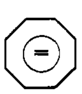
Reactions of Cyclooctatetraene Dianion with Aldehydes and Ketones and the Chemistry of Its Products[1]

Thomas S. Cantrell[2] and Harold Shechter

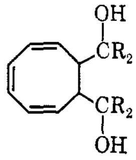
Contribution from the Department of Chemistry, The Ohio State University, Columbus, Ohio 43210. *Received April 27, 1967*

Abstract: Cyclooctatetraene dianion reacts as a 1,2- and a 1,4-dicarbanionic reagent with benzaldehyde, acetaldehyde, *o*-phthalaldehyde, acetone, benzophenone, and fluorenone to give 5,8-bis(α-hydroxyalkyl)-1,3,6-cyclooctatrienes, 7,8-bis(α-hydroxyalkyl)bicyclo[4.2.0]octadienes, and 2,4,6,8-tetraene-1,10-diols. The bicyclo[4.2.0]octadienes and the 2,4,6,8-tetraenediols are apparently formed by isomerization of the initial 7,8-disubstituted 1,3,5-cyclooctatrienes. Acid-catalyzed dehydration of the products of addition of cyclooctatetraene dianion to the aldehydes and ketones has been investigated. 5,8-Bis(α-hydroxyalkyl)-1,3,6-cyclooctatrienes convert to tricyclic ethers (3,3-dialkyl-9-alkylidene-2-oxa-7-tricyclo[4.3.1.$0^{4,10}$]decenes) or reverse aldolize to 7-(α-hydroxyalkyl)-1,3,5-cyclooctatrienes. 7,8-Bis(α-hydroxyalkyl)bicyclo[4.2.0]octadienes may dehydrate to conjugated decapentaenes, *o*-divinylbenzene derivatives, or carbon skeleton rearrangement products. 1,2-Dialkylidene-3,5,7-cyclooctatrienes and 1,4-dialkylidene-2,5,7-cyclooctatrienes were not isolated. Cyclooctatetraene dianion serves as an electron-transfer reagent to benzil and 9,10-phenanthrenequinone. Evidence for the structures and possible reaction mechanisms for formation of the varied products are presented.

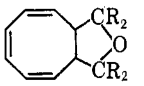
Cyclooctatetraene dianion (I) is of interest with respect to structural theory and its utility in chemical synthesis.[3] Reaction of I with aldehydes and ketones has been reported to give 7,8-bis(α-hydroxyalkyl)-1,3,5-cyclooctatrienes (II) which are dehydrated by *p*-toluenesulfonic acid to tetrahydrofurans (III).[4] The present investigation consists of a study of (1) the reactions of I with the following aldehydes and ketones: benzaldehyde, acetaldehyde, *o*-phthalaldehyde, acetone, benzophenone, fluorenone, benzil, and 9,10-phenanthrenequinone; and (2) the chemistry of the products formed thereby. The results of this research indicate that (1) I reacts with carbonyl groups as a 1,2- or a 1,4-dicarbanionic reagent or by electron transfer; and (2) the acid-catalyzed reactions of the carbonyl adducts are more varied and interesting than previously observed.[4]



I



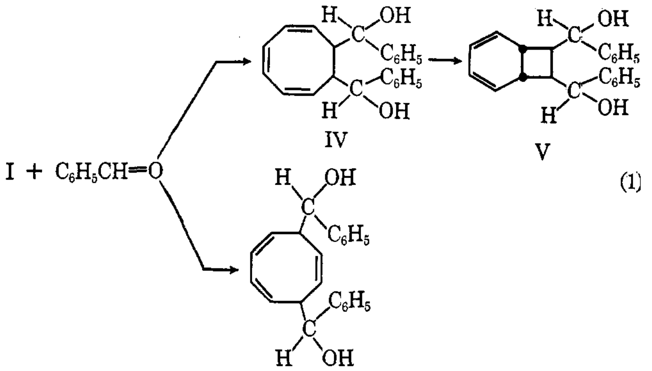
II



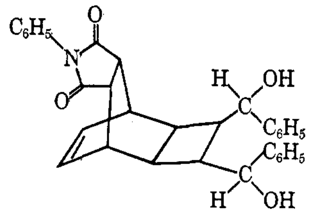
III

Discussion of Results

Benzaldehyde. Reaction of dilithium cyclooctatetraenide (I) with excess benzaldehyde in ethyl ether (eq 1) gives after hydrolysis 7,8-bis(α-hydroxybenzyl)bicyclo[4.2.0]octadiene (V, 15%) and 5,8-bis(α-hydroxybenzyl)-1,3,6-cyclooctatriene (VI, 66%). Dipotassium cyclooctatetraenide reacts similarly with benzaldehyde to yield V (12%) and VI (~70%). The structure of V is deduced from its analysis, its bicyclo[4.2.0]octadiene absorption [λ_{max} 274 mμ (ϵ 3100) and λ_{min} 236 mμ (ϵ 680)],[5] its absorption of 2 moles of hydrogen on catalytic hydrogenation, and its great reactivity with N-phenylmaleimide to give the corresponding adduct[6] VII in high yield.



(1)



VII

Bicyclo[4.2.0]octadienediol V is almost certainly formed by valence isomerization of an initially formed

---

[1] A portion of these results were described preliminarily by T. S. Cantrell and H. Shechter, *J. Am. Chem. Soc.*, **87**, 136 (1965). The present manuscript is abstracted in part from the Ph.D. dissertation of T. S. Cantrell, The Ohio State University, Columbus, Ohio, 1964.

[2] National Science Foundation Cooperative Fellow, 1961–1962 and 1963–1964, and National Science Foundation Graduate Fellow, 1962–1963.

[3] For a summary of the prior chemistry of I, see T. S. Cantrell and H. Shechter, *ibid.*, **89**, 5868 (1967), and the references therein.

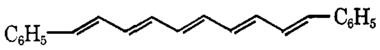
[4] V. D. Azatyan and R. S. Gyuli-Kevkhyan, *Dokl. Akad. Nauk Arm. SSR*, **20**, 81 (1955); V. Azatyan and R. S. Gyuli-Kevkhyan, *Izv. Akad. Nauk Arm. SSR, Otd. Khim.*, **14**, 451 (1961); G. Wittig and D. Wittenberg, *Ann.*, **606**, 1 (1957).

[5] (a) Bicyclo[4.2.0]octadienes absorb at 270–275 mμ.[5b–d] (b) A. C. Cope, A. C. Haven, F. L. Ramp, and E. R. Trumbull, *J. Am. Chem. Soc.*, **74**, 4867 (1952). (c) A. C. Cope and M. Burg, *ibid.*, **74**, 168 (1952). (d) J. L. Kice and T. S. Cantrell, *ibid.*, **85**, 2298 (1963). (e) 1,3,6-Cyclooctatrienes show a shoulder at 240–250 mμ or only end absorption; see ref 5d and A. C. Cope and F. A. Hochstein, *ibid.*, **72**, 2515 (1950). (f) 1,3,5-Cyclooctatrienes show λ_{max} 260–265 mμ; see ref 5b, 5e, and A. C. Cope and H. O. van Orden, *ibid.*, **74**, 175 (1952).

[6] (a) Substituted 1,3-cyclohexadienes, including bicyclo[4.2.0]octadienes, usually form adducts with maleic anhydride in the cold, whereas heat is necessary to effect such Diels–Alder reactions with 1,3,5-cyclooctatrienes and 1,3,5-cycloheptatrienes. (b) M. C. Kloetzel, *Org. Reactions*, **4**, 22 (1948).

7,8-disubstituted 1,3,5-cyclooctatriene (IV) as shown in eq 1. 1,3,5-Cyclooctatrienes bearing substituents at C-7 and C-8 have been reported.[7a,b] Reactions which might produce such compounds frequently give bicyclooctadienes or octatetraenes, the results of ring bridging or ring opening, respectively.[7c,b] The factors responsible for such isomerizations will be discussed later.

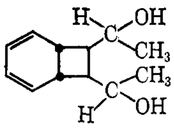
Diol V behaves unexpectedly on dehydration. Refluxing a benzene solution of V with iodine or *p*-toluenesulfonic acid yields 1,10-diphenyldecapentaene (VIII) as the only tractable product. Formation of VIII from V represents loss of the elements of hydrogen peroxide from the initial diol. The behavior of V on dehydration is similar to that for the product of *vicinal* addition of I to benzophenone (*vide infra*).



