β-Lactam Formation.—The β-lactam cyclization was carried out by the procedure of Sheehan and Hoff[5] using thionyl chloride in methylene chloride as the cyclizing agent. The thiazolidineacetates (III) were used for cyclization in the condition in which they were isolated from the hydrohalogenolysis reaction. Non-crystalline hydrochlorides cyclized just as well as their crystalline counterparts. The optimum reaction time at reflux temperature as set forth in Table III was determined from the yields of β-lactam after individual cyclization reactions had proceeded for varying periods of time. After working up the reactions by the Sheehan and Hoff[5] procedure, the products were obtained in benzene solution. This solution was shell-frozen and lyophilized to remove the solvent. A few products crystallized directly from the benzene and lyophilization was unnecessary. Such cases are noted by footnotes to Table III. All lyophilized products were obtained as fluffy yellow powders. The β-lactam content of these powders was always assessed by infrared analysis and the products showing little or no absorption at 5.5–5.6 μ were discarded. Chromatographic adsorption on alumina as described by Sheehan and Hoff was not necessary for preparative work. However, it was convenient to use chromatography to achieve the initial purification necessary to obtain seed crystals of new β-lactam preparations. Yield, crystallization solvents and analyses are reported in Table III.

Catalytic Hydrogenolysis of the Benzyl Esters and Formation of N-Ethylpiperidine Salts of the Penicillanic Acids (V).—A suspension of 2 g. of 10% palladium-on-carbon (Norite) catalyst in 100 ml. of purified dioxane was saturated with hydrogen at atmospheric pressure and 25°. To this suspension was then added 0.0025 mole of the benzyl ester IV and the hydrogenation was continued under the same conditions. The theoretical quantity of hydrogen was absorbed in about 2 hours and the reduction ceased. After removal of the catalyst by filtration, 0.283 g. (0.0025 mole) of N-ethylpiperidine was added to the filtrate. Concentration of the solution was carried out under vacuum with a bath temperature not exceeding 25°. Crystallization commenced when the volume was reduced to 5–10 ml. The products were collected and washed with cold dioxane.

For the diaminophenyl analog (V, R = 2,4-$(H_2N)_2C_6H_3$) the hydrogenolysis and reduction of the nitro groups were carried out using the same conditions and relative quantities of reagents as described in the preceding paragraph. However, after removal of the catalyst, no N-ethylpiperidine was added. The dioxane solution was shell-frozen and lyophilized and the product was obtained as a yellow, neutral powder. Yields and analyses are shown in Table IV.

WEST POINT, PA.
CAMBRIDGE, MASS.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF FORDHAM UNIVERSITY]

Ozonolysis of Polycyclic Aromatics. VII.[1] Dibenz[a,h]anthracene[2,3]

BY EMIL J. MORICONI, WILLIAM F. O'CONNOR, WILLIAM J. SCHMITT, GEORGE W. COGSWELL AND BRUNO P. FÜRER

RECEIVED OCTOBER 23, 1959

Corrected oxidation–reduction potentials for dibenz[*a,h*]anthracene-7,14-dione and dibenz[*a,h*]anthracene-5,6-dione are, respectively, 0.418 v. and 0.381 v. As previously suggested by us, ozone should therefore predominantly attack the 5,6-bond in dibenz[*a,h*]anthracene (I). Compound I, on absorption of one and two molar equivalents of ozone, yields, respectively, unstable, probably monomeric 5,6-ozonide Ia and stable, dimeric 5,6,12,13-diozonide Ib in inert solvents, and, respectively, monomeric, dimethoxy peroxide II and probably polymeric, tetramethoxy peroxide VIII in methanol solvent. Oxidation of Ia and II, and Ib and VIII gave, respectively, 2-(*o*-carboxyphenyl)-3-phenanthrene carboxylic acid (IV) and *p*-terphenyl-2,2′,5′,2″-tetracarboxylic acid (X). Reduction of Ia and II, and VIII, gave, respectively, 2-(*o*-formylphenyl)-3-phenanthrenecarboxaldehyde, and *p*-terphenyl-2,2′,5′,2″-tetracarboxaldehyde. The dimethyl ester V of IV was converted to X *via* 2-(*o*-carbomethoxyphenyl)-3-carbomethoxy-9,10-phenanthrenequinone (VII).

In several recent publications,[1,4a,4b] we have noted that the positions of *predominant* ozone attack on polycyclic aromatic hydrocarbons correspond to those of the *o*- or *p*-quinone with the lowest corrected quinone–hydroquinone oxidation–reduction potential (*i.e.*, those positions yielding the most stable of all possible dihydro structures).[5] Thus, for example, corrected oxidation–reduction potentials for benz[*a*]anthracene-7,12- and -5,6-dione are, respectively, 0.353 and 0.380 v. Reaction of benz[*a*]anthracene with one molar equivalent of ozone in methylene chloride, carbon tetrachloride and methylene chloride–methanol afforded a 64% yield of the 7,12-dione based on the amount of benz[*a*]anthracene utilized.[1,4b] Thus *predominant* ozone attack on benz[*a*]anthracene occurred at those positions (7,12-) whose corresponding quinone had the lowest oxidation–reduction potential.

In dibenz[*a,h*]anthracene (DBA = I), molecular orbital calculations predict the 7- and 14-carbon atoms to have the lowest carbon localization energies[6a,9] (reactivity numbers),[6b] the 7,14-positions to have the lowest *p*-localization energy,[7,10] and the 5,6-bond to have the lowest bond localization energy[7] (*o*-localization energy).[6a] Chemical

---

(1) Part VI, E. J. Moriconi, W. F. O'Connor and F. T. Wallenberger, THIS JOURNAL, **81**, 6466 (1959).

(2) For a preliminary report on part of this work see E. J. Moriconi, G. W. Cogswell, W. J. Schmitt and W. F. O'Connor, *Chemistry & Industry*, 1591 (1958).

(3) Presented in part at The Meeting-in-Miniature of The Metropolitan Long Island Subsection, American Chemical Society, New York Section, March, 1959, and at The Symposium on Ozone Chemistry, 136th National Meeting of The American Chemical Society, Atlantic City, N. J., Sept., 1959.

