absorption at 3.28 μ, 6.37 μ and 13.91 μ associated with C-9–C-10 unsaturation and at 7.23 μ and 7.33 μ due to the *gem*-dimethyl substituent at C-2.

Anal. Calcd. for $C_{12}H_{18}$: C, 88.82; H, 11.18. Found: C, 88.93; H, 11.12.

A phenyl azide adduct formed which did not give a sharp melting point, although it crystallized as distinctive colorless crystals from ethanol, m.p. 166–169°, mixed melting point with the *endo* isomer XIII, m.p. 137–159°.

Anal. Calcd. for $C_{18}H_{23}N_3$: C, 76.83; H, 8.24. Found: C, 77.11; H, 8.05.

A nitroso chloride dimer was prepared by the usual method and recrystallized from toluene, m.p. 163–165°, mixed melting point with the *endo* isomer, m.p. 155–159°.

Anal. Calcd. for $(C_{12}H_{18}ClNO)_2$: C, 63.29; H, 7.97. Found: C, 63.56; H, 7.60.

Reaction of the 2,2-dimethyl-1,2-dihydrodicyclopentadienes XXIII *and XXVI with phosphoric acid.* A small quantity of each isomer was distilled from 85% phosphoric acid at slightly reduced pressure. At first a small amount of hydrocarbon, probably starting material, appeared to distill with steam. The entire product was collected in each case and taken up in ether. The ether solutions were dried over magnesium sulfate and the ether was evaporated. In one run 1.7 g. of the *exo* isomer was distilled slowly from 2 ml. of phosphoric acid. The crude product after workup was distilled yielding a colorless liquid, b.p. 104–106° (30 mm.). During the reaction with phosphoric acid, the mixture being heated turned a greenish color and upon further heating this color was dispelled leaving a pale tan which darkened toward the end of the distillation. A very small sample (4–10 drops) of each starting material, the isomeric dimethyl compounds XXIII and XXVI, and of each phosphoric acid distillation product was reduced separately in 100 ml. of absolute ethanol using Adams' catalyst and hydrogen at ambient temperature and pressure. Two hours was allowed for each reduction and no attempt was made to measure hydrogen up-take. Each solution was filtered and concentrated. Using gas chromatography, samples of saturated and unsaturated starting materials and saturated and unsaturated reaction products, at 102° and a helium flow of about 70 cc./min. through a 1 m. × 6 mm. column of 20% Union Carbide Polypropylene Glycol-1025 on Chromosorb W (30-60 mesh). The retention times and approximate estimates of the relative proportions of the peaks observed for each sample are given below.

RETENTION TIMES

	Unsaturated			Saturated		
2,2-Dimethyl-*endo*-	9.4 min.			10.1 min. trace	12.1 min.	
Distilled from H_3PO_4	9.6 75%	12.0 6%	17.0 19%	10.2 5%	12.3 70%	17.3 25%
2,2-Dimethyl-*exo*	9.0			10.5	12.0 trace	
Distilled from H_3PO_4	9.2 30%	12.0 11%	17.2 59%	10.3 17%	12.2 15%	17.3 67%

The product from the 2,2-dimethyl-*exo* hydrocarbon which had been once distilled was estimated to be about 85% pure. A second distillation resulted in scarcely measurable purification and no change in boiling range. The product, dissolved in acetone, decolorized 3% aqueous permanganate. A sample of the mixed product, n_D^{25} 1.4975, was analyzed for carbon and hydrogen.

Anal. Calcd. for $C_{12}H_{18}$: C, 88.82; H, 11.18. Found: C, 88.61; H, 11.22.

Infrared analysis of this sample showed that all of the peaks associated with C-9-C-10 unsaturation in the starting material had disappeared. No absorption characteristic of hydrogen attached to an unsaturated carbon was observed, but a weak band at 5.97 μ suggests that the product contains a highly substituted unstrained double bond. The *gem*-dimethyl absorptions observed in the spectrum of the starting material are replaced by a C-methyl peak at 7.26 μ.

Acknowledgment. Support of this research by a grant from the Petroleum Research Fund administered by the American Chemical Society and, in part by a Research Grant (CY-4298) of the National Institutes of Health, U. S. Public Health Service, is gratefully acknowledged. The authors are indebted to Dr. Roger J. Philippe for assistance in the interpretation of several infrared traces.

