and the precipitated anthraquinone was filtered off; yield 0.41 g. (39%), m.p. 282–284°.

D. Alkaline Decomposition of Peroxidic Intermediate (VIII).—In another experiment the entire acetic acid ozonation reaction mixture was poured into 1500 ml. of water and the mixture of solids was removed by filtration and washed with dilute potassium hydroxide solution. A 71% yield of crude anthraquinone was obtained; it was recrystallized from acetic acid, m.p. 283–284°.

Miscellaneous Ozonations of Anthracene. A. With Catalytic Quantities of Ozone in Acetic Acid.—The usual volume of oxygen–ozone (but containing only 0.2% ozone) was passed through 10 mmoles of anthracene (I) in acetic acid solution. A total of 2 mmoles of ozone reacted and an 86% recovery of anthracene was made.

B. Anthraquinone Produced Directly in Nonprotolytic Solvents.—A solution of anthracene in methylene chloride was ozonized with 2.5 mole-equivalents of ozone in an oxygen mixture. The precipitated "ozonides" were filtered off and the filtrate was evaporated under reduced pressure at room temperature (rotar). The residue (0.82 g. from 0.89 g. of anthracene) was shown by infrared spectra comparison to consist of approximately 40% anthraquinone (XI, carbonyl peak at 5.98 μ). Some unidentified carboxylic acids were also present, none of which were XXXIV, XXXIII, or phthalaldehydic acid (XXX).

C. Ozonation with Large Excess of Ozone in Methylene Chloride.—Methylene chloride (300 ml.) was saturated with ozone at −78°. While the solution was kept saturated by the passage of more ozone–oxygen, a solution of 3 mmoles of anthracene in 60 ml. of methylene chloride was added dropwise to the ozonation mixture. The reaction mixture was worked up by procedure B. The anthraquinone yield was 18%.

D. Overozonation in Acetic Acid Solution.—More than ten mole-equivalents of ozone was passed through an acetic acid–anthracene ozonolysis mixture. After the reaction of 2.6 mole-equivalents of ozone, ozone absorption was very slow. The reaction mixture was worked up by procedure E, giving 38% crude or 35% pure (m.p. 285–286°) anthraquinone (XI), and 43% crude or 39% pure (m.p. 206–208°) phthalic acid (XXXIV). Most of the anthraquinone (30% yield) precipitated during the ozonation.

E. Test for Hydrogen in Exit Gases.—The ozonolysis was carried out as usual with ozone–oxygen in 90% acetic acid solution. The exit gases, after passing through the iodide trap, were led through a drying tower and into a sample gas collector. A sample taken after about 0.6 mole-equivalent of ozone had reacted was shown by its mass spectrum to contain no molecular hydrogen. This shows that the 1.5–2.0-mole ratio of molecular oxygen to anthraquinone was not due to loss of oxygen and hydrogen from XV.

F. Dianthrone (XXXV) from Ozonation of I in Glacial Acetic Acid.—The ozonation was carried out as usual with 10 mmoles of ozone in ozone–nitrogen and 10 mmoles of anthracene (I) in glacial acetic acid. Work-up was by procedure B, except that heat (steam bath) was used to evaporate the ozonation mixture under reduced pressure. From the petroleum ether eluate a 4-mmole recovery of anthracene was obtained. From the methylene chloride eluate pure anthraquinone (XI) was first obtained, after which a mixture shown by infrared spectra comparisons to be approximately 80% dianthrone[27] (XXXV, distinctive bands at 6.02, 7.41, 8.50, 12.70, 13.60, and 14.40 μ) and 20% anthraquinone (XI, distinctive bands at 5.98, 7.79, and 12.40 μ) was obtained. This amounted to a 34% yield of anthraquinone and an 8% yield of dianthrone (XXXV) based on the anthracene reacting. In addition, a small amount of an unknown compound was obtained. Infrared bands at 6.01 and 6.30 μ suggest that a diaryl ketone structure was present. No other characteristic bands for functional groups were present.

