Anal. Calcd for $C_{10}H_{16}$: C, 88.16; H, 11.84. Found: C, 88.01; H, 11.72.

1-Phenylbicyclo[3.3.1]nonane (35). A solution of 122 mg (1.0 mmol) of **13** and 4 ml of phenyllithium (Foote Co., 1.91 *M* benzene–ether, 70:30) in 25 ml of pentane was refluxed for 60 hr. The disappearance of alkene was followed by vpc (20% carbowax–10% KOH on Chromosorb W, 5 ft × 1/4 in.). The mixture was hydrolyzed; the pentane layer was separated, dried (Na_2SO_4), and concentrated. Analysis by vpc showed five products; the first four were shown to be derived from hydrolysis of phenyllithium, the latter being 1-phenylbicyclo[3.3.1]nonane. Collection of **35** by preparative vpc afforded 65 mg (33%); nmr (CCl_4) τ 2.82 (5 H), 7.65–9.4 (15 H).

Anal. Calcd for $C_{15}H_{20}$: C, 89.94; H, 10.06. Found: C, 89.74; H, 10.17.

Ethyl Cyclohexanol-3-propionate. 3-Hydroxycinnamic acid[36] (82 g, 0.5 mol) was hydrogenated in ethanol using ruthenium oxide as a catalyst.[37] The catalyst was removed by filtration and the crude product isolated by evaporation of the ethanol. Distillation of the crude product gave 75 g (75%) of ethyl cyclohexanol-3-propionate, bp 145–148° (2.75 mm); ir γ_{max} 3650, 3600–3200 broad, 1735 cm^{-1}; nmr τ 6.01 (2 H, q, J = 7), 6.5–7.0 (1 H, broad), 7.37 (1 H, s), 7.8 (t, J = 7, overlapping other resonance), 7.6–9.0 (16 H), 8.8 (t, J = 7).

Anal. Calcd for $C_{11}H_{20}O_3$: C, 65.97; H, 10.07. Found: C, 65.86; H, 10.16.

Ethyl Cyclohexanone-3-propionate. A solution of 20 g (0.10 mol) of ethyl cyclohexanol-3-propionate in 100 ml of reagent grade acetone was cooled to 0°. A solution of 113 g of CrO_3, 115 ml of H_2SO_4, and 500 ml of water (Jones Reagent) was added with stirring until the solution remained orange-brown in color (35 ml). Ethyl cyclohexanone-3-propionate was isolated in 76% yield (15.0 g); ir γ_{max} 1720, 1740 cm^{-1}; nmr τ 5.95 (2 H, q, J = 7), 7.5–8.6 (13 H, complex), 8.76 (3 H, t, J = 7).

Anal. Calcd for $C_{11}H_{18}O_3$: C, 66.64; H, 9.15; O, 24.21. Found: C, 66.69; H, 9.15.

Methyl Cyclohexanone-3-propionate (22). To 1.0 g (0.005 mol) of ethyl cyclohexanone-3-propionate was added 25 ml of methanol and a catalytic amount of hydrochloric acid. The solution was refluxed for 2 hr, cooled, and the solvent removed on a rotary evaporator. The residue was dissolved in ether, washed with 5% sodium bicarbonate solution, and dried (Na_2SO_4). Removal of solvent gave 0.80 g (89%) of the crude keto methyl ester. Purification of a small sample was effected by preparative vpc: ir γ_{max} 1720, 1745 cm^{-1}; nmr τ 6.58 (3 H, s), 7.6–9.16 (13 H, complex).

Anal. Calcd for $C_{10}H_{16}O_3$: C, 65.19; H, 8.75; O, 26.05. Found: C, 65.29; H, 8.77.

Oxidation of Bicyclo[3.3.1]non-1-ene. The method is that of von Rudloff.[38] A solution of 122 mg (1.0 mmol) of **13** in 10 ml of pentane was stirred overnight at room temperature with a solution of 3.2 g of sodium periodate, 0.15 g of potassium permanganate, and 5.0 g of potassium carbonate in 65 ml of water. The acidic product of this reaction was isolated and treated with a solution of diazomethane in ether. The solvent was removed, and vpc analysis of the residue showed that the major product was methyl cyclohexanone-3-propionate **22**. A sample purified by vpc gave an infrared spectrum identical with that synthesized above.

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[36] Obtained from Hi Laboratories, Whitmore Lake, Mich. This compound apparently contained sufficient mineral acid to cause esterification during the catalytic hydrogenation.

[37] The hydrogenation was done by J. Hudson.

[38] E. von Rudloff, *Can. J. Chem.*, **34**, 1413 (1956).

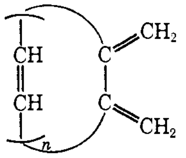
The Synthesis and Cycloaddition Reactions of 7,8-Dimethylene-1,3,5-cyclooctatrienes. The Synthesis of Dicyclooctatetraeno[1,2:4,5]benzene[1]

J. A. Elix, M. V. Sargent, and F. Sondheimer[2]

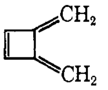
Contribution from the University Chemical Laboratory, Cambridge, England.
Received August 11, 1969

Abstract: 7,8-Dimethylene-1,3,5-cyclooctatriene (**4**) has been synthesized from 1,2-bis(hydroxymethyl)cyclooctatetraene (**6**), by conversion to 1,2-bis(bromomethyl)cyclooctatetraene (**7**) and subsequent zinc reduction. Treatment of **7** with potassium *t*-butoxide led to 7-methylene-8-bromomethylene-1,3,5-cyclooctatriene (**8**), while similar treatment of 1,2-bis(chloromethyl)cyclooctatetraene (**9**) gave 7-methylene-8-chloromethylene-1,3,5-cyclooctatriene (**10**). The exocyclic double bonds of **4**, **8**, and **10** proved to be the most reactive diene systems in thermal 1,4-cycloaddition reaction, and gave rise to fused cyclooctatetraene derivatives by addition to a variety of dienophiles. For instance, **4** and **8** have been converted to dicyclooctatetraeno[1,2:4,5]benzene (**27**). Although the possibility existed that **27** might represent a planar aromatic system, the spectral properties indicated that the eight-membered rings are nonplanar and do not possess delocalized π electrons.

Dimethylenecyclopolyenes of type **1** are an interesting class of compounds. The only representatives which had been studied when we commenced our work in this field were the first two members, 3,4-dimethylenecyclobutene (**2**)[3] and 5,6-dimethylene-1,3-cyclohexadiene (*o*-quinodimethane, *o*-xylylene) (**3**).[4,5]



1



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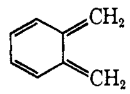

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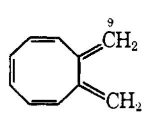

4

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[1] Unsaturated Eight-Membered Ring Compounds. VII. For Part VI, see J. A. Elix and M. V. Sargent, *J. Am. Chem. Soc.*, **91**, 4734 (1969).

[2] Author to whom inquiries should be addressed at the Chemistry Department, University College, London W.C.1, England.

[3] A. J. Blomquist and P. M. Maitlis, *Proc. Chem. Soc.*, 332 (1961); W. D. Huntsman and H. J. Wristers, *J. Am. Chem. Soc.*, **85**, 3308 (1963); 89, 342 (1967); M. L. Heffernan and A. J. Jones, *Chem. Commun.*, 120 (1966); B. A. W. Coller, M. L. Heffernan, and A. J. Jones, *Aust. J. Chem.*, **21**, 1807 (1968).

