150° (16 mm.) and had $n^{25}_D$ 1.5540 (reported[25] b.p. 127–130° (8 mm.) and $n^{20}_D$ 1.5585). The infrared spectrum of this product was identical with the product of part A and also with the spectra of the optically active samples of II.

**Hydrogenolysis of L(−)-Methylhydrobenzoin (I).**—A solution of the L(−)-methylhydrobenzoin (4 g.) in ethanol (50 ml.) was hydrogenolyzed for four hours at 200° with hydrogen at 1400 p.s.i. in the presence of copper–chromium oxide catalyst (2 g.). Processing yielded 1.5 g. of crude product and after distillation 0.87 g. (25%) of II which boiled at 54–58° (0.02 mm.) and had $[\alpha]^{20}_D$ 11.75° (*c* 2.1, chloroform). The infrared spectrum was identical with those of previous samples of II.

**1,2-Bis-(4-acetylphenyl)-propane. A.** *d,l*-Form.—Acetic anhydride (1.04 g.) was added during 15 minutes to a vigorously stirred mixture of *d,l*-1,2-diphenylpropane (1 g.), aluminum chloride (3.06 g.) and carbon bisulfide (10 ml.). The mixture then was refluxed for one hour and the solvent evaporated. The residue was treated with ice, hydrochloric acid and ether. Evaporation of the ether layer left a crystalline residue which was purified by five recrystallizations from pentane–benzene, m.p. 79–80°.

*Anal.* Calcd. for $C_{19}H_{20}O_2$: C, 81.39; H, 7.19. Found: C, 81.52; H, 7.40.

B. (+)-Form.—The reaction with the sample of (+)-1,2-diphenylpropane was carried out exactly as in part A. There was obtained after five recrystallizations, a product with m.p. 79–80° and $[\alpha]^{19}_D$ 35.3° (*c* 0.59, chloroform). The infrared spectrum of this product was identical with that of compound obtained in part A.

*Anal.* Calcd. for $C_{19}H_{20}O_2$: C, 81.39; H, 7.19. Found: C, 81.46; H, 7.24.

C. (−)-Form.—The reaction with (−)-1,2-diphenylpropane from the hydrogenolysis of I was carried out as in part A. Five recrystallizations yielded a product with m.p. 91–92° and $[\alpha]^{19}_D$ −158.3° (*c* 0.55, chloroform), and with infrared spectrum identical with those of the other samples of this derivative.

*Anal.* Calcd. for $C_{19}H_{20}O_2$: C, 81.39; H, 7.19. Found: C, 81.53; H, 7.32.

NEW BRUNSWICK, N. J.

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[25] K. Serijan and P. H. Wise, THIS JOURNAL, **73**, 4766 (1951).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF FORDHAM UNIVERSITY]

# Ozonolysis of Polycyclic Aromatics. VI.[1] Benz[a]anthracene and Benz[a]anthracene-7,12-dione. Correlation of Quinone–Hydroquinone Oxidation–Reduction Potentials with the Positions of Predominant Ozone Attack[2]

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Benz[a]anthracene (I) and benz[a]anthracene-7,12-dione (II) absorb, respectively, three and two molar equivalents of ozone to yield an unstable, probably monomeric ozonide (IV) in inert solvents, and a methoxyperoxidic oil and solid (crude VIII) in methanol from which was isolated a dimethoxy peracetal (VIII); IV, the peroxidic oil, and crude VIII have been oxidized to 1,2-anthraquinonedicarboxylic acid (V) and reduced to 1,2-anthraquinonedicarboxaldehyde (IX) and the cyclic hydroxylactone of 1-(or 2)-formyl-2-(1)-anthraquinonecarboxylic acid (X). Since the positions of predominant ozone attack on unsubstituted, polycyclic aromatics can be correlated with the positions of lowest corrected oxidation–reduction potential of the appropriate quinone–hydroquinone system, it is concluded that ozone attacks predominantly in a 1,2- or 1,4-addition *via* a rate-controlling transition state whose geometry corresponds to the most stable dihydro compound. These oxidation–reduction potentials qualitatively assess the order of decreasing ease of ozonolysis in the series: naphthacene > anthracene > I > phenanthrene ≃ dibenz[a,h]anthracene > pyrene > naphthalene > benzene.

Molecular orbital calculations predict that in the benz[α]anthracene molecule (I), the 7- and 12-carbon atoms have the lowest carbon localization energies[3a] (reactivity number),[3b] the 7,12-positions have the lowest paralocalization energy[3a,4a,5] and the 5,6-bond, the lowest bond localization energy[4b] (ortholocalization energy).[3a] Chemical evidence qualitatively supports this theory of chemical reactivity based on these three theoretical indices. Thus I undergoes substitution at the less sterically hindered 7-position[6] and addition at the 7,12-[7] and 5,6-positions.[8] Further, chromic acid,[9] perhydrol[10] and perbenzoic acid[11] oxidation of I gave benz[α]anthracene-7,12-dione (II) while oxidation with Milas reagent[12] gave a mixture of II and benz[α]anthracene-5,6-dione.[13]

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[1] Preceding papers in this series: (a) E. J. Moriconi, W. F. O'Connor and L. Taranko, *Arch. Biochem. and Biophys.*, **83**, 283 (1959); (b) E. J. Moriconi, W. F. O'Connor and F. T. Wallenberger, *Chemistry & Industry*, 22 (1959); (c) E. J. Moriconi, G. W. Cogswell, W. J. Schmitt and W. F. O'Connor, *ibid.*, 1591 (1958); (d) W. F. O'Connor, W. J. Schmitt and E. J. Moriconi, *Ind. Eng. Chem.*, **49**, 1701 (1957); (e) W. J. Schmitt, E. J. Moriconi and W. F. O'Connor, THIS JOURNAL, **77**, 5640 (1955).

[2] Presented in part at the Meeting-in-Miniature of the Metropolitan Long Island Subsection, American Chemical Society's New York Section, March, 1959 and at the 135th Meeting of the American Chemical Society, Boston, Mass., April, 1959.

[3] (a) M. J. S. Dewar, THIS JOURNAL, **74**, 3357 (1952); (b) M. J. S. Dewar, *Record Chem. Progr., Kresge-Hooker Sci. Lib.*, **19**, 1 (1958).

[4] (a) R. D. Brown, *J. Chem. Soc.*, 691 (1950); (b) R. D. Brown, *ibid.*, 3249 (1950).

[5] E. C. Kooyman and J. A. A. Ketelaar, *Rec. trav. chim.*, **65**, 859 (1946).

