3-phenyl-1,2-dibenzoylcyclopropane, 17393-16-7; *cis*-3-phenyl-1,2-dibenzoylcyclopropane, 17393-17-8; di-*p*-tolyl ketone, 611-97-2.

Acknowledgment.—The authors gratefully acknowledge support for this work received from the National Science Foundation.

Bicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylic Anhydride

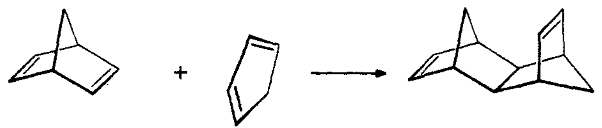
J. R. Edman and H. E. Simmons

Contribution No. 1432 from the Central Research Department, Experimental Station, E. I. du Pont de Nemours and Company, Wilmington, Delaware 19898

Received March 6, 1968

Bicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylic anhydride (norbornadiene-2,3-dicarboxylic anhydride) (**3**) has been synthesized and its Diels–Alder reactivity with butadiene, cyclopentadiene, and anthracene has been studied. The question of *exo* or *endo* attack on the norbornadiene ring is explored using deuterated cyclopentadiene and the pmr spectra of the adducts assigned. The photoisomerization of **3** to quadricyclane-2,3-dicarboxylic anhydride (**13**) and a cycloaddition reaction of **13** are reported.

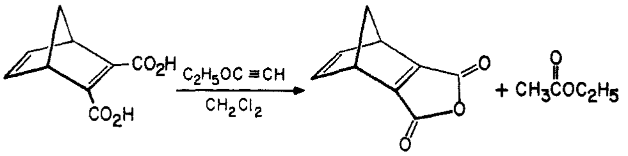
Stille and Frey[1] studied the Diels–Alder addition of cyclopentadiene to bicyclo[2.2.1]hepta-2,5-diene (norbornadiene) and established **1** as the structure of the major monoaddition product. They visualized this product as arising from *exo* addition with the methylene bridge of the cyclopentadiene ring directed away from the methylene bridge of norbornadiene. Such a mode of addition would be analogous to that of cyclopentadiene to norbornene.[2] Examination of models of norbornadiene and cyclopentadiene does not suggest why the proposed *exo* attack should be favored exclusively. The *endo*-5,6 protons which contribute to the *endo* steric hindrance in norbornene are no longer present in norbornadiene, and *endo* additions appear feasible in the latter. Furthermore, under the conditions that Stille and Frey ran their reactions (18 hr, 190°), the observed product **1** might simply represent the thermodynamically, but not kinetically, favored product.



1

We have synthesized bicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylic anhydride **3** and studied its reaction with cyclopentadiene. Anhydride **3** offers advantages over norbornadiene in that the two cyclopentene rings in the adduct can be chemically distinguished, and this allows assignment of the mode of cyclopentadiene addition. Anhydride **3** also reacts with cyclopentadiene at lower temperatures than norbornadiene, and there is better opportunity to distinguish between kinetically and thermodynamically controlled products.

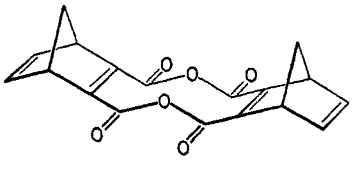
Synthesis and Reaction with Dienes.—Our preferred procedure for the synthesis of **3** is the dehydration of norbornadiene-2,3-dicarboxylic acid[3] in refluxing dichloromethane solution with ethoxyacetylene.[4] All other anhydride syntheses tried, including the carbodiimide method, gave poor yields. The crystalline anhydride **3** was obtained in a 70% yield and melts at 88–89°. It can be stored under nitrogen at −60° for at least 1 year, but slowly decomposes at room temperature.



2 3

The structure of **3** was established by its elemental analysis, molecular weight, infrared absorption spectrum (Figure 1a), pmr spectrum (Figure 1b), and photoisomerization to a quadricyclane anhydride. The characteristic infrared spectrum shows anhydride carbonyl absorptions at 1840 and 1770 cm^{-1}, with the carbonyl and hydroxyl absorptions found in **2** at 2540, 1700, and 1640 cm^{-1} missing.

In some runs a small amount of an ether-insoluble material was obtained which was assigned structure **4**.[5] The evidence for this structure is summarized in the Experimental Section.



4

The maleic anhydride double bond present in **3** readily undergoes Diels–Alder reactions with cyclopentadiene, butadiene, and anthracene.

The reaction with cyclopentadiene is unique in that it can occur in four distinct ways to give three isomeric adducts, **5**, **6**, and **7**. These additions are outlined in Scheme I.

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(1) J. K. Stille and D. A. Frey, *J. Amer. Chem. Soc.*, **81**, 4273 (1959).

(2) S. B. Soloway, *ibid.*, **74**, 1027 (1952).

(3) O. Diels and K. Alder, *Ann. Chem.*, **490**, 236 (1931).

(4) We thank Dr. T. Fukunaga for drawing this procedure to our attention. G. Eglinton, E. R. H. Jones, B. L. Shaw, and M. C. Whiting, *J. Chem. Soc.*, 1860 (1954).

(5) We are indebted to Professor J. R. Johnson for first suggesting this structure. As a referee has pointed out, two isomers are possible. There is no basis on which to favor **4** over the one with the methylene bridges *anti*. A melting point range of 1° does not favor a mixture while the broad pmr lines are consistent with a mixture.