[4] *Inter alia*, L. A. Errede, *J. Am. Chem. Soc.*, **83**, 949 (1961); K. Alder and M. Fremery, *Tetrahedron*, **14**, 190 (1961); D. A. Ben-Efraim and F. Sondheimer, *Tetrahedron Lett.*, 313 (1963); M. Avram, I. G.

In contrast to the four-membered ring compound **2**, the six-membered ring compound **3** proved to be too unstable for characterization, and its existence was inferred mainly from its transformation products.[4] It appeared of interest to prepare the next member of the series, 7,8-dimethylene-1,3,5-cyclooctatriene (**4**), in order to study its reactions and compare its properties with those of the lower vinylogs **2** and **3**.

We now describe a synthesis of **4**, as well as of the corresponding 9-bromo and 9-chloro derivatives (**8**, **10**). Some cycloaddition reactions of these substances have been investigated, and it has been found that they can be readily converted to fused cyclooctatetraene derivatives. For instance, **4** and **8** have been transformed to dicyclooctatetraeno[1,2:4,5]benzene (**27**). Our work has already appeared in preliminary form,[6,7] and is now described in detail. Since publication of our preliminary communications describing the synthesis and reactions of **4**,[6a] a different synthesis of this substance has been reported in preliminary form by Anet and Gregorovich.[8]

The starting material for our work was 1,2-bis(hydroxymethyl)cyclooctatetraene (**6**),[9,10] which we prepared by the photoinduced reaction of benzene with dimethyl acetylenedicarboxylate to give dimethyl cyclooctatetraene-1,2-dicarboxylate (**5**),[9,11] followed by reduction with lithium aluminum hydride and aluminum trichloride.[10] The diol **6** was converted in 53% yield to the corresponding dibromide **7** (mp 65–66°) by treatment with phosphorus tribromide and pyridine at 0–20°. 1,4 Reduction of **7** with zinc in dimethylformamide[12] at room temperature then led to 7,8-dimethylene-1,3,5-cyclooctatriene (**4**) in practically quantitative yield.

Dehydrobromination of the dibromide **7** with potassium *t*-butoxide in ether at −78–20° furnished 7-methylene-8-bromomethylene-1,3,5-cyclooctatriene (**8**) in 83% yield. Similar dehydrochlorination of the dichloride **9** (obtained in 90% yield from the dibromide **7** by reaction with lithium chloride in dimethylformamide at room temperature) led to 7-methylene-8-chloromethylene-1,3,5-cyclooctatriene (**10**) in almost quantitative yield. The dimethylenecyclooctatriene derivatives **4**, **8**, and **10** proved to be unstable pale yellow liquids. The structural assignments are based on the following spectroscopic evidence.

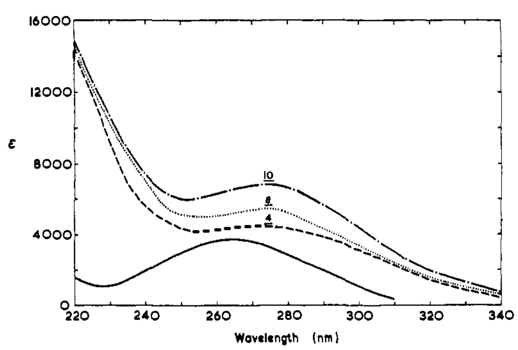
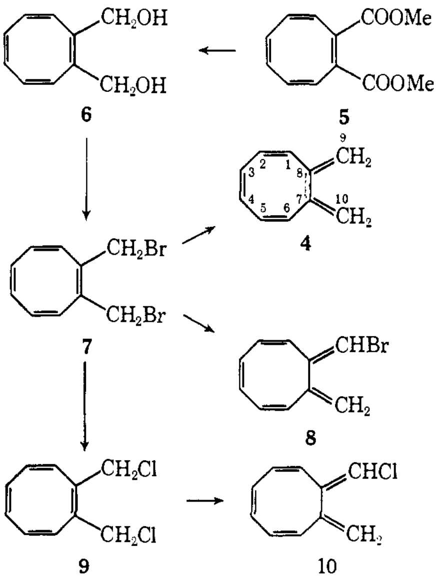
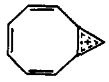
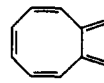


Figure 1. Electronic spectra (in EtOH) of 1,3,5-cyclooctatriene (solid line), 7,8-dimethylene-1,3,5-cyclooctatriene (**4**, dashed line), 7-methylene-8-bromomethylene-1,3,5-cyclooctatriene (**8**, dotted line), and 7-methylene-8-chloromethylene-1,3,5-cyclooctatriene (**10**, chain-dotted line).



The mass spectrum of the hydrocarbon **4** exhibited a prominent molecular ion peak at *m*/*e* 130, a base peak at *m*/*e* 129 (M − H) and a strong peak at *m*/*e* 128 (M − 2H). It is of interest to note that the spectrum also showed a strong peak at *m*/*e* 115, which may be due to the ion **11**. This structure has already been suggested by Le Goff and LaCount[10] for the ion responsible for the *m*/*e* 115 peak in the mass spectrum of cycloocta[c]furan (**12**), a compound closely related to **4**.


11



12

The mass spectrum of the bromo compound **8** exhibited strong molecular ion peaks at *m*/*e* 210 and 208, whereas the corresponding chloro compound **10** showed molecular ion peaks at *m*/*e* 166 and 164. The spectra of both **8** and **10** also showed prominent peaks at *m*/*e* 129, 128, and 115, the breakdown patterns being similar to that of the hydrocarbon **4** itself.

The electronic spectra of the three substances **4**, **8**, and **10**, given in Figure 1, exhibited maxima in the

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Dinulescu, D. Dinu, G. Mateescu, and C. D. Nenitzescu, *Chem. Ind.* (London), 555 (1962); *Tetrahedron*, **19**, 309 (1963).

(5) For molecular orbital calculations of 2 and 3, see J. D. Roberts, A. Streitwieser, and C. M. Regan, *J. Am. Chem. Soc.*, **74**, 4579 (1952); A. Streitwieser and J. I. Brauman, "Supplemental Tables of Molecular Orbital Calculations," Vol I, Pergamon Press, Oxford, 1965, pp 9–10; C. A. Coulson and A. Streitwieser, "Dictionary of π-Electron Calculations," Pergamon Press, Oxford, 1965, pp 106–107.

(6) (a) Synthesis and reactions of **4**: J. A. Elix, M. V. Sargent, and F. Sondheimer, *Chem. Commun.*, 508, 509 (1966); (b) synthesis of **8** and **10**: J. A. Elix, M. V. Sargent, and F. Sondheimer *J. Am. Chem. Soc.*, **89**, 180, 5081 (1967).

(7) See also F. Sondheimer, I. C. Calder, J. A. Elix, Y. Gaoni, P. J. Garratt, K. Grohmann, G. di Maio, J. Mayer, M. V. Sargent, and R. Wolovsky, Special Publication No. 21, The Chemical Society, London, 1967, p 75.

(8) F. A. L. Anet and B. Gregorovich, *Tetrahedron Lett.*, 5961 (1966).