Attempted ozonations of anthraquinone (XI) were carried out in methylene chloride at −30° and in 90% acetic acid at 14°, using two mole-equivalents of ozone. Titrations of the iodide trap showed that 86 and 98% of the ozone passed through the reaction mixture unchanged in methylene chloride and acetic acid solvents, respectively. The respective anthraquinone recoveries were 95 and 98%; m.p 282–283°. Identification was by the mixture melting point method

Attempted Oxidation of Anthracene (I) and Anthraquinone (XI) with Alkaline Hydrogen Peroxide.—A mixture of 1 g. of each (I and XI separately) in 20 ml. of 30% hydrogen peroxide and 60 ml. of 2–3% sodium hydroxide solution was heated with stirring over a steam bath for 2 hr., after which the mixture was filtered, and the filtrate was extracted with methylene chloride. The recovery of each (I or XI) was 97–99%; anthracene (I) m.p. 212–213°, anthraquinone (XI) m.p. 282–283°. Identifications were by the mixture melting point method.

Attempted Ozonation of Glacial Acetic Acid.—An ozone–nitrogen stream containing 4.44 mmoles of ozone was passed through glacial acetic acid at 16°. The exit gases passed through the iodide trap and into the oxygen analyzer.[8] Titration of the iodide trap with thiosulfate showed that 4.5 mmoles of ozone had passed through it, and the oxygen analyzer indicated that 4.0 mmoles of oxygen was produced, which is within experimental error.[8] An iodide test on the acetic acid showed only a trace of peroxide.

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[27] E. Barnett and M. Matthews, *J. Chem. Soc.*, 380 (1928).

Ozonation of 9,10-Dihaloanthracenes

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Ozonation of 9,10-dibromoanthracene gave anthraquinone, 1,4-dibromo-2,3-naphthalenedicarboxylic acid, and 3,6-dibromo-1,2,4,5-benzenetetracarboxylic acid (dibromopyromellitic acid). Approximately 2 moles of molecular oxygen was evolved per mole of anthraquinone produced when 2 mole equiv. or less of ozone was used. Bromine was also a product and reacted with ozone when more than 2 mole equiv. was employed. There is a definite, though not so great as originally reported, solvent effect involving the competition between atom and bond attack of ozone. Similar results were obtained with 9,10-dichloroanthracene, except that there was little, if any, solvent effect. Mechanisms are discussed.

A preliminary communication[1] reported the ozonation of 9,10-dibromoanthracene (Ia) to give dibromopyromellitic acid (Xa) as the major product and anthraquinone (VIII) as the minor product from methylene chloride solvent and to give the reverse when the solvent was 90% methylene chloride and 10% methanol. It was considered that this solvent effect of nonprotonic *vs.* protonic solvents determined whether initial bond attack[2] or atom attack[2] of ozone on the polycyclic system predominated. Unfortunately, the