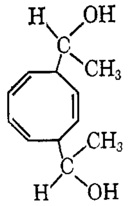
VIII

The major product of reaction of benzaldehyde and I (eq 1) is a viscous air-sensitive liquid. Its ultraviolet [λ_{max} 248 (sh) mμ (ϵ ~2000)],[5] infrared and nmr (phenyl: vinyl ratio = 5:3) spectrum is in accord with the 1,3,6-cyclooctatriene structure VI, the result of reaction at C-1 and C-4 of I.

Acetaldehyde. Acetaldehyde reacts with dilithium cyclooctatetraenide (I) to yield after hydrolysis a mixture of 7,8-bis(α-hydroxyethyl)bicyclo[4.2.0]octadiene (IX, ~25%) and 5,8-bis(α-hydroxyethyl)-1,3,6-cyclooctatriene (X, ~75%). The products are characterized from their ultraviolet and nmr spectra.

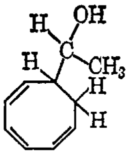


IX

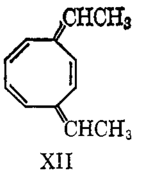


X

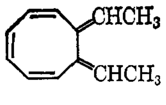
Attempted acid-catalyzed dehydration of the mixture of IX and X with *p*-toluenesulfonic acid results in reverse aldol condensation to give 7-(α-hydroxyethyl)-1,3,5-cyclooctatriene (XI) as an oxygen-sensitive liquid. 1,2-Diethylidene-3,5,7-cyclooctatriene (XII) and 1,4-diethylidene-2,5,7-cyclooctatriene (XIII) are not obtained in these experiments.[8] The structure of XI exclusive of the positions of the double bonds is proved from its catalytic hydrogenation followed by oxidation with chromic acid to give acetylcyclooctane. The unsaturation in XI is assigned from its ultraviolet [λ_{max} 268 mμ (ϵ 2300)][5] and nmr absorption. That the hydroxyethyl group is not attached to an olefinic carbon is shown by the nmr signal of the hydrogen bonded to the hydroxyl-bearing carbon; this hydrogen signal is an apparent quintet at τ 6.26, the result of two overlapping pairs of quartets, and indicates that the hydrogen is coupled to one other hydrogen besides that of methyl.



XI

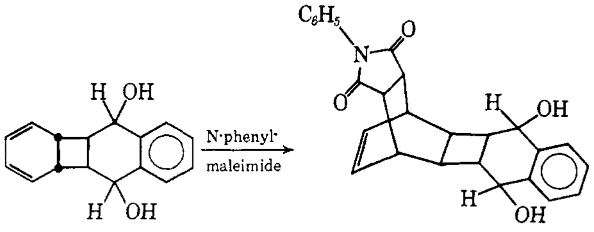


XII



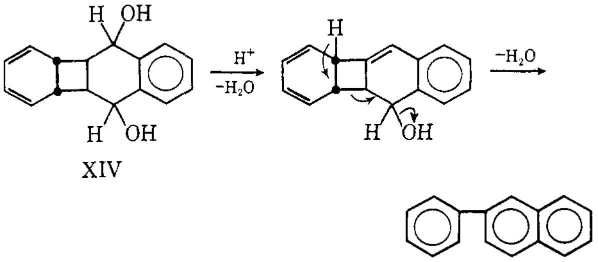
XIII

***o*-Phthalaldehyde.** *o*-Phthalaldehyde adds to dilithium cyclooctatetraenide (I) in ethyl ether to form 4,5-benzotricyclo[6.4.0.0^{2,7}]dodeca-9,11-diene-3,6-diol (XIV) in two crystalline modifications. XIV is identified from its analysis, its infrared, ultraviolet [λ_{max} 274 mμ (ϵ 3100)], and nmr spectra, and its rapid reaction with N-phenylmaleimide at room temperature to give the adduct XV (eq 2).



XIV XV (2)

Treatment of XIV with catalytic amounts of *p*-toluenesulfonic acid in refluxing benzene gives 2-phenylnaphthalene[9] (XVI) in 86% yield (eq 3); under these conditions 1,2,5,6-dibenzocyclooctatetraene is not obtained. A reasonable mechanism for conversion of XIV to XVI is summarized in eq 3.



XIV

XVI (3)

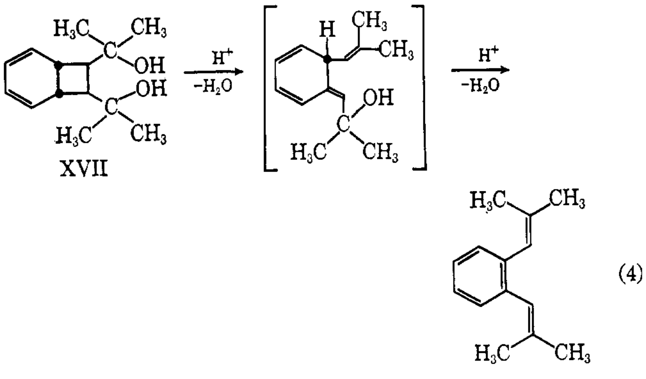
Acetone. Addition of dilithium cyclooctatetraenide (I) to excess acetone and acidification yield a mixture of 7,8-bis(2-hydroxy-2-propyl)bicyclo[4.2.0]octadiene (XVII) and 5,8-bis(2-hydroxy-2-propyl)-1,3,6-cyclooctatriene (XVIII). Attempts to separate the mixture by distillation or by chromatography on a variety of adsorbents were unsuccessful. The ultraviolet spectrum of the product has a maximum at 267 mμ (ϵ 2200) and corresponds to that obtained by addition of the spectra of the bicyclo[4.2.0]octadiene and 1,3,6-cyclooctatriene chromophores weighted 70:30, respectively. The nmr spectrum exhibits an olefinic hydrogen pattern corresponding exactly to that obtained by superimposing the vinyl portions of the spectra of 5,8-bis(2-cyano-2-propyl)-1,3,6-cyclooctatriene and a known bicyclo-[4.2.0]octadiene.[5d] Integration of the nmr spectrum of the mixture indicates that it consists of XVII and XVIII in a 62:38 ratio.

---

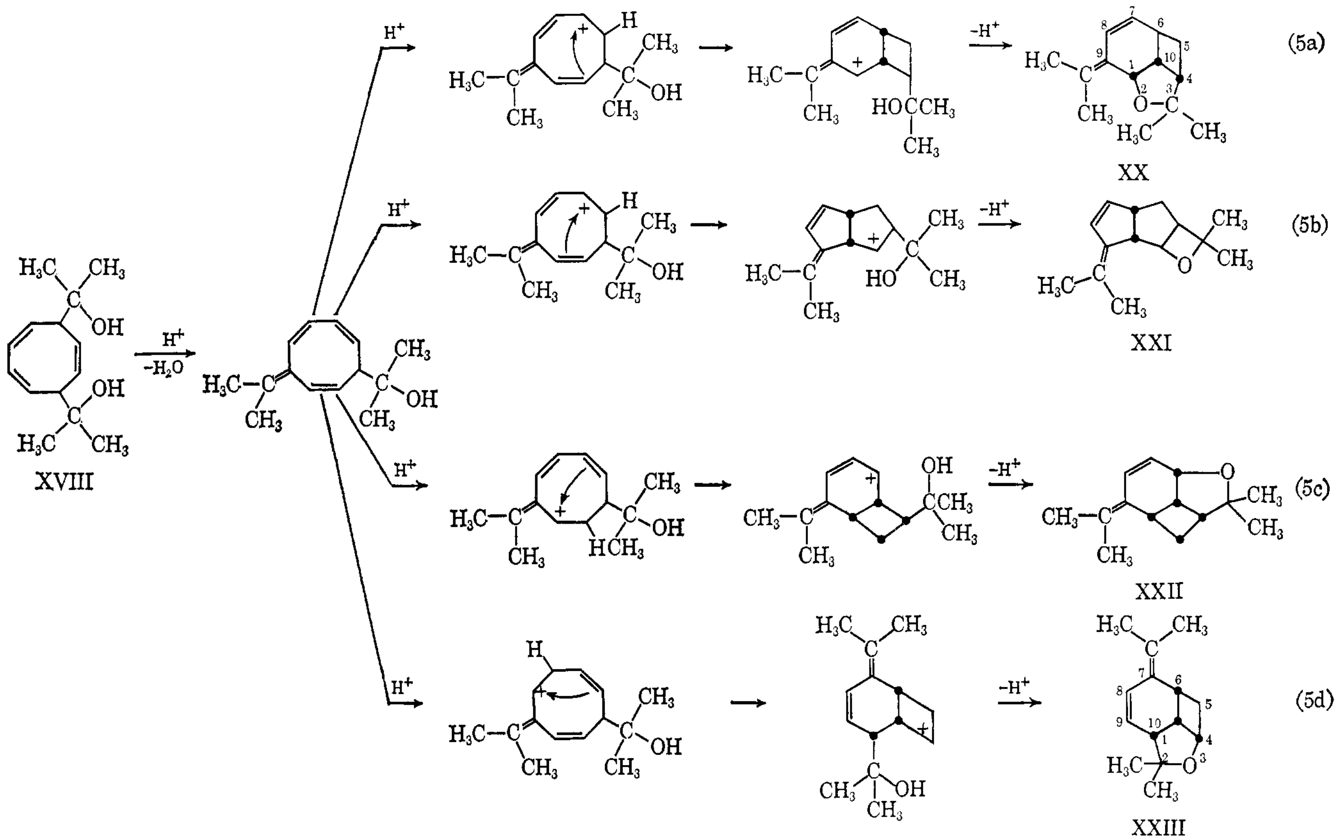
(7) (a) K. H. Conrow and D. Bak, *J. Org. Chem.*, **31**, 3958 (1966); (b) R. Huisgen and G. Boche, *Tetrahedron Letters*, 1769 (1965); (c) E. Vogel, O. Roos, and K. H. Disch, *Ann.*, **653**, 55 (1962), and references therein; (d) H. Meister, *Ber.*, **9**, 1688 (1963).