(9) J. E. Meili, Ph.D. Thesis, Massachusetts Institute of Technology, 1952; A. C. Cope and J. E. Meili, *J. Am. Chem. Soc.*, **89**, 1883 (1967).

(10) E. Le Goff and R. B. LaCount, *Tetrahedron Lett.*, 2787 (1965).

(11) E. Grovenstein and D. V. Rao, *ibid.*, 148 (1961); D. Bryce-Smith and J. E. Lodge, *Proc. Chem. Soc.*, 333 (1961); *J. Chem. Soc.*, 695 (1963); E. Grovenstein, T. C. Campbell, and T. Shibata, *J. Org. Chem.*, **34**, 2418 (1969).

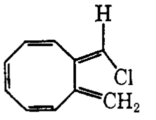
(12) The reaction is analogous to the 1,4 reduction of 1,4-dibromo-2-butene to butadiene with zinc in ethanol (see J. Thiele, *Ann.*, **308**, 339 (1899)). The use of zinc in dimethylformamide for this type of reduction was described by Alder and Fremery (ref 4), who employed it for generating 5,6-dimethylene-1,3-cyclohexadiene (3) from α,α′-dibromo-*o*-xylene.

269–275-nm region (ϵ 4500–6800) and strong end absorption (ϵ 14,100–14,900 at 220 nm). By comparison, the electronic spectrum of 1,3,5-cyclooctatriene (Figure 1) showed a maximum at 265 nm (ϵ 3700), but only relatively weak end absorption (ϵ 1600 at 220 nm).[13] Evidently, the maxima in the 270-nm region of **4**, **8**, and **10** are due to the cyclooctatriene chromophores, while the strong end absorption is due to the exocyclic *s-cis*-diene chromophores. The spectra indicate that the three substances exist in nonplanar conformations.

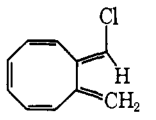
The infrared spectra of **4**, **8**, and **10** all showed strong bands at *ca.* 900 cm^{-1}, as well as medium-intensity bands at *ca.* 3080 cm^{-1}; these are characteristic of the hydrogen out-of-plane deformation and the carbon–hydrogen stretching, respectively, of a 1,1-disubstituted ethylene.[14]

The nmr spectrum (CCl$_4$, 100 MHz) of 7,8-dimethylene-1,3,5-cyclooctatriene (**4**) confirmed the presence of the *exo*-methylene protons, which gave rise to finely split bands at τ 4.93 (2 H) and 5.18 (2 H). The protons at positions 1,6 and 2,5 appeared as a quartet centered at τ 3.73 and 4.19 (J = 12 Hz). The magnitude of this coupling constant is compatible for pairs of *cis*-olefinic protons. The protons at positions 3 and 4 gave rise to a relatively narrow band at τ 4.22, which is superimposed on the high-field band of the quartet. The fact that the protons 3 and 4 exhibit little coupling with the protons 2 and 5 indicates that **4** probably exists in a nonplanar "tub" conformation, a conclusion which is in accord with the above described electronic spectrum.

The nmr spectra of the bromopentaene **8** and the chloropentaene **10** were more complex than that of **4**, but exhibited absorption in the same region. The bromo compound **8** appears to consist of a single stereoisomer, as the nmr spectrum showed a 1 H singlet at τ 3.76 due to the exomethine proton. In contrast, the chloro compound **10** appears to consist of a *ca.* 1:1 mixture of the "*cis*" isomer **10a** and the "*trans*" isomer **10b**. This follows from the fact that the singlet at τ 3.62 in the nmr spectrum of **10** due to the exomethine proton in one stereoisomer corresponds to only *ca.* 0.5 H; the signal due to the exomethine proton in the other isomer appears in the same region as the ring proton absorptions.



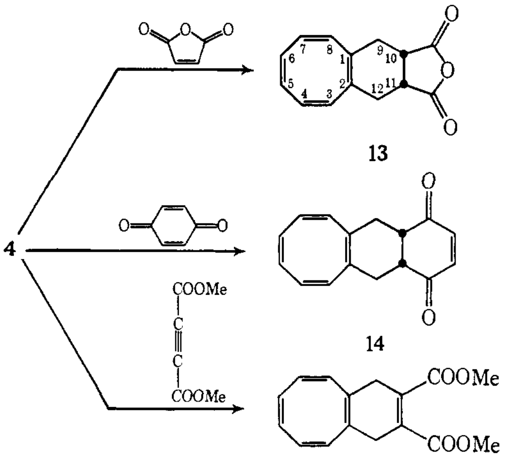
10a



10b

One of the most striking chemical properties of 7,8-dimethylene-1,3,5-cyclooctatriene (**4**) is its rapid reaction with atmospheric oxygen to form intractable, oxygen-containing products. Allowing the neat liquid to stand in daylight and air for 45 min resulted in the decomposition of *ca.* 50% and the appearance of a strong carbonyl band at 1720 cm^{-1} in the infrared spectrum. The bromo compound **8** and the chloro compound **10** also decomposed under these conditions, but more slowly than **4**. The decomposition of **8** appears to be autocatalyzed, the rate of reaction increasing sharply after *ca.* 2 hr (see Experimental Section).

The exocyclic double bonds of **4**, **8**, and **10** proved to be the most reactive diene systems in thermal 1,4-cycloaddition reactions and added readily to a variety of dienophiles. Thus, reaction of **4** with maleic anhydride in boiling cyclohexane led to 9,10,11,12-tetrahydrobenzocyclooctatetraene-*cis*-10,11-dicarboxylic anhydride (**13**, mp 144–145°) in 37% yield. The structure of this and the other adducts is based on microanalytical and spectroscopic evidence. In particular, the nmr spectrum (CDCl$_3$, 100 MHz) of **13** showed peaks at τ 4.17 and 4.22 (6 H) due to the olefinic protons, at τ 6.55 (2 H) due to the methine protons, and at τ 7.48 (4 H) due to the methylene protons. Similarly, **4** reacted with *p*-benzoquinone to give the adduct **14** (mp 123–124°) in 34% yield, and with dimethyl acetylenedicarboxylate to form the adduct **15** (mp 79.5–80.5°) in 52% yield.

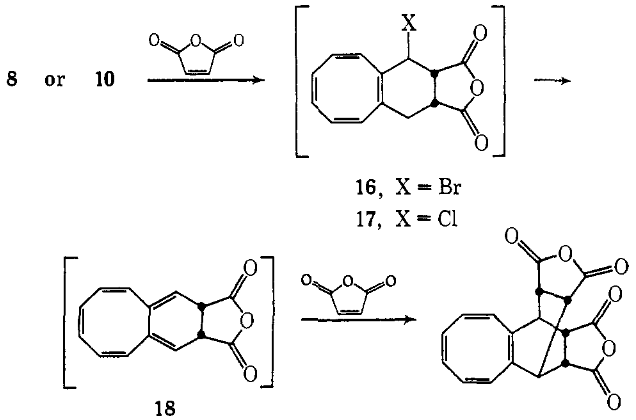


13

14

15

The reaction of 7-methylene-8-bromomethylene-1,3,5-cyclooctatriene (**8**) with an excess of maleic anhydride in boiling cyclohexane did not lead to the simple adduct **16**, but gave the bis adduct **19** (mp 313–314°) in 45% yield. Presumably, **16** was formed initially, but suffered dehydrobromination under the reaction conditions to give the dimethylenecyclooctatriene derivative **18**, which then reacted with a second molecule of maleic anhydride. The bis adduct **19** was also obtained (in 47% yield) by treatment of the chloro compound **10** with an excess of maleic anhydride, a reaction which presumably proceeds *via* the intermediate chloro adduct **17**.



