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10, 11-Dihydro-5*H*-dibenzo[*a, d*]cycloheptenylidene

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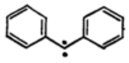
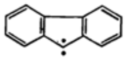
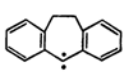
The photolysis of 5-diazo-10, 11-dihydro-5*H*-dibenzo[*a, d*]cycloheptene in *cis*-2-butene gave 5, 5′-bi(10, 11-dihydro-5*H*-dibenzo[*a, d*]cycloheptenyl) (81%), 10, 11-dihydro-5*H*-dibenzo[*a, d*]-cycloheptene (6%), and 10, 11-dihydro-5*H*-dibenzo[*a, d*]cyclohepten-5-one (6%). The ESR spectrum established the triplet ground state of this carbene. The absorption spectrum of this carbene was obtained successfully. These spectra are similar to that of diphenylmethylene. 5, 5-Dibromo-10, 11-dihydro-5*H*-dibenzo[*a, d*]cycloheptene was prepared by the bromination of the diazo compound at $-30°C$. The reaction of this dibromide with alkyllithium in the presence of olefin gave 5, 5′-bi(10, 11-dihydro-5*H*-dibenzo[*a, d*]cycloheptenylidene) and 5-alkyl-10, 11-dihydro-5*H*-dibenzo[*a, d*]cyclohepten-5-ol. No cyclopropane derivatives were obtained.

The photolysis of diphenyldiazomethane in the presence of olefins was found to give cyclopropanes nonstereospecifically,[1,2] and it was inferred that divalent carbon intermediates must be reacting in the triplet state.[3] Moreover, the triplet nature of diphenylmethylene (I) was explained by the resonance stabilization of the sp hybridization (D_{2d} symmetry) of the divalent carbon.[1] Nevertheless, the results of ESR study[4] show that the ground state is indeed triplet and indicates that carbene I does not have the D_{2d} structure visualized by Skell.[1] Moreover, this is confirmed by the addition reaction of fluorenylidene (II) to olefin.[5,6] These results show that the above hypothesis by Skell might not be satisfactory in explaining the relationship between the electronic state and its structure. It is, therefore, important to obtain further information on the carbene and on the carbenoid reaction. The photolysis of 5-diazo-10, 11-dihydro-5*H*-dibenzo[*a, d*]cycloheptene (IV) and the reaction of 5, 5-dibromo-10, 11-dihydro-5*H*-dibenzo[*a, d*]cycloheptene (V) with alkyllithium in the presence of olefin were also investigated. The mechanism of this carbenoid reaction[7] is discussed in connection with our previous proposal.[8] Furthermore, we investigated the electronic absorption spectra and ESR spectra of 10, 11-dihydro-5*H*-dibenzo[*a, d*]cycloheptenylidene (III) with the aim of establishing the electronic configuration of carbene III.


I


II


III

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[1] R. M. Etter, H. S. Skorovnek and P. S. Skell, *J. Am. Chem. Soc.*, **81**, 1008 (1959).

[2] G. L. Closs and L. E. Closs, *Angew. Chem.*, **74**, 431 (1962).

[3] W. Kirmse, "Carbene Chemistry," Academic Press Inc., New York, N. Y. (1964).

[4] A. M. Trozzolo, R. W. Murray and E. Wasserman, *J. Am. Chem. Soc.*, **84**, 4990 (1962).

[5] E. Funakubo, I. Moritani, T. Nagai, S. Nishida and S. Murahashi, *Tetrahedron Letters*, **1963**, 1069; S. Murahashi, I. Moritani and T. Nagai, This Bulletin, in press..

[6] M. Jones, Jr., and K. T. Rettig, *J. Am. Chem. Soc.*, **87**, 4013, 4015 (1965).

[7] W. Kirmse, *Angew. Chem.*, **77**, 1 (1965); G. L. Closs and R. A. Moss, *J. Am. Chem. Soc.*, **86**, 4042 (1964); G. L. Closs and J. J. Coyle, *ibid.*, **87**, 4270 (1965).

[8] S. Murahashi and I. Moritani *Tetrahedron*, in press.