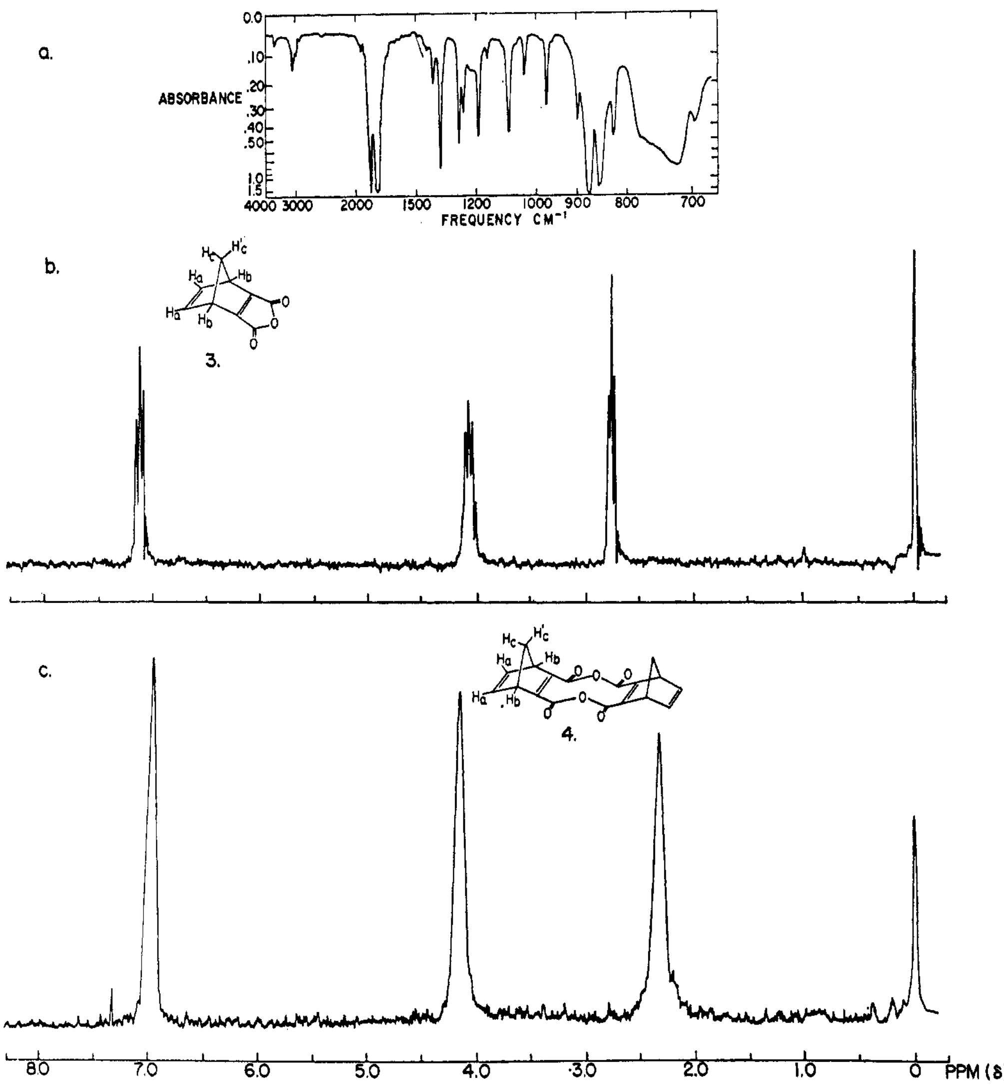
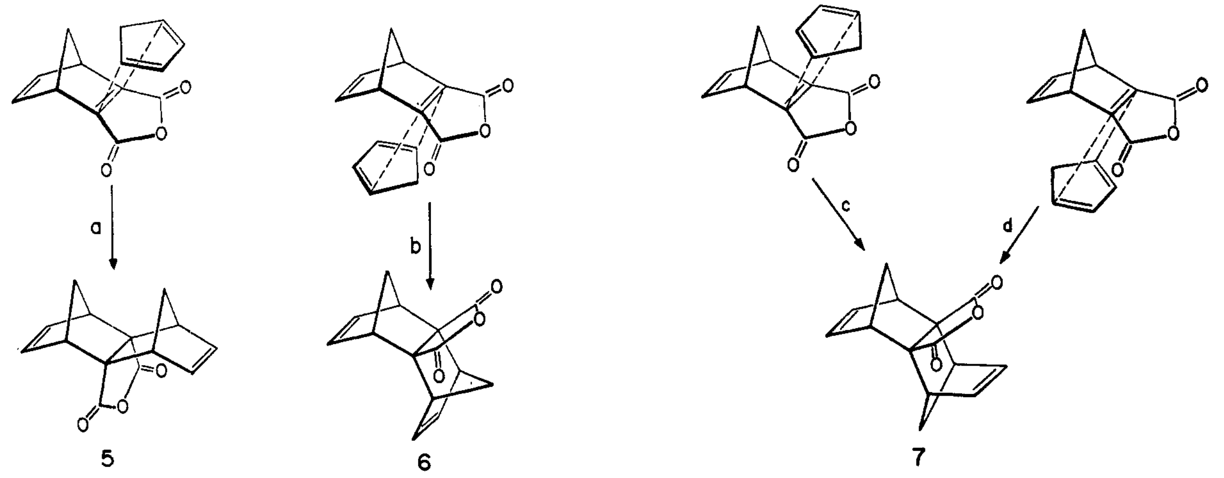


Figure 1.—(a) Infrared spectrum of **3** run in chloroform; (b) 60-Mc spectrum of **3** run in $CDCl_3$–TMS; (c) 60-Mc spectrum of **4** run in $CF_2ClC(OD)_2CF_2Cl$–TMS.

SCHEME I



These paths are labeled (a) *exo* Alder's rule; (b) *endo* anti-Alder's rule; (c) *exo* anti-Alder's rule; and (d) *endo* Alder's rule.

The reaction of maleic anhydride and cyclopentadiene[6] is known to produce under conditions of kinetic control the isomer which is derived from maximum overlap between the two π systems. Thus, it might be expected that paths a and d in Scheme I are operative and that **5** and **7** would be the products. However, path c is similar to the reaction envisioned for cyclopentadiene with norbornadiene,[1] and, furthermore, recent unpublished work[7] suggests that a step

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[6] M. C. Kloetzel, "Organic Reactions," Vol. IV, John Wiley & Sons, Inc., New York, N. Y., 1948, p 11.

[7] Private communication, Dr. Robert D. Thurn, Elastomer Chemicals Department, E. I. du Pont de Nemours and Co.

