

THE SYNTHESIS AND CERTAIN CHEMISTRY OF  
BENZOBICYCLO[2.2.0]HEXA-2,5-DIENE

by 45

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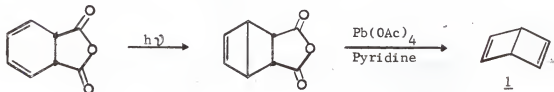
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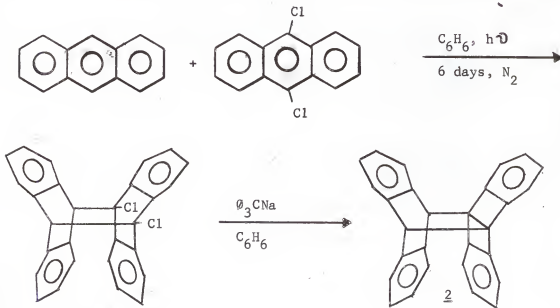
## INTRODUCTION

Small ring bicyclic molecules have been the subject of voluminous quantities of work due to their fascinating properties. Their geometry is of particular interest due to the bond deformations necessary to attain this geometry. The exact hybridization of the carbons is, to a certain extent, still not completely understood.

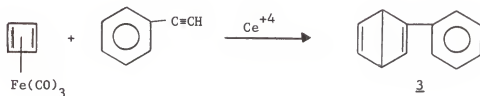
In 1867, J. Dewar<sup>23</sup> first proposed bicyclo[2.2.0]hexa-2,5-diene (1) as a possible structure for benzene. Nearly one hundred years later, van Tamelen and Pappas<sup>65</sup> reported the successful synthesis of 1. The next in this series of "Dewar" structures was a "Dewar anthracene" 2 synthesized by



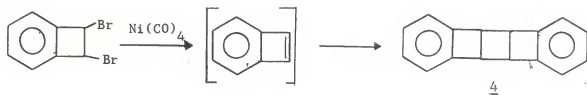
Applequist and Searle<sup>1</sup> in a 26% yield. A year following that report, Burt



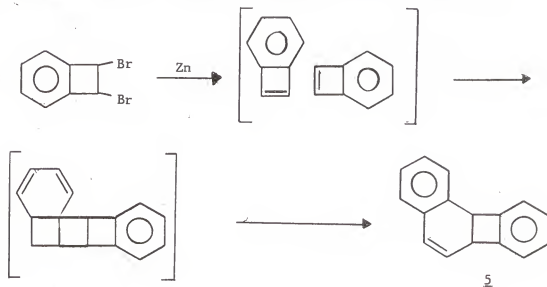
and Pettit<sup>12</sup> reported the synthesis of 2-phenylbicyclo[2.2.0]hexa-2,5-diene ("hemi-Dewar biphenyl") (3).



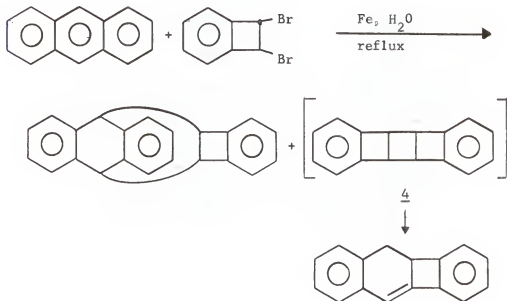
Systems in which a benzene ring is fused to "ladderane" structures have also received attention. Nenitzescu, *et al.*,<sup>2</sup> prepared 4 from 1,2-dibromobenzocyclobutene in the presence of nickel tetracarbonyl. Cava



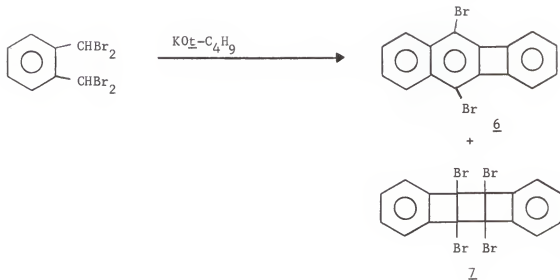
and Napier<sup>17</sup> investigated the dehalogenation of this same dibromide with zinc dust and did not obtain the linear benzobutadiene dimer, but apparently got the angular dimer which rearranged to 5 in 70-80% yield.



Another method debromination of trans-3,4-dibromobenzocyclobutene was carried out by Nozaki and Noyori<sup>50</sup> when they allowed the dibromide to react with a water suspension of iron powder in the presence of anthracene.

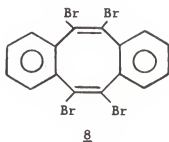


Jensen and Coleman<sup>38</sup> have reported that the action of potassium tert-butylate on  $\alpha, \alpha', \alpha', \alpha'$ -tetrabromo-o-xylene produces 6 (69%) and 7 (20%). However, Cava<sup>15</sup> found that the actual structure of the tetrabromide 7 by

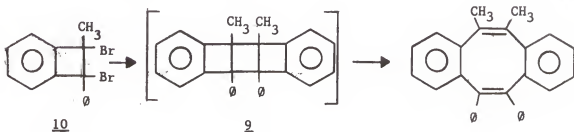




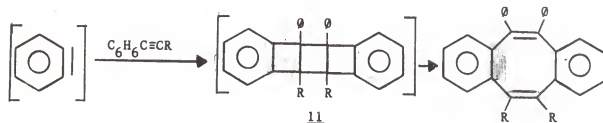
X-ray crystallography is 8. Blomquist and Bottomly<sup>9</sup> have proposed a



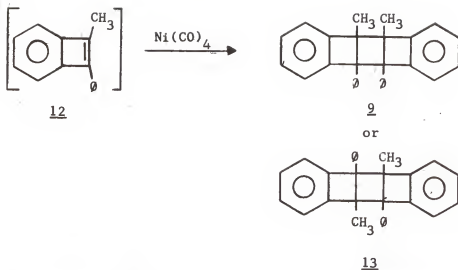
pentacyclic intermediate, 9, in the reaction of zinc, sodium or lithium amalgam, or sodium iodide with 10.



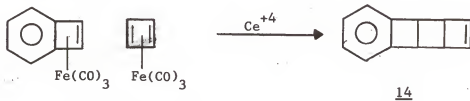
Intermediates of this type have also been proposed when benzyne is allowed to react with substituted alkynes. Stiles *et al.*,<sup>60</sup> have proposed the intermediacy of compounds having the general structure 11 when benzyne is produced in the presence of the appropriate alkyne. However, when



1-methyl-2-phenylbenzocyclobutadiene (12) was generated in the presence of nickel tetracarbonyl, a stable dimer having the structure of 9 or 13 was formed<sup>10</sup>.

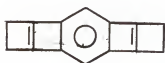
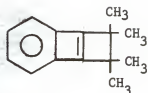
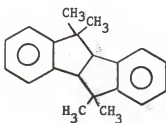
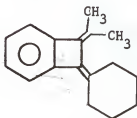
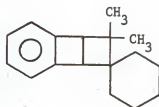


Merk and Pettit<sup>48</sup> produced 14 in a 75% yield by generating both benzocyclobutadiene and cyclobutadiene *in situ*.

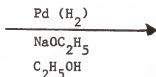


Lagidze and Petrov<sup>40</sup> assigned a benzocyclobutadiene structure 15 to a hydrocarbon "C<sub>14</sub>H<sub>10</sub>", m.p. 102°, which they obtained by the reaction of 1,4-diacetoxy-2-butyne with benzene and aluminum chloride, but subsequently favored structure 16<sup>41,42</sup>. Later, it was shown that Lagidze's "C<sub>14</sub>H<sub>10</sub>" hydrocarbon was 2-phenylnaphthalene (C<sub>16</sub>H<sub>12</sub>)<sup>25,34,45</sup>. Lagidze and Loladze<sup>43</sup> proposed structure 17 for the product from the reaction of 2,5-diacetoxy-2,5-dimethyl-3-hexyne with benzene and aluminum chloride. But Hancock and Scheuchenpflug<sup>33</sup> corrected the structure to 18. Similarly, the product resulting from the reaction of 1,4-diacetoxy-1-cyclohexyl-4-methyl-2-pentyne with benzene and aluminum chloride was reported by Lagidze and Kuprava<sup>44</sup> to be either 19 or 20. The structure of the product is not known but is

almost certain not to be 19 or 20<sup>14</sup>.

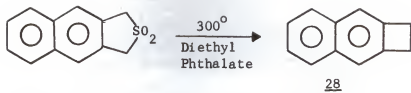
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By far the most well investigated system composed of a benzene ring fused to a cyclobutane ring is the benzocyclobutene system. Benzocyclobutene (21) was first prepared by Cava and Napier<sup>17</sup> by the action of hydrogen on palladium with 1,2-diiodobenzocyclobutene (22).

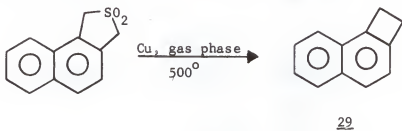
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1,2-Dimethylenebenzocyclobutene (23) was synthesized by Cava, Pohl, and Mitchell<sup>18</sup> by the pyrolysis of 24. Structure 23 can be isomerized to naphthalene by heat. Several 1,2-bis(benzylidene)benzocyclobutenes have been prepared by Blomquist and Hurby<sup>11</sup> by the action of strong base on the





Erickson<sup>20</sup> have reported the synthesis of naphtho[a]cyclobutene (29).



## OBJECTIVES OF THIS INVESTIGATION

The objectives of this investigation were to synthesize benzobicyclo-[2.2.0]hexa-2,5-diene to determine its spectral properties, and to study certain aspects of its chemistry.

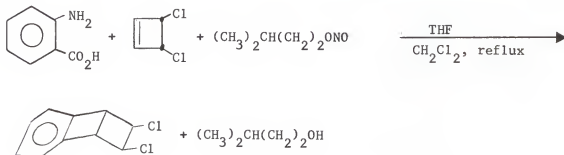
## DISCUSSION OF EXPERIMENTAL RESULTS

Benzobicyclo[2.2.0]hexa-2,5-diene ("hemi-Dewar naphthalene") (30) has not been reported heretofore. The term "hemi-Dewar naphthalene" will be used to denote benzobicyclo[2.2.0]hexa-2,5-diene. The approach taken in



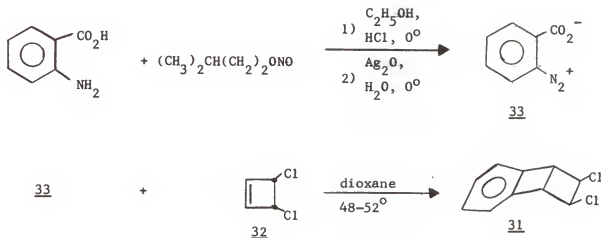
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this investigation was to prepare exo, cis-5,6-dichlorobenzobicyclo[2.2.0]-hex-2-ene (31) by the cycloaddition of benzyne with cis-3,4-dichlorocyclobutene<sup>4</sup> (32). Basically two methods were tried. One method was patterned after Friedman and Logullo's reaction of benzyne with anthracene where the benzyne precursor and the benzyne itself were all generated in situ<sup>31</sup>. How-



ever, only a 0.1% yield of the desired product was isolated. Several other products were formed in this reaction and were separated, to a certain extent, by column chromatography on basic, activity one alumina. One may have been an alcohol; another may have been an ether, as determined from the nuclear magnetic resonance (n.m.r.) spectrum of the fractions from the column chromatography. None were identified with certainty.