Results and Discussion

Formation of 10, 11-Dihydro-5*H*-dibenzo[*a*, *d*]cycloheptenylidene (III) and Its Chemical Reactivities. The reaction of 10, 11-dihydro-5*H*-dibenzo[*a*, *d*]cyclohepten-5-one (VI)[9,10] with *p*-toluenesulfonylhydrazine afforded the tosylhydrazone (VII) of VI in a 75% yield.[11] The diazo compound (IV) was prepared from VII in a 76% yield by the treatment with sodium methoxide in pyridine at 60°C. The photolysis of IV in *cis*-2-butene gave 5, 5′-bi(10, 11-dihydro-5*H*-dibenzo[*a*, *d*]cycloheptenyl) (VIII-a) (mp 266—266.5°C, 81% yield), 10, 11-dihydro-5*H*-dibenzo-[*a*, *d*]cycloheptene (IX)[10] (6% yield), and VI (6% yield). In the NMR spectrum of VIII-a the methine proton appears as a singlet at τ 5.22, and the methylene protons,[12] as multiplets at τ 6.07—6.43 and τ 6.79—7.13 (A_2B_2 system). In order to prepare an authentic sample of VIII-a, the following two reactions were carried out. The pyrolysis of IV in diglyme gave the same compound, VIII-a, in a 23% yield. However, the treatment of 5-chloro-10, 11-dihydro-5*H*-dibenzo-[*a*, *d*]cycloheptene (X)[10] with thiourea or copper powder gave a compound with a melting point of 271—272.5°C (VIII-b).

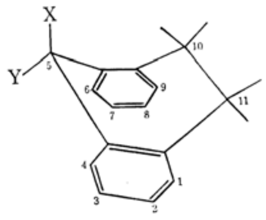
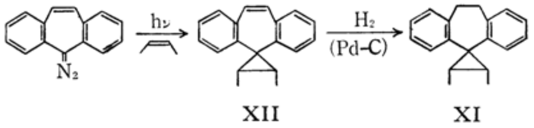


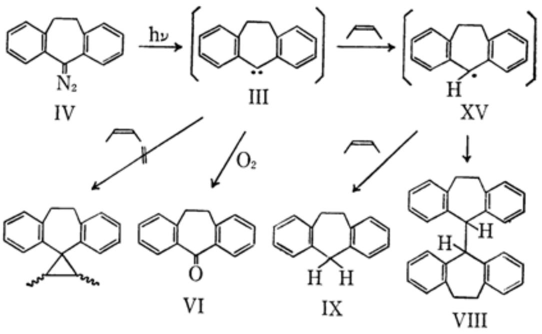
Fig. 1. The structure of 5, 5-disubstituted-10, 11-dihydro-5*H*-dibenzo[*a*, *d*]cycloheptene.

Although these two compounds show the same molecular weight, and the same results of elementary analysis, their NMR, ultraviolet[13] and infrared spectra are different. These results suggest that compounds VIII-a and VIII-b might be stereo-isomers. The treatment of VIII-a and VIII-b with zinc powder at 290°C gave the same product VI. This result also supports the idem of the presence of stereo-isomer. The flipping of seven-membered ring (Fig. 1) and the free rotation about the C_5–$C_{5'}$ of VIII may be difficult because of the steric repulsion between benzene rings. This steric repulsion could give stereo-isomers.

Although diphenylmethylene adds to olefin nonstereospecifically, no cyclopropane derivative was obtained. This result was confirmed by vpc comparing the retention time with that of an authentic sample. The authentic sample of *cis*-2, 3-dimethylspiro[cyclopropane-1, 5′-(10′, 11′-dihydro-5*H*′-dibenzo[*a*, *d*]cycloheptene)] (XI) was prepared by the hydrogenation of *cis*-2, 3-dimethylspiro [cyclopropane-1, 5′-5′*H*-dibenzo[*a*, *d*] cycloheptene)] (XII).[14] The *trans*-isomer (XIV) of XI was also prepared in the same manner.



It is noteworthy that ketazine was not obtained from the photolysis of IV in *cis*-2-butene, although the photolysis of diphenyldiazomethane gave ketazine in cyclohexane or petroleum ether.[15] Furthermore, the photolysis of IV in benzene gave VIII-a. The compounds VI, IX and VIII-a may be formed as is shown in Scheme 1. The hydrogen abstraction reaction and the lack of any addition reaction might be ascribed to the triplet character of carbene III.[16]



Scheme 1

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[9] W. Treibs and H-J. Klinkhammer, *Chem. Ber.*, **84**, 671 (1951).

[10] V. Mychajlyszyn and M. Protiva, *Collection Czechoslov. Chem. Commun.*, **24**, 207 (1959).

[11] Hydrazone of VI was not obtained from the reaction VI with hydrazine hydrate.

[12] When the carbon at C-5 has a sp^2 configuration or is substituted smaller alkyl group, the methylene protons are observed as a singlet (IV, VI, VII, IX). On the other hand, when substituent is replaced by larger groups the methylene protons are observed as two multiplet absorptions as A_2B_2 system (VIII, X, XI, XIII, XIV, XXI).

