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The Stereochemistry of 9,10-Dihydro-9,10-*o*-xylyleneanthracene Derivatives

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Ten derivatives of 9,10-dihydro-9,10-*o*-xylyleneanthracene (I) substituted at the methylene group(s) (II–XI) have been prepared and the stereochemistry of these new compounds has been examined by means of their spectrographic properties. Attention is focused on the conformational equilibrium of three possible forms as exemplified by Ia, Ib and Ic. All four ketones (VIII–XI) show absorption spectra which are conceivable only by assuming coplanarity of the 9,10-bridging groups, for example, IXb being preferred to IXa. The *trans*-configuration is tentatively assigned to the diol VII and the process of substitution on the methylene group of I is discussed.

A synthesis of 9,10-dihydro-9,10-*o*-xylyleneanthracene (I) has been described in our previous paper.[1] An equilibrium of three conformers as shown in Fig. 1 is considered for this system. The present paper will be concerned with the preparation of derivatives of this hydrocarbon substituted at the methylene group(s) and the resulting change in conformational equilibrium will be examined.

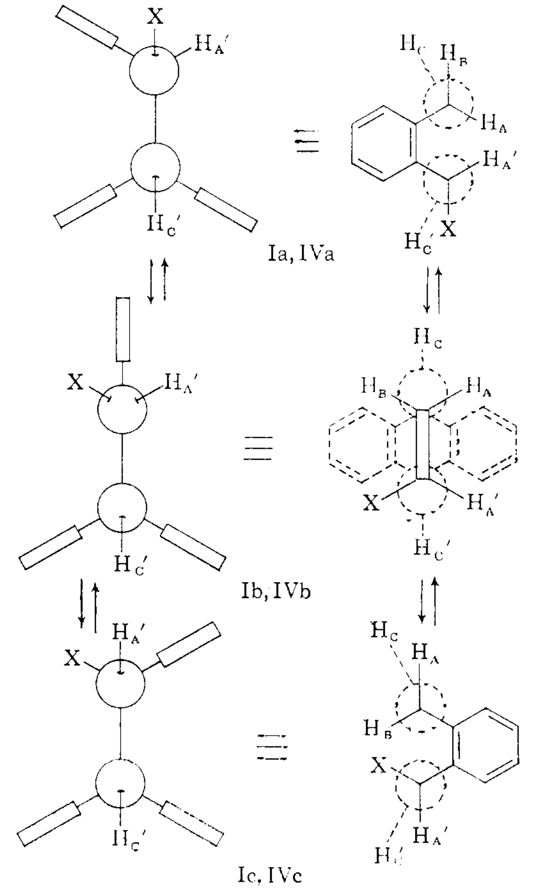

Fig. 1.—Conformations of I ($X = H_B'$) and IV (X = OAc).[2]

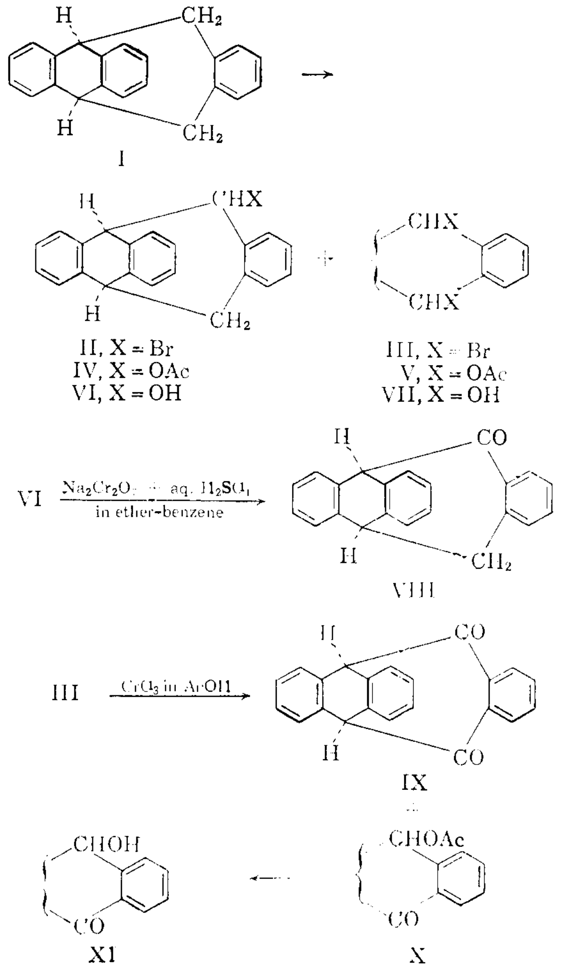

Fig. 2.—The preparation of derivatives of I.

