solution was diluted with water and the resinous precipitate was separated by decantation. The precipitate was taken up in warm ethanol and the solution was passed through a column of acid-washed Magnesol-Celite.[1a] The eluate was warmed and diluted to incipient opalescene with hot water. On standing overnight, crystalline macluraxanthone separated; the recovery was 17 mg., identified by its infrared spectrum.

An amount of 300 mg. of macluraxanthone in 25 ml. of ethanol was brought to reflux and about 100 mg. of *p*-toluenesulfonic acid was added. After refluxing 12 hr., the ethanol solution was reduced to a small volume under reduced pressure and diluted with water. Filtration and recrystallization of the crude precipitate gave pure starting material; the recovery was 148 mg., identified by its mixture melting point with an authentic sample and by its infrared spectrum. The above methods had been found suitable for the isomerization of osajin and pomiferin.[2]

The Attempt to Obtain a Diels–Alder Adduct of Macluraxanthone.—A solution of 100 mg. of macluraxanthone in xylene was refluxed for 2 hr. with a large excess of maleic anhydride. On processing, the pigment was recovered as the sole product; the recovery was 78 mg.

1,3,5,6-Tetrahydroxyxanthone.[7]—A mixture of 18.0 g. of anhydrous phloroglucinolcarboxylic acid, 18.0 g. of anhydrous pyrogallol, and 200 ml. of phosphorus oxychloride was warmed to 70° and 80.0 g. of freshly fused zinc chloride was added. The reaction mixture was stirred at 70° for 1.5 hr., cooled, and poured into 2.5 l. of ice and water and stirred for 0.5 hr. The precipitate was filtered, washed with 500 ml. of water, and recrystallized from ethanol–water. After vacuum drying at 78°, the crude xanthone was sublimed at 220–230° and 0.03 mm. The sublimate was recrystallized from ethanol–water, yielding 6.19 g., m.p. 352–354°; lit. m.p. 310°,[5] 320°,[35] 357°.[7]

1-Hydroxy-3,5,6-trimethoxyxanthone.—An amount of 1.00 g. of 1,3,5,6-tetrahydroxyxanthone was treated with ethereal diazomethane as described for the preparation of macluraxanthone dimethyl ether. Recrystallization from acetic acid–water yielded 0.71 g. of long yellow needles, m.p. 183–184°; lit m.p. 182–183°,[5] 185°.[7]

1,3,5,6-Tetraacetoxyxanthone.—A solution of 1.00 g. of 1,3,5,6-tetrahydroxyxanthone in 10 ml. of pyridine was cooled to 0° and 40 ml. of precooled acetic anhydride was added. The solution was kept at 0° overnight and then poured into 500 ml. of water. Filtration and recrystallization from acetic acid–water yielded 0.98 g. of long white needles, m.p. 248°, undepressed upon admixture with an authentic sample prepared by the method of Tanase.[5,35]

1-Hydroxy-3,5,6-triacetoxyxanthone.—An amount of 4.35 g. of triacetyl borate[36] was added to a solution of 1.00 g. of 1,3,5,6-tetrahydroxyxanthone in 40 ml. of acetic anhydride, and the mixture was refluxed for 15 min. The red solution was cooled and diluted to 100 ml. with absolute ether. On standing at 0° for 3 hr., bright yellow needles of the borate complex were deposited, which were filtered, washed well with ether, and decomposed by boiling in water. Filtration and recrystallization from acetic acid–water yielded 0.51 g. of long yellow needles, m.p. 168–169°.

Anal. Calcd. for $C_{13}H_5O_6(COCH_3)_3$: C, 59.07; H, 3.65; CH_3CO, 33.42. Found: C, 58.78; H, 3.68; CH_3CO, 33.33.

1,3,5,6-Tetramethoxyanthone.—A solution of 1.00 g. of 1,3,5,6-tetrahydroxyanthone in 75 ml. of acetone over 25 g. of potassium carbonate was brought to reflux and 15.0 ml. of dimethyl sulfate was added. The mixture was refluxed overnight and filtered, and the filtrate was reduced to dryness under reduced pressure. Recrystallization of the residue from methanol–water and ether–petroleum ether yielded 0.92 g. of white plates, m.p. 146–147°.

Anal. Calcd. for $C_{13}H_4O_2(OCH_3)_4$: C, 64.56; H, 5.10; OCH_3, 39.23. Found: C, 64.63; H, 5.30; OCH_3, 39.65.

Acknowledgment.—We gratefully acknowledge fellowship support from the Graduate School of The Ohio State University and the National Science Foundation. We wish to thank W. D. Ollis of the University of Bristol for enlightening discussions, Peter Yates of the University of Toronto for a sample of di-O-methylmangostin, and J. W. W. Morgan of the Forest Products Research Laboratories, Princes Risborough, England, for samples of jacareubin trimethyl ether and dihydrojacareubin dimethyl ether.

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Ozonolysis of Naphthalenes. The Aromatic Products[1]

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Ozonolyses of naphthalene, 2,3-dimethylnaphthalene, 2-hydroxynaphthalene, 2-methoxynaphthalene, and 2-ethoxynaphthalene in participating and nonparticipating solvents are reported. In methanol the first three compounds give the same product, 4-methoxy-2,3-benzodioxan-1-ol. 2-Methoxy- and 2-ethoxynaphthalene react differently to give 1,4-dimethoxy-2,3-benzodioxan. The above named peroxides can be converted to methyl phthalaldehydate, phthalaldehydic acid, and phthalic acid in high yields. In nonparticipating solvents the peroxidic ozonolysis products appear to be diozonides.

