# The Photochemistry of 7,8-Dimethylene-1,3,5-cyclooctatrienes. The Synthesis of Bicyclo[6.2.0]deca-1,3,5,7-tetraene[1]

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*Contribution from the University Chemical Laboratory,
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Abstract: Ultraviolet irradiation of 7,8-dimethylene-1,3,5-cyclooctatriene (**1**) led to bicyclo[6.2.0]deca-1,3,5,7-tetraene (**4**). Irradiation of 7-methylene-8-bromomethylene-1,3,5-cyclooctatriene (**2**) also gave **4**, as well as 5- (or 6-) methylene-6- (or -5-) bromomethylenetricyclo[5.1.0.0^{4,8}]oct-2-ene (**10**). Similar irradiation of 7-methylene-8-chloromethylene-1,3,5-cyclooctatriene (**3**) yielded 5- (or 6-) methylene-6- (or -5-) chloromethylenetricyclo[5.1.0.0^{4,8}]oct-2-ene (**11**) as well as 4- (or 5-) methylene-5- (or -4-) chloromethylene-*cis*-bicyclo[4.2.0]octa-2,7-diene (**12**). The structures **4**, **11**, and **12** were confirmed by catalytic hydrogenation. Diels–Alder reaction of **11** with dimethyl acetylenedicarboxylate led to dimethyl 2,3-benzotricyclo[5.1.0.0^{4,8}]octa-2,5-diene-10,11-dicarboxylate (**19**), a benz-fused derivative of semibullvalene (**20**). Similar Diels–Alder reaction of **12** with dimethyl acetylenedicarboxylate yielded a *ca.* 1:1 mixture of dimethyl 2,3-benzo-*cis*-bicyclo[4.2.0]octa-2,4,7-triene-10,11-dicarboxylate (**22**) and dimethyl benzocyclooctatetraene-10,11-dicarboxylate (**23**). Heating the mixture of **22** and **23** at 120° resulted in the complete conversion of **22** to **23**.

The syntheses of 7,8-dimethylene-1,3,5-cycloocta-triene (**1**), the 9-bromo derivative (**2**), and the 9-chloro derivative (**3**) were reported in the previous paper.[1] The results obtained by irradiating these substances are now described.[3] It was anticipated that the cyclobutene derivatives **4**, **5**, and **6**, respectively, would

1, R = H	**4**, R = H	**7**
2, R = Br	**5**, R = Br	
3, R = Cl	**6**, R = Cl	
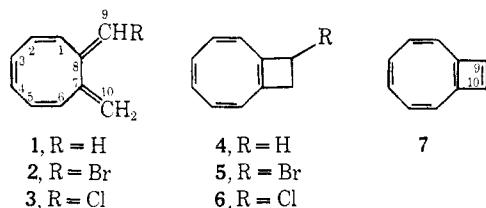
be obtained, since the photoinduced cyclization of conjugated dienes to cyclobutenes is a well-established reaction,[4] and the exocyclic double bonds in the starting materials had been found to be the most reactive in thermal cycloaddition reactions.[1] Substances **4**, **5**, and **6**, containing fused cyclooctatetraene and cyclobutene rings, are of interest *per se*, and are also potential precursors of the fully conjugated bicyclo[6.2.0]deca-1,3,5,7,9-pentaene (**7**). The last-mentioned substance is an isomer of naphthalene and azulene, and might represent an aromatic system.[5,6] In practice, we have found that irradiation of **1** indeed leads to **4**, the exocyclic double bonds being more photolabile than the endocyclic polyene system. On the other hand, introduction of the 9-chloro group deactivates the exocyclic diene grouping, and irradiation of **3** gave products de-

rived by reaction of the endocyclic double bonds. The behavior of the 9-bromo compound **2** on irradiation was more complex, both the hydrocarbon **4** and a product derived by reaction of the endocyclic double bonds being isolated.

Irradiation of a solution of **1** in methanol through silica with a Hanovia medium-pressure mercury vapor lamp in a nitrogen atmosphere at room temperature for 2 hr led to bicyclo[6.2.0]deca-1,3,5,7-tetraene (**4**), in 10% yield, as the only nonpolymeric product isolated. Substance **4** proved to be a yellow liquid, which was relatively stable in carbon tetrachloride solution at 0°, but rapidly decomposed in this solvent at 60° or in the neat
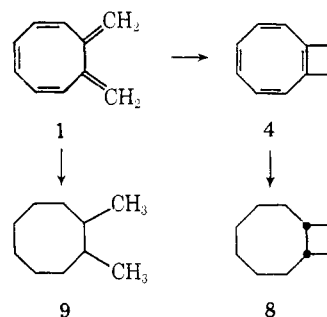
state at room temperature. The structural assignment **4** is based on the spectroscopic data and the results of catalytic hydrogenation.