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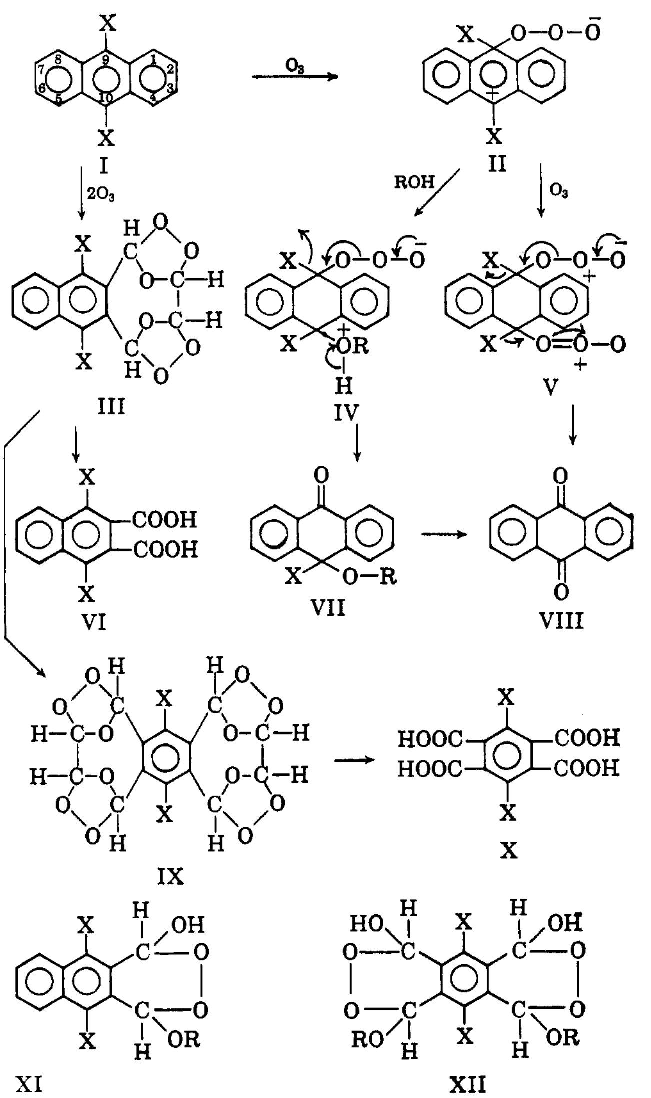
[1] F. Dobinson and P. S. Bailey, *Tetrahedron Letters*, **No. 13**, 14 (1960).

[2] P. S. Bailey, *Chem. Rev.*, **58**, 925 (1958).

SCHEME I



I–XI a, X = Br
b, X = Cl
c, R = CH_3
d, R = Ac
e, R = H
f, X = OCH_3

investigator in the early stages of the work[1] assumed that, because anthraquinone (VIII) came out pure from the methylene chloride reactions at the appropriate point in the work-up procedure, it also came out pure at this point from the methylene chloride–methanol reaction mixtures. Repetition of the early work has proven this to be untrue, and, although there is a definite solvent effect, it is not nearly so great as originally reported.[1] The present paper reports the experimental details of the ozonation of 9,10-dibromo- and 9,10-dichloroanthracenes (I) in several solvents and suggests possible mechanisms for the reactions involved.

In methylene chloride solvent 9,10-dibromoanthracene (Ia) absorbed 2 mole equiv. of ozone nearly quantitatively, after which the rate of absorption decreased and approximately an additional 2 mole equiv. of ozone slowly reacted. The yield of anthraquinone (VIII) was 15–20% regardless of whether ozone–oxygen or ozone–nitrogen[3,4] was used, whether 2 or 4 mole equiv. of ozone reacted, and whether an oxidative or a nonoxidative work-up procedure was used (expt. 1–4, Table I). Thus, anthraquinone (VIII) was produced by ozonation rather than by hydrogen peroxide oxidation. Further, it was found that Ia was partially converted to VIII and Ib by hydrogen peroxide in hydrochloric acid solution, but not by alkaline or neutral hydrogen peroxide. In the 2 mole equiv. of ozone reaction the acid product isolated (from initial bond attack) was 1,4-dibromo-2,3-naphthalenedicarboxylic acid (VIa) in 48% crude or 18% pure yield (expt. 1, Table I). It was not possible to identify the impurities in the crude acid product. From the 4 mole equiv. of ozone reaction the acid product isolated was dibromopyromellitic acid (Xa) in 76% crude or 66% pure yield (expt. 2, Table I). Small amounts of unidentified acids were present in crude Xa.

