

The Structure of the Product $C_{21}H_{12}O_6$ from *o*-Phenylene Thionocarbonate and Trimethyl Phosphite

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IN 1963 we reported a new method for the formation of olefins which involves the reaction of 1,2-thionocarbonates with phosphite esters.¹ In a more recent preliminary communication² we described various extensions of this synthesis, but noted that the thermal reaction of *o*-phenylene thionocarbonate (I) with trimethyl phosphite does

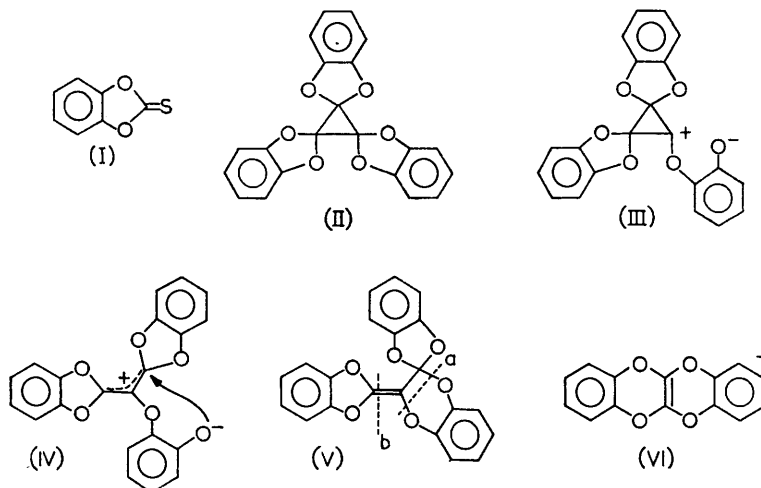
not appear to afford benzyne as an intermediate but instead a crystalline product $C_{21}H_{12}O_6$, m.p. 177.5—178.5°, formulated as (II) (20% yield). This product has been investigated further in the interim particularly because of the presence of a sharp absorption band in the infrared spectrum of medium intensity at 5.67μ (KBr disc) which is not

¹ E. J. Corey and R. A. E. Winter, *J. Amer. Chem. Soc.*, 1963, **85**, 2677.

² E. J. Corey, F. A. Carey and R. A. E. Winter, *J. Amer. Chem. Soc.*, 1965, **87**, 934.

readily explained by formula (II) and which has now been shown not to be due to an impurity, *e.g.* of *o*-phenylene carbonate.

It appeared possible that the substance $C_{21}H_{12}O_6$ might be a further rearrangement product of (II), formed by a cyclopropyl \rightarrow allyl cation type of rearrangement *via* (III) and (IV) which leads to



structure (V). Physical evidence indicates that this is probably the case. The infrared band at 5.67μ is explained satisfactorily in terms of (V) as a C=C stretching band displaced to lower wavelengths than normal for olefins because of the three oxygen substituents.³⁻⁵ Nuclear magnetic resonance data also favour (V) over (II) since the aromatic protons appear as two broadened peaks at 6.99 and 6.93 p.p.m. downfield from tetramethylsilane rather than as a single sharp peak as found for (I) and expected for (II).

Especially revealing is the mass spectrum of the desulphurization product. In addition to the molecular ion peak at m/e 360 of intensity 0.76 (relative to the most intense peak) major fragments appear at m/e 252 (0.27 intensity), 240 (1.0), and

196 (0.40) in addition to those of lower m/e containing only one aromatic ring. These peaks are indicative of structure (V) rather than (II). The peak at 252 corresponds to loss of *o*-benzoquinone from the molecular ion by fission at *a* in (V) and that at 240 corresponds to fission at *b* in (V). The peak at 196 is probably the xanthone

radical cation which can come from the molecular ion by *b* cleavage and rearrangement to (VI) followed by decarboxylation.

This preliminary account of our structural work on this problem was prompted by personal communication from Dr. R. Hull which revealed that the same reaction had been studied independently in his laboratory and that structure (V) rather than (II) was indicated by chemical as well as physical data.

We are continuing work in this area both to ascertain the validity of the path (II \rightarrow V)⁶ and whether (II) can be obtained as an intermediate. The photochemical generation of benzyne from (I) is also under study.

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³ S. M. McElvain and R. E. Starn, jun., *J. Amer. Chem. Soc.*, 1955, **77**, 4571.

⁴ S. M. McElvain and G. R. McKay, jun., *J. Amer. Chem. Soc.*, 1955, **77**, 5601.

⁵ R. W. Hoffmann and H. Hauser, *Tetrahedron Letters*, 1964, 197.

⁶ For a recent discussion of the cyclopropyl \rightarrow allyl cation type rearrangement see E. J. Corey and R. F. Atkinson, *J. Org. Chem.*, 1964, **29**, 3703.