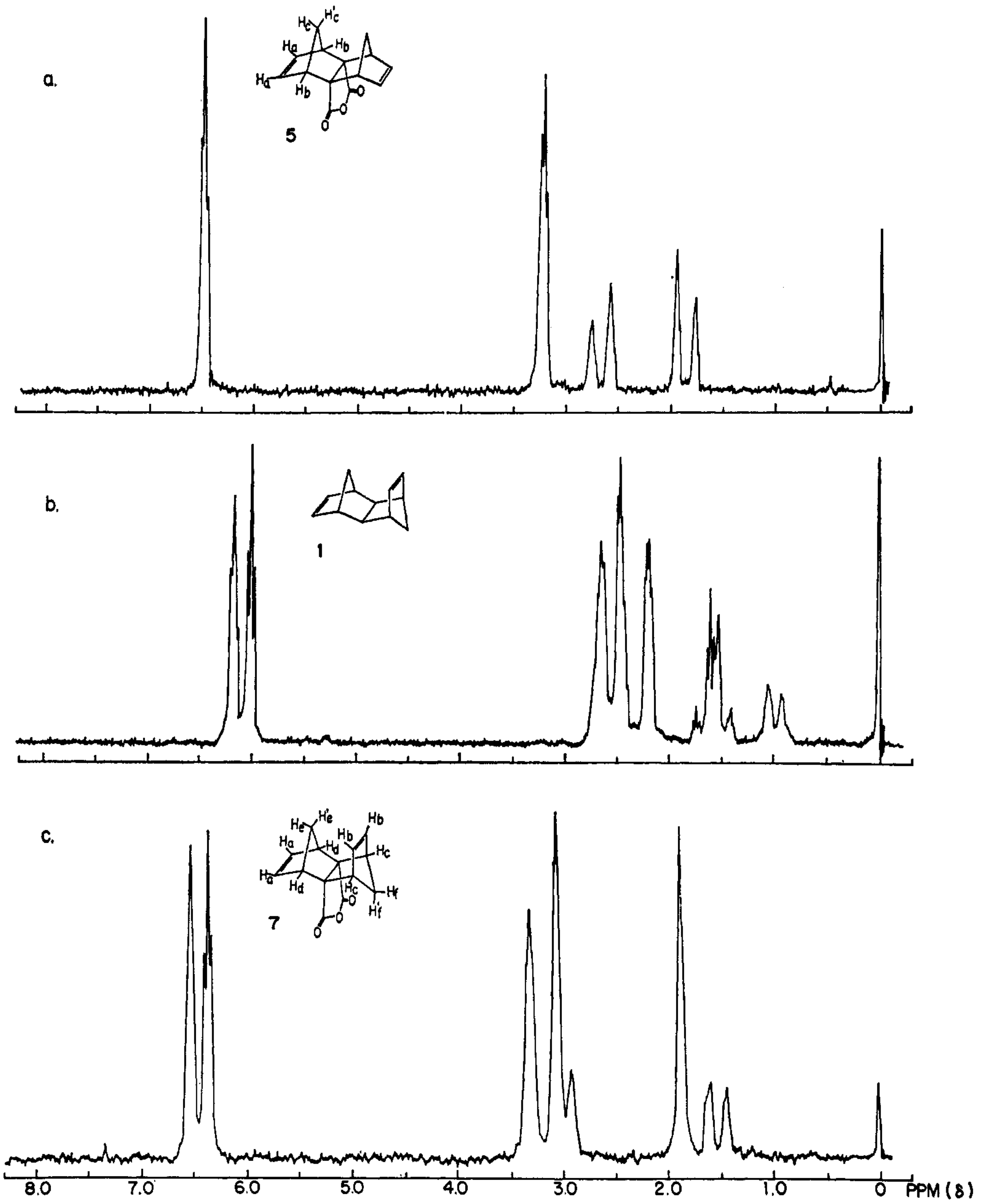

Figure 2.—(a) 60-Mc spectrum of **5** run in $CDCl_3$–TMS; (b) 60-Mc spectrum of **1** run in CCl_4–TMS; (c) 60-Mc spectrum of **7** run in $CDCl_3$–TMS.

analogous to b may also occur in this reaction. There is clearly no basis for excluding these latter paths which would give **7** and **6**, respectively.

The main point of interest then is the influence of the anhydride ring on the addition of cyclopentadiene to norbornadiene. If overlap of the cyclopentadiene π system with the maleic anhydride moiety contributes substantially to lowering the energy of the transition state of this reaction, results might be expected which differ from those observed in the addition of cyclopentadiene to norbornadiene.

In typical runs, the crude anhydride **3** was dissolved in benzene, excess cyclopentadiene was added, and the solution was maintained at 80° for 2 hr. The benzene was then evaporated, and the crude product mixture was chromatographed on neutral alumina. The main product was eluted first (60–70%) and a trace of a second product (1%) followed.[8] Elemental analyses and molecular weights established the 1:1 nature of the adducts, and the pmr spectrum (Figure 2c) clearly revealed the structure of the major isomer **7**. Structures **5** and **6** have only one set of vinyl, allylic, and methylene protons, whereas **7** has two sets of each. The pmr spectrum of **7** is discussed in detail below, but it is noted here that, except for the two protons at the ring junction in **1**, the patterns of the protons in **1** (Figure 2b) and **7** are similar.[9] The minor product, whose symmetrical nature is revealed by its pmr spectrum (Figure 2a), has been assigned structure **5**. Structure **5** is preferred over structure **6** for the minor product

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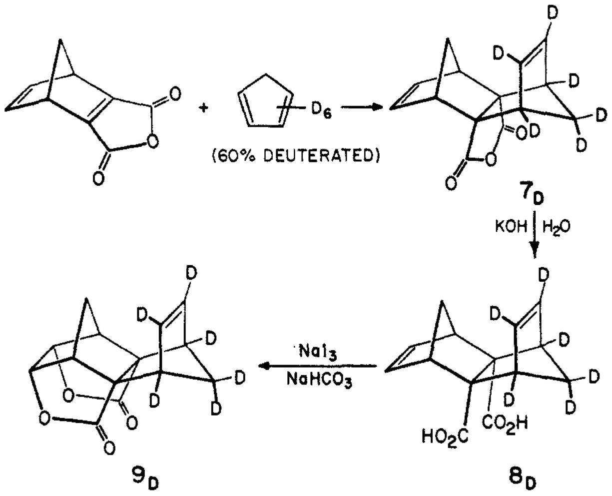
[8] The percentages are based on anhydride **3**. The fate of the other 30–40% is a soluble residue which is removed by chromatography. This residue would not crystallize. It is assumed to consist of di- and higher adducts, dicyclopentadiene, and conceivably compounds derived from **6**.

[9] At first glance the veracity of this statement is questionable. However, the methylene protons display the same anomalous relative chemical shifts in **1** as in **7**. The two protons in one pair have almost the same relative chemical shifts (they differ slightly compared to **7**) while the other pair has one proton at 1 ppm and the other proton at approximately 2.55 ppm (hid under the allylic protons). We thank Dr. Robert D. Thurn, Elastomer Chemicals Department, E. I. du Pont de Nemours and Co., for supplying the pmr spectrum of **1**.

since the material was stable to storage and could be recovered unchanged when reprecipitated with acid from a basic solution. Isomer **6**, presumably analogous to other bird-cage compounds,[10] would be expected to be unstable to these conditions. Furthermore, the minor product was stable to irradiation, whereas **6** is expected to photoisomerize very readily. Finally, a high C–H infrared stretching band is characteristic of this ring system[11] and the absorption at 3090 cm^{-1} has been assigned to the two crowded protons on the methylene bridges.

In an attempt to answer the question of kinetic control, the reaction of **3** with cyclopentadiene was carried out in ether at 0° and benzene at room temperature. The reactions were very slow at both temperatures; **5** and **7** were isolated in the benzene experiment but only starting material was recovered from the ether experiment.[12] It is concluded that the formation of both **5** and **7** is probably kinetically controlled. The question of which pathway, c or d, leads to **7** has been answered in the following way (Scheme II).

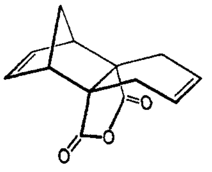
SCHEME II



The sequence shown in Scheme II was first established with unlabeled compounds. In the pmr spectrum of unlabeled **9** (Figure 3a and 3b), H_a and H_b are readily discernible, and the addition reaction can be followed by observing these protons in labeled $\mathbf{9}_D$ (Figure 3c). The establishment of $\mathbf{9}_D$ as the structure of the dilactone when labeled cyclopentadiene was added to **3** indicates that most of the addition took place *via* path c. The degree of labeling does not allow a quantitative measurement, but we estimate that at least 90% of the addition occurred by this path.[13]

It is concluded therefore that the transition state resembles starting materials more than products and that steric factors play a dominant role in determining the course of this reaction. Stille and Frey were correct in assuming c as the major path in the reaction of norbornadiene and cyclopentadiene, since d would be even more unlikely without the anhydride function. The fact that the minor isomer **5** also results from *exo* attack of the cyclopentadiene ring indicates that models belie the apparent vulnerability of the *endo* side of norbornadiene compared to the *exo* side.

The addition of butadiene to **3** was carried out in refluxing benzene using excess butadiene. A mixture of two adducts was obtained whose elemental analysis and molecular weight indicated their 1:1 nature. Based on its pmr spectrum (Figure 4), this mixture consists of **10** and **11**.



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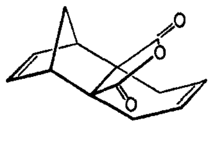
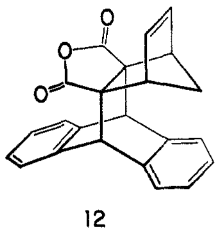


11

Although some variation in the ratio of the two isomers between runs was noted, an average value of 6:1[14] was found for **10**:**11**. This ratio was unchanged after the mixture was refluxed for 24 hr in benzene, suggesting that the products are formed under kinetic control. At high temperatures (above 300°), the mixture of **10** and **11** cracks to give cyclohexa-1,4-diene-1,2-dicarboxylic anhydride and cyclopentadiene. Based on the addition of cyclopentadiene to **3**, the major isomer of the butadiene addition is probably **10** (*exo* addition, Alder's rule). Significantly, however, a substantial amount of *endo* addition is observed in this reaction compared to that of cyclopentadiene.

