the ammonia had evaporated, water was added to the residue and the alkaline solution was acidified carefully at 0° with dilute HCl. The precipitate was isolated by ether extraction and evaporation of the dried extracts yielded 0.09 g of a colorless oil consisting of **4c** and **5c** in a ratio of 1:1 estimated by integration of the olefinic signals at 5.48 and δ 5.57.

The foregoing mixture was treated with 5 ml of formic acid containing 4 drops of concentrated H_2SO_4 at 20° for 1 hr. Work-up as described previously for **7** gave 0.04 g of a neutral compound, identified as **7** by pmr and vpc.

Registry No.—**4a,** 19990-29-5; **4a** (2,4-dinitrophenylhydrazone), 19990-30-8; **4b,** 19990-31-9; **4c,** 19990-32-0; **5a,** 19990-33-1; **5b,** 19990-34-2; **5c,** 19990-35-3; **6c,** 19990-36-4; **7,** 19990-37-5; **8,** 19990-38-6.

Bridged Polycyclic Compounds. LVII. The Photorearrangement of 7-Methylenedibenzobicyclo[2.2.2]octadiene. The Preparation and Properties of Dibenzotricyclo[4.2.1.0^{1,3}]octadiene[1]

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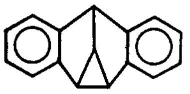
Received September 20, 1968

The photorearrangement of 7-methylenedibenzobicyclo[2.2.2]octadiene (3) yields dibenzotricyclo[4.2.1.0^{1,3}]-nonadiene (4) whose structure was determined by spectroscopic and chemical means. Upon hydrogenation cyclopropane 4 gives 5-methyldibenzobicyclo[3.2.1]octadiene (12). Treatment of 4 with perchloric acid in acetic acid gives dibenzobicyclo[4 2.1]nona-2,7-dien-6-ol acetate (15).

Our interest[1,2] in the chemistry of dibenzotricyclo-[3.3.0.0^{2,8}]octadiene (1) and its analogs naturally led us to the use of Ciganek's procedure[3] for the synthesis of **1** and its analogs by sensitized photorearrangements of dibenzobicyclo[2.2.2]octatriene (2) and its analogs. When 7-methylenedibenzobicyclo[2.2.2]octadiene (3) became available in our laboratory, we were attracted to a study of its photochemical behavior.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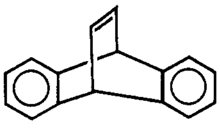
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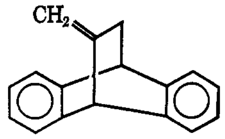
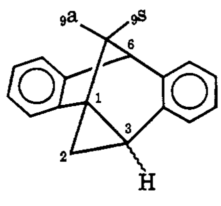


3

Irradiation of **3** in acetone gave a single compound whose pmr spectrum was initially difficult to interpret. However, at this time, a communication by Zimmerman and his coworkers appeared,[4] which suggested a general mechanism for the isomerization of divinylmethanes to vinylcyclopropanes. If a mechanism similar to that proposed by Zimmerman obtained in the phototransformation of **3**, one (or both) of the geometric isomers of the spirocyclopropane **4**, dibenzotricyclo[4.2.1.0^{1,3}]-nonadiene, would result. In one of the isomers (*exo* **4a**), the cyclopropane ring is *syn* to the methano bridge and, in the other (*endo* **4b**), *anti* to it. The pmr spectrum of the photoproduct is consistent with either **4a** or **4b**. The preparation of **3** by base-promoted dehydrohalogenation of 7-chloromethyldibenzobicyclo[2.2.2]octadiene (5) with potassium *t*-butoxide in dimethyl sulfoxide produced a hydrocarbon mixture that consisted largely (*ca.* 90%) of olefin **3**, contaminated with 7-methyldibenzobicyclo[2.2.2]octatriene (6).[5] When this mixture of olefins **3** and **6** was used for the photorearrangement reaction in acetone solution, two other cyclopropanes (compounds **7** and **8**)[6] were produced in addition to **4**.