[6] To form such derivatives of I (BA) as 7-nitro-BA [E. de Barnett and M. A. Matthews, *Chem. News*, **130**, 339 (1925); *C. A.*, **19**, 2335 (1925)]; 7-acetoxy-BA [L. F. Fieser and E. B. Hershberg, THIS JOURNAL, **60**, 1893 (1938)]; 7- or 12-acetyl-BA [J. W. Cook and C. L. Hewitt, *J. Chem. Soc.*, 1408 (1933)], on Friedel–Crafts acetylation at 0°; 7-bromo-BA [G. M. Badger and J. W. Cook, *ibid.*, 409 (1940)]; 7-chloro-BA [A. Müller and F. G. Hanke, *Monatsh. Chem.*, **158**, 435 (1949)]; 7-chloromethyl-BA [G. M. Badger and J. W. Cook, *J. Chem. Soc.*, 802 (1939)]; BA-7-aldehyde [L. F. Fieser and J. L. Hartwell, THIS JOURNAL, **60**, 2555 (1938)]; BA-7-mercaptan and BA-7-S-cysteine [J. L. Wood and L. F. Fieser, *ibid.*, **62**, 2674 (1940)]; 7-thiocyano-, and 12-thiocyano-BA [J. L. Wood and L. F. Fieser, *ibid.*, **63**, 2323 (1941); 7-carboxy-BA [A. Dansi, *Gazz. chim. ital.*, **67**, 85 (1937)]; and ethyl BA-7-acetate [A. Dansi and C. Ferri, *ibid.*, **69**, 195 (1939)].

[7] To form 7,12-disodium(dilithium)-7,12-dihydro-BA [W. E. Bachmann, *J. Org. Chem.*, **1**, 347 (1936)] from which was prepared 7,12-dihydro-BA [W. E. Bachmann, *ibid.*] and 7,12-dimethyl-7,12-dihydro-BA [B. M. Mikhailov, *Izvest. Akad. Nauk S.S.S.R., Otdel, Khim. Nauk*, 619 (1946); *C. A.*, **42**, 6350 (1948)]; and *endo*-7,12-BA-maleic anhydride adduct [E. Clar, *Ber.*, **65**, 518 (1932); R. N. Jones, C. J. Gokek and R. W. Sharpe, *Can. J. Research*, **26B**, 719 (1948)].

[8] To form *cis*-5,6-dihydroxy-5,6-dihydro-BA [G. M. Badger, *J. Chem. Soc.*, 456 (1949)], and 5,6-dihydrobenz[a]anthr-5,6-yleneacetic acid [G. M. Badger, J. W. Cook and A. R. M. Gibb, *ibid.*, 3456 (1951)].

[9] C. Graebe, *Ann.*, **340**, 259 (1905).

[10] R. T. Arnold and R. Larsen, *J. Org. Chem.*, **5**, 250 (1940).

[11] I. M. Roitt and W. A. Waters, *J. Chem. Soc.*, 3060 (1949).

[12] 20–40% hydrogen peroxide in *t*-butyl alcohol catalyzed by osmium tetroxide (0.01–0.5%).

[13] J. W. Cook and R. Schoental, *J. Chem. Soc.*, 47 (1950).

In a recent communication,[1b] we reported that Compound I dissolved in methylene chloride (−70°), 3:1 methylene chloride–methanol (−40 to −70°) or carbon tetrachloride (−20°), was oxidized to II in 35% yield on absorption of one molar equivalent of 3.4 volume per cent. ozone. Unreacted I (38%) was also recovered, in addition to small amounts of a peroxidic oil which on oxidation with alkaline hydrogen peroxide gave a 5% yield of 1,2-anthraquinonedicarboxylic acid (V). Thus, based on the amount of I utilized, 64% of I reacted with ozone predominantly in conjugate fashion at the 7,12-positions. It is reasonable to assume that the remaining 36% of I which did not produce II and V reacted at the 5,6-bond to give the undetected benzo[d]diphenic acid.[14] This would also account for most of the 50% of absorbed ozone which did not produce II and V.

Passage of 0.2 to 3.4 volume per cent. ozone in mole ratios of 0.5 to 1.5 moles of ozone per mole of I (Table II) produced II in amounts proportional to the amount of ozone used. Oxygen alone had no effect on I in solution. The oxidation of I to II therefore is most likely not ozone-catalyzed, and the oxidant most probably is ozone.[15]

The present paper records the experimental details of the ozonization of I, presents additional results of the ozonolysis of I and II in both inert and reactive solvents, and discusses the course of initial attack of ozone on unsubstituted aromatic systems.

## Ozonolysis Results

Ozonolysis of I with three molar equivalents of ozone, or of II with two molar equivalents of ozone, in methylene chloride or chloroform solution led to the same solid, unstable ozonide. This material decomposed rapidly, even at 0°, when dry, and more slowly when kept in suspension at the same temperature. Its infrared spectrum (Nujol) taken immediately after filtration showed strong carbonyl bands which broaden and smear out on standing a few minutes. On one occasion in over twenty runs, this material exploded while air drying. On several occasions, low temperature, vacuum drying caused the ozonide to char rapidly. All attempts to recrystallize this material from numerous solvents always depressed the initial melting point. Compound II can be considered a 1,2-disubstituted naphthalene derivative in which the substituents on the inner ring are electron withdrawing. Thus the greater susceptibility of the outer ring to oxidation, and the considerable double bond character of the 1,2- and 3,4-bonds of the outer ring would account for the direction of attack of the second and third moles of ozone at these bonds. The destruction of this outer ring would yield the unstable ozonide, presumably *via* Criegee's zwitterion (III),[16] of probable monomeric monoözonide structure (IV).[17]

In the presence of 2,4-dinitrophenylhydrazine, ozonolysis of I in acetic acid gave glyoxal 2,4-dinitrophenylhydrazone. Alkaline hydrogen peroxide oxidation of moist IV gave V.

Ozonolysis of I in methanol and methylene chloride–methanol gave a yellow oil on solvent evaporation at room temperature. The oil gave a strong hydroperoxide test with lead tetraacetate in methanol.[18] Further reaction of the ozonolysis products with methanol ultimately precipitated a solid material (crude VIII) from which could be obtained the dimethoxy peracetal VIII whose assigned monomeric structure is based on elementary analysis, molecular weight and methoxyl group determinations, negative hydroperoxide test and infrared spectrum.

Alkaline hydrogen peroxide oxidation of this peroxidic oil and crude VIII gave V; V was converted to 1,2-dicarbomethoxyanthraquinone (VI) with diazomethane, to 1,2-anthraquinonedicarboxylic anhydride (VII) with acetic anhydride and to anthraquinone (XI) on fusion with calcium oxide.

Hydriodic acid reduction of this peroxidic oil and crude VIII gave a mixture of products which could be oxidized to V. Vacuum sublimation of this mixture gave 1,2-anthraquinonedicarboxaldehyde (IX) and 1-(or 2)-formyl-2-(1)-anthraquinonecarboxylic acid (X)[19] formulated as the cyclic hydroxyactone[20] since its infrared spectrum showed a strong hydroxyl band at 2.94 $\mu$.

