

POLYMERIZATION STUDIES OF  
4-SUBSTITUTED-1,2,4-TRIAZOLINE-3,5-DIONES  
AND  
SYNTHESIS OF MODEL COMPOUNDS  
RELATED TO TRIPLE STRAND POLYMERS

By  
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This dissertation is dedicated to my parents.

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Abstract of Dissertation Presented to the  
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4-SUBSTITUTED-1,2,4-TRIAZOLINE-3,5-DIONES  
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By

Sam Richard Turner

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Chairman: Dr. George B. Butler  
Major Department: Chemistry

The research described in this dissertation consists of two main areas of investigation. The first area pertains to the use of azo dienophiles, particularly 4-phenyl-1,2,4-triazoline-3,5-dione, in polymerization studies. The second area involves attempts to synthesize model compounds related to proposed triple strand polymers.

A. Polymerization Studies of 4-Substituted-1,2,4-triazoline-3,5-diones

The copolymerization and reactivity of the very potent cycloadditionophile, 4-phenyl-1,2,4-triazoline-3,5-dione (PhTD), with electron rich coreactants were investigated. PhTD was found to spontaneously react with vinyl ethers at room temperature in methylene chloride solution. Ethyl vinyl ether (EVE) and isobutyl vinyl ether (IVE) were observed to copolymerize spontaneously with PhTD to form 1:1 alternating copolymers. Divinyl ether (DVE) was observed to form a mixture of the 2+2 cycloadduct and copolymer at room temperature. At 60°C, only copolymer was formed.

The structures of the copolymers were assigned from spectroscopic and chemical data. Some physical property characterizations of the

copolymers were made.

A propagation mechanism involving the coupling of dipolar intermediates was ascertained as the most probable mechanism of polymerization. Numerous experimental observations were in support of this proposed method of polymerization.

When the spontaneous copolymerizations of EVE and IVE were effected in acetone or cyclohexanone, the corresponding 1,3,4-tetrahydrooxadiazine compounds were obtained as well as the expected copolymers. These new heterocyclic ring structures were fully characterized. The compounds were believed to result from an interception of the initial 1,4-dipole intermediate by the weakly dipolarophilic alkyl ketone. DVE was noted to form only a trace of the corresponding oxadiazine structure.

The difference in the reactivity of EVE and DVE was explained in terms of the stability of the positive center of the 1,4-dipole.

Other olefinic compounds were reacted with PhTD. Vinyl acetate was observed to undergo a unique intramolecular rearrangement of the initially formed 1,4-dipole. Divinyl carbonate only resulted in 2:1 copolymers. N-vinyl carbazole spontaneously copolymerized to yield a 1:1 copolymer of significantly higher molecular weight than obtained in the vinyl ethers. The electron poor olefins, divinyl sulfone and acrylonitrile, were found to be unreactive with PhTD.

Some decomposition reactions of PhTD were studied. Attempts to catalytically homopolymerize PhTD were unsuccessful. The reaction of PhTD with nucleophiles like sodium cyanide in dimethylformamide and triethylamine resulted in the formation of 3,7-diphenyl-1,5-diazabicyclo[3.3.0]octa-2,4,6,8-tetraone as well as an unidentified oligomeric product.

A new bis dienophile, 4,4'-(4,4'-diphenylmethylene)-bis-1,2,4-triazoline-3,5-dione, for use in cycloaddition polymerizations was synthesized. It was found to spontaneously react with styrene to give a high polymer believed to have been formed by first a Diels Alder reaction and then an ene reaction.

#### B. Synthesis of Model Compounds Related to Triple Strand Polymers

Two dienes, 2-acetoxymethyl-1,3-butadiene and 2,3-di-(acetoxymethyl)-1,3-butadiene, were synthesized by a new sulfone pyrolysis procedure. The precursor acetoxysulfones were prepared in good yields from the corresponding bromides by use of silver acetate in acetonitrile. The Diels Alder reactions of these acetoxysulfones and the corresponding dihydroxy diene from the 2,3-diacetoxysulfone were studied with p-benzoquinone. A facile aromatization or dehydrogenation of the adduct, depending on the conditions, precluded its isolation.

2-Cyclohexene-1-one was found to react sluggishly with the 2-acetoxymethyl diene. Attempts to force the reaction yielded polymeric materials. Diazoquinone reacted with the disubstituted dienes to yield the expected Diels Alder adducts. Various attempts at catalytic hydrogenation of these adducts were not successful.

Tetracyanoethylene was found to be unreactive with  $\alpha$ -pyrone. Fumaronitrile and p-benzoquinone resulted in the expected adducts.

Bromination of 3,4-dimethylbutadiene sulfone and then dehydrobromination resulted in the corresponding 3,4-dimethylthiophene-1,1-dioxide. This compound was found to be unreactive with tetracyanoethylene, but it gave a double Diels Alder adduct with maleic anhydride.

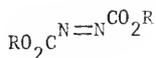
## CHAPTER I

### Introduction

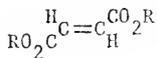
#### A. Polymerization Studies of Azo Dienophiles

##### Reactivity of azo dienophiles

Compounds containing dienophilic nitrogen to nitrogen double bonds have been extensively studied as reactants in cycloaddition reactions.<sup>1</sup> Normally these azo compounds have been shown to be more dienophilic than their carbon counterparts. For example azodicarboxylates, 1, have a stronger dienophilic reactivity than the corresponding fumarates, 2.<sup>1</sup>



1



2

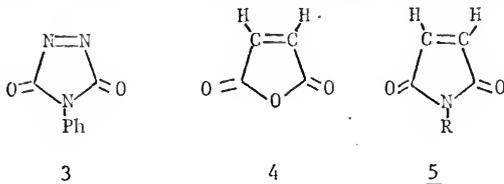
However, at the time this research was initiated only one report of the use of these compounds as monomers in polymerization studies was recorded.<sup>2</sup> This account involved the copolymerization of ethyl azo-bisformate with the comonomers tetrafluoroethylene, acrylonitrile and methyl methacrylate. In each case some incorporation of the azo compound into the polymer was verified by elemental analysis. No other structural characteristics were reported.

4-Phenyl-1,2,4-triazoline-3,5-dione (PhTD), 3, has been shown by Sauer and Schroder<sup>3</sup> to be the most reactive of the azo dienophiles and perhaps the most reactive dienophile known. The authors compared the reactivity of PhTD with tetracyanoethylene by utilizing competition experiments with 2-chloro-1,3-butadiene. PhTD was observed to react

about one thousand times faster than tetracyanoethylene, which had been previously described as one of the most potent dienophiles synthesized.<sup>4</sup> With the same diene, maleic anhydride, 4, was found to react only about one half as fast as the tetracyanoethylene.<sup>5</sup> However, with other dienes tetracyanoethylene reacted as great as  $10^6$  times faster than 4.

### Copolymerization studies

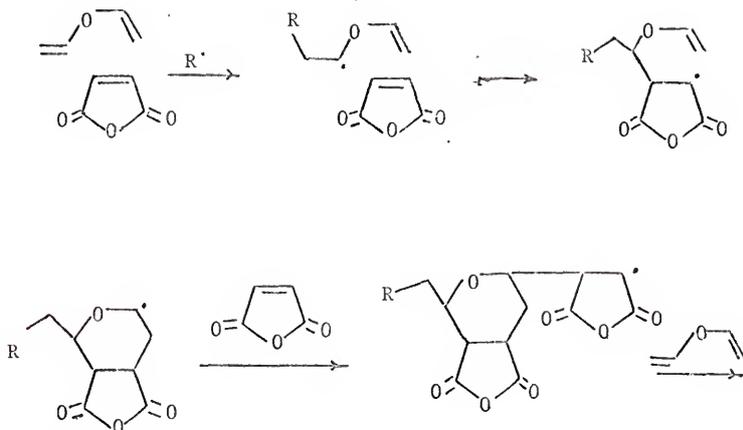
The structure of 4-substituted-1,2,4-triazoline-3,5 diones is very similar to that of the carbon to carbon double bond dienophiles maleic anhydride and N-substituted maleimides, 5. The latter compounds have been utilized extensively as comonomers in copolymerization studies. It was expected, then, "a priori" that these nitrogen analogues of maleic



anhydride and the maleimides would undergo similar copolymerizations with the appropriate electron rich comonomer.

Cyclocopolymerization, originally reported by Butler,<sup>6</sup> has evolved as an extremely important research area in polymer chemistry, not only because of the theoretical significance of the reaction but in the main because some of the cyclocopolymers have been shown to be active anti-tumor agents.<sup>7</sup> Because of this importance, the mechanistic and preparative aspects of cyclocopolymerization have undergone a careful systematic study. The general mechanism proposed was that of an alternating intra-inter molecular propagation<sup>6</sup> as shown below for the divinyl ether-maleic anhydride system which is the most thoroughly studied of all the

cyclocopolymerization systems. Since the initial mechanistic proposal, evidence consistent with the participation of a donor acceptor complex

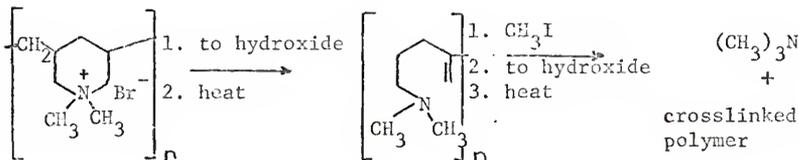


as a comonomer has been presented.<sup>8</sup> More recently the divinyl ether maleic anhydride system has been observed to polymerize thermally in the absence of a free radical initiator<sup>9</sup> and this has been interpreted as additional evidence for the participation of a donor acceptor complex in the copolymerization.

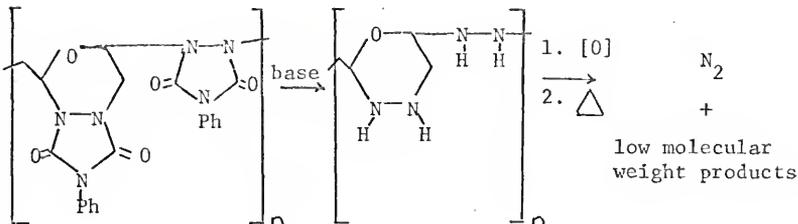
Since 4-substituted-1,2,4-triazoline-3,5-diones are known to be better dienophiles than the usual electron poor comonomers in cyclocopolymerization, it was thought that they might behave as electron acceptors in the presence of electron rich 1,4-dienes and participate in cyclocopolymerization. Furthermore, it seemed a distinct possibility, because of their great reactivity, that a spontaneous cyclocopolymerization might possibly be triggered.

The degradation approach to proving polymer structures is important.

For example, the cyclic structure resulting from the copolymerization of diallyl quaternary ammonium salts was verified by the following degradation procedure.<sup>10</sup>



No such proof of the cyclic structure of the cyclocopolymer systems has been possible to this time. If a 2:1 cyclocopolymer were to form, the unique characteristics of the triazoline dione moiety would offer a convenient handle to chemically probe the polymer structure by the general degradation procedure shown below.

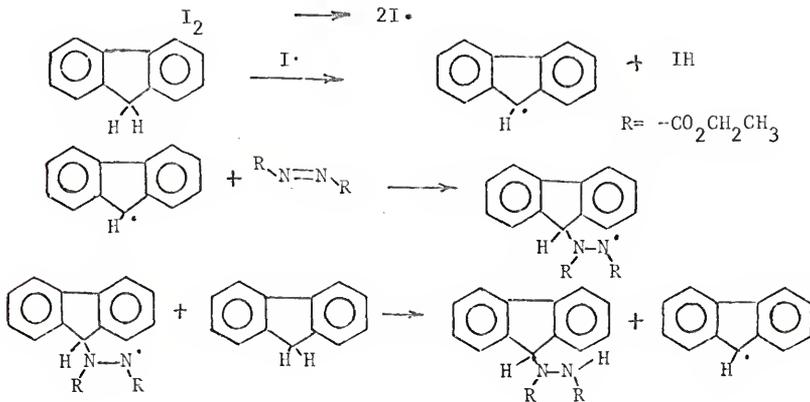


For the preceding reasons, as well as the desire to build new cyclic copolymer structures to be tested as anticancer agents, the behavior of 4-substituted-1,2,4-triazoline-3,5-diones with electron rich olefins was investigated.

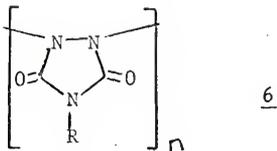
#### Nitrogen backboned polymers

At the commencement of this research no nitrogen backboned polymer had ever been reported. If homopolymerization of an azo dienophile

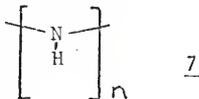
could be effected through the nitrogen to nitrogen double bond, obviously such a polymer with a nitrogen backbone would result. A report by Huisgen<sup>11</sup> of the participation of ethylazobisformate in a substitution reaction with fluorene proceeding by a free radical chain mechanism made a free radical polymerization of such an azo dienophile an attractive possibility.



By envisioning the results of such a successful polymerization of a 4-substituted-1,2,4-triazoline-3,5-dione, one would have at hand structure 6. Since such structures are readily hydrolyzable in strong



base, a polyhydrazine structure, 7, would be distinctly possible. These nitrogen backbone structures might possess practical value as well as, assuredly, possessing theoretical importance. As another



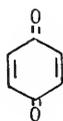
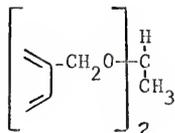
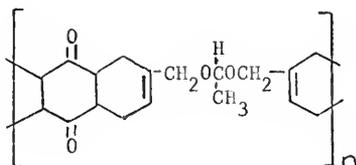
goal of this research, the homopolymerization of 4-substituted-1,2,4-triazolinc-3,5-diones, was investigated.

In the course of this work, Pirkle and Stickler<sup>12</sup> reported the homopolymerization of 4-n-butyl-1,2,4-triazoline-3,5-dione by initiation with visible irradiation. These authors presented strong evidence that the polymer obtained, indeed, possessed a nitrogen backbone.

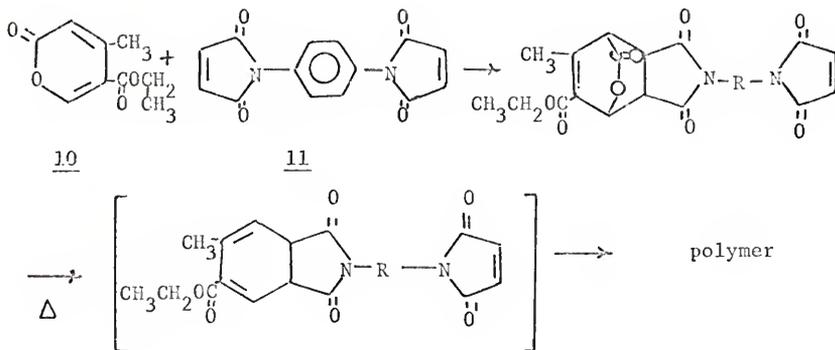
### Diels Alder polymers

Although the number of chemical reactions investigated in organic chemistry is immense, those that have been successfully adapted to yield high polymers are few. Two types of cycloaddition reactions have met with considerable success in producing high polymers, i.e., 1,3-dipolar cycloadditions<sup>13</sup> and Diels Alder reactions.<sup>14</sup>

The Diels Alder reaction has developed into the most profitable application of the use of cycloaddition reactions to form polymers.<sup>14</sup> To adapt the Diels Alder reaction to a polymer forming system whereby the polymer is built up by stepwise Diels Alder cycloadditions requires that the reactants be made difunctional. Two different approaches have been utilized. The first involves the reaction of a bis diene and a bis dienophile, generally referred to as an A-A, B-B system. One example<sup>15</sup> is the reaction of p-benzoquinone, 8, with the acetal prepared from 2-hydroxymethyl-1,3-butadiene and acetaldehyde, 9.

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The second general approach has utilized an A-B monomer or an intramolecular diene, dienophile. The reaction of the substituted  $\alpha$ -pyrone, 10, and p-phenylene bismaleimide, 11, is a good example of this approach.<sup>16</sup>



The main limitation and drawback to the use of the Diels Alder reaction has been the difficulty in obtaining high molecular weight products. In a polymerization propagation that follows step growth kinetics, as is the case in a Diels Alder polymerization,<sup>17</sup> the degree of polymerization  $\overline{DP}$  follows the Carothers equation<sup>18</sup>  $\overline{DP} = 1/1-p$ , where p is the extent of reaction. This means that the reaction must be practically quantitative before a high molecular weight product is obtained. For example a reaction with a 98% conversion only yields a  $\overline{DP}$  of 50 or, in other words, a low average molecular weight.

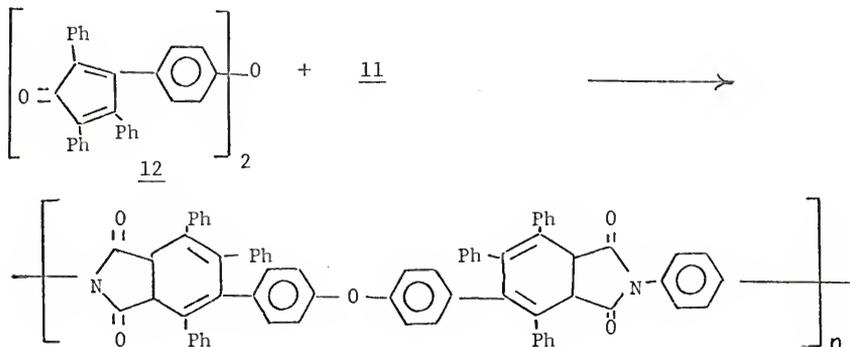
Hence, any stepwise polymerization reaction that is subject to side reactions of any significance will not be suitable for formation of high molecular weight products.

Two main reasons have been put forth for the inability, in most instances, of Diels Alder polymerizations to achieve high molecular weights.<sup>19</sup> The first involves the ease by which the retrodiene

reaction can occur and the second concerns the chain growth of the diene under the reaction conditions. Another complicating factor in some systems has been the precipitation of the rigid ladder type polymer causing a premature termination.<sup>15</sup>

Since the Diels Alder reaction is a thermally catalyzed reaction and these two complicating factors also are enhanced at higher temperatures, it is not surprising that the problem of obtaining high molecular weight has plagued its use in producing high polymers.

Stille<sup>20</sup> and coworkers have successfully circumvented the retrodiene reaction by employing bis dienes such as bis  $\alpha$ -pyrones and bis cyclopentadienones that lose carbon dioxide or carbon monoxide respectively and hence prevent the degradative retrodiene reaction from occurring. An example has been the successful use of 3,3'-(oxydi-p-phenylene)bis(2,4,5-triphenylcyclopentadienone), 12, and p-phenylene bismaleimide, 11.<sup>20</sup> A polymer with an intrinsic viscosity of 1.01 was obtained in four hours in refluxing 1,2,4-trichlorobenzene.



Another possible route to circumvent the bothersome side reactions would be to employ extremely reactive reactants that would not need to

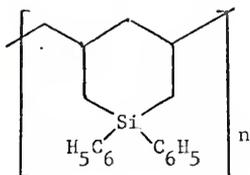
be heated in order to obtain the necessary high conversions. Obviously, a bis 1,2,4-triazoline-3,5-dione would be expected to serve in this capacity because of its fantastic reactivity. Hence another objective of this research was the synthesis, and polymerization with bis dienes, of such bis dienophiles.

### B. Triple Strand Polymer Model Compound Studies

#### Thermal stability of ladder polymers

The synthesis and study of thermally stable polymers have been extremely active areas of polymer chemistry research in recent years. The extensive accounts of such research recorded in the chemical literature attests to the theoretical and practical importance of this work. No attempts will be made to review these accounts since a recent book<sup>21</sup> and several reviews<sup>22,23,24</sup> are readily available.

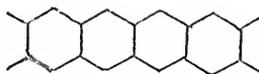
Physical polymer properties have generally been found to be related to the molecular weight of the polymer. These structure-property correlations have established that polymers with ladder or double strand structures, 14, possess extremely high thermal stability.<sup>23</sup> For example polydiallyldiphenylsilane, having structure 13 was observed to have enhanced thermal stability over its non-cyclic counterpart



13

prepared from the monoallyl derivative.<sup>25</sup> The reason advanced for the thermal stability of such cyclic structures is that thermal bond

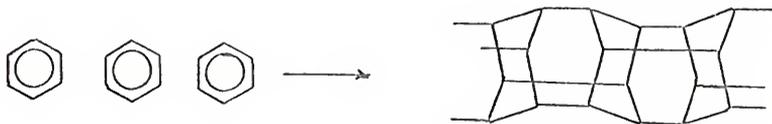
cleavage which occurs within the cyclic polymer repeat units of the backbone does not lead to a lower molecular weight polymer. It is obvious that thermal bond cleavage in the non-cyclic structures results in a lower molecular weight as depicted in 14a and 14b.

14a14b

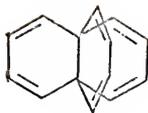
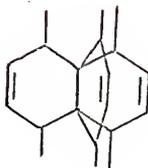
Therefore one goal that the polymer architect has striven for in the design of materials possessing thermal stability has been the synthesis of ladder or double strand polymers. Needless to say, many different researchers have been successful in using the double strand polymer concept in preparing materials resistant to thermal breakdown.

#### Possible triple strand polymers

As an extension of the ladder polymer concept of thermal stability a triple strand polymer would be expected to possess thermal properties reflected from a structure that requires three bond cleavages per ring to cause a decrease in molecular weight. Two possible approaches to constructing such a polymeric species are: 1) a formation of a tubular polycyclohexane, 15, from a triply initiated chain reaction of benzene

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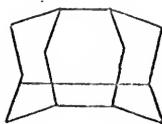
and 2) a triple 1,4-polymerization of a monomer such as 16 to yield structure 17.

1617

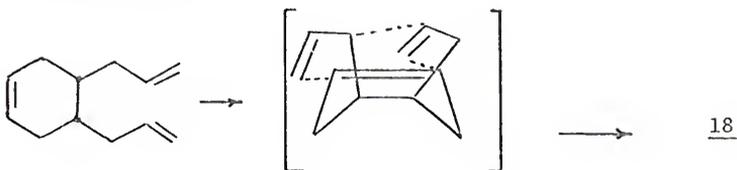
### Model compound studies

Generally, one of the objectives of this research was the preparation and studies of model compounds related to these two possible routes envisioned to triple strand polymers.

Much effort has been extended in the attempted synthesis of tetracyclo[4.4.0.1<sup>3,9</sup>.1<sup>4,8</sup>]dodecane, 18, the repeat unit of the tubular polycyclohexane polymer.

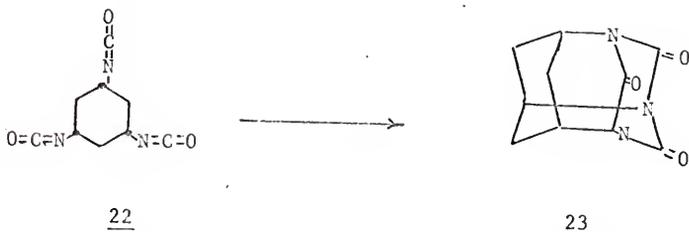
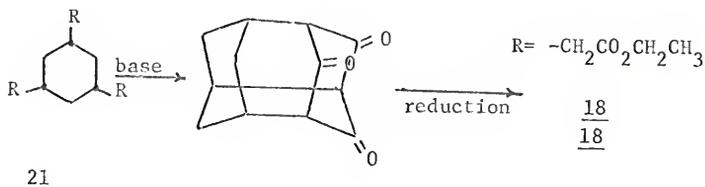
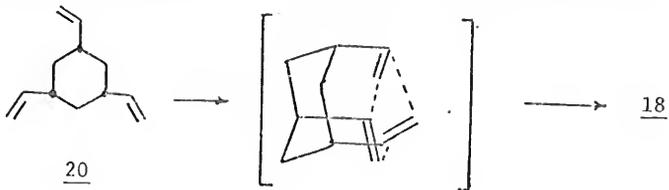
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The first approach has involved the homo Diels Alder reaction of cis 4,5-diallylcyclohexene derivatives, 19.<sup>26a</sup> To date this approach has not been successful.

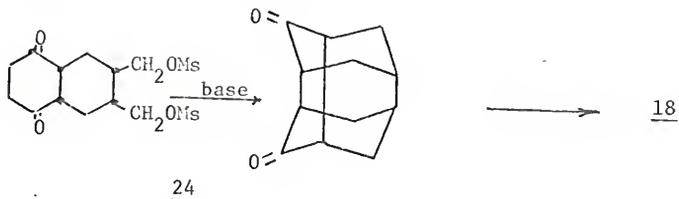
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The second approach has utilized 1,3,5-trisubstituted cyclohexane

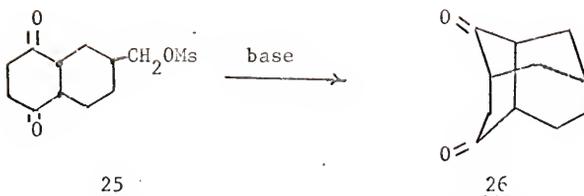
derivatives 20 and 21. The tri ester 21 has been successfully prepared and failed to undergo the desired cyclization to 18.<sup>26b</sup> A compound, which would lead to a nitrogen analogue of 18, 22, has been successfully prepared but also failed to yield the cyclic structure 23.<sup>27</sup>



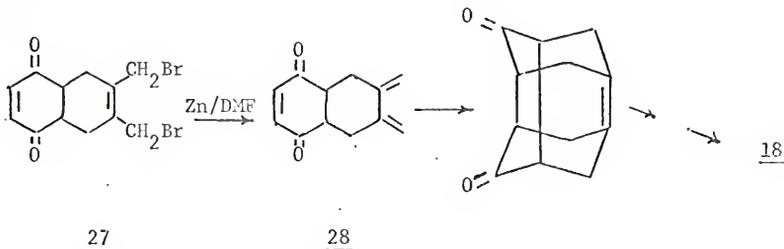
The synthesis of compounds such as 24, which are functionally capable of undergoing an intramolecular base catalyzed cyclization, is the basis of the third approach to 18. One objective of this work



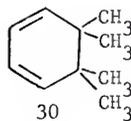
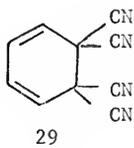
was the preparation of compound 24, and other related structures as 25, and cyclization of them to their respective cage structures 26.



A fourth approach to 18, which was also studied as a part of this research, was the possible intramolecular Diels Alder reaction of 28 to 18. A route to 28 was envisioned by the well documented 1,4-elimination of bromine by zinc in dimethylformamide<sup>28</sup> of 27,<sup>29</sup> the Diels Alder adduct of p-benzoquinone and 2,3-di(bromoethyl)-1,3-butadiene.



In order for a monomer like 16 to be polymerizable by a triple 1,4-initiation it is immediately obvious that monomers such as 29 and 30, which are steric models for 16, would have to be subject to a 1,4-polymerization. Hence another objective of this research was the synthesis of 5,5,6,6-tetrasubstituted cyclohexadienes like 29 and 30 and the study of their polymerizations.



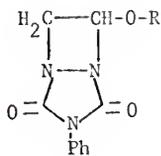
## CHAPTER II

### Polymerization Studies of 4-Substituted-1,2,4-triazoline-3,5-diones

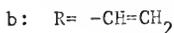
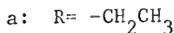
#### A. Copolymerization of Ethyl Vinyl Ether and Divinyl Ether with 4-Phenyl-1,2,4-triazoline-3,5-dione

##### Structure of the copolymers

4-Phenyl-1,2,4-triazoline-3,5-dione (PhTD), 3, spontaneously copolymerized with ethyl vinyl ether (EVE) in methylene chloride solution at room temperature and the product was shown to have a 1:1 composition by elemental analysis and nmr analysis. The copolymer was found exclusive of any 2+2 cycloadduct (1,2-diazetidene), 31a.

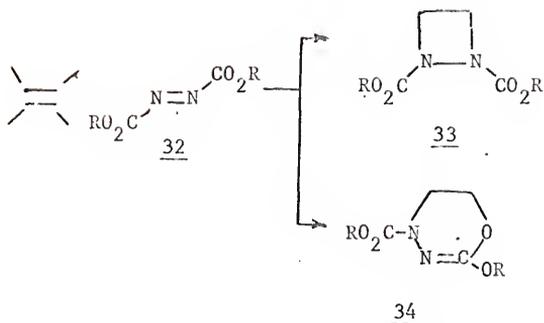


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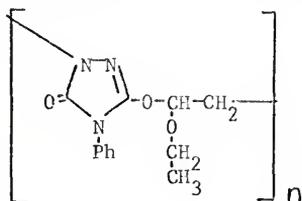
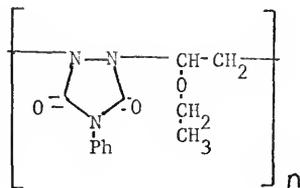


Cycloadditions of ethyl azobisformate, 32, a similar azo dienophile, have been shown to occur through both nitrogens to give 1,2-diazetidines, 33, or through one nitrogen and one carbonyl oxygen to give oxadiazines, 34. Therefore, structure 35, where propagation occurred through one nitrogen and one carbonyl oxygen, and structure 36, where propagation takes place through the nitrogen to nitrogen bond, appeared to be the most likely candidates for the structure of the copolymer.

The nmr spectrum (Fig. 1) did not distinguish between the two



possibilities since the observed resonance signals were consistent with either structure. The signals were  $\delta 7.50$  (broad, aromatic hydrogens, 5),  $\delta 6.05$  (broad, hydrogen adjacent to two electronegative atoms, 1),  $\delta 3.90$  (broad, methylene hydrogens of ether, 4) and  $\delta 1.20$  (broad, methyl hydrogens of ether, 3).

3536

The infrared data, however, indicated that 35 was the predominant repeat unit of the copolymer structure. A strong  $1610 \text{ cm.}^{-1}$  absorbance was observed and it was assigned to the  $-\text{C}=\text{N}-$  chromophore which is only present in 35. Oxadiazine structures like 34 have exhibited absorbances in the  $1630\text{-}1680 \text{ cm.}^{-1}$  region and they were assigned to the  $-\text{C}=\text{N}-$  chromophore.<sup>30</sup> A recent report on the infrared spectrum of N-cyclohexylacrylaldimine, 37, has assigned an observed  $1608 \text{ cm.}^{-1}$  band to the  $-\text{C}=\text{N}-$  chromophore.<sup>31</sup> Stickler and Pirkle<sup>12</sup> synthesized

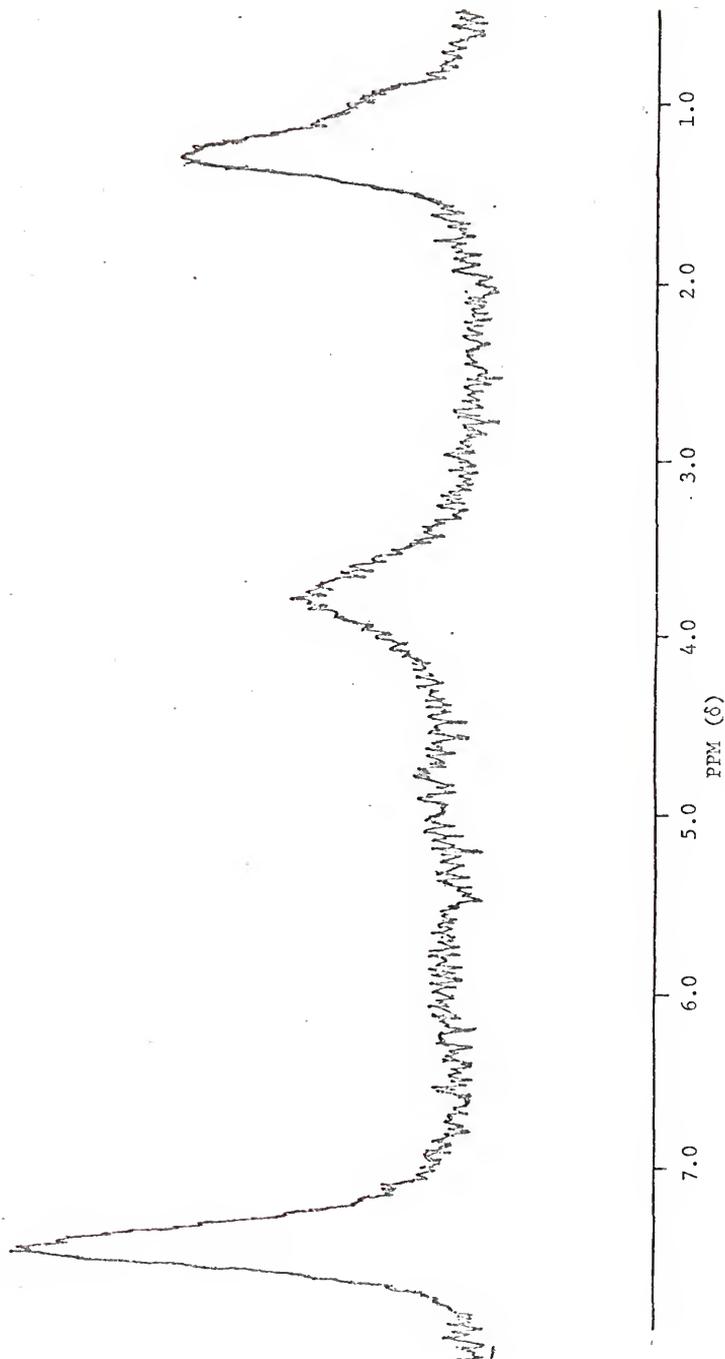
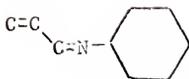
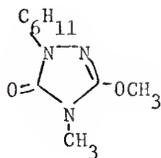


Figure 1. Nmr spectrum of the copolymer of ethyl vinyl ether and 4-phenyl-1,2,4-triazoline-3,5-dione.

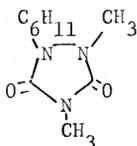


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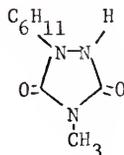
38, 39 and 40 as model compounds in a recent study of the homopolymerization of triazolone diones. A strong  $1605\text{ cm.}^{-1}$  absorbance was observed in 38 and not in 39 and 40.



38



39



40

Neither PhTD nor its precursor 4-phenyl urazole had an infrared absorbance in the  $1610\text{ cm.}^{-1}$  region. This information, along with that obtained from the model compounds, appears as solid evidence for the assignment of 35 as the predominant repeat unit of the copolymer.

In contrast to the EVE system, divinyl ether (DVE) and PhTD were observed to form a mixture of copolymer and an adduct at room temperature in methylene chloride. When the reaction was done at  $60^\circ\text{C}$  only copolymer was isolated.

The adduct from the room temperature reaction was isolated in pure form and was assigned as the 1,2-diazetidone, 3-phenyl-6-vinyloxy-1,3,5-triazabicyclo[3.2.0]hepta-2,4-dione, 31b. The infrared spectrum gave no  $1610\text{ cm.}^{-1}$  absorbance, but gave strong vinyl ether absorbances at  $1645\text{ cm.}^{-1}$  and  $1625\text{ cm.}^{-1}$ . The nmr (Fig. 2) spectrum gave resonance

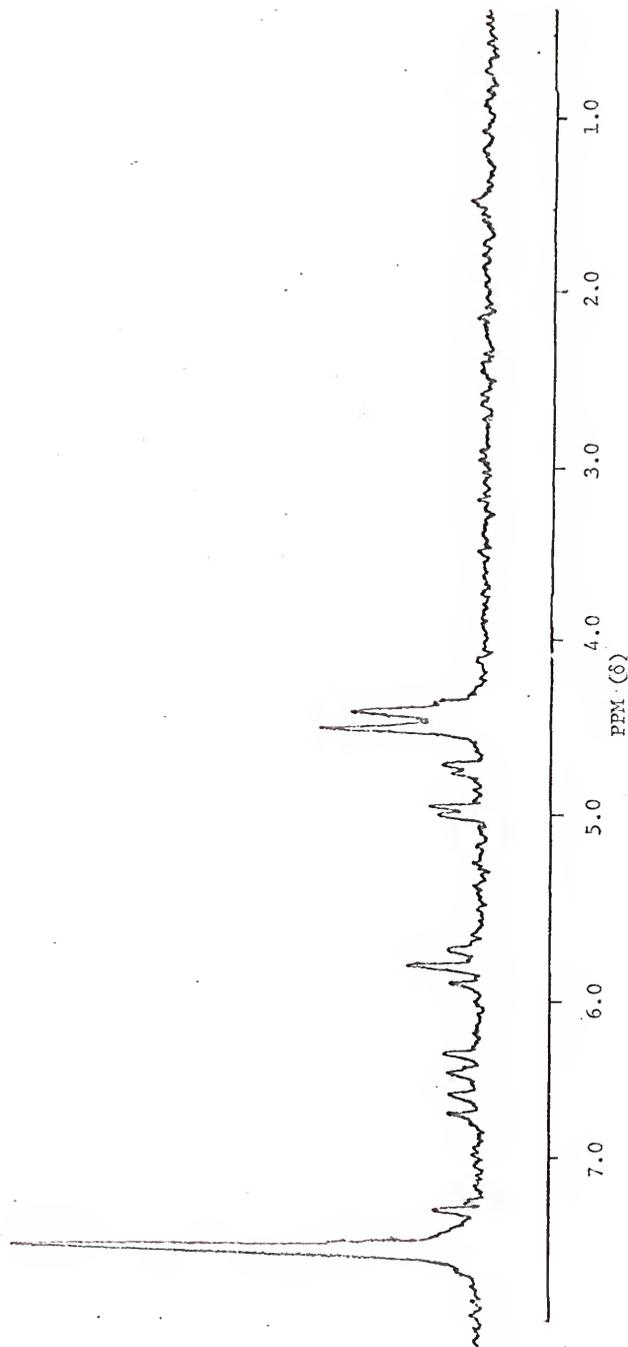
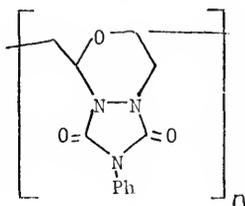
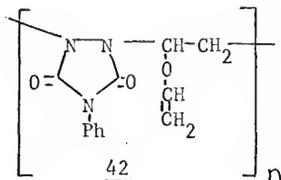
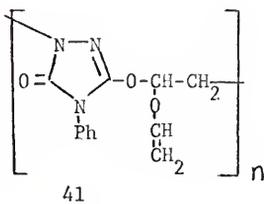


Figure 2. Nmr spectrum of 3-phenyl-6-vinyloxy-1,3,5-triazabicyclo[3.2.0]hepta-2,4-dione.

signals at  $\delta 7.40$  (singlet, aromatic hydrogens, 5),  $\delta 6.60$  (quartet, vinyl hydrogen, 1),  $\delta 5.90$  (triplet, hydrogen next to vinyloxy on ring, 1),  $\delta 4.50$  (multiplet, vinylic and ring methylene hydrogens, 4). The mass spectrum yielded the correct molecular ion and the elemental analysis agreed with the calculated value.

