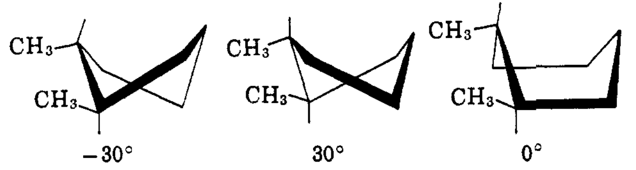
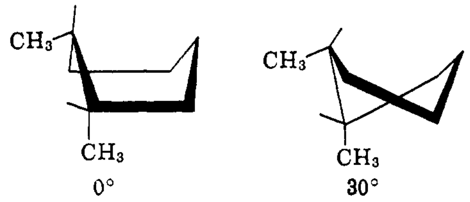
1,2-*trans*



1,2-*cis*



1,2-*cis*

Chair: $H° = 2.70$ kcal/mole, $\sigma = 1$; *dl*
Boat: $H° = 8.89$ kcal/mole, $\sigma = 1$; *dl*($\Theta = 30°$)

For chair ⇌ boat:

$$\Delta G^\circ_{cb} = 6.19 \text{ kcal/mole},\ K_{cb} = \exp(-6.19/RT)$$
$$N_{ea} = 1/(1 + K_{cb})$$

1,2-*trans*

Chairs: ee, $H° = 0.9$ kcal/mole, $\sigma = 2$; *dl*
aa, $H° = 3.6$ kcal/mole, $\sigma = 2$; *dl*

Boats: ba, $H° = 6.57$ kcal/mole, $\sigma = 2$; *dl* ($\Theta = 30°$)
bb, $H° = 8.66$ kcal/mole, $\sigma = 1$; *dl* ($\Theta = -30°$)

For chairs:

$$\begin{aligned} K &= \exp(-2700/RT) \\ N_{ee} &= 1/(1 + K) \qquad N_{aa} = 1 - N_{ee} \\ H^\circ_c &= \Sigma N_i H^\circ_i \\ S_c &= -R\,\Sigma(N_i \ln N_i) \end{aligned}$$

For boats:

$$\begin{aligned} K &= 2 \times \exp(-2090/RT) \\ N_{ba} &= 1/(1 + K) \qquad N_{bb} = 1 - N_{ba} \end{aligned}$$

H_b and S_b are calculated as for chairs

For chair ⇌ boat:

$$\begin{aligned} \Delta G^\circ &= H^\circ_{boat} - H^\circ_{chair} - T(S^\circ_{boat} - S^\circ_{chair}) \\ K_t &= \frac{(\text{boats})}{(\text{chairs})} = \exp(-\Delta G^\circ/RT) \\ N_{chairs} &= 1/(1 + K_t) \end{aligned}$$

The mole fraction of diequatorial chair (N_{ee}') in the mixture then is

$$N_{ee}' = N_{ee}'N_{chairs}$$

Then for axial–equatorial ⇌ diequatorial

$$K_{eq} = \frac{N_{ee}'}{N_{ea}} K_{obsd}$$

Similar calculations were carried out for the 1,3 and 1,4 isomers.

Enthalpy and entropy values were obtained by a least-squares fit of ln K *vs.* $1/T$. All correlation coefficients were ≥ 0.996.

Registry No.—*cis*-1,2-Dimethylcyclohexane, 2207-01-4; *trans*-1,2-dimethylcyclohexane, 6876-23-9; *cis*-1,3-dimethylcyclohexane, 638-04-0; *trans*-1,3-dimethylcyclohexane, 2207-03-6; *cis*-1,4-dimethylcyclohexane, 624-29-3; *trans*-1,4-dimethylcyclohexane, 2207-04-7.

Directional Effects of Substituents in the Ozonolysis of Naphthalenes. Synthesis of *o*-Phthalaldehydes

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A number of substituted naphthalenes have been ozonized and the selectivity of ozone attack determined quantitatively by conversion to the phthalic acids. Naphthalenes with electron-withdrawing substituents give predominance of attack on the ring not containing these substituents. Triphenylphosphine reduces these ozonolyses mixtures at low temperatures and results in good yields of the isolated *o*-phthalaldehydes. The cyclic peroxides that can be isolated from various naphthalenes are also reduced with triphenylphosphine to the corresponding *o*-phthalaldehydes.

Numerous investigations into the ozonolysis of naphthalene[1] and substituted naphthalenes[2] have been reported. These systems absorb 2 moles of ozone and lead to various *ortho*-disubstituted derivatives of benzene depending on reaction conditions and method of work-up. Further attack on the benzene ring is found to be extremely sluggish and for practical purposes may be considered to be negligible relative to the uptake of the first 2 mole equiv of ozone.