The reaction of **3** with anthracene in refluxing xylene gave a 95% yield of a 1:1 adduct. From the sharp melting point and simple pmr spectrum of the product, only one isomer was formed. Prolonged irradiation of this adduct gave no reaction, and this negative result together with the probable *exo* mode of addition suggests **12** as the structure of this adduct.



12

endo addition would place the double bond of the norbornene ring above one of the benzene rings,[15] and such a structure might have been expected to be photolabile.

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[10] L. De Vries and S. Winstein, *Chem. Ind.* (London), 405 (1960).

[11] D. Kivelison, S. Winstein, P. Bruck, and R. L. Hansen, *J. Amer. Chem. Soc.*, **83**, 2938 (1961).

[12] Compounds **5** and **7** were identified *via* a pmr spectrum of the crude reaction mixture. The concentration of **5** was very small and a quantitative determination was impossible. Refluxing benzene solutions of both **5** and **7** were stable for at least 2 hr.

[13] A careful comparison of the integrated areas of the absorptions of the olefinic proton, allylic proton, and methylenic proton pairs in $\mathbf{7}_D$ and $\mathbf{8}_D$ plus the integration in Figure 3c gave an average ratio of 2:5 for D/H. This means that 60% of the cyclopentene ring in $\mathbf{9}_D$ and of one cyclopentene ring in $\mathbf{7}_D$ and $\mathbf{8}_D$ is deuterated. Estimates based on the intensity of the C–D stretching band place the deuteration of the original cyclopentadiene ring at 60%. Allowing for 10% error, one can therefore say that at least 90% of the reaction proceeded by *exo* anti-Alder's rule.

[14] Obtained by integration of olefinic region of pmr spectrum. See Figure 4b.

[15] A referee has pointed out such a geometry should also cause an upfield shift of the olefinic protons which is inconsistent with their occurrence at 6.40 ppm in $CDCl_3$–TMS.

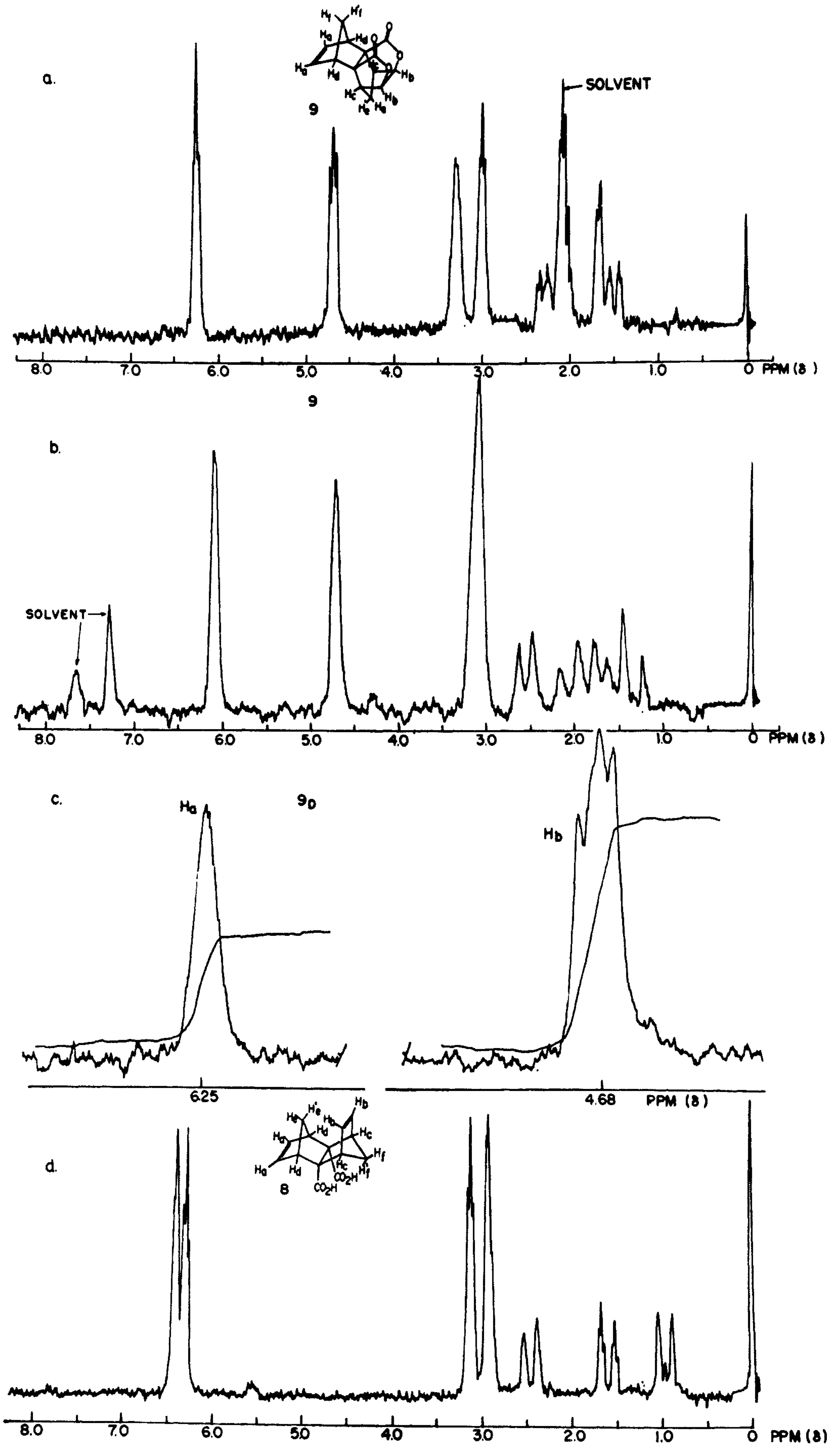


Figure 3.—(a) 60-Mc spectrum of 9 run in $(CD_3)_2CO$–TMS. The chemical shifts in Table I were calculated from this spectrum. (b) 60-Mc spectrum of 9 run in C_5D_5N–TMS with 1 drop of CF_3CO_2H. H_d and H_e are coincidental. J_{H_f,H'_f} and J_{H_e,H'_e} were calculated from this spectrum. (c) 60-Mc spectrum of H_a and H_b in compound 9_D run in $(CD_3)_2CO$–TMS. Sweep width 100 Mc. (d) 60-Mc spectrum of 8 run in $(CD_3)_2CO$–TMS.

