16α,17α-Epoxy-6α-methyl-4-pregnen-3,20-dione (VII).—One gram of the 6β-methyl isomer VI was refluxed in methanol (125 ml.) and potassium hydroxide (2.25 g.) for 35 minutes. Addition of a solution of sodium chloride, followed by filtration and drying, gave 870 mg. of crude VII, m.p. 152–155°. Crystallization from dichloromethane–methanol afforded 650 mg. of pure product, m.p. 153–156°, $[\alpha]D$ +150°; λ_{max}^{MeOH} 240 mμ, ε 16.100.

Anal. Calcd. for $C_{22}H_{30}O_3$: C, 77.15; H, 8.83. Found: C, 77.22; H, 8.84.

17α-Hydroxy-6α-methylprogesterone (VIII).—A solution of 500 mg. of VII in acetic acid (4.5 ml.) was treated with an excess of dry hydrogen bromide and then stored for 30 minutes at room temperature. The crude bromohydrin, recovered, by dilution with ice-water, was refluxed for 2 hours with twice its weight of Raney nickel in methanol. Filtration and removal of solvent gave a residue which, upon crystallization from aqueous acetone, weighed 305 mg. and melted at 218–220°, $[\alpha]D$ +78°; λ_{max}^{MeOH} 240 mμ, ε 16,000. These constants are in good agreement with those previously reported.[1d]

Anal. Calcd. for $C_{22}H_{32}O_3$: C, 76.77; H, 9.36. Found: C, 76.77; H, 9.51.

The 17α-acetate[1d] showed m.p. 203–205°, $[\alpha]D$ +54°; λ_{max}^{MeOH} 240 mμ, ε 16,000.

3β,5α-Dihydroxy-6β-methylpregnan-20-one (IX).—Six grams of IV in methanol were hydrogenated using 5% pal-

ladium-on-carbon catalyst. After removal of the catalyst and evaporation of the solvent, 5.8 g. of crude product was obtained melting at 206–209°. Crystallization from methanol yielded 5.4 g. of pure diol IX, m.p. 208.5–210.5°, $[\alpha]D$ +59.2.°

Anal. Calcd. for $C_{22}H_{36}O_3$: C, 75.81; H, 10.41. Found: C, 75.62; H, 10.47.

6β- and 6α-Methylprogesterone.—A solution of 1.82 g. of IX in 76 ml. of acetic acid was treated with 414 mg. of chromic acid dissolved in 15 ml. of 85% acetic acid and maintained at 45–48° for 1.5 hours. The mixture, worked up as usual, gave 1.1 g. of crude product with m.p. 225–230°. Several crystallizations from chloroform–methanol afforded 650 mg. of pure 5α-hydroxy-6β-methylpregnan-3,20-dione, m.p. 254–256°, $[\alpha]D$ +78°.[1e] The latter product (600 mg.) was dissolved in pyridine (8 ml.) and treated at 0° with 0.5 ml. of thionyl chloride. Recovery by dilution with ice-water and crystallization from methanol gave 350 mg. of 6β-methylprogesterone, m.p. 168–169°, $[\alpha]D$ +142°, which values agree with those of Ringold, *et al.*[1b]

Epimerization was effected by refluxing 1.0 g. of the β-isomer in 100 ml. of ethanol containing a few drops of 12 M hydrochloric acid for 40 minutes. After dilution with water, the crude product was collected and crystallized from methanol, affording 705 mg. of pure 6α-methylprogesterone,[1b] m.p. 118–120°, $[\alpha]D$ +178°.

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Bridged Polycyclic Compounds. XIII. Some Rearrangements of the Dibenzobicyclo[2.2.2]octadiene System

BY STANLEY J. CRISTOL AND RUTA K. BLY[1]

An attempt to prepare dibenzobicyclo[2.2.2]octadiene-*trans*-2,3-diol by means of performic acid oxidation of dibenzobicyclo[2.2.2]octatriene has failed because of a Wagner–Meerwein rearrangement which gave dibenzobicyclo[3.2.1]octadiene-*exo*-4-*syn*-8-diol. The same rearranged diol was obtained by the treatment of dibenzobicyclo[2.2.2]octadiene-2,3-epoxide with formic acid and subsequent hydrolysis. Reaction of the epoxide with alkali led to rearrangement and ring opening with 1,2,5,6-dibenzocycloheptatriene as the product. An investigation of this rearrangement showed that 1,2,5,6-dibenzocycloheptatriene-7-carboxaldehyde was an intermediate.

A number of investigators[2] have shown that reactions which involve a bicyclo[2.2.1]heptyl cation are frequently accompanied by skeletal rearrangements. Although the bicyclooctanes have not been studied as extensively, the limited amount of available information indicates that such rearrangements also occur with bicyclo[2.2.2]octyl cations.[3] The labile nature of these intermediates presents a problem when the preparation of the bicyclo[2.2.1]heptane and bicyclo[2.2.2]octane-*trans*-2,3-diols is attempted. The common synthetic

method for *trans*-diols, namely the peracid oxidation of the corresponding olefins followed by ring opening, proceeds *via* a carbonium ion intermediate and gives bicyclo[2.2.1]heptane-2,7-diol and bicyclo[3.2.1]octane-4,8-diol instead of the expected *trans*-2,3-diols.[2jkm,3c]

For the purpose of extending some studies of elimination reactions in bicyclic systems[4] we were interested in finding a synthetic route for the two above-mentioned *trans*-glycols and the related dibenzobicyclo[2.2.2]octadiene-*trans*-2,3-diol (IX). The reaction of dibenzobicyclo[2.2.2]octatriene (I) with peroxyformic acid has not been reported in the literature. However, Vaughan[5] has shown that some highly substituted dibenzobicyclo[2.2.2]octadienes undergo rearrangement under acid conditions to give dibenzobicyclo[3.2.1]octadiene derivatives, but that a positive charge on C_2 or C_3 does not always result in such a skeletal rearrangement. We found that treatment of dibenzobicyclo[2.2.2]octatriene (I) with peroxyformic acid gave,

(1) Previous paper in series: S. J. Cristol, J. R. Douglass, W. C. Firth, Jr., and R. G. Krall, THIS JOURNAL, **82**, 1829 (1960). This paper was presented at the 136th Meeting of the American Chemical Society in Atlantic City, N. J., September, 1959.

(2) (a) H. Meerwein and K. von Emster, *Ber.*, **53**, 1815 (1920); (b) **55**, 2500 (1922); (c) T. P. Nevell, E. de Salas and C. L. Wilson, *J. Chem. Soc.*, 1188 (1939); (d) S. Winstein and D. S. Trifan, THIS JOURNAL, **71**, 2953 (1949); (e) **74**, 1147 (1952); (f) **74**, 1154 (1952); (g) J. D. Roberts, C. C. Lee and W. H. Saunders, Jr., *ibid.*, **76**, 4501 (1954); (h) H. Kwart, *ibid.*, **75**, 5942 (1953); (i) H. Kwart and L. Kaplan, *ibid.*, **76**, 4072 (1954); (j) H. Kwart and W. E. Vosburgh, *ibid.*, **76**, 5400 (1954); (k) H. M. Walborsky and D. F. Loncrini, *ibid.*, **76**, 5396 (1954); (l) S. J. Cristol, W. K. Seifert and S. B. Soloway, *ibid.*, **82**, 2351 (1960); (m) S. B. Soloway and S. J. Cristol, *J. Org. Chem.*, **25**, 327 (1960).

(3) (a) W. von E. Doering and M. J. Farber, THIS JOURNAL, **71**, 1514 (1949); (b) M. S. Newman and Y. T. Yu, *ibid.*, **74**, 507 (1952); (c) H. Kwart and G. C. Gatos, *ibid.*, **80**, 881 (1958); (d) R. P. Arganbright, Ph.D. Thesis, University of Colorado, 1956.