The majority of studies have been concerned with substituted naphthalenes in which the substituents are electron releasing. These are attacked by ozone predominantly, and in some cases exclusively, in the substituted ring. The net result is that one generally isolates the same products from these naphthalene derivatives that can be obtained from the ozonolysis of naphthalene itself. On the other hand, little is recorded[3] in the literature on the ozonolysis of naphthalene derivatives containing electron-attracting substituents, which would be expected to give greater attack of ozone on the unsubstituted ring. One purpose of this work was to determine quantitatively the selectivity of ozone attack on a variety of naphthalenes with electron-withdrawing substituents. Since a high selectivity is desirable in order to avoid mixtures of products, this information would be of value in choosing appropriate naphthalene systems for conversion to a number of difficultly available benzene derivatives. Of particular interest was the synthesis of *o*-phthalaldehydes and certain phthalic acids.

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(1) (a) P. S. Bailey, S. S. Bath, F. Dobinson, F. J. Garcia-Sharp, and C. D. Johnson, *J. Org. Chem.*, **29**, 697 (1964); (b) C. D. Johnson and P. S. Bailey, *ibid.*, **29**, 703 (1964).

(2) P. S. Bailey, *Chem. Rev.*, **58**, 959 (1958). Reference 1a has a review of more recent work.

(3) Most simple monosubstituted naphthalenes with electron-withdrawing substituents have never been treated with ozone.

Initially, a series of monosubstituted naphthalenes was ozonized in a mixture of methanol and methylene chloride at −65°. The reaction conditions were constant in all runs, including molar concentration of the substituted naphthalene, ozone concentration, flow rate of the ozonized oxygen stream, and rate of stirring. Upon evaporation of the solvent, the residue was oxidized by hydrogen peroxide in water–formic acid to give the corresponding phthalic acids. The mole ratio of the substituted phthalic acid to phthalic acid was determined by vapor phase chromatography either on the mixture directly or on the esterified mixture. This ratio provides us with quantitative figures as to the per cent attack of ozone on the unsubstituted ring *vs.* the ring containing the substituent. The results are summarized in Table I and are arranged according to increasing rate of ozonolysis.

TABLE I

OZONOLYSIS OF SUBSTITUTED NAPHTHALENES

Compd	Time, min[a]	Acids, mole %: Substituted phthalic	Acids, mole %: Phthalic
1-Nitronaphthalene	225	95	5
2-Nitronaphthalene	162	87	13
Methyl 2-naphthoate	49	63	37
2-Bromonaphthalene	36	81	19
1-Chloronaphthalene	34	65	35
2-Chloronaphthalene	32	82	18
2′-Acetonaphthone	29	52	48
Naphthalene	22		
2-Methylnaphthalene	17	17	83
2-Methoxynaphthalene	16	0	100

[a] Required for the absorption of 2 mole equiv of ozone under reaction conditions; if all the ozone reacted that was passed through, 14.5 min would be required.

The over-all rates of ozonolysis in Table I (as represented by the time required for 2 moles of ozone to be absorbed) are consistent with the situation that Wibaut and Sixma[4] found to exist with substituted benzenes. They noted that electron-releasing groups on the benzene ring enhanced the rate of ozonolysis relative to benzene, whereas with electron-withdrawing substituents the rate was slower. In addition, the selectivity of ozone attack follows the same pattern observed for other types of electrophilic reactions with naphthalene derivatives.[5] Electron-withdrawing groups do indeed increase the predominance of attack on the unsubstituted ring as evidenced by the greater formation of substituted phthalic acids compared to phthalic acid. However, since the intimate mechanistic details of the ozonolysis of naphthalene derivatives are lacking, it becomes difficult to explain subtle differences, such as, for example, why 2-chloro- and 2-bromonaphthalene react with ozone in the unsubstituted ring to about the same extent as 2-nitronaphthalene and more than methyl 2-naphthoate and 2′-acetonaphthone.

The selectivity of ozone attack was also determined in acetic acid at 20° for 1-nitro-, 2-chloro-, and 2-methylnaphthalene which gave ratios of substituted phthalic to phthalic acid of 92:8, 76:24, and 25:75, respectively, compared with 95:5, 82 :18, and 17:83 in methylene chloride–methanol at −65°. The slightly lower selectivity can be accounted for in part by noting that ozone is an extremely energetic molecule which, at higher temperatures, would be expected to have less regard for electronic factors and, consequently, to be less discriminating as to which ring it attacks.

The utilization of the above data (Table I) in the synthesis of certain substituted phthalic acids is immediately obvious. As an example, 2-chloronaphthalene was converted to pure 4-chlorophthalic acid is an over-all yield of 41%. In addition, most pure phthalic acids used for the vpc determination of the product compositions were prepared from the corresponding naphthalenes by ozonolysis. Although the ozonolytic route is preferred in some cases when convenient, many substituted phthalic acids are, generally, more easily prepared by other methods.[6]

Customarily employed syntheses of *o*-phthalaldehydes, on the other hand, require laborious effort and result in low yields. The preparation of *o*-phthalaldehydes from substituted naphthalenes *via* an ozonolytic route would offer several advantages over other synthetic sequences provided that a good method of reduction could be found for the ozonolysis products. In formulating a reductive scheme, we decided to work with the various intermediates from the methanolic ozonolysis of naphthalene and substituted naphthalenes because of the well-characterized mechanism and high yields of products reported by Bailey[1] using this solvent.