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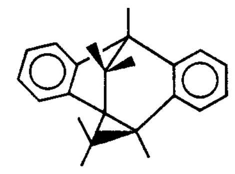
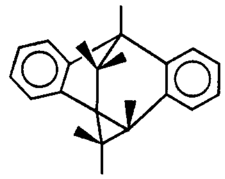

4a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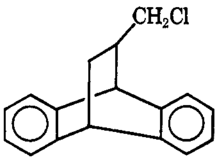

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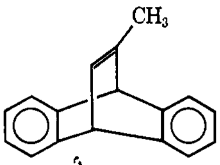

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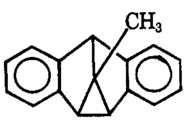

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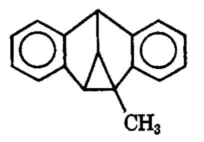

8

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(1) Previous paper in series: S. J. Cristol, R. J. Bopp, and A. E. Johnson, *J. Org. Chem.*, in press.

(2) See, for example, (a) S. J. Cristol and B. B. Jarvis, *J. Amer. Chem. Soc.*, **88**, 3095 (1966); **89**, 5885 (1967). (b) S. J. Cristol and B. B. Jarvis, *ibid.*, **89**, 401 (1967). (c) unpublished work of S. J. Cristol, W. Y. Lim, and A . R. Dahl.

(3) E. Ciganek, *J. Amer. Chem. Soc.*, **88**, 2882 (1966).

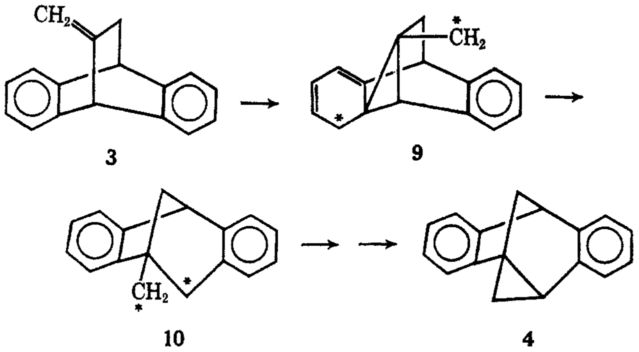
(4) H. E. Zimmerman, R. W. Binkley, R. S. Givens, and M. S. Sherwin, *ibid.*, **89**, 3933 (1967).

(5) The powerful base utilized in the dehydrohalogenation caused prototropic equilibration of **3** and **6**.

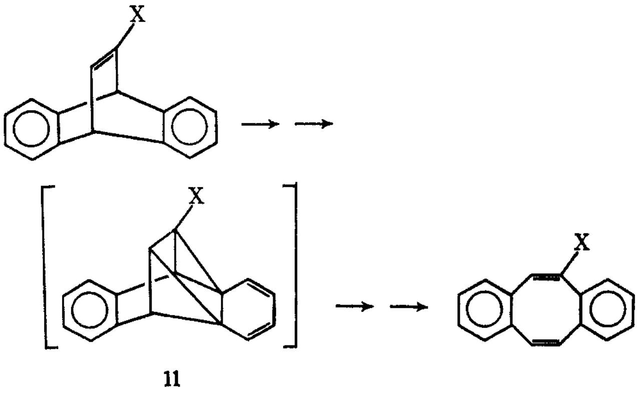
(6) The photochemical behavior of olefin **6** and other substituted ethenoanthracenes is currently under study in these laboratories. The resuts of these studies, as well as proofs of structure of compounds **6**, **7**, and **8**, will appear in a later paper.