## Experimental

Melting points were determined on a Kofler Micro Melting Point Apparatus. Microanalyses were performed by the Schwarzkopf Microanalytical Laboratory, Woodside, N.Y. The infrared spectra were determined in a Baird Associates infrared recording spectrophotometer, model B, by Dr. Robert L. Wagner, Chas. Pfizer and Co., Inc.

The ozonator used in this research has been described previously.[1e] The rate of gas flow was 50–60 liters per hour. The ozone content of the oxygen stream was determined at the beginning and at the end of each run, and the average value corrected by subtraction of the quantity of ozone appearing in the potassium iodide trap, was used to compute the ozone consumption. Thyodene (Magnus Chemical Co.) was used as an indicator in the iodimetry.[21]

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(14) After this work was submitted for publication, P. G. Copeland, R. E. Dean and D. McNeil [*Chemistry and Industry*, 329 (1959)] reported that on using 15% ozone, an undisclosed reaction temperature and solvent, and decomposing the ozonides by oxidative techniques, I gave 9% of II and benzo[d]diphenic acid (no yields) on absorption of one molar equivalent of ozone. Two molar equivalent absorption of ozone gave 16% of II and 17% of benzo[d]diphenic acid.

(15) One of the referees correctly suggests the possibility that oxygen may be entering into the reaction to some extent by an ozone-initiated autoxidation.

(16) R. Criegee and G. Wenner, *Ann.*, **564**, 9 (1949); R. Criegee and G. Lohaus, *ibid.*, **583**, 6 (1953); R. Criegee, G. Blust and H. Zinke, **87**, 766 (1954); R. Criegee, R. Kerckow and H. Zinke, *ibid.*, **88**, 1878 (1955).

(17) Analogous to that suggested by P. S. Bailey and F. J. Garcia-Sharp, *J. Org. Chem.*, **22**, 1008 (1957), for the explosive monoözonide obtained from the ozonolysis of naphthalene in an inert solvent.

(18) R. Criegee, H. Pilz and P. Flygare, *Ber.*, **72**, 1799 (1939); R. Criegee, *Fortschr. Chem. Forsch.*, **1**, 508 (1950).

(19) Two structural isomers are possible for III and X. Although no assignment has been made, steric considerations would tend to favor the presence of the aldehyde function on carbon 1 of the anthraquinone moiety.

(20) The close proximity of the carbonyl and carboxylic acid moieties in X and in the aldehyde-acid obtained from the ozonolysis of pyrene [M. S. Newman and H. S. Whitehouse, THIS JOURNAL, **71**, 3664 (1949); G. M. Badger, J. E. Campbell, J. W. Cook, R. A. Raphael and A. I. Scott, *J. Chem. Soc.*, 2326 (1950) R. E. Dessy and M. S. Newman, *Org. Syntheses*, **38**, 32 (1958)], and their rigid constraint in their respective positions probably force them into the cyclic, closed-chain structure as depicted in X. In 2′-formyl-2-biphenylcarboxylic acid [P. S. Bailey, THIS JOURNAL, **78**, 3811 (1956)], however, the aldehyde-acid exists in the open-chain structure, probably due to the freedom of rotation of the biphenyl moieties about the pivot bond.

(21) "Basic Manual of Applications and Laboratory Ozonization Techniques," The Welsbach Corporation, Ozone Processes Division, Philadelphia 2, Pa., First Revision, pp. 21–22.

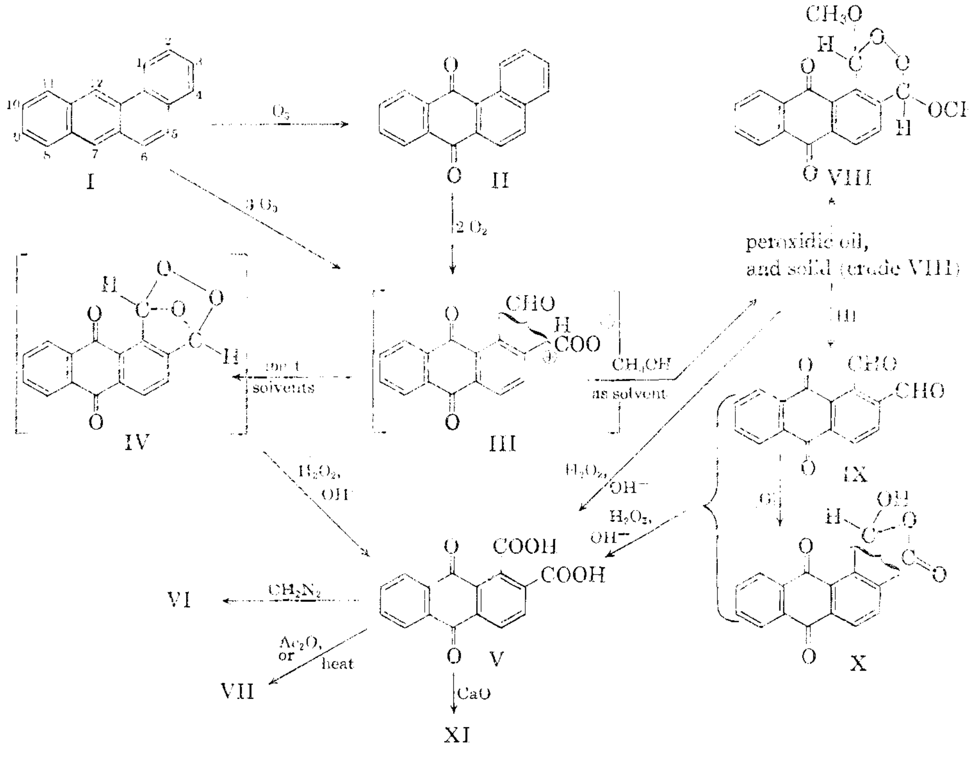
TABLE I

INFRARED ABSORPTION SPECTRA AND ANALYTICAL DATA FOR THE OZONE OXIDATION PRODUCTS OF BENZ[a]ANTHRACENE (I) AND BENZ[a]ANTHRACENE-7,12-DIONE (II)

| | Infrared[a] Wavelength, μ | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | OH | | C=O | | | | | | | |
| | Free | Associated | Substituents in 1- and/or 2-positions | p-Quinonoid | Ring conjugation[f] | Molecular formula | Carbon, % Calcd. | Carbon, % Found | Hydrogen, % Calcd. | Hydrogen, % Found |
| Anthraquinone | | | | 5.96s[e] | 6.26s | | | | | |
| Benz[a]anthracene-7,12-dione (II) | | | | 5.99s | 6.27s | | | | | |
| 1,2-Anthraquinonedicarboxylic acid (V) | 2.92[b] | 3.25–3.50s[c,d]<br>3.82–4.00m[c,d] | 5.78–5.87s[c] | 5.96s | 6.26s | | | | | |
| 1,2-Dicarbomethoxyanthraquinone (VI) | | | 5.77s | 5.95s | 6.28s | | | | | |
| 1,2-Anthraquinonedicarboxylic anhydride (VII) | | | 5.33s, 5.46m, 5.59s | 5.95s | 6.27s | $C_{16}H_6O_5$ | 69.07 | 68.82 | 2.17 | 2.43 |
| 1,2-Anthraquinonedicarboxaldehyde (IX) | | | 5.61s | 5.96s | 6.27s | $C_{16}H_8O_4$ | 72.73 | 72.80 | 3.05 | 3.08 |
| 1-(or 2)-Formyl-2-(1)-anthraquinonecarboxylic acid (X) | 2.94s | | 5.60–5.69s[c] | 5.96s | 6.27s | $C_{16}H_8O_5$ | 68.57 | 68.49,<br>68.97 | 2.88 | 3.27,<br>3.17 |