(4) (a) E. J. Moriconi, W. F. O'Connor and L. B. Taranko, *Arch. Biochem. and Biophys.*, **83**, 283 (1959); (b) E. J. Moriconi, W. F. O'Connor and F. T. Wallenberger, *Chemistry & Industry*, 22 (1959).

(5) This correlation is especially pertinent to those polycyclics whose most reactive positions are not the termini of the most reactive bond. The most reactive carbon atoms theoretically have the lowest carbon localization energy[6] and, experimentally, are the positions at which electrophilic, nucleophilic and radical substitution occurs; the most reactive bond has the lowest bond localization energy[6a,7] and is the site of attack by bond reagents, osmium tetroxide and diazoacetic ester.[8] Relevant polycyclic aromatics which have been ozonized include anthracene, naphthacene, benz[*a*]anthracene, pyrene and dibenz[*a,h*]anthracene.

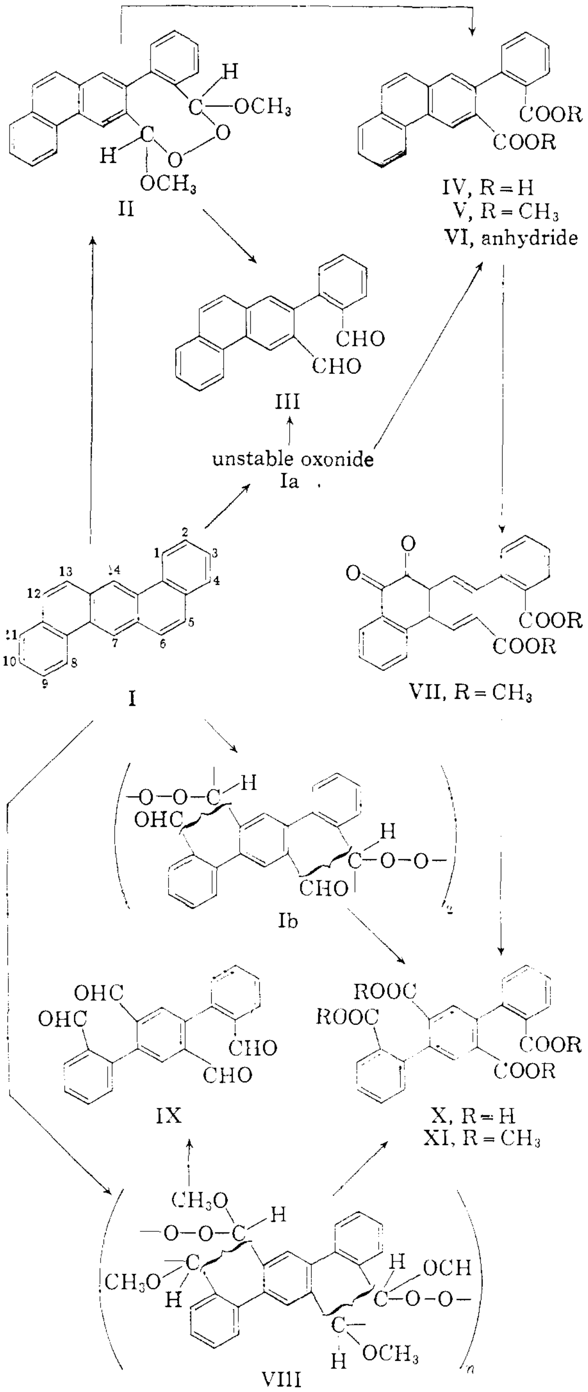
(6) (a) M. J. S. Dewar, THIS JOURNAL, **74**, 3357 (1952); (b) M. J. S. Dewar, *Record Chem. Progr. Kresge–Hooker Sci. Lib.*, **19**, 1 (1958).

(7) R. D. Brown, *J. Chem. Soc.*, 691, 3249 (1950); *Quart Revs.*, **6**, 63 (1952).

(8) G. M. Badger, *ibid.*, **5**, 147 (1951).

(9) G. W. Wheland, THIS JOURNAL, **64**, 900 (1942).

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



evidence at least qualitatively supports this theory of chemical reactivity based on these three theoretical indices.[11]

A preliminary report[2] showed that I in methylene chloride–methanol absorbed two moles of ozone per mole of I to give predominantly the 5,6- and 12,13-bond cleavage products. It was then predicted[1] that the corrected oxidation–reduction potential for DBA-5,6-dione would be lower than that for DBA-7,14-dione (0.418 v.)[16] and greater than 0.353 v. (for benz[*a*]anthracene-7,12-dione). We have since determined the corrected oxidation–reduction potential for DBA-5,6-dione to be 0.393 v.[17]

The present paper records the experimental details of the ozonization of I with one and two molar equivalents of ozone, in both inert and reactive solvents, and further discusses the course of initial attack of ozone on unsubstituted aromatic systems.

Experimental

Melting points were determined on a Kofler micro melting point apparatus unless otherwise stated. Capillary melting points are all corrected. Microanalyses were performed by The Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. The infrared spectra (KBr pellet, unless otherwise stated) were determined in a Baird Associates infrared recording spectrophotometer, model B, by Dr. Robert L. Wagner, Chas. Pfizer and Co., Inc., or a Perkin-Elmer model 21 spectrophotometer, by Mr. Joseph Tesar. Intensities are reported by the letters s (strong), m (medium) and w (weak) which follow the wave length in microns. The ozonator, ozonolysis flasks and ozonolysis procedure were as described in previous publications.[1]

The DBA (I) (m.p. 258–260°) was supplied by L. Light and Co., Ltd., Colnbrook, Bucks, England. The yellow-green color of this material which is due to other pentacyclic impurities[18] could be removed by recrystallization from benzene or selective oxidation with lead tetraacetate in acetic acid[19,20] to give colorless long plates or fine powder of DBA, m.p. 266–267° (lit.[21] m.p. 262°), in 60–70% yield. The high cost of I and the fact that in most biochemical studies the yellow-green material is used without further purification led us to use this material directly. The alumina was Woelm non-alkaline aluminum oxide, activity grade 1 unless otherwise specified. Fisher Scientific Co. certified grade methylene chloride, carbon tetrachloride and methanol were used as solvents and dried by conventional means. The solubility of I in chloroform and carbon tetrachloride is considerably lower than in methylene chloride (11.2 g. of I per liter of methylene chloride); I is virtually insoluble in methanol.