The second method involved isolation of the benzyne precursor, benzenediazonium-2-carboxylate (33), according to the method of Stiles, *et al.*<sup>61</sup>, and then allowing 33 to react with 32 in dry dioxane. This latter

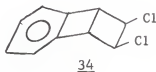
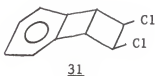


method afforded the desired product in yields varying from 2.4% to 11.3% depending on the ratio of 32 to 33 (see Table I, page 46). The impurities in the crude product seemed to be largely aromatic. By comparison of the nuclear magnetic resonance (n.m.r.) spectrum of the impure material with standard spectra, benzoic acid<sup>56</sup> seemed to be one of the impurities<sup>49</sup>. A thin layer chromatogram (t.l.c.) on silica gel G of the impure product with benzene as eluent showed four components present besides the desired product. This mixture was chromatographed on basic, activity one alumina with carbon tetrachloride as eluent. The first few fractions containing solid contained the purest product. The infrared spectrum of 31 was fairly simple (page 28) and is in agreement with a high degree of symmetry in the tricyclic structure.

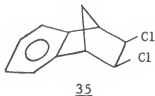
The structure of the product of the cycloaddition reaction was strongly



indicated to be 31 and not the endo, cis-dichloride 34 from analysis of the n.m.r. spectrum of the compound (page 32). The aromatic hydrogens were assigned to the finely split multiplet at  $\tau$  2.80. This is 0.2 p.p.m. lower field than the aromatic hydrogens of benzocyclobutene ( $\tau$  3.00)<sup>27</sup>. The bridgehead methine hydrogens were tentatively assigned to the finely



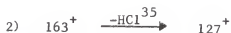
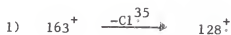
split multiplet at  $\tau$  5.55. This assignment was reinforced by the fact that the bridgehead hydrogens of the "hemi-Dewar naphthalene" 30 came at  $\tau$  5.58 (cf. page 32). The  $C_5$  and  $C_6$  hydrogens were assigned to the finely split multiplet at  $\tau$  5.92. The chemical shift of the  $C_5$  and  $C_6$  hydrogens of 31 compares well with those of 35 where the endo-5,6 hydrogens have a chemical shift of  $\tau$  6.00<sup>22</sup>.

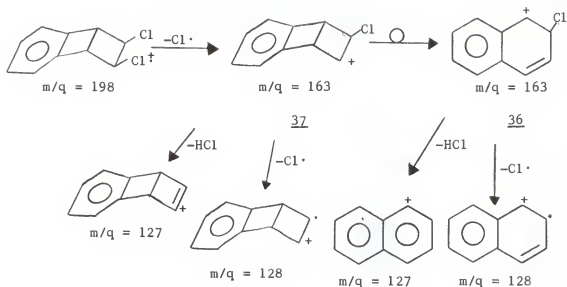


The  $C_5$  and  $C_6$  hydrogens of 31 being endo make a dihedral angle of  $120^\circ$  with the bridgehead hydrogens, whereas in 34 the same dihedral angle is about  $15^\circ$ . Consulting a graph of coupling constant ( $J$ ) vs. dihedral angle<sup>24</sup>, a dihedral angle of  $15^\circ$  would be expected to have a  $J$  of about 8 c.p.s. while an angle of  $120^\circ$  would have a  $J$  of about 2 c.p.s. The

multiplets corresponding to the methine and methylene of the tricyclic dichloride (page 32) had  $J=0.9$  c.p.s. and  $J=0.82$  c.p.s., respectively. Therefore, structure 31 was strongly favored over 34 as the structure of the dichloride.

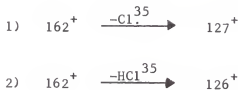
Mass spectral analysis of 31 (cf. Table I, Appendix), using a direct inlet, confirmed the presence of two chlorines on the molecule. As can be seen from the bar graph (page 42), the  $M^+-Cl$  peaks were in a ratio of 3:1, which was expected for a mono-chlorinated species in the mass spectrometer. Also the  $M^+$ ,  $M^+ + 2$ , and  $M^+ + 4$  peaks were in a ratio of 1:0.625:0.25 which was within experimental error of the actual ratio 1:0.655:0.106 for a dichloro species<sup>5</sup>, since the intensities of these peaks were quite small (page 42). The base peak ( $m/q = 128$ ) could correspond to either the radical-cation of naphthalene or to the radical-cation of "hemi-Dewar naphthalene". The former seems more reasonable, since to get to it from the parent radical-cation one could invoke a benzyl carbonium ion 36 which might be expected to be longer lived than the cyclobutyl carbonium ion 37 as shown in the following sequence. The only metastable peaks that have been reasonably assigned were 1)  $m/q = 100.5$  and 2)  $m/q = 99.1$ . These correspond to the processes:



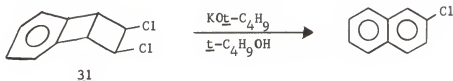


As to whether or not the  $m/q = 128$  peak corresponds to the radical-cation of naphthalene is still not very clear. Every peak in the naphthalene spectrum<sup>46</sup> has a corresponding peak in the spectrum of 31, but in the latter's spectrum the peaks are more intense. Many of these peaks in the mass spectrum of 31 were in the same relative ratios as the corresponding peaks in the mass spectrum of naphthalene. There are several peaks in the spectrum of 31 at lower mass units than  $m/q = 128$  that are not present in the spectrum of naphthalene.

Concerning the heated inlet mass spectrum of 31, in a communication from Professor R. W. Kiser<sup>39</sup>, he indicated through text and spectra that in the heated inlet ( $200^{\circ}$ ) spectrum the base peak was  $m/q = 162$  and that there were definite metastable peaks for the transitions:



Chemical proof of the nature of 31 was the dehydrochlorination of it to 2-chloronaphthalene in 69% yield. This was effected by heating a solution of 31 in potassium tert-butoxide-tert-butyl alcohol overnight. An independent synthesis of 2-chloronaphthalene from 2-aminonaphthalene was carried



out using the method of Fieser<sup>26</sup> for the diazonium salt preparation and that described by Chattaway and Lewis<sup>21</sup> for the Sandmeyer step. The n.m.r.

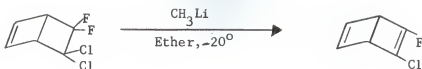


spectra of the products from the elimination reaction on 31 and that from the independent synthesis were identical.

The next step in this study was to investigate methods for converting 31 to benzobicyclo[2.2.0]hexa-2,5-diene (30) and benzobicyclo[2.2.0]hex-2-ene (38). The first approach was to make use of methyl lithium

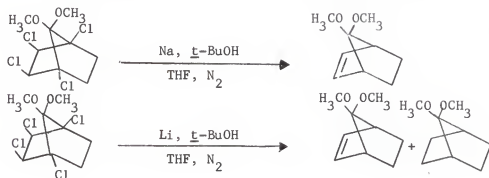


in dehalogenation, using the method of Schroder and Martini<sup>59</sup>, who obtained 70% yields in their dehalogenations of 5,5-dichloro-6,6-difluorobicyclohex-[2.2.0]hex-2-ene. When this was tried on 31, only starting material (85%



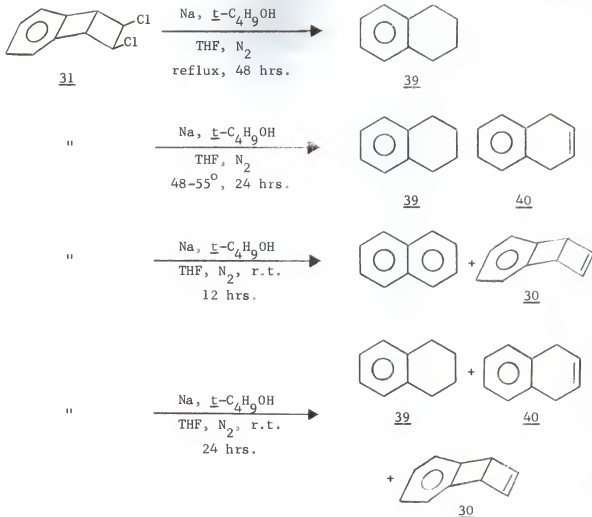
recovery) was obtained from the reaction.

The next procedure attempted was that of lithium or sodium and tert-butyl alcohol in tetrahydrofuran as a reductive dechlorination reagent. Gassman and Pape<sup>32</sup> had effectively used it on 7,7-dimethoxy-1,2,3,4-tetrachlorobicyclo[2.2.1]heptane and obtained product yields in excess of 60%. Several attempts were made using this method: 1) sodium, tert-butyl



alcohol, tetrahydrofuran under reflux for 48 hours (38.6% yield, 1,2,3,4-tetrahydronaphthalene (tetalin) (39)); 2) same reagents as 1), but heated at 48-54° for 24 hours (65% conversion of the starting material to a 1:8:1 mixture of 39 and 1,4-dihydronaphthalene (40)); 3) the same reagents were used as in 1), but they were allowed to react at room temperature for 12 hours (1:1:3 mixture of naphthalene, 30, and starting material 31 with a 44% conversion of starting material to naphthalene and 30).

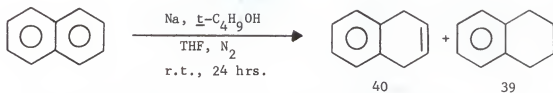
No starting material was found when 31 was allowed to react with sodium and tert-butyl alcohol in tetrahydrofuran for 24 hours at room temperature. A mixture of 30, 39, and 40 in a ratio of 1:1.2:2.5 was obtained in this



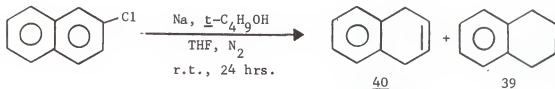
latter attempt. Upon standing in the freezer overnight the product mixture from the last reaction began to exhibit peaks in the n.m.r. spectrum corresponding to naphthalene.

It was then thought that the hydrogenated derivatives of naphthalene, 39 and 40, were being produced from the reduction of naphthalene which may be formed from the rearrangement of "hemi-Dewar naphthalene" (30). Naphthalene was subjected to the conditions of the last reaction. A quantity of material corresponding to 66% of the amount of starting material was obtained. It was a 2.5:1 mixture of 40 and 39, respectively, with a small

amount of starting material not discovered until purification of 40. There



was also a possibility that 31 could be producing 2-chloronaphthalene prior to conversion to 39 and 40. 2-Chloronaphthalene was subjected to these same conditions and 31.6% of the starting material was recovered along with 22.4% of a mixture of 40 and 39. Proof of the presence of 39 was obtained by comparing the published n.m.r. spectrum of 39<sup>56</sup> to the n.m.r. spectra of the

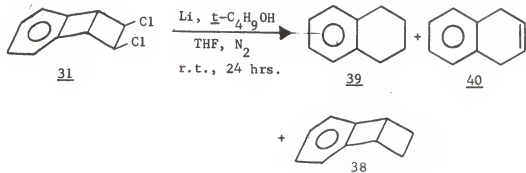


product mixtures of the dechlorination reactions. The same identification was made for naphthalene<sup>57</sup>.