Naphthalene (Ia) previously[1] has been ozonized by Harries,[3] Seekles,[4] and Wibaut and Kampschmidt.[5] In addition, the ozonolyses of 1,4- and 2,3-dimethylnaphthalene (Ib),[5,6] 1- and 2-methylnaphthalene,[7] 1- and 2-phenylnaphthalene,[8] 1- and 2-hydroxynaphthalene (Ic),[9a] and 2,3-dihydroxynaphthalene[9b] have been reported. Two moles of ozone per mole of the naphthalene compound readily were absorbed, after which absorption continued more slowly, apparently involving attack on the other ring; the homologs of naphthalene were attacked almost exclusively in the methylated ring by the first 2 mole equiv. of ozone.[5,7]

Until our earlier report,[1] only "nonparticipating" solvents (solvents which do not enter into the formation of the peroxidic ozonolysis product[10]) had been

(1) For a preliminary report on part of this work, see P. S. Bailey and F. J. Garcia-Sharp, *J. Org. Chem.*, **22**, 1008 (1957). More recent aspects were reported at the 18th Southwest Regional Meeting of the American Chemical Society, Dallas, Tex., December, 1962.

(2) Deceased, November 4, 1962.

(3) C. Harries, *Ann.*, **343**, 336, 372 (1905).

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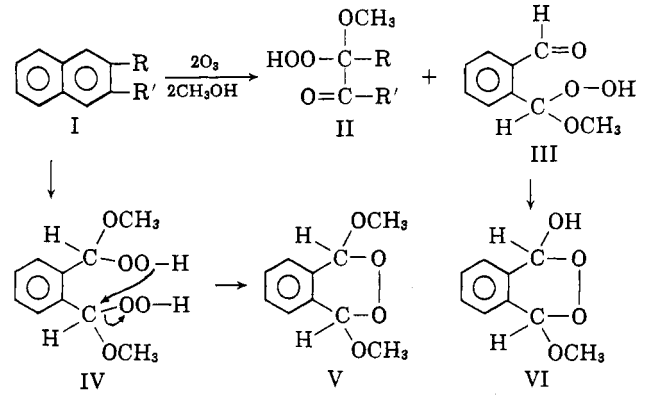
(9) (a) E. Bernatek and C. Frengen, *Acta Chem. Scand.*, **16**, 2421 (1962); (b) E. Bernatek and A. Vincze, to be published.

(10) P. S. Bailey, *Chem. Rev.*, **58**, 925 (1958).

employed in these ozonolyses, and the results had been interpreted variously.[5,6,11]

The ozonolyses of naphthalene (Ia), 2,3-dimethylnaphthalene (Ib), 2-naphthol (Ic), 2-ethoxy- (Ig), and 2-methoxynaphthalene (Ie) have now been studied, using both participating solvents such as methanol, and nonparticipating solvents such as methylene chloride. A more complete picture of the course of ozonolysis of the naphthalene ring system has thus been obtained.



a, R = R′ = H
b, R = R′ = CH_3
c, R = OH; R′ = H
d, R = H; R′ = OH
e, R = OCH_3; R′ = H
f, R = H; R′ = OCH_3
g, R = OEt; R′ = H

Naphthalene (Ia) in methanol solution absorbs 2 mole equiv. of ozone to produce peroxides IIa and III. The mechanism of this reaction and the fate of IIa and similar peroxides are discussed in the accompanying paper.[12] Peroxide III is not isolated as such, but cyclizes to 4-methoxy-2,3-benzodioxan-1-ol (VI) in good yield. The cyclization does not appear to occur at low temperatures, since the cyclic peroxide (VI) does not precipitate from the reaction mixture until it is brought to room temperature and recooled.

The structural assignment given VI is based upon elemental and methoxyl analyses, a molecular weight determination, the infrared spectrum which showed a hydroxyl but no carbonyl band, the n.m.r. spectrum (see Table I), a positive iodide test for a peroxide, but a negative lead tetraacetate test[10] for a hydroperoxide,

TABLE I

NUCLEAR MAGNETIC RESONANCE SPECTRA OF CYCLIC PEROXIDES[a]

Compound	Hydrogen	Shift, τ	Relative peak areas
4-Methoxy-2,3-benzodioxan-1-ol (VI)	Phenyl	2.5 (center)	4
	H	4.2	2
	OH	5.1	1[b]
	CH_3	6.1	3
1,4-Dimethoxy-2,3-benzodioxan (V)	Phenyl	2.5 (center)	2
	H	4.2	1
	CH_3	6.1	3
1,4-Diethoxy-2,3-benzodioxan	Phenyl	2.5 (center)	2
	H	4.2	1
	CH_2	6.2[c]	2
	CH_3	8.8[c]	3

[a] Run as saturated solutions in methylene chloride with trimethylsilane as internal standard. [b] Relative peak area slightly less than 1. [c] Center (typical ethyl group splittings).

(11) E. C. Kooyman, *Rec. trav. chim.*, **66**, 201 (1947).
(12) C. D. Johnson and P. S. Bailey, *J. Org. Chem.*, **29**, 703 (1964).

its conversion to methyl phthalaldehydate (X) and phthalaldehydic acid (XII) in good yield, and analogy to the phenanthrene peroxidic ozonolysis products.[13,14]

2,3-Dimethylnaphthalene (Ib) reacts with ozone in methanol in predominantly the same way that naphthalene (Ia) does. Although the isolated yield of crystalline peroxide VI was low, an infrared spectrum of the oily product showed that it was largely VI, together with methyl phthalaldehydate (X). A positive test also was given for phthalaldehyde (XVII). When the ozonolysis reaction mixture is brought to room temperature, an exothermal reaction occurs, probably due to decomposition of peroxide IIb. This apparently induces considerable decomposition of peroxide VI to methyl phthalaldehydate (X), and makes the isolation of VI from the mixture difficult. Good yields of the expected decomposition products of peroxide IIb[12] give additional evidence for the major course of the ozonolysis of Ib to IIb and VI.