DURHAM, N. C.

[CONTRIBUTION FROM THE UNIVERSITY OF GLASGOW]

Some Studies on Seven-Membered Ring Compounds

G. L. BUCHANAN AND DINBALA B. JHAVERI[1]

Received April 10, 1961

Acid-catalyzed rearrangement of the epoxides (IVa and IVb) of methyleneanthrone and benzalanthrone produces no ring expansion, but the products are identified as 10-hydroxymethyleneanthrone (VIa) and 10-formyl-10-phenylanthrone (IXa) respectively. Similar treatment of the epoxide (V) of 2-benzal-1-tetralone leads to 2-phenyl-4,5-benzocycloheptene-1,3-dione (X). A new explanation is offered for the alkali solubility of the 4,5-dihydroxy-2,3,6,7-dibenzocycloheptadienones XIII.

Pursuing our interest in tropones[2] and their hydroxy derivatives[3] we have been examining the ring expansion process which allowed Cook[4] to prepare the first known γ-hydroxytropone (I) by the action of moist silver oxide on benzalanthrone dibromide (II). Since this reaction must involve a carbonium ion intermediate, it was of interest to explore the acid-catalyzed opening of certain epox-

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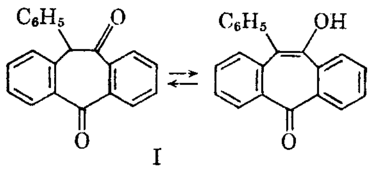
(1) Present address: Department of Pharmacology, Gordhandas Sunderdas Medical College, Parel, Bombay 18, India.

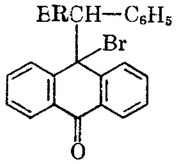
(2) G. L. Buchanan and D. R. Lockhart, *J. Chem. Soc.*, 3586 (1959).

(3) G. L. Buchanan, *J. Chem. Soc.*, 1060 (1954).

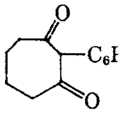
(4) J. W. Cook, *J. Chem. Soc.*, 2160 (1926); 58 (1928).



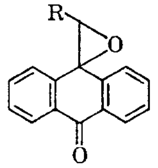
I



II



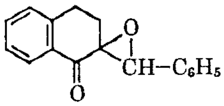
III



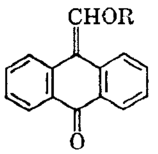
IVa. R = H
IVb. R = C_6H_5

ides as a potential route to seven-membered ring compounds,[5] and we have chosen to examine the epoxides IV and V.

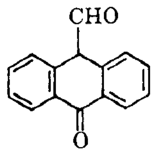
When methyleneanthrone epoxide (IVa) is treated with boron trifluoride, the product is 10-hydroxymethyleneanthrone (VIa).[6] This substance gives a monobenzoate[7] and a mono-2,4-dinitrophenylhydrazone, dissolves with effervescence in sodium carbonate solution and, in the presence of alkali, is oxidized by air to anthraquinone and formic acid.[8] Its infrared spectrum (Nujol) shows a very broad hydroxyl band (*ca.* 2800–2500 cm.$^{-1}$) with no carbonyl absorption above *ca.* 1600 cm.$^{-1}$ This indicates strong hydrogen bonding,[9] and on the above evidence we assign it structure VIa. In a more exhaustive examination, Rigaudy and Nedelec[10] show that although this substance, *in the solid state*, has structure VIa, *in solution*, it behaves as an equilibrium mixture of the tautomers VIa, VII and VIII.