Routes of preparation are summarized in Fig. 2. The monobromo compound II was obtained in a 63% yield with one equivalent of N-bromosuccinimide. Its acetolysis product IV was hydrolyzed and the resulting carbinol VI was oxidized by Brown's method[3] to the monoketone VIII in a 39% over-all yield based on IV. Bromination of I with two equivalents of N-bromosuccinimide gave a single isomer of the dibromo derivative III in 73% yield. Acetolysis of III was examined under two different conditions and *trans* configuration was tentatively assigned to the resulting diol VII as shown below. Oxidation of the dibromo compound III with chromic anhydride in acetic acid gave diketone IX and acetoxyketone X, the latter being further hydrolyzed to hydroxy ketone XI. The same diol (VII) was also produced by reduction of the diketone IX with sodium borohydride or with

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(1) K. Sisido, Y. Udô and H. Nozaki, *J. Org. Chem.*, **26**, 584 (1961).

(2) The left three formulas show side views of the molecules, while the right three show top views.

(3) H. C. Brown and C. P. Garg, *J. Am. Chem. Soc.*, **83**, 2952 (1961).

Raney nickel and hydrogen. No isomeric diol could be isolated.

When a molecular model of I is constructed, forms Ia and Ic are obtained with no appreciable distortion of valence angles. However, in the Ia conformation, for example, the H_A and H_A' protons come quite close together, and the H_B and H_C protons are *eclipsed*. Therefore, Pitzer strain[4] is expected to arise in conformations Ia and Ic, though no Baeyer strain has to be considered. The molecule is relieved of the Pitzer strain when the xylylene group is rotated up toward the symmetrical Ib position. Instead, however, negative Baeyer strain arises in Ib. Equivalency of methylene protons (H_A and H_B) in the hydrocarbon I is inferred from the n.m.r. splitting pattern of these protons as a doublet and of the methine protons as a triplet.[1] Therefore, the conformation is not fixed in either the Ia or Ic form.[5]

In monosubstituted derivatives such as II, IV and VI the conformational equilibrium should have been displaced in some way. In the n.m.r. spectrum of monoacetoxy derivative IV,[6] signals corresponding to the H_A' and H_C' protons were observed as sharp doublets with a coupling constant of 3.2 c.p.s. in contrast to the value of 6.8 c.p.s. for methylene and methine protons of I. The peaks for the H_A and H_B protons and for the H_C proton were poorly resolved multiplets and the peak of the acetate methyl group appeared in the normal region. Clearly the acetoxy group in IV results in a redistribution of the population of conformers so as to favor the Ia form with its acetoxy group in the "*exo*" position. In this connection, it should be noted that the dihedral angles of H_A' and H_C' protons are approximately 120°, 60°, and 0° in conformations IVa, IVb and IVc, respectively. Thus, the observed coupling constant of 3.2 c.p.s. would be abnormally low if the IVc conformation were to be assumed.[5] Moreover, if the acetate were "*endo*" or fixed in the Ic conformation, there should be strong diamagnetic shielding of the acetate methyl group by one of the benzene rings.[7]

This redistribution is not unexpected, since the repulsion between the non-bonded *endo* groups arises from H_A and H_A' protons in IVa, while from the acetoxy group and H_B proton in IVc. As known already, the acetoxy group of acetoxycyclohexane occupies the equatorial position in preference to the axial one[8] and this can be ascribed to the repulsion between an acetoxy group and a hydrogen atom being greater than that between two hydrogens in corresponding steric circumstances.

The spectroscopic properties of the ketonic derivatives VIII–XI are summarized in Table I.

TABLE I

THE ABSORPTION SPECTRA OF KETONES

ν_{max}, cm.$^{-1}$	VIII	IX	X, >C=O		XI	
	>C=O	>C=O	Ester	Ketone	—OH	>C=O
In CCl$_4$[a]	1680	1676	1743	1681	3500	1677
In CHCl$_3$[b]	1671	1669	1737	1671	3500	1669
Nujol mull	1680	1675	1740	1673	3470	1670
					3370	

λ_{max} mμ (log ϵ) in 100% ethanol

VIII	IX	X	XI
250 (3.88)	237sh. (4.42)	244sh. (4.08)	255sh. (3.94)
277sh. (3.49)	250sh. (4.32)	256sh. (4.03)	270sh. (3.66)
297sh. (3.22)	302 (4.13)	270sh. (3.61)	276sh. (3.49)
342 (2.72)	340sh. (3.88)	276sh. (3.50)	299sh. (3.15)
355sh. (2.58)		299sh. (3.16)	330sh. (2.77)
		342 (3.04)	342 (2.80)
		355sh. (2.99)	355sh. (2.67)
		375sh. (2.66)	