[a] KBr pellets; band intensities reported as s = strong, m = medium, w = weak. [b] Shoulder. [c] Broad bands. [d] This pattern is characteristic of hydrogen-bonded carboxylic acids.[22a] [e] Our value; Bellamy reports the carbonyl absorption at 5.95 μ.[22b] [f] This aromatic absorption which appears as a weak band at 6.16 μ in both anthracene and I, is considerably enhanced by ring conjugation with carbonyl groups.[22c]

**Reagents.**—Yellow benz[a]anthracene (I) from British Drug Houses, Ltd., Poole, England (U.S. Distributor, The Ealing Corp.), m.p. 153–155°, was twice recrystallized from methanol (charcoal) to yield an almost colorless product, m.p. 158–161°, lit.[23] m.p. 158–159°. The last trace of this yellow-colored impurity could be removed chromatographically over alumina, but this impurity neither depressed the m.p. nor had any adverse effect on the course or yield in the ozonolysis reaction. Yellow benz[a]anthracene-7,12-dione (II), m.p. 169–170°, (Distillation Products Industries No. 5143), was recrystallized once from methanol (charcoal), m.p. 169.5–170.5°; lit. m.p. 166°,[9] 168°.[24] The alumina was Woelms' non-alkaline aluminum oxide, activity grade 1. Fisher Scientific Co. certified grade methylene chloride, carbon tetrachloride and methanol, and reagent grade glacial acetic acid were used as solvents without further treatment.



**Concentration of Reagents.**—In all experiments, 1.14 g. or 2.28 g. of I, and 1.29 g. or 2.58 g. of II, respectively, 5.0

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(22) (a) L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 2nd edit., 1958, p. 163; (b) p. 150; (c) p. 73.

(23) E. Clar, "Aromatische Kohlenwasserstoffe," Springer-Verlag, Berlin, 2nd edit., 1952, p. 186.

(24) K. Dziewonski and E. Ritt, *Bull. intern. acad. Polonaise*, 181 (1927A); *Chem. Abstr.*, **22**, 2561 (1928).

or 10.0 millimoles of each, were dissolved or suspended in a total volume of 150–250 ml. of solvent. The yield of products was the same for either concentration.

**Ozonization of Benz[a]anthracene (I) to Benz[a]anthracene-7,12-dione (II).**—(a) Compound I dissolved in methylene chloride (−70°), 3:1 methylene chloride–methanol (−40 to −70°), or carbon tetrachloride (−20°) was treated with ozone (3.4% by volume) until one molar equivalent had been added. The resulting yellow to orange solution, which was acidic to litmus, was evaporated to dryness at room temperature. The crude material dissolved in the minimum amount of benzene was adsorbed on a 40 × 2.5 cm. alumina-packed column and eluted with 0.5–1.0 liter of benzene. As the elution of the colorless, fluorescent band of unreacted I proceeded, a bright orange zone developed on the column followed by several small zones of brown material. The larger portion of unreacted I was obtained by evaporation of the benzene eluate. In addition, the column was extruded, and the colorless, orange and brown zones separately extracted with benzene. The first (colorless) zone contained additional unreacted I; total recovery of I was 38%. The second zone was washed on a Büchner funnel with benzene and then with ether until the alumina was colorless. The combined filtrates were evaporated on a steam-bath, and after one recrystallization from methanol (charcoal) to remove traces of a red oil, gave 35% of II, m.p. 169–171°. The infrared spectrum of II and an authentic sample were identical and a mixed m.p. showed no depression. A similar extraction of the extruded brown zones with benzene and ether gave, on evaporation, an oil which was oxidized with 30% hydrogen peroxide–sodium hydroxide mixture to yield 5% of 1,2-anthraquinonedicarboxylic acid (V). V (fine needles) starts melting at approximately 221° with gradual formation of the anhydride (VII), as plates, m.p. 320–323°. The melting range of V is difficult to determine; lit.[25] m.p. of V, 267–269°, and its anhydride VII, 319–321°,[25] *vide infra* for oxidation procedure.

(b) Compound I suspended in glacial acetic acid (25°) was treated with one molar equivalent of ozone, at which time solution was complete. Water was added in small portions as solid material gradually precipitated until the appearance of a slight turbidity indicated precipitation of oily by-products. The residue was filtered and twice recrystallized from methanol (charcoal) to yield 22% of the less soluble, unreacted I. The methanolic mother liquors ultimately gave 12% of II, m.p. 169–171°.

Using procedure a, 5.0 millimoles of I was ozonized in 75 ml. of methylene chloride–25 ml. of methanol using 0.5, 1.0 and 1.5 molar equivalents of 0.2, 2.5 and 3.4 volume per cent. ozone. The results are summarized in Table II.

TABLE II

EFFECT OF OZONE CONCENTRATION AND MOLE RATIOS ON YIELDS OF BENZ[a]ANTHRACENE-7,12-DIONE (II) AND 1,2-ANTHRAQUINONEDICARBOXYLIC ACID (V)[a] IN THE OZONIZATION OF BENZ[a]ANTHRACENE (I)

| Ozone concentration vol. % $O_3$ in $O_2$ | Mole ratio ozone:I | Yield, % | | |
|---|---|---|---|---|
| | | Unreacted I recovered | II | V |
| 0 | .. | 100[b] | .. | .. |
| 0.2 | 0.5 | 65 | 18 | 2 |
| 0.2 | 1.0 | 28 | 30 | 8 |
| 2.5 | 0.5 | 70 | 20 | 2 |
| 2.5 | 1.0 | 32 | 35 | 7 |
| 2.5 | 1.5 | 5 | 52[c] | 12 |
| 3.4 | 1.0 | 38 | 35 | 5 |

[a] After alkaline hydrogen peroxide oxidation of by-product oil; see Experimental. [b] After passage of one hundred and twenty liters of oxygen through the solution. [c] After two recrystallizations from methanol to remove a trace of an orange oil which was eluted with this fraction.