Ozonolysis of I to Unstable 5,6-Ozonide Ia.—Compound I (2.78 g., 10.0 mmoles) dissolved in 500 ml. of dry methylene chloride (solution effected by stirring for 15 min. at room temperature) was treated with ozone (3.4% by volume) at −60 to −70° until one molar equivalent had been added. Many unsuccessful attempts were made to isolate the initial reaction product, presumably the ozonide. The mixture was evaporated to dryness at room temperature with an air blast to yield a light yellow residue which darkened rapidly on standing in air. This crude material was stirred in 100 ml. of methyl ethyl ketone (MEK) for 0.5 hour at

---

[11] Thus I undergoes substitution to form 7-nitro-DBA, and DBAnthranyl-7-pyridinium bromide,[12a] and addition to form 7,14-disodio-(dilithio)-7,14-dihydro-DBA.[13] 7,14-dihydro-DBA[12b,13] and DBA-7,14-*endo*-α,β-succinic acid.[12a] Further chromic acid oxidation leads to DBA-7,14-dione,[14] and reaction with osmium tetroxide yields *cis*-5,6-dihydro-5,6-DBAnthracenediol.[15]

[12] (a) J. W. Cook, *J. Chem. Soc.*, 3273 (1931); (b) 1594 (1933).

[13] W. E. Bachmann, *J. Org. Chem.*, **1**, 347 (1936).

[14] F. Weitzenböck, F. Klinger, *Monatsh. Chem.*, **39**, 315 (1911); E. Clar, *Ber.*, **62**, 350 (1929); J. Cason and L. F. Fieser, This Journal, **62**, 2681 (1940).

[15] (a) J. W. Cook and R. Schoental, *J. Chem. Soc.*, 170 (1948); (b) E. F. M. Stephenson, *ibid.*, 2620 (1949); (c) P. M. Bhargava, H. I. Hadler and C. Heidelberger, This Journal, **77**, 2877 (1955).

[16] The actual measured potential is 0.268 v.; L. F. Fieser and E. M. Dietz, *ibid.*, **53**, 1128 (1931). For the method and significance of the correction see G. E. K. Branch and M. Calvin, "The Theory of Organic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1941, pp. 303–314, and G. M. Badger, "Structure and Reactions of the Aromatic Compounds," University Press, Cambridge, 1954, pp. 87–96.

[17] The measured potential was 0.443 v. [E. J. Moriconi, N. O. Smith and W. F. O'Connor, unpublished information].

[18] J. W. Cook, *Proc. Roy. Soc.* (*London*), **B111**, 455 (1932).

[19] L. F. Fieser and E. B. Hershberg, This Journal, **60**, 1893 (1938).

[20] C. Heidelberger, P. Brewer and W. G. Dauben, *ibid.*, **69**, 1389 (1947).

[21] E. Clar, "Aromatische Kohlenwasserstoffe," Springer-Verlag. Berlin, 1952, p. 198.

room temperature, the mixture was filtered (filter paper since glass-frit filter funnels caused an immediate decomposition of the ozonide), and the filtrate poured into 100 ml. of 30–60° petroleum ether. Peroxidic material precipitated immediately. After refrigeration overnight, the white residue was filtered, recrystallized six to ten times from benzene–petroleum ether (30–60°), followed by a last, anhydrous ether wash to yield an amorphous powder, m.p. 162–163°. This material, probably monomeric ozonide Ia, showed strong carbonyl bands (Nujol) immediately after the last filtration, presumably from aldehydic decomposition products; Ia darkened within 30–60 minutes, even in vacuum, under nitrogen, in the cold, protected against light. Other recrystallizing solvents, such as toluene, acetone, chloroform, carbon tetrachloride and methanol did not prevent decomposition. The unstable ozonide (2.0 g., 61% yield) gave a negative hydroperoxide test,[22] a positive active oxygen test with sodium iodide,[23] and erratic carbon, hydrogen and oxygen analyses.

The MEK-insoluble material dissolved in hot 1:1 benzene–acetic acid, on cooling, gave 0.43 g. (15% recovery) of crude I, m.p. 250–255°.

Generally, the dry light-yellow, crude ozonide was immediately subjected to further reaction without purification.

Oxidation of Ia to 2-(*o*-Carboxyphenyl)-3-phenanthrenecarboxylic Acid (IV).—Crude Ia from 10.0 mmoles of I was suspended in 300 ml. of methanol, the mixture was made alkaline with 20–30 ml. of 20% sodium hydroxide, and 100 ml. of 30% hydrogen peroxide was added over a period of about one hour. The vigorous exothermic reaction was controlled with an ice-bath. After the exothermic reaction had subsided, the mixture was refluxed until no more reaction bubbles were evident; the hot solution was then filtered, and the residue washed with 50 ml. of hot water. The combined filtrates were carefully acidified with 20% hydrochloric acid to *p*H 4.5 (Hydrion), filtered again, and the filtrate acidified to *p*H 2.0 to precipitate fairly pure acid IV. This material was redissolved in hot 10% sodium bicarbonate solution, and the solution was successively charcoaled, filtered and re-acidified to yield a white powder, which on trituration with cold acetone gave pure white IV, m.p. 317–318° (capillary) after drying at 100° (3–5 mm.) (lit.[15b,c,24] m.p. 317–318) in 45% yield (1.55 g.); infrared spectrum: 2.93–3.00(m)[25] (free OH), 3.30–3.50(s)[26,27] (associated OH), and 5.90–5.95(s)[26] ($C{=}O$).