(4) (a) S. J. Cristol and N. L. Hause, THIS JOURNAL, **74**, 2193 (1952); (b) S. J. Cristol and E. F. Hoegger, *ibid.*, **79**, 3438 (1957); (c) S. J. Cristol and R. P. Arganbright, *ibid.*, **79**, 3441 (1957).

(5) (a) W. R. Vaughan, M. V. Anderson, Jr., and R. Q. Little, Jr., *ibid.*, **76**, 1748 (1954); (b) W. R. Vaughan and A. C. Schoenanthaler, *ibid.*, **79**, 5777 (1957).

after hydrolysis of the intermediate hydroxyformate, the rearranged dibenzobicyclo[3.2.1]octadiene-*exo*-4-*syn*-8-diol (VI) rather than IX. The same diol was obtained by the reaction of dibenzobicyclo[2.2.2]octadiene-2,3-epoxide (VII) with formic acid and subsequent hydrolysis.

We hoped to avoid rearrangement by choosing a synthetic method which would not involve a cationic center on the bridge carbon atoms. In view of the results of previous workers,[6] a promising possibility appeared to be the alkaline opening of the corresponding epoxides. However, when dibenzobicyclo[2.2.2]octadiene-2,3-epoxide (VII) was treated with aqueous sodium hydroxide, the product obtained was the hydrocarbon 1,2,5,6-dibenzocycloheptatriene (XIX) and was not the *trans*-2,3-diol IX. Although this reaction clearly had to be discarded as a possible route to the desired diol, the result was very interesting and seemed unprecedented in the literature. We therefore undertook an investigation to gain a better understanding of this rearrangement–ring opening reaction. The present article describes the results of this investigation.

Discussion.—The following outline shows a probable reaction sequence to give dibenzo[3.2.1]-octadiene-*exo*-4-*syn*-8-diol (VI) from I or VII.[7]
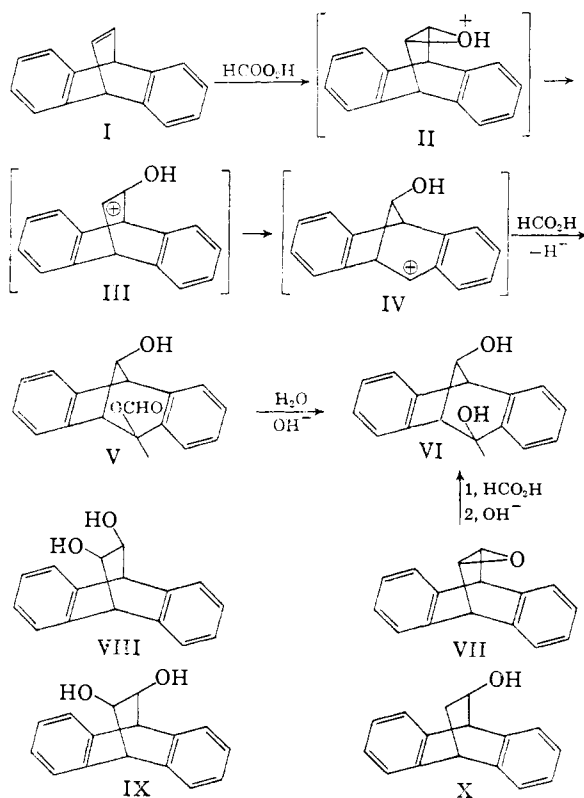

The structure of the epoxide VII, which was obtained by epoxidation of I with peroxybenzoic acid, was proved by reduction with lithium aluminum

(6) (a) D. Atherton and T. P. Hilditch, *J. Chem. Soc.*, 204 (1943); (b) F. A. Long and J. G. Pritchard, THIS JOURNAL, **78**, 2663 (1956).

(7) In this outline, structures III and IV may be separable species or may be resonance structures contributing to a hybrid non-classical cation; in addition, it is conceivable and consistent with our results that two or more of the represented steps may be telescoped.

hydride to an alcohol which was identical with an authentic sample of dibenzobicyclo[2.2.2]octadiene-2-ol (X). The authentic sample of X was prepared by the hydrolysis of the Diels–Alder addition product of anthracene and vinyl acetate according to the procedure of Wawzonek and Hallum.[8]

The diol VI gave a negative periodic acid test but reacted with acetic anhydride to give a diacetate. These facts indicate that VI is a diol with the hydroxyl groups on non-adjacent carbon atoms. Permanganate oxidation of the diol gave the products XI, XII and XIII.
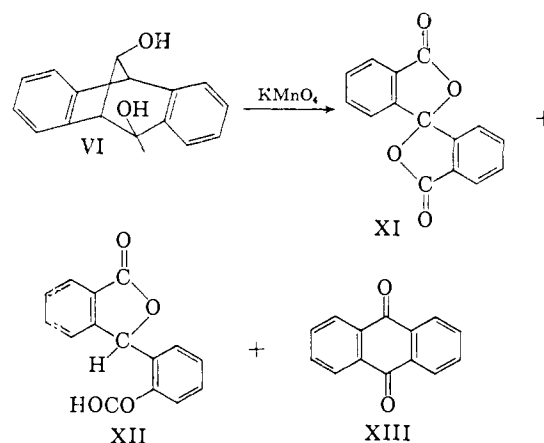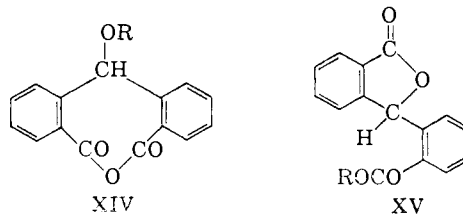

3,3'-Spirobiphthalide(XI) and anthraquinone (XIII) were identified by comparison with authentic samples.[5a] The physical properties of XII were in good agreement with those of 3-(*o*-carboxyphenyl)-phthalide described by Graebe and Julliard.[9] Our sample of XII gave methyl and ethyl esters[10] with properties agreeing with those reported[9] for the corresponding derivative of 3-(*o*-carboxyphenyl)-phthalide (XII).

First consideration of the oxidation products of VI suggested that this material is a mixture of compounds of different skeletal structures. Thus if the starting diol were of the dibenzobicyclo[3.2.1]octadiene system, we would expect to obtain XI and XII, whereas if it were a dibenzobicyclo[2.2.2]octadiene derivative, we would expect to obtain XIII. Judging from its physical properties VI did not appear to be a mixture; it had a sharp melting point which was the same whether it was purified by recrystallization or by chromatography. There is also the possibility that either XI and XII, or XIII,

(8) S. Wawzonek and J. V. Hallum, *J. Org. Chem.*, **18**, 288 (1953).

(9) C. Graebe and P. Julliard, *Ann.*, 214, 243 (1887).

(10) Graebe and Julliard refer to these derivatives as the "methyl and ethyl ethers" but do not suggest the exact structures of the compounds. From the carbon and hydrogen analyses they could be either XIV or XV. Since alkaline hydrolysis under mild conditions re-

generated 3-(*o*-carboxyphenyl)phthalide it appears that the correct structures are more likely those of the esters XV rather than the ethers XIV.

had been formed by way of a rearrangement. We found that permanganate oxidation of dibenzobicyclo[2.2.2]octadiene-*cis*-2,3-diol (VIII) gave anthraquinone (XIII) in 75% yield and gave no XI or XII; thus rearrangement had not occurred in the oxidation. On the other hand, permanganate oxidation of 1,2,5,6-dibenzocycloheptatriene gave as much as 52% of anthraquinone and only 35% of 3,3'-spirobiphthalide (XI). Similar rearrangements of seven- to six-membered ring systems have been reported by a number of other workers.[11] In view of these observations we feel that it is reasonable to assume that the anthraquinone obtained by the oxidation of the diol VI was the result of a rearrangement of an intermediate 1,2,5,6-dibenzocycloheptadiene derivative and that VI is a pure compound of the dibenzobicyclo[3.2.1]octadiene system.

