SYNTHESIS AND REACTIVITY IN THE CYCLOBUTENE SERIES

By

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CHAPTER I

DIELS-ALDER REACTIONS OF SUBSTITUTED CYCLOBUTENES

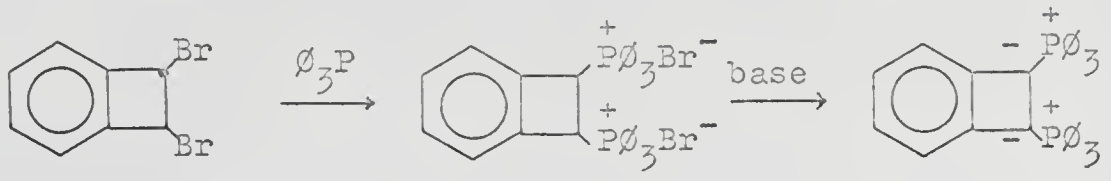
Introduction

The continuing interest in non-benzenoid aromatic compounds has resulted in a large number of significant advances in this area.* Application of the synthetic ingenuity of the organic chemist has yielded a variety of systems suitable for testing the predictions of the LCAO MO theory. Compounds which according to molecular orbital theory should possess appreciable aromatic character include a number of cyclically conjugated charged-ring systems. Monocyclic examples of these ring systems include the cyclopropenyl cation, the cyclobutadienyl dianion and dication, the cyclopentadienyl anion, the cycloheptatrienyl cation, and the cyclooctatetraenyl dianion and dication.

Stable salts of derivatives of the cyclopropenyl cation have been prepared and extensively studied by Breslow and co-workers,[5] although the parent ion is unknown. The cyclobutadienyl dianion has not been observed to date but a derivative of the benzocyclobutadienyl dianion has been obtained by treatment of salt 1 with n-butyllithium

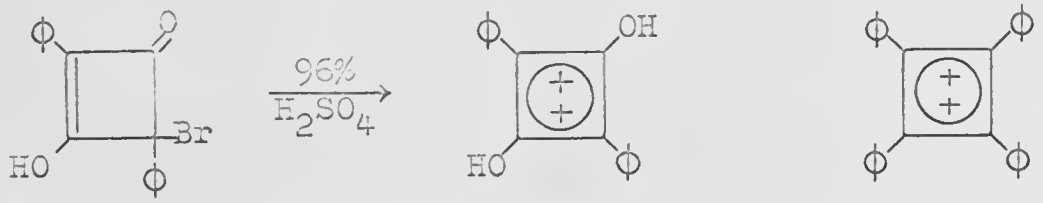
*For reviews see references 1-4.

or lithium ethoxide.[6] The bis-ylide 2 is reported to be



1 2

stable at -40° for at least several hours. The synthesis of the dibenzocyclobutadienyl dianion has been claimed[7] but the interpretation and significance of the data has been questioned.[8] Farnum has reported[9] the observation of a carbonium ion which is possibly cyclobutadienyl dication 4, although the evidence is not conclusive. The ion is formed

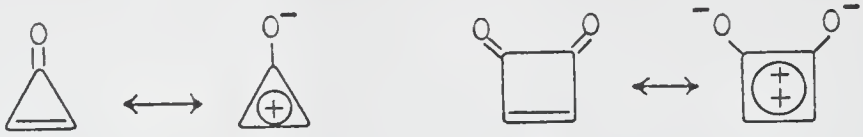


3 4 5

upon dissolution of α-bromoketone 3 in concentrated sulfuric acid. A claim[10] of the tetraphenylcyclobutadienyl dication (5) has been withdrawn[11] due to the results of an x-ray investigation.[12] A second report[11] of an ion which could be dication 5 appears more likely although again the data is not beyond question, pointing out the extreme difficulty in distinguishing between mono- and dication in this series. The parent ions have been obtained in the cases of the

cyclopentadienyl anion and the cycloheptatrienyl cation. In addition, a large number of stable salts (including inner salts) of these two ions have been prepared and studied.* The cyclooctatetraenyl dianion has been synthesized and studied by Katz.[13] The cyclooctatetraenyl dication and its derivatives are unknown. Efforts to prepare this ion by hydride abstraction from 1,3,5-cyclooctatriene, by reaction of cyclooctatetraene dichloride with stannic chloride, or by treatment of cyclooctatetraene with stannic bromide and bromine were unsuccessful.[14]

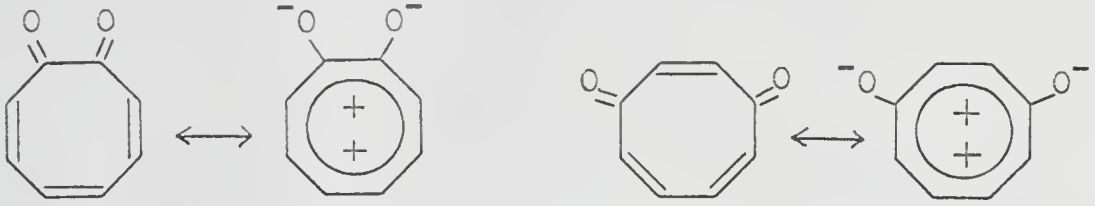
A series of exceedingly interesting compounds is composed of the carbonyl analogues of the positive ions mentioned above. For example, the carbonyl analogue of the cyclopropenyl cation is cyclopropenone (6a). Cyclopropenone should possess some degree of aromatic character as a consequence of contributions to the resonance hybrid by dipolar form 6b. Similar situations exist for cyclobutadienoquinone (7a and 7b), tropone (8a and 8b), and cyclooctatetraenoquinone (9a and 9b or 10a and 10b).



6a 6b 7a 7b

*See references 1, 2 and 4 for reviews.

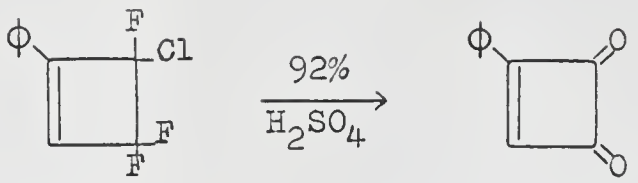
8a ⟷ 8b



9a ⟷ 9b

10a ⟷ 10b

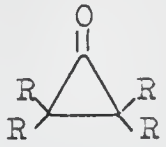
In good agreement with the theoretical predictions, derivatives of cyclopropenone have been synthesized by a variety of methods and exhibit the expected stability.[15] Unsubstituted cyclopropenone is unknown and an attempted synthesis by means of a route which afforded methylcyclopropenone was unsuccessful.[15a] The first derivative of the cyclobutadienoquinone ring system (7a) was prepared in 1955 by Smutny and Roberts.[16] Cyclobutene 11 is converted to phenylcyclobutadienoquinone (12) by 92 per cent sulfuric acid at 100°. The unusual stability of 12 is evidenced by its survival under the rather drastic conditions of its preparation. Following this initial synthesis, reports of a wide variety of derivatives of cyclobutadienoquinone have appeared[17] but the parent compound remains unknown. The



11 12

chemistry of tropone and its derivatives has been well established and indicates that the zwitterionic form 8b makes a considerable contribution to the ground state.* Neither the parent compounds nor any derivatives have been synthesized in the cases of the cyclooctatetraenoquinones 9a and 10a.

The fact that the dipolar resonance forms can contribute significantly to the stabilization of the carbonyl derivatives mentioned above is dramatically demonstrated in the instance of the cyclopropenone system. On the basis of ring strain alone, one would predict that cyclopropanones (13) would be more stable than cyclopropenones. Recent work[18] has shown that the reverse is actually the case. Cyclopropanones readily undergo reactions which result in relief of ring strain.



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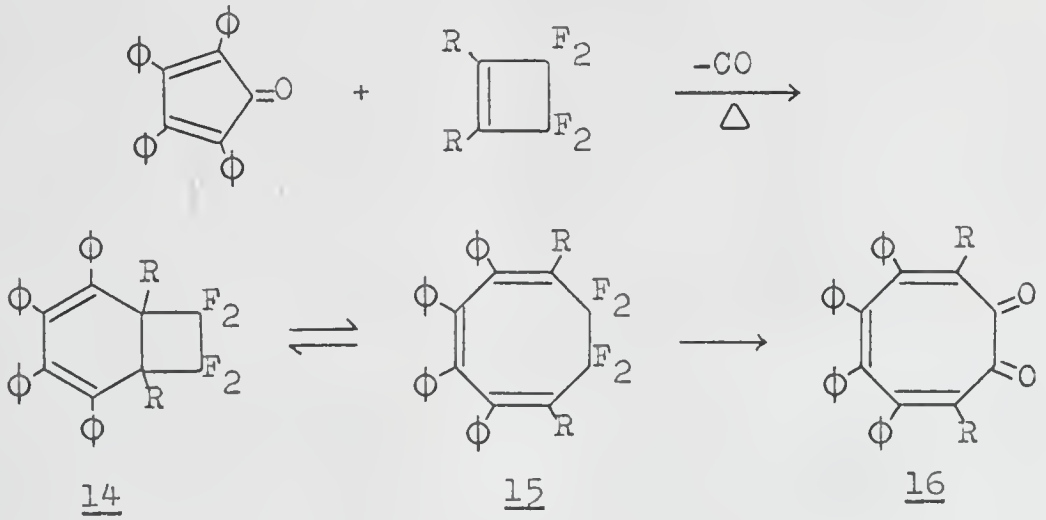
*For a review see reference 4.

The lack of available data concerning the cyclooctatetraenyl dication makes the synthesis of this ion a very desirable goal. The successful preparation[13] of the cyclooctatetraenyl dianion suggests that the delocalization energy of multicharged ions containing 4n+2 π-electrons may be sufficient to overcome the destabilizing electrostatic forces resulting from multiple positive or negative charges. The marked stability of carbonyl compounds 6a-8a indicates that a study of quinones 9a and 10a would provide information concerning the possible aromaticity of the cyclooctatetraenyl dication in addition to serving as logical precursors for the synthesis of derivatives of this ion.

A conceivable synthesis of derivatives of quinone 9a would involve entry into the cyclooctatriene ring system via a Diels-Alder reaction between a fluorine-substituted cyclobutene and a properly chosen diene. Chart I depicts

Chart I



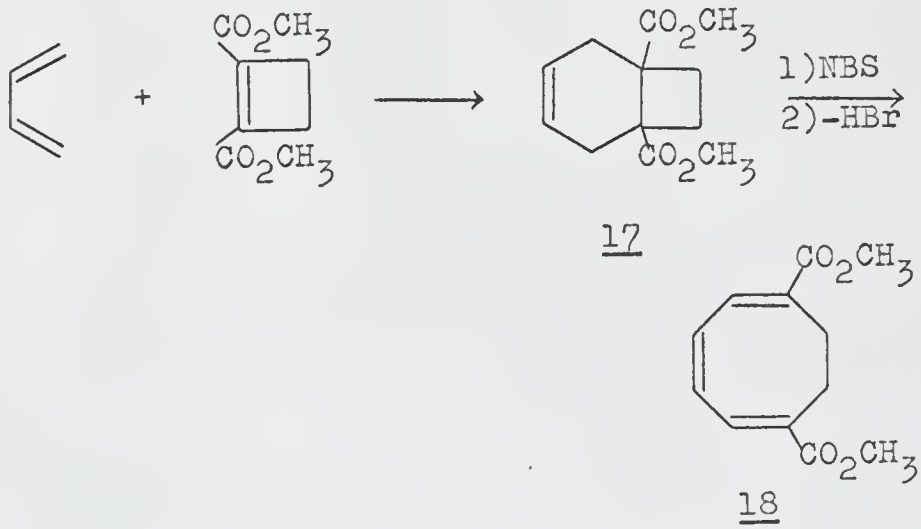
14 15 16

one such possible combination. Strong acid hydrolysis of the resulting cyclooctatriene 14 ⇌ 15 could result in quinone 16.

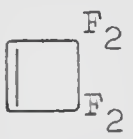
The work to be described in this chapter involves the attempted synthesis of cyclooctatrienes of the type 14 ⇌ 15 by means of Diels-Alder reactions utilizing cyclobutene derivatives as the dienophilic component.

Examples of the participation of cyclobutene or its derivatives in the Diels-Alder reaction are not numerous. Vogel[19,20] has shown that cyclobutenes in which the double bonds are substituted with activating carbomethoxy groups are excellent dienophiles. Reaction of 1,2-dicarbomethoxy-cyclobutene with butadiene leads to the bicyclic adduct 17, which can be converted to cyclooctatriene 18 by treatment with N-bromosuccinimide followed by elimination of hydrogen bromide (Chart II).[19] Shozda and Putnam[21] found that

Chart II



3,3,4,4-tetrafluorocyclobutene (19) reacts with dienes under reasonably mild conditions. Adducts were obtained with butadiene, 2,3-dimethylbutadiene, cyclopentadiene, furan, and 2,5-dimethylfuran. Cyclobutene adds to the extremely reactive 3,6-dicarbomethoxy-1,2,4,5-tetrazine to form an adduct, resulting from loss of nitrogen, in 83 per cent yield.[22] cis-3,4-Dichlorocyclobutene reacts with 9,10-dimethyl- and 9,10-dibromoanthracene to give normal Diels-Alder adducts in high yield.[23] The adduct from the dichlorocyclobutene and 9,10-dimethylanthracene was dechlorinated to the corresponding cyclobutene derivative which also proved to be a good dienophile. Studies of unsaturated four-membered cyclic sulfones have shown them to be moderately good dienophiles.[24] The fact that fused cyclobutadiene derivatives such as 20 react very readily with dienes[25] can not be considered informative regarding the dienophilic properties of related cyclobutenes.



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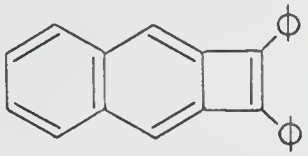


20

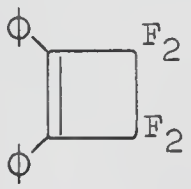
For the purposes of comparison, the available literature[26] describing cyclopropenes as dienophiles is somewhat more revealing. These compounds normally possess high dienophilic reactivity except in the case of geminally

substituted cyclopropenes which are unreactive, apparently for steric reasons.[26d,e]

Results and Discussion

A priori, the route to derivatives of the cyclooctatetraenoquinone ring system outlined in Chart I appeared feasible for a number of reasons. The fluorine-substituted cyclobutenes which were to be used as dienophiles show the remarkable thermal stability typical of fluorine-substituted four-membered rings.[27] This characteristic allows the use of long reaction times and relatively high reaction temperatures. Cyclobutenes in general should serve as reactive dienophiles as a result of angular strain. This strain should have a reaction promoting effect due to a reduction in angular deformation in the transition state leading to adduct formation. The reactivity of cyclopropene is not seriously impaired by the presence of bulky vinylic substituents,[26b,c,e] and it appeared likely that this would also be true for the cyclobutene series. Finally, the observations of Shozda and Putnam[21] with regards to the dienophilic reactivity of 19 indicate that the presence of four allylic fluorines on the cyclobutene ring does not prevent this olefin from participating in the Diels-Alder reaction.

The fluorocyclobutenes which were studied as possible precursors to fluorine-substituted cyclooctatrienes were 1,2-diphenyltetrafluorocyclobutene (21), 1,2-dimethyltetrafluorocyclobutene (22), and 3,3,4,4-tetrafluorocyclobutene (19). The reactivity of diphenylcyclobutadienoquinone (23) was also studied since adduct formation with this cyclobutene could conceivably result in a one-step synthesis of derivatives of 9a. In addition, some preliminary investigations were conducted on 1,2-diphenylcyclobutene (24) as a dienophile in order to gain some insight as to the factors influencing dienophilic reactivity in the cyclobutene series.



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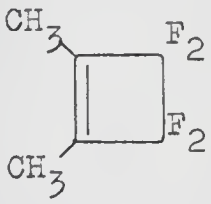

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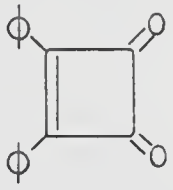

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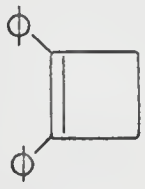
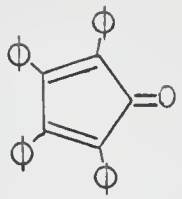


24

The dienes selected were ones which have been shown to give adducts with cyclopropenes. These dienes were (reference is to the adduct with a cyclopropene) tetraphenylcyclopentadienone (tetracyclone) (25),[26b] 1,3-diphenylisobenzofuran (26),[28] phencyclone (27),[28] 1,4-diphenyl-1,3-butadiene (28),[29] α-pyrone (29),[29] and 5,5-dimethoxytetrachlorocyclopentadiene (30).[28]



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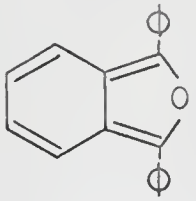

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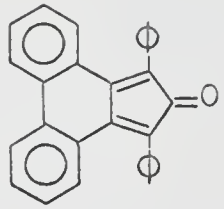

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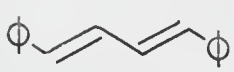

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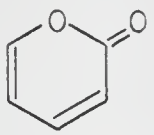

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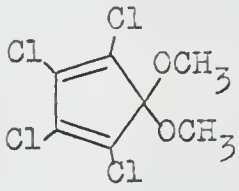

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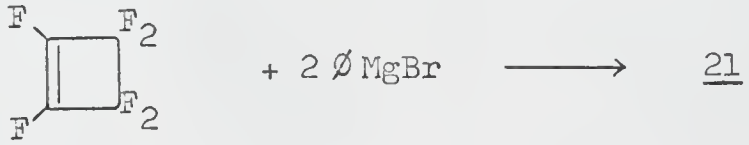
1,2-Diphenyltetrafluorocyclobutene (21)

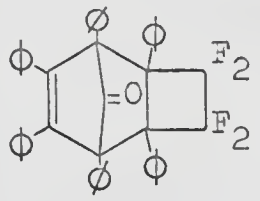
Cyclobutene 21 was prepared by the method of Park[30] involving the addition, elimination reaction of perfluorocyclobutene (31) with phenylmagnesium bromide.



31

The reaction of 21 with tetracyclone (25) under what are normally considered as forcing conditions for the Diels-Alder reaction failed to yield any detectable adduct formation. The lack of reaction was ascertained by the failure of the cyclobutene to discharge the characteristic violet color of 25 and by recovery of unchanged cyclobutene by chromatography (see Experimental Section). When mixtures of 21 and 25 were fused at temperatures as high as 295° the tetracyclone color was not discharged and gas evolution did not occur. The

absence of gas evolution is significant since if the bridged adduct 32 had been formed it would most likely have lost the carbon monoxide bridge at these extreme temperatures. Other



32

attempts at adduct formation with 21 and 25 are described in the Experimental Section.

The reaction of 1,3-diphenylisobenzofuran (26) with excess 21 in refluxing toluene for three days or in refluxing xylene for 29 days resulted in no Diels-Alder adduct formation. These results indicate that little hope exists for 21 as a dienophile since furan 26 is a very reactive diene commonly used for the trapping of transient dienophilic intermediates. In agreement with this observation, 21 failed to add to phencyclone (27) (where the formation of an additional aromatic nucleus in the product is a driving force for reaction) or to 1,4-diphenyl-1,3-butadiene (28).

1,2-Dimethyltetrafluorocyclobutene (22)

Cyclobutene 22 was prepared by the reaction of methyllithium with perfluorocyclobutene (31) as reported by Blomquist and Vierling.[17b]

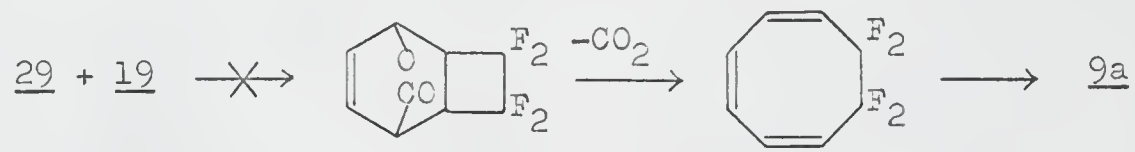
Refluxing a neat mixture of cyclopentadiene 30 and excess 22 for 9.5 days resulted in no isolable Diels-Alder

adduct. Similarly, refluxing a toluene solution of cyclopentadienone 25 with a large excess of 1,2-dimethyltetrafluorocyclobutene (22) failed to discharge the violet color of 25 and furnished no indication of Diels-Alder adduct formation.