(8) Such fulvene analogs are of interest with respect to their possible olefinic or aromatic character.

(9) Professor A. Streitwieser has informed us that he has obtained XIV of mp 215° from reaction of I with phthalaldehyde, but that it is unchanged after treatment with aqueous sulfuric acid in tetrahydrofuran. The cause of these differences in behavior of XIV is not known at present.



Dehydration of the mixture of XVII and XVIII with *p*-toluenesulfonic acid results in *o*-bis(2,2-dimethylvinyl)benzene (XIX, 36%; eq 4) and 3,3-dimethyl-9-isopropylidene-2-oxa-7-tricyclo[4.3.1.0^{4,10}]decene[10] (XX, 28%; eq 5a). These results differ from the previous report that the diol from I and acetone yields 2,2,5,5-tetramethyl-3,4-cyclooctatrienotetrahydrofuran on dehydration.[4,11]



The structural assignment of XIX rests on the following evidence: (1) analytical data; (2) infrared absorption at 13.4 μ, characteristic of an *ortho*-disubstituted benzene; (3) maximum ultraviolet absorption at 229 mμ (ϵ 22,000);[12] (4) nmr properties for four aromatic hydrogens (τ 2.95), two vinyl hydrogens as an apparent septet (τ 3.88, J = 1.3 cps), and two pairs of allylic methyl groups (τ 8.13 and 8.33; J = 1.3 cps); and (5) ozonolysis giving 61% of 2 moles of acetone. A plausible sequence for conversion of XVII to XIX is summarized in eq 4.

The data from which the structure of XX is assigned are: (1) quantitative analysis; (2) infrared absorption at 9.6 μ, characteristic of cyclic ethers; (3) maximum ultraviolet absorption at 244 mμ (ϵ 15,500), suggestive of a 3-isopropylidenecyclohexene chromophore;[13] and (4) the nmr spectrum, showing a doublet at τ 3.57 (area 1, J = 10.3 cps; hydrogen on C-8), pair of doublets centered at τ 4.42 (area 1, J = 10.3 cps, J = 4.0 cps; hydrogen on C-7), a doublet at τ 5.27 (area 1, J = 6.4 cps; hydrogen on C-1), a series of overlapping multiplets at τ 6.9–7.9 (area 5, hydrogens on C-4, C-5, C-6, and C-10), singlets at τ 8.13 and 8.17 (each of area 3, isopropylidene methyl groups), and a pair of partly overlapping singlets at τ 8.89 (area 6, methyl groups on C-8).

The first three pieces of evidence and the vinyl:methyl hydrogen ratio, as shown by nmr, indicate that the product is a tricyclic ether; structures XX–XXIII (eq 5a–d) are all consistent with this information and can arise from XVIII by mechanistically plausible pathways. Consideration of the nmr coupling constant permits distinction to be made and allows assignment of structure XX to the dehydration product. First XXI and other structures containing the bicyclo[3.3.0]octene nucleus are eliminated because of the large coupling constant observed between the hydrogens on C-7 and C-8. The magnitude of this coupling constant (10.5 cps) is typical of olefinic hydrogens on a six-membered ring, but con-

---

(10) *Chemical Abstracts* has recommended the name 2,2-dimethyl-6-isopropylidene-2a,3,3a,6,6a,6b-hexahydro-2H-cyclobuta[*cd*]benzofuran for XX.

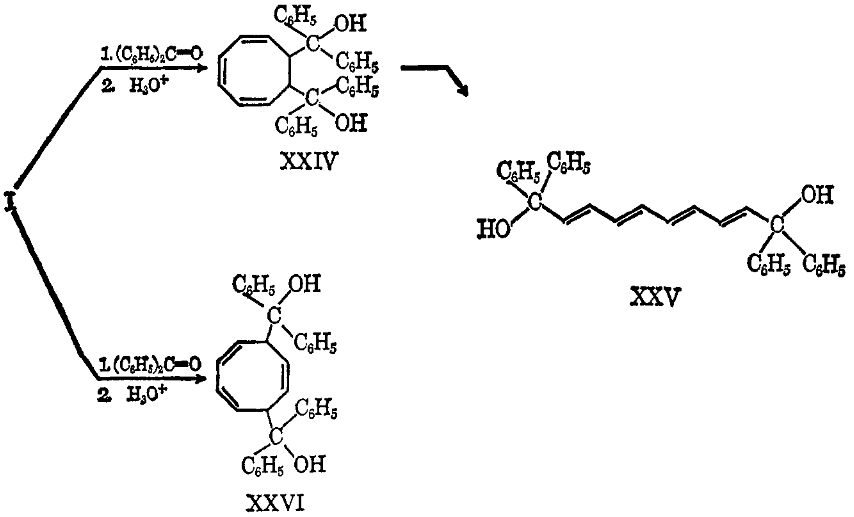
(11) The diol was assumed to be homogeneous.

(12) *o*-Divinylbenzene absorbs at λ_{max} 229 mμ (ϵ 23,000): F. W. Hoover, O. H. Webster, and C. T. Handy, *J. Org. Chem.*, **26**, 2234 (1961).

(13) 6-Methyl-3-isopropylidenecyclohexene has λ_{max} 243 mμ (ϵ 16,000): H. Pines and H. Eschinazi, *J. Am. Chem. Soc.*, **77**, 6314 (1955).

siderably larger than that for five-membered cycloolefins (5.4–7.0 cps).[14]

Secondly, in structure XXII the hydrogen on carbon attached to oxygen will be coupled to the adjacent olefinic hydrogen; since in the observed spectrum neither of the splittings of this olefinic hydrogen (10.5 and 4.0 cps) is identical with that of the hydrogen α to oxygen (6.4 cps), structure XXII is dismissed.



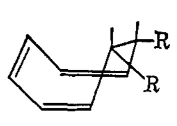
(6)

Finally, the reasons for preferring structure XX to XXIII are as follows. In structure XX the hydrogen on the oxygen-bearing carbon (C-1) should be coupled strongly only to the hydrogen on C-10, and its signal should appear as a doublet; on the other hand, the hydrogen on the oxygen-bearing carbon of XXIII (C-4) has three hydrogens on adjacent carbons, two on C-5 and one on C-10. Inspection of Dreiding models of XXIII indicates dihedral angles of $\sim 0°$ between the C-4 hydrogen and the β-hydrogen on C-5 as well as with the hydrogen on C-10, and of $\sim 120°$ with the α-hydrogen on C-5. The C-4 hydrogen should thus exhibit a signal of multiplicity at least four. Since the signal in question is clearly a doublet, XX is the apparent structure. Also, in formation of XX the intermediate monoalcohol is protonated at the terminal carbon of the triene system (eq 5a) whereas for the formation of XXII, the proton must attack an internal carbon of the triene system (eq 5c) of the monoalcohol. Electrophilic reagents usually attack the terminal position of polyenes preferentially and, therefore, XX is preferred on the ground that its formation is more reasonable mechanistically.

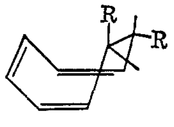
Benzophenone. Benzophenone reacts with dilithium cyclooctatetraenide (I) in ethyl ether (eq 6) to give, after acidification, 1,1,10,10-tetraphenyl-2,4,6,8-tetraene-1,10-diol XXV (28%) and 5,8-bis(α-hydroxybenzhydryl)-1,3,6-cyclooctatriene (XXVI, 64%).