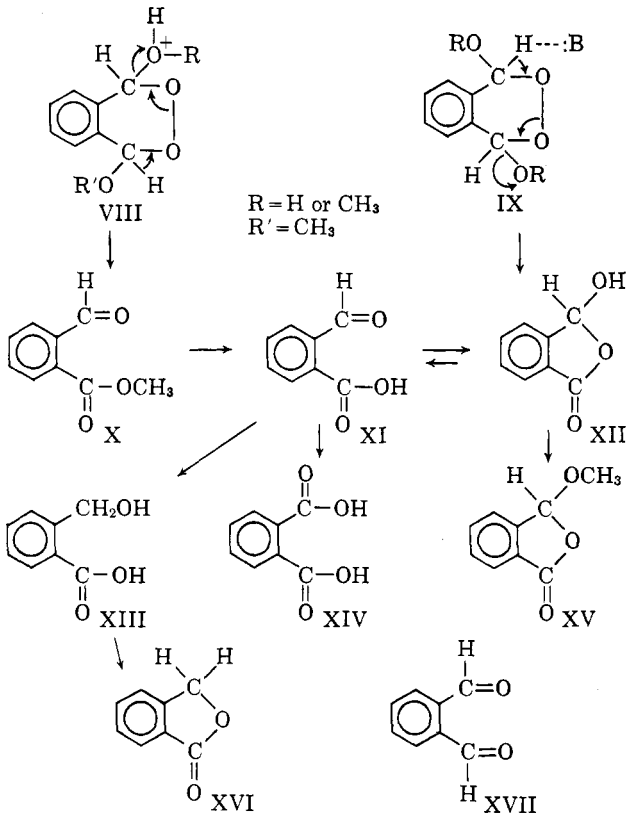
Ozonolysis of 2-naphthol (Ic) in methanol also results, at least predominantly, in cyclic peroxide VI. Whether the other peroxidic product is IIc or IId is discussed in the accompanying paper.[12]

In contrast, 2-methoxynaphthalene (Ie) and 2-ethoxynaphthalene (Ig) gave, at least largely, 1,4-dimethoxy-2,3-benzodioxan (V) under exactly the same conditions that naphthalene (Ia), 2,3-dimethylnaphthalene (Ib), and 2-naphthol (Ic) gave peroxide VI. The other products were methyl (from Ie) and ethyl (from Ig) glyoxalate (VIIe and g) in good yield. Ozonolysis of 2-methoxynaphthalene (Ie) in ethanol gave the diethoxy equivalent of V and methyl glyoxalate (VIIe). Peroxide VI was not converted to V under the conditions of these ozonolyses; a mineral acid was necessary to catalyze the conversion. For these and other reasons discussed in the accompanying paper,[12] we have concluded that Ie and Ig react in a different manner than do the other naphthalenes studied, to give initially VII and IV, rather than IIe or IIf (or ethoxy equivalents from Ig) and III, after which IV cyclizes to V through loss of hydrogen peroxide.

Ozonolyses of naphthalene (Ia) and 2,3-dimethylnaphthalene (Ib) in methanol to give useful nonperoxidic products without isolation of VI, as well as the conversions of VI and V to such products, also have been studied. When the methanolic reaction mixtures from ozonolyses of naphthalene or 2,3-dimethylnaphthalene were refluxed for several hours, the major product was methyl phthalaldehydate (X). When some hydrochloric acid was present, 3-methoxyphthalide (XV) also could be isolated. If the reaction mixtures were evaporated and hydrochloric acid or formic acid suspensions of the residues were refluxed, phthalaldehydic acid (XII) was obtained in excellent yield. High yields of this acid also were obtained if aqueous sodium hydroxide was added to the methanolic reaction mixture, and the solution then was refluxed and acidified. If hydrogen peroxide were present under acidic or basic conditions, phthalic acid (XIV) was obtained. Similar decompositions of the pure peroxides, VI and

(13) (a) P. S. Bailey, *J. Am. Chem. Soc.*, **78**, 3811 (1956); (b) P. S. Bailey and S. B. Mainthia, *J. Org. Chem.*, **23**, 1089 (1958).
(14) (a) J. P. Wibaut and T. J. de Boer, *Rec. trav. chim.*, **78**, 183 (1959); (b) M. G. Sturrock, E. L. Cline, and K. R. Robinson, *J. Org. Chem.*, **28**, 2340 (1963).

SCHEME I



V, gave high yields of phthalaldehydic acid or, with hydrogen peroxide, phthalic acid. (See Scheme I.)

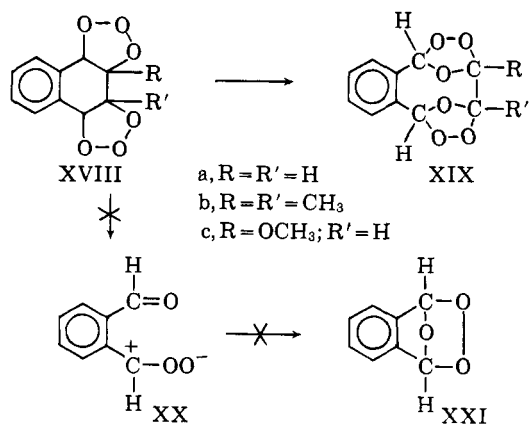
Logical mechanisms for the acid- and base-catalyzed rearrangements of VI and V are illustrated in structures VIII and IX. From VI either phthalaldehydic acid (XII) or methyl phthalaldehydate (X) could be produced, depending on whether the methoxyl or the hydroxyl group is eliminated. Under acidic or "neutral" conditions in methanol solution the major product is methyl phthalaldehydate. Thus, in VIII the major reaction must have been as shown, for had the decomposition occurred the alternative way, to give phthalaldehydic acid (XII), followed by esterification, the product would have been 3-methoxyphthalide (XV).[15] The small amount of 3-methoxyphthalide (XV) found under acidic conditions could have come either from a minor decomposition of VI to give phthalaldehydic acid (XII) followed by esterification to XV, or by hydrolysis of X to XII, followed by reesterification to XV.[15] Decomposition of V, of course, could give only methyl phthalaldehydate (X) initially. In the presence of base or with aqueous acidic solutions, hydrolysis of X occurs to give a high yield of phthalaldehydic acid (XII), and, with hydrogen peroxide present, XI (in equilibrium with XII) is oxidized to phthalic acid (XIV). In the base-catalyzed decomposition of VI, shown in IX, there is obviously no way of telling whether or not one of the two groups, hydroxy or methoxy, was preferentially eliminated.