λ_{max} mμ (log ϵ) in isoöctane

VIII	IX	X	XI
255sh. (3.87)	248 (4.40)	255sh. (4.00)	256sh. (3.89)
270sh. (3.40)	283 (3.57)	269sh. (3.55)	268sh. (3.51)
275sh. (3.32)	293 (3.56)	275sh. (3.41)	275sh. (3.34)
287sh. (3.13)	347 (3.51)	289 (3.29)	289 (3.23)
297sh. (3.10)	359sh. (3.50)	297 (3.26)	298sh. (3.16)
330sh. (2.90)	378sh. (3.33)	330sh. (3.18)	333sh. (2.96)
343 (2.91)		344 (3.21)	344sh. (3.03)
355sh. (2.80)		356sh. (3.18)	356sh. (2.98)
374sh. (2.39)		377sh. (2.95)	377sh. (2.76)

[a] Approximately 0.015 *M* solution. [b] Approximately 0.015 *M* solution.

The infrared absorptions indicate that the carbonyl groups are in conjugation with the central benzene ring in these ketones.[9] As demonstrated for the diketone IX in Fig. 3 the angle between the planes of the phthaloyl benzene ring and the carbonyl group[10] is about 71° in the IXa form and the resonance in that form is virtually completely damped.[11–13] The IXb form, on the other hand,

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(4) (a) W. G. Dauben and K. S. Pitzer in M. S. Newman, ed., "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956, p. 6; (b) H. H. Lau, *Angew. Chem.*, **73**, 423 (1961).

(5) The coupling constant of methylene and methine protons was 6.8 c.p.s. and this unusually high value for a 60° dihedral angle led the authors to assume a rapid flipping over of the xylylene group between Ia and Ic forms rather than a rigid Ib conformation. For the relationship of dihedral angle and coupling constant see (a) H. Conroy in R. A. Raphael, E. C. Taylor and H. Wynberg, ed., "Advances in Organic Chemistry: Methods and Results," Vol. II, Interscience Publishers, Inc., New York, N. Y., 1960, p. 311; and also (b) J. N. Shoolery in the NMR-EPR Staff of Varian Associates, "NMR and EPR Spectroscopy," Pergamon Press, Oxford, 1960, p. 115. This supposition is questionable, however, in view of recent developments which have shown that the older ideas relating dihedral angle to coupling constant require reinvestigations. See (c) J. I. Musher, *J. Am. Chem. Soc.*, **83**, 1146 (1961); and (d) K. L. Williamson and W. S. Johnson, *ibid.*, **83**, 4623 (1961). The authors are indebted to a referee of this manuscript for a valuable discussion of this problem.

(6) Other derivatives, II, III, V and VI, were too sparingly soluble in available solvents.

(7) The authors are grateful to another referee for this suggestion and for helpful discussions. For magnetic anisotropy of the benzene ring, see (a) W. S. Lindsay, P. Stokes, L. G. Humber and V. Boekelheide, *J. Am. Chem. Soc.*, **83**, 943 (1961); and (b) N. L. Allinger, M. A. Da Rooge and R. B. Hermann, *ibid.*, **83**, 1974 (1961).

(8) See for example E. L. Eliel, *J. Chem. Educ.*, **37**, 126 (1960).

(9) In the infrared absorption of the ketones VIII–XI the bands appearing near 1600 cm.$^{-1}$ showed much stronger intensities than those of non-ketonic derivatives I–VII. This is further evidence indicating that the carbonyl groups of the ketones are in conjugation with the adjacent benzene rings. The 1600 and 1580 cm.$^{-1}$ bands could not be differentiated with certainty. See L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd. edition, Methuen & Co. Ltd., London, 1958, p. 72.

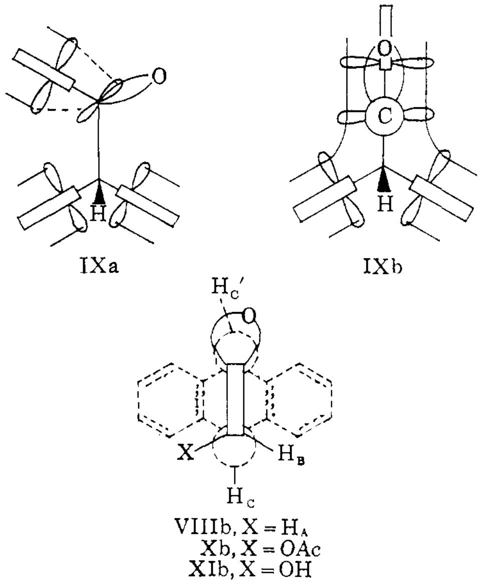
(10) This angle was obtained diagramatically, assuming the 120° bond angle of carbonyl carbon and the distance between the 9,10-carbons of dihydroanthracene as 2.94 Å. $[= 2 \times (1.40 + 1.54) \times \sin 30°]$. The C–C bond distances were taken from L. F. Fieser and M. Fieser, "Advanced Organic Chemistry," Reinhold Publishing Corp., New York, N. Y., 1961.