[13] The ultraviolet spectrum of VIII-b shows similar bands of VIII-a except a broad band at 298 mμ (see Experimental). This band at longer wavelength is similar to that of *p*-cyclophane with three or smaller methylene groups and may arise from the trans-annular interaction of nonconjugated aromatic rings. (See H. H. Jaffé and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," John Wiley & Sons, Inc., New York, N. Y. (1964), Chapter 15).

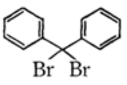
[14] S. Murahashi, I. Moritani and N. Nishino, *J. Am. Chem. Soc.*, **89**, 1257 (1967).

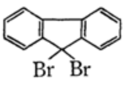
[15] W. Kirmse, L. Horner and H. Hoffmann, *Ann.*, **614**, 19 (1958); W. E. Parham and W. R. Hasek, *J. Am. Chem. Soc.*, **76**, 935 (1954).

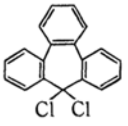
[16] H. E. Zimmerman and D. H. Paskovich, *ibid.*, **86**, 2149 (1964); V. Franzen and H. I. Joschek, *Ann.*, **633**, 7 (1960); W. Kirmse, L. Horner and H. Hofmann, *ibid.*, **614**, 19 (1958); E. Ciganek, *J. Am. Chem. Soc.*, **88**, 1979 (1966); D. M. Gale, W. J. Middleton and C. G. Krespan, *ibid.*, **88**, 3617 (1966).

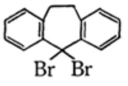
The Reaction of 5, 5-Dibromo-10, 11-dihydro-5*H*-dibenzo[*a*, *d*]cycloheptene (V) with Alkyllithium in the Presence of Olefin. Carbene I adds to olefin nonstereospecifically, while the reaction of dibromodiphenylmethane (XVI) with methyllithium proceeds stereospecifically.[2] The latter reaction has been explained by means of a S_N2-type transition state (XIX).[7] However, the fact that no cyclopropane derivatives are obtained from 9, 9-dibromofluorene (XVII) or 9, 9-dichloro-9*H*-tribenzo[*a*, *c*, *e*]cycloheptene (XVIII) with alkyllithium reveals that these reactions can not be explained in terms of a S_N2-type transition state (XIX) but must be explained in terms of concerted elimination reaction through a sp-like transition state (XX).[8]

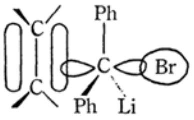
In order to ascertain this mechanism, the reaction of 5, 5-dibromo-10, 11-dihydro-5*H*-dibenzo[*a*, *d*]cycloheptene (V) with alkyllithium was carried out.