The n.m.r. spectrum assigned to 1,4-dihydronaphthalene (40) (page 34) was in agreement with the proposed structure. The olefin hydrogens were assigned to the multiplet at  $\gamma$  4.18, the methylene hydrogens were assigned to the unsymmetrical doublet at  $\gamma$  6.71, and the aromatic hydrogens were assigned to the tight multiplet at  $\gamma$  3.00. The ratio of the three sets of absorptions was 1:2:2.2, respectively. Coupling of the olefinic hydrogens to the methylene hydrogens was confirmed by spin decoupling these hydrogens. Naphthalene showed up in the n.m.r. spectrum (page 34) of this sample and was not separated.

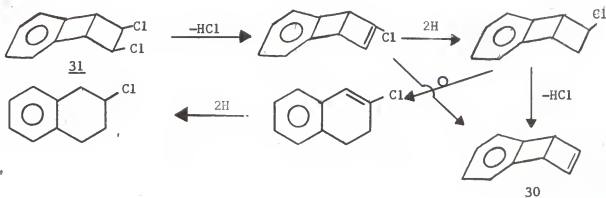
Considering that the use of lithium metal might give both the

"hemi-Dewar naphthalene" (30) and the benzobicyclo[2.2.0]hex-2-ene (38), lithium was allowed to react with 31 under the conditions used in the last sodium reaction and several products resulted. Of the material obtained

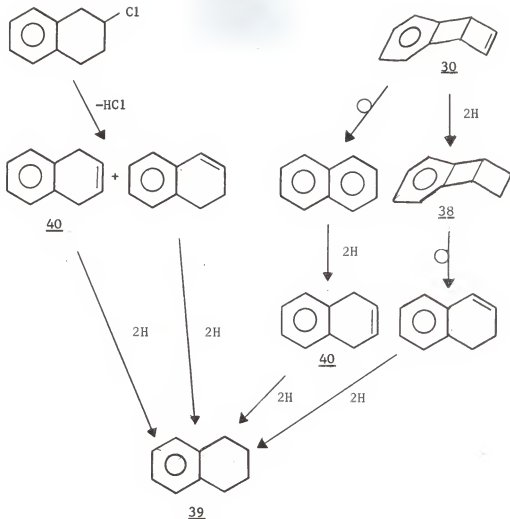


from this reaction (40-50% of the quantity of starting material used), besides 38, 39, and 40 (each one-fourth of obtained material) about one-fourth of it was an unknown material (possibly 1,2-dihydronaphthalene as determined from the n.m.r. spectrum of the mixture). No "hemi-Dewar naphthalene" was observed. The n.m.r. absorptions assigned to 38 were arrived at by comparing the n.m.r. spectrum of the above mixture to the n.m.r. spectrum of 38 (page 36) as produced in the diimide reduction of 30.

In the sodium and lithium *tert*-butyl alcohol reactions, possible routes by which 31 undergoes conversion to 30, 38, 39, and 40 are the following:

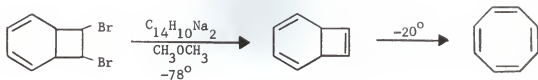




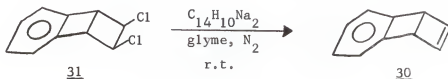


Due to the facile isomerization of the "hemi-Dewar naphthalene", separation of it from 39 and 40 was not attempted. A mild dehalogenation of 7,8-dibromobicyclo[4.2.0]octa-2,4-diene has been reported by Vogel<sup>66</sup>. He used a disodium-phenanthrene complex for his dehalogenation, obtaining in 45% yield bicyclo[4.2.0]octa-2,4,7-triene, which rearranged to cyclooctatetraene. Using this method "hemi-Dewar naphthalene" (30) was synthesized by first preparing the disodium-phenanthrene complex and then injecting the complex into a glyme solution of 31 at room temperature under nitrogen<sup>69</sup>. The "hemi-Dewar naphthalene" (30) was

easily distilled in a 34% yield from the unreacted starting material and the



phenanthrene. In the disodium-phenanthrene dechlorination reaction, the



mechanism can be considered as two one-electron transfers or a concerted two electron transfer by the complex to the dichloride 31 to effect the dechlorination.

The n.m.r. spectrum of 30 (page 32) exhibited a finely split multiplet at  $\tau$  2.95 (four aromatic hydrogens), a finely split multiplet at  $\tau$  3.43 (two olefinic hydrogens), and a finely split multiplet at  $\tau$  5.58 (two methine hydrogens). The n.m.r. spectrum (page 32) showed that the hydrogens on the bridgehead of the "Dewar" half of the molecule exhibited an absorption at a chemical shift very close to that for the same hydrogens of 31 ( $\tau$  5.55). The reason for the small coupling between the bridgehead hydrogens and the olefinic hydrogens of the "Dewar" half was due to the dihedral angle (about  $55^\circ$ ) between them. The graph of  $J$  vs. dihedral angle<sup>24</sup> predicts a  $J$  of about 2.3 c.p.s.; the observed  $J$  was 1.0 c.p.s. The chemical shift of the olefinic hydrogens of 30 was very close to that of the same hydrogens in van Tamelen's bicyclo[2.2.0]hexa-2,5-diene ("Dewar benzene") ( $\tau$  3.45)<sup>65</sup>. However, the bridgehead hydrogens in the "Dewar benzene" were

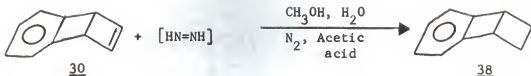
upfield 0.58 p.p.m. from the bridgehead hydrogens of the 30. The aromatic hydrogens of 30 were downfield about 0.2 p.p.m. from that of 41 ( $\gamma$  3.13)<sup>22</sup>. The olefinic hydrogens of 30 were chemically shifted very nearly the same amount as the corresponding hydrogens in 41 ( $\gamma$  3.43)<sup>22</sup>. The methine hydrogens of 30, however, were downfield over 0.8 p.p.m. from that of the corresponding hydrogen's of 41 ( $\gamma$  6.41)<sup>22</sup>.

41

The ultraviolet spectrum of 30 (page 38) was not sufficiently different than benzocyclobutene (22)<sup>17</sup> to warrant a postulation of homoconjugation of the olefinic double bond with the aromatic ring (cf. Table III, Appendix). The infrared spectrum of 30 (page 30) was also consistent with the assigned structure.

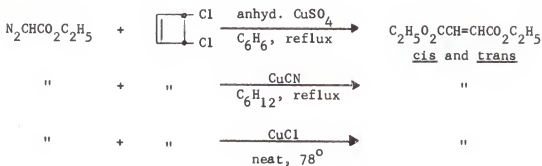
The rate constant for the isomerization of 30 to naphthalene was determined in carbon tetrachloride at  $38 \pm 0.2^\circ$ , the ambient temperature of the probe in the n.m.r. spectrometer. In the kinetic study, the decrease in 30 was followed by comparing the n.m.r. integration of the  $\gamma$  3.43 peak of 30 to the integration of a standard. The kinetic study indicated a first order reaction with a half-life of 3.96 hours and a rate constant of  $4.85 \pm 0.484 \times 10^{-5} \text{ sec.}^{-1}$ .

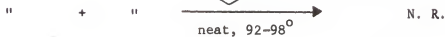
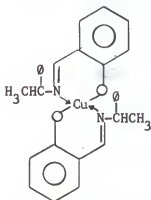
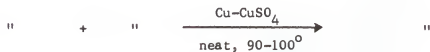
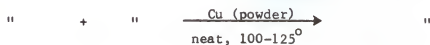
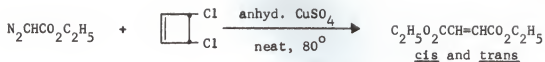
"Hemi-Dewar naphthalene" (30) was reduced to benzobicyclo[2.2.0]hex-2-ene (38) in a 47% yield by the use of diimide generated *in situ* from dipotassium azodicarboxylate<sup>62</sup> by the method of van Tamelen<sup>64</sup>. The n.m.r. spectrum of 38 (page 36) consisted of a multiplet centered at  $\gamma$  6.19 (two



methine hydrogens), a complex multiplet between  $\gamma$  7.33-8.28 (four methylene hydrogens), and an  $A_2B_2$  multiplet centered at  $\gamma$  2.93 (four aromatic hydrogens). The methylene and the methine hydrogens appeared at a lower field than the corresponding methylene ( $\gamma$  7.6-8.7) and methine ( $\gamma$  6.83) hydrogens of bicyclo[2.2.0]hex-2-ene<sup>47</sup>. The three largest absorptions in the ultraviolet spectrum of 38 (page 38) came at 262, 268, and 274  $m\mu$ , which were shifted to a lower wave length from the corresponding absorptions of 30 (cf. page 38). However, the shift was not great enough to cause the absorptions of 38 to correspond exactly to similar absorptions for benzocyclobutene (cf. Table III, Appendix).

Another facet of this study of the chemistry of organic small ring compounds, and, in particular, the reactions of cis-3,4-dichlorocyclobutene (32), was the attempted synthesis of cis-5,6-dichloro-2-carboxybicyclo[2.1.0]pentane. Ethyl diazoacetate<sup>58</sup> was allowed to react with 32 in the presence of various catalysts. The starting material 32 was recovered in





all cases in 22-85% recovery.

Polymer accompanied these seven reactions. None of the desired material was ever indicated by the spectra of the product mixtures. Diethyl fumarate was synthesized independently and its spectra compared with the products of these reactions. Other absorptions in the n.m.r. spectra were identified as diethyl maleate by comparison to that of a known sample<sup>6</sup>. A possible reason for the observation of no desired product from the above reactions was that the carbenoid species generated in these reactions was

not energetic enough to counter the electron withdrawal effect of the chlorines on the double bond in 32 so as to react with the double bond.

## SUMMARY

To prepare benzobicyclo[2.2.0]hexa-2,5-diene ("hemi-Dewar naphthalene") (30), exo,cis-5,6-dichlorobenzobicyclo[2.2.0]hex-2-ene (31) was synthesized by the cycloaddition of benzyne (generated in situ by heating benzene-diazonium-2-carboxylate) with cis-3,4-dichlorocyclobutene (32). "Hemi-Dewar naphthalene" (30) was prepared by the dechlorination of 31 with disodium-phenanthrene complex. The rate constant for the isomerization of 30 to naphthalene at 38° was found to be  $4.85 \pm 0.484 \times 10^{-5} \text{ sec.}^{-1}$ . This corresponded to a half-life of 3.96 hours. Hydrocarbon 30 was reduced to benzobicyclo[2.2.0]hex-2-ene (38) by diimide, generated in situ by the action of acid on dipotassium azodicarboxylate.

Other methods of dechlorination were attempted before the disodium-phenanthrene complex technique was tried. These consisted of sodium and tert-butyl alcohol in tetrahydrofuran, and lithium and tert-butyl alcohol in tetrahydrofuran. Compound 30 was found among the products, 1,2,3,4-tetrahydronaphthalene (39) and 1,4-dihydronaphthalene (40), from the sodium reactions. Hydrocarbon 30 was not found in the lithium reaction; however, hydrocarbons 38, 39, and 40 were present. The disodium-phenanthrene reaction proved to be best, because 30 could be distilled from the residual starting material and the phenanthrene with a minimum of rearrangement to naphthalene.

