Communication TO THE EDITOR

Ozonolysis of Naphthalene

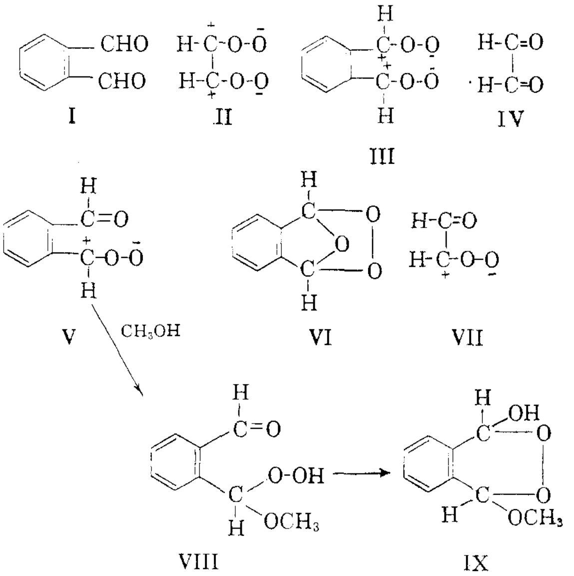
Sir:

Harries and Weiss[1] reported the isolation of diozonides of naphthalene and phenanthrene by ozonolyses of these substances in chloroform. It has been shown since then that phenanthrene yields a polymeric monoozonide upon ozonolysis in inert solvents.[2,3] Workers have continued to assume, however, that the ozonide of naphthalene is a diozonide, because two moles of ozone per mole of naphthalene are absorbed.[4-6]

In light of the Criegee mechanism[7] for ozonolysis, one would expect the naphthalene ring to be cleaved at the 1,2 and 3,4 bonds to yield one of the following pairs of fragments: I and II, III and IV, or V and VII. Fragments such as II and VII would be expected to decompose as soon as they are formed.[8] Instead of obtaining a diozonide, therefore, one should obtain one of the following: a monoozonide with two carbons less than in naphthalene (from cyclization of V), a polymer of V, I, or a polymer of III.

Ozonolysis of naphthalene in hexane at −70° resulted in the absorption of 2 molar equivalents of ozone and the precipitation in high yield of a colorless crystalline peroxidic material. The ozonide was too unstable to analyze. If allowed to dry in chunks, it exploded.

Ozonolysis of naphthalene in methanol at −70° (2 molar equivalents of ozone absorbed) followed by partial evaporation and cooling to −70° gave a 94% yield of a colorless crystalline peroxide (m.p. 115–117°; recrystallized from ethyl acetate and hexane, m.p. 126–127°, 85% yield). The material was assigned structure IX because of its elemental analysis (calcd. for $C_9H_{10}O_4$: C, 59.35; H, 5.52; methoxyl, 17.03; mol. wt. 182.17. Found: C, 59.39; H, 5.38; methoxyl, 16.89; mol. wt. 184, 190[9]), its infrared spectrum which showed a hydroxyl but no carbonyl bond, a negative lead tetraacetate test for hydroperoxides,[10] conversion to phthalic acid by acidic hydrogen peroxide and hydrolytic rearrangement under acidic or alkaline conditions to phthaldehydic acid.



The formation of IX obviously is a reaction of zwitterion V, involving cyclization of VIII. One may conclude, therefore, that the ozonide, likewise, was formed from zwitterion V and either was the monomeric monoozonide VI or a polymer of V. We believe it was VI because of its crystalline character and because of its explosiveness. The polymeric ozonide of phenanthrene was not explosive.[2] It has been reported previously that systems such as VI are very unstable.[11]

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[3] J. B. Wibaut and T. J. de Boer, *Koninkl. Ned. Akad. Wetenschap. Proc. Ser. B.*, *59*, 421 (1956).

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[5] J. B. Wibaut and L. W. F. Kampschmidt, *Koninkl. Ned. Akad. Wetenschap Proc.*, **53**, 1109 (1950).

[6] L. W. F. Kampschmidt and J. B. Wibaut, *Rec. trav. chim.*, *73*, 431 (1954).

[7] See P. S. Bailey, *J. Am. Chem. Soc.*, *78*, 3811 (1956) for out-line of mechanism and leading references.

[8] R. Criegee, P. de Bruyn, and G. Lohaus, *Ann.*, **583**, 25 (1953).

[9] Determined cryoscopically in 1,2-dibromoethane.

[10] R. Criegee, H. Pilz, and P. Flygare, *Ber.*, **72**, 1799 (1939).

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