XVI

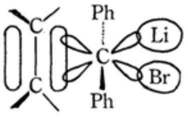

XVII


XVIII

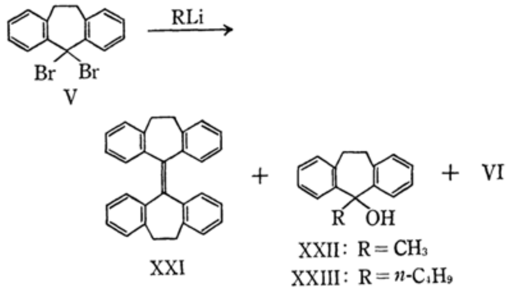

V



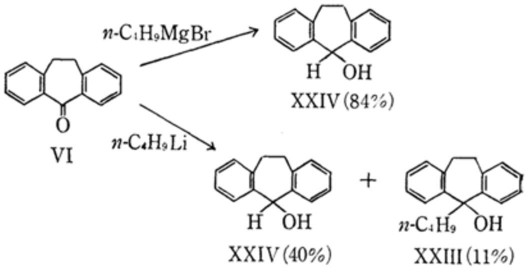
XIX



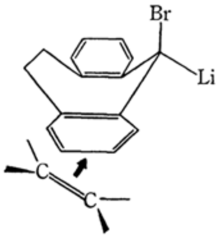
XX



Dibromide V was prepared by the bromination of IV in carbon disulfide at −30°C (quantitative yield). The reaction of V with 2.9 mol equivalents of methyllithium in *cis*-2-butene at −25—−30°C gave 5, 5′-bi(10, 11-dihydro-5*H*-dibenzo[*a*, *d*]-cycloheptenylidene) (XXI) (12%), 5-methyl-10, 11-dihydro-5*H*-dibenzo[*a*, *d*]cyclohepten-5-ol (XXII) (42%),[17,18] and ketone VI (10%). No cyclopropane derivatives were obtained. On the other hand, the reaction of dibromide V with 4 mol equivalents of *n*-butyllithium in the presence of ethyl vinyl ether gave XXI (14%), VI (13%), and 5-*n*-butyl-10, 11-dihydro-5*H*-dibenzo[*a*, *d*]cyclohepten-5-ol (XXIII). In these cases no formation of the cyclopropane derivatives was observed. In an attempt to synthesize an authentic sample of XXIII, the reaction of ketone VI with *n*-butylmagnesium bromide or *n*-butyllithium was investigated. However, the treatment of VI with *n*-butylmagnesium bromide gave no carbinol XXIII; however, it did afford 10, 11-dihydro-5*H*-dibenzo[*a*, *d*]-cyclohepten-5-ol (XXIV) in a 84% yield.[19] Moreover the reaction of VI with *n*-butyllithium gave alcohol XXIV (40%) and alcohol XXIII (11%). The reduction of ketone of VI with alkyllithium is an abnormal case, since this reaction might give a tertiary alcohol.[20]



It is noteworthy that the reaction of dibromide V with alkyllithium in olefin gave no cyclopropane derivatives, although the similar reaction of dibromide XVI gave cyclopropanes.[7,8] One may conclude that the carbenoid molecule can not be attacked through a sp-like transition state (XX) as is shown in XXV. Moreover, no hydrogen abstraction products were obtained. This shows that the reaction does not proceed through a free carbene, since a homolog of a carbene of this type does abstract a hydrogen atom from the solvent.[5,15,16]



XXV

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17) A. C. Cope and S. W. Fenton, *ibid.*, **73**, 1673 (1951).

18) The alcohol XXII was easily converted to 5-methylene-10, 11-dihydro-5*H*-dibenzo[*a*, *d*]cycloheptene[17] by heating at 190—200°C or treatment with hydrogen bromide in methylene chloride.

19) The reduction by Grignard reagent has been reported in respect to sterically hindered ketone, see M. S. Kharasch and O. Reinmuth, "Grignard Reactions of Nonmetallic Substances," Prentice-Hall, Inc., New York, N. Y. (1954), p. 160.

20) T. Eicher, "The Chemistry of the Carbonyl Group," ed. by S. Patai, Interscience Publishers, New York, N. Y. (1966), Chapter 13.

ESR and Electronic Absorption Spectra of 10, 11-Dihydro-5*H*-dibenzo[*a*, *d*]cycloheptenylidene(III). The powder of the diazo compound IV was irradiated with a 100-W high-pressure mercury lamp below 3000 Å at 77°K in a quartz Dewar. The spectra were obtained with a Japan Optic Lab. JES 3BX spectrometer with a 100-kc modulation, employing a frequency of 9137 Mc/sec. Resonance absorptions were observed at these magnetic fields; 939, 2260, 2417, 4572, 5247, and 7431 gauss. A broad line at the free spin value (3263 gauss) was also observed. This latter line is presumably due to doublet radicals resulting from further reactions. The intensities of the absorptions were not appreciably diminished when irradiation ceased. This indicates that the observed species are in the ground state. The spectra can be described by the Hamiltonian21):

$$\mathscr{H} = \beta g\vec{H}\vec{S} + DS_{Z^2} + E(S_{X^2} - S_{Y^2}) - 2/3D$$

The zero-field parameters obtained in this observation were found to be $D=0.3932\ \mathrm{cm}^{-1}$ and $E=0.0170\ \mathrm{cm}^{-1}$. The D value observed, larger than that of the phosphorescent triplet state of the aromatic hydrocarbons,22) indicates that one unpaired electron is largely localized in an *n*-orbital at C-5, the divalent carbon atom, and another delocalized in a π-orbital.

It has been observed that the D and E values of I are 0.405 and $0.019\ \mathrm{cm}^{-1}$ respectively.23) The nonzero value of E for I eliminates a structure with a D_{2d} symmetry. The angle between the axes of the divalent carbon was calculated to be ~150°C, a value supported by the examination of the ^{13}C hyperfine splittings.24) Since the value of E/D for III is similar to I, the angle of the axes to the hybrid at C-5 appears to be ~150°C. This value is greater than the internuclear angle of the seven-membered ring. This is presumably due to that fact that the angle at C-5 in III is bent bond.25) If the C-5 hybrids of III are sp^2, similar to ketone, it is clear that the π-orbital in C-5 is almost perpendicular to the π-orbitals of both benzene rings. Such a model is clearly inconsistent with the observed value of D. On the other hand, the enlargement of the angle of the axes of the hybrids at C-5 increases the s character of the bonds and the planarity of the seven-membered ring, thus contributing to the delocalization of the π electron of the C-5 atom with both benzene rings. Thus, it is reasonable to assume that the bonds to C-5 of III are the bent ones. The D value for III is smaller than that of I. The greater possibility of π-delocalization should reduce the density of the π electron on the C-5 atom, and thus reduce the value of D.

