Ozonation of Carbon–Hydrogen Bonds. Anthrone[1]

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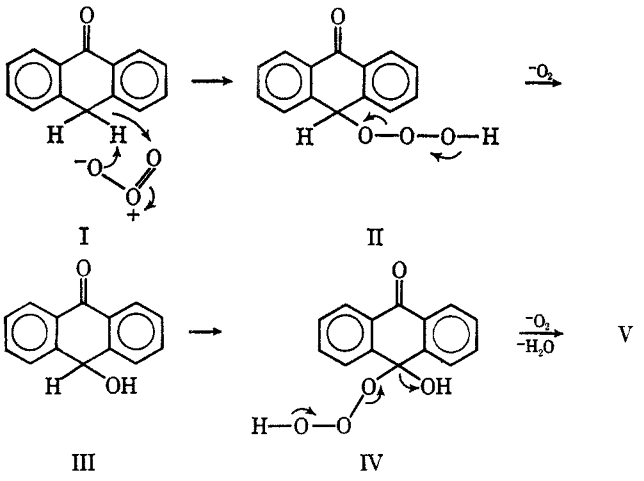
Evidence is presented to show that ozone attacks the methylene group of anthrone *via* a 1,3-dipolar insertion reaction to give intermediates of the type ROOOH, which immediately lose molecular oxygen. Ozone (2 moles) is required, 2 moles of molecular oxygen is evolved, and the final product is anthraquinone. In agreement with expectations based on this mechanism, 10-bromoanthrone, 10-nitroanthrone, and dibenzsuberone are much less reactive toward ozone than is anthrone. The attack of ozone on the methylene group of anthrone occurs to the extent of about 70%, the remainder of the reaction apparently involving the benzene rings. Just the opposite is true with fluorene, with which only about 25% of the ozonation involves the methylene group.

The oxidation of methyl, methylene, and methylidyne groups by ozone–oxygen mixtures is well known and has generally been assumed to occur by an ozone-initiated autoxidation.[3] An example is found in anthrone (I) (Scheme I), which was reported by Cavill *et al.*,[4] to yield only anthraquinone upon treatment with ozone–oxygen in chloroform solution.