The *exo*-4-*syn*-8-configuration of the hydroxyl groups in VI was established by means of the infrared spectrum which shows a moderately strong intramolecular hydrogen bonding ($\Delta\nu$ 63 cm.$^{-1}$).[12] Also, the diol reacted with phosgene to give a carbonate whose analysis and infrared spectrum were in agreement with the structure XVI.

XVI

XVIII   XVII = VI
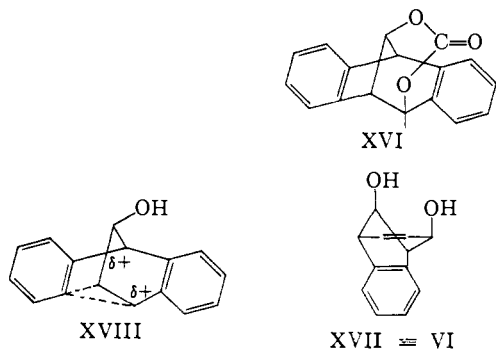
Only the *exo*-4-*syn*-8-configuration of the hydroxyl groups in the 4- and 8-positions could lead to intramolecular hydrogen bonding or the formation of a cyclic carbonate. It is of some interest that this diol is formed (presumably exclusively), even though both hydroxyl groups lie in axial positions in the rigid half-chair cyclohexene ring system (XVII). The structure of this diol is consistent with those reported for the ring opening of bicycloheptene oxides[2jkm] and bicyclooctene oxide[3c] and with other stereochemical results observed in many other Wagner–Meerwein rearrangements. The results may be explained on the basis of a nonclassical ion intermediate XVIII (of which III and IV are then to be considered as contributing resonance forms) with reaction occurring preferably at one of the two cationic positions and with displacement with inversion at that position or else by a presumed steric advantage of *exo* reaction on the classical intermediate IV. The latter may not appear plausible because of 1,3-diaxial interactions in the transition state, unless such interactions

are in fact stabilizing because of hydrogen bonding. We are presently studying a variety of addition reactions to I, and are looking at the stereochemistry of the rearranged addition products corresponding to VI and its epimers.

Attempts to prepare a cyclic acetal of VI and *p*-nitrobenzaldehyde were unsuccessful because, in the presence of *p*-toluenesulfonic acid catalyst, the diol rearranged to give 1,2,5,6-dibenzocycloheptatriene-7-carboxaldehyde. We shall return to this reaction later in the discussion.

Opening of dibenzobicyclo[2.2.2]octadiene-2,3-epoxide (VII) with hydroxide ion was attempted under several different sets of conditions. In all cases the major reaction product was 1,2,5,6-dibenzocycloheptatriene (XIX). Under relatively mild conditions some unreacted starting material was recovered, but an increase in temperature and base concentration resulted in considerable tar formation. The results are summarized

VII

$$ \xrightarrow[\text{aq.}]{7M \text{ NaOH, 150°}} $$

XIX (42%)

$$ \xrightarrow[\text{ethylene glycol}]{3\ M \text{ NaOH, reflux}} \text{XIX (46\%) + acid XX} $$

$$ \xrightarrow[50\%\ C_2H_5OH]{1\ M \text{ NaOH, reflux}} \text{XIX (45\%) + VII (6\%)} $$

Since the structure of the acid XX has not yet been established, we cannot speculate as to its origin and shall therefore discuss only the mechanism of the formation of XIX.

First, it was important to determine whether the epoxide VII had immediately undergone a skeletal rearrangement or if rearrangement was preceded by a reaction which gave another dibenzobicyclo-[2.2.2]octadiene derivative. If the latter were the case the two most likely intermediates would be 2-ketodibenzobicyclo[2.2.2]octadiene (XXI) and/or the originally expected dibenzobicyclo[2.2.2]octadiene-*trans*-2,3-diol (IX). The ketone XXI was prepared by the Oppenauer oxidation of the parent alcohol according to the procedure of Wawzonek and Hallum.[8] The *trans*-diol was not available, but we hoped to obtain some information about its probable behavior with alkali by studying the *cis* isomer VIII. The latter was prepared by low-temperature permanganate oxidation of dibenzobicyclo[2.2.2]octatriene (I). When XXI and VIII were heated under reflux with alkaline ethylene glycol the only products obtained were 9,10-dihydroanthracene-9-acetic acid (XXII) and 9,10-dihydroanthracene (XXIII), respectively. Similar results already have been reported by Vaughan and Yoshimine[13] who have treated the ketone XXI as well as 2,3-diketodibenzobicyclo[2.2.2]octadiene with alkali and have obtained XXII and XXIII, respectively. From the products of these reactions it is clear that the alkaline cleavage of both XXI and VII was not preceded by rearrangement of the carbon skeleton. With regard to the rear-
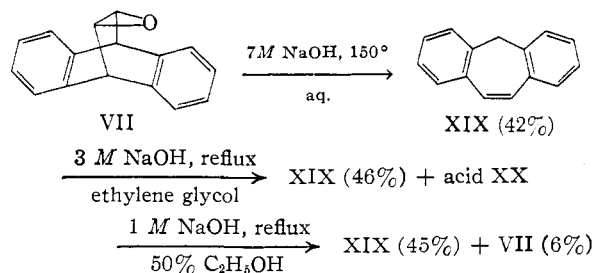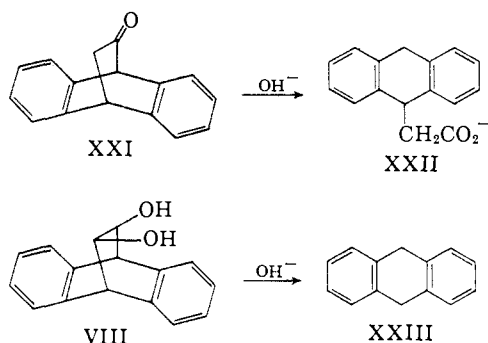
(11) (a) W. Treibs and H. J. Klinkhammer, *Ber.*, **83**, 367 (1950); (b) J. Rigaudy and L. Nedelec, *Compt. rend.*, **236**, 1287 (1953); *Bull. soc. chim.*, **638**, 543, 648 (1959); (c) W. von E. Doering and L. H. Knox, THIS JOURNAL, **79**, 352 (1957); (d) Y. Amiel and D. Ginsburg, *Tetrahedron*, **1**, 19 (1957).

(12) L. P. Kuhn, THIS JOURNAL, **74**, 2492 (1952).

(13) W. R. Vaughan and M. Yoshimine, *J. Org. Chem.*, **22**, 528 (1957).

XXI → XXII

VIII → XXIII

rangement of the epoxide VII to 1,2,5,6-dibenzo-cycloheptatriene (XIX) we can now say that the ketone XXI is definitely not an intermediate, and that it is also unlikely that the *trans* isomer of VIII is an intermediate.