The structure of XXV is assignable from its analysis, its ultraviolet absorption maxima at 320, 306, and 294 mμ (ϵ 65,000, 70,000, and 53,000), and its hydrogenation to 1,1,10,10-tetraphenyldecane-1,10-diol,[15] identical with an authentic sample. The stereochemistries of the olefinic centers in XXV are almost certainly *trans*. The ultraviolet spectra of all *trans* polyenes exhibit fine structure and usually three distinct maxima, whereas the isomers with one or more *cis* double bonds have a single long-wavelength maximum.[16] The spectrum of XXV contains three long-wavelength maxima and is quite similar in shape to those of typical all-*trans* polyenes.[15a]

XXV is apparently formed by decomposition of the intermediate 7,8-disubstituted 1,3,5-cyclooctatriene (XXIV). The previously reported cases of such ring openings involve cyclooctatrienes bearing unsaturated substituents,[17] and it was noted that the acyclic products are fully conjugated,[17] and presumably preferred for this reason. In the present case, however, there is no unsaturation in the α-carbon atom of the substituents, and the principal driving force must be the relief of steric strain in relatively weak bonds. The strain in the *cis* isomer (XXVII) of a rigid 7,8-disubstituted 1,3,5-cyclooctatriene results from repulsion of two substituents in an eclipsed conformation; in the *trans* isomer (XXVIII) one substituent is close to the π cloud above the C_3–C_4 double bond and strain is derived from interaction between the substituent and the π system. The strain in either isomer can be relieved by (1) bridging to a bicyclo[4.2.0]octadiene or (2) ring opening to the linear octatetraene. In the present case, apparently only the second course provides relief from the eclipsing effects of the two bulky α-hydroxybenzhydryl groups.[18]



XXVII



XXVIII

XXV forms a monoadduct (XXIX) with N-phenylmaleimide in refluxing tetrahydrofuran; however, reaction with a second mole of N-phenylmaleimide could not be made to occur. Evidently the terminal double bonds are hindered by the bulky α-hydroxybenzhydryl groups, and only the two internal double bonds participate in the Diels–Alder reaction. Acid-catalyzed dehydration of the adduct XXIX gives the yellow pentaene XXX (eq 7). The relatively short wavelength of the

---

[14] (a) O. L. Chapman, *J. Am. Chem. Soc.*, **85**, 2014 (1963); (b) G. V. Kriloff and H. Smith, *ibid.*, **85**, 2016 (1963); (c) P. Laszlo and P. von R. Schleyer, *ibid.*, **85**, 2017 (1963).

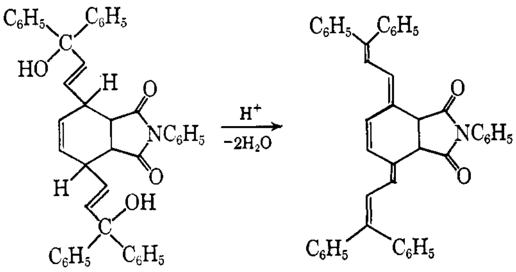
[15] M. Godchot, *Compt. Rend.*, **171**, 798 (1920).

[16] L. Zechmeister, *J. Am. Chem. Soc.*, **76**, 4144 (1954).

[17] A. C. Cope and D. J. Marshall, *ibid.*, **75**, 3208 (1953); H. Hover, *Tetrahedron Letters*, 256 (1962).

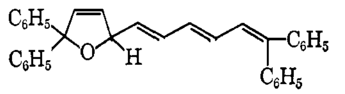
[18] In reactions of I with benzaldehyde, acetaldehyde, and acetone, bridging to bicyclo[4.2.0]octadienes occurs.

main ultraviolet absorption band (361 mμ) and the lack of fine structure make it likely that the stereochemistry of XXX is that shown.



XXIX XXX (7)

Brief warming of XXV with *p*-toluenesulfonic acid in benzene yields 2,2-diphenyl-5-(6,6-diphenylhexatrienyl)-2,5-dihydrofuran (XXXI). The dihydrofuran XXXI is unstable to acid and is destroyed by longer reaction times. The structure of XXXI is deduced from its analysis and its spectra. The analysis reveals that XXXI is formed from XXV by loss of *one* molecule of water. Its infrared spectrum shows no hydroxyl band, but does possess strong bands at 9.04 and 9.68 μ for an ether linkage.

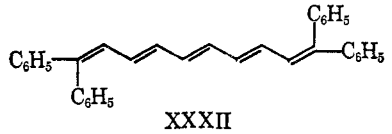


XXXI

Several cyclic ethers could be formed from XXV by cyclization of intermediate hydroxytetraenyl carbonium ions; these include three-, five-, seven-, nine-, and eleven-membered cyclic ether structures. These structures will all differ significantly in the positions of their ultraviolet absorption maxima. The ultraviolet spectrum of the actual product [$\lambda_{\max}$ 326 and 329 mμ (ϵ 44,000 and 16,500)] agrees with that predicted for a 1,1-diphenylhexatriene chromophore and lends support to structure XXXI.

The nmr spectrum of XXXI consists of signals for phenyl hydrogen at τ 2.71 and 2.78 (each of area 10), a one-hydrogen multiplet at τ 3.37, an unresolved multiplet at τ 3.74 (area 4, side-chain vinyl hydrogens), a multiplet at τ 4.22 (area 2, ring vinyl hydrogens), and a multiplet at τ 4.63 (area 1, tertiary allylic hydrogen on carbon bonded to oxygen). This spectrum indicates (1) the presence of tertiary doubly allylic hydrogen on carbon bonded to hydrogen, and (2) from the relative areas and chemical shifts, the location of *two* of the olefinic hydrogens on a ring. Only the five-membered ring structure XXXI is consistent with the spectrum. Preferential formation of XXXI is reasonable because of the general ease of closure yielding five-membered rings.

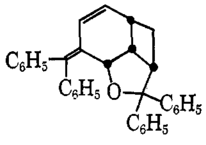
Reaction of XXV with iodine results in formation of 1,1,10,10-tetraphenyldecapentaene (XXXII) in ~10% yield. This elimination reaction results in over-all removal of hydrogen peroxide from XXV and thus parallels that of V under similar conditions.



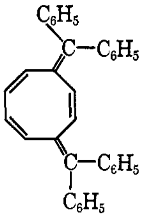
XXXII

Adduct XXVI, 5,8-bis(α-hydroxybenzhydryl)-1,3,6-cyclooctatriene, an air-sensitive glass, was not obtained completely analytically pure; the sensitivity of dialkylcyclooctatrienes to oxygen has been noted previously.[7a] The structure of XXVI follows from its ultraviolet spectrum (shallow maximum at 252 mμ), its nmr spectrum, and its method of formation.

Dehydration of XXVI by acid or by iodine yields the cyclic ether, 9-benzhydrylidene-3,3-diphenyl-2-oxatricyclo[4.3.1.$0^{4,10}$]dec-7-ene (XXXIII). None of the expected product, 5,8-bis(benzhydrylidene)-1,3,6-cyclooctatriene (XXXIV), was found. Use of milder or more vigorous conditions led to initial material or to intractables.



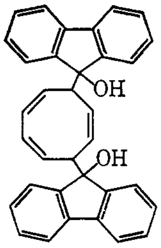
XXXIII



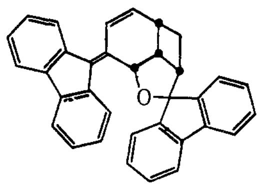
XXXIV

The infrared, ultraviolet, and nmr spectra of the product of dehydration of XXVI agree with the structure assigned, XXXIII. Its ultraviolet spectrum exhibits a maximum at 286 mμ (ϵ 19,000) indicative of a 3-benzhydrylidenecyclohexene chromophore;[19] its nmr absorption reveals the presence of only two vinyl hydrogens. The reasons for the decision in favor of structure XXXIII (see Experimental Section) are the same as those discussed for XX.

Fluorenone. Dilithium cyclooctatetraenide (I) and fluorenone in ethyl ether give 5,8-bis(9′-hydroxy-9′-fluorenyl)-1,3,6-cyclooctatriene (XXXV, 42%). No acyclic tetraene corresponding to XXV was found. The structure of XXXV is derived from its analytical and spectral properties. Its ultraviolet absorption [$\lambda_{\max}^{\text{ultraviolet}}$ 274, 295, and 307 mμ (ϵ 24,000, 10,700, and 6400)] is exactly that for two isolated fluorene chromophores.[20] The nmr spectrum of XXXV is compatible with the indicated structure. Dehydration of XXXV with *p*-toluenesulfonic acid yields a cyclic ether assigned structure XXXVI by analogy with XXXIII (see Experimental Section).