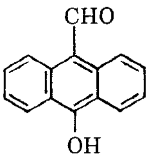
V



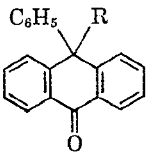
VIa. R = H
VIb. R = C_6H_5CO



VII



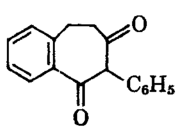
VIII



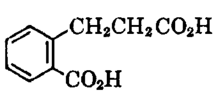
IXa. R = CHO
IXb. R = H
IXc. R = OH

Under similar conditions, benzalanthrone epoxide might be expected to yield Cook's dione I, the ketoaldehyde IXa or 10-benzoylanthrone. In fact the product of this reaction is IXa. It displays the reducing properties of an aldehyde and its infrared spectrum (Nujol) shows bands at 1660 cm.$^{-1}$ and at 2690 and 1725 cm.$^{-1}$ consistent with a ketoaldehyde of this structure. Although the reaction product is neutral, and unaffected by cold alkali, it dissolves in hot alkali, giving an orange-red solution, which on longer heating, slowly loses its color, depositing 10-hydroxy-10-phenylanthrone (IXc). The alkali-soluble intermediate is presumably 10-phenylanthrone (IXb), which undergoes aerial oxidation[11] to IXc. Under alkaline conditions it was not practicable to isolate the intermediate, but when the deformylation was effected by dilute acid, the product was identified as 10-phenylanthrone (IXb). Ring expansion of these anthrone derivatives could only take place *via* exocyclic carbonium ion intermediates and it is not surprising that in both cases the more stable C_{10} carbonium ion is preferred.

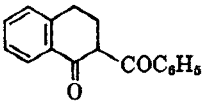
In contrast to the above, the epoxide (V) of 2-benzal-1-tetralone is smoothly isomerized by boron trifluoride or by sulfuric acid to the seven-membered β-diketone X.



X



XI



XII

The infrared spectrum of the product shows two carbonyl bands at 1715 and 1673 cm.$^{-1}$ (chloroform). It dissolves in, and is recoverable from, dilute alkali; it reacts with diazomethane forming a monomethyl ether; and it yields a mixture of benzoic acid and 2-(*o*-carboxyphenyl)propionic acid (XI) on oxidation. These results permit only two formulations of the product, namely X and XII, and the latter was eliminated by comparison

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[5] H. O. House and R. L. Wasson [*J. Am. Chem. Soc.*, **78**, 4398 (1956)] have prepared the β-diketone III by rearrangement of benzalcyclohexanone epoxide, and E. J. Corey *et al.*, [*J. Am. Chem. Soc.*, **83**, 1251 (1961)] have utilized an essentially similar ring expansion in their longifoline synthesis; however, the scope of the reaction has not been fully explored.

[6] Due to unavoidable delay in publishing our work, this observation has recently been anticipated by J. Rigaudy and L. Nedelec.[10]

[7] The infrared spectrum of this benzoate in Nujol shows bands at 1734 and 1660 cm.$^{-1}$, consistent with structure VIb.

[8] The latter was isolated as its sodium salt and identified as such by comparison of its infrared spectrum with that of authentic material.

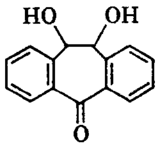
[9] Presumably intermolecular, but because of its insolubility we were unable to run a solution spectrum.

[10] J. Rigaudy and L. Nedelec, *Bull. soc. chim. France*, 400 (1960); 1204 (1960).

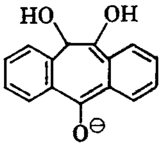
[11] A. Baeyer, [*Ann.*, **202**, 58 (1880)] has found that 10-phenylanthranol is readily oxidized to IXc, and in our experience the over-all conversion of IXa to IXc could be expedited by the addition of permanganate.

with authentic 2-benzoyl-1-tetralone.[12] The structure of the rearrangement product is therefore beyond doubt.[13]

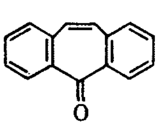
While this work was in progress, some incidental attempts were made to dehydrate the diol XIII to a hydroxytropone. These were unsuccessful, and will not be described here, since an identical investigation has recently been described in sufficient detail by other workers.[10] However, we were interested to observe that this diol is soluble in dilute alkali, and can be recovered on acidification.



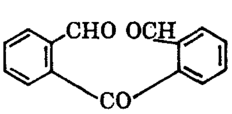
XIIIa. = *cis* series
b. = *trans* series



XIV



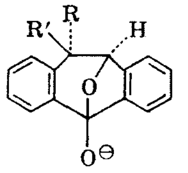
XV



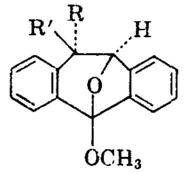
XVI

Treibs and Klinkhammer,[14] who first described this diol suggested that the anion had the structure XIV. This explanation is incompatible with our observation that the alkaline solution is not only colorless, but shows no long wave length absorption in the ultraviolet.[15] The diol XIII, prepared as described, is in fact the *cis* isomer XIIIa since it can also be obtained by the action of osmium tetroxide on the olefin XV.[6] The formation of the *cis*-glycol from the *trans*-dibromide of XV,[16] is thus a further example of Winstein's neighboring group participation effect,[17] and as expected, the *trans*-diol (XIIIb) is obtained from the same reactants when strictly anhydrous conditions are observed. Both diols have been characterized as diacetates and as acetonides, and both yield the same dialdehyde XVI, on periodate fission.