We were unable to prepare a pure sample of olefin **3** by fractional crystallization of the dehydrohalogenation mixture. Pure **3** was, however, readily obtained by utilizing the greater photoreactivity of **6**. When the mixture of **3** and **6** was irradiated for 4 days in acetone, a pmr spectrum showed that the yield of **4** was about 25%, and that **6** had completely reacted to give **7** and **8**. The cyclopropanes **4**, **7**, and **8** were separated from olefin **3** by chromatography on a silver nitrate impregnated column of alumina. Olefin **3** was now easily purified by crystallization and a pure sample upon irradiation gave only cyclopropane **4**.

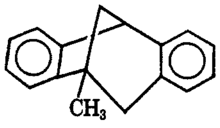
As indicated above, the Zimmerman mechanism[4] for the photosensitized rearrangement of divinylmethanes predicts the formation of **4** from **3**.



Under singlet conditions (cyclohexane solution) dibenzobicyclo[2.2.2]octatrienes undergo rearrangement to give dibenzocyclooctatetraenes[7] *via* di(arylvinyl)-bridged intermediates or transition states **11**,[8] rather than tricyclic compounds related to **1**, which are produced in the presence of triplet sensitizers. However, **3** was observed to give **4** not only in acetone or benzene solution, but also in cyclohexane. It seems possible that, as no ready path for isomerization analogous to **11** exists for **3**, its singlet lifetime is great enough to allow it to suffer intersystem crossing to its T_1 state, with consequent reaction *via* the Zimmerman mechanism. An interesting observation, which we are presently following up, is that irradiation of mixtures of **3** and **6** leads to methylcyclooctatetraene (from **6**) but to no photoproduct from **3**, at least initially.[9]



In beginning a study of the chemistry of **4**, we have studied its catalytic hydrogenation and addition of acetic acid. Hydrogenation of **4** over palladium on charcoal leads to a compound whose pmr spectrum (three-proton singlet) indicates a bridgehead methyl group and is otherwise consistent with structure **12**, 5-methyldibenzobicyclo[3.2.1]octadiene. It is of interest that hydrogenation of **1** leads to dibenzobicyclo[3.3.0]octa-2,7-diene (**13**);[2b,3] that is, rupture occurs between the benzylic carbon atoms. However, this is not the case with **4**, which follows the normal hydrogenolysis mode in cyclopropanes, where the bond most likely to be cleaved is that joining the two least substituted carbon atoms.[10] Also, models of both **4a** and **4b** suggest that steric factors would hinder the approach of the benzylic sites to the catalyst surface. The mode of cleavage unfortunately gives no insight into the **4a**–**4b** structural question.



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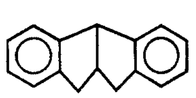

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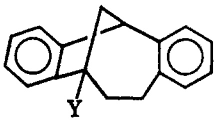
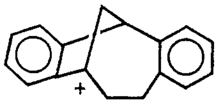
Treatment of **4** with perchloric acid in acetic acid gave dibenzobicyclo[4.2.1]nona-2,7-dien-6-ol acetate (**14**) which was converted by saponification into the corresponding alcohol **15**. Alcohol **15** could not be acetylated either by acetic anhydride in benzene–pyridine or by perchloric acid in acetic acid (the same conditions used for the ring-opening reaction). This evidence indicates that **15** is a tertiary alcohol.

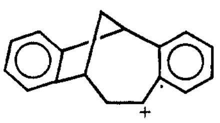
It would appear that electrophilic proton attack on **4** occurs in such a fashion as to give the tertiary benzylic cation **16** rather than the secondary benzylic cation **17** (or [3.2.1] cations), in spite of the fact that **16** is a bridgehead cation. Ion **16** does lie outside the limitations of Bredt's rule for bridgehead transient intermediates, as modified by Fawcett[11] (the sum of the number of atoms in the bridges should be seven or more) or by Wiseman[12] (the largest ring must contain seven or more members).



14, Y = OAc
15, Y = OH



16



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[7] P. W. Rabideau, J. B. Hamilton, and L. Friedman, *J. Amer. Chem. Soc.*, **90**, 4465 (1968).