XXXV



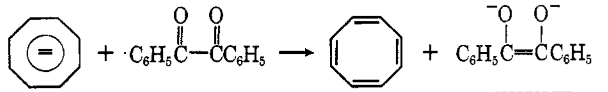
XXXVI

Benzil. Addition of benzil to I at 0° and acidification gives benzoin (57%) rather than the possible bicyclic diol. Evidently two electrons are transferred to benzil from I (eq 8) to give the enediolate XXXVII which on protonation (eq 9) yields the reduction product, ben-

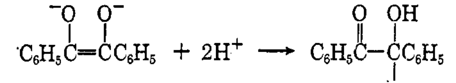
---

(19) 3-Benzhydrylidenecyclohexene absorbs at 281 mμ (ϵ 20,000): J. L. Kice and F. M. Parham, *J. Am. Chem. Soc.*, **80**, 3792 (1958).

(20) A linear tetraene such as XXV would exhibit maxima of much higher intensity.



I XXXVII (8)

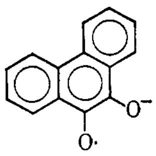


$$C_6H_5\overset{O^-}{\overset{|}{C}}=\overset{O^-}{\overset{|}{C}}C_6H_5 + 2H^+ \longrightarrow C_6H_5\overset{O}{\overset{\|}{C}}-\underset{H}{\overset{OH}{C}}C_6H_5 \qquad (9)$$

XXXVII

zoin. Reaction of I with benzil illustrates the behavior of cyclooctatetraene dianion as a reducing agent with respect to carbonyl compounds; a similar process occurs in the reduction of benzil by alkali metals to benzoin.[21]

9,10-Phenanthrenequinone. Reaction of cyclooctatetraene dianion (I) with 9,10-phenanthrenequinone results in an insoluble brown solid, pyrophoric in air when dry, which upon hydrolysis and acidification yields 9,10-phenanthrenequinone. It appears that one-electron transfer to 9,10-phenanthrenequinone is occurring, yielding the phenanthrenequinone radical anion



XXXVIII

XXXVIII which reverts to the parent quinone upon hydrolysis. The difference in behavior of 9,10-phenanthrenequinone and benzil to I is rationalizable on the basis that the quinone is the weaker electron acceptor. Additional study of reactions of quinones and 1,2-dicarbonyl compounds with I is in progress.

Experimental Section

All melting points are corrected; infrared spectra were obtained on a Perkin-Elmer Model 137 spectrophotometer and nmr spectra on a Varian A-60 spectrometer. Gas chromatographic separations were effected in an Aerograph A-90-P instrument with the columns described previously.[3]

Reaction of Dilithium Cyclooctatetraenide (I) with Benzaldehyde. A solution of dilithium cyclooctatetraenide in ether (300 ml, containing *ca.* 0.11 mole of I) was added in 30 min to a stirred solution of benzaldehyde (30 g, 0.28 mole) in ether (100 ml) at 0° under nitrogen. The mixture was stirred for 1 hr and allowed to warm to 25°. The solution was poured into ice water containing acetic acid (10 ml); the aqueous layer was extracted with ether and the extract combined with the ether layer from the previous separation. The ethereal solution was washed with water, dried, concentrated to *ca.* 50 ml, and stored at 5° overnight. The solid thus obtained was filtered and washed with cold ether. Recrystallization from ethyl acetate gave 7,8-bis(α-hydroxybenzyl)bicyclo[4.2.0]octa-2,4-diene (V, 4.7 g, 0.016 mole, 15%) as fine white needles, mp 175–176°. The infrared spectrum of V shows significant bands at 2.99 (s), 6.90 (m), 8.02 (m), 9.87 (s), 10.04 (s), 13.13 (s), 13.40 (s), 14.26 (vs), and 14.70 (vs) μ. The ultraviolet spectrum exhibits a maximum at 274 mμ (ϵ 3100) and a minimum at 237 mμ (ϵ 680).

Anal. Calcd for $C_{22}H_{22}O_2$: C, 83.02; H, 6.94. Found: C, 82.96; H, 6.96.

The ethereal mother liquor and washings from the filtration of V on evaporation gave crude 5,8-bis(α-hydroxybenzyl)-1,3,6-cyclooctatriene (VI) as an air-sensitive yellow syrup which analyzed erratically (low) for carbon and hydrogen. Chromatography of a portion (2.0 g) of this material on alumina, activity IV, did not yield crystalline material; 2% methanol in methylene chloride eluted VI as the same viscous oil (1.9 g, 66%). The infrared spectrum of VI has significant bands at 2.91 (m), 2.98 (s, br), 6.94 (m), 13.15 (s), and 14.4 (vs) μ; ultraviolet absorption occurs at 248 mμ (ϵ ~2000).

Hydrogenation of V. A solution of V (0.31 g, 1.0 mmole) in ethyl acetate (60 ml) was shaken over 10% palladium on charcoal under 1 atm of hydrogen until uptake ceased (2.5 hr); a total of 2.04 mmoles was absorbed. Filtration of the catalyst, evaporation of the solvent, and recrystallization of the white solid residue from ethyl acetate–hexane gave 7,8-bis(α-hydroxybenzyl)bicyclo[4.2.0]-octane as white chunky prisms, mp 162–163° (2.6 g, 85%).

Anal. Calcd for $C_{22}H_{26}O_2$: C, 81.99; H, 8.07. Found: C, 82.24; H, 7.89.

Reaction of V with N-Phenylmaleimide. A solution of V (0.32 g, 1.00 mmole) and N-phenylmaleimide (0.18 g, 1.105 mmoles) in tetrahydrofuran (4 ml) was stored at room temperature for 16 hr. The solvent was evaporated at room temperature, and the residue was triturated with ethanol and filtered to yield the crude adduct VII (0.46 g, 0.94 mmole, 94%), mp 271–275°. The product on recrystallization from acetone afforded VII as white prisms, mp 273–275° (0.38 g, 77%). Adduct VII absorbs at 3.00, 5.86, 7.21, and 8.41 μ.

Anal. Calcd for $C_{33}H_{29}NO_4$: C, 78.21; H, 5.90. Found: C, 78.23; H, 5.80.

Formation of 1,10-Diphenyldecapentaene (VIII) from V. A solution of V (0.40 g, 1.25 mmoles) and a trace of *p*-toluenesulfonic acid in benzene (10 ml) was refluxed for 2 hr. Cooling and filtration of the dark mixture yielded VIII as an orange solid. Recrystallization from chloroform gave the hydrocarbon (0.033 g, 0.11 mmole, 9%) as yellow-orange plates, mp 253–255° (lit.[22] 256°). Only three strong bands (10.1, 13.2, and 14.3 μ) are present in the infrared spectrum of VIII. The ultraviolet spectrum has maxima at 426, 402, and 381 mμ (ϵ 68,000, 71,000, and 46,000); lit.[22] 424, 403, and 387 mμ (ϵ *ca.* 70,000, 75,000 and 45,000).

Reaction of I with Acetaldehyde. A solution of dilithium cyclooctatetraenide (I) in ether (200 ml, containing 0.05 mole of I) was added in 20 min to stirred acetaldehyde (10 g, 0.23 mole) in ether (50 ml) at 0° under nitrogen. The mixture was stirred for 1 hr while being warmed to room temperature and then poured into ice water containing acetic acid (5 ml). The ether layer was washed with water, dried, and evaporated. The viscous orange residue (7.1 g) was distilled in a semimicro short-path apparatus. There was thus obtained a mixture of 7,8-bis(1-hydroxyethyl)bicyclo[4.2.0]octadiene (IX) and 5,8-bis(1-hydroxyethyl)-1,3,6-cyclooctatriene (X) as a viscous oil, bp 90–100° (bath temperature) (0.3 mm) (3.9 g, 0.0204 mole, 41%).

Anal. Calcd for $C_{12}H_{12}O_2$: C, 74.24; H, 9.28. Found: C, 74.82; H, 8.95.

The ultraviolet spectrum of the diol product shows λ_{max} 272 mμ (ϵ 2200) consistent for a 25:75 mixture of IX and X. The nmr spectrum of the mixture exhibits absorption at τ 4.10 (singlet), τ 3.8–4.5 (multiplets), τ 6.4–7.6 (multiplets), τ 8.84 (doublet, area 3, methyl hydrogens, J = 6.5 cps), and τ 9.0 (doublet, area 1, methyl hydrogens).