2-(*o*-Carbomethoxyphenyl)-3-carbomethoxyphenanthrene (V), m.p. 146.5–147.5°, as white rhombic crystals from methanol, was obtained in 50% yield by treating IV in anhyd. ether–methanol (1 g. of IV per 15 ml. of methanol and 17 ml. of ether) with an ethereal solution of diazomethane; infrared spectrum: 5.79(s) ($C{=}O$).

Anal. Calcd. for $C_{24}H_{18}O$: C, 77.82; H, 4.90. Found: C, 78.03; H, 4.94.

2-Phenylphenanthrene-3,2-dicarboxylic anhydride (VI), m.p. 263–265° (capillary), lit.[28] m.p. 257–259°, as small white needles from acetic anhydride, was obtained in 82% yield by dissolving IV in hot acetic anhydride; VI precipitated on cooling, and was recrystallized four times from acetic anhydride (charcoal); infrared spectrum: 5.69(s) and 5.79(s) ($C{=}O$'s).

Anal. Calcd. for $C_{22}H_{12}O_3$: C, 81.47; H, 3.73. Found: C, 81.62; H, 3.60.

5,8-Dihydro-5,8-dimethoxybenzo[*d*]phenanthro[2,3-*f*]-[1,2]dioxocin (II).—Compound I (2.78 g., 10.0 mmoles) first dissolved in 500 ml. of dry methylene chloride followed by the addition of 40–50 ml. of anhydrous methanol, was treated with ozone at −60 to −70° until one molar equivalent had been added. The color of the solution changed from pale green to pale yellow. No precipitation occurred on addition of the one molar equivalent of ozone and the solution gave a positive hydroperoxide test with lead tetraacetate.[22] On addition of a few drops of concentrated hydrochloric acid, the light yellow solution darkened slightly and now the hydroperoxide test was negative. About 200 ml. of methanol was added to the solution, and the methylene chloride–methanol solvent exchange was accomplished by slowly evaporating on a hot-plate for 3 to 4 hours, maintaining constant volume by the addition of further amounts of methanol. Finally, the solution was evaporated to a total volume of about 300 ml., at which time a fine yellow precipitate, m.p. 195–198° (1.95 g., 52%), of crude II appeared. This material was treated with 70–100 ml. of anhyd. ether (shaking for 0.5 hour), the mixture was filtered, and the filtrate was refrigerated for 4 days. After 2 or 3 days, the white, flaky precipitate of pure II appeared; yield 0.60 g. (16%), m.p. 203–204° (dried over P_2O_5 at 70–100° (3–5 mm.)); infrared spectrum (Nujol): absence of $C{=}O$ band; 7.56(m) (methyl ether),[29] and 9.13(s), 9.26(s) (ether).[30a,31] The ethyl ether-insoluble residue afforded a 20% yield of unreacted I.

Anal. Calcd. for $C_{24}H_{20}O_4$: C, 77.40; H, 5.41; O, 17.19; OCH_3, 16.66; mol. wt., 372. Found: C, 77.31; H, 5.71: O, 16.84; OCH_3, 15.39; mol. wt., 356 (Signer–Barger).

Alkaline hydrogen peroxide oxidation of II gave IV in 70% yield.

2 - (*o* - Formylphenyl) - 3 - phenanthrenecarboxaldehyde (III) could be prepared from I, Ia and II. The procedure which gave the highest yield was: Compound I (10.0 mmoles) was ozonized as in the preparation of II. To the cold reaction mixture was added 7.5 g. of sodium iodide and 8 ml. of glacial acetic acid. After the initially exothermic reaction had subsided (iodine liberated), the reaction was permitted to stand 0.5 hour with occasional stirring at room temperature. The liberated iodine was then reduced with excess 10% sodium thiosulfate solution. Vigorous stirring is required because of the two-phase system. The two layers were separated, and the methylene chloride solution was evaporated to dryness leaving brownish-yellow, crude III. Ten recrystallizations from 70% ethanol (charcoal) gave 1.30 g. (42%) of III, m.p. 157–158°, creamy white plates; infrared spectrum: 5.89(s) ($C{=}O$).[32]

Anal. Calcd. for $C_{22}H_{14}O_2$: C, 85.14; H, 4.55. Found: C, 85.31; H, 4.37.

Ozonolysis of I to 5,6,12,13-DBA-Diozonide (Ib).—Compound I (10.0 mmoles) dissolved in 500 ml. of dry methylene chloride absorbed slightly more than two molar equivalents of ozone (2.14) before iodine appeared in the potassium iodide trap and the blue-green color of the ozonolysis solution indicated it to be saturated with ozone. The crude ozonide precipitates during the addition of the second molar equivalent of ozone. A hydroperoxide test on the mother liquor and on the white ozonide (in acetic acid) was negative. The suspension was filtered on a medium frit funnel (*ca.* 1 hour), and while still wet, washed with 50 ml. of 2:1 anhydrous petroleum ether (30–60°)–ether. This ether wash is necessary to ensure a non-gummy product. The crude product (3.50 g., 94%), m.p. 120–137°, was treated with MEK, filtered, and the filtrate treated with 4:1 anhydrous (30–60°) petroleum ether–ether. On standing for 1–2 hours at 0°, the ozonide reprecipitated. This procedure of solution in MEK, filtration from any insoluble material and reprecipitation with ether was repeated as many as twenty times to yield on the average about 75 mg. (2%) of a white granular product, m.p. 134–136°. This material

---

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

[23] R. Criegee, G. Blust and G. Lohaus, *Ann.*, **583**, 4 (1953).

[24] An incorrect neutral equivalent of "224 (calcd. 233)" is also reported by these authors.[15c] The calcd. value is actually 171.

[25] Broad shoulder.

[26] Broad band.

[27] This pattern is characteristic of hydrogen bonded carboxylic acids (L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 2nd ed., 1958, p. 163).

[28] P. M. Bhargava and C. Heidelberger, THIS JOURNAL, **78**, 3671 (1956).

[29] P. S. Bailey, *ibid.*, **78**, 3811 (1956).