We succeeded in obtaining absorption spectra of I and III in various organic matrices at 77°K.26) Hutchison and Closs27) and Gibbons and Trozzolo28) observed the absorption spectrum of I independently. As is shown in Fig. 2 and Fig. 3, two absorption bands appeared in the ultraviolet and visible regions after the irradiation of the corresponding diazo compounds for a few minutes. The spectra thus obtained did not change at this temperature, but disappeared at a higher temperature. The spectra of I and III show similar characteristics, thus suggesting that the two carbenes have similar π electronic configurations. The long-wavelength

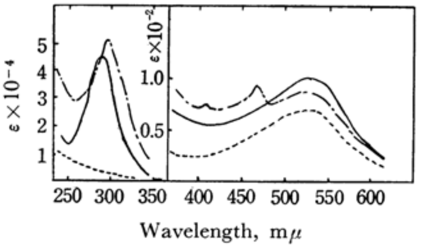

Fig. 2. Absorption spectra observed by the photolysis of diphenyldiazomethane in rigid media at 77°K; (——) before irradiation (—·—) after irradiation, and (----) after warming up to 25°C.

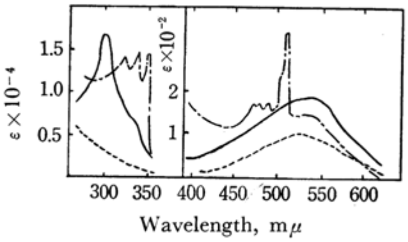

Fig. 3. Absorption spectra observed by the photolysis of 5-diazo-10, 11-dihydro-5*H*-dibenzo[*a*, *d*]-cycloheptene in rigid media at 77°K; (——) before irradiation, (—·—) after irradiation, and (----) after warming up to 25°C.

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21) K. W. H. Stevens, *Proc. Roy. Soc. (London)*, **A214** 235 (1952).

22) C. A. Hutchison Jr., and B. W. Mangum, *J. Chem. Phys.*, **29**, 952 (1958); **32**, 1261 (1960); **34**, 908 (1961).

23) R. W. Murray, A. M. Trozzolo, E. Wasserman and W. A. Yager, *J. Am. Chem. Soc.*, **84**, 3213 (1962); R. W. Brandon, G. L. Closs and C. A. Hutchison Jr., *J. Chem. Phys.*, **37**, 1878 (1962); E. Wasserman, L. C. Snyder and W. A. Yager, *ibid.*, **41**, 1763 (1964); R. W. Brandon, G. L. Closs, C. E. Davoust, C. A. Hutchison, Jr., B. E. Kohler and R. Silbey, *ibid.*, **43**, 2006 (1965).

24) E. Wasserman, A. M. Trozzolo, W. A. Yager and R. W. Murray, *J. Chem. Phys.*, **40**, 2408 (1964).

25) E. Wasserman, L. Barash, A. M. Trozzolo, R. W. Murray and W. A. Yager, *J. Am. Chem. Soc.*, **86**, 2304 (1964).

26) I. Moritani, S. Murahashi, M. Nishino, K. Kimura and H. Tsubomura, *Tetrahedron Letters*, **1966**, 373.

27) G. L. Closs, C. A. Hutchison, Jr., and B. E. Kohler, *J. Chem. Phys.*, **44**, 413 (1966).

28) W. A. Gibbons and A. M. Trozzolo, *J. Am. Chem. Soc.*, **88**, 172 (1966).

band of carbene III (486 mμ) is longer than that of carbene I (468 mμ), which may be consistent with the D value of III being smaller than that of I, and which may be attributed to a bent bond.

It was concluded, on the basis of the results of the UV and ESR spectral studies, that carbene III has a ground triplet state and an electronic configuration similar to that of carbene I. The bonds to C-5 in carbene III are bent, and the angle of the divalent carbon of III is ~150°. Moreover, the π-delocalization of III is slightly larger than that of I.

With regard to the chemical reactivity, carbene III shows a stronger hydrogen abstraction character than does diphenylmethylene.15)

The reaction of the bromide V with alkyllithium was found to proceed through a previously-proposed mechanism on XVII and XVIII.8)

Experimental

All melting points were uncorrected. The IR spectrum was recorded by the use of an EPI-S2 apparatus. The UV spectrum was recorded by the use of an EPS-2U apparatus. The NMR spectrum was recorded by the use of a JNM-4H-100 apparatus. The molecular weight was recorded by the use of a Mechrolab vapor pressure osmometer, model 301A, in a benzene solution.

