

Unsaturated Eight-Membered Ring Compounds. VI.¹

The Chemistry of Benzocyclooctatetraene

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Abstract: Benzocyclooctatetraene (I) can be conveniently synthesized by Diels–Alder addition of butadiene to 1,2-dehydrocyclooctatetraene (V) followed by dehydrogenation of the dihydro compound (VII) produced. By using 1,2-dimethylenecyclobutane as the diene the benzocyclooctatetraene (IX) was synthesized. The formation of benzocyclooctatetraeneiron tricarbonyl (X) and a benzocyclooctatetraeneiron hexacarbonyl tentatively formulated as XVII is described. The bromination of I afforded 3,4-dibromo-3,4-dihydrobenzocyclooctatetraene (XVIII) which underwent facile rearrangement to 1,2-benzocyclohepta-1,3,5-triene-7-aldehyde (XIX) on chromatography. Nitration gave a mixture of mononitro compounds thought to be the 4-, 5- and 3-nitro compounds XXIII, XXIV, and XXV, respectively. Reaction of I with tetracyanoethylene gave the adduct (XXVII), while reaction with dimethyl acetylenedicarboxylate afforded XXXII, formally by 1,6 addition. The mechanism of this reaction is discussed.

Although the chemistry of cyclooctatetraene has been extensively investigated in recent years,² benzocyclooctatetraene (I) has received comparatively little attention. The literature methods available for the synthesis of I are either tedious or afford low yields. Wittig's original synthesis³ of I involved four steps and gave an over-all yield of 0.7%. The method first described by Stiles,⁴ but recently modified by Friedman,^{5,6} in which benzyne generated by thermolysis of benzenediazonium-2-carboxylate undergoes addition to benzene in presence of silver ions, produces I in 5.4% yield. A third method⁷ based on the addition of dimethyl acetylenedicarboxylate to 7,8-dimethylenecycloocta-1,3,5-triene (II) suffers from the drawbacks that II is not very readily available, and that the final decarboxylation proceeds in only 3% yield. The lead tetraacetate oxidation of a mixture of cyclobutadieneiron tricarbonyl and (benzocyclobutadiene)iron tricarbonyl produces a 75% yield of the benzotricyclooctadiene III. On thermolysis or silver fluoroborate catalyzed ring-opening of III, a quantitative yield of I results.⁸ However cyclobutadieneiron tricarbonyl is not readily available since it is obtained from cyclooctatetraene in a four-step sequence.⁹ The best literature method for the synthesis of I is by the direct ultraviolet irradiation of benzobicyclo[2.2.2]octatriene (IV) (available in 20% yield from addition of benzene to benzyne generated by thermolysis of benzenediazonium-2-carboxylate at 45° in the absence of silver ions⁶), which gives I in 95% yield (19% over-all yield from anthranilic acid).¹⁰

(1) For the previous publication in this series see: J. A. Elix, M. V. Sargent, and F. Sondheimer, *J. Am. Chem. Soc.*, **89**, 5081 (1967).

(2) G. Schröder, "Cyclooctatetraen," Verlag Chemie, Würzburg, 1965.

(3) G. Wittig, H. Eggers, and P. Duffner, *Ann.*, **619**, 10 (1959).

(4) R. G. Miller and M. Stiles, *J. Am. Chem. Soc.*, **85**, 1798 (1962); M. Stiles, N. Burckhardt, and G. Freund, *J. Org. Chem.*, **32**, 3718 (1967).

(5) L. Friedman, *J. Am. Chem. Soc.*, **89**, 3071 (1967).

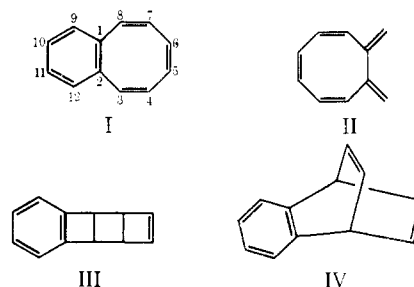
(6) L. Friedman and D. F. Lindow, *ibid.*, **90**, 2329 (1968).

(7) J. A. Elix, M. V. Sargent, and F. Sondheimer, *Chem. Commun.*, 508 (1966).

(8) W. Merk and R. Pettit, *J. Am. Chem. Soc.*, **89**, 4787 (1967).

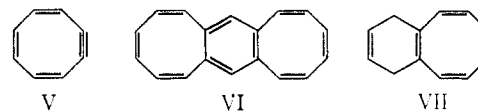
(9) G. F. Emerson, L. Watts, and R. Pettit, *ibid.*, **87**, 131 (1965).

(10) P. W. Rabideau, J. B. Hamilton, and L. Friedman, *ibid.*, **90**, 4465 (1968); see also H. E. Zimmermann, R. S. Givens, and R. M. Pagni, *ibid.*, **90**, 6096 (1968).



1,2-Dehydrocyclooctatetraene (V), generated by treatment of an ether solution of bromocyclooctatetraene with potassium *t*-butoxide, undergoes Diels–Alder reactions with a number of dienes.^{11–13} Reaction with 7,8-dimethylenecycloocta-1,3,5-triene (II), for example, gives after dehydrogenation, a 10% over-all yield of dicyclooctatetraeno[1.2:4.5]benzene (VI).¹³ Indeed Krebs and Byrd¹² have prepared I in 5% yield by treating a mixture of 1-diethylaminobutadiene and bromocyclooctatetraene with potassium *t*-butoxide.

We now describe a convenient and efficient synthesis of benzocyclooctatetraene, involving the intermediacy of 1,2-dehydrocyclooctatetraene. When a solution of butadiene and bromocyclooctatetraene¹⁴ in ether is treated with potassium *t*-butoxide for 60 hr, 9,12-dihydrobenzocyclooctatetraene (VII) is produced in 83% yield¹⁵ after chromatography. The dihydro compound was dehydrogenated to I in 68% yield (44.5% over-all yield from cyclooctatetraene) by boiling under reflux in



(11) A. Krebs, *Angew. Chem.*, **77**, 966 (1965).

(12) A. Krebs and D. Byrd, *Ann.*, **707**, 66 (1967).

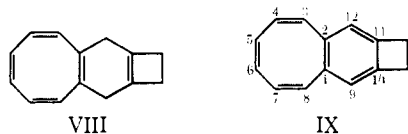
(13) J. A. Elix, M. V. Sargent, and F. Sondheimer, *Chem. Commun.*, 509 (1966).