[30] L. J. Bellamy,[27] (a) p. 116; (b) p. 73.

[31] We have noted that in unsymmetrical methoxy peroxides, two ether bands appear instead of the customary one. Thus, besides II, 1,4-dihydro-1,4-dimethoxyanthra[1,2-*d*]-*o*-dioxin-6,11-dione[1] also shows the presence of two ether bands at 9.13(m) and 9.27(m) (Nujol). In symmetrical methoxy peroxides, 1,4-dihydro-1,4-dimethoxyanthra-[2,3-*d*]-*o*-dioxin-6,11-dione,[4] 5,8-dihydro-5,8-dimethoxydibenzo[*d,f*][1,2]dioxocin (Bailey's compound IIIb),[29] and our compound VIII, ether bands appear, respectively, as singlets at 9.14(m) (Nujol), 9.19(s) (KBr) and 9.19(s) (KBr).

[32] Which should be compared with the 5.89s ($C{=}O$) band observed in 2,2′-biphenyldialdehyde [W. F. Forbes, F. T. Wallenberger, W. F .O'Connor and E. J. Moriconi, *J. Org. Chem.*, **23**, 224 (1958)].

approached the correct analysis for a diozonide only once in at least five attempts.

Anal. Calcd. for $C_{22}H_{14}O_6$: C, 70.58; H, 3.77; O, 25.64; mol. wt. (monomer), 374. Found: C, 70.22; H, 4.24; O, 25.03; mol. wt., 553, 541 (Signer–Barger, acetone); 430 (cryoscopic in benzene); decomposes in Rast camphor.

This material burns brightly in an open flame, gave an active oxygen test with sodium iodide,[23] and a negative hydroperoxide test with lead tetraacetate.[22] The infrared spectrum of this material in both Nujol and KBr pellet was virtually identical and showed the bands: 5.91(s) (C=O), 6.24(m)(C=O conjugated with an aromatic ring),[30b] 6.34(w) (shoulder), 7.15(m), 8.35(m), 8.90–8.95(w), 9.40–9.60(m),[26] 9.72(m), 10.95(w), 12.07(w),[26] 13.00–13.12(m),[26] 13.90(w) (shoulder).

A refrigerated sample (18 months) had turned cream-colored, but the m.p. remained constant, 134–135.5°.

The MEK-insoluble material by continued washing and extraction with MEK and ether can be purified to a product, m.p. 115–117°. The infrared spectrum (Nujol) was quite similar to Ib and showed such bands as 5.94(s) (C=O), and 6.27(m) (C=O conjugated with an aromatic ring).[30b] This compound was not further characterized.

Anal. Found: C, 67.48, 67.81; H, 4.39, 4.39.

Ozonolysis of I in chloroform (−50°) and carbon tetrachloride (−20°) with slightly greater than two molar equivalents of ozone gave a turbid yellow solution from which could ultimately be isolated (in lower yields) ozonides of m.p., respectively, 128–129° and 139–141°. The properties of these compounds were quite similar to Ib.

Oxidation of Ib to 2,2',5',2''—Tetracarboxy-*p*-terphenyl (X).—To 0.38 g. of crude Ib (after first precipitation from methylene chloride, chloroform or carbon tetrachloride) suspended in 25 ml. of ethanol was added 10 ml. of 30% hydrogen peroxide and 10 ml. of 10% sodium hydroxide solutions. The mixture turned dark brown in a few seconds, and a vigorous exothermic reaction commenced. In about 20 minutes the reaction had subsided, and the mixture was refluxed an additional 40 min. at which time oxygen evolution had ceased and solution (amber) was complete. This solution was acidified with 20% hydrochloric acid, evaporated to one-half its volume, and refrigerated overnight. The copious white precipitate was extracted with ether. This extract was evaporated until crystals appeared, and then refrigerated. Two recrystallizations from ether and a final recrystallization from ethanol (charcoal) gave 60 mg. (16%) of the dihydrate of X, m.p. 318–319° (capillary).

Anal. Calcd. for $C_{22}H_{14}O_8 \cdot 2H_2O$: C, 59.72; H, 4.10. Found: C, 60.24, 60.17, 59.91; H, 3.89, 4.27, 4.12.

This material when dried over P_2O_5 at 125° (3–5 mm.) for several hours gave X, m.p. 318–319°, with immediate formation of needles which do not melt below 360°. If the m.p. is taken rapidly, this phase change may take place without melting. A mixed m.p. of IV (m.p. 317–318°) and X (m.p. 318–319°) was depressed; infrared spectrum: 2.92(m) (free OH), 3.28(m) and 3.42(m) (associated OH), and 5.88(s) (C=O).

Anal. Calcd. for $C_{22}H_{14}O_8$: C, 65.03; H, 3.47; neut. equiv., 101.5. Found: C, 65.28; H, 3.82; neut. equiv., 107.[33]

Compound Ib in ethylene glycol dimethyl ether was also oxidized to X with a hot saturated solution of potassium permanganate.

2,2',5',2''-Tetracarbomethoxy-*p*-terphenyl (XI).—Compound X (0.174 g., 0.39 mmole) in 30 ml. of ether and 1 ml. of ethanol was esterified with excess diazomethane to yield 0.086 g. (47%) of XI, m.p. 154.5–156°, white plates after three recrystallizations from methanol (charcoal). The m.p. (146–147°) as reported in ref. 2 is incorrect; infrared spectrum: 5.79(s) (C=O).

Anal. Calcd. for $C_{26}H_{22}O_8$: C, 67.52; H, 4.79. Found: C, 67.53; H, 4.65.