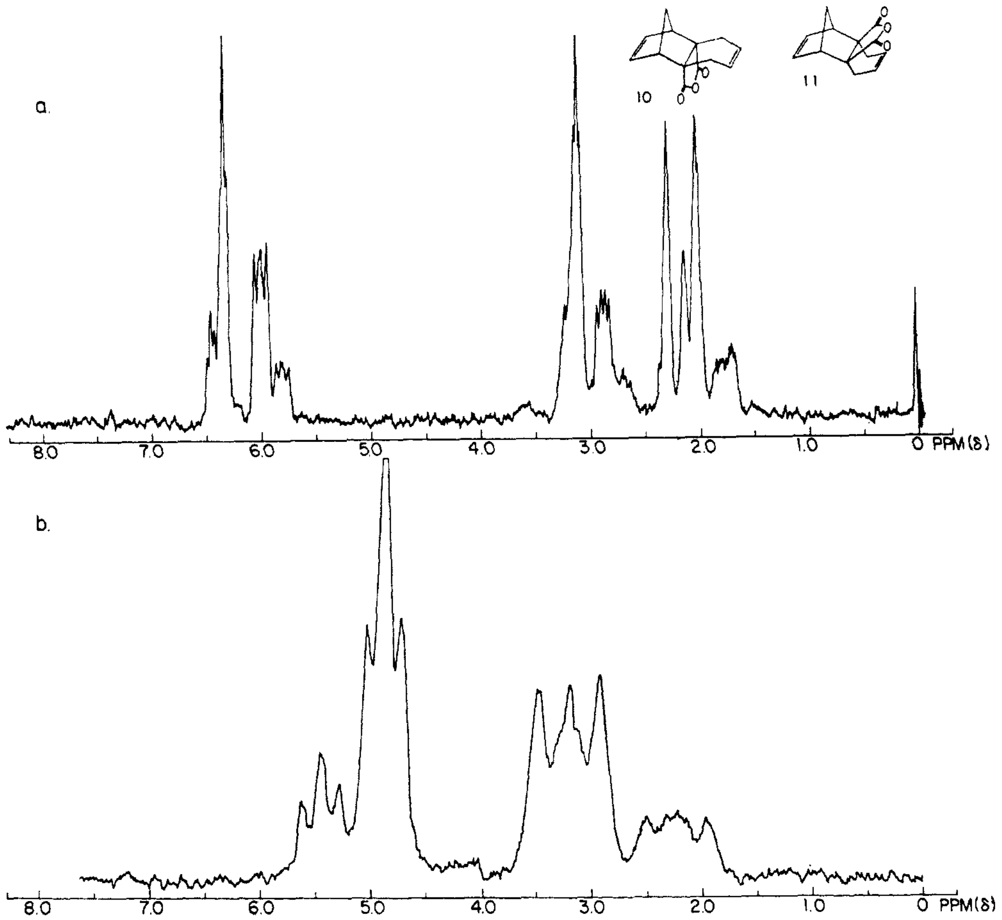
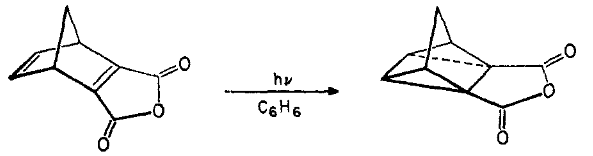


Figure 4.—(a) 60-Mc spectrum of **10** and **11** run in CDCl$_3$–TMS; (b) 60-Mc spectrum of **10** and **11** showing the olefinic protons only.

Irradiation of 3.—Of special interest[16] to us was the photoisomerization of **3** to tetracyclo[3.2.0.$0^{2,7}$.$0^{4,6}$]-heptane-1,5-dicarboxylic anhydride (quadricyclane-2,-3-dicarboxylic anhydride) (**13**). Although this photoisomerization of norbornadienes is well known,[17] irradiation of **3** in ether, acetonitrile, and acetone gave only polymer; however, the desired isomerization occurred cleanly in benzene (95% yield). The superiority of benzene as solvent is not clear, but it is unlikely that benzene is acting as a photosensitizer or serving as a quencher of some polymer-forming excited state.



3 **13**

Anhydride **13** is one of the more strained anhydrides known, and its physical and chemical properties reflect this strain. When the temperature of a crystalline sample of **13** is slowly raised (about 10°/min), no melting point is observed and charring occurs above 300°. If the sample is heated quickly (about 30–40°/min) or placed in a melting-point apparatus at 100° and then heated quickly, a mild explosion with charring and gas evolution occurs at about 110–116°. This behavior is quite characteristic. Under very mild thermal conditions either neat or in solvents, the anhydride polymerizes to polymer of unknown structure.

The thermally produced polymer is not a simple homopolymer, since elemental analysis shows excess oxygen and hydrogen (corresponding roughly to 1 mol of water, even when formed in dry solvents). The infrared spectrum suggests that perhaps anhydride functions are still present (absorptions at 1820 and 1740 cm^{-1}). The pmr spectrum of the polymer dissolved in D$_2$O–NaOD did not show any vinyl hydrogens. It was not possible to produce samples with consistent elemental analyses, and further structural work proved frustrating.

The thermal decomposition of **13** is unique for a quadricyclane in that little if any **13** reverts to **3** on heating. The rapid decomposition of **13** at ~110° was studied briefly. Samples were decomposed in this mildly explosive manner, and the gaseous products were identified by mass spectrometry. The material balance was poor, but it was evident that roughly equimolar amounts of carbon dioxide and carbon monoxide were formed. Small amounts of acetylene, cyclopentadiene, and ethylene were also produced, but no **3** was detected. The results suggest that at about 110° **13** initially loses carbon monoxide and carbon dioxide to give a high-energy intermediate that decomposes to a carbonaceous residue and traces of volatile hydrocarbons. The heat from this decomposition is probably sufficient to propagate the reaction. At lower temperatures, the rate of this unimolecular decomposition might be quite slow and a bimolecular reaction leading to polymer takes precedence.

(16) J. R. Edman, *J. Org. Chem.*, **32**, 2920 (1967).

(17) J. R. Edman, *J. Amer. Chem. Soc.*, **88**, 3454 (1966).[1]

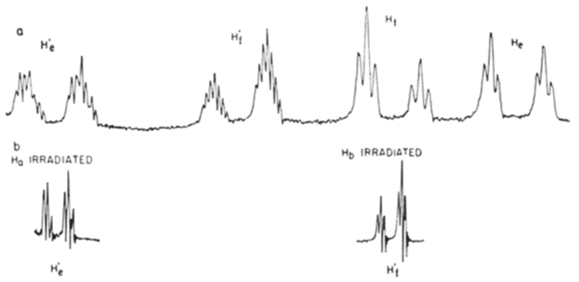
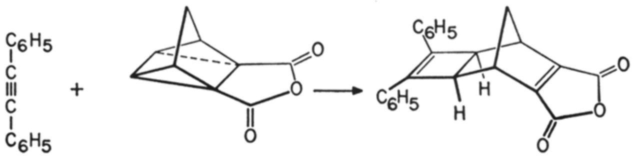


Figure 5.—(a) 100-Mc spectrum of **7** in C_6D_6 showing the methylene region only; (b) 100-Mc spectrum of **7** in C_6D_6 showing the decoupling of H′$_e$ (H_a irradiated) and H′$_f$ (H_b irradiated).

When samples of **13** were heated in deuterioacetonitrile at 60°, analysis showed that the polymer formed contained *ca.* 10% deuterium. This suggests a radical mechansim for the decomposition.

Finally, we prepared a photopolymer of bicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylic acid in benzene and compared its pmr spectrum in D_2O–NaOD with that of a sample of the quadricyclane anhydride polymer. The spectra were distinctly different, although neither polymer showed vinyl proton absorption. Unlike the anhydride **3**, the dicarboxylic acid **2** isomerizes cleanly when irradiated in ether[18] but polymerizes when irradiated in benzene.