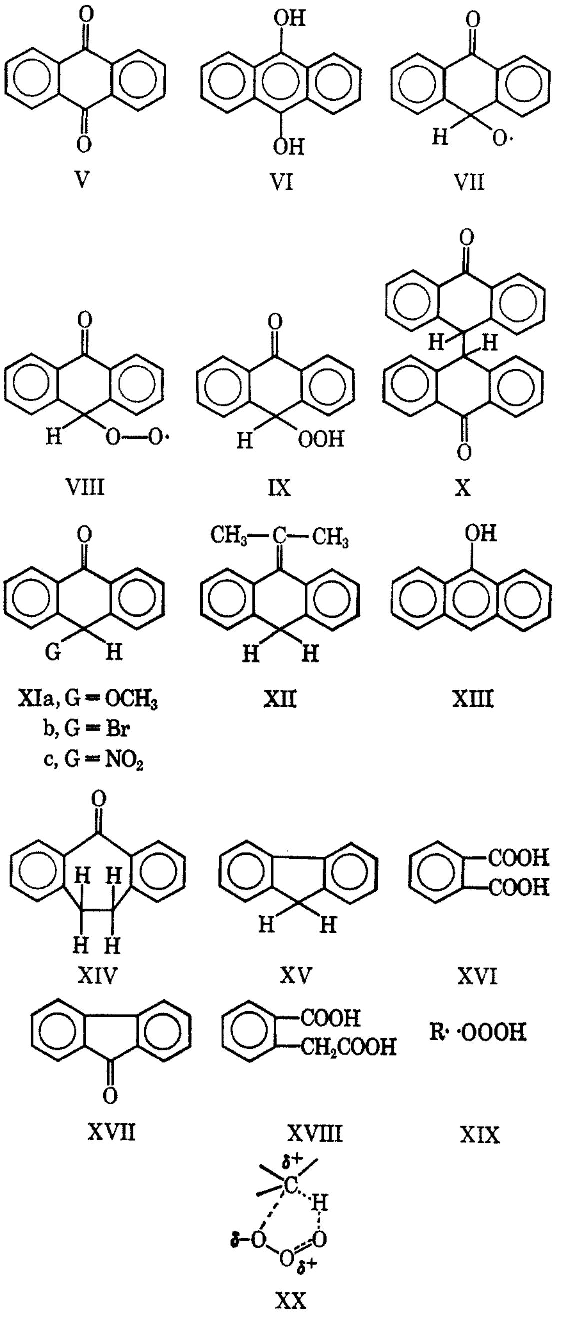
SCHEME I



In an earlier publication,[5] we showed that oxygen was not necessary for the conversion of benzaldehyde to perbenzoic acid by ozone, but that in its presence some autoxidation did occur. The evidence indicated, however, that the autoxidation was not initiated by ozone itself, but by radicals produced during decomposition of an initial aldehyde–ozone insertion product ($C_6H_5C(=O)OOOH$). Price and Tumolo[6] have similarly proposed such an insertion compound as an intermediate in the ozonation of ethers. We now report on the ozonation of anthrone, which was studied in order to test the generality of the reaction paths proposed for aromatic aldehydes and aliphatic ethers.

We have ozonized anthrone (I) with both ozone–oxygen and ozone–nitrogen mixtures, using different amounts of ozone and different temperatures. Most of the reactions were carried out in methylene chloride solution, although in a few cases carbon tetrachloride, methanol, and acetic acid (alone or with methylene chloride) were used. The results are shown in Tables I and II. The only products isolated were anthraquinone (V), dianthron-9-yl (X), and, under oxidizing work-up conditions, phthalic acid (XVI) (Chart I).

CHART I



Dianthronyl (X) also has been reported as a product of the ozonation of 9-isopropylidene-9,10-dihydro-

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[1] Presented in part at the Ozone Symposium held at the 19th Southwest Regional Meeting of the American Chemical Society, Houston, Texas, Dec. 1963.

[2] To whom inquiries should be directed.

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

[4] G. W. K. Cavill, A. Robertson, and W. B. Whalley, *J. Chem. Soc.*, 1567 (1949).

[5] H. M. White and P. S. Bailey, *J. Org. Chem.*, **30**, 3037 (1965).

[6] C. C. Price and A. L. Tumolo, *J. Am. Chem. Soc.*, **86**, 4691 (1964).

TABLE I

OZONATION OF ANTHRONE (I) WITH OZONE–OXYGEN[a]

Expt no.	Solvent	—O_3, mmoles—		Ratio[a] of O_3 reacted to I	Compd I producing dimer, mmoles	Compd I reacted with O_3, mmoles	Anthraquinone,[b] mmoles (%)	Ratio of O_3 reacted to I reacted	Available for bond —attack, mmoles—		Ratio of O_3 to I (for bond attack)	Other[b] product, etc.
		Used	Reacted						O_3[c]	I[d]		
1	CH_2Cl_2	2.5	2.5	0.25	7.4	2.6	1.6 (62)	1.0	0–0.9	1.0	0–0.9	...
2	CH_2Cl_2[e]	4.8	4.8	0.48	4.6	5.4	3.2 (59)	0.9	0–1.6	2.2	0–0.7	...
3	CH_2Cl_2	10.2	9.9	0.99	4.2	5.8	3.8 (66)	1.7	2.3–6.1	2.0	1.2–3.1	...
4	CH_2Cl_2	19.8	17.8	1.8	1.3	8.7	5.3 (61)	2.0	7.2–12.5	3.4	2.1–3.7	...
5	CH_2Cl_2	23.4	20.8	2.1	1.5	8.5	5.6 (66)	2.4	9.6–15.2	2.9	3.3–5.2	...
6	CH_2Cl_2[f]	23.7	23.2	2.3	0.3	9.7	6.2 (64)	2.4	10.8–17.0	3.5	3.1–4.9	...
7	CH_2Cl_2	81.9	22.6	2.3	0.5	9.5	5.8 (61)	2.4	11.0–16.8	3.7	3.0–4.5	...
8	CH_2Cl_2/CH_3OH[g]	10.6	10.0	1.0	4.1	5.9	3.6 (61)	1.7	2.8–6.4	2.3	1.2–2.8	...
9	CH_2Cl_2/CH_3OH	22.3	19.1	1.9	4.8	5.2	3.1 (60)	3.7	12.9–16.0	2.1	6.1–7.6	...
10	CH_3OH[g]	26.0	24.4	2.4	7.3	2.7	1.6 (59)	9.0	21.2–22.8	1.1	19.2–20.8	...
11	CCl_4[g]	24.1	8.2	0.8	5.3	4.7	2.4 (51)	1.7	3.4–5.8	2.3	1.5–2.5	...
12	CH_2Cl_2/CH_3COOH[f]	23.7	22.3	2.2	0.3	9.7	5.7 (59)	2.3	10.9–16.6	4.0	2.7–4.2	...
13	CH_3COOH[f]	24.7	21.6	2.2	0.2	9.8	5.0 (51)	2.2	11.6–16.6	4.8	2.4–3.5	...
14	90% CH_3COOH/HOH[f]	22.8	16.8	1.7	1.5	8.5	4.4 (52)	2.0	8.0–12.4	4.1	2.0–3.0	...
15	CH_2Cl_2	21.2	16.9	1.7	0.0	10.0	6.8 (68)	1.7	3.3–10.1	3.2	1.0–3.2	32% act oxygen[h]
16	CH_2Cl_2	10.6	9.7	1.0	4.7	5.3	3.4 (64)	1.8	2.9–6.3	1.9	1.5–3.3	8% XVI[i]
17	CH_2Cl_2	29.7	22.9	2.3	0.3	9.7	6.4 (66)	2.4	10.1–16.5	3.3	3.1–5.0	8% XVI[i]

