

- PART I. THERMAL "ENE" REACTIONS OF CYCLOPROPENES WITH
CLASSICAL ENEOPHILES
PART II. GENERATION AND REARRANGEMENT OF CYCLOPROPENYL
CARBINYL ANIONS

By

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TO BARBARA

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Abstract of Dissertation Presented to the Graduate Council
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This work consists of two main areas, the mechanistic investigation of the thermal "ene" reactions of cyclopropenes with some classical eneophiles and the synthesis and base catalyzed hydrolysis of several (2,3-diphenyl-2-cyclopropen-1-yl)carbinyltriphenylphosphonium salts.

In the "ene" reaction investigation, triphenylcyclopropene was reacted with the classical eneophiles maleic anhydride, dimethyl acetylenedicarboxylate and dimethyl azodicarboxylate. In each case, one to one adducts were isolated and characterized. Likewise, the unsymmetrically substituted cyclopropene 1,2-diphenyl-3-(9'-fluorenyl)-cyclo-

propene yielded a single adduct upon addition to dimethyl acetylenedicarboxylate. 3-d-Triphenylcyclopropene was shown to add in a stereospecific cis manner to the double bond of maleic anhydride.

The entropy of activation, ΔS^\ddagger , was determined for the dimerization of triphenylcyclopropene and for the addition of triphenylcyclopropene to dimethyl acetylenedicarboxylate at 120.4°. In the former case, ΔS^\ddagger was found to be -37 cal/mole and in the latter case, -26 cal/mole. The latter reaction was also employed to probe the intermolecular isotope effect (k_H/k_D), solvent effects and substituents effects. The isotope effect was found to be 1.25 at 100°. The reaction was insensitive to changes in solvent and the ρ -value was determined to be -0.31. These results are discussed in terms of zwitterionic, hydride transfer and concerted cyclic mechanisms and the conclusion is drawn that the concerted process best explains the experimental results.

Lastly, triphenylcyclopropene was found to add to dimethyl acetylenedicarboxylate at least 3000 times faster than the acyclic olefin, 1,2,3-triphenylpropene. This rate enhancement is discussed in terms of both ground state and transition state effects.

In the second investigation, a series of resonance stabilized phosphoranes afforded cyclopropenylcarbinylphosphonium salts when treated with diphenylcyclopropenium

perchlorate. Subsequent base (OH^-) catalyzed decomposition of these salts in aqueous dimethyl sulfoxide resulted in the formation of triphenylphosphonium oxide and products resulting from solvent capture of ring opened butadienyl anions. No products resulting from capture of an intermediate cyclopropenyl carbinyl anion were detected. The stereochemistry of the phenyl substituents in the butadiene products varied from salt to salt and steric effects appear to govern the product distribution. Several products were synthesized authentically via the Wittig reaction of the phosphoranes with E- and Z- α -phenylcinnamaldehyde.

1,2-Diphenylpropenylidene fluorene, obtained from hydrolysis of 9-(2,3-diphenyl-2-cyclopropen-1-yl)-fluorenyl-triphenylphosphonium perchlorate, was found to yield 1,2-diphenylfluoranthrene upon photolysis. This reaction was extended to the synthesis of the previously unknown ring system, phenanthro[9,10-b] fluoranthrene.

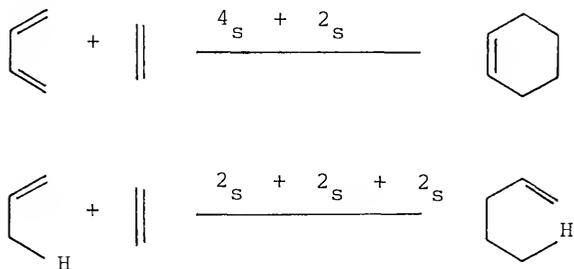
PART I

THERMAL "ENE" REACTIONS OF CYCLOPROPENES WITH
CLASSICAL ENEOPHILES

CHAPTER I

INTRODUCTION

The "ene" reaction, or indirect substitutive addition, has marked similarities to the well-known Diels-Alder reaction. The latter involves the cycloaddition of a diene and a dienophile, while the former reaction results from interaction of a molecule containing at least one allylic hydrogen (the "ene" component) and an eneophile. These reactions are illustrated for their simplest compounds in Scheme I.

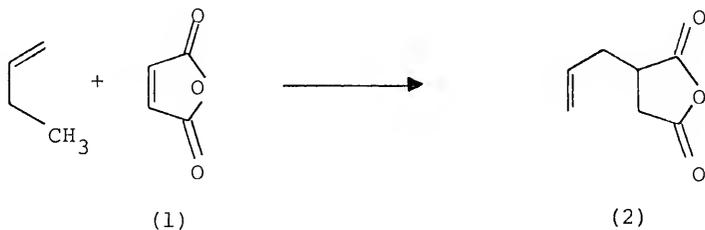


Scheme I

In both cases elevated temperature and/or pressure are required to promote reaction. It should be noted that the newly formed double bond occupies the same relative position in both products.

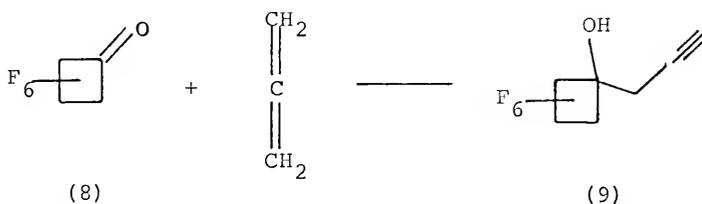
In the Diels-Alder reaction two new sigma bonds are formed and two double bonds are consumed, while in the "ene" reaction one new sigma bond is formed at the expense of one double bond. Also, both reactions are thermally allowed, concerted, suprafacial transformations under the orbital symmetry rules developed by Woodward and Hoffmann.¹ Accordingly, the Diels-Alder reaction is a $\pi^4_s + \pi^2_s$ cycloaddition and the "ene" reaction a $\pi^2_s + \pi^2_s + \sigma^2_s$ allylic hydrogen transfer.² In spite of these similarities, the Diels-Alder reaction has received far greater attention regarding its scope, stereochemical requirements, and mechanism than the "ene" reaction.

The "ene" reaction was first studied by Alder in 1943.³ He observed that propene reacted with maleic anhydride (1) at elevated temperature to give allyl succinic anhydride (2) as shown below. Although no mechanistic work was done, Alder envisioned the product as arising from attack by (1) at the terminal carbon of the carbon-carbon double bond of propene, migration of the double bond, and transfer of an allylic hydrogen to the anhydride.



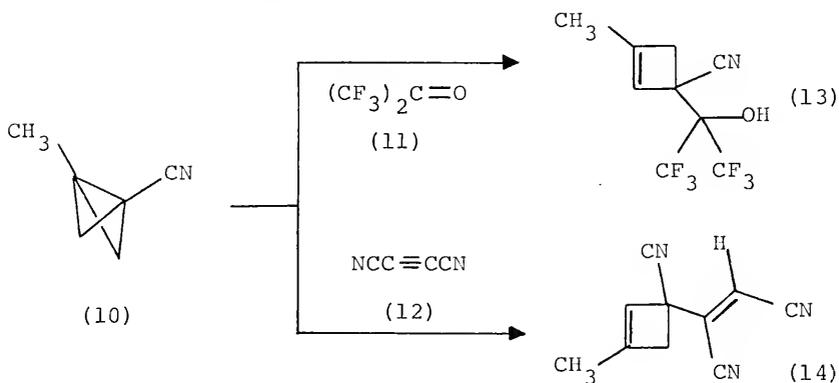
Preference for formation of the "ene" product in this example can be attributed to the fact that (3) normally possesses the more stable trans-configuration, which causes severe interactions in the transition state leading to the Diels-Alder product. The same reaction, run under ultra-violet light, yields only the Diels-Alder adduct (5).¹³ Irradiation of the trans-diethyl azodicarboxylate produces some of the cis-isomer in a photo-stationary equilibrium and this cis-isomer is more reactive in Diels-Alder cyclo-additions.¹⁴

Acetylenes and allenes also participate in the "ene" reaction but only if very powerful eneophiles such as benzyne (6), perfluor-2-butyne (7), or perfluorocyclobutanone (8) are employed. Allene reacts with perfluorocyclobutanone, yielding the acetylene (9) by attack of the eneophile at one of the terminal carbons.¹⁵



Substituted allenes such as tetramethylallene react differently; attack of the eneophile occurring at the central carbon.¹⁶ Acetylenes are generally less reactive than olefins. For example, 1-hexyne gives only a 4% yield of the "ene" product when treated with benzyne.

Although most systems employed in the "ene" reaction contain carbon-carbon multiple bonds, strained sigma bonds have also shown reactivity toward eneophiles. Bicyclo[1.1.0]butanes and bicyclo[2.1.0]pentanes, in which the zero bridge exhibits considerable unsaturation, react with a number of eneophiles. For example, 1-cyano-3-methylbicyclo[1.1.0]butane (10) reacts with hexafluoroacetone (11) and dicyanoacetylene (12) in refluxing ether to yield the cyclobutenes (13) and (14) respectively.^{17,18}

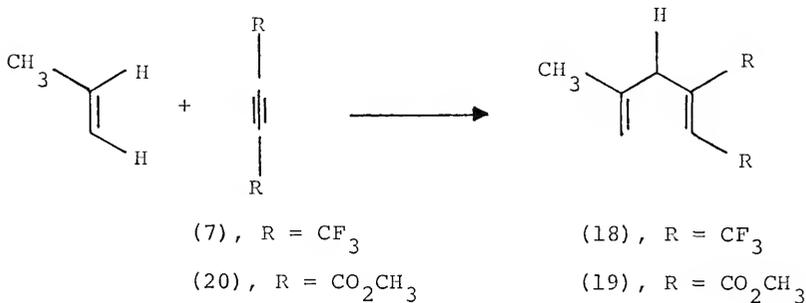


It is clear from the examples above that a wide variety of unsaturated and even some saturated compounds can be employed as the "ene" component in the "ene" reaction. The same versatility has been demonstrated for the eneophile. Since Alder's initial study using maleic anhydride, a number of olefins, alkynes, azo compounds and carbonyl compounds have been shown to have eneophilic character. The unifying feature of all eneophiles is the presence of one or more electron withdrawing groups bonded directly to the multiple

requiring higher temperatures and longer reaction times to produce "ene" adducts.

Acetylenes show enhanced eneophilic character over their olefinic counterparts. This enhanced reactivity may be attributed to the reduced pi-bond energy of the triple bond and to the greater stability of the newly formed vinylic carbon-hydrogen bond. Acetylene itself reacts with a variety of olefins, forming 1,4-dienes, but only under extreme conditions. Thus cis-2-butene reacts with acetylene at 350° and 2500 psi to give 3-methyl-1,4-pentadiene.²¹

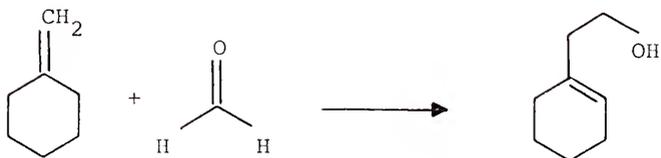
Acetylenes containing electron withdrawing groups show far greater reactivity. The "ene" adducts (18) and (19) are formed in the reactions of isobutene with (7) and dimethyl acetylenedicarboxylate (20) at 145° and atmospheric pressure.²² These eneophiles also react with allenes under mild conditions, affording good yields of the "ene" adducts.¹⁶



Benzyne (6) reacts readily with simple olefins such as 1-octene, cyclohexene, and isobutene.^{23,24} In fact, (6) is one of the most powerful eneophiles known and when employed with open chained dienes such as 2-methyl-1,3-butadiene, the "ene" reaction competes favorably with the Diels-Alder reaction.²⁴ In an extreme case, 2,5-dimethyl-2,4-hexadiene reacts with (6) to yield the "ene" adduct exclusively.²⁵ The absence of any Diels-Alder adduct was attributed to a trans-configuration of the isobutylene units in the diene.

Diethyl azodicarboxylate (3) has received the most attention among azo compounds found to have eneophilic character. The reaction of 1,3-cyclohexadiene with (3) has already been discussed.¹² The reaction of 1,4-cyclohexadiene with (3) also results in formation of an "ene" adduct.²⁶ Huisgen has studied the reaction of acyclic olefins with this eneophile and has found exclusive formation of the "ene" adducts.²⁷

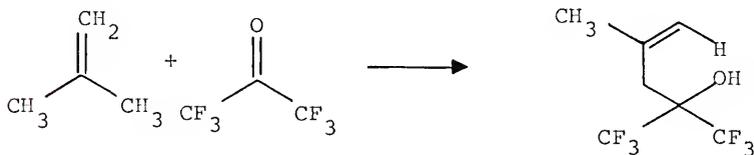
Some carbonyl compounds also show eneophilic character. The product that results from the "ene" reaction of an olefin with a carbonyl compound is an alcohol, arising from transfer of hydrogen from the "ene" component to the oxygen of the carbonyl compound. Arnold first observed this reaction when he treated methylenecyclohexane with formaldehyde, isolating as the sole product the unsaturated alcohol (21).⁶



(21)

Products resulting from reverse addition, that is vinyl ethers, have not been observed in this reaction. Presumably, this preference results from the greater gain in bond energy ($D(O-H) + D(C-C) = 190$ kcal./mole) in the observed reaction than in ether formation ($D(C-O) + D(C-H) = 177$ kcal./mole).²⁸

Although acetone shows no tendency to act as an enophile, its perfluoro derivative, hexafluoroacetone (11), has marked enophilic character, yielding the "ene" adduct (22) upon reaction with isobutylene at 25°.²⁹



(11)

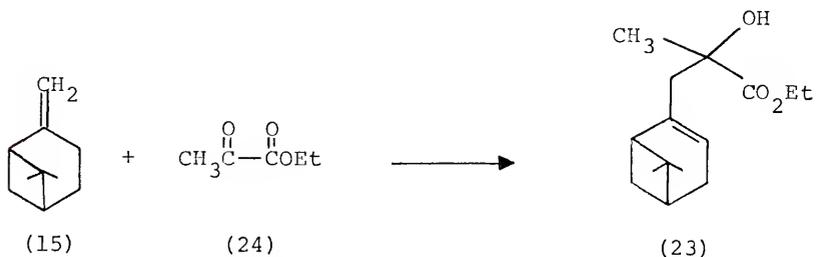
(22)

As shown previously, (11) also reacts with the strained sigma bond in bicyclo[1.1.0]butanes.¹⁷

Another perfluoroketone, hexafluorocyclobutanone (8), is perhaps the most reactive enophile known. Its tendency

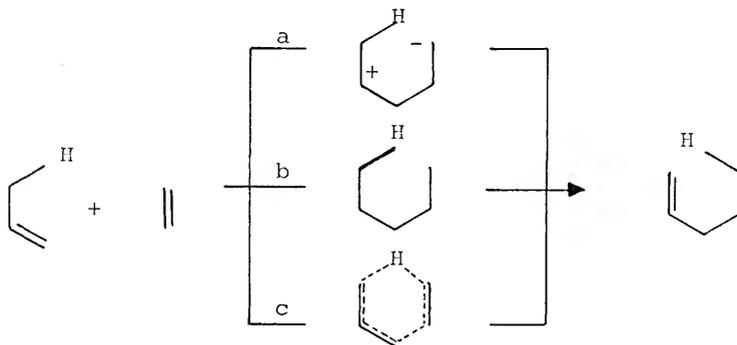
to undergo the "ene" reaction with allenes when most other eneophiles fail has been well documented.^{15,29}

Keto-esters should also act as eneophiles. This was demonstrated by Arnold when he isolated the "ene" adduct (23) in 55% yield from the reaction of methyl pyruvate (24) and β -pinene (15).^{30,31}



From the above discussion, it is obvious that a great deal of work has been done to expand the scope of the "ene" reaction. In addition, considerable attention has been focused on elucidating the mechanism of this reaction.

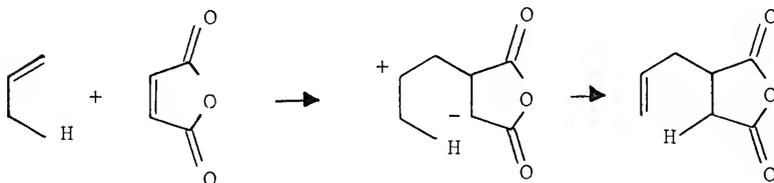
In general, three reaction mechanisms can be envisioned, shown for the simplest case in Scheme II.



Scheme II

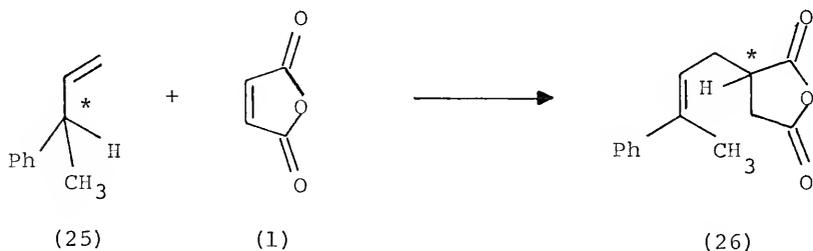
In mechanism (a) a zwitterionic intermediate is formed followed by intramolecular proton transfer. Mechanism (b) involves formation of a diradical intermediate followed by intramolecular hydrogen transfer. In mechanism (c), a concerted process involving a six-centered cyclic transition state is proposed.

An ionic mechanism was first proposed by Rondestvedt to account for the products observed in the reaction of olefins and α -substituted maleic anhydrides.³² He envisioned polarization of the reactants, with the negative dipole of the olefin attacking the positive dipole of the eneophile. The ionic intermediate formed would then yield the product by intramolecular proton abstraction. This mechanism accounted for the products obtained with α -substituted maleic anhydrides on grounds of steric and inductive effects but failed when the stereochemical orientation of the products was considered.

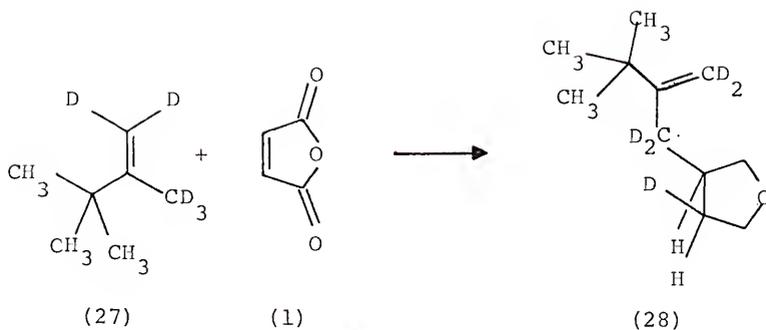


Arnold first proposed a concerted mechanism to account for the stereochemistry of the "ene" reaction. He observed that the reaction of β -pinene (15) with maleic anhydride (1)

yielded a mixture of two optically active products, one of which predominated.⁴ This concept was given support by Hill.⁷ He reacted the optically active olefin 3-phenyl-1-butene (25) with (1) and observed that an optically active product (26) was obtained. The transfer of optical activity from olefin to product is consistent with a concerted process. In addition, had an ionic intermediate been involved, it would be reasonable to assume that rearrangement to the more stable benzylic cation would occur. No products corresponding to such a rearrangement were observed.

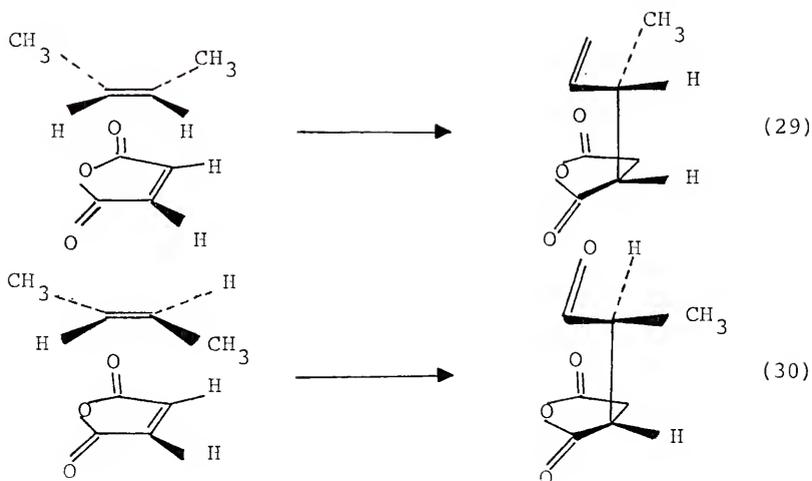


A concerted process would also predict cis-addition across the double bond of the enophile. This was shown to be the case by Friedrich.³³ The deuterated olefin (27) was treated with (1) and the product analysed by nmr spectroscopy. Comparison of the coupling constants in the product (28) with those obtained from the undeuterated product confirmed the cis-addition of deuterium and the alkyl component. However, because of partial deuterium scrambling, the limit of detectability for trans-deuterated (28) was approximately 30%. Therefore, the "ene" reaction was at least 70% stereoselective.

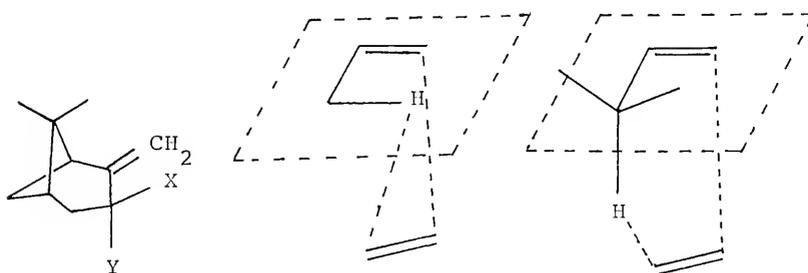


This result is consistent with a concerted mechanism, but a biradical or zwitterionic intermediate in which cis hydrogen transfer is preferred is also compatible.

The question of orientation in the transition state for a concerted mechanism has been studied by several workers. In their investigation of the reactions of optically active olefins with (1), Hill and Rabinovitz demonstrated that, not only was optical activity transferred to the product, but the bulky phenyl substituent was oriented away from the eneophile.⁷ This is to be expected on the basis of simple steric considerations. The preference for endo addition was demonstrated by Berson from a study of the reaction of both cis- and trans-2-butene with (1). Thus, cis-2-butene yielded the threo isomer (29) as the major product (80%) while trans-2-butene gave the erythro isomer (30) as the major product (57%).



Additional evidence supporting the concept of endo addition has been supplied by Hill et al. from a study of the reaction of cis- and trans-3-d- β -pinene with (1).⁵ This group determined that the configuration of the adduct in each case is constant with endoid addition, and further that a perpendicular orientation of the allylic carbon-hydrogen bond and the carbon-carbon double bond of the "ene" component is preferred over a cisoid orientation.



X = H; Y = D

Cisoid

Perpendicular

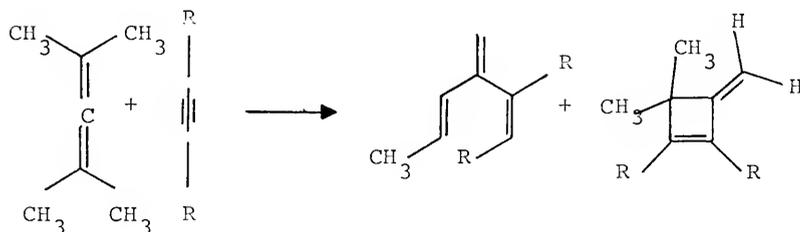
X = D; Y = H

Thus, the reaction of trans-3-d- β -pinene with (1) results in exclusive deuterium abstraction while cis-3-d- β -pinene yields exclusive hydrogen abstraction. Simultaneous to this work, Arnold arrived at the same conclusions through the study of cis- and trans-3-d- β -pinene with benzyne and methyl-phenylglyoxylate.³¹

Despite the evidence presented, Berson has been careful to point out that the stereochemical results do not prove a concerted mechanism because "the preservation of asymmetry in the product of the "ene" syntheses with optically active olefins are necessary but insufficient conditions, since a stepwise mechanism in which the carbon-carbon bond is formed first is also compatible with them."⁸

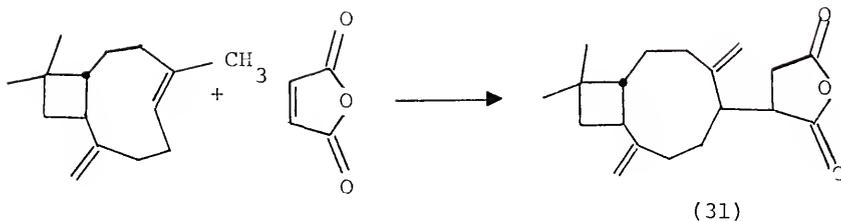
Other evidence for a concerted mechanism has been provided by Franzus.²⁶ In his study of the reactions of 1,3-cyclohexadiene and 1,4-cyclohexadiene with diethyl azodicarboxylate (3), he found the entropy of activation, ΔS^\ddagger , to be -31.8 eu in the former case and -40.7 eu in the latter. These large negative values are consistent with a concerted mechanism involving a highly ordered transition state. Huisgen studied the reactions of 1-p-tolyl-3-phenylpropene and 1-phenyl-3-p-tolylpropene with (3).²⁷ Varying the solvent from cyclohexane to nitrobenzene resulted in only a four-fold rate acceleration. This minimal effect on the rates of these reactions suggests a transition state involving little if any charge development.

A diradical mechanism does not appear likely in the "ene" reaction. The photochemical reaction of ketones and olefins to form oxetanes is known to proceed via a diradical triplet; however, in these reactions, "ene" adducts are absent.³⁴ On the other hand, the thermal "ene" reactions of olefins and ketones or aldehydes fail to produce any oxetane products. Nevertheless, a diradical intermediate appears necessary to account for the products obtained by Taylor from the "ene" reaction of tetramethylallene and perfluoro-2-butyne (7) or dimethyl acetylenedicarboxylate (20).¹⁶

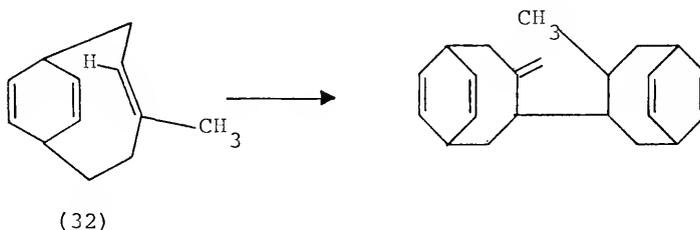


Dolbier has shown that the related reaction of allene with perfluorocyclobutanone proceeds via a concerted pathway.^{29,35} Thus, the result of Taylor appears to be unique for a specific example and not a general mechanism for the "ene" reaction of allenes.

Olefins showing the greatest reactivity in the "ene" reaction are those containing strained double bonds. The natural product, caryophyllene, which contains a strained trans-double bond and an exocyclic double bond, reacts smoothly with maleic anhydride (1) in refluxing benzene to produce the adduct (31).⁹



Although the exocyclic double bond is more accessible to the eneophile, it is not involved in the reaction. An even more spectacular example is the below room temperature dimerization via an intermolecular "ene" reaction of the bridged cis-trans-1,5-cyclooctadiene (32).³⁶

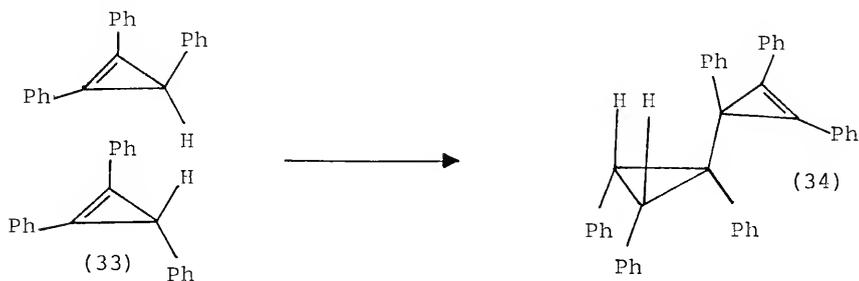


In both of these examples, relief of strain in the "ene" products provides the driving force for the facile reactions observed.

One system which contains a strained double bond and yet has received very little attention regarding its reactivity toward eneophiles is the cyclopropene series. This is surprising in light of the enormous interest in the thermally allowed Diels-Alder reactions of cyclopropene and its derivatives. In these reactions the cyclopropene functions as the dieneophile and the initial product of its

reaction with a diene contains a cyclopropane ring. The decrease in strain energy (27 kcal./mole) in going from cyclopropene to cyclopropane offers an attractive explanation for the facility of these Diels-Alder reactions.³⁷

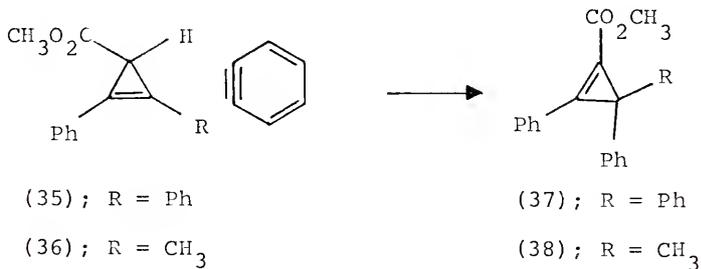
Two recent but familiar examples of "ene" reactions involving cyclopropenes only are the dimerizations of triphenylcyclopropene (33) and cyclopropene.^{38,39} Triphenylcyclopropene dimerizes in 20% yield in refluxing toluene to give the cyclopropylcyclopropene (34), resulting from transfer of hydrogen from one molecule to the least hindered face of the other.



A concerted process was proposed for the reaction since radical inhibitors failed to effect the rate of dimerization. Even more facile is the dimerization of the parent cyclopropene at -25° .³⁹ This is probably not a radical process either, since neither nitrobenzene nor benzoquinone effect the rate of dimerization.

In these cases, the cyclopropene moiety acts as both the "ene" component and the eneophile, and again strain relief would appear to provide the driving force for these

reasonably facile reactions. This would not be true if a different eneophile was employed. Nevertheless, Razin and Gupalo have reported that the cyclopropenes (35) and (36) react with benzyne to form the "ene" adducts (37) and (38).⁴⁰



Both "ene" adducts result from transfer of the cyclopropene hydrogen to the eneophile and migration of the cyclopropene double bond. Here, the extreme reactivity of benzyne may be responsible for the observed reaction.

The reactions of cyclopropenes with less reactive eneophiles remains an area of interest. This study was thus undertaken to investigate the reactivity of cyclopropenes with classic eneophiles and if appropriate cases could be found, to investigate the mechanism of the "ene" reactions through the use of product studies, kinetic results, deuterium isotope effects and competition reactions.

CHAPTER II

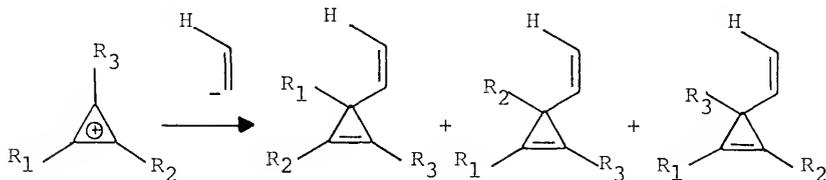
STRUCTURE AND STEREOCHEMISTRY OF SEVERAL CYCLOPROPENE "ENE" ADDUCTS

Introduction

The dimerizations of cyclopropene at -25° ³⁹ and of 1,2,3-triphenylcyclopropene (33) at 110° ³⁸ via the "ene" reaction are facile processes in which the relief of strain (27 kcal/mole) achieved in transforming a cyclopropene into a cyclopropane may provide the required driving force. However, strain relief is not required for the "ene" reactions of cyclopropenes to occur, as demonstrated by Razin and Gupalo.⁴⁰ These workers reacted 1,2,3-trisubstituted cyclopropenes with benzyne and obtained tetrasubstituted cyclopropenes as products. In addition, the substituent bound to the saturated carbon in the starting cyclopropene was found to reside on the double bond in the product cyclopropene, demonstrating that these reactions proceeded with migration of the cyclopropenyl double bond. Because of the extreme reactivity of benzyne, however, very little information can be gained regarding the reactivity of the cyclopropene system relative to acyclic allylic systems. One objective of this investigation is to determine whether the

bonding and geometry of the cyclopropene ring system increases its reactivity toward classical eneophiles. Comparison of the reactivities of suitably substituted cyclopropene and a similarly substituted acyclic model toward an appropriate eneophile should provide an answer to this question.

Secondly, there exists the possibility of a unique mechanism in these "ene" reactions; that of hydride transfer from the cyclopropene to the eneophile. In such a mechanism, an aromatic 2π cyclopropenium cation would be formed. Combination of the cation and anion would then lead to the "ene" adduct.



This mechanism is not unlikely in view of the fact that hydride ion abstraction from 1,2,3-trialkyl- and 1,2,3-triarylcyclopropenes is easily accomplished with triphenylmethyl perchlorate at room temperature.⁴¹ The hydride ion abstraction mechanism should be easily distinguished from a concerted process, in which little if any charge is created along the reaction pathway leading to products, by invest-

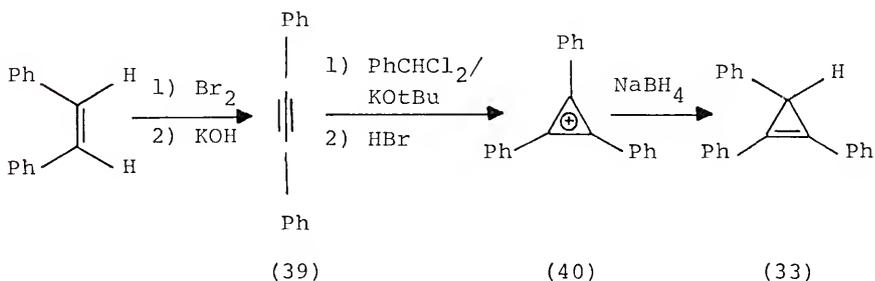
igating solvent effects on the rate of reaction. In addition, cyclopropenes bearing substituents ($R_1 = R_2 \neq R_3$) should, in the hydride abstraction mechanism, yield two products resulting from attack of the anion at C_3 or at either C_1 or C_2 of the cyclopropenium cation. In the concerted mechanism, only one product should result from such cyclopropenes.

Several criteria must be met by the cyclopropenes selected for this investigation. First, one of the substituents at C_3 must be hydrogen to fulfill the requirement that the "ene" component have an allylic hydrogen. Second, the cyclopropene should be relatively stable to the elevated temperatures required for the "ene" reaction. The parent cyclopropene ($R_1 = R_2 = H$), which dimerizes at -25° , would not be a suitable choice since the eneophiles chosen for this investigation could not compete favorably with this dimerization. Finally, the cyclopropene chosen for the initial investigation should have, for simplicity of product separation and identification, the same substituents at C_1 , C_2 , and C_3 . In this case, regardless of the mechanism operating, only one "ene" adduct should result.

One cyclopropene that meets all these requirements is 1,2,3-triphenylcyclopropene (33). This compound is symmetrically substituted, contains a hydrogen at C_3 , and has the desired thermal stability, dimerizing in 20% yield after heating in refluxing toluene (110°) for thirty-nine hours.³⁸ The classical eneophiles reviewed previously should compete favorably with this dimerization.

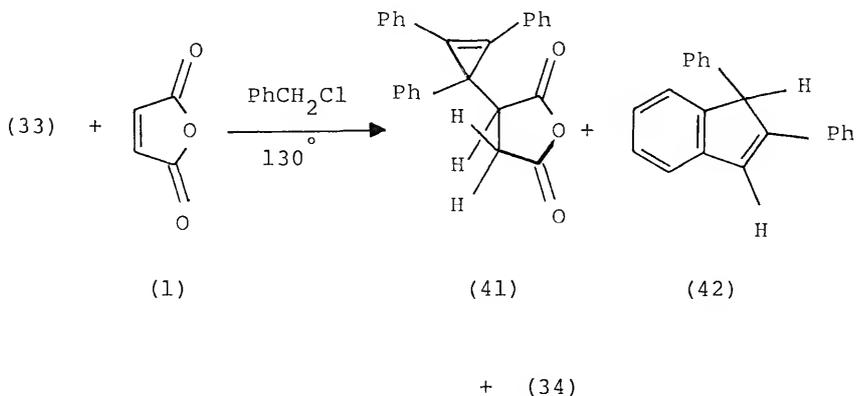
Preparation of 1,2,3-Triphenylcyclopropene (33) and its Thermal Reaction with Maleic Anhydride (1)

1,2,3-Triphenylcyclopropene (33) was prepared from trans-stilbene by the method of Battiste.⁴² Bromine addition followed by dehydrobromination yielded diphenylacetylene (39).⁴³ Reaction of (39) with benzal chloride and potassium-*t*-butoxide followed by treatment with hydrogen bromide gas gave the cyclopropenium salt (40), which upon sodium borohydride reduction afforded (33). This reaction sequence is shown below.



The first eneophile investigated was maleic anhydride (1), chosen because of its extensive use with various other "ene" reactants. After failure to obtain the desired "ene" adduct at room temperature or in refluxing benzene, the reaction was conducted in refluxing chlorobenzene (130°). In addition to the "ene" adduct 1-(1',2',3'-triphenylcyclopropenyl)-succinic anhydride (41), the triphenylcyclopropene dimer (34) and 1,2-diphenylindene were also isolated and characterized. Formation of (41) and (34) arise from the

"ene" reactions of (33) with maleic anhydride and with a second molecule of (33), respectively. Indene (42) presumably arises by the known acid-catalyzed rearrangement of triphenylcyclopropene via a ring opened allylic cation.⁴⁴ Thermal rearrangement of (33) under these conditions does not appear likely in light of the fact that Breslow reports a greater than 99% conversion of 3-d-1,2,3-triphenylcyclopropene (43) to its dimer in refluxing xylene (145°).



The assignment of structure (41) to the "ene" adduct of (33) and maleic anhydride is based on its spectral data. The 60 MHz nmr spectrum of (41) is given in Figure 1.1. Four of the aromatic protons are shifted slightly to lower field. These protons can be assigned to the ortho-positions of the phenyl substituents bound to the double bond of the cyclopropene ring. This ortho-deshielding effect is common for other 1,2-diarylcyclopropenes such as (33) and (34). The multiplets at δ 4.30, 3.07, and 2.92 can be assigned to

the three protons bound to the succinic anhydride portion of the molecule. These signals, are, in reality, all part of an ABX system, as revealed by the 100 MHz nmr spectrum given in Figure 1.2. Analysis of this system yielded the coupling constants shown in Table 1.1. The assignments are based upon comparison with a number of other substituted succinic anhydrides, which show that in every case, the cis-proton coupling constant is larger by 2-5 Hz than the corresponding trans-coupling constant.³³

Further support for these assignments was obtained from the nmr spectrum, given in Figure 1.3, of the "ene" adduct (44), isolated from the reaction of 3-d-1,2,3-triphenylcyclopropene (43), with (1). The ABX pattern observed in (41) collapsed into two doublets in (44). Good agreement is observed between the coupling constant ($J = 10.0$ Hz) in (44) and the cis-coupling constant ($J = 9.1$ Hz) in (41), indicating that in each of these adducts the elements of hydrogen or deuterium and triphenylcyclopropene have added in a cis-mode across the double bond of maleic anhydride. The mechanistic implications of this stereospecific addition will be discussed later. The line broadening of the up-field doublet in (44) is indicative of hydrogen-deuterium coupling and thus this signal can be assigned to H_A . The downfield doublet must then be due to H_X .

Additional evidence confirming the proposed structure of (41) is obtained from its infrared, ultraviolet, and mass spectral data. Carbon-oxygen stretching bands observed at

1865 (m) and 1780 (s) cm^{-1} are indicative of a cyclic anhydride. The ultraviolet spectrum showed maxima at 330 ($\epsilon = 19,800$) and 314 nm ($\epsilon = 24,700$), comparing favorably to the maxima observed for (33) and (34). This data is shown in Table 1.2. The mass spectrum of (42) showed a molecular ion at m/e 366.1263 (calcd. 366.1255) and a P+1 ion at m/e 367.1284 (calcd. 367.1288), confirming that (41) is a one to one adduct of (33) and maleic anhydride. In addition, a major fragment at m/e 267 indicates the presence of the triphenylcyclopropene ring.

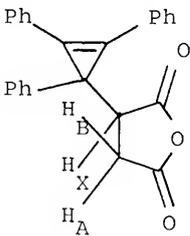
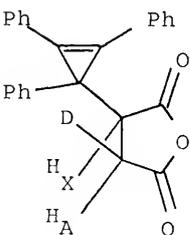
The Thermal "Ene" Reaction of (33)

with Dimethyl Acetylenedicarboxylate (20)

Since activated acetylenes, in general, show greater eneophilic character than similarly substituted olefins, the successful "ene" reaction of (33) with maleic anhydride presaged success with dimethyl acetylenedicarboxylate (20).

Treatment of (33) with a five-fold excess of (20) at 100° in chlorobenzene resulted in the formation of a single product, the expected "ene" adduct (45), in 57% yield. Unlike the previous example with maleic anhydride, no 1,2-diphenylindene (42) or dimer (34) were detected in this reaction.

TABLE 1.1
 PROTON COUPLING CONSTANTS OF "ENE" ADDUCTS (41) and (44)

Compound	J_{AB}^a	J_{AX}	J_{BX}
 (41)	18.5 Hz	9.1 Hz	6.9 Hz
 (44)	---	10.0 Hz	---

^aAt ambient temperature in CDCl₃.

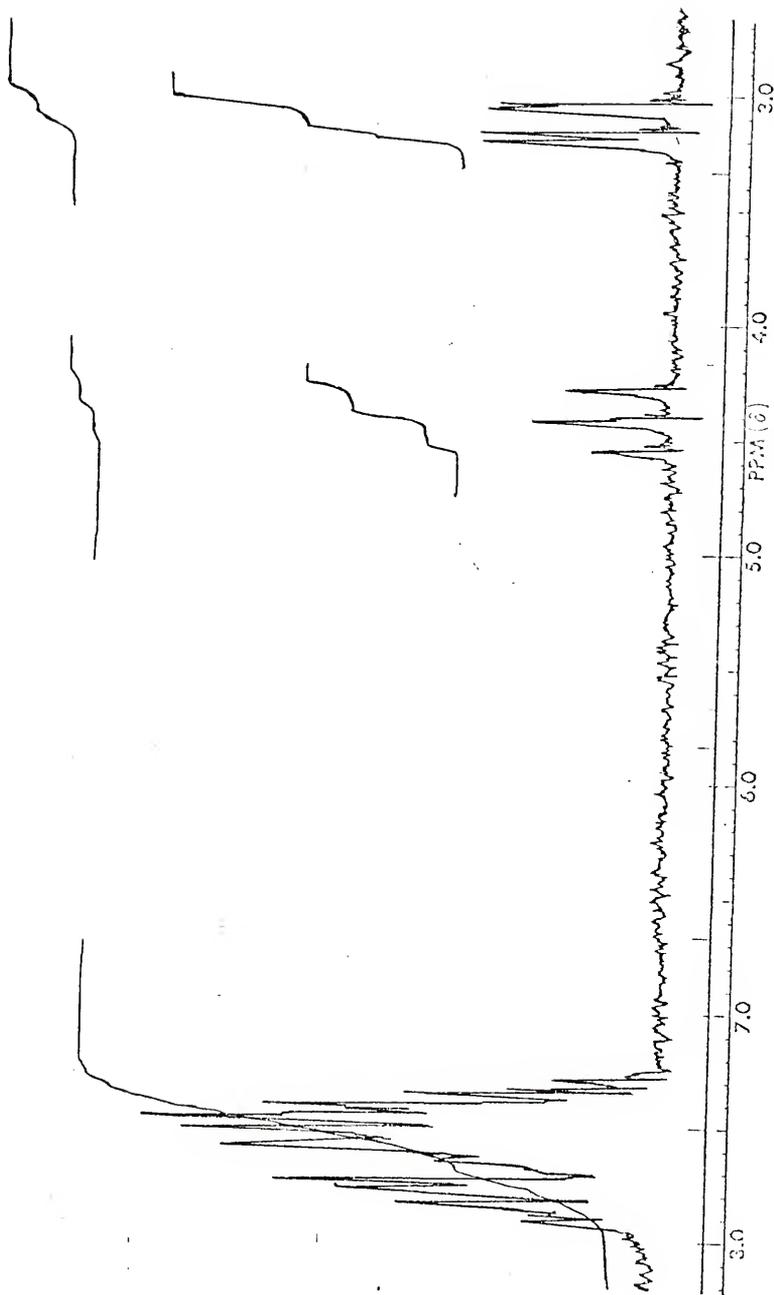


Fig. 1.1. Proton magnetic resonance spectrum of 1-(1',2',3'-triphenylcyclopropenyl)-succinic anhydride (41) in deuteriochloroform at ambient temperature.

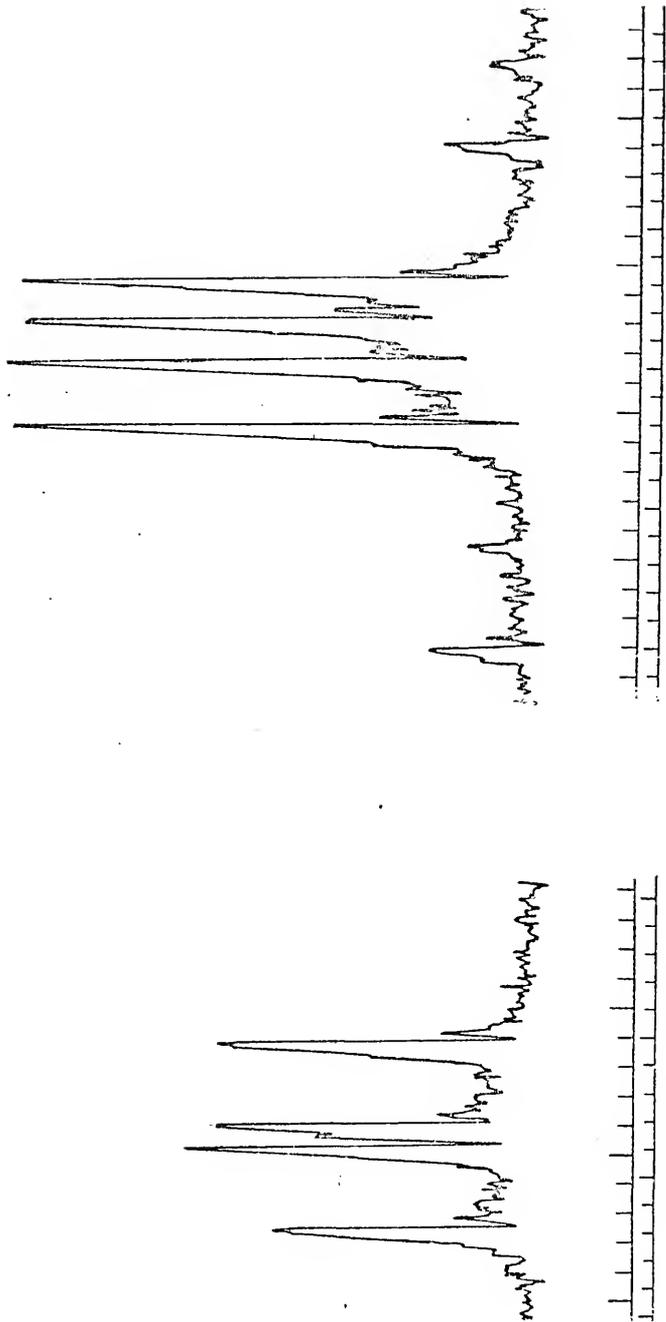


Fig. 1.2. 100 MHz proton magnetic resonance spectrum of the ABX portion of 1-(1',2',3',-triphenylcyclopropenyl)-succinic anhydride (4L) in deuteriochloroform at ambient temperature.

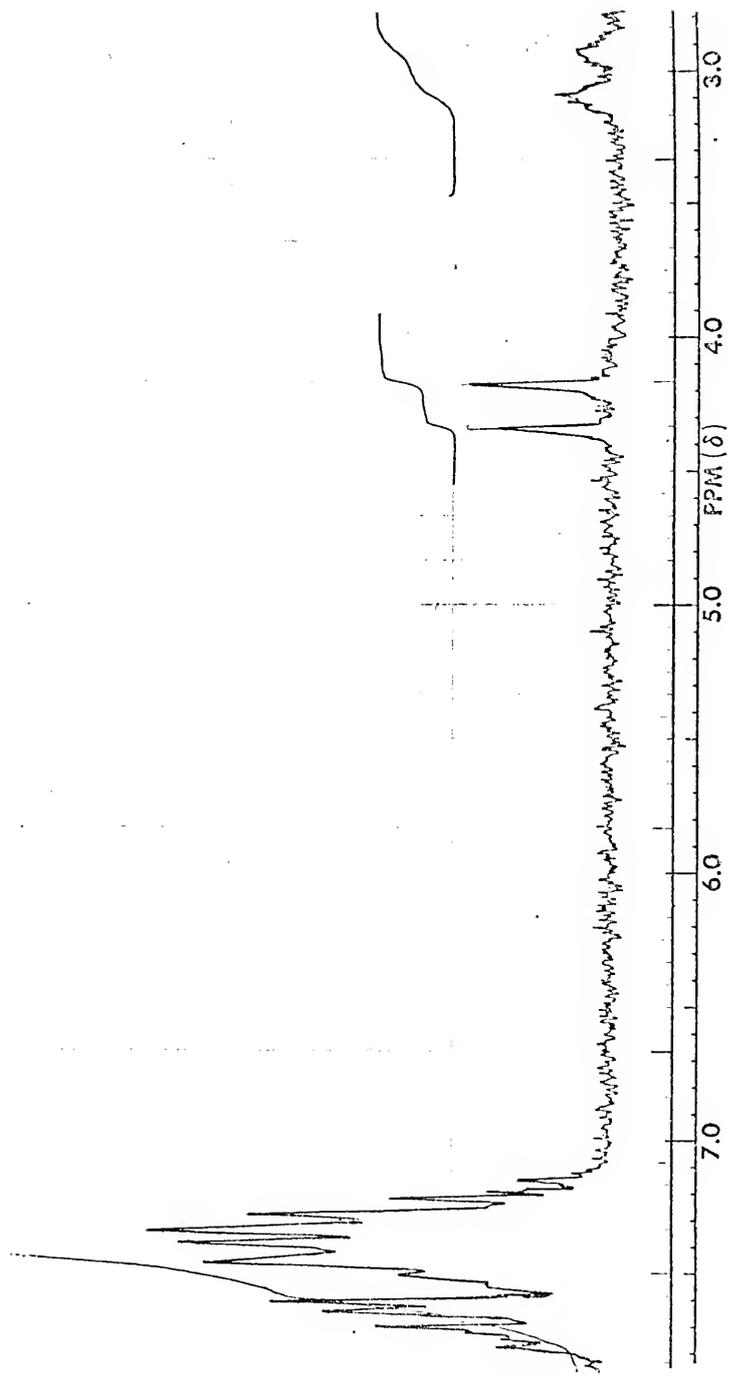
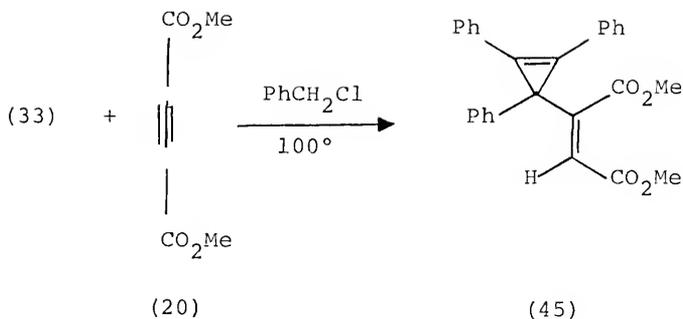


Fig. 1.3. Proton magnetic resonance spectrum of cis-1-(1',2',3'-tricyclopropenyl)-2-deutero-succinic anhydride (44) in deuteriochloroform at ambient temperature.