Attempts to synthesize phthalaldehyde (XVII) by iodide reduction of either the methanolic naphthalene ozonolysis reaction mixture or the pure peroxides VI and V failed. Only phthalaldehydic acid (XII) was obtained. Similarly, treatment of the ozonolysis reaction mixture with dinitrophenylhydrazine gave only the dinitrophenylhydrazone (DNP) of phthalaldehydic acid. Apparently, the acid- or base-catalyzed decompositions occur more rapidly than reduction. From sodium borohydride reduction of VI and V, fair yields of phthalide (XVI) were obtained, presumably from the base-catalyzed decomposition to phthalaldehydic acid (XI $\rightleftharpoons$ XII) followed by reduction to *o*-carboxybenzyl alcohol (XIII) and dehydration to XVI, or, less likely, by reduction to phthalaldehyde (XVII) followed by the Cannizarro reaction to XIII and dehydration to XVI.

Ozonolysis of naphthalene (Ia) in hexane or carbon tetrachloride gave a white crystalline peroxide which decomposes *violently* when left to dry in chunks. When washed thoroughly with solvent and finely divided, it decomposes more slowly to an oil, usually without violence. Attempts to recrystallize it convert it to an oil which is peroxidic, but usually nonexplosive; it is probably polymeric.

Harries[3] reported that the crystalline peroxide (from ozonolysis of naphthalene in chloroform) gave analyses for a diozonide, and Wibaut[5] isolated some glyoxime from treatment of the material with hydroxylamine. Since (1) the peroxide was very unstable and difficult to analyze, (2) Harries[3] had already erroneously reported that the ozonide of phenanthrene also gave analyses for a diozonide, (3) in our hands the naphthalene "ozonide" did not give glyoxime or any other derivative of glyoxal, (4) the active oxygen determination of the ozonide, though low, was closer to the value for XXI than for XIXa, and (5) ozonolysis of naphthalene in methanol resulted in complete cleavage to II and VI, it was suggested that complete cleavage occurred also in nonparticipating solvents to give XX, and hence XXI.[1]

In order to decide with certainty between structures XIXa and XXI, 2,3-dimethylnaphthalene (Ib) and 2-methoxynaphthalene (Ic) were ozonized in nonparticipating solvents. The infrared spectra of the resultant peroxides were different from each other and from that given by the naphthalene ozonide, thereby eliminating structure XXI. Further, the "ozonide" from 2,3-dimethylnaphthalene reacted with 2,4-dinitrophenylhydrazine to give the dinitrophenylhydrazones of both aliphatic and aromatic moieties. Thus, all carbon atoms were still present in the peroxide, and it was either a monomeric or a polymeric diozonide. It then became possible to analyze the carefully washed "ozonides," and, in both the case of naphthalene and of 2-methoxy-



(15) D. D. Wheeler, D. C. Young, and D. S. Erley, *J. Org. Chem.*, **22**, 547 (1957).

naphthalene, the "ozonide" gave analyses reasonably close to the value for a diozonide.

It also has been shown that when the ozonide from naphthalene is decomposed in ethanol, a good yield of ethyl formate is produced, indicating that all carbon atoms were still present. Because of the crystallinity and instability of these "ozonides" a monomeric (XIX) rather than a polymeric structure is favored.

In view of the recent necessary revision of the Criegee mechanism,[16] the formation of XIX rather than XXI is no longer surprising, since XVIII (or its "stepwise equivalents") can either undergo complete cleavage to a moiety such as XX, or rearrangement to XIX. Complete cleavage almost invariably occurs during ozonolysis in participating solvents, but rearrangement is frequently associated with nonparticipating solvents.[16]

Experimental[17]

The naphthalene compounds used were obtained commercially, and, if necessary, were recrystallized or distilled to give the melting or boiling points recorded in the literature. Ozonolysis solvents were pure and anhydrous.

4-Methoxy-2,3-benzodioxan-1-ol (VI). A. From Ozonolysis of Naphthalene (Ia) in Methanol.—Into a finely divided suspension of 6 g. of naphthalene in 50–100 ml. of methanol (or 50 ml. of methanol and 50 ml. of methylene chloride) cooled to −50° was passed on oxygen–ozone stream containing about 1.3 mmoles of ozone per liter. The naphthalene slowly dissolved and upon completion of the ozonolysis the solution turned blue. The solution was swept with nitrogen. The ozone uptake corresponded to 2.0 mole equiv. The solution was evaporated at room temperature, using a rotary evaporator, to a viscous oil. Upon addition of 10–30 ml. of water, crystallization occurred.

The crude white crystals which may melt as low as 90–95° (best yield 99%) or as high as 115° (best yield 95%) are recrystallized from acetone or ethyl acetate by addition of petroleum ether (b.p. 40–60°) or from chloroform. In the best experiment the yield of pure 4-methoxy-2,3-benzodioxan-1-ol (VI) melting at 126–127° was 91%.