[a] Anthrone (10 mmoles) was employed in each experiment, the reaction temperature was −35 ± 5°, and the work-up was by procedure A (Experimental Section) unless otherwise noted. [b] Yields are based on the millimoles of anthrone reacting with O_3. [c] The two figures shown represent the ozone available after 2 and 1 mole equiv, respectively, are used in the production of anthraquinone. [d] This figure represents the total number of millimoles of anthrone reacting with O_3 minus the millimoles of anthraquinone produced. [e] Reaction temperature, −7°. [f] Reaction temperature, 10°. [g] Reaction temperature, −15°. [h] The reaction mixture was immediately reduced with potassium iodide; see work-up procedure B in the Experimental Section. [i] The reaction mixture was worked up oxidatively (work-up procedure C in Experimental Section.) The yield of phthalic acid is based on an expected 1 mole equiv.

TABLE II

OZONATION OF ANTHRONE IN CH_2Cl_2 WITH OZONE–NITROGEN[a]

Expt no.	I, mmoles	—O_3, mmoles—		Ratio of O_3 reacted to I	Compd I producing dimer, mmoles	Compd I reacted with O_3, mmoles	Compd V,[b] mmoles (%)	Ratio of O_3 reacted to I reacted	Available for bond —attack, mmoles—		Ratio of O_3 to I (for bond attack)	O_2 evolved, mmoles	Ratio O_2 to V	Other[b] products
		Used	Reacted						O_3[c]	I[d]				
1	5.0	2.5	2.5	0.5	2.6	2.4	1.7 (71)	1.0	0–0.8	0.7	0–1.1	1.5	0.9	
2	5.0	5.1	4.6	0.9	3.0	2.0	1.1 (55)	2.3	2.4–3.5	0.9	2.7–3.9	...	...	
3	10.0	10.9	10.8	1.1	3.8	6.2	4.2 (68)	1.7	2.4–6.6	2.0	1.2–3.3	7.1	1.7	
4	5.0	5.5	5.2	1.0	1.9	3.1	1.7 (55)	1.7	1.8–5.3	1.4	1.3–3.8	2.5	1.5	
5	5.0	10.5	8.5	1.7	0.4	4.6	2.7 (59)	1.8	3.1–5.8	1.9	1.6–3.1	6.3	2.3	
6	2.4	5.2	4.9	2.0	0.4	2.0	1.2 (60)	2.5	2.5–3.7	0.8	3.1–4.6	2.3	1.9	
7	5.0	10.2	10.0	2.0	1.0	4.0	2.5 (63)	2.5	5.0–7.5	1.5	3.3–5.0	5.4	2.2	
8[e]	5.0	12.8	11.8	2.4	1.8	3.2	1.9 (59)	3.7	8.0–9.9	1.3	6.2–7.6[f]	6.4	3.4[f]	
9	10.0	2.6	2.6	0.3	7.9[g]	2.1	1.3 (62)	1.2	0–1.3	0.8	0–1.6	1.3	1.0	2% XVI[h]
10	10.0	12.7	12.7	1.3	3.7	6.3	3.8 (60)	2.0	5.1–8.9	2.5	2.0–3.6	...	...	5% XVI[h]
11	5.0	12.0	11.9	2.4	0.5	4.5	2.9 (65)	2.7	6.1–9.0	1.6	3.8–5.4	7.0	2.4	7% XVI[h]