Assignment of structure (45) to the "ene" adduct is based on its spectral data. The nmr spectrum of (45), given in Figure 1.4, is consistent with the assigned structure. As in the previous "ene" adduct (41), four of the aromatic protons are shifted to lower field by the ortho-deshielding effect common to 1,2-diarylcyclopropenes. The downfield singlet at δ 5.93 integrates for one proton and its position is in agreement with a vinyl proton bonded to the β -position of an α, β -unsaturated ester. The two upfield singlets at 3.65 and 3.50 each integrate for three protons and correspond to the methyl ester protons of (45).

Supporting evidence for structure (45) is provided by infrared, ultraviolet and mass spectral data. The cyclopropene double bond stretching frequency at 1840 (w) cm^{-1} is in agreement with the value observed for a number of other 1,2-diarylcyclopropenes.^{38,45} In addition, intense carbon-oxygen double bond stretching at 1730 (s) and 1710 (s) cm^{-1} as well as strong carbon-carbon double bond stretching at 1630 (s) cm^{-1} lend support to the proposed structure. The

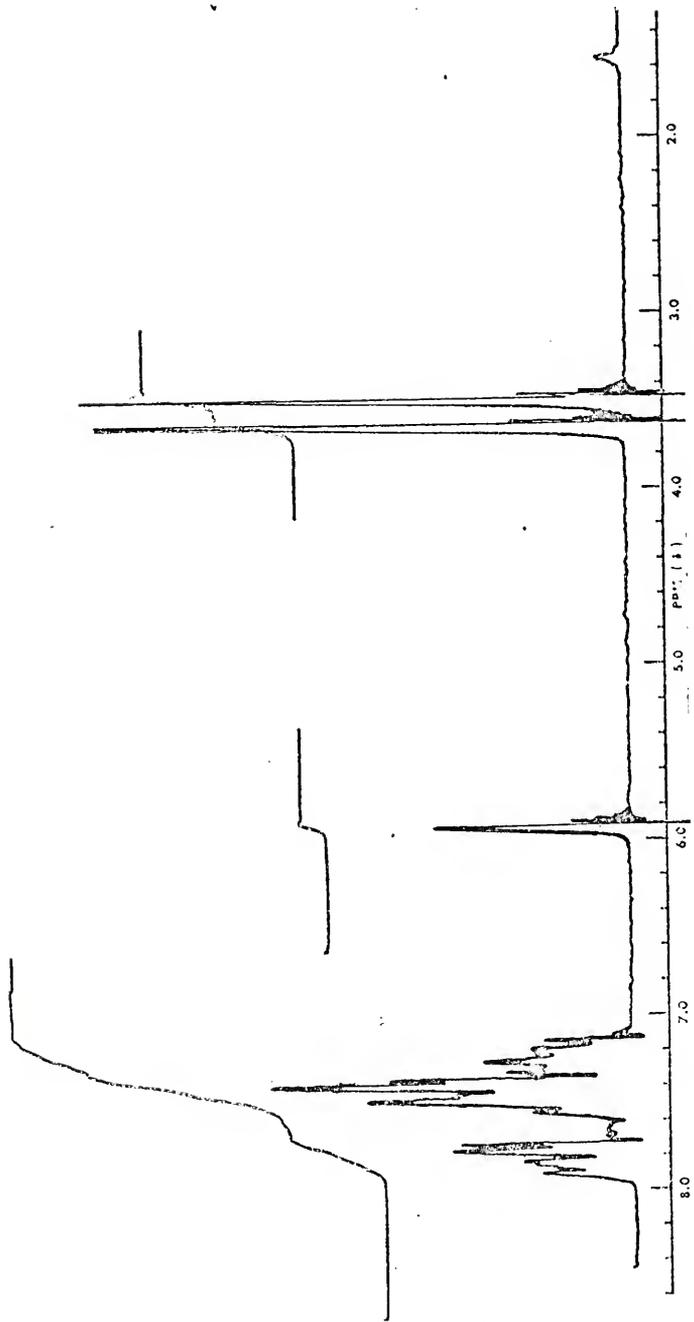


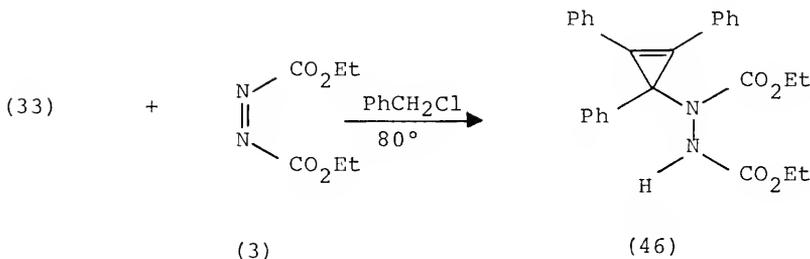
Fig. 1.4. Proton magnetic resonance spectrum of 1-(1',2',3'-triphenylcyclopropenyl)-dimethyl maleate (45) in deuteriochloroform at ambient temperature.

ultraviolet spectrum, given in Table 1.2, agrees with other 1,2-diarylcyclopropenes. The mass spectrum shows a parent ion at m/e 410, confirming that (45) is a one to one adduct of (33) and (20). A minor fragment ion at m/e 379 ($P-OCH_3$), is consistent with the methyl ester formulation while fragment ions at m/e 351 and m/e 292 correspond to sequential loss of two CO_2CH_3 radicals from the parent ion. The fragment that results from these losses is formally an acetylenic cyclopropenyl radical cation. An obscure and deep seated rearrangement with sequential loss of hydrogen radicals would then account for the intense fragment ions observed at m/e 291, 290, and 288 (base peak). Such a rearrangement would also explain why the fragment at m/e 267, associated with the triphenylcyclopropenium cation is only 8% of the base peak in this molecule.

The Thermal "Ene" Reaction of (33)
with Diethyl Azodicarboxylate (3)

The previous examples demonstrated the ability of triphenylcyclopropene (33) to undergo the "ene" reaction with the electron deficient olefin (1) and acetylene (20). A third class of eneophiles, those containing an electron deficient nitrogen-nitrogen double bond, was investigated using diethyl azodicarboxylate (3). This eneophile was synthesised according to the procedure of Rabjohn.⁴⁶ The reaction of (33) with (3) was accomplished in refluxing toluene and the "ene" adduct (46) was isolated in

71% yield as the sole product. Again, as in the previous example, none of dimer (34) or indene (43) was detected.



The spectral data of (46) confirm the assigned structure. The nmr spectrum is shown in Figure 1.5. The aromatic portion again reveals the characteristic ortho-deshielding effect common to 1,2-diarylcyclopropenes. The singlet at δ 6.78 is assigned to the amide nitrogen proton. The methylene protons of the ester groups appear as two overlapping quartets at 4.11 and 4.01 while the methyl protons appear as two triplets at 1.08 and 1.03.

The infrared, ultraviolet and mass spectral data further support the assigned structure. Nitrogen-hydrogen stretching, nitrogen-hydrogen bending and carbonyl stretching bands at 3230 (m), 1510 (m), and 1695 (s) cm^{-1} , respectively, are indicative of a secondary amide. In addition, the characteristic cyclopropene double bond stretching band is observed at 1820 (w) cm^{-1} . The ultraviolet spectrum of (46) exhibits maxima at 318 ($\epsilon = 20,300$) and 303 nm ($\epsilon = 24,000$). These values represent a slight

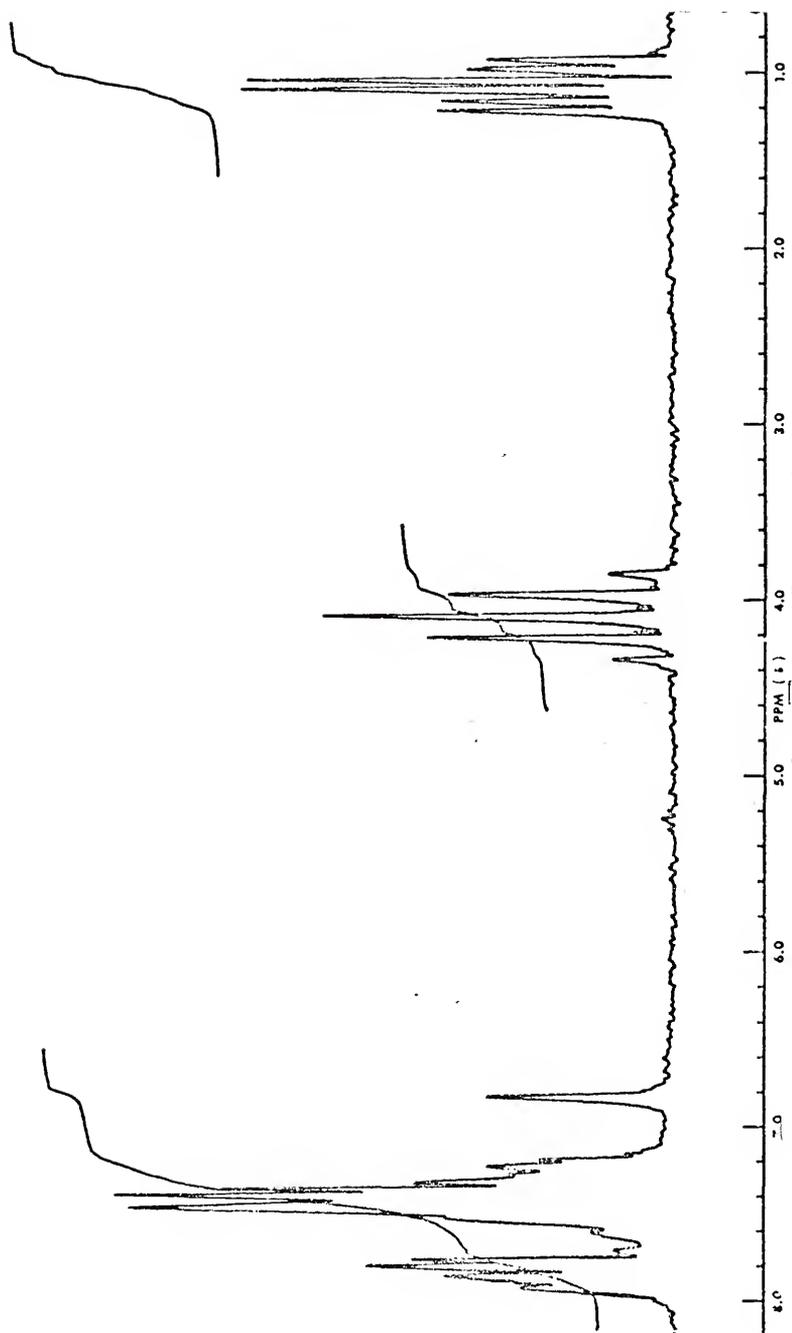
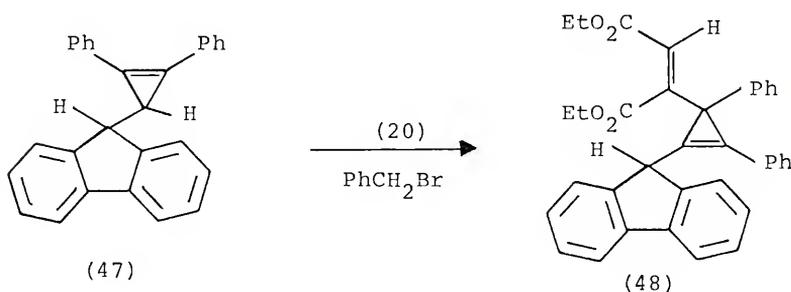


Fig. 1.5. Proton magnetic resonance spectrum of diethyl 1-(1',2',3'-triphenylcyclopropenyl)-hydrazodicarboxylate (46) in deuteriochloroform at ambient temperature.

hypsochromic shift relative to the maxima of (41) and (45) but agree favorably with the values observed for other 1,2-diarylcyclopropenes containing an electron withdrawing substituent at C₃.^{45,47} The mass spectrum shows a parent ion at m/e 442, confirming that (46) is a one to one adduct of (33) and (3). In addition, the triphenylcyclopropenium cation at m/e 267 is the base peak in this compound.

The Thermal "Ene" Reaction of 1,2-Diphenyl-3-(9'-fluorenyl)-cyclopropene

The unsymmetrically substituted cyclopropene (47) was prepared from fluorene and 1,2-diphenylcyclopropenium perchlorate by the method of Jones.⁴⁸ Treatment of (47) with one equivalent of dimethyl acetylenedicarboxylate (20) yielded a single "ene" adduct (48).



The spectral data of (48) confirm the assigned structure. The nmr spectrum showed a broad aromatic multiplet at δ 7.8-6.9 which integrated for eighteen protons. The olefinic proton appeared as a sharp singlet at 5.80 and the 9-fluorenyl proton as a broad singlet at 5.33, which is

TABLE 1.2

ULTRAVIOLET SPECTRA MAXIMA FOR TRIPHENYLCYCLOPROPENE (33)
AND "ENE" ADDUCTS (34), (41), (44), (45), (46), AND (48)

Compound	λ_{max}^a (ϵ)				
	I	II	III	IV	V
(33)	334 (22,800)	318 (28,800)	---	---	218 (27,800)
(34) ^b	330 (20,000)	318 (23,800)	---	---	225 (64,000)
(41)	330 (19,800)	314 (24,700)	295 ^c (18,800)	---	---
(44)	330 (19,300)	314 (23,600)	---	---	---
(45)	330 (16,000)	314 (17,600)	285 ^c (13,600)	235 (23,100)	228 (23,600)
(46)	318 (20,400)	303 (24,000)	290 (19,100)	---	---
(48)	---	300 (8,700)	287 (10,500)	255 (23,400)	---

^aAll spectra obtained in 95% ethanol; ^bReference 38; ^cInflections

considerably deshielded with respect to (47). The methyl ester protons appeared as sharp singlets at 3.60 and 3.55.

Supporting evidence for structure (48) is provided by infrared, ultraviolet and mass spectral data. The cyclopropene double bond stretching at 1845 (w) cm^{-1} , carbonyl stretching at 1730 (s) and 1705 (s) cm^{-1} , and olefinic stretching at 1635 (m) cm^{-1} all lend support to the proposed structure. The ultraviolet spectrum, given in Table 1.2, agrees with other cyclopropenes containing one aryl substituent bound to the cyclopropene double bond. The mass spectrum showed a parent ion at m/e 498, corresponding to a one to one adduct of (47) and (20).

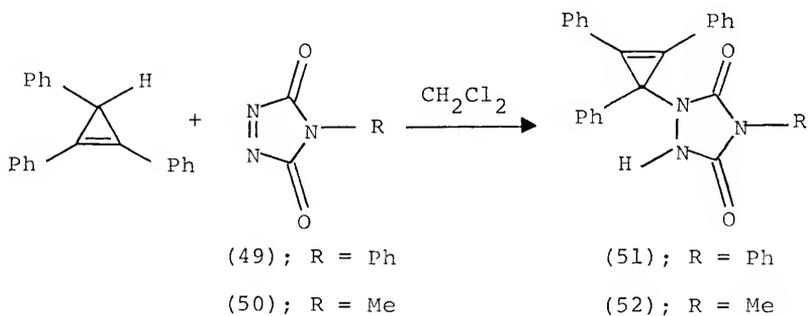
Attempted Thermal "Ene" Reactions of (33) with Various Other Eneophiles

Attempts to extend the scope of the "ene" reaction of (33) to a variety of other potential eneophiles met with little success. For example, treatment of (33) with 1,4-benzoquinone and 1,4-naphthaquinone resulted only in the recovery of starting material and dimer (34). The same result was obtained with diethyl maleate and diethyl fumarate. When bromomaleic anhydride and chloromaleic anhydride were employed as eneophiles, 1,2-diphenylindene (42) was isolated as the only product. None of the desired "ene" adduct could be detected in any of these reactions.

The reactions of (33) with 4-phenyl- and 4-methyl-1,2,4-triazoline-2,5-dione, (49) and (50) respectively, gave

questionable results. The addition of a methylene chloride solution of (49), which has a deep purple color, to a solution of (33) in the same solvent at 0° resulted in complete discharge of color within thirty minutes. A white powder was isolated from the reaction and the nmr spectrum (aromatic protons and a sharp singlet at δ 6.43), mass spectrum (parent ion at m/e 443) and infrared spectrum (strong carbonyl stretching) suggested that the desired adduct was obtained. However, lack of any significant absorption in the 300 to 330 nm region of the ultraviolet spectrum and the inability to obtain an adequate elemental analysis makes assignment of structure (51) to this material rather dubious.

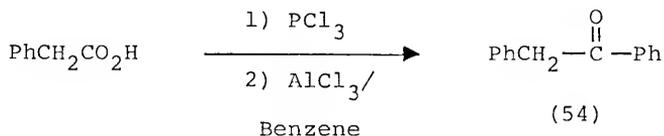
Likewise, the reaction of (50) with triphenylcyclopropene (33) resulted in immediate loss of color and isolation of a white powder. Again, the spectral data gave strong indication that the desired "ene" adduct (52) was formed, but all attempts to obtain an adequate elemental analysis on this compound also failed.

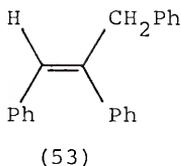
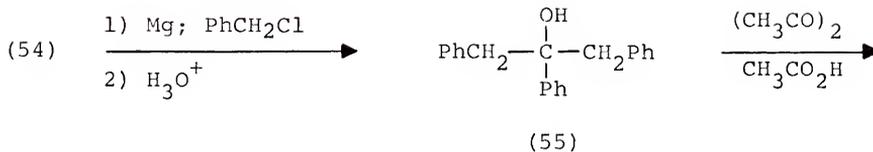


Decomposition of the "ene" adducts (51) and (52), coupled with their isolation as an admixture with the corresponding urazil compounds might explain the inability to obtain adequate analysis. When either (51) or (52) were spotted on thin layer plates and eluted, considerable streaking occurred. Some support for this explanation was obtained by dividing the streak into two portions and analyzing each by ultraviolet absorption. The top portion showed considerable enhancement of the typical cyclopropene absorptions in the 330-300 nm region whereas no absorptions in this region were observed for the bottom portion.

Comparison of the Reactivities of Tri-phenylcyclopropene and 1,2,3-Triphenylpropene Toward Dimethyl Acetylenedicarboxylate (20)

To determine whether the reaction of triphenylcyclopropene (33) with eneophiles is accelerated with respect to the reaction of a similarly substituted acyclic olefin, 1,2,3-triphenylpropene (53) was synthesized. This olefin was chosen because it, like (33), contains a diphenyl substituted double bond and a phenyl substituent at the allylic position, and was synthesized from phenylacetic acid as shown.





Phenylacetic acid was converted into its acid chloride followed by Friedel-Crafts substitution on benzene, yielding phenylbenzyl ketone (54).⁴⁹ Treatment of (54) with benzyl Grignard gave the tertiary alcohol (55), which upon dehydration afforded (53), shown by nmr spectroscopy to be a 4.25 to 1.00 mixture of the trans and cis isomers.⁵⁰ This mixture was employed without separation in the subsequent rate comparisons.

Dimethyl acetylenedicarboxylate (20) was chosen as the eneophile for this investigation because its reactivity is not so great as to preclude selectivity between the olefins and has already been shown to react cleanly with (33).

One to one solutions of each "ene" component and (20) were prepared in chlorobenzene with an internal standard (tetrachloroethane) added. The reactions were carried out at 119.9° and monitored by nmr spectroscopy, following the disappearance of the "ene" component. The reaction of (33) with (20) proceeded with a half-life of 0.8 hours, but

1,2,3-triphenylpropene (53) failed to show any measurable reaction after 125 hours.

The initial concentration of each reactant in these reactions was 0.5 M. If a minimum limit of detectability by nmr analysis of 5% is assumed, a lower limit for the half-life of the reaction of 1,2,3-triphenylpropene with dimethyl acetylenedicarboxylate (20) may be estimated to be 2400 hours. This treatment results in an estimated rate acceleration for the reaction of triphenylcyclopropane with (20) of 3000. The factors possibly responsible for the increased reactivity of (33) with respect to (53) toward the eneophile (20) will be discussed in Chapter III.

CHAPTER III

KINETIC AND MECHANISTIC INVESTIGATION OF THE "ENE" REACTIONS OF CYCLOPROPENES

Introduction

The reactivity of triphenylcyclopropene (33) with the classic eneophiles maleic anhydride (1), diethyl azodicarboxylate (3), and dimethyl acetylenedicarboxylate (20) prompted an investigation of the mechanism of these "ene" reactions with the objective of determining whether a concerted or stepwise process is operating. Several approaches were used to probe the mechanism of these reactions, including product studies, determination of the kinetic activation parameters (E_a^\ddagger and ΔS^\ddagger), competition reactions, solvent effects and deuterium isotope effects.

Results

In each of the thermal reactions of triphenylcyclopropene (33) with eneophiles (1), (3), and (20), discussed in Chapter II, only one "ene" adduct was isolated, although a substantial amount of the "self ene" dimer (34) was also formed during the reaction of (33) with (1). In this latter case, dimerization of (33) became competitive with adduct formation because of the substantially longer reaction time

and higher reaction temperature. The formation of a single adduct in these reactions is consistent with either a concerted or a step wise hydride-transfer mechanism, since in the latter case, a symmetrical cyclopropenium cation is involved as the product determining intermediate. However, the reaction of 1,2-diphenyl-3-(9'-fluorenyl)-cyclopropene (47) with (20) also led to the isolation of a single product, (48). The mechanistic implication of this result as well as the previously stated observation that the "ene" reaction of 3-d-triphenylcyclopropene (43) with maleic anhydride gave stereospecific cis-addition across the double bond of the eneophile will be explored later.

Two "ene" reactions, the dimerization of (33) and the reaction of (33) with (20) were subjected to kinetic investigation. The dimerization reaction was carried out on 0.5 molar solutions of (33) in bromobenzene and the reaction of (33) with (20) was conducted on bromobenzene solutions that were 0.5 molar in each reactant. Both reactions were carried out in sealed nmr tubes and the disappearance of (33) relative to an internal standard, toluene, was monitored. In this way, the concentration of (33) at a given time could be calculated and in turn, the rate constants determined using equation 1, the integrated rate expression for a second order reaction in which the initial concentrations of both reactants are equal, x being the concentration of (33) at time t and a_0 being the initial concentration of (33).

$$k = \frac{x}{a_0(a_0 - x)t} \quad \text{Equation 1}$$

From the rate constants for these reactions at two temperatures, the energies of activation, E_a^\ddagger , were calculated using equation 2, in which k_1 is the rate constant at absolute temperature T_1 , k_2 is the rate constant at absolute temperature T_2 , and R is the gas constant.

$$2.303 \log \frac{k_2}{k_1} = \frac{E_a^\ddagger}{R} \frac{(T_2 - T_1)}{(T_2 T_1)} \quad \text{Equation 2}$$

Employing the energies of activation calculated from equation 2, the entropies of activation, ΔS^\ddagger , were calculated from equation 3, where $\Delta H^\ddagger = E_a^\ddagger - RT$.

$$2.303 R \log \frac{k_1}{T_1} - 47.198 = \frac{-\Delta H^\ddagger}{T_1} + \Delta S^\ddagger \quad \text{Equation 3}$$

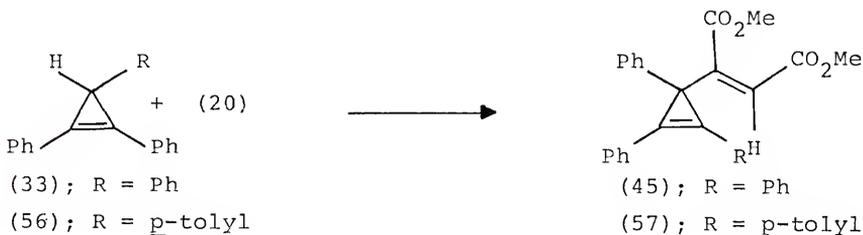
Using the entropy of activation, ΔS^\ddagger , the pre-exponential factor of the Arrhenius equation was calculated from equation 4.

$$\Delta S^\ddagger = 4.576 (\log A - 13.23) \quad \text{Equation 4}$$

The rate constants for the dimerization of (33) and the reaction of (33) with (20) and the accompanying E_a^\ddagger , ΔS^\ddagger , and $\log A$ values are given in Table 1.3.

The reaction of (33) with (20) was also used to probe the effect of solvent on the "ene" reactions of cyclopropenes. Thus, 0.5 molar solutions of each reactant in carbontetrachloride, bromobenzene, and nitrobenzene were prepared and heated at 100.0°. As before, the progress of the reaction was monitored by following the disappearance of (33) with respect to the internal standard, toluene. The rate of reaction was found to be insensitive to changes in solvent polarity, increasing by less than a factor of two as the solvent was changed from carbontetrachloride to nitrobenzene.

To determine what effect structural changes have on this "ene" reaction, a competitive study was conducted using the eneophile (20) and the "ene" components (33) and 1,2-diphenyl-3-*p*-tolylcyclopropene (56). A bromobenzene solution containing equal molar amounts of (33) and (56) and approximately 0.1 mole equivalents of (20) was heated in a sealed tube and the relative rates of formation of the "ene" adducts (45) and (57) were determined simply by isolating the adduct mixture and comparing the nmr integral heights of the allylic, methyl ester and tolyl-methyl protons.



The ratio of tolyl-methyl protons to olefinic protons was 1.60 and the ratio of methyl ester protons to tolyl-methyl protons was 3.78. In a product mixture containing equal amounts of (45) and (57), these ratios would be 1.50 and 4.00 respectively. Therefore, the adduct mixture was found to contain 53% (57) and 47% (45). To check the accuracy of this method, the ratio of methyl ester protons to olefinic protons was measured and determined to be 6.03. Regardless of the composition of the product mixture, the theoretical value of this ratio is 6.00.

The rate ratio for this reaction was calculated employing equation 5, where A stands for "ene" adduct and C stands for starting cyclopropene.

$$\frac{k_{(56)}}{k_{(33)}} = \frac{A_{(57)}}{A_{(45)}} \times \frac{C_{(33)}}{C_{(56)}} \quad \text{Equation 5}$$

From equation 5 and the percent composition of the "ene" adduct mixture, $k_{(56)}/k_{(33)}$ was found to be 1.13. A one point ρ value was calculated for the "ene" reaction using the Hammett equation,⁵¹ equation 6, where $k = k_{(56)}$, $k_0 = k_{(33)}$, and $\sigma = -0.17$ for a para-methyl substituent.⁵²

$$\log \frac{k}{k_0} = \sigma \rho \quad \text{Equation 6}$$

This treatment yields a value of $\rho = -0.31$. It may be more appropriate to employ σ^+ for the reaction at hand,

since the reacting center at C₃ of the cyclopropene ring can interact directly with the C₃-phenyl substituent.⁵³ For a para-methyl substituent, σ⁺ has a value of -0.31⁵⁰, and in this case, ρ⁺ = -0.17.

The intermolecular isotope effect was determined by reacting an equalmolar mixture of triphenylcyclopropene (33) and 3-d-triphenylcyclopropene (43) with approximately 0.1 mole equivalents of dimethyl acetylenedicarboxylate (20). After isolating the "ene" adduct, the composition of the product mixture was determined by nmr integration of the vinyl and methyl ester protons. The starting cyclopropenes were also isolated and the isotopic composition determined by comparing the nmr integration of the cyclopropenyl C₃-hydrogen with that of an accurately measured amount of toluene. This mixture was then used to obtain a duplicate value of the intermolecular isotope effect. The rate ratio is given by equation 7, where A stands for the "ene" adduct and C stands for the starting cyclopropene.

$$\frac{k_{(H)}}{k_{(D)}} = \frac{A_{(H)}}{A_{(D)}} \times \frac{C_{(43)}}{C_{(33)}} \quad \text{Equation 7}$$

The intermolecular isotope effect $k_{(H)}/k_{(D)}$ was found to be 1.25 ± 0.03 .

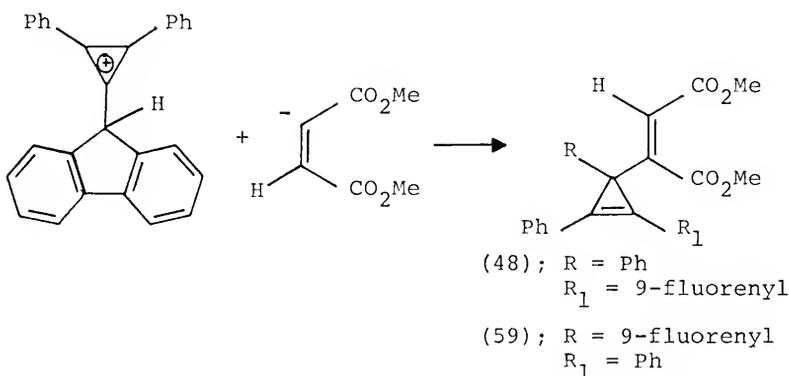
TABLE 1.3
 RATES OF FORMATION OF "ENE" ADDUCTS (34) AND (45)

Adduct	Run no.	Concn.	Temp. °C	Rate $10^{-6} k_2, \text{ m l}^{-1} \text{ s}^{-1}$	E_a		ΔS^\ddagger cal./mole log.A
					E_a kcal./mole	ΔS^\ddagger	
(34)	1	0.522 ^a	99.8	7.73 ± .23	18.0 ± 0.9	-36.7 ^c	5.2
	2	0.501	99.8	7.17 ± .28			
	1	0.481 ^a	120.4	25.2 ± .51	20.7 ± 0.4	-25.6 ^c	7.6
	2	0.481	120.4	26.4 ± .11			
(45)	1	0.521 ^b	100.1	169 ± 5.7	20.7 ± 0.4	-25.6 ^c	7.6
	2	0.254	100.1	156 ± 2.5			
	1	0.500 ^b	120.4	667 ± 7.7	20.7 ± 0.4	-25.6 ^c	7.6
	2	0.504	120.4	650 ± 3.8			

^aInitial molar concentration of triphenylcyclopropene (33). ^bInitial molar concentration of both triphenylcyclopropene (33) and dimethyl acetylenedicarboxylate (20). ^cAt 120.4°.

Discussion

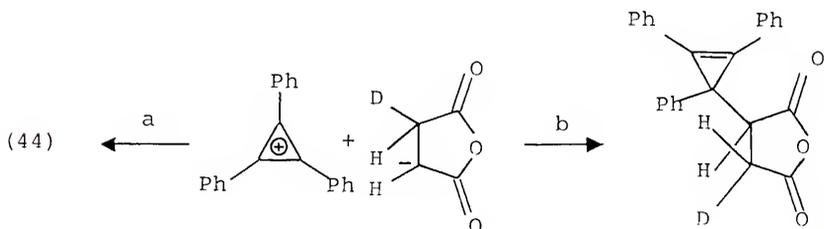
The results obtained from the investigation of the mechanism of the "ene" reactions of cyclopropenes point toward a concerted rather than a stepwise process. The formation of a single "ene" adduct from the reactions of (33) with the eneophiles (1), (3), and (20) is inconclusive, but the isolation of a single "ene" adduct from the reaction of (47) with (20) does appear to support a concerted process. If this reaction were proceeding by complete hydride transfer to the eneophile, the unsymmetrically substituted cyclopropenium cation (58) would be formed as the product determining intermediate. Subsequent combination of (58) with the corresponding anion would be expected to yield two products, (48) and (59).



Charge distribution and steric requirements in (58) might favor combination at one of the phenyl-substituted carbons to give (48), but complete absence of the thermody-

namically more stable product (59) appears unlikely in light of the fact that unsymmetrically substituted cyclopropenium salts containing three substituents other than hydrogen yield mixtures of cyclopropene products when treated with sodium borohydride, methyl lithium, or methyl magnesium iodide.⁵⁴ For example, diphenyl-methylcyclopropenium perchlorate, upon treatment with methyl lithium at -70° , gives approximately equal amounts of 1,2-diphenyl-3,3-dimethylcyclopropene and 1,3-diphenyl-2,3-dimethylcyclopropene, while the same salt with methyl magnesium iodide gives the same products in a seven to one ratio.⁵⁴ Sodium borohydride reduction of diphenyl-p-tolylcyclopropenium perchlorate yields a mixture of 1,3-diphenyl-2-p-tolylcyclopropene and 1,2-diphenyl-3-p-tolylcyclopropene in which the former predominates.⁵⁴

The stereospecific cis-addition of 3-d-triphenylcyclopropene (43) to maleic anhydride also supports a concerted mechanism. A stepwise process, involving hydride transfer, might be expected to yield a mixture of products resulting from cis- or trans- addition to maleic anhydride, represented by paths a and b respectively.



Likewise, hydride transfer from the cyclopropene to the eneophile, resulting in formation of a tight ion pair which could then collapse both regiospecifically and stereospecifically, is also consistent with formation of a single product from the unsymmetrical cyclopropene (47) and the stereospecific cis-addition of (33) and (43) across the double bond of maleic anhydride.

Even though the zwitterionic mechanism or tight ion pair mechanism could explain the formation of a single product in the reactions of unsymmetrical cyclopropenes with eneophiles, the negligible solvent effects observed for the reaction of (33) with dimethyl acetylenedicarboxylate (20) argues strongly against mechanisms involving significant charge generation. For reactions proceeding from neutral reactants to charged intermediates, it may be said that the more polar the solvent, the faster the reaction will be, since the intermediate ion or ion pairs will be better solvated by more polar solvents. The same is true if there is considerably more charge generated in the transition state than in the reactants; enhanced solvation of the transition state leading to a lowering of the energy of activation, which is reflected in an enhance rate. Since no significant rate increase was observed in the reaction of (33) with (20) when the solvent was changed from carbontetrachloride to bromobenzene to nitrobenzene, the dielectric constants of which are 2.22, 5.40, and 34.8,⁵⁶ respectively, a reaction pathway involving generation of a cyclopropenium cation or

zwitterionic intermediate is very unlikely. However, a concerted process involving some degree of charge separation in the transition state is not incompatible with this result since any positive charge generated in the cyclopropene moiety of the transition state would be dispersed throughout the ring, thus decreasing the demand for external solvation by polar solvents. Huisgen and Pohl have also investigated the effect of solvent on the "ene" reaction of 1,3-diarylpropenes with diethyl azodicarboxylate (3)²⁷ and observed only a four-fold rate enhancement on changing the solvent from cyclohexane to nitrobenzene. This result, coupled with product studies, led to the conclusion that a concerted process was operating.

The results from the competitive study involving the "enes" (33) and 1,2-diphenyl-3-p-tolylcyclopropene (56) and the eneophile (20) are also supportive of a concerted mechanism. The observed rate ratio, $k_{(56)}/k_{(33)} = 1.13$, indicates that this reaction is only slightly sensitive to substituent effects. A single point Hammett ρ value of -0.31 is determined for the "ene" reaction of 1,2-diphenyl-3-arylcyclopropenes with dimethylacetylene dicarboxylate (20). This value is consistent in both magnitude and sign with reactions involving cyclic transition states. For example, the rearrangement of p-substituted cinnamyl ethers at 180° exhibits a ρ value of -0.40 ⁵⁷ and the Diels-Alder reaction of 1-aryl-substituted butadienes with maleic anhydride at 45° displays a ρ value of -0.61 .⁵⁸

The small ρ value observed for the "ene" reaction leads to the conclusion that there is little charge development in the transition state. This conclusion may be biased, however, because any charge generated at C_3 of the cyclopropene in the transition state will not be localized at this carbon, but will be dispersed throughout the cyclopropene ring, thus decreasing the effect of substituents. Although additional substituents should be examined to obtain an accurate ρ value, there is no reason to believe that the one point ρ value determined for this "ene" reaction is not of the proper magnitude and sign.

The large negative entropies of activation observed for the dimerization of (33) and the reaction of (33) with (20), -36.7 eu and -25.6 eu, respectively, are also consistent with a concerted process. These values are in good agreement with the ΔS^\ddagger value of -36 eu observed for the Diels-Alder reaction of cyclopentadiene with maleic anhydride,⁵⁹ and the ΔS^\ddagger values of -40.7 and -31.8 eu obtained by Franzus for the "ene" reactions of 1,3- and 1,4-cyclohexadienes respectively with diethyl azodicarboxylate.²⁶

Although concerted, bimolecular processes are accompanied by large, negative entropies of activation, these values are, of themselves, insufficient to prove such a mechanism since reactions proceeding from neutral reactants to dipolar or ionic intermediates also exhibit similar entropy effects due to increased orientation of the surrounding solvent molecules. Of course, reactions proceeding

through a dipolar or ion pair intermediate would be sensitive to changes in solvent and that is not the case in these "ene" reactions.

Although the isotope effect, $k_{(H)}/k_{(D)} = 1.27$, observed for the reaction of (33) with (20), is relatively small in comparison to the intramolecular value of 2.8 reported by Huisgen²⁷ for the reaction of 1,4-dideuterio-1,4-dihydronaphthalene with diethyl azodicarboxylate or the intermolecular value of 1.99 reported by Dai and Dolbier²⁹ for the reaction of allene with perfluorocyclobutanone, the most satisfactory rationalization seems to require a concerted mechanism.

The primary isotope effect arises largely from the difference in zero-point energy between a bond to hydrogen and a corresponding bond to deuterium. The major portion of the kinetic isotope effect results from changes in the zero-point energy which occurs when reactants are converted into an activated complex. The difference in zero-point energy for C-H and C-D bonds is estimated from their corresponding zero-point vibration energy to be roughly 1.15 kcal/mole. If this stretching vibration is lost in the transition state, then the difference in E_a^\ddagger for the C-H bond and C-D bond will be 1.15 kcal/mole, which at 298°C corresponds to a rate factor of about seven. Although this is a somewhat simplified treatment, experimental data confirm that, for reactions involving a linear, symmetrical transition state, isotope effects of five to seven are generally observed.

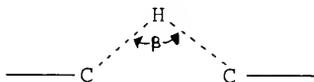
Obviously, the primary isotope effect of 1.25 observed for the "ene" reaction of (33) with (20) is smaller than the maximum effect, so that the reaction cannot proceed through a linear symmetrical transition state. Examples of small primary isotope effects are numerous and rationalization of these low values generally consider three possibilities.

First, the maximum isotope effect calculated from the zero-point energies of the C-H and C-D bonds assumes a symmetrical transition state. If the C-H bond is only slightly perturbed at the transition state and the stretching vibration is still strong, then the effect of deuterium substitution on the rate will be much smaller. The effect would be similar in the event of a very late, or product-like transition state in which the new bond to hydrogen is almost completely formed. This dependence of isotope effect on the position of the transition state is nicely demonstrated by the variable isotope effects observed for base-catalyzed proton removal from carbon, the variations rationalized in terms of the differences in basicity between the proton donors and proton acceptors.^{60,61}

Secondly, a significant primary isotope effect will be observed only if a C-H bond is broken in the rate-determining step.⁶² Slow formation of an intermediate followed by fast removal of a proton in the product-determining step usually results in a negligible intermolecular effect.

Finally, a broad group of reactions in which primary isotope effects are small are those proceeding via non-

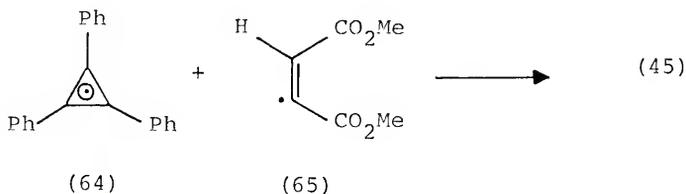
linear transition states.⁶³ Examples of this class include low isotope effects observed in 1,2-hydrogen shifts,⁶⁴ E₂ eliminations,⁶⁵ and other hydrogen transfer processes proceeding via three,⁶⁶ four, five, and six membered cyclic transition states. Theoretical explanations for and calculations of these low isotope effects observed for reactions proceeding through non-linear transition states have been discussed by O'Ferrall.⁶³ A qualitative agreement was obtained by correlating the isotope effect with the β -angles (63) of hydrogen migration in the transition state, the magnitude of the effect increasing from 0.9 to 3.0 as the β -angle increased from 60° to 120°. These effects were calculated assuming equality of bond breaking and bond formation in the transition state. Since the concerted "ene" mechanism proceeds through a six-membered cyclic transition state, small intermolecular isotope effects should be observed.



(63)

Considering the first possibility, a linear, unsymmetrical abstraction of hydrogen from (33) by dimethyl acetylenedicarboxylate (20) appears unlikely. Abstraction of a hydrogen from (33) should result in the formation of two

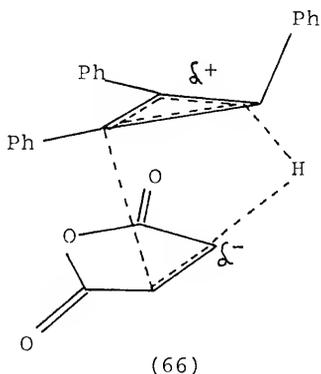
radical species (64) and (65). Although combination of these radicals could account for the observed product, one might question why only one product is observed when unsymmetrical cyclopropenes are employed. Also, (64) is much less stable than the corresponding cyclopropenium cation, owing to the presence of the odd electron in an anti-bonding molecular orbital,⁶⁷ and is known to undergo fast dimerization to bis-triphenylcyclopropene.⁶⁸ None of this product or the subsequent rearrangement product, hexaphenylbenzene was detected in this reaction. Further, Breslow has previously demonstrated that the dimerization of (33) via the "ene" reaction did not proceed by a radical mechanism.³⁸



A stepwise mechanism is more attractive than the radical mechanism, but as previously discussed, still cannot account for all of the experimental observations, especially the negligible solvent effects.

The mechanism most compatible with all the experimental results is a concerted one, involving a cyclic transition

state similar to that first described by Arnold⁶ to account for the condensation reactions of maleic anhydride with olefins. This process should not be interpreted as being completely synchronous; indeed, some charge development in the transition state might be anticipated and as previously discussed, would not be incompatible with the negligible solvent effects or small ρ -value observed in these "ene" reactions. Furthermore, the intermolecular kinetic isotope effect of 1.25 anticipates, by the treatment of O'Ferrall,⁶³ a β -angle of approximately 80° . This angle seems to be rather small for these reactions but to the extent that hydride character is developed in the transition state, that is bond breaking and bond formation become unequal, a larger and more reasonable β -angle would be predicted. The transition state (66), proposed for these reactions, is given below.



One might predict, from the mechanistic picture proposed here, that the ability of an electrophilic reagent to stabilize any negative charge developed in the transition state would be a factor in determining its ability to participate in the "ene" reaction involving the cyclic mechanism depicted on the preceding page. Indeed, this appears to be the case; maleic anhydride requiring higher reaction temperatures and longer reaction times than dimethyl acetylenedicarboxylate, which in turn is less reactive than diethyl azodicarboxylate.

Having concluded that the thermal "ene" reactions of the cyclopropenes (33) and (47) proceed via a concerted mechanism, the enhanced reactivity of triphenylcyclopropene (33) with respect to 1,2,3-triphenylpropene (53) toward the eneophile dimethyl acetylenedicarboxylate (20) must be rationalized.

One explanation for the disparity in rates may result from the differences in the orientation of the reacting centers in these molecules. Both Hill and Arnold have recently demonstrated that the preferred orientation of the "ene" component is the one in which the allylic carbon-hydrogen bond is perpendicular to the carbon-carbon double bond.^{5,31} In (33), this geometry is inherent, a consequence of the rigidity of the three membered ring system. In (53), however, models indicate that a perpendicular arrangement of either of the allylic hydrogens with the double bond results in non-bonded interactions between the

phenyl substituents and that these interactions are at a minimum when the allylic phenyl substituent is perpendicular to the double bond.

A second factor which may increase the reactivity of (33) with respect to (53) is the disposition of the phenyl substituents bound to the carbon-carbon double bond. Internal bond compression in the cyclopropene ring results in an external θ (C=C-Ph) angle of about 150° ,⁶⁹ compared to the estimated θ (C=C-Ph) angle of 120° for (53). This increased angle results in a greater intramolecular distance between the phenyl substituents, allowing them to assume a more planar alignment with the double bond in (33) than is possible in (53). Thus, in (53), where the phenyl substituents are more skewed, steric inhibition to approach by the eneophile could contribute to the decreased reactivity of this olefin.

An alternate explanation may be found in the electronic nature of the double bonds of the "ene" components. Electronic effects on the rates of the related Diels-Alder reaction have been extensively investigated. The general rule, originally proposed by Alder,⁷⁰ that electron withdrawing substituents at the double bond of the dieneophile enhances the rate of the Diels-Alder reaction, has firm experimental support. Sauer, for example, has found that the rate of reaction of cyclopentadiene with dieneophiles increases by a rate factor of greater than 10^7 in going from acrylonitrile to tetracyanoethylene.⁷¹

Recently a second class of Diels-Alder reactions, in which the electron demand is reversed, have been investigated. In these reactions, electron donating substituents at the double bond of the dieneophile enhance its reactivity toward electron deficient dienes. The reactivity of the electron-poor diene hexachlorocyclopentadiene with various dieneophiles demonstrates this type of electron demand. Thus, Sauer has found that the electron-rich system, cyclopentadiene, acting as a dieneophile, reacts by a factor of about 10^3 times faster with this diene than does the electron-poor dieneophile maleic anhydride.⁷² In addition, changes in the electronic nature of the diene has a pronounced effect on the rate of Diels-Alder reactions with a given dieneophile, as shown by the fact that maleic anhydride reacts 5×10^4 times faster with 9,10-dimethylantracene than with hexachloropentadiene.⁷²

A qualitative explanation for these two types of Diels-Alder reactions has been offered by Sustmann.⁷³ In the normal Diels-Alder reaction, the prominent bonding interaction is between the highest occupied molecular orbital (HOMO) of the diene and the lowest unoccupied molecular orbital (LUMO) of the dieneophile. By introducing electron withdrawing substituents in the dieneophile, and thus lowering its orbital energies, this interaction is enhanced. Likewise, electron donating groups in the diene will raise its orbital energies and again produce an increased interaction between its (HOMO) and the dieneophile (LUMO). This

interaction is increased more rapidly than the concomitant decrease in the interaction of the diene (LUMO) and dieneophile (HOMO), resulting in a net energy gain. In the inverse electron demand case, where the diene is now electron deficient and the dieneophile electron rich, just the opposite interactions predominate. Now, the major bonding interaction involves the diene (LUMO) and the dieneophile (HOMO). Electron donating groups in the dieneophile increase this interaction as do electron withdrawing groups in the diene.

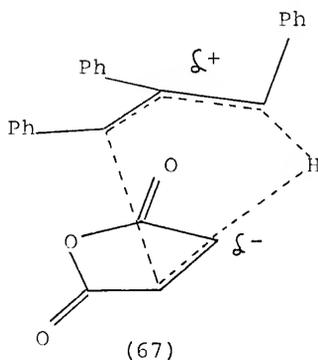
One class of dieneophiles that react readily with electron-poor dienes is the cyclopropene ring system. Battiste and co-workers⁷⁴ have shown that triphenylcyclopropene (33) reacts smoothly with the electron deficient dienes tetraphenylcyclopentadienone and 3,6-disubstituted tetrazines. Although strain relief undoubtedly plays an important part in these facile transformations, it cannot explain the differences in reactivities of cyclopropenes with these dienes. Whereas (33) reacts conveniently with 3,6-diphenyltetrazine in refluxing benzene in 80% yield, 3-carbomethoxy-1,2-diphenylcyclopropene gives only 32% reaction with the same diene after refluxing in benzene for fourteen days. Replacing the C₃-phenyl substituent in (33) with the electron withdrawing carbomethoxy substituent greatly reduces the reactivity of the cyclopropenyl double bond, demonstrating that the electron-rich nature of this double bond plays an important factor in its ability to interact with electron-poor dienes.

Photoelectron spectroscopy provides a quantitative measure of the orbital energies of the highest occupied molecular orbitals of unsaturated bonds. The ionization potentials for the compounds 1,2-diphenylcyclopropene, trans-stilbene, and cis-stilbene are 7.57,⁷⁵ 8.00,⁷⁶ and 8.20⁷⁶ eV respectively. The (HOMO) of 1,2-diphenylcyclopropene is, therefore, about 0.4 eV higher in energy than that of trans-stilbene and about 0.6 eV higher than that for cis-stilbene, and as a result, is better able to mix with the (LUMO) of electron-poor dienes.

The "ene" reaction is also subject to the same electronic influences found operating in the Diels-Alder reaction. Eneophiles bearing two electron withdrawing groups are more reactive than those containing only one such group and electron-rich "ene" components show greater reactivity than their electron-poor counterparts. In their "ene" reactions cyclopropenes participate as the "ene" component and therefore, the electron-rich nature of the cyclopropenyl double bond relative to the double bond of propenes, should facilitate reaction with electron-poor eneophiles just as electron-rich dienes are facilitated in their reactions with electron-poor dieneophiles.

The effects described above may be considered to be primarily identified as structural effects. The operation of specific stabilizing effects in the transition state (66) for reaction of (33) with (20) may also be considered. Relative to the transition state (67), involved in the

reaction of (53) with (20), (66) contains an extra bonding interaction in the "ene" component of the transition state that should provide added stabilization. Also, to the extent that charge is developed in the two transition states, the cyclopropenium character in (66) will allow greater stabilization than in (67). In the extreme case of complete hydride transfer from the "ene" component to the enophile, this added stabilization would be the difference in delocalization energy between a triphenylcyclopropenium cation and a 1,2,3-triphenylallylic cation.



Although it is difficult to access which, if any, of the aforementioned steric and electronic factors is most responsible for the enhanced reactivity of triphenylcyclopropene (33) toward dimethyl acetylenedicarboxylate (20), their cumulative effect at least offers a reasonable explanation for the observed results.

CHAPTER IV

EXPERIMENTAL

Physical Measurements

General

Melting points were taken on a Thomas-Hoover capillary melting point apparatus. All melting and boiling points are reported uncorrected.

Elemental analyses were performed by Atlantic Microlab, Incorporated, Atlanta, Georgia.

Spectra

Infrared spectra were recorded on a Perkin-Elmer 137 Infrared spectrophotometer as potassium bromide pellets or liquid films on sodium chloride or silver chloride plates. Infrared absorptions are given in cm^{-1} and are described as: w = weak, m = medium, s = strong, vs = very strong, sh = sharp, and b = broad.

Ultraviolet spectra were recorded on a Cary Model 15 recording spectrophotometer, using Beckman 1 cm cells. Reported maxima are given in nanometers and are followed by the extinction coefficient, (ϵ).

All nuclear magnetic resonance spectra were recorded in

deuteriochloroform (CDCl_3) with tetramethylsilane (TMS) as the internal standard unless otherwise stated. All spectra were obtained using a Varian A-60A or Varian XL-100 spectrometer.

Mass spectra were obtained on a Hitachi Perkin-Elmer RMU-6E instrument or on an AEI MS-30 high resolution instrument at an ionizing voltage of 70 electron volts.