3,3,4,4-Tetrafluorocyclobutene (19)[31,32]

As mentioned previously, cyclobutene 19 has been shown to react with dienes in a normal manner to give Diels-Alder products in reasonable yield.[21] However, 19 failed to react with α-pyrone (29) when a neat mixture of the two was heated in a sealed tube at 60-75° for 30 days. Adduct 33 could have provided a route to the unsubstituted 1,2-cyclooctatetraenoquinone (9a) via decarboxylation followed by acid hydrolysis (Chart III).

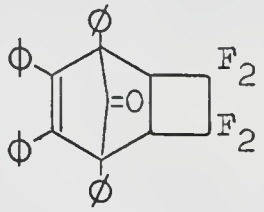
Chart III



33

Heating a benzene solution of tetracyclone (25) and excess 19 at 100° for 23 days in a sealed tube failed to discharge the violet color of the diene. Chromatography led to the isolation of a trace of impure white solid which turned violet at its melting point. The violet color very likely indicates a retro-Diels-Alder reaction in which the

tetracyclone is regenerated. It is thus possible that this material is in fact the bridged adduct 34 although insufficient material was obtained for characterization. It is evident that the formation of 34 in reasonable yield will require reaction temperatures in excess of 100°. Decarbonylation of 34 would provide a cyclooctatriene of structure



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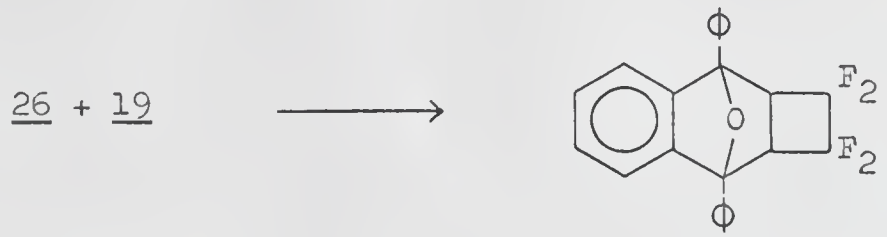
suitable for conversion to a derivative of the 1,2-quinone 9a.

When a benzene solution of 1,3-diphenylisobenzofuran (26) and excess 19 is heated in a sealed tube at 100° for 15 days a 64 per cent yield of adduct 35 is obtained. The structure of 35 was established by elemental analysis, spectral data, and the apparent retro-Diels-Alder reaction upon melting (see Experimental Section).



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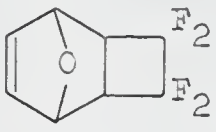
When heated at its melting point adduct 35 turns the bright-fluorescent yellow characteristic of furan 26. Attempts at conversion of 35 into a benzocyclooctatriene derivative by removal of the oxygen bridge were unsuccessful. This compound was resistant to deoxygenation with trimethylphosphite or concentrated sulfuric acid, with both reactions affording only unchanged starting material. Similarly, the adduct (36) formed by reaction of 19 with furan has been shown to be unreactive toward attempts at removal of the oxygen bridge.[33]



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The investigation of the Diels-Alder reactions of 19 has not been satisfactorily completed due to a lack of availability of this cyclobutene. The studies described above indicate that the pertinent synthetic routes employing 19 as a dienophile may be feasible. In particular, the reaction of 19 with tetracyclone is deserving of further study.

1,2-Diphenylcyclobutene (24)

Initial studies of the Diels-Alder reactions of 24 indicate that it is not a good dienophile. Cyclobutene 24

fails to react with tetracyclone in refluxing benzene. 1,2-Diphenylcyclobutene apparently forms an adduct with 1,3-diphenylisobenzofuran (26). However, the reaction is very slow and the product has not yet been obtained in sufficient yield and purity for full characterization. In contrast with the behavior of cyclopropene derivatives,[26e] cyclobutene 24 is not reduced by diimide.

The lack of dienophilic reactivity in cyclobutenes 21, 22 and 24 is somewhat surprising. The experiments described above were designed with a synthetic goal in mind and thus do not comprise a systematic study of the reactivity of cyclobutenes in the Diels-Alder reaction. The paucity of reported data concerning the use of cyclobutenes in the diene synthesis makes the assessment of the precise reasons for the observed inertness rather difficult. However, some general observations can be made.

Two pertinent factors concerning the Diels-Alder reaction are: a) the reactivity of the dienophile is normally increased by electron-withdrawing groups, and b) the reaction is very sensitive to steric factors. The observed[21] reactivity of 3,3,4,4-tetrafluorocyclobutene indicates that the fluorine substituents have no deleterious effect on the reactivity of the olefin although a direct comparison with cyclobutene is not available. It is very possible that the fluorines are actually serving to activate the cyclobutene by means of electron withdrawal. It thus

seems that the principle cause of lack of dienophilic reactivity in cyclobutenes 21 and 22 is a result of steric effects due to the presence of two substituents on the cyclobutene double bond. The steric factor takes on added importance when one considers that the dienes employed in the study of cyclobutenes 21 and 22 are all heavily substituted with bulky groups. The success of Vogel[19,20] in obtaining Diels-Alder adducts with 1-carbomethoxy- and 1,2-dicarbomethoxycyclobutene may be ascribed to the fact that the carbomethoxy group is an excellent dienophile activator. In addition, the dienes used in these syntheses (butadiene, 1,4-dichloro-1,3-butadiene and α-pyrone) were ones having relatively low degrees of substitution. A more complete appraisal of the relative effects of the fluorine substituents and steric factors must await the accumulation of additional data, particularly with regard to the reactivity of 1,2-diphenylcyclobutene. In any case, it must be kept in mind that a Diels-Alder reaction is composed of two components, diene and dienophile. Reactivity is thus a function of both elements and any comparison of dienophile reactivities should be for reactions where the diene is of constant or nearly constant structure.

The observed lack of reactivity of some of the cyclobutene derivatives described above prompts a comparison with the cyclopropene series. As mentioned earlier, cyclopropenes

(except those which are geminally substituted) are active dienophiles even when the double bond of the cyclopropene bears two phenyl substituents. A comparison of the two small ring compounds necessitates a discussion of three factors.

The first point involves the presence of ring strain in the dienophile. The pronounced angular strain of the cyclopropene ring[34] is considerably decreased in the Diels-Alder adduct where the three-membered ring has become saturated. This reduction in strain is already present in the transition state leading to adduct formation and thus has an accelerating effect on the reaction. This effect is less important in the cyclobutene series where angular distortion is not as large.

The second point concerns steric factors stemming from the orientation of substituents about the double bond of the dienophile. In 1,2-disubstituted cyclopropenes the vinylic substituents can more readily achieve coplanarity with the ring than can vinylic substituents in 1,2-disubstituted cyclobutenes (see Chapter III for a more detailed discussion of this point). While the ultraviolet spectrum of 1,2-diphenylcyclobutene (see Chapter III) indicates that the phenyl rings may be nearly coplanar with the cyclobutene ring they will not be as coplanar as the phenyl substituents in 1,2-diphenylcyclopropenes. While

this deviation in coplanarity in going from cyclopropene to cyclobutene may be small, it could have a large effect on the energy of the transition state for formation of the Diels-Alder adduct by providing steric hindrance to the approaching diene.

A third point relates to the electronic structure of small-ring compounds. Several models have been proposed to account for the stability, reactivity, and unusual bond angles of the cyclopropane ring.[35] It is possible that some measure of the high reactivity of cyclopropenes as compared to cyclobutenes in the diene synthesis is a result of the electronic structure of the three-membered ring. However, the precise nature and relative importance of this effect, or even whether or not such an effect exists, cannot be properly determined at this time. In addition, there exists no firm basis for prediction of whether this effect would be rate accelerating or rate retarding.

The factors discussed above provide a qualitative explanation for the differing reactivities of cyclopropenes and cyclobutenes. A determination of the relative importances of these factors will require a more detailed study.

Diphenylcyclobutadienoquinone (23)

Quinone 23 was prepared by sulfuric acid hydrolysis of 21 as described by Blomquist and LaLancette.[17a] The possibility that 23 could enter into the Diels-Alder reaction was investigated since adduct formation with this quinone could result in a one-step synthesis of the cyclooctatetraenoquinone ring system.

Diphenylcyclobutadienoquinone failed to form an adduct with furan 26 in refluxing benzene. Reaction with tetracyclone in refluxing toluene or xylene was unsuccessful. Fusing mixtures of 23 and tetracyclone at temperatures of approximately 200° resulted in the evolution of small amounts of gas but afforded no isolable adduct.

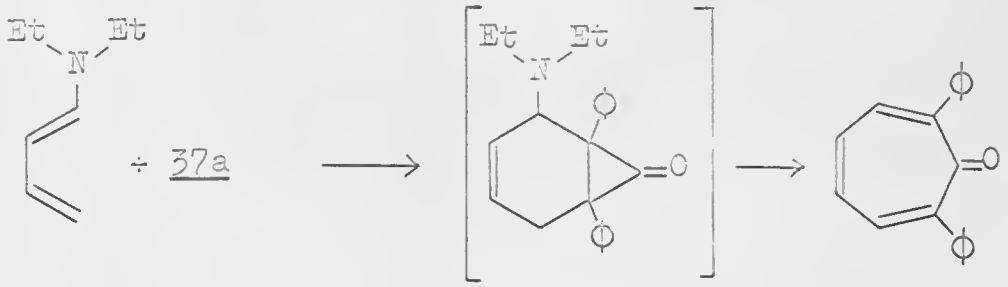
The failure of 23 to add to the dienes described above is not surprising. The data obtained for olefins 21 and 24 indicate that the presence of two vinylic phenyl substituents seriously affects the reactivity of cyclobutene derivatives. Furthermore, diphenylcyclopropenone (37a) does not enter into Diels-Alder reactions[28] although 1,2,3-triphenylcyclopropene is an excellent dienophile.[26b,c,e] The

37a 37b

inertness of 37a is probably due to the fact that the cyclopropenone is a resonance hybrid of forms 37a and 37b and addition to the double bond would involve loss of the aromatic system. Diphenylcyclobutadienoquinone would be predicted to be unreactive for the same reason.

Cycloaddition routes

Diphenylcyclopropenone (37a) reacts with 1-diethylamino-1,3-butadiene (38) to yield, after the loss of the elements of diethylamine, 2,7-diphenyltropone (39).[36] This 1,4-addition reaction could proceed by concerted cyclo-

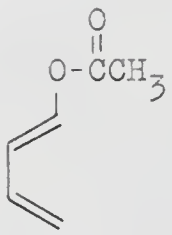


38 39

addition or by Michael-type addition followed by ring closure of the resulting dipolar species.[36]

Reaction of enamine 38 with diphenylcyclobutadienoquinone at room temperature resulted in immediate decomposition of the quinone and afforded no isolable product. Repetition of this experiment at -78° followed by warming to room temperature gave the same result. Butadiene 38 and 1,2-diphenyltetrafluorocyclobutene failed to react in refluxing benzene.

The destruction of quinone 23 by enamine 38 is undoubtedly due to attack on the cyclobutene ring by the nucleophilic nitrogen.[37] Replacement of the diethylamino group of 38 with an acetoxy group yields a butadiene which may also serve as a dipolarophile. However, reaction of 1-acetoxy-1,3-butadiene (40) with diphenylcyclobutadienoquinone in refluxing benzene yielded only unchanged quinone.



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CHAPTER II

STRUCTURE AND REACTIVITY OF DIPHENYLCYCLOBUTADIENOQUINONE MONOTOSYLHYDRAZONE

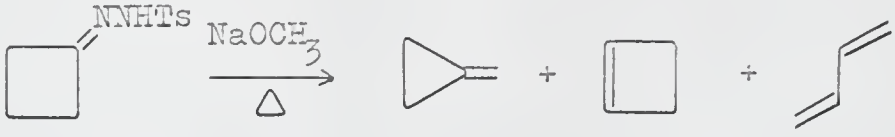
Introduction

Tosylhydrazone derivatives of carbonyl compounds have proved to be valuable synthetic intermediates. The tosylhydrazones are precursors of the corresponding diazo compounds which in turn may decompose to yield carbenes (Chart IV). The products derived from such carbenes are very

Chart IV

$$\text{>C=O} \xrightarrow{TsNHNH_2} \text{>C=NNHTs} \xrightarrow[(2)\ -Ts^-]{(1)\ \text{base}} \text{>C=}N_2 \xrightarrow{-N_2} \text{>C:}$$

often the result of intramolecular reactions such as insertion, ring expansion, ring contraction, and elimination. For example, solution pyrolysis of the sodium salt of cyclobutanone tosylhydrazone (41) affords methylenecyclopropane in 80 per cent yield.[38] Cyclobutene (20%) and trace amounts



41

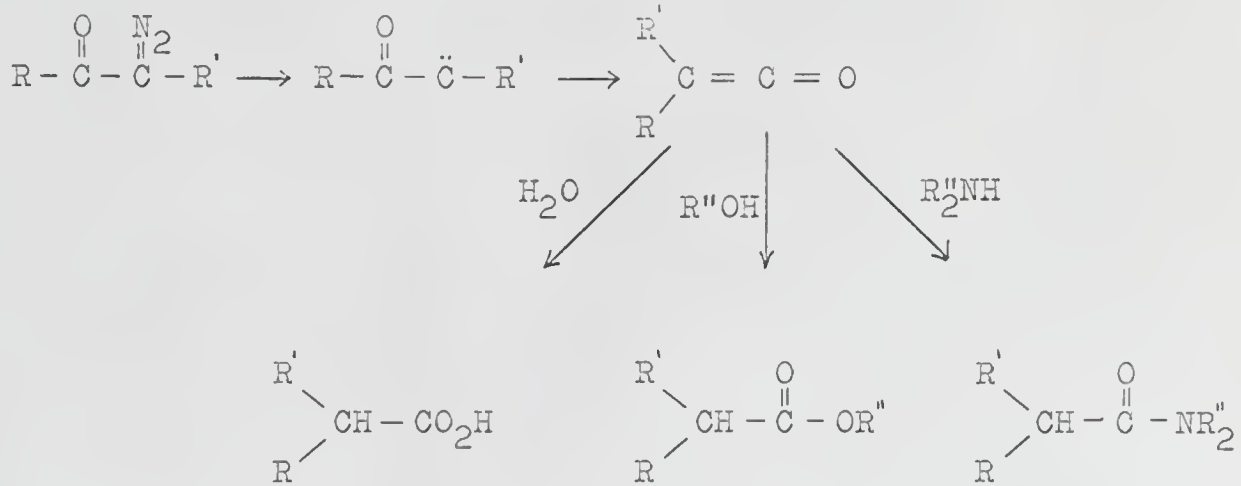
of butadiene are also obtained.

The monotosylhydrazone derivatives of α-diketones are of interest since they may be converted to the corresponding α-diazoketones which derive stability from resonance structures employing the carbonyl group (42a and 42b). These α-diazoketones undergo a number of reactions, being

42a 42b

decomposed by heat, light, and a variety of catalysts. One very important reaction is the Wolff rearrangement[39] where decomposition of the diazoketone in the presence of water, alcohols, or amines yields rearrangement products as shown in Chart V.

Chart V

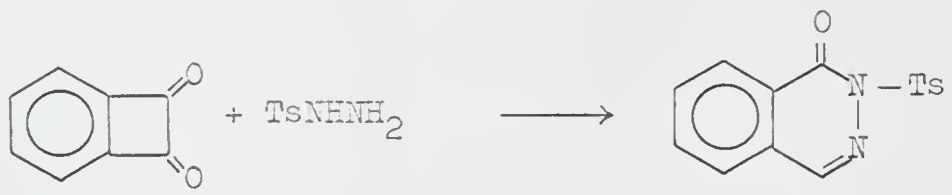


In this chapter the monotosylhydrazone derivative of diphenylcyclobutadienoquinone (23) has been studied with the

objective of generating the diazoketone and carbene derived from this derivative.

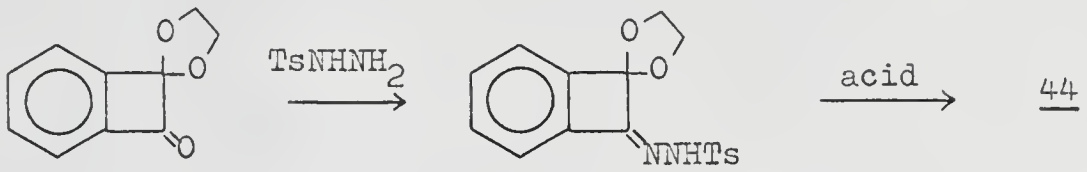
Results and Discussion

The monotosylhydrazone derivative of quinone 23 has been reported by Blomquist and LaLancette[17a] although the only data listed in support of the assigned structure was a correct elemental analysis. In view of results reported[40] for the benzocyclobutadienoquinone system (43) it was felt that proof of structure for this derivative was necessary. Quinone 43 reacts normally with 2,4-dinitrophenylhydrazine and o-phenylenediamine to give the bis-2,4-dinitrophenylhydrazone and quinoxaline, respectively.[40a] However, 43 fails to give normal carbonyl derivatives with hydroxylamine, hydrazine, or p-toluenesulfonylhydrazine (tosylhydrazine).[40b] The only products isolated from these reactions were those resulting from cleavage of the four-membered ring. For example, reaction of 43 with tosylhydrazine under neutral conditions afforded 2-tosylphthalazone (44). Similarly, monoketal 45 gave a normal tosylhydrazone derivative (46)



43 44

but acid hydrolysis of this derivative yielded the rearranged product 44.

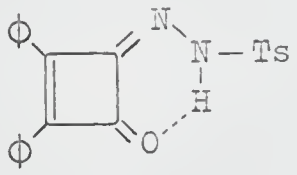


45 46

The data described above, coupled with the fact that both phenylcyclobutadienoquinone[41] and diphenylcyclobutadienoquinone[37] react with o-phenylenediamine to give rearranged quinoxaline derivatives resulting from cleavage of the four-membered ring, necessitated proof that 23 forms a normal toslyhydrazone derivative.

Treatment of quinone 23 with one equivalent of tosylhydrazine in acidic ethanol solution affords a bright-yellow, crystalline product (47) in yields of approximately 80 per cent. The melting point agreed with that reported[17a] for the assumed monotosylhydrazone derivative. The infrared spectrum showed absorption bands at 3.15 (N-H) and 5.67 μ (small ring C=O). The n.m.r. spectrum of 47 supported a normal monotosylhydrazone structure. Resonances were observed at τ 1.15 (broad singlet, N-H), 1.78-2.80 (complex multiplet, aromatic protons), and 7.58 (sharp singlet, CH_3), with area ratios of 1:14:3, respectively. Conclusive proof that 47 is indeed a normal tosylhydrazone derivative was obtained by sulfuric acid hydrolysis which regenerated quinone 23 in 59 per cent yield.

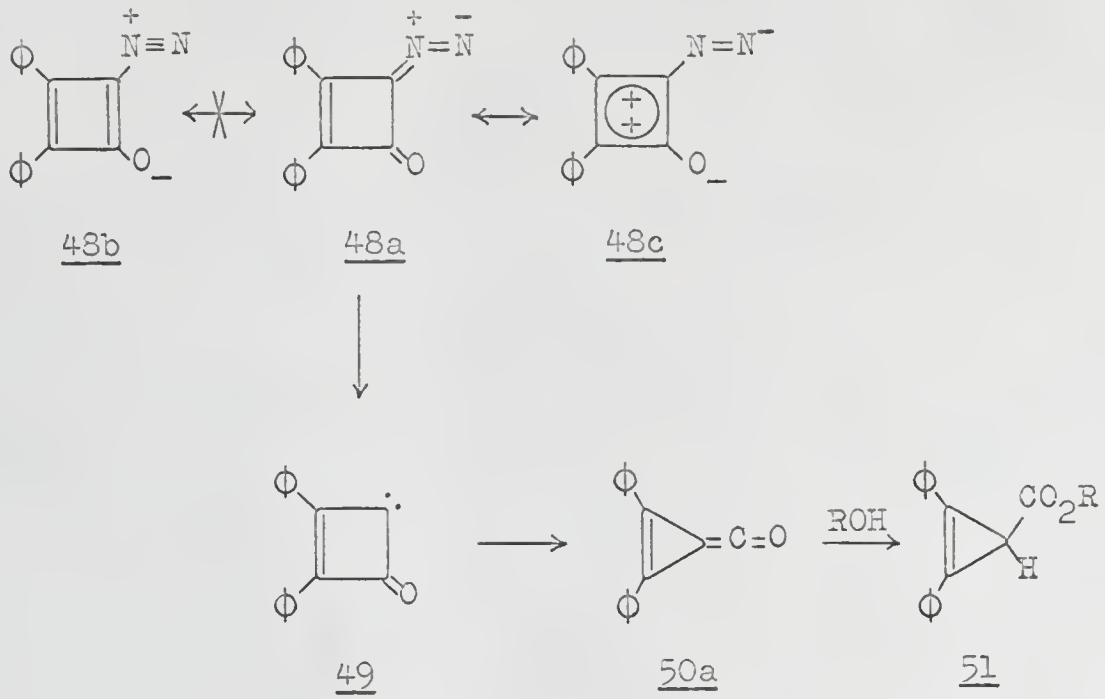
The nitrogen proton of 47 appears at considerably lower field in the n.m.r. spectrum than do the nitrogen protons of the tosylhydrazone derivatives examined in Chapter III (see Experimental Section). This low field absorption provides further support for structure 47 since it is very likely that the shift is due to intramolecular hydrogen bonding.