In the methylene chloride–methanol reactions (expt. 5–8) the ozone absorption was similar, except that it continued well past 4 mole equiv. (expt. 8). This is perhaps due to some ozone attack on methanol. The anthraquinone (VIII) yields from the 2 mole equiv. or less of ozone reactions (expt. 5–7) were considerably higher than those from methylene chloride solvent and did not vary whether ozone–oxygen or ozone–nitrogen[3,4] was used, or whether an oxidative or a nonoxidative work-up procedure was employed (expt. 6 and 7). In contrast to the results in methylene chloride solution, the anthraquinone yields from the methylene chloride–methanol reaction mixtures decreased somewhat as more ozone reacted (expt. 5–8), showing that a precursor to anthraquinone was being destroyed. Anthraquinone itself does not react appreciably under these conditions.[5] No ozone concentration effect, such as was found with anthracene,[5] was observed with the ozonation of Ia in either methylene chloride or methylene chloride–methanol solution. From an exhaustive ozonation of Ia in methylene chloride–methanol solution, the acid product (from initial bond cleavage) was dibromopyromellitic acid (Xa) in 73% crude or 51% pure yield (expt. 8). In glacial and aqueous acetic acid solutions the anthraquinone (VIII) yields were similar (expt. 9, 10) to those from the methylene chloride–methanol reaction mixtures (expt. 5).

It was obvious in all solvents that molecular bromine was a product. In one experiment, with methylene chloride–methanol solvent, approximately 1 mole of bromine per mole of anthraquinone (VIII) produced was found by titration with standard phenol solution.

With ozonations using 2 mole equiv. or less of ozone (expt. 1, 5, 9) approximately 2 moles of molecular oxygen were evolved per mole of anthraquinone (VIII) produced. The molecular oxygen to anthraquinone ratios were 2.6–3.4 in expt. 6 and 10. We believe this is due to the lesser solubility of the starting material (Ia) in the solvents employed and the resulting greater ability of bromine to compete with Ia for the ozone. In expt. 2, where 4 mole equiv. of ozone were employed, the ratio of molecular oxygen to anthraquinone was 6.4–8.5. The large increase is undoubtedly due to the reaction between ozone and molecular bromine which is

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[3] G. A. Cook, A. D. Kiffer, C. V. Klumpp, A. H. Malik, and L. A. Spence, *Advan. Chem. Ser.*, **21**, 44 (1959).

[4] P. S. Bailey and A. M. Reader, *Chem. Ind.* (London), 1063 (1961).

[5] P. S. Bailey, P. Kolsaker, B. Sinha, J. B. Ashton, F. Dobinson, and J. E. Batterbee, *J. Org. Chem.*, **29**, 1400 (1964).

TABLE I

OZONATIONS OF 9,10-DIHALOANTHRACENES (I)

Experiment	Compound	Solvent[a]	Temp., °C.	Starting I, mmoles	Reacting I, mmoles	Reacting O_3, mole equiv.[b,c]	O_2 yield, mmoles	Anthraquinone (VIII) yield, mmoles[d]	% yield of VIII[d,f]	O_2-anthraquinone ratio	Acid products,[e,f] %	Work-up procedure[g]
1	Ia	CH_2Cl_2	−30	6.0	6.0	2.0	2.3	0.9–1.2	15–20	1.9–2.6	VIa 48 C 18 P	A
2	Ia	CH_2Cl_2	−30	4.0	4.0	4.1	5.1	0.6–0.8	15–20	6.4–8.5	Xa 76 C 66 P	A
3	Ia	CH_2Cl_2	0	6.0	6.0	3.8[b]	. . .		15–18	. . .		A
4	Ia	CH_2Cl_2	−30	3.0	3.0	4.0[b]	. . .		15	. . .	. . .	F
5	Ia	CH_2Cl_2–CH_3OH (9:1)	−30	3.0	2.3	1.2	1.2	0.6–0.7	26–30	1.7–2.0	. . .	D
6	Ia	CH_2Cl_2–CH_3OH (9:1)	−30	3.0	3.0	2.0	2.1	0.7–0.8	23–27	2.6–3.0	. . .	D
7	Ia	CH_2Cl_2–CH_3OH (9:1)	−30	3.0	3.0	1.9[b]	. . .		23–28	. . .		A
8	Ia	CH_2Cl_2–CH_3OH (9:1)	−30	6.0	6.0	4.7[b]	. . .		19–22	. . .	Xa 73 C 51 P	B
9	Ia	gl. HOAc	15	2.5	1.9	1.2	1.2	0.5	26	2.4	. . .	D
10	Ia	HOAc–HOH (9:1)	20	2.5	1.8	1.2	1.7	0.5	28	3.4	. . .	D
11	Ib	CH_2Cl_2	−30	4.0	4.0	3.9	3.7	1.1–1.3	28–32	2.8–3.4	Xb 67 C 59 P	C
12	Ib	CH_2Cl_2	0	10.0	10.0	3.4[b]	. . .		27	. . .		A
13	Ib	CH_2Cl_2–CH_3OH (9:1)	−30	3.0	2.7	1.5			33–36		. . .	E
14	Ib	CH_2Cl_2–CH_3OH (9:1)	−30	6.0	6.0	3.6[b]	. . .		25–27	. . .	Xb 68 C 51 P	B
15	Ib	HOAc–HOH (9:1)	15	3.4	2.2	0.9	1.4	0.8	36	1.7	. . .	D