With the assumption that this was the case we considered three possible reaction paths for the rearrangement. The first of these is


VII → VI → XXIV → XXV → XXVI → XIX
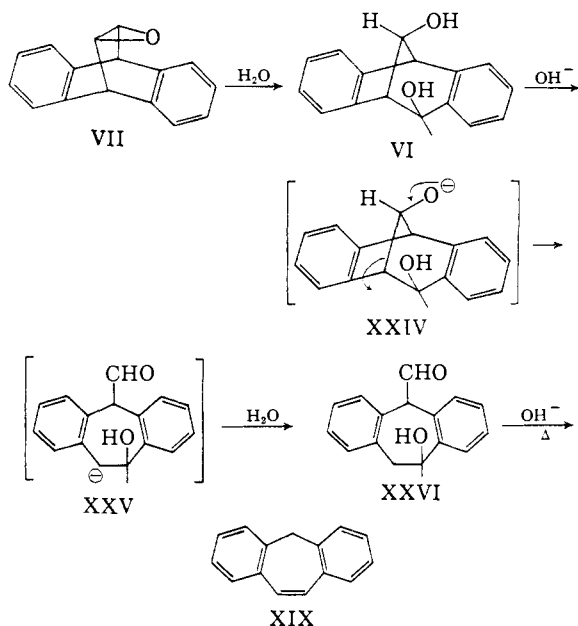
There were a number of analogies which made such a mechanism seem reasonable. We knew that VII gave the diol VI in acid solution, and Searles and co-workers[14] have reported that treatment of 1,3-diols with alkali at 150–200° causes cleavage of a carbon–carbon bond to give an alcohol and an aldehyde or a ketone. Alkaline cleavage like that suggested in the last step of this reaction path has been demonstrated by Shemyakin and Shchukina[15] and by Vaughan.[13] We could easily determine whether or not this mechanism was feasible by treating a sample of VI with alkali. When this reaction was performed we found that no 1,2,5,6-dibenzocycloheptatriene was obtained and only unreacted starting material and some tar were recovered. Since VI was one of the intermediates in this reaction path, it was definitely ruled out.

(14) S. Searles, Jr., E. K. Ives and S. Nukini, *J. Org. Chem.*, **24**, 1770 (1959).

(15) M. M. Shemyakin and L. A. Shchukina, *Quart. Revs.*, **10**, 261 (1956).

The second mode of reaction we considered was

VII → XXIX → XIX
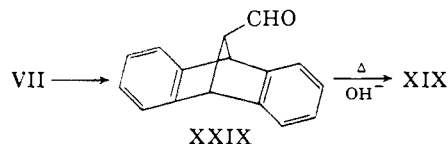
We considered the above reaction path because of a report by the Shell Chemical Corporation[16] who have shown that bicyclo[2.2.1]heptadiene gave cycloheptatriene when heated at 450–500°. A more detailed study of this reaction has recently been published by Woods.[17] If VII first rearranged to the dibenzobicyclo[2.2.1]heptadiene derivative XXIX *via* the well known epoxide to carbonyl compound rearrangement,[18] XXIX might conceivably undergo reaction with alkaline decarboxylation and rearrangement to give XIX. However, Vaughan and Yoshimine[19] have described the preparation of dibenzobicyclo[2.2.1]-heptadiene by dehydrogenation of the addition product of bicyclo[2.2.1]heptadiene and butadiene at 230°. This work indicates that the dibenzobicyclo[2.2.1]heptadiene system is stable even at considerably higher temperatures than were required to obtain XIX from the epoxide VII. Therefore, although this path has not been definitely disproved, it did not seem to be a very likely possibility and was not investigated further.

A third path that appears likely is


VII → XXX → XXXI → XXXII → XIX + HCO$_2^-$
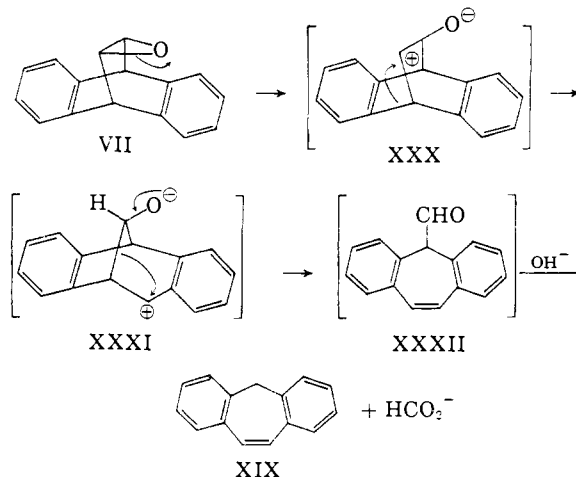
We note that the first steps in the above series of reactions do not require the participation of base. Therefore if this path were correct, it might be possible to obtain 1,2,5,6-dibenzocycloheptatriene-7-carboxaldehyde (XXXII) by heating the epoxide VII in the absence of alkali. When VII was heated in aqueous suspension the expected carboxaldehyde XXXII was in fact obtained. Heating of the epoxide in an ethylene glycol solution gave the corresponding acetal XXXIII instead.

(16) Shell Chemical Corporation, *Chem. Eng. News*, **35**, No. 11, 23 (1957).

(17) W. J. Woods, *J. Org. Chem.*, **23**, 110 (1958).

(18) S. Winstein and R. B. Henderson in R. C. Elderfield, "Heterocyclic Compounds," Vol. 1, John Wiley and Sons, Inc., New York, N. Y., 1950, pp. 47–52.

(19) W. R. Vaughan and M. Yoshimine, *J. Org. Chem.*, **22**, 7 (1957).
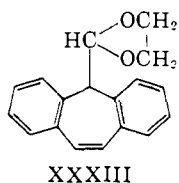
XXXIII

The reaction of both XXXII and XXXIII with alkali in ethylene glycol gave XIX and the acid XX. On the basis of this evidence we believe that the 1,2,5,6-dibenzocycloheptatriene(XIX) was obtained from dibenzobicyclo[2.2.2]octadiene-2,3-epoxide(VII) via this path.

The structure of the aldehyde XXXII was established by the following series of reactions.

XXXII   XXXIV

XXXV   XXXVI
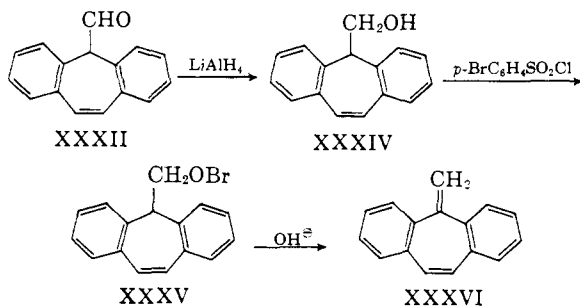
The product XXXVI gave no melting point depression with an authentic sample of 7-methylene-1,2,5,6-dibenzocycloheptatriene.[20] Additional support for the structure of the carboxaldehyde XXXII was provided by infrared and ultraviolet spectra, by the preparation of a 2,4-dinitrophenylhydrazone, and by silver oxide oxidation to a carboxylic acid.

During the course of this investigation we have obtained the aldehyde XXXII by two other methods in addition to the one already mentioned.

When an attempt was made to purify the epoxide VII by means of chromatography on Fisher alumina it was found that, after elution, the aldehyde XXXII was recovered instead of the epoxide. We believe that this rearrangement was caused by the electrophilic nature of alumina.

CHO

XXXII
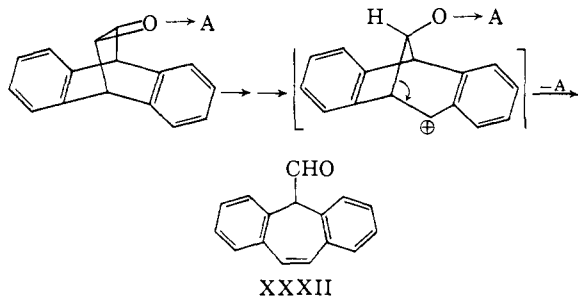
Rearrangement occurred if the solvent was carbon tetrachloride or chloroform. If ethyl acetate was used the starting epoxide was recovered unchanged. This may be due to the fact that ethyl acetate, because of its relatively high polar character, is adsorbed on the acid sites in preference to the epoxide. The rearrangement of VII on alumina provides a very convenient means of obtaining small amounts of the aldehyde in pure form.