Tetramethoxy Peroxidic Terphenyl Derivative VIII.—Compound I (10.0 mmoles) dissolved in 500 ml. of dry methylene chloride–50 ml. of methanol was treated with 2.14 molar equivalents of ozone at −60° as in the preparation of II. Although the solution is clear at the completion of the ozone absorption, a precipitate begins to form several hours thereafter. For maximum yields, the reaction mass is kept at 0° for 24 hours. This mixture was filtered on a medium porosity glass frit, and while still wet[34] was thoroughly washed with anhyd. ether and methanol. The white flaky material was then triturated several times with methanol to yield 1.66 g. (36%) of VIII, a white compact powder which after desiccation over P_2O_5 melted at 233–235° to a clear yellow liquid; infrared spectrum: absence of C=O band; 7.48(m) (methyl ether),[29] and 9.19(s) (ether).[31]

Anal. Calcd. for $C_{26}H_{26}O_8$: C, 66.94; H, 5.61; O, 27.44; OCH_3, 25.58. Found: C, 66.62; H, 5.80; O, 27.26; OCH_3, 25.22.

Compound VIII burns rapidly in an open flame but is stable to shock. It is stable at ambient temperatures for indefinite periods of time. The m.p. of a sample on the shelf 18 months remained unchanged. Unlike II, it could be pelleted with KBr without the appearance of carbonyl bands in the infrared; VIII was too insoluble for a hydroperoxide test, was insoluble in all conventional cryoscopic, and isothermal distillation analyses solvents, and decomposes in Rast camphor.

The procedure for the two molar equivalent addition of ozone to chloroform–methanol (−50°) and carbon tetrachloride–methanol (−20°) was the same as with methylene chloride–methanol. Thus, 0.354 g. of I in 150 ml. of chloroform–25 ml. of methanol gave 0.211 g. (36%) of VIII, m.p. 233–235°; Compound I (0.312 g.) in 150 ml. carbon tetrachloride–25 ml. methanol gave 0.100 g. (19%) of VIII, m.p. 234–236°.

Compound VIII (0.428 g., 0.92 mmole) in 30 ml. of ethanol was oxidized with 15 ml. of 30% hydrogen peroxide and 20 ml. of 10% sodium hydroxide to give ultimately 0.100 g. (25%) yield of the dihydrate of X.

Reduction of VIII to *p*-Terphenyl-2,2',5',2''-Tetracarboxaldehyde (IX).[35]—Compound VIII (0.200 g., 0.43 mmole) was refluxed for 6 hr. with 2 ml. of 50% hydriodic acid and 2.4 ml. of glacial acetic acid. Unreacted VIII was filtered from the mixture, and to the filtrate was added 25 ml. of water and excess 10% sodium thiosulfate solution. The mixture was filtered, and the residue first triturated with carbon disulfide to remove sulfur, and then recrystallized four times from MEK–petroleum ether to yield 50 mg. (34%) of IX, m.p. > 360°; infrared spectrum: 5.92(s) (C=O).

Anal. Calcd. for $C_{22}H_{14}O_4$: C, 77.18; H, 4.12. Found: C, 77.19; H, 4.42.

2-(*o*-Carbomethoxyphenyl)-3-carbomethoxy-9,10-phenanthrenequinone (VII).—Compound V (0.70 g., 1.9 mmoles) was ground in a mortar with 2.8 g. of potassium dichromate, and the whole made into a paste with 7 ml. of water. Concentrated sulfuric acid was slowly added with much stirring. After the spontaneous, exothermic reaction subsided, the mixture was heated until the green chromous salts were evident. The mixture was then added to ice, filtered and the residue washed with water to give 0.50 g. (66%) of crude VII. This material was converted to the bisulfite adduct by warming in a few ml. of a solution of 12 ml. of 40% sodium bisulfite and 3 ml. of ethanol. Just enough water was added to effect virtual solution. This solution was filtered and VII regenerated by the addition of a saturated solution of sodium carbonate. The insoluble quinone was filtered and recrystallized once from ethanol, m.p. 199–206°. This crude material was dissolved in benzene and chromatographed on alumina (activity grade III, 6% water by weight). The eluting solvent was benzene. The first fraction, m.p. 201–206° (containing fluorescent band under ultraviolet light), the second smaller fraction, m.p. 203–207° (to ensure removal of all fluorescent material), the trailing, m.p. 205–207°, and a dark brown band which remained at the top of the column were all discarded. The center fraction, m.p. 207–209°, was analytically pure VII; infrared spectrum: 5.82(s) (ester C=O; *cf.* V and XI), 5.95(s) and 6.29(m) [respectively, *o*-quinone; and ring conjugated C=O's; *cf.* DBA-5,6-dione (KBr, our work) with strong bands at 5.98μ and 6.28μ].

Anal. Calcd. for $C_{24}H_{26}O_6$: C, 71.99; H, 4.02. Found: C, 72.21; H, 4.21.

---

(33) Compound X was insoluble in Rast camphor.

(34) If this residue is ever permitted to be evaporated to dryness prior to the ether–methanol wash, a low-melting, gummy product is formed. This material could be worked up again using a large volume of triturating solvent ether and methanol but with a very large product loss.

(35) Previously named 2,2',5',2''-tetraformyl-*p*-terphenyl.[2]

Oxidation of VII to X.—Compound (0.091 g., 2.3 mmoles) was refluxed for 2 hours in 7.3 ml. of water containing 0.4 g. of potassium permanganate and 2 ml. of 20% sodium hydroxide. The usual isolation procedure[36] afforded 0.22 g. (22%) of X, m.p. and infrared spectra identical with X prepared from I *via* Ib and VIII. A mixed m.p. was not depressed.

A 55% yield of X from VII was also obtained by first hydrolyzing 0.100 g. of VII in 15 ml. of a solution obtained by treating 0.8 g. of sodium with 25 ml. of ethanol and 2.5 ml. of water. After two hours reflux, the acid intermediate (VII, R = H) was obtained by acidification and evaporation. Without further purification, alkaline potassium permanganate treatment of this crude acid gave X.

Direct oxidation of IV to X was achieved in very low yield by successive oxidations of IV either with excess alkaline potassium permanganate or with excess potassium dichromate (twice).

Discussion

Results.—Ozonolysis of I in methylene chloride, chloroform and carbon tetrachloride with one and two molar equivalents of ozone gave, respectively, white, unstable ozonide Ia (61% yield), and white, stable ozonide Ib (2% yield).