Bailey[1] elucidated, among others, the course of ozonolysis of naphthalene (I), 2-naphthol (V), and 2-methoxynaphthalene (VI) in methanol as is shown in Scheme I. He found that naphthalene (I) reacted with 2 moles of ozone to give hydroperoxidic moieties II and III. The methoxyhydroperoxide II could not be isolated but cyclized during the work-up to 4-methoxy-2,3-benzodioxan-1-ol (IV) in which form it was obtained in high yields. The ozonolysis of 2-naphthol (V) also led to peroxide IV, indicating the intermediacy of II in this case, too. In contrast, 2-methoxynaphthalene (VI) gave 1,4-dimethoxy-2,3-benzodioxane (VIII) and, since IV could not be transformed to VIII under the reaction conditions, it was concluded that the bis(methoxyhydroperoxide) VII must be the intermediate.

Attempts by Bailey[1] to obtain phthalaldehyde (IX) by reduction of the various species available from the above ozonolysis mixtures were not successful although Rieche and Schulz[7] were able to synthesize IX by hydrogenating peroxide IV using Lindlar catalyst. We reported[8] an improved reductive scheme for this system using dimethyl sulfide. Although good yields of phthalaldehyde (IX) were obtained on reduction of the ozonized methanolic solutions of naphthalene (68% as the bis[(2,4-dinitrophenyl)hydrazone], 40–50% isolated), substituted naphthalenes did not work as well. Since dimethyl sulfide operates only on the hydroperoxidic function, it must react at low enough

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[4] J. P. Wibaut and F. L. J. Sixma, *Rec. Trav. Chim.*, **71**, 761 (1952).

[5] P. B. D. de la Mare and J. H. Ridd, "Aromatic Substitution, Nitration and Halogenation," Academic Press Inc., New York, N. Y., 1959, pp 177–181.

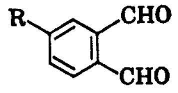
[6] E. H. Rodd, "Chemistry of Carbon Compounds," Vol. III, Part B, Elsevier Publishing Co., New York, N. Y., 1956, p 851.

[7] A. Rieche and M. Schulz, *Chem. Ber.*, **97**, 190 (1964).

[8] J. J. Pappas, W. P. Keaveney, E. Gancher, and M. Berger, *Tetrahedron Letters*, No. 36, 4273 (1966).