On warming an unpurified mixture of polymer and adduct to  $60^\circ\text{C}$ , a ring opening polymerization occurred. This was noted by the disappearance of the  $\delta 5.90$  triplet in the nmr spectrum and the formation of a product which gave identical spectral data as the original  $60^\circ\text{C}$  copolymer.

An elemental analysis of the copolymer was indicative of a 1:1 structure and for such a copolymer three structures were probable. The first two, 41 and 42, were analogous to the EVE case in which only one double bond is consumed and the third, 43, was preceded by cyclo-copolymerization in which both double bonds are consumed.



On the basis of spectroscopic and chemical evidence, repeat unit 41 appeared to predominate. First, the absence of upfield resonances in the nmr spectrum indicated that there were no methylene units flanked by saturated carbon atoms. Since a requirement for the cyclic structure 43 would be upfield resonances, this structure was eliminated. The resonance signals observed (Fig. 3),  $\delta 7.48$  (broad, aromatic hydrogens, 5),  $\delta 6.30$  (broad, vinylic hydrogen and hydrogen adjacent to two heteroatoms, 2) and  $\delta 4.20$  (broad, methylene and vinyl hydrogens, 4), were consistent with both structures 41 and 42.

The infrared spectrum of the copolymers, as in the EVE copolymers, showed a strong  $1610 \text{ cm.}^{-1}$  band and this was assigned to the  $-\text{C}=\text{N}-$  unit. Also present in the infrared spectrum were bands at  $1640 \text{ cm.}^{-1}$  and  $860 \text{ cm.}^{-1}$  due to the vinyl ether chromophore.<sup>32,33</sup>

As insurance that the  $1610 \text{ cm.}^{-1}$  band was not associated with the aromatic moiety, a copolymer of DVE and 4-methyl-1,2,4-triazoline-3,5-dione was prepared. This copolymer also exhibited the strong  $1610 \text{ cm.}^{-1}$  absorbance. The nmr spectrum of this copolymer is given in Fig. 4.

Catalytic hydrogenation of the DVE copolymer over palladium on alumina at atmospheric pressure resulted in the absorption of the theoretical amount of hydrogen for a structure like 41 or 42. The resulting material exhibited a new  $2770 \text{ cm.}^{-1}$  band due to the saturated carbon hydrogen stretch, and loss of  $1640 \text{ cm.}^{-1}$  and  $860 \text{ cm.}^{-1}$  bands of the pendant vinyl group in the infrared spectrum. The  $1610 \text{ cm.}^{-1}$  band also disappeared. New resonances appeared in the nmr spectrum at  $\delta 3.90$  and  $\delta 1.20$ . These signals had the same chemical shifts as the ethyl protons in the EVE copolymers.

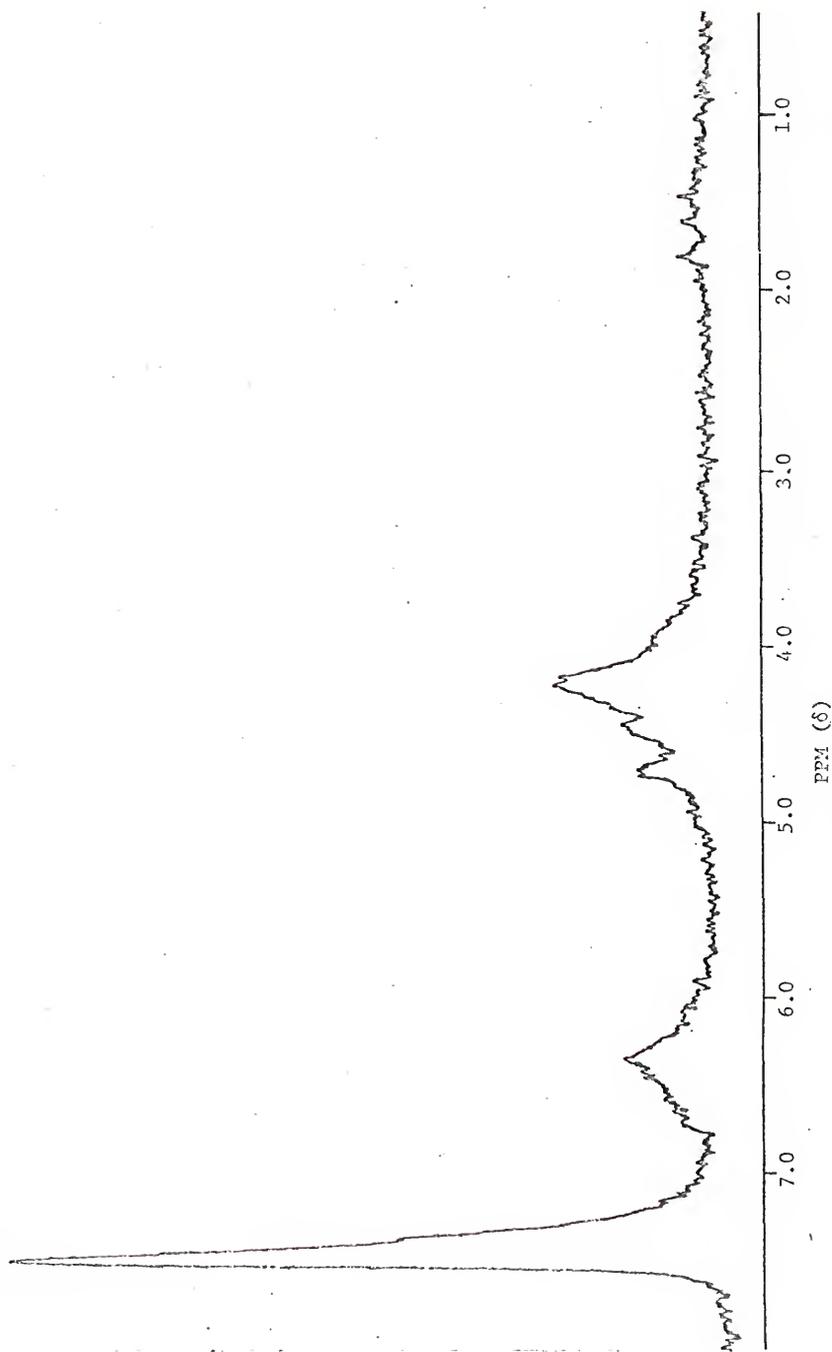


Figure 3. Nmr spectrum of the copolymer of divinyl ether and 4-phenyl-1,2,4-triazoline-3,5-dione.

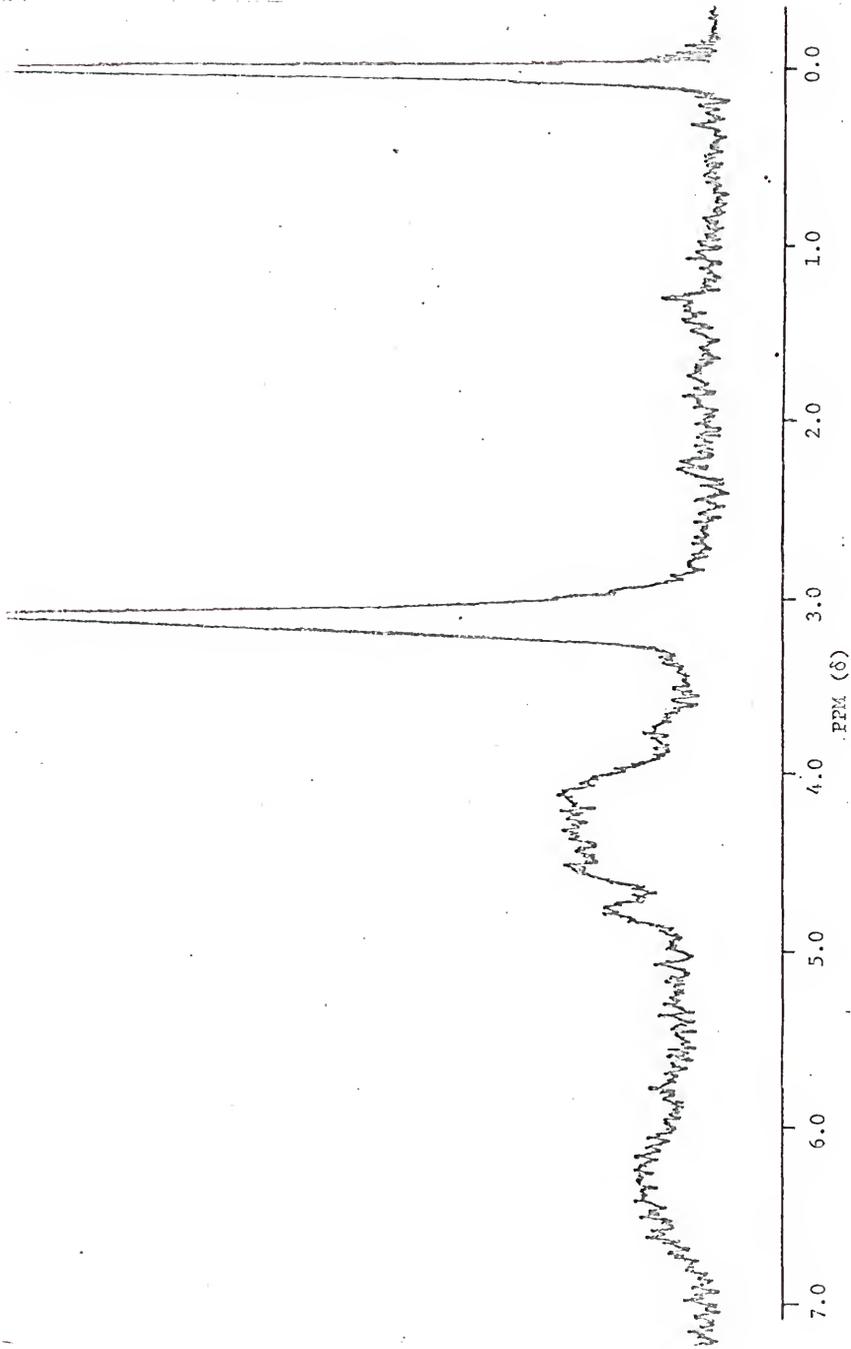


Figure 4. Nmr spectrum of the copolymer of divinyl ether and 4-methyl-1,2,4-triazoline-3,5-dione.

One discrepancy in the hydrogenation results was the disappearance of the  $1610 \text{ cm.}^{-1}$  band in the infrared spectrum. This was thought to be due to an isomerization over the alumina catalyst for the following reasons. The  $-\text{C}=\text{N}-$  linkage has been shown to be resistant to catalytic hydrogenation<sup>30</sup> when it appeared in oxadiazine structures like 34. The catalytic hydrogenation of the EVE copolymer was carried out as a control and although no hydrogen was absorbed, the loss of the  $1610 \text{ cm.}^{-1}$  band was noted. A plausible explanation is that the catalyst promotes an isomerization from structure 35 to the structure bonded through both nitrogens, 34. If this were the case, a decrease in the molecular weight of the copolymers should be observed since such a change would require bond breaking and then bond reformation. This was exactly what was observed as a DVE-PhTD copolymer had a molecular weight of 1590 before hydrogenation and 490 afterwards. An attempt to use palladium on carbon as the catalyst only gave a partial hydrogenation.

#### Physical characteristics of the copolymer

The copolymers of EVE-PhTD and DVE-PhTD were white, highly electrostatic solids which were soluble in most organic polar solvents. Maximum number average molecular weights ( $\bar{M}_n$ ) were normally in the 1000 to 3000 range and were measured by vapor pressure osmometry (VPO) in acetone solution. The polymeric materials were low melting and both copolymers softened around  $100\text{--}110^\circ\text{C}$ .

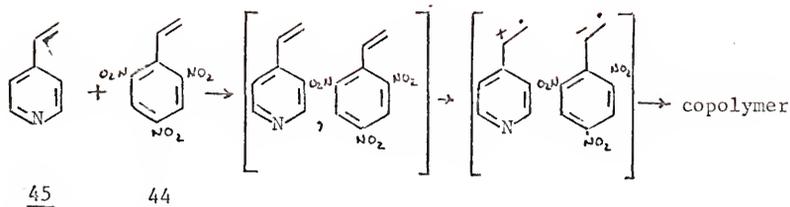
A molecular weight distribution ( $\bar{M}_w/\bar{M}_n$ ) of 3.36 was obtained for one DVE-PhTD sample from gel permeation chromatography (GPC). The determination was made in dimethylformamide and a calculation of the

$\bar{M}_n$  from the GPC trace gave a value of 2500 versus 2750 from the VPO. An attempted GPC analysis of an EVE-PhTD copolymer was unsuccessful due to what was believed to be a degradation of the polymer in the highly polar solvent.

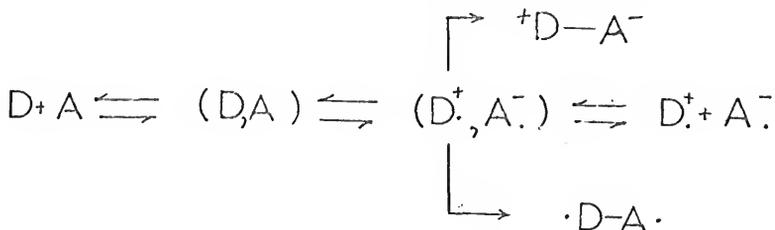
#### Spontaneous copolymerizations

Since the copolymerization of EVE and PhTD was certainly a spontaneous copolymerization, the literature was reviewed to obtain examples of previous spontaneous copolymerizations. Spontaneous copolymerizations are differentiated in this discussion from other types of photoinitiated spontaneous copolymerizations<sup>34</sup> and Lewis acid catalyzed spontaneous copolymerizations<sup>35</sup> by defining a spontaneous copolymerization as one that occurs when two olefinic monomers are mixed in bulk or in solution at room temperature or lower with no additional initiator involved.

All observations of spontaneous copolymerizations reported in the literature have involved an olefinic monomer pair in which one partner was electron rich and the other electron poor. Apparently, the first report of such a copolymerization was disclosed in a Canadian patent authored by Miller and Gilbert.<sup>36</sup> They reported the spontaneous copolymerization of vinylidene cyanide and alkyl vinyl ethers. No mechanistic interpretation of their results appeared. Yang and Gaoni<sup>37</sup> have prepared 1:1 copolymers from the spontaneous reaction of trinitrostyrene, 44, as the acceptor or electron poor olefin and either 4-vinyl pyridine, 45, 2-vinyl pyridine or p-dimethylaminostyrene as the donor or electron rich olefin. The authors suggested that the monomers formed an initial donor acceptor complex



which initiated the radical copolymerization of the monomers. Kosower<sup>38</sup> has suggested that the copolymerization is initiated by the formation of a ground state donor acceptor complex which goes to an excited ion pair state which then copolymerizes the surrounding ground state donor acceptor complexes according to the equation shown above. Such a mechanism is designated by Kosower to be a "T-Class Reaction" in which the electron transfer in the complex is brought about by thermal energy. The general equation<sup>38</sup> for this reaction,



proposed by Kosower, includes formation of a ground state complex (D,A) which experiences a thermally induced electron transfer to the excited ion pair form (D<sup>+</sup>, A<sup>-</sup>) and then can go to products or can disassociate to the separate ion pair excited state.

Butler and Sharpe<sup>9,39</sup> have reported two other systems which fit the definition of spontaneous copolymerization. One system in which this type reaction occurs is the cyclocopolymerization of maleic

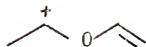
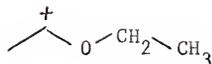
anhydride and DVE,<sup>9</sup> and the other is the cyclocopolymerization of divinyl sulfone and DVE.<sup>39</sup> Both systems are believed to form a donor acceptor complex which then goes to an excited state, couples to form a diradical and thus initiates the copolymerization of either complexed or uncomplexed comonomers.

#### Mechanism of EVE and DVE copolymerizations

PhTD has been shown to undergo 2+2 cycloadditions with both indene and p-dioxene.<sup>30</sup> The cycloaddition with indene has been shown to involve a dipolar intermediate since this 1,4-dipolar species has been trapped with water. p-Dioxene formed the expected 2+2 adduct plus a lot of discarded polymeric material.

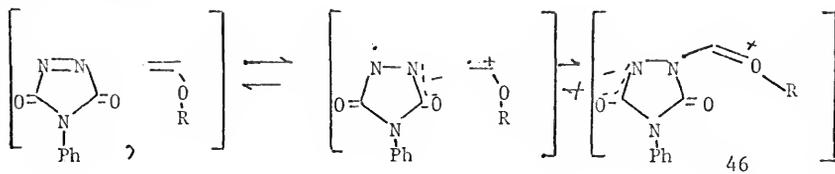
In light of these results and in light of the polymer structures, the most plausible propagation mechanism is believed to be the initial formation of a stable 1,4-dipole. This intermediate, in the EVE system, then went directly to copolymer, while in the DVE system it formed the 1,2-diazetidene 31b and copolymer. At 60°C, the diazetidine is proposed to open to the initial 1,4-dipole and couple intermolecularly to form the copolymer 41.

The difference in behavior between the EVE and DVE systems can be rationalized in terms of the stabilities of the positive centers of the respective 1,4-dipoles. The acid hydrolysis of EVE has been observed to be 350 times faster than the acid hydrolysis of DVE.<sup>40</sup> This difference is due to the stability of the corresponding oxonium ion intermediates, 47 versus 48. The same positive center stabilization occurs in the two 1,4-dipoles. Therefore it is believed that the more stable 1,4-dipole (EVE) has a more pronounced dipolar character and

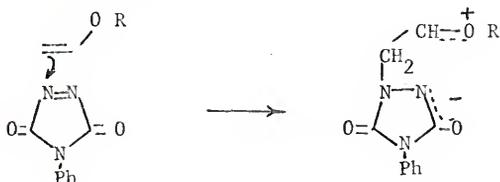
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links intermolecularly, while the energetically higher DVE dipole closes to the strained 1,2-diazetidene.

The exact nature of the transition state leading to the 1,4-dipole is not known. Kosower<sup>38</sup> has proposed that 2+2 cycloadditions which are dipolar in nature are "T Class Reactions" and they go through an excited charge transfer complex which then couples to the corresponding dipolar species. This dipole then closes to a four membered ring. The formation of the vinyl ether-PhTD intermediate 46 by this pathway is shown below.



The other possibility is an electrophilic attack of the electron poor PhTD on the electron rich olefin in which no complex is required to arrive at 46, i.e.,

46

The first observation that is consistent with the postulated 1,4-dipole is the non-cyclic structure of the DVE-PhTD copolymer. A diradical intermediate would have been expected to cyclize.<sup>6</sup> However, cyclization of the 1,4-dipole 46 would be highly unlikely since vinyl ethers are known to be resistant to anionic attack.

Copolymerizations of the two vinyl ethers with PhTD were found to be insensitive to a free radical inhibitor and a free radical initiator. The free radical initiator azobisisobutyronitrile (AIBN) had no effect on the molecular weight of the EVE copolymers (Table 1, exp. 11). The copolymer from the DVE case showed some increase in molecular weight, which some random coupling of pendant vinyl groups could easily explain (Table 2, exp. 3). The known free radical inhibitor, *m*-dinitrobenzene, had no effect on the copolymerization of DVE (Table 2, exp. 6).

An attempt to free radically copolymerize DVE and PhTD at -45°C by photolytic decomposition of benzoyl peroxide only resulted in a product identical to the ambient copolymerizations. Since the conversion was extremely low, the product was probably the result of a slow thermal reaction, because at the same temperature the same product was obtained without benzoyl peroxide.

In an attempt to exclude moisture from the system, a copolymerization of DVE and PhTD was effected under more rigorous conditions than the normal trials. It was felt that since water would terminate the dipolar step-growing chain that the elimination of moisture would lead to a higher molecular weight copolymer. The dry conditions included flame drying of glassware, predrying of monomers and transferring monomers and solvents in an inert and dry atmosphere. Although

TABLE I. COPOLYMERIZATIONS OF EVE AND PhTD

Exp. No.	Reaction Solvent	Temp. °C	Time (hr.)	Product and conversion	$\bar{M}_n^a$	IR <sup>b</sup> 1610 cm. <sup>-1</sup>
1	CH <sub>2</sub> Cl <sub>2</sub>	25	0.5	87.5 1:1 copolymer	1660	s
2	CH <sub>2</sub> Cl <sub>2</sub>	25	0.03	52.0 1:1 copolymer	410	s
3	CH <sub>2</sub> Cl <sub>2</sub>	25	0.25	75.7 1:1 copolymer	670	s
4	CH <sub>2</sub> Cl <sub>2</sub>	25	1.0	-	1175	s
5	CH <sub>2</sub> Cl <sub>2</sub>	25	4.0	-	1340	s
6	CH <sub>2</sub> Cl <sub>2</sub>	25	12.0	-	1260	m
7	CH <sub>2</sub> Cl <sub>2</sub>	25	24.0	77.0 1:1 copolymer	437	-
8 <sup>c</sup>	CH <sub>2</sub> Cl <sub>2</sub>	60	24.0	-	-	-
9 <sup>d</sup>	-	-	-	-	-	-
10	CH <sub>2</sub> Cl <sub>2</sub>	60	24.0	77.4 1:1 copolymer	820	-
11 <sup>e</sup>	CH <sub>2</sub> Cl <sub>2</sub>	60	24.0	78.2 1:1 copolymer	840	-

TABLE I (continued).

Exp. No.	Reaction Solvent	Conditions Temp. °C	Time (hr.)	Product and Conversion	$\bar{M}_n^a$	IR <sup>b</sup> 1610 cm. <sup>-1</sup>
12	DMF	25	0.5	50.3 1:1 copolymer	3900	s
13 <sup>f</sup>	THF	25	0.5	85.6 1:1 copolymer	940	s
14	THF	25	0.5	67.0 1:1 copolymer	2040	s
15	CH <sub>2</sub> Cl <sub>2</sub>	60	118	71.5 1:1 copolymer	923	w
16	CH <sub>2</sub> Cl <sub>2</sub>	60	166	77.5 1:1 copolymer	1120	w
17	CH <sub>2</sub> Cl <sub>2</sub>	60	211	76.2 1:1 copolymer	970	w

<sup>a</sup>VPO-acetate solution.

<sup>b</sup>s, (strong); m, (medium); w, (weak); -, (not present).

<sup>c</sup>Sample 1 dissolved and heated.

<sup>d</sup>Sample 1 hydrogenated.

<sup>e</sup>0.5 wt. % AIBN added.

<sup>f</sup>10 mol. % NaPh<sub>4</sub>B added.

TABLE 2. COPOLYMERIZATIONS OF DYE AND PHTD

Exp. No.	Reaction Solvent	Temp. °C	Conditions Time (hr.)	Product and Conversion	$\bar{M}_n$	IR <sup>b</sup> (cm. <sup>-1</sup> )
1	CH <sub>2</sub> Cl <sub>2</sub>	25	0.5	77.5 1:1 copolymer	450	1610 w m 860 m
2	CH <sub>2</sub> Cl <sub>2</sub>	60	24	77.8 1:1 copolymer	860	s m
3 <sup>c</sup>	CH <sub>2</sub> Cl <sub>2</sub>	60	24	80.8 1:1 copolymer	1590	s m
4	CH <sub>2</sub> Cl <sub>2</sub>	60	120	84.5 1:1 copolymer	3130	s m
5 <sup>d</sup>	CH <sub>2</sub> Cl <sub>2</sub>	60	24	86.0 1:1 copolymer	2540	s m m
6 <sup>e</sup>	CH <sub>2</sub> Cl <sub>2</sub>	60	24	65.8 1:1 copolymer	2130	s m m
7 <sup>d</sup>	CH <sub>2</sub> Cl <sub>2</sub>	60	120	85.8 1:1 copolymer	2760	s m m
8	CH <sub>2</sub> Cl <sub>2</sub>	25	22	85.7 1:1 copolymer and adduct	-	w m m
9	Dioxane	60	24	66.4 1:1 copolymer	1330	s m m

TABLE 2 (continued).

Exp. No.	Solvent	Reaction Temp. °C	Conditions Time (hr.)	Product and Conversion	$\bar{M}_n^a$	IR <sup>b</sup> (cm. <sup>-1</sup> )
10	DMF	60	24	31.2	-	1610 860
11 <sup>c</sup>	DMF	60	24	19.4	-	-
12	CH <sub>3</sub> CN	60	24	80.0	820	-
13	CH <sub>3</sub> CN	25	0.5	73.8	590	-
14 <sup>f</sup>	-	-	-	-	490	-

<sup>a</sup>VPO-acetate solution.

<sup>b</sup>s, (strong); m, (medium); w, (weak); -, (not present).

<sup>c</sup>0.5 wt. % AIBN added.

<sup>d</sup>Dry conditions.

<sup>e</sup>1 m-dinitrobenzene added.

<sup>f</sup>Polymer 6 hydrogenated.

a higher molecular weight material was obtained than in the normal trials, a control in which the glassware was not treated yielded even higher molecular weights (Table 2, exp. 7 vs. exp. 5).

Szwarc<sup>41</sup> has discussed in great detail the effect of trace amounts of water on ionic polymerizations and the conditions needed to conduct polymerizations in the absence of water and other impurities. Since the purification procedures needed for such experiments required special techniques and equipment, this approach was abandoned.

Surprisingly, the EVE-PhTD copolymerization conducted at 60°C resulted in a lower molecular weight product than in the room temperature trials. The 1610 cm.<sup>-1</sup> band in the infrared spectrum of the copolymer was absent, although the nmr spectrum was the same. The elemental analysis remained consistent with a 1:1 copolymer. The room temperature copolymerization was repeated for a 24 hour period and a molecular weight of 430 was obtained compared to 2440 for a thirty minute polymerization time. The 1610 cm.<sup>-1</sup> infrared band was absent in the product from the 24 hour run. A study of molecular weight versus time was conducted for the room temperature copolymerization and the results are shown in Fig. 5. A decrease in intensity of the 1610 cm.<sup>-1</sup> band paralleled the decrease in molecular weight. Table 1 gives the molecular weight versus time in tabular form. Copolymerizations conducted at 60°C for extended times showed a rebuilding of the chain length (Table 1, exps. 15, 16 and 17).

These results can easily be accommodated by the proposed copolymerization mechanism. The decrease in molecular weight is believed to result from a depolymerization back to the 1,4-dipole structure and then recombination through both nitrogens to give structure 36,

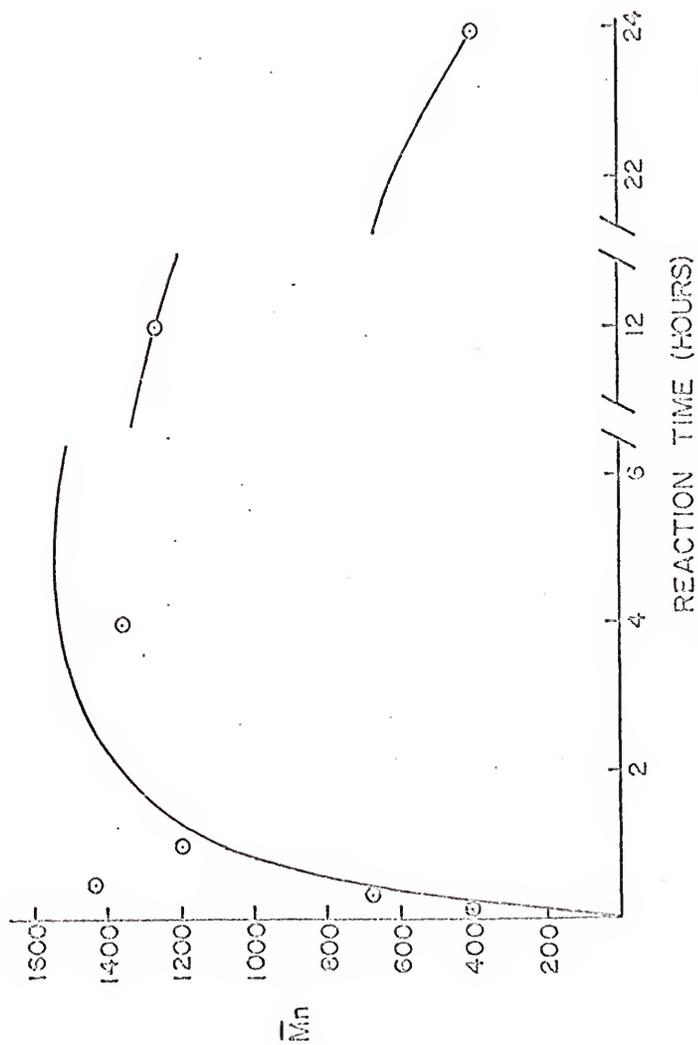


Figure 5. Plot of  $\bar{M}_n$  versus reaction time for EVE-PhTD in  $\text{CH}_2\text{Cl}_2$  at  $25^\circ\text{C}$ .

possibly a more stable structure. The DVE copolymer once formed was observed to be thermally stable at 60°C as noted by no decrease in molecular weight or decrease in the intensity of the 1610  $\text{cm}^{-1}$  absorbance. Since the activation energy to reformation of the vinyloxy 1,4-dipole would be expected to be higher than the ethyloxy because of the difference in stability of the positive center, this result is also consistent with the polymerization mechanism.

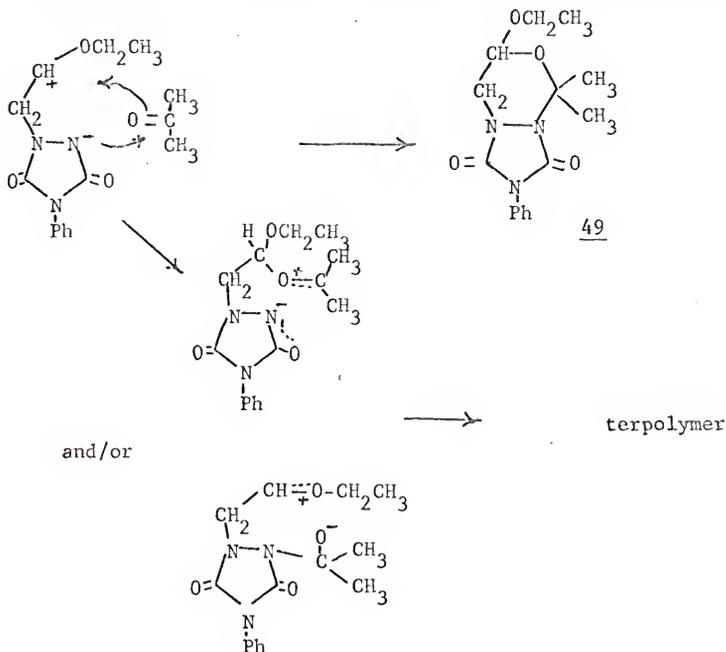
It is generally thought that dipolar reactions should show pronounced solvent effects. The results of a solvent study of the reaction rate are shown in Table 3. This study was conducted by observing the disappearance of the band in the visible spectrum of the PhTD. No pronounced rate differences were observed in going from the fairly non-polar solvent benzene to the strongly polar solvents dimethylformamide and acetonitrile. There was a distinctive rate difference between EVE and DVE. This was probably another manifestation of the difference in the stability of the positive center of the dipole.

Gompper<sup>42</sup> has recently reviewed cycloaddition reactions involving polar intermediates. He cites two cases in which significant solvent effects may not accompany such reactions. The first case involves reactants that are highly polar and thus experience significant solvation effects to effectively negate the solvation of the intermediate. The second case involves a system where the energies of activation of the first step and the second step are nearly the same and a change in solvent changes the rate determining step, but not necessarily the overall reaction rate.

Since both monomers are highly polar molecules, it is reasonable that they could experience enough ground state solvation to effectively cause the solvation of the intermediate to be undetectable.

One criterion which can conclusively demonstrate the presence of a dipolar intermediate is the interception of this intermediate before cycloproduct formation.<sup>42</sup> When EVE and PhTD were reacted at room temperature in acetone 3-oxa-2,2-dimethyl-4-ethoxy-8-phenyl-1,6,8-triazabicyclo[4.3.0]-nona-7,9-dione, 49, was formed in 42% yield. Along with this product was formed a copolymer which from the nmr spectrum appeared to have about 12% acetone incorporated.

This result is believed to be conclusive evidence for the existence for the 1,4-dipole since the product arises from the interception of the 1,4-dipole with the weakly dipolarophilic acetone. Apparently some



of the intercepted dipole did not close to the six membered adduct but proceeded to link intermolecularly with other similar segments or with other 1,4-dipoles to form the copolymer containing about 12% acetone.

TABLE 3. FIRST ORDER RATE CONSTANTS IN PhTD AT 25°C

A. Ethyl Vinyl Ether-PhTD<sup>a</sup>

Solvent	k(sec <sup>-1</sup> )	(D)
Acetone	5.36 x 10 <sup>-2</sup>	20.7
Dimethylformamide	6.02 x 10 <sup>-2</sup>	37.6
Dioxane	6.83 x 10 <sup>-2</sup>	2.2
Acetonitrile	2.22 x 10 <sup>-1</sup>	37.5
Methylene chloride	6.04 x 10 <sup>-1</sup>	9.1
Benzene	2.85 x 10 <sup>-1</sup>	2.3

B. Divinyl Ether-PhTD<sup>a</sup>

Dioxane	3.05 x 10 <sup>-3</sup>	2.2
Acetone	1.13 x 10 <sup>-2</sup>	20.7
Methylene chloride	4.20 x 10 <sup>-1</sup>	9.1

<sup>a</sup>10:1 vinyl ether to PhTD

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The infrared spectrum of 49, which is a new 1,3,4-tetrahydrooxa-diazine ring structure, showed strong absorbances at 2980-2880 cm.<sup>-1</sup> (saturated carbon hydrogen), 1770 and 1710 cm.<sup>-1</sup> (double carbonyl) and strong bands in the 1200-1000 cm.<sup>-1</sup> region due to the acetal linkage. The nmr spectrum (Fig. 6) gave resonance signals at  $\delta$ 7.40 (multiplet, aromatic hydrogens, 5),  $\delta$ 5.02 (quartet, hydrogen on acetal carbon, 1),  $\delta$ 3.73 (multiplet, methylene hydrogens, 4),  $\delta$ 1.85 (two equivalent singlets, nonequivalent methyl hydrogens from incorporated acetone, 6) and  $\delta$ 1.25 (triplet, methyl hydrogens from ether, 3). The elemental analysis agreed with the calculated value.