Smith found that quadricyclane undergoes an unusual kind of cycloaddition reaction with electron-poor olefins and acetylenes.[19] An attempt to extend this reaction to dicyanoquadricyclane[16] failed, and in the present work similar additions of quadricyclane dicarboxylic acid and its anhydride **13** were unsuccessful. These substituted quadricyclanes did not react readily with electron-rich double or triple bonds, although the reaction of diphenylacetylene with **13** gave adduct **14** in low yield, accompanied by much decomposition of the anhydride. Our observations support the view that this cycloaddition reaction must depend on the strain inherent in the quadricyclane molecule as well as its polarizability, since quadricyclane dicarboxylic acid did not react with diphenylacetylene.



13 14

Pmr Spectra.—The pmr spectra of the compounds described in this paper present some points of interest and are discussed in this section. Proton chemical shifts in several of the derivatives have been assigned by using deuterated cyclopentadiene in our syntheses. The data are summarized in Table I.

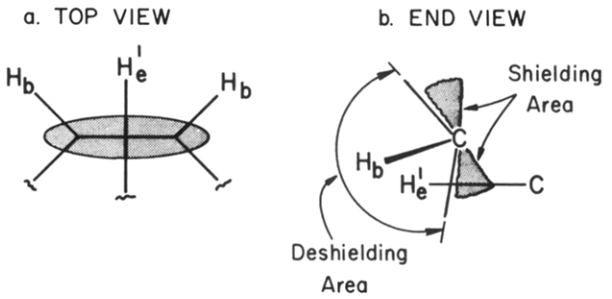


Figure 6.

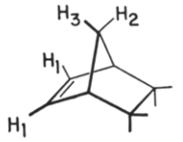
TABLE I

CHEMICAL SHIFT VALUES[a]

Compd	Protons and chemical shifts (*J*, cps)
3	H_a, 7.14; H_b, 4.08; H_c + H′$_c$, 2.77
4[b]	H_a, 6.99; H_b, 4.17; H_c + H′$_c$, 2.33
5	H_a, 6.48; H_b, 3.23; H′$_c$, 2.67; H_c, 1.87 ($J_{H'_c,H_c} = 11$)
7	H_a, 6.49; H_b, 6.32; H_c, 3.32; H_d, 3.06; H′$_e$, 3.00; H_e, 1.54; H′$_f$ + H_f, 1.86; ($J_{H'_e,H_e} = 10$; $J_{H_f,H_f'} = 10.2$)
8[c]	H_a, 6.43; H_b, 6.30; H_c, 3.13; H_d, 2.95; H′$_e$, 3.05; H_e, 0.96; H′$_f$, 2.46; H_f, 1.60 ($J_{H'_e,H_e} = 9$) ($J_{H'_f,H_f} = 15$)
9[c]	H_a, 6.25; H_b, 4.68; H_c, 3.29; H_d, 3.00; H′$_e$, 2.24; H_e, 1.58; H′$_f$, 2.15; H_f, 1.65[d] ($J_{H'_e,H_e} = 12.4$) ($J_{H'_f,H_f} = 10$)

[a] Run in $CDCl_3$ with TMS as internal standard unless otherwise noted. Chemical shifts are reported in ppm and are downfield from TMS at 0. [b] Run in $ClCF_2C(OD)_2CF_2Cl$. [c] Run in $(CD_3)_2CO$. [d] Assignment of H′$_f$ + H_f is tentative.

The chemical shifts of the methylene protons in **5**, **7**, and **8** are particularly of interest. The components of the pairs of methylene protons in these compounds were readily determined by decoupling experiments, and deuterium labeling further distinguished the pairs. Assignments were then made in the following way. It is well known that H_1 and H_2 in bicyclo[2.2.1]heptenes exhibit long-range coupling,[20] which is readily demonstrated by an expanded 100-Mc spectrum of the methylene region of **7** (Figure 5a). Irradiation caused the olefinic protons H_a and H_b to decouple from the *anti*-methylene protons H′$_e$ and H′$_f$ to give a simple triplet (Figure 5b). Once these protons have been assigned, it is evident that a large difference in chemical shift exists between H_e and H′$_e$ in **7** and **8**. This difference is apparently due to the unexpected deshielding of H′$_e$, since H_e appears at a typical chemical shift for this type of proton.[21]



This deshielding of H′$_e$ in **7** may arise from the double bond on which the two H_b protons are located, although conventional molecular models of this compound place H′$_e$ more in the shielding rather than the deshielding region of the double bond. Nevertheless, the actual situation may resemble that shown in Figure 6,[22] so that H′$_e$ is actually in the deshielding cone of the

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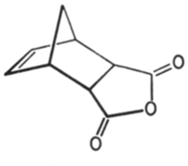
(18) S. J. Cristol and R. L. Snell, *J. Amer. Chem. Soc.*, **80**, 1950 (1958).

(19) C. D. Smith, *ibid.*, **88**, 4273 (1966).

(20) E. I. Snyder and B. Franzus, *ibid.*, **86**, 1166 (1964).

(21) As models, the chemical shifts of the methylene protons in *exo* and *endo*



were determined in $CDCl_3$–TMS: *exo*, 1.46 and 1.69 ppm; *endo*, 1.62 and 1.75 ppm.

(22) This explanation was first proposed by Dr. J. Mrowca.

double bond. A further deshielding of H$'_e$ could be due to repulsion between the electrons in the C–H bond and those in the π bond, which could reduce the electron density around this proton. Such an effect has been postulated in proton–proton interactions[23] and is demonstrated in the spectrum of **5**, where the H$'_c$ protons are shifted downfield, presumably because of this effect. Support for the H$'_e$ proton being in the deshielding cone of the double bond is found in the spectrum of the dilactone **9**. According to models, the net effect of forming the dilactone from the dicarboxylic acid is to move H$'_e$ away from the deshielding area and into the shielding area of the double bond (Figure 6b). This results in an upfield shift of 0.81 ppm for H$'_e$ in the dilactone.

Experimental Section

All melting points unless otherwise noted are uncorrected and were obtained on a Mel-Temp apparatus.

Bicyclo[2.2.1]heptadiene-2,3-dicarboxylic Anhydride (**3**) **and 3,12-Dioxapentacyclo[12.4.0.0^{5,10}.1^{6,9}.1^{15,18}]eicosa-5(10),7,14(1),-16-tetraene-2,4,11,13-tetrone** (**4**).—To 1.7 g of bicyclo[2.2.1]-heptadiene-2,7-dicarboxylic acid[3] suspended in 40 ml of dichloromethane with stirring at 30–35° was added 1 ml of ethoxyacetylene.[24] The dicarboxylic acid dissolved and the solution was stirred under nitrogen for 18 hr. The volume of the solution was then reduced by one-half with a nitrogen stream, and the solution was filtered to remove any insoluble material. The filtrate was treated with charcoal, filtered, and evaporated to give 1.1 g of **3** melting at 80–83°. One recrystallization from ether gave a pure sample, mp 88–89°.

Anal. Calcd for $C_9H_6O_3$: C, 66.72; H, 3.73; mol wt, 162. Found: C, 67.13; H, 3.68; mol wt, 162 (mass spectroscopy).

The success of this synthesis depends critically on the purity of the dicarboxylic acid and ethoxyacetylene used.