TABLE II

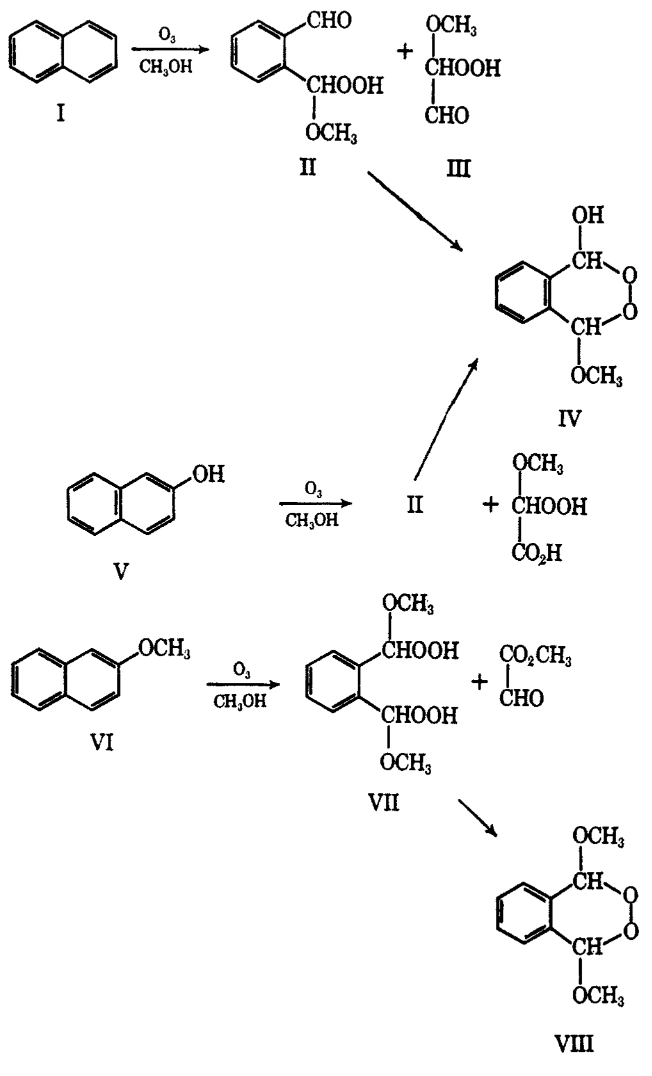
o-PHTHALALDEHYDES BY REDUCTION OF OZONOLYSIS MIXTURES WITH TRIPHENYLPHOSPHINE



Compd ozonized		Registry No.	*o*-Phthalaldehydes Bp, °C (mm)[a]	Mp, °C[b]	Yield, %[c]
Naphthalene	R = H		80–85 (0.5)	54–55[d]	57
2-Methoxynaphthalene	R = H		85–90 (1.0)		44
2,7-Dimethoxynaphthalene	R = OCH_3	6500-51-2	130–132 (1.0)	41–42[e]	58
2,6-Dimethylnaphthalene	R = CH_3	15158-36-8	100–105 (1.0)	37–38[f]	51
2-Chloronaphthalene	R = Cl	13209-31-9	88–95 (1.0)	77–78[g]	20
6-Bromo-2-naphthol	R = Br	13209-32-0	120–135 (1.0)	98–99[h]	60
2-Bromo-6-methoxynaphthalene	R = Br		125–130 (0.5)		61
Methyl 6-methoxy-2-naphthoate	R = CO_2CH_3	15158-39-1	145–150 (1.0)	103–104[i]	40
Methyl 2-naphthoate	R = CO_2CH_3		135–150 (1.0)		22

[a] Does not represent boiling point of pure product but of material distilled from reaction mixture. [b] Purest or analytical sample. [c] Of material having melting point within one or two degrees of purest sample. [d] J. C. Bill and D. S. Tarbell ("Organic Syntheses," Coll. Vol. IV, John Wiley and Sons, Inc., New York, N. Y., 1963, p 807) give mp 55.5–56°. [e] A. M. Khan, G. R. Proctor, and L. Rees [*J. Chem. Soc., Sect. C*, 990 (1966)] give mp 45°. [f] *Anal.* Calcd for $C_9H_8O_2$: C, 72.96; H, 5.44. Found: C, 72.95; H, 5.33. [g] *Anal.* Calcd for $C_8H_5ClO_2$: Cl, 21.03. Found: Cl, 20.89, 20.94. [h] K. Mislow and H. D. Perlmutter [*J. Am. Chem. Soc.*, **84**, 3591 (1962)] give mp 98–100°. [i] *Anal.* Calcd for $C_{10}H_8O_4$: C, 62.50; H, 4.20. Found: C, 62.56; H, 4.10.

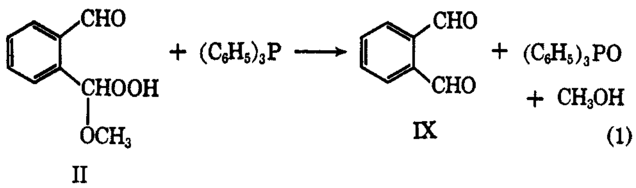
SCHEME I



temperatures before cyclization of hydroperoxides of types II and VII occurs.

However, the temperature at which cyclization takes place depends on a number of factors such as the substituents on the benzene ring, the acidity of the medium and the solvents used. For example, II should cyclize at lower temperatures in methanol–methylene chloride solvent than in methanol alone since a small amount of hydrochloric acid would be produced[9] during ozonolysis which would be expected to enhance ring closure. Dimethyl sulfide appears to commence reacting between −20 and −10° and would only be useful in the naphthalene series in certain situations where conditions were favorable.

One method of reduction, that has been found reliable, utilizes triphenylphosphine. Horner and Jurgeleit[10] found triphenylphosphine to be effective in the reduction of a variety of peroxidic and hydroperoxidic functions. Most important, triphenylphosphine reduces hydroperoxides readily below −50°, at which temperatures the rate of cyclization is extremely slow. The reaction can be visualized as shown in eq 1 in the case of methoxyhydroperoxide II.



(1)

Naphthalene and several substituted naphthalenes were ozonized in methanol or methanol–methylene chloride mixture at −65 to −70° and reduced below −50° with triphenylphosphine. The results are summarized in Table II. With the exception of 4-chlorophthalaldehyde and 4-carbomethoxyphthalaldehyde the yields of pure *o*-phthalaldehydes are reasonably good. In these cases some phthalaldehyde (IX) showed up as a contaminant because of partial attack on the substituted ring during the ozonolysis of 2-chloronaphthalene and methyl 2-naphthoate. Attempts to isolate the substituted dialdehydes from 1-chloro- and 1- and 2-nitronaphthalene were unsuccessful using a number of reductive methods including triphenylphosphine, trimethyl phosphite,[11] dimethyl sulfide,[8] and hydrogenation. Reduction with triphenylphosphine of the ozonolysis mixture of 2-acetyl-6-methoxynaphthalene proceeded normally. How-

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(9) (a) W. P. Keaveney, M. G. Berger, and J. J. Pappas, *J. Org. Chem.*, **32**, 1537 (1967); (b) C. R. Dick and R. F. Hanna, *ibid.*, **29**, 1218 (1964); (c) P. S. Bailey, P. Kolsaker, B. Sinha, J. B. Ashton, F. Dobinson, and J. E. Batterbee, *ibid.*, **29**, 1400 (1964).

(10) L. Horner and W. Jurgeleit, *Ann.*, **591**, 138 (1955).