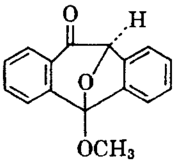
Like its *cis* epimer, the *trans*-diol dissolves in dilute alkali, and is quantitatively recovered, unepimerized, on acidification. When shaken with dimethyl sulfate and alkali, each gives rise to an individual methyl ether[18] whose infrared absorption spectrum (carbon tetrachloride) shows no bands in the 1700–1635-cm.$^{-1}$ region. These observations can only be accommodated by the bridged ring structures XVII a and b and XVIII a and b which represent the anions and methyl ethers of the *cis*- and *trans*-diols, respectively. On the other hand, both diols (XIII) show carbonyl absorption in the infrared, as 1643 cm.$^{-1}$ in Nujol, and at 1660 cm.$^{-1}$ in carbon tetrachloride. They are thus definitely represented by structures XIII a and b.



XVIIa. R = H, R' = OH
b. R = OH, R' = H

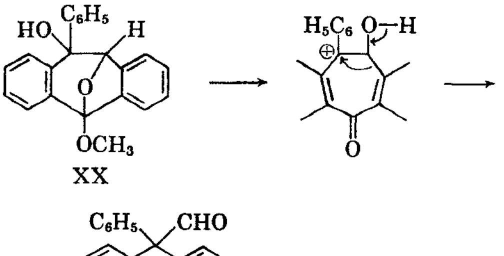


XVIIIa. R = H, R' = OH
b. R = OH, R' = H



XIX

On oxidation, both methyl ethers yield the same ketone (XIX). The latter reacts with phenyllithium, and since the product (XX) seemed to offer a route to Cook's diketone (I), some attempts were made to open the ketal under mild conditions. These yielded either starting material or 10-phenylanthrone (IXb) according to their degree of severity, and a plausible rationalization of this degradation is shown above.



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[12] We are indebted to Professor C. R. Hauser of Duke University, Durham, N. C., for a sample of 2-benzoyl-1-tetralone [C. R. Hauser, B. I. Ringler, F. W. Swamer, and D. F. Thompson, *J. Am. Chem. Soc.*, 69, 2650 (1947)].

[13] The infrared data indicates that X is not enolized, and in this respect it resembles 2-phenylcycloheptan-1,3-dione[6] III. Nevertheless, the reactions described here demonstrate that it *can* enolize and the ultraviolet spectrum supports this: $\lambda_{\max}$ (ethanol) 300 mμ (ϵ 5075); $\lambda_{\max\,(\text{ethanol})}^{(\text{alkaline})}$ 350 mμ (ϵ 10,000). In the absence of similar measurements on III, no useful comparison can be drawn, but it is pertinent to note that on models, enolization of III produces an unfavorable interaction between hydrogens on C_4 and C_7, which is not apparent in the enol form of X.

[14] W. Treibs and H. J. Klinkhammer, *Ber.*, 84, 671 (1951).

[15] In ethanol, the diols (XIII) shows $\lambda_{\max}$ 269 mμ (ϵ 9300): in 3*N* sodium hydroxide, there is a plateau at 260–270 mμ (ϵ 823) between the end absorption and the transparent long wave length (350 mμ) region.

[16] By the action of silver acetate in acetic acid, followed by hydrolysis.[14]

[17] See M. S. Newman, *Steric Effects in Organic Chemistry*, John Wiley and Sons Inc., New York, N. Y., 1956, p. 290 *et seq.*

[18] Their ultraviolet absorption characteristics [$\lambda_{\max}$ 268 mμ (ϵ 724)] show a striking resemblance to that of 1,2,4,5-dibenzocycloheptadiene [$\lambda_{\max}$ 266 mμ (ϵ 709)], and to those quoted above[15] for the diols XIII in alkaline solution.