[a] Where mixed solvents are used, the numbers refer to parts by volume of each component in the mixture. [b] All ozonations, except those of expt. 3, 4, 7, 8, 12, and 14, were with ozone–nitrogen mixtures.[3,4] [c] The ozone reacting is listed in moles per mole of starting dihaloanthracene (I). [d] The yields listed are of pure anthraquinone. [e] C stands for crude and P stands for pure. [f] Per cent yields are calculated on bases of reacting I. [g] See Experimental section.

reported to occur according to the following equation,[6] accounting for 4 moles of oxygen per mole of bromine produced, assuming that all of the bromine reacts: $Br_2 + 4O_3 \rightarrow 2BrO_2 + 4O_2$. The rest of the excess oxygen probably comes from decomposition of the bromine oxide according to the following equation[6]: $2BrO_2 \rightarrow Br_2 + 2O_2$.

It seems obvious, therefore, that at least the major reaction producing anthraquinone (VIII) requires 2 moles of ozone and releases 2 moles of molecular oxygen and 1 mole of bromine per mole of anthraquinone produced. We suggest that the initial ozone attack on the central ring of Ia is electrophilic, to give IIa, as was suggested in the case of anthracene.[5] Owing to deactivation of the 9-position of the anthracene ring by the bromo groups of Ia, this reaction does not occur to so great an extent with Ia as it did with anthracene.[5] In methylene chloride (a nonnucleophilic solvent) solution, at least, we believe that, next, IIa is attacked nucleophilically by a second ozone molecule to give Va, which loses a molecule of bromine and two molecules of oxygen to give anthraquinone (VIII). Since halogen rather than hydrogen groups are present in Ia, it is unlikely that reactions similar to those suggested for the major route of anthracene to anthraquinone[5] would occur in the present case. The accepted structure of the ozone molecule suggests that it should be able to attack organic molecules nucleophilically.[2]

The loss of halogen from V should be much easier than the loss of hydrogen from a similar intermediate in the ozonation of anthracene, and, thus, the reaction of V to anthraquinone (VIII) should occur in preference to the rearrangements suggested in the case of anthracene.[5] It is possible, however, that competing rearrangements of this sort account for the impurities in the crude dibromopyromellitic acid (Xa).

We suggest that, in the presence of methanol, acetic acid, or water (expt. 5–10), IIa is attacked by the nucleophilic solvent to give IVa rather than Va. Loss of hydrogen bromide and molecular oxygen would give VIIa. In one experiment the methylene chloride–methanol reaction mixture was poured into methanolic sodium methoxide solution. The anthraquinone obtained was contaminated with colorless crystals which decomposed to anthraquinone either on standing or during recrystallization; this substance may have been VIIcf. It was too unstable to purify. Hydrolysis during work-up of VIIac or VIIad to VIIae, followed by loss of hydrogen halide, would give anthraquinone (VIII). The bromine found in the reaction mixture would then be produced by the reaction of hydrogen bromide with a second mole equiv. of ozone to give bromine and oxygen. As said earlier, the decreasing yields of anthraquinone as more ozone is employed in expt. 5–8 must be due to the partial destruction of an intermediate to anthraquinone (VIII). This intermediate is perhaps VIIac, which would undergo ring attack by ozone much more easily than would anthraquinone.