[a] The reaction temperature ranged from −20 to −35°. Work-up was by procedure A (Experimental Section) unless otherwise noted. [b] Yields are based on the millimoles of anthrone reacting with O_3. [c] The two figures shown represent the ozone available after 2 and 1 mole equiv, respectively, are used in the production of anthraquinone. [d] This figure represents the total millimoles of anthrone reacting with O_3 minus the millimoles of anthraquinone produced. [e] The solvent was a methylene chloride–methanol mixture (50:50). [f] Some ozone must have reacted with methanol to produce oxygen. [g] Isolated as recovered anthrone; work-up procedure D. [h] The reaction mixture was worked up oxidatively. The yield of phthalic acid is based on an expected 1 mole equiv.

anthracene (XII) by Rigaudy and Thang.[7] It was assumed to have arisen through anthrone (I) as an intermediate. At first we thought that dianthronyl (X) was an ozonation product, but later found that it arose from unreacted anthrone during the period that the reaction mixtures were allowed to stand in order to complete the crystallization of anthraquinone. By means of thin layer chromatography we showed that immediately after ozonation some anthrone but no dianthronyl was present in the reaction mixture. As time progressed the anthrone slowly disappeared and at the same time dianthronyl appeared proportionately. It has previously been reported that solutions of anthrone (I) are oxidized to dianthronyl (X) upon standing.[8]

The fact that some unreacted anthrone (isolated as the dimer) was usually present even when a large excess of ozone was employed appears to be due to some evaporation of solvent in the ozone inlet tube at the bottom of the ozonation vessel, during the ozonation, leaving some solid anthrone on the walls of the tube. When the yields of anthraquinone (V) in Tables I and II were calculated on the basis of the anthrone which reacted during the ozonation (millimoles of starting

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(7) J. Rigaudy and K. V. Thang, *Bull. Soc. Chim. France*, 1620 (1959).

(8) A. Schönberg and A. Mustafa, *J. Chem. Soc.*, 657 (1945).

anthrone minus 2 mmoles of dianthronyl), it was found that 51–71% anthraquinone was obtained. That such a procedure is justified was verified by working up one run (Table II, expt 9) in such a way that unreacted anthrone (I) was isolated as such rather than as dianthronyl (X); the yield of anthraquinone (62%) was within the range found in other experiments. This range was essentially the same whether ozone–nitrogen or ozone–oxygen was used. Thus, the reactions involved ozone rather than oxygen as the principal oxidant, just as in the cases of aromatic aldehydes[5] and ethers.[6] Also, there appeared to be no solvent effect. The fact that the yields of anthraquinone (V) in expt 11, 13, and 14 of Table I were at the lower end of the range appears to be due to problems caused by the lower solubility of the starting material in the solvents employed.

The reactions competing with those yielding anthraquinone (V) appear to involve largely the attack of ozone on the benzene rings of anthrone (I). Anthraquinone (V) is extremely slowly attacked by ozone.[9] Although the only pure "bond-attack" product isolated, *via* an oxidative work-up procedure, was phthalic acid (XVI) in 2–8% yield (expt 16 and 17 of Table I and 9–11 of Table II), the presence of 32% peroxidic oxygen in the ozonation reaction mixture (expt 15 of Table I) indicates appreciably bond attack. The low yield of phthalic acid and the failure to isolate homophthalic acid is probably due to difficulty in converting the complicated peroxidic intermediates into identifiable products. This was also encountered in the ozonation of anthracene.[9]