**Ozonolysis of I and II to Unstable Ozonide IV.**—Compound I dissolved in methylene chloride (70°) or carbon tetrachloride (−20°) absorbed 3.0 ± 0.2 molar equivalents of ozone. A solid material began to precipitate in the reaction vessel after approximately one molar equivalent of ozone had been added. The end of the reaction was denoted by a color change of the bright orange solution (whose maximum intensity appeared after one molar equivalent of ozone had been added) to a faint yellow-green (due to dissolved ozone) and the sudden appearance of iodine in the potassium iodide trap. The suspension was flushed with nitrogen to free it of excess oxygen and dissolved ozone, and the residue filtered off into a glass frit. The pale green ozonide IV turned yellow on the frit as the solvent evaporated, and brown on further decomposition within 24 hr., even at 0°. This operation should be carried out in a hood behind a shield since the dry ozonide may explode. In other experiments, 1.14 g. of I gave a 68% yield of dry ozonide, decomposing at 134–136°. Generally, moist IV was immediately subjected to further reaction without drying.

Compound II dissolved in methylene chloride (−70°) or carbon tetrachloride (−20°) absorbed 2.0 ± 0.2 molar equivalents of ozone before the ozone began to pass through unabsorbed into the potassium iodide trap. Color changes of the solution during ozonation, ozone uptake, the instability of the dry ozonide, and its decomposition temperature, 134–136°, indicated the same ozonolysis product as obtained in the reaction of I with three molar equivalents of ozone.

Carbon, hydrogen and oxygen analyses of the dry ozonide gave erratic results.

**Glyoxal Formation.**—Compound I in glacial acetic acid was ozonized (three molar equivalents of ozone) in the presence of sulfuric acid and 2,4-dinitrophenylhydrazine[1e,26] to yield a small amount of insoluble material. This material was adsorbed on an alumina column and eluted with chloroform to yield 5–10 mg. of glyoxal 2,4-dinitrophenylhydrazone, m.p. 327–328°; no depression on admixture with an authentic sample.

**Oxidation of Moist IV to 1,2-Anthraquinonedicarboxylic Acid (V).**—The moist ozonide was added directly to a solution of 20 ml. of 10% sodium hydroxide and 20 ml. of 30% hydrogen peroxide contained in a large evaporating dish. A small amount of Dow Corning Corp. Antifoam AF Emulsion was successful in moderating the foam from the vigorous exothermic reaction. The color of the solution turned from pink to orange, and any solid present partly melted and floated atop the solution. At the end of the reaction, any remaining, possibly polymeric material was filtered off, and the filtrate was acidified with concd. hydrochloric acid. The light yellow 1,2-anthraquinonedicarboxylic acid monohydrate began to precipitate on cooling. The yield of anhydrous acid V did not exceed 5% of the theoretical.

Oxidation of moist IV with potassium permanganate in either alkaline or acidic media, or with hydrogen peroxide in acid media led to no isolable V.

**Ozonolysis of I to Liquid 1,2-Methoxyperoxidic Derivatives of Anthraquinone.**—Compound I suspended in methanol (−70°) or dissolved in methylene chloride–methanol (3:1) (−70°) also absorbed three molar equivalents of ozone before iodine began to appear in the potassium iodide absorber trap. No solid formed at the reaction temperature or at room temperature for periods extending to seven days. Partial evaporation also gave no precipitate. Hence the solution was evaporated to dryness to give a yellow oil which gave a strong hydroperoxide test with lead tetraacetate in methanol.[18] The oil did not solidify over a period of one week, and subsequent crystallization attempts from numerous solvents failed to produce a solid. In the early stages of this work, the yellow oil or a concentrated solution of this oil (either the reaction solution was evaporated to 50–60 ml. total volume, or the evaporated oil was dissolved in methanol) was used directly in further oxidation and reduction reactions. Elementary analysis, methoxyl group determination, positive hydroperoxide test and infrared spectrum suggest that this oil is a mixture of monomeric and polymeric methoxy hydroperoxides.[27]

**1,4-Dihydro-1,4-dimethoxyanthra[1,2-d]-*o*-dioxin-7,12-dione (VIII).**—Ultimately a solid methoxylated material was obtained in the following manner; ozonolysis (with, respectively, three or two molar equivalents of ozone) of I or II in 4:1 methylene chloride–methanol was carried out as usual. A few drops of concentrated hydrochloric acid was

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[25] R. Scholl and E. Schwinger, *Ber.*, **44**, 2992 (1911); R. Scholl and R. Neuberger, *Monatsh. Chem.*, **33**, 507 (1912).

[26] B. E. Gordon, F. Wopat, Jr., H. D. Burnham and L. C. Jones, Jr., *Anal. Chem.*, **23**, 1754 (1951).

[27] (a) P. S. Bailey, *J. Org. Chem.*, **22**, 1548 (1957); (b) *Ind. Eng. Chem.*, **50**, 993 (1958).

added to the light yellow solution which immediately darkened slightly, and which now gave a negative hydroperoxide test. The solution was then slowly evaporated to a volume of 30–40 ml. on a hot-plate. Most of the methylene chloride and some of the methanol distilled off. To the warm solution was added 20–30 ml. of methanol and the evaporation was continued to remove all the methylene chloride until crystallization began or until a final volume of 20–30 ml. was reached. A fine, light yellow precipitate, m.p. range 100–148° (crude VIII) with decomposition, formed within 15–20 minutes on standing. This solid material was filtered, suspended in 60 ml. of methanol and refluxed for 30 minutes (not all the solid dissolved). The suspension was cooled, filtered, and this trituration technique was repeated four times; each time the solid residue became lighter in color. Two final recrystallizations from acetone gave VIII as yellow, fluffy needles, m.p. 168–169°, in 8% yield from I; VIII gave a positive active oxygen test with potassium iodide. *Anal.* Calcd. for $C_{18}H_{14}O_6$ (VIII): C, 66.25; H, 4.32; $OCH_3$, 19.01; mol. wt., 326. Found: C, 65.98, H, 4.11; $OCH_3$, 18.42; mol. wt., 300 (Signer-Barger), 236 (Rast). Its infrared spectrum (Nujol) showed the absence of a hydroxyl bands at 5.96 and 6.31μ (Table I, ref. *f*), a methyl ether band at 7.52μ (m), (P. S. Bailey, *loc. cit.*[20]), and medium ether bands at 9.13 and 9.27μ.