Reactions

Diphenylacetylene (39)⁴³

A solution of trans-stilbene (45.0 g, 0.25 moles) in 750 ml of ether was prepared in a 1-liter three-necked round-bottomed flask equipped with a mechanical stirrer, reflux condenser, and dropping funnel. Bromine (14 ml, 43 g, 0.27 moles) was added dropwise over fifteen minutes to the stirred trans-stilbene solution. Stirring was continued for an additional hour, and the precipitate collected on a Buchner funnel and washed with ether until the washing were colorless. After air drying, 1,2-dibromo-1,2-diphenylethane (69.0 g, 80%) was obtained as a white solid, mp 234-236° (Lit.⁴³ mp 235-237°).

A solution of potassium hydroxide (90 g, 0.62 moles) in 150 ml of absolute ethanol was prepared in a 500-ml round-bottomed flask equipped with a reflux condenser and heated with an oil bath maintained at 130-140°. The dibromostilbene prepared above was added in small portions, replacing the reflux condenser after each addition. The reaction solution was heated at 130-140° for 24 hours and

then poured into 750 ml of cold water. The product was collected on a filter, washed with water, and dried over calcium chloride in a vacuum desiccator. Crude diphenylacetylene was obtained as a brown solid (37.8 g, 83%) and was dissolved in a minimum amount of hexane and chromatographed over a column of florex eluting with hexane. After removing the elutant under reduced pressure the residue was recrystallized from absolute ethanol, yielding diphenylacetylene (39) (31.7 g, 70%) as white prisms, mp 60-62° (Lit.⁴³ mp 60-61°).

1,2,3-Triphenylcyclopropenium
bromide (40) ⁴²

A solution of diphenylacetylene (39) (23.0 g, 0.129 moles) and potassium tert-butoxide (70.1 g, 0.620 moles) in 1500 ml of freshly distilled benzene (from P₂O₅) was prepared in a 3-liter three-necked round-bottomed flask equipped with a mechanical stirrer, dropping funnel, reflux condenser and nitrogen purge. Freshly distilled benzal chloride (48.4 g, 0.305 moles) in 150 ml of dry benzene was added dropwise over a period of 1 hour. The reaction mixture was refluxed for five hours, cooled to room temperature and quenched with 300 ml of water. The benzene layer was separated and dried over magnesium sulfate and the aqueous layer was extracted with ether and the extracts dried over magnesium sulfate. The benzene solution was filtered and concentrated to 200 ml, the ether extracts

filtered into the concentrated benzene solution and the resulting mixture diluted to 1500 ml with ether. The ether-benzene mixture was stirred and saturated with a stream of hydrogen bromide gas. The precipitate that formed was collected on a filter, washed with ether and dried under vacuum, yielding triphenylcyclopropenium bromide (40) (24.2 g, 54%) as a yellow-brown powder, mp 253-256°.

1,2,3-Triphenylcyclopropene (33)⁴²

1,2,3-Triphenylcyclopropene was prepared from triphenylcyclopropenium bromide by the method of Battiste.⁴² A suspension of triphenylcyclopropenium bromide (38.3 g, 0.110 moles) in absolute ethanol (200 ml) was prepared in a 1-liter three-necked round bottomed flask equipped with a dropping funnel, mechanical stirrer and nitrogen purge. A suspension of sodium borohydride (5.5 g, 0.15 moles) in 100 ml of absolute ethanol was added dropwise over a period of 1 hour. The reaction mixture was stirred for an additional three hours, cooled to 0°, and quenched with 250 ml of water. The product was collected on a filter, washed twice with cold 95% ethanol and air dried. The crude (33) thus obtained was placed on a column of alumina and eluted with hexane. After removing the elutant under reduced pressure, (33) (28.5 g, 96%) was obtained as a white solid, mp 107-109°. Recrystallization from ethanol yielded (33) (26.9 g, 91%) as white plates, mp 110-111° (Lit.³⁸ mp 110-112°).

3-(1',2',3'-Triphenylcyclopropyl)-1,2,3-triphenylcyclopropene (34)³⁸

A solution of triphenylcyclopropene (33) (0.268 g, 1.00 mmoles) in chlorobenzene (2 ml) was heated at reflux with magnetic stirring for 44 hours. After cooling the reaction mixture to room temperature, the solvent was removed under a stream of nitrogen and the oily residue that remained was dissolved in a 1:1 benzene-hexane solution and cooled. The precipitate that formed was collected on a filter, washed with hexane and recrystallized from the same solvent system. The precipitate was again collected on a filter, washed with hexane and dried under vacuum, yielding (34) (0.092 g, 34%) as colorless prisms, mp 179-180° (Lit.³⁸ mp 178.5-181°).

1-(1',2',3'-Triphenylcyclopropenyl)-succinic anhydride (41)

Triphenylcyclopropene (33) (0.268 g, 1.00 mmoles), freshly sublimed maleic anhydride (0.098 g, 1.00 mmoles) and bromobenzene (5 ml) were stirred at 130° for 40 hours. After cooling to room temperature, the reaction mixture was examined by thin layer chromatography. Several components were detected and separation by column chromatography was attempted. The solvent was evaporated under a stream of nitrogen and the reaction residue was placed on a column of silica gel and eluted with hexane, 4:1 hexane-benzene, benzene, and 7:3 benzene-chloroform. The collected

fractions (30 ml) were combined on the basis of their thin layer behavior. The first three components to elute were, in order of elution, (33) (0.043 g, 12%), 1,2-diphenylindene (42) (0.082 g, 22%), and dimer (34) (0.060g, 16%), identified by their nmr spectra and melting points. The final component to elute was identified as the "ene" adduct (41). Recrystallization from benzene-petroleum ether yielded colorless plates (0.147 g, 40%), mp 171-173°.

The nmr spectrum (CDCl_3) showed an aromatic multiplet at δ 8.00-7.30(15H) and an ABX multiplet characterized by the chemical shifts 4.30 (1H), 3.07 (1H), and 2.97 (1H), and the coupling constants $J_{\text{gem}} = 18.5$, $J_{\text{cis}} = 6.9$, and $J_{\text{trans}} = 9.1$ Hz.

The infrared spectrum (KBr) showed absorptions for carbon-hydrogen stretch at 3080 (w), 3060 (w), and 3030 (w), carbon-oxygen double bond stretch at 1860 (s) and 1760 (vs), along with other absorptions at 1600 (m), 1492 (s), 1445 (s), 1415 (w), 1220 (s), 1072 (s), 1050 (s), 900 (m), 758 (s), 733 (s), 690 (s), and 630 (w).

The mass spectrum showed a molecular ion at m/e 366.1263 (21%), (calcd., 366.1255), a P+1 ion at m/e 367.1284 (5%), (calcd., 367.1288), and other abundant fragments at m/e 325 (base peak), 267 (80%), and 105 (50%).

The ultraviolet spectrum (95% ethanol) showed maxima at 330 (19,800), 314 (24,700), 295 (18,800) along with strong end absorption.

cis-1-(1',2',3'-Triphenylcyclopropyl)-2-d-succinic anhydride (44).

3-d-1,2,3-Triphenylcyclopropene (43) (0.269 g, 1.00 mmoles), freshly sublimed maleic anhydride (2.94 g, 30.0 mmoles), and chlorobenzene (10 ml) were heated at reflux for 44 hours. The reaction mixture was cooled to room temperature and examined by thin layer chromatography. Several components were detected and separation of the "ene" adduct from the hydrocarbon products by column chromatography was attempted. The solvent was removed under a stream of nitrogen and the reaction residue placed on a column of silica gel. The hydrocarbon products were eluted with 9:1 hexane-benzene and when thin layer examination revealed that no more material was being eluted, the elutant was changed to 6:4 hexane-chloroform. The collected fractions (30 ml) were combined on the basis of their thin layer behavior. The solvent was removed under reduced pressure and the residue was recrystallized from benzene-petroleum ether, yielding (44) (0.161 g, 43%) as colorless plates, mp 174-175.

The nmr spectrum (CDCl_3) showed an aromatic multiplet at 7.90-7.15 (15H), a sharp doublet at 4.28 (1H, $J=10.0$ Hz), and a broad doublet 3.05 (1H, $J=10.0\text{Hz}$).

The infrared spectrum (KBr) showed carbon-hydrogen stretch at 3050 (w), carbon-oxygen stretch at 1860 (s) and 1780 (vs) and other absorptions at 1490 (m), 1445 (m),

1220 (m), 1090 (m), 1075 (m), 930 (s), 915 (s), 880 (m), 792 (m), 775 (m), 760 (s), 733 (m), and 690 (s) cm^{-1} .

The ultraviolet spectrum (95% ethanol) showed maxima at 330 (19,800), 314 (23,600), and 295 nm (18,600) along with a strong end absorption.

Dimethyl-1-(1',2',3'-triphenylcyclopropenyl)-maleate (45)

Triphenylcyclopropene (0.268 g, 1.00 mmoles) and freshly distilled dimethyl acetylenedicarboxylate (20) (0.710 g, 5.00 mmoles) were dissolved in chlorobenzene (15 ml) and stirred at 100° for 42 hours. The reaction mixture was cooled to room temperature and examined by thin layer chromatography. In addition to starting material, a new component was detected and separation by column chromatography was attempted. The solvent was removed under a stream of nitrogen and the reaction residue was placed on a column of silica gel and eluted with hexane. This failed to elute any material and the elutant was changed to benzene. The collected fractions (30 ml) were combined on the basis of their thin layer behavior. Removal of the solvent resulted in an oil which was taken up in benzene-petroleum ether and cooled. The precipitate was collected on a filter, washed with cold petroleum ether and air dried, yielding the adduct (45) (0.233 g, 57%) as colorless prisms, mp 121-122°.

Anal. Calcd. for $\text{C}_{27}\text{H}_{22}\text{O}_4$: C, 79.00; H, 5.40.

Found: C, 78.99; H, 5.44.

The nmr spectrum (CDCl_3) showed aromatic multiplets at δ 7.95-7.65 (4H) and 7.65-7.11 (11H), and sharp singlets at 5.93 (1H), 3.65 (3H), and 3.50 (3H).

The infrared spectrum (KBr) showed carbon-hydrogen stretch at 3030 (w), 2990 (w), and 2930 (w), cyclopropenyl carbon-carbon double bond stretch at 1840 (w), carbon-oxygen double bond stretch at 1730 (s) and 1710 (s), and carbon-carbon double bond stretch at 1630 (m), along with other absorptions at 1495 (m), 1440 (s), 1430 (s), 1345 (s), 1275 (s), 1240 (m), 1195 (s), 1170 (s), 1110 (s), 1035 (m), 976 (m), 879 (m), 866 (m), 791 (m), 767 (m), 753 (s), 734 (m), 706 (s), and 683 (s) cm^{-1} .

The mass spectrum showed a molecular ion at m/e 410 (7%), along with other abundant fragments at m/e 319 (15%), 318 (25%), 292 (26%), 291 (73%), 290 (38%), 288 (base peak), 276 (18%), 267 (8%), 215 (29%), and 77 (17%).

The ultraviolet spectrum (95% ethanol) showed maxima at 330 (16,000), 314 (17,600), 285 (13,600), 235 (23,100) and 228 nm (23,600).

Ethyl hydraazodicarboxylate⁴⁶

Hydrazine hydrate (20 g, 0.42 moles) and 95% ethanol (250 ml) were placed in a 1-liter three-necked round-bottomed flask equipped with two dropping funnels and a thermometer and cooled to 10° with an ice water bath. One dropping funnel was charged with ethyl chloroformate (87 g, 0.80 moles) and the other with potassium carbonate (55 g,

0.43 mmoles) and water (250 ml). Ethyl chloroformate was added dropwise with stirring while maintaining the temperature of the reaction solution between 15-20°. After approximately one-half of the ethyl chloroformate had been added, simultaneous dropwise addition of the potassium carbonate solution was begun, always maintaining an excess of ethyl chloroformate and a temperature below 20°. During the addition, a white solid formed. After all the reactants had been added, the precipitate on the upper walls of the flask was washed down with water and the reaction mixture was stirred for an additional hour. The solid was then collected on a filter, washed with cold water and dried in an oven at 80°, yielding ethyl hydrazodicarboxylate (43.1 g, 61%) as a white solid, mp 130-132° (Lit.⁴⁶ mp 131-133°).

Ethyl azodicarboxylate (3)⁴⁶

Ethyl hydrazodicarboxylate (43 g, 0.24 moles) and 70% nitric acid (100 ml) were placed in a 500-ml three-necked round-bottomed flask equipped with a thermometer, mechanical stirrer and gas outlet tube and cooled to 5° with an ice-water bath. Cold, fuming nitric acid (100 ml) was added and the reaction mixture stirred at 5° for 2 hours. The dark orange reaction mixture was then cautiously stirred into a mixture of ice (250 g), water (250 ml) and methylene chloride (250 ml). The organic layer was separated and the acid layer was extracted with three 100 ml

portions of cold water, stirred for ten minutes with cold 10% potassium carbonate solution (300 ml), washed twice more with cold water and dried over magnesium sulfate. After filtering, the solvent was removed under reduced pressure and the reaction residue was vacuum distilled. Ethyl azodicarboxylate (24.1 g, 58%) was collected as an orange oil at 106-111°/15 mm.

Diethyl-1-(1'2'3'-triphenylcyclopropenyl)-hydraazodicarboxylate (46)

Triphenylcyclopropene (0.268 g, 1.00 mmoles) and diethyl azodicarboxylate (0.174 g, 1.00 mmoles) were dissolved in toluene (20 ml) and heated at reflux for 14 hours. The reaction mixture was cooled to room temperature and examined by thin layer chromatography. Two components were detected, the faster moving of which was identified as (33). Separation was attempted by fractional crystallization. The solvent was removed under a stream of nitrogen and the residue was taken up in methylene chloride-petroleum ether and cooled. The precipitate was collected on a filter, washed with cold petroleum ether and air dried, yielding (46) (0.314 g, 71%) as a white powder, mp 138.5-141°. Recrystallization from ethanol-petroleum ether gave (46) (0.298 g, 67%) as small white prisms, mp 140-141°.

Anal. Calcd. for $C_{27}H_{26}N_2O_4$: C, 73.28; H, 5.92; N, 6.30.

Found: C, 73.24; H, 5.93; N, 6.41.

The nmr spectrum (CDCl_3) showed aromatic multiplets at δ 7.90-7.60 (4H), and 7.60-7.00 (11H), a sharp singlet at 6.78 (1H), overlapping quartets at 4.11 (2H, $J = 7.0$ Hz), and 4.01 (2H, $J = 7.0$ Hz), and two triplets at 1.08 (3H, $J = 7.0$ Hz) and 1.03 (3H, $J = 7.0$ Hz).

The infrared spectrum (KBr) showed absorptions for nitrogen-hydrogen stretch at 3230 (s), carbon-hydrogen stretch at 2910 (m), cyclopropenyl carbon-carbon double bond stretch at 1820 (w), carbon-oxygen double bond stretch at 1695 (s), along with other absorptions at 1510 (s), 1470 (m), 1425 (m), 1375 (m), 1350 (m), 1250 (s), 1155 (m), 1053 (s), 768 (m), 771 (s), 761 (s), 741 (m), 710 (s), and 693 (s) cm^{-1} .

The mass spectrum showed a molecular ion at m/e 442.5 (0.2%) along with other abundant fragments at m/e 325 (16%), 297 (16%), 280 (22%), 268 (24%), 267 (base peak), 77 (16%), and 29 (47%).

The ultraviolet spectrum (95% ethanol) showed maxima at 318 (20,350), 303 (24,000) and 290 nm (19,100) along with strong end absorption.

1,2-Diphenylcyclopropene-3-
carboxylic acid⁷⁷

Freshly distilled ethyl diazoacetate (14.9 ml, 16 g, 0.14 moles) was added dropwise over a 5 hour period to a mixture of diphenylacetylene (50 g, 0.28 moles), cyclohexane (30 ml) and anhydrous copper sulfate (0.07 g) prepared in

a 500-ml three-necked round-bottomed flask equipped with a mechanical stirrer, dropping funnel, reflux condenser and nitrogen purge and heated with an oil bath maintained at 125°. When the addition was complete, the reaction mixture was cooled to room temperature and 150 ml of a 10% methanolic potassium hydroxide solution (11 g of potassium hydroxide in 100 ml of methanol) was added dropwise. The resulting dark red solution was heated at reflux for 4 hours, cooled to room temperature and diluted with 1 liter of water. The unreacted diphenylacetylene was removed by extraction with hexane. The aqueous solution was cooled to 5° with an ice-water bath and acidified to a pH of less than four by the dropwise addition of concentrated hydrochloric acid. The crude cyclopropene acid was collected on a filter, washed with water and air dried. The crude acid was placed on a column of florex and eluted with chloroform. The solvent was removed and the residue recrystallized from acetone, yielding 1,2-diphenylcyclopropene-3-carboxylic acid (9.8 g, 38% based on diphenylacetylene consumed) as white prisms, mp 209-211° (Lit.⁷⁷ mp 209-211°).

Diphenylcyclopropenium perchlorate⁴⁷

A slurry of 1,2-diphenylcyclopropene-3-carboxylic acid (6.0 g, 25 mmoles) in acetic anhydride (20 ml) was added in one portion to an ice cold solution of perchloric acid in acetic anhydride, prepared by adding 6.6 ml of

cold 70% perchloric acid to 40 ml of ice cold acetic anhydride, in a 250-ml three-necked round-bottomed flask equipped with a mechanical stirrer and nitrogen purge. The resulting dark brown suspension was stirred at 0° for 2.5 hours. Ether was then added and the precipitate collected on a filter, washed extensively with ether and air dried to give diphenylcyclopropenium perchlorate (4.6 g, 61%) as a light tan solid, mp 148-150° (Lit.⁴⁷ mp 148.5-150.5°)

1,2-Diphenyl-3-(9'fluorenyl)-
cyclopropene⁴⁸

A solution of fluorene (1.664 g, 10.00 mmoles) in dry ether (15 ml) was prepared in a 100-ml three-necked round-bottomed flask equipped with a reflux condenser, syringe cap and nitrogen purge. n-Butyl lithium (7.4 ml, 10 mmoles) was added via syringe over a period of 30 minutes. The orange reaction mixture was then stirred at reflux for 1.5 hours, cooled to room temperature and added via syringe to a stirred suspension of diphenylcyclopropenium perchlorate (1.162 g, 4.000 mmoles) in ether (25 ml) at -78° prepared in a 50 ml round-bottomed flask equipped with a syringe cap, until the orange color remained. The reaction mixture was stirred at -78° for 30 minutes, warmed to room temperature, extracted with dilute hydrochloric acid, brine, and water, dried over anhydrous sodium sulfate, filtered and the solvent removed under reduced pressure.

The yellow residue was placed on a column of acidic alumina (activity 1) and eluted with hexane. The collected fractions (30 ml) were combined on the basis of their thin layer behavior. The solvent was evaporated and the residue recrystallized from benzene-petroleum ether. The product was collected on a filter, washed with petroleum ether and air dried to yield 1,2-diphenyl-3-(9'-fluorenyl)-cyclopropene (0.320 g, 22%) as white needles, mp 169-170° (Lit.⁴⁸ mp 170-171.5°)

Dimethyl-1-[2'-(9''-fluorenyl)-1',3'-
diphenylcyclopropenyl]-maleate (48)

A solution of 1,2-diphenyl-3-(9'-fluorenyl)-cyclopropene (0.064 g, 0.18 mmoles) and dimethyl acetylenedicarboxylate (0.026 g, 0.18 mmoles) in bromobenzene (3 ml) was heated at 100° for 18 hours. The reaction mixture was cooled to room temperature and examined by thin layer chromatography. In addition to a small amount of starting material, one major component was observed and separation by column chromatography was attempted. The solvent was removed under a stream of nitrogen and the reaction residue was placed on a column of silica gel and eluted with hexane to remove the unreacted (47). The elutant was then changed to 4:1 hexane-chloroform and 20 ml fractions were collected and combined on the basis of their thin layer behavior. The solvent was removed under reduced pressure, yielding (48)

as a waxy orange material (0.065 g, 72%). Attempts to crystallize this product from hexane, hexane-benzene, chloroform-hexane, and methanol were all unsuccessful.

The nmr spectrum (CDCl_3) showed an aromatic multiplet at δ 7.8-6.9 (18H), a singlet at 5.80 (1H), a broad singlet at 5.33 (1H), a singlet at 3.60 (3H), and a singlet at 3.55 (3H).

The infrared spectrum (film on AgCl) showed carbon-hydrogen stretch at 2950 (m), cyclopropene carbon-carbon double bond stretch at 1840 (w), carbon-oxygen double bond stretch at 1760 (s) and 1720 (s), and carbon-carbon double bond stretch at 1650 (m), along with other absorptions at 1490 (m), 1475 (m), 1450 (s), 1355 (m), 1035 (m), 978 (m), 887 (m), 762 (s), 745 (s), and 698 (s) cm^{-1} .

The mass spectrum showed a molecular ion at m/e 498.1830 (67%), (calcd., 498.1838) along with other abundant fragments at m/e 466 (22%), 439 (29%), 437 (63%), 407 (32%), 379 (45%), 376 (50%), 351 (25%), 302 (25%), 265 (20%), 189 (19%), 188 (22%), 180 (23%), 166 (31%), 165 (base peak), and 163 (12%).

The ultraviolet spectrum (95% ethanol) showed maxima at 300 (8,700), 287 (10,500) and 255 nm (23,400) along with strong end absorption.

Attempted reaction of Triphenyl-
cyclopropene (33) with 1,4-benzoquinone

Triphenylcyclopropene (0.268 g, 1.00 mmoles) and freshly sublimed 1,4-Benzoquinone (0.108 g, 1.00 mmoles) were dissolved in chlorobenzene (2 ml). A 1-ml aliquot of the resulting solution was sealed in an nmr tube and heated at 130° for 19 hours. The reaction mixture was cooled to room temperature and examined by nmr spectroscopy. In addition to starting material, the only new product was shown by comparison with an authentic sample to be the dimer (34). None of the desired "ene" adduct was detected and further investigation of this eneophile was discontinued.

Attempted Reaction of Triphenyl-
cyclopropene (33) with 1,4-Naphthaquinone

Triphenylcyclopropene (0.178 g, 0.664 mmoles) and freshly sublimed 1,4-naphthaquinone (0.105 g, 0.662 mmoles) were dissolved in benzene (2 ml) and heated at reflux for 24 hours. The reaction mixture was cooled to room temperature and examined by nmr spectroscopy. In addition to starting material, the only new product was a small amount of dimer (34), identified by comparison with an authentic sample. None of the desired "ene" adduct was detected and this reaction was not investigated further.

Attempted reaction of Triphenyl-
cyclopropene (33) with diethyl maleate

Triphenylcyclopropene (0.108 g, 0.403 mmoles) and diethyl maleate (0.138 g, 0.802 mmoles) were dissolved in chlorobenzene (2 ml) and a 1 ml aliquot of the resulting solution was sealed in an nmr tube and heated at 105° for 140 hours. The reaction mixture was cooled to room temperature and examined by nmr spectroscopy. The concentration of diethyl maleate was unchanged and the only new signal corresponded to the dimer (34). No "ene" adduct from the reaction of (33) with dimethyl maleate was detected and this reaction was not investigated further.

Attempted Reaction of Triphenyl-
cyclopropene (33) with Diethyl fumarate

Triphenylcyclopropene (0.108 g, 0.403 mmoles) and diethyl fumarate (0.138 g, 0.802 mmoles) were dissolved in chlorobenzene (2 ml) and a 1 ml aliquot of the resulting solution was sealed in an nmr tube and heated at 105° for 48 hours. The reaction mixture was cooled to room temperature and examined by nmr spectroscopy. The concentration of diethyl fumarate was unchanged and the only new signal corresponded to the dimer (34), and this reaction was not investigated further.

Attempted Reaction of Triphenyl-
cyclopropene with Bromomaleic anhydride

Triphenylcyclopropene (0.068 g, 0.25 mmoles) and bromomaleic anhydride (0.177 g, 1.00 mmoles), as supplied by Aldrich Chemicals, were dissolved in chlorobenzene (1 ml) and the resulting solution was sealed in an nmr tube and heated at 130°. After two hours, the reaction solution was cooled to room temperature and examined by nmr spectroscopy. The signal corresponding to the C₃ hydrogen of (33) was absent and a new signal corresponding to 1,2-diphenylindene was observed. The solvent was removed under a stream of nitrogen and the reaction residue was placed on a column of silica gel and eluted with hexane. After the solvent was removed, the residue was taken up in petroleum ether and cooled. The precipitate was collected on a filter and washed with cold petroleum ether and air dried, yielding 1,2-diphenylindene (0.059 g, 87%) as white needles, mp 177-178°.

Attempted Reaction of Triphenyl-
cyclopropene (33) with Chloromaleic anhydride

Triphenylcyclopropene (0.030 g, 0.11 mmoles) and chloromaleic anhydride (0.25 g, 0.53 mmoles), supplied as a 50% mixture with maleic anhydride by Aldrich Chemicals, were dissolved in chlorobenzene (1 ml) and the resulting solution was sealed in an nmr tube and heated at 130° for 5 hours. The reaction mixture was cooled to room temperature

and examined by nmr spectroscopy. The signal corresponding to the C₃ hydrogen of (33) was completely consumed and a new signal corresponding to 1,2-diphenylindene was observed. The solvent was removed under a stream of nitrogen and the residue dissolved in petroleum ether and cooled. The precipitate was collected on a filter, washed with cold petroleum ether and air dried, yielding 1,2,-diphenylindene (0.023 g, 77%) as white needles, mp 176-178°.

Attempted Reaction of Triphenyl-
cyclopropene (33) with 4-Phenyl-
1,2,4-Triazoline-3,5-dione (49)

A solution of 4-phenyl-1,2,4-triazoline-3,5-dione (0.525 g, 3.00 mmoles) in methylene chloride (25 ml) was added dropwise to a solution of triphenylcyclopropene (0.804 g, 3.00 mmoles) in methylene chloride (100 ml) prepared in a 250 ml three-necked round-bottomed flask equipped with a dropping funnel and nitrogen purge and cooled to 0° with an ice-water bath. The reaction mixture was stirred for 1 hour, after which time the dark red color of (49) was discharged and a pale yellow solution remained. The solvent was removed under reduced pressure and the residue dissolved in ether. Hexane was added and the precipitate that resulted was collected on a filter, washed with cold hexane and air dried to yield a white fluffy solid (1.157 g, 87%), mp 264.5-265.5°.

The nmr spectrum (CDCl_3) showed an aromatic multiplet at δ 7.85-7.00 (20H), and a singlet at 6.43 (1H).

The infrared spectrum (KBr) showed nitrogen-hydrogen stretch at 3450 (m), carbon-oxygen stretch at 1785 (s) and 1730 (vs) and other absorptions at 1600 (w), 1505 (m), 1405 (s), 1290 (m), 1140 (w), 1080 (w), 1025 (w), 763 (s), 750 (m), and 697 (s) cm^{-1} .

The mass spectrum showed a parent ion at m/e 443 (20%), along with other abundant fragments at m/e 366 (24%), 322 (82%), 267 (24%), and 119 (base peak).

The ultraviolet spectrum (95% ethanol) showed a broad maxima at 305 nm.

Attempted Reaction of Triphenyl-
cyclopropene (33) with 4-Methyl-
1,2,4-triazoline-3,5-dione (50)

A solution of 4-methyl-1,2,4-triazoline-3,5-dione (0.034 g, 0.30 mmoles) in methylene chloride (5 ml) was added dropwise to a solution of triphenylcyclopropene (0.081 g, 0.30 mmoles) in methylene chloride (5 ml) prepared in a 25-ml three-necked round-bottomed flask equipped with a dropping funnel and nitrogen purge and cooled to 0° with an ice-water bath. The reaction mixture was stirred at 0° for 45 minutes, during which time the dark red color of (50) was discharged and a pale yellow solution remained. The solvent was removed under reduced pressure and the

residue dissolved in ether. Hexane was added and the resulting precipitate was collected on a filter and washed with hexane, yielding a white fluffy solid (0.067 g, 58%), mp 238-243°.

The nmr spectrum (CDCl_3) showed an aromatic multiplet at δ 7.80-7.10 (15H), a singlet at 6.30 (1H), and a singlet at 3.0 (3H).

The infrared spectrum (KBr) showed nitrogen-hydrogen stretch at 3400 (m), carbon-oxygen double bond stretch at 1735 (s) and other absorptions at 1600 (m), 1545 (m), 1497 (m), 1445 (m), 1235 (w), 1075 (w), 1030 (w), 975 (w), 770 (m), 760 (m), 733 (w), and 697 (s).

The mass spectrum showed a molecular ion at m/e 381 (base peak) along with other abundant fragments at m/e 351 (71%), 304 (94%), 295 (79%), 267 (32%) and 105 (24%).

The ultraviolet spectrum (95% ethanol) showed maxima at 317 (8,660), 303 (10,500) and 287 nm (9890).

Phenylbenzyl ketone (54)⁴⁹

Phosphorous trichloride (56 g, 0.40 moles) was added to phenylacetic acid (54.4 g, 0.400 moles) in a 1 liter three-necked round-bottomed flask equipped with a reflux condenser and gas outlet tube leading to a potassium hydroxide trap. The reaction mixture was heated at 90-100° until gas evolution ceased, cooled to room temperature and examined by nmr spectroscopy. No phenylacetic acid was detected and the phenylacetic acid chloride was used in the

preparation of phenylbenzyl ketone without further purification.

Benzene (400 ml) was added to the phenylacetic acid chloride prepared in the previous reaction and the solution was decanted into a dry 1 liter round-bottomed flask and cooled to 10° with an ice-water bath. Aluminum chloride (60 g, 0.47 moles) was added in portions and the resulting solution was heated at reflux for 1 hour. The reaction mixture was then cooled to 10° and cautiously poured into a mixture of ice (500 g) and concentrated hydrochloric acid (200 ml). The organic layer was separated and the acid layer was extracted three times with ether. The ether extracts were combined with the original organic layer and washed twice with water, twice with 5% aqueous potassium carbonate and twice more with water, dried over anhydrous sodium sulfate, filtered and the solvent removed under reduced pressure. The brown solid that remained was distilled under reduced pressure. Phenylbenzyl ketone was collected as a colorless oil at 144-146°/1.5 mm which gave a white solid (63.1 g, 80%) on cooling. Recrystallization from methanol yielded (54) (57.6 g, 72%) as white needles, mp 50-52° (Lit.⁴⁹ mp 53-54°).

1,2,3-Triphenyl-2-propanol (55)⁵⁰

Magnesium (2.0 g, 0.082 g at) and dry tetrahydrofuran (20 ml) were placed in a dry 100 ml three-necked round-bottomed flask equipped with a mechanical stirrer, dropping

funnel, and reflux condenser. A solution of benzyl bromide (14.4 g, 0.0851 moles) in tetrahydrofuran (10 ml) was added dropwise at such a rate as to maintain a gentle reflux. When no more magnesium was being consumed, the Grignard solution was cooled and phenylbenzyl ketone (8.7 g, 0.044 moles) in tetrahydrofuran (20 ml) was added at such a rate as to maintain a gentle reflux. After the addition was complete, the reaction mixture was heated at reflux for an additional 2 hours, cooled to 10° with an ice-water bath and quenched with dilute hydrochloric acid. The organic layer was separated and the acid layer extracted with ether. The ether extract was combined with the original organic layer, washed three times with water, dried over calcium chloride, filtered and the solvent evaporated under reduced pressure. The residue was dissolved in aqueous ethanol and cooled. The precipitate was collected on a filter, washed with water, and dried under vacuum to yield (55) (7.7 g, 61%) as white needles, mp 82-84° (Lit.⁵⁰ mp 84°)

1,2,3-Triphenylpropene (53)

1,2,3-Triphenyl-2-propanol (2.0 g, 7.2 mmoles) was dissolved in a 2:1 mixture of acetic anhydride (30 ml) and acetyl chloride (15 ml) and heated at reflux for 90 minutes. The reaction mixture was cooled and cautiously poured into 150 ml of ice water. The aqueous mixture was extracted twice with ether and the ether extracts were combined, washed with water, dried over calcium chloride, filtered and the solvent removed under reduced pressure. The residue

was placed on a column of alumina and eluted with hexane. One large reaction (150 ml) was collected, the solvent removed under reduced pressure, and the residue (1.3 g, 69%) examined by nmr spectroscopy. From the nmr spectrum (CDCl_3), the product was shown to be a 4.25:1.00 mixture of trans- and cis- (53), respectively, by comparing the integral intensities of the allylic protons of the trans-isomer at 4.09 (Lit.⁵⁰ 4.04) with the allylic protons of the cis-isomer at 3.73 (Lit.⁵⁰ 3.71). Attempts to further separate these isomers by column chromatography failed and the mixture was used in the following competitive rate study.

Comparison of the Reactivities of

Triphenylcyclopropene (33) and 1,2,3-
Triphenylpropene (53) with Dimethyl
Acetylenedicarboxylate (20)

Two solutions, one containing triphenylcyclopropene (0.134 g, 0.499 mmoles) and dimethyl acetylenedicarboxylate (0.071 g, 0.500 mmoles) and an internal standard, tetrachloroethane (0.042 g, 0.25 mmoles) in chlorobenzene (1 ml) and the other containing 1,2,3-triphenylpropene (0.135 g, 0.499 mmoles) as a 4.25:1.00 mixture of the trans- and cis-isomers, respectively, and dimethyl acetylenedicarboxylate (0.071 g, 0.500 mmoles) and tetrachloroethane (0.045 g, 0.27 mmoles) in chlorobenzene (1 ml), were prepared and sealed in separate nmr tubes. The solutions were heated

at $119.9 \pm 0.1^\circ$ and the progress of the reactions were followed by monitoring the loss of (33) and (53) with respect to the internal standard. The reaction of (33) with (20) proceeded with a half-life of 0.8 hours, but no decrease in the nmr integration of either the cis- or the trans-isomer of (53) was detected after 125 hours.

Determination of the Rate Constants
for the "Self-Ene" Reaction of
Triphenylcyclopropene

Determination of the rate constants of the "self-ene" reaction of (33) were conducted on bromobenzene solutions approximately 0.5 molar in (33) and containing a known amount of toluene as an internal standard. The rate constants were obtained at two temperatures, $99.8 \pm 0.1^\circ$ and $120.4 \pm 0.1^\circ$. Details for the preparation of the solution used in determining the rate constant obtained in Run #1 at $99.8 \pm 0.1^\circ$ are given below and all other runs were conducted on solutions prepared in a similar manner.

Triphenylcyclopropene (33), (0.6702 g, 2.497 mmoles) and toluene (0.080 g, 0.87 mmoles) were placed in a 5-ml volumetric flask and freshly distilled, dry bromobenzene was added to the mark to yield a solution 0.4994 molar in (33) and 0.17 molar in toluene. Aliquots of the reaction mixture were then transferred to clean, dry nmr tubes. The tubes were attached to a vacuum pump and the reaction mixture was frozen with a dry ice-2-propanol bath,

evacuated, thawed, frozen again, evacuated, and sealed. NMR spectroscopy was employed to obtain six determinations of the initial integral intensities of the C_3 -hydrogen of (33) and the methyl hydrogens of toluene in each tube. The sample tubes were then placed in a constant temperature oil bath maintained at $99.8 \pm 0.1^\circ$ and the progress of the reaction was monitored by removing a sample tube after a known reaction time, cooling it in an ice-water bath, and obtaining the final integral intensities of the C_3 -hydrogen of (33) and the methyl hydrogens of toluene as before. An example of the initial and final integral intensities obtained in this manner for a typical point are given in Table 1.4.

A computer program, prepared by Dr. Roy B. King of this department, was then employed to convert the initial and final integral intensities for each point into values for $1/33$ observed and $1/33$ calculated, the latter values being obtained from least squares analysis and used by the computer to calculate the corresponding second order rate constants and standard deviation. The data from the computer print-out for each kinetic run are reproduced in Tables 1.5 and 1.6.

Graphic presentations of the data from each kinetic run of this "self-ene" reaction are presented in Figures 1.6-1.9. The straight line observed by plotting x/a_0-x , where x = concentration of (33) consumed and a_0-x = concentration of (33) remaining, versus time confirms the second order nature of this reaction.

Determination of the Rate Constants
for the "ene" Reaction of Triphenyl-
cyclopropene (33) with Dimethyl Acety-
lenedicarboxylate (20)

Rate constants for the thermal "ene" reaction of (33) with (20) at $100.1 \pm 0.1^\circ$ and $120.4 \pm 0.1^\circ$ were determined in a manner identical to that employed for the "self-ene" reaction of (33). In this case, however, bromobenzene solutions containing equal molar quantities of (33) and (20), approximately 0.5 molar in each component, and a known amount of the internal standard, toluene, were employed. Details for the preparation of the solution used in determining the rate constant obtained in Run #1 at $120.4 \pm 0.1^\circ$ are given below. All other runs were conducted on solutions prepared in a similar manner.

Dimethyl acetylenedicarboxylate (0.3706 g, 2.608 mmoles) was placed in a 5-ml volumetric flask. An equal molar amount of triphenylcyclopropene (0.6996 g, 2.608 mmoles) was then placed in the flask and bromobenzene was added. The internal standard, toluene (0.046 g, 0.50 mmoles), was added and additional bromobenzene was added to the mark. Aliquots of the reaction mixture were placed in clean, dry nmr tubes and the tubes were sealed under vacuum as before. The rate constants were determined from the initial and final nmr integral intensities of the C_3 -hydrogen of (33) and the methyl hydrogens of toluene. The kinetic data obtained from the computer printout for each kinetic run are

reproduced in Tables 1.7 and 1.8. Graphic presentations of the data are shown in Figures 1.10-1.13. Again, the straight line observed by plotting $x/a - x$ versus time confirms the second order nature of this reaction.

Comparison of the Reactivities of Tri-phenylcyclopropene (33) and 1,2-Diphenyl-3-p-tolylcyclopropene (56) toward Dimethyl Acetylenedicarboxylate (20)

A solution of triphenylcyclopropene (0.1706 g, 0.6365 mmoles), 1,2,-diphenyl-3-p-tolylcyclopropene (0.1795 g, 0.6365 mmoles) and dimethyl acetylenedicarboxylate (0.035 g, 0.25 mmoles) in bromobenzene (2 ml) was heated in a sealed tube at 100° for 20 hours. The reaction mixture was cooled to room temperature, removed from the tube and examined by thin layer chromatography. Two well separated spots were observed and separation was attempted by column chromatography. The solvent was removed under a stream of nitrogen and the residue was placed on a column of silica gel and eluted first with hexane and then with 3:1 hexane-chloroform. The fractions (30 ml) were collected and combined according to their thin layer behavior. The first component to elute was shown by nmr spectroscopy to be a mixture of unreacted (33) and (56). The second component was a mixture of dimers, identified by nmr spectroscopy. The final component was a mixture of the "ene" adducts (45) and (57).

The solvent was removed under reduced pressure and the last traces of solvent removed under vacuum, yielding a white solid (0.098 g, 94%).

Determination of the composition of the "ene" adduct mixture was based upon the nmr integration ratios (vinylic-H/tolyl methyl-H) and (tolyl methyl-H/methyl ester-H) obtained from the average of six integrations of each signal. These data are shown in Table 1.9. In this manner, the tolyl methyl and vinylic signals gave a ratio of 1.60 and the methyl ester and tolyl methyl peaks gave a ratio of 3.78. From these values, the mixture was determined to consist of 53% (57) and 47% (45). By employing equation 5 the rate ratio $k_{(56)}/k_{(33)}$ was calculated to be 1.13. To determine the accuracy of this method, the ratio of the methyl ester and vinylic peaks was calculated and found to be 6.03. Regardless of the product composition, this ratio has a theoretical value of 6.00.

TABLE 1.4
 EXAMPLE OF NMR INTEGRATION FOR DIMERIZATION OF (33)

Integration no.	Area C ₃ -H of (33)	Area CH ₃ of toluene
	Initial	
1	92.0	104.5
2	91.5	102.5
3	91.5	104.5
4	91.5	102.5
5	93.5	104.5
6	91.0	103.5
	Final	
1	40.5	104.5
2	40.0	104.5
3	40.0	102.5
4	41.0	104.5
5	39.0	103.5
6	41.0	102.5

TABLE 1.5

REPRODUCTION OF COMPUTER PRINTOUTS FOR THE "SELF-ENE"
REACTION OF (33) AT $99.8 \pm 0.1^\circ\text{C}$

t sec.	$\frac{1}{(33)}$ obs.	$\frac{1}{(33)}$ calcd.	Difference
Run no. 1			
94065	2.6965	2.6422	0.0542
166000	3.1509	3.1984	-0.0475
342620	4.5676	4.5641	0.0035
434130	5.1832	5.2716	-0.08844
511230	5.9459	5.8678	0.0782
Rate constant = 0.773195×10^{-5} moles/l-sec			
Standard Deviation = 0.226478×10^{-6}			
Concentration at zero time (calcd.) = 0.5222			
Concentration at zero time (obs.) = 0.4994			
Run no. 2			
48190	2.3325	2.3430	-0.0105
99562	2.7421	2.7116	0.0304
127720	2.8207	2.9137	-0.0929
192560	3.4828	3.3788	0.1039
269340	3.9234	3.9297	-0.0063
364780	4.5900	4.6145	-0.0246
Rate constant = 0.717487×10^{-5} moles/l-sec			
Standard deviation = 0.277091×10^{-6}			
Concentration at zero time (calcd.) = 0.5007			
Concentration at zero time (obs.) = 0.4998			

TABLE 1.6

REPRODUCTION OF COMPUTER PRINTOUTS FOR THE "SELF-ENE"
REACTION OF (33) AT $120.4 \pm 0.1^\circ\text{C}$

t sec.	$\frac{1}{(33)}$ obs.	$\frac{1}{(33)}$ calcd.	Difference
Run no. 1			
17160	2.5250	2.5101	0.0149
30405	2.8095	2.8442	-0.0348
45695	3.1766	3.2299	-0.0534
61730	3.7201	3.6344	0.0856
71635	3.8991	3.8843	0.0148
92510	4.3987	4.4109	-0.0122
132430	5.4031	5.4180	-0.0149
Rate constant = 0.252258×10^{-4} moles/l-sec			
Standard deviation = 0.514555×10^{-6}			
Concentration at zero time (calcd.) = 0.4814			
Concentration at zero time (obs.) = 0.4991			
Run no. 2			
13860	2.3581	2.4456	-0.0875
32385	2.9174	2.9348	-0.0175
79815	4.2549	4.1875	0.0674
112370	5.2233	5.0474	0.1759
168900	6.4019	6.5403	-0.1384
Rate constant = 0.264107×10^{-4} moles/l-sec			
Standard deviation = 0.115703×10^{-5}			
Concentration at zero time (calcd.) = 0.4809			
Concentration at zero time (obs.) = 0.5007			

TABLE 1.7

REPRODUCTION OF COMPUTER PRINTOUT DATA FOR THE "ENE"
REACTION OF (33) WITH (20) AT $100.1 \pm 0.1^\circ$

t sec.	$\frac{1}{(33)}$ obs.	$\frac{1}{(33)}$ calcd.	Difference
Run no. 1			
2163	2.2560	2.2834	-0.0274
5125	2.7722	2.7838	-0.0115
8145	3.3005	3.2939	0.0066
10310	3.5292	3.6797	-0.1305
14713	4.6257	4.4035	0.2223
31290	7.1444	7.2038	-0.0595
Rate constant = 0.168931×10^{-3} moles/l-sec			
Standard deviation = 0.572205×10^{-5}			
Concentration at zero time (calcd.) = 0.5214			
Concentration at zero time (obs.) = 0.5314			
Run no. 2			
4800	4.7198	4.7248	-0.0050
8000	5.2139	5.2240	-0.0101
13500	6.1149	6.0821	0.0328
19100	6.9380	6.9557	-0.0177
Rate constant = 0.156003×10^{-3} moles/l-sec			
Standard deviation = 0.252685×10^{-5}			
Concentration at zero time (calcd.) = 0.2515			
Concentration at zero time (obs.) = 0.2541			

TABLE 1.8

REPRODUCTION OF COMPUTER PRINTOUT DATA FOR THE "ENE"
REACTION OF (33) WITH (20) AT $120.4 \pm 0.1^\circ$

t sec.	$\frac{1}{(33)}$ obs.	$\frac{1}{(33)}$ calcd.	Difference
Run no. 1			
1003	2.6344	2.6694	-0.0351
1590	3.0817	3.0607	0.0210
2414	3.5980	3.6100	-0.0119
3241	4.2043	4.1612	0.0431
4410	4.9445	4.9405	0.0040
6000	5.9792	6.0003	-0.0212
Rate constant = 0.666577×10^{-3} moles/l-sec			
Standard deviation = -0.773045×10^{-5}			
Concentration at zero time (calcd.) = 0.4998			
Concentration at zero time (obs.) = 0.5216			
Run no. 2			
1270	2.8289	2.8102	0.0187
1645	3.0387	3.0540	-0.0153
2225	3.3898	3.4311	-0.0413
3077	3.9784	3.9850	-0.0066
4080	4.8154	4.6371	0.1783
4588	4.8335	4.9673	-0.1338
Rate constant = 0.650127×10^{-3} moles/l-sec			
Standard deviation = 0.381965×10^{-4}			
Concentration at zero time (calcd.) = 0.5039			
Concentration at zero time (obs.) = 0.5172			

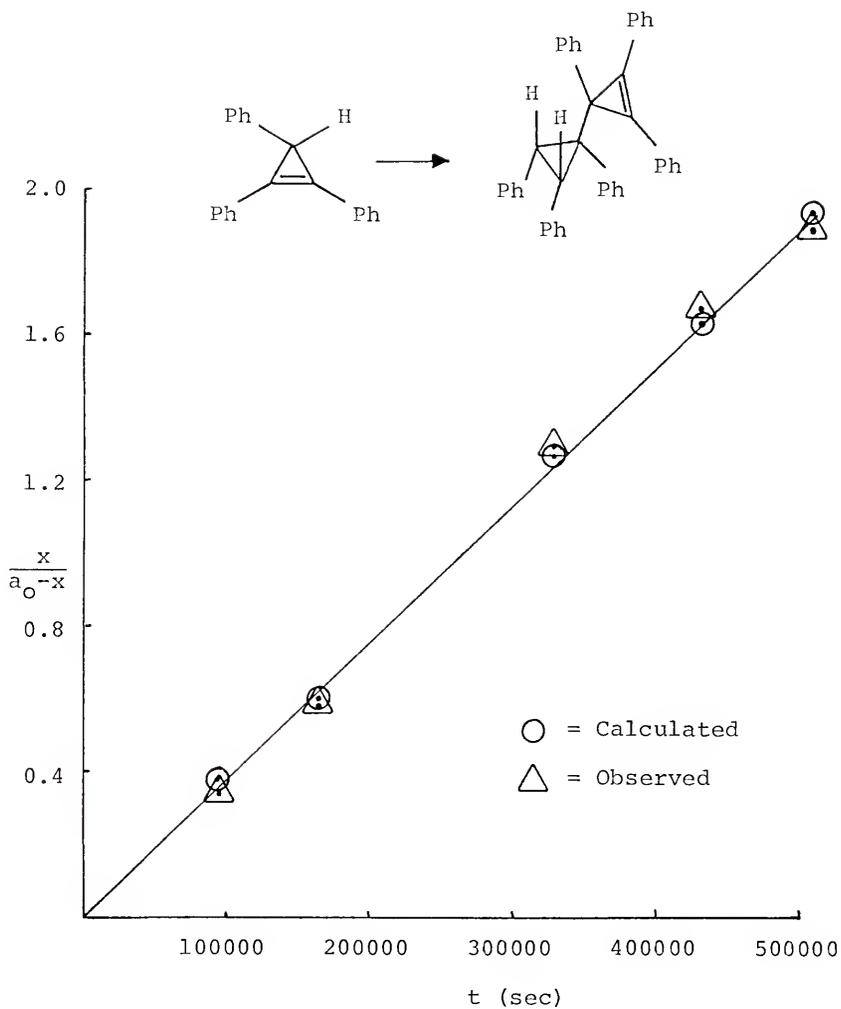


Fig. 1.6. Graphic presentation of kinetic run number 1 at $99.8 \pm 0.1^\circ$ for the "self-ene" reaction of (33).

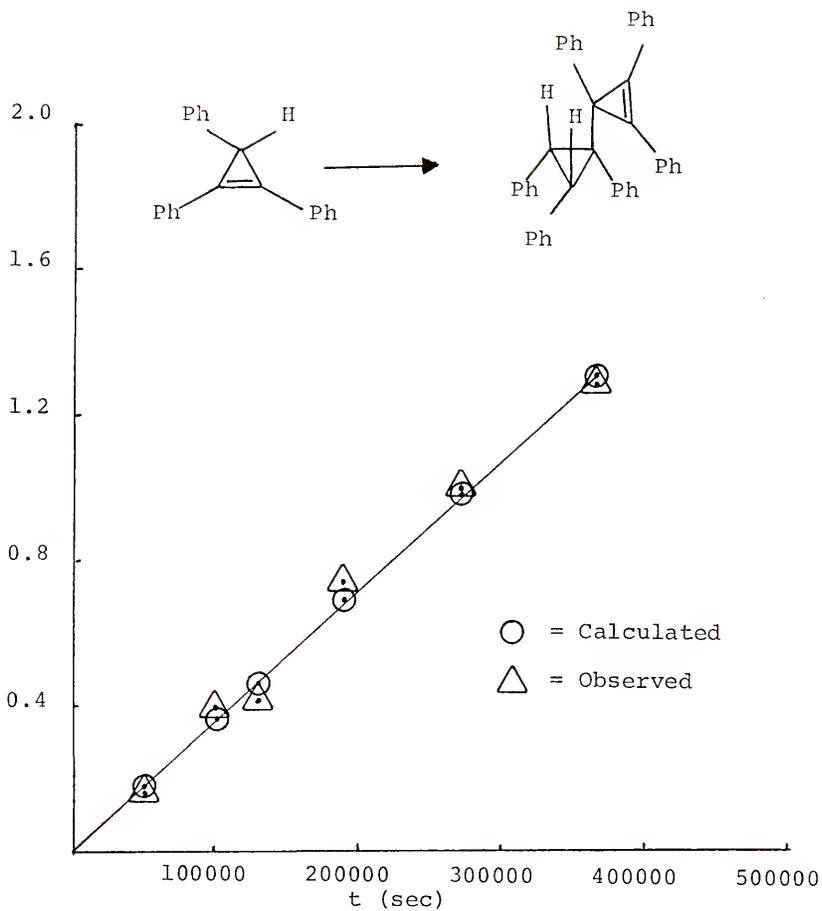


Fig. 1.7. Graphic presentation of kinetic run number 2 at $99.8 \pm 0.1^\circ$ for the "self-ene" reaction of (33).