16, X = Br

17, X = Cl

18

19

Treatment of either **8** or **10** with dimethyl acetylenedicarboxylate in boiling cyclohexane led to dimethyl

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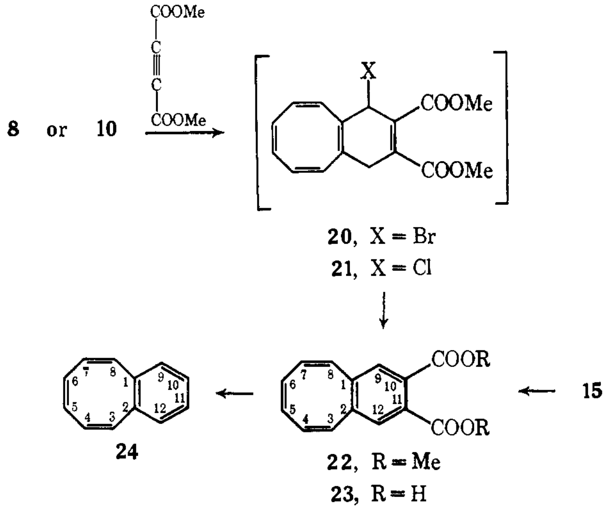
(13) See A. C. Cope and C. G. Overberger, *J. Am. Chem. Soc.*, **70**, 1433 (1948).

(14) See L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd ed, John Wiley & Sons, Inc., New York, N. Y., 1958, Chapter 3.

benzocyclooctatetraene-10,11-dicarboxylate (**22**) (mp 60.5–61.5°) in *ca.* 45% yield. In this case, dehydrohalogenation of the initially formed adduct (**20** or **21**) gives a benzenoid compound, which does not react further. The benzocyclooctatetraene derivative **22** was also obtained (in 81% yield) from the corresponding dihydro compound **15** by dehydrogenation with 2,3-dichloro-5,6-dicyano-*p*-benzoquinone in boiling benzene.



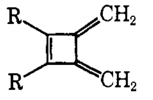
20, X = Br
21, X = Cl

24

22, R = Me
23, R = H

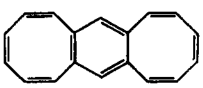
In order to relate the structure of one of the adducts to a known cyclooctatetraene derivative, the diester **22** was saponified to the corresponding dicarboxylic acid **23** (mp 175–178° dec), which was then decarboxylated with copper chromite at 260–270°.[15] The resulting benzocyclooctatetraene (**24**) (mp 49–50°), obtained in poor yield, was identified by direct comparison with an authentic sample.[16]

The 1,4-cycloaddition reactions of **4**, **8**, and **10** parallel those of 5,6-dimethylene-1,3-cyclohexadiene (**3**),[4] but are in marked contrast to the 1,2-cycloaddition reactions of 1,2-diphenyl-3,4-dimethylenecyclobutene (**25**)[17] and 1,2-dimethyl-3,4-dimethylenecyclobutene (**26**).[18, 19] The cycloaddition reactions of **4**, **8**, and **10** apparently involve only the exocyclic diene systems (making them (4 + 2) cycloadditions, compatible with orbital symmetry considerations),[20] and not all the peripheral ten π electrons, which would necessitate planar molecules. The observed relative stabilities and behavior in thermal cycloaddition reactions of the dimethylene derivatives of cyclooctatriene, cyclohexadiene, and cyclobutene (**4**, **3**, **2**) are presumably related to the fact that cyclooctatetraene is less stable than benzene, but more stable than cyclobutadiene.

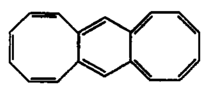


25, R = Ph
26, R = Me

7,8-Dimethylene-1,3,5-cyclooctatriene (**4**) and the 9-halogeno derivatives **8** and **10** appeared to be promising intermediates for the synthesis of dicyclooctatetraeno[1,2:4,5]benzene (**27**). There was a possibility that this tricyclic hydrocarbon might represent a planar aromatic system, since a possible contributing structure, **27b**, can be considered to be a perturbed [18]annulene.[21] Craig's rule[22] also predicts that **27** will be an aromatic system. In practice, it was found that **27** could be obtained simply from **4**, as well as from **8**.



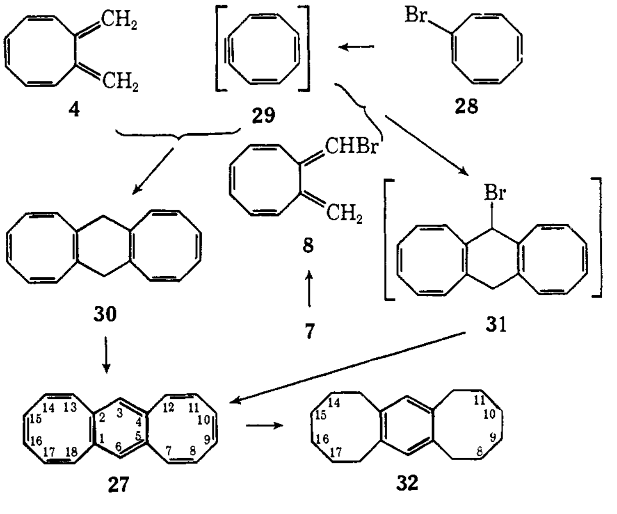
27a



27b

It has been shown by Krebs[23] that treatment of bromocyclooctatetraene (**28**)[24] with potassium *t*-butoxide in ether at room temperature leads to 1,2-dehydrocyclooctatetraene (1,3,5-cyclooctatrien-7-yne, **29**) as a transient intermediate, which undergoes cycloadditions with dienes.[1, 23] We have found that when **29** is generated in the presence of 7,8-dimethylene-1,3,5-cyclooctatriene (**4**), the expected adduct, dicyclooctatetraeno[1,2:4,5]-1,4-cyclohexadiene (**30**, mp 138–142°), can be isolated in 22% yield. Dehydrogenation of the adduct **30** with 2,3-dichloro-5,6-dicyano-*p*-benzoquinone in boiling benzene or with palladium–charcoal in boiling decalin then gave dicyclooctatetraeno[1,2:4,5]benzene (**27**, mp 179–181°) in *ca.* 35–50% yield.

A convenient one-step synthesis of **27** (in 11% yield) was accomplished by treatment of a mixture of bromocyclooctatetraene (**28**) and 1,2-bis(bromomethyl)cyclooctatetraene (**7**) with potassium *t*-butoxide in ether at room temperature. The initially formed 1,2-dehydrocyclooctatetraene (**29**) and 7-methylene-8-bromometh-



4
29
28
8
30
7
31
27
32

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(15) The conditions are modeled on those used by F. Fieser and M. M. Pechet [*J. Am. Chem. Soc.*, **68**, 2577 (1946)] for the decarboxylation of 1,2:5,6-dibenzocyclooctatetraene-3,8-dicarboxylic acid to the corresponding dibenzocyclooctatetraene.

(16) See part VI of this series (ref 1), and references cited there.

(17) A. T. Blomquist and Y. C. Meinwald, *J. Am. Chem. Soc.*, **81**, 667 (1959).