(11) J. Guy, *J. Chim. Phys.*, **46**, 469 (1949).

(12) For absorption spectra of diketones having similar phthaloyl chromophore, see (a) R. H. Thomson, *J. Chem. Soc.*, 1737 (1950); (b) V. C. Farmer, N. F. Hayes and R. H. Thomson, *ibid.*, 3600 (1956); (c) M. P. Cava and R. L. Shirley, *J. Org. Chem.*, **26**, 2212 (1961).

(13) For twisting effect see also ref. 12b. and (a) F. M. Dean, J. Staunton and W. B. Whalley, *J. Chem. Soc.*, 3004 (1959); (b) E. J. Hows, J. S. E. Holker, A. Kelly, A. D. G. Powell and A. Robertson *ibid.*, 3598 (1959).

allows maximum resonance between carbonyl function and the adjacent benzene ring. Accordingly, the most plausible assumption would be that conformations VIIIb–XIb are the predominating ones in the equilibrium of these ketones.


IXa IXb

VIIIb, X = H_A
Xb, X = OAc
XIb, X = OH

Fig. 3.—Conformations of ketones; for notations see ref. 2.

Stabilization of the "b" conformations may be explained in several ways: besides the resonance in the 9,10-bridging groups, the replacement of the tetrahedral methylene carbon with trigonal carbonyl carbon should have decreased the Baeyer strain of the "b" conformations to a considerable degree. An additional argument for this view comes from the anomalous ultraviolet spectra of these ketones with exceptionally high extinctions in the longer wave length absorptions in contrast to hydrocarbon I and its mono- and disubstitution products which invariably show normal benzenoid absorption as summarized in Table II. Stereoelectronic factors in the symmetrical "b" conformations as exemplified by IXb are favorable for strong homoconjugation[14] of the phthaloyl or α-keto-*o*-xylylene group with both dihydroanthracene benzene rings. Thus fully conjugated models such as IXb should be open to further theoretical treatments along the lines developed by Labhart and Wagnière[15] and by Wilcox and others.[16]

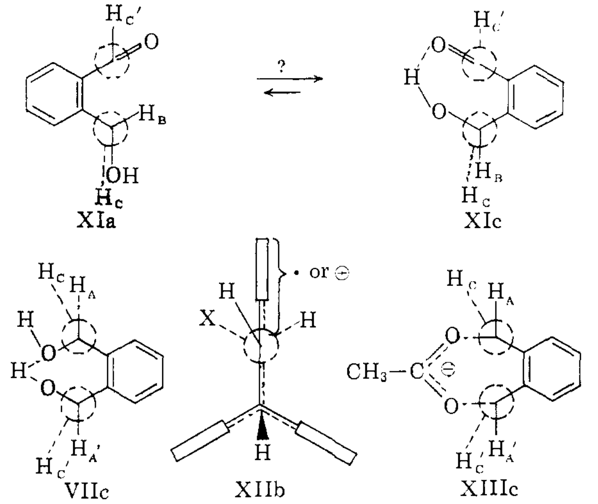
TABLE II

THE ULTRAVIOLET SPECTRA OF MONO- AND DISUBSTITUTED DERIVATIVES[a,b]

	λ_{max} mμ (log ε)	
II (X = Br)[c]	IV (X = OAc)[c]	VI (X = OH)[c]
259 (3.22)	263 (2.98)	262sh. (2.92)
266 (3.22)	273 (2.90)	266 (2.93)
274 (3.14)		273 (2.87)
III (X = Br)[d]	V (X = OAc)[c]	VII (X = OH)[c]
266sh. (3.47)	257sh. (2.97)	257sh. (2.99)
275sh. (3.29)	261 (3.01)	263 (3.05)
283sh. (3.05)	267sh. (2.94)	268sh. (2.94)
	272sh. (2.78)	271 (2.92)

[a] For ultraviolet absorptions of the hydrocarbon I see ref. 1. [b] X means a substituent at the methylene carbon. In the upper row are monosubstituted compounds and in the bottom row disubstituted compounds. [c] Measured in 100% ethanol. [d] Measured in isoöctane.