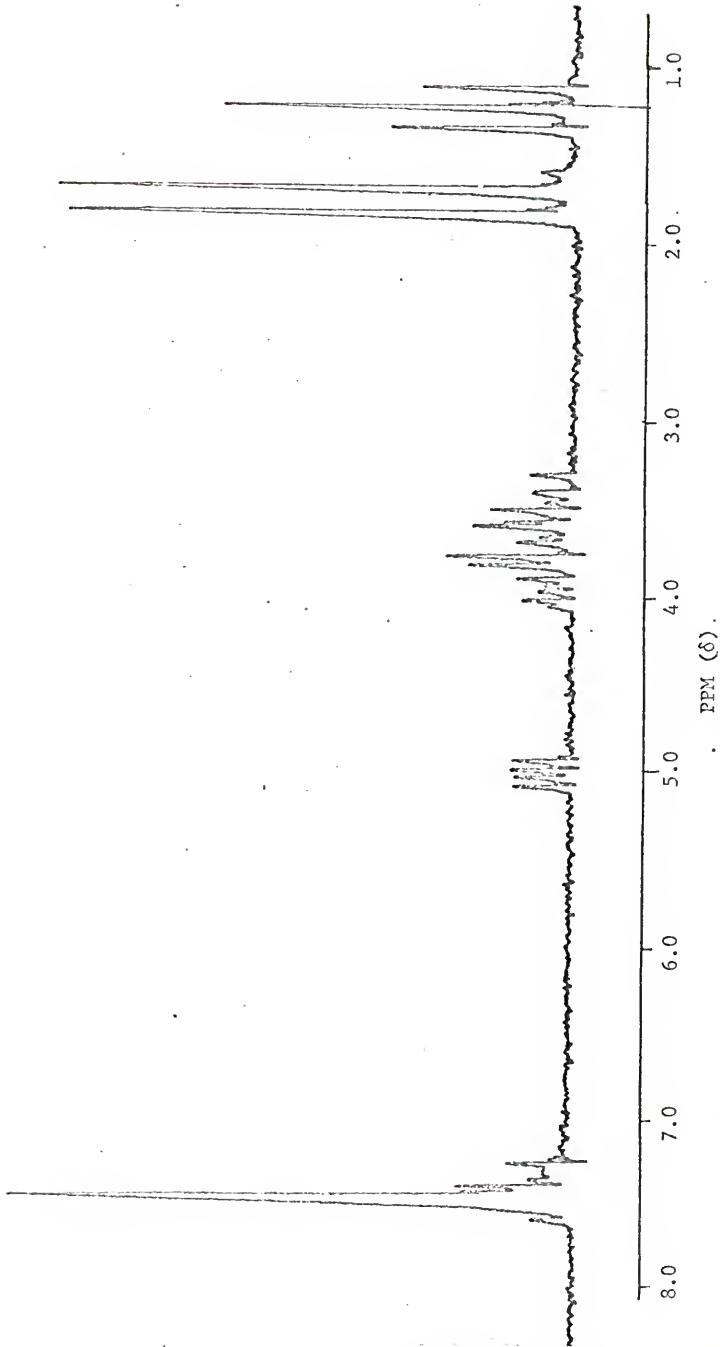
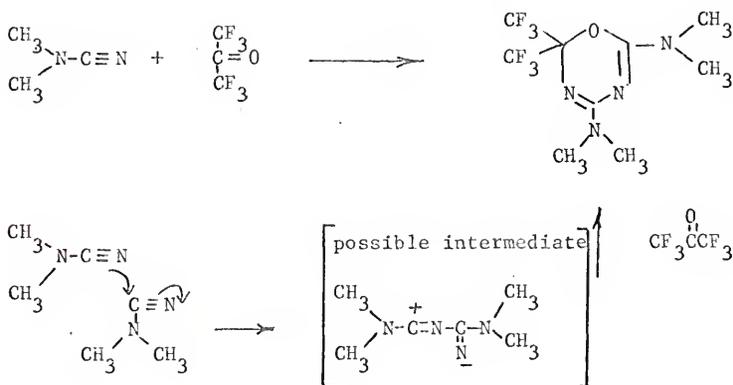


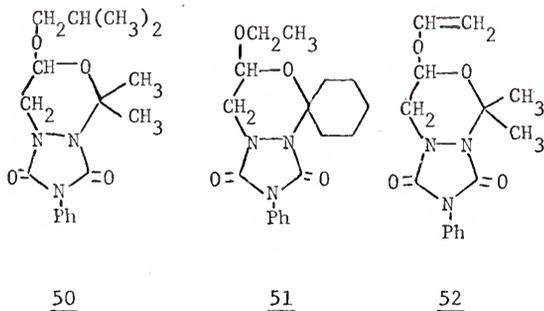
Figure 6. Nmr spectrum of 3-oxa-2,2-dimethyl-4-ethoxy-8-phenyl-L,6,8-triazabicyclo[4.3.0]nona-7,9-dione.

In previous studies<sup>42,43,44</sup> of the 1,4-dipoles, many different reactive dipolarophiles have been utilized to intercept the dipolar intermediates, i.e., isocyanates, acetylene dicarboxylate esters and ketenes, among many others. However, apparently only one case has been reported of a ketone performing this function and this involved the reaction of perhaloacetones with cyanamides to form 1,3,5-oxadiazines.<sup>45</sup>



To investigate the scope of this novel interception reaction, both the vinyl ether and the ketone solvent were varied. When isobutyl vinyl ether was substituted for ethyl vinyl ether 3-oxa-2,2-dimethyl-4-isobutoxy-8-phenyl-1,6,8-triazabicyclo[4.3.0]nona-7,9-dione, 50, was formed in 47% yield. The infrared spectrum was practically identical to that of 49 with only minor differences noted in the C-H stretching frequencies and in the fingerprint region of the spectrum. The nmr spectrum was similar to 49 except a doublet for the methyl groups of the isobutyl group was present at  $\delta 0.95$  (6), and the multiplet due

to the methylene protons was less complex because of the isobutyl group.



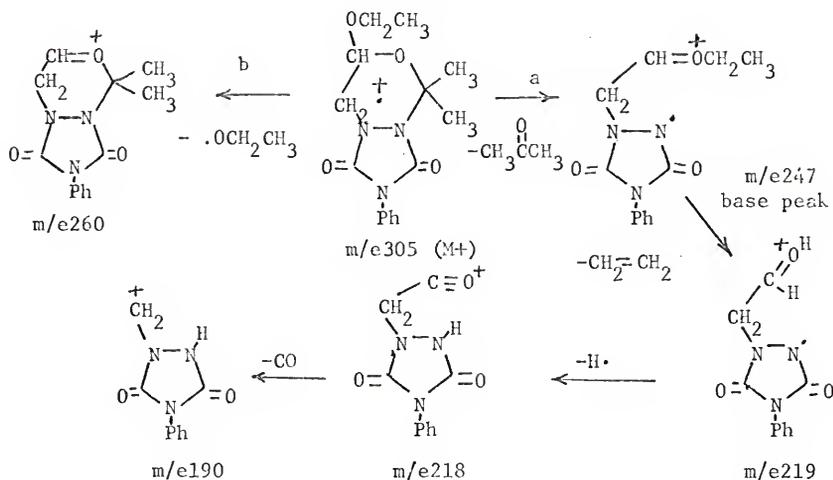
Changing the ketone solvent from acetone to cyclohexanone resulted in formation of 3-oxa-2-spirocyclohexyl-4-ethoxy-8-phenyl-1,6,8-triazabicyclo[4.3.0]nona-7,9-dione, 51, in 12% yield. Apparently the low yield resulted from the more complicated procedure for product isolation. The infrared spectrum appeared practically identical to 49 and 50. The nmr spectrum differed from that of 49 in that the nonequivalent methyl resonances at  $\delta$ 1.70 and  $\delta$ 1.85 were replaced by a broad multiplet resonance from  $\delta$ 1.50- $\delta$ 2.80 (10) from the cyclohexyl protons.

Divinyl ether, PhTD and acetone resulted in a small amount of the tetrahydrooxadiazine 52 and a trace of 1,2-diazetidene 31b. Both were identified by nmr with the oxadiazine spectrum resembling 49, 50 and 51, while the 1,2-diazetidene resonances were identical to those of the room temperature product of DVE-PhTD in methylene chloride 31b.

The mass spectral fragmentation patterns offered strong corroborative evidence for the proposed new 1,3,4-tetrahydrooxadiazine ring structures. The fragmentation patterns were very similar to known

cyclic acetal fragmentations.<sup>46</sup> They were different in that the molecular ion appeared. This could be due to the unique structure in which one ether linkage was inside the ring and the other was outside. Scheme I shows the fragmentation pattern for 49. The molecular ion  $m/e$  305 (1%) is believed to fragment by two pathways, a and b.

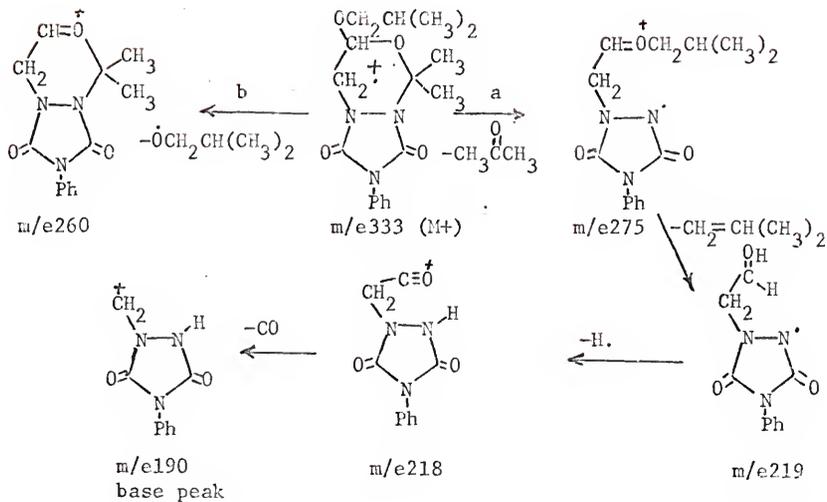
Scheme I



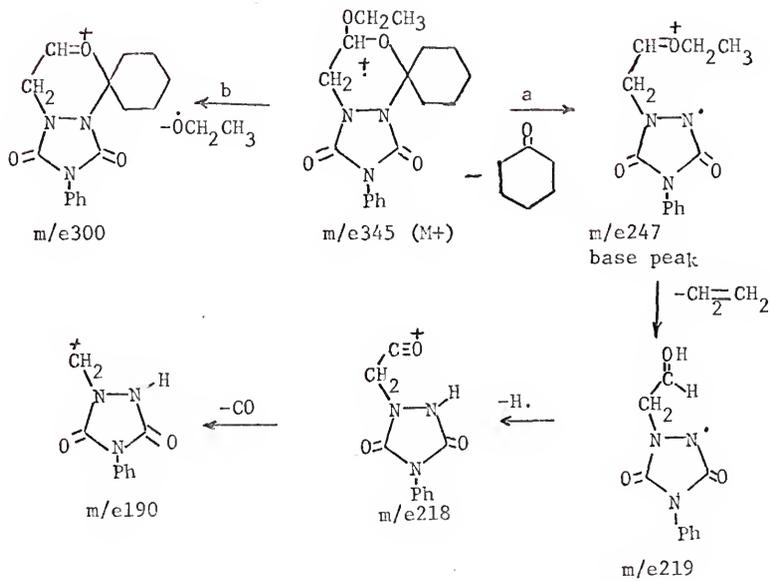
Pathway "a" involves loss of acetone to form  $m/e$  247, the base ion. This is followed by the loss of ethylene to  $m/e$  219 (8%) which then appears to rearrange and lose a hydrogen atom to  $m/e$  218 (22%). Ion  $m/e$  190 (59%) subsequently follows by loss of carbon monoxide. Pathway "b" involves loss of the ethoxy radical to form ion  $m/e$  260 (7%), a general cracking course for both acetals<sup>46</sup> and glucosides.<sup>47</sup>

Comparison of the fragmentation of 50 and 51 (Schemes II and III

Scheme II



Scheme III



respectively) with that of 49 shows similar ions resulting from the same double fragmentation pathway.

From these results (summarized in Table 4) it appears that the reactivity of the 1,4-dipole is quite sensitive to stabilization of its positive center. The high yields of oxadiazine when the carbonium ion stabilizing substituents, ethoxy and isobutoxy, are present and the low yield with vinyloxy are believed to mean that the intermediate has more pronounced dipolar character when its positive center is stabilized and hence can add across the weak dipolarophilic alkyl ketones. This is the same reasoning used to explain the earlier copolymerization results. In agreement with the above observations is the PhTD-indene<sup>30</sup> reaction in which no oxadiazine was reported even though the reaction was performed in acetone.

TABLE 4. SUMMARY OF INTERCEPTION REACTION RESULTS

<u>Vinyl Ether</u>	<u>Ketone</u>	<u>% Yield</u>	<u>M.P.</u>
$\text{CH}_2=\text{CH}-\text{O}-\text{CH}_2\text{CH}_3$	Acetone	42%	149-151°C
$\text{CH}_2=\text{CH}-\text{OCH}_2\text{CH}_3$	Cyclohexanone	12% <sup>a</sup>	170-171°C
$\text{CH}_2=\text{CH}-\text{O}-\text{CH}_2-\overset{\text{CH}_3}{\underset{\text{H}}{\text{C}}}-\text{CH}_3$	Acetone	47%	125-126°C
$\text{CH}_2=\text{CH}-\text{O}-\text{CH}=\text{CH}_2$	Acetone	trace <sup>b</sup>	---

(a) Yield lower possibly because of difficulty in work up.

(b) Identified from nmr. Also some 1,2-diazetidene formed.

By employing this unique property of these 1,4-dipoles, it was felt that information on the degradation of the EVE-PhTD copolymer could be obtained. When a high molecular weight sample of this

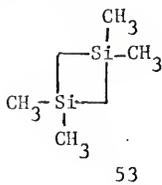
copolymer was refluxed in acetone, the usual decrease in molecular weight was observed along with a trace amount of oxadiazine 49. This was believed to result from degradation back to the initial 1,4-dipole which in turn was trapped by the acetone. This is interpreted to mean that, at least in part, the degradation is a reverse reaction of the original polymer formation.

Soluble salts are generally known to exhibit significant effects in either anionic or cationic polymerizations. It was felt that the ions of a soluble salt would effectively "tie up" some of the "living ends" of the propagating dipole and prevent their intermolecular coupling and hence lower the molecular weight. When the EVE-PhTD copolymerization was effected in tetrahydrofuran solution in the presence of 10 mole % of sodium tetraphenylboron, a significant change in the molecular weight was observed. A control in tetrahydrofuran yielded an average molecular weight of 2040 versus 940 for the sample containing the salt.

Another mechanistic pathway which merits consideration is that of a ring opening polymerization resulting from attack of the zwitterionic intermediate on an unopened 1,2-diazetidene. Although the data do not allow this mechanism to be disregarded, especially in the DVE case, the observation of molecular weight increase with time for both the DVE and EVE cases is not consistent with such a propagation mechanism. This evidence is particularly persuading for the EVE-PhTD copolymerizations because of two observations. The first observation resulted from an experiment conducted in an nmr tube. This experiment showed that when the reactants were mixed and inserted directly into the nmr cavity only copolymer was observed. The second observation was that

even though all the PhTD was consumed after 10 minutes in the PhTD-EVE copolymerization, the molecular weight increased over a 0.5 hour time period (Fig. 5). Since no adduct was present as indicated by the first experiment, the molecular weight growth is attributed to dipolar coupling. Wilson and Beaman<sup>48</sup> have recently observed a system in which the molecular weight increased after an addition polymerization was complete and attributed the phenomenon to a coupling of residual polymeric dipoles.

Another polymerization in which some dipolar coupling was postulated was the catalytically initiated polymerization of 1,1,3,3-tetramethyl-1,3-disilacyclobutane, 53.<sup>49</sup>



The vinyl ether-PhTD copolymerizations are believed to be the first reported cases of a dipolar coupling being the sole propagation mechanism.

#### Mechanism of termination

In all of the copolymerizations the highest molecular weights obtained were only in the vicinity of 3000 (Tables 1 and 2). These low molecular weights are thought to be a result of facile termination reactions. As was stated earlier, ionic polymerizations are readily subject to termination reactions by impurities such as water. At least two other termination reactions could occur. The first would be an intramolecular dipolar coupling to a macrocyclic structure and the

second is a type of disproportionation to an inactive species as shown below. Another possible consideration is that the dipoles are



so stabilized to result in a "living" structure. Unfortunately no experimental evidence was obtained supporting any of the possible termination reactions.

B. Copolymerization of 4-Phenyl-1,2,4-triazoline-3,5-dione with Other Monomers

Vinyl acetate and divinyl carbonate

To broaden the scope of the copolymerization and reaction characteristics of PhTD, its reactivity was investigated with several other olefinic systems. Vinyl acetate (VAC) and Divinyl carbonate (DVC) were chosen for investigation because these monomers were expected to be somewhat less reactive than the vinyl ethers.

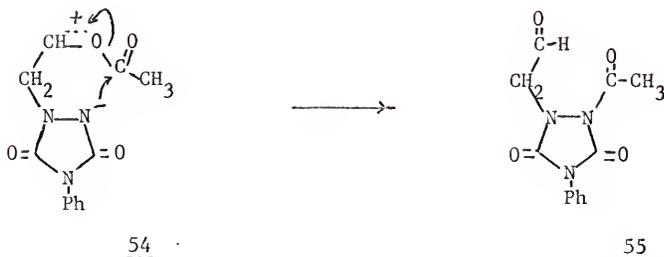
VAC was observed to react with PhTD at room temperature, but at a considerably slower rate than the vinyl ethers. The infrared spectrum of the product exhibited a medium intensity  $1610\text{ cm}^{-1}$  band. The nmr spectrum gave broad resonances at  $\delta 7.48$ ,  $\delta 4.32$  and  $\delta 2.16$ . Superimposed over these resonances were sharp singlets. A reaction conducted at  $60^\circ\text{C}$  in a sealed tube yielded as the major product an adduct which was assigned structure 55, 1-(formylmethyl)-2-acetyl-1,2,4-triazoline-3,5-

TABLE 5. COPOLYMERIZATIONS AND REACTIONS OF PhTD AND OTHER MONOMERS

Comonomer	Solvent	Conditions Temp. °C	Time (hr.)	Yield	$\bar{M}_n^a$	Product
Acrylonitrile	CH <sub>2</sub> Cl <sub>2</sub>	25	42	15.1	—	PhTD oligomeric species
Acrylonitrile	CH <sub>2</sub> Cl <sub>2</sub>	60	144	63.0	—	PhTD oligomeric species
Acrylonitrile <sup>b</sup>	CH <sub>2</sub> Cl <sub>2</sub>	60	24	31.8	—	Possibly some copolymer from elemental analysis
Acrylonitrile	CH <sub>2</sub> Cl <sub>2</sub>	60	24	33.0	—	
Divinyl sulfone	CH <sub>2</sub> Cl <sub>2</sub>	60	88	59.3	—	PhTD oligomeric species
Divinyl sulfone	CH <sub>2</sub> Cl <sub>2</sub>	60	24	33.5	—	PhTD oligomeric species
Divinyl sulfone <sup>b</sup>	CH <sub>2</sub> Cl <sub>2</sub>	60	24	29.0	—	No sulfur present from elemental analysis
N-vinyl carbazole	CH <sub>2</sub> Cl <sub>2</sub>	25	0.5	86.0	21,000 <sup>c</sup>	1:1 copolymer
N-vinyl carbazole	acetone	25	0.5	—	—	1:1 copolymer
Vinyl acetate	CH <sub>2</sub> Cl <sub>2</sub>	25	21	57.3	—	Copolymer and 55
Vinyl acetate	CH <sub>2</sub> Cl <sub>2</sub>	25	0.5	1.2	—	Not identified
Vinyl acetate	CH <sub>2</sub> Cl <sub>2</sub>	60	24	78.3	370	Mostly 55
Vinyl acetate	acetone	60	24	—	—	Mostly 55
Divinyl carbonate	CH <sub>2</sub> Cl <sub>2</sub>	25	14.5	44.9	—	2:1 copolymer
Divinyl carbonate	CH <sub>2</sub> Cl <sub>2</sub>	25	0.5	0.36	—	Not identified
Divinyl carbonate	CH <sub>2</sub> Cl <sub>2</sub>	60	24	73.5	1240	2:1 copolymer

<sup>a</sup>VPO-acetone solution<sup>b</sup>0.5 wt.%AIBN added<sup>c</sup>calculated from GPC

dione. This compound apparently arose from an internal trap of the intermediate 1,4-dipole 54.



The infrared spectrum of 55 showed two weak bands characteristic of an aldehyde carbon hydrogen stretch at  $2860 \text{ cm.}^{-1}$  and  $2750 \text{ cm.}^{-1}$ . A double carbonyl absorbance at  $1800 \text{ cm.}^{-1}$  and  $1730 \text{ cm.}^{-1}$  was also characteristic of the urazole type structure. The nmr spectrum (Fig. 7) gave resonance signals at  $\delta 9.56$  (singlet, aldehyde hydrogen, 1),  $\delta 7.50$  (singlet, aromatic hydrogens, 5),  $\delta 4.80$  (singlet, methylene hydrogens, 2) and  $\delta 2.60$  (singlet, methyl hydrogens, 3). The mass spectrum yielded the correct parent peak at  $m/e$  261 and the elemental analysis agreed with the 1:1 structure.

The broad nmr resonances and the  $1610 \text{ cm.}^{-1}$  infrared band were probably indicative of the formation of some copolymer in the room temperature reaction. The small amount of polymeric material is believed to be indicative of the low activation energy of the intramolecular six membered transition state rearrangement.

An attempt to trap the initial dipole before the intramolecular reaction occurred was made utilizing a large excess of phenyl isocyanate as the dipolarophile. Only 55 was isolated. The reaction was also performed in acetone so that the initial dipole could be trapped

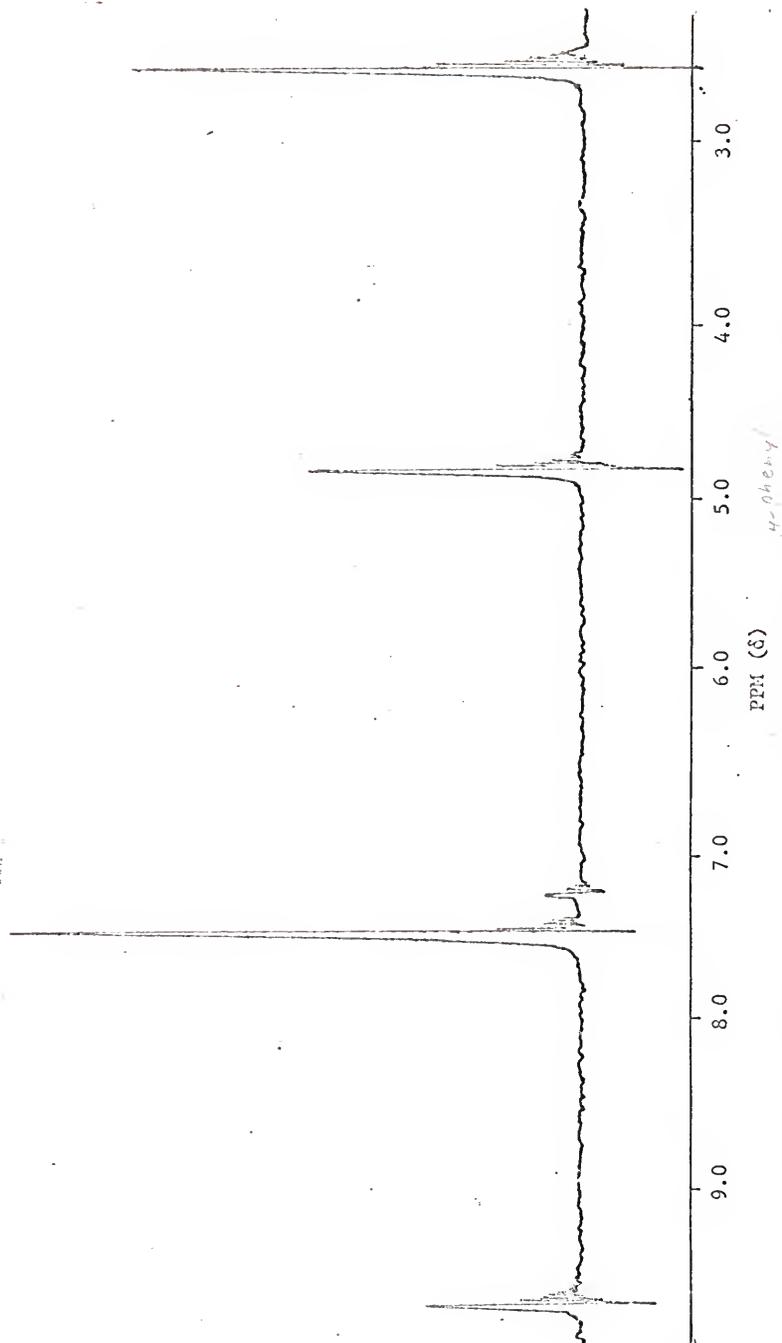
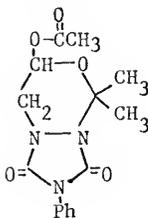


Figure 7. Nmr spectrum of 1-(formylmethyl)-2-acetyl-1,2,4-triazoline-3,5-dione.

to form an oxadiazine as was accomplished in the vinyl ethers. The majority of the reaction was 55. A few milligrams of material were isolated which gave an nmr spectrum with resonance signals at  $\delta 6.30$  (multiplet),  $\delta 3.75$  (doublet) and  $\delta 1.72$  (singlet). The spectrum was complicated by the presence of 55. The above resonances appeared in the ratio of 1:2:6. This could be evidence for the formation of a small amount of the oxadiazine 56.

56

DVC was found to react slowly at room temperature and at  $60^{\circ}\text{C}$  to give a material shown by elemental analysis to be a 2:1 structure. A strong  $1610\text{ cm.}^{-1}$  band was observed in the infrared spectrum and the nmr spectrum gave broad resonances at  $\delta 7.38$  (singlet, broad, 6) and  $\delta 5.31$ - $\delta 3.31$  (multiplet, broad, 1). A molecular weight of 1220 was obtained for the  $60^{\circ}\text{C}$  polymerization. No observations were indicative of the occurrence of a double internal trapping reaction analogous to the vinyl acetate reaction.

#### Divinyl sulfone and acrylonitrile

The normally electron poor olefins divinyl sulfone ( $\text{DVS}\text{O}_2$ ) and acrylonitrile (AN) were chosen for investigation to see if they would act as electron donors with PhTD.

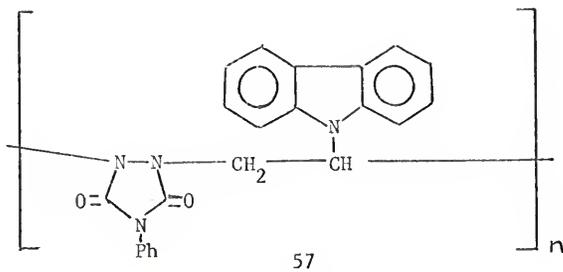
$\text{DVS}\text{O}_2$  appeared to give some reaction since more solid was obtained

in an attempted copolymerization at 60°C than was obtained with a control of PhTD. No sulfone absorbances were noted in the infrared spectrum and an elemental analysis only yielded a trace of sulfur.

AN showed no indication of reaction at room temperature or at 60°C for six days. At 60°C, with a free radical initiator present, some product appeared to result. An analysis of the infrared spectrum showed a new medium intensity 1610  $\text{cm.}^{-1}$  band. An elemental analysis yielded a higher nitrogen content than would result from a reaction only involving PhTD. No structure assignments were feasible.

#### N-vinyl carbazole

N-vinyl carbazole (NVC) was observed to spontaneously copolymerize at 25°C to yield an 86% yield of a 1:1 copolymer. The composition was established by elemental analysis. Only a weak-medium 1610  $\text{cm.}^{-1}$  absorbance was observed in the infrared spectrum. The nmr spectrum yielded two large broad resonances centered at  $\delta 8.50$  and  $\delta 5.80$ . Because of the weak 1610  $\text{cm.}^{-1}$  absorbance the polymer structure was thought to be 57.



Insolubility of the polymer in acetone precluded the usual vapor pressure osmometer molecular weight determination. However, calculation of the number average molecular weight from gel permeation chromatog-

raphy, calibrated with polystyrene, gave a value of 21,000. The weight average was calculated to be 54,000 and the molecular weight distribution ( $\overline{M}_w/\overline{M}_n$ ) was 2.57. In making the calculations a very dangerous assumption was necessary. It was assumed that polystyrene and the copolymer had similar coil dimensions in the solvent used for the determination. Although this assumption appeared to be valid in the DVE-PhTD copolymer, it was not necessarily valid in this case. The molecular weight obtained in this system is significantly higher than in the vinyl ether copolymers. No reasons are apparent for the change in structure and the change in molecular weight of the NVC system.

When the polymerization was conducted in acetone, a similar polymeric structure was obtained. Only a minute amount, if any, of the corresponding oxadiazine was observed. An nmr spectrum from a small amount of apparently non-polymeric material showed multiplets at  $\delta 4.50$  from methylene hydrogens and  $\delta 2.20$  from methyl hydrogens. Not enough material was isolated to identify and characterize this product. The failure of acetone to trap the probable intermediate dipole is probably due to the large steric effect of the vinyl carbazole moiety.

Stille and Aoki<sup>50</sup> have initiated the homopolymerization of electron donors by addition of catalytic amounts of strong electron acceptors. The homopolymerizations are proposed to be initiated by an excited ionic state of a charge transfer complex. Since NVC is known to readily homopolymerize, it was thought that the addition of a small amount of PhTD to a solution of NVC could possibly trigger a cationic homopolymerization of the NVC in which the initiation would

be effected by the positive end of the dipole. An attempted polymerization was unsuccessful.

C. Reactions and Attempted Homopolymerizations of 4-Phenyl-1,2,4-triazoline-3,5-dione

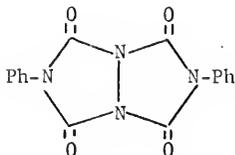
4-substituted-1,2,4-triazoline-3,5-diones have the potential to yield polymers possessing a nitrogen backbone if an initiation could be effected through the nitrogen to nitrogen double bond. This promise made the investigation of the behavior of the triazoline diones in the presence of radical and ionic initiating species an attractive proposal.

PhTD has been described<sup>51</sup> as decomposing instantly in basic solution, while in the presence of acid, water or alcohol the rate of decomposition was noted to be slower. Even in the presence of light or in solution at room temperature some decomposition was reported. No one has studied the decomposition products and their mechanisms of formation.

The thermal decomposition of PhTD at 60°C in a sealed tube was studied to determine if there was any appreciable decomposition that could compete with the copolymerizations. During the course of the reaction the color remained red and a few milligrams of a white crystalline solid formed in the bottom of the tube. Precipitation of the red solution yielded a small amount of tan-white solid 59.

The white crystalline solid did not melt when the temperature was raised to 300°C. The infrared spectrum gave no saturated carbon-hydrogen stretching absorbances and gave a double carbonyl at 1785 cm.<sup>-1</sup> and 1755 cm.<sup>-1</sup> The mass spectrum yielded a parent peak at m/e 322

and a base peak at  $m/e$  119 (phenyl isocyanate ion). Structure 58, 3,7-diphenyl-1,5-diazabicyclo[3.3.0]octa-2,4,6,8-tetraone, was assigned from this data. An elemental analysis perfectly agreed with the calculated value.

58

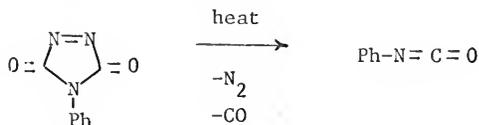
Two reports of 58 were found in the literature. Snyder<sup>52</sup> reported the formation of a bright orange solid, melting point 203-204°C, during a refluxing reaction of PhTD. In this case PhTD was generated by oxidation with *t*-butyl hypochlorite in acetone. The only structure proof presented was infrared data which included a double carbonyl and an aromatic absorbance. Koch and Fahr<sup>53</sup> reported the formation of 58 in a thermal reaction of PhTD in an apolar solvent. No structure proof or physical characteristics were presented.

The tan-white solid 59 isolated by precipitation into hexane had 3500  $\text{cm.}^{-1}$  and 1715  $\text{cm.}^{-1}$  absorbances in the infrared spectrum. The nmr spectrum gave broad resonances at  $\delta$ 7.50 (broad multiplet, 6) and  $\delta$ 4.48 (broad multiplet, 1). The number average molecular weight from vapor pressure osmometry was found to be 600. The elemental analysis did not correspond to any regular structure resulting from a homopolymerization of PhTD.

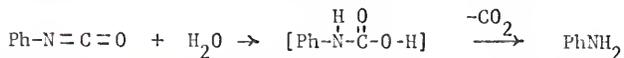
When PhTD was heated in a sealed tube in methylene chloride solution in the presence of azobisisobutyronitrile, results identical to reaction without the free radical initiator were obtained. An

attempt to initiate a free radical homopolymerization of PhTD by photolysis of benzoyl peroxide at  $-45^{\circ}\text{C}$  only resulted in a small amount of the oligomeric PhTD decomposition product 59.

In attempting to explain the mechanistic pathway for the thermal decomposition of PhTD to 59, the first reaction is probably the formation of phenyl isocyanate. Phenyl isocyanate could then in turn



react with water to form aniline. When a catalytic amount of aniline



was added to a methylene chloride solution of PhTD, some of the oligomeric decomposition product 59 resulted.

Another related experiment was to see what products were formed in the decomposition of PhTD by water, since PhTD had already been shown to readily decompose in water.<sup>51</sup> When PhTD, in dioxane solution, was added to water a vigorous reaction ensued and a large amount of oligomeric product 59 was obtained. A small amount of  $\text{N,N}'$ -diphenyl urea was also obtained. One of the products from the reaction is most assuredly phenyl isocyanate which then goes to aniline and then reacts with more phenyl isocyanate to yield the diphenyl urea.

Since aniline served as a catalyst for formation of the oligomeric product 59, an investigation using other nucleophilic species was initiated in hopes of effecting the formation of high polymer.

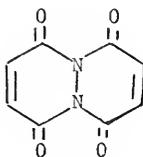
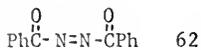
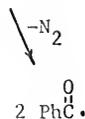
Triethylamine was used as the initiator and a similar product 59

was obtained. Surprisingly approximately 10% of 58 was isolated.

The strong nucleophilic reagent, sodium cyanide in dimethylformamide was then used as the initiator and a large yield 70-80 per cent of the tetraone 58 was obtained. A small amount of 59 was also obtained.

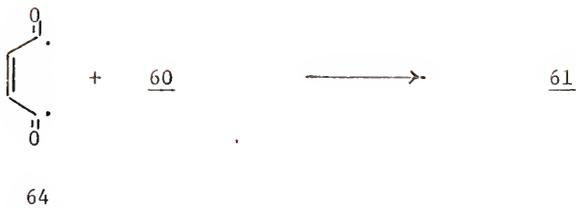
The rationalization of the formation of 58 from attack of a nucleophile on PhTD presents an interesting mechanistic problem that was not covered in the scope of this research. However, the following explanation is put forth as a possible mechanistic pathway of the unusual reaction.

Kealy<sup>54</sup> has observed the formation of 61 from the decomposition of diazoquinone 60. He did not propose a mechanism for the formation of 61, but only referred to earlier work on the decomposition of azo compounds by radical pathways. For example, Leffler and Bond<sup>55</sup> have studied the radical decomposition of dibenzoyl diimide 62 where 63 is one radical intermediate.

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For the diazoquinone, a probable diradical intermediate would be 64 which could couple with an intact molecule of diazoquinone 60 to yield 61.

If such a diradical intermediate 65 was involved in the formation of the tetraone 58 from a nucleophilic catalyzed reaction of PhTD



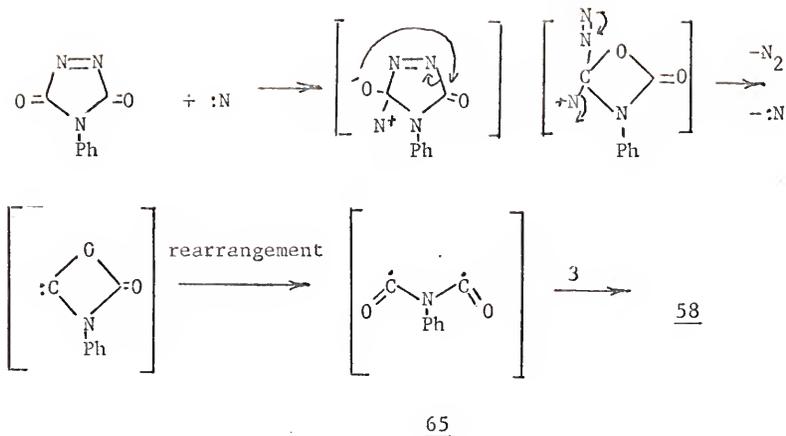
an unusual carbenoid mechanism could be involved as shown below. No proof has been gathered in support of this mechanism, although in the studies conducted on the radical decomposition of 62<sup>55</sup> much higher rates of decomposition were observed in strongly nucleophilic solvents like aniline. The reason for this could be a nucleophilic catalyzed reaction as was discussed for the formation of 58.