Reverse Aldolization of X. Formation of 7-(α-Hydroxyethyl)-1,3,6-cyclooctatriene (XI). A mixture of IX–X (4.9 g, 0.025 mole) and *p*-toluenesulfonic acid (0.2 g) was heated at 0.2 mm in a semimicro distillation apparatus. At a bath temperature of *ca.* 100°, a yellow oil distilled rapidly. When no more material was evolved, the distillate was redistilled through a short column to give XI (1.8 g, 48%) as a pale yellow, very air-sensitive oil, bp 62–64° (0.05 mm). The instability of XI precluded elemental analysis; its ultraviolet spectrum exhibits λ_{max} 268 mμ (ϵ 2400). The nmr spectrum of XI consists of signals at τ 4.01 (doublet, area 2, $J \cong 9.5$ cps), τ 4.43 (singlet, area 2), τ 4.6 (multiplet, area 2), τ 6.26 (apparent quintet, area 1, J = 5.8 cps), τ 6.60 (singlet, area 1, OH), τ 6.9–7.5 (multiplets, area 3, methylene hydrogens), and τ 8.84 (doublet, area 3, methyl hydrogens).

Hydrogenation of XI. A solution of XI (1.5 g) in ethyl acetate was shaken with 10% palladium on charcoal under 1 atm of hydrogen until uptake ceased (45 min). Filtration, evaporation of the solvent, and distillation gave cyclooctylmethylcarbinol [1.4 g, bp 77–80° (0.1 mm)]. This alcohol was converted by chromic acid[23] to cyclooctyl methyl ketone [bp 65–67° (0.1 mm)] and its subsequent semicarbazone. The infrared spectrum of the ketone was identical with that of an authentic sample prepared by oxidation of the carbinol obtained from cyclooctylmagnesium bromide and acetaldehyde. The mixture melting point of the two semicarbazone samples was undepressed.

---

(21) N. Bauld, *J. Am. Chem. Soc.*, **87**, 4788 (1965).

(22) R. Kuhn and K. Winterstein, *Helv. Chim. Acta*, **9**, 87 (1928).

(23) K. Bowden, I. M. Heilbron, E. R. H. Jones, and B. C. L. Weedon, *J. Chem. Soc.*, 39 (1946).

Reaction of I with Phthalaldehyde. A solution of I in ether (200 ml, containing *ca.* 0.05 mole of I) was added in 40 min to stirred phthalaldehyde (6.9 g, 0.050 mole) in ether (150 ml) at 0° under nitrogen. The cream-colored suspension was stirred for 2 hr while warming to room temperature and was then poured into ice water. The suspension was made faintly acidic with acetic acid and the ether layer separated. The aqueous layer was extracted with ether, and the combined ethereal solutions were washed thoroughly with water and dried. Evaporation of the ether gave an orange oil which, on trituration with benzene and cooling, partially crystallized. Filtration gave crude XIV as a pale yellow solid; recrystallization from ethanol–hexane gave 4,5-benzotricyclo[6.4.0.0^{2,7}]-dodeca-9,11-diene-3,6-diol (XIV, 0.44 g, 0.0018 mole, 3.6%) as white leaflets, mp 190–192°; $\lambda_{\max}^{\mathrm{KBr}}$ 3.07 (broad), 6.31 (w), 7.59 (m), 9.75 (s), 12.86 (s), 13.41 (s), and 14.60 (vs) μ. The product has $\lambda_{\max}$ 274 mμ (ϵ 3200) and 208 mμ (ϵ 11,000). The nmr spectrum in dimethyl sulfoxide consists of signals at τ 3.0 (singlet, area 4, aryl hydrogens), τ 4.48 (unresolved multiplet, area 2, vinyl hydrogens), τ 4.73 (multiplet, area 2, vinyl hydrogens), τ 5.53 (multiplet, area 2, hydrogens α to hydroxyls), and τ 6.85 (narrow multiplet, area 2, allylic hydrogens on C-1 and C-8); the signals of the hydrogens on C-2 and C-7 are hidden by the solvent absorption.

Anal. Calcd for $C_{16}H_{16}O_2$: C, 80.02; H, 6.67. Found: C, 80.30; H, 6.85.

When the reaction was conducted at −30° or below, with simultaneous addition of the dianion solution and the phthalaldehyde solution, there was obtained a polymorphic form of XIV, mp 214–215°; its infrared and ultraviolet spectra are identical with those of the product melting at 190°.

Reaction of XIV with N-Phenylmaleimide. A solution of XIV (0.14 g, 0.58 mmole) and N-phenylmaleimide (0.11 g, 0.62 mmole) in dry tetrahydrofuran (10 ml) was kept at room temperature 18 hr. Filtration of the white adduct and washing with cold tetrahydrofuran gave the crude adduct (0.17 g). Recrystallization from acetone gave XVI as white prisms, mp 319–321° dec; $\lambda_{\max}^{\mathrm{KBr}}$ 2.87 (m), 2.99 (m), 5.84 (s), and 7.22 (s) μ.

Anal. Calcd for $C_{26}H_{23}NO_4$: C, 75.54; H, 5.57. Found: C, 75.29; H, 5.70.

Dehydration of XIV to 2-Phenylnaphthalene. A solution of XIV (0.10 g, 0.4 mmole) and *p*-toluenesulfonic acid (*ca.* 5 mg) in benzene (15 ml) was flushed with nitrogen for 1 hr and then refluxed for 4 hr. Evaporation of the solvent under reduced pressure gave a tan semisolid which was chromatographed on a 16 × 100 mm column of alumina, activity I. Elution with 20% benzene–hexane yielded, after evaporation, a white solid (0.072 g, 86%), mp 101–103°. Recrystallization from ethanol gave white leaflets of 2-phenylnaphthalene, mp 102–103°, identified by comparison with an authentic sample (identical infrared spectra; no depression of mixture melting point).

Reaction of I with Acetone. A solution of I in ether (300 ml, containing *ca.* 0.075 mole of I) was added in 30 min to stirred acetone (14 g, 0.24 mole) in ether (50 ml) at 0° under nitrogen. The orange mixture was stirred for 1 hr while warming to room temperature and then poured into ice water. Sufficient acetic acid was added to make the system faintly acidic. The ether layer was separated and the aqueous layer extracted with ether. The combined ethereal solutions were washed with water and dried. Evaporation of the ether gave a mixture of 7,8-bis(2-hydroxy-2-propyl)-bicyclo[4.2.0]octadiene (XVII) and 5,8-bis(2-hydroxy-2-propyl)-1,3,6-cyclooctatriene (XVIII) as a viscous orange oil (16 g, 0.072 mole, 96%). The ultraviolet spectrum of the oxygen-sensitive diols showed a maximum at 268 mμ (ϵ 2200), indicative of a 70:30 ratio of XVII to XVIII. The nmr spectrum of the product reveals, in addition to a methyl singlet at τ 8.87, a complex pattern of olefinic hydrogen signals at τ 3.8–4.8 that corresponds exactly to that of superimposing the olefinic hydrogen signals of 5,8-bis(2-cyano-2-propyl)-1,3,6-cyclooctatriene[5d] upon the pattern shown by 7,8-dibromobicyclo[4.2.0]octadiene.

The 1,3,6-cyclooctatriene XVIII exhibits a doublet at τ 3.86 (area 2, J = 9.6 cps, hydrogens on C-2 and C-3), a singlet at τ 4.38 (area 2, hydrogens on C-6 and C-7), a pair of doublets at τ 4.78 (area 2, J = 9.6 and J' = 6.8 cps, hydrogens on C-1 and C-4), and a doublet at τ 7.24 (area 2, J = 6.8 cps, saturated hydrogens on C-5 and C-8). The chemical shifts and coupling constants are almost identical with those in the spectrum of the known 1,3,6-cyclooctatriene.[6b] Superimposed on this pattern is a narrow multiplet at τ 4.30 and a broad multiplet at τ 4.45 due to the olefinic hydrogens of the bicyclo[4.2.0]octadiene XVII. The area ratios of the various signals indicate a ratio of XVII to XVIII of 62:38. The diol mixture was dehydrated directly with acid to produce XIX and XX.

