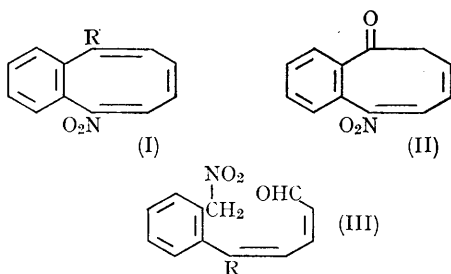


On the Formation and Rearrangement of Some Benzocyclo-octatetraene Derivatives

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In some instances, the addition of a reagent to the biphenylene system produces a derivative of benzocyclo-octatetraene rather than a derivative of the valency tautomer 4a, 8b-dihydrobiphenylene. Thus the reactions of acetyl nitrate and nitrosyl chloride with biphenylene have given mixtures of 2-nitrobiphenylene¹ with 3-acetoxy-8-nitrobenzocyclo-octatetraene (I, R = OAc), m.p. 115—116°, (40% yield) and 3-chloro-8-nitrobenzocyclo-octatetraene (I, R = Cl), m.p. 111—113°, (18% yield) respectively. In the latter case no nitroso-compounds were found.



Treatment of these derivatives with warm aqueous sodium carbonate gave low yields of 4-nitro-1-naphthol and 4-nitro-1-chloronaphthalene

respectively, with the loss of a two-carbon fragment from the cyclo-octatetraene ring. Passage of (I, R = Cl) through a column of basic alumina also resulted in its conversion into 4-nitro-1-chloronaphthalene. Basic hydrolysis of the acetoxy-derivative (I, R = OAc) under milder conditions gave a 25% yield of the ketone (II), m.p. 123—125°, D.N.P. derivative m.p. 175—177°, which on further reaction gave 4-nitro-1-naphthol.

Conversions of cyclo-octatetraene into side-chain derivatives of benzene are well known,² but the complete loss of a two-carbon fragment in this case indicates that the reaction is of a different type, and the isolation of acetaldehyde affords some evidence as to its mechanism. It is probable that the 7-8 double bond in (I), which cannot conjugate with the benzene ring, undergoes the facile nucleophilic attack which is characteristic of α -nitro-olefins.³ A retro-aldol reaction at this point would give the unsaturated aldehyde (III) which could lose acetaldehyde by further retro-aldol reactions. The loss of one molecule of acetaldehyde from (III) followed by recyclisation would give rise to a naphthalene derivative.

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¹ W. Baker, J. W. Barton, and J. F. W. McOmie, *J. Chem. Soc.*, 1958, 2666.

² R. A. Raphael in "Non-Benzenoid Aromatic Compounds", D. Ginsburgh, ed., Interscience, 1959, p. 469.

³ L. Haitinger, *Annalen*, 1878, **193**, 374.