(14) A. C. Cope and M. Burg, *J. Am. Chem. Soc.*, **74**, 168 (1952). However the method of G. E. Gream and R. Huisgen (private communication from Professor R. Huisgen to Professor F. Sondheimer) was found by us, to be much more convenient, and gave bromocyclooctatetraene in 81% yield based on cyclooctatetraene.

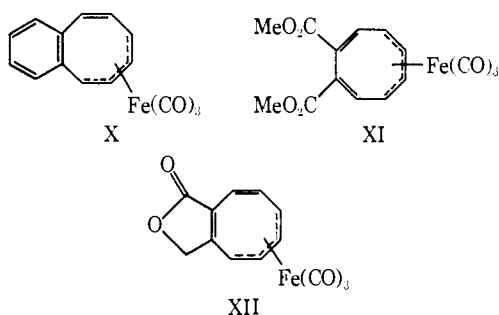
(15) Based on the bromocyclooctatetraene consumed.

benzene with 2,3-dichloro-5,6-dicyano-*p*-benzoquinone. Benzocyclooctatetraene prepared by this method had physical properties identical with those previously described.^{3,4,16}

In a similar fashion the generation of 1,2-dehydrocyclooctatetraene in the presence of 1,2-dimethylenecyclobutane¹⁷ gave a 13.3% yield¹⁵ of 10,11-cyclobuteno-9,12-dihydrobenzocyclooctatetraene (VIII) which was dehydrogenated in virtually quantitative yield to 10,11-cyclobutenobenzocyclooctatetraene (IX).¹⁸

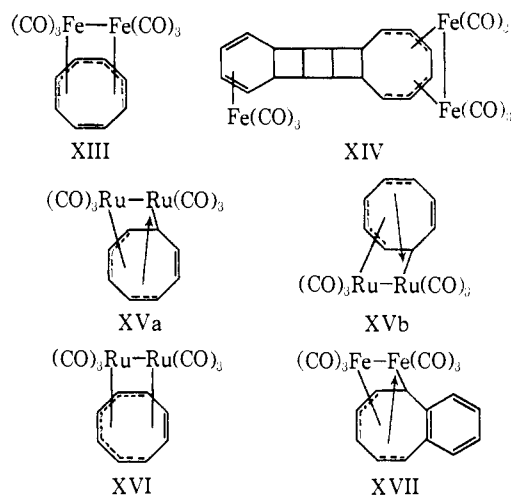


Iron Carbonyl Complexes of I. Benzocyclooctatetraene did not give iron carbonyl complexes on reaction with iron pentacarbonyl, but reacted readily with both diiron enneacarbonyl and triiron dodecacarbonyl in boiling benzene to form a mixture of two complexes; one an orange iron tricarbonyl complex, and the other a red diiron hexacarbonyl complex separable by preparative layer chromatography. The iron tricarbonyl complex is formulated as X on the basis of its spectroscopic properties. In particular, the nmr spectrum confirms that the complex is unsymmetrical and that one olefinic double bond is not involved in complex formation (the chemical shift being virtually unaltered from that observed for I). The electronic spectrum of the complex is compatible with structure X since it shows a band at 305 nm, characteristic of a complex containing an iron atom bound to a 1,3-diene group.¹⁹ Like the disubstituted cyclooctatetraeneiron tricarbonyl complexes XI and XII,¹⁹ complex X does not undergo the rapid intramolecular rearrangement in solution at room temperature which is characteristic of cyclooctatetraeneiron tricarbonyl (this is shown by the failure of X to exhibit any time-averaging phenomena in the nmr spectrum).



For the other complex, benzocyclooctatetraenediiron hexacarbonyl, the nmr spectrum indicates that the bonding in the eight-membered ring gives rise to a symmetrical species with a plane of symmetry along the long axis of the molecule, hence this complex must be closely related to the analogous cyclooctatetraenediiron hexacarbonyl,²⁰ cyclooctatetraenediruthenium hexacar-

bonyl,^{21,22} and 1,3,5,7-tetramethylcyclooctatetraenediiron hexacarbonyl²³ complexes. Pettit and his co-workers²⁰ proposed the symmetrical structure XIII for the cyclooctatetraenediiron hexacarbonyl complex, on the grounds of the Mössbauer and nmr spectra, and a similar structure XIV, involving a bis- π -allylic type of interaction has been proposed for a complex of a cyclooctatetraene dimer.²⁴ The X-ray evidence of Cotton and Edwards²² on the structure of the cyclooctatetraenediruthenium hexacarbonyl complex shows that the molecule possesses no symmetry in the crystal but consists approximately of a $(OC)_3Ru-Ru(CO)_3$ moiety bonded to the ring by a π -allyl-metal bond to one Ru, an olefin-metal bond and a carbon-metal σ bond to the other Ru, and an uncoordinated olefinic double bond in the ring, perpendicular to the Ru-Ru line. This unsymmetrical structure XVa cannot give rise to the observed nmr spectrum so these authors suggest that it is likely that the molecule may rearrange to XVI in solution, or it may be fluxional in the manner XVa \rightarrow XVb, the structure in the crystal being the one of lowest energy, separated from its mirror image by a low energy barrier *via* XVI. The state of affairs in the cyclooctatetraenediiron hexacarbonyl complex may be similar but awaits clarification.²² Hence we tentatively propose that the benzocyclooctatetraenediiron hexacarbonyl complex may be represented as XVII in the crystalline state, the observed nmr spectrum possibly arising by one of the mechanisms of Cotton and Edwards.



The benzocyclooctatetraenediiron hexacarbonyl complex proved to be unstable on prolonged storage in ether solution at room temperature in the dark. Benzocyclooctatetraeneiron tricarbonyl (X) is produced in addition to insoluble polymeric material. Due to the presence of the fused benzene ring, this thermal decomposition does not parallel that of the corresponding cyclooctatetraene complexes.^{19,21,23} The complex also decomposes at its melting point, with the liberation of carbon monoxide.

Bromination and Nitration of I. Benzocyclooctatetraene undergoes smooth addition of bromine at -78° in dichloromethane solution to give a product formulated as 3,4-dibromo-3,4-dihydrobenzocyclooctatet-

(16) The electronic spectrum was virtually identical with that reported by Stiles,⁴ but differed from that reported by Wittig.³

(17) A. T. Blomquist and J. A. Verdol, *J. Am. Chem. Soc.*, **77**, 1806 (1955).