INFRARED SPECTRA

exo, cis-5,6-Dichlorobenzobicyclo[2.2.0]hex-2-ene

(KBr pellet)

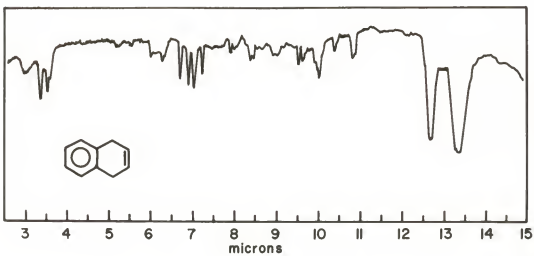
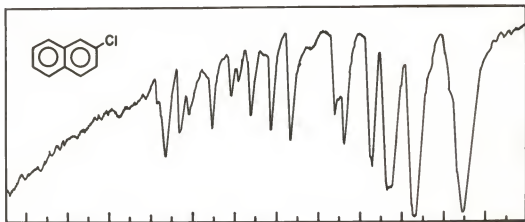
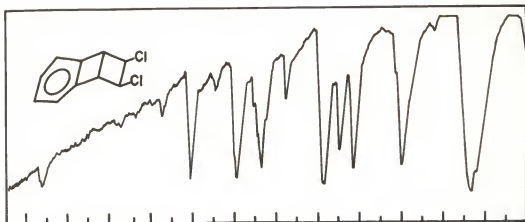
2-Chloronaphthalene

(KBr pellet)

1,4-Dihydronaphthalene (imp. Naphthalene)

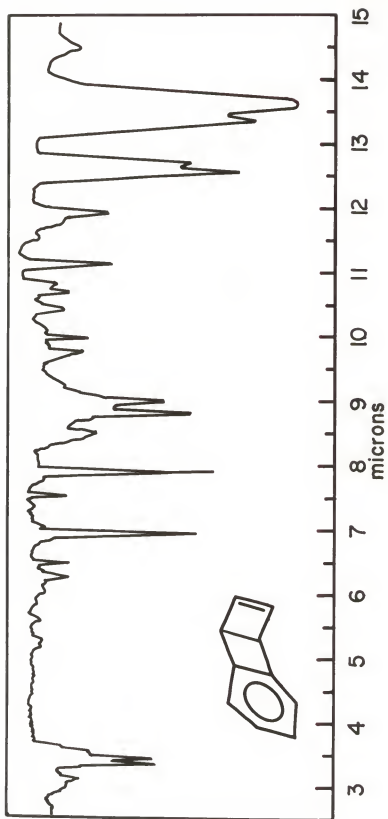
(neat)





INFRARED SPECTRA

Benzobicyclo[2.2.0]hexa-2,5-diene ("Hemi-Dewar  
Naphthalene") (imp. Naphthalene)  
(neat)



NUCLEAR MAGNETIC RESONANCE SPECTRA

exo, cis-5,6-Dichlorobenzobicyclo[2.2.0]hex-2-ene

(enlarged portions of spectrum were run

at sweep width of 50 c.p.s.)

(about 7% in  $\text{CCl}_4$  with TMS as internal standard)

2-Chloronaphthalene

(about 50% in  $\text{CCl}_4$  with TMS as internal standard)

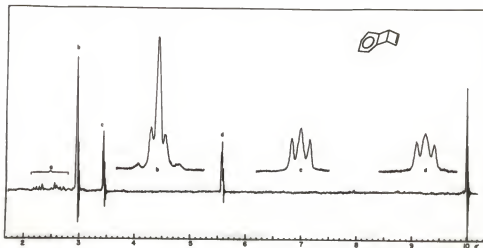
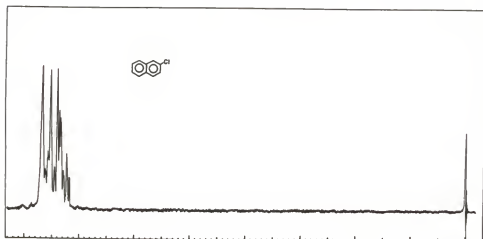
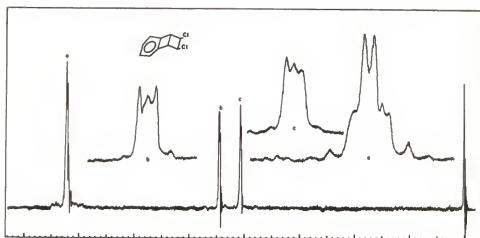
Benzobicyclo[2.2.0]hexa-2,5-diene ("Hemi-Dewar  
Naphthalene")

a) Naphthalene

(enlarged portions of spectrum were run

at sweep width of 50 c.p.s.)

(5% in  $\text{CCl}_4$  with TMS as internal standard)



NUCLEAR MAGNETIC RESONANCE SPECTRA

1,4-Dihydronaphthalene

a) Naphthalene

(sb = spinning side band)

(about 10% in  $\text{CCl}_4$  with TMS as internal standard)

Product Mixture from the Reductive Dechlorination  
of exo, cis-5,6-Dichlorobenzobicyclo[2.2.0]hex-2-  
ene using Sodium, tert-Butyl Alcohol, and Tetra-  
hydrofuran at Room Temperature for 12 hrs.

a) Starting Material

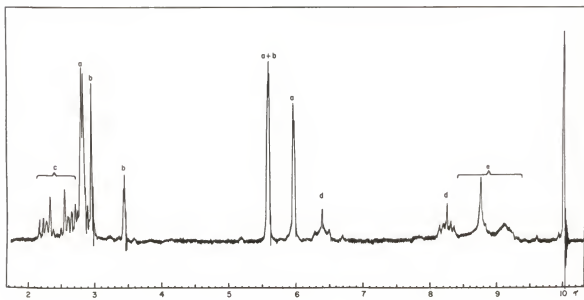
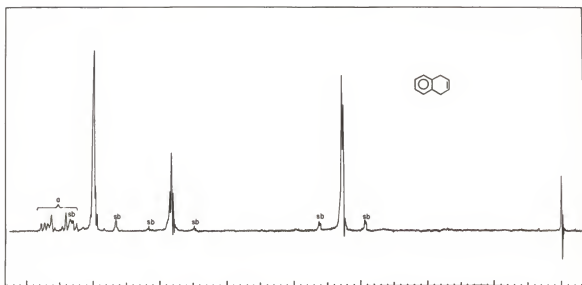
b) Benzobicyclo[2.2.0]hexa-2,5-diene

c) Naphthalene

d) Tetrahydrofuran

e) Polymer

(in  $\text{CCl}_4$  with TMS as internal standard)



NUCLEAR MAGNETIC RESONANCE SPECTRA

Benzobicyclo[2.2.0]hex-2-ene

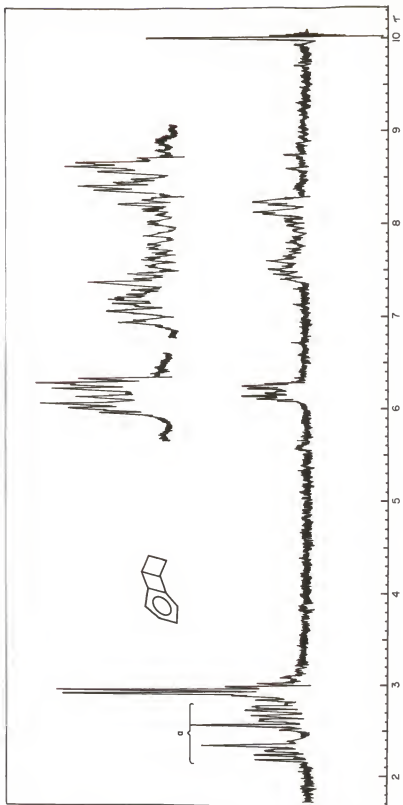
a) Naphthalene

(enlarged portions of spectrum were run

at sweep width of 250 c.p.s.)

(in  $\text{CCl}_4$  with TMS as internal standard)





ULTRAVIOLET SPECTRA

exo, cis-5,6-Dichlorobenzobicyclo[2.2.0]hex-2-ene

( $4.42 \times 10^{-4}$  M in cyclohexane)

Benzobicyclo[2.2.0]hex-2-ene

(imp. Contaminant from Binder

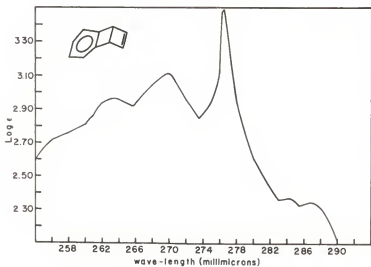
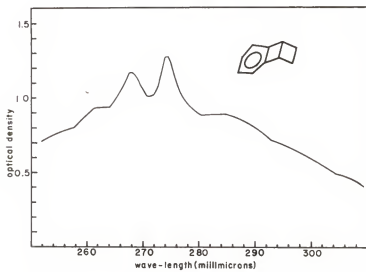
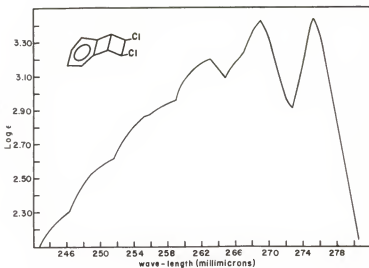
of T. L. C. Plates)

(cyclohexane)

Benzobicyclo[2.2.0]hexa-2,5-diene ("Hemi-Dewar

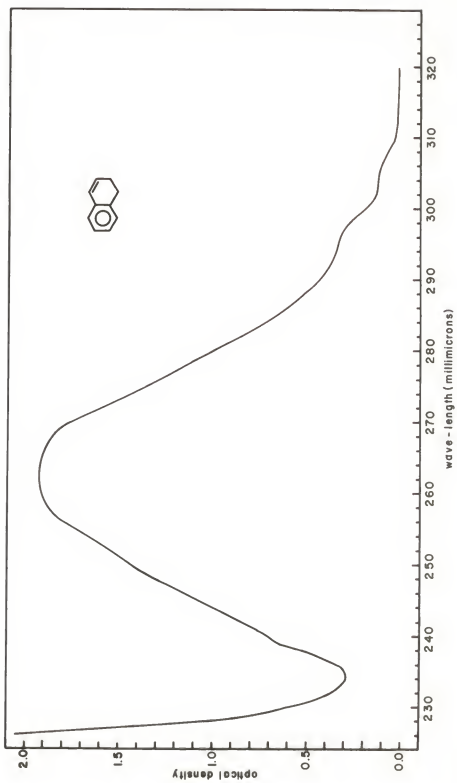
Naphthalene") (imp. Naphthalene)

( $1.235 \times 10^{-3}$  M in cyclohexane)



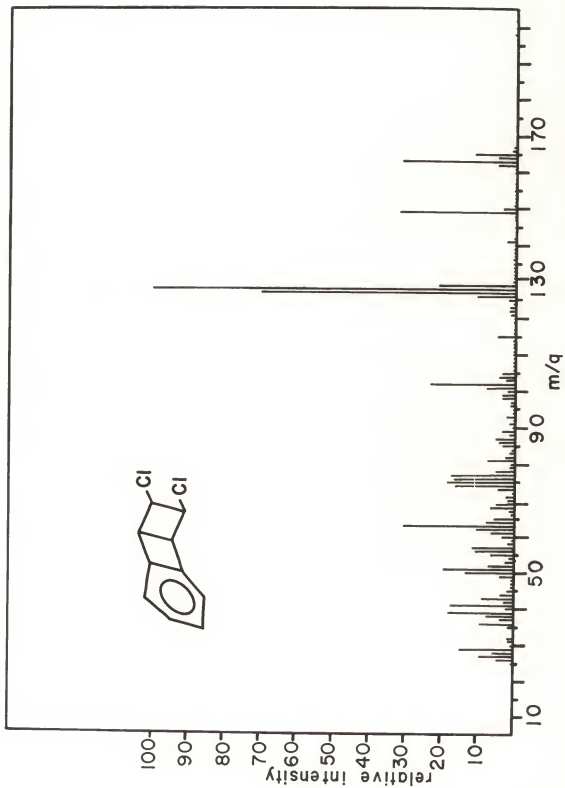
ULTRAVIOLET SPECTRA

1,2-Dihydronaphthalene  
(cyclohexane)



MASS SPECTRUM

Bar Graph of Mass Spectrum  
of exo,cis-5,6-Dichloro-  
benzobicyclo[2.2.0]hex-2-ene  
(70 ev.)