Although the solvent effect is not great, it appears to be definite and to involve competition between initial atom and initial bond attack, since anthraquinone can come only from atom attack and the major acidic products (VIa and Xa) can come only from bond attack. If one bases the degree of solvent effect on the quinone yields obtained, it amounts to about 10% (*i.e.*, 15–20% VIII from methylene chloride, expt. 1, *vs.* 26–30% VIII from nucleophilic solvents, expt. 5, 9, 10). It is more accurate to compare these experiments than to compare expt. 1 or 2 with 6, 7, and 8, since it has been shown that quinone yields decrease in methylene chloride–methanol solvent (and probably other nucleophilic solvents) as the amount of ozone reacting increases, whereas this is not true in the case of methylene chloride solvent. One arrives at a figure of 15% for the solvent effect if it is assumed that the impurities in the acid fractions are produced by atom attack, as was true with anthracene,[5] and yields of pure Xa in the two solvent types are compared (expt. 2, 8).

Since methylene chloride–methanol is as good a solvent for quinone formation as is 90% acetic acid, which was not true in the case of anthracene,[5] we believe that the nucleophilicity of the solvent is more important than its protonic character and that the solvent effect is caused by the stabilization of intermediate IIa (and the transition state leading to it) to give IVa, thus lowering the activation energy for atom attack and allowing it to compete more favorably with bond attack.

The ozonation results with 9,10-dichloroanthracene (Ib, expt. 11–15) were similar to those with Ia, except that the yields of anthraquinone (VIII) were higher than those from Ia (*cf.* expt. 2 with expt. 11, and expt. 5 and 10 with expt. 13 and 15) and the solvent effect, if any, was smaller (*cf.* expt. 11, 13). It is assumed that, since the quinone (VIII) yield did not decrease with increasing amount of ozone during ozonation of Ia in methylene chloride, the same is true with Ib. The higher yields of anthraquinone (VIII) from Ib than from Ia are logical on the basis that the carbonium ion initially produced (IIb and the transition state leading to it) would be stabilized to a greater extent by the adjacent chloro group than would be IIa by the adjacent bromo group, thus causing ozone attack at position 9 to be greater with Ib than Ia. This factor would not be as important when solvent stabilization of II (*i.e.*, IV) can occur; thus the solvent effect is not so great.

Bond attack[2] with the dihaloanthracenes (I) differs from that with anthracene[5] in that it occurs at least predominantly, first at one outer ring and then at the other outer ring, owing to the deactivating effect of the halogen groups on the central ring. By analogy to results with naphthalene,[7] the peroxidic ozonolysis products are probably III and IX from nonprotonic solvents and XI and XII from protonic solvents. Oxidation of III and XI would give VI, and oxidation of IX and XII would give X.

Experimental

The ozonation equipment and techniques are described in earlier publications.[4,5,8] Starting materials were obtained commercially and were purified by recrystallization or by chromatography to sharp, constant melting points. Solvents were pure and anhydrous, unless otherwise stated.

Ozonation of 9,10-Dihaloanthracenes (I).—A finely divided suspension of the dihaloanthracene (I) in the solvent (25–40 ml. per mmole of I) was ozonized either with ozone–oxygen (about

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[6] (a) M. Schmeisser and K. Joergen, *Angew. Chem.*, **71**, 523 (1959); (b) R. Schwarz and M. Schmeisser, *Ber.*, **70**, 1163 (1937).

[7] P. S. Bailey, S. S. Bath, F. Dobinson, F. J. Garcia-Sharp, and C. D. Johnson, *J. Org. Chem.*, **29**, 697 (1964).