10, 11 - Dihydro - 5*H*-dibenzo[*a*, *d*]cyclohepten-5-one *p*-Toluenesulfonylhydrazone (VII). To a solution of VI9,10) (30 g, 0.014 mol) in ethanol (200 m*l*), *p*-toluenesulfonylhydrazine (34 g, 0.018 mol) and a solution (15 m*l*) of concentrated hydrochloric acid were added. The reaction mixture was then refluxed for 8 hr. After cooling, a pale yellow material was filtered out. Recrystallization from acetone gave colorless prisms (41 g, 75% yield); mp 175°C (decomp). This material has characteristic infrared maxima at 3180 cm^{-1} (ν N–H) and 1170 cm^{-1} (ν S–O).

Found: C, 70.13; H, 5.27; N, 7.54%. Calcd for $C_{22}H_{20}SO_2N_2$: C, 70.18; H, 5.34; N, 7.44%.

5-Diazo - 10, 11 - dihydro - 5*H* - dibenzo[*a*, *d*]cycloheptene (IV). To a solution of VII (28 g, 0.077 mol) in dry pyridine (240 m*l*), sodium methoxide (4.2 g, 0.078 mol) was added. The mixture was then stirred for 1.5 hr at 70±2°C, and the solution was stirred into ice water (500 m*l*). A wine-red precipitate was then filtered out. After drying, recrystallization from petroleum ether (bp 40—70°C) gave IV (17 g, 76%), mp 71°C (decompt.). The infrared spectrum (Nujol mull) showed a band at 2050 cm^{-1} (ν N≡N). The ultraviolet spectrum in ethanol showed maxima at 237 mμ (4.23), 291 mμ (4.32), 326^{sh} mμ (3.76), and 540 mμ (2.08).

Found: C, 81.64; H, 5.40%. Calcd for $C_{15}H_{12}N_2$: C, 81.79; H, 5.49%.

Photolysis of 5-Diazo-10, 11-dihydro-5*H*-dibenzo-[*a*, *d*]cycloheptene (IV) in *cis*-2-Butene. A solution of IV (4.9 g, 0.022 mol) in *cis*-2-butene (150 m*l*) was placed in a 300-m*l* three-necked cylindrical flask equipped with a nitrogen inlet tube and a dry ice condenser topped with an azotometer, and photolyzed by 500-W high-pressure mercury lamp until the evolution of nitrogen had ceased (6 hr). After the evaporation of the solvent, the reaction mixture was dissolved in chloroform - *n*-hexane. The undissolved material was then filtered out; its recrystallization from chloroform-benzene gave 0.20 g of VIII-a. The evaporation of the solvent of the filtrate gave 4.20 g of a residue, which was dissolved in chloroform (30 m*l*) and then subjected to chromatography on alumina.

Elution with *n*-hexane gave 0.92 g of hydrocarbon, which was then subjected to vpc (Yanagimoto GCG 5DH, 3 mm × 1.5 m, Apieson L, 200°C). Four peaks were detected. The main peak (25%) was separated and identified as IX (6% yield), mp 76—77°C (reported mp 75°C).10) The NMR spectrum of IX has a singlet at τ 3.08 (8H), a singlet at τ 6.04 (2H), and a singlet at τ 6.93 (4H). Further elution with *n*-hexane-benzene (1 : 1) gave 3.31 g of VIII-a, mp 266—266.5°C (total yield 81%). This material was identified by comparing it with an authentic sample.

Found: C, 92.94; H, 6.83%; mol wt, 377. Calcd for $C_{30}H_{26}$: C, 93.22; H, 6.78%; mol wt, 386.5.

Finally, elution with benzene gave VI, which was converted to 2, 4-dinitrophenylhydrazone (0.51 g, 6%), mp 248—249°C.

Found: C, 64.60; H, 4.29%. Calcd for $C_{21}H_{16}O_4N_4$: C, 64.94; H, 4.15%.