(18) Attempts by a variety of methods to introduce a further double bond into IX met with failure.

(19) R. Grubbs, R. Breslow, R. Herber, and S. J. Lippard, *J. Am. Chem. Soc.*, **89**, 6864 (1967).

(20) C. E. Keller, G. F. Emerson, and R. Pettit, *ibid.*, **87**, 1388 (1965).

(21) F. A. Cotton, A. Davison, and A. Musco, *ibid.*, **89**, 6796 (1967).

(22) F. A. Cotton and W. T. Edwards, *ibid.*, **90**, 5412 (1968).

(23) F. A. Cotton and A. Musco, *ibid.*, **90**, 1444 (1968).

(24) G. N. Schrauzer and P. W. Glockner, *ibid.*, **90**, 2800 (1968).

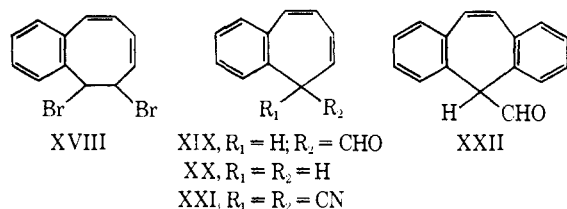
raene (XVIII) on the basis of its nmr spectrum and microanalysis. This structure is supported by the isolation of 1,2-benzocyclohepta-1,3,5-triene-7-aldehyde (XIX) on chromatography of XVIII or the mother liquors from the crystallization of XVIII. Structure XIX follows from the infrared (carbonyl at 1730 cm^{-1}) and nmr spectra, and the similarity of the electronic spectrum to those of 1,2-benzocyclohepta-1,3,5-triene³ (XX) and 7,7-dicyano-1,2-benzocyclohepta-1,3,5-triene²⁵ (XXI) (see Table I). The behavior of I on bromi-

Table I. Electronic Spectra of 1,2-Benzocyclohepta-1,3,5-trienes in Cyclohexane

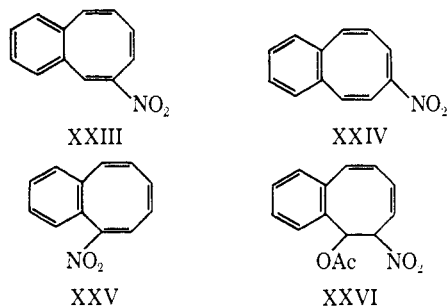
Compd	λ_{max} , nm (ϵ)	λ_{min} , nm (ϵ)
XIX ^a	280 (5900)	248 (3000)
XX ^b	275 (7400)	243 (2900)
XXI ^c	277 (8000)	243 (2600)

^a In ethanol. ^b These values are estimated from the reproduction of the spectrum in ref 3. ^c See ref 25.

nation thus closely parallels that of dibenzocyclooctatetraene, the dibromo compound of which also undergoes carbonium ion rearrangement to a cycloheptatrienaldehyde (XXII) on hydrolysis.²⁶



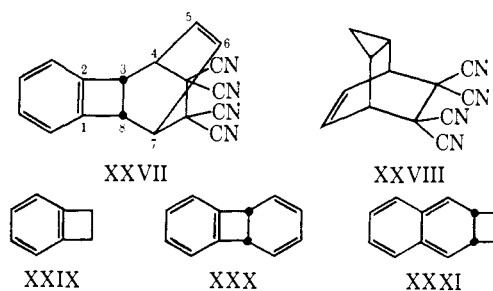
The nitration of I, under conditions similar to those used for the nitration of [18]annulene,²⁷ is somewhat more complex. Chromatography of the crude product gave a 13% yield of an oil which probably contained three monitro compounds. This could not be further resolved by chromatography in a variety of solvent systems. From the complex nmr spectrum (see Experimental Section), it is suggested that the mixture contains the three isomers XXIII, XXIV, and XXV. The low-



field singlet at τ 1.97 is presumed to be due to the 4-nitro isomer (XXIII), which thus comprises about 50% of the mixture. If substitution had occurred in the benzene ring (at the 10 position), the remaining 9 proton would still exhibit *meta* coupling. Since coupling is not observed between protons 3 and 5 in benzocycloocta-

tetraene the low-field singlet is best ascribed to proton 3, the nitro group thus occupying the 4 position. This nitration is analogous to that undergone by styrene,²⁸ and olefins in general, in the presence of acetyl nitrate. The ammonia work-up is probably effective in eliminating acetic acid from the initially formed acetoxynitro compound (e.g., XXVI \rightarrow XXIII).

Diels-Alder Reactions of I. Benzocyclooctatetraene reacted with tetracyanoethylene in boiling tetrachloroethane to give an adduct in 45% yield, the structure (XXVII) of which follows from the similarity of its nmr spectrum to that of the tetracyanoethylene-cycloheptatriene adduct²⁹ (XXVIII), and the resemblance of its electronic spectrum to that of benzocyclobutene (XXIX). Unlike the behavior of I on bromination and nitration, this reaction implicates the valence tautomer (XXX) as an intermediate. This is in marked contrast to the silver fluoroborate catalyzed reaction of maleic anhydride with the valence tautomer (III) of benzocyclooctatetraene where Diels-Alder addition occurs on the central ring of the *o*-xylylene intermediate XXXI.⁸



Reaction of I with dimethyl acetylenedicarboxylate in boiling xylene gave a 26% yield of the adduct XXXII, the spectroscopic properties of which are strikingly similar to those of XXXIII³⁰ and the parent hydrocarbon (XXXIV)^{31,32} (see Table II for electronic spectra).

Table II. Electronic Spectra of Bicyclo[4.2.2]deca-2,4,7,9-tetraenes in Ethanol

Compd	λ_{max} , nm (ϵ)	λ_{max} , nm (ϵ)	λ_{max} , nm (ϵ)
XXXII	258 sh (3400)	272 (3100)	282 (3100)
XXXIII ^{a,b}	260 (3900)	270 (4200)	281 (2900)
XXXIV ^c	258 (4200)	268 (4200)	280 (2900)
XXXV ^{a,d}	265 (3400)	272 (3300)	286 sh (3400)
XXXVI ^{e,f}	258.5 (4600)	268.5 (5000)	280 (2700)

^a In methanol. ^b See ref 30. ^c See ref 31. ^d See ref 33. ^e In hexane. ^f G. Schröder and W. Martin, *Angew. Chem. Intern. Ed. Engl.*, **5**, 130 (1966).