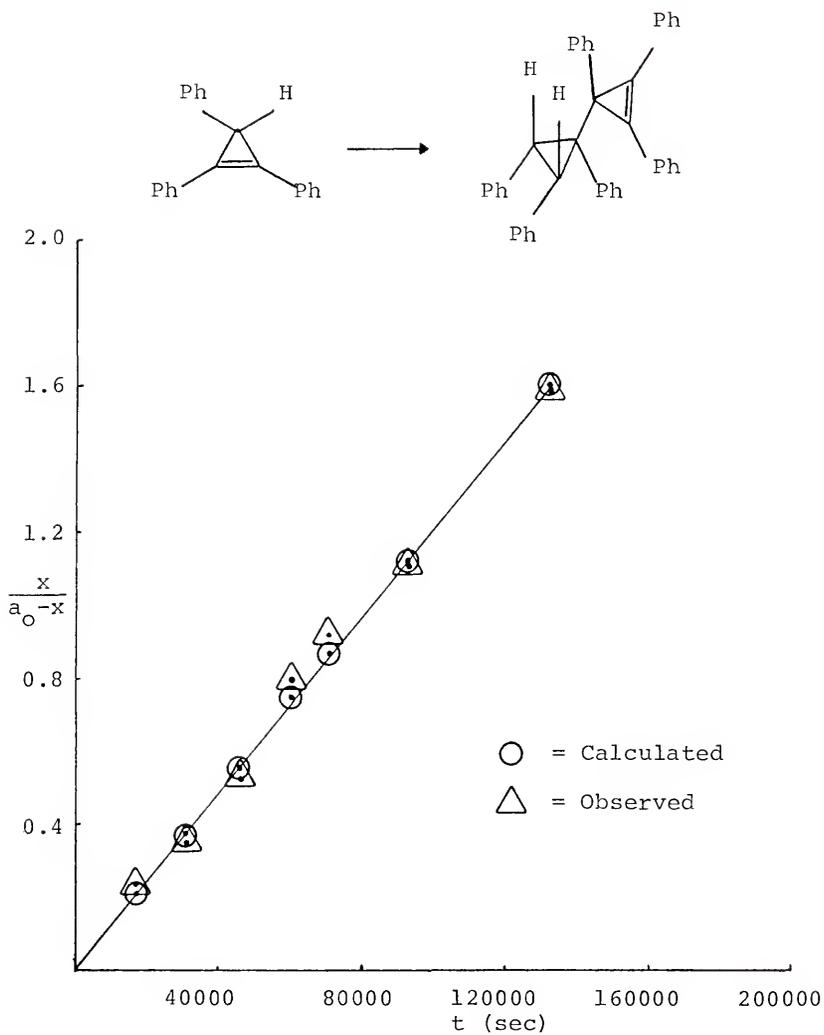


Fig. 1.8 . Graphic presentation of kinetic run number 1 at $120.4 \pm 0.1^\circ$ for the "self-ene" reaction of (33).

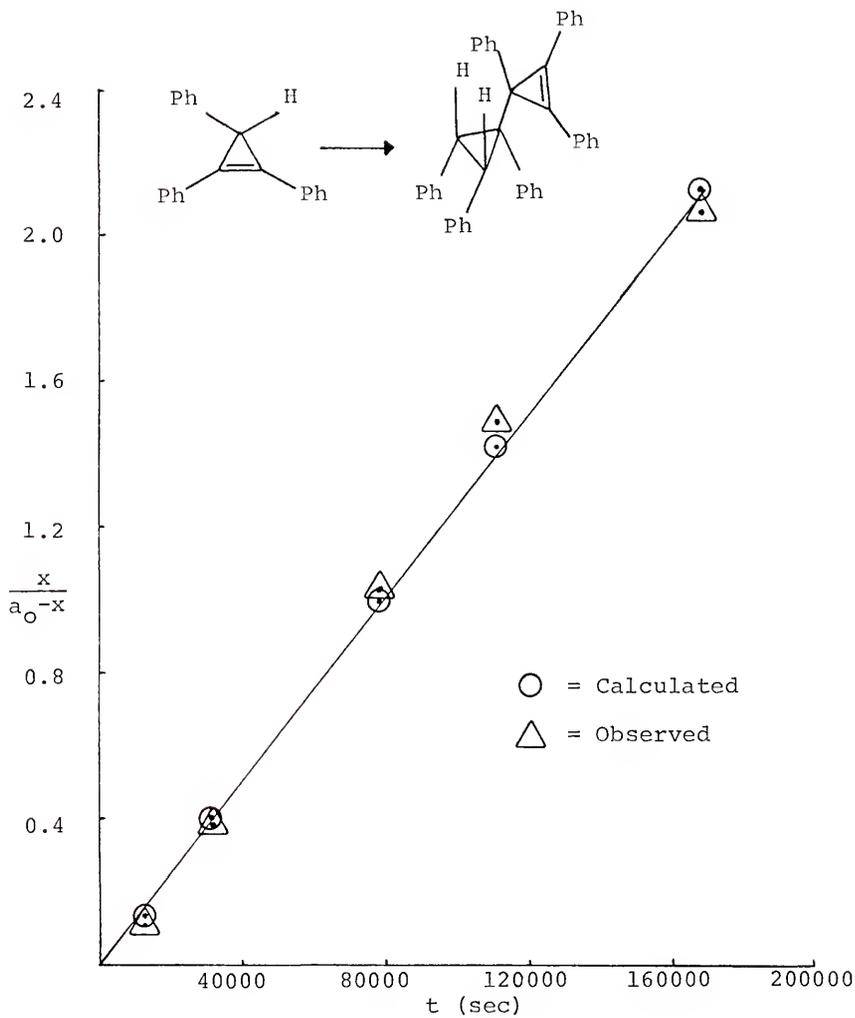


Fig. 1.9 . Graphic presentation of kinetic run number 2 at $120.4 \pm 0.1^\circ$ for the "self-ene" reaction of (33).

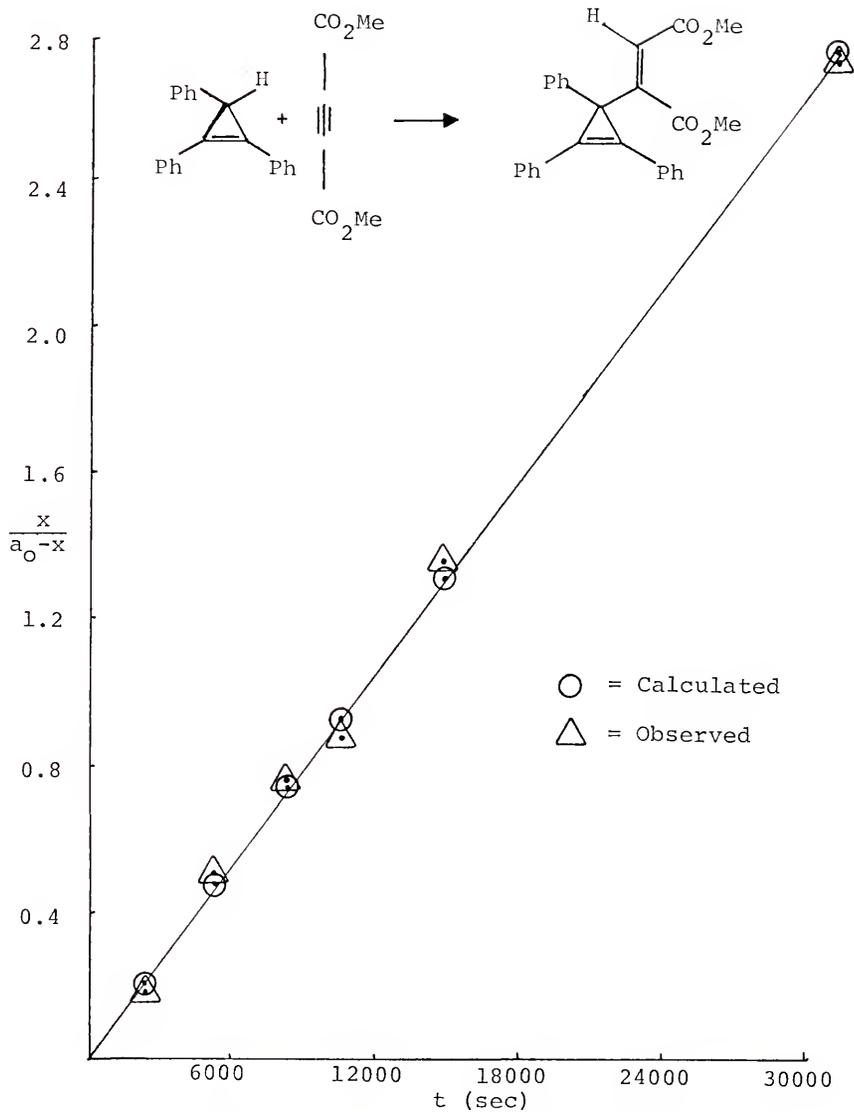


Fig. 1.10. Graphic presentation of kinetic run number 1 at $100.1 \pm 0.1^\circ$ for the "ene" reaction of (33) with (20).

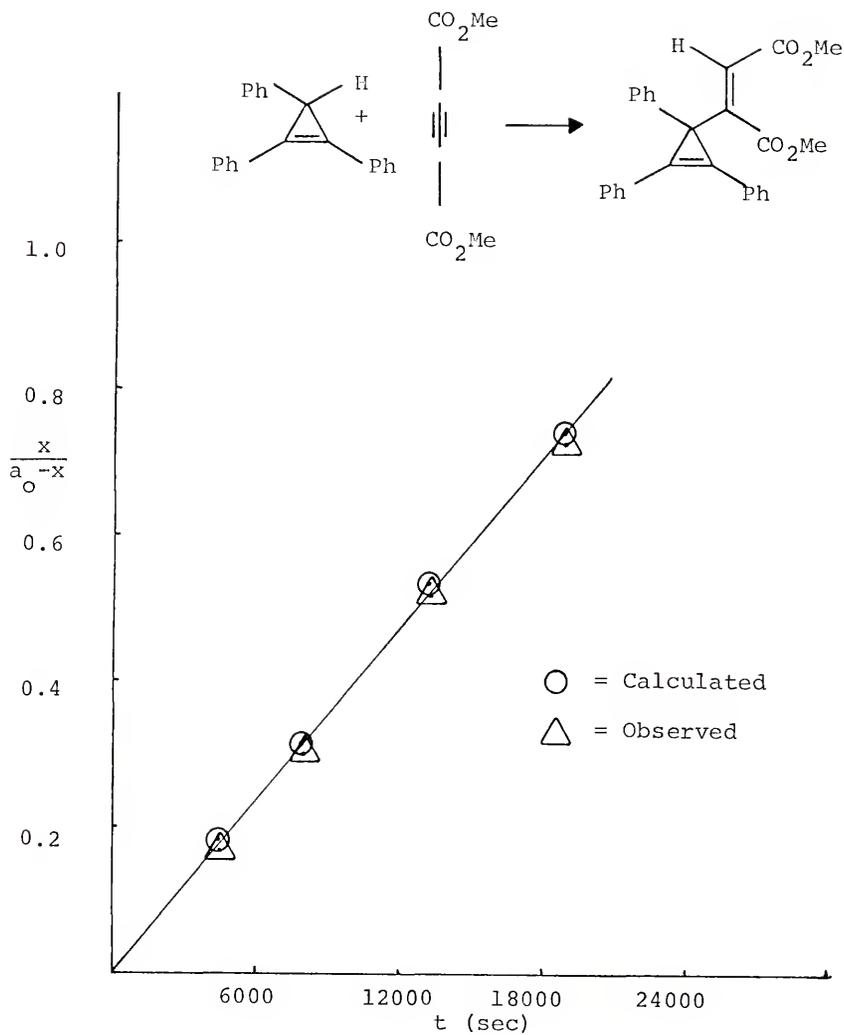


Fig. 1.11. Graphic presentation of kinetic run number 2 at $100.1 \pm 0.1^\circ$ for the "ene" of (33) with (20).

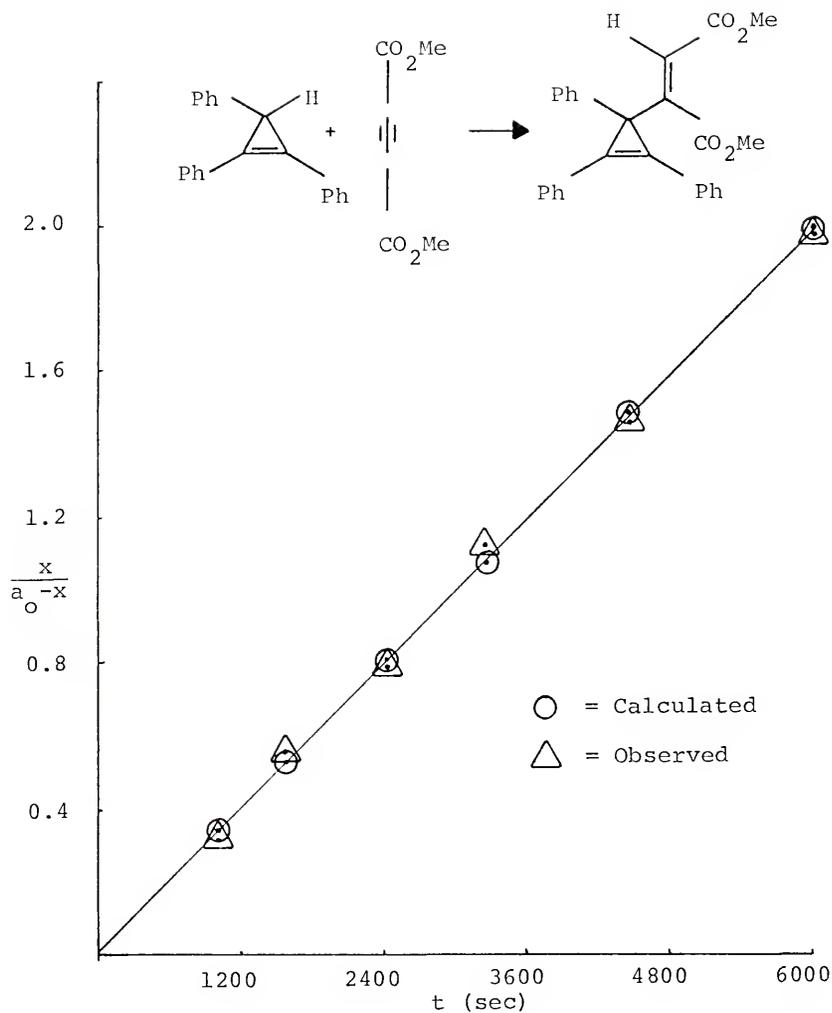


Fig. 1.12. Graphic presentation of kinetic run number 1 at $120.4 \pm 0.1^\circ$ for the "ene" reaction of (33) with (20).

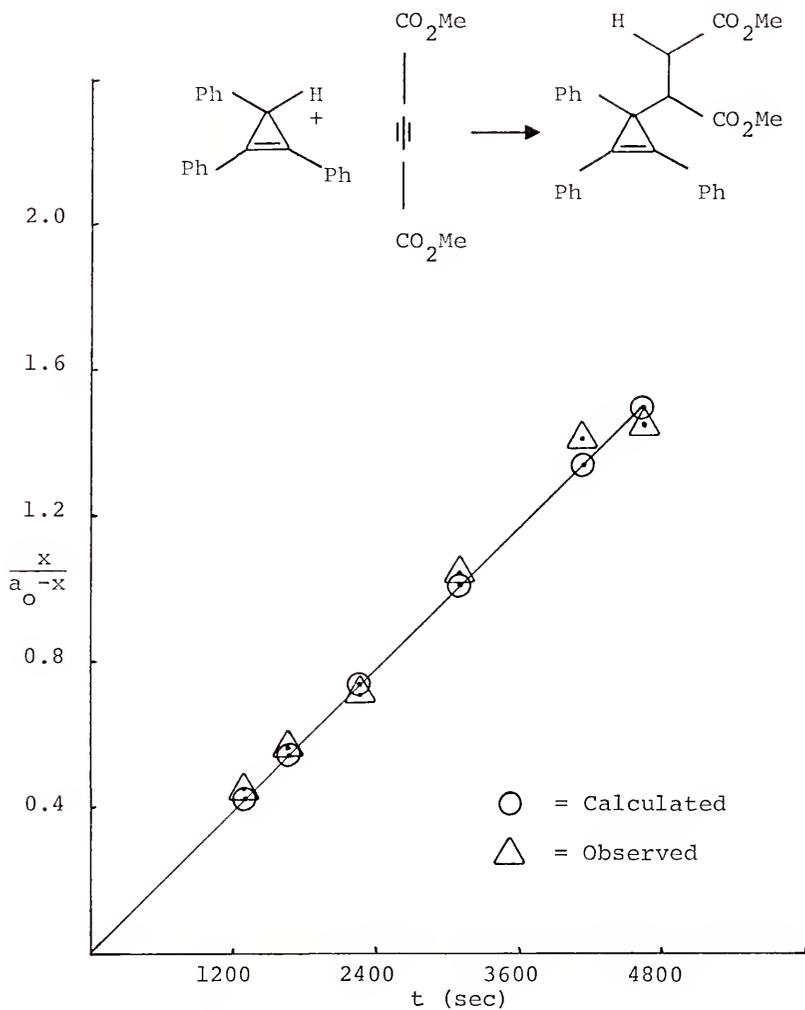


Fig. 1.13. Graphic presentation of kinetic run number 2 at $120.4 \pm 0.1^\circ$ for the "ene" reaction of (33) with (20).

TABLE 1.9

NMR INTEGRATION EMPLOYED IN DETERMINING THE RELATIVE REACTIVITIES OF CYCLOPROPENES
(33) AND (56) TOWARD DIMETHYL ACETYLENE DICARBOXYLATE

Integration no.	Area Vinyl-H	Area Methyl ester-H's	Area Tolyl methyl-H's
1	13.0	79.0	22.0
2	13.0	78.5	21.0
3	13.0	79.0	21.0
4	13.5	78.5	21.0
5	13.0	79.0	20.5
6	13.0	80.0	20.0
Average:	13.1	79.0	20.9
$\frac{\text{Methyl ester-H's}}{\text{Tolyl methyl-H's}} = 3.78 \qquad \frac{\text{Tolyl methyl-H's}}{\text{Vinyl-H}} = 1.60$			
$\frac{\text{Methyl ester-H's}}{\text{Vinyl-H}} = 6.03 \text{ (obs.)}; 6.00 \text{ (calcd.)}$			

Determination of the Intermolecular
Isotope Effect for the Reaction of Tri-
phenylcyclopropene (33) with Dimethyl
Acetylenedicarboxylate (20)

A solution of triphenylcyclopropene (0.3113 g, 1.160 mmoles), 3-d-triphenylcyclopropene (0.3124 g, 1.160 mmoles) and dimethyl acetylenedicarboxylate (0.049 g, 0.035 mmoles) in bromobenzene (3 ml) was heated at 100° for 23 hours, cooled to room temperature, and examined by thin layer chromatography. Two well separated components were detected and separation by column chromatography was attempted. The solvent was removed under a stream of nitrogen and the reaction residue placed on a column of neutral silica gel form. The fractions (30 ml) were collected and combined according to their thin layer behavior. The first component to elute was a mixture of unreacted cyclopropenes (0.3046 g). The next component was a mixture of dimers that were not characterized. The final component was a mixture of deuterated and non-deuterated "ene" adducts. The solvent was removed and the residue was recrystallized from hexane, yielding the "ene" adducts as a white solid (0.119 g, 85%).

The isotopic composition of the "ene" adduct mixture was determined from the nmr integration ratios of (methyl ester-H/vinylic-H), obtained from the average of six integrations of each signal. These values are shown in Table 1.10. In this manner, the methyl ester and vinylic signals

gave a ratio of 10.90:1.00, which corresponds to a product mixture containing 55.0% d_0 -(45) and 45.0% d_1 -(45). Employing this ratio and equation 7, the intermolecular deuterium isotope effect was calculated to be 1.22.

A second determination was obtained by employing the mixture of unreacted cyclopropenes. The isotopic composition of this mixture was determined by nmr spectroscopy from a comparison of the integral heights of the C_3 -hydrogen of (33) in an accurately weighed amount of the mixture with the integral height of the methyl protons in an accurately weighed amount of toluene. The mixture of cyclopropenes (0.3046 g, 1.133 mmoles) and toluene (0.0350 g, 0.379 mmoles) were dissolved in bromobenzene (2 ml) and the resulting solution was analysed by nmr spectroscopy. By averaging ten integrations of each peak, the integral intensities of the methyl protons of toluene and the C_3 -hydrogen of (33) were found to be 124.3 and 53.3 respectively, corresponding to a (methyl/ C_3 -H) ratio of 2.332. The calculated ratio based on a 1:1 mixture of (33) and 3-d-triphenylcyclopropene was 2.004 and the composition of the starting material was thus determined to be 42.9% d_0 and 57.1% d_1 . This mixture was then used to obtain a second determination of the intermolecular isotope effect in a manner identical to that described above. The integrations obtained from this second run are also given in Table 1.10. The methyl ester and vinylic signals gave a ratio of 12.46, which corresponds to a product

TABLE 1.10

NMR INTEGRATIONS EMPLOYED IN DETERMINING
THE KINETIC ISOTOPE EFFECT FOR THE "ENE"
REACTION OF (33) WITH (20)

Integration no.	Area Vinyllic-H	Area Methyl ester-H's
Run no. 1		
1	14.5	157.0
2	15.0	158.0
3	14.0	158.0
4	14.0	157.0
5	14.5	157.0
6	15.0	157.5
Average:	14.6	157.5
Run no. 2		
1	13.5	172.0
2	13.5	172.0
3	14.0	171.0
4	14.0	170.5
5	14.0	172.5
6	13.5	170.0
7	13.5	170.0
8	13.5	170.0
9	14.0	173.0
10	14.0	171.0
Average:	13.8	171.3

mixture containing 48.1% triphenylcyclopropene adduct and 51.9% 3-d-triphenylcyclopropene adducts. Employing this product composition and the composition of the starting material, an intermolecular isotope effect of 1.28 was calculated. Averaging the values obtained in these two runs, an intermolecular kinetic isotope effect of 1.25 ± 0.03 was obtained for this "ene" reaction.

Effect of Solvent on the Rate of the
Reaction of Triphenylcyclopropene (33)
with Dimethyl Acetylenedicarboxylate (20)

Solutions containing equal molar quantities of triphenylcyclopropene (33) and dimethyl acetylenedicarboxylate (20) were prepared in three solvents, carbontetrachloride, bromobenzene and nitrobenzene. An internal standard, toluene, was added, aliquots of the reaction mixtures were sealed under vacuum in nmr tubes, and initial ((33)/toluene) ratios were determined by comparison of the nmr integral heights of the C_3 -hydrogen of (33) and the methyl hydrogens of toluene. The reaction solutions were heated at $100.0 \pm 0.1^\circ$ and the progress of the reaction was monitored by removing the tubes at various times and determining the ratio of (33) to toluene as before. The rate constants for each solvent were determined and the results are summarized in Table 1.11.

TABLE 1.11
EFFECT OF SOLVENTS ON THE RATES OF THE REACTION
OF (33) WITH (20)

Solvent	Int. Conc. ^a	t sec	$k_p \times 10^{-4}$ m ³ l ⁻¹ -sec	k rel.
CCl ₄	0.485	3791	1.27	1.0
		7917	1.50	
		12702	1.37	
		$\overline{1.38}$ (avg)		
PhBr	0.600	3791	1.73	1.2
		7917	1.49	
		12702	1.65	
		$\overline{1.62}$ (avg)		
PhNO ₂	0.545	3791	1.94	1.5
		7917	2.18	
		12702	2.10	
		$\overline{2.07}$ (avg)		

^aMolar concentration of both triphenylcyclopropene (33) and dimethyl acetylenedicarboxylate (20).

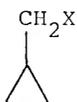
PART II

GENERATION AND REARRANGEMENT OF CYCLOPROPENYLCARBINYL ANIONS

CHAPTER I

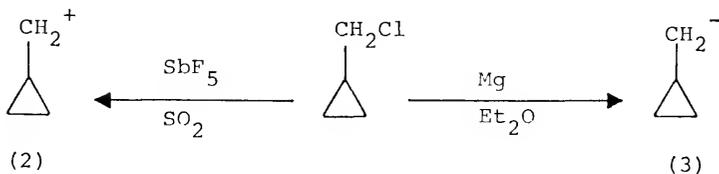
INTRODUCTION

In the last quarter of a century the most widespread and intensive investigative efforts in small ring chemistry have focused on the rearrangements of the cyclopropylcarbinyl system (1).



(1)

Two ionic species, the cyclopropylcarbinyl cation (2) and the cyclopropylcarbinyl anion (3) may be generated from (1) as shown below for their formation from cyclopropylcarbinylchloride.

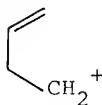


The cyclopropylcarbinyl cation (2) has received extensive attention from numerous workers.⁷⁸ It might be expected

that this cation could undergo ring expansion to form the cyclobutyl cation (4), since this rearrangement would convert a primary carbonium ion into a secondary cation and in the process relieve ring strain. Alternatively, (2) may undergo ring opening to the allylcarbinyl cation (5), again relieving strain, but retaining a primary cationic center.

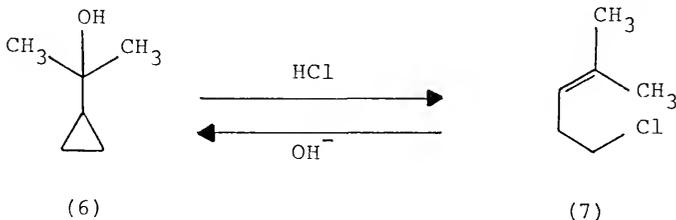


(4)



(5)

That the situation is actually more complicated was realized as early as 1928 by Breynants and Dewael.⁷⁹ These workers treated cyclopropyldimethylcarbinol (6) with hydrochloric acid and obtained the ring opened chloride (7). However, when (7) was hydrolyzed, the alcohol (6) was again formed.

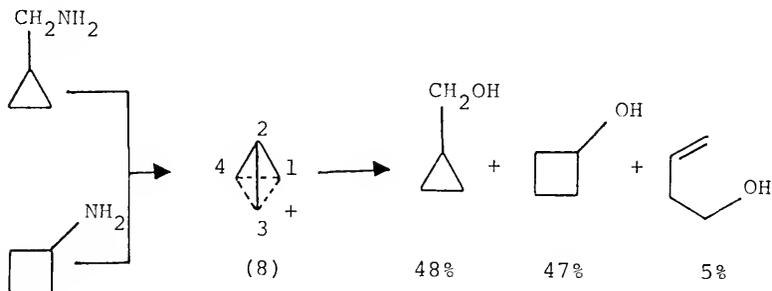


(6)

(7)

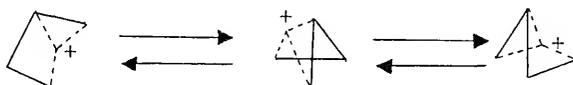
In 1951, Roberts⁸⁰ showed that deamination of either cyclopropylcarbinylamine or cyclobutylamine resulted in the formation of identical mixtures of alcohols and proposed

the intermediacy of a tricyclobutonium ion (8), in which all three methylene groups are equivalent, to account for his results.

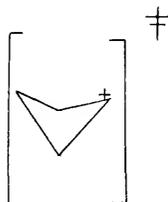


In subsequent work, Roberts and co-workers⁸¹ deaminated labeled cyclopropylcarbinylamine and found that in the major products, the cyclobutyl and cyclopropyl derivatives, the methylene groups approached but did not attain equivalence required of the tricyclobutonium ion (8). Based on this result, these investigators revised the concept of a single non-classical intermediate in favor of a rapidly equilibrating set of non-classical bicyclobutonium ions. The bicyclobutonium ion (9) is intermediate in structure between a cyclopropylcarbinyl cation and a cyclobutyl cation, resulting from partial ring expansion if approached from a cyclopropyl compound and partial ring contraction if approached from a cyclobutane substrate, and was argued to be more stable than either classical form. This ion predicts significant bonding between C_1 and C_4 , and hence significant

Olah and co-workers⁸⁵ employed nmr analysis to elucidate the structure of the cyclopropylcarbinyl cation. Their results suggested a nonclassical ion involving a set of equilibrating three-center bonded ions (12) with equilibration occurring through a puckered cyclobutonium ion (cyclobutyl cation intermediate or transition state).



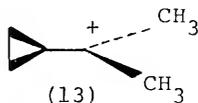
(12)



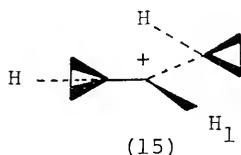
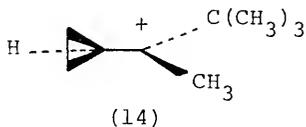
All of the cyclopropylcarbinyl ions presented above have merit in that they keep clearly in mind the considerable charge delocalization in these ions. However, they differ in their predictions of properties, and these predictions should be compared with conclusions about structure.

In 1965, Pittman and Olah^{86,87} observed that the methyl groups of the cyclopropylcarbinyl cation showed different

nmr absorptions, requiring that this ion have a structure in which the methyls are different. This result suggests that the ion has the bisected geometry (13).



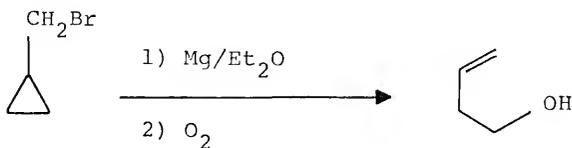
Additional evidence supporting the bisected ion was obtained from the observation that the cyclopropylmethyl-t-butylcarbiny l cation showed only one methyl and one t-butyl absorption, suggesting the presence of only the sterically more favorable conformational isomer (14).⁸⁶ Also, the large coupling constant ($J = 13$), observed between H_1 and H_α in the dicyclopropylcarbiny l cation has been cited as evidence favoring an anti relationship of these protons, found only in the bisected ion (15).⁸⁶



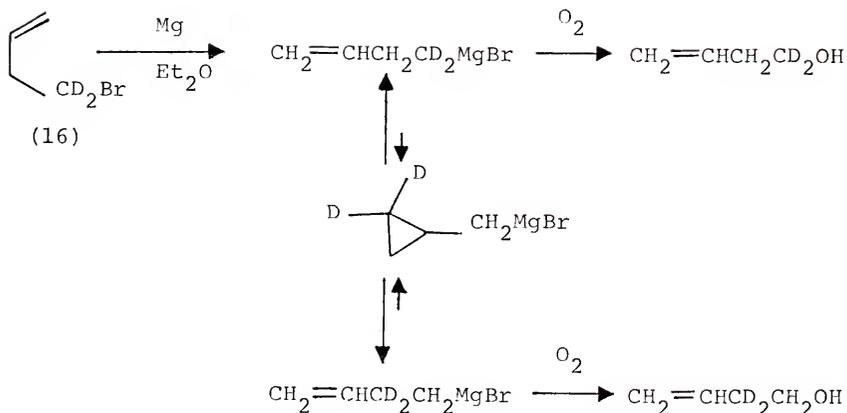
Both the symmetrical homoallylic ion (11) and the three-center bonded ion (12) are compatible with the bisected structure, since both ions predict equivalence of the C_3 and C_4 carbons. The bicyclobutonium ion, however, in which C_3

and C_4 are not equivalent, cannot be rationalized in terms of the bisected structure. Furthermore, the bicyclobutonium cation predicts considerable charge at C_2 , a result which is not compatible with the nmr data obtained by Olah.⁸⁵

The reactions of the cyclopropylcarbinyl anion (3), appear to proceed in a manner quite different from the cyclopropylcarbinyl cation (2). Roberts and Mazur⁸⁰ observed that products derived from the Grignard reagent prepared from cyclopropylcarbinyl bromide had the ring-opened allylcarbinyl structure. No ring expanded or cyclopropylcarbinyl products were detected. Also, nmr studies of the freshly prepared Grignard reagent showed the structure to be greater than 99% rearranged.⁸⁸



Roberts and co-workers⁸⁸ also showed that this reaction was reversible. Starting with deuterium labeled allylcarbinyl bromide (16), they prepared and oxygenated the Grignard reagent. Only open chain products were obtained but the deuterium label was scrambled in such a way as to show conclusively that the Grignard reagent rearranged after its formation and prior to conversion to products.

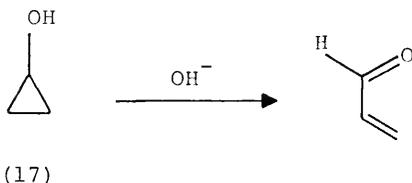


No deuterium label was found in the terminal position, indicating that a nonclassical bicyclobutanide anion did not intervene in this rearrangement, contrasting with the results obtained in the cyclopropylcarbinyl cation case, which, according to Roberts, involved intervention of (9). The absence of a bicyclobutanide anion is not surprising in light of the fact that this species would be a cyclic 4-electron system, for which the Hückel rule predicts zero delocalization energy.

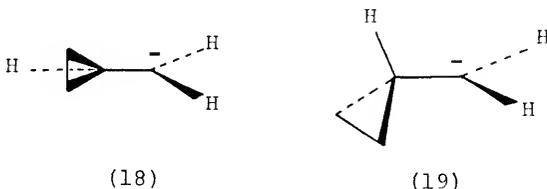
By preparing the Grignard reagent derived from cyclopropylcarbinyl bromide at low temperatures and quenching it after short reaction times, Roberts⁸⁸ was able to isolate products of both the cyclopropylcarbinyl and allylcarbinyl structures. However, the equilibrium constant between cyclopropylcarbinylmagnesium bromide and allylcarbinylmagnesium bromide was found to be about 8×10^{-6} at 24° , heavily favoring the ring-opened form. Relief of strain was sug-

gested to play the dominant role in the overwhelming preference for the ring-opened structure.

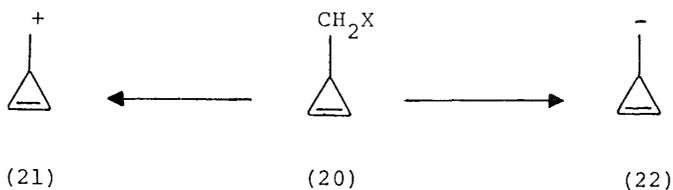
In a related system, Stahl and Cottle⁸⁹ have shown that cyclopropanol (17), on treatment with base, yields propanaldehyde as the sole product. Again, relief of strain was suggested as the dominant factor responsible for formation of only ring-opened products.



Although no experimental evidence has as yet been advanced concerning the preferred structure of the cyclopropylcarbinyl anion, Danen⁹⁰ has calculated the energies of both the bisected structure (18) and the perpendicular structure (19) and determined the perpendicular alignment to be slightly favored.

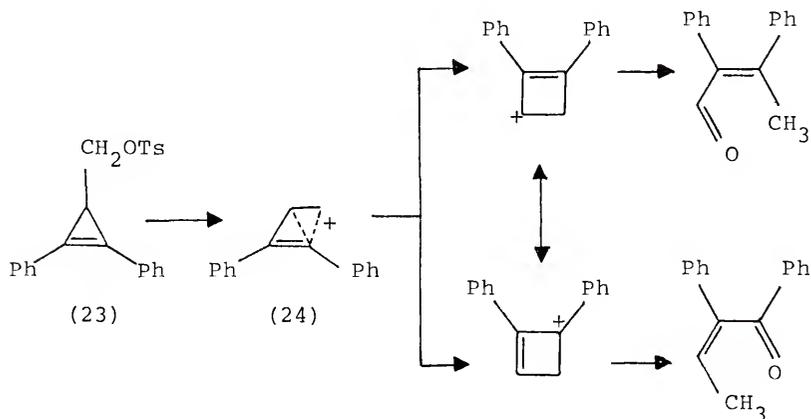


The cyclopropenylcarbinyl system (20), though closely related to the cyclopropylcarbinyl system (1), has not received the attention afforded to the latter. Again, two ionic species, the cyclopropenylcarbinyl cation (21) and the cyclopropenylcarbinyl anion (22) may be generated from (20).

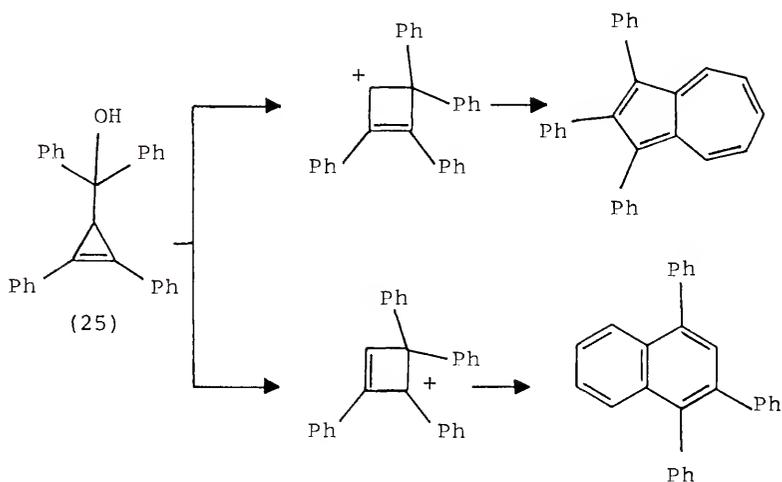


Breslow and co-workers⁹¹ have shown that diphenylcyclopropenylcarbinyl tosylate (23) solvolyzes only three times faster than the corresponding cyclopropylcarbinyl tosylate. It was concluded that (23) solvolyzed without significant participation of the double bond but gave a bicyclobutonium-type intermediate (24), similar to that proposed by Roberts for the reactions of cyclopropylcarbinyl derivatives. In addition, a *p*-methoxy substituent had little effect on the rate of this solvolysis, indicating that the *p* orbital of the developing positive charge at C_2 is orthogonal to the double bond at the time of the transition state. The only products observed in this reaction were derived from initially formed cyclobutenyl products. Breslow has suggested that the transition from starting material to (24) involves

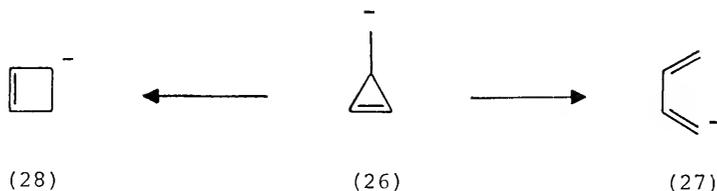
about 20 kcal/mole more strain relief than the corresponding conversion in the saturated series, thus accounting for lack of cyclopropenylcarbinyl products.



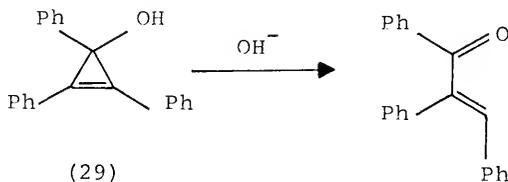
A similar ring expansion has been proposed by Breslow and Battiste⁹² to account for the products obtained from the acid catalyzed rearrangement of (25).



The cyclopropenylcarbinyl anion (26) has not been previously investigated in the all carbon system, but by analogy to the chemistry of the cyclopropylcarbinyl anion (3), one might expect products derived from the ring-opened butadienyl anion (27). Alternatively, by analogy to the chemistry of the cyclopropenylcarbinyl cation (21), products resulting from the ring expanded cyclobutenyl anion (28) might be expected.

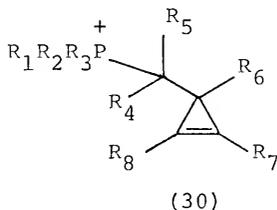


For the isoelectronic system, triphenylcyclopropenol (29), Breslow⁹¹ observed that treatment with base afforded only the ring-opened product, benzaldesoxybenzoin. This ring opening appeared to proceed in a stereospecific manner, since only the E-isomer was detected.

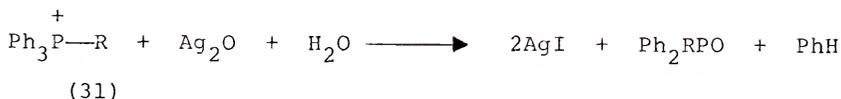


The present investigation was conducted with the objective of generating the cyclopropenylcarbinyl anion under a variety of conditions and to determine whether the products derived from the anion have the ring opened, ring expanded, or unrearranged structure.

One attractive approach to the generation of the cyclopropenylcarbinyl anion is the preparation and decomposition by base of cyclopropenylcarbinyl phosphonium salts, shown below for the general case (30).



As early as 1857, Cahours and Hoffmann⁹³ observed the decomposition by base of a quaternary phosphonium salt to give a hydrocarbon and a phosphine oxide. Michaelis and Soden⁹⁴ found that a phenyl group was preferentially cleaved from a triphenylalkylphosphonium iodide (31) upon treatment with aqueous silver oxide, while treatment of triphenylbenzylphosphonium iodide (32) with aqueous sodium hydroxide yielded toluene and triphenylphosphine oxide.



This work was extended by Meisenheimer⁹⁵ who listed the following groups in order of their ease of elimination upon hydrolysis of a quaternary phosphonium salt:

Allyl and benzyl > phenyl > methyl > ethyl > propyl.

Fenton and Ingold⁹⁶ studied the decomposition of a series of mixed phosphonium hydroxides and determined the following order for the ease of elimination of the hydrocarbon fragment:

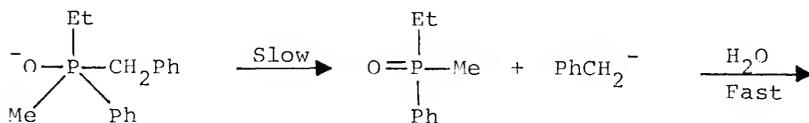
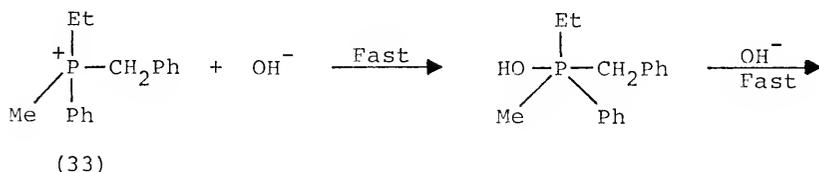
Benzyl > phenyl > methyl > ethyl > propyl.

Hoerner,⁹⁷ studying a series of aryltriphenylphosphonium halides, established the following order for loss of various aryl substituents:

o-, p-, m-nitrophenyl > p-chlorophenyl > p-carboethoxyphenyl > p-biphenyl > phenyl > p-methoxyphenyl > p-, m-tolyl > p-, m-aminophenyl.

It is readily apparent from all this work that the most stable anion is preferentially formed by carbon-phosphorous cleavage during the course of basic hydrolysis of quaternary phosphonium salts.

Recently, McEwen,⁹⁸ studying a series of *p*-*x*-benzyltribenzylphosphonium salts, and Hoffman,⁹⁹ studying a series of *p*-*x*-benzyltriphenylphosphonium salts, have both determined the reaction to be third order overall, first order in the phosphonium salt and second order in base. The mechanism of this reaction, proposed by these workers, is outlined for the phosphonium salt (33).



Hydrolysis of phosphonium salts of the general structure (30), in which R_4 and R_5 are capable of stabilizing negative charge should lead to the generation of a species containing the cyclopropenylcarbinyl anion structure. Product isolation and identification should then give an insight into the fate of this anion.

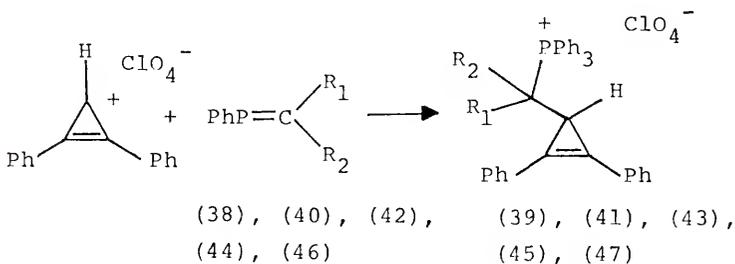
demonstrated by Wittig and Reiber¹⁰⁰ for the preparation of ethyltriphenylphosphonium iodide (35, X = I) from ylid (36) and methyl iodide.



To extend this method to the preparation of cyclopropenylcarbinyl phosphonium salts would simply require the preparation and isolation of stable ylids, followed by alkylation with a suitable cyclopropenium salt, which in the examples investigated here was diphenylcyclopropenium perchlorate (37).⁴⁷

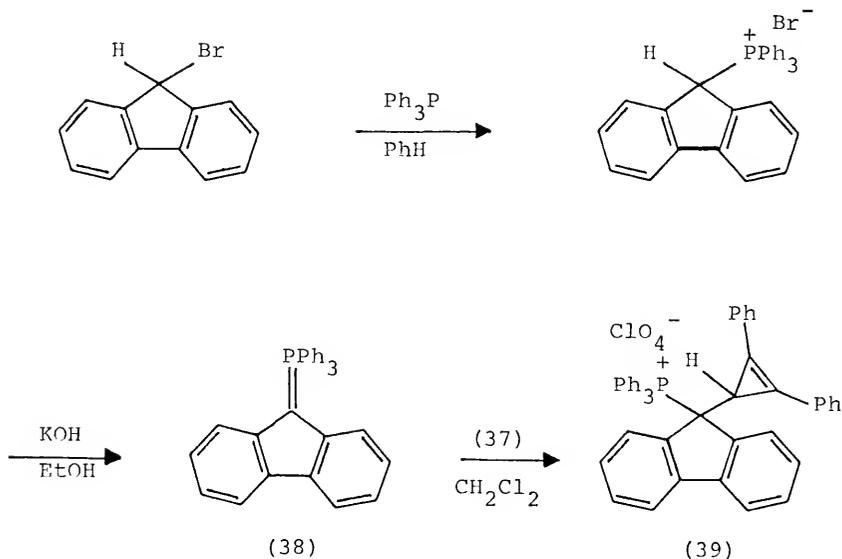
1,2-Diphenylcyclopropenylcarbinyl Phosphonium Salts

The diphenylcyclopropenylcarbinyl phosphonium salts (39), (41), (43), (45), and (47) were prepared by addition of the appropriate ylid to a suspension of cation (37) in methylenechloride at room temperature.



- (38) $R_1R_2 = \text{fluorenyl}$ (39) $R_1R_2 = \text{fluorenyl}$
 (40) $R_1 = \text{H}; R_2 = \text{CO}_2\text{Me}$ (41) $R_1 = \text{H}; R_2 = \text{CO}_2\text{Me}$
 (42) $R_1 = \text{Me}; R_2 = \text{CO}_2\text{Et}$ (43) $R_1 = \text{Me}; R_2 = \text{CO}_2\text{Et}$
 (44) $R_1 = \text{H}; R_2 = \text{COPh}$ (45) $R_1 = R_2 = \text{COPh}$
 (46) $R_1 = \text{H}; R_2 = \text{p-NO}_2\text{Ph}$ (47) $R_1 = \text{H}; R_2 = \text{p-NO}_2\text{Ph}$

The ylids (38),¹⁰¹ (40),¹⁰² (42),¹⁰³ (44),¹⁰⁴ and (46)¹⁰⁵ were prepared in two steps. Triphenylphosphine (34) was alkylated with the appropriate alkyl bromide and the resulting phosphonium salts were treated with base to generate the ylids. This procedure is outlined below for the preparation of fluorenylidetriphenylphosphorane (38) and the subsequent synthesis of (39).



The infrared spectra of salts (39), (41), (43), (45), and (47) showed the characteristic diphenylcyclopropene stretching absorption in the 1820-1850 cm^{-1} region. In addition, all of these salts showed medium to strong bands in the 1010-990 cm^{-1} region, which are reported to be characteristic of a phosphorous-phenyl bond, and intense perchlorate absorption in the 1110-1060 cm^{-1} region.

The ultraviolet spectra of these salts are reported in Table 2.1. As can be seen from this data, the compounds all exhibit the characteristic 1,2-diphenylcyclopropenyl absorption.

TABLE 2.1

 ULTRAVIOLET SPECTRA OF CYCLOPROPENYL CARBINYL
 PHOSPHONIUM SALTS IN METHYLENECHLORIDE

Phosphonium salt	$\lambda_{\text{max}}^{\text{a}}$	ϵ
	330 (sh) ^b	5400
	313	9300
	275	14200
	269 (sh)	14500

TABLE 2.1 (continued)

Phosphonium salt	λ_{\max}^a	ϵ
(41) $R_1 = H; R_2 = CO_2Me$	326 (sh)	15800
	311	22800
	277	13100
	270	11300
(43) $R_1 = Me; R_2 = CO_2Et$	325 (sh)	13800
	309	21500
	277	14800
	269 (sh)	12700
(45) $R_1 = H; R_2 = CPh$	328 (sh)	7800
	309	12700
	304	12900
	276	12300
	263	16500
(47) $R_1 = H; R_2 = p\text{-NO}_2\text{Ph}$	329 (sh)	13700
	310	21200
	277	13100
	268	12200

^aIn CH_2Cl_2 ; ^bShoulder

The nmr spectral data of these cyclopropenylcarbinyl phosphonium salts are recorded in Table 2.2. The aromatic protons of (41) and (43) appear as a broad singlet at δ 7.40 for the ring phenyls and a multiplet centered at 7.75 for the phenyls bound to phosphorous. For the other salts, the aromatic region is more complex due to the presence of additional aromatic protons, but the phenyls bound to phosphorous are still quite distinct, appearing as multiplets in the 7.80-7.70 region. For (47), the AA' portion of the AA'BB' system characteristic of p-nitrophenyl substituents appears as a doublet at lower field, 8.35, than the remaining aromatic protons.

One interesting spectral property of salts (41), (45), and (47) is the change in the phosphorous-hydrogen coupling constant J_{PCH} , observed with changes of R_2 . Allen and Millar¹⁰⁶ established that substitution on carbon had a major effect on J_{PCH} in (48).

	<u>X</u>	<u>J_{PCH}</u>
	OH	1.5
	OMe	4.0
+		
$\text{Ph}_3\text{P}-\text{CH}_2-\text{X}$	Cl	6.3
(48)	Br	6.3
	I	7.8

Phosphonium salts in which phosphorous is bound to an sp^3 hybridized carbon have negative geminal phosphorous-hydrogen coupling constants.^{107,108} These geminal coupling constants become more positive as the electronegativity of the groups bound to the sp^3 hybridized carbon is increased.¹⁰⁶ This increase in J_{PCH} is attributed to an increase in the \underline{s} character of the carbon-hydrogen bonds.¹⁰⁹ The trend observed in salts (41), (45) and (47) agrees with this explanation; the most negative geminal phosphorous-hydrogen coupling constant is observed for (47) and the least negative value is found for (45).

The vicinal phosphorous-cyclopropene hydrogen coupling constants J_{PCCH} vary from a value of 0.0 Hz for (39) to 6.5 Hz for (45). This trend can also be explained in terms of substituent electronegativity.

The vicinal coupling constants for vinyl phosphonium salts, in which the carbon-hydrogen bond can be assigned approximately 33% \underline{s} character, have been determined to be positive.^{110, 111} In these cyclopropenylcarbinyl salts, the vicinal carbon-hydrogen bond can be assigned 35% \underline{s} character,¹¹² and therefore the J_{PCCH} coupling constants observed here may also be assumed positive. The general trend that increasing \underline{s} character for a carbon-hydrogen bond results in increasing, that is less negative, phosphorous-hydrogen coupling appears to be valid not only for geminal coupling but also for vicinal coupling as well.

