Communications TO THE EDITOR

Ozonization of Anthracene[1]

Sir:

Badger[2] has classified ozone as a "double bond reagent" and Brown[3] has assumed that it makes a one-step attack of both reactive centers on both reactive centers of the unsaturated molecule, rather than a two-step attack. If so, it should attack anthracene at the 1,2-bond, because this bond, according to the molecular orbital theory, has the lowest "bond localization energy."[3,4]

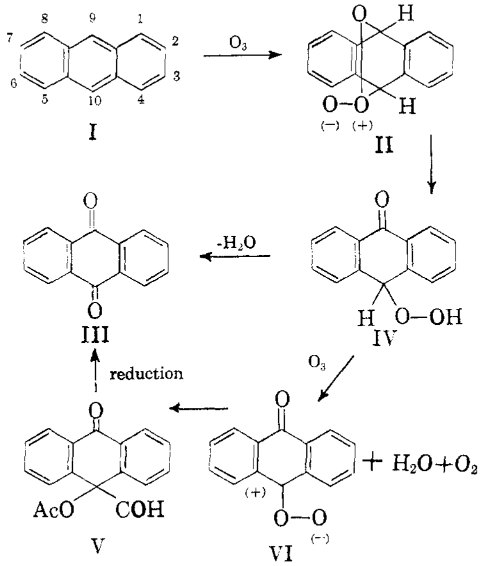
If the attack is by the two-step process, however, it should occur at the 9 and 10 positions, because these have the lowest "atom localization energies."[3,4] Diels-Alder type reagents also would attack at the 9 and 10 positions, even by a one-step mechanism, but ozone can probably be excluded from this category since it does not behave as such with ordinary conjugated systems.

The ozonization of anthracene in acetic anhydride to give anthraquinone has been reported.[5] The yield was not given, however, nor was it shown that ozone instead of oxygen actually was the reactant. We have ozonized anthracene in acetic acid at 10° with 5% ozone and have found that the ozone is readily absorbed. The reaction is complete after three moles per mole of anthracene react. Anthraquinone is produced in 69% yield. Some anthraquinone (28%) precipitates during the reaction. The remainder is produced by sodium iodide or bisulfite reduction of the peroxidic filtrate. Ozone rather than oxygen was shown to be the attacking agent not only by the fact that far more than catalytic amounts were absorbed but also by passing the same volume of 0.5–1% ozone through the reaction mixture and showing that the amount of anthraquinone produced was directly proportional to the amount of ozone employed.

These results are important for two reasons. This is the first established instance in which ozone has attacked the ends of a conjugated system rather than a specific double bond. The geometry of the system is such that the ozone molecule can reach across the ends of the system, i.e., from C-9 to C-10. Further, this is excellent evidence for the two-step mechanism and corroborates Wibaut's[6] experiments which indicate that the initial attack is electrophilic. Such can be the case only with the two-step mechanism.[3]

The following suggested mechanism for the anthracene reaction explains the essential fact that anthraquinone is produced both during the ozonolysis (presumably by decomposition of a peroxidic intermediate, e.g. IV) and by reduction of a peroxidic intermediate. Evidence for IV is the isolation of some anthrahydroquinone by sodium iodide reduction. Since anthraquinone is the principal reduction product, however, oxidation of IV to VI is proposed. This is to be expected since IV would be in equilibrium with a perhydroquinone structure.

The suggested mechanism does not explain the requirement of three moles of ozone per mole of anthracene. It seems likely that the 31% of anthracene which did not produce anthraquinone reacted by the one-step mechanism. This should result in destruction of both outer rings and account for a large portion of the total three moles of ozone.



Department of Chemistry
The University of Texas
Austin 12, Tex.

Philip S. Bailey
Joseph B. Ashton

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(1) Included in part in a paper presented before the International Ozone Conference, Chicago, Ill., November 28–30, 1956.

(2) Badger, *Quart. Revs.*, **5**, 155 (1951).

(3) (a) Brown, *Quart. Revs.*, **6**, 63 (1952). (b) Brown, *J. Chem. Soc.*, 3249 (1950).

(4) Dewar, *J. Am. Chem. Soc.*, **74**, 3357 (1952).

(5) Roitt and Waters, *J. Chem. Soc.*, 3060 (1949).

(6) For leading references see Bailey, *J. Am. Chem. Soc.*, **78**, 3811 (1956).

1,5-Diaryl-2,3-pyrrolidinediones. VII. Reassignment of Structure

Sir:

Since Schiff and Gigli[1] first reported the preparation of 1,5-diphenyl-2,3-pyrrolidinedione (Ia) a

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(1) R. Schiff and L. Gigli, *Ber.*, **31**, 1306 (1898).