Other substituted derivatives of the bicyclo[4.2.2]deca-2,4,7,9-tetraene system are also known.³³⁻³⁶ This apparent 1,6 addition of dimethyl acetylenedicarboxylate to I poses a mechanistic problem also encountered in the 1,4 addition of various species to cyclooctatetraene it-

(28) F. G. Bordwell and E. W. Garbisch, *J. Org. Chem.*, **27**, 2322 (1962).

(29) G. H. Wahl, *ibid.*, **33**, 2158 (1968).

(30) E. Vedejs, *Tetrahedron Letters*, 2633 (1968).

(31) M. Jones, Jr., *J. Am. Chem. Soc.*, **89**, 4236 (1967).

(32) M. Jones, Jr., and B. Failress, *Tetrahedron Letters*, 4881 (1968).

(33) E. Babad, D. Ginsburg, and M. M. Rubin, *ibid.*, 2361 (1968).

(34) E. Vogel, W. Grimme, W. Meckel, and H. J. Riebel, *Angew. Chem.*, **78**, 599 (1966); W. Grimme, H. J. Riebel, and E. Vogel, *ibid.*, **80**, 803 (1968).

(35) U. Krüerke, *ibid.*, **79**, 55 (1967).

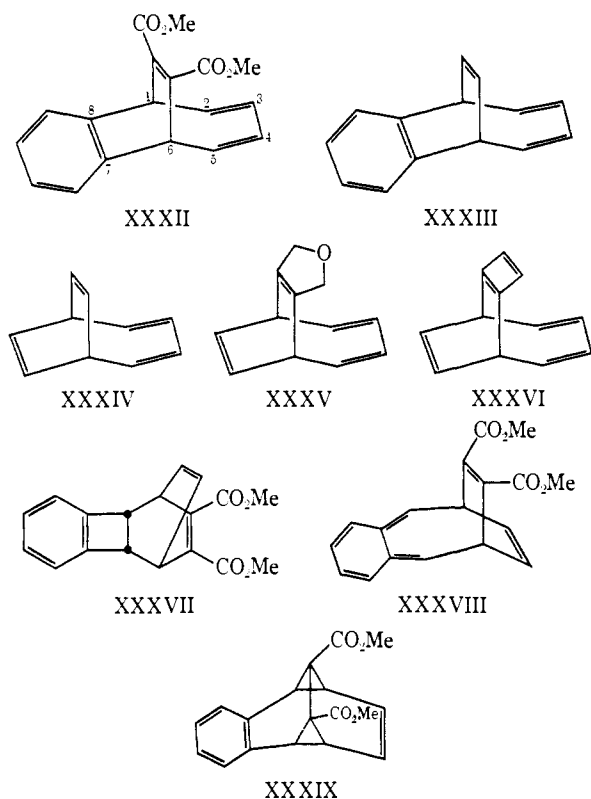
(36) H.-P. Löffler and G. Schröder, *ibid.*, **80**, 758 (1968).

(25) E. Ciganek, *J. Am. Chem. Soc.*, **89**, 1454 (1967).

(26) M. P. Cava, R. Pohlke, B. W. Erickson, J. C. Rose, and G. Fraenkel, *Tetrahedron*, **18**, 1005 (1962); M. Avram, I. G. Dinulescu, D. Dinu, G. Mateescu, and C. D. Nenitzescu, *ibid.*, **19**, 309 (1963).

(27) F. Sondheimer, R. Wolovsky, and Y. Amiel, *J. Am. Chem. Soc.*, **84**, 274 (1962).

self.^{30,37} In our case we prefer a mechanism in which I first undergoes valence tautomerism to XXX and Diels–Alder addition occurs in similar fashion to the tetracyanoethylene adduct (XXVII) to give the benzocyclobutene (XXXVII). Although in this case a conrotatory thermal benzocyclobutene-*o*-xylylene isomerization is precluded due to the constraints imposed by the ring system,⁵ we propose that under the relatively vigorous conditions employed, an *o*-xylylene intermediate (XXXVIII) is formed, possibly by a radical mechanism. Support for this hypothesis is found in the Diels–Alder reactions of benzocyclobutene itself.³⁸ The bicyclo[4.2.2]deca-2,4,7,9-tetraene system produced is now able to rearrange *via* a tetracyclo[4.4.0.0^{2,10}.0^{5,7}]-deca-3,8-diene intermediate (XXXIX) to the observed product (XXXII), with the regeneration of the aromatic sextet. This latter type of rearrangement of the bicyclic decatetraene system *via* a tetracyclic decadiene intermediate is now well authenticated,^{32–34,39} and the intermediate has been isolated in certain cases.^{33,39}



Experimental Section

All melting points were determined on a Kofler hot stage apparatus. Proton magnetic resonance spectra were measured on a Varian HA-100 (100 MHz) or a Perkin-Elmer R-10 (60 MHz) spectrometer in carbon tetrachloride solution unless stated otherwise. Electronic spectra were measured on a Cary 14-50 or a Unicam SP800 spectrophotometer. Infrared spectra were determined on a Perkin-Elmer 257 or a Unicam SP200 spectrophotometer, and mass spectra on an A.E.I. MS-9 spectrometer operating at 70 eV. Silica gel for preparative layer chromatography was Merck HF₂₅₄₋₂₆₆, and petroleum ether was the fraction bp 40–60°, unless otherwise stated.

(37) A. B. Evin, R. D. Miller, and G. R. Evanega, *Tetrahedron Letters*, 5863 (1968); L. A. Paquette and T. J. Barton, *J. Am. Chem. Soc.*, **89**, 5480 (1967), and references therein.

(38) F. R. Jensen, W. E. Coleman, and A. J. Berlin, *Tetrahedron Letters*, 15 (1962); see also G. Quinkert, K. Opitz, W.-W. Wiersdorff, and M. Finke, *Ann.*, **693**, 44 (1966), and references therein.

(39) S. Masamune, R. T. Seidner, H. Zenda, M. Wiesel, N. Nakatsuka, and G. Bigam, *J. Am. Chem. Soc.*, **90**, 5286 (1968). A bibliography of the tetracyclic decadiene system is given by these authors.