[8] (a) P. S. Bailey, *J. Am. Chem. Soc.*, **78**, 3811 (1956); (b) P. S. Bailey and S. S. Bath, *ibid.*, **79**, 3120 (1957).

4% ozone by weight) or ozone–nitrogen[3,4] mixtures. The ozone absorption was very nearly quantitative until 2 mole equiv. was absorbed, during which time the starting material slowly dissolved and reacted. With methylene chloride solvent a white precipitate formed during the ozonation. It proved best either to shake the reaction vessel intermittently or stir it magnetically[5] during the ozonation. Ozone absorption was much slower after 2 mole equiv. The iodide trap was titrated with standard thiosulfate, and the mole equivalents of ozone listed as reacting in Table I are the amounts obtained by subtracting that which reacted in the trap from the total amount employed. When ozone–nitrogen mixtures were used, the molecular oxygen yield was usually obtained, by procedures described previously.[4,5] Several different work-up procedures were employed. These are described below and the results are listed in Table I.

Procedure A. Oxidative Work-Up.—The reaction mixture was poured into 6% hydrogen peroxide solution (30–35 ml. per mmole of I) and the resulting mixture was refluxed for 1 hr., after which the organic solvent was removed by distillation, and refluxing was continued until the reaction mixture was no longer peroxidic (about 45 hr.). The resulting mixture was made alkaline with solid potassium hydroxide and the yellow precipitate which remained was extracted carefully with methylene chloride. The combined methylene chloride extracts were dried over anhydrous magnesium sulfate and evaporated, giving crude anthraquinone, m.p. 278–282°; recrystallized from ethanol, m.p. 285–286°; identifications were by comparison of infrared spectra with that of an authentic sample. The aqueous alkaline solution was acidified with hydrochloric acid. The 1,4-dibromo-2,3-naphthalenedicarboxylic acid (VIa) immediately precipitated. The dihalopyromellitic acids (X) remained in solution. The solution was saturated with sodium chloride and exhaustively extracted with ether. Evaporation of the ether gave crude X. Yields of pure X were calculated on the basis of the tetramethyl esters, which were obtained by refluxing methanol solutions (50 ml.) of X for 30 min., cooling, and adding ether (50 ml.) and excess ethereal diazomethane. The crude esters from ozonations in methylene chloride were shown by comparisons of infrared spectra with those of pure samples (ester band at 5.72 μ) to be 97–98% pure; those from ozonations in methylene chloride–methanol solutions were shown to be 80–83% pure. Yields of pure esters (and thus pure X) were calculated on this basis and are given in Table I.

Crude **1,4-dibromo-2,3-naphthalenedicarboxylic acid (VIa)** had m.p. 220–235°; recrystallized from ethanol (charcoal), m.p. 246–247°.

Anal. Calcd. for $C_{12}H_6Br_2O_4$: C, 38.5; H, 1.6; Br, 42.7. Found: C, 38.6; H, 1.7; Br, 43.2.

The material gave a positive Beilstein test for halogen and a positive test for *o*-dicarboxylic acids.[9]

Crude **3,6-dibromo-1,2,4,5-benzenetetracarboxylic acid (or dibromopyromellitic acid, Xa)** melted at 365–372°. The pure acid, recrystallized from 5 *N* hydrochloric acid, melted too high to obtain an accurate melting point.

Anal. Calcd. for $C_{10}H_4Br_2O_8$: C, 29.2; H, 1.0; Br, 38.8. Found: C, 29.3; H, 1.2; Br, 38.9.

The crude **tetramethyl ester** of Xa was purified by recrystallization from methanol, m.p. 195–196°.[10]

Anal. Calcd. for $C_{14}H_{12}Br_2O_8$: C, 35.9; H, 2.6; Br, 34.1; OCH_3, 26.5. Found: C, 36.0; H, 2.6; Br, 32.8; OCH_3, 26.2.