47

Attempts to convert 47 into the bistosylhydrazone derivative were unsuccessful (see Experimental Section).

Tosylhydrazone 47 is a reasonable precursor of diazodiphenylcyclobutenone (48a), which in turn could serve as a source of carbene 49. It is of interest that diazoketone 48a would not be expected to achieve resonance stabilization in the usual manner of α-diazoketones. The resonance form utilizing the carbonyl group (48b) should not be a major contributing form since it requires a cyclobutadiene nucleus. However, diazoketone 48a may achieve resonance stabilization as shown in form 48c. Cyclobutene 48a may thus be viewed formally as a derivative of the cyclobutadienyl dication.



48b 48a 48c

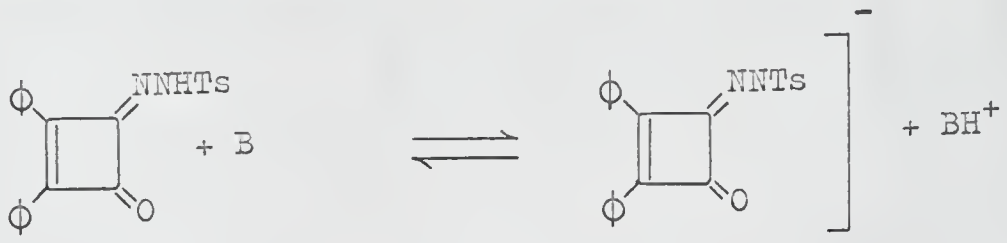
49 50a 51

Generation of carbene 49 under the conditions of the Wolff rearrangement could provide a new source of cyclopropene derivatives (51) via the intermediate ketene 50a. This ketene may be considered a derivative of methylenecyclopropene and might be sufficiently stable to permit isolation due to contributions to the resonance hybrid by form 50b.

50a 50b

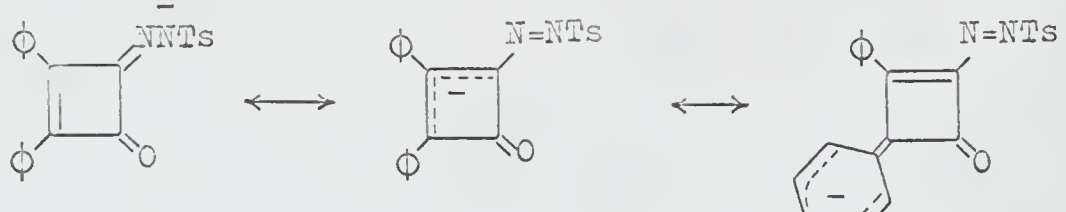
The conversion of the monotosylhydrazones of cyclic α-diketones to the corresponding α-diazoketones may be effected by treatment with aqueous sodium hydroxide[42] or more simply by chromatography of the tosylhydrazone on basic alumina.[43] The reaction involves the formation of the tosylhydrazone anion followed by elimination of the sulfinate anion to yield the neutral diazoketone.

When solutions of tosylhydrazone 47 in polar organic solvents were treated with aqueous sodium hydroxide, triethylamine, or n-butyllithium the organic solution turned an immediate dark red indicating formation of anion 52. The intense red color of anion 52 is accounted for by the



47 52

extended length of the conjugated system available for delocalization of the electron pair. This delocalization can take place as shown in resonance forms 52a-52c. Again,



52a 52b 52c

resonance forms involving a cyclobutadiene nucleus are avoided. Anion 52 proved to be exceedingly stable toward elimination of sulfinate anion.

When 52 was generated in a two-phase mixture of methylene chloride and aqueous sodium hydroxide (one equivalent) the organic layer became an immediate dark red. There was no visual change in the mixture after stirring at room temperature for three hours. Aqueous work-up afforded only the starting tosylhydrazone in 88 per cent recovery. Treatment of a chloroform solution of 47 with excess triethylamine again led to formation of a dark-red color. Addition of hexane caused precipitation of crystalline 47 (85% recovery). Attempted vacuum pyrolysis[44] of the lithium salt of 47 yielded only a black, carbonaceous residue with no volatile products observed.

Tosylhydrazone 47 was incompletely soluble in an aqueous sodium hydroxide solution (one equivalent). Stirring at room temperature resulted in the formation of an orange suspension. When stirring was stopped yellow solid settled beneath a bright-red aqueous solution. After stirring such a suspension at room temperature for six days the color of the mixture had changed to yellow and when stirring was stopped yellow solid settled beneath a colorless aqueous solution. Extraction with chloroform gave unchanged 47 (50% recovery) along with an intractable brown

gum. This brown gum showed infrared absorption at 4.74 microns characteristic of the diazo group[42,45] but all attempts at isolation of a pure material were unsuccessful. Acidification of the aqueous layer followed by extraction with chloroform gave a yellow, heat-sensitive solid which was not characterized. The fact that although the characteristic red color of the anion of 47 was no longer present 50 per cent of the tosylhydrazone was recovered indicates that the products formed stem from the reaction of the tosylhydrazone with two equivalents of base.

Attempted preparation of diazodiphenylcyclobutenone by chromatography of 47 on basic alumina was unsuccessful. The alumina column turned bright orange when a solution of the tosylhydrazone was added. This orange color traveled the length of the column but the eluants were yellow. Elution with chloroform until the eluants were colorless afforded only unchanged 47 (60% recovery). The alumina column remained a light-orange color after the tosylhydrazone had been completely eluted. The relatively low recovery of tosylhydrazone from this simple operation is very possibly due to a photolytic decomposition of the anion on the portion of the alumina surface which was exposed to light.

Preliminary studies of the decomposition of the sodium salt of 47 in aprotic media indicate that this will not be a productive method for the generation and study of carbene 49.

Decomposition of salts of 47 by photolysis could prove to be a more fruitful route.

CHAPTER III

THE SYNTHESIS AND VALENCE ISOMERIZATION OF 1,2-DIPHENYLCYCLOBUTENE

Introduction

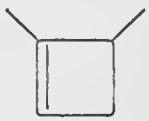
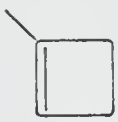
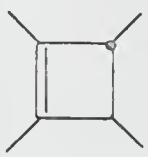
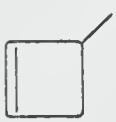
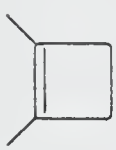
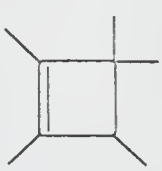
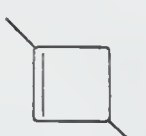
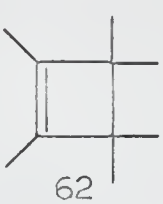
The thermal conversion of cyclobutenes to 1,3-butadienes has received a great deal of attention in recent years.[46] The reaction is of interest for several reasons. The stereospecificity of the valence isomerizations of cyclobutenes containing allylic substituents has been recognized for some time but theoretical grounds for the observed results have been advanced only recently.[47] Properly substituted cyclobutene derivatives provide a convenient source of experimental data with which to confirm the predictions of the Woodward-Hoffmann rules. In addition, the cyclobutene-butadiene isomerization is an ideal system with which to investigate subtle effects of substituents on the transition state of a unimolecular reaction. Very importantly from a kinetic viewpoint, cyclobutene isomerizations are characteristically homogeneous, unaffected by radical inhibitors, and free from side reactions; yielding normally a single butadiene isomer. The thermal isomerizations proceed at readily measurable rates in the temperature range of 25-200°, making kinetic studies of these systems experimentally feasible.

A great deal of the previous work on cyclobutene valence isomerizations has been qualitative in nature, dealing mainly with the stereochemistry of the resulting butadiene and occasionally with the relative ease of isomerization of cis-trans pairs of 3,4-disubstituted derivatives. More recently the importance of quantitative kinetic data has been recognized and a number of reports of results of this type have appeared.

The series of compounds which has been most completely studied is composed of the methyl-substituted cyclobutenes. Table 1 shows the members of this series for which kinetic data is available along with the rate constants calculated for 175°.[46] The data of Table 1 indicate that vinylic methyl substituents decrease the rate of isomerization. For example, 1-methyl- and 1,2-dimethylcyclobutene (54 and 56) both react more slowly than does cyclobutene (53). In addition, 1,3-dimethyl- and 1,4-dimethylcyclobutene (57 and 58) both isomerize at a lower rate than does 3-methylcyclobutene (55). The situation for allylic methyl substituents is more complex. The addition of a single allylic methyl group or two trans methyl groups in the 3 and 4 positions of the ring increases the rate of isomerization. On the other hand, a comparison of 1,2-dimethyl- and cis-1,2,3,4-tetramethylcyclobutene (56 and 60) indicates that the substitution of two cis methyl groups has little effect on the rate of isomerization.[53]

TABLE 1

RATES OF ISOMERIZATION OF METHYL-SUBSTITUTED CYCLOBUTENES AT 175°

Cpd.	$k \times 10^4$ ($sec.^{-1}$)	Ref.	Cpd.	$k \times 10^4$ ($sec.^{-1}$)	Ref.
 53	17	48	 58	16	52
 54	4.6	49	 59	56	46
 55	160	50	 60	0.94	46
 56	1.8	51	 61	2.6	46
 57	33	52	 62	0.45	46

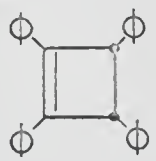
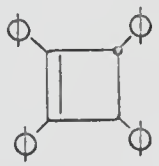
The rate differences observed for the compounds listed in Table 1 are probably due to a combination of steric and electronic factors. The steric factors are for the most part rate retarding and arise from increased methyl-methyl and methyl-hydrogen repulsions in the transition state for ring opening. These interactions can occur between two vinylic substituents and between a vinylic and an allylic substituent. In addition, the thermal ring opening of cyclobutene derivatives is a conrotatory process[47] and those compounds where an allylic methyl group must rotate inward will experience a steric deceleration of the rate of isomerization. The electronic effects of the methyl substituents are not as clearly defined. A lengthening of the ring double bond by stabilizing methyl substituents is in agreement with the trends observed although a consideration of steric interactions affords the same result and the relative weights of these two factors is difficult to assess. Methyl groups in allylic positions can be rate accelerating due to stabilization in the transition state of the developing π-centers. However, this rate increase can be effectively neutralized by the aforementioned steric repulsions. It is of interest to note that the substituent effects observed in Table 1 are fairly subtle, with the largest difference in reactivity being a factor of ca. 350.

The data of Table 1 suggest that eclipsing strain in the ground state does not significantly affect the rate at which these cyclobutene derivatives undergo ring opening. Thus, cis-1,2,3,4-tetramethylcyclobutene (60) reacts considerably slower than does trans-1,2,3,4-tetramethylcyclobutene (59), and hexamethylcyclobutene (62) is slowest of all. It thus seems that eclipsing effects in the ground state, although present to some degree, are overwhelmed by the electronic and steric effects operative in the transition state.

In contrast with the fairly small differences in reactivity observed for the methyl-substituted cyclobutenes, the addition of phenyl substituents to the cyclobutene ring may result in a much larger effect on the rate of isomerization. Table 2 shows the rate constants at 175° (calculated from the data reported in reference 54) for the valence isomerization of cis- and trans-1,2,3,4-tetraphenylcyclobutene (63 and 64). It is immediately evident from the data in Table 2 that the four phenyl substituents of 63 and 64 have a much greater effect on the rate of ring opening as compared to cyclobutene than was observed with any of the methyl-substituted compounds listed in Table 1. This enhanced reactivity indicates that a study of other members of the phenyl-substituted series may prove enlightening as to the precise nature of the substituent effects operative in

TABLE 2

RATES OF ISOMERIZATION OF CIS- AND TRANS-1,2,3,4-TETRAPHENYLCYCLOBUTENE AT 175°

Cpd.	$k \times 10^4$ ($sec.^{-1}$)	Ref.
 63	40,000	54
 64	80,000	54

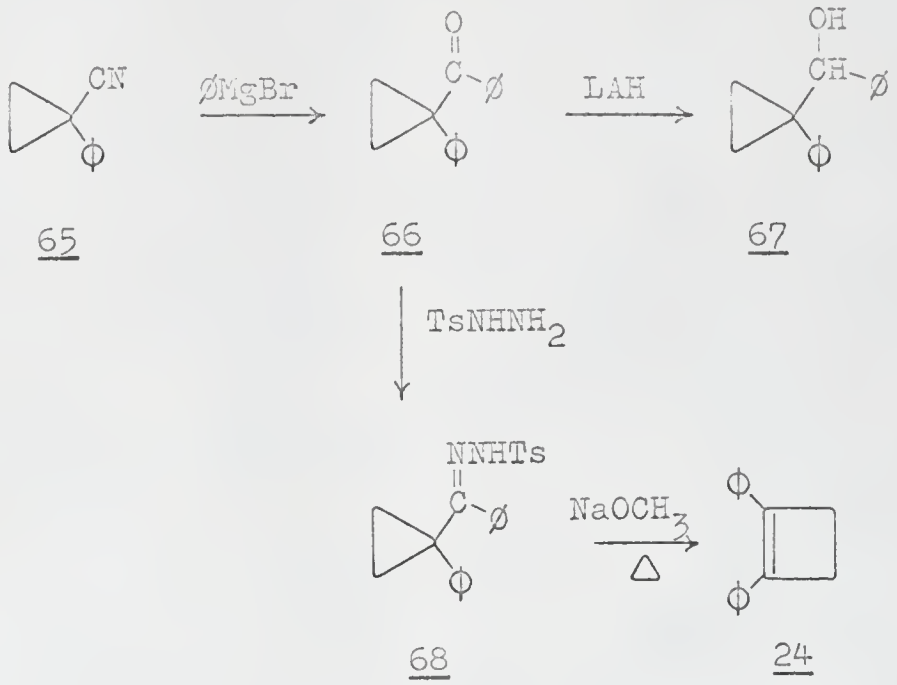
thermal isomerization of cyclobutene derivatives. The present chapter describes a kinetic study of another member of this series, 1,2-diphenylcyclobutene.

Results and Discussion

Synthesis and structure of 1,2-diphenylcyclobutene

A convenient source of 1,2-diphenylcyclobutene (24) was required not only for the study of the valence isomerization but also in connection with the Diels-Alder studies described in Chapter I. The synthetic route utilized in this work is outlined in Chart VI. Several other methods

Chart VI



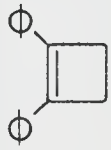
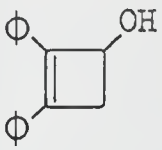
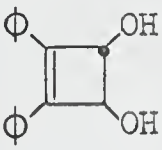
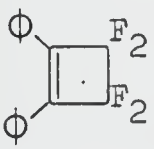
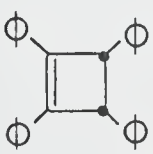
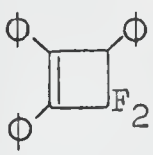
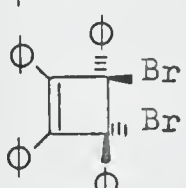
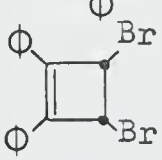
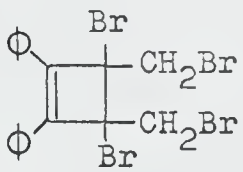
of preparation of this hydrocarbon have recently been reported.[55] The properties described below for 1,2-diphenylcyclobutene are identical in all respects with those listed by these workers. Reaction of 1-cyano-1-phenylcyclopropane (65)[56] with phenylmagnesium bromide followed by hydrolysis of the resulting ketimine salt gave 1-phenylcyclopropyl phenyl ketone (66).[57] Lithium hydride reduction of this ketone afforded 1-phenylcyclopropyl phenyl carbinol (67) in 81 per cent yield. Treatment of 66 with excess tosylhydrazine in ethanol containing trace amounts of acetic acid yielded tosylhydrazone 68 in yields of 66-71 per cent after seven days at reflux. The structures of 67 and 68 were confirmed by spectral and analytical data (see Experimental

Section). The slow rate of formation of tosylhydrazone 68 is undoubtedly due to steric hindrance at the reaction site as evidenced by the much faster rate of formation of the tosylhydrazone derivative of 1-phenylcyclopropyl methyl ketone (69) (vide infra). Conversion of 68 to 1,2-diphenylcyclobutene was effected by means of an aprotic-Bamford-Stevens reaction.[58] It has been previously demonstrated that tosylhydrazone derivatives of cyclopropyl aldehydes and ketones decompose under aprotic-Bamford-Stevens conditions to yield cyclobutene derivatives by ring expansion.[38,59] The base catalyzed decomposition of 68 in purified N-methyl-2-pyrrolidone at 120°, using freshly prepared sodium methoxide as the base, gave 1,2-diphenylcyclobutene in yields of 66-76 per cent.

The n.m.r. spectrum of 24 is in agreement with the assigned structure, showing a complex multiplet centered at τ 2.58 and a sharp singlet at 7.24 in the area ratio of 2.4:1.0, respectively. The position of the allylic protons compares favorably with the value of τ 7.46 reported for the allylic protons of cyclobutene.[60] The ultraviolet spectrum of 24 shows $\lambda_{max}^{isooctane}$ 227.5 mμ (ε 24,100), 236 sh. (13,500), 297 (18,400), 307 sh. (17,500) and 322 inf. (10,800). Table 3 lists other compounds containing the 1,2-diphenylcyclobutene chromophore which have been reported in the literature. It can be seen that allylic substituents

TABLE 3

ULTRAVIOLET MAXIMA OF COMPOUNDS CONTAINING THE 1,2-DIPHENYLCYCLOBUTENE CHROMOPHORE

	λ_{max} mμ (ε)		Ref.
	227.5 (24,100)	297 (18,400)	
		295	61
	228 (15,800)	292 (12,500)	62
	224 (8,600) 230 (8,000)	293 (17,750)	17a
		303 (19,500)	54,64
	220 (28,900)	294 (17,000)	63
		305 (20,000)	64,65
	238 (26,000)	303 (19,500)	62
		288 (19,500)	66

have only relatively minor effects on the position and intensity of the long-wavelength absorption band. All of the long-wavelength maxima fall in the range 288-305 mμ. The observed maximum at 297 mμ for 1,2-diphenylcyclobutene provides further support for the assigned structure.