(18) G. W. Griffin and L. I. Peterson, *ibid.*, **85**, 2268 (1963); R. Criegee, J. Dekker, W. Engel, P. Ludwig, and K. Noll, *Chem. Ber.*, **96**, 2362 (1963).

(19) 3,4-Dimethylenecyclobutene (**2**) itself gave no well-defined adducts with dienophiles (B. A. W. Coller, *et al.*, ref 3).

(20) 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).

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

(22) D. P. Craig, *J. Chem. Soc.*, 3175 (1951); "Theoretical Organic Chemistry," The Kekulé Symposium, Butterworths and Co., Ltd., London, 1959, p 20.

(23) A. Krebs, *Angew. Chem.*, 77, 966 (1965); A. Krebs and D. Byrd, *Ann.*, 707, 66 (1967).

(24) A. C. Cope and M. Burg, *J. Am. Chem. Soc.*, **74**, 168 (1952). See also footnote 14 in ref 1.

ylene-1,3,5-cyclooctatriene (**8**) presumably undergo cycloaddition to give the adduct **31**, which then suffers dehydrobromination under the basic conditions to give **27**.

The hydrocarbon **27** was obtained as pale yellow crystals, which could be readily sublimed at 100° (0.5 mm). Treatment with silver nitrate in ethanol led to a crystalline 1:1 adduct in *ca.* 75% yield, a reaction which is similar to that of cyclooctatetraene[25] and benzocyclooctatetraene (**24**)[26] with silver nitrate. The structure of **27** was confirmed by catalytic hydrogenation in methanol and ethyl acetate over a palladium–calcium carbonate catalyst, whereby dicycloocteno[1,2:4,5]benzene (**32**, mp 132–133°) was obtained in essentially quantitative yield.

The nmr spectrum ($CDCl_3$, 100 MHz) of **27** exhibited a singlet at τ 3.41 (2 H) due to the benzenoid protons, a doublet centered at τ 3.50 (4 H, $J = 12$ Hz) due to protons 7, 12, 13, and 18, a quartet centered at τ 3.92 and 4.03 (4 H, $J = 12$, *ca.* 1 Hz) due to protons 8, 11, 14, and 17, and a narrow multiplet at τ 4.12 (4 H, $J =$ *ca.* 1 Hz) due to protons 9, 10, 15, and 16. The absorptions of the eight-membered ring protons in the nmr spectrum of **27** are very similar to those of benzocyclooctatetraene (**24**), in which protons 3 and 8 appear as a doublet at τ 3.49 ($J = 12$ Hz), protons 4 and 7 as a quartet centered at τ 3.97 and 4.09 ($J = 12$, 2 Hz), and protons 5 and 6 as a narrow multiplet at τ 4.16 ($J = 2$ Hz).[1] The chemical shifts of the eight-membered ring protons in the nmr spectrum of **27** show that there is no diamagnetic ring current associated with these rings. The fact that little coupling occurs between protons 8 and 9 (and the other protons equivalent to these) indicates that the eight-membered rings in **27**, as in **24**, are nonplanar. The ultraviolet spectrum of **27** [λ_{max}^{EtOH} 254 nm (ϵ 24,700)] is compatible with this conclusion.

Dicyclooctatetraeno[1,2:4,5]benzene (**27**) is clearly not a planar aromatic 18-π-electron system. Presumably the gain in delocalization energy in a planar conformation is more than offset by the increase in strain energy. Moreover, simple resonance theory indicates that the gain in delocalization energy may be small, as the resonance structure **27b** demands the disruption of the aromatic sextet of the benzene ring. The substance is best represented by formula **27a**, containing nonplanar eight-membered rings.

Very recently, Lo and Whitehead[27] have published some calculations on the properties of **4** and **27**, which are in accord with our experimental findings.

Experimental Section

General Procedures. Melting points were determined on a Kofler hot-stage apparatus. Infrared spectra were measured on a Perkin-Elmer 257 or a Unicam SP 200 spectrophotometer, and electronic spectra on a Cary 14-50 or a Unicam SP 800 spectrophotometer. Nmr spectra were determined on a Varian HA-100 (100 MHz) or a Perkin-Elmer R-10 (60 MHz) spectrometer, tetramethylsilane being used as an internal standard. Mass spectra were measured with an A.E.I. MS-9 spectrometer operating at 70 eV.

1,2-Bis(bromomethyl)cyclooctatetraene (7). The method is modeled on that used by Cope, *et al.*,[28] for the preparation of bromomethylcyclooctatetraene from hydroxymethylcyclooctatetraene. A solution of phosphorus tribromide (5.0 g, 18.5 mmoles) in dry ether (40 ml) was added during 5 min to a stirred solution of 1,2-bis(hydroxymethyl)cyclooctatetraene (**6**) (3.4 g, 20.7 mmoles; prepared from **5** as described by Le Goff and LaCount[10]) in dry pyridine (1.32 g, 16.7 mmoles) and dry ether (25 ml) at 0° under nitrogen. Stirring was continued for 1 hr at 0° and then for 5 hr at 20°. The solution was diluted with ether and extracted successively with saturated sodium chloride solution, sodium bicarbonate solution, and again with saturated sodium chloride solution. The ether solution was then dried ($MgSO_4$) and evaporated. The residue in pentane was adsorbed onto a column of silicic acid (Mallinckrodt, 100 mesh; 15 × 2.5 cm), which was developed with pentane. A pale yellow band was eluted, which on evaporation and crystallization from pentane yielded 1,2-bis(bromomethyl)cyclooctatetraene (**7**, 3.2 g, 53%) as pale yellow prisms: mp 65–66°; nmr spectrum (CCl_4, 100 MHz), multiplet at τ 3.80–4.09 (6 H, olefinic protons) and multiplet at 5.76–6.02 (4 H, methylene protons).

Anal. Calcd for $C_{10}H_{10}Br_2$: C, 41.41; H, 3.48; Br, 55.11. Found: C, 41.55; H, 3.70; Br, 55.28.

7,8-Dimethylene-1,3,5-cyclooctatriene (4). Zinc powder (1.0 g) was added to a solution of **7** (330 mg) in dry dimethylformamide (5 ml), and the mixture was shaken at room temperature for 30 hr. The mixture was filtered, the filtrate was poured into cold water (50 ml) and extracted several times with carbon tetrachloride. The combined organic extracts were washed with cold water, dried ($MgSO_4$), and evaporated under reduced pressure (bath not above 25°). The product was adsorbed onto a column of silicic acid (Mallinckrodt, 100 mesh; 30 × 3 cm), which was developed with nitrogen-purged pentane. Fractions of 50 ml were collected. Fractions 4–7 were combined and cautiously evaporated under reduced pressure (bath not above 25°) in nitrogen. This procedure gave 7,8-dimethylene-1,3,5-cyclooctatriene (**4**, 140 mg, 95%) as a pale yellow liquid: infrared spectrum (film), bands at 3085 (m), 3000 (s), 1650 (w), 1600 (m), 1580 (m), 1445 (m), 1420 (m), 1400 (w), 1350 (w), 910 (s), 895 (vs), 850 (w), 810 (w), 795 (s), 780 (s), 750 (s), 720 (m), 675 (s), 655 (s), and 640 cm^{-1} (s); electronic spectrum, λ_{max}^{EtOH} 269 nm (ϵ 4500) and strong end absorption (ϵ 14,100 at 220 nm) (see Figure 1); nmr and mass spectra, see Discussion.