TABLE 6. SUMMARY OF CATALYZED PhTD REACTIONS

Exp. No.	Conditions	Products
1	90°C, vacuum	59 ( $\bar{M}_n = 1000$ )
2	Most electron poor comonomers	59 (small amounts)
3	CH <sub>2</sub> Cl <sub>2</sub> , 60°C, 70 hrs., sealed tube	59 (27%), 58 (1%)
4	CH <sub>2</sub> Cl <sub>2</sub> , 60°C, 24 hrs., sealed tube	59 (10.4%), 58 (trace)
5	water, dioxane, 25°C, 1 hr.	59 (61.5%, diphenyl urea, (7.8%)
6	aniline, CH <sub>2</sub> Cl <sub>2</sub> , 25°C	59 (22.0%) ( $M_n = 470$ )
7	triethyl amine, CH <sub>2</sub> Cl <sub>2</sub> , 25°C, 1 hr.	59 (24.5%), 58 (9.5%)
8	sodium cyanide, dimethylformamide 2.5 hrs., 25°C	59 (small amount) 58 (approximately 80.0%)

A summary of all the reactions and decompositions of PhTD is presented in Table 6.

While this research was being conducted, Stickler and Pirkle<sup>12</sup> reported the first synthesis of a nitrogen backboned polymer. Their



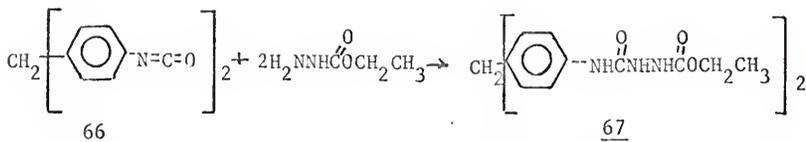
success resulted from a visible light irradiation of 4-n-butyl-1,2,4-triazoline-3,5-dione.

#### D. Diels Alder Polymers

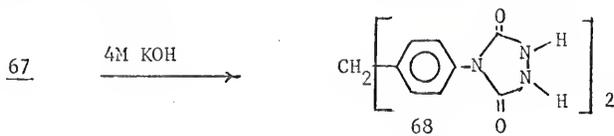
##### Synthesis of 4,4'-(4,4'-diphenylmethylene)-bis-1,2,4-triazoline-3,5-dione

Since the diisocyanate 66, 4,4'-diphenylmethane diisocyanate, was readily available from commercial sources, the bis triazolone dione selected as a target for synthesis was 69, 4,4'-(4,4'-diphenylmethylene)-bis-1,2,4-triazoline-3,5-dione. The synthesis of the diurethane precursor 67 was accomplished in a near quantitative yield by the addition of two moles of ethyl carbazate to 66. The infrared spectrum yielded strong N-H stretches at 3380  $\text{cm}^{-1}$  and 3305  $\text{cm}^{-1}$ . Strong carbonyl absorbances were observed at 1735  $\text{cm}^{-1}$  and 1685  $\text{cm}^{-1}$ . The nmr spectrum gave resonances at  $\delta$ 8.77 (singlet, hydrogens on nitrogen, 2),  $\delta$ 7.91 (singlet, hydrogens on nitrogen, 2),  $\delta$ 7.20 ( $A_2B_2$  quartet, aromatic hydrogens, 8),  $\delta$ 4.05 (quartet, methylene hydrogens, 4),

δ3.79 (singlet, methylene hydrogens, 2) and δ1.19 (triplet, methyl hydrogens, 6.). The product gave the correct elemental analysis.



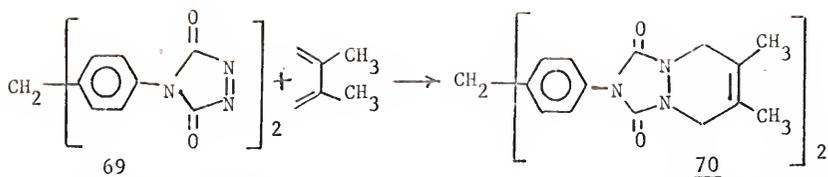
67 was quantitatively cyclized to the bis urazole 68 with 4M potassium hydroxide. The infrared spectrum yielded a broad band from



3320  $\text{cm.}^{-1}$  to 2760  $\text{cm.}^{-1}$ , a characteristic noted in the simple urazoles, and gave a double carbonyl absorbance at 1765  $\text{cm.}^{-1}$  and 1680  $\text{cm.}^{-1}$ . The nmr spectrum gave resonance signals at δ7.80-δ7.20 (broad with a sharp spike at δ7.38, aromatic hydrogens and hydrogens on nitrogen, 12) and δ4.03 (singlet, methylene hydrogens, 2). The elemental analysis agreed with the calculated value.

The oxidation of 68 to the bis triazoline dione 69 was accomplished in approximately 80% yield using dinitrogen tetroxide in the same manner as employed by Stickler and Pirkle<sup>12</sup> in the synthesis of the simple triazoline diones. The infrared spectrum showed an absence of any N-H stretching frequencies and yielded the characteristic double carbonyl at 1790  $\text{cm.}^{-1}$  and 1760  $\text{cm.}^{-1}$ . The nmr spectrum yielded, surprisingly, only two singlets, one at δ7.48 (aromatic hydrogens, 8) and δ4.18 (methylene hydrogens, 2).

69 reacted readily with reactive dienes. The reaction with 2,3-dimethyl-1,3-butadiene yielded 70. 70 was identified by its nmr spec-

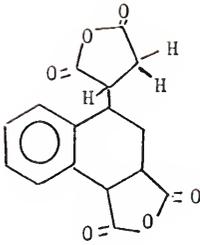
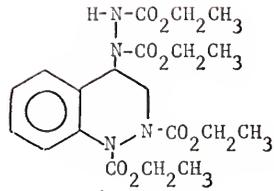
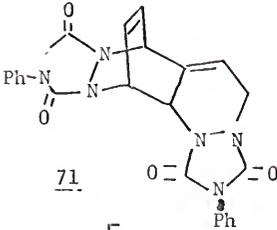
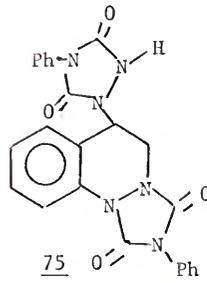
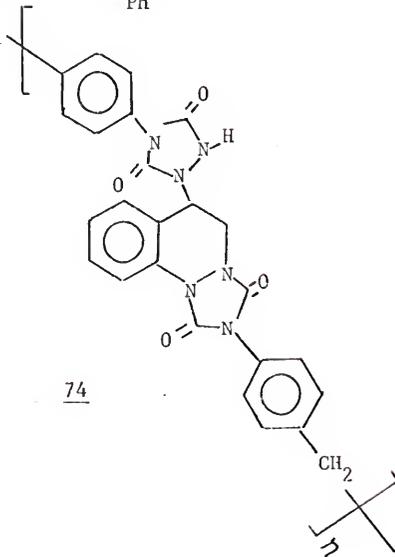


trum which showed resonance signals at  $\delta$ 7.33 (multiplet, broad, aromatic hydrogens, 8),  $\delta$ 4.00 (broad singlet, allylic next to nitrogen and benzylic hydrogens, 10) and  $\delta$ 1.75 (broad singlet, methyl allylic hydrogens, 12).

#### Diels Alder polymerization of styrene and 69

Cookson and coworkers<sup>51</sup> have investigated the Diels Alder reactions of triazoline diones and found that PhTD spontaneously reacted with styrene to yield the double Diels Alder adduct 71. Maleic anhydride<sup>56</sup> and ethyl azobisformate<sup>57</sup> have been shown to react with styrene in a Diels Alder fashion, but the final products in both cases were 72 and 73. These products resulted from an ene reaction after the first Diels Alder reaction. Cookson's results meant that styrene, potentially, would be an attractive bis diene to investigate with 69.

When styrene was reacted with 69 at room temperature in dimethylformamide solution, the deep red initial color faded to a much lighter red after two hours. After seven and one half hours, the red color, characteristic of unreacted 69, persisted. The solution was divided and the first half was precipitated into ether to yield a tannish, highly electrostatic powder. The second half was in turn divided into two portions and a discharge of the red color was noted after a few minutes. Precipitation into ether yielded an identical polymer (in-

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frared) as the portion precipitated while still red. The last portion was heated to reflux and immediately it began to darken. It was precipitated into ether and a much darker solid resulted.

The repeat structure of the polymer was assigned to 74, which results from a Diels Alder adduct which rearomatizes via an ene reaction as 72 and 73. This is contrary to what was expected a priori. The assignment was made from the infrared and nmr data and comparison to the model compound 75.

When PhTD and styrene were reacted in methylene chloride at room temperature 75 was formed rather than the reported Diels Alder adduct 71. The infrared spectrum gave an N-H stretch at  $3280\text{ cm.}^{-1}$  and the usual double carbonyls at  $1765\text{ cm.}^{-1}$  and  $1720\text{ cm.}^{-1}$ . The nmr spectrum (Fig. 8) gave resonance signals at  $\delta 8.38$  (doublet, hydrogen on nitrogen, 1),  $\delta 7.35$  and  $\delta 7.38$  (doublet and multiplet respectively, aromatic hydrogens, 4),  $\delta 5.70$  (triplet, benzyl hydrogen, adjacent to nitrogen, 1), and  $\delta 4.22$  (multiplet, methylene hydrogens, 2). The elemental analysis agreed with the 2:1 structure.

The polymer gave the double carbonyl in the infrared spectrum at  $1780\text{ cm.}^{-1}$  and  $1715\text{ cm.}^{-1}$ . The N-H stretch was very weak. The nmr spectrum (Fig. 9) showed resonances at  $\delta 8.40$  (doublet, broad, hydrogen on nitrogen, 1),  $\delta 7.37$  (singlet, broad, aromatic hydrogens, 12),  $\delta 5.67$  (singlet, broad, benzyl hydrogens adjacent to heteroatom, 1) and  $\delta 4.50$ - $\delta 3.80$  (multiplet, broad, two sets of methylene hydrogens, 4).

The polymer was soluble in both dimethylformamide and dimethylsulfoxide. The thermal decomposition was recorded using a Differential Scanning Calorimeter and was found to start at  $307^\circ\text{C}$ . An intrinsic viscosity determined in dimethylformamide at  $28^\circ\text{C}$  was 0.12. Calculation

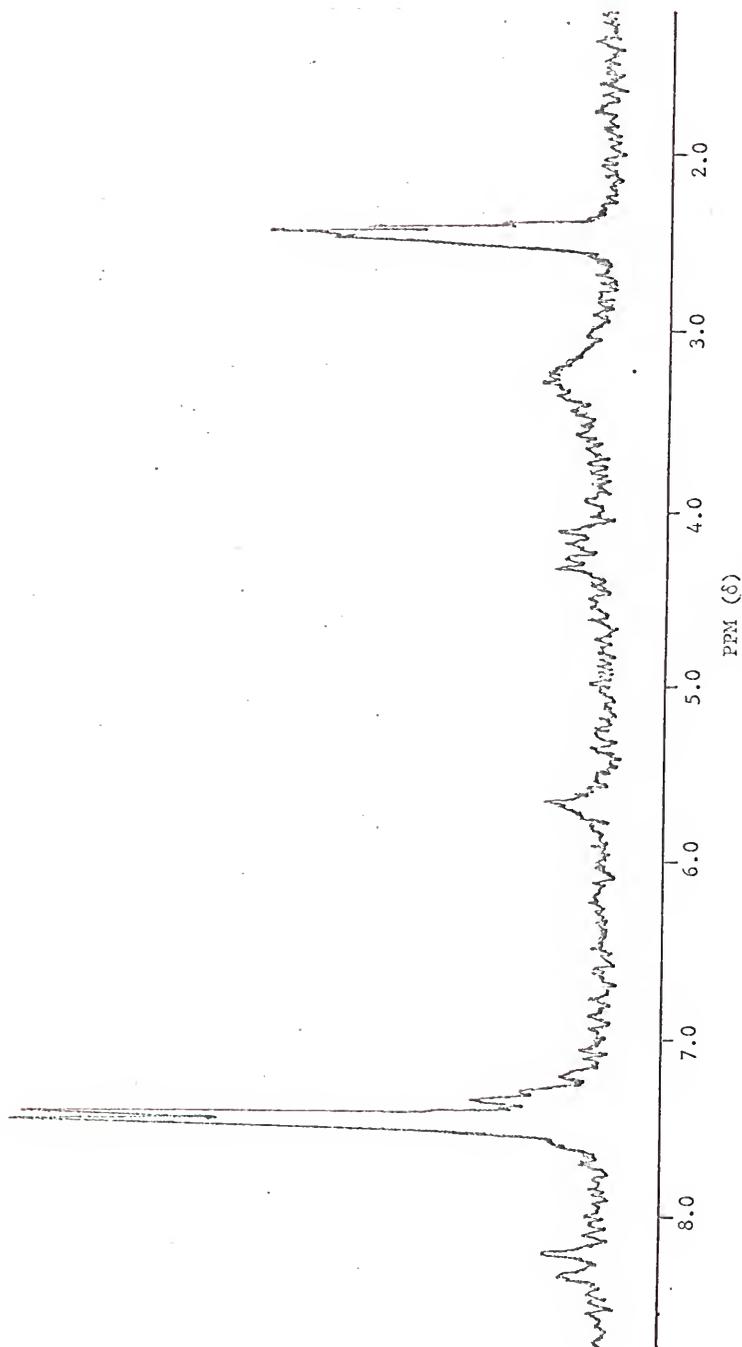


Figure 8. Nmr spectrum of the Diels Alder, the adduct of 4-phenyl-1,2,4-triazoline-3,5-dione and styrene.

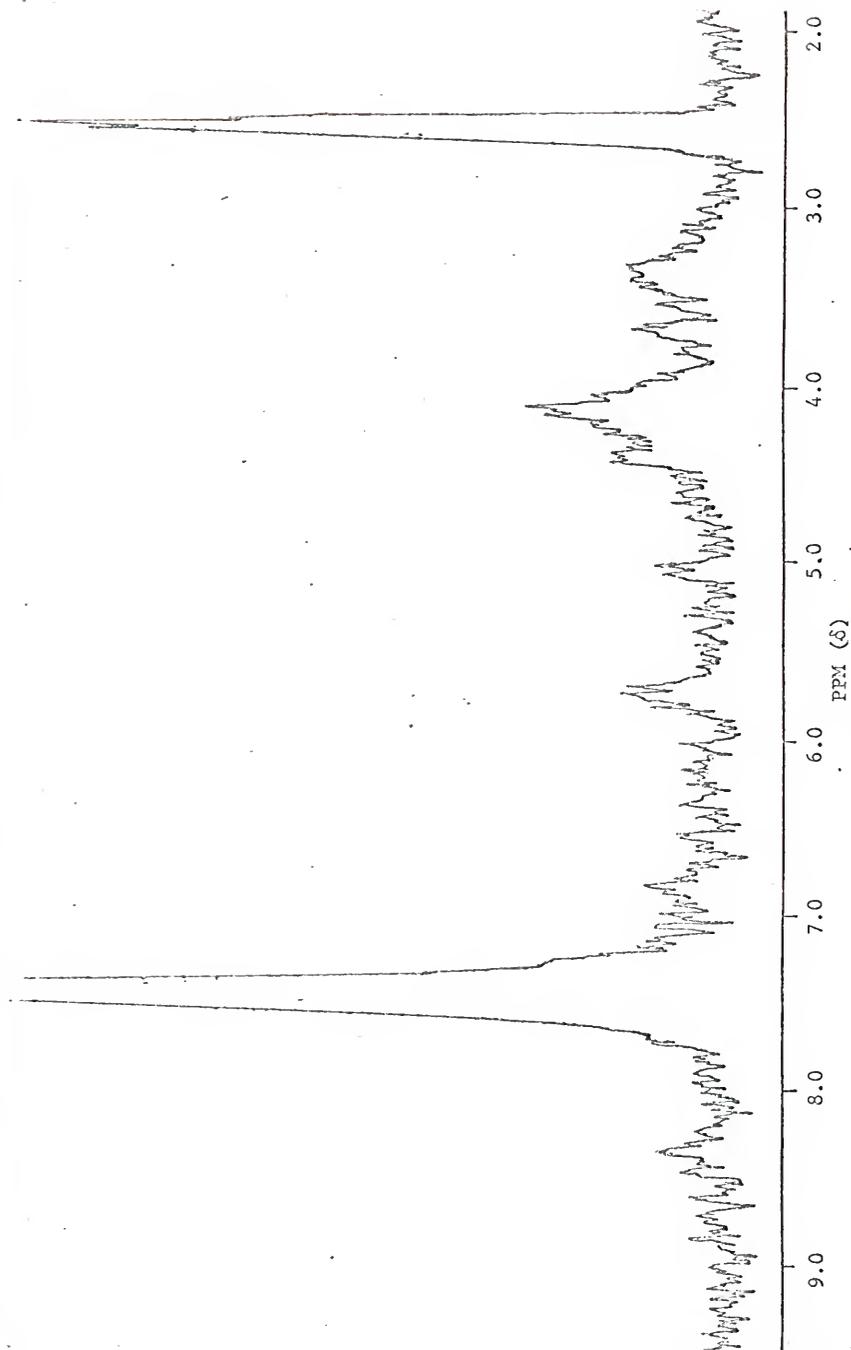
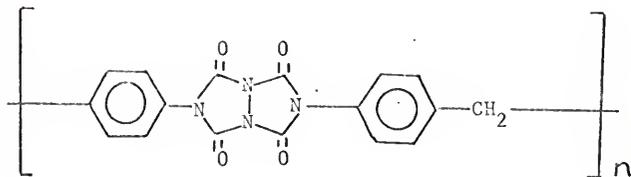


Figure 9. Nmr spectrum of the Diels Alder, ene polymer from styrene and bis triazoline dione.

from gel permeation chromatography showed a molecular weight distribution of 3.34 with the weight average molecular weight,  $\bar{M}_n = 36,000$ . These values were calculated from a calibration with a polystyrene standard, and again the assumption is made that the coil sizes are similar for the two polymers.

An attempted polymerization of 69 using sodium cyanide in dimethylformamide yielded a light brown polymeric material. The synthesis of a polymer with structure 76 was the object of this experiment. The infrared spectrum of this material was not similar to the monomeric tetraone 58 so apparently the desired decomposition and coupling reaction did not take place.



76

CHAPTER III

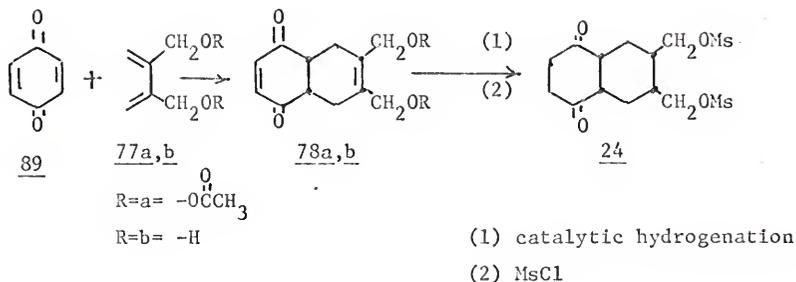
Triple Strand Polymer Model Compound Studies

A. Attempted Synthesis of Tetracyclo [4.4.0.1<sup>3,9</sup>.1<sup>4,8</sup>] Dodecane and Related Systems

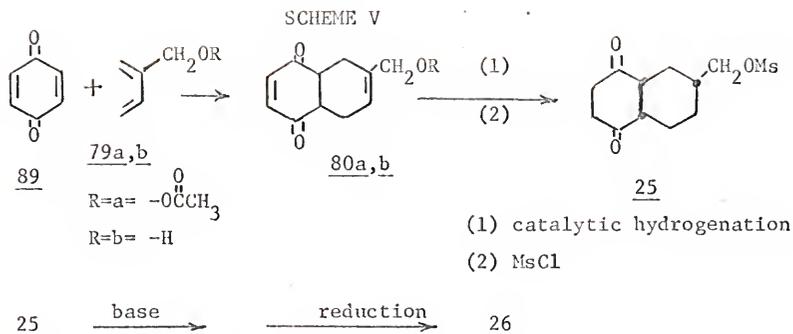
Synthetic schemes

The synthetic pathway for the attempted synthesis of the cage structure 18 is shown below in Scheme IV.

SCHEME IV

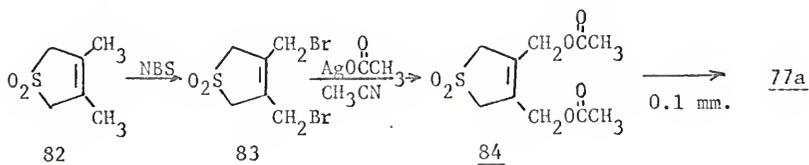


Scheme V is a proposed synthetic pathway to 25 which is the precursor to 26, a simplified cage structure related to 18.



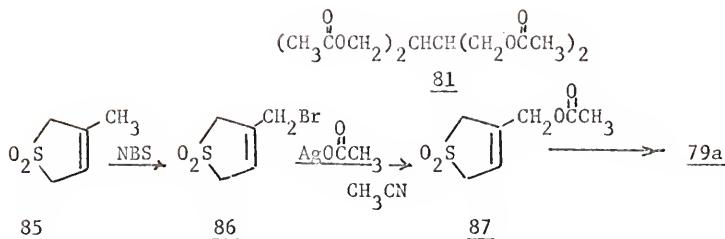
### Synthesis of dienes

The first step in Scheme IV required either 2,3-di(acetoxymethyl)-1,3-butadiene or 2,3-di-(hydroxymethyl)-1,3-butadiene, 77a and 77b. Both of these dienes had previously been synthesized by Bailey and Sorenson.<sup>58</sup> These authors prepared 77a by pyrolysis of 2,3-di-(acetoxymethyl)-1,4-diacetoxybutane, 81, at 480°C. Although the reported



yield was 84%, this was based on the recovery of unreacted starting material and the formation of a mono elimination product. Actually the conversion to 77a was only 16%. It was felt that the method of Butler and Ottenbrite<sup>29</sup> used in the preparation of 2,3-di-(bromomethyl)-1,3-butadiene would result in a more efficient preparation of 77a.

The first precursor to the desired dienes, 2,5-dihydro-3,4-dimethylthiophene-1,1-dioxide or commonly referred to as dimethyl-



butadiene sulfone, 82, was prepared by the method of Frank and Seven<sup>59</sup> in 90% yield. This was then brominated<sup>29</sup> with N-bromosuccinimide in 38% yield to 83. Treatment of this dibromide with silver acetate in acetonitrile resulted in a 73% yield (after recrystallization) of the diacetoxy sulfone 84. The elemental analysis of this compound agreed with the calculated and the infrared spectrum showed a strong carbonyl absorbance at  $1720\text{ cm}^{-1}$  for the ester group. The nmr spectrum yielded resonances consistent with the structure and they appeared at  $\delta 4.75$  (singlet, broadened, allylic hydrogens adjacent to acetoxy, 4),  $\delta 3.86$  (singlet, broadened, allylic hydrogens adjacent to sulfone, 4), and  $\delta 2.08$  (singlet, methyl protons, 6).

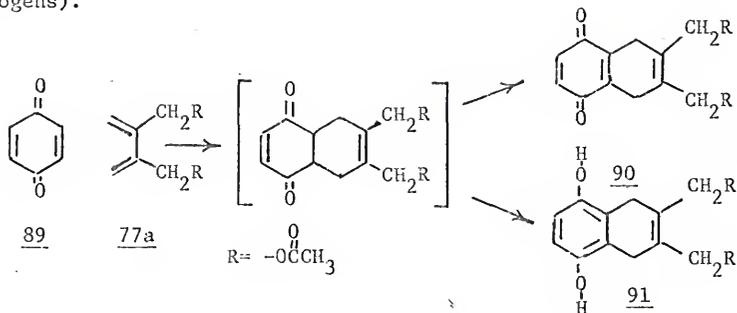
Pyrolysis of 84 was accomplished smoothly at  $200^\circ\text{C}$  and 0.1 mm pressure in 56.6% yield using a Hoskins furnace as the external heat supply. The white solid diene was purified by recrystallization and yielded the reported melting point.<sup>58</sup> Saponification<sup>58</sup> to 77b was accomplished in 90% yield.

By using the same general procedure as used in the preparation of 84, the sulfone precursor, 87, to the acetoxymethyl diene 79a was prepared in 74% yield. The bromomethyl sulfone 86 was prepared by the method of Krug and Yen<sup>60</sup> by bromination of isoprene sulfone 85 with N-bromosuccinimide. When 86 was reacted with silver acetate in



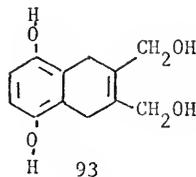
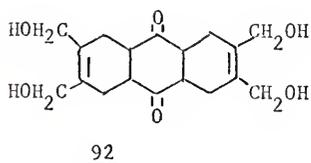
additional resonances at  $\delta 6.77$ ,  $\delta 6.75$ ,  $\delta 4.64$  and  $\delta 2.43$ . The  $\delta 3.23$  resonance was broadened considerably. This was apparently a mixture of unreacted quinone ( $\delta 6.77$ ), 90 and the desired Diels Alder adduct 78a. On addition of ethanol to the oil 90 was formed as a precipitate and no indication of 78a was found in a spectroscopic analysis.

The reaction of 77a and 89 was then performed in refluxing chloroform and the progress of the reaction was followed by nmr spectroscopy. Disappearance of resonances attributable to starting quinone and diene was observed and the appearance of signals at  $\delta 6.68$  (singlet, quinodial hydrogens, 2),  $\delta 4.65$  (singlet, allylic hydrogens adjacent to acetoxy, 4),  $\delta 3.27$  (multiplet, broad, bridgehead hydrogens, 2) and  $\delta 2.44$  (multiplet, broad, allylic hydrogens, 4) was noted. After 135 hours a conversion of 80% was calculated from the nmr spectrum. Removal of the chloroform yielded a yellow oil. This was chromatographed on silica gel and a white solid resulted that showed a strong  $3400\text{ cm}^{-1}$  band and a disappearance of the  $1650\text{ cm}^{-1}$  in the infrared spectrum. This indicated that 78a had rearranged to the hydroquinone derivative 91. The nmr spectrum gave resonances at  $\delta 6.64$  (singlet, aromatic hydrogens, 2),  $\delta 4.48$  (singlet, allylic hydrogens adjacent to acetoxy, 4),  $\delta 3.47$  (singlet, doubly allylic hydrogens, 4) and  $\delta 2.88$  (broad, hydroxyl hydrogens).



The reaction of the dihydroxy diene 77b with 89 failed to produce the desired Diels Alder adduct as an isolable material also. In refluxing chloroform a brownish solid formed whose nmr spectrum gave no resonances that could be assigned to a Diels Alder adduct.

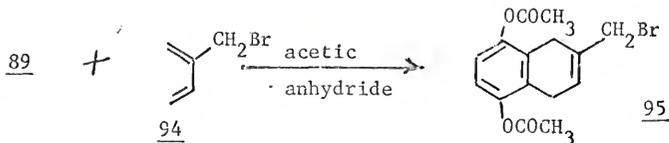
When the reaction was performed in tetrahydrofuran, a brownish-yellow oil was obtained which was initially chloroform soluble, but precipitated within a short time as a white solid. The absence of a quinone carbonyl in the infrared spectrum and the absence of bridgehead hydrogen resonances in the nmr spectrum was indicative that the desired Diels Alder adduct 77b was not present. The presence of a strong  $1710\text{ cm.}^{-1}$  absorbance in the infrared spectrum quite possibly may be due to some double Diels Alder adduct 92. There was, however, no



other indication of this. More likely, since the bridgehead protons did not appear in the nmr spectrum, 93 was formed.

The Diels Alder adducts of 89 and both 2-bromomethyl-1,3-butadiene, 94, and 79a were not isolable under the reaction conditions employed.

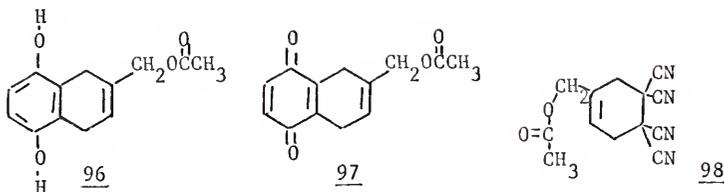
94, the bromine substituted diene,<sup>60</sup> reacted with 89 in acetic anhydride to give a 60% yield of the aromatized and acetylated product 95. All spectral characteristics were consistent with the structure



proposed. The infrared spectrum gave a strong  $1750\text{ cm.}^{-1}$  carbonyl from the ester functions. The nmr spectrum had resonances at  $\delta 7.00$  (singlet, aromatic hydrogens, 2),  $\delta 6.05$  (multiplet, vinylic hydrogen, 1),  $\delta 4.08$  (singlet, broad, allylic hydrogens adjacent to bromine, 2),  $\delta 3.30$  (singlet, broad, allylic hydrogens, 4) and centered at  $\delta 2.30$  (two singlets, nonequivalent methyl groups, 3 each). The mass spectrum gave the molecular ion and the molecular ion +2 in the correct percentage for one bromine atom, m/e 339 and m/e 341. The base peak m/e 176 corresponded to the loss of both acetoxy groups and the bromine atom.

In the reaction of the acetoxymethyl diene, 79a, with 89 in benzene at room temperature, quinhydrone,<sup>62</sup> the molecular complex of hydroquinone and quinone, was formed as an insoluble precipitate. It was identified by its melting point, nmr spectrum and mixed melting point with an authentic sample. On evaporation of the benzene a dark oil was formed, which on extraction with hot petroleum ether gave a bright yellow solid which quickly darkened. Column chromatography on silica gel resulted in a yellow oil which quickly darkened also. A thin layer chromatogram yielded two spots. The infrared spectrum gave a strong  $3500\text{ cm.}^{-1}$  absorbance indicative of a hydroxyl group. The nmr spectrum was very complex and from the methyl signal at  $\delta 2.10$ , three spikes were apparent indicating a mixture of three compounds. The bridgehead protons for the Diels Alder adduct appeared to be present as a multiplet at  $\delta 3.25$ . The downfield region centered at  $\delta 6.80$  appeared as a doublet. From these data it is believed that the initially formed Diels Alder adduct 80a aromatized to 96. From the color and the apparently three different methyl groups, some dehydrogenated material 97 was possibly present also. All attempts to separate the mixture were unsuccessful. When

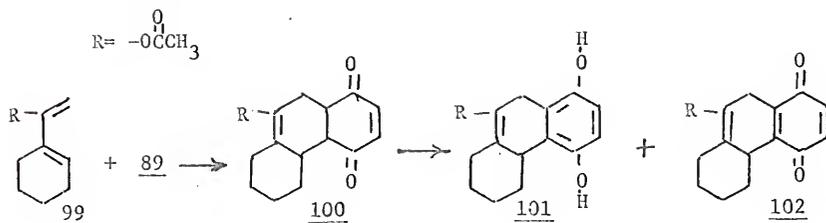
the reaction was carried out in ethanol a similar oily solid was obtained that yielded an infrared spectrum identical to the previous reaction in benzene.



The acetoxydiene 79a readily reacted with tetracyanoethylene to yield the Diels Alder adduct 98. Spectroscopic data and the elemental analysis were all consistent with the normal Diels Alder structure.

At the present time, there appears to be no plausible explanation why the Diels Alder adducts of *p*-benzoquinone, 89, and the dienes 77a, 77b, 79a and 94 isomerize so facily to the hydroquinone derivatives or dehydrogenate to the quinone like structures. Since quinhydrone appeared as a byproduct in the formation of 90 and 96, 89 probably acts as an oxidizing agent in the reactions.

Although these reactions appear to be the first time such reactions have been observed to occur spontaneously, Ansell and Knights<sup>63</sup> have reported the facile aromatizations of some Diels Alder adducts of 1,1'-acetoxyvinylcyclohexene, 99, and 89. They found that in ethanol



at room temperature the normal Diels Alder adduct 100, formed in 63% yield. In refluxing methanol, however, the authors observed the formation of 101 and 102. They offered no reasons for their observations but did report that most aromatizations of this nature are catalyzed by acid or by base. A previous synthesis of 100<sup>64</sup> revealed that melting the adduct and then resolidifying resulted in the formation of 101.

### 2-Cyclohexene-1-one and diazoquinone as dienophiles

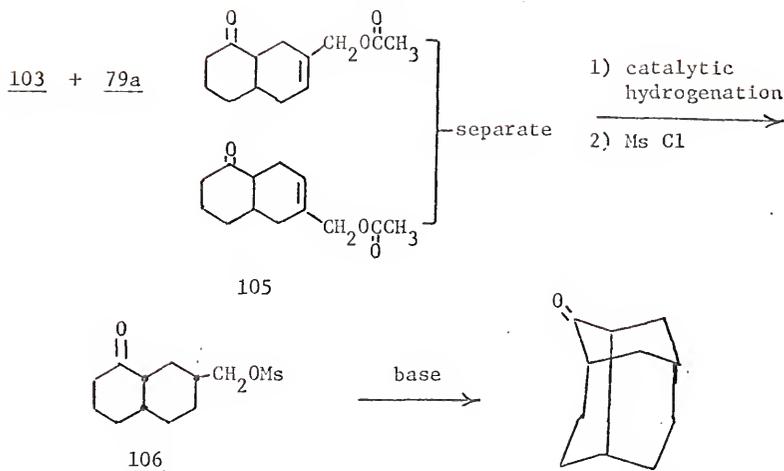
As an alternative approach to the synthesis of a precursor capable of undergoing the cyclization reaction to the cage structures, it was decided to employ dienophiles whose adducts were incapable of undergoing the facile aromatization reaction. The two dienophiles selected for this study were 2-cyclohexene-1-one, 103, and diazoquinone 104.

103104

If the normal Diels Alder adduct, 105, of 103 and 79a were to form then it would not be capable of aromatizing. Hence it was believed that the reactions shown in Scheme VI could be followed.

The synthesis of 103 was accomplished by bromination of cyclohexanone with N-bromosuccinimide<sup>65,66</sup> followed by dehydrobromination with collidine.<sup>67</sup> The bromination reaction was accomplished in a 53% yield, while the dehydrohalogenation gave a 58% yield of the desired  $\alpha,\beta$ -unsaturated ketone, an improvement over the 42% yield

## SCHEME VI



reported by the original investigators.<sup>67</sup> An attempted dehydrobromination using lithium bromide in dimethylformamide<sup>68</sup> resulted in a yellow viscous oil.

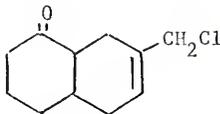
From earlier experiments with  $\underline{103}$  by Bartlett and Woods,<sup>69</sup> this dienophile was known to be quite sluggish in the Diels Alder reaction; therefore forcing reaction conditions were employed.

An autoclave attempt to form the adduct from neat reactants at 200°C resulted in a waxy, gummy, polymeric substance. This material gave a sharp carbonyl absorbance at 1710 cm.<sup>-1</sup> The nmr spectrum yielded broad resonances centered at  $\delta$ 7.00 (1) and  $\delta$ 1.00 (13).

In benzene solution, in a sealed tube at room temperature for four days, starting materials were recovered.  $\underline{103}$  and  $\underline{79a}$  were then reacted neat, in the presence of a small amount of hydroquinone, in a sealed tube at 190°C for three days. As in the autoclave reaction, a polymeric substance was isolated. It had the identical spectral characteristics of the former polymer.

Aluminum chloride had been found to be an effective catalyst for sluggish Diels Alder reactions.<sup>70</sup> When the Diels Alder reaction of 103 and 79a was attempted in the presence of a catalytic amount of anhydrous aluminum chloride, a vigorous exothermic reaction was noted and could only be controlled by use of an ice bath. On work up, an oil was obtained that yielded a double carbonyl absorbance at 1680  $\text{cm.}^{-1}$  and 1710  $\text{cm.}^{-1}$ . Chromatography on silica gel resulted in an oil with a strong 1705  $\text{cm.}^{-1}$  absorbance and no 1680  $\text{cm.}^{-1}$  absorbance. The nmr spectrum exhibited resonances consistent with structure 107 with  $\delta$ 5.85 (multiplet, vinyl hydrogen, 1),  $\delta$ 4.05 (singlet, allylic hydrogens next to chlorine, 2) and  $\delta$ 2.20 (multiplet, broad, ring hydrogens, 12). No resonances that could be assigned to the acetoxy methyl hydrogens were present.

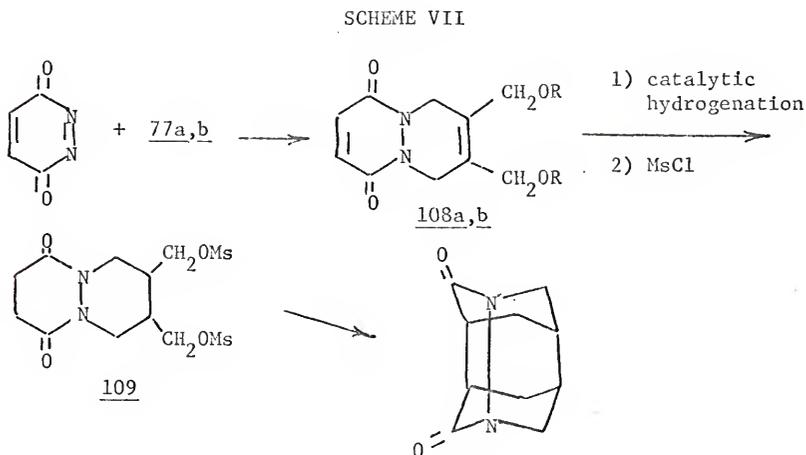
The mass spectrum gave a parent peak at  $m/e$  198 with a P+2 peak at  $m/e$  200 which was 35% of the parent. The theoretical P+2 intensity<sup>71</sup> for one chlorine atom is 32.6%. The base peak of the spectrum was  $m/e$  163 corresponding to loss of the allylic chlorine atom.