The insoluble precipitate removed from the reaction mixture could either be starting material or a new anhydride. The anhydride was sublimed to give an analytical sample, mp 195–196°.

Anal. Calcd for $C_{18}H_{12}O_6$: C, 66.72; H, 3.73; mol wt, 324. Found: C, 66.80; H, 3.64; mol wt, 318 (boiling point in benzene).

The pmr spectrum contained three broad singlets (Table I), and the ir spectrum in the carbonyl region resembled a linear anhydride rather than a maleic anhydride. The uv spectrum of **4** was identical with that of **3** except for a twofold increase in ϵ. The anhydride was assigned structure **4** on the basis of these data.

1,4,4,4A,5,8,8A-Hexahydro-1,4,5,8-*exo,endo*-dimethanonaphthalene-4A,8A-dicarboxylic Anhydride (**7**) **and 1,4,4A,5,8,8A-Hexahydro-1,4-5,8-*exo,exo*-dimethanonaphthalene-4A,8A-dicarboxylic Anhydride** (**5**).—Norbornadiene-2,3-dicarboxylic anhydride (2 g) and cyclopentadiene (0.95 ml) in 20 ml of benzene were heated at 80° for 2 hr. The benzene was then removed *in vacuo*. The tacky residue was dissolved in a minimum amount of ether and placed on a 4.5 × 76 cm column of neutral alumina packed with petroleum ether (bp 60–90°). The product was eluted with 1:20 ether–petroleum ether. The major product (**7**) eluted first and the minor product (**5**) second. In ideal cases a clean break occurred between **7** and **5**. In a run using 10 g of anhydride **3**, the yield of product **5** was about 100 mg.

The major product (**7**) was recrystallized twice from ether, mp 242–244°.

Anal. Calcd for $C_{14}H_{12}O_3$: C, 73.75; H, 5.31; mol wt, 228. Found: C, 73.84; H, 5.51; mol wt, 228 (mass spectroscopy).

The minor product (**5**) was recrystallized from ether, mp 216–219°.

Anal. Calcd for $C_{14}H_{12}O_3$: C, 73.75; H, 5.31; mol wt, 228. Found: C, 73.97; H, 5.01; mol wt, 228 (mass spectroscopy).

1,4,4A,5,8,8A-Hexahydro-1,4-methanonaphthalene-4A,8A-dicarboxylic Anhydride (**10** and **11**).—Butadiene was bubbled for 15 min through 200 ml of benzene. Norbornadiene-2,3-dicarboxylic anhydride (10 g) was then added to the benzene and the solution refluxed for 2 hr. The solvent was evaporated *in vacuo* and the residue taken up in ether. The ether solution was treated with charcoal, filtered, and cooled. The precipitate which formed was collected and air dried to yield 9.14 g, mp 100–110°. Two recrystallizations from ether raised the melting point to 124–127° (with softening). The pmr spectrum (Figure 4) represents a mixture of *exo* and *endo* isomers. An additional 4.8 g of product was obtained by evaporating the ether.

Anal. Calcd for $C_{13}H_{12}O_3$: C, 72.28; H, 5.60. Found: C, 72.39; H, 5.67.

When this mixture was heated *in vacuo* at *ca.* 300°, cyclopentadiene distilled and cyclohexa-1,4-diene-1,2-dicarboxylic anhydride sublimed out of the reaction zone. The cyclohexadiene anhydride[25] was identified by its melting point and ir and pmr spectra. The cyclopentadiene was identified by its boiling point, refractive index, and glpc retention time.

1,4,4A,9,9A,10-Hexahydro-9,10-benzeno-1,4-methanoanthracene-4A,9A-dicarboxylic Anhydride (**12**).—A solution of anthracene (1 g) and bicyclo[2.2.1]heptadiene-2,3-dicarboxylic anhydride (1 g) in 25 ml of xylene was refluxed for 24 hr. The solution was then cooled and filtered to give 1.9 g of crude product melting at 289–291°. One recrystallization from acetone with drying *in vacuo* gave an analytical sample, mp 286.5–288° cor.

Anal. Calcd for $C_{23}H_{16}O_3$: C, 80.77; H, 5.31. Found: C, 81.06; H, 4.90.

1,4,4A,5,8,8A-Hexahydro-1,4,5,8-*endo,exo*-dimethanonaphthalene-4A,8A-dicarboxylic Acid (**8**).—To 740 mg of potassium hydroxide (85% pellets) dissolved in 20 ml of water was added 500 mg of 1,4,4A,5,8,8A-hexahydro-1,4,5,8-*exo,endo*-dimethanonaphthalene-4A,8A-dicarboxylic anhydride (**7**). The resulting suspension was stirred vigorously at 60° for 40 min. The solution was then filtered to give 50 mg of unreacted starting material. The filtrate was acidified to pH 1 with dilute hydrochloric acid. A fine white precipitate was collected, washed thoroughly with water, and dried *in vacuo* over P_2O_5 for 24 hr to yield 415 mg. The material did not melt but charred over a wide range starting at ~200°.

Anal. Calcd for $C_{14}H_{14}O_4$: C, 68.35; H, 5.74. Found: C, 68.44; H, 5.67.

4,10-Dioxahexacyclo[11.2.1.0^{2,12}.0^{2,6}.0^{5,9}.0^{8,12}]hexadec-14-ene-3,11-dione (**9**).—To a solution of 500 mg (2.25 mmol) of 1,4,4A,-5,8,8A-hexahydro-1,4,5,8-dimethanonaphthalene-4A,8A-dicarboxylic acid (**8**) and 278 mg (4.5 mmol) of sodium bicarbonate was added 20 ml of water in which 624 mg (2.46 mmol) of I_2 had been dissolved by the addition of sodium iodide (about 1.6 g). The addition was carried out at 10° with stirring over 2 hr. The reaction mixture was stirred at room temperature for 24 hr and then refluxed for 18 hr. Filtration gave 240 mg of 4,10-dioxahexacyclo[11.2.1.0^{2,12}.0^{2,6}.0^{5,9}.0^{8,12}]hexadec-4-ene-3,11-dione as white leaflets. An analytical sample was prepared by sublimation, mp 300–315° dec.

Anal. Calcd for $C_{14}H_{12}O_4$: C, 68.91; H, 4.96; mol wt, 244. Found: C, 68.98; H, 5.11; mol wt (mass spectroscopy) 244.

Quadricyclane-2,3-dicarboxylic Anhydride (**13**).—Bicyclo-[2.2.1]heptadiene-2,3-dicarboxylic anhydride (**3**) (5 g) was dissolved in 300 ml of reagent-grade benzene. The solution was stirred under nitrogen and irradiated for 16 hr at 20° with a 3500-Å light source.[26] The benzene was then reduced to 60 ml by evaporation at 20° *in vacuo*. The benzene was diluted with 300 ml of petroleum ether, and the precipitate which formed was collected under nitrogen. The yield was 4.6 g of **13** which decomposed when heated quickly to 115°. The anhydride formed large white leaflets when recrystallized from ether, and on one occasion a sample of these leaflets decomposed with heat from the hand. A satisfactory carbon analysis could not be obtained.

Anal. Calcd for $C_9H_6O_3$: mol wt, 166. Found: mol wt, 166 (mass spectroscopy).