The mass spectrum of **4** was very similar to that of the precursor **1**,[1] initially showing a molecular ion peak at m/e 130, a base peak at m/e 129, and other prominent peaks at m/e 128 and 115. However, **4** polymerized far more rapidly than **1**, and peaks of mass greater than the molecular ion became apparent after a sample of **4** had been permitted to remain in the mass spectrometer for several minutes. The electronic spectrum of **4**, in contrast to **1**,[1] showed no maximum above 220 nm, like cyclooctatetraene itself.[7] The infrared spectrum of **4** exhibited bands at 2920 and 2870 cm^{-1}, assigned to the C–H stretching vibrations of the methylene groups.[8]

(1) Unsaturated Eight-Membered Ring Compounds. VIII. For Part VII, see J. A. Elix, M. V. Sargent, and F. Sondheimer, *J. Am. Chem. Soc.*, **92**, 962 (1970).

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(3) For preliminary communications, see J. A. Elix, M. V. Sargent, and F. Sondheimer, *J. Am. Chem. Soc.*, **89**, 180, 5081 (1967).

(4) See R. Srinivasan, *ibid.*, **84**, 4141 (1962); K. J. Crowley, *Proc. Chem. Soc.*, **334** (1962); *Tetrahedron*, **21**, 1001 (1965).

(5) See A. Rosowsky, H. Fleischer, S. T. Young, R. Partsch, W. H. Saunders, and V. Boekelheide, *ibid.*, **11**, 121 (1960).

(6) Neither **7**, nor derivatives of **7**, were known when we commenced our work. Recently, the 9-*t*-butoxy, the 9,10-di-*t*-butoxy, and the 9-*t*-butoxy-10-chloro derivatives of **7** have been prepared [G. Schröder and H. Röttele, *Angew. Chem.*, **80**, 665 (1968)], as well as a tribenzo derivative [P. J. Garratt and R. H. Mitchell, *Chem. Commun.*, 719 (1968)].

(7) See A. C. Cope and C. G. Overberger, *J. Am. Chem. Soc.*, **70**, 1433 (1948); B. Ekström, *Chem. Ber.*, **92**, 749 (1959).

(8) See L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd ed, John Wiley & Sons, Inc., New York, N. Y., 1958.

The nmr spectrum of **4** (CCl₄, 100 MHz) showed a complex multiplet (6 H) at τ 4.38–4.72 due to the olefinic protons and a sharp singlet (4 H) at 7.62 due to the methylene protons.
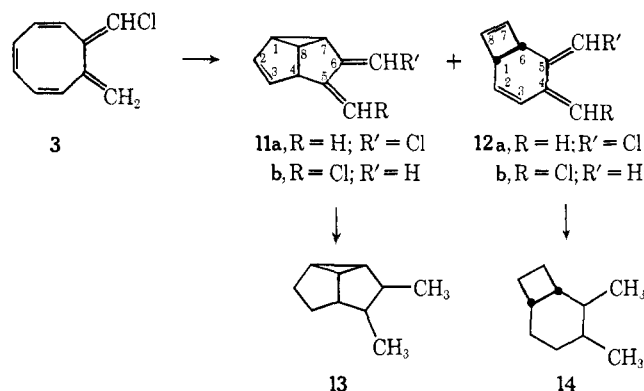
Hydrogenation of **4** in methanol over platinum resulted in the uptake of 3.9 molar equiv of hydrogen, and led to bicyclo[6.2.0]decane (presumably the *cis* isomer **8**)[9] as a colorless liquid which was homogeneous by vapor phase chromatography. The mass spectrum of **8** exhibited the expected molecular ion peak at *m/e* 138. The nmr spectrum (CCl₄, 100 MHz) showed only a broad band at τ 7.7–8.7 due to the methylene and methine protons, resonances due to olefinic or methyl protons being absent. By contrast, substance **1** on hydrogenation absorbed 4.8 molar equiv of hydrogen; the resulting 1,2-dimethylcyclooctane (**9**)[10] had a molecular ion peak at *m/e* 140 in the mass spectrum, and methyl proton resonances (6 H) at τ 9.11 and 9.18 in the nmr spectrum.

Attempts were made to convert **4** to the 9-bromo derivative **5** (*e.g.*, by bromination with N-bromosuccinimide), since subsequent dehydrobromination was then expected to lead to the fully conjugated bicyclo[6.2.0]-deca-1,3,5,7,9-pentaene (**7**). These experiments were unsuccessful, and we therefore decided to investigate whether irradiation of 7-methylene-8-bromomethylene-1,3,5-cyclooctatriene (**2**) would provide an alternative route to the bromo compound **5**. In practice, irradiation of **2** under the conditions used with **1** gave the hydrocarbon **4** as major product (*ca.* 7%). The conversion of **2** to **4** must involve photochemical cleavage of the C–Br bond, although it is not known whether this occurs before or after cyclization. A minor product (*ca.* 1%), which was not separated from **4**, proved to be

2 → **4** +

10a, R = H; R′ = Br
b, R = Br; R′ = H
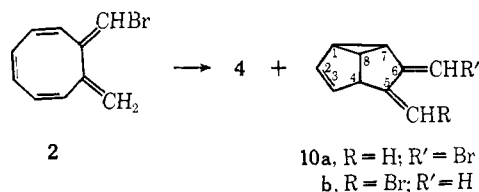
5-methylene-6-bromomethylenetricyclo[5.1.0.0⁴,⁸]oct-2-ene (**10a**) or the 5-bromomethylene-6-methylene isomer (**10b**), as evidenced by the great similarity of the nmr spectrum with that of the corresponding chloro compound **11** (see below and Experimental Section).