107

The mechanism is not known for the formation of 107 but one could speculate that the initial Diels Alder adduct, which appears to be present in small yield from the infrared spectrum, reacts with adventitious hydrogen chloride present. It is generally known that a trace amount of this impurity is contained in aluminum chloride.

The use of diazoquinone, 104, as a dienophile was believed to be an attractive course of action to pursue to obtain an adduct incapable of aromatizing. Scheme VII shows the intended reaction sequence. Kealy<sup>54</sup> had reported the synthesis of 104 and had reported it to be an extremely potent dienophile.



The synthesis of 104 was accomplished by oxidation of the potassium salt of maleic acid hydrazide with tert-butyl-hypochlorite at  $-77^{\circ}\text{C}$  in acetone. Reaction of 104 with the diacetoxydiene 77a at  $-55^{\circ}\text{C}$  for twelve hours yielded 45% of a light yellow crystalline solid which was consistent with structure 108a in every respect. The infrared spectrum gave the ester carbonyl at  $1730\text{ cm}^{-1}$  and the quinone amide carbonyl at  $1650\text{ cm}^{-1}$ . The nmr spectrum gave resonances at  $\delta 6.92$  (singlet, vinyl hydrogens, 2),  $\delta 4.80$  (singlet, allylic hydrogens adjacent to nitrogen, 4),  $\delta 4.57$  (singlet, allylic hydrogens adjacent to acetoxy, 4) and  $\delta 2.09$  (singlet, methyl hydrogens, 6). The elemental analysis agreed with the calculated value.

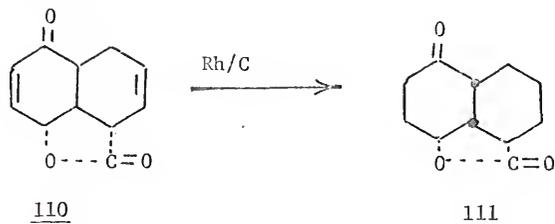
The reaction of 104 with the dihydroxy diene 77b yielded the

Diels Alder adduct 108b. Again all spectral characteristics were consistent with the assigned structure. The infrared spectrum gave absorbances for the hydroxyl groups at  $3480\text{ cm.}^{-1}$  and  $3400\text{ cm.}^{-1}$ . The amide like carbonyl appeared at  $1630\text{ cm.}^{-1}$ . The nmr spectrum had resonances at  $\delta 6.98$  (singlet, vinylic hydrogens, 2),  $\delta 4.51$  (singlet, allylic hydrogens adjacent to hydroxyl, 4),  $\delta 4.11$  (singlet, allylic hydrogens adjacent to nitrogen, 4) and  $\delta 3.50$  (broad, probably hydroxyl hydrogens, no integration). The elemental analysis agreed with the calculated values.

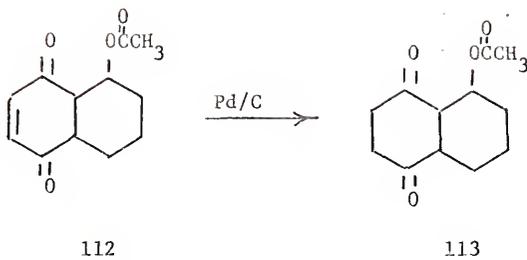
#### Attempted catalytic hydrogenation of Diels Alder adducts

The catalytic hydrogenations of the adducts 108a and 108b to the desired structure for the cyclizations were unsuccessful. Two catalyst systems were employed and both were chosen for their efficient reduction of double bonds and their inactivity toward hydrogenolysis of reactive substituent groups.

The catalyst system, 5% rhodium on carbon, has been successfully used in the reduction of compound 110 to 111.<sup>72</sup> Hydrogenation using 5% palladium on carbon has been found to be efficient in systems

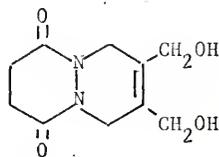


containing allylic acetoxy groups. Compound 112 was reduced to 113 using this system.<sup>73</sup>



The results of the hydrogenation attempts are shown in Table 7. In all cases, a mixture of products appeared to be present from the complex nmr spectra. Attempts at separation by column chromatography were almost unanimously unsuccessful.

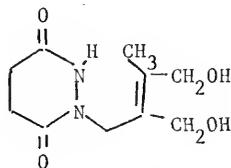
Two distinct trends, however, were apparent from these experiments. The first was that the quinone like double bond was easily hydrogenated and the tetrasubstituted double bond was highly resistant to reduction. In all atmospheric hydrogenations almost always approximately one-half of the theoretical hydrogen uptake was recorded in the first fifteen minutes. In experiment 3, the hydrogenation of 108b with 5% rhodium on carbon in ethyl acetate, a compound was isolated and purified and assigned structure 114. The nmr spectrum showed an absence of the



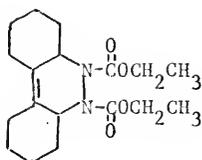
114

quinodial protons of the starting material and gave resonances at  $\delta 4.29$  (singlet, allylic hydrogens adjacent to hydroxyl, 4),  $\delta 4.10$  (singlet, allylic hydrogens, 4),  $\delta 3.87$  (singlet, broadened, hydroxyl hydrogens) and  $\delta 2.60$  (singlet, hydrogens adjacent to carbonyl, 4).

In a hydrogenation attempt under more forcing conditions, i.e., 5% rhodium on carbon at 35 psi., a white crystalline solid was isolated that melted at 151-4°C. The nmr spectrum was indicative of structure 115 which could result from the hydrogenolysis of a carbon nitrogen bond. The resonance signals recorded were  $\delta$ 4.31 and  $\delta$ 4.13 (two overlapping broad singlets, allylic hydrogens, 4),  $\delta$ 2.65 (singlet, hydrogens adjacent to the carbonyls, 4) and  $\delta$ 1.75 (broad singlet, allylic methyl hydrogens, 3). The mass spectrum gave the correct parent peak at m/e 228 and the base peak at m/e 210.

115

The resistance to hydrogenation of the tetrasubstituted double bond was not surprising since at least one report of a similar case is documented in the chemical literature. Gillis and Beck<sup>74</sup> attempted to hydrogenate 116 with Pd/C, Rainey nickel and Pd/Al<sub>2</sub>O<sub>3</sub> at 59 psi and were unsuccessful.

116

Hydrogenation of the double bonds of compound 90 was recognized as another route to 24. At atmospheric pressure hydrogenation with 5% rhodium on carbon in ethyl acetate resulted in the absorption

TABLE 7. CATALYTIC HYDROGENATION OF DIAZOQUINONE ADDUCTS

Experiment	Substrate	Conditions	Product
1	108a	Rh/C, ethyl acetate atmospheric pressure	unidentified oil 2250 cm. <sup>-1</sup> ir
2	108a	"	"
3	108b		<u>114</u>
4	108b	Rh/C, ethyl alcohol atmospheric pressure	unidentified oil 2250 cm. <sup>-1</sup> ir
5	108b	Pd/C, ethyl alcohol atmospheric pressure	"
6	108b	Pd/C, ethyl acetate atmospheric pressure	unidentified oil
7	108b	Rh/C, ethyl acetate 35 psi	<u>115</u>

of one third the theoretical amount of hydrogen. On work up a white solid was obtained with all spectral characteristics identical to its hydroquinone derivative 91.

Attempt to prepare precursor to intramolecular Diels Alder pathway

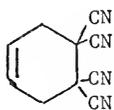
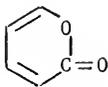
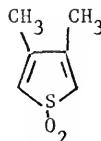
27, the Diels Alder adduct of 2,3-di(bromomethyl)1,3-butadiene and p-benzoquinone, was smoothly prepared by the method of Butler and Ottenbrite.<sup>29</sup> The 1,4-elimination of bromine from this compound by the use of zinc in dimethylformamide<sup>28</sup> to yield 28 was unsuccessful. Attempts to trap the intermediate diene with maleic anhydride and tetracyanoethylene were unsuccessful. In each case unidentifiable soluble polymeric material was obtained. Since Alder and Fremery<sup>28</sup> had postulated diradical intermediates in their investigation of the zinc dimethylformamide system, it is possible that the diene formed but then quickly polymerized.

## B. Attempted Synthesis of 5,5,6,6-Tetracyanocyclohexadiene

### Structures

#### Proposed syntheses

Two synthetic routes were investigated as possible means to generate 5,5,6,6-tetracyanocyclohexadiene, 29. Earlier work<sup>75</sup> had shown that the Diels Alder adduct of butadiene and tetracyanoethylene, 117, was resistant to halogenation reactions. The routes investigated

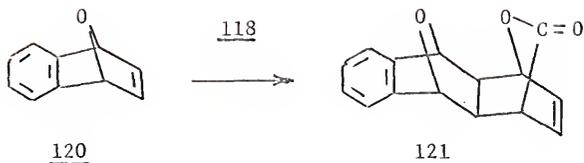
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were the reaction of tetracyanoethylene with  $\alpha$ -pyrone, 118, and with 3,4-dimethylthiophene-1,1-dioxide, 119, and then subsequent loss of carbon dioxide or sulfur dioxide to the desired tetrasubstituted diene.

#### Adducts of $\alpha$ -pyrone

118 was synthesized by the excellent preparation of Zimmerman and coworkers.<sup>76</sup> Surprisingly the cisoid diene failed to form the desired Diels Alder adduct with tetracyanoethylene under a variety of conditions. Upon mixing the two reactants, a strong reddish-brown color was always observed; however either starting materials or black tars were recovered from each reaction as summarized in Table 8.

The failure of tetracyanoethylene to form a Diels Alder adduct with 118 is surprising since this diene has been observed to be quite reactive with rather unreactive dienophiles. Fieser and Haddadin<sup>77</sup> observed 118 to react with the unusual dienophile 120 to yield 121.



Diels and Alder<sup>78</sup> observed the formation of the Diels Alder adduct with maleic anhydride. This reaction was successfully repeated.

Successful Diels Alder additions of 118 with both p-benzoquinone and fumaronitrile to yield 122 and 123 were observed. 122 was



characterized by the infrared spectrum which gave both a  $1750\text{ cm.}^{-1}$  ester carbonyl and a  $1655\text{ cm.}^{-1}$  quinone carbonyl. The nmr spectrum yielded resonances at  $\delta 6.82$  (singlet, quinone hydrogens, 2),  $\delta 6.57$  (triplet, vinylic hydrogens, 2),  $\delta 5.69$  (quartet, allylic hydrogens next to oxygen, 1),  $\delta 4.21$  (quartet, hydrogen next to carbonyl, 1) and  $\delta 3.60$  (two doublets, bridgehead hydrogens, 2). The elemental analysis was satisfactory for 122.

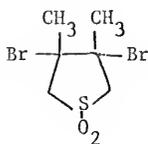
The fumaronitrile adduct, 123, gave weak infrared absorbances for the nitrile groups at  $2245\text{ cm.}^{-1}$  and  $2200\text{ cm.}^{-1}$ . The ester carbonyl absorbance was at  $1755\text{ cm.}^{-1}$ . The nmr spectrum gave resonances at  $\delta 6.92$  (multiplet, vinylic hydrogens, 2),  $\delta 5.80$  (multiplet, hydrogen adjacent to oxygen, 1),  $\delta 4.08$  (multiplet, unassigned, 2) and  $\delta 3.63$

(multiplet, unassigned, 1). A correct elemental analysis was obtained.

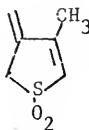
Both dimethyl maleic anhydride and tetraethylethylenetetracarboxylate failed to form the Diels Alder adduct also. It is probable that tetracyanoethylene along with these two dienophiles failed to react because of steric interferences. Under the forcing conditions, where the tars were obtained, it is possible that the adduct formed, lost carbon dioxide and then the resulting diene thermally polymerized under the severe reaction conditions.

#### Adducts of 3,4-dimethylthiophene-1,1-dioxide

3,4-Dimethylthiophene-1,1-dioxide, 119, was prepared by first the bromination of 2,3-dimethylbutadiene sulfone, 82, to the dibromide 124 and then dehydrohalogenation with sodium methoxide in tetrahydrofuran. The results of this reaction were not reproducible. Sometimes 119, the desired product, was formed in good yield, while at other times 125 was formed. The literature<sup>79</sup> preparation of 119 involved oxidation



124



125

of the corresponding thiophene to the thiophene dioxide. A reported dehydrobromination<sup>80</sup> of 124 with potassium hydroxide only yielded 125.

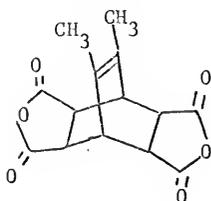
119 was found to be unreactive with tetracyanoethylene in the same manner as was  $\alpha$ -pyrone. However, maleic anhydride reacted with 119 in refluxing toluene to form 126.

This compound was identified by its infrared spectrum with an

TABLE 8. REACTIONS OF TETRACYANOETHYLENE WITH  $\alpha$ -PYRONE

Experiment	Solvent	Temperature	Time (hrs)	Product
1	neat	ambient	72	no reaction
2	tetrahydrofuran	reflux	48	no reaction
3	neat XS pyrone	140°C reflux	2	black tar
4	neat	100°C	24	black tar
5	xylene	reflux	48	black tar
6	toluene	reflux	44	black tar
7	benzene	reflux	45	black tar
8	tetrahydrofuran	sealed tube 60°	188	no reaction

anhydride carbonyl  $1850\text{ cm.}^{-1}$  and  $1780\text{ cm.}^{-1}$ . The nmr spectrum exhibited resonance signals at  $\delta 3.55$  (singlet, broad, hydrogens adjacent to carbonyl, 4),  $\delta 3.20$  (singlet, broad, hydrogens at bridgehead, 2) and  $\delta 1.62$  (singlet, allylic methyl hydrogens, 6). The mass spectrum yielded a molecular ion at  $m/e$  276.



## CHAPTER IV

### Experimental

#### A. General

All melting points and boiling points are uncorrected and reported in degrees centigrade. Melting points were determined in open capillary tubes on a Thomas-Hoover capillary melting point apparatus. Pressures are reported in millimeters of mercury. Elemental analyses were done by Galbraith Laboratories, Inc., Knoxville, Tennessee, Peninsular ChemResearch, Inc., Gainesville, Florida or Atlantic Micro-lab, Inc., Atlanta, Georgia.

Infrared spectra were recorded with either a Beckman IR 10 or a Beckman IR 8 Spectrophotometer. Visible spectra were recorded on a Beckman DK-2A Spectrophotometer. Proton nuclear magnetic spectra were obtained by use of a Varian A-60 Spectrometer and all resonances are given in the chemical shift parameter  $\delta$  and are measured from tetramethylsilane (TMS) as an internal standard. Mass spectral data were obtained using a Hitachi Perkin-Elmer RMU mass spectrometer.

All solvents were commercial reagent grade and used as received unless specifically noted. Polymer nonsolvents were technical grade and were filtered before use. All chemicals used as reactants were obtained commercially and used as received unless specifically designated as otherwise.

The comonomers divinyl ether, ethyl vinyl ether, isobutyl vinyl ether, styrene, acrylonitrile, divinyl sulfone and vinyl acetate were

obtained from commercial sources and distilled immediately prior to use. Divinyl carbonate and N-vinyl carbazole were obtained in high purity from commercial sources and used without further purification.

Number average molecular weights were obtained from a Mechrolab Model 302 Vapor Pressure Osmometer. Molecular weight distributions were obtained from a Waters Associates GPC 300 Gel Permeation Chromatograph. Thermal characteristics of the polymers were recorded by a Perkin-Elmer DSC1B Differential Scanning Calorimeter. Intrinsic viscosities were measured employing a Cannon-Ubbelohde semimicro dilution viscometer using standard procedures for operation and calculations.

## B. Copolymerizations and Related Reactions of 4-Substituted 1,2,4-triazoline-3,5-diones

### 1. Synthesis of 4-phenyl and 4-methyl-1,2,4-triazoline-3,5-diones

Ethyl carbazate<sup>81</sup>-Diethyl carbonate (2000 g., 1.80 mol.) and 88.0 g. (1.80 mol.) of 99% hydrazine hydrate were shaken together for approximately 20 minutes. Some exothermicity was observed and after this time the original two phase system blended into one phase. The solution was left standing overnight. Distillation at 95°C and 12 mm. yielded 147.7 g. (83.5%) of a clear liquid which solidified on standing to a white solid, m.p. 43-45.5° (lit.<sup>81</sup> 44-45.5°).

1-Ethoxycarbonyl-4-phenylsemicarbazide<sup>82</sup>-Ethyl carbazate (70.0 g., 0.67 mol.) was placed into a 500 ml. round-bottomed, three-necked flask with 350 ml. of benzene. The flask was equipped with a magnetic stirrer, a reflux condenser guarded by a calcium chloride drying tube, a dropping funnel and a thermometer. After refluxing to get the

ethyl carbazate into solution, the solution was cooled to 10°. Through the dropping funnel 70.0 g. (0.59 mol.) of phenyl isocyanate were introduced at a rate which kept the temperature between 10° and 20°. After all the isocyanate was added, the resulting white solid slurry was refluxed for 20 minutes and then cooled and filtered. After drying under vacuum 124 g. (89%) of the desired product m.p. 152-3° (lit.<sup>82</sup> m.p. 154°) were obtained.

4-Phenyl urazole<sup>82</sup>-To 275 ml. of hot 4M potassium hydroxide, 124 g. (0.55 mol.) of 1-ethoxycarbonyl-4-phenylsemicarbazide were added in small portions while shaking the potassium hydroxide solution on a steam bath. After the addition was completed, the solution was maintained on the steam bath for an additional 20 minutes. The solution was cooled and carefully acidified with concentrated hydrochloric acid. The precipitate was removed by vacuum filtration and extracted with 95% ethyl alcohol via a Soxhlet extractor. On cooling and then treating the mother liquor 69.2 g. (70.3% yield) of the urazole m.p. 204-7° (lit.<sup>82</sup> m.p. 206-7°) was obtained.

4-Phenyl-1,2,4-triazoline-3,5-dione, PhTD<sup>83</sup>-Anhydrous sodium sulfate, 25.0 g., was placed into a 500 ml. Erlenmeyer flask with 300 ml. of methylene chloride and 6.0 g. (0.034 mol.) of 4-phenyl urazole. The slurry was stirred by a magnetic stirrer and cooled to 0-5° with an ice-water bath. By means of a pipette attached to a gas cylinder with a tube, dinitrogen tetroxide was bubbled slowly through the solution. The temperature was kept below 5°. After a few minutes a deep red color developed. After all the urazole appeared to have been consumed, usually in about thirty minutes, the sodium sulfate was removed by vacuum filtration and the deep red solution was

evaporated using lukewarm water on a rotary evaporator. 4.8 g. (80% yield) of dark red crystalline PhTD was obtained. Purification was accomplished by sublimation at 70-75° under a vacuum of less than 0.5 mm. The red solid was stored in the absence of light in a freezer until it was used.

4-Methyl-1,2,4-triazoline-3,5-dione, MTD<sup>83</sup>-The same procedure used in the synthesis of PhTD was employed in the synthesis of MTD. This synthesis had been previously reported in the literature.<sup>83</sup> Methyl isocyanate was added to the ethyl carbazate and a quantitative yield of the corresponding semicarbazide derivative was obtained. This was cyclized with 4M potassium hydroxide to the corresponding 4-methyl urazole in a yield comparable to the phenyl derivative. Oxidation with dinitrogen tetroxide was accomplished in approximately 90% yield. The light red fluorescent appearing powder was purified by sublimation at less than 0.1 mm. and a temperature between 50 and 60°.

## 2. General copolymerization procedures

### a. Spontaneous copolymerizations

The following experimental procedure was typical of all spontaneous, room temperature copolymerizations unless specifically noted otherwise.

All glassware, i.e., Erlenmeyer flasks, syringes and volumetric flasks were scrupulously cleaned, rinsed with acetone, dried in an 80° oven and then allowed to cool to room temperature in a large desiccator. On removal from the desiccator the flasks were immediately capped with serum caps. Solvents were reagent grade and dried for a minimum of 24 hours over 3A molecular sieves.

Ethyl vinyl ether, EVE, PhTD copolymerization-A 50 ml. Erlenmeyer

flask equipped with a magnetic stirring bar and a rubber serum cap was charged with 0.499 g. (2.84 mmol.) of PhTD by removing the cap and adding as a solid. Next, 15 ml. of methylene chloride were introduced using a syringe and adding through the serum cap. This was followed by the addition of EVE (0.203 g., 2.83 mmol.) in the following manner. The vinyl ether was carefully weighed into a 10 ml. volumetric flask through a serum cap and then the flask was brought to volume with methylene chloride. A careful quantitative transfer to the reaction vessel was made using a syringe. The reaction mixture was stirred and within two minutes the dark red colored solution, characteristic of PhTD, was discharged to yellow. After 30 minutes the reaction mixture was precipitated by dropping slowly through a coarse filter frit into cold hexane. The hexane solution was filtered to yield 0.615 g. (86% yield) of a white-yellowish granular appearing solid. The solid appeared to soften at 100° and above 150° it darkened and decomposed. The number average molecular weight was determined to be 1660 by use of a Vapor Pressure Osmometer in acetone solution. The infrared spectrum (KBr) showed absorbances at 2980 (w), 1770 (w), 1715 (s), 1610 (s), 1500 (m), 1470 (m), 1420 (m), 1310 (m), 1130 (m), 1070 (w), 900 (w), 820 (w), 760 (m) and 700 (m) cm.<sup>-1</sup> The nmr spectrum (CDCl<sub>3</sub>) gave resonance signals at δ7.45 (s, broadened, 5), δ6.00 (m, broad, 1), δ3.83 (m, broad) and δ1.16 (t, broad, 3). The spectrum is shown in Fig. 1.

Anal. Calcd. for a 1:1 copolymer structure, C<sub>12</sub>H<sub>13</sub>N<sub>3</sub>O<sub>3</sub>: C, 58.30; H, 5.26; N, 17.00. Found: C, 58.08; H, 5.14; N, 17.16.

Table 1 contains a summary of experimental results of all EVE-PhTD copolymerizations.

b. Copolymerizations at 60°

The following experimental procedure was typical of all copolymerizations at 60° unless specifically noted otherwise.

The copolymerizations were effected in heavy walled 13 cm. x 3 cm. Pyrex tubes. All glassware i.e., Pyrex tubes, syringes and volumetric flasks was thoroughly cleaned, rinsed with acetone, dried in an 80° oven and then allowed to cool to room temperature in a large desiccator. On removal from the desiccator the volumetric flasks and the polymer tubes were sealed with serum caps. Solvents were reagent grade and were dried for a minimum of 24 hours over 3A molecular sieves. Copolymerizations were conducted in a 60° oil bath regulated by a Sargent NS1-12 controller to  $\pm 0.1^\circ$ .

Copolymerization of divinyl ether, DVE, and PhTD at 60°-A heavy walled Pyrex polymer tube, capped with a serum cap, was charged with 0.508 g. (2.81 mmol.) of PhTD by removing the cap and adding the solid. This was followed by the addition of 15 ml. of methylene chloride by means of a syringe. Next DVE (0.200 g., 2.82 mmol.) was carefully weighed into a 10 ml. volumetric flask using a syringe and adding through a serum cap. The flask was brought to volume with methylene chloride and then carefully transferred to the polymer tube by means of a syringe. The polymer tube was then placed on the high vacuum line and carried through a freeze-thaw degassing cycle using a  $10^{-4}$  mm. vacuum. The tube was sealed and warmed to room temperature before placing in the 60° bath. After 24 hours at 60° the originally red colored solution had changed to yellow. This color change normally took place within a few minutes after placing the tube in the bath. The tube was removed from the oil bath after 24 hours, cooled to room temp-

erature and opened. Precipitation of the copolymer was accomplished by filtering the reaction product through a coarse frit into rapidly stirred hexane. A white electrostatic polymeric material, 0.602 g. (86% yield), was obtained. This product softened at 105° and decomposed at 170°. The number average molecular weight was 1590. The infrared spectrum (KBr) showed absorbances at 1770 (m), 1720 (s), 1640 (m), 1610 (s), 1500 (m), 1470 (m), 1450 (m), 1425 (m), 1310 (m), 1160 (m), 1070 (m), 1000 (w), 945 (m), 855 (m), 760 (m) and 695 (m)  $\text{cm}^{-1}$ .

The nmr spectrum ( $\text{CDCl}_3$ ) gave resonance signals at  $\delta$ 7.39 (s, broad, 5),  $\delta$ 6.25 (m, broad, 2) and  $\delta$ 4.82- $\delta$ 3.50 (m, broad, 4). The nmr spectrum is shown in Fig. 3.

Anal. Calcd. for 1:1 copolymer structure  $\text{C}_{12}\text{H}_{11}\text{N}_3\text{O}_3$ : C, 58.80; H, 4.50; N, 17.20. Found: C, 58.60; H, 4.56; N, 17.17.

A summary of the DVE-PhTD copolymerizations is given in Table 2.

### 3. Copolymerizations of vinyl ethers and PhTD

Spontaneous copolymerization of DVE and PhTD-The standard method for spontaneous copolymerizations was followed with the flask charged with 0.502 g. (2.87 mmol.) of PhTD, 0.199 g. (2.85 mmol.) of DVE and 25 ml. of methylene chloride. A discharge of the red color was noted in 15 minutes and the contents were precipitated into hexane after 30 minutes. A white solid, 0.477 g. (77.5% yield), was obtained whose number average molecular weight was determined to be 450.

The infrared spectrum (KBr) exhibited absorbances at 1770 (m), 1710 (s), 1640 (w), 1610 (m), 1500 (m), 1425 (m), 1310 (w), 1160 (m), 1025 (w), 850 (w), 770 (m), and 695 (m)  $\text{cm}^{-1}$ . The nmr spectrum ( $\text{CDCl}_3$ ) gave resonance signals at  $\delta$ 7.49 (s, with upfield spikes, 5),  $\delta$ 6.50

(q, 1),  $\delta$ 5.71 (t, 1) and  $\delta$ 5.00- $\delta$ 3.80 (m,4).

Anal. Calcd. for  $C_{12}H_{11}N_3O_3$  (1:1 structure): C, 58.80; H, 4.50; N, 17.20. Found: C, 57.87; H, 4.45; N, 17.65.

Preparation of 3-phenyl-6-vinyloxy-1,3,5-triazabicyclo[3.2.0]hepta-2,4-dione-An identical procedure to the previous DVE-PhTD reaction at room temperature was followed. The reaction mixture was precipitated into hexane (not cooled) and after filtration of the solid the filtrate was placed into an ice-water bath for about two hours. A white solid crystallized out and filtration of this solid yielded 0.15 g. of pure 31b m.p. 128-29°.

The infrared spectrum (KBr) showed absorbances at 3080 (m), 3040 (w), 2990 (w), 1795 (m), 1730 (s), 1710 (s), 1645 (m), 1625 (m), 1600 (m), 1505 (m), 1455 (w), 1420 (m), 1365 (m), 1330 (m), 1290 (m), 1240 (m), 1200 (w), 1160 (s), 1130 (m), 1110 (m), 1070 (w), 1020 (m), 950 (m), 875 (m), 845 (m), 810 (w), 725 (m) and 655 (m)  $cm^{-1}$ .

The nmr spectrum ( $CDCl_3$ ) gave resonances at  $\delta$ 7.40 (s, 5),  $\delta$ 6.60 (q, 1),  $\delta$ 5.90 (t, 1) and  $\delta$ 4.50 (m, 4). The mass spectrum (70 eV) gave the following fragments,  $m/e$  (rel. intensity): 246 (10), 245 (M+, 69), 216 (3), 203 (6), 202 (9), 177 (8), 176 (9), 170 (3), 160 (3), 155 (8), 149 (17), 148 (6), 147 (12), 141 (12), 120 (22), 119 (100), 97 (5), 91 (23), 84 (5), 83 (14), 77 (8), 70 (44), 64 (4) and 57 (9).

Anal. Calcd. for  $C_{12}H_{11}N_3O_3$ : C, 58.80; H, 4.50; N, 17.20. Found: C, 58.88; H, 4.61; N, 17.24.

Attempted radical initiated copolymerization of PhTD and DVE by photolysis of benzoyl peroxide-A polymer tube was charged with 0.500 g. (2.84 mmol.) of PhTD, 0.032 g. of benzoyl peroxide (0.46 wt.%) and then 15 ml. of methylene chloride were added. The solution was frozen in

liquid nitrogen and then 0.201 g. (2.88 mmol.) of DVE was dissolved in 10 ml. of methylene chloride and introduced into the tube. The contents were frozen (two layers existed—one red and one white) and the tube was degassed on the high vacuum line and sealed. The tube was placed into a  $-45^{\circ}$  ethanol bath in which the temperature was maintained by circulating the ethanol through a dry ice isopropanol bath. The tube was irradiated for nine hours with a Hanovia Utility Ultraviolet Quartz Lamp. The solution gradually lightened in color over this time, but was still pink when the tube was removed and opened. The contents were filtered at dry ice temperature through a dry ice jacketed filter funnel and then quickly added to hexane which had been cooled to  $-10^{\circ}$ . A white solid precipitate formed and was removed by filtration and then dried in vacuo. The filtration was performed with care to keep the hexane from warming. The resulting solid, when redissolved in methylene chloride, gave an insoluble portion (0.195 g.) and a soluble portion (0.255 g.). Both solids gave very similar infrared spectra. The infrared spectra were very similar to the spontaneous copolymerization product of DVE-PhTD. The nmr spectrum gave identical resonance signals to the spectrum of the spontaneous copolymerization product of the two monomers.

Photolysis of DVE and PhTD-As a control the previous reaction was performed in the absence of benzoyl peroxide. After nine hours of irradiation 0.389 g. of soluble product were obtained and the spectral characteristics were identical to those from the previous reaction.

Copolymerization of DVE and PhTD at  $60^{\circ}$  under "dry conditions"-The normal procedure for the  $60^{\circ}$  copolymerization was followed with the following alterations and precautions taken.

Reagent grade methylene chloride was distilled from 3A molecular sieves through a twelve inch column into a flask containing more 3A sieves. The flask was immediately stoppered with a serum cap. The PhTD was dried for two hours in a drying pistol in vacuo at refluxing ether temperature and the DVE was distilled into 3A molecular sieves and left for 24 hours before use. A polymer tube and a 10 ml. volumetric flask were dried overnight in an oven and then connected to a vacuum pump, flamed out, cooled in a desiccator and then stoppered with serum caps. The PhTD was transferred to the polymer tube in a nitrogen flushed glove bag. The DVE was added in the usual manner by means of a syringe. The monomer charge was 0.500 g. (2.85 mmol.) of PhTD and 0.197 g. (2.81 mmol.) of DVE. After the customary freeze-thaw cycle on the high vacuum manifold the tube was sealed. The reaction was continued for 24 hours and 0.602 g. (86% yield) of product was obtained. The infrared absorbances of the copolymer were identical to those of other 60° DVE-PhTD copolymers. On dissolving for the molecular weight determination, an acetone soluble fraction (0.422 g.) and an acetone insoluble fraction were obtained. The molecular weight of the soluble fraction was determined to be 2540.

DVE-PhTD copolymerization in the presence of a free radical inhibitor-In the usual manner for 60° copolymerizations, a polymer tube was charged with 0.499 g. (2.85 mmol.) of PhTD, 0.200 g. (2.86 mmol.) of DVE and 0.010 g. (1.5 wt.%) of m-dinitrobenzene. After placing in the 60° oil bath the solution turned yellow as was usually observed in the 60° copolymerizations. Precipitation after 24 hours yielded 0.459 g. (71.5% yield) of polymeric material. The infrared spectrum of the polymeric material was identical to the other spectra from the DVE-PhTD 60° copolymerizations. The filtrate residue yielded a solid that gave

an infrared spectrum with the  $1610\text{ cm.}^{-1}$  and  $850\text{ cm.}^{-1}$  bands absent but identical in all other respects. The molecular weight of the polymer was determined to be 2130.

Spontaneous copolymerization of PhTD and DVE with a 2:1 feed composition-Following the usual procedure for the spontaneous room temperature copolymerizations 0.501 g. (2.85 mmol.) of PhTD and 0.098 g. (1.40 mmol.) of DVE were allowed to react for 30 minutes in methylene chloride. The red color persisted at the end of the reaction time and precipitation into hexane yielded 0.256 g. (44% yield) of product. The product was not sufficiently soluble in acetone to obtain a molecular weight. The infrared spectrum (KBr) showed a less intense  $1610\text{ cm.}^{-1}$  band and a very weak  $860\text{ cm.}^{-1}$  band when compared to the usual DVE-PhTD spontaneous products. The nmr spectrum gave the same signals as the 1:1 feed composition  $60^\circ$  DVE-PhTD copolymerizations with the aromatic region enhanced to approximately twice its absorbance in the 1:1 copolymers.

Copolymerization of PhTD and DVE at  $60^\circ$  with a 2:1 feed composition- A polymer tube was charged in the usual manner, but with 0.502 g. (2.86 mmol.) of PhTD and 0.099 g. (1.41 mmol.) of DVE. After 24 hours the usual yellow color was observed; however, considerable white fluffy solid was present. After filtering the insoluble portion (0.021 g.), precipitation into hexane yielded 0.545 g. (91.0% yield) of soluble product. The insoluble portion gave an infrared spectrum (KBr) with the following absorbances: 1775 (m), 1710 (m), 1600 (m), 1495 (m), 1420 (m), 1395 (m), 1290 (m), 1245 (m), 1145 (m), 1105 (m), 1070 (m), 1045 (m), 1020 (m), 940 (m), 875 (m), 835 (m), 795 (m), 775 (m), 740 (m) and  $690\text{ (m) cm.}^{-1}$

Anal. Calcd. for  $C_{20}H_{16}N_6O_5$  (2:1 copolymer): C, 57.20; H, 3.82; N, 20.00. Found: C, 54.45; H, 3.70; N, 19.02.

The soluble portion gave an infrared spectrum (KBr) showing absorbances at 1775 (m), 1715 (s), 1640 (w), 1610 (m), 1495 (m), 1420 (s), 1310 (m), 1290 (m), 1265 (m), 1150 (m), 1070 (m), 1025 (m), 940 (w), 860 (w), 765 (m) and 695 (m)  $cm^{-1}$ .

Anal. Calcd. for  $C_{12}H_{11}N_3O_3$  (1:1 copolymer): C, 58.80; H, 4.50; N, 17.20. Found: C, 55.63; H, 4.10; N, 18.85.

Copolymerization of DVE and MTD at 60°-Using the typical procedure for 60° copolymerizations, MTD (0.324 g., 2.86 mmol.) and DVE (0.198 g., 2.83 mmol.) were reacted in a sealed tube in methylene chloride for 24 hours. The red color faded as usual to yellow. Precipitation into hexane yielded 0.264 g. (50.0% yield) of yellowish-white powdery electrostatic product. The infrared spectrum (KBr) gave 2950 (w), 1770 (m), 1720 (s), 1640 (m), 1610 (s), 1510 (m), 1480 (m), 1400 (m), 1230 (m), 1160 (m), 1115 (w), 1030 (w), 995 (w), 860 (m), 770 (m) and 750 (m)  $cm^{-1}$ . The nmr spectrum ( $CDCl_3$ ) gave resonance signals at  $\delta$ 6.33 (broad, 2),  $\delta$ 4.33 (broad, 4) and  $\delta$ 3.03 (s, 3). The nmr spectrum is shown in Fig. 4.

Copolymerization of DVE and MTD at 60° with free radical initiator-This experiment was identical to the preceding copolymerization except for the addition of 0.5 wt. % of azobisisobutyronitrile. A yellowish-white powder was obtained as before and its infrared spectrum was identical to the reaction performed without initiator. A molecular weight of 900 was obtained.

Spontaneous copolymerization of MTD and EVE-In the usual manner for room temperature polymerizations 0.452 g. (4.00 mmol.) of MTD and 0.283 g. (3.95 mmol.) of EVE were polymerized for 30 minutes in 25 ml.

of methylene chloride. The red color was not completely discharged after this time, but was still a faint pink. Precipitation of the methylene chloride solution into hexane resulted in a pink jelly like material. Redissolving in methylene and precipitating into ether and then redissolving this product into acetone and precipitating into ether yielded only a few milligrams of solid product. The infrared spectrum (KBr) yielded absorbances at 2980 (w), 1770 (m), 1705 (s), 1470 (s), 1400 (m), 1270 (broad, w), 1240 (broad, w), 1100 (m), 1050 (broad, m), 760 (m) and 720 (w)  $\text{cm.}^{-1}$

Copolymerization of PhTD and isobutyl vinyl ether, IVE-The comonomers PhTD (0.500 g., 2.80 mmol.) and IVE (0.280 g., 2.80 mmol.) were reacted in the usual manner for spontaneous copolymerizations. Within 10 minutes the red color had discharged to yellow. Precipitation into hexane yielded 0.400 g. (51.5% yield) of a white electrostatic polymer. The infrared spectrum (KBr) showed absorbances at 3080 (w), 2975 (m), 2960 (w), 2880 (w), 1770 (m), 1720 (s), 1610 (m), 1500 (m), 1420 (m), 1250 (w), 1170-1000 (m, broad), 910 (w), 760 (m) and 685 (m)  $\text{cm.}^{-1}$  The nmr spectrum ( $\text{CDCl}_3$ ) gave resonance signals at  $\delta$ 7.30 (m, broad),  $\delta$ 6.20 (m, weak, broad),  $\delta$ 4.00- $\delta$ 3.00 (m, broad),  $\delta$ 1.70 (broad, m) and  $\delta$ 0.80 (m, broad). The spectrum was not integrated because of its complex nature.