Compound Ia decomposed rapidly (visibly darkened), under vacuum, nitrogen and at 0° within an hour. The infrared spectrum (Nujol) showed strong carbonyl bands which undoubtedly are aldehydic decomposition products and which broaden and smear out with passage of time. In solution however, Ia could be kept at least for several weeks without visible signs of decomposition or decrease in yields.

Compound Ib however showed the stability, when pure, of trimeric[37] or hexameric phenanthrene ozonide.[38] The low molecular weight of Ib, and the strong carbonyl absorption at 5.91 μ suggests a dimer. The infrared spectra in Nujol and KBr pellet were virtually identical and showed no progressive signs of decomposition; Ib when refrigerated was stable for long periods of time.

Treatment of I in methylene chloride–methanol gave 5,8-dihydro-5,8-dimethoxybenzo[*d*]phenanthro[2,3-*f*][1,2]-dioxocin (II) in 20% yield based on I utilized. Its assigned monomeric structure is based on elementary analysis, molecular weight and methoxyl determinations, negative hydroperoxide test, and infrared spectrum.

In the same solvent, with two molar equivalents of ozone, compound I gave the tetramethoxy peroxidic terphenyl derivative VIII in 36% yield. Both II and VIII showed the absence of carbonyl absorption in the infrared (Nujol); VIII was more stable than II, however, since it could also be pelleted with KBr without the appearance of carbonyl bands (aldehydic decomposition products). Compound VIII was insoluble in all conventional cryoscopic and isothermal distillation solvents, and decomposed in Rast camphor. It is probably polymeric.[39]

The position of attack of ozone upon I is supported by the oxidation and reduction products of Ia and II, and Ib and VIII.

Reduction of Ia and II with sodium iodide in acetic acid afforded 2-(*o*-formylphenyl)-3-phenanthrenecarboxaldehyde (III) while hydriodic acid reduction of VIII gave *p*-terphenyl-2,2′,5′,2″-tetracarboxaldehyde (IX).

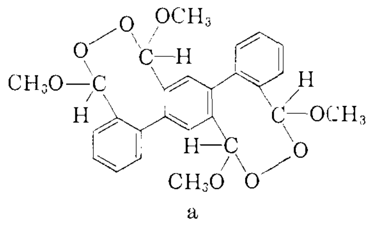
Alkaline hydrogen peroxide oxidation of Ia and II gave white 2-(*o*-carboxyphenyl)-3-phenanthrenecarboxylic acid (IV), respectively, in 45% (from I) and 70% yields. This acid is identical (mixed m.p. and superimposable infrared spectra) with the pale-yellow acid obtained by the peracetic acid oxidation of DBA-5,6-dione.[15b,c]

Compound IV was converted to V, its methyl ester, with diazomethane and to VI, its anhydride with acetic anhydride.

Potassium dichromate–sulfuric acid oxidation of V in a minimum amount of water gave 2-(*o*-carbomethoxyphenyl)-3-carbomethoxy-9,10-phenanthrenequinone (VII), the further oxidation and hydrolysis of which with alkaline permanganate gave X. This last step essentially proves the position of attack by the second mole of ozone to be at the 12,13-bond in I and relates compounds I-VI to VIII-XI.

Mechanism.—The two current opposed views in the literature as to the mode of initial attack by ozone on unsubstituted aromatic systems[40] would suggest a two-step, electrophilic, 1,4-conjugate addition to the most reactive carbon atoms in anthracene,[41,42] naphthacene,[4] and benz[*a*]anthracene[4b] to give predominantly quinones, and a one-step, 1,2-bond addition to the most reactive bonds in pyrene[43] and I[2] to give predominantly bond cleavage products. Such a view leaves unexplained why, under identical conditions and where both chemical evidence and localization theory predict similar reactivity of the 5,6-bonds in benz[*a*]anthracene and I,[44] ozone predominantly oxygenates the 7,12-positions of the former, and cleaves the 5,6-bond in the latter.

The continuing correlation between the predominant position and ease of initial ozone at-



a

---

[36] R. L. Shriner, R. C. Fuson and D. Y. Curtin, "The Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 4th ed., 1956, p. 218.

[37] J. P. Wibaut and Th. J. DeBoer, *Koninkl. Ned. Akad. Wetenschap. Proc. Ser. B*, **59**, 421 (1956); *Rec. trav. chim.*, **78**, 183 (1959).

[38] P. S. Bailey and S. B. Mainthia, *J. Org. Chem.*, **21**, 1335 (1956); **23**, 1089 (1958).

[39] A possible structure for the corresponding monomer from which it is derived would be (a) and should be named: 14,17-dihydro-5,8,14,17-tetramethoxy-5*H*,8*H*-benzo[1,2-*e*:4,5-*e*]bis[2,3]benzodioxocin.

[40] See P. S. Bailey, *Chem. Revs.*, **58**, 925 (1958), for leading references and a discussion of these mechanisms.

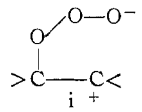
[41] I. M. Roitt and W. A. Waters, *J. Chem. Soc.*, 3060 (1949).

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

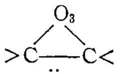
[43] H. Vollmann, H. Becker, M. Corell and H. Streeck, *Ann.*, **531**, 65 (1937); H. Vollmann and H. Becker, U. S. Patent 2,127,096, Aug. 16, 1938; L. F. Fieser and F. C. Novello, THIS JOURNAL, **62**, 1855 (1940); R. E. Dessy and M. S. Newman, *Org. Syntheses*, **38**, 32 (1958).

[44] Theoretically the 5,6-bond in benz[a]anthracene has a slightly lower bond localization energy (and consequently a slightly greater reactivity) than the corresponding bond in I.[6a] However, the rate of osmium tetroxide addition to the former is slightly less than that to I [G. M. Badger, *J. Chem. Soc.*, 456 (1949)]. As a first approximation, both bonds have the same reactivity.

tack, and corrected oxidation–reduction potentials[1,3,4] seems too consistent to be fortuitous.[45] If our conclusion that ozone initially attacks unsubstituted aromatic systems *via* a rate-controlling transition state whose geometry corresponds to the most stable dihydro product[1,3,4] is correct, then in the absence of relevant kinetic data, Criegee[46] with customary foresight has suggested a most appealing alternative: that the formation of (i) (electrophilic) and (ii) (nucleophilic)[47] occurs "nearly simultaneously so the initial ozonide



i



ii

comes together by a kind of four center reaction."[48] This viewpoint suggests that the difference between opposed schools may be more apparent than real.