**Oxidation of the 1,2-Methoxyperoxidic Oil and Crude VIII to V.**—The peroxidic oil or crude VIII was treated with a solution of 10 ml. of 10% sodium hydroxide and 10 ml. of 30% hydrogen peroxide. Antifoam AF Emulsion (Dow Corning Corp.) was added to ensure smooth oxidation. If the reaction subsided before the bulk of the material was oxidized, additional amounts of the oxidation mixture were added. The color of the solution was pink to orange, and a pink solid, probably the sodium salt of V, sometimes precipitated. After the reaction was completed, most of the precipitate dissolved on warming the solution or on further addition of several ml. of 10% sodium hydroxide. A small amount of an insoluble material (probably unreacted II) was filtered off and the solution acidified with concd. hydrochloric acid. On cooling and after standing for several hours, almost pure V was obtained. Recrystallization from water (1 g. in 250 ml.) or acetone–water, removed traces of inorganic material. On cooling V, recrystallized as the monohydrate in fine silky needles. Drying for 1–2 hours at 105° gave anhydrous V. Yields of V from I and II were, respectively, 30–65% and 65–88% of theory. A solution of V in cold sulfuric acid turned red on boiling[24,25] while the addition of alkaline bisulfite solution to V gave a red vat.[28] Peroxide oxidations in acid media were unsatisfactory. Thus, hydrogen peroxide (30% and 90%) oxidation in acetic acid of the peroxidic oil and crude VIII gave V in only 5–7% yields. Similar oxidations in formic acid and formic–acetic acids[27b] gave equally low yields of V.

**1,2-Dicarbomethoxyanthraquinone** (VI), m.p. 209–210.5°, lit.[25] m.p. 208° from methanol, was quantitatively obtained from V and diazomethane in ethereal solution.

**1,2-Anthraquinonedicarboxylic anhydride** (VII), m.p. 331–331.5°, lit.[29] m.p. 320° (approx.) from nitrobenzene, was obtained by dissolving V in warm acetic anhydride; VII precipitated rapidly and quantitatively from the warm solution in a few minutes.

**Anthraquinone** (XI).—Fusion of V with moist calcium oxide followed by extraction of the sublimate with alkaline bisulfite gave anthraquinone; after one recrystallization from ethanol, m.p. 280–282°, no depression on mixed m.p. with an authentic sample.

**Anthraquinonedicarboxaldehyde (IX) and the Cyclic Hydroxylactone of 1-(or 2)-Formyl-2-(1)-anthraquinonecarboxylic Acid (X).**—The peroxidic oil was dissolved in 50–100 ml. of methanol and the solution added to a mixture of 5 g. of potassium iodide and 5 ml. of glacial acetic acid. Alternatively, this same peroxidic oil was warmed with 47% hydriodic acid (1 ml. of HI per 0.1 g. of oil). In either case, an immediate exothermic reaction began, accompanied by the liberation of iodine. After about 5 min., the reaction subsided and a solution of 1 *N* sodium thiosulfate was added until the iodine color had disappeared. Further addition of water gave a viscous dark brown to dark blue oil (possibly the hydroquinone). The supernatant solution was decanted, and the oil was triturated with 50–60 ml. of methanol. Oily impurities dissolved and a yellow solid appeared. After filtration, this material was boiled in benzene to remove still adhering traces of an oil and, after filtering again, the solid was once recrystallized from acetic acid–water (charcoal to give a yellow-brown mixture (50–60% over-all yield of crude 1,2-anthraquinonedicarboxaldehyde (IX) from I). Vacuum sublimation (bath temp. 180–220°, 10 mm.) of this mixture gave three fractions and a dark brown residue. Each of the three fractions was resublimed: the yellow, resublimed first fraction, dec. 250–300° (sealed tube), analyzed for IX, while the last fraction resublimed, m.p. 245–248.5°, analyzed for X. Analytical and spectral data are summarized in Table I. It is quite possible that X could have been formed as an oxidation product of IX in the working-up procedure. The resublimed middle fraction (probably a mixture of IX and X) and residue were discarded.

In the reduction of crude VIII, the solid was suspended in water (20 ml. of $H_2O$ per 0.1 g. of solid) and gently warmed to 40–50° with 47% hydriodic acid solution (1 ml. of HI per 0.1 g. of solid) for 15–20 min. After standing overnight at room temperature, the solid was filtered off, recrystallized from acetic acid–water (approximately 60% over-all yield of crude IX–X mixture from I) and sublimed as previously described.

Crude IXX m-ixture was oxidized with alkaline hydrogen peroxide to V in approximately 40% over-all yield from I.

## Discussion

Differing views as to the nature of the initial attack of ozone on unsaturated systems[30] either classify ozone: (i) as a double bond reagent[31] assuming a one-step, four-center[4b,32,33] attack on the most olefinic bond (*i.e.*, the bond with the lowest bond localization energy[4b,32] or alternatively (ii) considers the reaction as an electrophilic,[34] two-step[35] attack of ozone at the most reactive centers). Recently Criegee[36] has suggested a possible compromise between these views in noting the probability that step 1 (electrophilic attack) and step 2 (nucleophilic attack) to form "primary ozonides" could occur nearly simultaneously *via* a kind of a four-center reaction.

The reactive centers of anthracene, naphthacene, I, pyrene and dibenz[a,h]anthracene are not associated with the most reactive bonds.[37] The behavior of these hydrocarbons toward ozone might conceivably permit selection of (i) or (ii) as the more probable mechanism. As compiled in Table III, however, the results show an almost even division between alternatives. Ozone attacks predominantly[38] the most reactive (conjugate) posi-

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[28] E. H. Rodd, "Chemistry of Carbon Compounds," Vol. IIIB, Elsevier Press, New York, N. Y., 1957, p. 1381.

[29] A. Fairbourne, *J. Chem. Soc.*, 1573 (1921).

[30] For a discussion of these mechanisms, see P. S. Bailey, *Chem. Revs.*, **58**, 925 (1958).

[31] G. M. Badger, *Quart. Revs.*, **5**, 155 (1951).

[32] R. D. Brown, *ibid.*, **6**, 63 (1952).

[33] A. Maggiolo, "Organic Ozone Reactions and Techniques," The Welsbach Corporation, Ozone Processes Division, Philadelphia 2, Pa., pp. 5, 9; E. A. Blair and A. Maggiolo, "Reactions of Ozone. Nature of the Initial Attack of Ozone on Olefins as Elucidated by Steric Considerations," Abstracts of Papers, p. 6-P, 134th American Chemical Society Meeting, Chicago, Ill., September 7–12, 1958. A preprint of this paper is gratefully acknowledged.

[34] (a) J. P. Wibaut and L. W. F. Kampschmidt, *Konikl. Ned. Akad. Wetenschap.*, **53**, 1109 (1950); (b) J. P. Wibaut, F. J. L. Sixma, L. W. F. Kampschmidt and H. Boer, *Rec. trav. chim.*, **69**, 1355 (1950); (c) F. J. L. Sixma, H. Boer and J. P. Wibaut, *ibid.*, **70**, 1005 (1951); (d) J. P. Wibaut and F. J. L. Sixma, *ibid.*, **71**, 761 (1952).

[35] (a) P. S. Bailey and J. B. Ashton, *J. Org. Chem.*, **22**, 98 (1957); (b) P. S. Bailey, *Chemistry & Industry*, 1148 (1957).

[36] R. Criegee, *Record Chem. Progr., Kresge-Hooker Sci. Lib.* **18**, 111 (1957).

