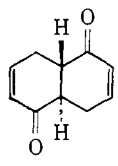
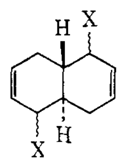
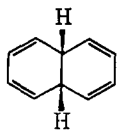
Entry into the desired $C_{10}H_{10}$ series was managed by utilizing the hexalindione III[5] as starting material. Reduction of the diketone was carried out by soxhlet extraction into a suspension of a 100-fold molar excess of lithium aluminum hydride in refluxing ether. The desired dienediol IV (X = OH),[6] a white solid (mp 212–14°) obtained in quantitative yield, was converted back to starting material with Jones reagent. The diol was directly converted with 48% aqueous hydrobromic acid–petroleum ether to two (tlc) unrearranged diene dibromides IV (X = Br)[6] in 70% yield.[7] Through the action of N-bromosuccinimide in carbon tetrachloride, the dibromide was transformed into the allylic tetrabromide V, a mixture of various undefined racemates.[6] Dehalogenation of V was brought about by 0.5% lithium-amalgam in ether.[8] A hydrocarbon (VI) was isolated by preparative vpc (10 ft × 0.25 in., 5% DC550 on Chromosorb G) and was found to be at room temperature a liquid which decomposed with exceeding ease to naphthalene. The new polyene exhibited maximal ultraviolet absorption in methanol at 231 mμ and revealed surprisingly simple nmr behavior in that two virtually unsplit signals appeared at τ 4.1 and 7.2 (4:1 proton ratio, 60 Mc in $CDCl_3$).[9] On the basis of its chemical and spectral behavior, VI is best regarded as *trans*-9,10-dihydronaphthalene (VII).

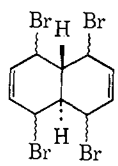

III



IV

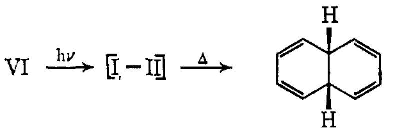


VII



V

On being photolyzed in pentane at room temperature for 2 min by means of unfiltered light (2537 A) from a Rayonet photochemical reactor, hydrocarbon VI gave rise to a large number of products, among which the following were identified by vpc and ultraviolet methods: deca-1,3,5,7,9-pentaene, *trans*-1-phenylbuta-1,3-diene, naphthalene, 1,2-dihydronaphthalene, *cis*-9,10-dihydronaphthalene, bicyclo[4.2.2]deca-2,3,7,9-tetraene,[10] and bullvalene.[11] The appearance of *cis*-9,10-dihydronaphthalene (and its photoproducts[11]) in comparatively major amount suggested its formation by a thermal, disrotatory process from transient cyclodecapentaene, itself formed in a conrotatory[12] event from excited-state *trans*-9,10-dihydronaphthalene. On the strength of this surmise, and with the aim of preserving the unstable isomer under modified conditions, low-temperature photolysis experiments were initiated. At −190°, no *cis*-9,10-dihydronaphthalene was detected after irradiation of the *trans* isomer in ethyl ether–isopentane–ethanol; however, after being warmed to *ca.* room temperature and recooled to −190°, the photolysis mixture exhibited the characteristic ultraviolet absorption (λ_{max} 247 mμ) of the *cis* isomer.[4] Diimide reduction,[13] carried out at the lowest possible temperature, converted the elusive cyclodecapentaene to cyclodecane, which was isolated and purified by preparative vpc, then identified and compared with authentic material by appropriate vpc and mass spectral means. In the low-temperature photolysis–reduction sequence, the final product was composed of *ca.* 40% cyclodecane (vpc); after room-temperature irradiation, only traces of cyclodecane are apparently formed by diimide reduction of total product. Although the trapping and identification of cyclodecapentaene seem unequivocal, questions concerning the geometry, conformation, and electronic character of the hydrocarbon remain open and await future answers. However, it appears that a central issue, namely the nature of the balance between stabilizing, 10-π-electron aromaticity, on the one hand, and destabilizing strain and/or steric effects, on the other, has been largely resolved.



Acknowledgment. The authors are indebted to ARO(D) for grant support (Project No. CRD-AA-5227-C).

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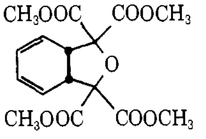
(5) W. S. Johnson, J. D. Bass, and K. L. Williamson, *Tetrahedron*, **19**, 861 (1963).

(6) Infrared and nmr spectral characteristics of this intermediate were completely consistent with the assigned structure.

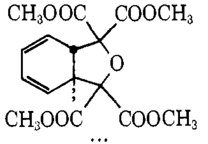
(7) The two compounds were shown to be closely related isomers by separation employing column chromatography on Florisil, then generation of the same product mixture (tlc) from each in the succeeding reaction with NBS.