It was expected that the C–Cl bond in 7-methylene-8-chloromethylene-1,3,5-cyclooctatriene (**3**) would be more resistant to photochemical cleavage than the C–Br bond in **2**, and the irradiation of **3** was therefore investigated. As expected, no appreciable C–Cl bond cleavage occurred, but the endocyclic triene system in **3** was now more photolabile than the exocyclic chlorodiene system. The photoreaction gave rise to 10.9% of 5-methylene-6-chloromethylenetricyclo[5.1.0.0⁴,⁸]oct-2-ene (**11a**) or the 5-chloromethylene-6-methylene isomer (**11b**), as well as 2.8% of 4-methylene-5-chloromethyl-ene-*cis*-bicyclo[4.2.0]octa-2,7-diene (**12a**) or the 4-chloromethylene-5-methylene isomer (**12b**) as unstable pale yellow liquids. The structures **11** and **12** are based on the spectroscopic properties and reactions of the sub-

(9) Other syntheses of **8** have been reported since this work was carried out [S. Masamune, C. G. Chin, K. Hojo, and R. T. Seidner, *J. Am. Chem. Soc.*, **89**, 4804 (1967)].

(10) A. C. Cope and H. C. Campbell, *ibid.*, **74**, 179 (1952).

3 → **11a, R = H; R′ = Cl** + **12a, R = H; R′ = Cl**
b, R = Cl; R′ = H   **b, R = Cl; R′ = H**

13   **14**

stances, but in neither case was it possible to determine which of the two exocyclic carbon atoms was bonded to chlorine.

The high-resolution mass spectra of both **11** and **12** showed the expected molecular ion peaks. The infrared spectrum of **11** exhibited a prominent peak at 880 cm⁻¹, assigned to the exomethylene group.[8] The nmr spectrum (CCl₄, 100 MHz) of **11** was particularly instructive; it consisted of a singlet (1 H) at τ 3.72 (exomethine proton), two quartets (1 H each) at 4.44 and 4.63 (protons 2 and 3; $J_{2,3}$ = 5 Hz, $J_{2,1}$ = $J_{3,4}$ = 1 Hz), two singlets (1 H each) at 5.28 and 5.50 (exomethylene protons), a quartet (1 H) at 6.44 (proton 4; $J_{4,8}$ = 6 Hz, $J_{4,3}$ = 1 Hz), a quartet (1 H) at 7.33 (proton 8; $J_{8,1}$ = $J_{8,4}$ = $J_{8,7}$ = 6 Hz) partially overlapping with a triplet (1 H) at 7.50 (proton 7; $J_{7,1}$ = $J_{7,8}$ = 6 Hz), as well as a sextet (1 H) at 7.71 (proton 1; $J_{1,7}$ = $J_{1,8}$ = 6 Hz, $J_{1,2}$ = 1 Hz).

The infrared spectrum of **12** showed bands at 1560 cm⁻¹ assigned to the C=C stretching vibration of the cyclobutene ring, as well as at 900 and 890 cm⁻¹ due to the exomethylene group.[8] The nmr spectrum (CCl₄, 60 MHz) of **12** consisted of two narrow bands (ratio *ca.* 1:4; total 1 H) at τ 3.37 and 3.55 (exomethine proton), a multiplet (4 H) at 3.75–4.10 (olefinic ring protons), two narrow bands (1 H each) at 4.86 and 5.11 (exomethylene protons), and a multiplet (2 H) at 6.24–6.51 (bridgehead protons). The fact that the exomethine proton gives rise to two bands in a ratio of *ca.* 1:4 indicates that **12** is a *ca.* 1:4 mixture of two isomers. We believe that these are most probably stereoisomers, since the precursor **3** consisted of a mixture of stereoisomers,[1] but the possibility that they are positional isomers (**12a** and **12b**) cannot be excluded.

The structures **11** and **12** were confirmed by catalytic hydrogenation. Reduction of **11** in methanol over a palladium–calcium carbonate catalyst resulted in hydrogenolysis of the chlorine group in addition to saturation of the double bonds. The main product was 2,3-dimethyltricyclo[5.1.0.0⁴,⁸]octane (**13**), a colorless liquid which exhibited the expected molecular ion peak at *m/e* 136 in the mass spectrum. Compound **13** was contaminated with *ca.* 5% of another substance, which showed a molecular ion peak at *m/e* 138 in the mass spectrum. This substance was the major product when the reduction of **11** was carried out in acetic acid over platinum, and presumably arose by cleavage of the cyclopropane ring. Hydrogenation of **12** in methanol over palladium–calcium carbonate also resulted in hydrogenolysis of the chlorine group; the product was 2,3-dimethyl-*cis*-bicyclo[4.2.0]octane (**14**), a colorless

liquid showing the expected molecular ion peak at m/e 138 in the mass spectrum.