Although structurally 1,2-diphenylcyclobutene resembles cis-stilbene the ultraviolet spectra of the two hydrocarbons are considerably different. It can be seen in Figure 1 that the spectrum of 24 more closely resembles the spectrum of trans-stilbene than that of cis-stilbene. This resemblance is most notable in the position of the long-wavelength absorption band and in the vibrational structure of both the 227.5 and 297 mμ bands. The long-wavelength band of trans-stilbene appears at 294 mμ (ε 27,950) in heptane.[67] The spectrum of cis-stilbene (ethanol) shows structureless absorption bands at 224 mμ (ε 24,400) and 280 mμ (ε 10,450).[67] As is the case for cis-stilbene, the short-wavelength band of 24 is more intense than the long-wavelength band. However, the 297 mμ band of 24 is considerably more intense than is the 280 mμ band of cis-stilbene. The above bathochromic and hyperchromic shifts observed in the ultraviolet spectrum of 24 as compared with the spectrum of cis-stilbene, coupled with the similarities in the spectra of 24 and trans-stilbene, are interpreted to mean that the phenyl rings of 24 are nearly coplanar with the

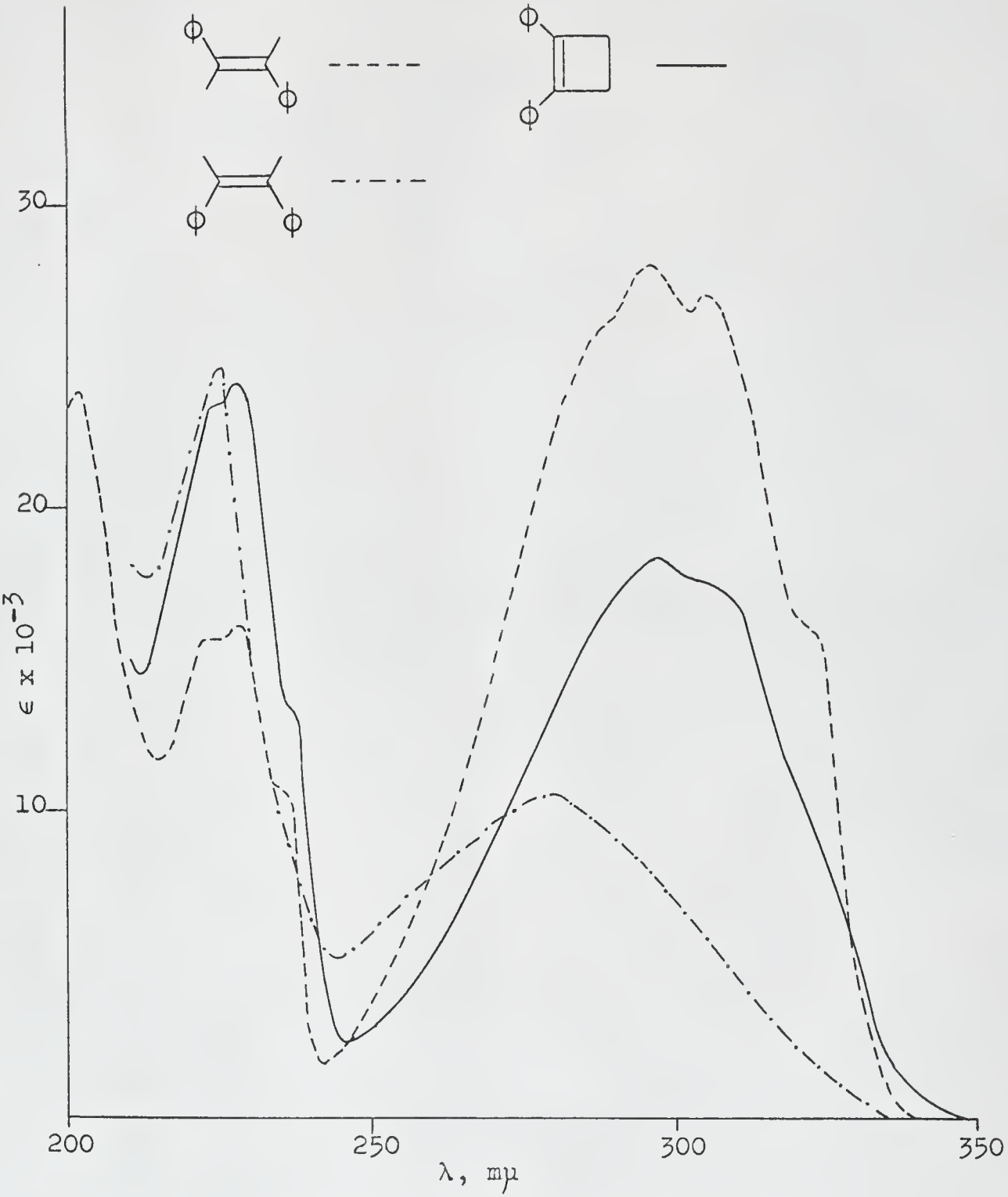


Fig. 1.-The ultraviolet spectra of cis- and trans-stilbene[67,68] and 1,2-diphenylcyclobutene.

cyclobutene ring. It should be noted that the shifts observed in the spectrum of 24 as compared with cis-stilbene may be due in part to electronic effects resulting from the angular strain present in the cyclobutene ring, although these effects should be relatively small.

The above coplanarity of the phenyl rings in 24 is made possible by the angular distortions present in the strained cyclobutene ring. These distortions result in a Ø-C=C bond angle which is larger than the corresponding bond angle in cis-stilbene. In general, the smaller the size of a cycloalkene ring containing three to six carbon atoms the less steric crowding present between vinylic substituents.[69,70]

Further support for the above conclusion concerning the planarity of 1,2-diphenylcyclobutene is provided by the n.m.r. spectrum of 24, in which the aromatic protons appear as a complex multiplet centered at τ 2.58. The aromatic protons of trans-stilbene appear as a complex multiplet centered at τ 2.6 whereas the aromatic protons of cis-stilbene appear as a sharp singlet at 2.82.[71]

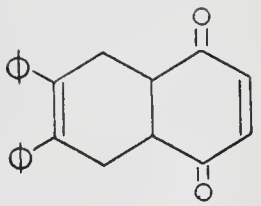
Valence isomerization of 1,2-diphenylcyclobutene. Structure of the product

The product of the thermal isomerization of 1,2-diphenylcyclobutene has been shown by chemical and spectral means to be the expected 2,3-diphenyl-1,3-butadiene (70).

Crystalline 70 could not be isolated from pyrolyses of neat samples of 24 due to extensive polymer formation in reactions run for ca. five half-lives (see Experimental Section). Later work demonstrated that 70 could probably be isolated from pyrolyses conducted in dilute solution under the conditions used for the kinetic study of the isomerization (vide infra). However, in view of the other data obtained, an experiment of this type was not considered necessary.

Chemical proof of the structure of the isomerization product was obtained as shown in Chart VII. Refluxing a xylene solution of 24 for 26 hours (ca. 8.5 half-lives) in the presence of an equivalent of p-benzoquinone afforded a 25 per cent yield of 6,7-diphenyl-4a,5,8,8a-tetrahydro-1,4-naphthoquinone (71), m.p. 161-163° (lit.[72] m.p. 163°). Similarly, refluxing a xylene solution of 24 for 26 hours in the presence of an equivalent of 1,4-naphthoquinone gave a 52 per cent yield of 2,3-diphenyl-1,4,4a,9a-tetrahydro-9,10-anthraquinone (72), m.p. 165-166.5° (lit.[72] m.p. 175-176°). Quinone 72 was further characterized by oxidation to 2,3-diphenyl-9,10-anthraquinone (73), m.p. 211.5-212.5° (lit.[72] m.p. 211-212°). Addition of bromine to a chloroform solution of a sample 24 that had been heated at 190° for seven minutes (ca. three half-lives) afforded 1,4-dibromo-2,3-diphenyl-2-butene (74) in 40 per cent yield, m.p. 148-150.5° (lit.[72] m.p. 145-147°).

Chart VII



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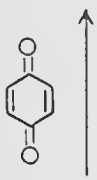
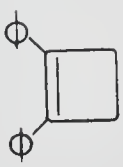
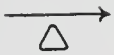
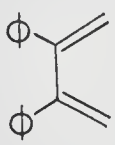




24





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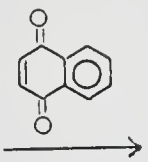

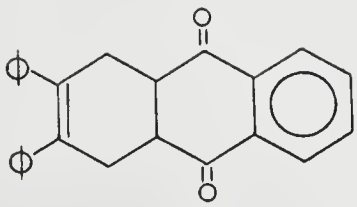

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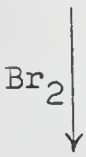

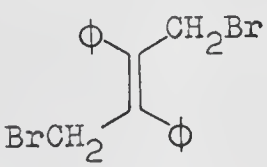

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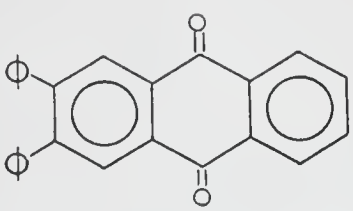


73

Spectral proof of the structure of the isomerization product was obtained by analysis of the ultraviolet and n.m.r. spectra of pyrolysis mixtures. A neat sample of 24 was heated in an open tube at 190° for three minutes (ca. 1.3 half-lives) and the n.m.r. spectrum of the resulting material examined immediately. The appearance of an AB quartet centered at τ 4.67 (J = 1.8 cps) indicated formation of butadiene 70. A comparison of the relative areas of the cyclobutene and butadiene methylene protons indicated that 54 per cent of the cyclobutene had undergone isomerization, a value which is in agreement with the calculated half-life at this temperature. Further spectral evidence for the formation of 70 in pyrolyses of 24 was obtained from the ultraviolet spectra of the infinity points determined in connection with the kinetic studies. The spectra of these infinity points were identical with that reported[73] for 2,3-diphenyl-1,3-butadiene. For example, pyrolysis of a 6×10^{-3} M n-propanol solution of 24 at 140° for 48 hours (15.7 half-lives) afforded a solution which had a single ultraviolet maximum at 242 mμ (ϵ 18,000). Reported[73] for 2,3-diphenyl-1,3-butadiene: $\lambda_{max}^{cyclohexane}$ 243 mμ (ϵ 18,100). The quantitative agreement of the above ultraviolet data indicates that the thermal isomerization of 1,2-diphenylcyclobutene affords 2,3-diphenyl-1,3-butadiene as the sole product.

Valence isomerization of 1,2-diphenylcyclobutene. Kinetics of the reaction

The procedure used for the rate studies and the method of treatment of the data obtained are described in the Experimental Section.

Initial studies of the valence isomerization of 24 in decalin showed that the reaction is first-order and afforded values for the rate constant, k, of 0.548×10^{-4} $sec.^{-1}$ at 138.4 ± 0.2° and 2.79×10^{-4} $sec.^{-1}$ at 155.1 ± 0.2°. It was considered desirable to determine the rate constant and related values to a higher degree of accuracy. The isomerization was thus studied in greater detail using isooctane as the solvent. The decalin previously employed had proved difficult to purify and caused a bathochromic shift of the ultraviolet band of 24 used to follow the isomerization. All values of the reaction parameters reported here have been calculated from the rate constants obtained in isooctane. These values are in good agreement with those previously reported[74] on the basis of the rate constants in decalin.

The rate constants were determined in isooctane from 135-150° in 5° intervals. Points were taken from time = 0 to time = 180 minutes in intervals of 30 minutes. Two separate solutions of approximately equal concentration in 24 were prepared and the rate of isomerization at each of

the four temperatures studied for each solution. The data obtained from a solution 5.91×10^{-3} M in 24 are labeled Run A and the data obtained from a 6.11×10^{-3} M solution are labeled Run B. Figures 2 and 3 show plots of log $(D_\infty - D_o)/(D_\infty - D)$ against time for Runs A and B, respectively. The rate constants obtained from these plots are listed in Table 4. A plot of log k_{ave} against 1/T (Figure 4) yields the value of 33,400 cal./mole for the Arrhenius activation energy, E_a, and the value of log A = 13.46 for the frequency factor, A. The entropy of activation, $\Delta S^{\neq}$, is determined to be +0.3 E.U. at 150°. The rate expression for the thermal isomerization of 1,2-diphenylcyclobutene is then: $k = A \exp(-E_a/RT) = 10^{13.46} \exp(-33{,}400/RT)$ sec.$^{-1}$.

TABLE 4

RATE CONSTANTS FOR THE ISOMERIZATION OF 1,2-DIPHENYLCYCLOBUTENE IN ISOOCTANE

Temperature °C ± 0.1	$k \times 10^4$ (sec.$^{-1}$) Run A	Run B	k_{ave}
135.0	0.368	0.373	0.371
140.0	0.613	0.645	0.629
145.0	0.983	1.005	0.994
150.0	1.60	1.62	1.61

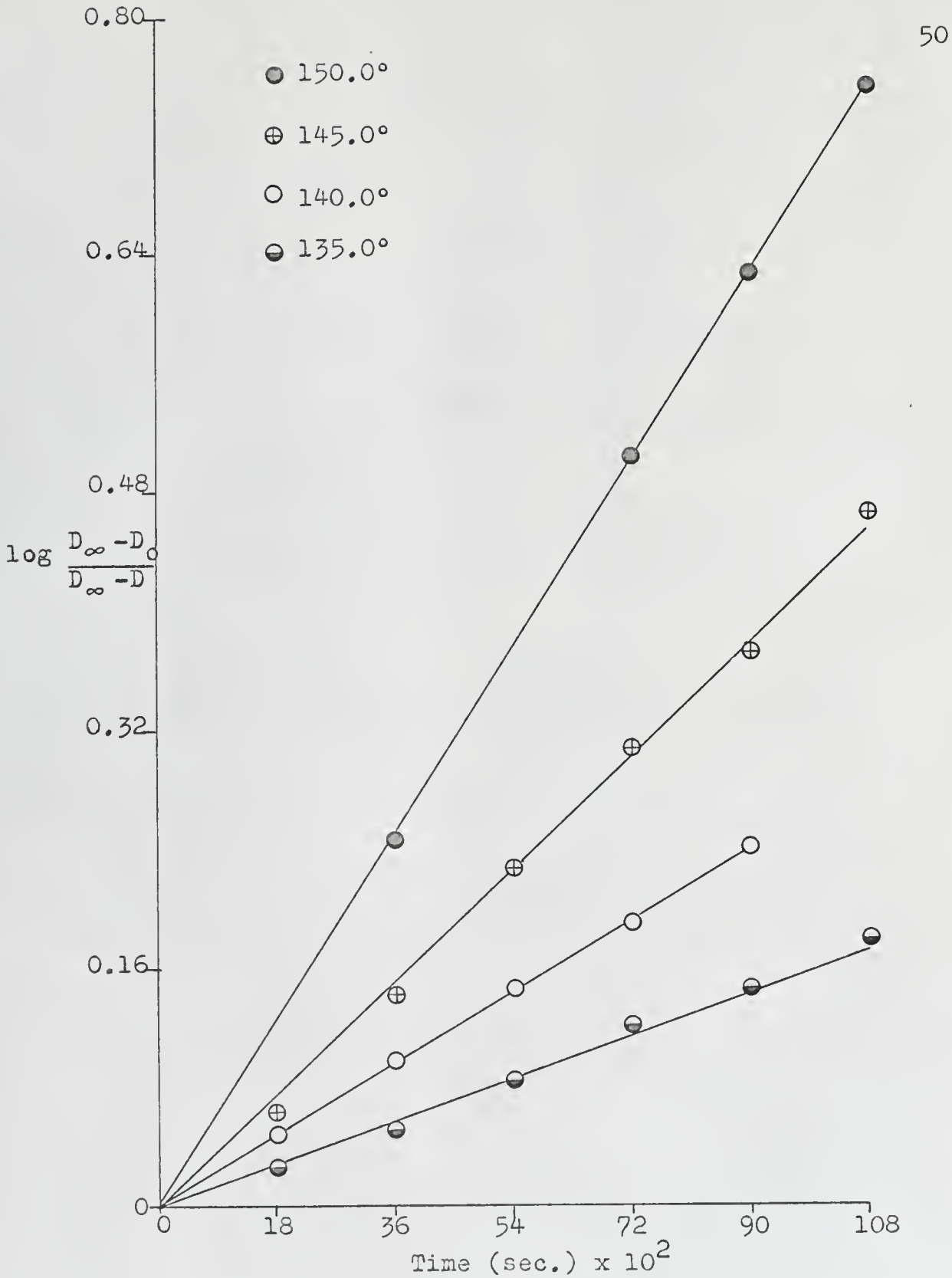


Fig. 2.-First-order kinetic plots for the thermal isomerization of 1,2-diphenylcyclobutene in isooctane (Run A).

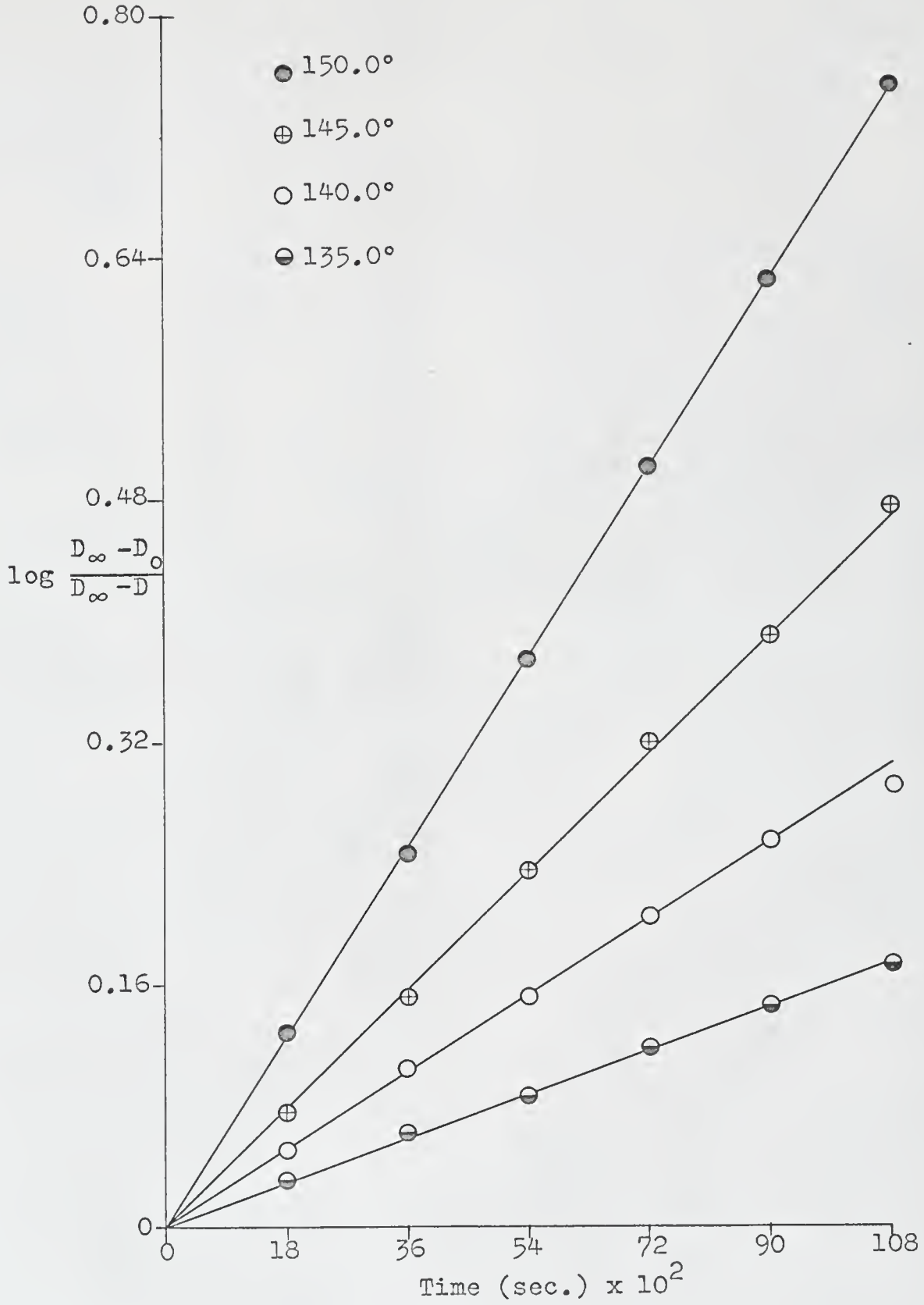


Fig. 3.-First-order kinetic plots for the thermal isomerization of 1,2-diphenylcyclobutene in isooctane (Run B).