In regard to the mechanism of the ozonation of anthrone to anthraquinone, data from the ozone–nitrogen reactions show that an average of 2 moles of molecular oxygen were evolved per mole of anthraquinone produced (Table II, expt 3–7, 11).[10] This means that 2 moles of ozone reacted with anthrone per mole of anthraquinone produced and suggests the reaction course I → III → V. Although we were not able to isolate III in the reaction mixture, for reasons to be mentioned later, such hydroxy compounds have been isolated from the ozonation of compounds similar to anthrone.[4] By analogy to the ozonation of aromatic aldehydes[5] and ethers,[6] we suggest that the first step is the 1,3-dipolar insertion of ozone at a carbon–hydrogen bond of the methylene group of I, to give unstable intermediate II, which then loses molecular oxygen to give III. Similar reactions of III, *via* IV, would give anthraquinone (V). An alternative to the second step would be attack on tautomer VI, as shown in the paper on ozonation of anthracene.[9] In favor of the insertion mechanism for the first step is the lower reactivity of 10-bromo- (XIb) and 10-nitroanthrone (XIc) toward ozone in comparison to anthrone. Whereas methylene chloride solutions of anthrone at $-35 \pm 5°$ absorbed, on the average, 92% of 2 mole equiv of ozone, methylene chloride solutions of the bromo- and nitroanthrones, under similar conditions, absorbed only 35 and 4% of the ozone, respectively (Table III). Previously,[5] the 1,3-dipolar insertion mechanism had been proposed because of similar observations with aromatic aldehydes[5] and ethers.[6] Electron-repelling substituents facilitated and electron-withdrawing substituents impeded the reaction. 10-Methoxyanthrone (XIa) appeared to absorb ozone slightly less efficiently than anthrone (77% of 2 mole equiv), but the yield of anthraquinone (68%) was higher than the average (62%) obtained from anthrone. Here the inductive effect of the methoxy group should slow down an electrophilic ozone attack, but the resonance effect should stabilize a potential positive charge on the attached carbon atom in the transition state (XX) of the 1,3-dipolar insertion reaction. Dibenzsuberone (XIV) also reacted with ozone very sluggishly (27% of 2 mole equiv absorbed). This was expected, since a potential positive charge on a methylene carbon atom would be dissipated by only one benzene ring in the transition state, rather than by two as in the case of anthrone.

Fluorene was much less reactive toward the insertion reaction than anthrone. Under similar reaction conditions as used for anthrone it absorbed only 72% of the 2 mole equiv of ozone employed. Much more bond attack occurred than with anthrone. The yield of fluorenone (XVII) was only 19–24% and a homophthalic acid (XVIII) yield of 64% has been reported by other workers.[11a] This was at first surprising since one might expect a greater delocalization of positive charge in the transition state (XX) of fluorene than of anthrone, which has a carbonyl group. However, the fluorenyl system, as well as other cyclopentadienyl systems, are notoriously reluctant to give up elections, as required for the developing positive charge in the transition state (XX) for 1,3-dipolar insertion.[11b]

The fact that there is little difference in the results using ozone–oxygen or ozone–nitrogen mixtures indicates that very little autoxidation occurs in the of oxygen. This also appeared to be true in the case of ethers,[6] but not with aromatic aldehydes.[5] Thus, the predominant fate of the 1,3-dipolar insertion intermediate (II, $C_6H_5C(=O)OOOH$, etc.) must be different in the case of the aromatic aldehydes from in the other cases. For the aldehyde ozone insertion intermediate, we proposed cleavage of oxygen bonds to give largely peroxy ($C_6H_5C(=O)OO\cdot$) radicals which abstracted hydrogen from aldehyde molecules, thereby initiating autoxidation in the presence of molecular oxygen.[5] In the present case, very little of this (involving VII or VIII) appears to occur. For example, there is no evidence for any appreciable formation of hydroperoxide IX (from VIII). If it were produced, it should easily dehydrate to anthraquinone,[9] thus requiring only 1 mole equiv of ozone for the production of anthraquinone from anthrone. The stoichiometry of the reaction and the absence of appreciable autoxidation favor the decomposition path for the insertion product illustrated in II.

The requirement of 2 moles of ozone reacting per mole of anthrone (I) to produce anthraquinone (V) appears to fit all of the experiments except those which employed less than 1 mole of ozone per mole of starting anthrone (expt 1 and 2 of Table I and 1 and 9 of Table II). In the cases of expt 1 and 2 of Table I and

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

[10] An exception is expt 8 of Table II in which the solvent contained methanol. Apparently some ozone attack on the solvent occurred, producing molecular oxygen.

[11] (a) P. G. Copeland, R. E. Dean, and D. McNeil, *J. Chem. Soc.*, 3230 (1960); (b) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961, pp 269–271. We thank one of the referees for reminding us of this.