TABLE 2.2
 PROTON MAGNETIC RESONANCE DATA FOR CYCLOPROPENYL-CARBINYL PHOSPHONIUM SALTS

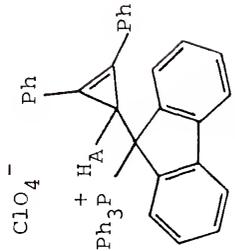
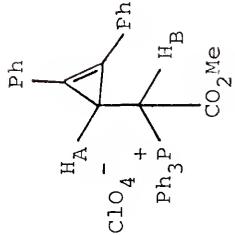
Phosphonium Salt	Proton	Chemical Shift a,b	J _{H_AH_B} ^c	J _{H_CH_D}	J _{PCH}	J _{PCCH}
 (39)	H _A	3.91 (s) ^d	----	----	----	0.0
 (41)	H _A	2.87 (t)	5	----	----	5
	H _B	4.68 (d,d)	5	----	11	----
	CH ₃	3.41 (s)	----	----	----	----

TABLE 2.2 (continued)

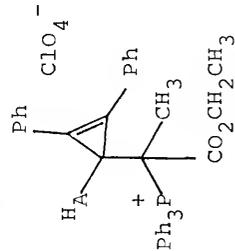
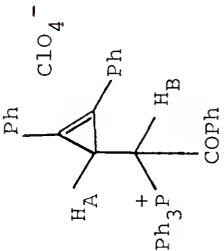
Phosphonium Salt	Proton	Chemical Shift ^{a,b}	$J_{H_A H_B}$	$J_{H_C H_D}$	J_{PCH}	J_{PCCH}
 (43)	H_A CH_3^e CH_2^f CH_3^f	3.38 (d) 1.43 (d) 4.05 (d,q) 1.00 (t)	--- --- --- ---	--- --- 7.0 7.0	--- --- --- ---	3 18 1.5 ---
 (45)	H_A H_B	3.05 (d,d) 6.30 (d,d)	4.5 4.5	--- ---	--- 9.0	6.5 ---

TABLE 2.2 (continued)

Phosphonium Salt	Proton	Chemical Shift ^{a,b}	$J_{H_A H_B}$	$J_{H_C H_D}$	J_{PCH}	J_{PCCH}
	H _A	3.17 (d,d)	6.0	---	---	1.0
	H _B	5.13 (d,d)	6.0	---	16.0	---

(47)

^a60 MHz spectra in Deuteriochloroform at ambient temperature; ^bIn δ ; ^cIn cycles per second; ^d(s) = singlet, (d) = doublet, (t) = triplet, (d,d) = doublet of doublets, (d',d) = doublet of doublets, (d',q) = doublet of quartets; ^eGeminal methyl protons; ^fEthyl ester protons.

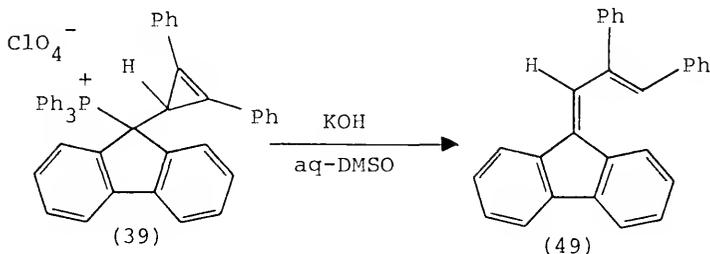
However, differences in conformation, resulting in different P-C-C-H angles may also play an important part in determining the vicinal coupling constants and the true origin of the variations observed remains an open question.

CHAPTER III

GENERATION AND REARRANGEMENT OF CYCLOPROPENYLCARBINYL ANIONS

Base Catalyzed Decomposition of Cyclo- propenylcarbiny Phosphonium Salt (39)

Hydrolysis of (39) with potassium hydroxide in aqueous dimethyl sulfoxide afforded triphenylphosphine oxide and the ring opened product 1,2-diphenylpropenyldene-fluorene (49), isolated in 52% yield as a yellow solid.

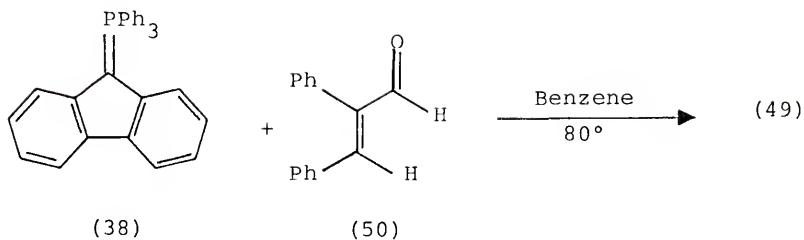


The nmr spectrum of (49) showed a low field multiplet at 8.15, tentatively assigned to the proton vicinal to the fluorene ring. A three proton multiplet at 7.61 may be assigned to the terminal hydrogen and the fluorenyl C_4 - and C_5 - hydrogens, which have been shown to appear at slightly lower field than the other fluorenyl protons in a number of fluorene compounds. The remaining protons appeared as a sixteen proton multiplet at 7.40-7.05.

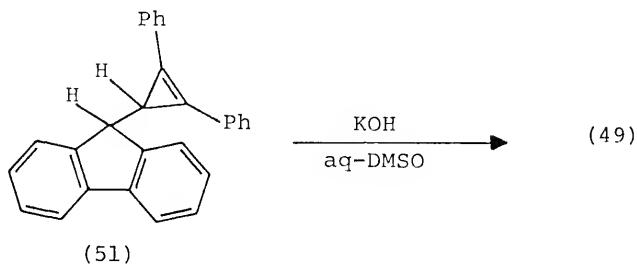
The mass spectrum of (49) gave a parent ion at m/e 356, which was also the base peak. Only one fragment greater than 20% intensity was observed, that occurring at m/e 279, corresponding to loss of a phenyl radical from the parent ion. A weak fragment at m/e 165 can be assigned to the fluorenyl cation. A metastable at m/e 76 indicates that this fragment is formed directly from the parent ion.

The ultraviolet spectrum of (49) in ethanol exhibited maxima at 353, 292, 257, and 228 nm. During the course of obtaining this data, an interesting observation was made. The initial solution of (49) in ethanol was yellow, but over a period of several days this color dissipated until a colorless solution remained. This loss of color led to an investigation of the photochemistry of (49) and related compounds and these results will be presented in Chapter IV.

The structure assigned to (49) was confirmed by authentic synthesis. E- α -phenylcinnamaldehyde (50) was prepared from benzaldehyde and phenylacetaldehyde by the method of Alder.¹¹³ The Wittig reaction of (50) with fluorenylid-enetriphenylphosphorane (38) in refluxing benzene afforded, in addition to triphenylphosphine oxide, a single yellow solid, shown by comparison of its melting point, nmr, infrared, ultraviolet and mass spectra to be identical to (49). The successful synthesis of (49) by this route not only confirmed the ring opened structure of this compound but also confirmed the cis-relationship of the phenyl substituents.

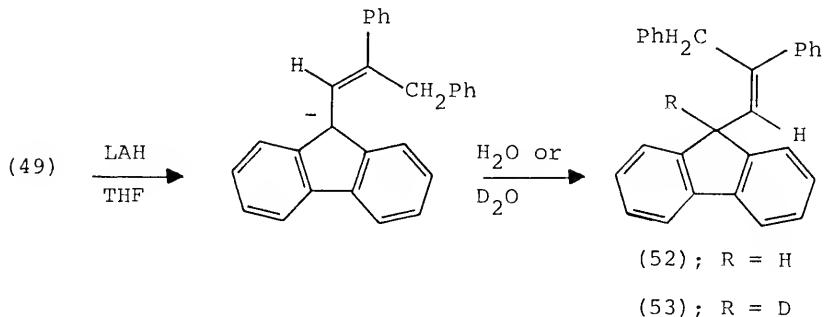


The ring opened compound (49) was also obtained as the sole product when 1,2-diphenyl-3-(9'-fluorenyl)-cyclopropene (51) was treated with potassium hydroxide in aqueous dimethyl sulfoxide. No products containing either ring expanded or unrearranged structures were observed.



To further establish the structure of (49), this compound was reduced with lithium aluminum hydride in refluxing tetrahydrofuran. A red reaction mixture resulted, which was quenched with water to give 9-(2',3'-diphenylprop-1'-enyl) fluorene (52). When the reaction was quenched with D_2O , (53) was obtained containing deuterium incorporated at the 9-fluorenyl position. Presumably, these products result from hydride attack at the terminal position of (49), giving the

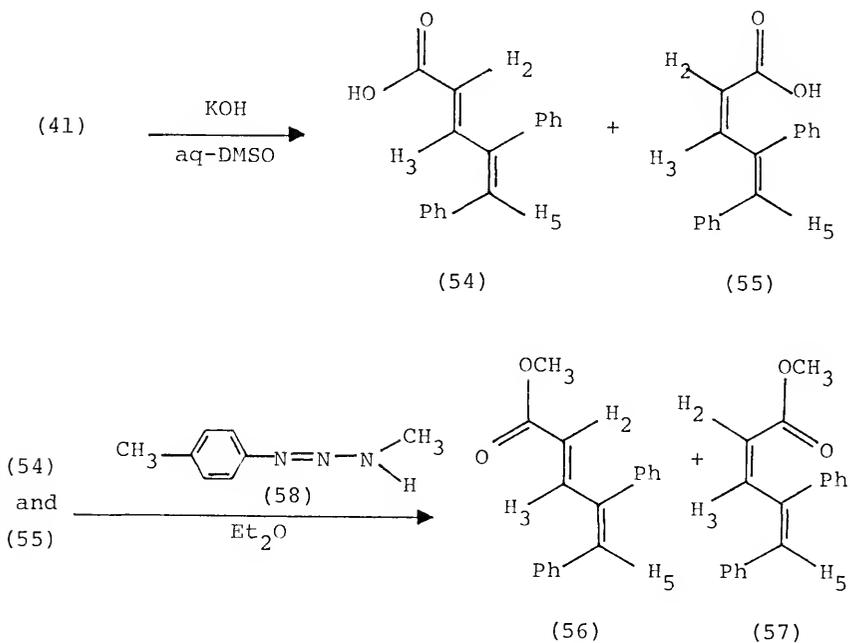
more stable fluorenyl-allyl anion. No products containing a fluorenylidene structure, which would result if the anion were quenched at the other allylic position, were observed in these reactions, indicating that most of the charge must be located at the fluorenyl end of the anion.



The aromatic portion of the nmr spectrum of (52) and (53) consisted of a multiplet at δ 7.75 (2H) and a broad multiplet at 7.60-7.10 (16H). The two lowfield protons may be assigned to the protons bound to C_4 and C_5 of the fluorene ring. The benzylic protons in these compounds appeared as a singlet at 4.33. In (52), the olefinic proton appeared as a doublet at 5.71 ($J = 10.0$ Hz), coupled to the 9-fluorenyl proton. In (53), this signal collapsed to a singlet at 5.68. The 9-fluorenyl proton in (52) appeared as a doublet at 4.98 ($J = 10.0$ Hz), whereas in (53), this signal was completely absent.

Base Catalyzed Decomposition of Cyclo-
propenylcarbinyl Phosphonium Salt (41)

Hydrolysis of salt (41) with potassium hydroxide in aqueous dimethyl sulfoxide afforded a 1:1 mixture of the ring opened acids E,E-4,5-diphenyl-2,4-pentadienoic acid (54) and Z,E-4,5-diphenyl-2,4-pentadienoic acid (55) in 88% yield. These acids could not be separated by chromatography techniques or by fractional recrystallization and were converted into their respective methyl esters (56) and (57) with the triazine (58) and separated by column chromatography.



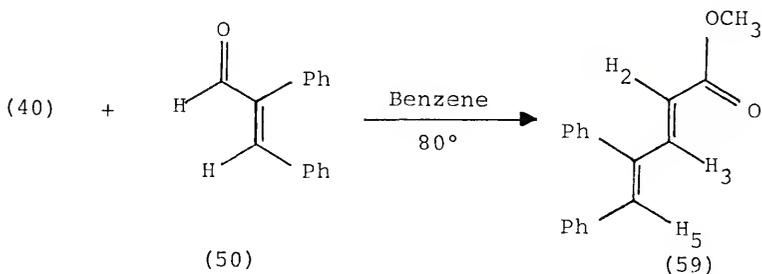
The nmr spectral data for (56) and (57) are summarized in Table 2.3. In (56), the H_2-H_3 coupling constant is 15.5 Hz, while in (57) this coupling constant is 12 Hz. Since trans coupling constants are generally larger than cis coupling constants in olefinic compounds, these protons can be assigned a trans relationship in (56) and a cis relationship in (57). Furthermore, H_3 in (56) appears at lower field than in (57). This is to be expected if (56) has the assigned structure because H_3 is cis to the ester function and should be deshielded with respect to H_3 in (57). By expanding the spectra of these compounds additional small coupling of both H_2 and H_3 to H_5 was observed.

The aromatic region of both (56) and (57) appeared as a sharp singlet. By analogy to the stilbene series, in which the cis-isomer appears as a sharp spike and the trans-isomer as a multiplet, it would seem that the phenyl substituents in (56) and (57) should be assigned the cis configuration. Indeed, this was the assumption under which the authentic synthesis of (56) was attempted.

House¹¹⁴ has shown that the Wittig reaction between a stable ylid such as (40) and a carbonyl compound containing substituents that differ greatly in size results in the stereoselective formation of the α,β -unsaturated ester in which the largest substituent is trans to the ester function. For example, the reaction of acetaldehyde with (40) gave a mixture of cis- and trans-methyl 2,3-dimethyl-2-propenoates

in 96.5% and 3.5% yield, respectively. To extend this reaction to the synthesis of (56) would require simply the substitution of α -phenylcinnamaldehyde for acetaldehyde.

Proceeding under the assumption that (56) contained the phenyl substituents cis, its authentic synthesis was attempted via the Wittig reaction of E- α -phenylcinnamaldehyde (50) with ylid (40). This resulted in the formation of triphenylphosphine oxide and a single product, methyl E,Z-4,5-diphenyl-2,4-pentadienoate (59).



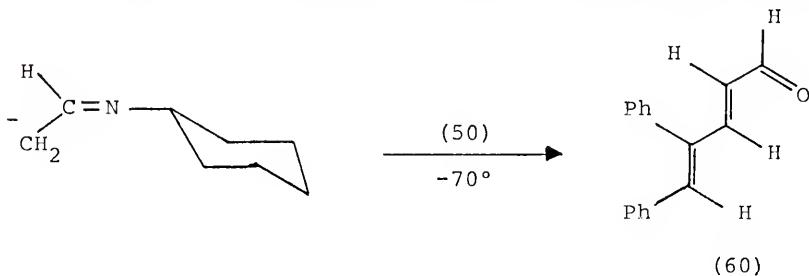
That this product was not (56) was readily apparent from its nmr spectrum. Instead of a sharp singlet for the phenyl protons, (59) exhibited a complex multiplet. However, (59) did display an H₂-H₃ coupling of 16.0 Hz, indicating the desired trans stereochemistry about the internal double bond. The complete nmr spectral data for (59) is presented in Table 2.3.

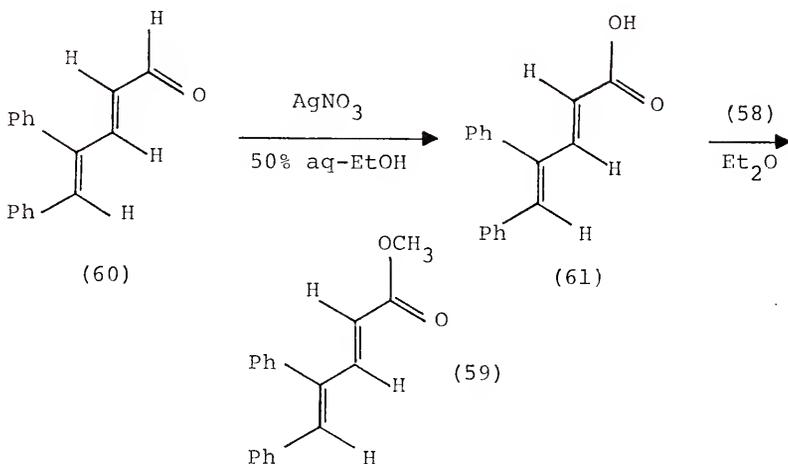
Failure to obtain (56) from this reaction could result from two possibilities. First, the stereochemistry of the phenyl substituents in (56) could actually be cis, in which case the diene (59) must contain the phenyl substituents

trans. This would be the case if the stereochemistry of (50) is wrongly assigned, or, if during the course of the Wittig reaction, (50) isomerized to the Z-isomer prior to conversion to products. Second, the structures assigned to (56), (59) and (50) may all be correct and no isomerization is occurring in the Wittig reaction.

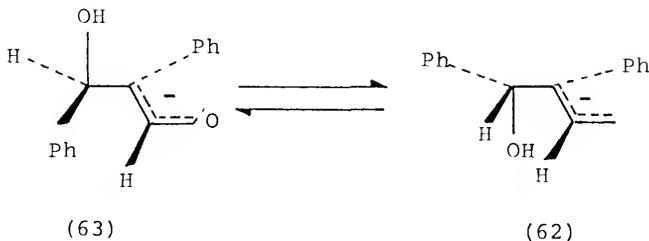
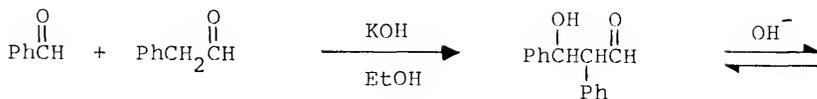
To determine whether isomerization occurred under the conditions of the Wittig reaction, the aldehyde (50) was heated in refluxing benzene for several hours. The recovered material was completely unrearranged, eliminating the possibility of thermal isomerization.

Further evidence that no rearrangement occurred in this reaction was obtained from the synthesis of (59) from (50) by an alternate route. Aldehyde (50) was homologized to 4,5-diphenyl-2,4-pentadienal (60) by a directed aldol condensation.¹¹⁵ Oxidation of (60) gave (61) which was esterified by treatment with triazine (58). Directed aldol condensations involving α,β -unsaturated carbonyl compounds have previously been shown to occur without rearrangement under the conditions employed in this reaction.¹¹⁶ Since this reaction sequence also gave (59), it is safe to conclude that no rearrangement occurred in the Wittig reaction.





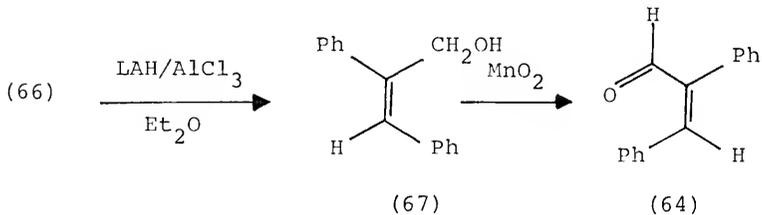
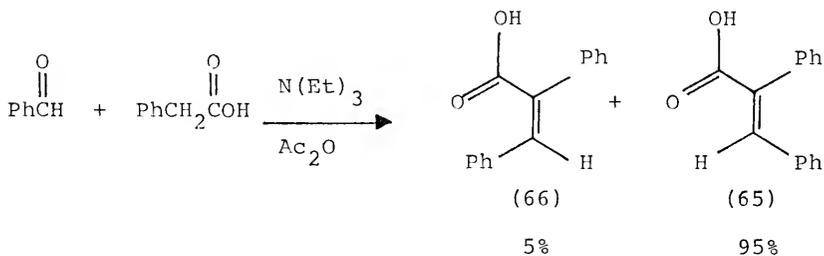
Next, the possibility that the aldehyde (50) had been assigned the wrong stereochemistry was explored. Initially, (50) was prepared from benzaldehyde and phenylacetaldehyde via a Claisen-Schmidt condensation reaction. The stereochemistry of the products obtained in this type of reaction is such that the carbonyl function is trans to the larger substituent at the β -carbon. This stereochemistry has been explained in terms of preferential dehydration of the enolate anion in conformation (62) rather than (63). In (62) there is less steric interference between the planar enolate anion and the large substituent at the β -carbon, and this configuration is therefore energetically favored.¹¹⁷ Based upon this explanation, the expected product from the reaction of benzaldehyde and phenylacetaldehyde is (50).



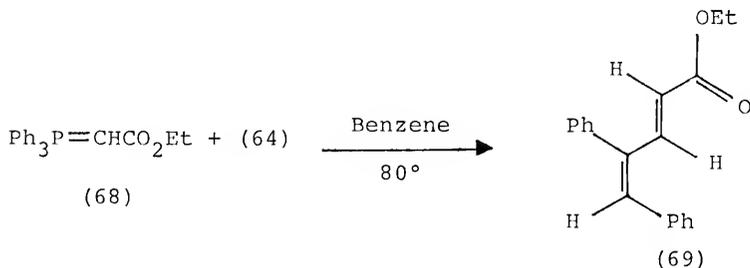
Additional evidence that the assigned structure of (50) is correct was obtained from the reaction of diphenylcyclopropenium salt (37) with aqueous potassium hydroxide. This reaction had been previously reported to afford α -phenylcinnamaldehyde, and indeed the product obtained was identical to (50).

Having determined that the stereochemistry of (50) and (59) is correct, the synthesis of *Z*- α -phenylcinnamaldehyde (64) was undertaken according to the reaction sequence shown below. Condensation of benzaldehyde with phenylacetic acid yielded a mixture of *E*- α -phenylcinnamic acid (65) and *Z*- α -phenylcinnamic acid (66) in the ratio 95:5 respectively.¹¹⁸ Isolation of the minor product (66) and reduction with aluminum hydride afforded the alcohol (67),¹¹⁹ which upon oxidation with manganese dioxide gave the desired aldehyde (64). Interestingly, attempted preparation of (64) by conversion of (66) to the corresponding acid chloride with oxalyl

chloride followed by reduction with lithium tri-*t*-butoxy-aluminum hydride gave (50), which was also obtained from the same reaction sequence starting with acid (65).

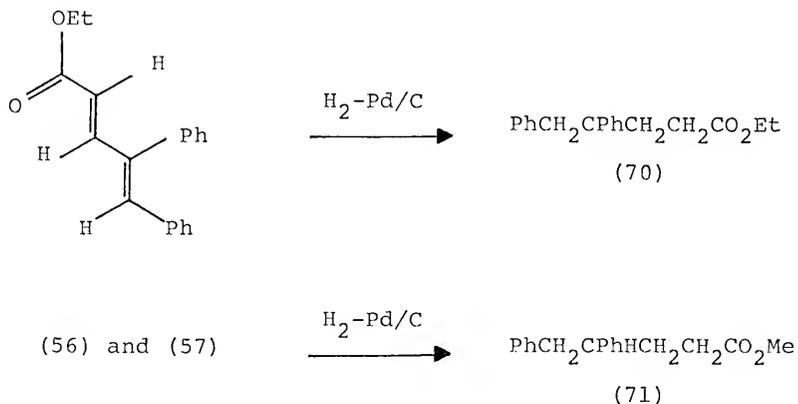


The authentic synthesis of an *E,E*-4,5-diphenyl-2,4-pentadiene ester was achieved via the Wittig reaction of (64) with ylid (68).



The nmr spectral data of ethyl *E,E*-4,5-diphenyl-2,4-pentadienoate (69) are presented in Table 2.3. Except for the fact that (69) is an ethyl rather than a methyl ester, its nmr spectrum is identical to that of (56).

That the esters (54) and (55) obtained from the hydrolysis of salt (41) and the ester (59) are all isomeric 2,4-pentadienoates was confirmed by hydrogenation. The ethyl ester corresponding to (59) was hydrogenated over 5% palladium on charcoal, yielding the saturated ethyl ester (70). The mixture of esters (56) and (57), upon hydrogenation under the same conditions, yielded the corresponding saturated methyl ester (71).



From the nmr spectral data of these unsaturated esters, it is quite apparent that they are structurally identical. The aromatic protons of both esters appear as identical multiplets at δ 6.85-7.35 and integrate for ten protons. The

benzyl protons appear as an unresolved multiplet at 2.85 (3H) and the remaining internal protons appear as a second unresolved multiplet at 2.04 (4H). These signals are identical in shape and chemical shift in both (70) and (71). The ethyl ester protons of (70) appear as a quartet at 3.97 (2H, $J = 7.0$ Hz) and a triplet at 1.08 (3H, $J = 7.0$ Hz), while the methyl ester protons of (71) are a sharp singlet at 3.55 (3H).

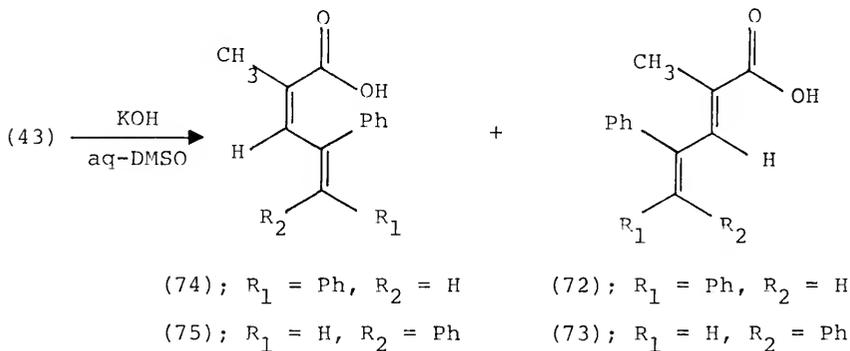
To determine whether the acids obtained from the hydrolysis of salt (41) are kinetic rather than thermodynamic products, ester (59) was hydrolyzed under the same reaction conditions. Only unrearranged acid was recovered, indicating that during the hydrolysis of salt (41), initial formation of acids containing the phenyl substituents cis followed by isomerization to acids (54) and (55) did not occur.

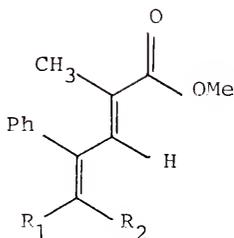
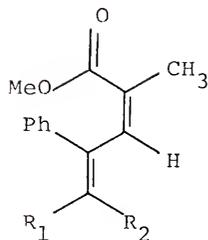
Additional information regarding the mechanism of the hydrolysis of salt (41) was obtained by conducting the reaction in deuterated medium containing sodium deuterioxide. The reaction mixture was quenched with dilute hydrochloric acid and the mixture of acids analyzed by nmr spectroscopy. The H_2 and H_5 signals associated with acids (54) and (55) were completely absent, indicating deuterium incorporation at both positions. Furthermore, the H_3 signal, which appeared as a doublet of doublets in (54) and (55), collapsed to a singlet at 8.00 for the E,E-isomer and a singlet at 7.05 for the Z,E-isomer. Hydrolysis of ester (59) in

deuterated medium containing sodium deuterioxide failed to incorporate deuterium at either C₂ or C₅, indicating that deuterium incorporation in the previous case must occur prior to product formation.

Base Catalyzed Decomposition of Cyclo-
propenylcarbiny Phosphonium Salt (43)

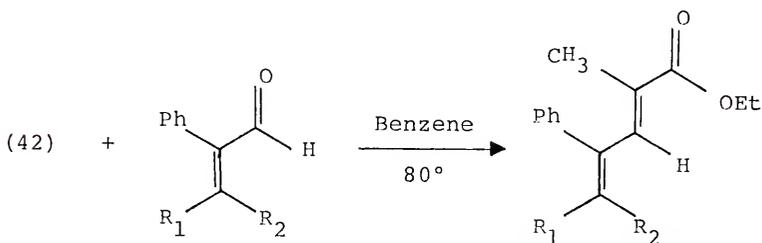
Hydrolysis of salt (43) with potassium hydroxide in aqueous dimethyl sulfoxide afforded a mixture of products tentatively identified as the isomeric ring opened 2-methyl-4,5-diphenyl-2,4-pentadienoic acids (72)-(75). This mixture could not be separated and the acids were converted into their corresponding methyl esters (76)-(79) as previously described. Unfortunately, this ester mixture could not be separated by a variety of chromatographic techniques.



(76); $R_1 = \text{Ph}$, $R_2 = \text{H}$ (77); $R_1 = \text{H}$, $R_2 = \text{Ph}$ (78); $R_1 = \text{Ph}$, $R_2 = \text{H}$ (79); $R_1 = \text{H}$, $R_2 = \text{Ph}$

The C_2 -methyl protons in this mixture of esters appeared as four distinct signals at δ 1.67 (d, $J = 1.5$ Hz), 1.53 (d, $J = 1.5$ Hz), 1.17 (s), and 1.05 (s) and gave a combined integration for three protons.

Ethyl esters (80) and (81), corresponding to (76) and (77), respectively, were prepared authentically via the Wittig reaction of ylid (42) with aldehydes (50) and (64).

(50); $R_1 = \text{Ph}$, $R_2 = \text{H}$ (80); $R_1 = \text{Ph}$, $R_2 = \text{H}$ (64); $R_1 = \text{H}$, $R_2 = \text{Ph}$ (81); $R_1 = \text{H}$, $R_2 = \text{Ph}$

The nmr spectra of these esters confirmed the presence of esters (76) and (77) in the ester mixture (76)-(79). The C_2 -methyl protons in (80) appeared as a doublet at δ 1.67

TABLE 2.3
 PROTON MAGNETIC RESONANCE DATA OF ISOMERIC 4,5-DIPHENYL-2,4-PENTADIENE ESTERS

Compound ^a	Ar	H ₂	H ₃	H ₅	CH ₂	CH ₃
(56)	7.33 (s, 10H)	5.88 (d,d)	7.98 (d,d)	6.87 (d,d)	----	3.68 (s)
		J = 15.5 Hz	J = 15.5 Hz	J = 0.8 Hz		
		J = 0.8 Hz	J = 1.0 Hz	J = 1.0 Hz		
(57)	7.32 (s, 10H)	6.07 (d,d)	7.00 (d,d)	6.86 (d,d)	----	3.22 (s)
		J = 12.0 Hz	J = 12.0 Hz	J = 1.2 Hz		
		J = 1.2 Hz	J = 1.8 Hz	J = 1.8 Hz		
(59)	6.80-7.45 (m, 10H)	5.48 (d)	7.69 (d)	6.88 (s)	----	3.67 (s)
		J = 16.0 Hz	J = 16.0 Hz	J = 16.0 Hz		

TABLE 2.3 (continued)

Compound	Ar	N ₂	H ₃	H ₅	CH ₂	CH ₃
(69)	7.33 (s, 10H)	5.85 (d, d)	8.00 (d, d)	6.87 (d, d)	4.18 (q)	1.25 (t)
		J = 15.5 Hz	J = 15.5 Hz	J = 0.8 Hz	J = 7.0 Hz	J = 7.0 Hz
		J = 0.8 Hz	J = 1.0 Hz	J = 1.0 Hz		

^aAt ambient temperature in CDCl₃. Chemical shifts are in δ .

($J = 1.5$ Hz) and in (81) as a doublet at 1.52 ($J = 1.5$ Hz). These signals are identical in both shape and chemical shift to the doublets observed in the ester mixture. Protons H_3 and H_5 were quite distinct in (80) and (81), H_3 appearing as a distorted triplet in both compounds at δ 7.47 and 7.60 respectively, while H_5 appeared as a broad singlet at 6.81 in (80) and 6.87 in (81). These signals were obscured by the aromatic protons in the original methyl ester mixture. The aromatic protons appeared as a multiplet in (80) at 7.43-7.00 and as a singlet in (81) at 7.32.

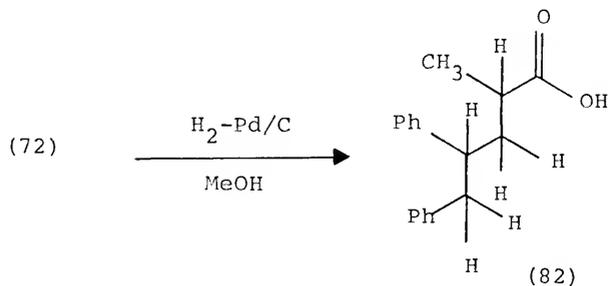
The singlets at 1.17 and 1.05, observed in the ester mixture (76)-(79) may be tentatively assigned to esters (78) and (79), although a specific assignment can not be made from the available data.

In addition to the signals discussed above, a number of small peaks in the δ 2.3-3.0 region were also present in both the acid mixture (72)-(75) and the ester mixture (76)-(79). The source of these signals could not be separated and must remain unidentified. The signals integrate for 1.5 protons relative to the combined C_2 -methyl protons and for approximately two protons relative to the C_2 -methyl spikes tentatively assigned to (78) and (79). This latter ratio remained unchanged during several repetitions of the hydrolysis of salt (43) in which both the reaction time and concentration of base were varied, raising the possibility that these signals correspond to a single unidentified compound and that the spikes assigned to (78) and (79) may in

reality be a doublet corresponding to this compound. Although this possibility must be considered, by analogy to the results from hydrolysis of phosphonium salt (41), the Z,E- and Z,Z-isomers (78) and (79) are expected in the product mixture.

An authentic synthesis of ethyl Z,Z-4,5-diphenyl-2-methylpentadienoate was attempted by the Reformatsky reaction between aldehyde (50) and ethyl 2-bromopropionate. Dehydration of the alcohol mixture followed by hydrolysis of the resulting esters yielded a complex mixture of acids from which only (72) could be separated. The nmr spectrum of the acid mixture did contain the signals at 1.17 and 1.05, originally observed in the acid mixture (72)-(75), but neither the Z,E- nor the Z,Z-isomer could be separated and identified.

Hydrogenation of the E,Z-acid (72) over palladium on charcoal gave the saturated acid 4,5-diphenyl-2-methylpentanoic acid (82), presumably as a pair of erythro and threo diastereomers, although these could not be separated.

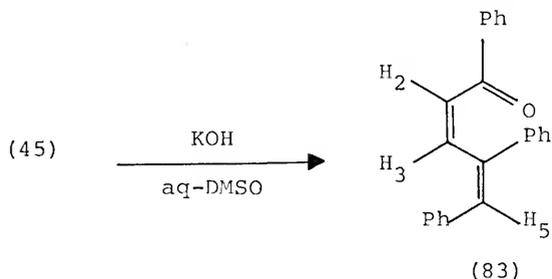


The nmr spectrum of (82) showed a broad singlet at δ 11.20 (1H) for the acidic proton, a multiplet at 7.35-6.85 for the aromatic protons and a broad singlet at 3.92 for the benzylic protons. The remaining protons were a broad multiplet at 2.54-1.50 (3H), and a doublet at 1.07 (3H, $J = 7.0$ Hz, C_2 -methyl).

When the acid mixture (72)-(75) was hydrogenated under identical conditions and the crude product analyzed by nmr spectroscopy, all of the signals assigned to (82) were observed, but in addition, a number of other signals in the 1.2-0.9 region were also present. After chromatographic techniques failed to separate this apparent mixture, it was distilled. The only product which could be isolated and identified was the saturated acid (82).

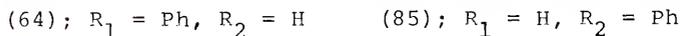
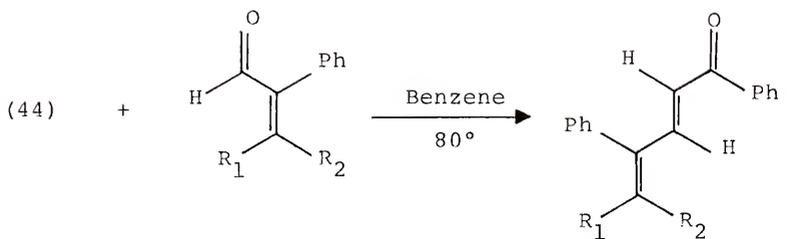
Base Catalyzed Decomposition of Cyclopropenylcarbinyl Phosphonium Salt (45)

Hydrolysis of salt (45) with potassium hydroxide in aqueous dimethyl sulfoxide afforded, in 17% yield, a single product, identified from its spectral data as the ring opened ketone, *Z,E*-1,4,5-triphenyl-2,4-pentadienone (83).



The nmr spectral data for (83) are presented in Table 2.4. The aromatic protons appeared as a multiplet at δ 7.75-7.50 (2H), and a broad singlet at 7.20-7.45 (13H). The two proton multiplet was assigned the ring protons ortho to the carbonyl function. Protons H₂ and H₃ appeared as an AB quartet at 6.87 (H₃) and 6.05 (H₂, J_{2,3} = 6.5 Hz), the magnitude of J_{2,3} confirming their cis orientation. The stilbene proton H₅ appeared as a singlet at 6.38. The mass spectrum of (83) showed a molecular ion at m/e 310 with a major ion fragment at m/e 233 (P - 77) and base peak at m/e 205 (P - 105).

The reactions of ylid (44) with aldehydes (50) and (64) yielded the isomeric 2,4-pentadienones (84) and (85). With (50), the reaction proceeded smoothly, affording only (84). However, with (64), both stereoisomers were obtained in a 70:30 ratio, respectively, indicating that isomerization of the isomeric α -phenylcinnamaldehydes, when it occurs, proceeds from the Z-isomer to the E-isomer. Ramirez¹⁰⁴ has shown that the charge in this ylid is highly delocalized from the ylid carbanion through the carbonyl group. Reversible Micheal type addition to (64) could account for this isomerization.¹²⁰



The nmr spectral data for (84) and (85) are presented in Table 2.4. The aromatic protons of (84) appeared as multiplets at δ 7.95-7.70 (2H) and 7.65-6.80 (15H). In (85) the two proton multiplet also occurred at 7.95-7.70 but the remaining aromatic protons appeared as a broad singlet at 7.55-7.30. In (84), H_3 and H_5 are obscured by the phenyl absorptions, while in (85), these protons appeared as a doublet at 8.15 ($J = 15.0$ Hz) and a singlet at 7.00, respectively. The remaining vinyl proton, H_2 , appeared as a doublet at 7.02 ($J = 15.0$ Hz) in (84) and as a doublet at 6.58 ($J = 15.0$ Hz) in (85). The large $J_{2,3}$ value supports the assignment of these protons as trans. The deshielding of H_3 in (84) and (85) with respect to this proton in (83) further supports the assignment of H_3 cis to the carbonyl substituent in (84) and (85). It is also interesting to note that H_5 in (83) is observed at higher field than in (84) or (85), indicating that steric interactions between

TABLE 2.4
 PROTON MAGNETIC RESONANCE SPECTRAL DATA OF 1,4,5-TRIPHENYL-2,4-PENTADIENONES
 (83), (84) and (85)

Compound ^a	Ar	H ₂	H ₃	H ₅
(83)	7.75-7.50 (2H, m) 7.45-7.25 (13H, bs)	6.05 (d, J = 6.5 Hz)	6.87 (d, J = 6.5 Hz)	6.38 (s)
(84)	7.95-7.70 (2H, m) 7.65-6.80 (15H, bm)	7.02 (d, J = 15.0 Hz)	b	b
(85)	7.95-7.70 (2H, m) 7.55-7.30 (13H, bs)	6.58 (d, J = 15.0 Hz)	8.15 (d, J = 15.0 Hz)	7.00 (s)

^aAmbient temperature in CDCl₃.

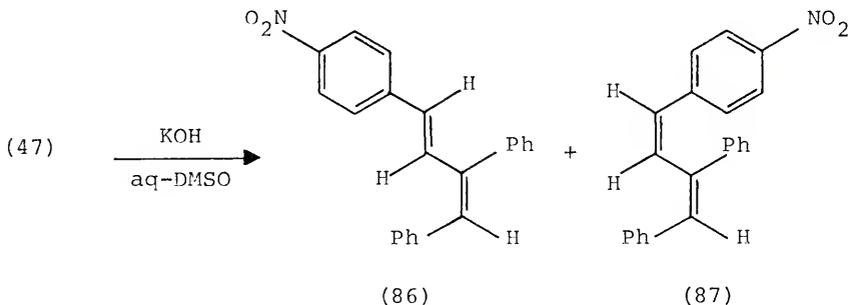
^bObscured by aromatic protons. Chemical shifts in δ -values.

the C₄ phenyl substituent and the benzoyl substituent may reduce the coplanarity of the conjugated system in (83) and thereby reduce the effect of extended conjugation to C₅.

The mass spectra of (84) and (85) also indicate that they are isomers of (83). The molecular ions for both (84) and (85) appear at m/e 310, while each compound also displays an abundant fragment ion at m/e 233 and a base peak at m/e 205.

Base Catalyzed Hydrolysis of Cyclo-
propenylcarbinyl Phosphonium Salt (47)

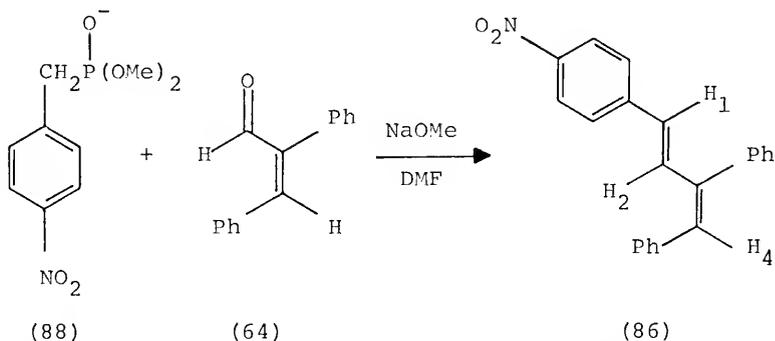
Hydrolysis of salt (47) with potassium hydroxide in aqueous dimethyl sulfoxide afforded an intensely blue reaction mixture. After chromatography, two distinct components were isolated. The first, an orange oil, was tentatively identified as a mixture of the ring-opened dienes (86) and (87). The second component was a dark blue solid.



The nmr spectrum of the diene mixture showed two doublets in the 7.62-8.12 region which can be assigned to the ring

protons ortho to the nitro substituent. The remaining aromatic protons appeared as a narrow multiplet, indicating the possible absence of cis-phenyl dienes in this mixture. In addition, the mass spectrum of this diene mixture showed a parent ion at m/e 327, corresponding to the proposed dienes.

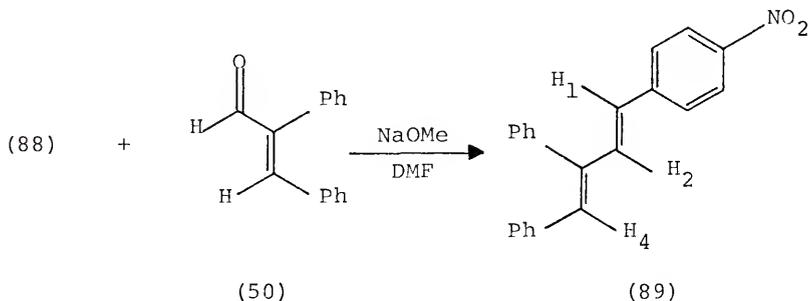
After exhaustive column chromatography, a small quantity of one of the components in the diene mixture was separated. This material was identified as *E,E*-1-(4'-nitrophenyl)-3,4-diphenyl-1,3-butadiene (86), by comparison of its physical data with authentic (86), prepared from the phosphonate (88) and aldehyde (64) employing the Horner modification of the Wittig reaction.



The nmr spectrum of (86) supported the assigned stereochemistry. The aromatic region showed a doublet at δ 8.10 ($J = 9.0$ Hz), corresponding to the ring protons ortho to the nitro substituent, and a narrow multiplet at 7.45-7.17 (13H). Proton H_1 appeared as a doublet at δ 6.45 ($J_{1,2} = 16.0$ Hz), the large coupling constant supporting the trans-stereochemistry assigned to the C_1 - C_2 double bond. The H_2 signal was

partially obscured by the phenyl absorptions, but H_4 was found as a broad singlet at δ 6.68, indicating unresolved coupling to H_2 .

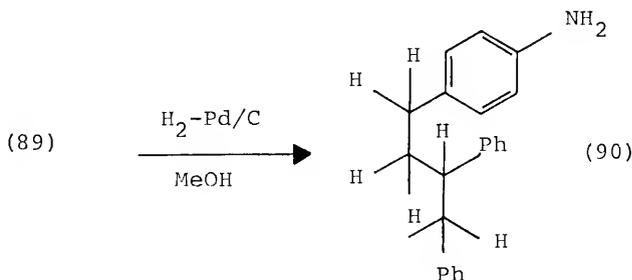
Evidence that dienes containing cis-phenyl substituents were not present in detectable amounts in the diene mixture was provided by the synthesis of *E,Z*-1-(4'-nitrophenyl)-3,4-diphenyl-1,3-butadiene (89) and comparison of its nmr spectrum to that of the diene mixture.



The ring protons ortho to the nitro substituent in (89) appear as a doublet at δ 8.18, slightly deshielded with respect to these protons in (86). Although this deshielding is only 0.08 ppm, it is sufficient to allow the detection of (89) if present in the diene mixture. Furthermore, the aromatic region of (89) is a complex multiplet which would be readily apparent in the diene mixture. Finally, H_2 in (89) appears as a doublet at δ 6.18 ($J = 16.0$ Hz), a region void of proton signals in the diene mixture from the above phosphonium salt hydrolysis.

This nmr comparison does not completely rule out the presence of (89) or the corresponding Z,Z-isomer in the diene mixture since the limit of detectability by this method is about 5%. However, it does indicate that, if present, these isomers must be very minor components.

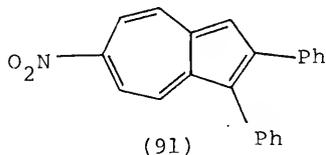
To demonstrate that the diene component obtained in the hydrolysis of salt (47) was a mixture of ring opened 1,3-butadienes, it was hydrogenated over 5% palladium on charcoal and the product compared to the product obtained from hydrogenation of (89). In both cases, the saturated amine (90) was the sole hydrogenation product.



The nmr spectrum of (90) showed an aromatic multiplet at δ 7.20-6.85 (10H), assigned to the benzene ring protons, and an AA'BB' multiplet centered at 6.55, assigned to the aniline ring protons. The amine protons appeared as a singlet at 3.18 (2H), and the three benzyl protons bound to C₃ and C₄ as a broad singlet at 2.80 (3H). The remaining internal protons comprised a broad absorption at 2.60-1.65 (4H).

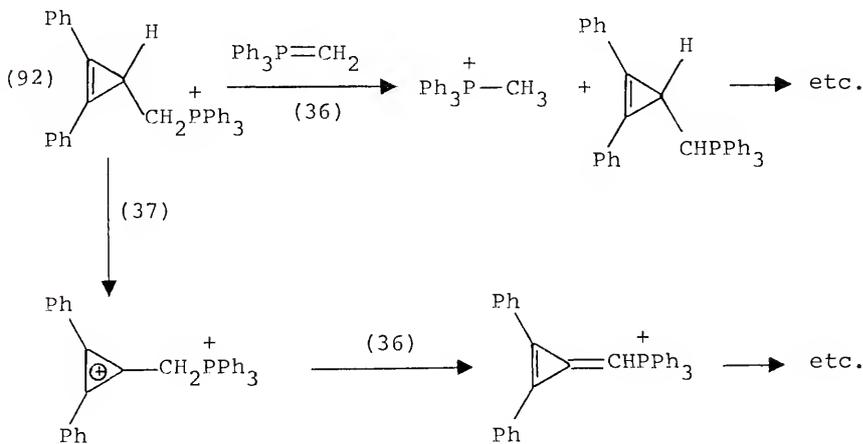
The mass spectrum of (90) showed a molecular ion at m/e 301 and a base peak at m/e 106, corresponding to the aminotropylium cation. It is interesting to note that the intensity of the tropylium cation at m/e 91 is only 9%, demonstrating the enhanced stability of the former fragment ion.

The intense blue color of the second component, isolated from the hydrolysis of salt (47), is characteristic of a number of azulene derivatives. Elemental analysis of a recrystallized sample, although incorrect, confirmed the presence of nitrogen and oxygen. The nmr spectrum revealed two distinct aromatic multiplets. This material gave a broad absorption maxima at 571 nm in its visible spectrum and the mass spectrum showed a molecular ion at m/e 325, two mass units smaller than the molecular ion of the ring opened dienes and consistent with the additional degree of unsaturation required for the azulene ring system. Further purification could not be accomplished because of insufficient material and identification was not pursued further. Although purely speculative, one attractive structure for this blue solid is the azulene (91).

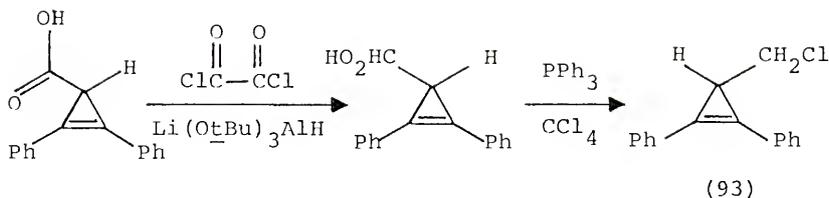


Generation and Rearrangement of 1,2-Diphenyl-
cyclopropenylcarbinyl Magnesium Bromide

The phosphonium salts (39), (41), (43), (45), and (47) all contain substituents capable of stabilizing negative charge generated at the cyclopropenylcarbinyl carbon during the course of hydrolysis. All attempts to prepare the parent 1,2-diphenylcyclopropenylcarbinyl phosphonium salt (92) from the reaction of methylenetriphenylphosphorane (36) with cation (37) failed to yield any recognizable product. The problem here may be that the ylid (36) is a strong base and could react with any (92) formed initially.



An alternate approach to (92) was attempted. 3-Chloromethyl-1,2-diphenylcyclopropene (93) was prepared from 1,2-diphenylcyclopropene carboxylic acid as shown on the following page.



The acid was converted into its acid chloride with oxalyl chloride, which was then reduced without purification to the cyclopropenylcarbonyl alcohol.⁹¹ Treatment of the alcohol with triphenylphosphine in carbontetrachloride afforded the previously unknown chloride (93).

The nmr spectrum of (93) showed an aromatic multiplet at δ 7.75-7.20 (10H), a triplet for the cyclopropene ring proton at 2.50 ($J = 5.5$ Hz) and the methylene protons as a doublet at 3.68 ($J = 5.5$ Hz).

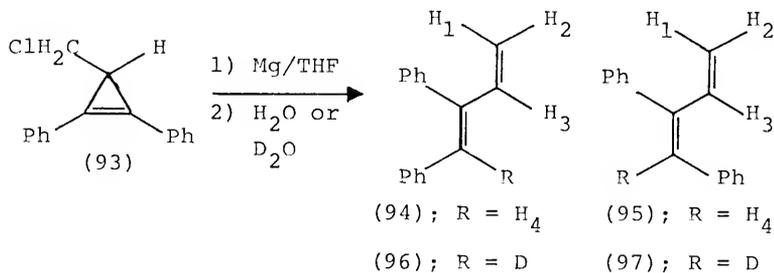
The infrared spectrum of (93) showed a moderate absorption at 1830 cm^{-1} , characteristic of diphenylcyclopropenes as well as a broad, intense absorption at $760\text{-}730\text{ cm}^{-1}$, characteristic of carbon-chlorine bond stretching.

The ultraviolet spectrum displayed maxima characteristic of 1,2-diphenyl substituted cyclopropenes at 327 ($\epsilon = 24700$) and 309 nm ($\epsilon = 32200$).

The mass spectra showed a molecular ion at m/e 240 and a base peak at m/e 205 (P-Cl). Other major fragment ions appeared at m/e 191, corresponding to the 1,2-diphenylcyclopropenium cation and m/e 178, corresponding to the diphenyl acetylene radical cation.

The chlorocyclopropene (93) was treated with triphenylphosphine in refluxing benzene, toluene and acetone. Regardless of the solvent, none of the desired phosphonium salt (92) could be detected. In each case (93) was recovered and the preparation of salt (92) was abandoned.