The course of the photorearrangement of 3 is not without precedent, since irradiation of 1,3,5-cyclooctatriene (15) is known to give tricyclo[5.1.0.0^{4,8}]oct-2-ene (16) and cis-bicyclo[4.2.0]octa-2,7-diene (17), as well as other products.[11,12] The cis stereochemistry of the

15   16   17
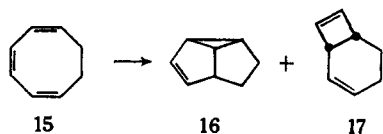
ring junction in 12 is assigned by analogy with 17, and this is the stereochemistry to be expected from orbital symmetry considerations.[13]

Although compounds 11 and 12 are of no value for the synthesis of 7, they could be converted to interesting benz-fused derivatives by Diels–Alder reaction of the exocyclic diene systems with dimethyl acetylenedicarboxylate. Thus, treatment of 11 with this ester in boiling cyclohexane gave 91% of dimethyl 2,3-benzotricyclo[5.1.0.0^{4,8}]octa-2,5-diene-10,11-dicarboxylate (19) as a colorless liquid. This reaction presumably involves the adduct 18a or 18b as an intermediate, which undergoes dehydrochlorination under the reaction condi-


18a, R = H; R' = Cl
b, R = Cl; R' = H

19

20   19a
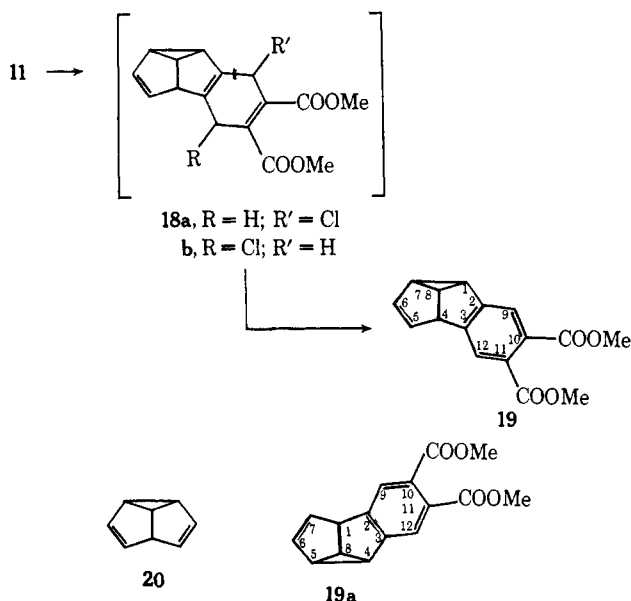
tions. The nmr spectrum (CCl$_4$, 100 MHz) of 19 substantiated the structural assignment, showing two singlets (1 H each) at τ 2.41 and 2.64 (protons 9 and 12), a quartet (1 H) at 4.40 (proton 5; $J_{5,6}$ = 5.5 Hz, $J_{5,4}$ = 2.5 Hz), a quartet (1 H) at 4.79 (proton 6; $J_{6,5}$ = 5.5 Hz, $J_{6,7}$ = 2.5 Hz), a quartet (1 H) at 6.08 (proton 4; $J_{4,8}$ = 6.5 Hz, $J_{4,5}$ = 2.5 Hz), a singlet (6 H) at 6.18 (methyl protons), a quartet (1 H) at 6.68 (proton 8; $J_{8,1}$ = $J_{8,4}$ = $J_{8,7}$ = 6.5 Hz), a triplet (1 H) at 6.91 (pro-

ton 1; $J_{1,7}$ = $J_{1,8}$ = 6.5 Hz), and a sextet (1 H) at 7.19 (proton 7; $J_{7,1}$ = $J_{7,8}$ = 6.5 Hz, $J_{7,6}$ = 2.5 Hz).

Compound 19 is a benz-fused derivative of semibullvalene (20).[14,15] The degenerate Cope rearrangement which occurs in 20 is precluded in 19 by the fused benzene ring. Although vinylcyclopropyl rearrangement of 19 to 19a appears possible, it could not be detected by nmr spectroscopy at room temperature or at 100° (the nmr spectrum in toluene-d_8 at 100° was essentially identical with that at room temperature).

Reaction of 12 with dimethyl acetylenedicarboxylate in boiling cyclohexane led to 52% of a pale yellow liquid, consisting of an inseparable mixture (ca. 1:1) of dimethyl 2,3-benzo-cis-bicyclo[4.2.0]octa-2,4,7-triene-10,11-dicarboxylate (22) and dimethyl benzocycloocta-

12 →

21a, R = H; R' = Cl
b, R = Cl; R' = H

22   +   23
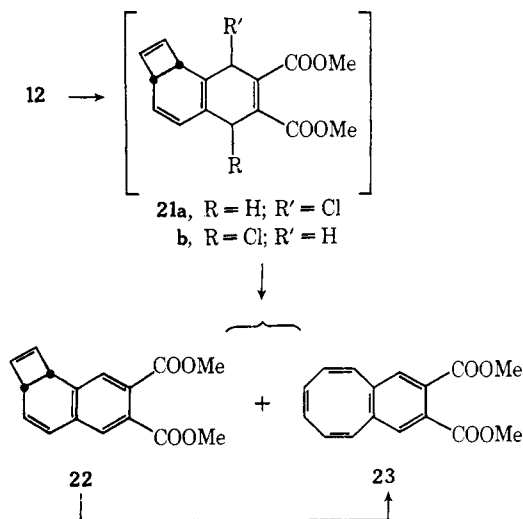
tetraene-10,11-dicarboxylate (23).[1] These substances are presumably derived from the primary adduct 21a or 21b, which undergoes dehydrochlorination under the reaction conditions. The structural assignments are based mainly on the nmr spectrum (CCl$_4$, 100 MHz) of the mixture, which showed all the bands of authentic 23,[1] as well as the following ones assigned to 22: two singlets at τ 2.55 and 2.63 (benzenoid protons), a multiplet at ca. 4.0 (olefinic protons), and a multiplet at ca. 6.2 (bridgehead protons). The electronic spectrum (λ_{max}^{ether} 238 and 290 nm; relative optical density, ca. 6:1) also supported the assigned structures, the lower wavelength maximum being assigned to 23,[1] and the higher one to 22.