Anal. Calcd. for $C_9H_{10}O_4$: C, 59.33; H, 5.53; methoxyl, 17.04; mol. wt., 182. Found: C, 59.39; H, 5.38; methoxyl, 16.89, 17.10; mol. wt. (cryoscopic in ethylene bromide), 184, 190.

The yields varied from 40 to 91%, but were usually around 80%. In several cases the work-up procedure was to allow the reaction mixture to come to room temperature, recool to −78°, and filter the precipitated crystalline peroxide (VI) after several hours. No precipitate of VI was ever obtained unless the reaction mixture first was brought to room temperature.

The pure peroxide (VI) was stable to shock, burned quickly in an open flame, and gave a weak but definite iodide test for a peroxide, but a negative hydroperoxide test with lead tetraacetate.[10] It was very soluble in methanol, acetone, ethyl acetate, and ether, and almost insoluble in benzene, carbon tetrachloride, chloroform, and hexane. Its infrared spectrum (taken in methylene chloride or Nujol mull) showed no carbonyl band, but did show a hydroxyl band at 2.8, an ether band at 9.2, and a band at 7.4 μ similar to that present in the cyclic peroxides from ozonolysis of phenanthrene in methanol.[13] The n.m.r. spectrum gave the results shown in Table I. The sample appeared to contain a trace of the dimethoxyperoxide (V) since the hydroxyl peak was slightly too small.

B. From Ozonolysis of 2-Naphthol (Ic) in Methanol.—The ozonolysis was carried out with a solution of 10 g. of 2-naphthol in 160 ml. of methanol. A red coloration was immediately produced, but then slowly disappeared; 2 mole equiv. of ozone reacted. The reaction mixture was evaporated under reduced pressure, and the white solid residue was dried (wt. 12.7 g.) and recrystallized from an ethyl acetate–petroleum ether mixture to give 4.8 g. (38%) of crude peroxide melting at 110–115°. Further recrystallization raised the melting point to 126–127°. The material was shown to be the same as that obtained from the naphthalene ozonolysis by a mixture melting point and by comparison of infrared spectra. From a careful examination of infrared spectra, the initial solid appeared to be largely VI (judging from the hydroxyl peak and a distinctive peak at 9.6 μ), contaminated with some methyl phthalaldehydate (X, peaks at 5.65 and 5.83 μ). No other compound, such as V (distinctive peaks at 7.5 and 7.6 μ), appeared to be present.

During the warming of the ozonolysis solution to room temperature an exothermal reaction occurred and carbon dioxide (detected in a baryta trap) was evolved. This does not occur in the naphthalene ozonolysis, and probably accounts partially for the higher yields of VI isolated from naphthalene.

C. From Ozonolysis of 2,3-Dimethylnaphthalene (Ib) in Methanol.—The ozonolysis was carried out as in A and B. 2,3-Dimethylnaphthalene (3 g.) in 60 ml. of methanol was used and 2.0 mole equiv. of ozone was taken up. On warming, the solution underwent a vigorous exothermal reaction. The solution was evaporated and the solvent was trapped at −78°. It was tested for biacetyl with 2,4-dinitrophenylhydrazone, but no precipitation occurred.

The residue, a yellow oil (3.5 g.), was shown by its infrared spectrum to consist approximately of equal amounts of cyclic peroxide VI and methyl phthalaldehydate (X, see preceding experiment). This amounts to a 50% yield of VI. The oil crystallized partially from a methylene chloride–petroleum ether mixture to give a 39% yield of crude VI, m.p. 104–111°.

In another experiment, when the ozonolysis was carried out in a solution of methanol and chloroform, the oily residue partially crystallized upon addition of water and, after recrystallization from an ethyl acetate–petroleum ether mixture, gave a 62% yield of impure VI, m.p. 102–105°. The aqueous mother liquor gave a black coloration when treated first with ammonia and then with glacial acetic acid,[4] indicating the presence of phthalaldehyde (XVII). This was present only in traces, however, since none could be isolated by steam distillation.

Identifications of crude VI were by infrared spectra.

Ozonolysis of naphthalene (Ia) in ethanol gave only an intractable oil.

1,4-Dimethoxy-2,3-benzodioxan (V). A. From Ozonolysis of 2-Methoxynaphthalene (Ie).—A suspension of 10 g. of 2-methoxynaphthalene in 100 ml. of methylene chloride and 80 ml. of methanol was ozonized at −60°, as described in the naphthalene experiments; 2 mole equiv. of ozone were absorbed. Evaporation of the reaction mixture and trituration of the solid residue with a small amount of methanol gave 8.4 g. (68% yield) of 1,4-dimethoxy-2,3-benzodioxan (V), m.p. 100–102°. Recrystallization from ethyl acetate–petroleum ether gave a 50% yield of the pure peroxide melting at 111–112°. An infrared spectrum (methylene chloride or Nujol mull) showed no hydroxyl or carbonyl bands but did show doublet ether bands typical of acetals at 9.1–9.3, and characteristic bands at 7.4, 7.5, and 7.6 μ similar to bands for the analogous phenanthrene peroxides.[13] The n.m.r. spectrum of the compound is described in Table I.

Anal. Calcd. for $C_{10}H_{12}O_4$: C, 61.21; H, 6.17; O, 32.62; methoxyl, 31.64. Found: C, 61.26; H, 6.06; O, 32.62; methoxyl, 31.15.

Similar results were obtained using methanol only as a solvent.