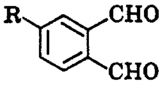
(11) W. S. Knowles and Q. E. Thompson, *J. Org. Chem.*, **25**, 1031 (1960).

ever, isolation of 4-acetylphthalaldehyde could not be effected because of polymer formation.[12]

The infrared and nmr spectra of the pure *o*-phthalaldehydes are compiled in Table III. In the nmr, formyl protons of the *ortho*-oriented aldehyde functions exhibit chemical shifts in the range δ 10.29–10.62. The appearance at lower field from benzaldehyde (δ 10.02) and terephthalaldehyde (δ 10.17) would be anticipated from the findings of Klinck and Stothers[13] who measured the chemical shifts of formyl protons in a variety of *ortho*-, *meta*-, and *para*-substituted benzaldehydes.

TABLE III

SPECTRAL DATA OF *o*-PHTHALALDEHYDES



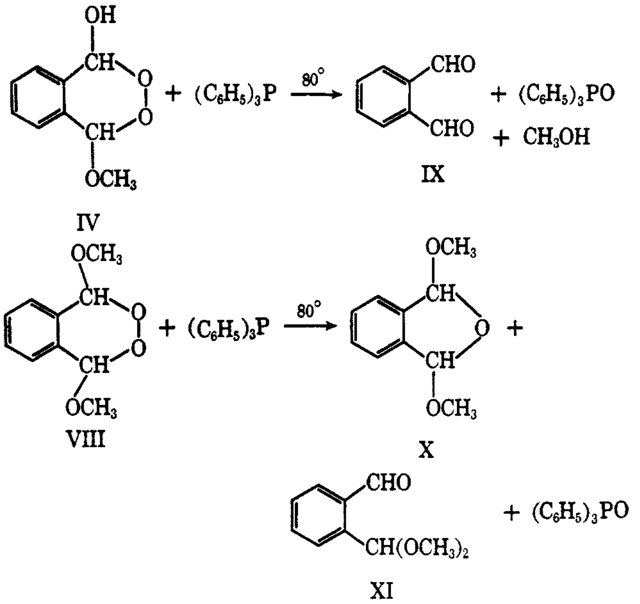
R	Infrared bands,[a] cm^{-1}		Nmr Proton	Chemical shifts[b] (δ), ppm	Rel peak areas
H	2841	1590	Formyl	10.53	1
	2755	1276	Aromatic	7.5–8.2	2
	1699	1192			
	1608	860			
OCH_3	2849	1253	Formyl	10.29	1
	2747	1098		10.56	1
	1696	1036	Aromatic	7.1–8.0	3
	1600	836	CH_3	3.93	3
	1576				
CH_3	2841	1578	Formyl	10.43	1
	2755	1280		10.51	1
	1699	1154	Aromatic	7.4–8.0	3
	1608	833	CH_3	2.51	3
Cl	2857	1570	Formyl	10.47	1
	2762	1190		10.54	1
	1704	831	Aromatic	7.4–8.1	3
	1595				
Br	2857	1570	Formyl	10.45	1
	2762	1190		10.51	1
	1704	893	Aromatic	7.8–8.2	3
	1595	826			
CO_2CH_3	2857	1298	Formyl	10.51	1
	2762	1193		10.62	1
	1741	1124	Aromatic	7.9–8.7	3
	1708	830	CH_3	4.01	3
	1446				

[a] Determined in chloroform. [b] Determined in deuteriochloroform at 37°.

In addition to working at low temperatures with the hydroperoxides, triphenylphosphine also was effective in reducing cyclic peroxides to *o*-phthalaldehydes in refluxing benzene. A slight difference was found to exist between the two cyclic peroxides, IV and VIII, in their reaction with triphenylphosphine, Scheme II.

The peroxide IV was reduced to phthalaldehyde (IX) with little or no acetal formation, whereas the dimethoxy peroxide VIII gave little phthalaldehyde (IX) and mostly acetal, probably of structures X and XI. In the latter case hydrolysis with 2 *N* hydrochloric acid was required to obtain the free dialdehyde.

SCHEME II



The substituted cyclic peroxides from the methanolic ozonolysis of several substituted naphthalenes were isolated and characterized as to whether they were similar to IV (hydroxymethoxy peroxides) or to VIII (dimethoxy peroxides). Peroxides of type IV were obtained from 2-chloronaphthalene, 2,6-dimethylnaphthalene, and 6-bromo-2-naphthol, while 2,7-dimethoxynaphthalene, 2-bromo-6-methoxynaphthalene, methyl 6-methoxy-2-naphthoate and 2-acetyl-6-methoxynaphthalene gave peroxides of type VIII. These would be the anticipated structures in accordance with the results of Bailey.[1] Because of the number of isomers involved, the substituted hydroxymethoxy peroxides (type IV) could not be easily recrystallized to a single constant-melting product. The substituted dimethoxy peroxides (type VIII), on the other hand, were readily purified (Table IV). Their nmr spectra are listed in Table V.