EXPERIMENTAL[19]

Methyleneanthrone epoxide (IVa). A solution of 1 g. of methyleneanthrone[20] in 10 ml. of ethanol was warmed on the steam bath for 2 or 3 min., with 2 ml. of 10% aqueous sodium hydroxide and 2 ml. of 15% hydrogen peroxide. The red solution was then set aside, and the product allowed to crystallize: yield 0.7 g. (63%). It crystallized from ethanol in needles, m.p. 128–129°.

Anal. Calcd. for $C_{15}H_{10}O_2$: C, 81.1; H, 4.5. Found: C, 81.1; H, 4.7.

10-Hydroxymethyleneanthrone (VIa). A solution of 1 g. of methyleneanthrone epoxide (IVa) in 15 ml. of benzene was treated with 1 ml. of boron trifluoride etherate, and after a few minutes at room temperature, the red precipitate which formed was filtered off, dissolved in dilute alkali, filtered, and reprecipitated by acid. The product was purified by sublimation at 110–160° under 3×10^{-4} mm., m.p. 185–187°.[21]

Anal. Calcd. for $C_{15}H_{10}O_2$: C, 81.1; H, 4.5. Found: C, 81.4; H, 4.6.

The 2,4-dinitrophenylhydrazone crystallized from acetic acid in dark green needles, m.p. > 300°.

Anal. Calcd. for $C_{21}H_{14}N_4O_5$: C, 62.7; H, 3.5; N, 13.9. Found: C, 62.3; H, 3.8; N, 14.0.

The benzoate, formed by the Schotten-Baumann method was crystallized from ethanol in colorless needles, m.p. 165–166°.

Anal. Calcd. for $C_{22}H_{14}O_3$: C, 81.0; H, 4.3. Found: C, 80.7; H, 4.3.

Oxidation of IVa. Air was bubbled thru a solution of 1 g. of 10-hydroxymethyleneanthrone in aqueous sodium hydroxide solution. After 50 hr., the crude anthraquinone so precipitated was filtered off and purified by crystallization from benzene, m.p. 278–280°. A mixed melting point with anthraquinone showed no depression.

The filtrate was acidified with sulfuric acid, distilled, and the distillate titrated to neutral point with sodium hydroxide. On evaporation, this neutral solution yielded a white powder whose infrared spectrum (potassium chloride disk) was identical in all significant respects with that of authentic sodium formate.

10-Formyl-10-phenylanthrone (IXa). A solution of 2.98 g. of benzalanthrone epoxide[22] in 30 ml. of benzene was treated with 2.15 ml. of boron trifluoride etherate and left at room temperature for 10 min. The red solution was then diluted with ether, washed with water until neutral, dried over anhydrous magnesium sulfate, and concentrated under vacuum. The yellow crystalline solid which separated was recrystallized from ethanol, m.p. 130–131°: yield 1.4 g. (47%).

Anal. Calcd. for $C_{21}H_{14}O_2$: C, 84.5: H, 4.7. Found: C, 84.8; H, 4.8.

The product reduces ammoniacal silver nitrate solution and Fehling's solution and rapidly decolorizes alkaline potassium permanganate solution. A 50-mg. sample was dissolved in 2 ml. of acetic acid, treated with 2 drops of 6*N* sulfuric acid, heated to the boiling point, and allowed to stand for 1 hr. The solution was diluted with water until crystallization commenced, and the product was recrystallized from ethanol, m.p. 139–140°. Its infrared spectrum was identical with that of authentic 10-phenylanthrone.[23]

When a sample of 10-formyl-10-phenylanthrone was warmed with dilute sodium hydroxide solution, it rapidly dissolved forming a red solution. On further warming (1 hr. at 100°) the color faded and a precipitate was formed. This product was filtered off, washed with water, dried, and crystallized from benzene–ether petroleum (b.p. 60–80°), m.p. 214–215°. The melting point was undepressed on admixture with an authentic sample of 10-hydroxy-10-phenylanthrone,[24] and the infrared spectra of the two samples were superposable.

Anal. Calcd. for $C_{20}H_{14}O_2$: C, 83.9; H, 4.9. Found: C, 84.2; H, 4.9.