Allowing neat **4** to stand in daylight and air, and determining the ϵ value of the 269-nm maximum at intervals, gave the following results: 49% decomposition after 45 min, 67% after 1.5 hr, and over 90% after 3 hr. The infrared spectrum (film), determined after a sample had been allowed to stand for 45 min, showed a prominent carbonyl band at 1720 cm^{-1}.

7-Methylene-8-bromomethylene-1,3,5-cyclooctatriene (8). A solution of **7** (1.2 g, 4.1 mmoles) in dry ether (70 ml) was cooled to −78°, and added to a stirred suspension of potassium *t*-butoxide (0.78 g, 7.0 mmoles) in ether (10 ml) at −78°. The stirred mixture was permitted to warm to room temperature and was then allowed to stand for 1 hr. It was poured into water (100 ml), and the ether layer was washed several times with water. Evaporation of the dried ($MgSO_4$) extract under reduced pressure gave 7-methylene-8-bromomethylene-1,3,5-cyclooctatriene (**8**, 0.72 g, 83%) as a yellow liquid: infrared spectrum (film), bands at 3080 (m), 3000 (s), 1605 (m), 1585 (m), 1450 (m), 1400 (w), 1160 (s), 1140 (m), 900 (s), 790 (vs), 770 (vs), 730 (s), 710 (s), and 660 cm^{-1} (s); electronic spectrum, λ_{max}^{EtOH} 275 nm (ϵ 5400) and strong end absorption (ϵ 14,800 at 220 nm) (see Figure 1); nmr spectrum (CCl_4, 100 MHz), singlet at τ 3.76 (1 H, exomethine proton), multiplet at 3.84–3.98 (3 H), and finely split band at 4.20 (3 H) (ring olefinic protons), as well as finely split bands at 4.98 and 5.10 (1 H each, exomethylene protons); mass spectrum, see Discussion.

Allowing neat **8** to stand in daylight and air, and determining the ϵ value of the 275-nm maximum at intervals, gave the following results: 3% decomposition after 1 hr, 7.5% after 2 hr, and 56% after 3 hr.

1,2-Bis(chloromethyl)cyclooctatetraene (9). The dibromide **7** (0.16 g, 0.55 mmole) was added to a suspension of anhydrous lithium chloride (0.75 g, 17.7 mmoles) in dimethylformamide (5 ml), and the mixture was allowed to stand at room temperature for 72 hr. Cold water (50 ml) was then added, and the mixture was extracted several times with ether. The combined ether extracts were washed repeatedly with water, dried (Na_2SO_4), and evaporated. The resulting 1,2-bis(chloromethyl)cyclooctatetraene (**9**, 0.10 g, 90%) was a pale yellow liquid: nmr spectrum (CCl_4, 100 MHz), multiplet at τ 3.88–4.12 (6 H, olefinic protons) and multiplet at 5.69–5.99 (4 H, methylene protons); mass spectrum, molecular ion peaks at *m/e* 202 and 200.

Anal. Calcd for $C_{10}H_{10}Cl_2$: Cl, 35.26. Found: Cl, 35.30.

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[26] G. Wittig, H. Eggers, and P. Duffner, *Ann.*, **619**, 10 (1958).

[27] D. H. Lo and M. A. Whitehead, *J. Am. Chem. Soc.*, **91**, 238 (1969).

[28] A. C. Cope, R. M. Pike, and D. F. Rugen, *ibid.*, **76**, 4945 (1954).

7-Methylene-8-chloromethylene-1,3,5-cyclooctatriene (10). A solution of the dichloride **9** (0.70 g, 3.5 mmoles) in ether (70 ml) was treated with potassium *t*-butoxide (0.78 g, 7.0 mmoles) in ether (10 ml), initially at −78°, as described above for the preparation of **8** from **7**. The resulting 7-methylene-8-chloromethylene-1,3,5-cyclooctatriene (**10**, 0.56 g, 97%) was a pale yellow liquid: infrared spectrum (film), bands at 3085 (m), 3070 (m), 3010 (s), 1650 (w), 1605 (m), 1575 (m), 1550 (m), 1440 (w), 1410 (w), 1380 (w), 1280 (s), 900 (s), 880 (s), 870 (s), 825 (s), 800 (s), 780 (s), 770 (s), 720 (m), 700 (m), and 650 cm^{-1} (s); electronic spectrum, $\lambda_{\max}^{\text{EtOH}}$ 274 nm (ϵ 6800) and strong end absorption (ϵ 14,900 at 220 nm) (see Figure 1); nmr spectrum (CCl_4, 60 MHz), singlet at τ 3.62 (*ca.* 0.5 H, exomethine proton), finely split bands at 3.84 (*ca.* 3.5 H) and at 4.12 (3 H) (exomethine and ring olefinic protons), and finely split bands at 4.93 and 5.05 (1 H each, exomethylene protons); mass spectrum, see Discussion; high-resolution mass spectrum, molecular ion peaks at *m/e* 166.036 and 164.039 (calcd for $^{12}C_{10}{}^{1}H_9{}^{37}Cl$: 166.036; calcd for $^{12}C_{10}{}^{1}H_9{}^{35}Cl$: 164.039).

When a sample of neat **10** was allowed to stand in daylight and air for 30 min and the infrared spectrum (film) was redetermined, the intensities of the bands at 3085, 3070, 900, 880, and 870 cm^{-1} had diminished considerably and a prominent carbonyl peak at 1685 cm^{-1} had appeared.

9,10,11,12-Tetrahydrobenzocyclooctatetraene-*cis*-10,11-dicarboxylic Anhydride (13). A solution of **4** (70 mg, 0.54 mmole) and maleic anhydride (55 mg, 0.56 mmole) in cyclohexane (5 ml) was boiled under reflux for 4 hr. The resulting solution was then concentrated to *ca.* half its volume, and cooled. The resulting pale yellow crystalline solid was collected and recrystallized from ether–pentane to give 9,10,11,12-tetrahydrobenzocyclooctatetraene-*cis*-10,11-dicarboxylic anhydride (**13**, 46 mg, 37%) as pale yellow prisms: mp 144–145°; infrared spectrum ($CHCl_3$), bands at 1845 and 1780 cm^{-1} (anhydride); electronic spectrum, end absorption only; nmr spectrum, see Discussion; mass spectrum, molecular ion peak at *m/e* 228.

Anal. Calcd for $C_{14}H_{12}O_3$: C, 73.67; H, 5.30. Found: C, 73.62; H, 5.58.