The acid (Xa) was further identified by catalytic dehalogenation (Pd–$BaSO_4$) to give pyromellitic acid, m.p. 270–271°. Identification was by a mixture melting point with an authentic sample.[11]

Procedure B. Oxidative Work-Up.—This procedure was exactly the same as procedure A, except that after the ozonation the reaction mixture was evaporated and the residue was taken up in 50 ml. of methanol, 30 ml. of 30% hydrogen peroxide, and 70 ml. of 5% aqueous sodium hydroxide solution. The resulting mixture was stirred for 36 hr., after which time active oxygen was no longer present.

3,6-Dichloro-1,2,4,5-benzenetetracarboxylic acid (or dichloropyromellitic acid, Xb) melted too high to obtain an accurate melting point. It was recrystallized from 5 *N* hydrochloric acid.

Anal. Calcd. for $C_{10}H_4Cl_2O_8$: C, 37.2; H, 1.2; Cl, 22.0. Found: C, 36.9; H, 1.5; Cl, 21.5.

The pure **tetramethyl ester of Xb** (recrystallized from methanol) melted at 176–177°.[12]

Anal. Calcd. for $C_{14}H_{12}Cl_2O_8$: C, 44.3; H, 3.2; Cl, 18.7; OCH_3, 32.7. Found: C, 44.6; H, 3.2; Cl, 18.7; OCH_3, 32.7.

Procedure C. Oxidative Work-Up.—This procedure was exactly the same as procedure A, except that the oxidizing mixture was 100 ml. of 4% aqueous sodium hydroxide and 30 ml. of 30% hydrogen peroxide, and it was necessary to reflux the mixture for only 3 hr. to destroy all active oxygen.

Procedure D. Nonoxidative Work-Up.—After ozonation, 5–10 ml. of water was added to the reaction mixture, and the resulting mixture was stirred at room temperature (27°) until no more active oxygen was present (2–3 hr.). The reaction mixture was evaporated to dryness (rotar) and the residue was dissolved in 75–150 ml. of carbon tetrachloride and chromatographed on acid-washed alumina (Merck). Elution with 400–800 ml. of petroleum ether (b.p. 40–60°) gave unchanged dihaloanthracene (Xa, m.p. 218–221°; Xb, m.p. 209–211°). Elution with 300–600 ml. of methylene chloride gave the fraction from which pure anthraquinone (VIII) was obtained by recrystallization from ethanol.

Procedure E. Nonoxidative Work-Up.—This procedure was exactly the same as procedure D, except that after the ozonation, the reaction mixture was evaporated (rotar), the residue was taken up in carbon tetrachloride, and the carbon tetrachloride solution was refluxed until it was no longer peroxidic, and then was chromatographed.

Procedure F. Nonoxidative Work-Up.—The precipitated ozonide was filtered off and the filtrate was evaporated, giving anthraquinone (VIII) melting at 280–282°.

Determination of Bromine in Ozonation Mixture.—A solution of 3 mmoles of 9,10-dibromoanthracene (Ia) in 90 ml. of methylene chloride and 10 ml. of methanol was ozonized with 2 mole equiv. of ozone from ozone–oxygen. The solution was titrated with standard phenol solution (American Hospital Supply Corp., Evanston, Ill.); 0.26 mmole of phenol reacted, indicating 0.78 mmole of bromine. On the basis of the anthraquinone yield in expt. 6 and 7 (Table I), this represents approximately a quantitative yield of the expected bromine.

Treatment of 9,10-Dibromoanthracene (Ia) with Hydrochloric Acid and Hydrogen Peroxide.—A mixture of 0.266 g. of 9,10-dibromoanthracene (Ia), 90 ml. of methylene chloride, 10 ml. of methanol, 5 drops of concentrated hydrochloric acid, and 5 drops of 30% hydrogen peroxide was heated on the steam bath for 6 hr. Evaporation of the reaction mixture gave material, the infrared spectrum of which indicated it to be a mixture of 9,10-dibromoanthracene (Ia), 9,10-dichloroanthracene (Ib), and anthraquinone (VIII). 9,10-Dibromoanthracene was recovered unchanged after treatment with alkaline or neutral hydrogen peroxide.

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