[8] H. E. Zimmerman, R. S. Givens, and R. M. Pagni, *ibid.*, **90**, 4191, 6096 (1968).

[9] S. J. Cristol and G. O. Mayo, work in progress.

[10] R. L. Augustine, "Catalytic Hydrogenation," M. Dekker, Inc., New York, N. Y., 1965, pp 133–134, and references therein.

[11] F. S. Fawcett, *Chem. Rev.*, **47**, 219 (1950).

[12] J. R. Wiseman, *J. Amer. Chem. Soc.*, **89**, 5966 (1967).

Experimental Section[13]

7-Methylenedibenzobicyclo[2.2.2]octadiene (3).—To a solution of 7-chloromethyldibenzobicyclo[2.2.2]octadiene (**5**)[15] (5.00 g, 19.6 mmol) in 100 ml of dry dimethyl sulfoxide (decanted from molecular seives) was added potassium *t*-butoxide (4.0 g, 35 mmol). After 1 day, the solution was poured into ice-cold water. Extraction with ether followed, and the organic layer was washed with four portions of water and dried ($MgSO_4$). The solvent was removed by rotary evaporation and the residue was crystallized from 95% ethanol (charcoal). The product (3.91 g, 92% yield) had mp 102–104°. Pmr analysis indicated that the product contained about 90% olefin **3**[16] and about 10% 7-methyldibenzobicyclo[2.2.2]octatriene (**6**).

Photorearrangement of Olefin 3. A. In Acetone.—The olefin mixture (3.06 g, 14.0 mmol), prepared by dehydrohalogenation of the chloromethyl compound **5**, was dissolved in enough reagent grade acetone to completely fill a long-necked round-bottom quartz flask (about 500 ml). Nitrogen was bubbled through the solution for 20 min. The solution was irradiated for 1 week. The acetone was removed by rotary evaporation and the orange residue was chromatographed on Merck 71707 alumina in order to remove the colored material. A hydrocarbon mixture (812 mg) was eluted by petroleum ether (bp 60–70°). The mixture consisted of 17% olefin **3**, 70% cyclopropane **4** (19% yield), 4% cyclopropane **8**, and 9% cyclopropane **7** (pmr analysis). The cyclopropanes were separated from the olefin by chromatography on a 10% silver nitrate impregnated column of Merck 71707 alumina.[17] Good separation resulted when the weight ratio of support to olefin was about 30:1. The oily cyclopropanes were eluted by olefin-free petroleum ether (bp 60–70°) and hydrocarbon **3** was recovered by elution with benzene.

Olefin **3** (recovered in this way from several photoreactions) was purified by recrystallization from 95% ethanol to mp 104.5–106.0°; uv max (C_2H_5OH) 272 mμ (ϵ 1985), 265 (1630), and 259 (1080). This material (2.012 g, free of olefin **6** and the cyclopropanes) was irradiated for 5 days in 120 ml of reagent grade acetone. A pmr spectrum of the colorless oil (1.255 g, 62.4%) eluted during the chromatography on Merck 71707 alumina indicated the presence of olefin **3** (59.2%) and cyclopropane **4** (40.8%) only. The yield of **4** was therefore 512 mg (25.4% of theoretical) or 40.3% based on unrecovered starting material.

An analytical sample of cyclopropane **4**, mp 50.0–51.5°, was prepared by another chromatography on silver nitrate–alumina and a short-path distillation (80°, 0.6 mm): uv max (C_2H_5OH) 276 mμ (ϵ 1870), 269 (1950), and 258 (1340); pmr[18] H_{9s} (τ 8.97, doublet, J = 10 Hz, dihedral angle $H_6C_6C_9H_{9s} \simeq 90°$, shielded by cyclopropane ring[19]), H_{9a} (τ 7.04, doublet of doublets, J = 4, 10 Hz, geminal coupling and vicinal coupling with H_6, somewhat deshielded by cyclopropane ring), H_6 (τ 6.37, doublet, J = 4 Hz), H_3 (τ 7.80, doublet of doublets, J = 6, 8 Hz, cyclopropano and benzylic), and 2 H_2 (τ 8.23, doublet of doublets, J = 6, 7 Hz) (τ 9.23, doublet of doublets, J = 7, 8 Hz).