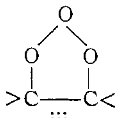
Acknowledgment.—This research was supported by a grant C-3325 (C2) from the U. S. Public Health Service, National Cancer Institute. Grateful acknowledgment is hereby made to the donor of said funds. We are indebted to Dr. L. T. Capell of the "Chem. Abstracts" Service for the systematic nomenclature used herein. E. J. M. wishes to thank Prof. R. Criegee for his interest, helpful suggestions and many stimulating discussions.

---

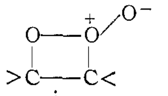
[45] F. T. Wallenberger [*Tetrahedron Letters*, **9**, 5 (1959)] has recently suggested the use of theoretical resonance energy decrease accompanying the reaction to correlate and predict the specificity of the ozonization of polycyclic aromatics. We are indebted to Dr. Wallenberger for providing us with a preprint of his communication.

[46] R. Criegee, *Record Chem. Prog. Kresge–Hooker Sci. Lib.*, **18**, 111 (1957).

[47] Nucleophilic attack on the carbonium ion may occur by the terminal or central oxygen atom to give respectively, iii or iv.



iii



iv

[48] Bailey's π-complex mechanism[40,42b] also shows how this might be accomplished but does not indicate why it should.

NEW YORK 58, N. Y.

[CONTRIBUTION FROM THE PROCTER & GAMBLE CO., MIAMI VALLEY LABORATORIES]

The Reaction of Diborane with Di-*t*-butylethylene and Di-*t*-butylacetylene

BY TED J. LOGAN AND THOMAS J. FLAUTT

RECEIVED SEPTEMBER 14, 1959

The reaction of di-*t*-butylethylene (*trans*-2,2,5,5-tetramethyl-3-hexene) with diborane yields 2,2,5,5-tetramethyl-3-hexylborane, $C_{10}H_{21}BH_2$, a monoalkylborane. Oxidation and hydrolysis of this product lead to the corresponding alcohol, 2,2,5,5-tetramethyl-3-hexanol. Heating of the hydroborated olefin prior to oxidation, however, results in the unexpected formation of a C_{10}-diol, namely, 2,2,5,5-tetramethyl-1,4-hexanediol, as the end product. Nuclear magnetic resonance spectra enabled this structural assignment to be made. The same product is obtained in a 20% yield from the hydroboration, thermal isomerization and oxidation of di-*t*-butylacetylene (2,2,5,5-tetramethyl-3-hexyne). An explanation of the unexpected results is offered.

Hennion[1] discovered that secondary and tertiary alkyl groups attached to boron may be thermally isomerized to the corresponding primary alkyl groups. Brown[2] found that trialkylboranes, formed by the reaction of B_2H_6 with non-terminal olefins, undergo a similar thermal isomerization to the corresponding 1-alkylboranes. The over-all conversion of internal olefins to primary alcohols is then completed by oxidation and hydrolysis.

Brown[2] suggested that the isomerization of internal boranes to the terminal derivatives could proceed through a thermally induced equilibrium of the trialkylborane with olefin and dialkylborane, and that conversion to the more stable terminal derivative is achieved by a series of addition and elimination reactions. According to this mechanism boron atom migration past a quaternary carbon atom could not occur. Hennion's proposed mechanism,[1] on the other hand, would permit such a migration.

The present study was undertaken to establish whether or not this boron migration could occur and to learn more about the migration mechanism in general. This object was not fully realized because it was found that the isomerization of hydroborated di-*t*-butylethylene proceeds abnormally. A product is obtained which can be oxidized to a C_{10}-diol, instead of the expected monoalcohol. Di-*t*-butylethylene was chosen for study because it is well described in the literature[3–6] and because the boron atom in its hydroborated product must pass a quaternary carbon atom in order that the 1-alkylborane and, ultimately, a primary alcohol can be produced.

trans-Di-*t*-butylethylene reacts with B_2H_6 to form 2,2,5,5-tetramethyl-3-hexylborane, $C_{10}H_{21}BH_2$,[7] identified by its infrared spectrum and elemental

---

[1] G. F. Hennion, P. A. McCusker, E. C. Ashby and A. J. Rutkowski, A.C.S. Abstracts of Papers, 130th Meeting, Atlantic City, N. J., September, 1956, p. 53-O; also, THIS JOURNAL, **79**, 5190 (1957).

[2] H. C. Brown and B. C. Subba Rao, *J. Org. Chem.*, **22**, 1137 (1957).

[3] G. F. Hennion and T. F. Banigan, Jr., THIS JOURNAL, **68**, 1202 (1946).

[4] F. L. Howard, T. W. Mears, A. Fookson and P. Pomerantz, *ibid.*, **68**, 2121 (1946).

[5] F. L. Howard, T. W. Mears, A. Fookson, P. Pomerantz and D. B. Brooks, *J. Research Natl. Bur. Standards*, **38**, 365 (1947).

[6] W. H. Puterbaugh and M. S. Newman, THIS JOURNAL, **81**, 1611 (1959).

[7] This is the first reported example of the preparation of a monoalkylborane by hydroboration of an olefin. Brown has previously reported the preparation of dialkylboranes from the reaction of B_2H_6 with substituted olefins (ref. 9 and A.C.S. Abstracts of Papers, 135th Meeting, Boston, Mass., April, 1959, p. 39-O); unsubstituted olefins invariably lead to the trialkylboranes. NOTE ADDED IN PROOF.—Brown has recently reported that "reaction with tetrasubstituted olefins appears to halt at the monoalkylborane, RBH_2, stage," THIS JOURNAL, **81**, 6428 (1959).