Adduct 14 from 7,8-Dimethylene-1,3,5-cyclooctatriene (4) and *p*-Benzoquinone. A solution of **4** (260 mg, 2.0 mmoles) and *p*-benzoquinone (216 mg, 2.0 mmoles) in cyclohexane (20 ml) was boiled under reflux for 5 hr. The residue obtained on evaporation was adsorbed onto a column of silica gel (B.D.H., 40 × 2.5 cm), which was developed with pentane–ether (3:1). Fractions of 100 ml were collected. Fractions 7–9 on evaporation yielded a pale yellow solid (84 mg) consisting of a mixture of the adduct **14** and *p*-benzoquinone. Fractions 10–15 on evaporation and crystallization from cyclohexane (charcoal) gave the adduct **14** (160 mg, 34%) as colorless needles: mp 123–124°; infrared spectrum ($CHCl_3$), band at 1685 cm^{-1} (C=O); electronic spectrum, $\lambda_{\max}$ 290 mμ (ϵ 810) and strong end absorption; nmr spectrum ($CDCl_3$, 100 MHz), peaks at τ 3.22, 3.26 (2 H, six-membered ring olefinic protons) and at 4.08, 4.18 (6 H, eight-membered ring olefinic protons), a broad multiplet centered at *ca.* 6.7 (2 H, methine protons), and a broad multiplet centered at *ca.* 7.7 (4 H, methylene protons); mass spectrum, molecular ion peak (weak) at *m/e* 238, base peak at *m/e* 234 (M − 4 H).

Anal. Calcd for $C_{16}H_{14}O_2$: C, 80.64; H, 5.92. Found: C, 80.35; H, 5.72.

Dimethyl 9,12-Dihydrobenzocyclooctatetraene-10,11-dicarboxylate (15). A solution of **4** (430 mg, 3.3 mmoles) and dimethyl acetylenedicarboxylate (350 mg, 2.5 mmoles) in cyclohexane (50 ml) was boiled under reflux for 48 hr (an excess of **4** was used, in order to facilitate the separation of the product **15** by chromatography). The residue obtained on evaporation was adsorbed onto a column of silica gel (B.D.H., 40 × 2.5 cm), which was developed with 1.5 l. of pentane–ether (9:1) and then with 2.5 l. of pentane–ether (4:1). Fractions of 250 ml were collected. Fractions 8–13 on evaporation and crystallization from pentane yielded dimethyl 9,12-dihydrobenzocyclooctatetraene-10,11-dicarboxylate (**15**, 470 mg, 52% based on **4**) as pale yellow needles: mp 79.5–80.5°; infrared spectrum ($CHCl_3$), bands at 1720 (ester) and 1655 cm^{-1} (double bond); electronic spectrum, end absorption only; nmr spectrum ($CDCl_3$, 60 MHz), finely split peaks at τ 4.13 and 4.21 (6 H, olefinic protons), a singlet at 6.21 (6 H, methyl protons), and a singlet at 7.05 (4 H, methylene protons); mass spectrum, molecular ion peak at *m/e* 272.

Anal. Calcd for $C_{16}H_{16}O_4$: C, 70.57; H, 5.92. Found: C, 70.49; H, 5.90.

Bis Adduct 19 from 7-Methylene-8-bromomethylene-1,3,5-cyclooctatriene (8) or 7-Methylene-8-chloromethylene-1,3,5-cyclooctatriene (10) and Maleic Anhydride. A solution of **8** (1.08 g, 5.2 mmoles) and maleic anhydride (1.20 g, 12.2 mmoles) in cyclohexane (100 ml) was boiled under reflux for 60 hr. Evaporation and crystallization from acetone–cyclohexane (charcoal) gave the bis adduct **19** (0.75 g, 45%) as pale yellow needles: mp 313–314°; infrared spectrum ($CHCl_3$), bands at 1860 and 1780 cm^{-1} (anhydride); electronic spectrum, end absorption only; nmr spectrum (CD_3COCD_3, 100 MHz), multiplet at τ 4.13–4.52 (6 H, olefinic protons), a finely split band at 6.21 (4 H, methine protons adjacent to anhydride groups), and a finely split band at 6.57 (2 H, allylic methine protons); mass spectrum, molecular ion peak at *m/e* 324.

Anal. Calcd for $C_{18}H_{12}O_6$: C, 66.67; H, 3.73. Found: C, 67.06; H, 3.93.

Treatment of **10** (0.7 g, 4.3 mmoles) with maleic anhydride (1.2 g, 12.2 mmoles) in boiling cyclohexane (100 ml) for 60 hr, and isolation as before, yielded the same bis adduct **19** (0.65 g, 47%), mp and mmp 313–314°.

Dimethyl Benzocyclooctatetraene-10,11-dicarboxylate (22). A. From 7-Methylene-8-bromomethylene-1,3,5-cyclooctatriene (8). A solution of **8** (720 mg, 3.45 mmoles) and dimethyl acetylenedicarboxylate (490 mg, 3.45 mmoles) in cyclohexane (100 ml) was boiled under reflux for 60 hr. The residue obtained by evaporation was adsorbed onto a column of silica gel (B.D.H., 40 × 2 cm), which was developed successively with 1.5 l. of pentane–ether (9:1), 1 l. of pentane–ether (17:3), and 1.5 l. of pentane–ether (4:1). Fractions of 250 ml were collected. Fractions 9–13 on evaporation and crystallization from pentane gave dimethyl benzocyclooctatetraene-10,11-dicarboxylate (**22**, 400 mg, 43%) as colorless prisms: mp 60.5–61.5°; infrared spectrum (Nujol), band at 1725 cm^{-1} (ester); electronic spectrum, $\lambda_{\max}^{\text{EtOH}}$ 242 nm (ϵ 22,800) and λ_{infl} *ca.* 290 nm (ϵ 2100); nmr spectrum ($CDCl_3$, 100 MHz), singlet at τ 2.64 (2 H, benzenoid protons), a doublet centered at 3.45 (2 H, *J* = 12 Hz, protons 3 and 8), a quartet centered at 3.82, 3.94 (2 H, *J* = 12, *ca.* 1 Hz, protons 4 and 7), a narrow multiplet at 4.10 (2 H, *J* = *ca.* 1 Hz, protons 5 and 6), and a singlet at 6.11 (6 H, methyl protons); 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, 70.83; H, 5.02.

B. From 7-Methylene-8-chloromethylene-1,3,5-cyclooctatriene (10). A solution of **10** (350 mg, 2.1 mmoles) and dimethyl acetylenedicarboxylate (500 mg, 3.5 mmoles) in cyclohexane (100 ml) was boiled under reflux for 60 hr. Isolation and chromatography as described under A yielded **22** (255 mg, 44%), mp 60–61°, undepressed on admixture with the above described sample.

C. From Dimethyl 9,12-Dihydrobenzocyclooctatetraene-10,11-dicarboxylate (15). A solution of **15** (470 mg, 1.73 mmoles) and 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (600 mg, 2.64 mmoles) in benzene (60 ml) was boiled under reflux for 75 min. The cooled solution was adsorbed onto an alumina column (Spence grade H, 40 × 2.5 cm), which was eluted with pentane–ether (1:1). The eluate (1 l.) was evaporated and the residue was crystallized from pentane. The resulting **22** (380 mg, 81%) showed mp 60–61°, undepressed on admixture with the sample obtained by method A. Further proof of identity was obtained by comparison of the infrared and nmr spectra.

Benzocyclooctatetraene-10,11-dicarboxylic Acid (23). The diester **22** (207 mg) was added to 50% aqueous ethanol (20 ml) containing potassium hydroxide (2 g), and the mixture was boiled under reflux for 30 min. Concentration to small volume and acidification with dilute hydrochloric acid gave a solid, which was collected and crystallized from aqueous methanol. The resulting benzocyclooctatetraene-10,11-dicarboxylic acid (**23**, 162 mg, 87%) formed colorless plates: mp 175–178° dec (rapid heating); infrared spectrum ($CHCl_3$), band at 1705 cm^{-1} (carboxylic acid); electronic spectrum, $\lambda_{\max}^{\text{EtOH}}$ 242 nm (ϵ 18,400).