EXPERIMENTAL<sup>68</sup>

Dimethyl Acetylenedicarboxylate. This was prepared according to the method of Huntress, Lesslie, and Bornstein<sup>36</sup> in 65-73% yield, b.p. 87-93°/16.5-18 mm.,  $n_D^{25}$  1.4432 (lit.<sup>36</sup> b.p. 95-98°/19 mm.,  $n_D^{25}$  1.4444). The infrared compared well to that of a known sample<sup>55</sup>.

cis-3,4-Dichlorocyclobutene. The preparation of this compound was carried out according to the procedure of Avram, Dinulescu, Elian, Farcasiu, Marica, Mateescu, and Nenitzescu<sup>4</sup>.

1. Chlorination of Cyclooctatetraene. Since the cyclooctatetraene contained a stabilizer, the reaction was conducted under gentle reflux. One-third of the sulfuryl chloride was added and the solution heated to reflux until the gases that evolved were given off rapidly. The rest of the sulfuryl chloride was added at a rate sufficiently slow to keep the reaction under gentle reflux. In the neutralization, a saturated solution of sodium bicarbonate was used instead of calcium carbonate used by the Nenitzescu<sup>4</sup>. This reaction was performed under nitrogen<sup>69</sup> using one, two, three, and four times literature quantities in various runs.

2. Diels-Alder Reaction. After the dimethyl acetylenedicarboxylate was added, the carbon tetrachloride solution was heated under reflux for 5 hours for runs with amounts of starting materials at four times the literature quantities. Runs of a smaller size were heated under reflux for three hours.

3. Pyrolysis and Purification of Product. After evaporation of the carbon tetrachloride, the residue was distilled, taking three fractions: 1. bath temp. 110-160°, b.p. 35-115°/60 mm.; 2. bath temp. 160-195°, b.p. 115-170°/60 mm.; 3. bath temp. 135-195°, b.p. 91-155°/8-59 mm. The



pyrolysis step was done on a scale of one, two, three, and four times literature quantities in various runs. Fraction 2 from the pyrolysis was distilled on a 15 cm. semi-micro spinning band distillation column. Two fractions were collected: 1. 59-77°/58-60 mm.; 2. 77-78°/60 mm.,  $n_D^{25}$  1.4979 (lit.<sup>4</sup>  $n_D^{25}$  1.4983). From 93.2 g. of cyclooctatetraene an average of 14-31 g. of a mixture of cis-3,4-dichlorocyclobutene and trans,trans-1,4-dichlorobutadiene (15-29% yields) from which 6.2-20 g. (5.7-18.4% yields) of pure cis-3,4-dichlorocyclobutene was obtained in the final distillation.

Benzenediazonium-2-carboxylate. This was prepared according to the procedure of Stiles, Miller, and Buckhardt<sup>61</sup>. Yields of 33-61% of brown to light buff needles were obtained. Caution: this compound is explosive when subjected to friction, especially when scraped on hard surfaces. The infrared spectrum compared well to that reported<sup>61</sup>.

exo,cis-5,6-Dichlorobenzobicyclo[2.2.0]hex-2-ene. To a solution of 13.2 g. (107 mmoles) of cis-3,4-dichlorocyclobutene in 100 ml. of dioxane (distilled from sodium) was added 3.14 g. (21.2 mmoles) of freshly prepared benzene-diazonium-2-carboxylate. The resultant slurry was magnetically stirred at 48-52° under nitrogen<sup>69</sup> until the mixture became homogeneous (3.25-4.5 hours depending on the purity of the benzyne precursor). The solution was dark brown at this point. The dioxane and the cis-3,4-dichlorocyclobutene were distilled off under vacuum, using a 33 cm. Vigreux column and not allowing the pot temperature to rise above 70°, leaving a dark brown viscous residue. This residue was dissolved in about 100 ml. of ether and filtered to a clear solution. The ether was evaporated in a molecular still, and the product was sublimed at room temperature and about 0.05 mm. pressure from the residue as a white crystalline solid mixed with a light yellow oil. The

oil was separated from the solid by rubbing the mixture on a piece of absorbent paper. This afforded 0.48 g. (11.3% yield) of crude product. Further purification was effected by subliming half of the total yield at room temperature and about 0.05 mm. pressure, cleaning the cold finger of the sublimation chamber and subliming the rest. The second half of the sublimate was the purer sample (m.p. about 70-79<sup>o</sup>), which was purified further by repeated sublimations.

The first half was impure and was purified by column chromatography using neutral, Woelm alumina, activity one, with carbon tetrachloride as an eluent and a fairly fast elution rate. The first few fractions (containing solid) contained the purest product (m.p. 60-79<sup>o</sup>) from the chromatography. This was purified further by repeated sublimations. The melting point of the product was 79-79.5<sup>o</sup> (sealed tube). The n.m.r. (page 32), infrared (page 28), mass (page 42), and ultraviolet spectra (page 38) all agreed with the proposed structure for the compound.

Anal. Calcd. for C<sub>10</sub>H<sub>8</sub>Cl<sub>2</sub>: C, 60.35; H, 4.02

Found: C, 60.39; H, 4.14

In runs of this preparation, various ratios of the cis-3,4-dichlorocyclobutene to benzenediazonium-2-carboxylate were used. The following is a table of these ratios and their respective yields. These yields are based on the product sublimed from crude product mixture with the benzenediazonium-2-carboxylate as the limiting reagent as described in the above procedure.

TABLE I

YIELDS ON VARIOUS RUNS OF THE REACTION OF THE BENZENEDIAZONIUM-  
2-CARBOXYLATE WITH cis-3,4-DICHLOROCYCLOBUTENE.

<u>CYCLOBUTENE: DIAZONIUM SALT</u>	<u>YIELD, %</u>
3.7:1	7.3
5.5:1	4.5
8.0:1	10.4
4.0:1	10.0
5.0:1	11.3
12.5:1	8.9
1.5:1	2.4

Reductive Dechlorination Reaction of *exo,cis*-5,6-Dichlorobenzobicyclo-  
[2.2.0]hex-2-ene.

1. Sodium, *tert*-Butyl Alcohol and Tetrahydrofuran at Reflux for 48 hours. A mixture of 65 mg. (0.33 mmoles) of *exo,cis*-5,6-dichlorobenzo-  
bicyclo[2.2.0]hex-2-ene, 244 mg. (3.3 mmoles) of *tert*-butyl alcohol (dis-  
tilled from sodium), and 15 mg. (6.6 mg. atoms) of sodium in 27 ml. of  
tetrahydrofuran (distilled from calcium hydride) under nitrogen<sup>69</sup> was heated  
under reflux with stirring for 48 hrs. About five ml. of methyl alcohol was  
added to the brown slurry to destroy the excess sodium. The reaction mix-  
ture was quenched in 200 ml. of ice and the reaction flask was washed out  
with 70 ml. of water and the water washings added to the ice. The entire  
ice-water mixture was extracted with four 50 ml. portions of ether. The  
ether was washed with three 50 ml. portions of water followed by 30 ml. of  
saturated sodium chloride solution. The ether was dried over magnesium sul-  
fate and evaporated to yield a dark yellow oil. Seventy-seven percent of the  
23 mg. of oil was shown by n.m.r. spectroscopy to be tetralin by comparison  
with that of a known sample<sup>8</sup>. The rest of the oil appeared to be polymer by  
n.m.r. spectroscopy. The yield as calculated from the n.m.r. spectrum was 39%.

2. Sodium, tert-Butyl Alcohol and Tetrahydrofuran at 48-54° for 24 hours. A mixture of 80 mg. (0.4 mmoles) of exo,cis-5,6-dichlorobenzo-bicyclo[2.2.0]hex-2-ene, 0.297 g. (4.0 mmoles) of tert-butyl alcohol (distilled from sodium), 0.183 g. (8.0 mg. atoms) of sodium in 35 ml. of tetrahydrofuran (distilled from calcium hydride) was heated at 48-54° for 24 hours. The work up was the same as in part 1. The n.m.r. spectrum of the crude product mixture showed the presence of tetralin and 1,4-dihydronaphthalene in a ratio of 1.8:1. There was obtained 49 mg. of crude product mixture, of which 32 mg. were the products as determined from integration of the n.m.r. spectrum.

3. Sodium, tert-Butyl Alcohol and Tetrahydrofuran at Room Temperature for 12 hours. The amounts of reactants were the same as used in part 2 and the work up was the same as used in part 1. Forty-nine milligrams of product residue was obtained and 35.5 mg. of it was actual product and starting material as determined from integration of the n.m.r. spectrum. The components were naphthalene, benzobicyclo[2.2.0]hexa-2,5-diene ("hemi-Dewar naphthalene") (30), and starting material in a ratio of 1:1:3 as determined by n.m.r. spectroscopy (page 34). The part of the n.m.r. spectrum assigned to naphthalene was done so by comparison to that of a known sample<sup>57</sup>.

4. Sodium, tert-Butyl Alcohol and Tetrahydrofuran at Room Temperature for 24 hours. The same amounts of materials were used as in part 2 and the same work up was employed as in part 1. The products found were tetralin, 1,4-dihydronaphthalene, and benzobicyclo[2.2.0]hexa-2,5-diene in a 1:2.5:1 ratio as indicated by n.m.r. spectroscopy.

5. Lithium, tert-Butyl Alcohol and Tetrahydrofuran at Room Temperature for 24 hours. Eighty milligrams (0.4 mmoles) of exo,cis-5,6-dichlorobenzo-

bicyclo[2.2.0]hex-2-ene, 0.377 ml. (4.0 mmoles) of tert-butyl alcohol, and 0.555 g. (80 mg. atoms) of lithium were stirred in 35 ml. of tetrahydrofuran for 24 hours under nitrogen<sup>69</sup> at room temperature. The work up was the same as in part 1. After a trap-to-trap distillation (25°/0.1 mm.) on crude product mixture (63 mg.), the n.m.r. of the distillate (about 40 mg.) indicated the presence of tetralin, 1,4-dihydronaphthalene, benzobicyclo[2.2.0]hex-2-ene, and an unknown exhibiting a multiplet at  $\tau$  4.2-4.6, a multiplet overlapping both the  $\tau$  7.1-7.4 multiplet of tetralin and the  $\tau$  7.33-8.28 multiplet of benzobicyclo[2.2.0]hex-2-ene, and a tight multiplet at  $\tau$  2.88. This latter material was not identified, but possibly could be 1,2-dihydronaphthalene. All four materials were present in the distillate from the trap-to-trap distillation in equivalent amounts.

Dechlorination Reactions of *exo,cis*-5,6-Dichlorobenzobicyclo[2.2.0]hex-2-ene.