If the hydroxy ketone XI were in the "a" or "c" conformation (see Fig. 4), there might be stabilization of the XIc form with *endo*-hydroxy group through intramolecular hydrogen bonding. The infrared spectrum (Table I) clearly excludes this possibility, providing additional evidence for the predominance of the XIb conformation.


XIa XIc

VIIc XIIb XIIIc

Fig. 4.—Possible products or intermediates in disubstitution; for notation see ref. 2.

Supposedly any substitution on the methylene carbon of I and its derivatives would take place, with relief of the Pitzer or Baeyer strain, *via* resonance-stabilized radicals or cations as shown by XIIb (Fig. 4) having planar 9,10-bridging groups. This conformation is quite similar to the preferred one of ketones VIII–XI mentioned above.

Single compounds were obtained in all disubstituted derivatives III, V and VII, and no isomer could be isolated. The configuration of the dibromide III might probably be *trans* but, irrespective of this, the participation of a bridged cation XIIIc (Fig. 4) or the transformation of cation XIIb (X = OAc) into XIIIc appeared probable during the introduction of the second acetoxy group. In light of the classic work of Winstein and his co-workers,[17] attempts were made to obtain *cis*-diol monoacetate by the action of silver acetate in acetic acid containing 4% of water. The diol obtained after hydrolysis was found identical with VII prepared from diacetoxy compound V by lithium aluminum hydride treatment or from diketone IX by reduction. The diol VII is the thermodynamically more stable isomer, as equilibration by means of aluminum isopropoxide in 2-propanol

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[14] (a) R. C. Cookson and N. S. Wariyar, *ibid.*, 2302 (1956); (b) R. C. Cookson and N. Lewin, *Chemistry & Industry*, 984 (1956); (c) H. Birnbaum, R. C. Cookson and N. Lewin, *J. Chem. Soc.*, 1224 (1961); (d) S. Winstein, L. de Vries and R. Orloski, *J. Am. Chem. Soc.*, **83**, 2020 (1961), and references cited there.

[15] H. Labhart and G. Wagnière, *Helv. Chim. Acta*, **42**, 2219 (1959).

[16] (a) C. F. Wilcox, Jr., S. Winstein and W. G. McMillan, *J. Am. Chem. Soc.*, **82**, 5450 (1960); (b) C. F. Wilcox, Jr., and A. C. Craig, *J. Org. Chem.*, **26**, 2491 (1961).

[17] For a review see W. Lwowski, *Angew. Chem.*, **70**, 483 (1958).

containing acetone[18] resulted in total recovery of the unchanged material.

Inspection of a molecular model of diol VII showed that the *cis* form might exist in the hydrogen-bonded *endo–endo* conformation, VIIc (Fig. 4), rather than in the alternative one with *exo–exo*-hydroxy groups. The crowded hydroxy groups in the former conformation may be linked together by hydrogen bonding, while repulsions should be operating between the *endo*-hydrogens in the latter conformation.

In the infrared spectrum of diol VII a sharp singlet due to monomeric hydroxy group was observed at 3500 cm.$^{-1}$ in dilute solutions and no hydrogen bonding could be detected. This would imply that the *cis*-diol exists in the *exo–exo* conformation or that the *trans* configuration should be ascribed to the diol VII and accordingly to the diacetate V. The above-mentioned considerations and the failure of attempted acetalization in various ways[19] might support the latter view. If this be the case, the planar cation (XIIb, X = OAc) should be more stable than the bridged cation XIIIc.

Experimental[20]

9,10-Dihydro-9,10-*o*-xylyleneanthracene (I).—The preparation of the hydrocarbon (I)[1] was modified as follows: a solution of 6.0 g. of 1,3-dihydroisothianaphthene-2,2-dioxide[21] (35 mmoles) and 6.5 g. of anthracene (36 mmoles) in 80 ml. of diethyl phthalate was heated at about 290° for 1.5 hr. in an atmosphere of nitrogen. The reaction mixture was hydrolyzed by heating at 90° with 350 ml. of 15% sodium hydroxide solution for 15 hr. with stirring. The solids remaining undissolved were collected by filtration, and the filtrate was extracted with 300 ml. of benzene. The solids were dissolved in the benzene extract and this solution was washed with 5% hydrochloric acid, sodium bicarbonate solution, and finally with water, dried over calcium chloride, and concentrated *in vacuo*. The solid residue was recrystallized from 30 ml. of benzene, whereupon a part of unchanged anthracene separated out. To the evaporation residue of the mother liquor were added 80 ml. of ethanol and 4.0 g. of picric acid, the mixture was boiled for 10 min., and the resulting red solution was allowed to stand overnight. The precipitated crystals were collected and recrystallized twice from ethanol to afford 2.6 g. (26% based on the starting sulfone) of colorless needles, m.p. 179°.