(20) A. C. Cope and S. W. Fenton, THIS JOURNAL, **73**, 1673 (1951).

As was mentioned earlier in the discussion, the diol VI, while stable in alkali or in formic acid, undergoes rearrangement to XXXII in the presence of p-toluenesulfonic acid. This rearrangement probably occurs in the following manner.

VI
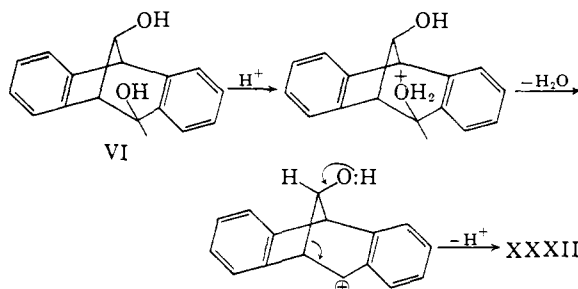
XXXII

The question of whether the ion IV is an intermediate in the rearrangement of VII to VI and of VI to XXXII is under investigation.

Experimental

Dibenzobicyclo[2.2.2]octatriene (I).—cis-2,3-Dichlorodibenzobicyclo[2.2.2]octadiene was prepared from cis-acetylene dichloride and anthracene as described by Cristol and Hause.[4a] Dehalogenation of the dichloride was carried out by a modified procedure of Cristol and Hause.[4a] Sodium (ca. 20 g.) was added in small pieces to a solution of 16 g. (0.058 mole) of the dichloride in 400 ml. of n-amyl alcohol at reflux temperature. The addition was continued until the sodium began to sink to the bottom of the reaction flask forming one ball instead of floating as separate globules on top of the solution. The reaction mixture was cooled and washed with water, and the solvent removed under reduced pressure. Recrystallization of the residue from ethanol gave 10.5 g. (88%) of product, m.p. 119–120.5°.

Dibenzobicyclo[3.2.1]octadiene-exo-4-syn-8-diol (VI).—To a solution of 5.0 g. (24.5 mmoles) of dibenzobicyclo[2.2.2]octatriene (I) in 20 ml. of formic acid and 30 ml. of ether was added with stirring 4.2 g. of 30% hydrogen peroxide. The solution was heated under reflux for 4 hours. The ether and formic acid were then removed under reduced pressure. The oily residue was dissolved in 50 ml. of 1 N ethanolic potassium hydroxide and heated under reflux for 4 hours. The solution was cooled, diluted with an equal volume of water, and extracted with five 50-ml. portions of ether. The ether extract was washed with dilute sulfuric acid and with water until the washings tested neutral to litmus and then dried over anhydrous sodium sulfate. Evaporation of the ether gave 4.9 g. of a dark oily residue. The residue was dissolved in carbon tetrachloride and purified by chromatography using 185 g. of activated alumina as adsorbent. Elution with carbon tetrachloride and chloroform gave 1.12 g. (22%) of starting olefin and a small amount of anthraquinone. The column was then eluted with ethyl acetate to remove some dark oily material. Finally elution with ethanol gave 3.45 g. (59%) of the diol VI, m.p. 135–140°. Recrystallization from benzene gave a product melting at 145–146°. The product gave a negative periodic acid test.

Anal. Calcd. for $C_{16}H_{14}O_2$: C, 80.76; H, 5.88. Found: C, 80.51; H, 6.05.

In another experiment the procedure was modified as follows. After saponification of the hydroxyformate, the reaction mixture was extracted with ether. When most of the ether was evaporated a small amount of Skellysolve B was added to the sirupy residue. This caused the prod-

uct to crystallize. The product was filtered, washed with a small amount of Skellysolve B and recrystallized from benzene. The yield of pure product was 62%, m.p. 145–146°.

The diacetate of VI was obtained in 91% yield by heating 100 mg. (0.42 mmole) of the diol on a steam-bath for 3 hours with 2 ml. of acetic anhydride and 50 mg. of powdered, fused sodium acetate, m.p. 168–170°.

Anal. Calcd. for $C_{20}H_{18}O_4$: C, 74.52; H, 5.63. Found: C, 74.50; H, 5.60.

Dibenzobicyclo[2.2.2]octadiene-2,3-epoxide (VII).—A dried solution of 9.5 g. (68.8 mmoles) of peroxybenzoic acid in 300 ml. of chloroform was added with cooling to 12 g. (58.3 mmoles) of I. The solution was allowed to stand at 5–10° for 5 days. At this time titration with sodium thiosulfate showed that 61.5 mmoles of perbenzoic acid had been consumed. The chloroform solution was washed with several portions of 10% sodium hydroxide and with water and dried over anhydrous sodium sulfate. Evaporation of the chloroform under reduced pressure gave 12.6 g. of a pale yellow residue, m.p. 110–150°. Recrystallization from chloroform gave 8.1 g. (62%) of VII as a colorless material, m.p. 154–165°. Additional recrystallization gave 6.7 g. (52%) of a product which softened slightly at 154° and melted with a 3 to 5° range between 160 and 170° (depending upon the rate of heating). The melting point was highest when the temperature was increased rapidly or if the compound was not placed in the heating bath until the temperature reached about 140°. Further recrystallization did not improve the melting point. The infrared spectrum showed a strong peak at 11.97 μ and no peaks in the 5.5 to 6.5 μ region.

Anal. Calcd. for $C_{16}H_{12}O$: C, 87.24; H, 5.49. Found: C, 87.01; H, 5.46.

Reduction of VII.—Four-hundred milligrams of lithium aluminum hydride was added in one portion to a solution of 500 mg. (2.29 mmoles) of the epoxide in 10 ml. of dried and purified tetrahydrofuran. The reaction mixture was heated under reflux for 5 days. The excess hydride was decomposed with ethyl acetate, and the mixture was poured into 15 ml. of cold 15% sodium hydroxide. The product was extracted with ether, and the ether extract washed with water and dried. Evaporation of the ether gave 443 mg. (88%) of a pale yellow solid, m.p. 132–136° with a slight softening at 110°. The product was dissolved in carbon tetrachloride and purified by means of alumina chromatography. Elution with ethyl acetate gave 327 mg. (65%) of a colorless compound, m.p. 135–141°. After recrystallization from methanol–water the product melted at 139–141° and gave no melting point depression with dibenzobicyclo[2.2.2]octadiene-2-ol.[8]

Treatment of VII with Formic Acid.—Four milliliters of formic acid was added with stirring to 1.00 g. (4.54 mmoles) of VII in 6 ml. of ether. An exothermic reaction took place as the epoxide gradually dissolved. The solution was allowed to stand at room temperature for 5 hours. The ether was evaporated under reduced pressure, and the residue washed with several portions of water. The oily product was dissolved in chloroform and dried. Evaporation of the solvent gave 980 mg. of a viscous oil. All efforts to obtain a crystalline product were unsuccessful.

Ten milliliters of 1 M ethanolic potassium hydroxide was added to 376 g. of the above product and the solution was heated under reflux for 5 hours. The solution was diluted with water and extracted with ether. The ether extract was washed with water and dried. Evaporation of the solvent gave 300 mg. (89%) of a crystalline material, m.p. 140–144°. Recrystallization from benzene gave a product which melted at 145–146° and gave no melting point depression with the dibenzobicyclo[3.2.1]octadiene-*exo*-4-*syn*-8-diol (VI) obtained directly from I.