1. Methyl Lithium in Ether. To 24 ml. of a 1.63 molar ether solution of methyl lithium (39.2 mmoles) at -30° under nitrogen<sup>69</sup> 80-120 mg. (0.4-0.6 mmoles) of *exo,cis*-5,6-dichlorobenzobicyclo[2.2.0]hex-2-ene was added by means of a Gooch rubber tube with a 10 ml. Erlenmeyer flask. The mixture was stirred under nitrogen<sup>69</sup> for 24 hours at -38° to 5°. The mixture was washed with 50 ml. of a 20% ammonium chloride solution in a nitrogen<sup>69</sup> atmosphere at about 0°. The ether was dried over magnesium sulfate in the freezer. After filtration of the magnesium sulfate and evaporation of the ether, there was obtained a brown solid (78 mg.) which the n.m.r. spectrum indicated to be about 85% starting material and about 15% polymer. The uncertainty in the amount of starting material used, was due to the fact that during the addition of the methyl lithium-ether solution, pressure

built up in the system and expelled from the Gooch tube, the Erlenmeyer flask used for addition of the dichloride. Then an uncertain quantity of the starting material in the flask was spread onto the bench top.

2. Disodium-Phenanthrene Complex in Glyme. To a magnetically stirred solution of 2.021 g. (11.79 mmoles) of phenanthrene in 10 ml. of freshly distilled glyme (distilled from calcium hydride and then from lithium aluminum hydride) in a 25 ml. dry two-necked flask, fitted with a rubber septum and a gas inlet, was added 0.700 g. (30.4 mg. atoms) of sodium while cooled in an ice bath. The sodium was cut immediately prior to addition and added quickly so as to present a clean surface to the phenanthrene solution. After a few minutes of stirring under nitrogen<sup>69</sup>, the solution became very dark green. Thirty minutes was allowed for the reaction of the sodium with the phenanthrene.

The green solution was then removed from the flask by means of a syringe through the septum and charged into a stirred solution of 0.782 g. (3.93 mmoles) exo, cis-5,6-dichlorobenzobicyclo[2.2.0]hex-2-ene (75-90% pure) in 10 ml. of anhydrous glyme under nitrogen<sup>69</sup> at room temperature in a 50 ml. two-necked flask fitted as the 25 ml. flask used for the complex formation. The first few drops were decolorized and a white precipitate formed immediately. As the entire disodium-phenanthrene solution was added, the mixture became dark red. After 30 min. of stirring under nitrogen<sup>69</sup>, the mixture became brown and never lightened much more during the 1.25 hr. reaction time.

The reaction mixture was dissolved in 100 ml. of ether which was washed with four 50 ml. portions of water and dried over magnesium sulfate in the freezer. Filtration of the magnesium sulfate and evaporation on a rotary

evaporator to near dryness gave a yellow solid residue. Any residual ether or glyme was evaporated by means of an oil pump and collected in a Dry Ice cooled trap. The product was distilled using a trap-to-trap apparatus at room temperature and 0.1-0.2 mm. pressure and collected in a trap cooled at liquid nitrogen temperature. The length of time of distillation was determined by stopping when a little of the starting material began to sublime on to the inside of the upper portion of the vacuum adaptor used for the distillation. The yield of the product as a clear, colorless liquid was 171 mg. (34%). The unreacted starting material was recovered by subliming about one-fourth to one-third of the residual solid from the distillation and chromatographing the sublimate on basic, activity one alumina with Skelly "B" as the eluent. A fair correlation between percent yield and conditions used is shown in the following table.

TABLE II  
YIELDS ON VARIOUS RUNS OF THE DECHLORINATION OF exo, cis-5,6-DICHLOROBENZOBICYCLO[2.2.0]HEX-2-ENE WITH THE DISODIUM-PHENANTHRENE COMPLEX.

<u>TIME OF SODIUM REACTING WITH PHENANTHRENE, min.</u>	<u>YIELD, %</u>
3	18.8
15	23.0
30	28.0
30	34.0

In one run, not listed in the above table, the solvent for complex formation was 3 ml. of glyme. The amount of phenanthrene used was 0.312 g. (1.75 mmoles), and the amount of sodium used was 0.104 g. (4.5 mmoles). The complex was then added slowly to a 5 ml. glyme solution of 70 mg.

(0.35 mmoles) of exo,cis-5,6-dichlorobenzobicyclo[2.2.0]hex-2-ene. Only about a 4.5% yield of product was obtained from this run. These results seemed to indicate the necessity of a large excess of the complex to effect a good yield.

The n.m.r. (page 32), infrared (page 30), and ultraviolet (page 38) spectra of the product were recorded and are in agreement with the proposed structure.

3. Sodium in Glyme. A mixture of 30 mg. (0.5 mmoles) of exo,cis-5,6-dichlorobenzobicyclo[2.2.0]hex-2-ene and 9 mg. (0.39 mg. atoms) of sodium were stirred under nitrogen<sup>69</sup> in 1 ml. of glyme at room temperature for 25 min. Two milliliters of methyl alcohol were added to destroy the excess sodium, and the reaction mixture was dissolved in 10 ml. of ether which was washed with four 5 ml. portions of water, and dried over magnesium sulfate in the freezer. The ether was filtered and evaporated to a slightly yellow, oily solid (28 mg.). The n.m.r. spectrum of this solid indicated it to contain mainly starting material (77.5% recovery) with some benzobicyclo[2.2.0]hexa-2,5-diene (6.1% yield) by integration.

Dehydrochlorination of exo,cis-5,6-Dichlorobenzobicyclo[2.2.0]hex-2-ene. Thirty milligrams (0.15 mmoles) of exo,cis-5,6-dichlorobenzobicyclo[2.2.0]hex-2-ene was dissolved in 4.5 ml. of tert-butanol (distilled from sodium). To this was added 24 mg. (0.6 mg. atoms) of potassium and the mixture heated under reflux overnight. Water (25 ml.) was then added and the mixture was extracted with three 25 ml. portions of pentane. The pentane extracts were washed with three 100 ml. portions of water, dried over anhydrous magnesium sulfate, and distilled to near dryness. The rest of the solvent was evaporated on a rotary evaporator to give 11 mg. (69% yield) of crude



2-chloronaphthalene, m.p. 35-58° (lit.<sup>21</sup> m.p. 58°).

Reduction of Naphthalene. A mixture of 3.0 g. (23.4 mmoles) of naphthalene, 17.35 g. (0.234 moles) of tert-butyl alcohol (distilled from sodium), 10.764 g. (0.468 g. atoms) of sodium, and 335 ml. of tetrahydrofuran (distilled from calcium hydride) was stirred under nitrogen<sup>69</sup> for 24 hrs. at room temperature. The cloudy solution was decanted away from the sodium (which was destroyed separately) into 1500 ml. of ice. The ice mixture was extracted with four 500 ml. portions of ether. The ether was then washed with three 500 ml. portions of water and 300 ml. of saturated sodium chloride solution. The ether was dried over anhydrous magnesium sulfate, filtered, and evaporated to 2.182 g. of a dark yellow oil of which 2.0 g. were tetralin and 1,4-dihydronaphthalene in a 1:2.6 ratio, as determined by integration of the n.m.r. spectrum of the mixture. After separating the 1,4-dihydronaphthalene (retention time 11.6 min.) from the tetralin (retention time 10.0 min.) by vapor phase chromatography (6 ft.; 10% Apiezon L on Chromosorb W; detector block 230°; injection port 42, 223°; column temperature 120°; helium flow rate 150 ml./min.), it was found that a trace of naphthalene was present in the material with the higher retention time. The n.m.r. (page 34) and infrared (page 28) spectra were consistent with the assigned structure for the 1,4-dihydronaphthalene.

2-Chloronaphthalene. This was prepared from 2-aminonaphthalene using the general procedure of Fieser<sup>26</sup> for the preparation of diazonium salts. The Sandmeyer reaction procedure of Chattaway and Lewis<sup>21</sup> was used for converting the diazonium salt to 2-aminonaphthalene in a 45.5% yield of 2-chloronaphthalene, m.p. 57-58° (lit.<sup>21</sup> m.p. 58°). The infrared spectrum (page 28) compared well with that of a known sample<sup>55</sup>. The n.m.r. spectrum (page 32)

was consistent with the structure. Upon dilution of the carbon tetrachloride solution, the entire n.m.r. spectrum of 2-chloronaphthalene, consisting of a complex multiplet, seemed to shift downfield. All the peaks in this complex multiplet seemed to shift within the multiplet so as to give a different appearance to it.

Reduction of 2-Chloronaphthalene. A mixture of 0.5 g. (3.08 mmoles) of 2-chloronaphthalene, 2.28 g. (30.8 mmoles) of tert-butyl alcohol (distilled from sodium), and 1.41 g. (61.6 mg. atoms) of sodium were stirred under nitrogen<sup>69</sup> in 142 ml. of tetrahydrofuran (distilled from calcium hydride) at room temperature for 24 hrs. Thirty milliliters of methyl alcohol were added to destroy the excess sodium and the mixture was poured onto 600 ml. of ice. Water (140 ml.) was used to wash out the reaction flask and the beaker into the ice mixture. The ice mixture was extracted with four 200 ml. portions of ether, the ether was washed with two 150 ml. portions of water, and 100 ml. of saturated aqueous sodium chloride solution, and dried over anhydrous magnesium sulfate. The magnesium sulfate was filtered and the ether was evaporated to a yellow oil which was trap-to-trap distilled (25°/0.1 mm.). In the product mixture 0.158 g. (31% yield) of 2-chloronaphthalene was found along with 0.112 g. of a mixture of tetralin and 1,4-dihydronaphthalene, as determined by n.m.r. spectroscopy.

Determination of the Kinetics of the Isomerization of Benzobicyclo[2.2.0]hexa-2,5-diene to Naphthalene. A sample of 5-10 mg. of benzobicyclo[2.2.0]hexa-2,5-diene was dissolved in 0.2 ml. of carbon tetrachloride (distilled from phosphorous pentoxide) to give a 0.17-0.39 M solution. Using a capillary tube containing a 10% solution of methylene chloride in carbon tetrachloride as a standard, the amount of benzobicyclo[2.2.0]hexa-2,5-diene

present at various times was determined by integration. The n.m.r. spectral absorption corresponding to the  $\gamma$  3.42 absorption of benzobicyclo[2.2.0]-hexa-2,5-diene and the methylene chloride singlet were integrated and a ratio of the areas obtained. The temperature at which the study was done was  $38 \pm 0.2^\circ$ , the ambient probe temperature. The rate data is in Table II, Appendix, and the calculated first-order rate constant is  $4.85 \pm 0.484 \times 10^{-5}$  sec.<sup>-1</sup>.

Reduction of Azobenzene by Diimide. A mixture of 3.74 g. (44.5 mmoles) of azodicarbonamide and 8.9 ml. of a solution consisting of a 1:1 weight ratio of potassium hydroxide and water was used to prepare a dipotassium azodicarboxylate salt according to the procedure of Thiele<sup>62</sup>. Continuous stirring with a magnetic stirrer seemed to enhance the rate of reaction. This salt was filtered in a sintered glass funnel, washed several times with cold methanol, washed into a clean filter flask with 15 ml. of ice water and reprecipitated with 40 ml. of cold methanol. This yellow slurry was added to 3.483 g. (19.1 mmoles) of azobenzene in 60 ml. of methanol under nitrogen<sup>69</sup>. Acetic acid (5.35 g., 89.0 mmoles) dissolved in 37 ml. of methanol was slowly added to the reaction mixture over a period of three hours at room temperature. This mixture was stirred under nitrogen<sup>69</sup> an additional 2.75 hours. It was then extracted with 500 ml. of ether which was washed with four 200 ml. portions of water and dried over anhydrous magnesium sulfate under nitrogen<sup>69</sup> in the freezer. The magnesium sulfate was filtered and the ether evaporated on a rotary evaporator to give 3.49 g. of a light orange-white heterogeneous solid. The n.m.r. spectrum of this solid indicated it to be composed of 87.5% of hydrazobenzene and 12.5% of azobenzene. This reduction was done several times. Below is a table of the various

ratios of azodicarbonamide to azobenzene used. Recovery of azobenzene and yield of hydrobenzene in each case was determined by n.m.r. spectroscopy.