9,12-Dihydrobenzocyclooctatetraene (VII). A vigorous stream of butadiene was passed through absolute ether (250 ml) for 0.75 hr, and pulverized potassium *t*-butoxide⁴⁰ (5 g) and bromocyclooctatetraene¹⁴ (5.00 g) were added, and the stoppered flask was set aside in the dark for 60 hr. The suspension was filtered off and washed with ether, and the filtrate and washings were extracted with saturated brine (50 ml) and dried (MgSO₄). The ether was removed under reduced pressure and the oily residue chromatographed over silica gel (British Drug Houses, 750 g). Petroleum ether (bp 30–40°) eluted unreacted bromocyclooctatetraene (2.57 g), and petroleum ether (bp 30–40°)–2% ether eluted VII (1.82 g, 83%)¹⁵ as a yellow oil. The electronic spectrum (EtOH) had a band at 213 nm with a long tail, similar to cyclooctatetraene itself. The infrared spectrum (film) had bands at 3135 (m), 2998 (s), 2955 (m), 2921 (m), 2872 (m), 2815 (m), 1658 (m), 1455 (w), 1427 (m), 1392 (w), 1378 (w), 1170 (w), 1119 (w), 982 (w), 968 (w), 947 (m), 923 (m), 788 (s), 751 (s), 738 (s), 690 (s), and 660 (m) cm⁻¹. The nmr spectrum (100 MHz) had two singlets at τ 4.26 and 4.38 (total 8 H) due to the olefinic protons, and a singlet at 7.48 (4 H) due to the methylene protons. The mass spectrum showed a molecular ion at m/e 156.0905 (calcd for C₁₂H₁₂: 156.0939). Prominent peaks were apparent at m/e 155, 141, 128, 115 (base peak), and 91.

Benzocyclooctatetraene (I). The foregoing dihydro compound (1.82 g) and 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (2.7 g) were heated under reflux in dry benzene (120 ml) for 1.2 hr. The cooled solution was poured onto a column of alumina (Spence grade H, 2.5 × 70 cm) and I was eluted with petroleum ether (bp 30–40°)–50% ether. After crystallization from aqueous ethanol, it gave pale yellow prisms (1.22 g, 68%), mp 49.5–50° (lit.³ 50–51°). The electronic spectrum (EtOH) had λ_{max} 234 and 275 nm (ϵ 21,600 and 920) and λ_{min} 224 and 266 nm (ϵ 20,400 and 890). The infrared spectrum (CCl₄) exhibited bands at 3058 (m), 3012 (s), 2958 (m), 2924 (m), 1654 (w), 1642 (w), 1630 (w), 1609 (w), 1492 (s), 1447 (s), 1401 (m), 1221 (w), 1173 (m), 1110 (m), 1042 (m), 968 (w), 950 (m), 942 (s), 919 (w), and (CS₂) 810 (s), 770 (s), 760 (s), 737 (s), 692 (s), 678 (w), and 646 (s) cm⁻¹. The nmr spectrum (100 MHz) showed an A₂B₂ pattern centered at τ 2.87 and 3.10 (4 H) for the benzenoid protons, a doublet centered at 3.49 (2 H, J = 12.0 Hz) due to protons 3 and 8, a quartet centered at 3.97, and 4.09 (2 H, J = 12.0 and 2.0 Hz) due to protons 4 and 7, and a narrow multiplet centered at 4.16 (2 H, J = 2.0 Hz) due to protons 5 and 6. The silver nitrate complex of I formed colorless needles from ethanol, mp 167.5–168° dec (lit.³ 167–167.5° dec).

10,11-Cyclobuteno-9,12-dihydrobenzocyclooctatetraene (VIII). Potassium (1.5 g) was dissolved in dry *t*-butyl alcohol and the solution evaporated under reduced pressure. The residual solid was dried by heating at 100° (0.5 mm) for 2 hr. The potassium *t*-butoxide so obtained was covered with absolute ether and a solution of bromocyclooctatetraene (4.60 g) and 1,2-dimethylenecyclobutane¹⁷ (2.0 g) in absolute ether (50 ml) was added. The reaction mixture was set aside for 70 hr and the ethereal solution was washed repeatedly with saturated brine, dried (MgSO₄), and concentrated. The residue (3.5 g) was adsorbed on to a column of silicic acid (Mallinckrodt, 100 mesh analytical reagent, 3 × 30 cm) and eluted with petroleum ether (bp 30–40°, 50 ml) followed by petroleum ether (bp 30–40°)–1% ether (250 ml), petroleum ether (bp 30–40°)–2% ether (250 ml), and petroleum ether (bp 30–40°)–5% ether (250 ml); 100-ml fractions were collected. Fraction 2 contained unreacted 1,2-dimethylenecyclobutane (86 mg), and fractions 4–7 contained bromocyclooctatetraene (1.38 g). Fractions 9–12 contained the product (0.424 g, 13.3%)¹⁵ which was obtained as a pale yellow oil after short-path distillation, bp 80° (bath) (0.5 mm). The electronic spectrum (EtOH) had λ_{max} 209 nm (ϵ 26,300) and λ_{inf} 258 nm (ϵ 1200). The infrared spectrum (film) showed bands at 3050 (s), 3000 (s), 2950 (vs), 2900 (s), 1650 (w), 1640 (m), 1440 (m), 1265 (m), 800 (m), 765 (s), 735 (w), 710 (w), and 690 (vs) cm⁻¹. The mass spectrum exhibited a prominent molecular ion at m/e 182 and other prominent peaks at m/e 167, 165, 153, 152, 141, 128, 115, and 91. The nmr spectrum (60 MHz) showed peaks at τ 4.06 (2 H) and 4.18 (4 H) due to the olefinic protons, and singlets at 7.53 (4 H) due to the methylene protons on the six-membered ring, and 7.60 (4 H) due to the methylene protons on the four-membered ring.

Anal. Calcd for C₁₄H₁₄: C, 92.3; H, 7.7. Found: C, 92.0; H, 7.9.

(40) Prepared by dissolving clean potassium in dry *t*-butyl alcohol, removing the *t*-butyl alcohol under reduced pressure, and drying the butoxide at 120° (0.3 mm).