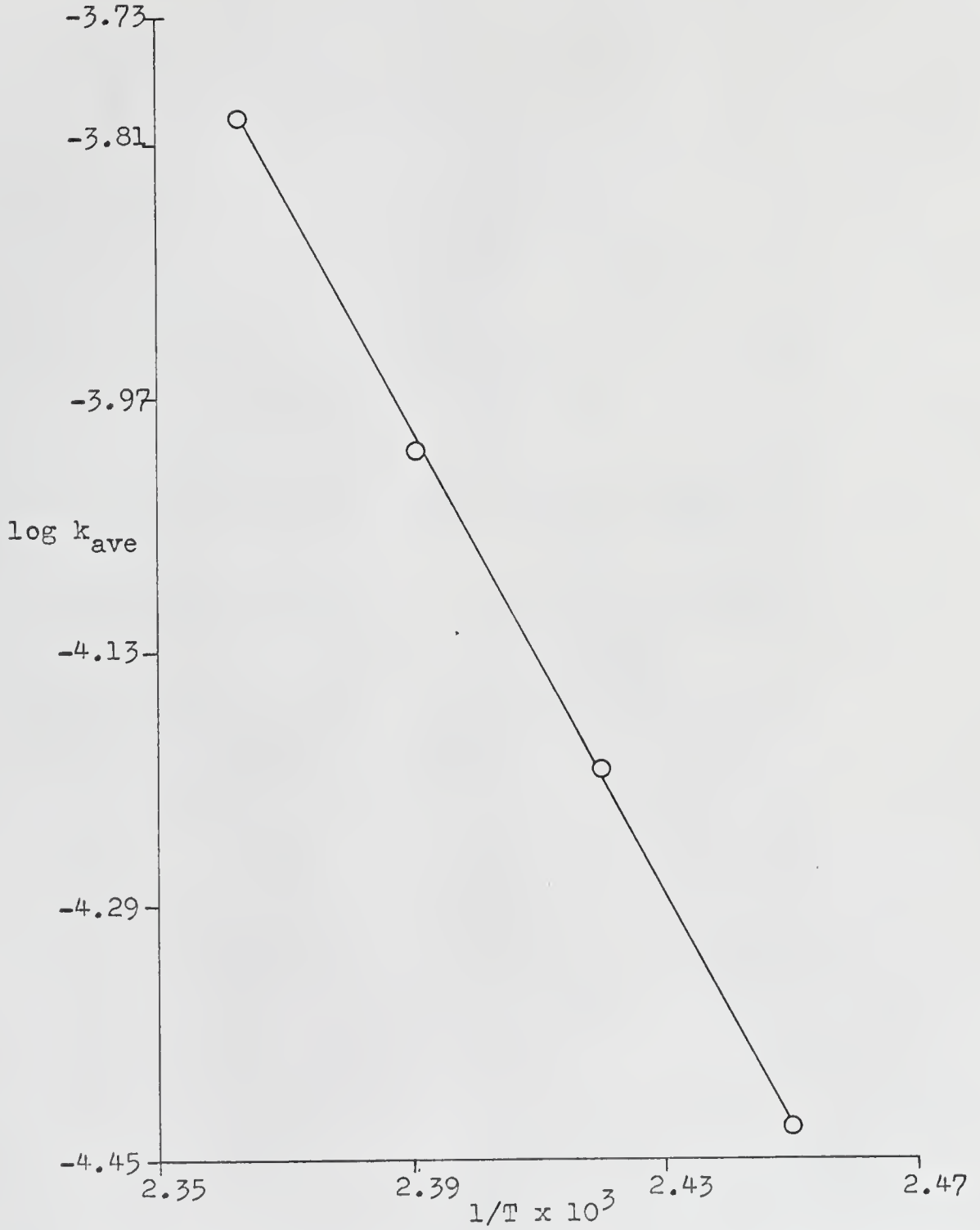


Fig. 4.-Arrhenius plot for the thermal isomerization of 1,2-diphenylcyclobutene in isooctane.

The frequency factor, log A = 13.46, is normal for a unimolecular reaction in which the entropy of activation is approximately zero.[75] The observed entropy of activation, $\Delta S^{\neq}$ = 0.3 E.U., is in agreement with that found for other cyclobutene valence isomerizations. For example, for cyclobutene $\Delta S^{\neq}$ = -1.4 E.U.,[48] for trans-1,2,3,4-tetramethylcyclobutene $\Delta S^{\neq}$ = 0,[46] and for cis-1,2,3,4-tetramethylcyclobutene $\Delta S^{\neq}$ = 0.3 E.U.[46]

The rate constants of unimolecular reactions in which there is no great change in polarity between reactant and product are normally solvent independent.[76,77] A study of the rate of isomerization of 24 in n-propanol and in n-propionitrile afforded the values $k_{140°} = 0.657 \times 10^{-4}$ sec.$^{-1}$ and $k_{140°} = 0.610 \times 10^{-4}$ sec.$^{-1}$, respectively. These values are within experimental error of the rate constants obtained in isooctane (Table 4) and the valence isomerization of 24 is thus solvent independent. The rates of isomerization of cyclobutenes 59,[46] 60,[46] 63,[54] and 64[54] have also been shown to be independent of the solvent used.

Table 5 lists the pertinent kinetic values for 1,2-diphenylcyclobutene and related compounds. Although reaction rates in solution are not strictly comparable to those in the gas phase, unimolecular reactions of the type under consideration here normally give closely agreeing results in the two phases.[76,77]

TABLE 5

SUBSTITUENT EFFECTS OF THE KINETICS OF CYCLOBUTENE VALENCE ISOMERIZATION

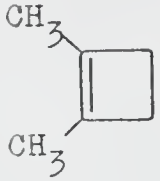
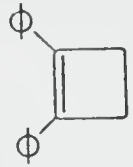
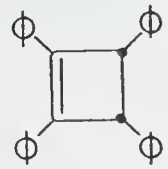
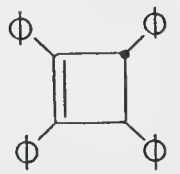
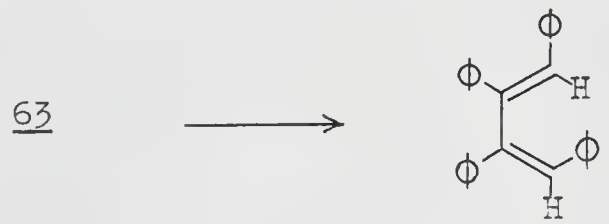
Compound	T(°C)	k x 10^4 ($sec.^{-1}$)	E_a (kcal./mole)	log A	$k_{150°} \times 10^4$ ($sec.^{-1}$)	Rel. k 150°	Ref.
 a 53	150	1.9-2.0	32.5	13.1	1.9-2.0	1	48
 a 56	149.7	0.162	36.0	13.8	0.17	0.09	51
 b 24	150	1.61	33.4	13.5	1.61	0.8	

Table 5 (cont'd)

Compound	T(°C)	k x 10^4 ($sec.^{-1}$)	E_a (kcal./mole)	log A	$k_{150°} \times 10^4$[e] ($sec.^{-1}$)	Rel. k 150°	Ref.
 63 [c]	50	0.8	25	12.8[f]	7,000	3,500	54
 64 [d]	24	0.5	21	11.1[f]	20,000	10,000	54

[a]Kinetic data obtained in the vapor phase.
[b]Solvent isooctane.
[c]Solvent unspecified.
[d]Solvent THF.
[e]Calculated from data at other temperatures where necessary.
[f]Calculated from data in Ref. 54.

It is obvious from the data in Table 5 that the rate of isomerization of 1,2-diphenylcyclobutene is essentially the same as that of cyclobutene. As a consequence, the greatly enhanced rates of isomerization of 63 and 64 as compared to cyclobutene are due entirely to the presence of allylic phenyl substituents. Even in the case of cis-1,2,3,4-tetraphenylcyclobutene (63), where conrotatory ring opening must result in the sterically hindered cis,trans-1,2,3,4-tetraphenylbutadiene (75), the rate of isomerization at 150° is 3.5×10^3 greater than for cyclobutene.



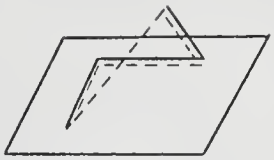
63 ⟶ 75

The finding that 1,2-dimethylcyclobutene (56) isomerizes at one-tenth the rate of cyclobutene has been attributed to a lengthening of the ring double bond by stabilizing methyl substituents, resulting in a decrease in ring strain and thus a decrease in the rate of ring opening.[51] However, as mentioned previously, steric factors will also be important here as the transition state for ring opening will involve increased methyl-methyl and methyl-hydrogen interactions. If steric repulsions in the transition state and lengthening of the ring double bond by stabilizing substituents are the only factors operating one

would predict that 1,2-diphenylcyclobutene would isomerize at a rate even slower than that of 56. It thus appears that there must be an additional effect operative in the isomerization of 24. At the present it seems most likely that the vinylic phenyl substituents of 1,2-diphenylcyclobutene serve to stabilize the transition state for ring opening by overlap with the developing double bonds. This stabilization, although minor relative to the effects of allylic phenyl substituents, is sufficiently large to counterbalance both steric interactions in the transition state and electronic stabilization of the ground state.

The normal A factors and relatively low activation energies which are characteristic of the valence isomerizations of cyclobutene derivatives tend to rule out a transition state resembling a biradical.[78] The simplest representation of the transition state for ring opening involves a planar arrangement of the four carbon atoms of the ring with stabilization of the developing π-centers by the ring double bond (76). It has been pointed out[52,78] that a skew arrangement (77) of the four ring carbon atoms is more favorable since it allows a greater degree of overlap between the ring double bond and the incipient π-centers. In addition, the skew arrangement allows the greatest amount of overlap between the orbitals being formed by rupture of the σ-bond,[65,79]

76

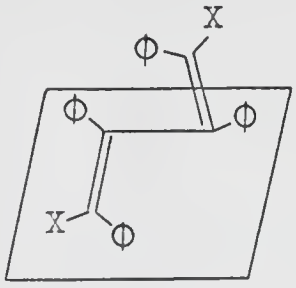


77

and is also the most favorable array for minimization of steric repulsions. Recent work has provided experimental support for the skew transition state. Freedman[65,79] has shown that room temperature solutions of butadienes 78 and 79, which exist in a cisoid-skew conformation (82) for steric reasons,[80] consist of an equilibrium mixture of the butadienes and the corresponding cyclobutenes (80 and 81).

78, X=Br
79, X=Cl

80, X=Br
81, X=Cl



82

The facile thermal conversion of butadienes to cyclobutenes is normally observed only for fluorine-containing derivatives.[27] The ease with which butadienes 78 and 79 are converted to the corresponding cyclobutenes is due to the fact that the ground state conformation of the dienes (82) is very similar to that proposed for the transition state (77) for ring opening and ring closure.

The observed rate of isomerization of 1,2-diphenylcyclobutene is also compatible with a skew transition state. In a planar transition state (76) phenyl-phenyl and phenyl-hydrogen interactions increase significantly as the 3,4-bond of the ring ruptures and overlap between the phenyl rings and the developing double bonds is hindered. However, in a skew transition state (77) the phenyl rings are twisted out of plane with one another and can thus effectively stabilize the incipient double bonds.

The small pre-exponential factor found for the isomerization of trans-1,2,3,4-tetraphenylcyclobutene indicates a negative entropy of activation which is consistent with extensive phenyl stabilization of developing π-centers in the transition state.[81]

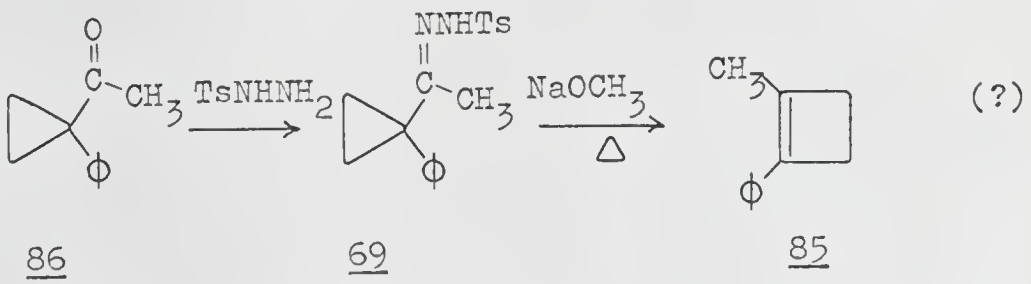
1-Phenylcyclobutene (83)

Attempts to study the rate of valence isomerization of 1-phenylcyclobutene (83) have thus far been unsuccessful due to the high tendency of this compound to polymerize.

The thermal isomerization of 83 was observed in the heated injector chamber of a gas chromatograph. The product of the isomerization was identified as the expected 2-phenyl-1,3-butadiene (84) by a comparison of its retention time with that of a known sample. The extent of valence isomerization at various injector port temperatures is described in the Experimental Section.

1-Methyl-2-phenylcyclobutene (85)

An attempt was made to prepare the unknown 1-methyl-2-phenylcyclobutene (85) by using a reaction scheme analogous to that employed for 1,2-diphenylcyclobutene. Treatment of 1-phenylcyclopropyl methyl ketone (86)[57a] with tosylhydrazine in glacial acetic acid at room temperature afforded tosylhydrazone 69 in 77 per cent yield. The thermal decomposition of the sodium salt of 69 appeared to proceed at a much slower rate than did the decomposition of the corresponding



86 69 85

salt of 68. V.p.c. analysis of the product of this reaction showed five major components and at least seven minor components (see Experimental Section). Spectral data indicated that 85 was very likely present in the reaction product but isolation of this material was not achieved.

CHAPTER IV

EXPERIMENTAL

General.-Melting points were determined on a Thomas-Hoover capillary melting point apparatus. All melting and boiling points are uncorrected. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tennessee. Analytical vapor phase chromatography was performed using helium as the carrier gas with an Aerograph Model 600-D Hy-Fi instrument (Wilkens) equipped with a hydrogen flame ionization detector. All v.p.c. analyses were performed on ether solutions and retention times are reported relative to the ether peak.

Spectra.-Infrared spectra were recorded on either a Perkin-Elmer Infracord spectrophotometer or with a Beckman IR10 instrument. Ultraviolet and visible spectra were determined on a Cary 14 recording spectrophotometer. Nuclear magnetic resonance spectra were obtained with Varian 4300-2 and A-60A instruments. Tetramethylsilane was used as an internal reference and chemical shifts are reported in tau values.

1,2-Diphenyltetrafluorocyclobutene (21).[17a,30,82] A solution of phenylmagnesium bromide was prepared under an

argon atmosphere from 13.4 g. (0.552 g.-atom) of magnesium and 91.0 g. (0.580 mole) of bromobenzene in 250 ml. of absolute ether. The water-cooled condenser used in the preparation of the Grignard reagent was exchanged for a dry-ice condenser and the ether solution cooled to 0°. Perfluorocyclobutene (31) (Peninsular ChemResearch, Inc.) (35.8 g.; 0.221 mole) was bubbled into the ether solution over a period of two hours. The reaction mixture was then maintained at 0° for 2 hours, at room temperature for 3 hours, and at reflux for 30 minutes. The mixture was cooled to 0° and 100 ml. of 10 per cent hydrochloric acid added with care. The ether layer was separated and the aqueous layer extracted with ether. The combined ether solutions were washed with 5 per cent sodium bicarbonate solution and saturated saline solution. After drying over sodium sulfate the ether was removed on a rotary evaporator yielding a red oil. 1-Phenylpentafluorocyclobutene was removed by distillation [b.p. 66° (15 mm.), n_D^{21} 1.4639 (lit.[30] b.p. 67-68°/15 mm., n_D^{25} 1.4606)]; the infrared spectrum (neat) showed a strong absorption for the fluorine-substituted double bond at 5.85 microns. The residue from the distillation was filtered through 400 g. of alumina (Merck 71707) using hexane as the eluant. Removal of the solvent from the eluate (600 ml.) afforded a colorless oil. Crystallization from hexane

gave 16.34 g.(27%) of 1,2-diphenyltetrafluorocyclobutene as colorless crystals, m.p. 56.5-58° (lit.[17a,30,82] m.p. 58°).

Attempted reaction of 1,2-diphenyltetrafluorocyclobutene (21) with tetraphenylcyclopentadienone (25).-The reaction of 21 with cyclopentadienone 25 under a variety of experimental conditions failed to yield any detectable Diels-Alder product. These reactions are briefly summarized below.

A. Refluxing 25 with a 1.20 mole excess of cyclobutene 21 in xylene for 20 days failed to discharge the characteristic violet color of 25. The only isolable materials were unchanged 21 and 25.

B. A mixture of 25 and a 1.20 mole excess of 21 was heated in a Wood's metal bath. The temperature of the bath was raised from room temperature to 225° over a two hour period, maintained at 225° for 3 hours, and then heated to and maintained at 295° over a period of 3 hours. Gas evolution was not observed and the violet color of the tetracyclone was still present when the reaction was discontinued.

C. Refluxing 25 with a 4.0 mole excess of 21 in 1,2,4-trimethylbenzene for 12 days resulted only in the decomposition of the tetracyclone. The only material isolated was unchanged 21.

Attempted reaction of 1,2-diphenyltetrafluorocyclobutene (21) with 1,3-diphenylisobenzofuran (26).

A. Refluxing 26 with a 1.04 mole excess of 21 in toluene for 3 days failed to discharge the fluorescent-

yellow color of the furan and resulted in no detectable adduct formation.

B. Refluxing 26 with a 1.03 mole excess of 21 in xylene for 29 days yielded no evidence for formation of a Diels-Alder adduct. In addition to starting materials, o-dibenzoylbenzene, the product of air oxidation of 26, was isolated in 20 per cent yield (based on furan 26), m.p. 145-147° (lit.[83] m.p. 146-147°). The infrared spectrum (KBr) of this material showed strong carbonyl stretching absorption at 6.03 μ (lit.[84] carbonyl absorption at 6.05 μ).

Attempted reaction of 1,2-diphenyltetrafluorocyclobutene (21) with phencyclone (27).-A mixture of 21 (0.222 g.; 0.798 mmole) and phencyclone (0.264 g.; 0.691 mmole) in 12 ml. of xylene was refluxed for 6.5 days. Over this period of time the dark-green color of the phencyclone gradually faded until the color of the xylene solution was yellow. Chromatography on alumina (Merck 71707) using hexane as the eluant resulted in the recovery of 0.199 g. (90%) of unchanged 21. The nature of the product(s) formed by decomposition of the phencyclone was not investigated.

Attempted reaction of 1,2-diphenyltetrafluorocyclobutene (21) with 1,4-diphenyl-1,3-butadiene (28).-A mixture of 21 (0.167 g.; 0.601 mmole) and 1,4-diphenyl-1,3-butadiene (0.124 g.; 0.602 mmole) in 10 ml. of xylene was refluxed for 20 days. The xylene solution was concentrated to a volume

of 3 ml. and ether added. Cooling afforded 0.064 g. (52% recovery) of unchanged 28 which was identified by a comparison of melting point and infrared spectrum with that of a known sample.

1,2-Dimethyltetrafluorocyclobutene (22).[17b] A solution of methyllithium was prepared under an argon atmosphere from 10.6 g. (1.53 g.-atoms) of lithium wire and 116 g. (0.817 mole) of methyl iodide in 325 ml. of dry ether. The water-cooled condenser used during the preparation of the lithium reagent was exchanged for a dry-ice condenser and the ether solution cooled to -36° in a dry ice-ethylene dichloride bath. Perfluorocyclobutene (31) (40 g.; 0.25 mole) was bubbled into the ether solution over a period of 30 minutes. The reaction mixture turned grey and finally dark green by the time the addition was complete. The solution was stirred at -36° for 4 hours, at 0° for 2 hours, and at room temperature for 17 hours. The mixture was cooled to 0° and carefully decomposed by addition of 150 ml. of 10 per cent hydrochloric acid. The ether layer was separated and the aqueous layer extracted with ether. The combined ether solutions were washed with 5 per cent sodium bicarbonate solution and saturated saline solution. After drying over sodium sulfate the ether was removed by slow distillation. Distillation of the black residue under argon at atmospheric pressure gave 16.5 g. (43%) of 1,2-dimethyltetrafluorocyclobutene, b.p. 97-98°, n_D^{22} 1.3493 (lit.[17b] b.p. 100-104°, $n_D^{27.5}$ 1.3478).

The infrared spectrum (neat) showed absorption bands at 6.95 (m), 7.17 (m), 7.24 (m), 7.48 (s), 8.25 (s), 9.12 (s), 9.72 (s), 10.86 (s), and 11.57 (m) μ.

The material prepared above was obtained as a pink liquid. This color was changed to brown by exposure to air or by addition of acetone, but did not change when the product was stored in a stoppered flask. In an attempt to remove this pink color the material was filtered through a column of alumina (Merck 71707) using petroleum ether (b.p. 20-40°) as the eluant. The pink color was removed leaving a black band at the top of the alumina column. The eluate was initially colorless but turned pink upon standing for three hours. Removal of the petroleum ether and distillation of the residue under argon at atmospheric pressure gave 22 as a pale-pink liquid. The pink color of this material was not nearly as intense as was the color of the initial product. It appears that the pink color is due to the decomposition of a trace impurity.