5, 5′-Bi(10, 11-dihydro-5*H*-dibenzo[*a*, *d*]cycloheptenyl) (VIII). Method A: A mixture of X (1.5 g, 0.0065 mol)10) and thiourea (0.5 g, 0.007 mol) was heated at 140—150°C for 6 hr. To the mixture benzene (50 m*l*) was then added, and the mixture was refluxed for 30 min. The reaction mixture was filtered, and an insoluble material was washed with methanol. The evaporation of the solvent of the filtrate gave 0.1 g of VIII-b,29) mp 271.5—272.5°C (reported mp 269°C).10) The infrared spectrum has bands at 1166, 1105, 939, 800, 765, 741, 724, and 699 cm^{-1}. The ultraviolet spectrum in *n*-hexane exhibits maxima at 232^{sh} mμ (log ε=4.22), 270^{sh} mμ (3.51), 273^{sh} mμ (3.52), 276^{sh} mμ (3.53), and 298 mμ (3.62).

Found: C, 92.75; H, 6.92%; mol wt, 367. Calcd for $C_{30}H_{26}$: C, 93.22; H, 6.78%; mol wt, 386.5.

Method B: A mixture of X (0.60 g, 0.0026 mol)10) and copper powder (0.2 g) in benzene (10 m*l*) was heated under reflux for 4 hr. After cooling, the mixture was filtered, and the filtrate was concentrated to 4 m*l*. The colorless compound, VIII-b, was filtered and recrystallized from *n*-hexane-dichloromethane, mp 271.5—272.5°C.

Method C: A solution of IV (2.0 g, 0.0091 mol) in diethyleneglycol dimethyl ether (50 m*l*) was heated under reflux for 2 min. The mixture was poured into water (100 m*l*), and the precipitate was filtered. Recrystallization from benzene or chloroform gave VIII-a29) (0.4 g, 23%), mp 266—266.5°C. The infrared spectrum has bands at 1049, 1035, 937, 756, 740, 723, and 698 cm^{-1}. The ultraviolet spectrum in *n*-hexane exhibits maxima at 266 mμ (log ε=4.19), 269 mμ (4.16), 273^{sh} mμ (4.08), and 275^{sh} mμ (3.99).

Photolysis of 5-Diazo-10, 11-dihydro-5*H*-dibenzo-[*a*, *d*]cycloheptene (IV) in Benzene. A solution of IV (2.0 g, 0.009 mol) in benzene (400 m*l*) was photolyzed. After the filtration of an undissolved yellow polymer (0.15 g), the reaction mixture was concentrated

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29) A mixture of VIII and zinc powder was heated at 290°C by metal bath. The reaction mixture was sublimed and ketone VI was obtained.

to *ca*. 50 m*l*. The benzene solution was then subjected to alumina chromatography. Elution with benzene gave VIII-a (0.46 g, 27%).

5, 5-Dibromo-10, 11-dihydro-5*H*-dibenzo[*a*, *d*]-cycloheptene (V). To a solution of IV (11 g, 0.050 mol) in carbon disulfide (100 m*l*), a solution of bromine (8 g, 0.050 mol) in 80 m*l* of carbon disulfide was added at −20°C with stirring. The carbon disulfide was evaporated *in vacuo*, and 50 m*l* of ether was added. After the evaporation of the ether, the resulting yellow needles were recrystallized from petroleum ether (bp 40—70°C), mp 80°C (decomp.). In the air the decomposition occurred easily to give the ketone VI. In the NMR spectrum the phenyl protons (8H) appear as a multiplet at τ 2.67—3.18, and the methylene proton (4H), as a singlet at τ 6.89.

The Reaction of 5, 5-Dibromo-10, 11-dihydro-5*H*-dibenzo[*a*, *d*]cycloheptene (V) with Methyllithium in the Presence of *cis*-2-Butene. A solution of *cis*-2-butene (100 m*l*) and V, which had been prepared in situ by the bromination of IV (4.5 g, 0.020 mol) with bromine (3.3 g, 0.021 mol) in dry ether (420 m*l*) was cooled to −25°C and stirred. To this solution methyllithium (0.059 mol) in ether (115 m*l*) was added over 20-min period. After stirring the solution at −25°C for additional 30 min, water was added to the reaction mixture. The organic layer was separated, and the aqueous layer was extracted with ether. The ether extracts were combined, washed with water, and dried. After the removal of the solvent, the residue was crystallized from benzene to give 0.47 g of XXI (12% based on IV), mp 291—292.5°C. The infrared spectrum of XXI has bands at 1483, 1442, 1090, 940, 772, 753, 746, 715, and 650 cm^{-1}. The ultraviolet spectrum in ethanol exhibits maximum at 274 mμ ($\log \varepsilon = 4.4$).