TABLE III

YIELDS ON VARIOUS RUNS OF THE REDUCTION OF AZOBENZENE BY DIIMIDE.

<u>AZODICARBONAMIDE:AZOBENZENE</u>	<u>YIELD, %</u>	<u>RECOVERY, %</u>
2.3:1	67	4.6
1.2:1	70	24.5
1.6:1	22	67.5
2.3:1	87.5	12.5

Benzobicyclo[2.2.0]hex-2-ene. The dipotassium azodicarboxylate was prepared according to the method of Thiele<sup>62</sup>. To 0.780 g. (9.4 mmoles) of cool azodicarbonamide was added 2.50 ml. of a cold 1:1 weight ratio of potassium hydroxide:water solution. The slurry was stirred in an ice-water bath with a magnetic stirrer until all the liberated ammonia was evolved. This was filtered using cold methyl alcohol (distilled from magnesium dimethoxide) to transfer the thick slurry. The yellow crystals were washed with cold methyl alcohol in a Buchner funnel, and the crystals were dissolved and washed through the funnel with about 5 ml. of ice water. The yellow salt was reprecipitated by adding about 9 ml. of methyl alcohol (distilled from magnesium dimethoxide) to the aqueous filtrate. This slurry was added to a solution containing 1.0 ml. of absolute methyl alcohol and 120 mg. (0.94 mmoles) of benzobicyclo[2.2.0]hexa-2,5-diene (containing 30% of naphthalene) under nitrogen<sup>69</sup> at room temperature in a 25 ml. three-necked flask fitted with a gas inlet adaptor, a constant pressure addition funnel, a ground glass stopper, and a magnetic stirrer. Two drops of a solution of 0.792 ml. (18.0 mmoles) of acetic acid in 8 ml. of absolute methyl alcohol were added and the slurry was stirred under nitrogen<sup>69</sup>. The yellow slurry

became a white slurry within 15 min. after the addition. This was stirred for 7 hours at room temperature under nitrogen<sup>69</sup>. The mixture was washed from the flask with 30 ml. of ether, shaken, separated, and washed with five 15 ml. portions of water. The ether was dried over magnesium sulfate in the freezer, filtered, and evaporated on the rotary evaporator to give 88 mg. of yellow oil containing 61.1 mg. (47% yield) of the desired product and 16.9 mg. of naphthalene as determined by n.m.r. spectroscopy.

An attempt was made to separate the naphthalene from the product by the use of vapor phase chromatography (6 ft.; Apiezon L on Chromosorb W; injection port 42, 232<sup>o</sup>; detector block 235<sup>o</sup>; column temperature 150<sup>o</sup>; helium flow rate, 80 ml./min.). However, the product rearranged to 1,2-dihydronaphthalene as indicated by the ultraviolet spectrum (page 40) which corresponded well to the reported spectrum of this compound<sup>29</sup>.

The product was separated from the naphthalene by thick layer chromatography on pre-coated Silica Gel F<sub>254</sub> preparative thick layer chromatography plates using hexane as the eluent. However, the sample obtained from this separation was contaminated with the binder from the thick layer plates. The ultraviolet spectrum was taken of this sample (page 38), since the binder appeared to be merely saturated hydrocarbons as indicated by n.m.r. spectroscopy. An attempt was made to distill the product from the contaminant but the quantity of material was so small compared to the original 61.1 mg., due to possible losses by evaporation during the thick layer chromatography, that distillation did not prove to be feasible.

Ethyl Diazoacetate. This was prepared according to the procedure of Searle<sup>58</sup>. An 84% yield of light yellow liquid was obtained,  $n_D^{25}$  1.461 (lit.<sup>58</sup>  $n_D^{25}$  1.462). The infrared spectrum compared favorably to that of a

known sample<sup>54</sup>.

Reaction of cis-3,4-Dichlorocyclobutene with Ethyl Diazoacetate.

1. Anhydrous Cupric Sulfate in Benzene. A solution of 2.5 g. (22.0 mmoles) of ethyl diazoacetate in 2.19 ml. of benzene was added slowly over a period of 1.5 hours to a mixture of 0.02 g. (1.25 mmoles) of cupric sulfate and 5.0 g. of cis-3,4-dichlorocyclobutene in 2.19 ml. of benzene heated under reflux. The addition was fairly rapid at first and considerable nitrogen was evolved. After a few drops were added the color of the solution became brown and remained brown throughout the reaction. At the end of the addition, the solution was filtered and the filtrate evaporated. A trap-to-trap distillation (25°/0.75-0.85 mm.) of the viscous brown residue yielded a 22.8% (0.108 g.) recovery of cis-3,4-dichlorocyclobutene and a 10% (0.462 g.) yield of diethyl fumarate and diethyl maleate in a 1.5:1 ratio as determined by n.m.r. spectroscopy. The nitrogen was collected over water in a 97.5% yield.

2. Cuprous Cyanide in Hexane. To a stirred, heated solution of 1.00 g. (2.1 mmoles) of cis-3,4-dichlorocyclobutene and 0.0318 g. (0.355 mmoles) of cupric cyanide in 3 ml. of hexane was added 0.775 g. (6.8 mmoles) of ethyl diazoacetate in 3 ml. of hexane at such a rate to maintain a vigorous flow of nitrogen. After the addition, the brown mixture was heated under reflux for an additional 30 min., filtered, and the solvent evaporated. The brown residue was trap-to-trap distilled (25-100°/0.5 mm.) to give cis-3,4-dichlorocyclobutene (0.534 g., 53.4% recovery), diethyl fumarate (0.067 g., 5.7% yield), and diethyl maleate (0.0566 g., 4.8% yield). This analysis was done by vapor phase chromatography (6 ft.; 20% Carbowax on acid washed Chromosorb W; injection port 55, 323°; detector block, 302°; helium flow

rate, 60 ml./min.). The nitrogen from the reaction was collected over water in a quantitative yield.

3. Cuprous Chloride, Neat Liquids. To a stirred, heated (72-78<sup>o</sup>) slurry of 1.50 g. (12.2 mmoles) of cis-3,4-dichlorocyclobutene and 0.053 g. (0.535 mmoles) of cuprous chloride was slowly added 1.17 g. (10.2 mmoles) of ethyl diazoacetate over a 40 min. period. The mixture was trap-to-trap distilled at 100<sup>o</sup> and 0.55-0.65 mm. The n.m.r. spectrum of the distillate indicated the presence of only starting material (about 0.85 g., 57% recovery), diethyl fumarate, and diethyl maleate (about 0.393 g., 22.8% combined yield). The n.m.r. spectrum of the distillation residue indicated the presence of only the diethyl fumarate and maleate in an unknown ratio. The nitrogen from the reaction was collected over water in an 84% yield.

4. Anhydrous Cupric Sulfate, Neat Liquids. To a stirred slurry of 2.46 g. (20 mmoles) of cis-3,4-dichlorocyclobutene and 0.446 g. (2 mmoles) of cupric sulfate at 80<sup>o</sup> was added, in five min., 0.246 (2.0 mmoles) of ethyl diazoacetate. The reaction mixture was poured into ether and the cupric sulfate removed by filtration. The ether was distilled and the resultant liquid was trap-to-trap distilled (25<sup>o</sup>/0.35 mm.). The distillate was starting material (2.09 g., 81% recovery) and the residue consisted of residual starting material, diethyl fumarate, diethyl maleate, and an unknown material exhibiting several small peaks (a singlet at  $\tau$  5.22, a singlet  $\tau$  7.38 and absorptions under the methyl triplets of the diethyl fumarate and diethyl maleate) in the n.m.r. spectrum. The nitrogen given off in this reaction was collected over water in 95% yield.

5. Copper Powder, Neat Liquids. To a stirred mixture of 2.843 g.

(23.2 mmoles) of cis-3,4-dichlorocyclobutene and 0.147 g. (2.32 mg. atoms) of copper powder at 100-125<sup>o</sup> was added 0.320 g. (2.8 mmoles) of ethyl diazoacetate in 15 min. The starting material (2.454 g.) was distilled (28<sup>o</sup>/0.15-0.2 mm.) from the brown reaction mixture to leave a brown residue. After adding ether to this residue and filtering the copper catalyst from the ether solution, the ether was evaporated and the residue was chromatographed on activity one, basic alumina. None of the desired material could be found for certain among the fractions from the chromatography. However, one of the fractions did give an n.m.r. spectrum that looked suspiciously like the desired compound, but there was so little of this material that it was not worth saving. Another fraction gave an n.m.r. spectrum that resembled the expected one for the mixture of diethyl fumarate and diethyl maleate. The rest of the fractions contained only polymer. The amount of nitrogen liberated was not determined in this run.

6. Copper-Cupric Sulfate, Neat Liquids. To a stirred mixture of 7.989 g. (64.1 mmoles) of cis-3,4-dichlorocyclobutene, 0.204 g. (3.2 mg. atoms) of copper, and 0.501 g. (3.2 mmoles) of cupric sulfate heated to 90-100<sup>o</sup> was added dropwise over 75 min. 0.741 g. (6.5 mmoles) of ethyl diazoacetate. The starting material was removed by trap-to-trap distillation (22<sup>o</sup>/0.03 mm.). The resulting brown residue was treated with ether and the catalyst removed by filtration. The ether was evaporated to leave a brown residue. Trap-to-trap distillation (20<sup>o</sup>/0.02 mm.) of this residue produced more starting material (7.66 g., 97% total recovery), but not the desired product. This latter distillation residue was chromatographed on basic alumina, activity one. Two fractions from this column gave n.m.r. spectra similar to the fraction mentioned in reaction 5. There was more of



this material than in reaction 5 (above) but the n.m.r. spectrum could not be rationalized to fit the structure of the desired material. The nitrogen evolved was collected over water in an 83% yield.

7. Bis[N- $\alpha$ -Phenylethylsalicylaldiminato] copper (II), Neat Liquids. To a stirred mixture of 4.79 g. (35.7 mmoles) of cis-3,4-dichlorocyclobutene and 0.90 g. (1.71 mmoles) of bis[N- $\alpha$ -Phenylethylsalicylaldiminato] copper (II)<sup>51</sup> at 96-98<sup>o</sup> was added dropwise over a period of 30 min. a solution of 4.79 g. (35.7 mmoles) of cis-3,4-dichlorocyclobutene and 0.89 g. (7.8 mmoles) of ethyl diazoacetate. The mixture was stirred for an additional hour at 92-98<sup>o</sup> and allowed to stir at room temperature overnight. The resultant homogeneous solution was trap-to-trap distilled (27<sup>o</sup>/0.025 mm.) to give cis-3,4-dichlorocyclobutene as distillate. From column chromatography on basic, activity one alumina of the distillation residue was obtained fractions containing polymer and decomposed copper complex. These were indicated by n.m.r. spectroscopy. The amount of nitrogen evolved was not determined in this reaction.