The benzocyclooctatetraene derivative 23 presumably arose by valence tautomerism of 22. This was confirmed by the observation that boiling a solution of the mixture of 22 and 23 in tetrachloroethylene (bp 121°) for 72 hr resulted in the complete conversion of 22 to 23. Hence, the 2,3-benzobicyclo[4.2.0]octa-2,4,7-triene derivative 22 exhibits thermal stability to valence tautomerism intermediate between that of the parent cis-bicyclo[4.2.0]octa-2,4,7-triene (24) (which undergoes

(11) W. R. Roth and B. Peltzer, Angew. Chem., 76, 378 (1964); Ann., 685, 56 (1965); J. Zirner and S. Winstein, Proc. Chem. Soc., 235 (1964); O. L. Chapman, G. W. Borden, R. W. King, and B. Winkler, J. Am. Chem. Soc., 86, 2660 (1964).

(12) For the mechanism of the reaction leading to cyclopropane derivatives from conjugated trienes, see J. Meinwald and P. H. Mazzocchi, ibid., 89, 1755 (1967).

(13) See R. B. Woodward, Special Publication No. 21, The Chemical Society, London, 1967, p 217; R. Hoffmann and R. B. Woodward, Accounts Chem. Res., 1, 17 (1968).

(14) See H. E. Zimmerman and G. L. Grunewald, J. Am. Chem. Soc., 88, 183 (1966); H. E. Zimmerman, R. W. Binkley, R. S. Givens, G. L. Grunewald, and M. A. Sherwin, ibid., 91, 3316 (1969).

(15) Since our work was published in preliminary form (ref 3), the synthesis of the unsubstituted benzosemibullvalene by irradiation of benzobarrelene has been described [H. E. Zimmerman, R. S. Givens, and R. M. Pagni, ibid., 90, 4191, 6096 (1968); P. W. Rabideau, J. B. Hamilton, and L. Friedman, ibid., 90, 4465 (1968)].

rapid tautomerism at 0°)[16] and of the 2,3:4,5-dibenzo derivative 25 (which requires heating at 350°).[17]
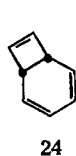
24
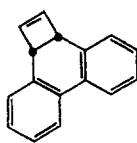
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Experimental Section[18]

Irradiation of 7,8-Dimethylene-1,3,5-cyclooctatriene (1). A solution of 7,8-dimethylene-1,3,5-cyclooctatriene (1, 220 mg)[1] in methanol (500 ml) was irradiated with a Hanovia medium-pressure mercury vapor lamp (2 A, 125 W) through silica for 2 hr at room temperature in an atmosphere of nitrogen. The solution was poured into water (1 l.) and extracted with ether. The extract was washed several times with water, dried (MgSO₄), and evaporated under reduced pressure (outer temperature not above 25°). The product was adsorbed onto a column of silicic acid (Mallinckrodt, 15 × 3 cm), which was developed with pentane; 50-ml fractions were collected. A yellow band moved slowly down the column and was collected in fractions 7–9. Cautious evaporation of these fractions yielded bicyclo[6.2.0]deca-1,3,5,7-tetraene (4, 22 mg, 10%) as a mobile yellow liquid: infrared spectrum (film), bands at 3010 (s), 2920 (s), 2870 (m), 1635 (m), 1620 (m), 1445 (m), 1430 (m), 795 (m), 785 (m), 760 (s), and 685 cm⁻¹ (m); electronic spectrum (ethanol), no maximum above 220 nm; nmr and mass spectra, see Discussion. On exposure of the neat liquid to daylight and air at room temperature, *ca.* 60% decomposition had occurred after 4 min and 90% after 30 min (as determined by weighing the amount of ether-soluble product).

Hydrogenation of Bicyclo[6.2.0]deca-1,3,5,7-tetraene (4). A solution of 4 (18 mg) in methanol (10 ml) was added to a suspension of prereduced platinum oxide (30 mg) in methanol (30 ml). The mixture was stirred in hydrogen at atmospheric pressure and room temperature until uptake ceased (3.9 molar equiv of hydrogen absorbed in 6 hr). Water was then added and the product was extracted with ether. The extract was washed repeatedly with water, dried (MgSO₄), and evaporated, to yield *cis*-bicyclo[6.2.0]decane (8, 13.5 mg, 71%) as a colorless liquid with a decalin-like odor; nmr and mass spectra, see Discussion. Vapor phase chromatography, using a 6 ft × ⅛ in. column (10% Apiezon L on 60–80 W support) at a column temperature of 145°, an injector temperature of 210°, and a hydrogen flow rate of 70 ml/min, showed that 8 was homogeneous. Under these conditions, the retention times of *trans*-decalin, *cis*-decalin, and 8 were 5.2, 6.5, and 6.9 min, respectively.