Attempted reaction of 1,2-dimethyltetrafluorocyclobutene (22) with 5,5-dimethoxytetrachlorocyclopentadiene (30).-A mixture of 2.844 g. (18.5 mmoles) of 22 and 1.033 g. (3.91 mmoles) of freshly distilled (b.p. 93°/2.5 mm.) 5,5-dimethoxytetrachlorocyclopentadiene[85] was heated at the reflux temperature of the cyclobutene (bath temperature

125°) for 9.5 days. The infrared spectrum (neat) of the resulting amber oil showed only those absorption bands which are contained in the spectra of the starting materials. The cyclobutene was removed by warming under a stream of argon. The infrared spectrum of the resulting oil was identical with that of an authentic sample of 30.

Attempted reaction of 1,2-dimethyltetrafluorocyclobutene (22) with tetraphenylcyclopentadienone (25).-A suspension of 0.315 g. (0.842 mmole) of tetracyclone in 3.264 g. (21.2 mmoles) of 22 was heated under an argon atmosphere at the reflux temperature of the cyclobutene (bath temperature 125°) for 15 hours. At the end of this time the tetracyclone had crystallized on the sides of the reaction flask and the cyclobutene remained as a clear, colorless liquid. Toluene (4 ml.) was added and the resulting solution refluxed an additional 205 hours (total reaction time 220 hours). The resulting solution still retained the dark violet color of the tetracyclone. Alumina chromatography gave only unchanged 25.

Attempted reaction of 3,3,4,4-tetrafluorocyclobutene (19)[31] with α-pyrone (29).-A mixture of 19 (2.000 g.; 15.9 mmoles) and α-pyrone (1.430 g.; 14.9 mmoles) was heated in a sealed tube for 18 days at 60° and for an additional 12 days at 75°. Alumina chromatography of the reaction mixture afforded unchanged α-pyrone as the only isolable material (no attempt was made to recover the low boiling cyclobutene).

Reaction of 3,3,4,4-tetrafluorocyclobutene (19) with tetraphenylcyclopentadienone (25).-A mixture of 19 (1.00 g.; 7.93 mmoles) and tetracyclone (0.703 g.; 1.83 mmoles) dissolved in 5 ml. benzene was heated in a sealed tube at 100°. The hot benzene solution contained a considerable amount of undissolved tetracyclone. After 23 days at 100° the appearance of the mixture had not changed and the reaction was discontinued. The reaction mixture was chromatographed on a column of alumina (Merck 71707) packed in hexane. Elution with mixtures of benzene-hexane gave a trace of white solid (contaminated with tetracyclone) which eluted prior to the tetracyclone. This material had m.p. 152-210° (melt violet) but was obtained in insufficient quantity for characterization. The only other material isolated was unchanged 25.

Reaction of 3,3,4,4-tetrafluorocyclobutene (19) with 1,3-diphenylisobenzofuran (26).-A mixture of (19) (1.00 g.; 7.93 mmoles) and 1,3-diphenylisobenzofuran (0.631 g.; 2.34 mmoles) dissolved in 5 ml. of benzene was heated in a sealed tube at 100° for 15 days. Addition of ether to the resulting benzene solution gave 0.595 g. (64%) of the Diels-Alder adduct 35, m.p. 175-198° (melt bright yellow). Two recrystallizations from benzene-hexane gave the analytical sample, m.p. 197-199°.

Anal. Calcd. for $C_{24}H_{16}F_4O$: C, 72.72; H, 4.07. Found: C, 72.96; H, 4.24.

The infrared spectrum (KBr) showed absorption bands at 3.25 (m), 6.26 (m), 6.68 (m), 6.85 (s), 7.40 (s), 7.65 (s), 7.88 (m), 8.04 (s), 8.40 (s), 8.63 (m), 8.95 (s), 9.03 (s), 9.13 (s), 9.48 (m), 10.00 (s), 10.40 (m), 10.62 (m), 10.77 (m), 11.02 (w), 11.16 (m), 11.44 (m), 11.86 (m), 12.52 (s), 12.88 (s), 13.27 (s), 13.44 (s), 14.30 sh. (s), 14.40 (s), and 14.78 (s) μ.

The n.m.r. spectrum ($CDCl_3$) showed a complex multiplet at τ 2.18-3.23 (aromatic protons) and a broad multiplet at 6.17-6.70 (methine protons), with an area ratio of 14.0:2.18, respectively.

The product with m.p. 175-198° obtained above is possibly a mixture of the exo and endo isomers. A small amount of material with m.p. 155-159° (melt bright yellow) was isolated from this product as white needles. The predominant product (m.p. 197-199°) formed hard white crystals. The Diels-Alder reaction of 19 with cyclopentadiene affords a 1:1 mixture of the exo and endo isomers.[21] The reaction of 19 with furan affords only a single isomer.[21] The problem of stereochemistry in the present system was not further investigated.

Attempted deoxygenation of 35 with trimethyl phosphite.-A mixture of 96 mg. (0.242 mmole) of adduct 35 and 188 mg. (1.52 mmoles) of trimethyl phosphite dissolved in 2 ml. of benzene was refluxed for 24 hours. Addition of

petroleum ether (b.p. 30-60°) to the cooled benzene solution gave 80 mg. (83% recovery) of unchanged 35.

Attempted sulfuric acid hydrolysis of 35.-To 3 ml. of hot (100°) concentrated sulfuric acid was added 97 mg. (0.245 mmole) of 35. The resulting suspension was stirred at 100° for 1.5 hours. The mixture was poured onto ice and the organic materials extracted into chloroform. The chloroform solution was dried over sodium sulfate and concentrated on a rotary evaporator. Addition of hexane gave 65 mg. (67% recovery) of unchanged 35.

Attempted reaction of 1,2-diphenylcyclobutene (24) with tetraphenylcyclopentadienone (25).-A benzene solution of 1,2-diphenylcyclobutene (0.018 g.; 0.0875 mmole) and tetraphenylcyclopentadienone (0.027 g.; 0.0702 mmole) was heated at reflux for 5 days. At the end of this period the characteristic dark-violet color of the tetracyclone had not decreased in intensity. No attempt was made to recover starting materials.

Attempted diimide reduction of 1,2-diphenylcyclobutene (24).[86] To a stirred solution of 1,2-diphenylcyclobutene (0.250 g.; 1.21 mmoles) in 25 ml. of 1:1 dimethoxyethane (freshly distilled)-methanol was added 0.469 g. (2.42 mmoles) of freshly prepared potassium azodicarboxylate.[87] The reaction was carried out under an argon atmosphere. To this stirred suspension was added 0.5 ml. of glacial acetic

acid over a period of 10 minutes. Stirring at room temperature for 4.5 hours resulted in a clear colorless solution. This solution was poured into 40 ml. of water and the resulting oil extracted into 75 ml. of hexane. The hexane solution was washed with three 25 ml. portions of water, separated, and dried over sodium sulfate. Removal of the solvent on a rotary evaporator yielded a colorless oil which crystallized from methanol at -78° to give 0.226 g. (90% recovery) of unchanged 24 which was identified by its melting point, mixed melting point with an authentic sample, and qualitative ultraviolet spectrum.

Diphenylcyclobutadienoquinone (23).-The procedure followed was that described by Blomquist and LaLancette.[17a] In a typical preparation, an etched flask was heated to 100° and then charged with 20 ml. of 96 per cent sulfuric acid. 1,2-Diphenyltetrafluorocyclobutene (21) (4.66 g.; 16.8 mmoles) was added in one portion. Copious evolution of hydrogen fluoride began immediately. After stirring at 100° for 30 minutes the mixture was poured onto ice and the organic materials extracted into chloroform. The chloroform solution was washed with water and dried over magnesium sulfate. Removal of the solvent on a rotary evaporator gave a yellow oil which crystallized from chloroform-hexane to give 2.61 g. (67%) of quinone 23 as bright-yellow plates or needles, m.p. 95-98.5°. Recrystallization from chloroform-

hexane raises the melting point to 97-98.5° (lit.[17a] m.p. 97-97.2°).

The infrared (KBr) and ultraviolet (acetonitrile) spectra of this material were identical with those reported in reference 17a. The n.m.r. spectrum ($CDCl_3$) showed only aromatic protons as two multiplets centered at τ 1.91 and 2.41.

Attempted reaction of diphenylcyclobutadienoquinone (23) with 1,3-diphenylisobenzofuran (26).-An equimolar mixture of 23 and furan 26 dissolved in benzene was refluxed for 52 hours. Addition of ether to the cooled benzene solution resulted only in the isolation of unchanged starting materials.

Attempted reaction of diphenylcyclobutadienoquinone (23) with tetraphenylcyclopentadienone (25).-Attempts to obtain a Diels-Alder adduct by reaction of quinone 23 with tetracyclone were unsuccessful. The various experiments performed are summarized briefly below.

A. Refluxing 25 with a 1.4 mole excess of quinone 23 in xylene for 5 days resulted in no adduct formation. Concentrating and cooling the xylene solution caused the precipitation of unchanged tetracyclone. Trituration of this material with chloroform gave trace amounts of a very insoluble yellow solid with m.p. > 300°. Elemental analysis of this yellow solid gave: C, 79.85; H, 4.61. The

possibility that this compound is the photodimer mentioned by Blomquist and LaLancette[37] was not investigated.

B. Refluxing 25 with a 1.4 mole excess of quinone 23 in toluene for 19 days failed to yield any detectable Diels-Alder adduct. In addition to starting materials, very small amounts of the yellow solid described in A were isolated.

C. A solid mixture of 25 and a 2.0 mole excess of quinone 23 was fused at 210° for 5 minutes. The molten mixture evolved a very small amount of gas but evolution ceased within 5 minutes and the tetracyclone color was not discharged. Workup gave only unchanged starting materials.

D. A Pyrex test tube containing a solid mixture of tetracyclone and a 1.3 mole excess of quinone 23 was immersed in a Wood's metal bath. The bath temperature was initially 75° and was raised slowly over a period of 3 hours to 225°. At 200-205° evolution of small amounts of gas was observed. The temperature was maintained at 225° for an additional 1.5 hours. At the end of this time the violet color of the tetracyclone had not been discharged. Examination of the mixture resulted only in the recovery of unchanged starting materials.

1-Diethylamino-1,3-butadiene (38).-The procedure followed was as described by Hünig and Kahanek.[88] Distillation of the crude reaction mixture on a spinning-band

column gave enamine 38 as a light-yellow oil in 42 per cent yield, b.p. 55-62° (12 mm.), n_D^{21} 1.5258 (lit.[88] b.p. 64-66°/ 10 mm., lit.[89] n_D^{21} 1.5239). The infrared spectrum (neat) showed strong absorption bands at 6.15, 10.08 and 18.84 μ (lit.[89] strong absorption bands at 6.10, 10.14 and 10.93 μ).

The identity of the product obtained above was further demonstrated by its condensation with diphenylcyclopropenone (37a) in refluxing benzene to afford 2,7-diphenyltropone (39)[36] in yields of 29-44 per cent. Tropone 39 crystallized from absolute ethanol as pale-yellow plates, m.p. 131-132.5° (lit.[90] m.p. 133°). The infrared spectrum (KBr) was identical with that reported by Mukai.[90]

Reaction of 1-diethylamino-1,3-butadiene (38) with diphenylcyclobutadienoquinone (23).-A solution of 0.125 g. (1.00 mmole) of freshly distilled 38 in 2 ml. benzene was added in one portion to a solution of 0.200 g. (0.855 mmole) of quinone 23 in one ml. of benzene. The mixture turned very dark immediately. The benzene solution was refluxed under argon for 12 hours. Work-up of the reaction mixture as described in reference 36 resulted only in the isolation of dark-red intractable tars.

Repetition of the above experiment by slowly adding a solution of enamine 38 to a stirred solution of quinone 23 at -78°, stirring for 3 hours, and then allowing the mixture to warm to room temperature gave the same result as found above.

Attempted reaction of 1-diethylamino-1,3-butadiene (38) with 1,2-diphenyltetrafluorocyclobutene (21).-A solution of 0.125 g. (1.00 mmole) of freshly distilled 38 in 3 ml. of benzene was added in one portion to a solution of 0.250 g. (0.900 mmole) of cyclobutene 21 in 2 ml. of benzene. The mixture was refluxed under argon for 64 hours. The benzene solution was diluted with 30 ml. of ether and then washed with two 10 ml. portions of 5 per cent hydrochloric acid and one 10 ml. portion of saturated saline solution. After drying over sodium sulfate the solvent was removed on a rotatory evaporator to yield a yellow oil. Crystallization from hexane gave 0.159 g. (two crops) of unchanged 21 (64% recovery). The melting point and infrared spectrum of this material were identical with those of a known sample.

1-Acetoxy-1,3-butadiene (40).-1-Acetoxy-1,3-butadiene was prepared as described in the literature.[91] The product was a colorless liquid, b.p. 36-38° (12.5 mm.), n_D^{20} 1.4688 (lit.[91] b.p. 42-43°/16 mm., n_D^{20} 1.46870). The diene was stored under argon in the dark at 0° with a trace of phenanthrenequinone added.

Attempted reaction of 1-acetoxy-1,3-butadiene (40) with diphenylcyclobutadienoquinone (23).-To a solution of 0.132 g. (0.564 mmole) of quinone 23 in 3 ml. of benzene was added in one portion a solution of 0.122 g. (1.09 mmoles) of 1-acetoxy-1,3-butadiene (40) in 2 ml. of benzene. The

resulting solution was refluxed under argon for 12 hours. Removal of the solvent under a stream of argon gave a yellow oil which crystallized upon addition of petroleum ether (b.p. 30-80°). The yellow solid thus obtained was identified as unchanged 23 by its melting point and infrared spectrum. The recovery was 0.123 g. (93%).

Diphenylcyclobutadienoquinone monotosylhydrazone (47).-The procedure of Blomquist and LaLancette[17a] was used with minor modifications. A mixture of diphenylcyclobutadienoquinone (23) (0.500 g.; 2.14 mmoles) and tosylhydrazine (0.420 g.; 2.26 mmoles) was dissolved in 15 ml. of absolute ethanol containing 1 per cent by weight hydrogen chloride. After stirring at room temperature for 18.5 hours the precipitated yellow solid was collected by filtration and washed with absolute ethanol and hexane. The yield of 47 was 0.712 g. (83%), m.p. 184-187° (dec.) (lit.[17a] m.p. 188-189°).

Elemental analysis of the monotosylhydrazone as obtained above gave consistently low values for the carbon content. In addition, a single analysis for nitrogen and sulfur also gave values which were less than theoretical. Shown below is the analytical data for a sample of 47 prepared by recrystallization from chloroform-hexane, m.p. 185.5-187° (dec.).

Anal. Calcd. for $C_{23}H_{18}N_2O_3S$: C, 68.65; H, 4.51; N, 6.96; S, 7.97. Found: C, 66.95; H, 4.31; N, 6.32; S, 7.66.

The infrared spectrum (KBr) showed absorption bands at 3.15 (s), 3.29 (m), 5.67 (s), 5.99 (w), 6.26 (s), 6.35 (m), 6.46 (m), 6.69 (w), 6.77 (m), 6.95 (m), 7.13 (s), 7.38 (s), 7.47 (s), 7.73 (m), 8.22 (w), 8.39 (m), 8.59 (s), 9.17 (s), 9.34 (m), 9.57 (s), 9.75 (s), 10.01 (m), 10.16 (w), 10.70 (m), 10.87 (w), 11.56 (s), 12.18 (s), 12.35 (s), 12.75 (s), 13.08 (s), 13.45 (s), 14.15 (s), and 14.55 (s) μ.

The ultraviolet spectrum (acetonitrile) showed λ_{max} at 225 mμ (ε 23,600), 285 (26,900), 297 sh. (26,100), and 335 sh. (12,600). The spectrum showed no maxima in the visible region. The yellow color of the compound can be accounted for by the fact that the maximum at 285 mμ trails to 440 mμ.

The n.m.r. spectrum ($CDCl_3$) showed resonance signals at τ 1.15 (broad singlet, N-H), 1.78-2.80 (complex multiplet, aromatic protons), and 7.58 (sharp singlet, CH_3), with area ratios of 0.91:14:2.90, respectively.

Monotosylhydrazone 47 can also be prepared in acetic acid at room temperature. However, the yield, purity, and crystalline form of the product are superior when ethanol is used as the solvent. Diethyl α,α'-diphenylsuccinate, the product of the reaction between ethanol and the bisketene

form of quinone 23,[17a] was not formed in any detectable amount during the preparation of tosylhydrazone 47 in ethanol. Methanol also appears to be a suitable solvent for the preparation of 47.[17a]

Sulfuric acid hydrolysis of diphenylcyclobutadienoquinone monotosylhydrazone (47).-Tosylhydrazone 47 (200 mg.; 0.497 mmole) was dissolved in 96 per cent sulfuric acid (5 ml.) and the resulting dark-brown solution stirred at room temperature for one hour. The solution was poured onto ice and the aqueous mixture extracted with chloroform. The chloroform layer was washed with 5 per cent sodium bicarbonate solution and dried over sodium sulfate. Removal of the solvent on a rotary evaporator yielded an orange oil which crystallized from chloroform-hexane to give 69 mg. of a yellow solid, m.p. 88-91°. This material was triturated with boiling hexane containing a small amount of chloroform and filtered while hot to remove a trace amount of insoluble orange solid. The filtrate was evaporated to dryness and the above procedure repeated. Removal of the solvent gave a yellow oil which crystallized from chloroform-hexane to give 34 mg. of a yellow solid, m.p. 93-96.5°. The infrared spectrum of this material was identical with that of a known sample of diphenylcyclobutadienoquinone (23). The qualitative ultraviolet spectrum exhibited maxima and relative peak intensities which were identical with those of

a known sample of the quinone. The yield of crude 23 was 59 per cent; the yield of purified 23 was 29 per cent.

Attempted preparation of the bistosylhydrazone derivative of diphenylcyclobutadienoquinone (23).

A. A mixture of 0.100 g. (0.248 mmole) of tosylhydrazone 47 and 0.050 g. (0.269 mmole) of tosylhydrazine was dissolved in 5 ml. of chloroform. Five ml. of absolute ethanol containing 1 per cent by weight hydrogen chloride was added and the resulting solution stirred at room temperature for 13 hours. The solution was concentrated and cooled to give 0.066 g. (66% recovery) of unchanged 47, which was identified by its melting point and infrared spectrum.

B. A suspension of 0.200 g. (0.497 mmole) of tosylhydrazone 47 and 0.100 g. (0.537 mmole) of tosylhydrazine in 6 ml. of absolute ethanol containing 6 drops of glacial acetic acid was heated at reflux for 48 hours. Undissolved solid was present in the reaction mixture during the entire reflux period. The mixture was cooled to room temperature and filtered to give 0.038 g. of yellow crystals, m.p. 217-219° (dec.). Two recrystallizations from chloroform-hexane gave this compound as small yellow needles, m.p. 224.5-225.5° (dec.). The elemental analysis of this material did not agree with that calculated for a bistosylhydrazone derivative.

Anal. Calcd. for $C_{30}H_{26}N_4O_4S_2$: C, 63.15; H, 4.59; N, 9.82. Found: C, 69.21; H, 4.99; N, 9.83.

The infrared spectrum (KBr) showed absorption bands at 3.23 (s), 5.91 (w), 6.09 (s), 6.27 (m), 6.36 (w), 6.47 (s), 6.77 (m), 6.94 (s), 7.30 (s), 7.38 (s), 8.45 (s), 8.56 (s), 8.80 (w), 9.33 (s), 10.02 (w), 11.48 (m), 11.68 (m), 12.30 (m), 12.68 (m), 13.32 (m), and 14.58 (s) μ.

The qualitative ultraviolet spectrum (acetonitrile) showed λ_{max} at 228 mμ (relative ε 1.38), 307 (1.92), and 392 (1.00).

The structure of this product remains unassigned. Blomquist and LaLancette[17a] report the isolation of a compound (m.p. 239-240°) which was presumed to be the bistosylhydrazone derivative of quinone 23. This material was obtained from the mother liquors of a preparation of the monotosylhydrazone and gave a correct elemental analysis for nitrogen.