Failure to obtain any of the salt (92) led to an attempt to generate cyclopropenylcarbinyl magnesium chloride. This approach proved successful. Treatment of chloride (93) with magnesium in refluxing tetrahydrofuran yielded a dark orange reaction mixture. The Grignard reagent was quenched with water and a mixture of ring opened dienes, identified as (94) and (95) was obtained in 80% yield. NMR analysis of the crude reaction products failed to reveal any unrearranged products. The diene mixture was separated by gas chromatography and shown to consist of a 55:45 mixture of (94) and (95) respectively. When the Grignard reagent was quenched with D_2O , an identical mixture of dienes (96) and (97), containing deuterium incorporated at C_1 was obtained.



The nmr spectral data for these dienes are presented in Table 2.5. Both (94) and (96) showed a ten proton aromatic multiplet at δ 7.40-6.80 while in (95) and (97), the aromatic protons appeared as a spike at 7.30. A broad singlet at δ 6.57 and 6.55 in (94) and (95) respectively, which is absent in the deuterated dienes (96) and (97) is assigned to H_4 on the basis of its chemical shift and lack of multiplicity. By contrast, H_3 appeared as a doublet of doublets in (94) and (96) at 6.72 ($J_{1,3} = 17.0$ Hz; $J_{2,3} = 10.4$ Hz) and as a doublet of doublets in (95) and (97) at 7.02 ($J_{1,3} = 16.8$ Hz; $J_{2,3} = 11.2$ Hz). Additional long range coupling to H_4 of approximately 1.0 Hz was observed for both dienes (94) and (95) when the H_3 signal was expanded. In the deuterated dienes, this coupling was absent. The methylene protons, H_1 and H_2 , in (94) appeared as doublets of doublets at 4.81 ($J_{1,3} = 1.4$ Hz; $J_{1,3} = 17.0$ Hz) and 5.13 ($J_{1,2} = 10.4$ Hz). These doublets were not well defined, suggesting possible long range coupling to H_4 . When the H_1 and H_2 signals were expanded, the additional couplings $J_{1,4} = 0.9$ Hz and $H_{2,4} = 0.7$ Hz were observed. These long range couplings were also absent in the deuterated diene (96). The H_1 and H_2 signals in trans-1,2-diphenyl-1,3-butadiene (95) were more complex. However, when expanded, the splitting pattern became evident. A line reproduction of the expanded H_1 and H_2 signals for (95) is presented in Figure 2.1. At slightly higher field (δ 5.19), H_1 appeared as a doublet of doublets of doublets characterized by the coupling constants $J_{1,3} = 16.8$ Hz, $J_{1,2} =$

1.7 Hz, and $J_{1,4} = 0.6$ Hz, while H_2 (δ 5.31) exhibited a doublet of triplets characterized by the coupling constants $J_{2,3} = 11.2$ Hz, $J_{1,2} = 1.7$ Hz, and $J_{2,4} = 1.7$ Hz. When the long range coupling was removed, either by replacing H_4 with deuterium as in (97), or by irradiating the H_4 signal, the H_1 and H_2 signals were each reduced to a pair of doublets.

From the nmr spectral data it is clear that H_4 does not couple strongly to the remaining olefinic protons, thereby eliminating other isomeric diphenylbutadienes such as 1,3- or 1,4-diphenyl-1,3-butadienes as possible products. The other isomeric compound, 2,3-diphenyl-1,3-butadiene was eliminated from consideration by its authentic synthesis¹²¹ and comparison of its nmr spectrum with that of (94) and (95).

The mass spectra of dienes (94) and (95) showed a prominent molecular ion at m/e 206, consistent with the molecular weight of these compounds. Other abundant fragment ions at m/e 205, 204, 191, 178, and 128 can all be explained by the intermediacy of a cyclopropane radical cation. Less abundant fragment ions at m/e 104 and 102 can be accounted for by a second, weakly competing process.

The tropylium cation, m/e 91, is the base peak in the spectrum of (94) and an abundant fragment in (95). This fragment ion can be rationalized by the process shown on the following page, which is supported by the presence of a metastable at m/e 29.

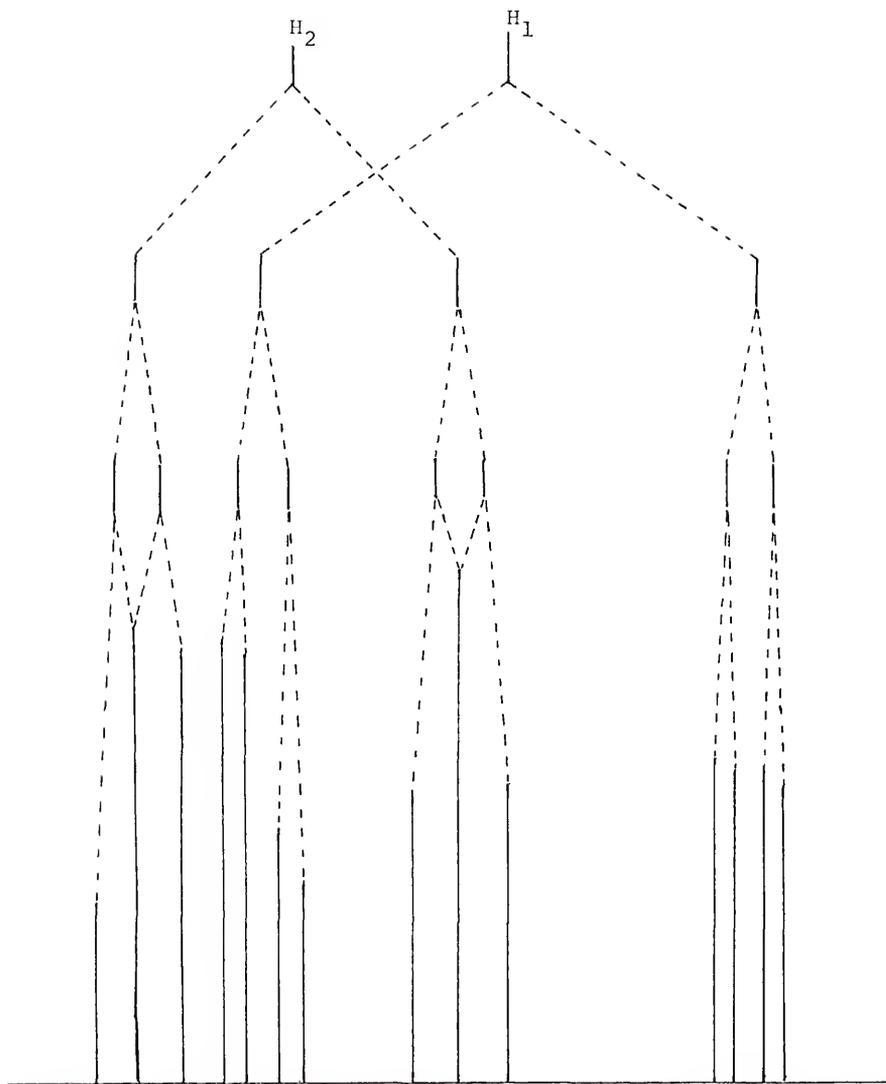


Fig. 2.1. Line reproduction of the expanded nuclear magnetic resonance absorptions of H₁ and H₂ in Z-1,2-diphenyl-1,3-butadiene (95).

TABLE 2.5
 PROTON MAGNETIC RESONANCE SPECTRAL DATA OF 1,2-Diphenyl-1,3-BUTADIENES
 (94), (95), (96), AND (97)

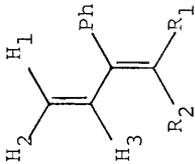
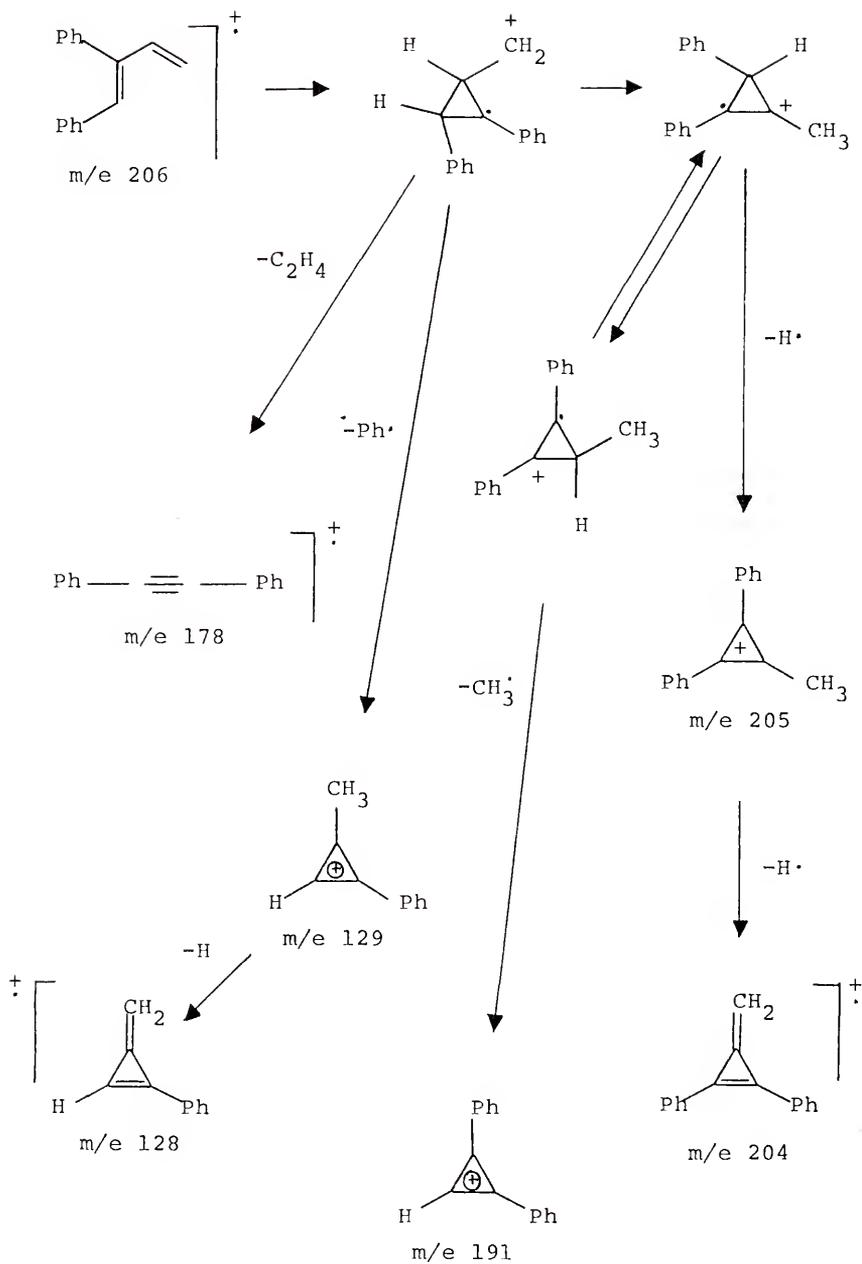
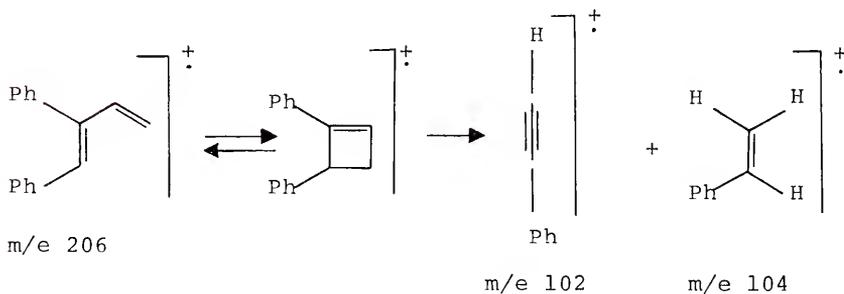
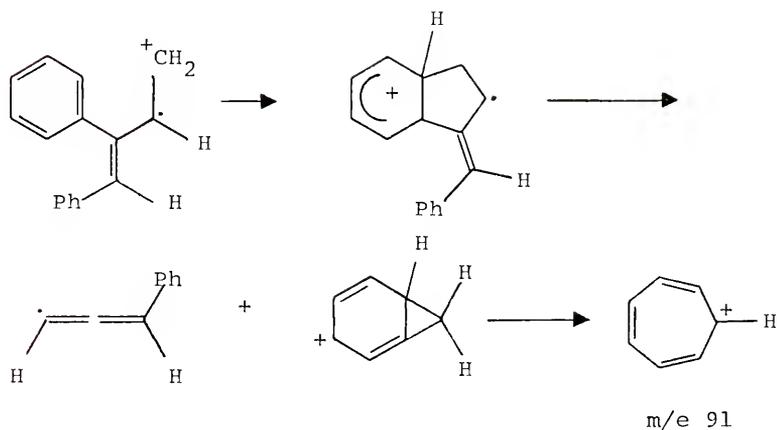
Compound ^a	Ar	H ₁	H ₂	H ₃	H ₄	J values
	(94), R ₁ = Ph; R ₂ = H ₄	4.81 (d, d, d)	5.13 (d, d, d)	6.72 (d, d, d)	6.57 (bs)	H ₁ H ₂ = 1.4 Hz H ₁ H ₃ = 17.0 Hz H ₁ H ₄ = 0.9 Hz H ₂ H ₃ = 10.4 Hz H ₂ H ₄ = 0.7 Hz H ₃ H ₅ = 1.0 Hz
	(95), R ₁ = Ph; R ₂ = H ₄	4.81 (d, d, d)	5.13 (d, d, d)	6.72 (d, d, d)	6.57 (bs)	H ₁ H ₂ = 1.4 Hz H ₁ H ₃ = 17.0 Hz H ₁ H ₄ = 0.9 Hz H ₂ H ₃ = 10.4 Hz H ₂ H ₄ = 0.7 Hz H ₃ H ₅ = 1.0 Hz
	(96), R ₁ = Ph; R ₂ = H ₄	4.81 (d, d, d)	5.13 (d, d, d)	6.72 (d, d, d)	6.57 (bs)	H ₁ H ₂ = 1.4 Hz H ₁ H ₃ = 17.0 Hz H ₁ H ₄ = 0.9 Hz H ₂ H ₃ = 10.4 Hz H ₂ H ₄ = 0.7 Hz H ₃ H ₅ = 1.0 Hz
	(97), R ₁ = Ph; R ₂ = H ₄	4.81 (d, d, d)	5.13 (d, d, d)	6.72 (d, d, d)	6.57 (bs)	H ₁ H ₂ = 1.4 Hz H ₁ H ₃ = 17.0 Hz H ₁ H ₄ = 0.9 Hz H ₂ H ₃ = 10.4 Hz H ₂ H ₄ = 0.7 Hz H ₃ H ₅ = 1.0 Hz
	(98), R ₁ = Ph; R ₂ = H ₄	4.81 (d, d, d)	5.13 (d, d, d)	6.72 (d, d, d)	6.57 (bs)	H ₁ H ₂ = 1.4 Hz H ₁ H ₃ = 17.0 Hz H ₁ H ₄ = 0.9 Hz H ₂ H ₃ = 10.4 Hz H ₂ H ₄ = 0.7 Hz H ₃ H ₅ = 1.0 Hz

TABLE 2.5 (continued)

Compound	ν	H_1	H_2	H_3	H_4	J values
(96), $R_1 = \text{Ph}$, $R_2 = \text{D}$	7.40-6.85 (m, 10H)	4.83 (d,d)	5.10 (d,d)	6.72 (d,d)	---	$H_1H_2 = 1.4$ Hz
						$H_1H_3 = 17.0$ Hz
						$H_2H_3 = 10.4$ Hz
(95), $R_1 = H_4$; $R_2 = \text{Ph}$	7.30 (s)	5.19 (d,d,d)	5.31 (d,t)	7.02 (d,d)	---	$H_1H_2 = 1.7$ Hz
						$H_1H_3 = 16.8$ Hz
						$H_1H_4 = 0.6$ Hz
						$H_2H_3 = 11.2$ Hz
						$H_2H_4 = 1.7$ Hz
$H_3H_4 = 1.0$ Hz						
(97), $R_1 = \text{D}$; $R_2 = \text{Ph}$	7.32 (s)	5.19 (d,d)	5.32 (d,d)	7.03 (d,d)	---	$H_1H_2 = 1.7$ Hz
						$H_1H_3 = 16.8$ Hz
						$H_2H_3 = 11.2$ Hz

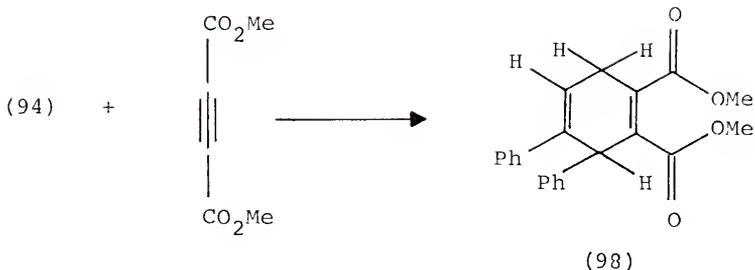
^aAt ambient temperature in CDCl_3 . All chemical shifts are δ -values. s = singlet, bs = broad singlet, m = multiplet, d,d = doublet of doublets, d,t = doublet of triplets, d,d,d = doublet of doublets of doublets.





Additional evidence concerning the structure of the dienes (94) and (95) obtained from the Grignard reagent was provided by their authentic synthesis from methylindene-triphenylphosphorane and the α -phenylcinnamaldehydes (50) and (64), respectively. The dienes obtained from either reaction were, in every respect, identical.

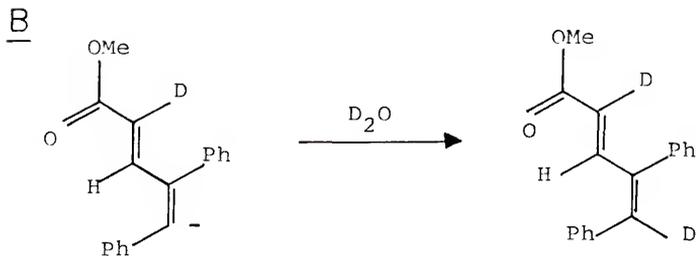
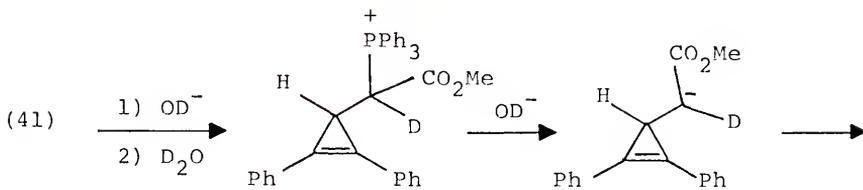
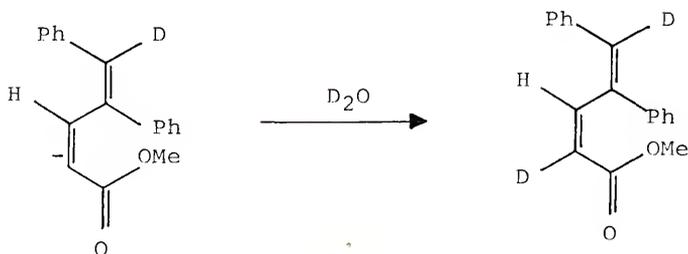
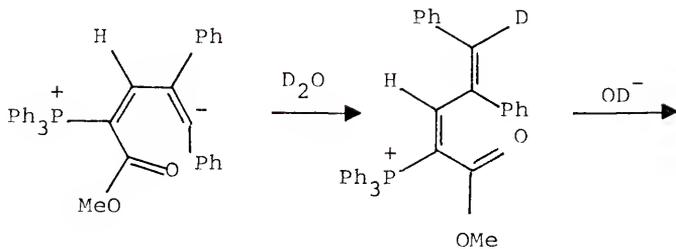
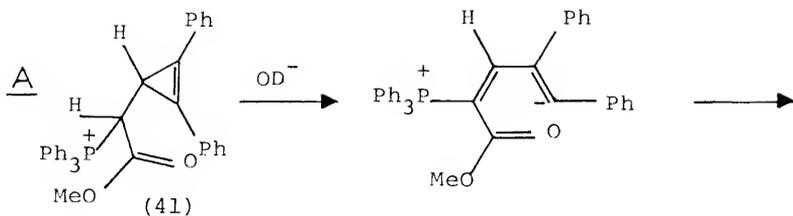
Finally, *E*-1,2-diphenyl-1,3-butadiene was reacted with dimethyl acetylenedicarboxylate to give the 1:1 Diels-Alder adduct (98) in 78% yield, finalizing the ring opened structure.

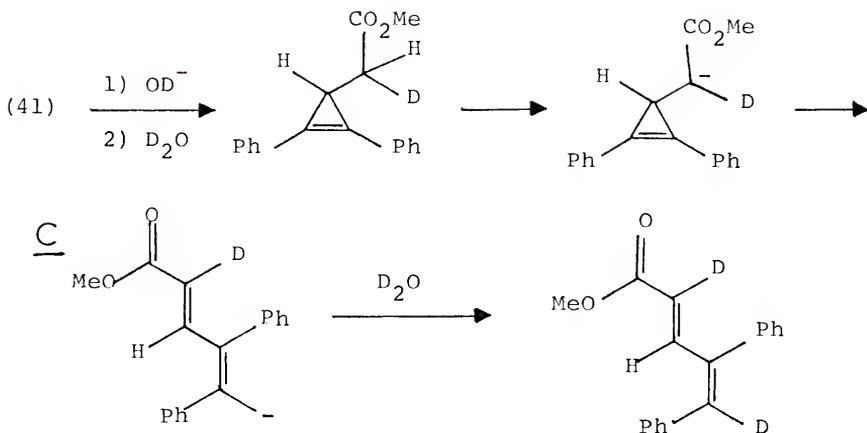


Discussion

The products from the basic hydrolysis of cyclopropenylcarbinyl phosphonium salts (39), (41), (43), (45), and (47) are all 1,3-butadienes and their formation may best be explained in terms of the general mechanism for phosphonium salt decomposition followed by irreversible ring opening of an extruded cyclopropenylcarbinyl anion and solvent capture of the resulting butadienyl anion. The specific products in each case can be rationalized by considering steric and conformational effects in the butadienyl anions.

Some evidence for the intermediacy of a cyclopropenylcarbinyl anion was obtained from the hydrolysis of salt (41) in deuterated medium. Deuterium was found to be incorporated at both the 2- and 5-positions of the ring opened dienes and this incorporation was shown by control experiments to occur before or during the product forming step, but not after product formation. Several mechanistic possibilities are compatible with this result and are shown on the following page.

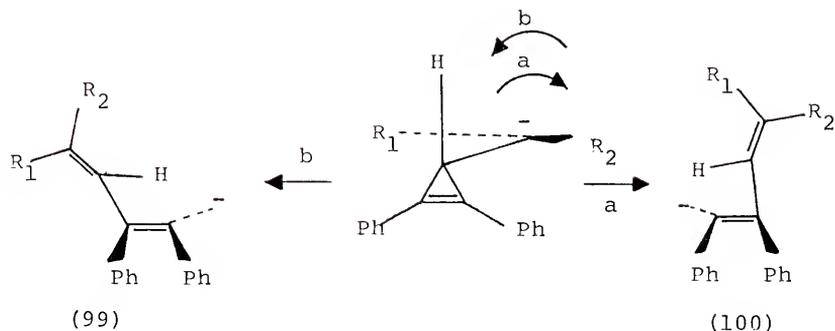




In A, ring opening followed by solvent capture would yield a butadienylphosphonium salt which could then undergo decomposition to give a butadienyl anion. Capture by solvent would give the products containing deuterium at both the 2- and 5-positions. Although this mechanism accounts for the products observed, one might question why products arising from nucleophilic attack at the terminal position of the butadienyl phosphonium salt are not observed in light of the fact that vinyl phosphonium salts are readily attacked by nucleophiles at the terminal carbon.

The available data does not allow distinction between mechanisms B and C. However, decomposition prior to exchange is unlikely since ylids (40) and (42) are prepared from their phosphonium salt precursors with aqueous potassium hydroxide or sodium hydroxide without any accompanying decomposition. It appears, then, that mechanism B best accounts for the deuterium incorporation and that the cyclopropenylcarbinyl ylid is a likely intermediate in this reaction.

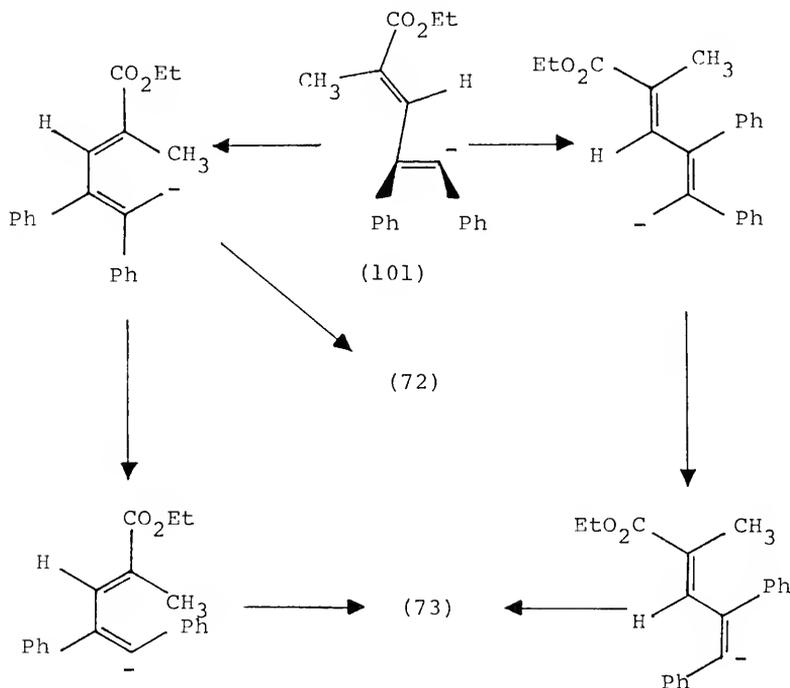
The stereochemistry of the products from each salt can be explained by invoking controlled ring opening of the intermediate cyclopropenylcarbinyl anions coupled with the effects of non-bonded steric interactions and conformational effects in the subsequent butadienyl anions. No calculations have been conducted concerning the preferred conformation of the cyclopropenylcarbinyl anion, but Danen⁹⁰ has calculated the energies of both the bisected and perpendicular cyclopropylcarbinyl anion and has shown that the perpendicular conformation is slightly preferred. By analogy, the perpendicular conformation for the cyclopropenylcarbinyl anion may be assumed. From this conformation, rotation of the anion center and concomittant cleavage of a cyclopropene side bond can occur in either of two directions, giving both cis and trans stereochemistry about the newly formed double bond, as observed in the products from decomposition of salts (41), (43) and (47). Of course, when the substituents R and R₁ are equal, as in salt (39), the direction of rotation is inconsequential. The relatively low yield of products isolated from the decomposition of the benzoyl salt (45) makes a diffinitive statement difficult in this case.



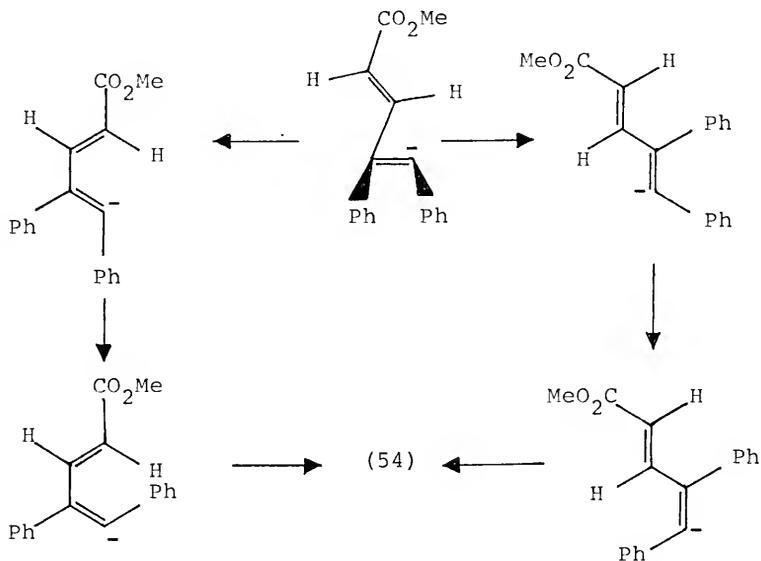
The butadienyl anions (99) and (100), generated from cyclopropene cleavage, will be formed initially in an energetically unfavorable perpendicular conformation and should then collapse into either a planar cisoid or transoid conformation. In the fluorenyl case, only in the cisoid conformation are non-bonded interactions as a minimum, and from this conformation, cis-trans isomerization of the type observed for the α -stilbene anion¹²² is precluded by steric effects. Therefore, the observed product (49), containing the phenyl substituents cis, is entirely consistent with the above mechanistic arguments.

The two products (72) and (73), identified from the hydrolysis of salt (43) can also be explained by similar arguments. The perpendicular butadienyl anion (101) can collapse to either the cisoid or transoid anion since replacement of the fluorenyl ring system by methyl and

carboethoxy substituents should decrease the non-bonded interactions in the transoid anion. In the cisoid form, isomerization of the phenyl substituents is hindered to some degree by the methyl substituent at C₂ and solvent capture might lead predominantly to the E,Z-diene (72). In the transoid form, non-bonded interactions should not be as severe as in the fluorenyl case and phenyl isomerization could compete with solvent capture, resulting in formation of the E,E-diene (73).



Products containing only trans-phenyl substituents were obtained from the hydrolysis of salts (41), (45) and (47). The E,E-dienes can be explained as before. Collapse of the perpendicular butadienyl anion can again give either the cisoid or transoid anions. In these cases, however, phenyl isomerization is relatively unhindered by non-bonded interactions in either planar diene conformation since the bulky C₂ substituent has been replaced by hydrogen, and hence only trans-phenyl products are observed.



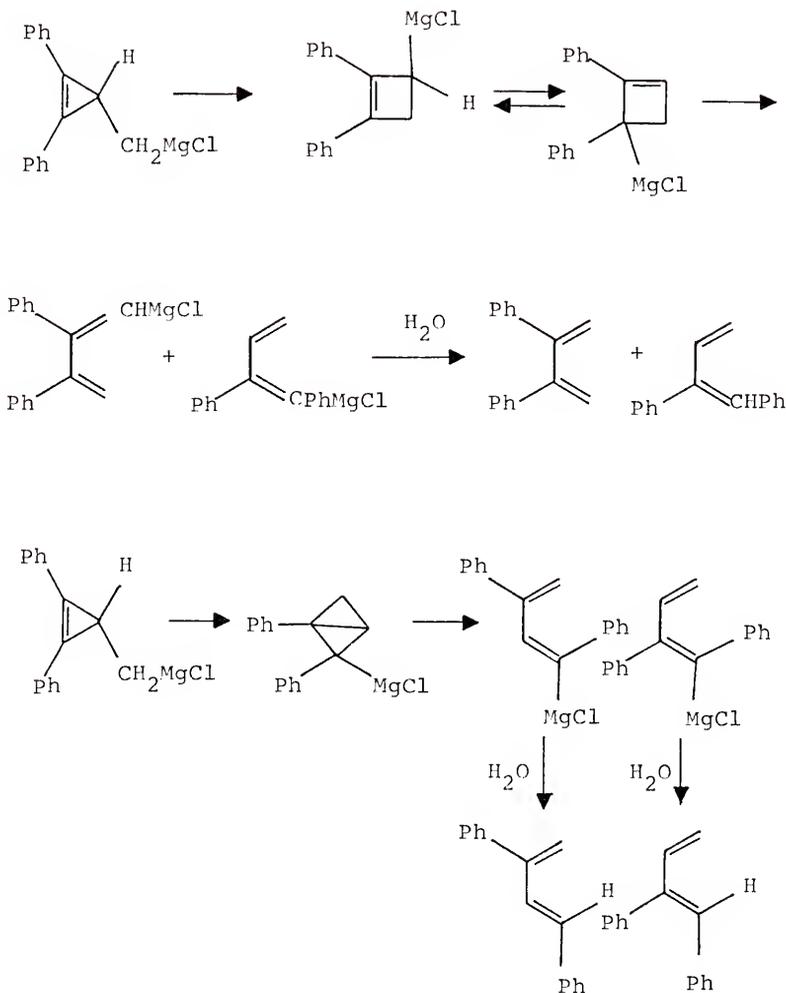
The second perpendicular butadienyl anion, in which the C₂ and C₃ hydrogens are cis might also collapse to two planar dienyl anions. In the cisoid form, however, electronic and

steric interactions could hinder both phenyl isomerization and solvent capture, and the Z,E-dienes might arise solely from the transoid form.

It is evident that the products obtained from each phosphonium salt can be explained in terms of a simple ring opening of the cyclopropenyl anion to butadienyl anions, without intervention of non-classical or ring expanded anion intermediates. The same may be said for the results obtained from the Grignard reagent prepared from the cyclopropenylcarbinyl chloride (94). Only 1,2-diphenyl-1,3-butadienes were observed, strongly suggesting that alternate mechanisms shown on the following page are not operating.

In the first case, either ring expansion prior to or after Grignard formation would produce a cyclobutenyl Grignard which could exist in either of two allylic forms. Ring opening and subsequent trapping with water should give a mixture of 1,2- and 2,3-diphenylbutadienes. Since none of the latter was observed, ring expansion of the initially formed cyclopropenylcarbinyl magnesium chloride appears to be unlikely mechanistic pathway.

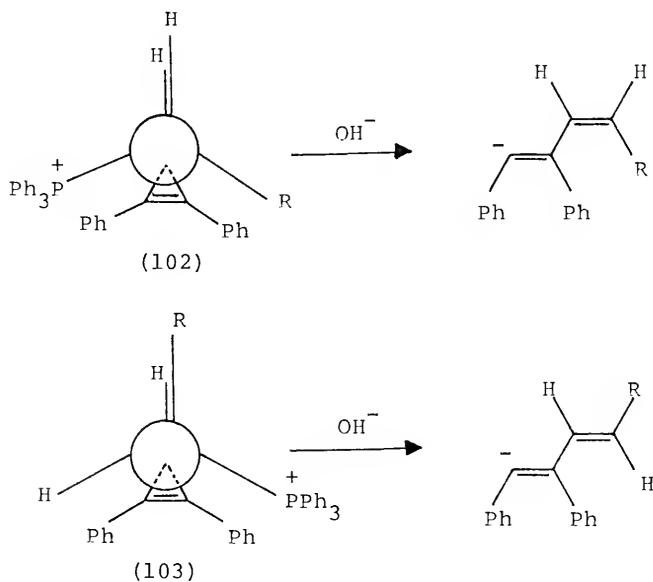
In the second alternate mechanism, the initial Grignard reagent might collapse to a bicyclobutyl Grignard. This species could undergo ring opening in either of two ways to produce a mixture of 1,3- and 1,2-diphenylbutadienes. Again, the presence of only 1,2-diphenylbutadienes in the product mixture argues against this mechanism.

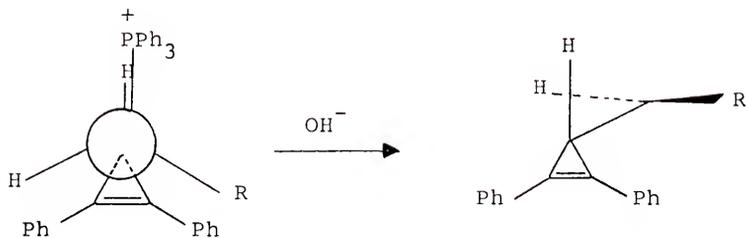


A concerted phosphorous-carbon bond-cyclopropene ring cleavage, leading directly to a butadienyl anion without the intermediacy of a cyclopropenylcarbinyl anion can not be ruled out by these results. In the fluorenyl case, however, products resulting from capture of a cyclopropenylcarbinyl anion would not be observed, since 1,2-diphenyl-

3-(9'-fluorenyl)-cyclopropene was demonstrated to afford the ring opened product (49) under the conditions of hydrolysis.

A concerted process can only occur from conformations (102) and (103), in which the developing negative charge can interact directly with a cyclopropene side bond without rotation. Models indicate that in either conformation, non-bonded interactions between the phenyl rings bound to phosphorous and the cyclopropene phenyl substituents are at a maximum and that these interactions are minimal when the cyclopropene ring and the triphenylphosphinyl groups are anti, as in conformation (104).





(104)

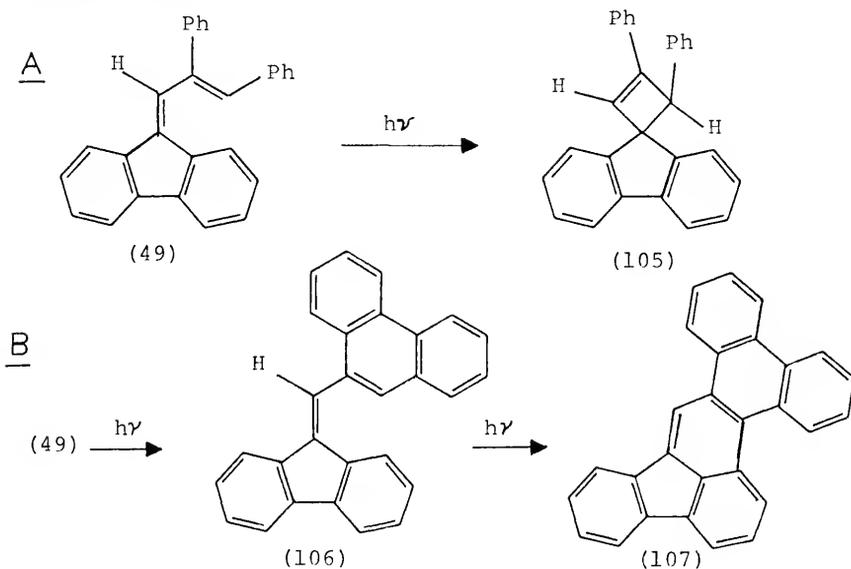
In conclusion, the preceding results show that the fate of the cyclopropenylcarbinyl anion parallels that of the cyclopropenylcarbinyl anion in that only products resulting from ring opening are observed.

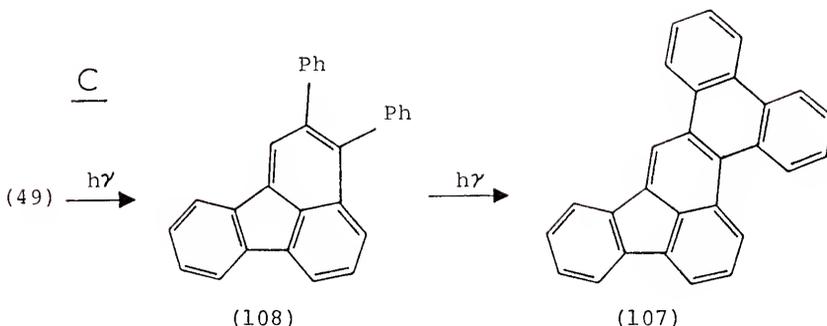
CHAPTER IV

PHOTOCHEMICAL SYNTHESIS OF FLUORANTHRENES

On characterization of compound (49), obtained either from the hydrolysis of salt (39) or from the Wittig reaction of α -phenylcinnamaldehyde (50) with ylid (38), it was observed that the initial yellow color of an ethanol solution of (49) disappeared when exposed to light. This interesting observation led to an investigation of the photochemical behavior of (49) and related compounds.

Several possible photochemical reactions of (49) are outlined below.

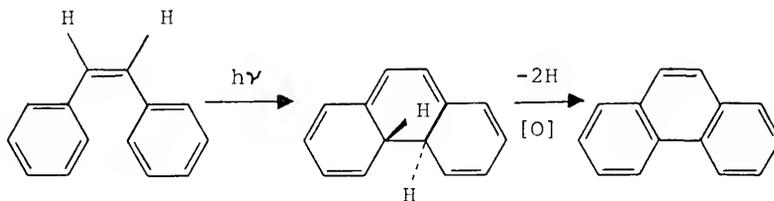




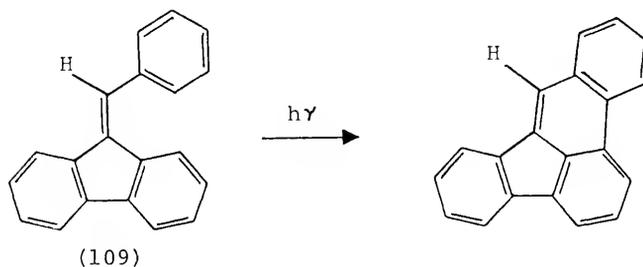
Pathway A involves a butadiene to cyclobutene isomerization, yielding the spiro compound (105), which could arise from either a concerted, disrotatory ring closure or a diradical process and should be readily distinguished from the possible polycyclic products by nmr or mass spectrographic means. Pathways B and C involve photodehydrocyclizations. In B, a cis-stilbene to phenanthrene conversion would give (106), which could undergo a second photodehydrocyclization to give the completely cyclized product (107). In pathway C this reaction sequence is reversed, the first photo conversion leading to the fluorene compound (108), which may or may not proceed on to (107) via a second photodehydrocyclization. In all, then, three products, (106), (107) and (108), arising from photodehydrocyclizations should be considered as possible products.

The photoconversion of cis-stilbene and related compounds to phenanthrene derivatives have been extensively investigated and reviewed.¹²³ These reactions involve photocyclization to give a dihydrophenanthrene intermediate,

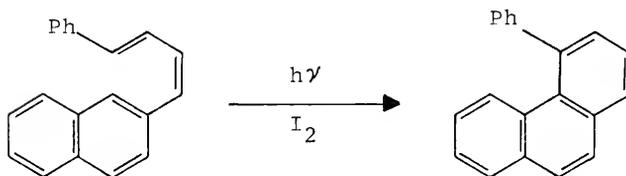
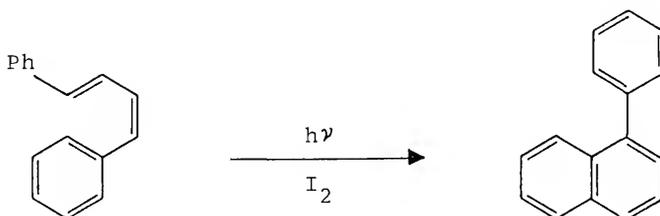
which is readily oxidized by oxygen or another oxidizing agent to give the phenanthrene product.



Photocyclizations of the type required for conversion of (106) into (107) or conversion of (49) into (108) are less well known. Scholz and co-workers¹²⁴ have shown that a related compound (109) affords the benzofluoranthrene ring system in very poor yield. This system is not strictly analogous to (49), however, since it does not contain a terminal double bond. There are no other examples of photosynthesis of the fluoranthrene ring system by dehydrocyclizations.



Aromatic hydrocarbons containing butadiene side chains have been reported to undergo photodehydrocyclizations. For example, substituted 1,4-diphenylbutadienes have been shown to yield naphthalenes upon photolysis.¹²⁵ In addition, 1-(2'-naphthalene)-4-phenylbutadiene has been shown to give 1-phenylphenanthrene under similar conditions.¹²⁶

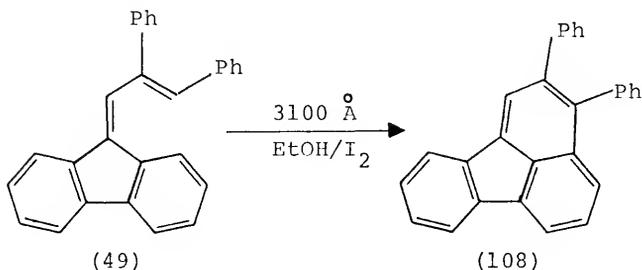


Results

Photolysis of (49) in ethanol at 3100 \AA in the presence of iodine resulted in the formation of a single photoproduct in 56% yield. This product was assigned the 2,3-diphenyl-

fluoranthrene structure (108) on the basis of the evidence presented below.

The nmr spectrum of (108) exhibited only aromatic absorptions, the phenyl protons appearing as two sharp spikes at δ 7.05 and 7.10 and the fluoranthrene ring protons as a multiplet at 8.05-7.20. Absence of any signal corresponding to a benzyl proton clearly excludes (105) from structural consideration.

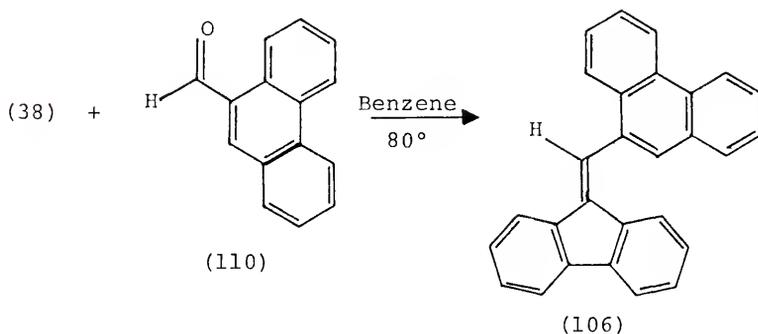


From the mass spectral evidence it was also clear that (108) resulted from a photodehydrocyclization process. The molecular ion at m/e 354 was two mass units less than that of (49). In addition, the molecular ion was also the base peak, which would be expected for a polycyclic aromatic compound. There were no major fragment ions associated with the mass spectrum of (108), but a doubly charged molecular ion at m/e 177 was quite apparent. Double charged molecular ions are rare, but seem to occur most frequently

in polycyclic systems capable of extensive delocalization of the charge associated with the molecular radical cation.

The ultraviolet spectrum of (108) showed low energy maxima at 365 and 350 nm, indicating extended conjugation. The complete ultraviolet spectral data for this compound are presented in Table 2.6.

From the nmr and mass spectral data presented above, it is clear that (108) arises via a photodehydrocyclization process; however, this data does not allow distinction between (108) and (106), since both compounds contain only aromatic protons and have the same molecular formula, $C_{28}H_{18}$. Therefore, the synthesis of (106) was undertaken. This was accomplished in 65% yield from the Wittig reaction of (110) with ylid (38).

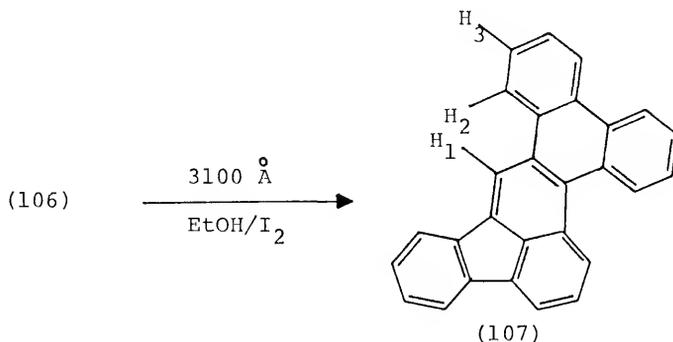


The nmr spectrum of (106) consisted of a multiplet at δ 8.83-8.50 (2H) and a broad multiplet at 8.13-6.60 (16H). The lowfield multiplet, which can be assigned to the protons

bound to C₄ and C₅ of the phenanthrene ring, is completely absent in (108). Furthermore, the sharp spikes associated with the phenyl protons in (108) are absent in (106).

As expected, the mass spectrum of (106) displayed a molecular ion at m/e 354 which was also the base peak, and again there were no major fragment ions in the spectrum. However, a doubly charged molecular ion was observed at m/e 177.

The successful photosynthesis of the fluoranthrene ring system from (49), coupled with the results of Scholz,¹²⁴ mentioned previously, suggested that (106) might afford the unknown phenanthro [9,10-b] fluoranthrene ring system on photolysis. Photodehydrocyclization of (106) in ethanol at 3100 Å in the presence of ethanol did, in fact, give the completely cyclized product (107) in 30% yield.



The nmr spectrum of (107) exhibited only aromatic absorptions, although there was some detail. Thus, a

sharp spike at δ 9.30 was assigned to H₁ with confidence. Similarly the multiplet at 8.97-8.50 (5H) was assigned to H₂, H₅, H₆, H₉ and H₁₀, all of which occupy positions analogous to H₄ and H₅ of phenanthrene. The other ten protons appeared as a broad multiplet at 8.30-7.17.

The mass spectrum of (107) displayed a molecular ion at m/e 352, which was also the base peak and two mass units less than for the molecular ion of (106). No other major fragment ions were detected, but doubly and triply charged molecular ions were observed at m/e 176 and 117.3, respectively.

The ultraviolet spectrum of (108) exhibited two low energy maxima at 386 and 367 nm along with a number of higher energy maxima. The complete ultraviolet spectral data for this compound are given in Table 2.6.

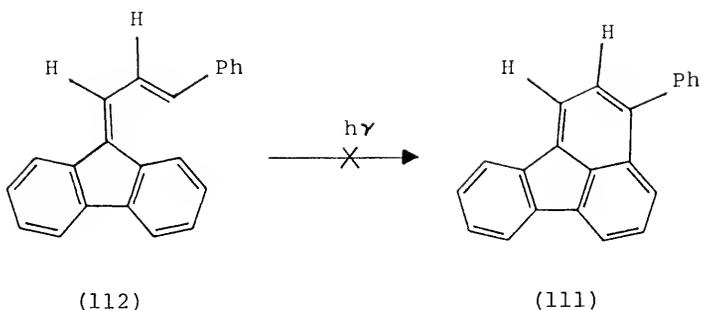
These two photochemical syntheses, coupled with the sketchy work of Scholz,¹²⁴ offer a convenient two step synthesis into the heretofore difficultly synthesized fluoranthrene ring system. The general applicability of this method, however, appears to be limited. All attempts to prepare 3-phenylfluoranthrene (111) via photodehydrocyclization of the fluorenylidene (112), prepared from the Wittig reaction of cinnamaldehyde with ylid (38), failed and the recovery of starting material was almost quantitative.

TABLE 2.6

ULTRAVIOLET SPECTRA OF FLUORENYLIDENE
DERIVATIVES (49), (107), (108) AND (109).

Compound	λ_{\max} ^a	ϵ
(49)	353	12,500
	292 (sh)	9,800
	257	31,900
	228	35,350
(107)	337	12,700
	295	17,200
	255	68,200
	249	69,800
	229	56,800
(108)	386	15,900
	367	14,800
	313	40,100
	306	49,500
	301	52,600
	265 (sh)	44,800
	254	52,500
	226	34,100
(109)	365	9,800
	350	9,400
	332 (sh)	6,000
	289	16,800
	277	29,700
	250	35,300
	223	30,000

^aIn 95% ethanol. (sh) = shoulder peak

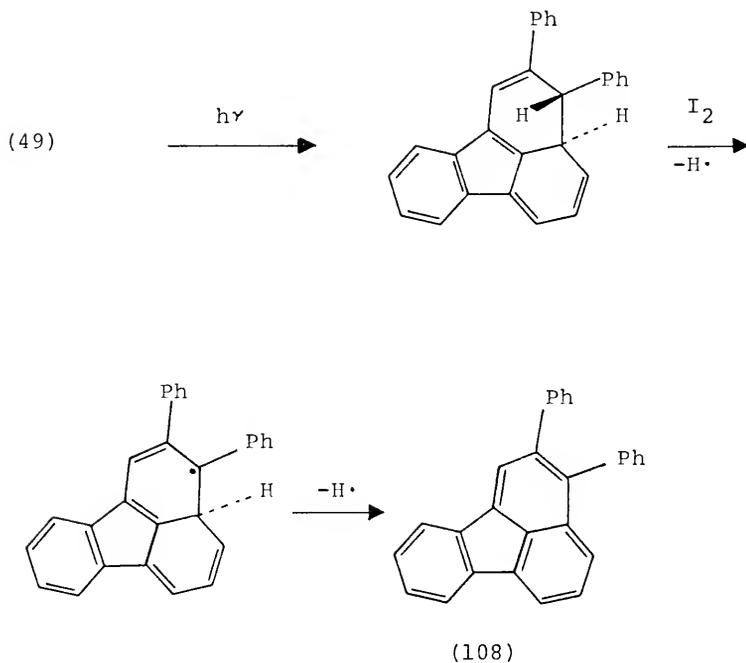


The only apparent difference in (112) and the fluorenylidene compounds (49), (106) and (109) which undergo photoconversion to fluoranthrene derivatives is the absence of a bulky substituent beta to the fluorene ring. In (49), this substituent is a phenyl group while in (109) and (106), the beta carbon is incorporated in the benzene and phenanthrene substituents, respectively.