9,10-Dihydro-9,10-[α-bromo-*o*-xylylene]-anthracene (II).—A mixture of 500 mg. of the hydrocarbon I (1.77 mmoles), 400 mg. of N-bromosuccinimide[18] (1.80 mmoles) and 12 ml. of dry carbon tetrachloride was heated and irradiated for 6 hr. with a tungsten lamp. After evaporation of the solvent *in vacuo* the resulting residue was treated with water and extracted with benzene. The benzene extracts were combined, washed with water, dried over magnesium sulfate, and concentrated *in vacuo*. Three recrystallizations of the residue from ethyl acetate gave 400 mg. (63%) of colorless crystals, m.p. 141–142°.

Anal. Calcd. for $C_{22}H_{17}Br$: C, 73.14; H, 4.74. Found: C, 73.09; H, 4.77.

9,10-Dihydro-9,10-[α,α'-dibromo-*o*-xylylene]-anthracene (III).—In the same way as above, 500 mg. of the hydrocarbon I (1.77 mmoles) was treated with 870 mg. of N-bromosuccinimide (3.91 mmoles). Chromatographic purification of the brown product on an alumina column, followed by two recrystallizations from benzene–ligroin (b.p. 80–100°), afforded 570 mg. (73%) of colorless crystals, m.p. 216–217° dec.

Anal. Calcd. for $C_{22}H_{16}Br_2$: C, 60.03; H, 3.67. Found: C, 60.07; H, 3.79.

9,10-Dihydro-9,10-[α-acetoxy-*o*-xylylene]-anthracene (IV).—A mixture of 130 mg. of the monobromo compound II (0.36 mmole) and 300 mg. of anhydrous potassium acetate dissolved in 3 ml. of acetic anhydride and 3 ml. of glacial acetic acid was heated at 90° for 3 hr. After removing the solvents by distillation, the residue was treated with water and extracted with benzene. The combined benzene extracts were washed with sodium bicarbonate solution and water, dried over magnesium sulfate, and concentrated *in vacuo*. Upon chromatographic purification of the residue on an alumina column, 100 mg. (82%) of a resinous product was obtained from elutions with benzene. One recrystallization of this product from ethanol gave colorless needles, m.p. 171.5–172°, with an excellent recovery; infrared absorptions (Nujol): 1744, 1242 cm.$^{-1}$.

Anal. Calcd. for $C_{24}H_{20}O_2$: C, 84.68; H, 5.92. Found: C, 84.33; H, 5.93.

The n.m.r. spectrum obtained on a 56.4-Mc. instrument in carbon tetrachloride solution using water as an external reference showed the following peaks: a multiplet at δ −2.40 p.p.m., wt. 12, assigned to aromatic protons; a doublet at δ −1.29 p.p.m., wt. 1, assigned to H_A' proton (Fig. 1); a doublet at δ +0.23 p.p.m., wt. 1, assigned to H_C' proton; a poorly resolved multiplet at δ +0.51 p.p.m., wt. 1, assigned to H_C proton; a poorly resolved multiplet at δ +1.39 p.p.m., wt. 2, assigned to H_A and H_B protons; and a sharp singlet at δ +2.39 p.p.m., wt. 3, assigned to the acetoxy methyl group. The coupling constant of H_A' and H_C' protons was 3.2 c.p.s.

9,10-Dihydro-9,10-[α,α'-diacetoxy-*o*-xylylene]-anthracene (V).—Similarly, as above, 200 mg. of the dibromide III (0.45 mmole) was treated with 500 mg. of anhydrous potassium acetate in 5 ml. of acetic anhydride and 5 ml. of glacial acetic acid. Chromatography of the reaction products on an alumina column followed by two recrystallizations from methanol–ethanol, gave 130 mg. (72%) of colorless crystals, m.p. 212–214°.

Anal. Calcd. for $C_{26}H_{22}O_4$: C, 78.37; H, 5.57. Found: C, 78.33; H, 5.70.

9,10-Dihydro-9,10-[α-hydroxy-*o*-xylylene]-anthracene (VI).—A mixture of 100 mg. of the acetoxy compound IV (0.29 mmole) and 10 ml. of a 10% ethanolic solution of potassium hydroxide was allowed to stand overnight at room temperature and then refluxed for 1 hr. The mixture was diluted with water, distilled to remove most of the ethanol, and extracted with benzene. This benzene solution was washed with 5% sulfuric acid, saturated sodium bicarbonate solution, and then with water, dried over magnesium sulfate, and concentrated. Two recrystallizations of the residue from benzene–ethanol gave 50 mg. (57%) of colorless solid, m.p. 191–192°; infrared spectrum (Nujol): 3450, 1030 cm.$^{-1}$; (0.008 *M* carbon tetrachloride solution): 3510, 1028 cm.$^{-1}$.