Catalytic hydrogenation of the DVE-PhTD copolymer with 5% Rh/C in ethyl acetate-A catalytic hydrogenation flask for an atmospheric pressure hydrogenation apparatus was charged with 0.149 g. of the DVE-PhTD copolymer, 50 ml. of ethyl acetate and 0.115 g. of 5% Rh/C catalyst. At atmospheric pressure only 5 ml. of hydrogen were absorbed. Application of a small pressure via the mercury measuring column gave an uptake of 21.1 ml., whereas a blank under the same conditions absorbed 11.2 ml.

The net, 9.9 ml., was only 66.0% of the theoretical 15 ml. for a 1:1 copolymer with structure 41. An nmr spectrum of the product ( $\text{CDCl}_3$ ) showed resonance signals at  $\delta 7.38$ ,  $\delta 6.10$ - $\delta 5.30$ ,  $\delta 4.80$ - $\delta 3.20$ , and  $\delta 1.40$ - $\delta 0.83$ .

Catalytic hydrogenation of the DVE-PhTD copolymer with 5% Pd/Al<sub>2</sub>O<sub>3</sub> in ethyl acetate-The catalytic hydrogenator was charged with 0.168 g. of the DVE-PhTD copolymer, 0.135 g. of 5% Pd/Al<sub>2</sub>O<sub>3</sub> and 75 ml. of ethyl acetate. The hydrogen uptake was exactly equal to the theoretical after subtraction for the blank. The infrared spectrum had three distinctive changes, i.e., the 1640  $\text{cm.}^{-1}$  band, the 1610  $\text{cm.}^{-1}$  band, and the 850  $\text{cm.}^{-1}$  band disappeared. The nmr spectrum ( $\text{CDCl}_3$ ) gave resonances at  $\delta 7.38$ , a much decreased resonance at  $\delta 6.50$ , a broader resonance from  $\delta 5.00$  to  $\delta 3.00$  and a large resonance at  $\delta 1.20$ . No integration was taken because of the broadness. The original molecular weight of 1590 was reduced to 490.

Catalytic hydrogenation of the EVE-PhTD copolymer with 5% Pd/Al<sub>2</sub>O<sub>3</sub> in ethyl acetate-The same procedure used for hydrogenation of the DVE-PhTD copolymer was followed. The hydrogenation flask was charged with 0.165 g. of EVE-PhTD copolymer, 75 ml. of ethyl acetate and 0.127 g. of 5% Pd/Al<sub>2</sub>O<sub>3</sub>. At first it appeared as if more hydrogen than the blank was absorbed; however after a couple of hours the amount measured was identical to that measured for the blank. The infrared spectrum was identical to the original copolymer except the strong 1610  $\text{cm.}^{-1}$  had disappeared.

4. Interception of the 1,4-dipole of PhTD and vinyl ethers by Ketone solvents

Spontaneous reaction of PhTD and EVE in acetone-PhTD (0.500 g., 2.85 mmol.) was placed into a 50 ml. Erlenmeyer flask equipped with a magnetic stirring bar and a serum cap. Using a syringe, acetone (15 ml.) was introduced and a deep red solution resulted. EVE (0.199 g., 2.80 mmol.) dissolved in 10 ml. of acetone was added in like manner. After 30 minutes the dark red color had faded to a slight pink-tinged solution. The acetone was removed on a rotary evaporator at ambient temperature. The solid product was dissolved in methylene chloride (15 ml.) and then precipitated by slowly dropping into 300 ml. of hexane. A white polymeric solid was removed by filtration and the resulting yellow filtrate carefully evaporated to dryness on a rotary evaporator. The light yellow crystalline product (0.361 g., 42% yield) was recrystallized from absolute ethenol to give pure 49, m.p. 149-51°.

The infrared spectrum (KBr) showed absorbances at 2980-2880 (m), 1770 (s), 1710 (s), 1600 (w), 1490 (m), 1420 (s), 1390 (m), 1280 (w), 1250 (m), 1245 (w), 1205 (w), 1170 (m), 1150 (m), 1130 (m), 1080 (w), 1030 (m), 990 (m), 950 (m), 880 (w), 855 (w), 815 (w), 780 (m), 740 (m), 710 (m), 690 (m), 650 (m) and 610 (m)  $\text{cm.}^{-1}$

The nmr spectrum ( $\text{CDCl}_3$ ) showed resonance signals at  $\delta$ 7.40 (m, 5),  $\delta$ 5.02 (q, 1),  $\delta$ 3.73 (m, 4),  $\delta$ 1.85 (s, 3),  $\delta$ 1.70 (s, 3) and  $\delta$ 1.25 (t, 3). The mass spectrum (70 eV) gave the following fragments,  $\underline{m/e}$  (rel. intensity) 305 ( $\text{M}^+$ , 4), 260 (7), 248 (17), 247 (100), 219 (8), 218 (22), 205 (7), 191 (13), 190 (59), 177 (2), 174 (2), 159 (4), 149 (2), 148 (4), 128 (4), 120 (18), 119 (27), 99 (11), 81 (10), 77 (7), 72 (26) and 71 (24). Anal. Calcd. for  $\text{C}_{15}\text{H}_{19}\text{N}_3\text{O}_4$ : C, 59.00; H, 6.24; N, 13.79.

Found: C, 59.03; H, 6.33; N, 13.79.

The white polymeric solid was formed in 40% yield (0.283 g.). It was reprecipitated twice from methylene chloride into hexane. The nmr spectrum was characteristic of the EVE-PhTD copolymers with broad resonances centered at  $\delta$ 7.41,  $\delta$ 6.00,  $\delta$ 4.00 and  $\delta$ 1.15. A new resonance appeared at  $\delta$ 2.12 as a broad singlet. It did not decrease in intensity after the two reprecipitations and was assigned to acetone incorporated into the polymer. A calculation based on its relative intensity indicated about 20% incorporated.

Spontaneous reaction of PhTD and IVE in acetone-The experimental procedure followed was identical to the EVE case except isobutyl vinyl ether (IVE) was used in place of EVE. The light yellow product was recrystallized from absolute ethanol to give pure 50, m.p. 125-6° in 47% yield.

The infrared spectrum (KBr) showed absorbances at 2980-2880 (m), 1770 (s), 1710 (s), 1600 (w), 1490 (s), 1470 (m), 1445 (m), 1415 (s), 1380 (s), 1280 (m), 1250 (m), 1245 (m), 1205 (m), 1170 (s), 1130 (s), 1090 (m), 1035 (s), 1015 (m), 990 (m), 950 (m), 915 (w), 880 (w), 855 (w), 815 (w), 780 (m), 740 (m), 710 (w), 690 (m) and 610 (w)  $\text{cm}^{-1}$ .

The nmr spectrum ( $\text{CDCl}_3$ ) showed resonance signals at  $\delta$ 7.42 (m, 5),  $\delta$ 5.00 (q, 1),  $\delta$ 3.50 (m, 4),  $\delta$ 1.85 (s, 3),  $\delta$ 1.70 (s, 3) and  $\delta$ 0.95 (d, 6). The mass spectrum (70 eV) gave the following fragments,  $\text{m/e}$  (rel. intensity) 333 ( $\text{M}^+$ , 1), 276 (4), 275 (20), 261 (1), 260 (7), 219 (6), 218 (30), 191 (30), 190 (100), 177 (1), 162 (1), 149 (1), 148 (1), 141 (1), 135 (2), 134 (1), 120 (15), 119 (22), 100 (2), 91 (8), 84 (5), 77 (5), 71 (18), 59 (24), 58 (3), 57 (30) and 56 (29).

Anal. Calcd. for  $\text{C}_{17}\text{H}_{23}\text{N}_3\text{O}_4$ : C, 61.30; H, 6.90; N, 12.61.

Found: C, 61.49; H, 6.98; N, 12.47.

Spontaneous reaction of PhTD and EVE in cyclohexanone—The experimental procedure followed was identical to the two previous cases with a change in the work up due to the high boiling point of cyclohexanone. The cyclohexanone was removed by vacuum distillation at 60°. The resulting oily residue was dissolved in methylene chloride and added slowly to hexane as before. The gummy polymeric material formed was filtered and the filtrate evaporated to obtain a white solid which was readily purified by recrystallization from absolute ethanol to give a 12% yield of pure 51. The actual yield was probably much higher but was lowered by the complicated work up procedure. The white needle like crystalline solid melted at 170–71°. The infrared spectrum (KBr) yielded absorbances at 2980–2860 (m), 1775 (s), 1715 (s), 1600 (w), 1490 (m), 1420 (s), 1385 (m), 1365 (m), 1335 (w), 1285 (w), 1260 (m), 1250 (m), 1220 (m), 1170 (m), 1150 (m), 1135 (s), 1070 (m), 1020 (m), 980 (m), 970 (m), 910 (m), 870 (w), 850 (w), 825 (w), 800 (m), 770 (m), 740 (m), 685 (m), 660 (w) and 640 (w) cm.<sup>-1</sup>

The nmr spectrum (CDCl<sub>3</sub>) gave resonance signals at  $\delta$ 7.40 (m, 5),  $\delta$ 5.10 (q, 1),  $\delta$ 3.70 (m, 4),  $\delta$ 1.50– $\delta$ 2.80 (broad m, 11) and  $\delta$ 1.25 (t, 3). The mass spectrum (70 eV) yielded the following fragments, m/e (rel. intensity) 345 (M<sup>+</sup>, 2), 300 (3), 248 (18), 247 (100), 219 (11), 218 (21), 214 (3), 205 (8); 191 (12), 190 (37), 177 (3), 162 (1), 149 (1), 148 (4), 135 (2), 128 (5), 121 (2), 120 (21), 119 (29), 99 (15), 91 (10), 81 (14), 77 (7), 71 (26) and 56 (16).

Anal. Calcd. for C<sub>18</sub>H<sub>23</sub>N<sub>3</sub>O<sub>4</sub>: C, 62.60; H, 6.67; N, 12.17. Found: C, 62.73; H, 6.76; N, 12.32.

Spontaneous reaction of PhTD and DVE in acetone—The experimental

procedure followed was identical to the EVE case. The reaction mixture was precipitated into hexane and the solid polymeric material was removed by filtration. The polymeric material gave an nmr spectrum ( $\text{CDCl}_3$ ) with broad bands centered at  $\delta 7.48$ ,  $\delta 4.48$  and two upfield multiplets at  $\delta 2.20$  and  $\delta 1.80$ , possibly from incorporated acetone.

The filtrate was evaporated to dryness and an nmr spectrum ( $\text{CDCl}_3$ ) of the small amount of solid was indicative of two products. Signals for the 1,2-diazetidene, 3lb, were present. Also resonances were present at  $\delta 6.42$  (q, 1),  $\delta 5.25$  (t, 1), centered at  $\delta 4.30$  (complex m, after subtracting for 3lb, 4) and  $\delta 1.75$  (s, 6) which were characteristic of the oxadiazine. No other characterization of this product was possible because of its small yield.

##### 5. Reactions and copolymerizations of PhTD and other monomers

Reaction of PhTD with vinyl acetate, VAC, at 60°—The normal procedure for the 60° copolymerizations in sealed tubes was followed. PhTD (0.503 g., 2.86 mmol.) and VAC (0.249 g., 2.90 mmol.) were reacted for 24 hours in 25 ml. of methylene chloride solution. The red color of PhTD disappeared after four hours. Precipitation in hexane yielded a white solid and as the filtrate cooled under the water aspirator vacuum a white solid began to crystallize from solution. After cooling this filtrate in a freezer for two hours, filtration yielded 30% of pure 55, m.p. 130–31°. The white granular solid gave an infrared spectrum (KBr) that showed absorbances at 3080 (w), 3005 (w), 2990 (w), 2890 (w), 2860 (w), 2750 (w), 1800 (m), 1730 (s), 1600 (w), 1495 (m), 1425 (s), 1390 (m), 1370 (m), 1325 (m), 1275 (s), 1240 (m), 1175 (m), 1145 (m), 1090 (m), 1040 (w), 1000 (w), 995 (m), 950 (m), 875 (m), 810 (m),

755 (m), 690 (m) and 640 (m) cm.<sup>-1</sup>

The nmr spectrum (CDCl<sub>3</sub>) gave resonance signals, all singlets, at  $\delta$ 9.56 (s, 1),  $\delta$ 7.50 (s, 5),  $\delta$ 4.80 (s, 2) and  $\delta$ 2.60 (s, 3). The mass spectrum (70 eV) gave the following fragments,  $m/e$  (rel. intensity) 262 (14), 261 (M<sup>+</sup>, 100), 220 (11), 219 (86), 191 (11), 176 (11), 175 (11), 132 (18), 131 (36), 122 (11), 121 (14), 120 (18), 119 (79), 104 (89), 93 (25), 91 (32) and 77 (54).

Anal. Calcd. for C<sub>12</sub>H<sub>11</sub>N<sub>3</sub>O<sub>4</sub>: C, 55.20; H, 4.22; N, 16.09.  
Found: C, 55.34; H, 4.28; N, 15.95.

The initial solid, 0.186 g., yielded an nmr spectrum which indicated it was in the most part 55. Also present were broadened resonances at  $\delta$ 7.75,  $\delta$ 4.50 (weak) and  $\delta$ 2.15. The melting point was recorded as 110-13°. Evaporation of the final filtrate yielded an additional 0.119 g. of impure 55. By combining all three products, the total yield of the reaction was 71%.

Reaction of PhTD and VAC at room temperature-The normal room temperature copolymerization procedure was followed with 0.499 g. (2.84 mmol.) of PhTD and 0.246 g. (2.89 mmol.) of VAC in 25 ml. of methylene chloride. The flask was stirred for 21 hours and upon precipitation of the contents (still pink) 0.426 g. (57.3% yield) of a white solid was obtained. The infrared spectrum was practically identical to the 60° product. The nmr spectrum was identical to the first precipitated product from the 60° reaction verifying it to be impure 55.

Reaction of PhTD and VAC at 60° in acetone-The normal 60° reaction conditions were employed with acetone in the place of methylene chloride as the solvent. PhTD (0.502 g., 2.86 mmol.) and VAC (0.252 g., 2.96 mmol.) were reacted in 25 ml. of acetone. Precipitation into hexane gave a gummy solid which was dissolved and reprecipitated in hex-

ane. The filtered solid gave spectral data indicative of 55. The filtrate was evaporated and a small amount of solid was obtained which yielded an nmr spectrum showing some other compound with the following additional resonances  $\delta$ 7.42 (d, one peak from 55),  $\delta$ 6.20 (t, 1),  $\delta$ 3.75 (d, broad, 2),  $\delta$ 2.17 (s, broad, 3) and  $\delta$ 1.80 (s, broad, 6). Since only a very small amount of solid was formed, no other characterizations were made.

Reaction of PhTD and VAC at 60° in the presence of phenyl isocyanate-This reaction was conducted in an identical manner to the 60° PhTD-VAC reaction in methylene chloride with the addition of 2.18 g. (18.30 mmol.) of phenyl isocyanate. On opening the polymer tube after 24 hours at 60°, the sharp odor of phenyl isocyanate was noted. Precipitation into hexane yielded a light yellow solid that gave an oily solid which had a strong phenyl isocyanate odor. After setting overnight this oil changed to a white solid. This solid was identified as diphenyl urea from its melting point, i.e., 238-40° (lit.<sup>62</sup> m.p. 241-42°).

Copolymerization of PhTD and DVC at room temperature-In a manner analogous to other room temperature polymerizations 0.499 g. (2.85 mmol.) of PhTD and 0.326 g. (2.86 mmol.) of DVC were reacted for 14.5 hours. The flask was wrapped with aluminum foil to protect the light sensitive divinyl carbonate. The solution, which remained red, was precipitated into hexane and the reddish precipitate obtained was extracted twice with 50 ml. of anhydrous ethyl ether. A white solid was left after the unreacted monomers had been extracted and filtration yielded 0.370 g. (44.9%). The infrared spectrum (KBr) gave the following absorbances: 3080 (w), 1775 (s), 1720 (s), 1650 (w), 1610 (m), 1600 (m), 1500 (m), 1415 (s), 1300 (m), 1250 (s), 1150 (m), 1100 (w),

1070 (m), 1025 (w), 980 (m), 940 (w), 890 (m), 760 (m) and 690 (m)  $\text{cm.}^{-1}$ . The nmr spectrum ( $\text{CDCl}_3$ ) exhibited resonance signals at  $\delta 7.38$  (s, broad, 6) and  $\delta 5.31$ - $\delta 3.31$  (m, broad, 1).

Anal. Calcd. for  $\text{C}_{21}\text{H}_{16}\text{N}_6\text{O}_7$  (2:1 structure): C, 54.35; H, 3.45; N, 18.10. Found: C, 54.45; H, 3.87; N, 18.10.

Copolymerization of PhTD and DVC at  $60^\circ$ -In the same manner as followed for all  $60^\circ$  copolymerizations, a polymer tube was charged with 0.500 g. (2.86 mmol.) of PhTD and 0.326 g. (2.86 mmol.) of DVC and 25 ml. of methylene chloride. After about 18 hours the resulting solution was clear and colorless, in contrast to all other reactions with PhTD when the solutions were yellow. Precipitation into hexane yielded a white solid, 0.608 g. (73.5% yield). The infrared and nmr spectra were identical to the room temperature trial. A molecular weight determination yielded a value of 1240.

Attempted copolymerization of PhTD with divinyl sulfone,  $\text{DVS}\text{O}_2$ , at  $60^\circ$ -A polymer tube was charged with 0.499 g. (2.84 mmol.) of PhTD, 0.320 g. (2.72 mmol.) of  $\text{DVS}\text{O}_2$  and 0.004 g. (0.5 wt. %) of AIBN. The polymerization was carried out in the usual manner and after 24 hours at  $60^\circ$  0.229 g. (29% yield) of a white solid were obtained. The infrared spectrum (KBr) was very similar to PhTD decomposition products except that some minor differences were recorded for the 1140  $\text{cm.}^{-1}$  and 1290-1260  $\text{cm.}^{-1}$  bands. The nmr spectrum ( $\text{CDCl}_3$ ) gave resonance signals at  $\delta 7.37$  (s, broad with spike at  $\delta 7.28$ , 7),  $\delta 6.50$  (m, broad, 1),  $\delta 5.89$  (m, broad, 1) and  $\delta 4.50$ - $\delta 3.80$  (m, broad, 1).

Anal. Calcd. for  $\text{C}_{12}\text{H}_{11}\text{N}_3\text{O}_4\text{S}$  (1:1 structure): C, 49.20; H, 3.73; N, 14.31; S, 10.95. Found: C, 56.67; H, 3.91; N, 20.69; S, trace.

Attempted copolymerization of PhTD with acrylonitrile, AN, at room temperature--In the usual manner for room temperature polymerizations 0.501 g. (2.86 mmol.) of PhTD, 25 ml. of methylene chloride and 0.155 g. (2.88 mmol.) of AN were reacted for 42 hours. The solution remained red and precipitation yielded only 0.099 g. (15.1% yield) of a yellow-white solid. The infrared spectrum was identical to the product from the PhTD homopolymerization experiments, indicating no reaction with the AN.

Attempted copolymerization of PhTD with AN at 60°--The same procedure was used as followed in other 60° copolymerizations. The feed was 0.500 g. (2.66 mmol.) of PhTD, 0.151 g. (2.79 mmol.) of AN and 25 ml. of methylene chloride. The solution was still red when the contents of the tube were precipitated after six days at 60°. A tannish-white solid (0.409 g., 63% yield) was obtained, whose infrared spectrum was identical to that of the preceding room temperature experiment, indicating that no reaction had occurred.

Attempted copolymerization of PhTD with AN at 60° with AIBN--A polymer tube was charged with 0.500 g. (2.86 mmol.) of PhTD, 0.155 g. (2.88 mmol.) of AN, 0.003 g. (0.5 wt. %) of AIBN in 25 ml. of methylene chloride. A polymerization time of 24 hours was used and, on precipitation, 0.211 g. (31.8% yield) of a light yellow solid was obtained. The infrared spectrum (KBr) gave no absorbance that could be attributed to a nitrile. Some weak absorbance at  $1610\text{ cm.}^{-1}$  was the only apparent difference from PhTD decomposition products. The nmr spectrum ( $\text{CDCl}_3$ ) gave resonance signals at  $\delta 7.32$  (s, broad, 5),  $\delta 6.00$ – $\delta 3.00$  (very broad, approximately 2 or 3).

Anal. Calcd. for  $\text{C}_{11}\text{H}_8\text{N}_4\text{O}_2$  (1:1 structure): C, 57.90; H, 3.50;

N, 24.58. Found: C, 56.74; H, 3.64; N, 23.49.

Spontaneous copolymerization of N-vinyl carbazole, NVC, and PhTD at room temperature-In the usual manner for the 25° copolymerizations 0.502 g. (2.86 mmol.) of PhTD and 0.547 g. (2.83 mmol.) of NVC were reacted in 25 ml. of methylene chloride. The reaction discharged its red color within two minutes after the comonomers were mixed. Precipitation yielded 0.899 g. (85.7% yield) of a white electrostatic solid. The infrared spectrum (KBr) gave the following absorbances: 3060 (m), 1780 (m), 1725 (s), 1610 (m), 1600 (m), 1480 (m), 1410 (s), 1320 (m), 1255 (m), 1215 (m), 1155 (m), 1065 (w), 1020 (w), 740 (s), 720 (m) and 685 (m)  $\text{cm}^{-1}$ . The nmr spectrum ( $\text{CDCl}_3$ ) gave one large broad resonance signal  $\delta$ 8.50- $\delta$ 5.80. Analysis of the polymer by gel permeation chromatography in dimethylformamide solvent resulted in a  $\bar{M}_w$  of 54, 000,  $\bar{M}_n$  of 21,000 and a molecular weight distribution,  $\bar{M}_w/\bar{M}_n$ , of 2.57. This value was calculated from a calibration of the column by a polystyrene standard.

Anal. Calcd. for  $\text{C}_{22}\text{H}_{16}\text{N}_4\text{O}_2$  (1:1 copolymer): C, 71.25; H, 4.34; N, 15.21. Found: C, 71.59; H, 4.56; N, 15.43.

Attempted homopolymerization of NVC by PhTD-A solution of 1.659 g. (8.60 mmol.) of NVC dissolved in 50 ml. of methylene chloride was prepared and divided into two 25 ml. portions. To one portion, 0.5 mol. % of PhTD (0.004 g. in five ml. of methylene chloride) was added and stirred for 30 minutes. Precipitation into hexane yielded no solid formation. A control with no PhTD behaved similarly.

## 6. Determination of rate constants for PhTD-vinyl ether copolymerizations in various solvents

The procedure used for determination of the rate constant in PhTD in its reaction with EVE in acetone solution is outlined below. It is an example of the experimental technique employed in determining the effect of solvents of various polarities on the rate of the PhTD-vinyl ether reactions and copolymerizations.

PhTD (0.0176 g.) was weighed into a 10 ml. volumetric flask so that a 0.010 M solution resulted when brought to volume with dry spectro grade acetone. A 0.10 M solution of EVE was prepared by weighing 0.1800 g. of EVE into a 25 ml. volumetric flask and then bringing to volume. A 10-fold excess of EVE was used because of the difficulties encountered in weighing and transferring the EVE due to its high volatility. The extinction coefficient ( $\epsilon$ ) and  $\lambda_{\max}$  were determined by filling the sample cell with one ml. of the PhTD solution and one ml. of acetone and then scanning the 500-550  $\mu\mu$  region using a Beckman DK-2A spectrophotometer. A previous report<sup>83</sup> in the literature pointed out a visible absorbance in this range. This determination of  $\lambda_{\max}$  was made after setting a baseline of solvent versus solvent.

The instrument was set at the determined  $\lambda_{\max}$  (523  $\mu\mu$  for acetone-PhTD) and the sample cell was filled with one ml. of the PhTD solution and then one ml. of the EVE solution was added. The cell was shaken and immediately inserted into the spectrophotometer and the readings of absorbance commenced. The initial concentration of reactants was 0.05 M EVE and 0.005 M PhTD. A plot of the amount of PhTD consumed, calculated from the extinction coefficient, versus time is shown in Fig. 10. The reaction was found to be first order in PhTD and the first order rate constant was determined by taking the slope of the plot of  $\ln [\text{PhTD}]_0/[\text{PhTD}]$  or  $A_0/A$  versus time as shown in Fig. 11.

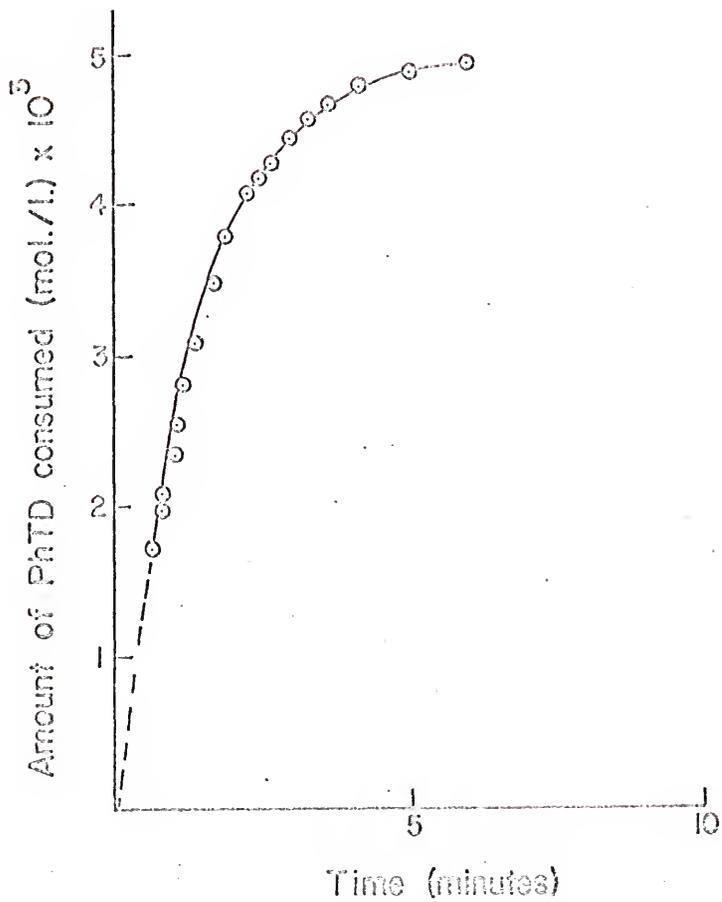


Figure 10. Plot of consumption of PhTD versus time for EVE-PhTD in dioxane at 25°C.

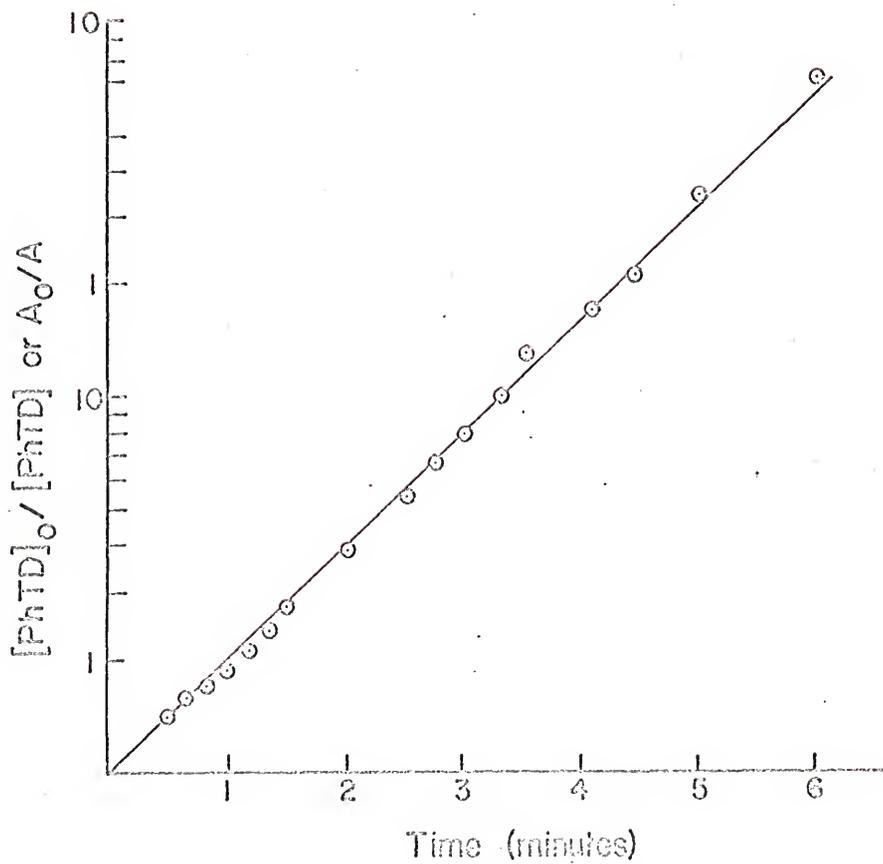


Figure 11. Logarithmic plot of  $[\text{PhTD}]_0 / [\text{PhTD}]$  or  $A_0 / A$  versus time for EVE-PhTD in dioxane at  $25^\circ\text{C}$ .

## 7. Reactions of PhTD

Thermal decomposition of PhTD at 60°-A polymer tube was sealed containing 0.500 g. (2.86 mmol.) of PhTD in 25 ml. of methylene chloride. After 24 hours the tube remained red with some white solid present. The white solid was removed by filtration and the red solution precipitated into hexane to yield 0.052 g. of a tan-white solid. The insoluble white crystalline solid failed to melt at 300°. From the following data it was assigned to structure 58. The infrared spectrum (KBr) was characterized by absorbances at 3060 (m), 1785 (s), 1755 (s), 1625 (w), 1500 (m), 1435 (s), 1340 (m), 1295 (w), 1175 (s), 1075 (m), 1020 (m), 925 (w), 780 (w), 750 (m), 735 (m), 725 (m), 695 (m) and 650 (m)  $\text{cm.}^{-1}$ . The mass spectrum (70 eV) gave the following fragments,  $\text{m/e}$  (rel. intensity) 322 ( $\text{M}^+$ , 11), 321 (57), 150 (2), 149 (22), 146 (6), 145 (3), 120 (17), 119 (100), 91 (41), 90 (6), 84 (5), 77 (6), 70 (18), 65 (17), 64 (46), 63 (19), 52 (17), 51 (35), 50 (15) and 49 (11).

Anal. Calcd. for  $\text{C}_{16}\text{H}_{10}\text{N}_4\text{O}_4$ : C, 59.60; H, 3.11; N, 17.48.

Found: C, 59.60; H, 3.08; N, 17.48.

The tan-white solid which had been formed by precipitation into hexane yielded the following spectroscopic data. The infrared spectrum (KBr) gave absorbances at 3500 (m), 1715 (s), 1630 (w), 1600 (w), 1495 (m), 1420 (m), 1280-1220 (w, broad), 760 (m) and 695 (m)  $\text{cm.}^{-1}$ . The nmr spectrum ( $\text{d}_6$ -acetone) yielded resonance signals at  $\delta$ 7.50 (m, 6) and  $\delta$ 4.48 (m, broad, 1). The molecular weight was determined to be 600.

Anal. Calcd. for  $\text{C}_8\text{H}_5\text{N}_3\text{O}_2$  (homopolymer of PhTD): C, 54.80; H, 2.86; N, 24.00. Found: C, 54.47; H, 3.68; N, 21.52.

Attempted free radical polymerization of PhTD with AIBN at 60°-The previous reaction was repeated with 0.5 wt. % of AIBN present. Products

identical in every respect to those of the previous reaction were obtained.

Attempted radical polymerization of PhTD by photolysis of benzoyl peroxide-A polymer tube was sealed in the usual manner with 0.501 g. (2.86 mmol.) of PhTD and 0.003 g. of benzoyl peroxide. The tube was inserted into an ethanol bath at  $-45^{\circ}$  for nine hours while it was irradiated by a Hanovia lamp with ultraviolet radiation. The red color persisted in the solution and precipitation into hexane yielded 0.257 g. (51.4% yield) of a faint pink solid and a red filtrate. An infrared spectrum of the solid was identical to that of an authentic pure sample of the PhTD indicating no reaction had occurred.

Reaction of PhTD with water-PhTD (0.598 g., 3.41 mmol.) dissolved in 25 ml. of dioxane was slowly added to 50 ml. of rapidly stirred water. Immediate reaction occurred resulting in a murky tan solution. The reaction was left to continue for one hour. The solids were removed by filtration and the filtrate was evaporated on the rotary evaporator at a temperature less than  $40^{\circ}$ . All the solids were extracted with methylene chloride and a small amount of insoluble white solid was obtained. The methylene chloride soluble portion was precipitated into hexane, redissolved and precipitated again and 0.392 g. (65.7% yield) of product was obtained. Its spectral characteristics were identical to other PhTD oligomeric products. The white solid, insoluble in methylene chloride, 0.046 g. (7.7% yield) was identical in all respects to an authentic sample of N, N'-diphenyl urea.

Attempted homopolymerization of PhTD with aniline-An Erlenmeyer flask was charged with 0.620 g. (3.54 mmol.) of PhTD dissolved in 30 ml. of methylene chloride. A solution of 0.0189 g. of aniline dissolved in

10 ml. of methylene chloride was prepared. Two mls. of this solution were injected into the PhTD solution and after one hour a small aliquot gave no precipitate in hexane. Two additional mls. of the aniline solution were added and after 100 minutes no precipitate was noted on sampling and dropping into hexane. A total of five ml. more were added over the next 25 minutes and after 2.5 hours total reaction time precipitation into hexane yielded 0.133 g. (21.5% yield) of a brown precipitate. The molecular weight was determined to be 470. The infrared spectrum (KBr) was identical to the other PhTD oligomeric products.

Attempted homopolymerization of PhTD with triethylamine-Into an Erlenmeyer flask were introduced 0.620 g. (3.54 mmol.) of PhTD dissolved in 25 ml. of methylene chloride. A triethylamine solution was prepared by dissolving 0.024 g. of triethylamine in 10 ml. of methylene chloride. Five ml. of the amine solution were injected via a syringe and the solution became turbid within five minutes. The reaction was allowed to continue for 17 hours at the ambient temperature. The mixture was filtered and then precipitated into hexane. The methylene chloride insoluble portion amounted to 0.059 g. (9.5% yield) and the methylene chloride soluble portion was 0.152 g. (24.5% yield) of a light tan material. The light tan material gave an infrared spectrum (KBr) identical to other PhTD oligomeric products. The infrared spectrum of the methylene chloride insoluble product was identical to the tetraone  
58.

Reaction of PhTD with sodium cyanide in dimethylformamide-A saturated solution of sodium cyanide in dimethylformamide was prepared<sup>84</sup> by dissolving 0.49 g. of the anhydrous salt in 50 ml. of dimethylformamide. A 50 ml. Erlenmeyer flask was then charged with 0.518 g.

(2.96 mmol.) of PhTD and 20 ml. of dimethylformamide and 2 ml. of the salt solution were injected via a syringe. The reaction immediately turned dark and some gas evolution was noted. After about one hour of reaction the solution appeared black with a considerable amount of white solid present. After a total reaction of 2.5 hours the solid was removed by filtration and the filtrate precipitated by slow addition to ether. On filtration this yielded a brown solid. The initially insoluble solid 0.140 g. (27.1% yield) gave an infrared spectrum (KBr) identical to the tetraone 58. The brown solid 0.240 g. (46.3% yield) gave an infrared spectrum very similar to 58. This solid was stirred with 25 ml. of acetone for 0.5 hours and the residue was much lighter in color with a dark brown acetone solution which on evaporation yielded a dark brown solid. The infrared spectrum of the dark brown solid was very similar to other PhTD oligomeric products. The acetone insoluble tan-white material was extracted on a Soxhlet extractor for several hours and seemed to exhibit partial solubility. Both the soluble and insoluble portions from the extraction had infrared spectra characteristic of the tetraone 58.