[37] See appropriate section in ref. 23.

[38] The positions of predominant ozone attack on these aromatic systems are based on products isolated. Since the yields are never quantitative, the positions noted are obviously not the sole positions of attack.

tions in anthracene,[11,5a] naphthacene,[1a] and I,[1b] and the most reactive bonds in pyrene[20,39] and dibenz[a,h]anthracene.[1c]

The positions of predominant ozone attack, however, can be correlated with the oxidation–reduction potential of the quinone–hydroquinone systems involving the positions in question. These potentials may be taken as a measure of the stability of a dihydro compound (quinone structure) relative to the parent hydrocarbon (hydroquinone structure). Table III compares the potentials measured for the *o*- and *p*-quinones with the positions of predominant ozone oxidation, and shows that the positions of lowest corrected oxidation–reduction potential (*i.e.*, the most stable of all possible dihydro structures) are the ones that are predominantly oxygenated.[40] This correlation supports the view that initial ozone attack involves, in the rate-controlling step, a transition state whose geometry corresponds to the most stable dihydro compound.

TABLE III

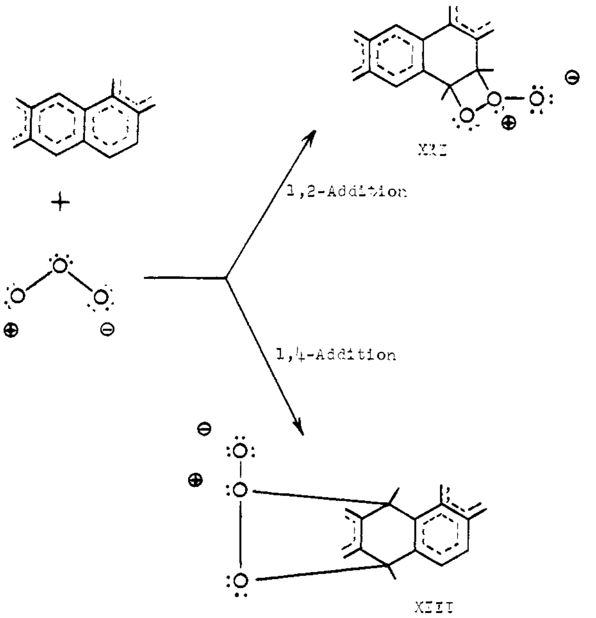
MOST REACTIVE POSITIONS AND BONDS IN POLYCYCLIC AROMATICS[37]; OXIDATION–REDUCTION POTENTIALS OF *o*- AND *p*-QUINONES[a]

| Aromatic compound[b] | Most reactive positions | Most reactive bond | Oxidation–reduction potentials[d] Positions | Corrected $E_0$ in volts[e] | Positions of predominant ozone attack[38] |
|---|---|---|---|---|---|
| Naphthalene | 1,2 | 1,2 | 1,2 | 0.501 | 1,2[i] |
| | | | 1,4 | .534 | |
| Anthracene | 9,10 | 1,2 | 9,10 | .254 | 9,10[11,35] |
| | | | 1,2 | .415 | |
| | | | 1,4 | .451 | |
| Phenanthrene | 9,10 | 9,10 | 9,10 | .410 | 9,10[1d,1e] |
| | | | 1,2 | .585 | |
| | | | 1,4 | .598 | |
| | | | 3,4 | .571 | |
| Benz[a]anthracene (I) | 7,12 | 5,6 | 7,12 | .353 | 7,12[1b] |
| | | | 5,6 | .380 | |
| Chrysene | 6 | 5,6 | 5,6 | .440 | 5,6[14] |
| | | | 6,12 | .442[f] | |
| Dibenz[a,h]-anthracene | 7,14 | 5,6 | 7,14 | .418 | 5,6[1c] |
| Pyrene | 1,3,6,8 | 4,5 | 4,5 | .424[g] | 4,5[20,39] |
| | | | 1,8 | .664[f,j] | |
| | | | 1,6 | .666[f,j] | |
| Naphthacene | 5,12 | ..[c] | 5,12 | −.215[h] | 5,12[1a] |

[a] Data from L. F. Fieser in H. Gilman's "Organic Chemistry," Vol. 1, 2nd edit., John Wiley and Sons, Inc., N.Y., 1945, p. 159, unless otherwise stated. [b] The *C.A.* numbering system is employed. [c] No bond reaction data is available but probably the 1,2-bond. [d] Measured in alcoholic solution. [e] For the method and significance of correction see G. E. K. Branch and M. Calvin, "The Theory of Organic Chemistry," Prentice-Hall, Inc., New York, N. Y., p. 303 et seq., and G. M. Badger, "Structure and Reactions of the Aromatic Compounds," University Press, Cambridge, 1954, pp. 87–96. [f] Not an *o*- or *p*-quinone and in this sense may be inadmissible for comparison with such quinones. [g] Data from G. M. Badger and H. A. McKenzie, *Nature*, **172**, 485 (1953). [h] Corrected oxidation-reduction potential from E. Clar's calculated value (ref. 23, p. 38). [i] L. Seekles, *Rec. trav. chim.*, **42**, 706 (1923); L. W. Kampschmidt and J. P. Wibaut, *ibid.*, **73**, 431 (1954). [j] Unpublished information, E. J. Moriconi, W. F. O'Connor and N. O. Smith.

In the absence of relevant kinetic data, a definite selection among mechanisms i, ii or Criegee's compromise is still not possible. However, we favor the view that ozone attacks unsubstituted polycyclic aromatics predominantly in a 1,2- or 1,4-addition to the *o*- or *p*-carbon atoms whose corresponding dihydro structure is most stable. It does this most probably *via* Criegee's mechanism.[36] Further, within the framework of this mechanism, we prefer the second step, nucleophilic attack on the carbonium ion to occur with the central oxygen atom to give, respectively, primary ozonides XII and XIII. Although the alternative five-membered ring structures cannot be ruled out, XIII has at least its structural precedent in transannular photoöxides and maleic anhydride adducts of polynuclear aromatic hydrocarbons.

Bailey was the first to suggest the possibility of 1,4-addition of ozone to anthracene[35a] and 2,5-diphenylfuran.[41] Although he offered structure XIII as a possible alternative to his two-step, π-complex mechanism in such 1,4-additions of ozone to *aromatic* systems,[30,35a,41] he seemingly eliminated structure XII as the initial intermediate of 1,2-addition of ozone[35b] in view of the preferential course of the ozonolysis of unsymmetrical *olefins*.[42] The obvious difference in character of both systems (even to ease of ozonolysis[30]) suggest to us that it is much more likely that different mechanisms are operative in the two systems.