TABLE III

OZONATION OF SUBSTITUTED ANTHRONES, FLUORENE, AND DIBENZSUBERONE[a]

			Compound, mmoles		Ozone, mmoles		Yield of keto product, mmoles (%)
Compd	Solvent	Temp, °C	Starting	Reacting	Starting	Reacting	
XIa	CH_2Cl_2[b]	−25	2.5	2.5	5.2	4.0	1.7 (68[c])
XIb	CH_2Cl_2[b]	−30	5.0	*d*	10.4	3.6	*e*
XIc	CH_2Cl_2[b]	−30	5.0	*d*	10.1	0.4	*e*
XIV	CH_2Cl_2[b]	−30	10.0	*d*	22.0	6.0	*e*
XV	CH_2Cl_2[f]	−40	10.0	5.8	22.4	16.0	1.1 (19[g])
XV	CH_2Cl_2/CH_3OH[f]	−35	10.0	3.8	21.4	18.4	0.9 (24[g])
XV	CH_2Cl_2/CH_3OH[f]	−30	10.0	7.8	22.8	17.3	1.8 (23[g])

[a] Ozone–oxygen was used. [b] Volume of solvent, 150 ml. [c] Anthraquinone. [d] Very little reacted. [e] Not determined. [f] Volume of solvent, 100 ml; with mixtures, 1:1. [g] Fluorenone.

of expt 1 of Table II, the *total* amount of ozone absorbed was less than 2 moles per mole of anthraquinone (V) produced. In expt 9 of Table II, if 2 mole equiv of ozone were required for the anthraquinone produced, there would be none left for attack on the benzene ring. The logical explanation is that with insufficient ozone, the reaction stops at the stage leading to intermediate III which, however, is difficult to isolate because it is easily oxidized to anthraquinone by atmospheric oxygen during the work-up procedure. A similar phenomenon was observed in the ozonation of anthracene with insufficient ozone.[9] The fact that in expt 1 and 9 of Table II, only 1 mole of molecular oxygen was evolved per mole of anthraquinone produced is strong evidence for this proposal. This phenomenon also appears to occur, but to a lesser degree, in experiments where 1.0–1.7 moles of ozone per mole of anthrone was employed (expt 3, 8, 11, 15, and 16 of Table I and 3 and 4 of Table II). In these cases, if 2 mole equiv of ozone was used per mole of anthraquinone, less than 2 mole equiv would be available for attack on the benzene rings.

Thus, with minor exceptions, particularly in regard to the mode of decomposition of II, the mechanism of the attack of ozone on the methylene and methylidyne groups of anthrone and similar compounds appears to be similar to that which occurs during the ozonation of ethers[6] and aromatic aldehydes.[5]

Hamilton and Ribner[12] recently reported that ozonation of *cis*- and *trans*-1,2-dimethylcyclohexane occurred with 79–85% retention of configuration to the corresponding tertiary alcohols. They, however, proposed a partial radical character for the reaction, giving a transition state of type XIX, in which they assumed that most of the radicals never became free enough to cause much loss of stereospecificity.[12,13]

To our minds the results of Hamilton and Ribner constitute confirmation of the 1,3-dipolar insertion mechanism. The ROOOH intermediate may not only decompose to alcohol, as shown in II, but also to alkoxy radicals to some extent. The alkoxy radicals could abstract hydrogen from other hydrocarbon molecules, also giving the tertiary alcohol, with retention of configuration, and alkyl radicals. The small amount of racemization occurring is probably due to the alkyl radicals, which may react with oxygen to give hydroperoxide or with hydroxy radicals to give alcohol. Any hydroperoxide produced could easily be converted to alcohol, or, in the case of secondary hydroperoxides, be partially dehydrated to ketones, as found.[12] The fact that Hamilton and Ribner[12] found no appeciable temperature effect supports the 1,3-dipolar insertion mechanism more than their own. An increase in temperature should increase the yield of free radicals from a transition state of type XIX, thus decreasing the stereospecificity of the reaction. Finally, a radical attack by ozone, as implied by Hamilton and Ribner,[12,13] seems highly unlikely since ozone is not paramagnetic.[14]

Experimental Section

The ozonation setup and equipment are described in earlier papers.[9,15-17] Solvents were pure and anhydrous, unless otherwise stated. Thin layer chromatography (tlc) was carried out on silica gel G layers. Chromatograms of neutral materials were eluted with a benzene–chloroform solution and visualized with a chloroform solution of iodine. Chromatograms of acids were eluted with a 100:16:12 solution of 95% ethanol, 25% ammonium hydroxide, and water and visualized with bromocresol green.