Some of these cyclic peroxides were subjected to reduction with triphenylphosphine and the substituted *o*-phthalaldehydes were isolated in good yields (Table VI).

In general, the best method for obtaining *o*-phthalaldehydes from naphthalenes is to reduce the ozonolysis mixture directly with triphenylphosphine (Table II). In certain cases, however, it is preferable to go through the hydroxymethoxy peroxides (type IV) where these can be isolated readily and in good yields, such as from 2-chloronaphthalene. The scheme involving the use of dimethoxy peroxides (type VIII) as intermediates for the preparation of *o*-phthalaldehydes is the least desirable.

Experimental Section[14]

Apparatus.—The ozone source was a Welsbach T-816 laboratory ozonator, using Air Products' pure dry oxygen as the feed gas. Ozone concentration at a gas flow rate of 1.0 l./min was around 60–70 mg/l. and was determined iodimetrically.

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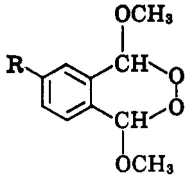
[12] These systems are quite labile and require extremely mild conditions for their preparation. See, for example, the synthesis of *p*-acetylbenzaldehyde: W. K. Detweiler and E. D. Amstutz, *J. Am. Chem. Soc.*, **72**, 2882 (1950).

[13] R. E. Klinck and J. B. Stothers, *Can. J. Chem.*, **40**, 1071, 2329 (1962).

[14] Melting points and boiling points are uncorrected. Infrared spectra were determined by means of a Perkin-Elmer 137 spectrophotometer. Nmr spectra were obtained on a Varian A-60A spectrometer.

TABLE IV

DIMETHOXY PEROXIDES FROM OZONOLYSIS OF SUBSTITUTED NAPHTHALENES

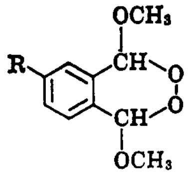


Compd ozonized		Registry No.	Mp, °C	Yield, %	Anal., % C Calcd	C Found	H Calcd	H Found
2,7-Dimethoxynaphthalene	R = OCH_3	15158-40-4	124–125	40	58.40	58.38	6.24	5.95
2-Bromo-6-methoxynaphthalene	R = Br[a]	15158-41-5	140–141	48	43.66	43.53	4.03	4.21
2-Acetyl-6-methoxynaphthalene	R = $\overset{\overset{O}{\|}}{C}CH_3$	15180-25-3	119–120	11	60.50	60.56	5.92	5.85
Methyl 6-methoxy-2-naphthoate	R = CO_2CH_3[b]	15158-42-6	150–151	3	56.69	56.87	5.55	5.66

[a] Calcd: Br, 29.05. Found: Br, 28.90. [b] Calcd: mol wt, 254. Found: mol wt, 260.

TABLE V

NMR SPECTRA OF DIMETHOXY PEROXIDES



R	Hydrogen	Chemical shifts[a] (δ), ppm	Rel peak areas
H	OCH_3	3.64	3
	H	5.54	1
	Aromatic	7.1–7.5	2
OCH_3	OCH_3	3.63	3
		3.65	3
	H	5.52	2
	R	3.80	3
	Aromatic	6.7–7.4	3
Br	OCH_3	3.64	6
	H	5.51	2
	Aromatic	7.0–7.6	3
$\overset{\overset{O}{\|}}{C}CH_3$	OCH_3	3.67	6
	H	5.59	2
	R	2.60	3
	Aromatic	7.2–8.1	3
CO_2CH_3	OCH_3	3.68	6
	H	5.58	2
	R	3.92	3
	Aromatic	7.2–8.2	3

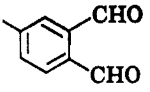
[a] Determined in deuteriochloroform at 37°.

The reactor used in the ozonolyses was "Mini-Lab" assembly no. 10104 (Ace Glass).

Materials.—Substituted naphthalenes which were not available commercially were prepared by literature methods. 2-Nitronaphthalene[15] was synthesized by the Sandmeyer reaction, as was 1-chloronaphthalene[16] (commercial material contains substantial amounts of 2-chloronaphthalene). Methyl 2-naphthoate was prepared by esterification[17] of 2-naphthoic acid, and 2,7-dimethoxynaphthalene[18] and 2-bromo-6-methoxynaphthalene[19] from the corresponding naphthols. 2-Acetyl-6-methoxynaphthalene[20] and 6-methoxy-2-naphthoic acid[21] were obtained from 2-methoxynaphthalene. Esterification[17] of 6-methoxy-2-naphthoic acid gave the methyl ester.[22]

TABLE VI

o-PHTHALALDEHYDES BY REDUCTION OF CYCLIC PEROXIDES WITH TRIPHENYLPHOSPHINE



Cyclic peroxide		Yield, %
4-Methoxy-2,3-benzodioxan-1-ol (IV)	R = H	72
6(or 7)-Chloro-4-methoxy-2,3-benzodioxan-1-ol[a,b]	R = Cl	37
6(or 7)-Methyl-4-methoxy-2,3-benzodioxan-1-ol[b]	R = CH_3	80
6(or 7)-Bromo-4-methoxy-2,3-benzodioxan-1-ol[b]	R = Br	68
1,4,6-Trimethoxy-2,3-benzodioxane[c]	R = OCH_3	63
6-Bromo-1,4-dimethoxy-2,3-benzodioxane[c]	R = Br	55

[a] Contains about 18% by weight of 4-methoxy-2,3-benzodioxan-1-ol (IV). [b] Probably a mixture of isomers. [c] Hydrolysis of reaction mixture with 2 *N* hydrochloric acid is necessary to isolate free dialdehyde.