Permanganate Oxidation of VI.—To a suspension of 480 mg. (2.02 mmoles) of VI in 15 ml. of water was added with stirring during a 2-hour period 1.48 g. (9.4 mmoles) of potassium permanganate. The reaction mixture was stirred at room temperature for an additional 3 hours. The temperature was then raised to 60° and the reaction continued until the purple color of the permanganate disappeared completely. The precipitate was filtered, dried and washed with several portions of warm chloroform. Evaporation of the chloroform gave 43 mg. (10%) of anthraquinone, m.p. 265–270°. Recrystallization from chloro-

form gave a product which melted at 282–284° and gave no melting point depression with an authentic sample of anthraquinone. The aqueous filtrate was extracted with ether. Evaporation of the ether gave only a small amount of a high melting residue (above 360°) which was not identified. The aqueous phase was acidified with 3 M hydrochloric acid. The solution was digested at 50–60° for a day. A white precipitate was formed.

Part of the product dissolved rapidly in alkali and was precipitated immediately upon acidification. The yield of this material was 111 mg. (22%), m.p. 199–203°. Recrystallization from chloroform–Skellysolve gave a melting point of 202.5–203.5°. This product was identified as 3-(*o*-carboxyphenyl)-phthalide (XII).[9] The infrared spectrum showed two strong absorption bands in the carbonyl region (5.59 and 5.87 μ). A potentiometric titration showed a pK_a of 4.85.

Anal. Calcd. for $C_{15}H_{10}O_4$: C, 70.86; H, 3.96; sapon. equiv., 127. Found: C, 71.29; H, 4.32; sapon. equiv., 132.

The methyl and ethyl esters of XII were prepared according to the procedure of Graebe and Julliard.[9] The melting points were 155–156.5° for the methyl ester (lit. 154–155°) and 100–101° for the ethyl ester (lit. 99.5°).

Anal. (methyl ester): Calcd. for $C_{16}H_{12}O_4$: C, 71.63; H, 4.51. Found: C, 71.70; H, 4.70.

A small amount of the ethyl ester was saponified by heating under reflux for 2 hours in a 0.5 M sodium hydroxide solution in 50% ethanol. Most of the ethanol was evaporated under reduced pressure and the solution acidified. A colorless material precipitated which melted at 199–203° and gave no melting point depression with XII.

The remainder of the oxidation product of VI dissolved in alkali only very slowly and reprecipitation with acid required digestion for several hours. The yield of this product was 206 mg. (41%), m.p. 205–210°. Recrystallization from ethanol gave a material which melted at 210–212° and gave no melting point depression with 3,3′-spirobiphthalide (XI).[5]

The Carbonate of Dibenzobicyclo[3.2.1]octadiene-*exo*-4-*syn*-8-diol (XVI).—Two milliliters of dry pyridine and 10 ml. of purified dioxane were placed in a three-necked flask, equipped with a dropping funnel with a pressure-equalizing side arm, and saturated with dry phosgene at room temperature. The excess phosgene was passed into 20% potassium hydroxide. The flow of the phosgene was stopped and a solution of 520 mg. (2.18 mmoles) of the diol VI in 10 ml. of dioxane was added through the dropping funnel. A slight evolution of heat was observed, but the reaction was not strongly exothermic. The bubbling of phosgene was resumed and continued until the reaction mixture cooled down to room temperature; this required about 5 hours. A heavy white precipitate was formed during the reaction. Water was added slowly to the reaction mixture. The crystalline precipitate dissolved and a gummy substance separated, wt. 375 mg. The solution was decanted and allowed to stand at room temperature overnight. A second fraction of a white crystalline product precipitated, wt. 56 mg., m.p. 220–230°. The oily first fraction was dissolved in chloroform and slowly reprecipitated with Skellysolve B. An additional 6 mg. of crystalline product was obtained, m.p. 225–230°. The total yield of the carbonate XVI was 62 mg. (11%). Two recrystallizations from carbon tetrachloride–chloroform gave a melting point of 232–234°. The infrared spectrum showed a carbonyl absorption peak at 5.70 μ. The two peaks at 2.88 and 3.04 μ which were present in the spectrum of the starting diol and assigned to the hydroxyl groups were now absent.

Anal. Calcd. for $C_{17}H_{12}O_3$: C, 77.26; H, 4.58. Found: C, 77.05; H, 4.70.

Attempted Preparation of the Acetal of the Diol VI and *p*-Nitrobenzaldehyde.—The procedure was the same as that used earlier[2k,21] for the preparation of the acetal of *exo*-2-*syn*-7-norbornanediol (XXVIII) and *p*-nitrobenzaldehyde. The diol (920 mg., 3.86 mmoles), 600 mg. (3.97 mmoles) of *p*-nitrobenzaldehyde and a catalytic amount of *p*-toluenesulfonic acid were used. The crude yield was 1.47 g. of a reddish-brown oil. Seven recrystallizations from Skellysolve-B gave 0.25 g. of a crystalline product, m.p. 108–111°.

(21) K. Alder and H. Wirtz, *Ann.*, **601**, 138 (1956).

This compound was the carboxaldehyde XXXII and not the expected acetal.

The Treatment of VII with Alkali in Aqueous Suspension. —One gram (4.54 mmoles) of the epoxide VII and 30 ml. of 7 M aqueous sodium hydroxide were sealed in a Pyrex bomb tube and rocked at 140–150° for 16 hours. The tube was cooled and opened and the reaction mixture filtered. The precipitate, which consisted of a dark brown oily substance, powdered glass and some gelatinous inorganic materials, was washed with water and extracted with hot carbon tetrachloride. Evaporation of the solvent gave 850 mg. of a dark partially crystalline residue. The crystalline part melted at about 116–126°. Recrystallization from ethanol gave 367 mg. (42%) of crude dibenzocycloheptatriene (XIX), m.p. 116–126°. Additional recrystallization gave 320 mg. (38%) of pure product, m.p. 132–134° (lit.[22] 134°). The ultraviolet spectrum showed a maximum at 285 mμ (log ϵ 4.13) and a minimum at 245 mμ (log ϵ 3.40) (lit.[23] λ_{max} + 285 mμ, log ϵ 4.17; λ_{min} 245 mμ, log ϵ 3.43).

Anal. Calcd. for C₁₅H₁₂: C, 93.70; H, 6.29. Found: C, 93.80; H, 6.08.

The product XIX was hydrogenated over a palladium-on-charcoal catalyst in acetic acid. The yield of 1,2,5,6-dibenzocycloheptadiene was 81%, m.p. 70–72°. Two recrystallizations from ethanol gave a melting point of 74–75° (lit.[22] 78–79°).

Bromination of XIX was carried out according to the procedure of Treibs and Klinkhammer.[22] The yield of 3,4-dibromo-1,2,5,6-dibenzocycloheptadiene was 44%. The melting point was between 155 and 163° (depending upon the rate of heating) with evolution of a gas and a range of about 3°. Treibs and Klinkhammer have reported a melting point of 160°.