### 8. Diels Alder Polymerization Study

#### a. Synthesis of monomer

Reaction of ethyl carbazate with 4,4'-diphenylmethylenediisocyanate- 4,4'-diphenylmethane diisocyanate (11.9 g., 0.047 mol.), freshly distilled before use, was dissolved in 30 ml. of benzene. This solution was dropped slowly into a solution of the ethylcarbazate (9.95 g., 0.095 mol.) in 100 ml. of benzene. The isocyanate was added at room temperature and the rate of addition was controlled to maintain the temperature

at 45° or below. After the addition was complete the voluminous white slurry was refluxed gently for two hours. The white solid was removed by vacuum filtration and then dried "in vacuo" to yield 21.2 g. (97.0% yield) of product with a m.p. 240-244° (with decomposition).

A sample was purified for analysis by dissolving in dimethylformamide and precipitating into ether. The infrared spectrum (KBr) exhibited absorbances at 3380 (s, broad), 3305 (s, broad), 3025 (w), 3000 (w), 2940 (w), 1735 (s), 1685 (s), 1645 (s), 1605 (s), 1560 (s), 1510 (s), 1415 (m), 1370 (w), 1315 (m), 1305 (m), 1225 (s), 1115 (w), 1095 (w), 1055 (m), 1035 (m), 900 (w), 850 (w), 760 (m) and 615 (m)  $\text{cm.}^{-1}$

The nmr spectrum ( $d_6$ -dimethyl sulfoxide) gave resonance signals at  $\delta$ 8.77 (s, 2),  $\delta$ 8.57 (s, 2),  $\delta$ 7.91 (s, 2),  $\delta$ 7.20 (q, 8),  $\delta$ 4.05 (q, 4),  $\delta$ 3.79 (s, 2), and  $\delta$ 1.19 (t, 6).

Anal. Calcd. for  $C_{21}H_{25}N_6O_6$ : C, 55.00; H, 5.54; N, 18.35.

Found: C, 55.25; H, 5.77; N, 18.16.

Preparation of 4,4'-(4,4'-diphenylmethylene)-diurazole-On a steam bath, 5 g. (1.09 mmol) of the bis semicarbazide was added slowly to 25 ml. of 4 M potassium hydroxide. The addition, which was assisted with frequent swirling, took about one hour and the reaction was left on the steam bath for an additional hour. On removal from the steam bath it was noted that all the bis carbazide had gone into the basic solution except for a few white particles floating on the surface which were filtered. The solution was then cooled to 10-15° and 50% hydrochloric acid was slowly added. On addition of each drop, a polymeric like portion of solid would form which could be put back into solution with vigorous stirring. Attempted stirring with a magnetic stirring bar resulted in the precipitating solid adhering to it. (This problem

was eliminated in later preparations by diluting the original volume of the solution to be acidified by about four fold.) As the reaction mixture was neutralized and just made acidic, a voluminous white precipitate resulted. This was removed by filtration and dried about 30 minutes on the water aspirator and then dried overnight at 70° "in vacuo". A quantitative yield of the bis urazole was formed. This product was recrystallized with water/5% methanol to yield white needles, m.p. 320° (decomposition). The infrared spectrum (KBr) was very similar to the 4-phenyl urazole and gave the following absorbances: 3410 (m), 3320-2760 (s, broad), 1765 (m), 1680 (s), 1510 (s), 1440 (s), 1210 (m), 1120 (m), 1095 (m), 1030 (w), 1010 (w), 865 (m), 785 (m), 760 (m), 710 (m), 690 (w) and 640 (m)  $\text{cm.}^{-1}$ . The nmr spectrum ( $\text{d}_5$ -dimethylsulfoxide) gave a broad resonance from  $\delta 7.80$ - $\delta 7.20$  with a sharp spike at  $\delta 7.38$  equivalent to 12 protons and another resonance at  $\delta 4.03$  (s, 2).

Anal. Calcd. for  $\text{C}_{17}\text{H}_{14}\text{N}_6\text{O}_4$ : C, 55.75; H, 3.83; N, 22.90.

Found: C, 55.73; H, 3.93; N, 22.94.

Preparation of 4,4'-(4,4'-diphenylmethylene)-bis-1,2,4-triazoline-3,5-dione-The bis urazole (2.30 g., 6.25 mmol.) was placed into a 500 ml. Erlenmeyer flask with 25 g. of sodium sulfate and 250 ml. of methylene chloride. The solution was stirred in an ice-water bath and cooled to 5°. Dinitrogen tetroxide was bubbled slowly through the stirring slurry until a dark red color persisted (about 30 minutes). The sodium sulfate was removed by filtration and the dark red filtrate was evaporated on a rotary evaporator using lukewarm water. A light pink solid was formed (1.80 g., 79.8% yield). The solid had the following melting characteristics: 160-180° pink color changed to tan and up to 320° there was no

decomposition. The infrared spectrum gave absorbances at 3620 (m), 3060 (m), 2960 (w), 2930 (w), 2570 (w), 2330 (w), 2260 (w), 1925 (w), 1900 (m), 1875 (w), 1845 (m), 1790 (s), 1760 (s), 1710 (m), 1635 (m), 1600 (w), 1510 (s), 1460 (m), 1430 (m), 1415 (m), 1385 (s), 1300 (m), 1180 (s), 1175 (s), 1150 (s), 1100 (w), 1070 (w), 1020 (m), 955 (m), 895 (m), 845 (m), 810 (m), 790 (m), 730 (s), 715 (m), 675 (s), 630 (m), 625 (w) and 620 (m)  $\text{cm.}^{-1}$ . The nmr spectrum ( $d_6$ -acetone) yielded resonances at  $\delta 7.48$  (s, 8) and  $\delta 4.18$  (s, 2). Since the nmr spectrum indicated the bis triazoline dione to be free of impurities, it was used without further purification.

#### b. Polymerization studies

Copolymerization of styrene and bis triazoline dione-A 100 ml. round-bottom flask was charged with 50 ml. of dimethylformamide and 1.30 g. (3.60 mmol.) of the bis triazoline dione. By means of a dropping funnel 0.374 g. (3.60 mmol.) of freshly distilled styrene, dissolved in 25 ml. of dimethylformamide, were added over a two hour period. The dark red color of the original solution lightened considerably over this time. After 7.5 hours no further color change was noted so the solution was warmed for 10 minutes with an infrared lamp. No change appeared to be effected so the solution was divided into two equal parts. One portion was precipitated into ether yielding a light pink colored solid, which after washing with ether appeared tannish colored (solid A) and after drying weighed 0.493 g.

The second portion of the original mixture was left stirring overnight and no significant change was noted. This was divided into two more portions. To the first was added 0.05 g. of styrene and after 10 minutes the residual red color was discharged to yellow. Precipitation

into ether and drying yielded 0.306 g. (solid B) of a light tannish solid. The second portion was heated via a heating mantle to reflux for 15 minutes and during this period the solution turned to a dark brown color. Precipitation into ether resulted in 0.574 g. of a dark brown solid (solid C).

Solid A gave an infrared spectrum (KBr) with absorbances at 1780 (m), 1715 (s), 1605 (w), 1515 (m), 1495 (w), 1415 (m), 1135 (w), 1100 (w), 1020 (w), 815 (w) and 750 (w)  $\text{cm.}^{-1}$ . The nmr spectrum ( $d_6$ -dimethylsulfoxide) yielded resonance signals at  $\delta$ 8.40 (d, broad, 1),  $\delta$ 7.37 (s, broad, 12),  $\delta$ 5.67 (s, broad, 1), and  $\delta$ 4.50- $\delta$ 3.80 (m, broad, 4). A DSC thermogram recorded a decomposition temperature of 307°. The intrinsic viscosity in dimethylformamide at 28° was 0.12. Number average and weight average molecular weights, calculated from a gel permeation chromatogram, gave 36,000 and 120,000 respectively. The determination was made in dimethylformamide and was based on a calibration curve determined with standard polystyrene samples.

The infrared spectra from solids B and C were identical to A. No other characterizations were done on B and C.

Reaction of styrene and PhTD-A 50 ml. Erlenmeyer flask was charged with 0.500 g. (2.86 mmol.) of PhTD, 0.151 g. (1.43 mmol.) of styrene and 25 ml. of methylene chloride. After five minutes the red color discharged to yellow which then went on to give a colorless solution. After 15 minutes a white precipitate began to form and at 45 minutes the reaction was stopped and the resulting solid was removed by filtration (solid A). The filtrate was stripped off on a rotary evaporator and the resulting solid (solid B) remained soluble in methylene chloride, but on dissolution immediately began to precipitate.

Solid A had a melting point of 250-52°. The infrared spectrum (KBr) gave absorbances at 3280 (m), 1765 (m), 1720 (s), 1600 (w), 1585 (w), 1495 (m), 1460 (w), 1420 (m), 1365 (w), 1325 (w), 1310 (w), 1270 (w), 1250 (w), 1215 (w), 1160 (w), 1130 (m), 1095 (w), 1075 (w), 1020 (w), 860 (w), 790 (w), 750 (m), 725 (m), 685 (m) and 640 (w)  $\text{cm.}^{-1}$ . The nmr spectrum ( $d_6$ -dimethylsulfoxide) yielded resonances at  $\delta$ 8.38 (d, 1),  $\delta$ 7.35 and  $\delta$ 7.38 (d and m respectively, 14),  $\delta$ 5.70 (t, broad, 1) and  $\delta$ 4.22 (m, 2).

Anal. Calcd. for  $\text{C}_{24}\text{H}_{17}\text{N}_4\text{O}_4$  (2:1 adduct): C, 63.48; H, 3.96; N, 18.50. Found: C, 63.41; H, 4.01; N, 18.38.

Solid B gave an infrared spectrum identical to solid A. It gave a melting point of 222-26°. No further analysis was performed.

Reaction of sodium cyanide in dimethylformamide with 4,4'-(4,4'-diphenylmethylene)-bis-1,2,4-triazoline-3,5-dione-The bis triazoline di-one (0.188 g., 0.52 mmol.) was dissolved in 25 ml. of dimethylformamide and then one ml. of concentrated sodium cyanide in dimethylformamide solution was injected via a syringe. A very slight gas evolution was noted and the only other change was loss of the red color to brown. Addition of another 0.5 ml. of the salt solution gave no significant change. The reaction was left for 24 hours and then precipitated into ether. A dark oily brown solid formed, which after washing with acetone and methylene chloride, yielded a light brown powder. The infrared spectrum (KBr) gave the following absorbances 2250 (w), 1700 (m), 1680 (m), 1650 (m), 1510 (m), 1370 (m), 1170 (m), 1020 (w) and 750 (w)  $\text{cm.}^{-1}$ . No further effort was invested in characterizing this product.

C. Syntheses Related to Triple Strand Model Compound Studies1. Preparation of dienes

Preparation of 2,3-dimethyl-1,3-butadiene sulfone, 82<sup>59</sup>-Into a 500 ml. autoclave, precooled in an isopropanol dry ice bath, were placed 60 ml. of methanol, 3.0 g. of hydroquinone, 78.0 g. (1.22 mol.) of sulfur dioxide and 100.0 g. (1.22 mol.) of 2,3-dimethyl-1,3-butadiene. The autoclave was heated to 85° for four hours and the resulting solid was recrystallized from absolute methanol. Approximately 135 g. (80% yield) of white crystals m.p. 134-37° (lit.<sup>59</sup> m.p. 136-37°) were obtained. Recrystallization of the solid obtained on evaporation of the mother liquor raised the yield to approximately 90%.

Preparation of 2,3-di-(bromomethyl)-1,3-butadiene sulfone, 83<sup>29</sup>-Into a 3 l. round-bottomed flask, 640 ml. of chloroform (reagent grade, washed 4 times with water and dried over magnesium sulfate and then distilled) were added. To the chloroform, 64.9 g. (0.443 mol.) of dimethylbutadiene sulfone, 82, and 159.0 g. (0.886 mol.) of N-bromosuccinimide were added. Benzoyl peroxide (5.0 g., 0.021 mol.) was added as an initiator. The white slurry turned yellow and then amber during reflux and after 3-10 hours of reflux it returned to the original light yellow. The reaction mixture was allowed to cool and the resulting succinimide was removed by filtration. Most of the chloroform was removed on a rotary evaporator and the oily residue was refiltered to remove the remaining succinimide. Further evaporation on the rotary evaporator removed the remaining chloroform. An equal amount of 95% ethanol was added to the oily residue and the mixture was shaken vigorously for several minutes (until the oily residue appeared as a white solid). The product was placed in the refrigerator

and shaken occasionally for 2 days. After filtering and recrystallizing from benzene 50.6 g. (37.6% yield) of slightly yellow crystals m.p. 120-21° (lit.<sup>29</sup> m.p. 124-125°) were obtained.

Preparation of 2,3-di-(acetoxymethyl)-1,3-butadiene sulfone, 84-  
7.0 g. (0.023 mol.) of the dibromosulfone, 7.6 g. (0.046 mol.) of silver acetate and 75 ml. of acetonitrile were placed into a 200 ml. round-bottomed flask equipped with a magnetic stirring bar and a reflux condenser. The acetonitrile was gently refluxed for three hours. At first, a white color was noted in the solution. This darkened during the reaction. The silver bromide formed was removed by filtration yielding a yellow filtrate. The acetonitrile was removed on a rotary evaporator leaving a brownish oil. About 50 ml. of chloroform were added to the oil, and the resulting solid, which seemed to be residual silver salts, was filtered. The filtrate was evaporated on the rotary evaporator and a yellowish white solid was obtained. The crude yield was 5.0 g. (86%). Recrystallization twice from absolute ethanol yielded 4.2 g. (72.5%) of white flaky crystals, m.p. 90-2°. The infrared spectrum (KBr) showed absorbance bands at 3040 (w), 2995 (w), 2950 (w), 1720 (s), 1655 (w), 1475 (w), 1388 (m), 1362 (s), 1312 (s), 1255 (s), 1230 (s), 1185 (s), 1139 (s), 1094 (m), 1019 (s), 960 (m), 920 (m), 884 (m) and 810 (w) cm.<sup>-1</sup>

The nmr spectrum (CDCl<sub>3</sub>) exhibited resonance signals at δ4.75 (s, broadened, 4), δ3.86 (s, broadened, 4) and δ2.08 (s, 6).

Anal. Calcd. for C<sub>10</sub>H<sub>14</sub>O<sub>6</sub>S: C, 45.80; H, 5.35. Found: C, 45.70; H, 5.21.

Preparation of 2,3-di-(acetoxymethyl)-1,3-butadiene, 77a-A 9 inch pyrolysis tube with a 14/35 ST female joint was charged with 4.0 g.

(0.015 mol.) of the diacetoxy sulfone. The tube was connected by a double male 14/35, 14/20 ST joint to an adapter which led to a receiver flask immersed in an ice bath. The system was evacuated to less than 0.1 mm. and then the pyrolysis tube was inserted into a preheated Hoskins furnace at 200°. After a few minutes, liquid was seen collecting in the adapter leading to the receiver. The pyrolysis was stopped after one hour and 1.70 g. (56.5%) of the diene were obtained.

After recrystallization from anhydrous ethyl ether, a white solid m.p. 41-4° (lit.<sup>58</sup> m.p. 43-4°) was observed. The infrared spectrum was identical to that reported. The nmr spectrum (CDCl<sub>3</sub>) exhibited resonance signals at  $\delta$ 5.35 (s, 4),  $\delta$ 4.80 (s, 4) and  $\delta$ 2.12 (s, 6).

Preparation of 2,3-di-(hydroxymethyl)-1,3-butadiene, 77b<sup>58</sup>

A 100 ml. round-bottomed flask was charged with 2.7 g. (0.014 mol.) of the diacetoxy diene, 1.9 g. (0.048 mol.) of sodium hydroxide and a few milligrams of diphenyl amine. The reaction flask was equipped with a condenser and was placed on a steam bath for 2.5 hours. On removal the solution was extracted 12 hours with ether on a continuous extractor. The ether was removed on a rotary evaporator and to the resulting oily residue 125 ml. of toluene were added. This solution was refluxed for three hours on a Dean-Stark trap to remove water. As the toluene was removed on a rotary evaporator, a white solid was formed which was removed by filtration to yield 1.4 g. (89.6%) of product with m.p. 63-4.5° (lit.<sup>58</sup> m.p. 63-4°). The infrared spectrum was identical to that reported. The nmr spectrum (CDCl<sub>3</sub>) exhibited resonance signals at  $\delta$ 5.30 (s, 4),  $\delta$ 4.37 (s, 4) and  $\delta$ 1.88 (s, 2).

Preparation of isoprene sulfone, 85<sup>59</sup>-Isoprene (81.6 g., 1.20 mol.),

purified by distillation after washing twice with 100 ml. portions of 10% acidified ferrous ammonium sulfate, was placed into a one l. autoclave that was precooled in a dry ice-isopropanol bath. To the isoprene 113 g. (1.77 mol.) of sulfur dioxide, 4.0 g. of hydroquinone and 88 ml. of methyl alcohol were added. The sealed autoclave was placed into a shielded autoclave reactor for 2.5 hours. Filtration and then work up of the mother liquor resulted in 175.9 g. of crude product. On recrystallization from methyl alcohol 150.0 g. of the sulfone were obtained m.p. 62-64° (lit.<sup>59</sup> m.p. 63-64°).

Preparation of 2-bromomethyl-1,3-butadiene sulfone, 86<sup>60</sup>-To 1.6 l. of chloroform (dried over anhydrous calcium chloride) in a three l. round-bottomed flask, 132.0 g. (1.0 mol.) of isoprene sulfone, 178 g. (1.0 mol.) of N-bromosuccinimide and 12.0 g. (0.050 mol.) of benzoyl peroxide were added. The reaction was stirred and appeared as a white slurry at the start. The original preparation called for a reaction temperature of 75° which was not possible since chloroform boils at 61.2°. Vigorous boiling and frothing started after several minutes at chloroform reflux and after two hours the reaction appeared dark red. The reaction was stopped after 24 hours and the solvent was removed on a rotary evaporator. Succinimide crystals were filtered off before all the solvent was evaporated. An equal amount of 95% ethyl alcohol was added and the flask was vigorously shaken for several minutes. The yellowish, cloudy mixture was left in the refrigerator for 24 hours and a crude product of light, fluffy yellowish-white solid was removed by filtration. Only 41.0 g. were obtained compared to 80.0 g. expected from the procedure. The product had a melting range of 74-78° versus lit.<sup>60</sup> 78-84°. Care was taken in handling the solid because it was a strong lachrymator.

Preparation of 2-bromomethyl-1,3-butadiene<sup>60</sup> -The literature procedure was modified to the following method: 41.0 g. (0.195 mol.) of the halogenated isoprene sulfone were placed into a 500 ml. round-bottomed three-necked flask equipped with a Claisen head and a receiver immersed in an ice bath. The sulfone was heated via a heating mantle and 12.2 g. (43% yield) of a brownish liquid were collected between 35° and 85° at 10 mm. The infrared spectrum was as reported and an nmr spectrum indicated approximately 90% purity. This diene was used without further purification because it was a horrible lachrymator as reported!

Preparation of 2-acetoxymethyl-1,3-butadiene sulfone, 87- 14.3 g. (0.067 mol.) of the monobromo sulfone and 12.0 g. (0.072 mol.) of silver acetate were placed into a 250 ml. round-bottomed flask with 125 ml. of acetonitrile. The flask was equipped with a magnetic stirring bar and a reflux condenser. The reaction was refluxed for three hours with stirring. The solids were removed by filtration and the acetonitrile was removed on a rotary evaporator. Addition of chloroform to the dark oil resulted in the formation of some solid which when removed by filtration turned dark. On evaporation of the chloroform a yellow brown oil was obtained in 74% yield. This oil polymerized to a rubbery solid after a few hours; therefore it was used immediately after its formation. The infrared spectrum (neat, salt plates) had absorbances at 3080 (m), 2980 (m), 2940 (m), 1735 (s), 1655 (w), 1550 (w), 1435 (m), 1400 (m), 1380 (m), 1305 (s), 1230 (s), 1150 (m), 1125 (s), 1030 (m), 970 (m), 900 (m), 780 (m) and 650 cm.<sup>-1</sup>

The nmr spectrum (CDCl<sub>3</sub>) gave resonance signals at  $\delta$ 6.06 (s, broad, 1),  $\delta$ 4.69 (s, 2),  $\delta$ 3.81 (s, 4) and  $\delta$ 2.10 (s, 3).

Anal. Calcd. for  $C_7H_{10}O_4S$ : C, 44.30; H, 5.27. Found: C, 44.41; H, 5.03.

Preparation of 2-acetoxymethyl-1,3-butadiene, 79a-Pyrolysis of the acetoxymethyl sulfone was accomplished by using a thermo-regulated horizontal Hoskins furnace. The pyrolysis was done at 200° at a pressure of 0.5-1.0 mm. A nine inch 14/35 ST pyrolysis tube was loosely packed with 6 mm. glass beads and these beads were then coated with 7.0 g. (0.037 mol.) of the sulfone to be pyrolyzed. The pyrolysis tube was connected to an adapter via a double male 14/35, 14/20 ST connector tube. The receiver was placed in a dry ice trap. The system was evacuated before its insertion into the preheated furnace. 3.90 g. (84% yield) of crude diene was collected which was purified by distillation at one mm. and 25°. The infrared characteristics were identical to those reported.<sup>61</sup>

## 2. Diels Alder Reactions of the Dienes with p-Benzoquinone

Reaction of p-benzoquinone, 89, with 2,3-di-(acetoxymethyl)-1,3-butadiene in acetic anhydride at room temperature-In a 50 ml. round-bottomed flask; the diacetoxymethyl diene (1.40 g., 7.06 mmol.), quinone (1.0 g., 9.25 mmol.) and 25 ml. of acetic anhydride were stirred together for 20 days. After this time 200 ml. of water were added to the solution and a brownish oil fell to the bottom of the flask. This oil was observed to crystallize overnight. A reddish-brown solid (0.5 g.) was obtained on filtration which was recrystallized from absolute ethanol to yield a reddish-brown solid m.p. 128-30°, which was identified as 90 by the following spectroscopic data. The infrared spectrum (KBr) exhibited the following absorbances: 2955 (w), 1725 (s), 1655 (s), 1605 (m), 1595 (m), 1485 (w), 1455 (m), 1425 (m), 1410 (m),

1380 (m), 1340 (w), 1308 (s), 1285 (m), 1245 (s), 1225 (s), 1140 (w), 1120 (m), 1030 (s), 1000 (m), 960 (m), 925 (m), 895 (w), 840 (m), 820 (m), 665 (m) and 620 (m)  $\text{cm}^{-1}$

The nmr spectrum ( $\text{CDCl}_3$ ) gave resonance signals at  $\delta 6.75$  (s, 2),  $\delta 4.78$  (s, 4),  $\delta 3.23$  (s, 4) and  $\delta 2.12$  (s, 6).

Anal. Calcd. for  $\text{C}_{16}\text{H}_{16}\text{O}_6$ : C, 63.20; H, 5.26. Found: C, 63.83; H, 5.02.

Reaction of 89 with 77a in benzene at room temperature-A small flask was charged with 0.77 g. (3.89 mmol.) of the diene 77a, 0.76 g. (2.00 mmol.) of 89 and 15 ml. of benzene. The flask was left at room temperature for 16 days. Removal of the solvent resulted in a brownish oily residue. An nmr spectrum gave resonance signals at  $\delta 6.77$  (s),  $\delta 6.75$  (s),  $\delta 6.67$  (s),  $\delta 4.78$  (s),  $\delta 4.64$  (s),  $\delta 3.23$  (broad, with a sharp peak in middle),  $\delta 2.43$  (m, broad) and  $\delta 2.05$  (s). This spectrum was indicative of a mixture of 90 and the desired Diels Alder adduct 78a. The oily residue was dissolved in ethanol and immediately a brownish-red precipitate was formed. Its spectral characteristics were identical to 90.

Reaction of 89 with 77a in refluxing chloroform-A 10 ml. round-bottomed flask was charged with a few boiling chips, 0.25 g. (1.26 mmol.) of the diacetoxy diene 77a and 0.136 g. (1.26 mmol.) of quinone 89. These reactants were dissolved in eight ml. of chloroform and the reaction brought to reflux. The reaction was followed by nmr by removing an aliquot, blowing off a small portion of the chloroform with nitrogen and replacing it with  $\text{CDCl}_3$ , and then taking an nmr spectrum. After 135 hours over 80% of the starting materials had been converted to desired Diels Alder adduct as exemplified by the

disappearance of  $\delta$ 5.34 and  $\delta$ 4.80 singlet resonances of the diene and the formation of  $\delta$ 6.68 (s),  $\delta$ 4.65 (s),  $\delta$ 3.27 (broad m) and  $\delta$ 2.44 (broad) in the ratio of 2:4:2:4 respectively. All these peaks were similar to the known dibromo adduct 27. After 135 hours, the reaction was stopped and the solvent was removed and a yellow oil remained. Thin layer chromatography indicated that chloroform would remove remaining starting material and that ethyl acetate would move the desired compound. This was done on a silica gel column and a yellow oil was obtained which on redissolving in chloroform yielded a chloroform insoluble white crystalline substance m.p. 147-8°. This substance was believed to be 91. The infrared spectrum (KBr) gave absorbances at 3400 (s), 1730 (s), 1620 (m), 1485 (m), 1425 (m), 1390 (m), 1360 (m), 1340 (m), 1310 (s), 1290 (s), 1255 (s), 1235 (m), 1195 (m), 1145 (w), 1110 (w), 1025 (m), 990 (m), 955 (m), 930 (m), 895 (w), 845 (w), 800 (m), 745 (m), 695 (w), 640 (w) and 610 (w) cm.<sup>-1</sup>

The nmr spectrum ( $d_6$ -acetone) gave resonance signals at  $\delta$ 6.64 (s, 2),  $\delta$ 4.48 (s, 4),  $\delta$ 3.47 (s, 4),  $\delta$ 2.88 (s, broad, 4) and  $\delta$ 2.10 (covered by solvent).

Reaction of 2,3-di-(hydroxymethyl)-1,3-butadiene, 77b, with 89 in refluxing chloroform-A 50 ml. round-bottomed flask was charged with 0.31 g. (2.73 mmol.) of the dihydroxy diene 77b, 10 ml. of chloroform and 0.293 g. (2.71 mmol.) of 89. This mixture was allowed to reflux gently overnight. After 15 hours a brownish precipitate was formed and removed by filtration. On cooling, the filtrate yielded a few milligrams of unreacted diene. The brownish solid was extracted with boiling chloroform and a small amount of yellowish-white solid was obtained that gave a broad melting point around 150°. An nmr spectrum ( $d_6$ -

dimethylsulfoxide) gave no indication of the desired adduct.

Reaction of 77b and 89 in tetrahydrofuran in a pressure bottle at 65°—A pressure bottle was charged with 0.20 g. (1.76 mmol.) of the dihydroxy diene 77b and 0.19 g. (1.85 mmol.) of the quinone 89. Tetrahydrofuran was added (10 ml.) and the bottle was flushed with nitrogen, sealed and placed into a 65° oil bath for 24 hours. The solvent was then removed on a rotary evaporator and a brownish-yellow oily like material was obtained which turned darker after a few minutes. The product was initially soluble in chloroform, but after a few minutes it precipitated out yielding a white solid which turned brown between 250° and 290° and did not melt or decompose below 325°. This solid was partially acetone soluble and the soluble portion gave an infrared spectrum (KBr) with absorbances at 3480-3100 (broad, s), 2950-2860 (broad, m), 1670 (s), 1600 (w), 1510 (m), 1460 (m), 1420 (m), 1380 (m), 1360 (m), 1280 (m), 1250 (m), 1210 (m), 1190 (m), 1140 (m), 1095 (m), 1040 (m), 1015 (m), 985 (m), 950 (m), 935 (m) and 710 (broad, m) cm.<sup>-1</sup>

The nmr spectrum (d<sub>6</sub>-acetone) gave resonance signals at δ6.70 (d, 1), δ4.18 (s, broad, 1), δ2.82 (s, 4), δ2.52 (broad, 2).

The few milligrams of acetone and chloroform insoluble material gave an infrared spectrum (KBr) with absorbances at 3350 (broad, s), 2950-2890 (broad, m), 1710 (s), 1420 (m), 1355 (w), 1325 (w), 1260 (m), 1240 (m), 1210 (m), 1170 (w), 1140 (w), 1085 (m), 995 (m) and 795 (m).

Reaction of 2-bromomethyl-1,3-butadiene, 94, with 89—Into a 200 ml. three-necked round-bottomed flask, 60 ml. of acetic anhydride, 11.0 g. (0.075 mol.) of the bromodiene and 8.0 g. (0.075 mol.) of 89 were added. The reaction was left stirring at room temperature and after 36 hours a precipitate began to form. After 96 hours the reaction

was stopped and the solid removed by filtration and 10.0 g. (57.7% yield) of a yellow solid were obtained. The material was readily recrystallized from benzene to give a light yellow powder m.p. 154-6°. This solid was identified as 95, the aromatized and acetylated Diels Alder adduct by the following spectral data. The infrared spectrum (KBr) showed absorbance bands at 2890-2800 (m, broad), 1750 (s), 1365 (s), 1180-1110 (s, broad), 1015 (s), 940 (w), 885 (m) and 815 (m)  $\text{cm}^{-1}$ .

The nmr spectrum gave resonance signals at  $\delta$ 7.00 (s, 2),  $\delta$ 6.05 (broad m, 1),  $\delta$ 4.08 (broad s, 2),  $\delta$ 3.30 (broad s, 2) and  $\delta$ 2.30 (two s, 3 each). The mass spectrum (70 eV) gave the following fragments  $\frac{m}{e}$  (rel. intensity), 341 (1), 339 (M+, 1), 299 (6), 297 (6), 261 (12), 259 (12), 257 (12), 255 (30), 237 (6), 216 (15), 176 (100), 162 (9), 131 (9), 115 (9), 92 (9) and 43 (76).

Anal. Calcd. for  $\text{C}_{15}\text{H}_{15}\text{O}_4\text{Br}$ : C, 53.50; H, 4.40; Br, 23.60. Found: C, 52.57; H, 4.45; Br, 21.38. (sample appeared to decompose slightly before it was sent for analysis.)

Reaction of 2-acetoxymethyl-1,3-butadiene with 89 at room temperature in benzene-A 50 ml. pear-shaped flask was charged with 1.0 g. (8.00 mmol.) of the acetoxymethyl diene 79a, 0.84 g. (7.70 mmol.) of recrystallized 89 and then 10 ml. of benzene. The flask was flushed with dry nitrogen, stoppered and left for one week in the dark. At this time the solution was yellow and a greenish crystalline solid appeared in the bottom of the flask. After another week the insoluble solid was clear and was removed by filtration. The nmr spectrum ( $d_6$ -acetone) of this solid exhibited two equivalent sharp singlets at  $\delta$ 6.80 and  $\delta$ 6.68 (4 each) and a broad singlet at  $\delta$ 2.83 (2). The melting point was 170-71°. Quinhydrone<sup>62</sup>, m.p. 171°, fits all the characteristics of this

product.

After evaporation of the filtrate on a rotary evaporator, an oily residue was obtained which on extraction with petroleum ether yielded a yellow solid which darkened immediately on isolation. Thin layer chromatography yielded two spots and then column chromatography on silica gel with acetone/petroleum ether resulted in a yellow oil that darkened immediately. An infrared spectrum gave two prominent absorbances at  $3500\text{ cm.}^{-1}$  and  $1600\text{ cm.}^{-1}$ . The nmr spectrum ( $\text{CDCl}_3$ ) gave resonance signals at  $\delta 6.65$  (m),  $\delta 5.75$  (m),  $\delta 4.50$  (2, broad singlets),  $\delta 2.90$  (s) and  $\delta 2.10$  (m). The spectrum was not integrated and no further work was invested in isolation and identification of the product.

Reaction of 79a with 89 in refluxing ethanol-A small flask was charged with 0.25 g. (2.30 mmol.) of 89, 10 ml. of absolute ethanol and 0.3 g. (2.40 mmol.) of the diene 79a. The flask was equipped with a condenser and then the reaction mixture was refluxed for 12 hours. After stopping, petroleum ether was added until a cloudy appearance persisted and then the flask was put aside in a freezer. A brown oil appeared in the bottom which was separated and chromatographed on silica gel. Three fractions were taken and all were yellow-brownish oils. The middle fraction gave an infrared spectrum containing strong -OH absorbances at  $3500\text{ cm.}^{-1}$  and a broad carbonyl at  $1710\text{-}1650\text{ cm.}^{-1}$ . The spectrum was practically identical to the one from the previous reaction in benzene. Since the product was not the desired Diels Alder adduct, it was not characterized further.

Reaction of tetracyanoethylene with 79a-A 25 ml. round-bottomed flask was charged with 0.6 g. (4.70 mmol.) of the diene and 0.6 g. (4.70 mmol.) of tetracyanoethylene. These reactants were dissolved in

10 ml. of tetrahydrofuran and a yellow-brown complex of tetrahydrofuran and tetracyanoethylene was observed. The flask was stoppered and left for 24 hours. The solvent was removed on a rotary evaporator and a brownish oil was obtained, which when chloroform was added gave a light brown precipitate (unreacted tetracyanoethylene) and a yellow-brown solution. The chloroform was evaporated at reduced pressure to yield 1.1 g. (91.6% yield) of a crude brown solid. Two recrystallizations from 95% ethanol yielded a white crystalline solid m.p. 135-36°. The infrared spectrum (KBr) showed absorbances at 2990 (m), 2905 (w), 2340 (w), 2250 (w), 1730 (s), 1465 (m), 1445 (m), 1432 (m), 1352 (m), 1330 (w), 1312 (m), 1240 (s), 1220 (s), 1180 (m), 1115 (m), 1020 (m), 1000 (m), 905 (m), 870 (m), 830 (m), 790 (m), 700 (w), 650 (w) and 625 (w)  $\text{cm.}^{-1}$

The nmr spectrum ( $\text{CDCl}_3$ ) gave resonance signals at  $\delta$ 5.89 (m, 1),  $\delta$ 4.51 (s, 2),  $\delta$ 3.10 (s, 4) and  $\delta$ 2.10 (s, 3).

Anal. Calcd. for  $\text{C}_{13}\text{H}_{10}\text{N}_4\text{O}_2$ : C, 61.40; H, 3.94; N, 22.02.

Found: C, 61.20; H, 4.02; N, 22.30.

### 3. Preparation and reactions of 2-cyclohexene-1-one, 103, and di-azoquinone, 104

Preparation of  $\alpha$ -bromocyclohexanone<sup>65,66</sup> - In a two l. three necked round-bottomed flask, 40.0 g. (0.41 mol.) of cyclohexanone, 73.0 g. (0.71 mol.) of N-bromosuccinimide and 2.0 g. of benzoyl peroxide were dissolved in 250 ml. of carbon tetrachloride and the resulting solution was reacted for one hour at 75°. The first observation was development of a yellow color which preceded a period of exothermicity and vigorous boiling during which a fluffy white solid formed on the sides of the flask. After the solid formed, the mixture was gently refluxed for the

remainder of the hour. The mixture was cooled and the solid, which was water soluble, an indication that it was succinimide, was removed by filtration. The carbon tetrachloride was removed under reduced pressure. Further distillation at 65° and 2 mm. (reported<sup>65</sup> 74°, 3 mm.) resulted in 38.5 g. (53% yield) of a colorless liquid which rapidly turned yellow on standing. The product was stored in the absence of light in a refrigerator and used as quickly as possible. Storage for three months resulted in a dark brown solid.

Reaction of  $\alpha$ -bromocyclohexanone with lithium bromide in dimethylformamide<sup>68</sup>—A 500 ml. three-necked round-bottomed flask was set up with a nitrogen flush, a magnetic stir bar, a condenser and a thermometer.  $\alpha$ -Bromocyclohexanone (35.0 g., 0.198 mol.), 200 ml. of dimethylformamide and 16.1 g. (0.185 mol.) of lithium bromide were introduced and the flask immersed in an oil bath at approximately 130°. The inside temperature rose to 120–130°. The reaction was followed by thin layer chromatography and after 18 hours the disappearance of starting materials was noted and the reaction stopped. To the dimethylformamide solution 200 ml. of water were added and then the aqueous solution was extracted three times with 75 ml. of ether. The ether extractions were combined and washed three times with 50 ml. of water. Evaporation of the ether yielded 10.9 g. of a yellow oily product with a phenolic odor. Vacuum distillation yielded only a few drops of a liquid with a phenolic odor and a viscous yellow oily residue which did not distill at 135° and two mm. was isolated. The viscous oil was soluble in carbon tetrachloride and chloroform. The infrared spectrum gave absorbances at 3400 (m, broad), 2950–2820 (s), 1710–1650 (m, broad), 1440 (w), 1320 (w), 1085 (w), 900 (w) and 740 (w). The nmr spectrum

gave an enormous multiplet centered at  $\delta$ 2.00 and smaller multiplets at  $\delta$ 5.70 and  $\delta$ 6.70. No further work was done on this substance.