The 3- and 4-nitrophthalic acids and trimellitic acid were commercial samples which were purified further. 4-Chlorophthalic acid was prepared by the method of Blicke and Smith[23] and also by the ozonolysis of 2-chloronaphthalene. The 3-chloro- and 4-bromophthalic acids were isolated from the ozonolyses of 1-chloro- and 2-bromonaphthalene, respectively, according to the procedure described below for 4-chlorophthalic acid. 4-Acetylphthalic acid was prepared by the ozonolysis of 2-acetyl-6-methoxynaphthalene as described below, and 4-methyl- and 4-methoxyphthalic acid from 2,6-dimethylnaphthalene and 2,7-dimethoxynaphthalene, respectively, using this same procedure. All the substituted naphthalenes and phthalic acids had the melting points reported in the literature and showed less than 1% impurities by vapor phase chromatography.

4-Methoxy-2,3-benzodioxan-1-ol (IV) and 1,4-dimethoxy-2,3-benzodioxane (VIII) were prepared according to Bailey.[1]

Ozonolysis of Substituted Naphthalenes (Table I).—The substituted naphthalene (0.01 mole) was dissolved in a mixture of 35 ml of methanol and 45 ml of methylene chloride and cooled to −65°. A stream of ozonized oxygen (66.0 mg of ozone/l.) was passed into the solution at a rate of 1.0 l./min. The amount of unreacted ozone was determined every 15 min by collecting it in a potassium iodide trap and titrating. After the reaction of 2 mole equiv of ozone, the uptake of ozone stopped and the solution turned blue. From the titration of the traps and the time required to reach a blue coloration, it was possible to obtain an approximate time required for ozonolysis of the substituted naphthalene. The system was then swept with nitrogen and the solvents were removed under

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vacuum keeping the pot temperature below 25°. To the residue was added 10 ml of 50% hydrogen peroxide in 20 ml of water and 20 ml of formic acid. This mixture was heated on the steam bath for 4 hr and then evaporated to dryness under vacuum. The oxidative procedure was repeated again with 10 ml of 50% hydrogen peroxide in 20 ml of water and 20 ml of formic acid. For 1-substituted naphthalenes, such as 1-chloro- and 1-nitronaphthalene, the oxidation was carried out a total of four times to ensure complete reaction. The solvents were always evaporated after each oxidation. The residue was then dissolved in 5 ml of methanol and analyzed by vapor phase chromatography (F & M Model 810) programmed at 10°/min between 140 and 240° using a 6-ft 20% SF 96 on 60/80 Diatoport S column. The phthalic acids were converted to the anhydrides on the column. The chromatograms were compared to those of synthetic mixtures of phthalic acids and the percentages of substituted and unsubstituted phthalic acid in the reaction mixture determined. The results are summarized in Table I. In some cases, the oxidized reaction mixture was esterified with methanol and compared to esterified synthetic mixtures of phthalic acids by vapor phase chromatography. The ratio of substituted phthalic acid to phthalic acid determined in this way was within 1% of the figures shown in Table I.

4-Chlorophthalic Acid.—A suspension of 8.13 g (0.05 mole) of 2-chloronaphthalene in 35 ml of methanol and 50 ml of methylene chloride was ozonized as described above. The solid that remained after the second oxidation was taken up in 50 ml of ether and the ether extracted with six 50-ml portions of water. The ether was dried and evaporated; the residue which remained was triturated in chloroform, filtered, and dried to yield 4.11 g (41%) of 4-chlorophthalic acid, mp 148–149° (lit.[23] mp 150°). This product contained less than 1% phthalic acid as an impurity.

4-Acetylphthalic Acid.—A solution of 2.00 g (0.01 mole) of 2-acetyl-6-methoxynaphthalene in 35 ml of methanol and 45 ml of methylene chloride was ozonized as above. The solid that remained after oxidation was triturated with chloroform, washed with a little water, and dried to yield 1.31 g (63%) of 4-acetylphthalic acid, mp 211° dec (lit.[24] mp 210°).

6 (or 7)-Chloro-4-methoxy-2,3-benzodioxan-1-ol.—The above ozonolysis was repeated with 8.13 g (0.05 mole) of 2-chloronaphthalene in 35 ml of methanol and 50 ml of methylene chloride. The white solid which remained after removal of solvents was triturated several times in water, filtered, and dried. The cyclic peroxide weighed 7.70 g (73%) and melted at 115–130°. The infrared was similar to the infrared of 4-methoxy-2,3-benzodioxan-1-ol (IV). This solid was analyzed without further purification.