2-Benzal-1-tetralone epoxide (V). A solution of 6 g. of 2-benzal-1-tetralone[25] in 60 ml. of ethanol was treated with 12 ml. of 8% aqueous sodium hydroxide solution and 12 ml. of 15% hydrogen peroxide. The reaction mixture was warmed briefly on the steam bath and allowed to stand at room temperature for 16 hr. It was then diluted with an excess of water and thoroughly extracted with ether. The combined ethereal extracts were washed with water, dried, and concentrated *in vacuo*, yielding the epoxide (5.1 g.; 78%) which crystallized from ethanol in cubes, m.p. 107°.[26] ν_{C-H} (carbon tetrachloride) 1695 cm.$^{-1}$

Anal. Calcd. for $C_{17}H_{14}O_2$; C, 81.6; H, 5.6. Found: C, 81.9; H, 5.6.

2-Phenyl-4,5-benzocyclohepten-1,3-dione (X). (a) To 10 ml. of ice cold concd. sulfuric acid was added 1 g. of 2-benzal-1-tetralone epoxide (V), and the mixture was swirled for a few minutes until the solid dissolved. The resulting red solution was allowed to stand for 1 hr. at 0° and then poured onto crushed ice. The precipitated dione was washed with water, dried in air, and crystallized from petroleum ether (b.p. 40–60°), m.p. 86–87°; yield 0.9 g. (90%).

Anal. Calcd. for $C_{17}H_{14}O_2$: C, 81.6; H, 5.65. Found: C, 81.8; H, 5.85.

(b) A solution of 0.3 g. of the epoxide (V) in 7 ml. of dry benzene was treated with 6 ml. of boron trifluoride etherate, and allowed to stand for 15 min. at room temperature. The solution was then diluted with ether, washed with water, and dried over magnesium sulfate. The solvent was removed *in vacuo* leaving a colorless oil, which solidified on titration with petroleum ether (b.p. 40–60°). The product recrystallized from the same solvent in needles, m.p. 85–86° and was identical in all respects with the sample prepared above; yield 0.1 g. (33%).

Methyl ether of X. An excess of diazomethane in ether was added to 1 g. of the dione X, dissolved in ether, and the solution was set aside for 2 days. The solution was then washed with dilute sodium hydroxide solution and finally with water, and dried. Removal of the solvent furnished the crude ether which crystallized from methanol in plates, m.p. 84–86° (depressed to 60–65° on admixture with the dione X); yield 0.5 g. (48%).

Anal. Calcd. for $C_{18}H_{16}O_2$: C, 81.8; H, 6.1. Found: C, 82.0; H, 6.1.

$\nu_{C=O}$ (Nujol) 1660 cm.$^{-1}$ λ_{max} (ethanol 290 mμ (ϵ 13,000)

Oxidative cleavage of the dione (X). A solution of 0.1 g. of the diketone (X) in aqueous sodium hydroxide was treated with 2 ml. of 30% hydrogen peroxide, and allowed to stand at room temperature for 17 hr. The solution was then acidified, extracted with ether, and the ethereal extract was washed with water, dried, and evaporated. The solid residue was sublimed, and thus separated into volatile and involatile fractions. The former (10 mg.) had a m.p. of 120–121° and was identical (mixed melting point) with benzoic acid. The

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(19) Melting points are uncorrected. Microanalyses were carried out in this department by Mr. J. M. L. Cameron and his staff.

(20) E. Clar, *Ber.*, **69**, 1686 (1936).

(21) Rigaudy and Nedelec[10] quote a m.p. of 206–208°.

(22) E. Weitz, *Ann.*, **418**, 34 (1919).

(23) E. Barnett and J. W. Cook, *J. Chem. Soc.*, **123**, 2631 (1923).

(24) A. Baeyer, *Ann.*, **202**, 58 (1880).

(25) W. S. Rapson and R. G. Shuttleworth, *J. Chem. Soc.*, 636 (1940).