Hydrogenation of 7,8-Dimethylene-1,3,5-cyclooctatriene (1). A solution of 1 (35 mg) in glacial acetic acid (10 ml) was added to a suspension of prereduced platinum oxide (30 mg) in glacial acetic acid (30 ml). The mixture was stirred in hydrogen at atmospheric pressure and room temperature until uptake ceased (4.8 molar equiv of hydrogen absorbed in 4 hr). Water was then added and the product was extracted with ether. The extract was washed with water and repeatedly washed with saturated sodium bicarbonate solution. The extract was dried (MgSO₄) and evaporated. Distillation at 100° (bath temperature) (50 mm) gave 1,2-dimethylcyclooctane (9, 23 mg, 61%) as a colorless liquid, homogeneous by vapor phase chromatography: n^{20}D 1.4542 (lit.[10] n^{25}D 1.4558); nmr spectrum (CCl₄, 100 MHz), complex series of peaks at τ 8.20–8.73 (14 H, methine and methylene protons) and singlets at 9.11 and 9.18 (3 H each, methyl protons); mass spectrum, molecular ion peak at *m/e* 140.

Irradiation of 7-Methylene-8-bromomethylene-1,3,5-cyclooctatriene (2). A solution of 2 (260 mg)[1] in methanol (250 ml) was irradiated for 2 hr as described above for 1. The product, isolated with ether as previously, was adsorbed onto a column of silicic acid (Mallinckrodt, 15 × 2.5 cm); the column was developed with pentane, 100-ml fractions being collected. Fractions 6 and 7 gave bicyclo[6.2.0]deca-1,3,5,7-tetraene (4, 8 mg), which had infrared and nmr spectra identical with those of the material obtained by

irradiation of 1. Fractions 8 and 9 yielded an approximately 1:1 mixture (7 mg) of 4 (*ca.* 7% total yield) and 5- (or 6-) methylene-6- (or -5-) bromomethylenetricyclo[5.1.0.0⁴,⁸]oct-2-ene (10, *ca.* 1.3% yield); nmr spectrum (CCl₄, 100 MHz), bands of 4 and following bands due to 10: singlet at τ 3.55 (1 H, exomethine proton), two quartets at 4.36 and 4.66 (1 H each, protons 2 and 3), two singlets at 5.22 and 5.42 (1 H each, exomethylene protons), quartet at 6.33 (1 H, proton 4), and multiplet at 7.24–7.80 (3 H, protons 1, 7, and 8); mass spectrum, peaks at *m/e* 210 and 208 (molecular ions of 10), as well as at 130, 129, 128, and 115 (due to 4).

Further elution of the column gave several other products which were not identified.

Irradiation of 7-Methylene-8-chloromethylene-1,3,5-cyclooctatriene (3). A solution of 3 (230 mg)[1] in ether (500 ml) was irradiated as above for 2 hr. The solutions from three such experiments were combined and evaporated under reduced pressure (bath not above 25°). The product was adsorbed onto a column of silicic acid (Mallinckrodt, 30 × 2.75 cm), which was developed with pentane; 50-ml fractions were collected. Fractions 3 and 4 on careful evaporation afforded 4- (or 5-) methylene-5- (or -4-) chloromethylene-*cis*-bicyclo[4.2.0]octa-2,7-diene (12, 19 mg, 2.8%) as a pale yellow liquid: infrared spectrum (CCl₄), bands at 3130 (w), 3070 (m), 3050 (s), 1620 (m), 1560 (m), 1380 (m), 1270 (m), 920 (s), 900 (s), 890 (m), 860 (s), and 690 cm⁻¹ (s); electronic spectrum (ethanol), λ_{max} 262 nm (ε 9600); nmr spectrum, see Discussion; mass spectrum, molecular ion peaks at *m/e* 166.036 and 164.039 (calcd for $^{12}C_{10}{}^1H_9{}^{37}Cl$: 166.036; calcd for $^{12}C_{10}{}^1H_9{}^{35}Cl$: 164.039).

Fractions 7–9 on evaporation yielded 5- (or 6-) methylene-6- (or -5-) chloromethylenetricyclo[5.1.0.0⁴,⁸]oct-2-ene (11, 75 mg, 10.9%) as a pale yellow liquid: infrared spectrum (CCl₄), bands at 3060 (m), 3040 (m), 3010 (m), 1620 (m), 1430 (s), 1375 (m), 1345 (m), 1320 (m), 920 (m), 910 (m), and 880 cm⁻¹ (s); electronic spectrum (ethanol), λ_{max} 264 nm (ε 5900); nmr spectrum, see Discussion; mass spectrum, molecular ion peaks at *m/e* 166.036 and 164.039 (calcd for $^{12}C_{10}{}^1H_9{}^{37}Cl$: 166.036; calcd for $^{12}C_{10}{}^1H_9{}^{35}Cl$: 164.039).