Dehydration of XVII and XVIII. Preparation of *o*-Bis(2,2-dimethylvinyl)benzene (XIX) and 3,3-Dimethyl-9-isopropylidene-2-oxatricyclo[4.3.1.0^{4,10}]dec-7-ene (XX). The mixture of diols XVII and XVIII (33 g) was heated with *p*-toluenesulfonic acid (0.30 g) in a vacuum distillation apparatus (1 mm). The crude mixture of XIX and XX distilled as a yellow oil (12.4 g) at 58–92 (1 mm). This oil was fractionally distilled through a 300-mm wire spiral column to effect preliminary separation. The following fractions were collected.

A. *o*-Bis(2,2-dimethylvinyl)benzene (XIX, 6.2 g, 0.033 mole, 36% based on nmr analysis of the diol mixture), a colorless liquid, bp 59–61° (0.5 mm), was obtained pure by preparative gas chromatography on column A. The retention time at 200° was 6.5 min. The infrared spectrum shows strong bands at 6.10 (m), 6.94 (s), 7.29 (s), 11.96 (vs), and 13.37 (vs) μ; $\lambda_{\max}^{\mathrm{ultraviolet}}$ 229 mμ (ϵ 23,000). The nmr spectrum consists of signals at τ 2.94 (singlet, area 4, aryl hydrogens), τ 3.87 (apparent septet, area 2, vinyl hydrogens, J = 1.3 cps), and τ 8.13 and 8.33 (pair of doublets, J = 1.3 cps, area 6 each, isopropylidene methyl hydrogens).

Anal. Calcd for $C_{14}H_{18}$: C, 90.33; H, 9.68. Found: C, 90.01; H, 9.49.

B. 3,3-Dimethyl-9-isopropylidene-2-oxatricyclo[4.3.1.0^{4,10}]-dec-7-ene (XX, 3.3 g, 0.016 mole, 28% based on nmr analysis of the diol mixture) was obtained as a pale yellow oil, bp 77–80° (0.5 mm). Purification was effected by preparative gas chromatography on column A (retention time 9.5 min at 220°).

Anal. Calcd for $C_{14}H_{20}O$: C, 82.37; H, 9.81. Found: C, 81.93; H, 10.07.

XX has significant infrared bands at 6.10 (w), 6.23 (w), 7.29 (m), 7.34 (m), 9.60 (m), 10.33 (s), and 12.04 (s) μ. The nmr spectrum consists of a pair of doublets centered at τ 3.58 (area 1, J = 10.3 and J' = 0.8 cps, hydrogen on C-8), a quartet at τ 4.42 (area 1, J = 10.3 and J' = 4.0 cps, hydrogen on C-7), a doublet at τ 5.27 (J = 6.4 cps, area 1, hydrogen on C-1), a series of overlapping multiplets at τ 6.9–7.9 (area 5, hydrogens on C-5, C-6, C-7, and C-10), sharp singlets at τ 8.13 and 8.17 (each of area 3, isopropylidene methyls), and a slightly broadened singlet at τ 8.90 (area 6, methyls on C-3).

Ozonation of XIX. A stream of ozone in oxygen (*ca.* 2.5%, 2.3 equiv) was bubbled through a solution of XIX (0.80 g, 0.0043 mole) in 95% ethanol (70 ml) at 0°. The mixture was stirred with zinc dust (5 g) for 1 hr at room temperature and was then distilled at 100-mm pressure until 40 ml of distillate had been collected (receiver at −78°). The distillate on treatment with 2,4-dinitrophenylhydrazine (2.4 g) in 30% ethanol (40 ml) containing sulfuric acid yielded acetone 2,4-dinitrophenylhydrazone, mp 125–126° (1.24 g, 0.0052 mole, 61% of 2 moles/mole of XIX).

Reaction of I with Benzophenone. A solution of I in ether (400 ml, containing *ca.* 0.125 mole of I) was added in 30 min to a stirred solution of benzophenone (50 g, 0.275 mole) in ether (400 ml) at 0° under nitrogen. The thick suspension was stirred for 20 min, warmed to room temperature, and then poured onto an equal volume of ice water containing acetic acid (15 ml). The aqueous layer was extracted with ether and the extract combined with the original ether layer. The ether solution was washed with water, dried, concentrated to *ca.* 100 ml, and stored at 5° overnight. The suspension was filtered, and the solid was washed with cold ether. Recrystallization from benzene–ethyl acetate gave 1,1,10,10-tetraphenyldeca-2,4,6,8-tetraene-1,10-diol (XXV, 16.1 g, 0.0345 mole, 28%) as tiny white needles, mp 220–221°. XXV exhibits infrared maxima at 2.86 (m), 6.80 (m), 6.92 (m), 10.02 (s), 10.31 (s), 10.83 (s), 12.77 (s), 13.00 (s), 13.29 (s) and 14.3 (vs) μ; the ultraviolet spectrum has maxima at 320, 306, and 294 mμ (ϵ 65,000, 70,000, and 53,000). The low solubility of XXV precludes determination of its nmr spectrum.

Anal. Calcd for $C_{34}H_{30}O_2$: C, 86.81; H, 6.38. Found: C, 87.02; H, 6.22.

The ethereal mother liquor and washes above were evaporated to a thick orange oil (39 g, 0.083 mole, 67%) consisting mostly of the diol XXVI. A portion (4.0 g) of this oil was chromatographed on a 26 × 250 mm column of alumina, activity III. Elution with 1:4 ether–hexane gave unchanged benzophenone (0.23 g). Elution with 1:2 ether–hexane gave 5,8-bis(α-hydroxybenzhydryl)-1,3,6-cyclooctatriene (XXVI, 3.6 g, 64% based on I) as a faintly yellow glass. The substance is readily oxidized by air and low analyses for carbon and hydrogen were always obtained.

Anal. Calcd for $C_{34}H_{30}O_2$: C, 86.81; H, 6.38. Found: C, 84.13; H, 6.04.

The ultraviolet spectrum of XXVI has a shallow maximum at 252 mμ (ϵ 7000), a minimum at 247 mμ, and strong end absorption.

The nmr spectrum consists of a multiplet at τ 2.7 (area 20, phenyl hydrogens), a doublet at τ 3.86 (area 2, vinyl hydrogens, J = 8.6 cps), a singlet at τ 4.21 (area 2, vinyl hydrogens), a multiplet at τ 4.46 (area 2, vinyl hydrogens), a multiplet at τ 7.18 (area 2, tertiary hydrogens), and a broad singlet at τ 7.48 (area 2, hydroxyls). The pattern of ring vinyl and tertiary hydrogens greatly resembles that of a known 5,8-disubstituted 1,3,6-cyclooctatriene.[5b]

Reaction of XXV with N-Phenylmaleimide. A solution of XXV (0.47 g, 1.00 mmole) and N-phenylmaleimide (0.36 g, 2.0 mmoles) in toluene (10 ml) was flushed with nitrogen and refluxed for 6 hr. A white solid precipitated from solution during the latter stages of refluxing. The solution was cooled and filtered, giving the mono-adduct XXIX (0.69 g, 0.83 mmole, 83%) as white needles. Recrystallization from xylene gave the analytical sample as silky white needles, mp 301–303° dec. The infrared spectrum of XXIX displays principal bands at 5.81 (s), 6.70 (m), 7.17 (s), 8.31 (s), 9.42 (vs), and 10.28 (s) μ.

Anal. Calcd for $C_{44}H_{37}NO_4$: C, 82.30; H, 5.78. Found: C, 82.46; H, 6.20.

Dehydration of XXIX. A solution of XXIX (0.20 g, 0.30 mmole) in acetic acid (10 ml) was treated with concentrated hydrochloric acid (two drops) and refluxed for 2 hr. Cooling and filtration gave crude XXX as a lemon yellow solid. Recrystallization from benzene–ethyl acetate led to XXX (0.12 g, 62%) as yellow needles, mp 314° dec; $\lambda_{\max}^{\text{KBr}}$ 5.84 (s), 7.20 (s), 8.35 (s), 13.08 (s), 13.18 (s), 13.77 (s), 14.14 (s), and 14.4 (vs) μ; $\lambda_{\max}^{\text{ultraviolet}}$ 361 and 264 mμ (ε 36,000 and 21,500).

Anal. Calcd for $C_{44}H_{33}NO_2$: C, 86.98; H, 5.43. Found: C, 86.58; H, 5.38.