(8) R. Criegee and G. Louis, *Chem. Ber.*, **90**, 417 (1957).

(9) A satisfying nmr parallel is found in the *cis* and *trans* isomeric pair ii (R. E. Benson, W. J. Linn, and O. W. Webster, *J. Am. Chem. Soc.*, **85**, 2032 (1963)) and iii (obtained by Dr. G. V. Parry in this laboratory by ultraviolet irradiation of ii). Whereas tetraester ii, like *cis*-9,10-dihydronaphthalene,[4] exhibits extensive splitting in the vinyl and methine proton regions (τ 3.9–4.1, 4.2–4.5, and 5.98–6.02, all multiplets in the integrated ratio 2:2:2), isomer iii revealed singlets in the vinyl (τ 3.9) and methine (τ 6.50) regions.



ii



iii

(10) M. Jones, Jr., and L. T. Scott, *J. Am. Chem. Soc.*, **89**, 150 (1967), also detected VI as a secondary product in their synthetic route to this isomer. We are grateful to these investigators for supplying information in advance of publication.

(11) W. von E. Doering and J. W. Rosenthal, *ibid.*, **88**, 2078 (1966).

(12) R. B. Woodward and R. Hoffman, *ibid.*, **87**, 395 (1965), and references cited therein.

(13) The reagent was generated by addition of cold acetic acid to disodium azodicarboxylate in methanol at acetone–Dry Ice temperature, both before and after addition of cold irradiation product (see E. E. van Tamelen, R. S. Dewey, and R. J. Timmons, *ibid.*, **83**, 3725 (1961), for close precedents). Reduction presumably occurred at −70° and/or during the warming to room temperature.

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Received October 28, 1966

Synthesis of a Triquinocyclopropane

Sir:

Recently there has been a great deal of interest in derivatives of trimethylenecyclopropane.[1] We wish to report the synthesis of the triquinocyclopropane **2**,

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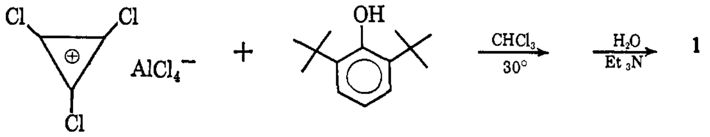
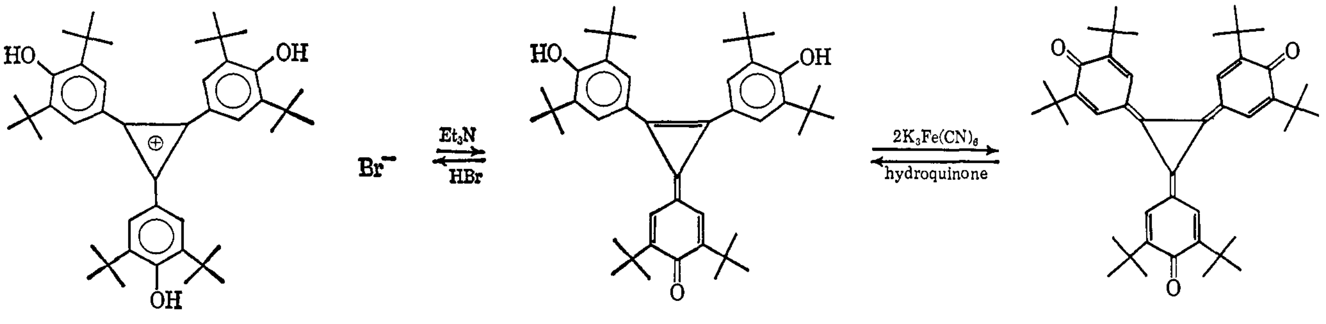
(1) (a) E. A. Dorko, *J. Am. Chem. Soc.*, **87**, 5518 (1965); (b) G. Köbrich and H. Heinemann, *Angew. Chem. Intern. Ed. Eng.*, **4**, 594 (1965);(c) P. A. Waitkus, L. I. Peterson, and G. W. Griffin, *J. Am. Chem. Soc.*, **88**, 181 (1966).

a trimethylenecyclopropane derivative of unprecedented stability. **2** was obtained by the oxidation of the quinocyclopropene **1**, which was in turn synthesized from trichlorocyclopropenium tetrachloroaluminate[2] and 2,6-di-*t*-butylphenol.