In another experiment the crude solid obtained from evaporation of the reaction mixture was triturated with water (50 ml.) with overnight stirring. The solid was filtered and traces of oil were removed by passage of the filtrate through a short cellulose column. To the clear, aqueous, only slightly peroxidic solution was added excess phenylhydrazine in aqueous acetic acid (10%), and after several hours the phenylhydrazone of methyl glyoxalate (VIIe) was removed by filtration (m.p. 125°), recrystallized from methanol and then benzene, m.p. 142° (60% yield). The compound was identified by a mixture melting point and comparison of infrared spectra with an authentic sample (m.p. 138°) prepared by the ozonolysis of dimethyl fumarate.[18]

Methyl glyoxalate (VIIe) was also found by v.p.c. in high yield.[12]

B. From Ozonolysis of 2-Ethoxynaphthalene (Ig) in Methanol.—The ozonolysis was carried out in the usual manner with 1.78 g. of Ig. The solution was evaporated and the residual oil was allowed to stand at 5° under water. Fine needles of V melting at 105–107° precipitated in 35% yield and were identified by

(16) P. S. Bailey, S. B. Mainthia, and C. J. Abshire, *J. Am. Chem. Soc.*, **82**, 6136 (1960).

(17) Melting points are corrected. Most elemental and group analyses were performed by commercial laboratories. The ozonation apparatus and procedure were described in earlier papers.[12]

(18) C. Harries, *Ber.*, **36**, 1936 (1903).

the mixture melting point method and comparison of infrared spectra. The remaining oil was shown by its infrared spectrum to be approximately a 50:50 mixture of V and methyl phthalaldehydate (X, see earlier spectral discussion).

The aqueous layer, when treated with phenylhydrazine as in the preceding experiment, gave an 89% yield of the phenylhydrazone of ethyl glyoxalate (VIIg) melting at 129–131°; identification was by a mixture melting point and comparison of infrared spectra with an authentic sample (m.p. 129–131°) prepared by ozonolysis of diethyl fumarate.[18]

C. From Ozonolysis of Naphthalene (Ia) in Methanol.—The ozonolysis was carried out with 2.14 g. of naphthalene in 40 ml. of methanol and 6 drops of concentrated hydrochloric acid. The isolated peroxide weighed 1.97 g., m.p. 90–93°. An infrared spectrum (in methylene chloride) showed the material to be largely the dimethoxy peroxide (V) contaminated with VI (see earlier spectral discussion). Fractional recrystallization from ethyl acetate–petroleum ether gave a small amount of pure VI, the rest being impure V which could not be further separated from traces of VI (infrared spectra). The experiment was repeated using one drop of hydrochloric acid. The infrared spectrum of the product showed a smaller amount of the dimethoxy peroxide (V) to be present. Further ozonolyses in the presence of formic acid, acetic acid, and dimethyl carbonate gave only peroxide VI contaminated with methyl phthalaldehydate (X, infrared spectra). Pure peroxide VI in methanol behaved similarly when the above reagents were added.

1,4-Diethoxy-2,3-benzodioxan.—Ozonolysis of 2-methoxynaphthalene (Ie) in ethanol–methylene chloride in the same way as described for the preparation of V gave a 48% yield of the peroxide, m.p. 73–80°. The infrared spectrum in methylene chloride showed only a trace of ethyl phthalaldehydate. Several recrystallizations from ethanol raised the melting point to 103°. The infrared spectrum showed neither a carbonyl nor a hydroxyl band. The n.m.r. spectrum demonstrated the absence of methoxyl hydrogen atoms (Table I).

Anal. Calcd. for $C_{12}H_{16}O_4$: C, 64.27; H, 7.19; O, 28.54; OCH_2CH_3, 40.19. Found: C, 64.30; H, 7.10; O, 28.79; OCH_2CH_3, 40.50.

In a further experiment, a 46% yield of methyl glyoxylate (VIIe) was isolated in the same way as described for the ozonolysis of 2-methoxynaphthalene in methanol.

Methyl Phthalaldehydate (X). A. From Ozonolysis of Naphthalene (Ia) in Methanol.—The ozonolysis solution obtained from 15 g. of naphthalene in 200 ml. of methanol as described earlier was refluxed overnight, after which it gave a negative peroxide test with iodide ion. The solution was evaporated, the residue was taken up in ether, and the extract was dried over magnesium sulphate and evaporated. Distillation of the residue gave 9.8 g. of an oil (51%), b.p. 118–128° (10 mm.), $n^{20}D$ 1.5250. The infrared spectrum in methylene chloride was compared with those of pure methyl phthalaldehydate [prepared from silver phthalaldehydate by treatment with methyl iodide, b.p. 102° (3 mm.), $n^{20}D$ 1.5403] and 3-methoxyphthalide [XV, prepared by refluxing a methanol solution of phthalaldehydic acid, b.p. 102° (2–3 mm.)]. This showed the oil to be methyl phthalaldehydate contaminated with a small amount of 3-methoxyphthalide (indicated by characteristic bands at 9.4 and 7.8 μ).

B. From Ozonolysis of 2,3-Dimethylnaphthalene (Ib) in Methanol.—The ozonolysis and work-up were carried out as in the preceding experiment. The yield of crude methyl phthalaldehydate (X) contaminated with XV was 72%. Treatment of the ozonolysis solution, in another instance, with 2,4-dinitrophenylhydrazine gave a 78% yield of the 2,4-dinitrophenylhydrazone of methyl phthalaldehydate, m.p. 240°; the infrared spectrum was essentially identical with that of pure phenylhydrazone, m.p. 260°.

C. From 1,4-Dimethoxy-2,3-benzodioxan (V).—A solution of 3 g. of V, 10 ml. of methanol, and 5 ml. of pyridine underwent an exothermal reaction after standing a few minutes. It was refluxed then for 4 hr. until free of active oxygen, and evaporated. Distillation of the residue gave 1.8 g. of practically pure methyl phthalaldehydate (X), b.p. 120° (5 mm.), $n^{20}D$ 1.5360. Identification was by comparison of the infrared spectrum with that of pure X.