Monotosylhydrazone 47 is stable under the reaction conditions employed above. Refluxing 47 in absolute ethanol containing a trace of glacial acetic acid for 71 hours resulted only in the recovery of unchanged monotosylhydrazone.

Attempted preparation of diazodiphenylcyclobutenone (48a).

A. To a solution of 0.201 g. (0.498 mmole) of tosylhydrazone 47 in 5 ml. of methylene chloride was added 5.00 ml. of a 0.100 N sodium hydroxide solution (1.00 equivalents). The methylene chloride layer turned an immediate dark red. The mixture was stirred for 3 hours at room temperature. At the end of this time the methylene chloride layer was still dark red and the aqueous layer was pale yellow. The methylene chloride layer was separated and water added. Upon shaking the organic solution turned yellow. The organic layer was separated, dried over sodium sulfate, and the solvent removed on a rotary evaporator. Recrystallization of the yellow residue from chloroform-hexane gave 0.176 g. (88% recovery) of unchanged 47 which was identified by its melting point and infrared spectrum.

B. Addition of excess triethylamine to a chloroform solution of tosylhydrazone 47 gave a dark-red solution. Addition of hexane caused precipitation of unchanged 47 (85% recovery).

C. A solution of 0.300 g. (0.747 mmole) of tosylhydrazone 47 in 4 ml. of tetrahydrofuran was cooled to 0°. To this stirred solution was added 0.53 ml. of a 1.59 M solution of n-butyllithium (0.843 mmole) in hexane under an atmosphere of argon. The solution turned dark-red

immediately but no precipitate formed. The solvent was removed on a rotary evaporator to yield an amorphous red solid which was dried further at 0.2 mm. The reaction flask was connected to a water-cooled condenser, evacuated to 0.2 mm., and immersed in a bath at 100°. The temperature of the bath was raised to 140° over a period of one hour and maintained at 140° for an additional hour. During this time the solid in the flask turned from red to black in color but no material distilled or sublimed into the condenser. Examination of the residue in the flask revealed only the presence of carbonaceous material.

D. A chloroform solution of tosylhydrazone 47 (0.168 g.; 0.418 mmole) was added to an 11 x 1.1 cm. column of basic alumina (Merck 71707) packed in chloroform. The alumina column turned bright orange upon contact with the tosylhydrazone solution. The orange color traveled the length of the column but the eluates were yellow. The column was eluted with chloroform (400 ml.) until the eluates were colorless. Removal of the solvent on a rotary evaporator gave a yellow residue which was crystallized from chloroform-hexane (three crops) to give 0.100 g. (60% recovery) of unchanged 47. Removal of the solvent from the final filtrate left no residue.

E. A mixture of 0.200 g. (0.497 mmole) of tosylhydrazone 47 and 5.00 ml. of an 0.100 N sodium hydroxide

solution (1.01 equivalents) was stirred in a stoppered flask at room temperature. The tosylhydrazone was insoluble in the basic solution but formed a fine suspension with stirring. This suspension was orange after 10 minutes and orange with a metallic luster after one hour. Yellow solid settled beneath a bright-red aqueous solution when stirring was stopped. After 6 days the suspension was yellow and, when stirring was stopped, yellow solid settled beneath a colorless aqueous solution. After 7 days at room temperature the mixture was extracted with chloroform. The chloroform layer was separated, washed twice with water and dried over magnesium sulfate. Removal of the solvent on a rotary evaporator gave a yellow solid which was recrystallized from chloroform-hexane to yield 0.100 g. (three crops, 50% recovery) of unchanged 47 which was identified by its melting point and infrared spectrum. Removal of the solvent from the final residue gave a brown, intractable residue. The infrared spectrum ($CHCl_3$) of this residue showed a strong band at 4.74 microns but all attempts to isolate a solid product were unsuccessful. Acidification of the combined aqueous layers followed by extraction with chloroform gave a yellow heat-sensitive solid which decomposed upon attempted recrystallization.

1-Cyano-1-phenylcyclopropane (65).-The procedure followed was that of Tilford, Van Campen and Shelton.[56] A 2-l. three-necked flask fitted with a dry-ice condenser, gas-inlet tube, dropping funnel, and magnetic stirrer was cooled to -36° in a dry ice-ethylene dichloride bath. Approximately 500 ml. of liquid ammonia was slowly condensed in the flask. After the addition of 0.5 g. of ferric nitrate, 40.7 g. (1.77 g.-atoms) of sodium metal (Baker reagent) was added with stirring over a period of 30 minutes. Four hours after the addition of sodium was complete the initial blue color of the solution had faded to gray and freshly distilled phenylacetonitrile (100 g.; 0.85 mole) was added over a 20 minute period. The cooling bath was changed to a dry ice-chloroform bath (-64°) and 156 g. (0.83 mole) of ethylene dibromide in 500 ml. of dry ether was added over a period of 1.5 hours. At the end of addition the cooling bath was removed and the ammonia allowed to evaporate over a period of 6 hours while the original volume was maintained by the addition of dry ether. The resulting ether solution was refluxed for two hours. The mixture was cooled to room temperature and 400 ml. of water and 500 ml. of benzene were added. The organic layer was separated, dried over sodium sulfate and the ether and benzene removed by slow distillation. Distillation of the residue on a spinning-band column gave a forerun of 23 g.

of unchanged phenylacetonitrile, b.p. 109-120° (17 mm.), n_D^{20} 1.5250 (lit.[92] n_D^{25} 1.5211), followed by 50.3 g. (42%) of 1-cyano-1-phenylcyclopropane as a colorless oil, b.p. 125-131° (17 mm.), n_D^{20} 1.5381 (lit.[93] b.p. 125°/15 mm., n_D^{20} 1.5382). The infrared spectrum of this material was identical with that reported in reference 93.

1-Phenylcyclopropyl phenyl ketone (66).[57] A solution of phenylmagnesium bromide was prepared under an argon atmosphere from 2.92 g. (0.120 g.-atom) of magnesium and 19.60 g. (0.125 mole) of bromobenzene in 125 ml. of dry ether. To this solution was added 15.00 g. (0.105 mole) of 1-cyano-1-phenylcyclopropane (65) dissolved in 75 ml. of ether over a period of 45 minutes. The ether solution refluxed gently during the addition. The stirred reaction mixture was then refluxed for 72 hours. The mixture was cooled to 0° and 150 ml. of 10 per cent hydrochloric acid was added, causing the formation of copious amounts of solid material. Benzene (100 ml.) was added and the ether removed by distillation. An additional 100 ml. of benzene was added and the two-phase mixture refluxed with stirring for 14 hours. At the end of this time all solid material had dissolved and the benzene solution was dark green. The benzene layer was separated and the aqueous layer extracted twice with ether. The combined organic solutions were washed with 5 per cent sodium bicarbonate solution, causing the color to

change from green to red-brown. The organic layer was washed with saturated saline solution and dried over magnesium sulfate. Removal of the solvents on a rotary evaporator yielded a black oil. Short-path distillation gave 18.0 g. of a yellow oil, b.p. 130-135° (0.45 mm.). Crystallization from 95 per cent ethanol gave 10.25 g. (44%) of 1-phenylcyclopropyl phenyl ketone as slightly yellow crystals, m.p. 66-71°. Further recrystallization from 95 per cent ethanol gives colorless crystals, m.p. 73-74° (lit.[57a] m.p. 73.6-73.9°). The infrared spectrum of this material was identical with that reported in reference 57b.

1-Phenylcyclopropyl phenyl carbinol (67).-To a stirred mixture of 1.71 g. (0.0450 mole) of lithium aluminum hydride in 150 ml. of absolute ether at 0° was added 4.70 g. (0.0212 mole) of 1-phenylcyclopropyl phenyl ketone (66) in 75 ml. of absolute ether over a period of 30 minutes. The reaction mixture was stirred at 0° for 30 minutes, at room temperature for one hour, and at reflux for 45 minutes. The solution was cooled to 0° and decomposed by addition of ethyl acetate followed by 10 per cent hydrochloric acid. The ether layer was separated and the aqueous layer extracted with ether. The combined ether solutions were washed twice with water and dried over sodium sulfate. Removal of the solvent on a rotary evaporator gave a colorless oil. Distillation yielded 3.84 g. (81%) of 1-phenylcyclopropyl phenyl

carbinol as a colorless, very viscous oil, b.p. 130-133° (0.50-0.65 mm.), n_D^{21} 1.5822.

Anal. Calcd. for $C_{16}H_{16}O$: C, 85.68; H, 7.19. Found: C, 85.60, H, 7.07.

The infrared spectrum (neat) showed absorption bands at 2.89 (s), 3.27 (m), 3.46 (w), 6.26 (w), 6.70 (m), 6.90 (m), 9.66 (m), 9.78 (m), 12.66 (w), 13.12 (m), 14.05 (s), and 14.35 (s) μ.

The n.m.r. spectrum exhibited resonance signals at τ 2.97 (singlet, aromatic protons), 5.67 (singlet, OH), 6.75 (singlet, CH), and 9.22 (unresolved doublet, cyclopropyl protons), with area ratios of 10:1:1:4, respectively.

1-Phenylcyclopropyl phenyl ketone tosylhydrazone (68).-A mixture of 1-phenylcyclopropyl phenyl ketone (66) (2.595 g.; 11.7 mmoles) and tosylhydrazine (3.270 g.; 17.6 mmoles) was heated to reflux in 25 ml. of absolute ethanol containing 6 drops of glacial acetic acid. Colorless crystals separated from the hot solution after two days at reflux. After refluxing for seven days the solution was cooled and filtered to yield 3.316 g. of colorless crystals. This material was triturated with 20 ml. of boiling ethanol, cooled, and filtered to give 3.240 g. (71%) of tosylhydrazone 68 as colorless crystals, m.p. 191-193° (dec.). The analytical sample was prepared by one recrystallization from absolute ethanol and had m.p. 191-193° (dec.). The melting

point of this material varies with crystalline form. The small crystals obtained by recrystallization have m.p. 191-193° but the large, very hard crystals which separate from hot ethanol during the preparation have melting point as high as 198°. The yield of 68 by the procedure described above was consistently 66-71 per cent.

Anal. Calcd. for $C_{23}H_{22}N_2O_2S$: C, 70.75; H, 5.68. Found: C, 70.91; H, 5.80.

The infrared spectrum (KBr) showed absorption bands at 3.06 (m), 3.26 (w), 6.27 (m), 6.70 (m), 6.93 (m), 7.30 (s), 7.43 (m), 7.55 (m), 8.53 (s), 9.35 (m), 9.48 (m), 9.72 (m), 10.13 (m), 11.28 (m), 12.40 (m), 12.94 (s), 13.23 (s), 14.14 (s), and 14.40 (s) μ.

The n.m.r. spectrum ($CDCl_3$) exhibited the following resonance signals: a broad singlet at τ 1.92 (N-H, relative area 1.07), two multiplets centered at 2.23 and 2.95 (aromatic protons, combined relative area 14.0), a sharp singlet at 7.57 (CH_3, relative area 3.14), and a pair of unresolved multiplets centered at 8.53 and 8.75 (cyclopropyl protons, relative area 3.82).

Attempts to improve the yield of tosylhydrazone or to shorten the reaction time required were unsuccessful. These experiments are briefly described below.

A. Refluxing equimolar amounts of ketone and tosylhydrazine in ethanol containing a trace of acetic acid for 45 minutes yielded essentially no product.

B. Repeating the experimental conditions in A but refluxing for 72 hours gave a 19 per cent yield of tosylhydrazone.

C. Repeating the experimental conditions in A but refluxing for 166 hours gave a 39 per cent yield of tosylhydrazone.

D. Refluxing the ketone with a 1.07 mole excess of tosylhydrazine in glacial acetic acid for 61 hours gave a black solution which yielded no product but from which 82 per cent of the starting ketone was recovered.

E. Refluxing the ketone with a 1.55 mole excess of tosylhydrazine in n-butanol containing a trace of acetic acid for 70 hours yielded a deep-violet solution and a 7 per cent yield of relatively impure tosylhydrazone.

1,2-Diphenylcyclobutene (24).[55] To a solution of tosylhydrazone 68 (2.745 gl; 7.03 mmoles) in 50 ml. of dry N-methyl-2-pyrrolidone was added 0.435 g. (8.07 mmoles) of freshly prepared sodium methoxide. The solution was stirred for 3 minutes and then immersed in a bath at 120°. Nitrogen evolution began immediately and was essentially complete after 12 minutes. The solution was dark orange after 2 minutes of heating, red after 4 minutes, and light orange after 7 minutes. After 12 minutes at 120° the solution was cooled and poured into 75 ml. of water. The resulting oil was extracted into hexane. The hexane solution was washed

3 times with water and dried over sodium sulfate. Removal of the solvent on a rotary evaporator yielded a yellow oil which was dissolved in hexane and filtered through a column of alumina (Merck 71707) using hexane as the eluant. The resulting colorless oil was crystallized from methanol at -78° to give 1.105 g. (76%) of 1,2-diphenylcyclobutene as colorless plates, m.p. 51-53.5°. The analytical sample was obtained by two further recrystallizations from methanol and had m.p. 53-54°. The yield of 24 by this method of preparation was consistently 66-76 per cent.

Anal. Calcd. for $C_{16}H_{14}$: C, 93.16; H, 6.84. Found: C, 93.04; H, 6.97.

The infrared spectrum (KBr) showed absorption bands at 3.21 (m), 3.35 (m), 6.25 (m), 6.68 (m), 6.91 (m), 7.50 (m), 8.26 (m), 9.32 (m), 9.61 (w), 9.79 (w), 10.80 (m), 10.93 (m), 12.46 (w), 12.99 (m), 13.33 (s), 14.13 (w), and 14.53 (s) μ.

The ultraviolet spectrum (isooctane) showed λ_{max} at 224 mμ sh. (ϵ 23,200), 227.5 (24,100), 236 sh. (13,500), 297 (18,400), 307 sh. (17,500), and 322 inf. (10,800).

The n.m.r. spectrum ($CDCl_3$) showed a complex multiplet centered at τ 2.58 (aromatic protons) and a sharp singlet at 7.24 (methylene protons), with an area ratio of 2.4:1.0, respectively.

Thermal isomerization of 1,2-diphenylcyclobutene (24) in the presence of p-benzoquinone.-A mixture of 0.055 g. (0.267 mmole) of 1,2-diphenylcyclobutene and 0.027 g. (0.250 mmole) of p-benzoquinone dissolved in 3 ml. of xylene was refluxed for 26 hours. The xylene was removed under a stream of argon and the residue triturated with boiling hexane. Filtration of the hot solution gave a white solid which was dissolved in boiling methanol and filtered while hot to remove a trace of insoluble material. Cooling afforded 0.020 g. (25%) of 6,7-diphenyl-4a,5,8,8a-tetrahydro-1,4-naphthoquinone (71) as pale-yellow crystals, m.p. 160-162° (lit.[72] m.p. 163°). Recrystallization from methanol gives pale-yellow needles, m.p. 161-163°. The infrared spectrum (KBr) showed absorption due to carbonyl stretching vibration at 5.93 μ.

Thermal isomerization of 1,2-diphenylcyclobutene (24) in the presence of 1,4-naphthoquinone.-A mixture of 0.107 g. (0.519 mmole) of 1,2-diphenylcyclobutene and 0.080 g. (0.507 mmole) of freshly sublimed 1,4-naphthoquinone dissolved in 3 ml. of xylene was refluxed for 26 hours. The xylene was removed under a stream of argon and the residue recrystallized from acetone and then from methanol to give 0.095 g. (52%) of 2,3-diphenyl-1,4,4a,9a-tetrahydro-9,10-anthraquinone (72) as a white, amorphous solid, m.p. 165-166.5° (lit.[72] m.p. 175-176°). The infrared spectrum (KBr) showed absorption due to carbonyl stretch at 5.92 μ.

To a solution prepared by dissolving one potassium hydroxide pellet in 5 ml. of absolute ethanol was added 24 mg. (0.066 mmole) of quinone 72. The resulting solution was dark red. When air was bubbled through the solution for 15 minutes the red color disappeared and yellow needles precipitated. Filtration gave 17 mg. (70%) of 2,3-diphenyl-9,10-anthraquinone (73), m.p. 211.5-212.5° (lit.[72] m.p. 211-212°). The infrared spectrum (KBr) showed absorption due to carbonyl stretch at 5.98 μ.

Thermal isomerization of 1,2-diphenylcyclobutene (24): bromination of the product.-1,2-Diphenylcyclobutene (0.042 g.; 0.204 mmole) was heated in an open tube at 190° for 7 minutes. The resulting yellow oil, which was not entirely fluid, was dissolved in chloroform and a solution of bromine in carbon tetrachloride added until the bromine color persisted. Upon warming under a stream of argon to remove the solvent the solution turned a deep blue. The solvent was removed and the residue dissolved in boiling acetone and filtered to remove insoluble blue solid. The process of warming the filtrate and filtering was repeated until blue precipitate was no longer formed. The resulting acetone solution was evaporated to dryness and the residue dissolved in boiling ethanol. The hot solution was filtered to remove a trace of insoluble material and cooled to give 0.030 g.

(40%) of 1,4-dibromo-2,3-diphenyl-2-butene (74) as glistening needles, m.p. 148-150.5° (lit.[72] m.p. 145-147°).

Heating a neat sample of 24 at 155° for 3.5 hours afforded a yellow gum. This material was dissolved in chloroform and treated with a bromine-carbon tetrachloride solution until the bromine color persisted. Upon warming the solution became very dark with evolution of hydrogen bromide. Removal of the solvent under a stream of argon gave a blue residue which formed a hard, amorphous, metallic-blue mass when acetone was added. None of the desired dibromide could be isolated.

Thermal isomerization of 1,2-diphenylcyclobutene (24): n.m.r. spectrum of the product.-A neat sample of 1,2-diphenylcyclobutene was heated in an open tube at 190° for 3 minutes (ca. 1.3 half-lives). The resulting fluid oil was dissolved in $CDCl_3$ and the n.m.r. spectrum determined immediately. The spectrum showed a complex multiplet centered at τ 2.74 (aromatic protons), an AB quartet (J = 1.8 cps) centered at 4.67 (butadiene methylene protons), and a sharp singlet at 7.24 (cyclobutene methylene protons). A comparison of the relative areas of the cyclobutene and butadiene methylene protons indicated that 54 per cent of the cyclobutene had undergone isomerization. When the extent of isomerization was calculated by comparing the relative area of the aromatic protons with that of the cyclobutene methylene protons the

value of 58 per cent was obtained. The similarity of the above two values indicates that little, if any, polymerization has taken place. Polymer was not detectable in the spectrum described above.

When a neat sample of 24 was heated under argon at 155° for 3.5 hours a yellow gum resulted. The n.m.r. spectrum ($CDCl_3$) of this material showed, in addition to aromatic protons, small peaks at τ 6.54, 7.24, and 8.73. A large, relatively broad peak was centered at τ 8.00. There was no detectable absorption in the vinyl region of the spectrum.

Kinetic runs.-The rate of valence isomerization of 1,2-diphenylcyclobutene was determined by following the decrease in optical density of the long-wavelength ultraviolet band of this compound as a function of time. This absorption band appeared at 297 mμ in isooctane, n-propanol, and n-propionitrile and at 299.5 mμ in decalin. Extrapolation of the ultraviolet spectrum of the product of the isomerization, 2,3-diphenyl-1,3-butadiene (70), as reported by Cope,[73] showed that absorption at 297 mμ was insignificant with $\epsilon < 200$. The spectra of the infinity points of the kinetic runs (9.3-15.7 half-lives) characteristically showed optical densities at 297 mμ which were 1-2 per cent of the optical densities at zero time. A plot of optical density against concentration for isooctane solutions of

1,2-diphenylcyclobutene was linear over the concentration range of 0.529×10^{-5} M to 5.29×10^{-5} M, indicating that Beer's law is obeyed in this range. The solutions used for analysis of the kinetic runs were within this concentration range.

The sample vials used for the kinetic studies were prepared from Pyrex tubing having i.d. 6 mm. and o.d. 8 mm. The length of these tubes before sealing was 20-21 cm. and the length after sealing was 16-17 cm. Before using the vials were thoroughly cleaned, soaked in concentrated ammonium hydroxide, and rinsed with distilled water containing a trace of ammonium hydroxide. The vials were then dried at 125° for at least 24 hours. Each vial was charged with exactly 2 ml. of a ca. 6×10^{-3} M solution of 1,2-diphenylcyclobutene by means of a micro buret (5 ml.). The solutions were degassed three times under vacuum and sealed under vacuum. The solutions were stored at -78° in the dark until just prior to use, when they were allowed to warm to room temperature before immersion in the constant temperature bath. Samples stored in this fashion for 8 days showed no change in the optical density at 297 mμ.