(26) A. Hassner, N. H. Cromwell, and S. J. Davis, [*J. Am. Chem. Soc.*, **79**, 230 (1957)] report that this compound has a m.p. of 77–77.5°. Our material shows no change at this temperature and is presumably a stereoisomer. It is clearly different from 2-benzal-1-tetralone (which also melts at 107°) since a mixed melting point is depressed to *ca.* 80°, and the infrared spectra are nonidentical. Isomeric epoxides have been reported by E. Weitz and A. Scheffer [*Ber.*, **54**, 2327 (1921)].

latter crystallized from water in needles (40 mg.) of m.p. 168°, and was shown to be 2-(*o*-carboxyphenyl)propionic acid (XI) by comparison (infrared and mixed melting point) with authentic material prepared from 1,2-dihydronaphthalene.[27]

Anal. Calcd. for $C_{10}H_{10}O_4$: C, 61.85; H, 5.2. Found: C, 62.1; H, 5.0.

cis - 4,5 - Dihydroxy - 2,3,6,7 - dibenzocycloheptadiene - 1 - one (XIIIa). A solution of 0.3 g. of 2,3,6,7-dibenzocycloheptatrien-1-one (XV) in 2.5 ml. of dry benzene was treated with 0.38 g. of osmium tetroxide in 2 ml. of dry benzene containing 0.22 ml. of pyridine. The reaction mixture was allowed to stand at room temperature for 6 days, and the black precipitate which formed was then suspended in 32 ml. of ethanol, and treated with 7 g. of sodium sulfite in 16 ml. of water. This mixture was boiled under reflux for 30 min., and filtered. The filtrate was concentrated and yielded on cooling the *cis*-diol which crystallized from benzene in needles, m.p. 130–131°. This material was identical in all respects with that prepared by the literature route.[14]

Diacetate of cis-diol (XIIIa). A solution of 0.2 g. of the *cis* diol in 3.7 ml., of acetic anhydride was refluxed for 3 hr., then cooled, and flooded with water. The precipitated diacetate was crystallized from ethanol in needles, m.p. 156; yield 0.19 g. (73%).

Anal. Calcd. for $C_{19}H_{16}O_5$: C, 70.4; H, 5.0. Found: C, 70.4; H, 5.5.

Acetonide of cis-diol (XIIIa). A mixture of 0.44 g., of the *cis*-diol, 8 ml. of acetone and 0.32 ml. of concd. sulfuric acid was shaken for 6 hr. at room temperature. Solid sodium carbonate was then added to neutralize the mineral acid, the mixture was filtered, and the filtrate evaporated to dryness *in vacuo*. The acetonide crystallized from petroleum ether (b.p. 60–80°), in plates, m.p. 152–153°; yield 0.2 g. (23%).

Anal. Calcd. for $C_{18}H_{16}O_3$: C, 77.1; H, 5.75. Found: C, 77.45; H, 5.85.

trans-4,5-Diacetoxy-2,3,6,7-dibenzocycloheptadien-1-one. A suspension of 1 g. of the dibromide[14] of XV in 40 ml. of anhydrous acetic acid[28] was stirred at 60–65° for 4 hr. with 0.1 g. of dry silver acetate. The cooled reaction mixture was filtered and the filtrate, on dilution with water, afforded the *trans*-diacetate which crystallized from ethanol in long needles, m.p. 196°; yield 0.7 g. (77%).

Anal. Calcd. for $C_{19}H_{16}O_5$: C, 70.4; H, 5.0. Found: C, 70.4; H, 5.0.

trans-4,5-Dihydroxy-2,3,6,7-dibenzocycloheptadiene-1-one (XIIIb). A solution of 1 g. of the *trans*-diacetate and 1.5 g. of potassium hydroxide in 100 ml. of methanol was boiled under reflux for 15 min. Thereafter the solution was taken to dryness under reduced pressure, and the solid residue dissolved in water. This solution was acidified with mineral acid, extracted with ether and the ethereal extract washed with water, dried and evaporated, yielding the *trans*-diol (XIIIb) (0.50 g. 90%) which crystallized from benzene-petroleum ether (b.p. 60–80°) in needles, m.p. 155–156°.

Anal. Calcd. for $C_{15}H_{12}O_3$: C, 75.0; H, 5.0. Found: C, 75.1; H, 5.2.

The acetonide of the *trans*-diol was prepared by the method already described for the *cis* isomer. It crystallized from ethanol in needles, m.p. 99–100°.

Anal. Calcd. for $C_{18}H_{16}O_3$: C, 77.1; H, 5.75. Found: C, 77.85; H, 6.0.