The chlorine analysis indicated approximately 82% by weight of the chloro cyclic peroxide and 18% by weight of IV. No attempt was made to purify the chloro cyclic peroxide further or to determine whether the 6 or 7 isomer (or a mixture of the two) was formed.

6(or 7)-Methyl-4-methoxy-2,3-benzodioxan-1-ol.—A mixture of 4.69 g (0.03 mole) of 2,6-dimethylnaphthalene in 35 ml of methanol and 50 ml of methylene chloride was ozonized in the usual manner at −65°. The solvents were removed under vacuum and the solid that remained was triturated several times in water, filtered, and dried. The cyclic peroxide weighed 2.20 g (37%) and melted at 130–134°.

Anal. Calcd for $C_{10}H_{12}O_4$: C, 61.21; H, 6.17. Found: C, 61.23; H, 5.96.

No attempt was made to characterize the structure as to whether the 6 or 7 isomer was formed (or a mixture of the two).

6(or 7)-Bromo-4-methoxy-2,3-benzodioxan-1-ol.—A mixture of 6.69 g (0.03 mole) of 6-bromo-2-naphthol in 80 ml of methanol was ozonized at −65°. The solution was swept with nitrogen and then warmed to 20° and kept at this temperature for 15 min with cooling. The solution was cooled to 0° and added to 150 ml of cold water. The total mixture was cooled again to −20° for 15 min and the solid filtered, washed with water, and dried. The bromo cyclic peroxide weighed 4.60 g (59%) and had mp 166–171° dec.

Anal. Calcd for $C_9H_9BrO_4$: C, 41.41; H, 3.47; Br, 30.61. Found: C, 41.27; H, 3.37; Br, 30.85.

No attempt was made to characterize the structure as to whether the 6 or 7 isomer was formed (or a mixture of the two).

Synthesis of Dimethoxy Peroxides (Table IV).—A mixture of 0.020 mole of the substituted naphthalene in 35 ml of methanol and 45 ml of methylene chloride was cooled to −65° and reacted with 2 mole equiv of ozone. Upon evaporation of solvents, the residue was triturated with water and filtered. The solid was washed with a small amount of methanol, dried, and recrystallized from benzene–petroleum ether (bp 30–60°).

Synthesis of *o*-Phthalaldehydes. A. By Reduction of Ozonolysis Mixture (Table II).—A solution of 0.030 mole of the substituted naphthalene in Table II in 35 ml of methanol and 50 ml of methylene chloride (for naphthalene and 6-bromo-2-naphthol the solvent was 85 ml of methanol) was cooled to −65 to −70° and treated with 2 mole equiv of ozone. The system was swept with nitrogen and 15.74 g (0.060 mole) of triphenylphosphine added over 15 min, keeping the temperature below −60°. The mixture was warmed to −50°, held at this temperature for 1 hr, and then warmed to room temperature. The solvent was removed under vacuum, and 30 ml of ether was added to the residue. The triphenylphosphine oxide was filtered off and washed with an additional 30 ml of ether. Upon evaporation of the ether the residue was heated with 30 ml of 2 *N* hydrochloric acid on the steam bath for 15 min, swirling the mixture every 2 or 3 min. The mixture was cooled and extracted with ether. The ether was washed with saturated sodium bicarbonate solution, dried, and evaporated. The residue was distilled at the temperature indicated in Table II to give the crude *o*-phthalaldehydes which upon one or two recrystallizations from *n*-heptane gave products melting within 1–2° of the pure sample. In the case of methyl 6-methoxy-2-naphthoate and methyl 2-naphthoate the reaction mixture upon removal of solvents was treated directly with the 2 *N* hydrochloric acid on the steam bath for 30 min. The 4-carbomethoxyphthalaldehyde was extracted with chloroform instead and upon distillation was recrystallized from *n*-heptane–benzene.

B. By Reduction of Cyclic Peroxides (Table VI).—A mixture of 0.010 mole of cyclic peroxide and 0.010 mole of triphenylphosphine in 25 ml of anhydrous benzene was refluxed for 2 hr under an atmosphere of nitrogen. The benzene was removed under vacuum and 10 ml of ether added to the residue. The triphenylphosphine oxide was filtered off and washed with 10 ml of ether. The ether was evaporated and in the case of hydroxymethoxy peroxides (type IV) the residue distilled and the *o*-phthalaldehyde recrystallized from *n*-heptane. In the case of the dimethoxy peroxides (type VIII) the residue was treated with 10 ml of 2 *N* hydrochloric acid on the steam bath for 15 min and extracted with ether. The ether was washed with sodium bicarbonate solution, dried, and evaporated. The *o*-phthalaldehyde was obtained by distillation and recrystallization.

Registry No.—IV, 15158-33-5; VIII, 15158-34-6; IX, 643-79-8.

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