Anal. Calcd for $C_{17}H_{14}$: C, 93.53; H, 6.47. Found: C, 93.44; H, 6.51.

In other runs, it was found that a 4-day reaction time gave similar results. Also, the deaeration had no apparent effect on the yield.

B. In Benzene.—The mixture of olefins **3** and **6** (487 mg, *ca.* 90% **3** and 10% **6**) was irradiated at 2537 Å in 100 ml of thiophene-free benzene in a quartz tube for 5 days. Olefin **3** was converted into **4** in 21% yield, while the endocyclic olefin **6** was totally transformed to 2-methylcyclooctatetraene (pmr analysis).[9]

C. In Cyclohexane.—A solution of pure olefin **3** (397 mg, free of olefin **6**) in 35 ml of spectral grade cyclohexane was placed in a quartz tube. Prepurified nitrogen was bubbled through the solution for 20 min and then the solution was irradiated (2537 Å) under nitrogen for 3 days. At this time pmr analysis showed the presence of 43% cyclopropane **4** and 57% unreacted **3**.

Hydrogenation of Dibenzotricyclo[4.2.1.0^{1,3}]nonadiene (4).—Cyclopropane **4** (475 mg, 218 mmol) was hydrogenated in the presence of 10% palladium on charcoal (494 mg) in 50 ml of 95% ethanol at atmospheric pressure in the Brown[2] apparatus.[20] The reaction required about 4 hr. The catalyst was removed by filtration and the solvent was removed by rotary evaporation. The pmr spectrum indicated that no starting material remained and that the major product (>80%) was 5-methyldibenzobicyclo[3.2.1]octadiene (**12**). The colorless oil was crystallized from 95% ethanol, mp 47.5–50.0°. An analytical sample of **18** was sublimed (60°, 1.5 mm): pmr[15] 3 H (τ 8.55, singlet), H_1 (τ 6.13, doublet, J = 4 Hz), H_{4x} (τ 7.00, doublet, J = 17 Hz), H_{4n} (τ 7.42, doublet of doublets, J = 17, 1 Hz, geminal coupling and "W" [21] coupling with H_{8a}), H_{8a} (τ 7.73, multiplet, J = 4, 10, 1 Hz), and H_{8s} (τ 8.04, doublet, J = 10 Hz, geminal coupling).

Anal. Calcd for $C_{17}H_{16}$: C, 92.68; H, 7.32. Found: C, 92.80; H, 7.43.

Addition of Acetic Acid to Dibenzotricyclo[4.2.1.0^{1,3}]nonadiene (4).—Cyclopropane **4** (278 mg, 1.275 mmol) was dissolved in 16 ml of 0.1 *M* perchloric acid in acetic acid. The solution was allowed to stand at room temperature for 21 hr. The reaction was quenched by addition of water. The slurry was extracted by chloroform and the combined extracts were washed with water and aqueous sodium bicarbonate and dried ($MgSO_4$). The solvent was removed by rotary evaporation. A pmr spectrum of the oily residue showed only one acetate methyl singlet (τ 7.98), H_1 (τ 5.74, doublet, J = 7 Hz), and 6 $H_{4,5,9}$ (τ 7–9, unresolved multiplets). Spin decoupling showed only that H_1 couples with a proton, presumably H_{9a}, which absorbs at τ 7.3. Acetate **14** (dibenzobicyclo[4.2.1]nona-2,7-dien-6-ol acetate) was not purified but was saponified by potassium hydroxide (1.5 ml of a 1 *M* solution) in refluxing ethanol (20 ml) overnight. Most of the ethanol was removed by rotary evaporation. The residue was extracted by chloroform. The organic layer was washed with water until neutral and then dried ($MgSO_4$), filtered, treated with decolorizing charcoal, and filtered again. The chloroform was removed and dibenzobicyclo[4.2.1]nona-2,7-dien-6-ol (**15**) was crystallized from ethanol (charcoal) as needles: mp 161–163° (three more crystallizations raised this to 163–163.5°) (220 mg, 73% yield over-all): pmr H_1 (τ 5.89, doublet, J = 7.5 Hz), 7 $H_{4,5,9,OH}$ (τ 7 to 9, unresolved multiplet, expansion on HA-100 showed no singlet or doublet 3 H absorptions; H_1 couples with a proton, H_{9a}, which absorbs at τ 7.4).