Oxidation of XIX was performed in the same manner as that of VI using 57 mg. (0.30 mmole) of XIX and 177 mg. (1.11 mmoles) of potassium permanganate in 15 ml. of water. The reaction was run at 70° for 8 hours. The products were 27 mg. (52%) of anthraquinone (XIII) and 26 mg. (35%) of 3,3′-spirobiphthalide (XI).[11d]

Treatment of VII with Alkali in Ethylene Glycol. — The epoxide VII (750 mg., 3.4 mmoles) and 2.5 g. (62 mmoles) of sodium hydroxide were added to 20 ml. of ethylene glycol. The temperature of the reaction mixture was gradually increased until it reached the reflux point. The hydroxide and most of the epoxide went into solution. A white material slowly sublimed into the condenser. The reaction was continued overnight. The sublimate was rinsed out of the condenser and washed several times with water. The yield was 442 mg., m.p. 85–125°. Recrystallization from ethanol gave 300 mg. (46%) of a product which melted at 127–130°. Several additional recrystallizations from ethanol gave a melting point of 131–133°. The product gave no melting point depression with the 1,2,5,-6-dibenzocycloheptatriene (XIX) obtained in the previous experiment. The infrared spectra of the two products were also identical.

The alkaline reaction mixture was cooled to room temperature, diluted with 50 ml. of water and extracted with ether. Evaporation of the ether extract gave 102 mg. of a brown tar. The aqueous phase was acidified with hydrochloric acid. The solution turned cloudy and, after digestion for an hour at 50–60°, a white precipitate was formed. The yield of this product was 120 mg., m.p. 194–196°. Recrystallization from chloroform–carbon tetrachloride or from benzene–Skellysolve gave a melting point of 200–201°. The infrared spectrum showed a strong carbonyl absorption peak at 5.76 μ and a peak at 2.94 μ which probably is due to a hydroxyl group.

Anal. Found: C, 75.43, 76.60; H, 5.71, 5.70.

Treatment of VII with Alkali in 50% Ethanol.—One gram (4.54 mmoles) of the epoxide was dissolved in 30 ml. of a 1 N sodium hydroxide solution in 50% ethanol and heated under reflux for 85 hours. The reaction mixture was cooled and the light brown precipitate filtered. Fractional recrystallization from ethanol–water gave 378 mg. (45%) of 1,2,5,6-dibenzocycloheptatriene (XIX) and 60 mg. of starting material.

Dibenzobicyclo[2.2.2]octadiene-*cis*-2,3-diol (VIII).—A solution of 7.5 g. (3.6 mmoles) of dibenzobicyclo[2.2.2]-octatriene (I) in 300 ml. of acetone and 60 ml. of water was cooled to −11° in an ice–salt-bath. To the cold solution was added with vigorous stirring 3.8 g. (2.4 mmoles) of potassium permanganate at such a rate that the temperature of the reaction mixture was maintained at −10°. The precipitated manganese dioxide was filtered and the filtrate treated with a small amount of sodium bisulfite. The acetone was evaporated on a steam-bath. A yellow oily material separated. The aqueous solution was decanted, and the product allowed to dry in air. It gradually became crystalline. Recrystallization from benzene gave 1.6 g. (24%) of the diol, m.p. 195–200°. Further recrystallization from benzene raised the melting point to 201–202°. Chromatography of the mother liquors on alumina gave, after elution with benzene, 3.3 g. (44%) of unreacted starting material and, after elution with chloroform, 0.5 g. of anthraquinone.

The Diels–Alder addition product of vinylene carbonate and anthracene was prepared according to the method of Newman and Addor.[24] Hydrolysis of the carbonate gave a product which melted at 202° and gave no melting point depression with the diol obtained in the above oxidation.

The diacetate of VIII was prepared in the same manner as the diacetate of VI. The yield was 94%, m.p. 158–160°.

Anal. Calcd. for C₂₀H₁₈O₄: C, 74.52; H, 5.63. Found: C, 74.49; H, 5.55.

Permanganate Oxidation of VIII.—The procedure was the same as that of the oxidation of the diol VI using 238 mg. (1.00 mmole) of the diol VIII and 740 mg. (4.68 m-moles) of potassium permanganate. The reaction was carried out at room temperature for about 18 hours. The yield of crude anthraquinone, m.p. 250–260°, was 187 mg. (90%). Purification by chromatography on alumina gave 153 mg. (74%) of a product which melted at 278–282°. Recrystallization from chloroform raised the melting point to 283–285°. The product gave no melting point depression with an authentic sample of anthraquinone.

Treatment of VIII with Alkali in Ethylene Glycol.—The procedure was analogous to the reaction of the epoxide VII with alkali in ethylene glycol, using 250 mg. (1.05 m-moles) of VIII, 1.5 g. (37.5 mmoles) of sodium hydroxide and 10 ml. of ethylene glycol. The reaction time was 10 hours at reflux temperature. The product sublimed into the condenser. The crude yield was 151 mg. (80%), m.p. 99–109°. Three recrystallizations from ethanol gave a product which melted at 105–107° and gave no melting point depression with 9,10-dihydroanthracene. The infrared spectrum agreed with that of an authentic sample.

Treatment of 2-Ketodibenzobicyclo[2.2.2]octadiene (XXI) with Alkali in Ethylene Glycol.—The procedure was the same as described for the epoxide VII using 800 mg. (3.64 mmoles) of XXI,[8] 3 g. (75 mmoles) of sodium hydroxide and 20 ml. of ethylene glycol. The reaction time was 15 hours. This time, sublimation of a volatile product did not occur. The reaction mixture was diluted with 50 ml. of water, extracted with ether to remove some dark tar, and acidified. A white product precipitated, yield 810 mg. (93%), m.p. 168–171°. Recrystallization from methanol–water raised the melting point to 170–171°. May and Mosettig[25] have reported a melting point for 9,10-dihydroanthracene-9-acetic acid of 168.5–169°.

Treatment of the acid with dimethylamine and thionyl chloride gave a product which melted at 135.5–136.5°. The reported[25] melting point for 9,10-dihydroanthracene-9-N,N-dimethylacetamide is 134–135°.

Treatment of the Diol VI with Alkali.—The diol VI was treated with sodium hydroxide in both water and ethylene glycol exactly in the same manner as the epoxide VII. In both cases only the starting material and some dark tar could be isolated.

The Effect of Heat and Water upon VII.—One gram of the epoxide and 15 ml. of water were sealed in a Pyrex bomb-tube and heated for 12 hours at 140°. The reaction mixture was cooled to room temperature and the tube opened. The water was decanted and the semi-oily product dried in air. A crystalline material separated when the oil was triturated with a few drops of carbon tetrachloride.

(22) W. Treibs and H. J. Klinkhammer, *Ber.*, **84**, 671 (1951).

(23) T. W. Campbell, R. Gisig and H. Schmid, *Helv. Chim. Acta*, **36**, 1493 (1953).

(24) M. S. Newman and R. W. Addor, THIS JOURNAL, **77**, 3789 (1955).

(25) E. L. May and E. Mosettig, *ibid.*, **70**, 1077 (1948).

The product was filtered and washed with a small amount of Skellysolve B. The crude yield of 1,2,5,6-dibenzocycloheptatriene-7-carboxaldehyde (XXXII) was 400 mg. (40%), m.p. 90–104°. Several recrystallizations from Skellysolve B gave a product which melted at 112–114°. The infrared spectrum showed a strong peak at 5.78 μ which was absent in the spectrum of the starting material. The peak at 11.97 μ assigned to the epoxy group was no longer present. The infrared spectrum was identical with that of the product obtained in the attempted preparation of the cyclic acetal of the diol VI with p-nitrobenzaldehyde in the presence of p-toluenesulfonic acid. A mixed melting point of these two products showed no depression. The ultraviolet spectrum was very similar to that of 1,2,5,6-dibenzocycloheptatriene (XIX).[23]

Anal. Calcd. for $C_{16}H_{12}O$: C, 87.24; H, 5.54. Found: C, 87.28; H, 5.49.

The 2,4-dinitrophenylhydrazone melted at 221–223°.

Anal. Calcd. for $C_{22}H_{16}N_4O_4$: C, 65.99; H, 4.03. Found: C, 65.99; H, 4.24.