7,8-Diphenyltricyclo[4.2.1^{2,5}.0]nona-3,7-diene-3,4-dicarboxylic Anhydride (**14**).—Diphenylacetylene (500 mg) was melted at 75° and quadricyclane anhydride (300 mg) was added with stirring. The resulting mixture was kept for 2 hr at 75° and then cooled. The solid mass was ground and treated with 30 ml of boiling ether. Filtration gave a quantity of insoluble polymer which was discarded. The ether filtrate was cooled in Dry Ice

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[23] S. Winstein, P. Carter, F. A. L. Anet, and A. J. R. Bourn, *J. Amer. Chem. Soc.*, **87**, 5247 (1965).

[24] Humphrey Chemical Co., North Haven, Conn.

[25] K. Alder and K. H. Backendorf, *Ber.*, **71B**, 2199 (1938).

[26] Cylinderical reactor from Southern New England Ultraviolet equipped with 16 F8T5-BLB lamps.

and filtered to give 50 mg of light yellow product. A second recrystallization from ether gave a sample melting at 208–209°.

Anal. Calcd for $C_{23}H_{16}O_3$: C, 81.24; H, 4.74. Found: C, 81.03; H, 4.93.

The uv spectrum of compound **14** in ether has maxima at 2070 Å (ε 4.3 × 10^4), 2250 (5 × 10^4), and 3085 (3 × 10^4). The 3085-Å band is very broad and tails into the visible. *cis*-Stilbene, except for additional fine structure, displays much the same spectrum: 2030 Å (ε 2.4 × 10^4), 2280 (1.6 × 10^4), and a broad absorption with maxima at 2941 (2.79 × 10^4) and 3080 (2.64 × 10^4).[27]

The *exo* configuration of the fused cyclobutene ring was assigned by comparing the pmr spectrum of **14** with that of 7,8-diphenyltricyclo[4.2.1^{2,5}.0]nona-3,7-diene.[28]

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[27] H. H. Jaffé and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," John Wiley & Sons, Inc., New York, N. Y., 1962, pp 276, 277.

[28] G. N. Schrauzer and P. Glockner, *Chem. Ber.*, **97**, 2451 (1964).

Deuterated Cyclopentadiene.—Sodium hydride (3 g) dispersed in mineral oil was carefully added with stirring to 20 ml of dry cyclopentadiene in 100 ml of ether. When hydrogen evolution ceased, 40 ml of deuterium oxide was added and the mixture was stirred vigorously for 2 hr. The ether–cyclopentadiene layer was then distilled under vacuum, dried over magnesium sulfate, and recycled. After three such treatments the ether layer contained about 2–3 ml of cyclopentadiene (based on glpc-peak areas).

Isolation of a small sample by preparative glpc and quantitative comparison of the C–D stretching *vs.* the C–H stretching in its ir spectrum led to the assignment of approximately 60% deuteration.

Registry No.—**1,** 15914-94-0; **3,** 17397-31-8; **4,** 17397-35-2; **5,** 17414-28-7; **7,** 17397-36-3; **8,** 17397-32-9; **9,** 17411-01-7; **10,** 17414-29-8; **11,** 17397-33-0; **12,** 17458-12-7; **13,** 17447-99-3; **14,** 17397-34-1.

Cyclopentadienylidene. Stereochemistry of the Addition Reaction

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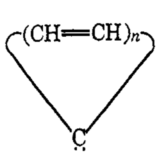
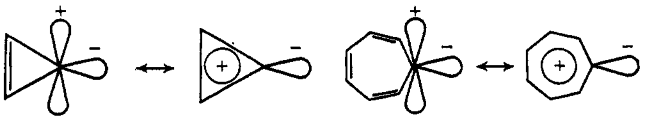
Photolysis of diazocyclopentadiene in *cis*- and *trans*-4-methylpentene-2 led to the formation of *cis*-1-methyl-2-isopropylspiro[2.4]heptadiene-4,6 and *trans*-1-methyl-2-isopropylspiro[2.4]heptadiene-4,6, respectively. No *cis* product was formed from the *trans* olefin, but some *trans* product was found in the product mixture from the *cis* olefin reaction. Under conditions where the spiro[2.4]heptadienes do not photointerconvert, the extent of formation of *trans* product from *cis* olefin is small (1–2%). This nonstereospecificity could not be greatly increased by carrying out the photolysis in large excesses of hexafluorobenzene or octafluorocyclobutane diluents, nor could it be much decreased by means of 2,5-dimethylhexadiene-2,4 or acrylonitrile diluents. It is concluded that the photolysis of diazocyclopentadiene leads to a singlet cyclopentadienylidene which reacts more rapidly with olefinic substrate than it crosses to its triplet ground state.

It is well known that a carbene's ability to discriminate between various olefinic substrates may be greatly enhanced by the proper choice of carbenic substituent groups, *e.g.*, chlorine or fluorine.[1] More recently, attempts have been made to generate carbenes in which unique chemistry might be anticipated due to the incorporation of the carbenic center in a potentially aromatic system. Three such systems, of basic structure I, have been studied.

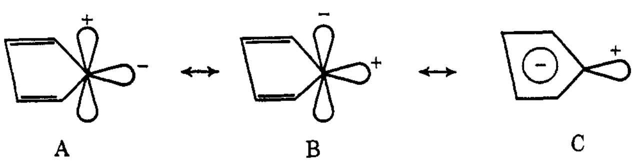


I

For I, $n = 1$, cyclopropenylidene, and I, $n = 3$, cycloheptatrienylidene, it was hoped that the singlet carbene would derive important stabilization from the aromaticity expressed by the resonance hybrids which are shown below.



Important contributions of the charge delocalized forms would be signaled by *nucleophilic* behavior of the carbenes toward olefins. Thus far, in keeping with prediction, only olefins with electron-poor π bonds have proven to be suitable substrates for these systems.[2] For the system I, $n = 2$, cyclopentadienylidene, the situation is more complex. The ground state of the carbene is known to be a triplet in which one unpaired electron is localized in the in-plane sp^2 orbital, while the other electron is in the π system.[3] The singlet state of the carbene may be expressed as the resonance hybrid II.



II

Although, ordinarily, a singlet carbene would be expected to adopt an electronic configuration in which the lone pair populates the inplane sp^2 orbital, IIA, rather than a p orbital, IIB, recent calculations indicate that the alternative configurations are within 0.2 eV. The resulting extensive configuration interaction will lead to mixing of IIA and IIB, and the singlet cyclopentadienylidene is therefore best represented as the entire resonance hybrid II.[4] An important question is: how much of a contribution is made by the charge delocalized canonical form IIC? Were II adequately

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[1] R. A. Moss and R. Gerstl, *J. Org. Chem.*, **32**, 2268 (1967), and references therein.

[2] Cyclopropenylidene: see W. M. Jones, M. E. Stowe, E. E. Wells, Jr., and E. W. Lester, *J. Amer. Chem. Soc.*, **90**, 1849 (1968), and references therein. Cycloheptatrienylidene: see W. M. Jones and C. L. Ennis, *ibid.*, **89**, 3069 (1967); T. Mukai, T. Nazakawa, and K. Isobe, *Tetrahedron Lett.*, 565 (1968).

[3] E. Wasserman, L. Barash, A. M. Trozzolo, R. W. Murray, and W. A. Yager, *J. Amer. Chem. Soc.*, **86**, 2304 (1964).

[4] Private communication from Professor Roald Hoffmann, Cornell University.