Anal. Calcd for $C_{17}H_{16}O$: C, 86.41; H, 6.83. Found: C, 86.40; H, 6.89.

Attempted Acetylation of Dibenzobicyclo[4.2.1]nona-2,7-dien-6-ol (15).—Alcohol **15** (214 mg, 0.907 mmol), acetic anhydride (2.0 ml, 21 mmol), and 10 ml each of dry pyridine and benzene were combined and allowed to stand at room temperature for 2 days. The mixture was poured onto a slurry of ice and concentrated hydrochloric acid. After 1 hr the mixture was transferred to a separatory funnel with the aid of more benzene and the organic layer was washed with 10% hydrochloric acid and then sodium bicarbonate solution and finally dried ($MgSO_4$). The solvent was removed by rotary evaporation and the colorless solid residue was subjected to pmr analysis. Only absorptions due to starting material were observed in the spectrum.

The recovered alcohol **15** was then dissolved in 25 ml of a 0.1 *M* solution of perchloric acid in acetic acid. The solution was allowed to stand at room temperature overnight. Pmr analysis of the colorless solid, mp 158–160°, recovered from the reaction mixture indicated that only alcohol **15** was present.

Registry No.—**3**, 19978-14-4; **4**, 19978-15-5; **12**, 19978-16-6; **15**, 19978-17-7.

Acknowledgments.—This work was supported by the National Science Foundation. The authors wish to thank Professor A. D. Norman and Professor R. A. Newmark for help in interpretation of the pmr spectra.

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(13) Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. Melting points were taken on a Thomas–Hoover capillary melting point apparatus and are uncorrected. The irradiations were carried out in an air-cooled Rayonet[14] photoreactor using lamps emitting radiation mainly at 2537 Å. Ultraviolet spectra were obtained on a Cary 14 recording spectrometer. Proton magnetic resonance spectra were obtained on Varian A-60, A-60A, and HA-100 spectrometers. All chemical shifts are in τ units. Tetramethylsilane was used as an internal standard. The coupling constants given are observed values. Spin–decoupling experiments were conducted on the A-60A and HA-100 instruments.

(14) Southern New England Ultraviolet Co., Middletown, Conn.

(15) K. Alder and E. Windemuth, *Ber.*, **71**, 1939 (1938).

(16) V. J. Shiner and J. S. Humphrey, *J. Amer. Chem. Soc.*, **85**, 2416 (1963).

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(18) Compare with spectrum of dibenzobicyclo[3.2.1]octadiene in S. J. Cristol, J. R. Mohrig, and D. E. Plorde, *J. Org. Chem.*, **30**, 1956 (1965).

(19) D. J. Patel, M. E. H. Howden, and J. D. Roberts, *J. Amer. Chem. Soc.*, **85**, 3218 (1963), and references therein.

(20) Delmar Laboratories, Maywood, Ill.

(21) A. Rassat, C. W. Jefford, J. M. Lehn, and B. Waegell, *Tetrahedron Lett.*, 233 (1964).