One possible explanation for the lack of fluoranthrene products upon irradiation of (112) may be that the absence of a large substituent beta to the fluorene ring allows the butadiene portion of this molecule to assume a preferred transoid configuration, from which cyclization cannot occur. Until other fluorenylidene derivatives have been investigated and general trends established, an adequate explanation for the failure of (112) to undergo dehydrocyclization must remain a matter of conjecture.

Although no mechanistic investigation of these photo-dehydrocyclizations was conducted, it may be assumed that

the oxidation step takes place after the cyclization step as has been shown in the dehydrocyclization of stilbene by Fischer.¹²⁷



CHAPTER V

EXPERIMENTAL

9-Fluorenyltriphenylphosphonium bromide¹⁰¹

A solution of 9-bromofluorene (11.2 g, 0.0456 moles) and triphenylphosphine (12.0 g, 0.0458 moles) in dry benzene (75 ml) was prepared in a 200-ml round-bottomed flask equipped with a reflux condenser. The reaction solution was heated at reflux for twenty hours, cooled to room temperature, and the precipitate collected on a filter and washed with hot benzene. The crude salt was dissolved in hot chloroform and titrated with ethyl acetate until crystallization just began. After allowing the solution to cool to room temperature, the product was filtered, washed with cold ethyl acetate and dried under vacuum. 9-Fluorenyltriphenylphosphonium bromide (20.4 g, 88%) was obtained as white prisms, mp 276-279° (Lit¹⁰¹ mp 277-278°).

9-Fluorenylidetriphenylphosphorane (38)¹⁰¹

A solution of potassium hydroxide (0.084 g, 3.3 mmoles) in ethanol (4 ml) was added dropwise to a solution of fluorenyltriphenylphosphonium bromide (0.200 g, 0.490 mmoles) in

hot ethanol (6 ml). After addition was complete, the reaction mixture was stirred for an additional five minutes and then cooled to room temperature. The precipitate was collected on a filter, washed with cold ethanol and dried under vacuum, affording 9-fluorenylidene-triphenylphosphorane (0.145 g, 90%) as bright yellow plates, mp 252-253° (Lit.¹⁰¹ mp 253-254°).

Carbomethoxymethylidene-triphenyl-
phosphorane (40)¹⁰²

Carbomethoxymethyl-triphenylphosphonium bromide (10.0 g, 0.0241 moles) was dissolved in water (300 ml) and benzene (200 ml), and phenolphthalein (3 drops) was added. The two phase solution was stirred vigorously and titrated with dilute aqueous sodium hydroxide to the phenolphthalein endpoint. The benzene layer was separated, washed with water, dried over anhydrous magnesium sulfate, filtered and concentrated to approximately 50 ml under reduced pressure. Petroleum ether was added dropwise until crystallization just began. The solution was allowed to cool to room temperature and the precipitate was collected on a filter, washed twice with cold petroleum ether and air dried. Carbomethoxymethylidene-triphenylphosphorane (4.1 g, 50%) was obtained as colorless prisms, mp 204-206° (Lit.¹⁰² mp 205-206°).

α-Carboethoxyethyl-triphenylphosphonium
bromide¹⁰³

A solution of triphenylphosphine (10.5 g, 0.0401 moles)

and ethyl 2-bromopropionate (7.24 g, 0.0398 moles) in benzene (100 ml) was prepared on a 250-ml round-bottomed flask equipped with a reflux condenser. The solution was heated at reflux for six hours, cooled to room temperature and the solvent removed under reduced pressure. The orange oil that remained was placed on a column of silica gel and eluted with chloroform. The elutant was removed under reduced pressure, giving α -carboethoxyethyltriphenylphosphonium bromide (7.8 g, 44%) as a colorless oil. This salt was used in the subsequent preparation of α -carboethoxyethylidene-triphenylphosphorane without further purification.

α -Carboethoxyethylidene-triphenyl-
phosphorane (42)¹⁰³

The salt (7.8 g, 0.018 moles) obtained in the preceding reaction was dissolved in water (100 ml). Benzene (100 ml) and phenolphthalein (3 drops) were added and the two phase solution was stirred vigorously and titrated with dilute sodium hydroxide to the phenolphthalein endpoint. The yellow benzene layer was separated, washed with water, dried over anhydrous sodium sulfate, filtered and concentrated to approximately 40 ml under reduced pressure. Petroleum ether was added dropwise until crystallization just began. The solution was allowed to cool to room temperature and the precipitate was collected on a filter, washed twice with petroleum ether and air dried. α -Carboethoxyethylidene-

triphenylphosphorane (42) (5.54 g, 85%) was obtained as pale yellow prisms, mp 161-163° (Lit.¹⁰³ mp 161-164°).

Phenacyltriphenylphosphonium
bromide¹⁰⁴

A solution of triphenylphosphine (5.2 g, 0.020 moles) and 2-bromoacetophenone (4.0 g, 0.020 moles) in benzene (30 ml) was prepared in a 100-ml round-bottomed flask equipped with a reflux condenser. The solution was heated at reflux for four hours and cooled to room temperature. The precipitate that formed was collected on a filter, washed with hot benzene and air dried to give crude phenacyltriphenyltriphenylphosphonium bromide (9.0 g, 98%) as a white powder, mp 263-267°. Recrystallization from chloroform-ethyl acetate afforded the salt (8.7 g, 95%) as white needles, mp 274-276° (Lit¹⁰⁴ mp 269-271°).

Phenacylidenetriphenylphosphorane (44)¹⁰⁴

Phenacyltriphenylphosphonium bromide (8.7 g, 0.019 moles) was dissolved in water (300 ml). Benzene (200 ml) and phenolphthalein (2 drops) were added and the two phase solution was stirred vigorously and titrated with a 2% aqueous sodium hydroxide solution to the phenolphthalein endpoint. The benzene layer was separated, washed with water, dried over anhydrous sodium sulfate, filtered and concentrated to approximately 50 ml under reduced pressure. Hexane was added

dropwise until crystallization was induced. The solution was allowed to cool to room temperature and the precipitate was collected on a filter, washed with hexane and dried under vacuum. Phenacylidenetriphenylphosphorane (5.0 g, 69%) was obtained as white prisms, mp 182-184° (Lit.¹⁰⁴ mp 178-180°).

p-Nitrobenzyltriphenylphosphonium
bromide¹⁰⁵

A solution of triphenylphosphine (5.2 g, 0.020 moles) and p-nitrobenzylbromide (4.3 g, 0.020 moles) in benzene (100 ml) was prepared in a 200 ml round-bottomed flask equipped with a reflux condenser. The solution was heated at reflux for five hours and cooled to room temperature. The precipitate was collected on a filter, washed with hot benzene and air dried. The crude salt was recrystallized from chloroform-ethyl acetate, affording p-nitrobenzyltriphenylphosphonium bromide (7.9 g, 85%) as colorless prisms, mp 166-168° (Lit.¹⁰⁵ mp 168-170°).

p-Nitrobenzylidenetriphenylphosphorane (46)¹⁰⁵

A solution of p-nitrobenzyltriphenylphosphonium bromide (2.39 g, 0.500 mmoles) in dry methylene chloride (10 ml) was prepared in a 25-ml three-necked round-bottomed flask equipped with a mechanical stirrer, syringe cap and nitrogen purge. The salt solution was stirred for five minutes under nitrogen

and then a 1.6 M solution of n-butyl lithium (4.0 ml, 6.4 mmoles) was added via syringe. The resulting blood red reaction mixture was stirred at room temperature for two hours and washed with water. The organic layer was separated, dried over anhydrous magnesium sulfate, filtered and the solvent removed under reduced pressure. The reaction residue was taken up in hot benzene and filtered to remove unreacted p-nitrobenzyltriphenylphosphonium bromide. The benzene solution was chilled in an ice-water bath and the precipitate was collected on a filter, washed with cold benzene and dried under vacuum. p-Nitrobenzylidenetriphenylphosphorane (46) (1.23 g, 77%) was obtained as red needles, mp 169-171° (Lit.¹⁰⁵ mp 171-172°).

9-(2',3'-Diphenyl-2'-cyclopropen-1'-yl)-

fluorenyltriphenylphosphonium perchlorate (39)

A solution of 9-fluorenylidenetriphenylphosphorane (38) (0.852 g, 1.99 mmoles) in methylenechloride (10 ml) was added dropwise under nitrogen to a stirred suspension of diphenylcyclopropenium perchlorate (37) (0.580 g, 1.99 mmoles) in methylenechloride (20 ml) over a period of ten minutes. As the ylid was added, the cyclopropenium salt dissolved and a dark green solution resulted. The reaction mixture was stirred for an additional three hours and then concentrated to approximately 5 ml under reduced pressure. The concentrated solution was added dropwise to 100 ml of

cold ether and the precipitate that resulted was collected on a filter, washed with ether and air dried to give (39) (1.278 g, 89%) as a white powder, mp 163-167°. Recrystallization from chloroform-ethyl acetate afforded (39) as colorless prisms, mp 169-171°.

Anal. Calcd. for $C_{46}H_{34}PClO_4$: C, 77.04; H, 4.78; Cl, 4.94.

Found: C, 76.91; H, 4.66; Cl, 4.99.

The nmr spectrum ($CDCl_3$) showed a broad aromatic multiplet at δ 7.9-6.8 (33H) and a singlet at 3.91 (1H).

The infrared spectrum (KBr) showed carbon-hydrogen stretching at 3100 (w), cyclopropene stretching at 1850 (w), intense perchlorate absorption at 1085 (vs) and other absorptions at 1500 (m), 1455 (s), 1035 (w), 1020 (w), 990 (w), 751 (s), 724 (m) and 688 (s) cm^{-1} .

The ultraviolet spectrum (CH_2Cl_2) showed maxima at 333 (5400), 313 (9300), 275 (14200) and 269 nm (14500) along with strong end absorption.

Carbomethoxy-(2,3-diphenyl-2-cyclopropen-1-yl)-methyltriphenylphosphonium perchlorate (41)

A solution of carbomethoxymethylidenetriphenylphosphorane (40), (1.002 g, 3.000 mmoles) in methylenechloride (10 ml) was added dropwise under nitrogen to a stirred suspension of diphenylcyclopropenium perchlorate (37) (0.870 g, 2.99 mmoles) in methylene chloride (15 ml). The reaction mixture was

stirred under nitrogen for four hours and the solvent removed under reduced pressure. The brown reaction residue was dissolved in methanol and chilled with an ice-water bath. The precipitate was collected on a filter, washed with cold methanol and air dried to give (41) as a tan solid, mp 173-177°. Recrystallization from methanolether-chloroform yielded (41) (1.68 g, 90%) as pale tan prisms, mp 176-178°.

Anal. Calcd. for $C_{36}H_{30}PCl_6$: C, 69.18; H, 4.84.

Found: C, 68.90; H, 4.83.

The nmr spectrum ($CDCl_3$) showed a complex aromatic multiplet at δ 7.70-7.28 (25H), a doublet of doublets for the cyclopropenylcarbonyl proton at 4.68 (1H, $J = 11.0$ Hz, $J' = 5.0$ Hz), a singlet for the methyl ester protons at 3.41 (eH) and a triplet for the cyclopropenyl proton at 2.87 (1H, $J = J' = 5.0$ Hz).

The infrared spectrum (KBr) showed carbon-hydrogen stretching frequencies at 3040 (w) and 2900 (w), cyclopropene stretching frequency at 1830 (w), strong carbonyl absorption at 1740 (s), intense, broad perchlorate absorption at 1095 (vs) and other absorptions at 1435 (m), 760 (s), 727 (m) and 688 (s) cm^{-1} .

The ultraviolet spectrum (CH_2Cl_2) showed maxima at 326 (15,800), 311 (22,800), 277 (13,100) and 270 nm (11,300) along with strong end absorption.

α -Carboethoxy- α -(2,3-diphenyl-2-cyclopropen-1-yl)-
ethyltriphenylphosphonium perchlorate (43)

A solution of α -carboethoxyethylidenetriphenylphosphorane (42) (0.724 g, 2.00 mmoles) in methylene chloride (15 ml) was added dropwise under nitrogen to a stirred suspension of diphenylcyclopropenium perchlorate (0.580 g, 1.99 mmoles) in methylene chloride (10 ml). The reaction mixture was stirred under nitrogen for three hours and the solvent was then removed under reduced pressure. The orange reaction residue was dissolved in chloroform and titrated with ether until cloudy. The solution was stirred over night and the precipitate that formed was collected on a filter, washed with ether and air dried to yield crude (43) (1.184 g, 91%) as a white powder, mp 189.5-192°. Recrystallization from chloroform-ethyl acetate afforded (43) (1.043 g, 80%) as colorless prisms, mp 193-194.5°.

Anal. Calcd. for $C_{38}H_{34}PClO_6$: C, 69.88; H, 5.25; Cl, 5.43.

Found: C, 69.82; H, 5.28; Cl, 5.50.

The nmr spectrum ($CDCl_3$) showed a broad aromatic multiplet at δ 7.90-6.90 (25H), a doublet of quartets for the methylene ester protons at 4.05 (2H, $J = 7.0$ Hz, $J' = 1.5$ Hz), a doublet for the cyclopropene proton at 3.38 (1H, $J = 3.0$ Hz), a doublet for the cyclopropenylcarbiny methyl protons at 1.43 (3H, $J = 18.0$ Hz) and a triplet for the methyl ester protons at 1.00 (3H, $J = 7.0$ Hz).

The infrared spectrum (KBr) showed carbon-hydrogen stretching frequencies at 3050 (w), 2990 (w) and 2920 (w), cyclopropene stretching at 1830 (w), strong carbonyl absorption at 1750 (s), broad perchlorate absorption at 1087 (vs) and other absorptions at 1490 (m), 1450 (s), 1340 (s), 1220 (vs), 780 (m), 770 (s), 757 (s), 693 (s) and $\delta 25$ (s) cm^{-1} .

The ultraviolet spectrum (CH_2Cl_2) showed maxima at 325 (13,800), 309 (21,500), 277 (14,800) and 269 nm (12,700) as well as strong end absorption.

α -(2,3-Diphenyl-2-cyclopropen-1-yl)phenacyl-
triphenylphosphonium perchlorate (45)

A solution of phenacylidetriphenylphosphorane (44), (0.760 g, 2.00 mmoles) and diphenylcyclopropenium perchlorate (0.580 g, 2.00 mmoles) in methylene chloride (10 ml) was stirred under nitrogen for seven hours. The reaction mixture was then concentrated under reduced pressure to approximately 3 ml and added dropwise to cold ether. The precipitate was collected on a filter, washed with cold ether and air dried to give (45) (1.230 g, 92%) as a pale yellow powder, mp 160-165°. Recrystallization from chloroform-ethyl acetate afforded (45) (1.029 g, 77%) as colorless prisms, mp 173-175°. Solvent could not be completely removed from this phosphonium salt.

Anal. Calcd. for $\text{C}_{41}\text{H}_{32}\text{PClO}_5$: C, 73.37; H, 4.81;

Cl, 5.28

Found: C, 71.37; H, 4.57; Cl, 5.39.

The nmr spectrum (CDCl_3) showed a broad aromatic multiplet at 8.15-6.96 (30H), a doublet of doublets for the cyclopropenylcarbinyl proton at 6.30 (1H, $J = 4.5$ Hz, $J' = 9.0$ Hz) and a second doublet of doublets for the cyclopropene proton at 3.05 (1H, $J = 4.5$ Hz, $J' = 6.5$ Hz).

The infrared spectrum (KBr) showed carbon-hydrogen stretching at 2970 (w), cyclopropene stretching at 1830 (w), carbonyl stretching at 1670 (s) and perchlorate absorption at 1090 (vs) along with other absorptions at 1600 (m), 1490 (m), 1440 (s), 1000 (s), 752 (vs), 725 (s) and 691 (s) cm^{-1} .

The ultraviolet spectrum (CH_2Cl_2) showed maxima at 328 (7,800), 309 (12,700), 304 (12,900), 276 (12,300) and 263 nm (16,500) along with strong end absorption.

α -(2,3-Diphenyl-2-cyclopropen-1-yl)-p-nitrobenzyltriphenylphosphonium perchlorate (47)

A solution of p-nitrobenzylidenetriphenylphosphorane (46) (0.794 g, 2.00 mmoles) in methylene chloride (10 ml) was added dropwise under nitrogen to a stirred suspension of diphenylcyclopropenium perchlorate (0.580 g, 1.99 mmoles) in methylene chloride (10 ml). The reaction mixture was stirred under nitrogen for five hours and then added dropwise to ether (150 ml). The tan precipitate that resulted was collected on a filter, washed with cold ether and air

dried, yielding crude (47) (1.10 g, 80%) as a pale tan powder, mp 181-186°. Recrystallization from chloroform-ethyl acetate afforded (47) (0.976 g, 71%) as pale tan crystals, mp 187-190°.

Anal. Calcd. for $C_{40}H_{31}PClNO_6$: C, 69.81; H, 4.54; N, 2.04.

Found: C, 69.55; H, 4.45; N, 1.89.

The nmr spectrum ($CDCl_3$) showed a broad aromatic multiplet at δ 8.1-6.7 (29H), a doublet of doublets for the benzyl proton at 5.13 (1H, $J = 6.0$ Hz, $J' = 16.0$ Hz) and a second doublet of doublets for the cyclopropene proton at (1H, $J = 6.0$ Hz, $J' = 1.0$ Hz).

The infrared spectrum (KBr) showed carbon-hydrogen stretching at 2940 (w), cyclopropene absorption at 1825 (w), nitro stretching at 1535 (s) and perchlorate absorption at 1095 (vs) along with other absorptions at 1580 (m), 1435 (s), 1345 (s), 858 (m), 755 (m), 723 (m) and 688 (s) cm^{-1} .

The ultraviolet spectrum (CH_2Cl_2) showed maxima at 329 (13,700), 310 (21,200), 277 (13,100), and 268 nm (12,200) along with strong end absorption.

Hydrolysis of Phosphonium Salt (39)

Phosphonium salt (39) (0.177 g, 0.287 mmoles) was added in portions to a stirred solution of potassium hydroxide (0.112 g, 2.00 mmoles) in dimethyl sulfoxide (5 ml) and water (1 ml). The orange-red reaction mixture was stirred

at room temperature for three hours and then extracted with methylene chloride. The organic layer was separated, dried over anhydrous magnesium sulfate, filtered, and the solvent removed under reduced pressure. The yellow reaction residue was dissolved in ethanol and cooled overnight. The precipitate was collected on a filter, washed with cold ethanol and dried under vacuum, affording 1,2-diphenylpropenylidene fluorene (49) (0.053 g, 52%) as yellow needles, mp 132-135°. A second recrystallization gave an analytical sample (0.041 g, 40%) as yellow needles, mp 142.5-143.5°.

Anal. Calcd. for $C_{28}H_{20}$: C, 94.34; H, 5.66.

Found: C, 94.30; H, 5.67.

The nmr spectrum ($CDCl_3$) showed a low field multiplet at δ 8.15 (1H), a multiplet at 7.61 (3H) and a broad multiplet at 7.45-7.05 (16H).

The infrared spectrum (KBr) showed carbon-hydrogen stretching at 2950 (w), olefinic stretching at 1600 (w) and 1580 (w) along with other absorptions at 1560 (w), 1435 (s), 920 (m), 905 (m), 780 (s), 758 (m), 731 (s), 705 (s) and 690 (s) cm^{-1} .

The mass spectrum showed a molecular ion at m/e 356 (100%) along with other abundant fragments at 279 (60%), 278 (38%), 265 (14%), and 165 (16%).

The ultraviolet spectrum (95% ethanol) showed maxima at 353 (12,500), 292 (9,800), 257 (31,900) and 228 nm (35,500).

E- α -phenylcinnamaldehyde (50)¹¹³

A solution of benzaldehyde (52.2 g, 0.494 moles) and potassium hydroxide (4.0 g, 0.071 moles) in ethanol (100 ml) was prepared in a 500-ml three-necked round-bottomed flask equipped with a dropping funnel, thermometer and nitrogen purge and cooled to 5° with an ice-water bath. Phenylacetaldehyde (52.5 g, 0.438 moles) was added dropwise over a period of five hours while maintaining the reaction temperature at 5-10°. The reaction mixture was stirred for an additional 2.5 hours and the solid that formed was collected on a filter and washed with cold ethanol. The washings were combined with the mother liquor and poured into water (500 ml) and extracted three times with ether. The ether extracts were combined, dried over sodium sulfate, filtered and the solvent was removed under reduced pressure. The reaction residue was vacuum distilled and the fraction at 136° at 0.5 mm was collected, combined with the original solid and recrystallized from methanol. The product was collected on a filter, washed with cold methanol and dried under vacuum, giving E- α -phenylcinnamaldehyde (50) (52.7 g, 58%) as white plates, mp 92-93° (Lit.¹¹³ mp 94°).

Authentic Synthesis of 1,2-Diphenylpropenylidene fluorene (49)

A solution of fluorenylidene triphenylphosphorane (38) (1.704 g, 4.00 mmols) and E- α -phenylcinnamaldehyde

(50) (0.832 g, 4.00 mmoles) in benzene (30 ml) was heated at reflux for 37 hours. The reaction solution was cooled to room temperature and the solvent removed under reduced pressure. The reaction residue was examined by thin layer chromatography, and shown to consist of two components, the slower moving of which was identified as triphenylphosphine oxide, by comparison with authentic material. The residue was placed on a column of alumina and eluted with 5% chloroform in hexane. The collected fractions (100 ml) were combined according to thin layer behavior and the solvent removed under reduced pressure. The residue was dissolved in ethanol, cooled and the precipitate collected on a filter, washed with cold ethanol and air dried, yielding (49) (0.740 g, 52%) as bright yellow needles, mp 142-143°. The nmr, infrared, and ultraviolet spectra of this material confirmed that it was identical to (49) obtained from hydrolysis of salt (39). The melting point of a mixture of the two samples was not depressed.

Base Catalyzed Isomerization of 1,2-Diphenyl-3-(9'-fluorenyl)-cyclopropene (51)

The cyclopropene (51) (0.070 g, 0.20 mmoles) was added in portions to a solution of potassium hydroxide (0.14 g, 2.5 mmoles) in dimethyl sulfoxide (5 ml) and water (1 ml). The resulting orange reaction mixture was stirred at room temperature for three hours and extracted with

methylene chloride. The organic layer was separated, washed with water, dried over anhydrous sodium sulfate, filtered and the solvent evaporated under reduced pressure. The residue was dissolved in ethanol and cooled. The precipitate was collected on a filter, washed with cold ethanol and air dried, giving (49) (0.057 g, 81%) as yellow needles, mp 141-143°.

9-(2',3'-Diphenylprop-1'-enyl)-fluorene (52)

A sample of (49) (0.250 g, 0.702 mmoles) was refluxed with excess lithium aluminum hydride (ca 1 g) in anhydrous tetrahydrofuran (40 ml) for 20 hours. The red reaction mixture was quenched with saturated ammonium chloride solution. The organic layer was separated, washed with water, dried over anhydrous sodium sulfate, filtered, and the solvent evaporated under reduced pressure. The residue was dissolved in benzene-hexane and cooled. The precipitate was collected on a filter, washed with cold hexane and dried under vacuum, yielding (51) (0.080 g, 32%) as colorless prisms, mp 125-127°. Recrystallization from hexane gave an analytical sample, mp 130-131.5°.

Anal. Calcd. for $C_{28}H_{22}$: C, 93.81; H, 6.19.

Found: C, 93.62; H, 6.22.

The nmr spectrum ($CDCl_3$) showed a multiplet for the C_4 - and C_5 -fluorenyl protons at δ 7.75 (2H), an aromatic multiplet at 7.60-7.10 (16H), a doublet for the olefinic proton at 5.75

(1H, $J = 10$ Hz), a doublet for the 9-fluorenyl proton at 4.98 (1H, $J = 10$ Hz) and a singlet for the benzyl protons at 4.37 (2H).

The infrared spectrum (CDCl_3) showed carbon-hydrogen stretching at 2940 (w), olefinic stretching at 1590 (w) and other absorptions at 1485 (w), 1380 (m), 1030 (m), 935 (m), 905 (m), 769 (s), 753 (s), 745 (s), 728 (s), 721 (s), and 693 (s) cm^{-1} .

The mass spectrum showed a molecular ion at m/e 358 (25%) along with other prominent fragments at m/e 267 (base peak), 178 (18%) and 165 (20%).

9-(2',3'-Diphenylprop-1'-enyl)-9-d-fluorene (53)

A sample of (49) (0.511 g, 1.44 mmoles) was refluxed with excess lithium aluminum hydride (ca 0.5 g) in anhydrous tetrahydrofuran (35 ml) for 18 hours. The red reaction mixture was cooled to 0° and quenched by cautious addition of D_2O . The organic layer was separated, washed with water, dried over anhydrous sodium sulfate, filtered and the solvent evaporated under reduced pressure. The residue was placed on a column of alumina and eluted with 1:1 benzene-hexane. The collected fractions (30 ml) were combined according to thin layer behavior, the solvent removed under reduced pressure and the residue dissolved in hot hexane. The solution was cooled and the precipitate was collected on a filter, washed with cold hexane and dried under vacuum, giving (53)

(0.150 g, 32%) as colorless prisms, mp 129.5-130.5°.

Anal. Calcd. for $C_{28}H_{21}D$: C, 93.55; H, 6.45.

Found: C, 93.50; H, 6.46.

The nmr spectrum ($CDCl_3$) confirmed deuterium incorporation at the 9-fluorenyl position, showing a multiplet for the C_4 - and C_5 -fluorenyl protons at δ 7.75 (2H), an aromatic multiplet at 7.65-7.05 (16H), a singlet for the olefinic proton at 5.68 (1H) and a singlet for the benzyl protons at 4.30 (2H).

Hydrolysis of Phosponium Salt (41)

A solution of (41) (1.0 g, 1.6 mmoles) and potassium hydroxide (1.0 g, 18 mmoles) in dimethyl sulfoxide (4 ml) and water (1 ml) was stirred at room temperature for two hours. The reaction mixture was then poured into water and extracted with methylene chloride. The methylene chloride extract was washed with water, dried over anhydrous magnesium sulfate, filtered and the solvent evaporated, giving triphenylphosphine oxide (0.421 g, 95%) as a pale white solid, mp 156-157°. The aqueous layer was acidified to pH ca 2 with dilute hydrochloric acid and extracted with ether. The ether extracts were combined, washed with water, dried over anhydrous sodium sulfate, filtered and the solvent removed under reduced pressure, affording a mixture of E,E- and Z,E-4,5-diphenylpentadienoic acids (54) and (55), (0.350 g, 88%) as a cream colored solid. Examination by nmr spectroscopy revealed

that this was a 1:1 mixture of (54) and (55). These acids could not be separated by thin layer chromatography using benzene, chloroform, benzene-chloroform, acetone, ethyl acetate, ethyl acetate-chloroform or acetone-chloroform as elutants.

The nmr spectrum (CDCl_3) of this mixture showed a broad singlet for the acid proton at δ 10.34 (2H), a doublet for H_3 of acid (54) at 7.98 (1H), a sharp spike for the aromatic protons at 7.33 (20H), a broad singlet for H_5 at 6.87 (2H), and two doublets for the H_2 protons of (54) and (55) at 5.88 (1H, $J = 16.0$ Hz) and 6.07 (1H, $J = 12.0$ Hz), respectively.

The infrared spectrum (KBr) of this mixture showed broad oxygen-hydrogen stretching from 3200-2850 (s), carbonyl stretching at 1710 (s) and olefinic absorption at 1610 (s) along with other absorptions at 1490 (m), 1435 (m), 1420 (m), 1380 (s), 1295 (s), 1215 (m), 945 (m), 794 (w), 772 (m), 751 (m), and 700 (s) cm^{-1} .

Esterification of Acid Mixture (54) and (55)

A 0.5 M ethereal solution of 3-methyl-p-tolyltriazine (58) (6 ml) was added dropwise to a solution of the acid mixture (54) and (55), (0.348 g, 1.39 mmoles) in ether (10 ml) prepared in a 50-ml three-necked round-bottomed flask equipped with a bubbler. The reaction was monitored until nitrogen evolution ceased and then was stirred for an additional hour.

The reaction mixture was then washed with 5% aqueous hydrochloric acid, 5% aqueous sodium bicarbonate, and water. The organic layer was separated, dried over anhydrous sodium sulfate, stirred with norite and filtered. The solvent was evaporated under reduced pressure and the pale orange reaction residue (0.317 g, 82%) was analyzed by nmr spectroscopy. No acid proton signal was detected and two new methyl ester signals were observed in approximately equal intensity. Separation was attempted by column chromatography. The ester mixture was placed on a column of silica gel and eluted with 9:1 hexane-chloroform. The collected fractions (20 ml) were combined according to their nmr spectroscopic appearance.

The first component to elute from the column was methyl *E,E*-4,5-diphenyl-2,4-pentadienoate (56) (15 mg) as a white solid, mp 61-62°.

The nmr spectrum (CDCl_3) of (56) showed a doublet of doublets for H_3 at δ 7.98 (1H, $J_{2,3} = 16.0$ Hz, $J_{3,5} = 1.0$ Hz), a sharp spike for the aromatic protons at 7.33 (10H), a distorted triplet for H_5 at 6.87 (1H, $J_{3,5} = 1.0$ Hz, $J_{2,5} = 0.8$ Hz), a doublet of doublets for H_2 at 5.88 (1H, $J_{2,3} = 16.0$ Hz, $J_{2,5} = 0.8$ Hz) and a sharp singlet for the methyl ester protons at 3.68 (3H).

The infrared spectrum (KBr) showed carbon-hydrogen stretching at 2970 (w) and 2950 (w), carbonyl stretching at 1700 (s) and olefinic stretching at 1610 (m) along with other absorptions at 1475 (w), 1435 (m), 1425 (m), 1265 (s),

1160 (s), 924 (w), 874 (w), 791 (w), 770 (m), 751 (s) and 703 (s) cm^{-1} .

The mass spectrum showed a molecular ion at exact mass 264.1143 (calcd; 264-1149).

The ultraviolet spectrum (95% ethanol) showed maxima at 314 (17,000) and 239 nm (19,000) along with strong end absorption.

After a mixture of the esters was eluted (0.236 g), a small quantity of ester (57) (17 mg) was collected as a colorless oil.

Anal. Calcd. for $\text{C}_{18}\text{H}_{16}\text{O}_2$: C, 81.79; H, 6.10.

Found: C, 81.62; H, 6.17.

The nmr spectrum (CDCl_3) of (57) showed a sharp spike for the aromatic protons at δ 7.32 (10H), a doublet of doublets for H_3 at 7.00 (1H, $J_{2,3} = 12.0$ Hz, $J_{3,5} = 1.8$ Hz), a distorted triplet for H_5 at 6.86 (1H, $J_{2,5} = 1.2$ Hz, $J_{3,5} = 1.8$ Hz), a doublet of doublets for H_2 at 6.07 ($J_{2,3} = 12.0$ Hz, $J_{2,5} = 1.2$ Hz) and a sharp singlet for the methyl ester protons at 3.22 (3H).

The ultraviolet spectrum (95% ethanol) showed maxima at 310 and 274 nm, along with strong end absorption. The extinction coefficients were not calculated because the concentration of the sample was not accurately known.

Methyl E,Z-4,5-diphenyl-2,4-pentadienoate (59)

A solution of E- α -phenylcinnamaldehyde (50) (0.331 g, 1.59 mmol) was added dropwise to a solution of carbomethoxy-

methylidetriphenylphosphorane (40), (0.531 g, 1.59 mmoles) in benzene (15 ml) prepared in a 50-ml three-necked round-bottomed flask equipped with a reflux condenser and nitrogen purge. The reaction mixture was heated at reflux for 37 hours, cooled to room temperature and examined for unreacted aldehyde by nmr spectroscopy. No aldehyde was detected and the solvent was removed under reduced pressure. The reaction residue was dissolved in hot methanol and cooled. The precipitate was collected on a filter, washed with cold methanol and air dried, giving (59) (0.265 g, 63%) as white needles, mp 85-89°. A second recrystallization from methanol gave an analytical sample of (59) mp 88.5-89.5°.

Anal. Calcd. for $C_{18}H_{16}O_2$: C, 81.79; H, 6.10.

Found: C, 81.77; H, 6.14.

The nmr spectrum ($CDCl_3$) showed a doublet for H_3 at δ 7.69 (1H, $J_{2,3} = 16.0$ Hz), a broad aromatic multiplet at 7.55-6.80 (10H), a broad singlet for H_5 at 6.88 (1H), a doublet for H_2 at 5.48 (1H, $J_{2,3} = 16.0$ Hz) and a singlet for the methyl ester protons at 3.67 (3H).

The infrared spectrum (KBr) showed carbon-hydrogen stretching at 2920 (w), carbonyl stretching at 1720 (s), olefinic stretching at 1605 (s) and other absorptions at 1425 (m), 1300 (s), 1282 (m), 1205 (m), 1175 (s), 1097 (m), 861 (m), 852 (m), 785 (w), 760 (m), 751 (w), 718 (m), 697 (s) and 692 (s) cm^{-1} .

The mass spectrum showed a molecular ion at m/e 264 (34%) along with other abundant fragments at m/e 206 (25%),

205 (base peak), 204 (51%), 203 (38%), 202 (27%), 191 (8%), 190 (13%), 178 (9%), 165 (7%), 159 (metastable), 128 (10%), 91 (8%) and 77 (9%).

Cyclohexylacetalimine

Acetaldehyde (44 g, 1.0 moles) was chilled to -20° with an acetone-dry ice bath and added dropwise under nitrogen to cyclohexylamine (99 g, 1.0 moles) also at -20° . The reaction mixture was stirred under nitrogen at -20° for an additional hour and then warmed to room temperature. Anhydrous sodium sulfate was added and the reaction mixture was vacuum distilled. The fraction at 33° at 5 mm afforded cyclohexylacetalimine (119 g, 94%) as a colorless oil. This material was used in the next reaction without further purification.

E,Z-4,5-Diphenyl-2,4-pentadienal (60)¹¹⁵

To a solution of diisopropylamine (3.65 ml) in dry ether (26 ml) was added 16.2 ml of a 1.6 M solution of *n*-butyl lithium in hexane, maintaining the temperature below -10° . Cyclohexylacetalimine (3.24 g, 0.0259 moles) in ether (26 ml) was then added dropwise. After 15 minutes, the temperature was lowered to -70° and a solution of E- α -phenylcinnamaldehyde (4.50 g, 21.6 μ moles) in ether (120 ml) was added dropwise. After the addition, the temperature was raised to 20° , then lowered to -10° and water (45 ml)

was added. The ethereal layer was separated and stirred for 16 hours with benzene (30 ml), acetic acid (11 ml) and water (27 ml). The organic layer was separated, washed with dilute aqueous sodium hydroxide and finally brine, dried over anhydrous sodium sulfate, filtered and the solvent removed under reduced pressure. The residue was crystallized from ethanol to give (60) (3.2 g, 83%) as pale yellow prisms, mp 89-94°. A second recrystallization from ethanol gave (60) (2.38 g, 62%) as white prisms, mp 96-97° (Lit.¹¹⁵ mp 92-94°).

The nmr spectrum (CDCl₃) showed a doublet for the aldehydic proton at δ 9.65 (1H, J = 8.0 Hz), a broad multiplet for the aromatic protons and H₃ and H₅ at 7.6-6.7 (12H) and a quartet for H₂ at 5.78 (1H, J = 16.0 Hz, J' = 8.0 Hz).

E,Z-4,5-Diphenyl-2,4-pentadienoic acid (61)

To a solution of sodium hydroxide (0.32 g) and silver nitrate (0.72 g) in 50% aqueous ethanol (12 ml) was added E,Z-4,5-diphenyl-2,4-pentadienal (60) (0.468 g, 2.00 mmoles). The reaction mixture was stirred at reflux for two hours, cooled to room temperature, filtered, washed with water, and cooled to 0°. The pH was adjusted to ca 3 with dilute hydrochloric acid and the acidic solution extracted with ether. The ether extract was separated, washed with water, brine, and water again, dried over anhydrous sodium sulfate, filtered and the ether removed under reduced pressure. The

residue was dissolved in hot ethanol and the solution cooled. The precipitate was collected on a filter, washed with cold ethanol and dried under vacuum. E,Z-4,5-Diphenyl-2,4-pentadienoic acid (61) (0.425 g, 85%) was obtained as white needles, mp 167.5-168.5°.

The nmr spectrum (CDCl₃) showed a singlet for the acidic proton at δ 11.02 (1H), a doublet for H₃ at 7.67 (1H, J = 16.0 Hz), a broad multiplet for H₅ and the aromatic protons at 7.4-6.7 (11H), and a doublet for H₂ at 5.48 (1H, J = 16.0 Hz).

Esterification of E,Z-4,5-Diphenyl-2,4-pentadienoic acid (61)

E,Z-4,5-Diphenyl-2,4-pentadienoic acid (61) (0.425 g, 1.61 mmoles) was esterified with 3-methyl-p-tolyltriazine (58) in a manner identical to that previously described for the esterification of the mixture of acids (54) and (55). A white needlelike solid (0.387 g, 86%) was obtained and shown by nmr spectroscopy to be identical to ester (59) obtained from the Wittig reaction of E- α -phenylcinnamaldehyde and ylid (40), mp 87-89°.

E- and Z- α -Phenylcinnamic Acid (65) and (66)¹¹⁸

A solution of benzaldehyde (60 g, 0.57 moles) and phenylacetic acid (50.0 g, 0.37 moles) in triethylamine (40 ml) and acetic anhydride (40 ml) was stirred at reflux

for 1 hour and then cooled to room temperature. Concentrated hydrochloric acid (80 ml) was added and the resulting paste was dissolved in ether (500 ml). The ethereal solution was washed twice with water and extracted three times with 500 ml portions of 2% aqueous sodium hydroxide. The alkaline extracts were combined and acidified with glacial acetic acid (100 ml). The resulting solid was collected on a filter and the mother liquor saved. The solid was washed with water, air dried and recrystallized from ether-petroleum ether. The product was collected on a filter, washed with cold petroleum ether and dried under vacuum, giving E- α -phenylcinnamic acid (65) (58 g, 70%) as white needles, mp 173-174° (Lit.¹¹⁸ mp 173-174°).

The nmr spectrum (CDCl₃) showed a singlet for the acidic proton at δ 11.00 (1H), a singlet for the olefinic proton at 8.02 (1H) and a multiplet for the aromatic protons at 7.75-6.98 (10H).

The infrared spectrum (KBr) showed an intense carbonyl absorption at 1680 (s) cm⁻¹.

The mother liquor from above was treated with concentrated hydrochloric acid (100 ml) and cooled at 5° for 24 hours. The coagulated solid was collected on a filter, washed with water and air dried. After recrystallization from ether-petroleum ether, Z- α -phenylcinnamic acid (9.2 g, 11%) was obtained as a granular white solid, mp 135-137° (Lit.¹¹⁸ mp 139-140°).

The nmr spectrum (CDCl_3) showed a singlet for the acidic proton at 11.50 (1H), a narrow multiplet for the aromatic protons at 7.53-7.25 (10H), and a singlet for the olefinic proton at 7.08 (1H).

The infrared spectrum (KBr) showed an intense carbonyl absorption at 1712 cm^{-1} .

Z-2,3-Diphenylpropene-1-ol (67)¹¹⁹

To a solution of anhydrous aluminum chloride (1.50 g, 11.2 mmoles) in dry ether (100 ml) was added a solution of lithium aluminum hydride (ca 1.0 g, 22 mmoles) in dry ether (30 ml). The mixture was stirred and a solution of Z- α -phenylcinnamic acid (66) (2.50 g, 11.1 mmoles) in dry ether (25 ml) was added and the resulting reaction mixture was heated at reflux for 1 hour. The mixture was then cooled to 0° , quenched with 50 ml of 20% aqueous sodium potassium tartrate, and the mixture filtered. The ether layer was separated and washed successively with water, 5% aqueous sodium hydroxide and water. After drying over anhydrous sodium sulfate, the ether was evaporated under reduced pressure and the residue dissolved in petroleum ether and cooled. The precipitate was collected on a filter, washed with cold petroleum ether and air dried to yield Z-2,3-diphenylpropene-1-ol (1.48 g, 64%) as white prisms, mp $76.5\text{--}77.5^\circ$ (Lit.¹¹⁹ mp $77\text{--}78^\circ$).

Z- α -Phenylcinnamaldehyde (64)

Z-2,3-Diphenylpropene-1-ol (2.4 g, 11 mmoles) and freshly prepared manganese dioxide (7.00 g, 66 mmoles) were stirred for 24 hours in dry petroleum ether (75 ml). The mixture was filtered and the manganese dioxide was copiously washed with methylene chloride. The washings were combined with the mother liquor, dried over anhydrous sodium sulfate, filtered and the solvent evaporated under reduced pressure. The residue was placed on a column of silica gel and eluted with 9:1 hexane-chloroform. The solvent was removed under reduced pressure and the residue was dissolved in hot petroleum ether (65-110°). The solution was chilled and the product collected on a filter, washed with cold petroleum ether and air dried. Z- α -phenylcinnamaldehyde (64) (1.34 g, 64%) was obtained as pale yellow needles, mp 120.5-121.5°. An analytical sample was obtained by sublimation (80° at 2 mm).

Anal. Calcd. for C₁₅H₁₂O: C, 86.51; H, 5.81.

Found: C, 86.40; H, 5.82.

The nmr spectrum (CDCl₃) showed a singlet for the aldehydic proton at δ 10.07 (1H), a singlet for the olefinic proton at 7.38 (1H) and a sharp spike for the aromatic protons at 7.25 (10H).

The infrared spectrum (KBr) showed carbon-hydrogen stretching at 2970 (w), carbonyl stretching at 1695 (s) and other absorptions at 1490 (m), 1440 (m), 1340 (m),

1060 (m), 1025 (m), 940 (m), 912 (m), 842 (w), 778 (s), 737 (m), and 700 (s) cm^{-1} .

The mass spectrum showed a molecular ion at m/e 208 (32%) along with other abundant fragments at m/e 207 (18%), 179 (27%), 178 (24%), 140 (14%), 149 (base peak), 102 (16%) and 77 (12%).

The ultraviolet spectrum (95% ethanol) showed maxima at 298 (14,200) and 226 nm (12,600) along with strong end absorption.

Attempted Isomerization of E- and Z- α -

Phenylcinnamaldehydes (50) and (64)

Separate solutions of (50) and (64) (0.100 g) in benzene (1 ml) were sealed under vacuum in nmr tubes and heated at 80° for 48 hours. The solutions were cooled to room temperature and examined by nmr spectroscopy. To the limits of detectibility, ca 95%, no isomerization of either isomer was observed.

Ethyl E,E-4,5-Diphenyl-2,4-pentadienoate (69)

A solution of Z- α -phenylcinnamaldehyde (64) (0.055 g, 0.26 mmoles) and carboethoxymethylidetriphenylphosphorane (68) (0.091 g, 0.26 mmoles) in benzene (5 ml) was stirred at reflux for 16 hours. The reaction mixture was cooled to room temperature and the solvent evaporated under reduced pressure. The residue was examined by silica gel thin layer

chromatography. Two components were detected and the slower moving component was identified as triphenylphosphine oxide by comparison to authentic material. The residue was placed on a column of silica gel and eluted with 9:1 hexane-chloroform. The fractions were combined according to their thin layer behavior and the solvent was removed under reduced pressure. The residual oil was dissolved in hot ethanol and the solution chilled. The precipitate was collected on a filter, washed with cold ethanol and air dried. Ethyl E,E-4,5-diphenyl-2,4-pentadienoate (69) (0.048 g, 66%) was obtained as white needles, mp 68-70°.

Anal. Calcd. for $C_{19}H_{18}O_2$: C, 81.98; H, 6.52.

Found: C, 81.98; H, 6.57.

The nmr spectrum ($CDCl_3$) showed a doublet of doublets for H_3 at δ 8.00 (1H, $J_{2,3} = 15.5$ Hz, $J_{3,5} = 1.0$ Hz), a sharp spike for the aromatic protons at 7.33 (10H), a doublet of doublets for H_2 at 5.85 (1H, $J_{2,3} = 15.5$ Hz, $J_{2,5} = 0.8$ Hz), a broad singlet for H_5 at 6.87 (1H), a quartet for the methylene ester protons at 4.18 (2H, $J = 7.0$ Hz) and a triplet for the methyl ester protons at 1.25 (3H, $J = 7.0$ Hz).

The infrared spectrum (KBr) showed carbon-hydrogen stretching at 3000 (m) and 2940 (m), carbonyl stretching at 1740 (s), olefinic stretching at 1630 (m) and other absorptions at 1610 (m), 1500 (m), 1450 (m), 1310 (m), 1285 (m), 1263 (m), 1182 (s), 1040 (m), 928 (m), 884 (m), 793 (w), 772 (m), 758 (m) and 702 (s) cm^{-1} .

The mass spectrum showed a molecular ion at m/e 278 (10%) along with other abundant fragments at m/e 205 (28%), 204 (9%), 179 (8%), 150 (11%), 149 (base peak), 91 (4%), 77 (5%) and 57 (9%).

Hydrolysis of Methyl E,Z-4,5-diphenyl-
2,4-pentadienoate (59)

A solution containing methyl E,Z-4,5-diphenyl-2,4-pentadienoate (59) (0.528 g, 2.00 mmoles) and potassium hydroxide (ca 1.0 g, 18 mmoles) in dimethyl sulfoxide (8 ml) and water (2 ml) was stirred at room temperature for three hours. The reaction mixture was then diluted with 50 ml of water and acidified to a pH of about 2 with dilute hydrochloric acid. The mixture was extracted with ether, the organic layer separated, washed with water and dried over anhydrous sodium sulfate. After evaporating the solvent under reduced pressure, the residue was dissolved in hot aqueous ethanol and the solution chilled. The product was collected on a filter, washed with cold water and dried under vacuum to yield E,Z-4,5-diphenyl-2,4-pentadienoic acid (0.480 g, 96%) as white needles, mp 167.5-168.5°. The nmr spectrum ($CDCl_3$) confirmed this to be unrearranged acid.

Hydrolysis of Phosphonium Salt (41) in
Deuterated Medium

Deuterium oxide (1.5 ml was placed in a dry 25-ml round-

bottomed flask equipped with a calcium chloride drying tube and cooled to 0-5° with an ice-water bath. Freshly cut sodium (ca 100 mg) was cautiously added in portions to the stirred deuterium oxide. After all the sodium dissolved, dimethyl sulfoxide (6.5 ml) was added and the solution warmed to room temperature. Phosphonium salt (41) (0.347 g, 0.555 mmoles) was then added in one portion and the reaction mixture was stirred at room temperature for 3 hours, diluted with water and acidified to a pH of about 2 with dilute hydrochloric acid. The acidic mixture was extracted with ether, the organic layer separated, washed with water, dried over anhydrous sodium sulfate and filtered. The ether was evaporated under reduced pressure and the residue examined by nmr spectroscopy.

The nmr spectrum (CDCl_3) showed a broad singlet for the acidic proton at δ 10.67 (2H), a broad singlet for H_3 of the E,E-acid at 8.00 (1H), a sharp spike for the aromatic protons at 7.34 (20H), and a broad singlet for H_3 of the Z,E-acid at 7.04 (1H).

Hydrolysis of Methyl E,Z-4,5-diphenyl-

2,4-pentadienoate (59) in Deuterated Medium

Deuterium oxide (1.5 ml) was cooled to 0-5° with an ice-water bath. Freshly cut sodium (ca 100 mg) was cautiously added in portions to the stirred deuterium oxide. After all the sodium dissolved, dimethyl sulfoxide (6.5 ml) was

added and the solution warmed to room temperature. Methyl E,Z-4,5-diphenyl-2,4-pentadienoate (59) (0.264 g, 1.00 mmoles) was added in one portion and the reaction mixture stirred at room temperature for 3 hours. The mixture was diluted with water, acidified to a pH of about 2 with dilute hydrochloric acid, and extracted with ether. The ether extracts were combined, filtered and the ether evaporated under reduced pressure. The residue was dissolved in hot aqueous ethanol and cooled. The precipitate was collected on a filter, washed with cold water and dried under vacuum. E,Z-4,5-diphenyl-2,4-pentadienoic acid (0.240 g, 91%) was obtained as white needles, mp 167-169°.

The nmr spectrum (CDCl₃) confirmed that this product had not incorporated deuterium.

Hydrogenation of Ethyl E,Z-4,5-diphenyl-2,4-pentadienoate

Ethyl E,Z-4,5-diphenyl-2,4-pentadienoate (0.556 g, 2.00 mmoles) was dissolved in methanol (25 ml) and hydrogenated under reduced pressure over an excess of 10% palladium on charcoal for 4 hours at room temperature. The reaction mixture was then filtered through a celite pad and the solvent removed under reduced pressure. Ethyl 4,5-diphenylpentanoate (70) (0.515 g, 91%) was obtained as a colorless oil. An analytical sample was obtained by vacuum distillation (125° at 0.5 mm).

Anal. Calcd. for $C_{19}H_{22}O_2$: C, 80.81; H, 7.85.

Found: C, 80.63; H, 7.85.

The nmr spectrum ($CDCl_3$) showed an aromatic multiplet at δ 7.4-6.9 (10H), a quartet for the methylene ester protons at 3.97 (2H, $J = 7.0$ Hz), an unresolved multiplet for the benzyl protons at 2.85 (3H), an unresolved multiplet for the remaining internal protons at 2.04 (4H) and a triplet for the methyl ester protons at 1.08 (3H, $J = 7.0$ Hz).

The infrared spectrum (film of $AgCl$) showed carbon-hydrogen stretching at 2880 (s), 2870 (s) and 2850 (s), carbonyl stretching at 1730 (s) along with other absorptions at 1930 (w), 1855 (w), 1565 (w), 913 (m), 857 (m), 805 (m), 761 (s), 737 (s) and 702 (s) cm^{-1} .

The mass spectrum showed a weak molecular ion at m/e 282 (0.5%) along with other abundant fragments at m/e 237 (10%), 191 (67%), 177 (23%), 149 (53%), 145 (21%), 129 (metastable), 110 (metastable), 117 (base peak), 105 (8%), 104 (10%), 103 (10%), 91 (47%), 77 (20%), 71 (metastable), 65 (17%) and 51 (13%).

Hydrogenation of Methyl E,E-4,5-diphenyl-
2,4-pentadienoate (56) and Methyl Z,E-
4,5-diphenyl-2,4-pentadienoate (57)

A mixture of esters (56) and (57) (0.026 g, 0.098 mmoles) was dissolved in methanol (5 ml) and hydrogenated under reduced pressure over an excess of 10% palladium on

charcoal at room temperature for 4 hours. The reaction mixture was filtered through a celite pad and the solvent removed under reduced pressure. Methyl 4,5-diphenylpentanoate (71) (0.023 g, 89%) was obtained as a colorless oil. An analytical sample was obtained by distillation (125° at 0.5 mm).