Anal. Calcd. for $C_{22}H_{18}O$: C, 88.56; H, 6.08. Found: C, 88.61; H, 6.21.

9,10-Dihydro-9,10-[α,α'-dihydroxy-*o*-xylylene]-anthracene (VII). (a) **From Diacetate V.**—To a suspension of 100 mg. of lithium aluminum hydride in 10 ml. of dry ether was added dropwise a solution of 100 mg. of the diacetoxy derivative V (0.25 mmole) in 6 ml. of dry benzene under vigorous stirring at 0–5° during 15 min. and then the mixture was heated at reflux for 3 hr. After cooling, 20 ml. of ethyl acetate was added and the reaction mixture was worked up in the usual way. Two recrystallizations of the evaporation residue from benzene–ligroin (b.p. 50–70°) afforded 60 mg. (76%) of colorless fine crystals, m.p. 110–113°.

Anal. Calcd. for $C_{22}H_{18}O_2$: C, 84.05; H, 5.77. Found: C, 83.69; H, 5.99.

(b) **From Dibromide III with Silver Acetate in Aqueous Acetic Acid.**—A mixture of 350 mg. of the dibromide III (0.80 mmole), 270 mg. of silver acetate (1.62 mmoles) and 12 ml. of acetic acid containing 4% water was stirred at 90° for 15 min.[22] After cooling, the reaction mixture was fil-

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[18] E. L. Eliel and R. S. Ro, *J. Am. Chem. Soc.*, **79**, 5992 (1957).

[19] For methods of acetalization of diols see (a) R. I. T. Cromartie and Y. K. Hamied, *J. Chem. Soc.*, 3622 (1961); and (b) K. C. Brannock and C. R. Lappin, *J. Org. Chem.*, **21**, 1366 (1956).

[20] Microanalyses were performed by Miss Kenko Ogawa. All temperatures are uncorrected. The N-bromosuccinimide used contained 80% active bromine. The chromic acid solution in the preparation of IX and X was obtained by dissolving 5.0 g. of chromic anhydride in 3.5 ml. of glacial acetic acid and 3.5 ml. of water.

[21] M. P. Cava and A. A. Deana, *J. Am. Chem. Soc.*, **81**, 4266 (1959).

[22] For this procedure, see L. F. Fieser, "Experiments in Organic Chemistry," 3rd. edition, D. C. Heath & Co., Boston, Mass., 1957, p. 188.

tered, the filtrate was diluted with 50 ml. of water and extracted with benzene. The extract was washed with 10% sodium hydroxide solution and then with water, dried over magnesium sulfate and concentrated *in vacuo*. On chromatographic separation of the residue on an alumina column, 200 mg. (63%) of the diacetoxy derivative V, m.p. and mixed m.p. 212–214°, was first eluted with benzene and then 40 mg. of α-hydroxy-α'-acetoxy compound was eluted with benzene–ethanol. The latter product formed a waxy solid and could not be isolated pure, but the infrared absorptions (Nujol) at 3480, 3400, 1740, 1242 and 1036 cm.$^{-1}$ showed the presence of both hydroxy and acetate groups. This solid (30 mg.) was refluxed with 2 ml. of sodium hydroxide 10% solution and 4 ml. of ethanol for 20 min. Recrystallizations of the reaction product from benzene–ligroin (b.p. 50–70°) gave 20 mg. of fine crystals, m.p. and mixed m.p. 110–113°.

(c) **From Diketone IX with Sodium Borohydride.**—To a mixture of 250 mg. of the diketone IX (0.81 mmole) and 20 ml. of ethanol was added slowly a solution of 150 mg. of sodium borohydride in 2 ml. of ethanol and 2 ml. of water at 0–5° under stirring. The reaction mixture was heated gradually and then refluxed for 15 min. After cooling, 60 ml. of 2 *N* hydrochloric acid was added and the whole was extracted with benzene. The benzene solution was washed with saturated sodium bicarbonate solution and water, dried over magnesium sulfate, filtered, and concentrated *in vacuo*. Three recrystallizations of the residue from benzene–ligroin (b.p. 50–70°) gave 180 mg. (71%) of colorless fine crystals, m.p. and mixed m.p. 110–113°.