Hydrogenation of 5- (or 6-) Methylene-6- (or -5-) chloromethylenetricyclo[5.1.0.0⁴,⁸]oct-2-ene (11). A. With Palladium–Calcium Carbonate in Methanol. A solution of 11 (26 mg) in ethanol (10 ml) was added to a suspension of 10% palladium–calcium carbonate (100 mg) in methanol (30 ml). The mixture was stirred in hydrogen at atmospheric pressure and room temperature for 24 hr, when 3.7 molar equiv of hydrogen had been absorbed. Water was then added and the product was extracted with ether. The extract was washed repeatedly with water, dried (MgSO₄), and evaporated, to yield 2,3-dimethyltricyclo[5.1.0.0⁴,⁸]octane (13, 13 mg, 60%) as a colorless liquid: mass spectrum, prominent peak at *m/e* 136 (due to 13) and weak peak at *m/e* 138 (due to contaminant). Vapor phase chromatography under the conditions described for 8 indicated a purity of 95% (retention time, 3.9 min), 5% of another substance (retention time, 4.8 min) being present.

B. With Platinum in Acetic Acid. A solution of 11 (12 mg) in glacial acetic acid (10 ml) was added to a suspension of prereduced platinum oxide (100 mg) in glacial acetic acid (30 ml), and the mixture was stirred in hydrogen at atmospheric pressure and room temperature for 24 hr. Water was then added and the product was extracted with ether. The extract was washed with water and several times with saturated sodium bicarbonate solution. Evaporation of the dried (MgSO₄) extract gave a colorless liquid (6 mg, 60%); mass spectrum, prominent peak at *m/e* 138, weak peak at *m/e* 136. Vapor phase chromatography as before indicated the contaminant mentioned in A (retention time, 4.8 min) to be the major component, and substance 13 (retention time, 3.9 min) to be the minor component.

Hydrogenation of 4- (or 5-) Methylene-5- (or -4-) chloromethylene-*cis*-bicyclo[4.2.0]octa-2,7-diene (12). A solution of 12 (10 mg) in methanol (10 ml) was added to a suspension of 10% palladium–calcium carbonate (100 mg) in methanol (30 ml), and the mixture was stirred in hydrogen at atmospheric pressure and room temperature for 24 hr. Water was then added and the product was extracted with ether. The extract was washed repeatedly with water, dried (MgSO₄), and evaporated, to give 2,3-dimethyl-*cis*-bicyclo[4.2.0]octane (14, 6 mg, 71%) as a colorless liquid with a decalin-like odor; mass spectrum, prominent molecular ion peak at *m/e* 138. Vapor phase chromatography under the conditions described for 8 indicated 14 to be homogeneous (retention time, 5.4 min).

Reaction of 5- (or 6-) Methylene-6- (or -5-) chloromethylenetricyclo[5.1.0.0⁴,⁸]oct-2-ene (11) with Dimethyl Acetylenedicarboxylate. A solution of 11 (40 mg) and dimethyl acetylenedicarboxylate (50 mg) in cyclohexane (10 ml) was boiled under reflux for 48 hr. The

(16) R. Huisgen and F. Mietzsch, *Angew. Chem.*, 76, 36 (1964); E. Vogel, H. Keefer, and W. Roth, *ibid.*, 76, 432 (1964).

(17) E. Vogel, W. Frass, and J. Wolpers, *ibid.*, 75, 979 (1963).

(18) For general procedures, see ref 1.

solvent was then evaporated under reduced pressure and the residue was chromatographed on a column of silica gel (B.D.H., 40 × 2 cm). The column was developed with 1.75 l. of pentane–ether (9:1) and then with pentane–ether (1:1), 100-ml fractions being collected. Fractions 18–26 on evaporation afforded dimethyl 2,3-benzotricyclo[5.1.0.0^{4,8}]octa-2,5-diene-10,11-dicarboxylate (19, 60 mg, 91%) as a colorless liquid. The analytical sample was obtained by thin layer chromatography on silica gel plates (Merck kieselgel HF$_{254+366}$, 20 × 20 × 0.09 cm), developed with pentane–ether (9:1): infrared spectrum (CCl$_4$), bands at 2995 (w), 2950 (s), 1732 (vs), 1435 (s), 1355 (m), 1280 (s), 1200 (s), 1140 (m), 1115 (s), 1095 (m), 1030 (m), and 825 cm^{-1} (m); electronic spectrum (ethanol), λ_{max} 218 nm (ϵ 26,800) and λ_{infl} ca. 270 nm (ϵ 7000); nmr spectrum, see Discussion; mass spectrum, molecular ion peak at m/e 270.

Anal. Calcd for C$_{16}$H$_{14}$O$_4$: C, 71.10; H, 5.22. Found: C, 70.64; H, 5.22.