Anal. Calcd. for $C_{18}H_{20}O_2$: C, 80.56; H, 7.51.

Found: C, 80.49; H, 7.49.

The nmr spectrum ($CDCl_3$) showed an aromatic multiplet at δ 7.4-6.9 (10H), a singlet for the methyl ester protons at 3.55 (3H), an unresolved multiplet for the benzylic protons at 2.85 (3H) and an unresolved multiplet for the remaining internal protons at 2.04 (4H).

Hydrolysis of Phosponium Salt (43)

To a solution of potassium hydroxide (ca 0.5 g, 9 mmoles) in dimethyl sulfoxide (8 ml) and water (2 ml) was added the phosponium salt (43) (1.304 g, 2.00 mmoles) in portions. The yellow reaction mixture was stirred at room temperature for 2 hours and then extracted with ether. The aqueous layer was diluted with water and acidified to a pH of about 2 with dilute hydrochloric acid. The acidic solution was extracted with ether, the organic layer separated, dried over anhydrous sodium sulfate, filtered and the solvent removed under reduced pressure. The residual oil (0.454 g, 86%) was examined by nmr spectroscopy.

The nmr spectrum (CDCl_3) showed a broad singlet for the acid proton at δ 9.55 (1H), a broad aromatic multiplet at 7.8-7.0 (12H), a series of signals at 3.0-2.5 (1.5H), and a series of signals at 1.65 ($J = 1.5$), 1.52 ($J = 1.5$ Hz), 1.17 ($J = 0$ Hz) and 1.05 ($J = 0$ Hz) which gave a combined integration of three protons.

All attempts to separate this reaction mixture by fractional recrystallization or by chromatographic techniques failed.

Esterification of the Acid Mixture (72)-(75)

Obtained from the Hydrolysis of Phosphonium

Salt (43)

To a solution of the acid mixture (0.454 g, 1.72 mmoles), obtained from the hydrolysis of phosphonium salt (43), in ether (15 ml) was added dropwise 6 ml of a 1.0 M ethereal solution of 3-methyl-p-tolyltriazine (58). The reaction was monitored until nitrogen evolution ceased and then stirred for an additional hour. The reaction solution was washed with 5% hydrochloric acid and then 5% aqueous sodium carbonate. The ether layer was separated, dried over anhydrous sodium sulfate, stirred with norite and filtered. The ether was evaporated under reduced pressure and the residual oil (0.333 g, 70%) was analyzed by nmr spectroscopy.

The nmr spectrum (CDCl_3) showed no acidic proton, a broad aromatic multiplet at δ 7.8-7.0 (12H), four methyl

ester signals at 3.87-3.71 (3H), a series of signals at 3.02.5 (1.5H), a doublet at 1.65 ($J = 1.5$ Hz), a doublet at 1.52 ($J = 1.5$ Hz), a singlet at 1.17 and a singlet at 1.05. The last four signals integrated for a total of three protons and showed relative intensities of 3.6:1.0:4.5:4.2.

This complex reaction mixture could not be separated by fractional recrystallization or chromatographic techniques.

Ethyl E,Z-4,5-diphenyl-2-methyl-2,5-pentadienoate (80)

A solution of α -carboethoxyethylidetriphenylphosphorane (42) (1.448 g, 4.00 mmoles) and E- α -phenylcinnamaldehyde (50) (0.083 g, 4.00 mmoles) in benzene (30 ml) was stirred at reflux for 30 hours, cooled to room temperature and the solvent evaporated under reduced pressure. The reaction residue was placed on a column of silica gel and eluted with 1:1 benzene-hexane. The fractions collected were combined according to their thin layer behavior, the solvent evaporated, and the residue dissolved in hot ethanol. Ethyl E,Z-4,5-diphenyl-2-methyl-2,4-pentadienoate (80) (0.783 g, 67%) was obtained as a colorless oil.

Anal. Calcd. for $C_{20}H_{20}O_2$: C, 82.16; H, 6.94.

Found: C, 82.08; H, 6.90.

The nmr spectrum ($CDCl_3$) showed a distorted triplet for H_3 at δ 7.47 (1H), an aromatic multiplet at 7.35-6.80 (10H),

a broad singlet for H_5 at 6.81 (1H), a quartet at 4.18 (2H, $J = 7.0$ Hz), a doublet for the C_2 -methyl protons at 1.65 (3H, $J = 1.5$ Hz) and a triplet at 1.20 (3H, $J = 7.0$ Hz).

The infrared spectrum (KBr) showed carbon-hydrogen stretching at 2895 (s), carbonyl stretching at 1710 (s) and olefinic stretching at 1620 (m), along with other absorptions at 1442 (m), 1365 (m), 1255 (s), 1119 (m), 1033 (m), 983 (m), 931 (m), 805 (w), 780 (w), 755 (s), 718 (s) and 697 (s) cm^{-1} .

The ultraviolet spectrum (95% ethanol) showed maxima at 314 (19,200) and 227 nm (12,600) along with strong end absorption.

Ethyl E,E-4,5-diphenyl-2-methyl-2,4-pentadienoate (81)

A solution of α -carboethoxyethylidetriphenylphosphorane (42) (0.064 g, 0.19 mmoles) and Z- α -phenylcinnamaldehyde (64), (0.040 g, 0.19 mmoles) in benzene (5 ml) was stirred at reflux for 20 hours, cooled to room temperature and the solvent evaporated under reduced pressure. The reaction residue was placed on a column of silica gel and eluted with 9:1 hexane-chloroform. The fractions were combined according to their thin layer behavior. The solvent was evaporated, yielding ethyl E,E-4,5-diphenyl-2-methyl-2,4-pentadienoate (81) (0.044 g, 79%) as a colorless oil. An

analytical sample was obtained by vacuum distillation at 105° at 0.6 mm.

Anal. Calcd. for $C_{20}H_{20}O_2$: C, 82.16; H, 6.89.

Found: C, 82.16; H, 6.90.

The nmr spectrum ($CDCl_3$) showed a distorted triplet for H_3 at δ 7.60 (1H), a sharp spike for the aromatic protons at 7.32 (10H), a doublet for H_5 at 6.87 (1H, $J = 2.0$ Hz), a quartet at 4.22 (2H, $J = 7.0$ Hz), a doublet for the C_2 -methyl protons at 1.52 (3H, $J = 1.5$ Hz) and a triplet at 1.28 (3H, $J = 7.0$ Hz).

The infrared spectrum (film on AgCl) showed carbon-hydrogen stretching at 3020 (m), carbonyl stretching at 1740 (s) and olefinic stretching at 1670 (w), along with other absorptions at 1645 (w), 1530 (m), 1470 (m), 1250 (s), 1117 (s), 1020 (m), 964 (w), 902 (w), 758 (s), 748 (s), 710 (w) and 693 (s) cm^{-1} .

Hydrolysis of Ethyl E,Z-4,5-diphenyl-
2-methyl-2,4-pentadienoate (80)

Ester (80) (0.953 g, 3.27 mmoles) was added in one portion to a stirred solution of potassium hydroxide (1.7 g, 24 mmoles) in dimethyl sulfoxide (16 ml) and water (4 ml) and the reaction mixture stirred at room temperature for 18 hours. The solution was diluted with water, acidified to a pH of about 2 with dilute hydrochloric acid and extracted with ether. The ether layer was separated, dried

over anhydrous sodium sulfate, filtered and the ether evaporated under reduced pressure. The residue was dissolved in hot aqueous ethanol and chilled. The precipitate was collected on a filter, washed with cold water and dried under vacuum. E,Z-4,5-diphenyl-2-methyl-2,4-pentadienoic acid (72) (0.846 g, 98%) was obtained as white needles, mp 157-159°. The product was analyzed by nmr spectroscopy.

The nmr spectrum (CDCl₃) showed a broad singlet for the acid proton at δ 11.06 (1H), a distorted triplet for H₃ at 7.46 (1H), an aromatic multiplet at 7.35-6.80 (10H), a singlet for H₅ at 6.79 (1H) and a doublet for the C₂-methyl protons at 1.65 (3H, J = 1.5 Hz), confirming that the acid was unrearranged.

Hydrolysis of Ethyl E,E-4,5-diphenyl-2-methyl-2,4-pentadienoate (81)

Ester (81) (0.137 g, 0.469 mmoles) was added in one portion to a stirred solution of potassium hydroxide (1.7 g, 6.1 mmoles) in dimethyl sulfoxide (20 ml) and water (5 ml) and the reaction mixture stirred at room temperature for 18 hours. After this time, the solution was diluted with water, acidified to a pH of about 2 with dilute hydrochloric acid and extracted with ether. The ether layer was separated, dried over anhydrous sodium sulfate, filtered and the solvent evaporated under reduced pressure. The residue was dissolved in hot aqueous ethanol, chilled and the precipitate collected

on a filter, washed with cold water and dried under vacuum. E,E-4,5-diphenyl-2-methyl-2,4-pentadienoic acid (73) (0.109 g, 87%) was obtained as white needles, mp 169-170.5°. The product was confirmed to be unrearranged by nmr spectroscopic analysis.

The nmr spectrum (CDCl_3) showed a broad singlet for the acidic proton at δ 10.89 (1H), a distorted triplet for H_3 at 7.61 (1H), a sharp spike for the aromatic protons at 7.32 (10H), a doublet for H_5 at 6.88 (1H, $J = 2.0$ Hz) and a doublet for the C_2 -methyl protons at 1.52 (3H, $J = 1.5$ Hz).

Attempted Preparation of Ethyl Z,Z-4,5-
diphenyl-2-methyl-2,4-pentadienoic acid (74)

To acid etched zinc (4.0 g, 0.062 g atm) and benzene (5 ml) in a 250-ml three-necked round-bottomed flask equipped with a reflux condenser and nitrogen purge was added a solution of E- α -phenylcinnamaldehyde (10.4 g, 0.0500 moles) and ethyl 2-bromopropionate (10.9 g, 0.0598 moles) in benzene (65 ml) at such a rate as to maintain a gentle reflux. After the addition was complete, the reaction mixture was heated at reflux for an additional hour, cooled to room temperature and quenched with 6% acetic acid (100 ml). The organic layer was separated, washed with water, saturated sodium bisulfate solution and water, dried over anhydrous sodium sulfate, filtered and the solvent evaporated. The residue was placed on a column of silica gel and eluted with 9:1 hexane-chloroform. The solvent was removed under reduced

pressure, giving ethyl 3-hydroxy-4,5-diphenyl-2-methyl-4-pentenoate (9.5 g, 61%) as a viscous oil. This alcohol (9.5 g, 0.031 moles) and *p*-toluene-sulfonic acid (0.4 g) were dissolved in benzene (250 ml) and heated at reflux until the theoretical amount of water (0.56 ml) was collected in a Dean-Stark trap. The reaction solution was cooled to room temperature, washed with water, saturated sodium bisulfate solution and water, dried over anhydrous sodium sulfate, filtered and the solvent evaporated. The residue was examined by nmr spectroscopy. In addition to a doublet for the C₂-methyl protons of (80), a number of other signals in the δ 1.6-1.0 region were observed. The complex mixture could not be separated and was hydrolyzed with potassium hydroxide in methanol. The ester mixture (2.6 g, 8.9 mmoles) and potassium hydroxide (1.0 g, 18 mmoles) were dissolved in methanol (40 ml) and heated at reflux for 2.5 hours. The solution was cooled to room temperature, extracted with ether and acidified to pH of about 2 with dilute hydrochloric acid. The acidic solution was extracted with ether, the organic layer separated, washed with water, dried over anhydrous sodium sulfate, filtered and the solvent evaporated. The residual oil (2.2 g, 94%) was examined by nmr spectroscopy.

The nmr spectrum (CDCl₃) showed a doublet for the C₂-methyl protons of (72) at δ 1.65 ($J = 1.5$ Hz) along with a number of other signals in the 1.5-1.0 region. The residue

was dissolved in acetonitrile and chilled. The product was collected on a filter, washed with cold water and dried under vacuum. Acid (72) (0.7 g, 30%) was obtained as white needles mp 160-161°. Further separation of the remaining complex mixture was unsuccessful.

Hydrogenation of E,Z-4,5-Diphenyl-2-methyl-2,4-pentadienoic acid (72)

E,Z-4,5-Diphenyl-2-methyl-2,4-pentadienoic acid (72) (0.264 g, 1.00 mmoles) was dissolved in methanol (20 ml) and hydrogenated under reduced pressure over an excess of 10% palladium on charcoal for 4 hours at room temperature. The reaction mixture was then filtered through a celite pad and the solvent removed under reduced pressure. 4,5-Diphenyl-2-methyl-pentanoic acid (82) (0.230 g, 91%) was obtained as a colorless oil. An analytical sample was obtained by vacuum distillation (150-155° at 0.5 mm).

Anal. Calcd. for $C_{18}H_{20}O_2$: C, 80.56; H, 7.51.

Found: C, 80.28; H, 7.47.

The nmr spectrum ($CDCl_3$) showed a broad singlet for the acidic proton at δ 11.20 (1H), an aromatic multiplet at 7.35-6.85 (10H), a broad singlet for the benzyl protons at 3.92 (3H), a broad multiplet at 2.53-1.50 (3H) and a doublet at 1.07 (3H, $J = 7.0$ Hz).

The infrared spectrum (film on AgCl) showed carbon-hydrogen stretching at 2930 (s) and 2890 (s), carbonyl

stretching at 1715 (s) and other absorptions at 1490 (m), 1455 (m), 1385 (m), 1285 (m), 1070 (w), 1030 (w), 754 (s), 742 (m) and 702 (s) cm^{-1} .

The mass spectrum showed a weak molecular ion at m/e 268 (0.7%) along with other abundant fragments at m/e 178 (14%), 177 (94%), 129 (39%), 91 (base peak) and 77 (9%).

Hydrogenation of Acid Mixture (72)-(75) Obtained
from Hydrolysis of Phosphonium Salt (43)

The acid mixture obtained from hydrolysis of phosphonium salt (43) (0.132 g, 0.500 mmoles) was dissolved in methanol (15 ml) and hydrogenated under reduced pressure over an excess of 10% palladium on charcoal for 4 hours at room temperature. The reaction mixture was then filtered through a celite pad and the solvent removed under reduced pressure. The residual oil (0.125 g, 89%) was examined by nmr spectroscopy. In addition to the doublet at 1.07 ($J = 1.07$) associated with the C_2 -methyl protons of 4,5-diphenyl-2-methyl-pentanoic acid, a number of other signals in the 1.2-0.9 region were observed. Attempted separation by column chromatography was unsuccessful and the mixture was distilled. Acid (82) (0.043 g) was obtained as a colorless oil and identified by nmr spectroscopy.

Hydrolysis of Phosphonium Salt (45)

Phosphonium salt (45) (0.355 g, 0.500 mmoles) was added in one portion to a stirred solution of potassium

hydroxide (0.56 g, 10 mmoles) in dimethyl sulfoxide (4 ml) and water (1 ml). The reaction mixture was stirred at room temperature for 1.5 hours, diluted with water, and extracted with chloroform. The organic layer was separated, dried over anhydrous sodium sulfate, filtered and the solvent evaporated. The yellow reaction residue was examined by alumina thin layer chromatography. Two components were detected, the slower moving of which was identified as triphenylphosphonium oxide. The residue was placed on a column of alumina and eluted with 9:1 hexane-chloroform, collecting 20-ml fractions. The fractions were combined according to their thin layer behavior, the solvent evaporated and the residue dissolved in hot petroleum ether-chloroform. The solution was chilled and the precipitate collected on a filter, washed with cold petroleum ether and air dried. *Z,E*-1,4,5-Triphenyl-2,4-pentadienone (83), (0.027 g, 17%) was obtained as yellow needles, mp 187-188°.

Anal. Calcd. for $C_{23}H_{18}O$: C, 89.00; H, 5.84

Found: C, 88.73; H, 5.82

The nmr spectrum ($CDCl_3$) showed a two proton multiplet at δ 7.75-7.50, a multiplet at 7.45-6.80 (13H), a doublet for H_3 at 6.87 (1H, $J = 6.5$ Hz), a singlet for H_5 at 6.38 (1H) and a doublet for H_2 at 6.05 (1H, $J = 6.5$ Hz).

The infrared spectrum (KBr) showed carbon-hydrogen stretching at 2950 (w), carbonyl stretching at 1680 (s)

and olefinic stretching at 1590 (s) along with other absorptions at 1300 (m), 1225 (s), 1035 (s), 887 (m), 795 (w), 764 (m), 710 (s) and 694 (s) cm^{-1} .

The mass spectrum showed a prominent molecular ion at m/e 310 (80%) along with other abundant fragments at m/e 233 (79%), 206 (18%), 205 (base peak), 204 (33%), 203 (29%), 202 (22%), 178 (13%), 127 (18%), 105 (93%) and 77 (73%).

E,Z-1,4,5-Triphenyl-2,4-pentadienone (84)

A solution of E- α -phenylcinnamaldehyde (50) (0.416 g, 2.00 mmoles) and phenacylidenetriphenylphosphorane (44) (0.760 g, 2.00 mmoles) in benzene (5 ml) was stirred at reflux for 21 hours. The solvent was evaporated and the residue was placed on a column of alumina and eluted with 9:1 hexane-chloroform. The yellow fractions were combined, the solvent evaporated and the residue dissolved in hot petroleum ether-chloroform. The solution was chilled and the precipitate collected on a filter, washed with cold petroleum ether and air dried. E,Z-1,4,5-triphenyl-2,4-pentadienone (0.391 g, 63%) was obtained as yellow needles, mp 130-132°. An analytical sample was obtained by recrystallization from petroleum ether, mp 133-134°.

Anal. Calcd. for $\text{C}_{23}\text{H}_{18}\text{O}$: C, 89.00; H, 5.84

Found: C, 88.91; H, 5.89

The nmr spectrum (CDCl_3) showed a multiplet at δ 7.95-7.70 (2H), a multiplet at 7.65-6.80 (15H), and a doublet for H_2 at 7.02 (1H, $J = 15.0$ Hz).

The infrared spectrum (KBr) showed carbon-hydrogen stretching at 2970 (w), carbonyl stretching at 1730 (s) and olefinic stretching at 1530 (s) along with other absorptions at 1440 (m), 1300 (s), 1217 (s), 1025 (s), 998 (s), 869 (m), 850 (m), 790 (m), 779 (w), 761 (m), 740 (w), 712 (s), 702 (s) and 692 (s) cm^{-1} .

The mass spectrum showed a prominent molecular ion at m/e 310 (75%) along with other abundant fragments at m/e 233 (63%), 206 (18%), 205 (base peak), 204 (34%), 203 (25%), 202 (19%), 178 (11%), 105 (78%), and 77 (53%).

E,E-1,4,5-Triphenyl-2,4-pentadienone (85)

A solution of *Z*- α -phenylcinnamaldehyde (64) (0.416 g, 2.00 mmoles) and phenacylidetriphenylphosphorane (44) (0.760 g, 2.00 mmoles) in benzene (5 ml) was stirred at reflux for 24 hours. The solvent was evaporated and the residue placed on a column of alumina and eluted with 9:1 hexane-chloroform. The yellow fractions were combined and the solvent removed under reduced pressure. The residue (0.466 g, 66%) was dissolved in hot chloroform-petroleum ether and cooled to room temperature. The product was collected on a filter, washed with cold petroleum ether and air dried, yielding E,Z-1,4,5-triphenyl-2,4-pentadienone (84) (0.135 g, 22%) as yellow needles, mp 132-134°. The mother liquor was evaporated and the residue dissolved in hot petroleum ether. The solution was chilled and the pre-

cipitate collected on a filter, washed with cold petroleum ether and air dried. E,E,1,4,5-triphenyl-2,4-pentadienone (85) (0.252 g, 41%) as yellow needles, mp 80-82°.

Anal. Calcd. for $C_{23}H_{18}O$: C, 89.00; H, 5.84.

Found: C, 89.11; H, 5.84.

The nmr spectrum ($CDCl_3$) showed a multiplet at δ 7.95-7.70 (2H), a multiplet at 7.55-7.30 (13H), a doublet for H_3 at 8.15 (1H, $J = 15.0$ Hz), a singlet for H_5 at 7.00 (1H), and a doublet for H_2 at 6.58 (1H, $J = 15.0$ Hz).

The infrared spectrum (KBr) showed carbon-hydrogen stretching at 2920 (w), carbonyl stretching at 1645 (s) and olefinic stretching at 1530 (s) along with other absorptions at 1435 (m), 1278 (s), 1215 (s), 1020 (s), 930 (m), 880 (m), 791 (w), 778 (m), 763 (m), 746 (m), 708 (s) and 698 (s) cm^{-1} .

The mass spectrum showed a prominent molecular ion at m/e 310 (82%) along with other abundant fragments at m/e 233 (60%), 206 (16%), 205 (base peak), 204 (27%), 203 (24%), 202 (18%), 178 (9%), 105 (77%) and 77 (50%).

Hydrolysis of Phosponium Salt (47)

Phosponium salt (47) (0.600 g, 0.872 mmoles) was added in one portion to a solution of potassium hydroxide (ca 0.50 g, 8.9 mmoles) in dimethyl sulfoxide (4 ml) and water (1 ml) and the reaction solution stirred for 2 hours at room temperature. An intense blue color appeared immediately and persisted throughout the course of the

reaction. The solution was diluted with water and extracted with chloroform. The organic layer was separated, washed with water, dried over sodium sulfate, filtered and the solvent evaporated. The residue was placed on a column of silica gel and eluted with 7:3 hexane-chloroform. The first material to elute was an orange oil, (0.210 g, 75%). The nmr spectrum (CDCl_3) of this oil indicated the presence of two components. The oil was re-chromatographed over silica gel, eluting with 9:1 hexane-chloroform. The collected fractions (20 ml) were combined according to their nmr spectroscopic behavior. A small quantity (0.019 g) of E,E-1-(4'-nitrophenyl)-3,4-diphenyl-1,3-butadiene (86) was isolated as an orange-yellow oil.

The nmr spectrum (CDCl_3) showed a doublet for the protons ortho to the nitro substituent at δ 8.11 (2H), a narrow multiplet for the remaining aromatic protons at 7.45-7.17 (12H), a doublet for H_1 at 6.45 (1H, $J = 16.0$ Hz) and a singlet for H_4 at 6.67 (1H). H_2 was partially obscured by the aromatic multiplet.

The second component to elute in the original chromatography was triphenylphosphine oxide.

The third component collected was a dark blue solid (0.041 g, 14%), mp 103-108° (dec). This material was not completely identified.

The nmr spectrum (CDCl_3) showed only aromatic protons as two distinct multiplets at 7.67 (4H) and 7.03 (11H).

The visible spectrum (CH_2Cl_2) showed a broad absorption at 570 nm.

The mass spectrum showed a molecular ion at m/e 325 (7%) along with other abundant fragments at m/e 295 (11%), 278 (38%), 277 (base peak), 263 (28%), 201 (21%), 199 (31%), 185 (14%), 183 (45%), 177 (10%), 153 (10%), 152 (18%), and 151 (18%).

E,Z-1-(4'-Nitrophenyl)-3,4-diphenyl-
1,3-butadiene (89)

A mixture of triethyl phosphite (6.64 g, 40.0 mmoles) and α -bromo-p-nitrotoluene (8.64 g, 40.0 mmoles) in a 30 by 2.5-cm test tube equipped with a cold finger condenser and a few boiling chips was heated at reflux for 1.5 hours. The mixture was then transferred to a 100-ml round bottomed flask equipped with a reflux condenser and nitrogen purge and containing sodium methoxide (2.2 g, 41 mmoles) in dimethyl formamide (25 ml) at 0°. The resulting dark purple mixture was stirred at 0° and a solution of E- α -phenylcinnamaldehyde (8.1 g, 39 mmoles) in dimethyl formamide (25 ml) was added dropwise over a 10 minute period. After the addition, the reaction solution was stirred at reflux for 1.5 hours, cooled to room temperature and poured into 40% aqueous methanol (100 ml). The solid was collected on a filter, washed with cold water and then with cold methanol and air dried. The solid was recrystallized from

methanol-chloroform to give E,Z-1-(4'-nitrophenyl)-3,4-diphenyl-1,4-butadiene (89) (7.4 g, 56%) as orange needles, mp 155-156°.

Anal. Calcd. For $C_{22}H_{17}NO_2$: C, 80.71; H, 5.23; N, 4.28.

Found: C, 80.64; H, 5.27; N, 4.22.

The nmr spectrum ($CDCl_3$) showed a doublet at δ 8.09 (2H), an aromatic multiplet at 7.55-6.75 (14H) and a doublet at 6.13 (1H, $J = 16.0$ Hz).

The infrared spectrum (KBr) showed carbon-hydrogen stretching at 2900 (w) and olefinic stretching at 1585 (s) along with other absorptions at 1500 (s), 1330 (s), 1180 (m), 981 (m), 973 (m), 867 (m), 837 (m), 780 (m), 759 (m), 747 (m), 701 (s) and 695 (s) cm^{-1} .

The mass spectrum showed a prominent molecular ion at m/e 327 (97%) along with other abundant fragments at m/e 280 (28%), 202 (32%), 191 (48%), 178 (16%), 165 (16%), 91 (base peak) and 77 (11%).

Authentic Synthesis of E,E-1-(4'-Nitrophenyl)-3,4-diphenyl-1,3-butadiene (86)

A mixture of triethyl phosphite (0.294 g, 1.77 mmoles) and α -bromo-p-nitrotoluene (0.382 g, 1.77 mmoles) was heated at reflux for 1.5 hours in a 10 by 1-cm test tube equipped with a cold finger condenser and a few boiling chips. The mixture was cooled to room temperature and transferred to a

25-ml three-necked round-bottomed flask equipped with a reflux condenser and nitrogen purge and containing sodium methoxide (0.097 g, 1.80 mmoles) and dimethyl formamide (5 ml). The purple solution was stirred at 0° and a solution of Z- α -phenylcinnamaldehyde (64) (0.370 g, 1.78 mmoles) in dimethyl formamide (5 ml) was added dropwise over a 10 minute period. The reaction mixture was then heated at reflux for 1.5 hours, cooled to room temperature, diluted with water and extracted with ether. The ether layer was separated, dried over anhydrous sodium sulfate, filtered and the solvent evaporated. The residue (0.352 g, 62%) was dissolved in hot petroleum ether and cooled to room temperature. The precipitate was collected on a filter, washed with cold petroleum ether and air dried, yielding (89) (0.170 g, 30%) as yellow needles, mp 155-156°.

The mother liquor from above was evaporated and the yellow oil that remained was chromatographed over a column of alumina, eluting with 95:5 hexane-chloroform. The solvent was evaporated, yielding E,E-1-(4'-nitrophenyl)-3,4-diphenyl-1,3-butadiene (86) (0.107 g, 18%) as a yellow oil.

Anal. Calcd. for $C_{22}H_{17}NO_2$: C, 80.71; H, 5.23; N, 4.28.

Found: C, 80.63; H, 5.33; N, 4.26.

The nmr spectrum ($CDCl_3$) showed a doublet for the phenyl protons ortho to the nitro substituent at δ 8.12 (2H), a narrow aromatic multiplet at 7.4-7.2 (12H), a broad

singlet for H_4 at 6.70 (1H) and a doublet for H_1 at 6.49 (1H, $J = 16.0$ Hz). H_2 was partially obscured by the aromatic signal.

The infrared spectrum (film on AgCl) showed carbon-hydrogen stretching at 2920 (m) and 2870 (w), olefinic stretching at 1580 (s) and other absorptions at 1505 (s), 1355 (s), 1180 (w), 1110 (m), 922 (w), 791 (w), 755 (m), 749 (s) and 699 (s) cm^{-1} .

The mass spectrum showed a molecular ion at m/e 327 (41%) along with other prominent fragments at m/e 298 (26%), 280 (14%), 203 (32%), 202 (33%), 191 (46%), 178 (18%), 165 (17%), 91 (base peak) and 77 (16%).

Hydrogenation of E,Z-1-(4'-Nitrophenyl)-
3,4-diphenyl-1,3-butadiene (89)

E,Z-1-(4'-Nitrophenyl)-3,4-diphenyl-1,3-butadiene (89), (0.654 g, 2.00 mmoles) was dissolved in methanol (100 ml) and hydrogenated under reduced pressure over an excess of 10% palladium on charcoal for 4 hours at room temperature. The reaction mixture was then filtered through a celite pad and the solvent evaporated under reduced pressure. 1-(4'-aminophenyl)-3,4-diphenylbutane (90), (0.537 g, 89%) was obtained as a pale yellow oil. An analytical sample was obtained by vacuum distillation at 140-145° at 0.5 mm.

Anal. Calcd. for $C_{22}H_{23}N$: C, 87.66; H, 7.69;
N, 4.64.

Found: C, 87.63; H, 7.67; N, 4.61.

The nmr spectrum (CDCl_3) showed an aromatic multiplet at δ 7.20-6.86 (10H), an AA'BB' multiplet for the aniline ring protons at 6.55 (4H), a broad singlet for the amine protons at 3.18 (2H), a broad singlet for the benzylic protons at 2.80 (3H), and a broad multiplet for the remaining protons at 2.60-1.65 (4H).

The infrared spectrum (film on AgCl) showed nitrogen-hydrogen stretching at 3300 (m), and 3270 (m) along with other absorptions at 1950 (w), 1870 (w), 1810 (w), 1750 (w), 1600 (m), 1520 (s), 1495 (m), 1445 (s), 1275 (s), 1180 (m), 1077 (m), 1035 (m), 825 (s), 757 (s), 734 (m) and 700 (s) cm^{-1} .

The mass spectrum showed a molecular ion at m/e 301 (14%) along with other abundant fragments at m/e 120 (12%), 106 (base peak) and 91 (9%).

Hydrogenation of Diene Mixture Obtained from

Hydrolysis of Phosponium Salt (47)

The diene mixture obtained from the hydrolysis of phosphonium salt (47), (0.164 g, 0.502 mmoles) was dissolved in methanol (25 ml) and hydrogenated under reduced pressure over an excess of 10% palladium on charcoal for 4 hours at room temperature. The reaction mixture was filtered through a celite pad and the solvent removed under reduced pressure. The residue (0.123 g, 80%) was analyzed by nmr spectroscopy and shown to be identical to (90) obtained from hydrogenation of (89).

1,2-Diphenylcyclopropenylcarbinol⁹¹

Oxalyl chloride (30 g, 0.24 moles) was added dropwise during the course of 30 minutes to 1,2-diphenylcyclopropene carboxylic acid (6.87 g, 0.0295 moles) in a 500-ml three-necked round-bottomed flask equipped with a reflux condenser, mechanical stirrer and gas outlet. The resulting solution was stirred at reflux for 2 hours and then the excess oxalyl chloride was removed under vacuum. A mixture of benzene-hexane (1:1) (15 ml) was added to the residual oil and then removed under vacuum. This process was repeated 4 times to remove the last traces of oxalyl chloride. The diphenylcyclopropene carboxylic acid chloride thus produced was used without further purification.

A solution of lithium aluminum tri-t-butoxy hydride (ca 25 g) in diglyme (120 ml) was added dropwise during the course of 1 hour to a solution of the acid chloride in diglyme (100 ml) at 0°. The reaction mixture was stirred at 0° for an additional 2 hours and then poured into 300 ml of cold water. The suspension that resulted was stirred for 5 minutes and then filtered. The paste that was collected was washed extensively with ethanol. The washings were combined and the volume reduced to 100 ml. Water was added until the solution became turbid. The solution was cooled at 0° overnight and the precipitate collected on a filter, washed with cold water and dried under vacuum. 1,2-Diphenylcyclopropenylcarbinol (4.5 g, 69%)

was obtained as white silken needles, mp 70-71° (Lit.⁹¹
mp 69-70.5°).

3-Chloromethyl-1,2-diphenylcyclopropene (93)

A solution of 1,2-diphenylcyclopropenylcarbinol (2.22 g, 10.0 mmoles) and triphenylphosphine (2.88 g, 11.0 mmoles) in dry carbon tetrachloride (10 ml) was heated at reflux with stirring for 29 hours. The reaction mixture was cooled to room temperature and 50 ml of pentane was added. The precipitate was collected on a filter and air dried to give triphenylphosphine oxide (2.58 g, 92%) as a white solid. The mother liquor was evaporated and the residue chromatographed on a column of silica gel, eluting with 9:1 hexane-chloroform. The fractions were combined on the basis of their thin layer behavior. The solvent was evaporated and the residual oil dried under vacuum. 3-Chloromethyl-1,2-diphenylcyclopropene (93), (1.9 g, 79%) was collected as a colorless oil.

The nmr spectrum (CDCl₃) showed an aromatic multiplet at δ 7.8-7.2 (10H), a doublet at 3.68 (2H, J = 5.5 Hz) and a triplet at 2.50 (1H, J = 5.5 Hz).

The infrared spectrum (film on AgCl) showed carbon-hydrogen stretching at 2970 (m), and 2850 (m), cyclopropene stretching at 1820 (m) and other absorptions at 1660 (s), 1585 (m), 1470 (s), 1435 (s), 1250 (s), 1070 (m), 1025 (s), 1008 (s), 915 (m), 882 (w), 837 (w), 755 (s), 740 (s), 725 (s) and 687 (s) cm⁻¹.

The ultraviolet spectrum (95% ethanol) showed maxima at 327 (24,700), 309 (32,200), 239 (21,300) and 227 nm (22,600).

The mass spectrum showed a P + 2 ion at m/e 242 (17%), a molecular ion at m/e 240 (58%) and other abundant fragments at m/e 205 (base peak), 204 (27%), 202 (24%), 191 (37%), 189 (18%), 179 (11%), 105 (37%), 91 (15%) and 77 (33%).

Attempted Preparation of 1,2-Diphenylcyclopropenylmethyltriphenylphosphonium Perchlorate (92)

A solution of the cyclopropenylcarbonyl chloride (93), (0.623 g, 2.60 mmoles) and triphenylphosphine (0.682 g, 2.60 mmoles) in benzene (5 ml) was heated at reflux for 18 hours. The reaction mixture was cooled to room temperature and examined by nmr spectroscopy. No change from the starting solution was observed. The solvent was removed under reduced pressure and replaced by acetone (5 ml). The solution was heated at reflux for 16 hours, cooled to room temperature and examined by nmr spectroscopy. Again no change from the starting solution was observed. The same result was found when toluene was employed as the solvent.

Reaction of 3-Chloromethyl-1,2-diphenylcyclopropene (93) with Magnesium

A solution of 3-chloromethyl-1,2-diphenylcyclopropene

(0.159 g, 0.662 mmoles) in dry tetrahydrofuran (5 ml) was added dropwise under nitrogen to magnesium (1.0 g, 0.04 g at) and tetrahydrofuran (5 ml). The reaction solution was then heated at reflux for 2 hours, cooled to 0° and quenched with 2 ml of water. The excess magnesium was consumed with dilute sulfuric acid and the organic layer was separated, washed with water, 5% aqueous sodium carbonate and water, dried over anhydrous sodium sulfate, filtered and the solvent evaporated. The residue was examined by nmr spectroscopy, which indicated the presence of two olefinic compounds. The residue was placed on a column of silica gel and eluted with 95:5 hexane-chloroform. The fractions collected were combined according to their thin layer behavior. The solvent was evaporated, yielding a pale yellow oil (0.108 g, 80%). NMR spectroscopy indicated that no separation had occurred, and separation was attempted by gas phase chromatography employing a six foot 30% SE-30 on carbowax column with an injector temperature of 180°, a column temperature of 170° and a detector temperature of 220°. Two components in a 55:45 ratio were separated and collected.

The first component, Z-1,2-diphenyl-1,3-butadiene (94) was collected as a colorless solid, mp 54-55.5°.

Anal. Calcd. for C₁₆H₁₄: C, 93.16; H, 6.84.

Found: C, 93.11; H, 6.87.

The nmr spectrum (CDCl_3) showed an aromatic multiplet at δ 7.40-6.80 (10H), a doublet of doublets at 6.72 (1H, $J = 17.0$, $J' = 10.4$ Hz), a broad singlet at 6.57 (1H), a doublet of doublets at 5.13 (1H, $J = 10.4$ Hz, $J' = 1.4$ Hz) and a doublet of doublets at 4.81 (1H, $J = 17.0$ Hz, $J' = 1.4$ Hz).

The infrared spectrum (KBr) showed carbon-hydrogen stretching at 2950 (w), aromatic overtones from 1970-1750 (w) and olefinic stretching at 1590 (m) along with other absorptions at 1495 (m), 1063 (s), 1020 (s), 990 (s), 908 (s), 882 (m), 850 (w), 780 (s), 756 (s), 724 (s), 710 (m) and 692 (s) cm^{-1} .

The mass spectrum showed a prominent molecular ion at m/e 206 (82%) along with other abundant fragments at m/e 205 (18%), 204 (21%), 203 (19%), 191 (31%), 190 (14%), 178 (29%), 165 (13%), 129 (16%), 128 (39%), 115 (19%), 104 (10%), 102 (12%), 91 (base peak), 77 (18%) and 51 (18%).

The second component, E-1,2-diphenyl-1,3-butadiene (95) was collected as a colorless oil.

Anal. Calcd. for $\text{C}_{16}\text{H}_{14}$: C, 93.16; H, 6.84.

Found: C, 93.12; H, 6.75.

The nmr spectrum (CDCl_3) showed an aromatic singlet at δ 7.30 (10H), a doublet of doublets at 7.02 (1H, $J = 16.8$ Hz, $J' = 11.2$ Hz), a broad singlet at 6.55 (1H), a doublet of triplets at 5.31 (1H, $J = 11.2$ Hz, $J' = 1.7$ Hz) and a doublet of doublets at 5.19 (1H, $J = 16.8$ Hz, $J' = 1.7$ Hz).

The infrared spectrum (film of AgCl) showed carbon-hydrogen stretching at 2940 (m), and 2870 (m) and olefinic stretching at 1595 (m), along with other absorptions at 1490 (m), 1440 (m), 1078 (m), 1035 (w), 1010 (w), 918 (s), 783 (m), 767 (m), 740 (s) and 700 (s) cm^{-1} .

The mass spectrum showed a molecular ion at m/e 206 (base peak) along with other abundant fragments at m/e 205 (45%), 204 (15%), 203 (17%), 202 (13%), 191 (30%), 178 (20%), 165 (16%), 128 (33%), 115 (26%), 105 (9%), 104 (11%), 103 (9%), 102 (14%), 101 (13%), 91 (76%), 77 (15%) and 51 (14%).

The Grignard reagent was prepared as before from (93), 1.0 g, 4.2 mmoles) and magnesium (0.7 g, 0.03 g atm) and quenched with D_2O . Work-up as in the previous reaction yielded an oil (0.638 g, 73%). This was separated into its two components by gas phase chromatography as before.

The first component, Z-1-d-1,2-diphenyl-1,3-butadiene (96), was collected as a colorless solid, mp 54-56°.

The nmr spectrum (CDCl_3) showed an aromatic multiplet at δ 7.40-6.85 (10H), a doublet of doublets at 6.72 (1H, $J = 17.0$ Hz, $J' = 10.4$ Hz), a doublet of doublets at 5.01 (1H, $J = 10.4$ Hz, $J' = 1.4$ Hz) and a doublet of doublets at 4.83 (1H, $J = 17.0$ Hz, $J' = 1.4$ Hz).

The second component, E-1-d-1,2-diphenyl-1,3-butadiene, (97) was collected as a colorless oil.

The nmr spectrum (CDCl_3) showed an aromatic singlet at δ 7.32 (10H), a doublet of doublets at 7.03 (1H, $J = 16.8$ Hz, $J' = 11.2$ Hz), a doublet of doublets at 5.32 (1H,

$J = 11.2 \text{ Hz}$, $J' = 1.7 \text{ Hz}$) and a doublet of doublets at 5.19 (1H, $J = 16.8 \text{ Hz}$, $J' = 1.7 \text{ Hz}$).

Authentic Synthesis of Z-1,2-Diphenyl-1,3-butadiene (94)

A solution of 5 ml of phenyl lithium in hexane (2.0M) and ether (20 ml) was prepared in a 100 ml round bottomed flask equipped with a dropping funnel, syringe cap and nitrogen purge. The solution was stirred and cooled to -78° with an acetone-dry ice bath. Methyltriphenylphosphonium bromide (3.57 g, 10.0 mmoles) was added in one portion and the bright yellow reaction mixture that resulted was warmed to room temperature and stirred for 2 hours. E- α -phenylcinnamaldehyde (50), (2.08 g, 10.0 mmoles) in ether (20 ml) was then added dropwise during the course of 5 minutes. The dropping funnel was replaced by a reflux condenser and the reaction mixture was stirred at reflux for 16 hours, cooled to room temperature, filtered and the solid washed with ether. The ether washings were combined with the mother liquor and washed with water, dried over anhydrous sodium sulfate, filtered and the ether evaporated. The residue was placed on a column of silica gel and eluted with 9:1 hexane-chloroform. The fractions (30 ml) were combined according to their thin layer behavior and the solvent evaporated, yielding a pale yellow oil (1.30 g, 63%). Gas phase chromatography as before indicated two components present in a 92:8 ratio.

The major component was collected as a colorless solid, mp 55-56° and was identified by its spectral data as Z-1,2-diphenyl-1,3-butadiene (94).

The minor component was collected as a colorless oil and was identified by its spectral data as E-1,2-diphenyl-1,3-butadiene (95).

2,3-Diphenyl-1,3-butadiene¹²¹

Commercial sodium hydride in oil (50%, 2.4 g) and dry dimethyl sulfoxide (30 ml) were stirred at 75° for 30 minutes in a 250-ml three-necked round-bottomed flask equipped with a dropping funnel, reflux condenser and nitrogen purge. The mixture was cooled to 30° and a solution of diphenylacetylene (4.45 g, 0.0250 moles) in dry dimethyl sulfoxide (20 ml) was added dropwise over a period of 30 minutes. The brown-red reaction mixture was then heated at 65° for 2.5 hours, cooled to room temperature and poured into ice water. The aqueous mixture was extracted five times with ether, the extracts combined, dried over anhydrous sodium sulfate, filtered and the ether evaporated. The residue was placed on a column of alumina and eluted with 7:1 hexane-benzene. The fractions (50 ml) were combined according to their thin layer behavior, the solvent evaporated and the residue dissolved in hot methanol. After cooling the solution to 0°, the precipitate was collected on a filter, washed with cold methanol and air dried, yielding 2,3-diphenyl-1,3-butadiene

(0.520 g, 10%) as a white solid, mp 45-47° (Lit.¹²¹ mp 47-48°).

The nmr spectrum (CDCl₃) showed an aromatic multiplet at δ 7.5-7.0 (10H), a doublet at 5.5 (2H, J = 1.5 Hz) and a doublet at 5.26 (2H, J = 1.5 Hz).

1,2-Dicarbomethoxy-3,4-diphenyl-1,4-cyclohexadiene (98)

A solution of Z-1,2-diphenyl-1,3-butadiene (94), (0.78 g, 3.4 mmoles) and dimethyl acetylenedicarboxylate (0.60 g, 4.2 mmoles) in benzene (3 ml) was sealed in a pressure tube and heated at 100° for 24 hours. The solution was cooled and removed from the tube. The solvent was evaporated and the residue dissolved in hot ethanol and chilled. The precipitate was collected on a filter, washed with cold ethanol and dried under vacuum to yield 1,2-dicarbomethoxy-3,4-diphenyl-1,4-cyclohexadiene (98), (0.921 g, 78%) as white prisms, mp 118.5-120°.

Anal. Calcd. for C₂₂H₂₀O₄: C, 75.84; H, 5.79.

Found: C, 75.70; H, 5.85.

The nmr spectrum (CDCl₃) showed an aromatic doublet at δ 7.08 (10H), a triplet at 6.06 (1H, J = 3.5 Hz), a triplet at 4.87 (1H, J = 6.0 Hz), a singlet at 3.68 (3H), a singlet at 3.50 (3H) and a complex multiplet at 3.28 (2H).

The infrared spectrum (KBr) showed carbon-hydrogen stretching at 2940 (m) and 2870 (m), carbonyl stretching at 1710 (s) and other absorptions at 1485 (m), 1430 (m),

1270 (s), 1080 (s), 1035 (m), 1022 (m), 856 (m), 823 (m), 763 (m), 756 (m), 742 (s) and 700 (s) cm^{-1} .

The mass spectrum showed a weak molecular ion at m/e 348 (8%) along with other abundant fragments at m/e 341 (5%), 317 (24%), 316 (63%), 257 (37%), 239 (18%), 238 (base peak), 229 (32%), 228 (25%), 105 (13%), 91 (18%), 77 (17%) and 59 (20%).

Photolysis of 1,2-Diphenylpropenylidene-fluorene (49)

1,2-Diphenylpropenylidene-fluorene (49) (0.088 g, 0.25 mmoles) was dissolved in ethanol (100 ml) and photolyzed through a pyrex filter with 3100 \AA light for 24 hours in the presence of 2 mole equivalents of iodine. The solvent was evaporated and the residue placed on a column of silica gel and eluted with 9:1 hexane-chloroform. The fractions (40 ml) were combined according to their thin layer behavior, the solvent evaporated and the residue recrystallized from ethanol-chloroform. 2,3-Diphenylfluoroanthrene (108) (0.049 g, 56%) was obtained as pale yellow prisms, mp 168-169°.

Anal. Calcd. for $\text{C}_{28}\text{H}_{18}$: C, 94.88; H, 5.12.

Found: C, 94.75; H, 5.19.

The nmr spectrum (CDCl_3) showed an aromatic multiplet at δ 8.1-7.8 (4H), an aromatic multiplet at 7.8-7.4 (4H) and two sharp spikes at 7.4-7.2 (10H).

The infrared spectrum (KBr) showed carbon-hydrogen stretching at 2910 (w) along with other absorptions at 1450 (m), 1445 (m), 1260 (m), 898 (w), 804 (m), 782 (s), 770 (w), 757 (s), 744 (m), 712 (m) and 700 (s) cm^{-1} .

The ultraviolet spectrum (95% ethanol) showed maxima at 365 (9,800), 350 (9,400), 332 (6,000), 289 (16,800), 277 (29,700), 250 (35,300) and 223 nm (30,000).

The mass spectrum showed a molecular ion at m/e 354 (base peak) along with other abundant fragments at m/e 353 (22%), 351 (10%), 178 (15%), 177 (17%), 176 (22%), and 162 (9%).

9-Phenanthrenylidene fluorene (106)

A solution of phenanthrene-9-carboxaldehyde (0.412 g, 2.00 mmoles) and fluorenylidene triphenylphosphorane (38) (0.852 g, 2.00 mmoles) in benzene (10 ml) was stirred at reflux for 24 hours. The reaction mixture was cooled to room temperature and examined by thin layer chromatography. In addition to starting material, two new components were detected, one of which was identified as triphenylphosphine oxide by comparison to authentic material. The solvent was evaporated and the residue placed on a column of silica gel and eluted with 9:1 hexane-chloroform. The fractions (40 ml) were combined according to their thin layer behavior. The solvent was evaporated and the residue recrystallized from ethanol. The product was collected on a filter, washed

with cold ethanol and air dried, yielding (106) (0.330 g, 47%) as yellow needles, mp 182.5-183.5°.

Anal. Calcd. for $C_{28}H_{18}$: C, 94.88; H, 5.12

Found: C, 94.83; H, 5.13.

The nmr spectrum ($CDCl_3$) showed an aromatic multiplet at δ 8.83-8.50 (2H) and a second aromatic multiplet at 8.17-6.60 (16H).

The infrared spectrum (KBr) showed carbon-hydrogen stretching at 2910 (w) along with other absorptions at 1420 (m), 950 (m), 780 (m), 770 (s), 755 (m), 740 (s), 725 (s) and 718 (s) cm^{-1} .

The ultraviolet spectrum (95% ethanol) showed maxima at 337 (12,700), 295 (17,200), 255 (68,200), 249 (69,800) and 229 nm (56,800).

The mass spectrum showed a molecular ion at m/e 354 (base peak) as the only prominent peak. Doubly and triply charged molecular ions at m/e 177 and m/e 118, respectively, were also observed.

Photolysis of 9-Phenanthrenylidene fluorene (106)

A solution of (106) (0.100 g, 0.284 mmoles) and iodine (0.144 g, 0.566 mmoles) in ethanol (100 ml) was photolyzed through a pyrex filter with 3100 Å light for 20 hours. The solvent was removed under reduced pressure and the residue examined by thin layer chromatography. Two components were detected and separation by column chromatography was attempted. The reaction residue was placed on a column of

alumina and eluted with 95:5 hexane-chloroform. The fractions (20 ml) were combined according to their thin layer behavior. The first component was shown by nmr spectroscopy to be starting material (106). The second component (0.030 g, 30%) was identified as phenanthro [9,10-b] fluoranthrene (108), mp 199.5-200.5°.

Anal. Calcd. for $C_{28}H_{16}$: C, 95.44; H, 4.56.

Found: C, 95.28; H, 4.67.

The nmr spectrum ($CDCl_3$) showed a singlet at δ 9.03 (1H), a multiplet at 8.97-8.50 (5H) and a multiplet at 8.30-7.17 (10H).

The ultraviolet spectrum (95% ethanol) showed maxima at 386 (15,900), 367 (14,800), 313 (40,100), 306 (49,500), 301 (52,600), 265 (44,800), 254 (52,500) and 226 nm (34,100).

1-Phenylpropenylidene fluorene (112)

A solution of cinnamaldehyde (0.538 g, 4.00 mmoles) and fluorenylidene triphenylphosphorane (38) (1.704 g, 4.00 mmoles) in benzene (10 ml) was stirred at reflux for 24 hours. The solvent was removed under reduced pressure and the residue dissolved in hot ethanol and chilled. The precipitate was collected on a filter, washed with cold ethanol and air dried, yielding (112) (0.896 g, 80%) as yellow needles, mp 155-157°.

Anal. Calcd. for $C_{22}H_{16}$: C, 94.25; H, 5.75.

Found: C, 94.12; H, 5.76.

The infrared spectrum (KBr) showed carbon-hydrogen stretching at 2940 (w) and olefinic stretching at 1610 (m) along with other absorptions at 1445 (s), 1425 (s), 1340 (w), 952 (s), 775 (s), 746 (s), 737 (s), 720 (s) and 683 (s) cm^{-1} .

The mass spectrum showed a molecular ion at m/e 280 (base peak) along with other abundant fragments at 279 (69%), 278 (17%), 276 (14%), 203 (27%), 202 (22%), 165 (16%), 138 (13%) and 127 (10%).

Attempted Photolysis of 1-Phenylpropenylidene-
fluorene (112)

1-Phenylpropenylidenefluorene (112) (0.108 g, 0.386 mmoles) and iodine (0.050 g, 0.197 mmoles) in ethanol (200 ml) was photolyzed through a pyrex filter with 3100 Å light for 72 hours. The solvent was removed under reduced pressure and the residue examined by thin layer chromatography. Only one component was detected. The residue was dissolved in hot ethanol and chilled. The precipitate was collected on a filter, washed with cold ethanol and air dried. Starting material (0.101 g, 94%) was recovered as yellow needles, mp 156-158°.

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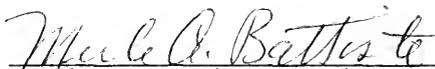
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