Periodate fission of diols to the keto dialdehyde XVI. A solution of 0.24 g. of sodium metaperiodate in 4.5 ml. of water was added to 0.11 g. of diol dissolved in 4 ml. of ethanol, warmed briefly to give a clear solution and then left overnight. The reaction mixture was then filtered, and the filtrate was concentrated *in vacuo* to a gum (50 mg., 50%) which crystallized from petroleum ether (b.p. 60–80°) in needles, m.p. 118–119°.

Anal. Calcd. for $C_{15}H_{10}O_3$: C, 75.6; H, 4.2. Found: C, 75.8; H, 4.4.

Both isomers yielded identical products, which showed no depression in a mixed melting point determination, and had superposable infrared spectra. $\nu_{C=O}$ 1680 and 1660 cm.$^{-1}$. (Nujol).

Methyl ethers (XVIII). A mixture of 1.2 ml. of dimethyl sulfate and 0.12 g. of diol dissolved in 4.5 ml. of 10% aqueous sodium hydroxide was stirred vigorously for 30 min. and then extracted with ether. The ether solution was washed with water, dried, and evaporated under reduced pressure. The solid product was crystallized from petroleum ether (b.p. 60–80°). The methyl ether obtained from the *cis*-diol had a m.p. of 134°.

Anal. Calcd. for $C_{16}H_{14}O_3$: 75.6; H, 5.55. Found: C, 75.8; H, 5.9.

The corresponding derivative of the *trans*-diol had a m.p. of 214–215°.

Anal. Calcd. for $C_{16}H_{14}O_3$: C, 75.6; H, 5.55. Found: C, 75.15; H, 5.8.

Oxidation of methyl ethers to XIX. A solution of 0.56 g. of the *cis*-methyl ether (XVIIIa) in 5 ml. of dry pyridine was treated with 0.63 g. of chromium trioxide in 6 ml. of dry pyridine, and the mixture allowed to stand at room temperature for 17 hr. The reaction mixture was then poured into ice water and extracted with ether. The ethereal extract was thoroughly washed with water, dried and concentrated *in vacuo,* affording 0.4 g., (70%) of the solid ketone (XIX) which was crystallized from alcohol in cubes, m.p. 136–137°.

Anal. Calcd. for $C_{16}H_{12}O_3$: C, 76.2; H, 4.8. Found: C, 76.2; H, 4.7.

The infrared spectrum (carbon tetrachloride) showed one C=O maximum at 1713 cm.$^{-1}$ and no OH absorption.

When the corresponding *trans* compound (XVIIIb) was oxidized by the same procedure, the product was identical with that described above.

4-Phenyl-4-hydroxy-1-methoxy1, 5-oxide-2,3,6,7-dibenzocycloheptadiene (XX). A stirred solution of 0.18 g. of the ketone XIX in 10 ml. of dry ether was treated, under nitrogen, with an ethereal solution containing 0.11 g. of phenyllithium,[29] and then heated to reflux for 30 min. The cooled reaction mixture was poured onto crushed ice, and extracted with ether. The combined ether extracts were washed with water, dried, and solvent removed under reduced pressure. The solid product crystallized from petroleum ether (b.p. 60–80°) to yield the phenylcarbinol (0.19 g.; 82%) in needles, m.p. 177–178°.

Anal. Calcd. for $C_{22}H_{18}O_3$: C, 80.0; H, 5.5. Found: C, 79.8; H, 5.4.

The infrared spectrum (carbon tetrachloride) showed a maximum at 3540 cm.$^{-1}$, but no carbonyl band.

Attempted hydrolysis of XX. A solution of 0.52 g. of the phenylcarbinol (XX) in 10 ml. of acetic acid was treated with 10 ml. of 6*N* sulfuric acid, refluxed for 45 min., and finally concentrated to *ca.* 10 ml. under vacuum. The yellow solid which separated during this process was collected, washed with water, dried and crystallized from alcohol in needles, m.p. 139–140°. It was identified as 10-phenylanthrone by mixed melting point with an authentic sample.[23]

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(27) F. Straus and A. Rohrbacher, *Ber.*, **54**, 69 (1921).

(28) Glacial acetic acid was refluxed for 3 hr. with one tenth of its weight of acetic anhydride, and distilled. The fraction boiling at 118° was collected and used as anhydrous acetic acid.

(29) J. C. W. Evans and C. F. H. Allen, *Org. Syntheses*, **Coll. Vol. II**, 517 (1943).