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EFFECT OF SOLVENTS UPON THE INITIAL OZONE ATTACK ON POLYCYCLIC AROMATICS

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Recent studies[1-9] concerning the ozonation of polycyclic aromatic compounds have indicated that the major ozone attack occurs with some systems at the positions of lowest ortho (or bond) localization energy[10] and with other systems at the positions of lowest para localization energy[10]. These findings have been explained in two analogous ways: (1) the preferred ozone attack occurs via a rate-controlling transition state whose geometry corresponds to the most stable dihydro compound (i.e. 1,2 or 1,4) as measured by the appropriate corrected quinone -- hydroquinone redox potentials[5,8]; (2) the preferred ozone attack occurs at the ortho or para

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positions corresponding to the lowest calculated resonance energy decrease accompanying the formation of the transition state[4].

Although these suggestions were able to correlate the data at hand at the time, they do not consider the possibility that the type of ozone attack, transition state and intermediate produced may vary with the type of solvent employed during the ozonation. The yields of ozonation products from some of the polycyclic aromatics were significantly low[2,3,5-8] and in some cases no information was given concerning the solvents employed[2,3].

Results of ozonation studies with anthracene suggest, but do not prove, the existence of a solvent effect. Ozonation of anthracene in acetic acid resulted in yields up to 69% of anthraquinone[9], whereas ozonation in carbon tetrachloride led to 62-67% yields of phthalic acid and only 6-14% yields of anthraquinone[11].

Using 9,10-dibromoanthracene as our aromatic species we have now obtained proof that there are two competing types of initial ozone attack and that the one which predominates can be determined by the type of solvent employed. Ozonation of this substance in methanol-methylene chloride medium followed by an oxidative work-up using hydrogen peroxide resulted in 79-80% yields of anthraquinone (m.p. 284-286°). Two mole-equivalents of ozone were absorbed during the reaction and some molecular bromine was released. Hydrogen peroxide was shown not to attack the starting material under the reaction conditions employed. Ozonolysis in methylene chloride followed by an oxidative work-up procedure gave only 18-22% yields of

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[11] P. S. Bailey, J. B. Ashton and F. Dobinson, unpublished results.

anthraquinone and 75-82% yields of 3,6-dibromobenzene-1,2,4,5-tetracarboxylic acid (m.p. above 300°). Found: C, 29.34; H, 1.20; Br, 38.94. $C_{10}H_4Br_2O_8$ requires: C, 29.15; H, 0.98; Br, 38.80%. This acid was made previously by the nitric acid oxidation of 1,4-dibromo-2,5-diethyl-3,6-dimethylbenzene[12]. We established its identity by catalytic dehalogenation to pyromellitic acid (m.p. 270-271°) which showed no depression in a mixture melting point with an authentic sample. Thus the position of major ozone attack has been changed from one aromatic ring to another simply by changing the type of solvent used. This could happen only if a drastic change in the mechanism of the ozone attack accompanied the solvent change.

The major attack in methylene chloride appears to involve essentially a four-center ozone attack leading to a transition state similar to that described by Moriconi, Wallenberger and coworkers[4,5,8] and producing a five-membered ring intermediate (II). Probably a π complex of type I is a precursor to the transition state leading to II. After the attack at the 1,2-bond the reaction continues at the 3,4 and 5,6 and 7,8 bonds. The presence of bromo groups at the 9 and 10 positions inhibits a four-center attack on the middle ring.

A reasonable explanation for the results in the presence of methanol is that the ozone molecule is polarized by the solvent (e.g. III) and makes an ionic attack at the reactive 9 position. This would involve a different transition state, leading to the formation of an intermediate sigma complex (IV). The route from IV to products is uncertain. Either

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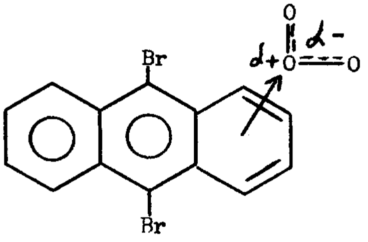
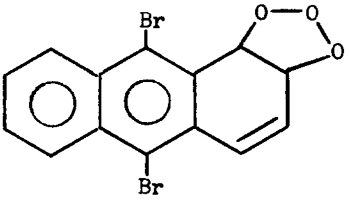
[12] E. Philippi, Liebigs Ann. **428** 286 (1922).



I



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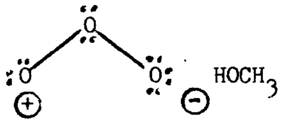

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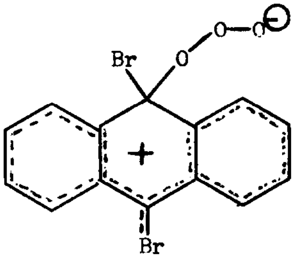

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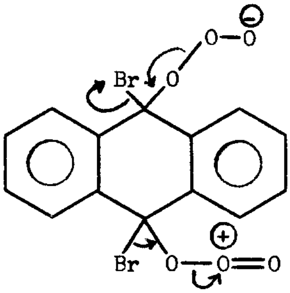
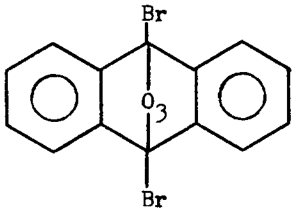


V



VI

a second ozone molecule could attack nucleophilically[13] to give V which

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[13] A. H. Riebel, R. E. Erickson, C. J. Abshire and P. S. Bailey, J. Amer. Chem. Soc. 82, 1801 (1960).

could go to products as shown, or else a 1,4-addition could be completed to give VI which could decompose to products through the reducing action of methanol.

The competition between an ionic and a four-center attack of ozone seems to be quite general. The yield of product from an ozone attack in a 1,2 sense with dibenz [a, h] anthracene was considerably lower in the presence of methanol than with pure methylene chloride solvent[8]. We shall report later further evidence for this competition with anthracene, pyrene and certain furans.

The observation of the type of solvent effect described here is novel in ozonation reactions. We feel that it is important not only because of its mechanistic implication but also because of its potential utility in organic syntheses.

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