The anthrone (I) used was the best grade available from K & K Laboratories (Plainview, N. Y.) or Aldrich Chemical Co. (Milwaukee, Wis.), recrystallized from benzene–petroleum ether (bp 60–70°) (3:1), mp 151–152° (lit.[18] mp 154–155°). The fluorene (XV) used was Eastman Practical grade of 98% purity, chromatographed over alumina (petroleum ether), mp 114–115° (lit.[19] mp 115–116°). The dibenzsuberone (XIV) was from the Aldrich Chemical Co.

10-Nitroanthrone (XIc) was synthesized by the procedure of Meyer,[20] mp 143–144° dec. **10-Bromoanthrone** (XIb) was prepared by the method of Goldman,[21] mp 148–149°. **10-Methoxyanthrone** (XIa) was prepared by the method of Meyer,[22] mp 99–101°.

Ozonation Procedures.—A solution of 5–10 mmoles of anthrone (I) in 100 ml of methylene chloride (or other solvents shown in Tables I and II) was ozonized at −40 to 10° either with an ozone–nitrogen stream[9,16,17] containing the desired amount of ozone or with the desired number of liters of an ozone–oxygen stream of known (about 3%) ozone concentration. The ozone actually reacting was measured by substracting that which passed into the potassium iodide trap from the total amount employed. Molecular oxygen analyses were by previously described methods.[9,16,17] Work-up was by one of the following procedures.

Work-Up Procedure A.—The reaction mixture was filtered. Some pure anthraquinone (V) was obtained in this manner and was identified by its melting point (282–285°) and its infrared spectrum which showed a unique peak at 12.40 μ and was identical with that of an authentic sample. The filtrate was partially evaporated on the steam bath and set aside to crystallize.

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[12] (a) G. A. Hamilton and B. S. Ribner, Abstracts of Papers presented at the 153rd Meeting of the American Chemical Society, Miami Beach, Fla., April 1967, paper 0–120. (b) Paper 57, presented at the International Oxidation Symposium, San Francisco, Calif., Aug 28–Sept 1, 1967.

[13] See also *Chem. Eng. News*, 49 (April 24, 1967).

[14] R. Trambarulo, S. N. Ghosh, C. A. Burrus, Jr., and W. Gordy, *J. Chem. Phys.*, **21**, 851 (1953).

[15] P. S. Bailey, *J. Am. Chem. Soc.*, **78**, 3811 (1956).

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

[17] A. M. Reader, P. S. Bailey, and H. M. White, *J. Org. Chem.*, **30**, 784 (1965).

[18] K. H. Meyer, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p 60.

[19] M. Orchin, *J. Am. Chem. Soc.*, **67**, 499 (1945).

[20] Reference 18, p 390.

[21] F. Goldmann, *Ber.*, **20**, 2436 (1887).

[22] K. H. Meyer, *Ann.*, **379**, 68 (1911).

The various precipitates which formed over a period of several days by repeated evaporations and crystallizations were shown by their infrared spectra and thin layer chromatograms to contain anthraquinone (V) and dianthron-9-yl (X).

In one case, X was separated and purified by fractional crystallization from benzene. It was identified by its melting point (267–269°), its elemental analysis, and its infrared spectrum, which showed major bands at 6.04 (aromatic carbonyl), 6.26 (aromatic "double bond"), and 12.70 μ and was identical with that of an authentic sample prepared by the method of Barnett and Matthews.[23] In addition, the nmr spectrum of X (in $CDCl_3$) showed a multiplet of 16 protons at τ 2.6 (aromatic) and a singlet of two protons at 5.2 ppm.

Anal. Calcd for $C_{28}H_{18}O_2$: C, 87.0; H, 4.7; mol wt, 386. Found: C, 87.5; H, 4.6; mol wt, 362.

In most cases the precipitated mixtures of anthraquinone (V) and dianthronyl (X) were not separated but were analyzed by comparison of peak heights in the infrared spectra with those of standard solutions of the known compounds. The peaks used were 12.40 μ for anthraquinone and 12.70 μ for dianthronyl. The results are shown in Tables I and II.

Thin Layer Chromatography.—In two experiments, one using ozone–oxygen and the other ozone–nitrogen, the ozonation reaction mixtures were immediately spotted on a tlc plate, along with authentic samples of anthrone (I) and dianthronyl (X). Anthrone, but not dianthronyl, was found to be present. After the reaction mixtures had stood for 3 days and were similarly treated, the chromatograms showed dianthronyl, but no anthrone. In another instance, pure anthrone (10 mmoles) was dissolved in methylene chloride (100 ml). A chromatogram of the solution showed only anthrone. After 2 days, the solution was concentrated on a steam bath to 50 ml and a chromatogram showed the formation of considerable dianthronyl; after 3 days, the chromatogram indicated equal amounts of anthrone and dianthronyl.