10,11-Cyclobutenobenzocyclooctatetraene (IX). The foregoing hydrocarbon (182 mg) and 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (227 mg) were dissolved in dry benzene (35 ml) and boiled under reflux for 1.25 hr. The cooled solution was adsorbed on to a column of alumina (British, 2 × 30 cm) and eluted with petroleum ether (bp 30–40°)–50% ether. The eluate (250 ml) was evaporated and the residual oil crystallized rapidly to give the product (179 mg, 99%). The analytical sample was obtained by sublimation at 70° (0.5 mm) to give colorless prisms, mp 77–78°. The electronic spectrum (cyclohexane) had λ_{\max} 212, 236, and 290 nm (ϵ 15,900, 17,500, and 2120), and λ_{\min} 219 and 267 nm (ϵ 13,800 and 1370). The infrared spectrum (film) exhibited bands at 3000 (s), 2930 (s), 2850 (s), 1640 (m), 1470 (s), 1420 (m), 1410 (m), 1210 (m), 1200 (m), 900 (s), 890 (s), 875 (s), 790 (m), 780 (s), 770 (s), 750 (m), 690 (s), and 640 (s) cm^{-1} . The mass spectrum gave a base peak at *m/e* 180 due to the molecular ion, and prominent peaks at 179, 178, 165, and 152. The nmr spectrum (60 MHz) showed a singlet at τ 3.32 (2 H) due to protons 9 and 12, a doublet centered at 3.41 (2 H, $J = 11$ Hz) due to protons 3 and 8, a doublet centered at 4.01 (2 H, $J = 11$ Hz) due to protons 4 and 7, which also showed further fine coupling with $J = ca.$ 2 Hz, a multiplet centered at 4.01 (2 H, $J = ca.$ 2 Hz) due to protons 5 and 6, and a singlet at 6.85 (4 H) due to the methylene protons.

Anal. Calcd for $\text{C}_{14}\text{H}_{12}$: C, 93.3; H, 6.7. Found: C, 93.15; H, 6.8.

Reaction of I with Triiron Dodecacarbonyl. A solution of I (0.195 g) in benzene (5 ml) was boiled under reflux with triiron dodecacarbonyl (1.06 g) for 48 hr in an atmosphere of nitrogen. The solution was filtered and the solid washed exhaustively with hot benzene (20 ml). The combined filtrates were concentrated and the residue adsorbed on a silica gel plate (1000 × 20 × 0.1 cm) and eluted with petroleum ether. Two distinct bands separated: a faster moving yellow band, and a slower moving red-orange band. I (10 mg) was recovered from a still faster moving band which could be detected under ultraviolet light. The yellow band yielded benzocyclooctatetraeneiron tricarbonyl (X) (0.22 g, 62.3%) on concentration. Recrystallization of the solid from petroleum ether afforded yellow-orange prisms, mp 77–79°. The electronic spectrum (Et_2O) had λ_{\max} at 237.5 and 270 nm (ϵ 24,100 and 20,300) and λ_{\min} 305 nm (ϵ 12,400). The infrared spectrum (film) had bands at 2045 (s), 1995 (s), 1950 (s, doublet), 1500 (m), 1450 (m), 1025 (m), 1000 (m), 975 (m), 780 (m), and 760 (m) cm^{-1} . The nmr spectrum (60 MHz) exhibited a singlet at τ 2.87 (4 H) due to the aromatic protons, and a series of broad singlets at 3.92 (2 H) olefinic protons, 5.10 (2 H), 5.40 and 6.27 (each 1 H) due to the complexed olefinic protons, in accord with the proposed structure. The mass spectrum had a molecular ion at *m/e* 293.998 (calcd for $\text{C}_{12}\text{H}_{10}\text{FeO}_3$: 293.998). Peaks were also evident at *m/e* 266 (–CO), 238 (2–CO), and 210 (3–CO). The red band yielded benzocyclooctatetraeneiron hexacarbonyl (81 mg, 15.6%) on concentration. Recrystallization of the solid product from petroleum ether gave red prisms, mp 109–111° dec (liberation of CO). The electronic spectrum (Et_2O) showed λ_{\max} at 225 nm (ϵ 26,400) and λ_{\min} 260 and 320 nm (ϵ 15,800 and 4400) with tailing into the visible region. The infrared spectrum (film) showed bands at 2050 (s), 2005 (s, doublet), 1960 (s, triplet), 1660 (m), 1490 (m), 1480 (m), 1430 (w), 1350 (w), 1025 (s), 1005 (m), 985 (m), and 745 (m) cm^{-1} . The nmr spectrum (60 MHz) exhibited a singlet at τ 3.17 (4 H) due to the aromatic protons, a double doublet centered at 5.44 (2 H, $J = 4.0$ and 2.0 Hz), a pair of overlapping quartets centered at 5.70 (2 H, $J = 9.0$, 4.0 and 2.0 Hz), and a doublet centered at 7.09 (2 H, $J = 9.0$ Hz), due to the "complexed" olefinic protons. The mass spectrum had a molecular ion at *m/e* 433.918 (calcd for $\text{C}_{12}\text{H}_{10}\text{Fe}_6\text{O}_6$: 433.918). Peaks were also prominent at *m/e* 406 (–CO), 378 (2–CO), 350 (3–CO), 322 (4–CO), 294 (5–CO), and 266 (6–CO). A solution of this compound (81 mg) in ether was allowed to stand at room temperature in the dark for 1 month. Some insoluble material was produced but 33 mg of the compound was recovered unchanged, (60% decomposition) and 5 mg of the complex X, identical with authentic material, was isolated.

Reaction of I with Diiron Enneacarbonyl. A solution of I (100 mg) in benzene (5 ml) was heated under reflux with diiron enneacarbonyl (0.36 g) for 12 hr in a nitrogen atmosphere. The solid material was filtered off, washed thoroughly with benzene, and the combined filtrates were concentrated under reduced pressure. The residue was adsorbed on to a silica gel plate (20 × 20 × 0.1 cm) and eluted with petroleum ether. The same bands separated as were described in the previous experiment. Concentration yielded (i) benzocyclooctatetraene (44.5 mg), (ii) benzocyclooctatetraene-

iron tricarbonyl (14.2 mg, 16.3%), and (iii) benzocyclooctatetraene-iron hexacarbonyl (5.4 mg, 4.2%).

Attempted Reaction of I with Iron Pentacarbonyl. A solution of iron pentacarbonyl (0.40 g) and benzocyclooctatetraene (0.20 g) in benzene (5 ml) was boiled under reflux for 24 hr. No carbonyl complexes could be detected but I (0.12 g) was recovered.