The experiment was repeated by heating the epoxide in ethylene glycol for 4 hours at reflux. Addition of water to the solution caused the precipitation of a material which melted at 170–185°. The infrared spectrum showed no peaks in the carbonyl region. Except for a few small deviations, probably due to impurities, the spectrum was identical with that of the acetal of the aldehyde XXXII and ethylene glycol.

The Acetal XXXIII of the Aldehyde XXXII and Ethylene Glycol.—One hundred milligrams (0.45 mmole) of XXXII was added to 10 ml. of ethylene glycol and heated under reflux overnight. The solution was cooled to room temperature and water was added until precipitation was complete. The crude yield was 80 mg. (67%), m.p. 170–190°. Recrystallization from ethanol gave 62 mg. (52%) of a product which melted at 191–193°.

Anal. Calcd. for $C_{18}H_{16}O_2$: C, 81.79; H, 6.10. Found: C, 81.65; H, 6.14.

Treatment of XXXII with Alkali in Ethylene Glycol.—The procedure was exactly the same as that of the treatment of the epoxide VII with alkali. One hundred milligrams (0.45 mmole) of the aldehyde, 0.3 g. (7.5 mmoles) of sodium hydroxide and 3 ml. of ethylene glycol were used. The solution was heated under reflux for 10 hours. The crude yields were 60 mg. (69%) of XIX and 12 mg. of the acid XX.

1,2,5,6-Dibenzocycloheptatriene-7-methanol (XXXIV).—A solution of 92 mg. (0.42 mmole) of XXXII in 10 ml. of anhydrous ether was added drop-wise to a slurry of 0.20 g. of lithium aluminum hydride in 10 ml. of ether. The mixture was heated under reflux for 3 hours. After the usual work-up, including ether extraction, there was obtained 90 mg. (97%) of crude product, m.p. 78–85°. Recrystallization from Skellysolve B gave 68 mg. (73%) of pure XXXIV, m.p. 86–87°. The infrared spectrum showed a strong peak at 3.20 μ and no peaks in the carbonyl region. The ultraviolet spectrum was almost superimposable upon that of the starting aldehyde.

Anal. Calcd. for $C_{16}H_{14}O$: C, 86.45; H, 6.35. Found: C, 86.66; H, 6.52.

The p-Bromobenzenesulfonate XXXV of XXXIV.—A solution of 72 mg. (0.32 mmole) of XXXIV in 2 ml. of dry pyridine with 85 mg. (0.33 mmole) of p-bromobenzenesulfonyl chloride gave a crude yield of XXXV of 92 mg. (64%), m.p. 135–155°. Addition of more water to the aqueous mother liquor gave 10 mg. (14%) of unreacted starting material. Recrystallization from ethanol gave 62 mg. (43%) of XXXV, m.p. 163–166°. Additional recrystallization from ethanol raised the melting point to 168°.

Anal. Calcd. for $C_{22}H_{17}BrO_3S$: C, 59.87; H, 3.88. Found: C, 59.92; H, 3.81.

7-Methylene-1,2,5,6-dibenzocycloheptatriene (XXXVI).—Sixty-two milligrams (0.14 mmole) of XXXV was heated under reflux with 10 ml. of 1 M ethanolic sodium hydroxide. The p-bromobenzenesulfonate gradually went into solution and was completely dissolved after about 5 hours. The reaction was continued overnight. The solution was then diluted with water. A white precipitate was formed. The crude yield was 29 mg. (83%), m.p. 111–117°. Re-

crystallization from ethanol gave 16 mg. of XXXVI, m.p. 118–120°. The product showed no melting point depression with 7-methylene-1,2,5,6-cycloheptatriene.[20] Also the infrared spectrum was superimposable on that of the authentic sample. The ultraviolet spectrum was in good agreement with the spectrum published by Bergmann and co-workers.[26]

1,2,5,6-Dibenzocycloheptatriene-7-carboxylic Acid.—To a solution of 100 mg. (0.45 mmole) of the aldehyde XXXII and 200 mg. of silver nitrate in 10 ml. of aqueous ethanol at 70° was added 100 mg. of sodium hydroxide. The solution was stirred for 5 minutes at 70°. The mixture was allowed to cool to room temperature, diluted with an equal volume of water and filtered. The filtrate was acidified with nitric acid, the major portion of the ethanol was allowed to evaporate at 60°, and the solution was allowed to stand at this temperature for 2 hours. A white precipitate slowly formed. The crude yield of this material was 40 mg. (37%), m.p. 190–215°. The product was dissolved in 1 M sodium hydroxide, filtered, and reprecipitated with nitric acid, yielding 30 mg. of material, m.p. 215–225°. Three successive recrystallizations from chloroform–Skellysolve B raised the melting point to 234–237°. The infrared spectrum showed a carbonyl absorption peak at 5.86 μ. The ultraviolet spectrum closely resembled that of the starting aldehyde.

Anal. Calcd. for $C_{16}H_{12}O_2$: C, 81.33; H, 5.12. Found: C, 81.42; H, 5.27.

When the dark precipitate of silver and silver oxide was extracted with chloroform, 52 mg. of an alkali-insoluble oil was obtained. If the procedure was modified by first dissolving the aldehyde in ethanolic sodium hydroxide and then adding the silver nitrate, only a trace of the above acid was obtained. The product was instead a neutral carbonyl compound which was unstable to recrystallization from chloroform–carbon tetrachloride. Judging from its ultraviolet spectrum this material is not a 1,2,5,6-dibenzocycloheptatriene derivative.

Alumina-catalyzed Rearrangement of the Epoxide VII.—A solution of 600 mg. (2.73 mmoles) of the epoxide VII in carbon tetrachloride was passed through a column packed with 65 g. of Fisher alumina. A yellow color developed slowly on the upper part of the column. The column was eluted with carbon tetrachloride until evaporation of the eluate left no residue. The weight of the material recovered in this manner was 32 mg., m.p. 155–160°. A mixed melting point with the starting material gave no depression.

The column was then eluted with a 10% solution of ethyl acetate in carbon tetrachloride. Twenty 15–20 ml. fractions were collected. Evaporation of the solvent gave a total of 286 mg. of residue. The first eleven fractions consisted of a white or pale yellow crystalline material; the melting points ranged from 95 to 108°. The later fractions became gradually more yellow and somewhat oily. When the amount of residue per fraction decreased to about 10 mg., the eluent was changed to pure ethyl acetate. An additional sixteen fractions were collected which gave 206 mg. of a yellow, semi-oily residue. The fractions were dissolved in a small amount of chloroform and recombined as follows: (a) 1–11, 124 mg.; (b) 12–20, 162 mg.; (c) 21–32, 180 mg. The chloroform was evaporated and the product was purified by recrystallization from Skellysolve B and treatment with activated charcoal. Fractions b and c required several recrystallizations before the mixed melting points of the crystalline materials with each other showed no depression. The combined yield of purified product was 315 mg. (52.5%), m.p. 109–111°. The infrared spectrum was superimposable upon that of 1,2,5,6-dibenzocycloheptatriene-7-carboxaldehyde.

It was found that the yields were decreased if too much alumina was used or if the material was left on the column overnight. When an attempt was made to shorten the procedure by omitting the washing of the column with carbon tetrachloride, it was found that a considerable amount of the epoxide was recovered unreacted. The optimum yield of aldehyde was obtained if the solvents were passed through the column at a rate such that the total reaction time was 8 to 10 hours.

(26) E. D. Bergmann, E. Fischer, D. Ginsburg, Y. Hirshberg, D. Lavie, M. Mayot, A. Pullman and B. Pullman, *Bull. soc. chim.*, 18, 681 (1951).