Anal. Calcd for $C_{14}H_{10}O_4$: C, 69.42; H, 4.16. Found: C, 69.13; H, 4.20.

Benzocyclooctatetraene (24). An intimate mixture of **23** (100 mg) and copper chromite (200 mg) was placed in a sublimation tube and covered with a further quantity (100 mg) of copper chromite.[15] The tube was evacuated (0.3 mm) and the contents were heated at 260–270° for 1 hr. The crystals (colorless prisms, mp 49–50°) which had formed in the cool part of the tube proved to be benzocyclooctatetraene (**24**, 2 mg, 3%), identified by direct comparison with an authentic sample (mp 49.5–50°).[16]

Dicyclooctatetraeno[1,2:4,5]-1,4-cyclohexadiene (30). A solution of **4** (750 mg, 5.7 mmoles) and bromocyclooctatetraene (**28**, 1.25 g, 6.8 mmoles)[24] in dry ether (25 ml) was added to a suspension of potassium *t*-butoxide (750 mg, 6.7 mmoles, dried at 100–120° for 6 hr) in dry ether (25 ml), and the mixture was stirred at room temperature for 72 hr. A red-brown precipitate was removed by filtration, the filtrate was evaporated, and the residue was adsorbed onto a column of silicic acid (Mallinckrodt, 30 × 25 cm). The column was developed with 1 l. of pentane and then with 1.5 l. of pentane–ether (19:1), fractions of 250 ml being collected. Fractions 3 and 4 on evaporation gave unchanged bromocyclooctatetraene (880 mg, 70%). Fraction 7 on evaporation and crystallization from pentane yielded dicyclooctatetraeno[1,2:4,5]-1,4-cyclohexadiene (**30**, 295 mg, 22%) as pale yellow prisms: mp 138–142°; nmr spectrum ($CDCl_3$, 100 MHz), peaks at τ 4.10 and 4.20 (12 H, olefinic protons) and at τ 7.42 (4 H, methylene protons); mass spectrum, molecular ion (base) peak at *m/e* 232.

Anal. Calcd for $C_{18}H_{16}$: C, 93.06; H, 6.94. Found: C, 93.11; H, 6.73.

Dicyclooctatetraeno[1,2:4,5]benzene (27). A. From Dicyclooctatetraeno[1,2:4,5]-1,4-cyclohexadiene (30) by Dehydrogenation with 2,3-Dichloro-5,6-dicyano-*p*-benzoquinone. A solution of **30** (166 mg, 0.72 mmole) and 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (165 mg, 0.73 mmole) in benzene (50 ml) was boiled under reflux for 1 hr. The cooled solution was adsorbed onto a column of alumina (Spence, grade H, 30 × 2.5 cm), which was eluted with pentane–ether (1:1). Evaporation of the eluate (500 ml) and sublimation of the residue at 100° (0.5 mm) yielded dicyclooctatetraeno[1.2:4.5]-benzene (**27**, 78 mg, 47%) as pale yellow prisms: mp 179–181°; infrared spectrum (KBr), bands at 3000 (s), 1655 (w), 1630 (w), 1500 (m), 1420 (w), 1395 (w), 1210 (m), 1170 (m), 965 (m), 925 (m), 900 (vs), 795 (m), 775 (m), 755 (vs), 715 (m), and 685 cm^{-1} (vs); electronic spectrum, λ_{max}^{EtOH} 254 nm (ϵ 24,700); nmr spectrum, see Discussion; mass spectrum, molecular ion (base) peak at *m/e* 230.

Anal. Calcd for $C_{18}H_{14}$: C, 93.87; H, 6.13. Found: C, 93.53; H, 5.93.

B. From Dicyclooctatetraeno[1,2:4,5]-1,4-cyclohexadiene (30) by Dehydrogenation with Palladium–Charcoal. A mixture containing **30** (72 mg) and 10% palladium–charcoal (35 mg) in decalin (20 ml) was boiled under reflux for 4 hr, the system being flushed continuously with a stream of carbon dioxide. The mixture was cooled, filtered, and evaporated under reduced pressure (0.5 mm). Sublimation of the residue at 100° (0.5 mm) gave **27** (26 mg, 36%), mp 178–181°. Identity with the sample obtained by method A was established by mixture melting point determination, as well as by comparison of the infrared and nmr spectra.

C. From 1,2-Bis(bromomethyl)cyclooctatetraene (7) and Bromocyclooctatetraene (28). A solution of **7** (900 mg, 3.1 mmoles) and **28** (600 mg, 3.3 mmoles) in dry ether (10 ml) was added to a suspension of potassium *t*-butoxide (1.2 g, 10.7 mmoles), and the mixture was stirred at room temperature for 72 hr. The resulting precipitate was removed by filtration, the filtrate was evaporated, and the residue was adsorbed onto a column of silicic acid (Mallinckrodt, 30 × 2.5 cm). The column was developed with 1 l. of pentane and then with 1 l. of pentane–ether (19:1), fractions of 150 ml being collected. Fraction 9 on evaporation and crystallization from pentane yielded **27** (78 mg, 11%), mp 179–181°, identified with the sample obtained by method A by mixture melting point determination and spectral comparison (infrared, nmr).

Silver Nitrate Adduct of Dicyclooctatetraeno[1,2:4,5]benzene (27). A solution of **27** (20 mg, 0.087 mmole) and silver nitrate (35 mg, 0.21 mmole) in ethanol (3 ml) was boiled under reflux for 45 min. Cooling and recrystallization of the precipitate from methanol gave the 1:1 adduct as pale yellow prisms, which decomposed gradually >200° on attempted melting point determination.

Anal. Calcd for $C_{18}H_{14}\cdot AgNO_3$: C, 54.02; H, 3.53. Found: C, 54.00; H, 3.61.

Dicycloocteno[1,2:4,5]benzene (32). A solution of **27** (50 mg) in ethyl acetate (10 ml) and methanol (20 ml) was added to a suspension of a 5% palladium–calcium carbonate catalyst (*ca.* 100 mg) in methanol (20 ml), and the mixture was stirred in hydrogen at atmospheric pressure and room temperature until uptake ceased (5.6 molar equiv of hydrogen absorbed). The catalyst was removed by filtration, the solvent was evaporated under reduced pressure, and the residue was crystallized from methanol–ether. The resulting dicycloocteno[1,2:4,5]benzene (**32**, 51 mg, 97%) formed colorless needles: mp 132–133°; electronic spectrum, λ_{max}^{EtOH} 263 nm (ϵ 505), 271 (1000), 275 (830), and 280 (1240); λ_{infl}^{EtOH} 255 nm (ϵ 260), 259 (365), and 267 (655); nmr spectrum (CCl_4, 100 MHz), singlet at τ 3.27 (2 H, benzenoid protons), three peaks at 7.26, 7.32, and 7.38 (8 H, benzylic protons), complex multiplet centered at 8.33 (8 H, methylene protons 8, 11, 14, 17), and complex multiplet at 8.63 (8 H, methylene protons 9, 10, 15, and 16); mass spectrum, molecular ion (base) peak at *m/e* 242.

Anal. Calcd for $C_{18}H_{26}$: C, 89.19; H, 10.81. Found: C, 89.22; H, 10.54.

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