Diethyl Fumarate. To a large excess of absolute ethyl alcohol (dried further with soda-lime) was added in one portion 1.408 g. (9.2 mmoles) of fumaryl chloride. After swirling and filtering the white precipitate that formed, the solution was evaporated on a rotary evaporator to a pale yellow oil (0.813 g., 51.2% yield). The infrared spectrum and the n.m.r. spectrum compared well with that of a known sample<sup>52,7</sup>.

8. Bis[N- $\alpha$ -Phenylethylsalicylaldimiato] copper (II). This was prepared according to the procedure of Sacconi and Ciampolini<sup>51</sup>. Very dark brown crystals in 15.6% yield were obtained, m.p. 146-147.6<sup>o</sup> (lit.<sup>51</sup>, m.p. 140-141<sup>o</sup>).

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68. All melting points were taken on a Kofler Hot Stage and are corrected. Boiling points are uncorrected. Infrared spectra were taken on a Perkin Elmer 137 recording spectrophotometer. Nuclear magnetic resonance spectra were determined using an A-60 Varian recording spectrometer. Ultraviolet spectra were determined using a Cary 11 spectrophotometer. Microanalysis was done at Galbraith Laboratories, Inc., Knoxville, Tennessee. The mass spectrum was determined by Professor R. W. Kiser, University of Kentucky, Lexington, Kentucky using a Perkin Elmer Hitachi RMU 6 mass spectrometer. The gas chromatographic analyses were performed using a F and M Model 500, temperature programmed gas chromatograph.
69. The nitrogen was deoxygenated with a hot copper tower and dried with a potassium hydroxide-calcium chloride tower.

## VITA

David G. Frickey was born in Portsmouth, New Hampshire, on October 2, 1942. He moved with his parents in 1945 to Bremerton, Washington, where he was reared and where he lived until his second year of undergraduate school. He attended Our Lady Star of the Sea Grade School, in Bremerton, from which he graduated in 1956. He attended O'Dea High School in Seattle, Washington, graduating in 1960.

In 1960 he entered Seattle University where he majored in Chemistry under the direction of Rev. Ernest P. Bertin S. J., department chairman. He did his undergraduate research on silico-dihydroanthracenes under the direction of Dr. David H. Read. He received his Bachelor of Science degree in 1965.

He then entered graduate school at Kansas State University in the Fall of 1965 to work on an advanced degree in organic chemistry. His research program was directed by Dr. Richard N. McDonald.

He is a member of the American Chemical Society.

## APPENDIX



TABLE I

MASS SPECTRUM<sup>39</sup> OF exo,cis-5,6-DICHLOROBENZOBICYCLO[2.2.0]HEX-2-ENE

70 ev, direct solids inlet, room temp.

<u>m/q</u>	<u>Relative Abundance</u>	<u>m/q</u>	<u>Relative Abundance</u>	<u>m/q</u>	<u>Relative Abundance</u>	<u>m/q</u>	<u>Relative Abundance</u>
25	0.5	55.5	0.1	82 <sup>-</sup>	2.6	115	5.0
26	4.5	56	10.1	82 <sup>+</sup>	0.5	116	0.4
27	9.3	56.5	0.1	82.5	0.3	117	0.1
28	5.5	57	11.7	83 <sup>-</sup>	0.3	118	0.0
29	14.7	57.5	0.1	83 <sup>+</sup>	1.2	119	0.2
30	0.6	58	1.1	83.5	0.1	120	0.1
31	1.1	59	0.3	84 <sup>-</sup>	0.7	121	1.2
32	1.7	60	2.8	84 <sup>+</sup>	0.7	122	1.5
33	0.1	61	6.2	85 <sup>-</sup>	3.1	123	1.7
34	0.1	61.5	0.4	85 <sup>+</sup>	1.2	124	0.2
35	2.3	62	10.8	86	4.4	125	1.7
36	9.5	62.5	0.9	87	5.2	126	10.7
37 <sup>-</sup>	0.8	63	30.6	88	1.6	127	70.5
37 <sup>+</sup>	3.7	63.5	9.3	89	3.5	128	100.0
37.5	0.1	64	7.3	90	0.4	129	11.2
38 <sup>-</sup>	3.0	64.5	0.6	91	1.2	130	0.7
38 <sup>+</sup>	7.3	65	5.5	92	0.5	131	0.1
39	17.9	66	0.9	93	3.0	132	0.3
40 <sup>-</sup>	1.9	66.5	0.1	94	0.4	133	0.1
40 <sup>+</sup>	1.9	67	1.1	95	0.6	134	0.1
41	17.5	67.5	0.1	96 <sup>-</sup>	1.0	135	0.5
42	2.9	68	6.8	96 <sup>+</sup>	0.3	136	0.5
43	8.5	68.5	0.5	97 <sup>-</sup>	1.3	137	0.1
44	3.8	69 <sup>-</sup>	5.3	97 <sup>+</sup>	0.5	138	0.2
45	1.6	69 <sup>+</sup>	2.0	98	3.6	139	0.5
46	0.4	69.5	0.2	99	3.5	140	0.1
46.5	0.1	70	1.7	100	1.9	141	2.5
47	0.4	70.5	0.1	101	8.0	142	0.4
47.5	0.0	71	2.3	102	23.7	143	0.1
48	0.5	72	0.4	103	2.5	144	0.1
49	3.7	73	4.4	104	4.4	145	0.1
49.5	0.9	74	16.6	105	3.8	146	0.0
50	23.4	75	18.9	106	0.4	147	0.1
50.5	0.7	76	16.8	107	0.3	148	0.2
51	29.3	77	17.5	108	0.3	149	32.3
51.5	1.0	78	5.1	109	0.3	150	3.4
52	7.1	79	1.1	110	0.3	151	0.7
52.5	0.0	80	1.1	111	0.5	152	0.2
53	2.6	80.5	0.2	112	0.3	153	0.2
54	1.1	81	7.9	113	0.6	154	0.3
55	6.5	81.5	1.3	114	0.6	155	0.7

TABLE I (cont.)

<u>m/q</u>	Relative <u>Abundance</u>
156	0.2
157	0.1
158	0.0
159	0.0
160	0.3
161	0.3
162	5.0
163	31.5
164	5.0
165	11.5
166	1.2
167	0.1
168	0.0
to	to
197	0.1
198	0.4
199	0.04
200	0.25
201	0.02
202	0.1
203	0.04

TABLE II

REARRANGEMENT DATA FOR BENZOBICYCLO[2.2.0]HEX-2,5-DIENE

<u>Time (min.)</u>	<u>Area, <math>\gamma</math> 3.43 Absorption</u>	<u>Area, Methylene Chloride Singlet</u>	<u>Ratio of Areas (Amt. "Hemi-Dewar")</u>
0	26.1	52.0	0.504
63.5	24.8	57.3	0.433
123.5	22.2	60.1	0.352
308.0	22.1	109.4	0.203
362.0	18.8	116.6	0.161
425.5	26.1	181.0	0.144
547.5	13.8	152.3	0.090

<u>Time (min.)</u>	<u>Log of Ratio</u>	<u><math>k \times 10^5 \text{ sec.}^{-1}</math></u>
0	-0.298	----
63.5	-0.362	3.94
123.5	-0.454	4.84
308.0	-0.693	4.90
362.0	-0.792	5.26
425.5	-0.841	4.90
547.5	-1.044	5.26

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Average  $k = 4.85 \pm 0.484 \times 10^{-5} \text{ sec.}^{-1}$

TABLE III

COMPARISON OF ULTRAVIOLET SPECTRA OF SELECTED COMPOUNDS








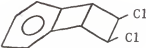
<u>Compound</u>	<u><math>\lambda_{\max.}</math>, m<math>\mu</math></u>	<u>log. <math>\epsilon_{\max.}</math></u>	<u>Solvent</u>
 benzocyclobutene <sup>17</sup>	260.0	3.09	95% ethanol
	265.5	3.28	
	271.5	3.27	
 o-xylene <sup>63</sup>	262.8	2.43	iso-octane
	266.0 (shoulder)	2.36	
	271.0	2.34	
 naphthalene <sup>30</sup>	221.0	4.98	95% ethanol
	266.6	3.70	
	275.8	3.72	
	286.6	3.60	
	311.6	2.40	
 benzene <sup>28</sup>	230.0	1.18	cyclohexane
	235.0	1.48	
	240.0	1.74	
	244.1	2.00	
	249.0	2.28	
	255.0	2.36	
	260.9	2.20	
	268.5	0.98	
 benzobicyclo[2.2.0]- hexa-2,5-diene	257.8 (shoulder)	2.75	cyclohexane
	263.4	2.97	
	270.0	3.12	
	276.5	3.15	
	284.5	2.37	
	287.0	2.32	
 benzobicyclo[2.2.1]- hepta-2,5-diene <sup>67</sup>	216.8	3.36	cyclohexane
	230.0 (shoulder)	3.03	
	262.4 (shoulder)	2.63	
	268.6	2.76	
	275.4	2.73	

TABLE III (cont.)

<u>Compound</u>	<u><math>\lambda_{\text{max.}}</math>, <math>m\mu</math></u>	<u><math>\log. \epsilon_{\text{max.}}</math></u>	<u>Solvent</u>
 benzobicyclo[2.2.0]- hex-2-ene	262	-----*	cyclohexane
	268	-----*	
	274	-----*	
	285	-----*	
 <u>exo, cis</u> -5,6-Dichloro- benzobicyclo[2.2.0]- hex-2-ene	244.0 (shoulder)	2.20	cyclohexane
	249.0 (shoulder)	2.53	
	255.5 (shoulder)	2.86	
	257.5 (shoulder)	2.92	
	261.0 (shoulder)	3.12	
	263.0	3.19	
	267.0 (shoulder)	3.23	
	269.0	3.42	
	275.3	3.44	

\*No extinction coefficients were determined due to an impurity (see Experimental).

THE SYNTHESIS AND CERTAIN CHEMISTRY OF  
BENZOBICYCLO[2.2.0]HEXA-2,5-DIENE

by

DAVID GEORGE FRICKEY

B. S., Seattle University, 1965

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AN ABSTRACT OF A MASTER'S THESIS

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MASTER OF SCIENCE

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KANSAS STATE UNIVERSITY  
Manhattan, Kansas

1969

exo,cis-5,6-Dichlorobenzobicyclo[2.2.0]hex-2-ene (31) was prepared by the cycloaddition of benzyne to cis-3,4-dichlorocyclobutene (32) in 11.3% yield. The n.m.r., infrared, ultraviolet, and mass spectra agreed with the proposed structure. When 31 was treated with potassium tert-butoxide in tert-butyl alcohol, 2-chloronaphthalene was produced in 69% yield. When 31 was treated with sodium and tert-butyl alcohol in tetrahydrofuran under a number of conditions, various ratios of benzobicyclo[2.2.0]hexa-2,5-diene (30), 1,2,3,4-tetrahydronaphthalene (39), 1,4-dihydronaphthalene (40), and naphthalene were found as the products.

However, when 31 was treated with a disodium-phenanthrene complex or with sodium in glyme, only 30 was produced in 34% and 6% yields, respectively. The n.m.r., infrared, and ultraviolet spectra of 30 agreed with the proposed structure.

A kinetic study on the rearrangement of 30 to naphthalene in carbon tetrachloride at 38° determined the half-life of the reaction to be 3.96 hours. This half-life was derived from a rate constant of  $k = 4.85 \pm 0.484 \times 10^{-5} \text{ sec.}^{-1}$  for the rearrangement.