Reaction of 4- (or 5-) Methylene-5- (or -4-) chloromethylene-cis-bicyclo[4.2.0]octa-2,7-diene (12) with Dimethyl Acetylenedicarboxylate. A solution of 12 (14 mg) and dimethyl acetylenedicarboxylate (20 mg) in cyclohexane (5 ml) was boiled under reflux for 48 hr. The solvent was then evaporated under reduced pressure, and the residue was adsorbed onto a thin layer plate (Merck kieselgel HF$_{254+366}$, 20 × 20 × 0.09 cm), which was developed with pentane–ether (9:1). Three bands could be detected under ultraviolet light, the first in order of elution being due to unchanged 12 and the second to dimethyl acetylenedicarboxylate. The third band on extraction with chloroform, filtration, and evaporation

gave a pale yellow liquid (12 mg, 52%) consisting of about equal parts of dimethyl 2,3-benzobicyclo[4.2.0]octa-2,4,7-triene-10,11-dicarboxylate (22) and dimethyl benzocyclooctatetraene-10,11-dicarboxylate (23),[1] as evidenced by careful examination of the nmr spectrum (see Discussion): electronic spectrum (ether), λ_{max} 238 and 290 nm (relative optical density, ca. 6:1); mass spectrum, prominent molecular ion peak at m/e 270. The mixture of 22 and 23 could not be separated by thin layer chromatography on silica gel or alumina plates in a variety of solvent systems.

Valence Tautomerism of Dimethyl 2,3-Benzobicyclo[4.2.0]octa-2,4,7-triene-10,11-dicarboxylate (22) to Dimethyl Benzocyclooctatetraene-10,11-dicarboxylate (23). A solution of the 1:1 mixture of 22 and 23 (8 mg) in tetrachloroethylene (10 ml) was boiled under reflux for 72 hr. Removal of the solvent under reduced pressure gave 23 (8 mg), the infrared, electronic, nmr, and mass spectra of which were identical with those of an authentic sample.[1] Thin layer chromatography indicated that no decomposition had occurred during the reaction.

The Synthesis of [3,4-c]Furooctalene, [1,2:5,6]Di[c]furocyclooctatetraene, and 1,2-Benzo[5,6-c]furocyclooctatetraene[1]
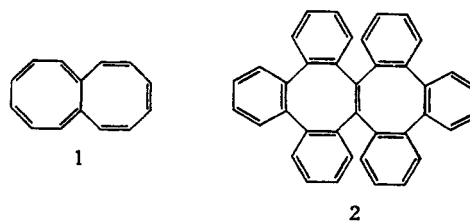
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Abstract: Oxidation of 1,2-bis(hydroxymethyl)cyclooctatetraene (3) with manganese dioxide gave cyclooctatetraene-1,2-dicarboxaldehyde (4), besides other products. Wittig reaction of 4 with furan-3,4-bis(methylenetriphenylphosphonium chloride) (9) and lithium ethoxide led to [3,4-c]furooctalene (10). The spectral properties of 10 show that the eight-membered rings are nonplanar and do not possess delocalized π electrons. Diels–Alder reaction of 10 with dimethyl fumarate yielded a monoadduct (12), derived by addition to the terminal eight-membered ring. Wittig reaction of furan-3,4-dicarboxaldehyde (13) with the furan salt 9 gave [1,2:5,6]di[c]furocyclooctatetraene (14). The related dimethyl [1,2:5,6]di[c]furocyclooctatetraene-3,8-dicarboxylate (16) was obtained by the reaction between 13 and furan-3,4-diacetic acid (15). Wittig reaction between o-phthalaldehyde (19) and the furan salt 9 led to 1,2-benzo[5,6-c]furocyclooctatetraene (20), a substance which was also obtained by the reaction between furan-3,4-dicarboxaldehyde (13) and o-xylylenebis(triphenylphosphonium bromide) (7). Diels–Alder reaction of 14 and 20 with dimethyl fumarate gave adducts (18 and 21, respectively) derived by addition to the furan rings.

Octalene (bicyclo[6.6.0]tetradecaheptaene, 1) is a compound of considerable interest. It is a 14-π-electron system, formally derived from [14]annulene[3] by formation of a cross-linkage, and calculations made some time ago indicated it to be an aromatic system.[4] However, more recent theoretical work has led to the

conclusion that octalene in fact should not be aromatic.[5] The only derivative of octalene known when we commenced our work was hexabenzoctalene (2),[6] the properties of which threw no light on the possible aromaticity

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(1) Unsaturated Eight-Membered Ring Compounds. IX. For Part VIII, see J. A. Elix, M. V. Sargent, and F. Sondheimer, *J. Am. Chem. Soc.*, 92, 969 (1970).

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(3) See F. Sondheimer, *Proc. Roy. Soc.* (London), A297, 173 (1967), and references cited therein.

(4) D. P. Craig, *J. Chem. Soc.*, 3175 (1951); A. Rosowsky, H. Fleischer, S. T. Young, R. Partsch, W. H. Saunders, and V. Boekelheide, *Tetrahedron*, 11, 121 (1960); A. Streitwieser, "Molecular Orbital Theory for Organic Chemists," John Wiley & Sons, Inc., New York, N. Y., 1961, Chapter 10.

(5) M. J. S. Dewar and G. J. Gleicher, *J. Am. Chem. Soc.*, 87, 685 (1965); N. L. Allinger and C. Gilardeau, *Tetrahedron*, 23, 1569 (1967).

(6) W. Tochtermann, *Angew. Chem.*, 75, 418 (1963).