Reaction of  $\alpha$ -bromocyclohexanone with collidine<sup>67</sup>-Freshly distilled  $\alpha$ -bromocyclohexanone (15.0 g., 0.085 mol.) was placed into a 100 ml. round-bottomed flask equipped with a condenser. Collidine (15.0 g., 0.124 mol.) was added and the reaction vessel was immersed into a 180° oil bath for five minutes. During this period, the reaction mixture hissed and puffed up into the condenser as a solid. The solid residue was washed with 55 ml. of benzene and then the resulting slurry filtered. The solid was washed with 55 ml. of hot benzene and the combined filtrates were washed with a total of 60 ml. of 2 N hydrochloric acid twice. The benzene was dried over magnesium sulfate and then removed on a rotary evaporator. Vacuum distillation, 62-64.5°, 10 mm. (lit.<sup>67</sup> 61-62°, 10 mm.) resulted in 4.7 g. (58.2% yield, lit.<sup>67</sup> 42%) of the desired 103.

Autoclave reaction of 2-cyclohexene-1-one, 103, with 2-acetoxy-methyl-1,3-butadiene-A 25 ml. autoclave was charged with 1.0 g. (8.00 mmol.) of the diene 79a and 1.0 g. (10.40 mmol.) of cyclohexenone, 103. The autoclave was flushed with dry nitrogen, closed and then placed into an oil bath at 200° for 48 hours. The pressure rose to 100 psig. Upon cooling and opening, a waxy, gummy polymeric material was isolated. The material was soluble in acetone and chloroform. The infrared spectrum (KBr) gave absorbances at 2930 (s), 1710 (s), 1450-1375 (m, broad), 1290 (m), 1245 (m), 1000 (w), 800 (w) and 750 (w). An nmr spectrum (CDCl<sub>3</sub>) resulted in broad resonances centered at  $\delta$ 7.00 and  $\delta$ 1.70 in the respective relative intensities of 1:13.

Reaction of 103 with 79a in a sealed tube at room temperature-A tube prepared for sealing was charged with 1.0 g. of 103 (10.4 mmol.), 1.0 g. (8.00 mmol.) of the diene 79a and 10 ml. of benzene. The tube was evacuated and carried through a degassing cycle before sealing. After four days at room temperature the color had changed to a reddish-brown. The tube was opened and the solvent removed; an nmr spectrum of the oily residue indicated only starting materials.

Aluminum chloride catalyzed reaction of 103 with 79a-To 3.02 g. (32.0 mmol.) of cyclohexenone in 10 ml. of methylene chloride, 3.5 g. of aluminum chloride were added. Much boiling and frothing occurred and the reaction turned reddish-brown. Then 4.00 g. (32.0 mmol.) of the diene 79a was added and the boiling was so vigorous that the mixture had to be cooled in an ice bath. After four hours the dark reddish-brown solution was poured over ice and the organic layer was separated in a separatory funnel. The methylene chloride was dried over magnesium sulfate and then removed on a rotary evaporator. An infrared spectrum of the crude reaction product gave a broad double carbonyl absorbance at 1680 and 1710  $\text{cm.}^{-1}$ . The product was chromatographed on a silica gel column with benzene. An oil yielding only a 1705  $\text{cm.}^{-1}$  carbonyl absorbance was separated. Other infrared absorbances of this oil were at 2940 (m), 2880 (m), 1705 (s), 1440 (m), 1260 (m), 1170 (w), 1100 (w), 1050 (w), 1020 (w) and 670 (m)  $\text{cm.}^{-1}$ . The nmr spectrum showed a broad multiplet centered at  $\delta$ 2.20 (12), a singlet at  $\delta$ 4.05 (2) and a multiplet at  $\delta$ 5.85 (1). The mass spectrum indicated a halogen by its peak at  $m/e$  198 and  $M+2$  at  $m/e$  200 which was 35% of  $M$ . One chlorine theoretically would give an isotope effect of 32.6%. The base peak at  $m/e$  corresponded to loss of a chlorine atom. From these data this product is believed to be 107.

Reaction of 103 with 79a in a sealed tube at 190°-A tube prepared for sealing was charged with 2.0 g. (16.0 mmol.) of the diene 79a, 1.53 g. (16.0 mmol.) of the unsaturated cyclic ketone and a few milligrams of hydroquinone. The tube was sealed after degassing one time and placed into a 190° oil bath for three days. After cooling and opening 1.2 g. of a tan solid were isolated. This solid was purified by dissolving in chloroform and precipitating into pentane. At 210° it softened and began to turn brown and at 270° it decomposed. The infrared spectrum gave absorbances at 2920 (s), 2860 (m), 1710 (m), 1680 (m), 1445 (m), 1370 (w), 1229 (m), 1150 (w) and 749 (w)  $\text{cm.}^{-1}$ . The nmr spectrum ( $\text{CDCl}_3$ ) exhibited resonance signals at  $\delta 7.50$ - $\delta 6.50$  (broad, 1) and  $\delta 3.70$ - $\delta 0.75$  (broad, 14). The substance was very similar, if not identical, to that isolated from the autoclave reaction. No further work was invested in this material.

Preparation of t-butyl hypochlorite<sup>85</sup>-Fresh commercial Clorox bleach (500 ml.) was stirred in a one l. three necked flask, which was placed into an ice bath and cooled to below 10°. A solution of t-butyl alcohol (37 ml., 0.39 mol.) and glacial acetic acid (24.5 ml., 0.43 mol.) was added quickly to the rapidly stirring bleach and the stirring was continued for three minutes. In a darkened hood, the mixture was poured into a one l. separatory funnel. The lower clear aqueous layer was washed once with 50 ml. of 10% sodium carbonate solution and then 50 ml. of water. The product was dried over 2.0 g. of calcium sulfate and filtered to yield 18.2 g. (43.2%, lit.<sup>85</sup> 70-80%) of the hypochlorite which was stored in a brown glass stoppered bottle in the freezer.

Preparation of the potassium salt of maleic acid hydrazide<sup>54</sup>  
Maleic acid hydrazide (112.0 g., 1.0 mol.) was dissolved in a solution

of 66.0 g. (1.16 mol.) of potassium hydroxide in 400 ml. of water by warming the mixture on a hot plate. The solution was then evaporated to dryness under vacuum. The product was dried for 96 hours at 97° in a vacuum oven. A total of 130.0 g. of the salt was obtained.

Preparation of diazoquinone, 104<sup>54</sup>-Into a 250 ml. three-necked round-bottomed flask equipped with a low temperature thermometer and a calcium chloride drying tube, 100 ml. of dry acetone were added along with a magnetic stir bar. The flask was placed into a dry ice acetone bath and cooled to -75°. 4.40 g. (0.40 mol.) of t-butyl hypochlorite were added and after stirring for several minutes 6.0 g. (0.04 mol.) of the potassium salt of maleic acid hydrazide were added. The mixture was left stirring at -77° for approximately 3.5 hours. The solution was observed to gradually turn to a green color. The solids were filtered under nitrogen and through a dry ice jacketed coarse filter frit and the green filtrate was collected in the filter flask which was cooled to -77° in a dry ice acetone bath.

Reaction of 104 with 2,3-di-(acetoxymethyl)-1,3-butadiene-To the just prepared diazoquinone, 1.5 g. (7.60 mmol.) of freshly prepared and recrystallized diacetoxymethyl diene 77a were added after being dissolved and precooled to -77° in acetone. The green color did not disappear immediately upon addition of the diene. The mixture was left at -77° for 0.5 hours and then placed into a cold box at -55° for 12 hours. During this time the temperature slowly climbed to -10°. The flask was removed from the cold box and 1.0 g. (45.4% yield) of light yellow crystalline solid m.p. 142-44° was removed by filtration. The solid was recrystallized from absolute ethanol to give light yellow needle like crystals m.p. 146-49°. The infrared spectrum (KBr) gave absorbances at

2960 (w), 1730 (s), 1675 (m), 1650 (s), 1595 (m), 1480 (w), 1445 (m), 1425 (m), 1395 (m), 1375 (m), 1360 (m), 1345 (m), 1335 (m), 1290 (m), 1250 (s), 1235 (s), 1220 (s), 1135 (m), 1030 (m), 1000 (m), 960 (m), 945 (m), 930 (m), 905 (m), 850 (m), 775 (m), 670 (m), 620 (m) and 600 (m)  $\text{cm.}^{-1}$

The nmr spectrum ( $\text{CDCl}_3$ ) gave resonance signals at  $\delta 6.92$  (s, 2),  $\delta 4.80$  (s, 4),  $\delta 4.57$  (s, 4) and  $\delta 2.09$  (s, 6).

Anal. Calcd. for  $\text{C}_{14}\text{H}_{16}\text{N}_2\text{O}_6$ : C, 54.50; H, 5.20; N, 9.10.

Found: C, 54.35; H, 4.98; N, 9.01.

Reaction of 104 with 2,3-di-(hydroxymethyl)-1,3-butadiene-The procedure followed was identical to the previous reaction in which the diacetoxy diene was used. 1.0 g. (52.0% yield) of cream colored fluffy solid was obtained with m.p. of 159-63°. Recrystallization from absolute ethanol yielded a yellowish cream colored solid m.p. 166-69°. The infrared spectrum (KBr) exhibited absorbances at 3480 (s), 3400 (s), 3070 (m), 3010 (w), 2850 (w), 1630 (s), 1585 (m), 1440 (s), 1350 (m), 1275 (m), 1260 (m), 1235 (m), 1155 (m), 1110 (m), 1030 (m), 1015 (s), 955 (w), 950 (m), 920 (w), 860 (m), 790 (m), 750 (w), 695 (m) and 650 (m)  $\text{cm.}^{-1}$

The nmr spectrum ( $d_6$ -dimethylsulfoxide) gave resonance signals at  $\delta 6.98$  (s, 2),  $\delta 4.51$  (s, 4),  $\delta 4.11$  (s, 4) and  $\delta 3.50$  (broad, no accurate integration).

Anal. Calcd. for  $\text{C}_{10}\text{H}_{12}\text{N}_2\text{O}_4$ : C, 53.50; H, 5.35; N, 12.50.

Found: C, 53.57; H, 5.50; N, 12.50.

#### 4. Catalytic hydrogenation of Diels Alder adducts

Butadiene-89 adduct<sup>72</sup>-The catalytic hydrogenation of the Diels

Alder adduct of 1,3-butadiene and p-benzoquinone was studied to obtain a model compound and to become familiarized with the hydrogenation equipment. The catalytic hydrogenation vessel was charged with 0.190 g. (1.17 mmol.) of the adduct, 40 ml. of ethyl acetate and then 0.08 g. of 5% Rh/C catalyst. After connecting to the apparatus, the flask was flushed five times with nitrogen and once with hydrogen before filling with hydrogen for the reaction. This was the procedure used for all the hydrogenations at atmospheric pressure. After the theoretical uptake of hydrogen was observed, no further or additional hydrogen was absorbed. The catalyst was removed by filtration and the filtrate evaporated in vacuo to yield 0.160 g. of a low melting solid m.p. 40-50°, (lit.<sup>72</sup> 42.5-48.5°).

2,3-di-(acetoxymethyl)-1,3-butadiene, 77a, and diazoquinone, 104, at atmospheric pressure, ethyl acetate, 5% Rh/C-The hydrogenation reactor was charged with 0.2227 g. (0.72 mmol.) of the adduct, 50 ml. of ethyl acetate and 0.094 g. of 5% Rh/C catalyst. The theoretical hydrogen uptake was 35.4 ml. and after two hours of reaction 36.1 ml. were absorbed. The catalyst was removed by filtration and the solvent removed on a rotary evaporator to yield a clear oil. An infrared spectrum (salt plates) of the oil showed 1735  $\text{cm}^{-1}$  and 1675  $\text{cm}^{-1}$  carbonyl absorbances. The nmr spectrum was complex ( $d_6$ -acetone) and gave absorbances at  $\delta$ 4.50- $\delta$ 2.80 (complex m, 9),  $\delta$ 2.10 (sharp s on top of solvent),  $\delta$ 2.00- $\delta$ 1.20 (m, 6) and  $\delta$ 1.20- $\delta$ 0.40 (m, 2). Column chromatography on silica gel resulted in a clear oil yielding an infrared spectrum identical to the original material except for new absorbances at 2250 and 920  $\text{cm}^{-1}$ . The reaction was repeated with similar results.

2,3-di-(hydroxymethyl)-1,3-butadiene, 77b, and diazoquinone, 104, atmospheric pressure, ethyl acetate, 5% Rh/C-The reaction was carried out in the previous manner using 0.2055 g. (0.93 mmol.) of the adduct 108b and 0.112 g. of the 5% Rh/C catalyst in 50 ml. of ethyl acetate. Within 10 minutes exactly half of the theoretical uptake was observed and an additional several hours of reaction only gave a total of 89% of the theoretical uptake. From evaporation of the solvent a broad melting solid 132-37° was obtained which after recrystallization from absolute ethanol yielded a white solid m.p. 133-36°. This compound was identified as 114 from the following data. The infrared spectrum (KBr) gave absorbances at 3400 (s, broad), 2980-2850 (m, broad), 1650 (s, broad), 1440 (s, broad), 1320 (w), 1265 (s), 1230 (m), 1200 (m), 1175 (m), 1160 (m), 1110 (w), 1080 (w), 1045 (m), 1005 (s), 925 (m), 905 (m), 840 (m), 770 (w), 740 (s), 695 (w) and 665 (m) cm.<sup>-1</sup>

The nmr spectrum (CDCl<sub>3</sub>-d<sub>6</sub>-dimethylsulfoxide) gave resonances at δ4.29 (s, 4), δ4.10 (s, 4), δ3.87 (s, broad, approximately 4) and δ2.60 (s, 4). The mass spectrum gave a parent peak at m/e 226.

108b, atmospheric pressure, ethyl alcohol, 5% Rh/C-The same procedure was followed with 0.1627 g. (0.74 mmol.) of adduct, 0.089 g. of catalyst and 50 ml. of absolute ethanol as the reactor charge. The hydrogen uptake was 53.3 ml. compared to 35.4 ml. required for two double bonds. The uptake was identical for three equivalents. The product was a clear oil which gave an infrared spectrum with absorbances at 3410 (s, broad), 2980-2890 (m, broad), 2250 (m), 1690-1650 (s, broad), 1450-1400 (s, broad), 1315 (m), 1265 (m), 1240 (m), 1185 (m), 1155 (m), 1125 (m), 1105 (m), 1045 (m), 980 (m), 925 (m), 890 (m), 875 (w), 840 (m), 735 (m) and 650 (m) cm.<sup>-1</sup> The nmr spectrum (CDCl<sub>3</sub>) possessed

resonances at  $\delta$ 4.20- $\delta$ 3.20 (broad m, 6),  $\delta$ 2.62 (s, two spikes, 4),  $\delta$ 2.32- $\delta$ 1.60 (m, broad, 2) and  $\delta$ 1.40- $\delta$ 0.86 (septet, 2). No other analyses were performed.

108b, atmospheric pressure, ethyl alcohol, 5% Pd/C-The reaction was performed almost exactly as the previous reaction except the 5% Pd/C catalyst was used. Almost three equivalents of hydrogen were taken up and the oil isolated gave an infrared spectrum identical to the previous product. The nmr spectrum was very similar with resonances at  $\delta$ 4.68- $\delta$ 3.30 (m, broad, 7),  $\delta$ 2.60 (s, 4) and  $\delta$ 0.98 (sextet, 3). The mass spectrum gave m/e 211 as the parent peak and m/e 195 as the base peak. The oil was not characterized further.

108b, atmospheric pressure, ethyl acetate, 5% Pd/C-Using the same procedure, 0.0887 g. of 5% Pd/C and 50 ml. of ethyl acetate along with 0.2241 g. (1.02 mmol.) of 108b were put into the reactor and after 7.5 hours 90% of the theoretical absorption of hydrogen was measured. An infrared spectrum (salt plates, neat) of the resulting oil gave absorbances at 3500-3380 (s, broad), 2975-2880 (s, broad), 1690-1620 (s, broad), 1450-1400 (s, broad), 1315 (m), 1270 (s), 1235 (m), 1190 (s), 1160 (m), 1105 (m), 1045 (s), 985 (m), 910 (w), 890 (m), 875 (m), 840 (m) and 735 (m)  $\text{cm}^{-1}$ . The nmr spectrum ( $\text{CDCl}_3$ ) gave resonances at  $\delta$ 4.20- $\delta$ 3.20 (m, broad, 5),  $\delta$ 2.60 (s, 4),  $\delta$ 1.70 (s, 2) and  $\delta$ 1.10- $\delta$ 0.77 (m, 2). The mass spectrum gave a parent peak at m/e 212. No further attempts were made to characterize this oil.

108b, 35 psi., ethyl acetate, 5% Rh/C-A Paar Hydrogenator was charged with 0.4766 g. (2.16 mmol.) of the dihydroxy adduct, 0.1728 g. of 5% Rh/C and 50 ml. of ethyl acetate. The system was flushed three times with hydrogen and set at 35 psi and left rocking for 24 hours. On

filtering the catalyst and evaporation of the solvent, an oil was obtained with some solid material. Recrystallization from ethanol yielded a white solid and a brown oil. The solid was crystalline with a m.p. of 151-54°. The infrared spectrum (KBr) gave the following absorbances: 3420 (s, broad), 2980 (m), 2930 (m), 2870 (m), 1675 (s), 1635 (s), 1440 (m), 1420 (m), 1310 (w), 1260 (m), 1225 (m), 1180 (m), 1155 (m), 1120 (w), 1105 (w), 1040 (w), 1000 (s), 945 (w), 910 (m), 890 (m), 830 (m), 730 (m), 685 (w) and 645 (w)  $\text{cm.}^{-1}$

The nmr spectrum ( $\text{CDCl}_3$ , with one drop of  $d_6$ -dimethylsulfoxide) gave resonances at  $\delta 4.31$  and  $\delta 4.13$  (two overlapping broad singlets, 6),  $\delta 2.65$  (s, 4) and  $\delta 1.75$  (s, broad, 3). The mass spectrum (70 eV) gave the following major fragments:  $\underline{m/e}$  228,  $\underline{m/e}$  226,  $\underline{m/e}$  210 (base peak),  $\underline{m/e}$  194 and  $\underline{m/e}$  179.

The brown oil gave an nmr spectrum ( $\text{CDCl}_3$ ) with resonance signals showing  $\delta 4.50$ - $\delta 3.30$  (m, broad, 9),  $\delta 2.60$  (d, 5),  $\delta 1.75$  (d, 2),  $\delta 1.00$  (m, broad, 8). No further characterizations of the oil were attempted.

2,3-di-(acetoxymethyl)-1,3-butadiene and p-benzoquinone, 90, 5% Rh/C, ethyl acetate, atmospheric pressure-In a similar procedure to that used for the diazoquinone adducts, 0.2017 g. (0.66 mmol.) of 90 and 0.1046 g. of 5% Rh/C were added with 50 ml. of ethyl acetate to the reaction flask. The theoretical hydrogen uptake was 48.3 ml. and after five minutes 19 ml. were taken up and after two additional hours no further hydrogen uptake was noted. A brownish solid was obtained which was recrystallized from chloroform to give a white-silvery solid m.p. 143-45°. The infrared spectrum was identical to 91. No further effort was exerted in characterization of this compound.

5. Syntheses for attempted intramolecular Diels Alder reaction

Reaction of 89 with 2,3-di-(bromomethyl)-1,3-butadiene<sup>29</sup>-Freshly prepared 2,3-di-(bromomethyl)-1,3-butadiene (3.0 g., 0.013 mol.) and 4.0 g. (0.037 mol.) of p-benzoquinone were dissolved in 30 ml. of acetic anhydride. Over a five day period at room temperature a yellowish-white precipitate appeared. The solid was removed by filtration and the product washed several times with water. The acetic anhydride filtrate was stirred with water and the resulting solid formed was combined with the original residue. After recrystallization from benzene 3.1 g. (74.5% yield) of the desired adduct m.p. 153-55° (lit.<sup>29</sup> m.p. 154-56°) were obtained.

Reaction of the adduct of 89 and 2,3-di-(bromomethyl)-1,3-butadiene with zinc in dimethylformamide<sup>28</sup>-Zinc dust was purified by treating it three times with 5% hydrochloric acid. This was followed by washings with water, methyl alcohol and anhydrous ether. The zinc was then dried in a vacuum oven.

To remove moisture, all glassware was flamed under a sweep of dry nitrogen. Into a 100 ml. three-necked round-bottomed flask, 2.5 g. (7.2 mmol.) of the dibromide adduct were added along with dimethylformamide (dried over molecular sieves for 24 hours). To this solution 2.0 g. of the purified zinc dust were added. After 24 hours of vigorous stirring, the reaction was stopped and the zinc dust removed by filtration. The dimethylformamide was added slowly to 400 ml. of water with stirring and a cloudy white precipitate formed which darkened on filtration. After isolation it was insoluble in both dimethylformamide and dimethylsulfoxide. The infrared spectrum (KBr) gave absorbances at 2900-2850 (m), 1705 (s), 1665 (s), 1400 (m), 1240 (m),

1120 (m), 975 (w) and 885 (w)  $\text{cm}^{-1}$ . From the insolubility and broad infrared bands, this solid was believed to be a crosslinked polymer.

Zinc/dimethylformamide reaction in the presence of tetracyanoethylene—A predried 100 ml. three-necked round-bottomed flask was charged with 75 ml. of dry dimethylformamide, 2.3 g. (18.0 mmol.) of tetracyanoethylene, 3.1 g. (8.90 mmol.) of the dibromide adduct and 2.0 g. of treated zinc dust. On addition of the tetracyanoethylene to the dimethylformamide, a deep red color developed which persisted until the reaction was stopped after 48 hours. The excess zinc dust was removed by filtration and the filtrate was precipitated by addition of 200 ml. of water. The brownish solid isolated gave an infrared spectrum identical to tetracyanoethylene. The initial filtrate residue appeared to contain organic material along with the excess zinc. However, attempts to dissolve this material were unsuccessful. Seemingly, cross-linked polymeric material had been formed.

Zinc/dimethylformamide reaction in presence of maleic anhydride—The dibromide adduct (1.8 g., 5.18 mmol.) was put into a dried 200 ml. three-necked flask with 75 ml. of dry dimethylformamide and 1.0 g. (10.2 mmol.) of freshly sublimed maleic anhydride. Zinc dust (2.0 g.) was added and the mixture stirred under a positive nitrogen pressure. The reaction turned to a reddish-yellow color and began to get cloudy during the first hour. After 24 hours, the reaction was stopped and the zinc was allowed to settle to the bottom and the suspended solid was removed by filtration and washed with water to remove zinc salts. The product was not soluble in organic solvents and was soluble in 50% potassium hydroxide. An infrared spectrum gave broad absorbances at

1750  $\text{cm.}^{-1}$  and 1650  $\text{cm.}^{-1}$  Further attempts to work up and purify this product were not carried out.

6. Attempted preparation of 5,5,6,6-tetrasubstituted cyclohexadienes

Preparation of coumalic acid<sup>86</sup> -Malic acid, 200 g. (1.49 mol.) was placed into a two l. round-bottomed flask with 170 ml. of concentrated sulfuric acid. To this suspension three 50 ml. portions of 30% fuming sulfuric acid were added at 45 minute intervals. The frothy mixture was put into a 90° water bath for two hours. During this time it was occasionally shaken and the color changed from cream to yellow to a dark brown. The solution was poured, with stirring, into 800 g. of crushed ice and a light yellow suspension was formed. On filtering and drying over water 83.3 g. of the coumalic acid m.p. 185-90° (lit.<sup>86</sup> m.p. 195-200°) were obtained. Recrystallization from 400 ml. of methanol and Norite gave 40.0 g. of a yellow powder m.p. 206-208° (lit.<sup>86</sup> m.p. 206-209°).

Preparation of  $\alpha$ -pyrone<sup>76</sup> -Coumalic acid (79.5 g., 0.567 mol.) was charged into a 30 cm. x 10 cm. cylindrical flask which was inverted over a paddlewheel-powder stopcock. This was attached directly to a Vycor tube (60 cm. x 2.5 cm.) packed with approximately 15 g. of copper turnings. On top of the copper and above the heat zone a two cm. layer of six mm. Berl saddles was held in place by copper wire. The Vycor tube was run through a Hoskins Furnace (heat zone 32 cm.) and attached directly to a 500 ml. receiver which was immersed in an ice water bath. The receiver was connected to a two l. gas surge reservoir followed by two dry ice traps and a high capacity vacuum pump. After evacuation, the furnace was brought to 650° and the coumalic acid was dropped slowly

through with the rate control such that the pressure remained below 10 mm. Occasional back release of air was found to loosen stoppage of the powdered acid at the stopcock.

A black oily product was collected in the receiver. Vacuum distillation at 75-76.5° and 1.3 mm. (lit.<sup>76</sup> 83°, 2.6 mm.) yielded 30.0 g. (54.8% yield, lit.<sup>76</sup> 63.9%) of colorless product. The product was noted to become yellow in a few hours, even in the refrigerator.

Reactions of  $\alpha$ -pyrone and tetracyanoethylene-

a. Neat, room temperature- $\alpha$ -Pyrone (2.0 g., 20.8 mmol.) was added to a 50 ml. three-necked round-bottomed flask and the flask was cooled to 5° in an ice water bath. Tetracyanoethylene (2.6 g., 20.2 mmol.) was added and the mixture immediately turned a dark brownish-red color. After this the flask was removed from the bath and allowed to warm to room temperature and then it was left for an additional two hours. An nmr spectrum indicated only unreacted starting materials.

b. Refluxing tetrahydrofuran-Tetrahydrofuran, 50 ml., and tetracyanoethylene (2.5 g, 20.0 mmol.) were mixed in a 100 ml. round-bottomed flask and a yellow colored solution resulted. To this solution 2.0 g. (20.8 mmol.) of  $\alpha$ -pyrone were added and no noticeable color change was noted at room temperature for 24 hours. Refluxing at 68-69° for an additional 24 hours resulted in a darkening of the yellow color. However an nmr spectrum of the reaction mixture indicated only unreacted starting materials.

c. Neat, 146°, excess  $\alpha$ -pyrone-A 50 ml. round-bottomed three-necked flask was charged with 810 g. (83.5 mmol.) of  $\alpha$ -pyrone and 6.0 g. (41.7 mmol.) of tetracyanoethylene and then flushed with nitrogen. The excess  $\alpha$ -pyrone was used to help put the tetracyanoethylene

into solution and to guard against getting a "double" Diels Alder reaction. The temperature was gradually increased to 140° and was stirred smoothly for approximately two hours. After this time the mixture became black and tarry. This substance was extracted with chloroform and a brown oil was obtained which was identified as unreacted  $\alpha$ -pyrone by its nmr spectrum. The black solid was not characterized further.

d. Neat, 100°-A small flask was charged with 1.5 g. (11.70 mmol.) of tetracyanoethylene and 3.5 g. (36.4 mmol.) of  $\alpha$ -pyrone. After flushing with nitrogen the flask and contents were inserted into a 100° oil bath. After three hours a thin layer chromatogram of an aliquot indicated no reaction had occurred. After 24 hours the temperature was raised to 110° and a black solid appeared to start forming. The flask was removed from the oil bath and the black solid was rinsed with ether, which when evaporated gave a dark brown oil indicative of unreacted  $\alpha$ -pyrone. The black solid was soluble in dimethylsulfoxide, but an nmr spectrum in this solvent gave no indication of the desired adduct.

e. Refluxing xylene-Into a 100 ml. round-bottomed flask were introduced the following: 65 ml. of p-xylene, 6.0 g. (62.5 mmol.) of  $\alpha$ -pyrone, 4.5 g. (35.1 mmol.) of tetracyanoethylene. The tetracyanoethylene formed a dark yellow-brown complex with the solvent. The solution was refluxed for 48 hours and after this time a black solid was filtered from the dark reddish-brown xylene. The xylene was removed in vacuo to yield large plate like brownish crystals which had a m.p. of 197-99°, tetracyanoethylene (lit.<sup>4</sup> m.p. 200°). These crystals were soluble in benzene with formation of a yellow color, a characteristic of tetracyanoethylene. From these observations it appeared no adduct was present and no further attempts to characterize these two

solids were made.

f. Refluxing benzene-Tetracyanoethylene (1.0 g., 7.82 mmol.) and  $\alpha$ -pyrone (1.0 g., 10.3 mmol.) were dissolved in 15 ml. of benzene and refluxed for 45 hours. A black solid was isolated which was not characterized.

g. Refluxing toluene-Tetracyanoethylene (1.0 g., 7.82 mmol.) and  $\alpha$ -pyrone (1.0 g., 10.3 mmol.) were refluxed in 15 ml. of toluene for 44 hours. A black solid tarry like substance was again isolated and was not further characterized.

h. Tetrahydrofuran sealed tube-A heavy walled Pyrex tube was charged with 2.0 g. (14.6 mmol.) of freshly recrystallized tetracyanoethylene, 1.5 g. (15.6 mmol.) of recently distilled  $\alpha$ -pyrone and 15 ml. of dry tetrahydrofuran. The tube was carried through a freeze-thaw cycle for degassing the contents and then sealed. The tube and its contents (dark yellow-brown) were placed into a 60° oil bath for 188 hours. On removal the contents had only darkened somewhat. An nmr analysis verified that no reaction had occurred.

Reaction of  $\alpha$ -pyrone and fumaronitrile-Fumaronitrile (1.0 g., 12.8 mmol.) and  $\alpha$ -pyrone (1.0 g., 11.9 mmol.) were placed into 15 ml. of toluene and refluxed for four days. The reaction turned cloudy on cooling and a white solid was removed by filtration. Recrystallization from ethanol-ethyl acetate resulted in a white crystalline solid m.p. 201-203°. The infrared spectrum (KBr) gave absorbances at 3100 (w), 3045 (m), 2950 (m), 2245 (m), 2200 (w), 1755 (s), 1605 (w), 1365 (s), 1345 (m), 1300 (w), 1265 (m), 1205 (m), 1135 (m), 1120 (m), 1030 (m), 1010 (m), 1000 (s), 980 (s), 900 (m), 800 (m), 725 (m) and 655 (m) cm.<sup>-1</sup>

The nmr spectrum (d<sub>6</sub>-acetone) gave resonance signals at  $\delta$  9.2

(m, 2),  $\delta$ 5.80 (m, 1),  $\delta$ 4.08 (m, 2) and  $\delta$ 3.63 (m, 1).

Anal. Calcd. for  $C_9H_6N_2O_2$ : C, 62.01; H, 3.45; N, 16.02. Found: C, 61.52; H, 3.62; N, 15.89.

Reaction of p-benzoquinone with  $\alpha$ -pyrone-A small flask was charged with p-benzoquinone (1.0 g., 9.25 mmol.) and  $\alpha$ -pyrone (4.6 g., 54.6 mmol.), stoppered and set aside. After three days the reaction had darkened and another 1.0 g. of quinone was added. After two weeks, the insoluble portion was removed by filtration and the 1.2 g. of crude product were recrystallized from chloroform to yield 1.0 g. (56% yield) of light yellow crystals m.p. 149-52°. The infrared spectrum gave absorptions at 3050 (w), 2950 (w), 1750 (s), 1655 (s), 1610 (m), 1380 (w), 1355 (m), 1325 (m), 1280 (m), 1265 (m), 1225 (w), 1205 (w), 1160 (m), 1115 (m), 1100 (m), 1060 (w), 1005 (m), 965 (m), 940 (m), 865 (m), 825 (m), 805 (m), 745 (w), and 700 (m)  $cm^{-1}$ .

The nmr spectrum ( $CDCl_3$ ) showed resonances at  $\delta$ 6.82 (s, 2),  $\delta$ 6.57 (t, 2),  $\delta$ 5.69 (q, 1) and  $\delta$ 3.60 (q, 2).

Anal. Calcd. for  $C_{11}H_8O_4$ : C, 64.70; H, 3.90. Found: C, 64.73; H, 3.99.

Reaction of  $\alpha$ -pyrone with dimethyl maleic anhydride-Dimethyl maleic anhydride (1.0 g., 7.95 mmol.) and  $\alpha$ -pyrone (1.0 g., 11.9 mmol.) were refluxed for five days in 15 ml. of toluene. On removal of the toluene on a rotary evaporator a yellow liquid was obtained. An nmr spectrum indicated only starting materials. No further effort was put into the reaction.

Reaction of  $\alpha$ -pyrone with tetracthylethylenetetra-carboxylate-The tetra ester (1.0 g., 3.16 mmol.) and  $\alpha$ -pyrone (1.0 g., 11.9 mmol.) were refluxed for five days in 15 ml. of toluene. A yellowish-brown

oil was obtained after the solvent was removed. A thin layer chromatogram indicated starting materials. The oil was set aside and after one year large crystals were noted formed in the bottom. No characterizations were attempted.

Reaction of 2,3-dimethyl-1,3 butadiene sulfone with bromine<sup>80</sup>

A 250 ml. three-necked round-bottomed flask was charged with 20.0 g. (0.137 mol.) of the sulfone and 50 ml. of dry chloroform. Bromine, 21.8 g. (0.137 mol.), dissolved in 50 ml. of chloroform was added via a dropping funnel in small increments. A white solid (37.3 g., 89% yield) was isolated m.p. 230-33° (lit.<sup>80</sup> m.p. 215°).

Preparation of 3,4-dimethylthiophene-1,1-dioxide-A 100 ml. three-necked flask was equipped with a reflux condenser and drying tube with a nitrogen flush inlet. Into the flask were introduced 50 ml. of tetrahydrofuran (distilled from lithium aluminum hydride and stored over molecular sieves), 2.0 g. (33.0 mmol.) of sodium methoxide followed by 5.0 g. (1.63 mmol.) of the dibromide. Stirring was accomplished via a magnetic stirrer. A slight exothermicity was noted on the bromide addition. The reaction was heated at reflux with a fast nitrogen sweep for five hours. After cooling the residual solid was removed by filtration under a nitrogen flush. The solid was soluble in water, formed a precipitate on addition of silver nitrate and weighed 3.40 g. The theoretical amount of sodium bromide formed during the reaction was 3.38 g. Approximately 1.3 g. (45% yield) of crude product were obtained m.p. 95-107°. Recrystallization from ethanol and petroleum ether gave a white solid m.p. 114-115° (lit.<sup>79</sup> m.p. 114°).

An nmr spectrum (CDCl<sub>3</sub>) gave resonance signals at δ6.32 (s, 2) and δ2.06 (s, 6).

Preparation of 2-hydro-3-methylene-4-methylthiophene-1,1-dioxide-

Under the identical conditions as the previous reaction, 9.7 g. (31.8 mmol.) of the dibromide, and 3.8 g. (36.3 mmol.) of sodium methoxide were reacted in 150 ml. of tetrahydrofuran. The reaction turned yellow and then very dark and on filtration sodium bromide was obtained. The black filtrate changed to yellow overnight and the yellow solid thus obtained, 3.3 g., was recrystallized from ethanol-petroleum ether to give a yellow solid m.p. 105-108° (lit.<sup>79</sup> m.p. 110°). The nmr spectrum (CDCl<sub>3</sub>) gave resonance signals at δ6.69 (s, 1), δ5.60 (m, 1), δ5.44 (m, 1), δ4.00 (m, 2) and δ2.10 (s, 3).

Reaction of 3,4-dimethyl-thiophene-1,1-dioxide with tetracyano-

ethylene-A 25 ml. pear-shaped flask was charged with 0.115 g. (0.80 mmol.) of the diene, 0.111 g. (0.89 mmol.) of tetracyanoethylene, a couple of carborundum chips and 10 ml. of dry tetrahydrofuran. The solution was refluxed for four days with the color darkening over this time. On evaporation of the tetrahydrofuran and redissolving the reaction mixture in chloroform the tetracyanoethylene was recovered quantitatively.

Reaction of 3,4-dimethylthiophene-1,1-dioxide with maleic anhydride-

Into a 25 ml. pear-shaped flask were placed 0.143 g. (1.49 mmol.) of maleic anhydride and 0.222 g. (1.54 mmol.) of the diene. Toluene (10 ml.) was added and the mixture was brought to reflux. After a few hours small crystals appeared on the sides of the flask. The reaction was stopped after 24 hours and a few milligrams of the brownish crystals were obtained, m.p. 280°. Removal of the toluene gave a dark oil which gave an infrared spectrum featuring a double carbonyl anhydride and two bands at 1625 cm.<sup>-1</sup> and 1595 cm.<sup>-1</sup> characteristic of a diene.

The infrared spectrum (KBr) of the solid gave absorbances at 3005 (m), 2990 (m), 2940 (m), 2875 (w), 1850 (s), 1780 (s), 1660 (m), 1430 (m), 1380 (w), 1310 (m), 1210 (s), 1145 (m), 1080 (m), 1030 (m), 900 (s), 790 (m), 725 (m) and 670 (m)  $\text{cm.}^{-1}$

The nmr spectrum ( $d_6$ -dimethylsulfoxide) gave resonance signals at  $\delta$ 3.55 (s, broad, 4),  $\delta$ 3.20 (s, broad, 2) and  $\delta$ 1.62 (s, 6). The mass spectrum (70eV)  $\underline{m/e}$  (rel. intensity) gave fragments 277 (14), 276 ( $M^+$ , 72), 249 (4), 248 (28), 176 (30), 175 (70), 174 (44), 159 (12), 131 (72), 130 (94), 117 (10), 115 (16), 107 (10), 106 (100), 105 (56), 99 (26), 92 (10) and 91 (82).

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