Bromination of I. A solution of I (0.20 g) in dry dichloromethane (5 ml) was cooled to –78° and treated dropwise over 10 min with bromine (0.13 g) in dry dichloromethane (2 ml) with stirring. Stirring was continued for a further 5 min and the solvent was removed under reduced pressure at room temperature. The oily residue was crystallized from acetone–petroleum ether to give colorless needles of 3,4-dibromo-3,4-dihydrobenzocyclooctatetraene (XVIII) (190 mg, 46.6%), mp 68–70°. The infrared spectrum (CCl_4) exhibited bands at 3075 (m), 3019 (s), 2960 (w), 2925 (w), 1484 (s), 1448 (m), 1385 (m), 1349 (w), 1200 (m), 1147 (s), 1102 (m), 1048 (w), 902 (s), and (CS_2) 831 (m), 809 (m), 791 (s), 763 (s), 720 (s), 690 (w), and 644 (m) cm^{-1} . The nmr spectrum (100 MHz) showed a multiplet at τ 1.98–2.30 (1 H) due to proton 12, a multiplet at 2.62–3.17 (3 H) due to protons 9, 10, and 11, a doublet centered at 3.26 (1 H, $J = 12$ Hz) due to proton 8, a double doublet centered at 3.74 (1 H, $J = 12.0$, and 4.0 Hz) due to proton 7, a complex multiplet at 3.90–4.60 (3 H) protons 3, 5, and 6, and a hexet centered at 4.95 (1 H) due to proton 4.

Anal. Calcd for $\text{C}_{12}\text{H}_{10}\text{Br}_2$: C, 45.90; H, 3.21. Found: C, 45.82; H, 3.28.

The residue (190 mg) was adsorbed on to a silica gel plate (1000 × 20 × 0.1 cm) and eluted with 5% ether–petroleum ether. The base line became black but a slow moving yellow band developed gradually. This was collected to give a liquid which was subjected to a short-path distillation, bp 50° (bath) (0.1 mm), and gave 1,2-benzocyclohepta-1,3,5-triene-7-aldehyde (XIX) (40 mg, 38.9%) as a colorless liquid. Similar results were obtained when pure crystalline XVIII was chromatographed under these conditions. The electronic spectrum of XIX (EtOH) had λ_{\max} 280 nm (ϵ 5900), and λ_{\min} 248 (ϵ 3000). The infrared spectrum (CHCl_3) showed bands, *inter alia*, at 1730 (saturated CHO), 1695, 1640, and 1590 ($\text{C}=\text{C}$) cm^{-1} . The nmr spectrum (60 MHz) exhibited a singlet at τ 0.39 (1 H) due to the aldehyde proton, a multiplet at 2.37–3.07 (5 H) due to the four aromatic and one olefinic protons, a complex multiplet (seven major peaks) at 3.45–4.18 (3 H) olefinic protons, and a doublet at 6.22 (1 H, $J = 7$ Hz) due to the methine proton. The mass spectrum had a molecular ion at *m/e* 170.0732 (calcd for $\text{C}_{12}\text{H}_{10}\text{O}$: 170.0732).

Nitration of I. To a solution of I (0.15 g) in acetic anhydride (4.0 ml) cupric nitrate trihydrate (0.36 g) was added and the mixture stirred at room temperature for 0.5 hr. The reaction mixture was then poured into cold dilute aqueous ammonia, and the suspension extracted several times with ether. The total extracts were washed once with dilute aqueous ammonia and several times with water and dried (Na_2SO_4). Concentration gave a yellow oil which was adsorbed on to a silica gel plate (20 × 20 × 0.1 cm) and eluted with 30% ether–petroleum ether. The front moving yellow band was removed, extracted into ether, and concentrated to give a yellow oil (24 mg, 13%). This mixture could not be resolved further by repeated tlc in a variety of solvent systems, however the mass spectrum showed only the presence of mononitro compounds with a molecular ion at *m/e* 199.0635 (calcd for $\text{C}_{12}\text{H}_9\text{NO}_2$: 199.0633). The electronic spectrum (EtOH) had λ_{\max} 227 nm (ϵ 12,800) and λ_{\min} 253 and 302 nm (ϵ 6900 and 3400). The infrared spectrum (film) had *inter alia*, bands at 1525 and 1330 (NO_2) cm^{-1} . The nmr spectrum (60 MHz) exhibited a singlet at τ 1.97 (0.5 H), a very complex multiplet at 2.38–3.13 (about 5 H), and peaks at 3.28, 3.32, 3.48, 3.57, 3.80, and 3.93–4.03 (total 3.5 H).

Reaction of I with Tetracyanoethylene. I (0.30 g) and tetracyanoethylene (0.25 g) were dissolved in *syn*-tetrachloroethane (5 ml) and boiled under reflux for 4 hr. The reaction mixture was cooled and the crystalline adduct filtered off. Recrystallization of the product from chloroform–petroleum ether gave the adduct (XXVII) as colorless needles (0.253 g, 45%), mp 262–264°. The electronic spectrum (EtOH) exhibited bands at λ_{\max} 211, 261, 266.5, and 273 nm (ϵ 9800, 1500, 2100, and 2000, respectively).⁴¹ The infrared spectrum (Nujol) had, *inter alia*, bands at 2225 (CN), 1630 ($\text{C}=\text{C}$), 790, 760, and 738 (substitution pattern) cm^{-1} . The nmr spectrum (DMSO-*d*₆, 60 MHz) showed a multiplet at τ 2.72–2.92 (4 H) due to the aromatic protons, a multiplet at 5.55–5.73 (2 H)

(41) Benzocyclobutene (XXIX) has λ_{\max} (EtOH) 260, 265.5, and 271.5 nm (ϵ 1230, 1900, and 1860, respectively).⁴²

(42) M. P. Cava and D. R. Napier, *J. Am. Chem. Soc.*, **78**, 500 (1956).

protons 4 and 7, and a multiplet at 6.01–6.13 (2 H) protons 3 and 8. When CDCl_3 was used as solvent the olefinic protons appeared as a triplet ($J = 3.0$ Hz). The mass spectrum showed a molecular ion at m/e 282.0907 (calcd for $\text{C}_{18}\text{H}_{10}\text{N}_4$: 282.0905).