3-Methoxyphthalide (XV) from Ozonolysis of 2,3-Dimethylnaphthalene (Ib) in Methanol.—A suspension of 10 g. of 2,3-dimethylnaphthalene in 180 ml. of methanol was ozonized at −60° as previously described. To the reaction mixture was added 5 ml. of concentrated hydrochloric acid and the resulting solution was stirred at 0° for 5 days, after which it was no longer peroxidic. The reaction mixture was evaporated; the residue was dissolved in ether and washed with sodium bicarbonate solution. The dried ethereal extract was distilled, giving 6.5 g. of an oil boiling at 125–128° (10 mm.). After several days the oil partially crystallized to give 0.5 g. of 3-methoxyphthalide (XV), m.p. 44–45°, after recrystallization from petroleum ether. It was identified by comparison of its infrared spectrum and by a mixture melting point with an authentic sample of XV.

Phthalaldehydic Acid (XII). A. From Ozonolysis of Naphthalene (Ia), Alkaline Work-Up.—A suspension of 2.0 g. of naphthalene in 40 ml. of methanol was ozonized in the usual manner. To the reaction mixture was added 10 ml. of aqueous sodium hydroxide solution (10%). The resulting mixture was refluxed for 0.5 hr., acidified with 2 *N* hydrochloric acid, and extracted with ether. Evaporation and recrystallization from water gave 2.1 g. (88%) of phthalaldehydic acid, m.p. 99°, identified by a mixture melting point with an authentic sample.

B. From Ozonolysis of Naphthalene, Acidic Work-Up.—The ozonolysis reaction mixture from 6 g. of naphthalene was evaporated free of methanol, and a mixture of the residue and 20 ml. of 50% formic acid was refluxed for 3 hr. On cooling, a 5% recovery of naphthalene was obtained, and on further cooling and evaporation tan crystals (91% crude yield), m.p. 91–95°, were deposited. Recrystallization from water (charcoal) gave an 86% yield of phthalaldehydic acid (XII) melting at 97–98°, identified by the mixture melting point method.

C. From Ozonolysis of 2,3-Dimethylnaphthalene (Ib).—The ozonolysis was carried out as usual with a suspension of 10 g. of 2,3-dimethylnaphthalene in 80 ml. of methylene chloride and 50 ml. of methanol at −60°. The reaction mixture was evaporated and a mixture of the residue, 50 ml. of water and 6 ml. of concentrated hydrochloric acid was refluxed for 4 hr. Volatile materials were removed by steam distillation, and the reaction mixture was evaporated to dryness with an air jet. The gummy residue was crystallized from water giving a 70% yield of phthalaldehydic acid (XII), m.p. 93–95°, identified by the mixture melting point method.

D. From 4-Methoxy-2,3-benzodioxan-1-ol (VI) and 1,4-dimethoxy-2,3-benzodioxan (V).—Aqueous hydrochloric acid solutions of the pure peroxides were refluxed as in preceding experiments. Evaporation and cooling of the reaction mixtures gave 82–92% yields of phthalaldehydic acid (XII), melting at 97–98°. Identification was by the mixture melting point method.

Phthalic Acid (XIV). A. From Ozonolysis of Naphthalene (Ia) and Oxidative Work-Up in Alkali.—To the ozonolysis solution from 2 g. of naphthalene and 40 ml. of methanol was added 10 ml. of aqueous sodium hydroxide (10%) and 8 ml. of 30% hydrogen peroxide. The mixture was refluxed for 0.5 hr., acidified, partially evaporated, and cooled, giving a solid which recrystallized from water to give a 73% yield of phthalic acid (XIV), m.p. 200°. Sublimation gave phthalic anhydride, m.p. 131°, identified by a mixture melting point with an authentic sample.

B. From Ozonolysis of Naphthalene and Oxidative Work-Up in Acid.—The ozonolysis reaction mixture (from 5 g. of naphthalene) was evaporated, and a mixture of the residue, 20 ml. of 50% formic acid, and 6 ml. of 30% hydrogen peroxide was refluxed for 6 hr. A tan precipitate was obtained when the reaction mixture was cooled. Trituration of the precipitate with hexane and evaporation of the hexane gave a 5% recovery of naphthalene. Recrystallization of the precipitate from water (charcoal) gave an 88% yield of phthalic acid, m.p. 198–200°. Identification was as described in the preceding experiment.

C. From 4-Methoxy-2,3-benzodioxan-1-ol (VI).—A mixture of 2 g. of VI, 10 ml. of 10% aqueous sulfuric acid, and 1 ml. of 30% hydrogen peroxide was refluxed for 3 hr. On cooling, a 93% yield of phthalic acid, melting at 200°, was deposited. Identification was by the mixture melting point method.

Reductions. A. Active Oxygen Determinations Using Iodide Reduction.—The naphthalene compound (0.01 mole) was dissolved in methanol (60 ml.) and ozonized at −70°. In this low concentration the aliphatic hydroperoxide appeared to be more stable than in the previously described experiments where the concentration was much higher. The blue color due to excess ozone was discharged with nitrogen at −70°. In the cold determinations, sodium iodide in acetic acid (3.6 g. in 15 ml.) was added at the low temperature while nitrogen was bubbled through. The temperature then was allowed to rise. Iodide liberation was not vigorous until the temperature rose above 0°. In the room temperature determinations, the reaction mixture

TABLE II

ACTIVE OXYGEN DETERMINATIONS ON OZONOLYSIS MIXTURES

Mixture	Temp., °C.	Mole equiv. of active oxygen
Ia reaction mixture	−78	1.0
	R.T.[a]	1.0
Ib reaction mixture	−78	1.4
	R.T.	1.0
Ie reaction mixture	−78	1.2
	R.T.	1.2
Pure VI	R.T.	0.2
Pure V	R.T.	very slight

[a] Room temperature.

was allowed to come to room temperature, kept there for 1 hr., recooled to −70°, and then treated with sodium iodide. Titrations were with 0.1 *N* sodium thiosulfate at room temperature, air being displaced from the flask by carbon dioxide. Results are shown in Table II.