(d) **From Diketone IX with Raney Nickel and Hydrogen.**—A mixture of about 100 mg. of freshly prepared Raney nickel (W-6 grade), 20 ml. of ethanol, 0.4 ml. of triethylamine, 50 mg. of the diketone IX (0.16 mmole) and 5 ml. of benzene was shaken in an atmosphere of hydrogen for 1 hr. at room temperature.[23] After removing the catalyst by filtration, the solution was concentrated *in vacuo*. Recrystallizations of the residue from benzene–ligroin (b.p. 50–70°) gave 45 mg. (89%) of crystals, m.p. and mixed m.p. 110–113°. These samples showed infrared spectra which were all completely identical either in carbon tetrachloride solution or in Nujol mull. Principal absorptions were observed in 0.008 *M* carbon tetrachloride solution at 3500, 1028 and 1000 cm.$^{-1}$.

9,10-Dihydro-9,10-[α-oxo-*o*-xylylene]-anthracene (VIII).—To a solution of 70 mg. of the monohydroxy compound VI (0.24 mmole) in 5 ml. of ether and 5 ml. of benzene was added 0.12 ml. of chromic acid solution (equivalent to VI) prepared from 5.0 g. of sodium dichromate dihydrate and 3.75 ml. of concentrated sulfuric acid and diluted to 25 ml.[3] After stirring at 25° for 5 hr., the reaction mixture was poured into water and extracted with benzene. The combined extracts were washed with saturated sodium bicarbonate solution and then with water, dried over magnesium sulfate, and evaporated. Two recrystallizations from benzene–ethanol afforded 45 mg. (69%) of colorless crystals, m.p. 192.5–193.5°. A mixture with an equal amount of VI melted at about 180–183°.

Anal. Calcd. for $C_{22}H_{16}O$: C, 89.16; H, 5.44. Found: C, 88.82; H, 5.82.

9,10-Dihydro-9,10-*o*-phthaloylanthracene (IX).—A mixture of 500 mg. of the hydrocarbon I (1.77 mmoles), 870 mg. of N-bromosuccinimide[18] (3.91 mmoles) and 15 ml. of dry carbon tetrachloride was heated and irradiated for 5 hr. and the crude dibromide III was subjected to the following oxidation. To a solution of the dibromide in 5 ml. of glacial acetic acid was added dropwise 1.3 ml. of the chromic acid solution[18] containing 7.22 mmoles of chromic anhydride at room temperature and then the mixture was heated at 90° for 1.5 hr. The resulting dark green solution was poured into 2 *N* sulfuric acid and extracted with benzene. The benzene solution was washed with saturated sodium bicarbonate solution and water, dried over magnesium sulfate, and concentrated *in vacuo*. Chromatography of the brown solid residue on alumina and elution with benzene afforded the diketone IX, besides a considerable amount of anthraquinone which was identified by mixed melting point and by infrared spectrum. Repeated recrystallizations of the diketone from ethanol–benzene gave 125 mg. (23%) of analytical sample, m.p. 213–214°.

Anal. Calcd. for $C_{22}H_{14}O_2$: C, 85.14; H, 4.55. Found: C, 85.06; H, 4.51.

Phthalic acid was isolated from sodium bicarbonate washings and was characterized by infrared spectrum and mixed melting point.

9,10-Dihydro[α-oxo-α'-acetoxy-*o*-xylylene]-anthracene (X).—In the same way as above 500 mg. of the hydrocarbon I (1.77 mmoles) was treated with 870 mg. of N-bromosuccinimide[18] (3.91 mmoles) and the products were oxidized with a smaller amount (0.45 ml.) of chromic acid solution[18] containing 2.50 mmoles of chromic anhydride. Chromatographic separation of the reaction products on alumina gave the diketone IX and the acetoxy ketone X fractions. Recrystallization of the latter from benzene-ethanol gave 55 mg. (9%) of colorless crystals, m.p. 186–187°.

Anal. Calcd. for $C_{24}H_{18}O_3$: 81.34; H, 5.12. Found: C, 81.22; H, 5.12.

From the diketone fraction, 110 mg. (20%) of a pure sample, m.p. and mixed m.p. 213–214°, was obtained.

9,10-Dihydro-9,10-[α-oxo-α'-hydroxy-*o*-xylylene]-anthracene (XI).—A mixture of 90 mg. of the acetoxyketone X (0.25 mmole), 5 ml. of 10% sodium hydroxide and 10 ml. of ethanol was heated at reflux for 1 hr. After cooling, the reaction mixture was poured into water and extracted with benzene. Working up the benzene solution, followed by two recrystallizations of the evaporation residue from benzene-ligroin (b.p. 50–70°) gave 55 mg. (69%) of colorless crystals, m.p. 194–195°.

Anal. Calcd. for $C_{22}H_{16}O_2$: C, 84.59; H, 5.16. Found: C, 84.28; H, 5.00.

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(23) For this procedure, see H. Adkins and H. R. Billica, *J. Am. Chem. Soc.*, **70**, 695 (1948).