Reaction of I with Dimethyl Acetylenedicarboxylate. A solution of I (0.30 g) and dimethyl acetylenedicarboxylate (0.30 g) in xylene (5 ml) was boiled under reflux for 48 hr. The xylene was removed under reduced pressure and the residue adsorbed on to an alumina plate (Merck, $1000 \times 20 \times 0.1$ cm) and eluted with 30% ether-petroleum ether. Benzocyclooctatetraene (0.25 g) was obtained from the front-running band (which appeared as a dark band under ultraviolet light). A second band (which appeared as a bright-blue fluorescent band under short-wavelength ultraviolet light) was

removed, extracted with chloroform and concentrated, to give the adduct XXXII (25 mg, 26%) as a pale yellow oil. This oil crystallized on standing to form very pale yellow prisms, mp $75\text{--}77^\circ$. The electronic spectrum (EtOH) had λ_{max} 213, 272, and 282 nm (ϵ 12,100, 3100, and 2200) and λ_{inf} 258 nm (ϵ 3400). The infrared spectrum (CHCl_3) had, *inter alia*, bands at 1725 ($\text{C}=\text{O}$), 1655, and 1590 ($\text{C}=\text{C}$) cm^{-1} . The nmr spectrum (60 MHz) exhibited a singlet at τ 2.86 (4 H) due to the aromatic protons, a hexet centered at 3.71 (2 H) protons 2 and 5, an asymmetric hexet at 4.35 (2 H) protons 3 and 4, a doublet centered at 5.76 (2 H, $J = 8.5$ Hz) due to protons 1 and 6, and a singlet at 6.26 (6 H) methoxyl protons. The mass spectrum had a molecular ion at m/e 296.1050 (calcd for $\text{C}_{18}\text{H}_{16}\text{O}_4$: 296.1049).

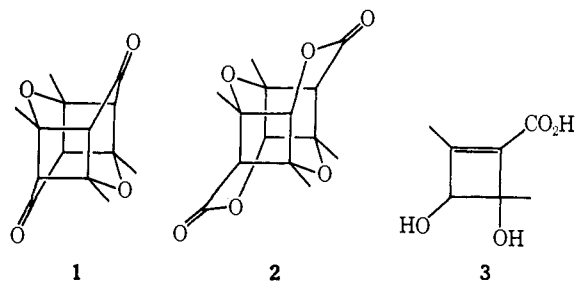
Photodimeric Cage Compounds. IV. Transformations of the Cyclobutenes Formed on Degradation of the Photodimers of 2,6-Dimethyl- and 2,6-Diethyl-4-pyrone¹

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Abstract: 3,4-Dihydroxy-2,4-dimethyl-1-cyclobutenecarboxylic acid (**3**), a degradation product from the photodimer of 2,6-dimethyl-4-pyrone, is converted by acid to 5,5-bis[2-(3,5-dimethylfuryl)]-4-methylpentanone (**4**), by pyrolysis to 1,6-dimethyl-3-[2-(4-oxopentyl)]-2,4-dioxabicyclo[3.2.0]hept-6-ene-7-carboxylic acid (**7**), and by base to 2-methyl-5-oxo-1-cyclopentenecarboxylic acid (**10**). The formation of the pyrolysis product and of an acetal on treatment with acetone establish that the cyclobutene is the *cis* isomer. On hydrogenation it gives two diastereomeric 2,3-dihydroxy-2,4-dimethylcyclobutanecarboxylic acids (**17**), whose stereochemistry is assigned on the basis of their conversion to the two diastereomers of 4-hydroxy-3-methyl-5-oxohexanoic acid lactone (**20**). These lactones were synthesized independently, and stereochemical assignments were made to them on the basis of equilibration studies. Analogous observations have been made on hydrogenation of the corresponding degradation product from the photodimer of 2,6-diethyl-4-pyrone.

The photodimer of 2,6-dimethyl-4-pyrone has been shown to have the cage structure **1**.³ In the course of the structural elucidation **1** was converted to the dilactone **2**, which on hydrolysis gave 3,4-dihydroxy-2,4-dimethyl-1-cyclobutenecarboxylic acid, **3**. This com-



ound, which combines several reactive functional groups in a small compass, undergoes a variety of interesting transformations, which we describe here.

(1) Paper III: P. Yates, E. S. Hand, P. Singh, S. K. Roy, and I. W. J. Still, *J. Org. Chem.*, in press.

(2) (a) Lash Miller Chemical Laboratories, University of Toronto, Toronto, Ontario, Canada; Alfred P. Sloan Foundation Fellow, 1957–1960; (b) National Institutes of Health Fellow, Harvard University, 1957–1958; (c) Commonwealth Scholar, University of Toronto, 1963–1966.

(3) P. Yates and M. J. Jorgenson, *J. Amer. Chem. Soc.*, **85**, 2956 (1963).

Treatment of **3** with hot 10% hydrochloric acid gave a crystalline product with the empirical formula $\text{C}_6\text{H}_8\text{O}$. Its molecular formula was indicated to be $\text{C}_{18}\text{H}_{24}\text{O}_3$ by the fact that it formed a 2,4-dinitrophenylhydrazone, $\text{C}_{24}\text{H}_{28}\text{N}_4\text{O}_6$. The infrared spectrum of the compound $\text{C}_{18}\text{H}_{24}\text{O}_3$ showed bands at 5.86, 6.21 (w), 6.33 (w), and 7.33 μ . The ultraviolet spectrum of the 2,4-dinitrophenylhydrazone showed a long-wavelength maximum at 362 $m\mu$ (ϵ 22,900), demonstrating the presence of an unconjugated carbonyl group in the parent compound, which was also indicated by the band at 5.86 μ in the infrared spectrum of the latter. The band at 7.33 μ in this spectrum suggested that the carbonyl function was a methyl ketone, and this was confirmed by a positive iodoform test. The absence of a carbonyl band in the infrared spectrum of the 2,4-dinitrophenylhydrazone and of a hydroxyl stretching band in the infrared spectrum of the parent compound, led to the assignment of two of the oxygen atoms in the latter to ether linkages. The weak bands at 6.21 and 6.33 μ in the infrared spectrum of the parent compound, a maximum in its ultraviolet spectrum at 225 $m\mu$ (ϵ 14,000), and its resistance to catalytic hydrogenation favored the assignment of these two oxygen atoms to furan rings.^{4–6} These con-

(4) C. N. R. Rao, "Chemical Applications of Infrared Spectroscopy," Academic Press, New York, N. Y., 1963, p 324.