The reduction mixture of compound Ia (cold), after titration, was acidified and extracted with ether. The ether extract was extracted with dilute sodium carbonate solution, which then was acidified and extracted with ether. Evaporation of the ethereal layer and recrystallization of the residue from water gave phthalaldehydic acid melting at 95–99° (48% yield), identified by the mixture melting point method.

B. Catalytic reduction of VI was attempted using 2.1 g. of peroxide in 50 ml. of methanol and palladium on barium sulfate catalyst. One mole equiv. of hydrogen was absorbed. From the reaction mixture was obtained an 8% yield of yellow crystals, m.p. 54–56°. The recorded[4] melting point for phthalaldehyde is 53°.

C. Sodium Borohydride Reductions of VI and V.—To a solution of 3 g. of peroxides VI or V in 30 ml. of ethanol was added slowly a suspension of 1 g. of sodium borohydride in 15 ml. of ethanol. The mixture was kept at 0° for 3 hr. and at room temperature overnight. Evaporation of the solution and treatment of the residue with dilute sulfuric acid gave colorless crystals of phthalide (XVI), m.p. 70–72°. Yields were 36% from VI and 44% from V. Identification was by the mixture melting point method.

Ozonolysis of Naphthalene (Ia) in Nonparticipating Solvents.—A suspension of 2 g. of finely divided naphthalene in 30 ml. of purified *n*-hexane was ozonized at −60° with intermittent shaking. The ozone uptake was nearly quantitative until 2 mole equiv. of ozone was absorbed, after which iodine was released vigorously in the iodide trap and the ozonolysis mixture became blue. Baryta and palladious chloride traps attached to the ozonolysis vessel detected no carbon dioxide or monoxide evolved either during the reaction or during the warming to room temperature. The reaction mixture was flushed with oxygen and the copious crystalline peroxidic precipitate was filtered and washed with hexane. If allowed to dry in chunks it *exploded violently.* When dried in a finely divided state it decomposed slowly, without violence, to a gummy material. The material gave a strong iodide test for active oxygen, burned violently in a flame, exploded when hit with a hammer, and was soluble in ethanol, methanol, acetone, benzene, chloroform, and methylene chloride. On evaporation of these solvents, or on addition of hexane, only an oil was obtained. The oil was peroxidic but no longer explosive. The infrared spectrum (methylene chloride) showed a band in the carbonyl region, indicating decomposition had occurred.

Ozonolysis of naphthalene in carbon tetrachloride apparently gave the same material, as shown by infrared spectra. The material seemed to be purer and more stable. After it was washed several times with carbon tetrachloride, then with ether, and dried, it had a melting point of 78–80°. It was quickly and carefully analyzed.

Anal. Calcd. for $C_8H_6O_3$ (XXIa): C, 64.00; H, 4.03. Calcd. for $C_{10}H_8O_6$ (XIXa): C, 53.57; H, 3.60. Found: C, 54.96, 55.27; H, 4.53.

Attempts to obtain glyoxime from the ozonide by Wibaut's method[5b] failed. When the ozonide was treated with 2,4-dinitrophenylhydrazine reagent, a good yield of the hydrazone of phthalaldehydic acid was obtained. Paper chromatography (Whatman No. 1 paper; solvent, *n*-butyl alcohol 4, water 5, ethanol 2 parts by volume; spots developed by spraying with ethanol–potassium hydroxide mixture) showed it to be pure. No spot for glyoxal 2,4-dinitrophenylhydrazone was observed.

Reaction of the carefully washed "ozonide" with methanol, in which it slowly dissolved, gave carbon dioxide (0.3 mole equiv.) and methyl formate (0.5 mole equiv., detected by v.p.c., see accompanying paper[12]). From the reaction mixture was isolated a 10% yield of crude phthalic acid (XIV); it also gave a positive test for phthalaldehyde (XVII).[4]

The ozonide was then dissolved in ethanol. No carbon dioxide was evolved, suggesting that carbon dioxide had come previously from oxidation of methanol by the "ozonide." V.p.c. showed the presence of ethyl formate.[12]

Ozonolysis of 2-methoxynaphthalene (Ie) in carbon tetrachloride at −20° (0.5 g. in 50 ml.) resulted in the uptake of 2 mole equiv. of ozone and the precipitation of the "ozonide." Carefully washed with ether, the "ozonide" melted at 50–54°, gave a positive active oxygen test, exploded when hit with a hammer, and slowly decomposed to a probable polymeric peroxide. The freshly dried material was analyzed immediately and carefully.

Anal. Calcd. for $C_{11}H_{10}O_7$ (XIXc): C, 51.97; H, 3.97. Found: C, 50.00; H, 4.43.

The infrared spectrum in methylene chloride differed from that of the naphthalene "ozonide" (XIXa).

Ozonolysis of 2,3-dimethylnaphthalene in *n*-hexane or carbon tetrachloride gave a similar "ozonide", but its infrared spectrum differed from that of the naphthalene or 2-methoxynaphthalene "ozonides." When the thoroughly washed "ozonide" was treated with 2,4-dinitrophenylhydrazine reagent and the mixture was examined by paper chromatography as described previously, three spots were found, one due to phthalaldehydic acid (red), one for biacetyl (blue), and a third faint spot apparently due to phthaldehyde.

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