Work-Up Procedure B. Reductive.—The cold (−40°) ozonation reaction mixture was swept with nitrogen, after which an excess of potassium iodide solution was added. The reaction mixture was treated with glacial acetic acid and allowed to come to room temperature, after which the methylene chloride was removed over a steam bath, the remaining acetic acid solution was titrated with standard thiosulfate solution, and the percentage of active oxygen (peroxide) was calculated. The results are shown in expt 15 of Table I.

Work-Up Procedure C. Oxidative.—Since it was shown in a separate experiment that dianthronyl (X) is oxidized to anthraquinone by alkaline hydrogen peroxide, the usual work-up procedure A was carried out. After all of the anthraquinone and dianthronyl had crystallized from the reaction mixture, which had been evaporated to a low volume, the remainder was treated with 30 ml of 10% sodium hydroxide, 15 ml of 30% hydrogen peroxide, and 25 ml of methylene chloride (for a 10-mmole run), and the resulting solution was refluxed for 12 hr. The aqueous and methylene chloride layers were separated and the aqueous layer was acidified with hydrochloric acid and extracted with ether (continuously or with many small portions). Tlc showed that the ether extract contained phthalic acid but no appreciable amount of homophthalic acid (XVIII). Evaporation of the ether solution and recrystallization of the residue from 10% hydrochloric acid gave phthalic acid (XVI) melting at 204°. It was further identified by comparison of its infrared spectrum with that of authentic sample. The results are shown in expt 16 and 17 of Table I and expt 10 and 11 of Table II. The results were no different when the acidified aqueous layer was evaporated and the residue was extracted in a Soxhlet extractor with acetone.

Work-Up Procedure D.—In this instance, the ozonation reaction mixture was immediately evaporated to a low volume, after which about 50 ml of methanol was added and the reaction mixture was cooled and filtered. The first crop of crystals was largely anthraquinone. By concentration of the reaction mixture, crystallization of anthrone occurred. Identifications were by comparison of infrared spectra with those of authentic samples. After all of the anthraquinone and anthrone had precipitated, the remainder of the reaction mixture was worked up by procedure C. The results are shown in expt 9 of Table II.

Oxidation of Dianthron-9-yl (X) with Alkaline Hydrogen Peroxide.—A solution of 0.2 g of dianthronyl (X), 20 ml of methanol, 20 ml of 30% hydrogen peroxide, and 20 ml of 10% sodium hydroxide was refluxed overnight, after which it was cooled and extracted with methylene chloride. The methylene chloride extract was washed, dried, and evaporated and the residue was crystallized from ethanol; 0.2 g of nearly pure anthraquinone was obtained and identified by its infrared spectrum.

Ozonation of 10-Substituted Anthrones and Dibenzsuberone.—A solution of 2.5 or 5.0 mmoles of the substituted anthrone or of dibenzsuberone in 150 ml of methylene chloride was ozonized with ozone–oxygen at about −30° by the usual procedure. The amount of ozone reacting was measured by subtracting that which passed into the potassium iodide trap from that in the ozone–oxygen stream employed. Only in the case of 10-methoxyanthrone (XIa) was the reaction mixture worked up. This was done by evaporation to dryness and crystallization of the residue from ethanol; the material melted at 282–285° and was identified as anthraquinone by comparison of its infrared spectrum with that of an authentic sample. The results are shown in Table III.

Ozonation of Fluorene.—The ozonation was carried out as in the preceding experiments using solutions of 10 mmoles of fluorene (XV) in 100 ml of solvent. The reaction mixture was evaporated to dryness and the residue was extracted first with hot petroleum ether and then with sodium bicarbonate solution. The bicarbonate solution was extracted with chloroform and the chloroform and petroleum ether extracts were dried and chromatographed on a neutral alumina column with benzene elution. First, came the fluorescent fraction (ultraviolet light) of fluorene (mp 114–115°), followed by the yellow fraction of fluorenone (XVII), mp 82° (lit.[24] mp 83–84°). Identifications were made by comparison of infrared spectra with those of authentic samples. The results are shown in Table III.

Registry No.—I, 90-44-8; V, 84-65-1; X, 434-84-4; XIa, 14629-83-5; XV, 86-73-7; XVII, 486-25-9.

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