Prediction, based on oxidation–reduction potentials, that the 5,6-bond of chrysene and the 5,12-positions of naphthacene should show reactivity toward ozone has been most recently substantiated.[1a,14] Further, the order of decreasing ease of ozonolysis for unsubstituted, aromatic systems can now be qualitatively reassessed *via* these oxidation–reduction potentials and expanded to: naphthacene (*p*-, −0.215 v.) > anthracene (*p*-, 0.254 v.) > I (*p*-, 0.353 v.) > phenanthrene (*o*-, 0.410 v.) ≃ dibenz[a,h]anthracene (*o*-, <0.418 v. >0.343 v.) > pyrene

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(39) H. Vollman, H. Becker, M. Corell and H. Streeck, *Ann.*, **531**, 65 (1937); H. Vollman and H. Becker, U. S. Patent 2,127,096, Aug. 16, 1938; L. F. Fieser and F. C. Novello, THIS JOURNAL, **62**, 1855 (1940).

(40) G. M. Badger (ref. 31) has previously pointed out the correlation between bond order or bond localization energy in aromatic systems, and the oxidation–reduction potential of the corresponding *o*-quinone.

(41) P. S. Bailey and H. O. Colomb, Jr., THIS JOURNAL, **79**, 4238 (1957).

(42) P. S. Bailey and S. S. Bath, *ibid.*, **79**, 3120 (1957).

(*o*-, 0.424 v.) > naphthalene (*o*-, 0.501 v.) > benzene (*o*-, 0.71 v.).

To summarize: The observed correlation of oxidation–reduction potentials with both the ease and position of ozone attack does offer for the first time, a reasonably consistent explanation why ozone adds *predominantly* 1,4- to some aromatic compounds and *predominantly* 1,2- to others.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, FORDHAM UNIVERSITY]

# Intramolecular Hydrogen Bonding of *vic*-Diols in Cyclic Systems. II.[1] OH···O and OH··· π-Electron Bonding in *cis*- and *trans*-1,2-Diaryl-1,2-acenaphthenediols[2]

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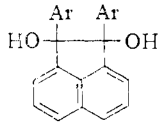
The syntheses and intramolecularly bonded OH absorption frequencies (3μ region) of a series of *cis*- and *trans*-1,2-diaryl-1,2-acenaphthenediols are reported in which the 1,2-aryl substituents vary in bulk and electronic effect [Aryl = H (I), phenyl (Ia), 4-methylphenyl (Ib), 2,4-dimethylphenyl (Ic), 2,4,6-trimethylphenyl (Id), and α-naphthyl (Ie)]. In both *cis*- and *trans*-diols, the higher frequency band (3584–3600 cm.$^{-1}$) is assigned to a weak OH · · · π bond to the naphthalene ring of the acenaphthene system. The lower frequency band (3512–3542 cm.$^{-1}$) in the *cis*-diols, and the 3544 cm.$^{-1}$ band in *trans*-Ie diol are assigned to a stronger OH · · · O bond between *vic*-OH groups. In the aryl substituted *trans*-diols, the intermediate frequency band (3549–3574 cm.$^{-1}$) is assigned to a OH · · · π electron bond to the aromatic ring of the aryl substituent situated on the adjacent carbon atom.

## Introduction

In the first paper of this series,[1] it was found that shifts in the fundamental OH vibrational frequency[3] (3μ region) of a series of *cis*- and *trans*-9,10-diaryl-9,10-dihydro-9,10-phenanthrenediols in which the 9,10-diaryl substituents varied in bulk and electronic effects could be interpreted in terms of the non-bonded steric effects of the aryl substituents upon the O–C–C angles at the 9,10-positions.

This paper records and interprets the Δν(OH) measurements of a series of similarly substituted *cis*- and *trans*-1,2-diaryl-1,2-acenaphthenediols.



I, Ar = H
Ia, Ar = phenyl
Ib, Ar = 4-methylphenyl (*p*-tolyl)
Ic, Ar = 2,4-dimethylphenyl (*m*-xylyl)
Id, Ar = 2,4,6-trimethylphenyl (mesityl)
Ie, Ar = α-naphthyl

The aryl-substituted *trans*-diols were prepared by a Grignard reaction[7–10,22] on acenaphthenequinone (Table I). The congruent *cis*-diols (*cis*-Ia,Ib,Ic,Ie) were synthesized by a magnesium–magnesium iodide,[10–13] or zinc dust–potassium hydroxide[9,11] reduction of the appropriate 1,8-diaroylnaphthalene (Table II) which in turn had been prepared by a lead tetraacetate or potassium dichromate oxidation of the corresponding *trans*-diol (Table III). Unlike their analogs in the phenanthrenediol series,[1,11,12] these methods of syntheses are unequivocal in that the appropriate technique gave only a single isolable isomer.[7,13] We were unable to prepare *cis*-Id diol since all attempts to obtain the intermediate 1,8-di-(2,4,6-trimethylbenzoyl)-naphthalene (IId) by either the oxidation of *trans*-Id diol or the Friedel–Crafts aroylation of mesitylene with naphthalic anhydride were unsuccessful. *cis*-1,2-Acenaphthenediol (*cis*-I) was prepared both by the catalytic hydrogenation of acenaphthenequinone[14] and selenium dioxide oxidation of acenaphthene,[15] while a lithium aluminum hydride reduction of acenaphthenequinone gave *trans*-1,2-acenaphthenediol (*trans*-I)[16] accompanied by a small amount of *cis*-I.

## Experimental

Melting points are uncorrected. Microanalyses were performed by the Schwarzkopf Microanalytical Laboratory, Woodside, N.Y. Δν(OH) measurements were made with a

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[1] Part I, E. J. Moriconi, F. T. Wallenberger, L. P. Kuhn and W. F. O'Connor, *J. Org. Chem.*, **22**, 1651 (1957).

[2] Presented in part at the Meeting-in-Miniature Metropolitan Long Island Subsection, American Chemical Society, New York Section, March, 1958, and at the 134th Meeting of the American Chemical Society, Chicago, Ill., September, 1958.

[3] These concentration independent Δν(OH) values (in cm.$^{-1}$) are a direct measure of intramolecular hydrogen bond strength between *vic*-OH groups; see L. P. Kuhn[4–6] for a detailed account of the relationship between molecular structure and intramolecular hydrogen bond formation as measured by Δν(OH) values.

[4] L. P. Kuhn, THIS JOURNAL, **74**, 2492 (1952).

[5] L. P. Kuhn, *ibid.*, **76**, 4323 (1954).

[6] L. P. Kuhn, *ibid.*, **80**, 5950 (1958).

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[10] (a) P. D. Bartlett and R. F. Brown, *ibid.*, **62**, 2927 (1940); (b) R. F. Brown, *ibid.*, **76**, 1279 (1954).

[11] M. Gomberg and W. E. Bachmann, *ibid.*, **49**, 236 (1927); W. E. Bachmann, *ibid.*, **54**, 1969 (1932).

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[14] K. M. Jack and H. G. Rule, *J. Chem. Soc.*, 188 (1938).

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