3 1 2

Previous work from these laboratories showed that aryltrichlorocyclopropenes and diarylcyclopropenones could be obtained by the reaction of $C_3Cl_3^+AlCl_4^-$ with benzene and substituted benzenes.[2b] More recently we have found that triarylcyclopropenium ions are formed in this reaction when activated aromatic compounds react with $C_3Cl_3^+$ salts.[3] If one of the aromatic rings bears a *p*-hydroxyl group, deprotonation to a quinocyclopropene can often be effected.[3,4]

When 2,6-di-*t*-butylphenol in chloroform was allowed to react with $C_3Cl_3^+AlCl_4^-$, then hydrolyzed and treated with triethylamine, **1**[5] was formed in yields up to 70%. The quinocyclopropene **1**, an orange-red solid, showed the following ultraviolet-visible absorption maxima in acetonitrile solution: λ 310 mμ (log ϵ 4.40), 323 (4.42), 386 sh (4.56), and 406 (4.86). The infrared showed an absorption of medium strength at 1820 cm^{-1} and a strong band at 1595 cm^{-1}, both of which appear to be characteristic for the quinocyclopropene system.[3] **1** was quite insoluble in solvents commonly used for nmr spectra, but was soluble in trifluoroacetic acid. The proton nmr spectrum in this solvent showed singlets at τ 1.60 and 8.30 in a 1:9 ratio, as expected for the aromatic and *t*-butyl hydrogens in the protonated form of **1**.

Upon treatment with hydrogen bromide in ether, **1** was converted to the corresponding triarylcyclopropenium bromide, **3**. The infrared spectrum of **3** showed a strong band at 1590 cm^{-1} and a very strong, broad absorption at 1370 cm^{-1}, characteristic for carbon–carbon ring expansion in triarylcyclopropenium salts.[6] The ultraviolet spectrum in CH_3CN showed λ_{max} 241 mμ (log ϵ 4.50), 288 (4.14), 352 (4.73), and 370 (4.79); the spectrum is similar to that reported for trianisylcyclopropenium bromide.[7]

Oxidation of **1** in benzene with lead dioxide or aqueous basic potassium ferricyanide immediately gave an intense blue-green solution, which was evaporated to give crude **2**. Recrystallization from dichloromethane–acetonitrile afforded pure **2** as a dark blue powder, stable to above 250° in air, decomposing without melting at about 280°.

The ultraviolet-visible spectrum of **2** in benzene showed λ_{max} 307 mμ (log ϵ 4.13), 316 (4.15), 390 (4.62), 625 sh (4.43), and 685 (4.68). The infrared spectrum showed only six bands of strong or moderate intensity between 625 and 2500 cm^{-1}, at 1590, 1465, 1355, 1250, 1090, and 900 cm^{-1}, suggesting a highly symmetrical structure. Bands characteristic for hydroxyl or cyclopropene are absent. The nmr spectrum of **2** in CCl_4 consists of two singlets at τ 2.50 and 8.60 in 1:9 ratio. All of the spectral evidence is compatible with the assigned structure.

Upon treatment with hydroquinone, solutions of **2** are reduced to **1**. Spectroscopic studies indicate that the two-electron oxidation–reduction involving **1** and **2** is rapid in both directions and is essentially quantitative.

A diradical structure can be written for **2**, with two of the rings fully aromatic rather than quinonoid. Electron spin resonance measurements indicate that **2** does not contain unpaired electrons at 25°. The possibility that a diradical state may become populated at higher temperatures is under investigation.

Acknowledgments. This work was supported by a grant from the National Science Foundation.

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(2) (a) S. W. Tobey and R. West, *J. Am. Chem. Soc.*, **86**, 1459 (1964); (b) *ibid.*, **86**, 4215 (1964); (c) R. West, S. W. Tobey, and A. Sadô, *ibid.*, **88**, 2488 (1966).

(3) Unpublished work by R. West and D. C. Zecher.

(4) Two quinocyclopropenes have previously been reported. See A. S. Kende, *J. Am. Chem. Soc.*, **85**, 1882 (1963); B. Föhlisch and P. Bürgle, *Tetrahedron Letters*, 2661 (1965).

(5) All new compounds gave elemental analyses in good agreement with those calculated for the assigned structures.

(6) R. Breslow, H. Höver, and H. W. Chang, *J. Am. Chem. Soc.*, **84**, 3168 (1962); J. Chatt and R. G. Guy, *Chem. Ind.* (London), 212 (1963).

(7) R. Breslow and H. W. Chang, *J. Am. Chem. Soc.*, **83**, 2367 (1961).

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Received November 5, 1966

Synthesis of a Diquinocyclopropanone and a Diquinoethylene

Sir:

The reaction between trichlorocyclopropenium tetrachloroaluminate[1] and aromatic hydrocarbons leading

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(1) (a) S. W. Tobey and R. West, *J. Am. Chem. Soc.*, **86**, 4215 (1964); (b) R. West, A. Sadô, and S. W. Tobey, *ibid.*, **88**, 2488 (1966).