Found: C, 93.65; H, 6.25%; mol wt, 378. Calcd for $C_{30}H_{24}$: C, 93.71; H, 6.29%; mol wt, 384.5.
The filtrate was subjected to vpc (Yanagimoto, GCG 3DH, 5 mm × 2m, Apieson L, 255°C). Five compounds were detected. Two of these compounds were separated and identified as VI (10%) and 5-methylene-10, 11-dihydro-5*H*-dibenzo[*a*, *d*]cycloheptene⁽17⁾ (42%), which may be formed from XXII.⁽18⁾ The absence of the cyclopropane derivative XI was confirmed.

5-Methyl-10, 11-dihydro-5*H*-dibenzo[*a*, *d*]cyclohepten-5-ol (XXII). To a solution of ketone VI (4.0 g, 0.017 mol) in ether (50 m*l*) a solution of methyllithium (0.020 mol) in ether (70 m*l*) was added over a 20-min period at 0°C. After treatment in the usual manner, XXII was obtained (4.1 g, 95%), mp 142.5—143°C (reported mp 142—143°C).⁽17⁾ The infrared spectrum (Nujol mull) has a characteristic band at 3365 cm^{-1} (νO–H). The NMR spectrum of XXII consists of a multiplet at τ 2.0—3.0 (8H), a multiplet at τ 6.63—7.01 (4H), a singlet at τ 7.77 (1H), and a singlet at τ 8.17 (3H).

The Reaction of 5, 5-Dibromo-10, 11-dihydro-5*H*-dibenzo[*a*, *d*]cycloheptene (V) with *n*-Butyllithium in the Presence of Ethyl Vinyl Ether. To a mixture of ethyl vinyl ether (200 m*l*) and V (prepared from IV (11.0 g, 0.050 mol) and bromine (8 g, 0.050 mol)) in ether (550 m*l*) 0.20 mol of *n*-butyllithium in ether (200 m*l*) was added at −35°C. The reaction mixture was then treated as has been described for the reaction of V with methyllithium. The dimer XXI (2.62 g, 14%) the ketone VI (1.2 g, 13%), and the alcohol XXIII (0.61 g, 4.6%) were thus obtained. No cyclopropane derivative XI was detected.

The Reaction of 10, 11-Dihydro-5*H*-dibenzo[*a*, *d*]-cyclohepten-5-one (VI) with *n*-Butyllithium. Into a stirring solution of VI (15 g, 0.072 mol) in 100 m*l* of ether there was added 0.11 mol of *n*-butyllithium in 90 m*l* of ether at −30°C. After treatment in the usual manner, crystallization from petroleum ether (bp 50—70°C) afforded 6.1 g of XXIV (40%), mp 92—92.5°C (reported mp 93°C).⁽10⁾ The chromatography of the filtrate of alumina gave 2.1 g of XXIII (11%), mp 86°C (recrystallized from petroleum ether (bp 50—70°C)). The infrared spectrum (Nujol mull) shows the characteristic band at 3335 cm^{-1} (ν O–H). The NMR spectrum has a multiplet at τ 2.2—3.2 (8H), a multiplet at τ 6.55—6.87 (2H), a multiplet at τ 6.98—7.33 (2H), a triplet at τ 7.95 (2H, *J*=8 cps), a multiplet at τ 8.75—9.15 (4H), and a triplet at 9.25 (3H, *J*=6 cps).

Found: C, 85.88; H, 8.33%. Calcd for $C_{19}H_{22}O$: C, 85.67; H, 8.33%.

Hydrogenation of *cis*-2, 3-Dimethylspiro[cyclopropane-1, 5′-(10′, 11′-dihydro-5′*H*-dibenzo[*a*, *d*]-cycloheptene)] (XII). To a solution of XII (210 mg) in 50 m*l* of ethanol, 150 mg of palladium-charcoal were added, and the mixture was hydrogenated. After the filtration of the catalyst, the solvent was removed. When the resulting oil was subjected to preparative vpc, pure XI was obtained. The infrared spectrum shows characteristic bands at 1384, 1167, 1156, 1105, 1076, 939, 776, 753, and 738 cm^{-1}. The NMR spectrum has a multiplet at τ 2.8—3.2 (8H, phenyl protons), a multiplet at τ 6.2—6.7 (2H, methylene protons), a multiplet at τ 7.0—7.4 (2H, methylene protons), a multiplet at τ 8.0—8.25 (1H, cyclopropyl proton), a multiplet at τ 8.7—8.95 (1H, cyclopropyl proton), a doublet at τ 8.67 (3H, methyl protons, *J*=6.5)), and a doublet at τ 9.13 (3H, methyl protons, *J*=6.5 cps).

Found: C, 91.71; H, 8.35%. Calcd for $C_{19}H_{20}$: C, 91.88; H, 8.12%.

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