Reaction of XXV with *p*-Toluenesulfonic Acid. A solution of XXV (1.00 g, 2.03 mmoles) in benzene (30 ml) was flushed with nitrogen for 30 min and heated to boiling. *p*-Toluenesulfonic acid (20 mg) was added, and the solution was refluxed under nitrogen for 5 min. Evaporation of the solvent gave a viscous orange oil which partially solidified on standing. Trituration with 10% benzene–hexane and filtration yielded 0.72 g of a yellow-tan solid. The material was recrystallized from oxygen-free 20% benzene–hexane at 5° and seeding. There was thus obtained 2,2-diphenyl-5-(6,6-diphenylhexatrienyl)-2,5-dihydrofuran (XXXI, 0.66 g, 1.45 mmoles, 71%) as a dull cream-colored solid, mp 120–126°. Two more recrystallizations (with the use of charcoal) gave XXXI as tiny off-white clusters of prisms, mp 131–132°.

Anal. Calcd for $C_{34}H_{32}O$: C, 90.32; H, 6.19. Found: C, 90.82; H, 6.31.

The infrared spectrum of XXXI exhibits absorption at 9.60 (vs), 9.78 (s), 10.03 (vs), 13.1 (vs), and 14.3 (vs) μ. The ultraviolet spectrum reveals maxima at 326 and 239 mμ (ε 42,000 and 16,500). The nmr spectrum consists of a singlet at τ 2.73 (area 10, phenyl hydrogens), a singlet at τ 2.79 (area 10, phenyl groups on the side chain), a multiplet at τ 3.74 (area 4, vinyl hydrogens on the side chain), a multiplet at τ 4.22 (area 2, ring vinyl hydrogens), and a broad multiplet at τ 4.63 (area 1, methine hydrogen).

Reaction of 1,1,10,10-Tetraphenyldecatetraene-1,10-diol (XXV) with Iodine. A solution of XXV (1.60 g, 3.4 mmoles) and iodine (0.1 g) in benzene (100 ml) was flushed with nitrogen and refluxed under nitrogen for 2 hr. Evaporation of the solvent gave a brown residue which was chromatographed directly on a 20 × 220 mm column of alumina, activity I. Elution with 10% benzene–hexane yielded 1,1,10,10-tetraphenyldecapentaene (XXXII, 0.15 g, 0.34 mmole, 10%) as tiny yellow needles. Recrystallization from benzene–hexane gave short yellow needles, mp 226–228° (lit.[24] mp 227–228°). The infrared spectrum of XXXII shows major bands at 6.73, 6.95, 9.92, 12.80, 13.09, and 14.42 μ. The ultraviolet spectrum possesses maxima at 420 and 407 mμ (ε 69,900 and 67,000); the reported values[24] are 423 and 406 mμ (ε 70,000 and 66,000).

Dehydration of 5,8-Bis(α-hydroxybenzhydryl)-1,3,6-cyclooctatriene (XXVI). A solution of diol XXVI (5.00 g, 0.0106 mole) and *p*-toluenesulfonic acid (0.1 g) in dry benzene (100 ml) was flushed with nitrogen for 40 min and refluxed under nitrogen for 6 hr. The water was collected in a Dean–Stark trap as formed. Evaporation of the benzene led to a semisolid residue which was triturated with 1:1 benzene–hexane and filtered to give crude 9-benzhydrylidene-3,3-diphenyl-2-oxatricyclo[4.3.1.$0^{4,10}$]dec-7-ene (XXXIII, 2.17 g, 0.0047 mole, 45%) as a pale yellow solid, mp 228–230°. Recrystallization from ethyl acetate yielded pure XXXIII as fine white prisms, mp 230–231°.

Anal. Calcd for $C_{34}H_{28}O$: C, 90.32; H, 6.19. Found: C, 90.59; H, 6.36.

The infrared spectrum of XXXIII has bands at 6.73 (m), 6.93 (m), 9.51 (m), 10.09 (s), 10.30 (s), 10.40 (m), 12.41 (m), 12.65 (m), 12.98 (s), 13.08 (s), 13.32 (s), and 14.2 (vs) μ. The ultraviolet spectrum exhibits maxima at 287 (ε 20,500) and 208 mμ. The nmr spectrum (in $CHBr_3$ at 125°) consists of a multiplet centered at τ 2.76 (area 20, phenyl hydrogens), multiplets at τ 3.5 and 4.2 (each of area 1, vinyl hydrogens), a multiplet at τ 5.2 (area 1, hydrogen on C-1), and complex overlapping multiplets at τ 5.7–6.2 and 6.7–7.0 (total area 5, hydrogens on C-4, C-5, C-6, and C-10).

Compound XXXIII is also obtained by refluxing a benzene solution of XXVI with iodine (10% yield).

Reaction of I with Fluorenone. A solution of I in ethyl ether (150 ml, containing 0.04 mole of I) was added to fluorenone (18 g, 0.010 mole) in ether (300 ml) at −20° under nitrogen. The pale blue-green suspension was stirred for 1 hr while warming to room temperature, and then poured onto an ice–water slush. The two-phase system was brought to pH 6 with acetic acid. The ether layer was separated and the aqueous layer washed with ether. The combined ether layers were washed with water, dried, and concentrated to 50 ml under nitrogen. Cooling and scratching caused crystallization to occur; filtration, further concentration of the mother liquors, and recooling gave additional white solid. This material was recrystallized from oxygen-free ethanol–hexane mixtures, working as rapidly as possible. There was thus obtained 5,8-bis(9′-hydroxy-9-fluorenyl)-1,3,6-cyclooctatriene (XXXV) as white prisms, mp 230–232° dec (6.3 g, 0.016 mole, 42%); infrared absorption at 2.9 (s, br), 6.96 (s), and 9.14 (s); ultraviolet absorption at $\lambda_{\max}$ 274, 295, and 307 mμ (ε 24,000, 10,700, and 6400).

Anal. Calcd for $C_{34}H_{26}O_2$: C, 87.55; H, 5.33. Found: C, 87.19; H, 5.31.

Dehydration of XXXV. A solution of diol XXXV (0.48 g, 1.0 mmole) and *p*-toluenesulfonic acid (20 mg) in dry benzene (20 ml) was flushed with nitrogen for 15 hr and then refluxed under nitrogen for 2 hr. Evaporation of the benzene under reduced pressure and trituration of the residue gave crude XXXVI as a yellow solid, mp 262–266°. Recrystallization from ethyl acetate gave pure XXXVI as white chunky prisms, mp 265–266° (0.19 g, 44%); maximum ultraviolet absorption at 329 and 305 mμ.

Anal. Calcd for $C_{34}H_{24}O$: C, 91.19; H, 5.36. Found: C, 90.80; H, 5.18.

Reaction of I and Benzil. A solution of benzil (12 g, 0.057 mole) in ether (150 ml) was added dropwise to stirred I in ether (200 ml, containing *ca.* 0.06 mole of I) at 0° under nitrogen. The solution was stirred at 0° for 20 min and then at room temperature for 1 hr. The solution was poured into ice water and the two-phase solution filtered. The gray solid obtained was washed with cold ether and extracted with hot benzene. Evaporation of the benzene extracts to dryness and recrystallization of the residue from ethanol gave benzoin (5.8 g), mp 130–131°, identified by comparison with an authentic sample (infrared spectra, mixture melting point). The benzene-insoluble residue amounted to 0.8 g. The ethereal mother liquor was washed with water, dried, and evaporated to *ca.* 15 ml. Filtration gave additional benzoin (1.3 g, total yield 7.1 g, 0.033 mole, 57%). Evaporation of the ether from the mother liquor gave an orange oil (5 ml) whose infrared spectrum indicated that it was a mixture of cyclooctatetraene and cyclooctatrienes.

Reaction of I and Phenanthrenequinone. Phenanthrenequinone (7.3 g, 0.035 mole) was added to I in ether (250 ml, containing *ca.* 0.04 mole of I) at 0° under nitrogen. The suspension was warmed to room temperature, then stirred and refluxed for 18 hr. The initially mustard yellow suspension became faintly green, and finally deep yellow-brown at the end of the reflux period. Direct filtration of a 50-ml portion of the reaction mixture gave a yellow solid which became green as the ether evaporated and as the solid came in contact with air. On standing in air, the green solid spontaneously ignited.

The remainder of the reaction mixture was poured into ice water; the result was a yellow upper ether layer and a dark green aqueous layer containing a slimy green mass suspended at the interface. The ether layer was separated, washed with water, dried, and evaporated. The residue was identified as a mixture of cyclooctatetraene and cyclooctatrienes. The aqueous layer was acidified with hydrochloric acid, whereupon the green colloidal mass coagulated and became dark brown. This material was filtered, washed several times with water and once with ethanol, and recrystallized from ethyl acetate to give phenanthrenequinone (4.18 g, 58%) identified by its melting point and infrared spectrum.

---

(24) G. Wittig and A. Klein, *Ber.*, **69**, 2037 (1936).