Optical densities were measured with a Cary 14 recording spectrophotometer. Temperature was measured with an N.B.S. calibrated thermometer and was corrected for stem exposure. The maximum temperature deviation was 0.1°C.

Time was measured with a Precision Scientific "Time It" timer. Isooctane was Fisher or Mallinckrodt spectrophotometric grade and was not further purified. n-Propanol was Fisher reagent grade purified by drying over sodium sulfate and then distilling. n-Propionitrile was Eastman practical grade purified by heating to reflux with and then distilling from phosphorous pentoxide. Decalin was Fisher reagent grade or Aldrich research grade purified by stirring with concentrated sulfuric acid for 24 hours and then washing with concentrated sulfuric acid until the acid layer was no longer yellow. The decalin was then filtered through alumina and vacuum distilled from phosphorous pentoxide. All of the solvents described above, except for decalin, were transparent in the ultraviolet region above 220 mμ. The decalin contained a considerable amount of aromatic impurities but was transparent in the region under investigation.

Following pyrolysis the isomerization reaction was quenched by immersion of the vial in a dry ice-acetone bath. The vials were then stored at -78° until analyzed. The analyses were performed immediately after completion of a run and were effected by opening the tube, rinsing the contents into a 25 ml. volumetric flask, and diluting 1 ml. of this solution to 10 ml. The solutions obtained in this fashion had optical densities at 297 mμ ranging from 0.16 to 0.87. Points were measured from time = 0 to time = 180

minutes in intervals of 30 minutes over the temperature range 135-150°. Under these conditions the extent of isomerization at time = 180 minutes varied from 33 per cent (135°) to 81 per cent (150°). The rate constants were obtained graphically from equation 1[94] by plotting log $(D_\infty - D_o)/(D_\infty - D)$ against time where D is optical density.

$$k = \frac{2.303}{t} \log \frac{D_\infty - D_o}{D_\infty - D} \qquad (1)$$

These plots were linear over the entire concentration range studied. The Arrhenius activation energy, E_a, was determined in the usual fashion. The entropy of activation, $\Delta S^{\neq}$, was determined from equations (2), (3), and (4)[95] where k_r is the rate constant, k is Boltzmann's constant, h is Planck's constant, and κ, the transmission coefficient, is assumed to be unity.[96]

$$\Delta H^{\neq} = E_a - RT \qquad (2)$$

$$\Delta F^{\neq} = RT \ln \kappa \frac{kT}{k_r h} \qquad (3)$$

$$\Delta S^{\neq} = \frac{\Delta H^{\neq} - \Delta F^{\neq}}{T} \qquad (4)$$

1-Phenylcyclobutanol (86).-The procedure followed was as described by Burger and Bennett.[97] A solution of phenyllithium was prepared under an argon atmosphere from bromobenzene (26.00 g.; 0.165 mole) and lithium wire (2.25 g.; 0.324 g.-atom) using absolute ether (150 ml.) as the solvent.

A solution of cyclobutanone (Columbia) (5.16 g.; 0.0737 mole) in absolute ether (50 ml.) was added over a period of one hour. The addition reaction was very exothermic. The mixture was stirred at room temperature for 21 hours, cooled to 0°, and decomposed with 100 ml. of water. The ether layer was separated and the aqueous layer extracted twice with ether. The combined ether solutions were washed with saturated saline solution and dried over sodium sulfate. Removal of the ether on a rotary evaporator gave a brown oil. Distillation gave 9.90 g. of a colorless oil, b.p. 79-86° (0.25-0.35 mm.), which had partially crystallized by the time the distillation was completed. Crystallization from hexane at 0° gave 8.53 g. (78%) of 1-phenylcyclobutanol as colorless prisms, m.p. 39-42° (lit.[97] m.p. 41-42°). The infrared spectrum (KBr) showed absorption bands at 2.97 (s) (OH); 6.25 (w), 6.34 (w), 6.70 (m) and 6.92 (m) (aromatic C=C stretching vibrations); 13.12 (s) and 14.35 (s) μ (monosubstituted benzene ring).

1-Phenylcyclobutene (83).[97,98] The method of preparation was as described by Burger and Bennett.[97] A mixture of 3.054 g. (20.6 mmoles) of 1-phenylcyclobutanol (86) and ca. 15 mg. of p-toluenesulfonic acid monohydrate was heated at 115° under reduced pressure. The colorless oil which rapidly distilled had b.p. 63° (2-3 mm.) and n_D^{21} 1.5728

(lit.[98] b.p. 68-70°/3.5 mm., n_D^{26} 1.5657). The infrared spectrum (neat) contained bands at 5.91, 6.18, 6.25 and 6.35 μ (lit.[98] 5.90, 6.17, 6.23 and 6.33 μ). The n.m.r. spectrum was in complete accord with that reported by Wilt.[59b]

The samples of 1-phenylcyclobutene as prepared above would crystallize when stored at 0°. This olefin was always stored in the dark at 0° due to its tendency to polymerize. Thin layer chromatography (using Eastman Chromagram Type K 301R and developing with hexane) indicated that material stored in this fashion would remain free of polymer for approximately 24 hours. Analysis of material which had been stored in this manner for 48 hours revealed the presence of a single mobile spot (cyclobutene) and a spot with an R_f value of zero (polymer). The rate of polymerization was much more rapid when the compound was handled at room temperature.

2-Phenyl-1,3-butadiene (84).[99] The procedure followed was that of Marvel and Woolford.[99a] Methylphenylvinyl carbinol[99a] (10.00 g.; 0.0676 mole), aniline hydrobromide (1.00 g.), and hydroquinone (0.15 g.) were mixed together in a round-bottom flask and the flask connected to a short Vigreux column. With stirring, the pressure was reduced to 13 mm. and the mixture was heated first to 100° and then over a period of 1.5 hours the temperature was slowly raised

to 155°. The colorless oil which distilled was collected in a receiver cooled in an ice-salt bath. The yield of crude material was 5.28 g. (wet). The oil was dissolved in ether and dried over magnesium sulfate. The ether was removed under reduced pressure and the residue redistilled to give 3.41 g. (39%) of 2-phenyl-1,3-butadiene as a colorless oil, b.p. 52-56° (7 mm.), n_D^{20} 1.5487 (lit.[99e] b.p. 55-64°/15 mm., n_D^{20} 1.5489).

A mixture of diene 84 (0.250 g.; 1.92 mmoles) and 1,4-naphthoquinone (0.270 g.; 1.71 mmoles) in benzene (3 ml.) was refluxed for 3 hours. The benzene was removed under a stream of nitrogen and the residue triturated with 5 ml. of boiling 95 per cent ethanol. The mixture was cooled to 0° and filtered to give 0.426 g. (87%) of 2-phenyl-1,4,4a,9a-tetrahydro-9,10-anthraquinone as slightly yellow needles, m.p. 142-144° (lit.[99a-d] m.p. 144°). Recrystallization from 95 per cent ethanol gives white needles, m.p. 143-144°.

A solution of maleic anhydride (0.227 g.; 2.32 mmoles) in benzene (4 ml.) was added in one portion to 0.302 g. (2.32 mmoles) of diene 84. The mixture was allowed to stand at room temperature for 12 hours. Addition of hexane to the benzene solution afforded 0.423 g. (80%) of 4-phenyl-Δ^4-tetrahydrophthalic anhydride as colorless crystals, m.p. 102-105.5° (lit.[99a,c-e] m.p. 105°).

The valence isomerization of 1-phenylcyclobutene (83) to 2-phenyl-1,3-butadiene (84).-The thermal isomerization of cyclobutene 83 was conducted in the heated injector chamber of a gas chromatograph. The product of the isomerization is apparently the expected 2-phenyl-1,3-butadiene (84), although this identification is based solely on a comparison of retention times. The v.p.c. analyses were carried out using a column of 5 per cent SE-30 on 60/80 Chromosorb W (5 ft. x 1/8 in.) maintained at 110°. At this column temperature the retention time of 1-phenylcyclobutene was 4.3 minutes and that of a known sample of 2-phenyl-1,3-butadiene was 2.0 minutes.

The pyrolysis of 83 was studied by injecting an ether solution of this olefin at various injector temperatures. The extent of isomerization was calculated from the relative peak areas of the cyclobutene and diene, assuming that the sensitivity of the detector toward each of the two hydrocarbons was identical. The cyclobutene was stable to an injector temperature of 210° with the chromatogram showing only a single peak at retention time 4.3 minutes. At 225° the cyclobutene:butadiene ratio was 80:1. At 272° the ratio was 1:1. At 300° the cyclobutene:butadiene ratio was 1:75. At 315° the cyclobutene was completely converted to butadiene with the chromatogram showing only a single peak at a retention time of 2.0 minutes.

The chromatograms described above indicated that diene 84 is the sole product of the thermal isomerization of cyclobutene 83. In all experiments the only two peaks present were the ones at 2.0 and 4.3 minutes.

1-Phenylcyclopropyl methyl ketone (86).[57a] A solution of methylmagnesium bromide was prepared under an argon atmosphere by adding a solution of 18.1 g. (0.191 mole) of methyl bromide in 75 ml. of dry ether to 3.074 g. (0.127 g.-atom) of magnesium covered with 50 ml. of ether. To this solution was added 15.00 g. (0.105 mole) of 1-cyano-1-phenylcyclopropane (65) in 75 ml. of ether over a period of 30 minutes. The addition reaction was mildly exothermic with the reaction mixture turning initially yellow and then dark-green by the end of addition. The mixture was refluxed under argon for 72 hours. Dry ether was added periodically to replace losses. After 12 hours at reflux the solution was yellow and thick with suspended solid. The solution was cooled to 0° and 150 ml. of 10 per cent hydrochloric acid was added with care. The resulting two-phase mixture was refluxed with stirring for 14 hours. The yellow ether layer was separated and the aqueous layer extracted with ether. The combined ether solutions were washed with 5 per cent sodium bicarbonate solution and saturated saline solution. After drying over sodium sulfate the ether was removed on a rotary evaporator to yield a brown oil. Distillation gave

14.21 g. (85%) of 1-phenylcyclopropyl methyl ketone as a colorless oil, b.p. 84-87° (3.4 mm.), n_D^{20} 1.5240 (lit.[57a] b.p. 122°/25 mm., n_D^{20} 1.5280). The infrared spectrum of this material was identical with that reported in reference 93. This spectrum showed no absorption near 4.5 μ indicating that the product was free of unreacted nitrile.

The 2,4-dinitrophenylhydrazone derivative was obtained in 75 per cent yield and had m.p. 125-127° (lit.[57a] m.p. 129.2-130.2°).

1-Phenylcyclopropyl methyl ketone tosylhydrazone (69).-A mixture of 8.91 g. (0.0557 mole) of 1-phenylcyclopropyl methyl ketone (86) and 10.49 g. (0.0564 mole) of tosylhydrazine dissolved in 70 ml. of glacial acetic acid was stirred at room temperature. The product began to precipitate within 5 minutes after the reaction was started. After stirring at room temperature for 16 hours the bright-pink acetic acid solution was thick with suspended solid. Filtration gave 7.67 g. of slightly pink crystals which were washed with hexane, m.p. 119-123°. The filtrate was concentrated under reduced pressure to a volume of ca. 15 ml. and filtered to give 7.48 g. of red crystals which were washed with a mixture of ethanol-hexane (1:4) until nearly colorless, m.p. 118-121°. The above two crops were combined and triturated with 50 ml. of boiling ethanol-hexane (1:4).

The mixture was cooled to 0° and filtered to give 14.54 g. of colorless crystals, m.p. 119.5-122°, which were washed with 25 ml. of ice-cold ethanol-hexane (1:4). Repetition of this procedure gave 14.15 g. (77%) of tosylhydrazone 69 as colorless crystals, m.p. 120-123°. The analytical sample was obtained by recrystallization from ethanol-hexane and had m.p. 123.5-125°.

Anal. Calcd. for $C_{18}H_{20}N_2O_2S$: C, 65.84; H, 6.14. Found: C, 66.02; H, 6.02.

The infrared spectrum (KBr) showed absorption bands at 3.15 (s), 6.13 (w), 6.28 (m), 6.74 (m), 6.96 (m), 7.07 (w), 7.23 (s), 7.37 (m), 7.48 (s), 7.58 (s), 7.68 (m), 7.81 (m), 8.27 (w), 8.42 (m), 8.56 (s), 8.69 (s), 8.94 (w), 9.18 (m), 9.30 (m), 9.62 (s), 9.75 (s), 9.84 (m), 10.17 (m), 10.58 (w), 10.77 (s), 10.85 sh. (s), 11.03 (s), 11.74 (w), 11.90 (w), 12.02 (m), 12.23 (s), 12.53 (w), 12.86 (m), 13.00 (s), 14.12 (s), 14.19 sh. (s), and 14.36 (s) μ.

The n.m.r. spectrum ($CDCl_3$) exhibited the following resonance signals: absorption in the range τ 2.04-2.98 with the strongest peak at 2.80 (N-H plus aromatic protons, total relative area 10.0), a singlet at 7.55 ($ArCH_3$, relative area 2.89), a sharp singlet at 8.33 ($N{=}C{-}CH_3$, relative area 2.81), and a pair of triplets (split further) centered at 8.82 and 9.00 (cyclopropyl protons, combined relative area 4.18).

Thermal decomposition of the sodium salt of 1-phenylcyclopropyl methyl ketone tosylhydrazone (69).-To a suspension of 1.34 g. (24.8 mmoles) of sodium methoxide in 75 ml. of dry N-methyl-2-pyrrolidone (NMP) was added a solution of 7.00 g. (21.3 mmoles) of 1-phenylcyclopropyl methyl ketone tosylhydrazone in 75 ml. of NMP. The resulting solution was stirred at room temperature for several minutes and then immersed, with stirring, in a bath at 130°. The bath temperature dropped to 110° but climbed to 125° over a period of 10 minutes. Gas evolution began when the temperature reached 125°. The reaction mixture was maintained at 125° for 50 minutes. At the end of this time gas evolution had ceased completely. The NMP solution remained yellow throughout the entire reaction period. The solution was cooled, poured into 150 ml. of water, and the aqueous mixture extracted with two 100 ml. portions of hexane. The combined hexane solutions were washed with five 50 ml. portions of water, separated, and dried over magnesium sulfate. Removal of the solvent on a rotary evaporator yielded a yellow oil which was separated into two fractions by distillation at reduced pressure.

Fraction A (0.423 g.) was a colorless oil possessing an aromatic odor, b.p. 34-60° (1.5 mm.), n_D^{20} 1.5466. The qualitative ultraviolet spectrum (isooctane) showed λ_{max} at 221 mμ (relative ϵ 1.83), 238.5 (2.55), 243.5 (2.50), 249

(2.95), 259 (1.56), and 269 sh. (1.00). The n.m.r. spectrum (CCl_4) was very complex, showing absorption in the ranges τ 1.98-2.30, 2.50-3.13, 4.03-5.62, and 6.58-9.43. The ratio of the areas of the non-aromatic to the aromatic protons was 1.33:1. V.p.c. analysis (5 ft. x 1/8 in. column composed of 5 per cent SE-30 on 60/80 Chromosorb W maintained at 115°) with an injector port temperature of 200° showed five major components with retention times (minutes) of 1.6, 1.9, 2.2, 4.7, and 5.1. Also present were at least seven minor components with retention times of 1.1, 1.2, 2.7, 2.9, 3.4, 4.1, and 6.5. When the temperature of the injector port is raised to 360°, the peak at 4.7 disappears, the peak at 2.2 increases, and new peaks appear at 7.1 and 7.6.

Fraction B (0.903 g.) was a colorless oil possessing a slight aromatic odor, b.p. 60-62° (1.5 mm.), n_D^{20} 1.5629. The qualitative ultraviolet spectrum (isooctane) showed λ_{max} at 214 mμ (relative ϵ 1.11), 221 (0.94), 255 sh. (1.34), 259 (1.45), 269 sh. (1.00), and 294 (0.03). The n.m.r. spectrum (CCl_4) was considerably less complex than that of Fraction A, showing a multiplet at τ 2.52-3.13, a broad multiplet at 7.20-7.75, a multiplet centered at 8.03 and a sharp singlet at 8.60. Minor absorptions were observed at τ 2.02-2.28 and 8.67-9.33. The ratio of the areas of the

non-aromatic to the aromatic protons was 1.40:1. V.p.c. analysis (same column and temperature as for Fraction A) with an injector port temperature of 200° showed two major components with retention times (minutes) of 4.9 and 5.2. In addition, there was present at least four minor components with retention times of 1.5, 2.1, 3.4, and 6.5. When the temperature of the injector port is raised to 360°, the peak at 4.9 almost completely disappears, a major peak appears at 2.1, and smaller peaks appear at 7.0 and 7.5.

CHAPTER V

SUMMARY

The Diels-Alder reactivity of a series of cyclobutene derivatives was studied with the goal of obtaining a synthetic route to the cyclooctatetraenoquinone ring system (9a or 10a). 1,2-Diphenyl- and 1,2-dimethyltetrafluorocyclobutene (21 and 22) were found to be completely inert toward a variety of dienes. Studies of 3,3,4,4-tetrafluorocyclobutene (19) indicate that routes employing this olefin may be more productive. A preliminary investigation of the Diels-Alder reactivity of 1,2-diphenylcyclobutene (24) suggests that it is not a good dienophile. The contrast in dienophilic activity between the cyclobutene series and the cyclopropene series is explained mainly by a consideration of the effects of ring strain and steric hindrance to reaction. Diphenylcyclobutadienoquinone (23) was found to be unreactive toward a number of dienes. The lack of reactivity of this quinone is due in part to the fact that addition to the cyclobutene double bond would involve loss of the aromatic system resulting from contributions to the ground state by the dipolar resonance form of the quinone. Attempted synthesis of the cyclooctatetraenoquinone ring

system by cycloaddition reactions of 1-diethylamino- and 1-acetoxy-1,3-butadiene (38 and 40) was unsuccessful.

The monotosylhydrazone derivative (47) of diphenylcyclobutadienoquinone was prepared with the objective of converting this derivative into diazodiphenylcyclobutenone (48a). The structure of the tosylhydrazone was demonstrated by chemical and spectral means. Solutions of this derivative turned a deep red, indicating formation of the corresponding anion, when treated with a variety of bases. The conversion of this anion to cyclobutene 48a was not achieved as the ion proved to be exceedingly stable toward elimination of sulfinate anion.

1,2-Diphenylcyclobutene (24) was synthesized by the thermal decomposition of the sodium salt of 1-phenylcyclopropyl phenyl ketone tosylhydrazone (68). The ultraviolet and n.m.r. spectra of this olefin indicate that the phenyl rings are nearly coplanar with the cyclobutene ring. The product of the thermal isomerization of 24 was shown to be the expected 2,3-diphenyl-1,3-butadiene (70) by chemical and spectral means. The rate of valence isomerization of 24 was determined in isooctane, n-propanol, and n-propionitrile and was found to be solvent independent. The data in isooctane afforded the rate expression: $k = A \exp(-E_a/RT) = 10^{13.46} \exp(-33{,}400/RT)$ sec.$^{-1}$. The entropy

of activation was determined to be +0.3 E.U. The observed rate of isomerization of 1,2-diphenylcyclobutene is compared with the kinetic data reported for other cyclobutene derivatives. The transition state of cyclobutene valence isomerizations and the factors which influence reactivity are discussed. The data obtained for 1,2-diphenylcyclobutene are best explained by means of a skew transition state.

An attempt to prepare 1-methyl-2-phenylcyclobutene (85) by a route analogous to that used in the preparation of 1,2-diphenylcyclobutene was unsuccessful. Thermal decomposition of the sodium salt of 1-phenylcyclopropyl methyl ketone tosylhydrazone (69) afforded a number of products. Spectral data indicated that the desired cyclobutene was very likely formed in this reaction but isolation of this material was not achieved.

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BIOGRAPHICAL SKETCH

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This dissertation was prepared under the direction of the chairman of the candidate's supervisory committee and has been approved by all members of that committee. It was submitted to the Dean of the College of Arts and Sciences and to the Graduate Council, and was approved as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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