

Formation of Benzo-1,3-dithiolium Carbene from Benzyne and Carbon Disulphide

By JYUZO NAKAYAMA

(The Institute of Physical and Chemical Research, Wako-shi, Saitama 351, Japan)

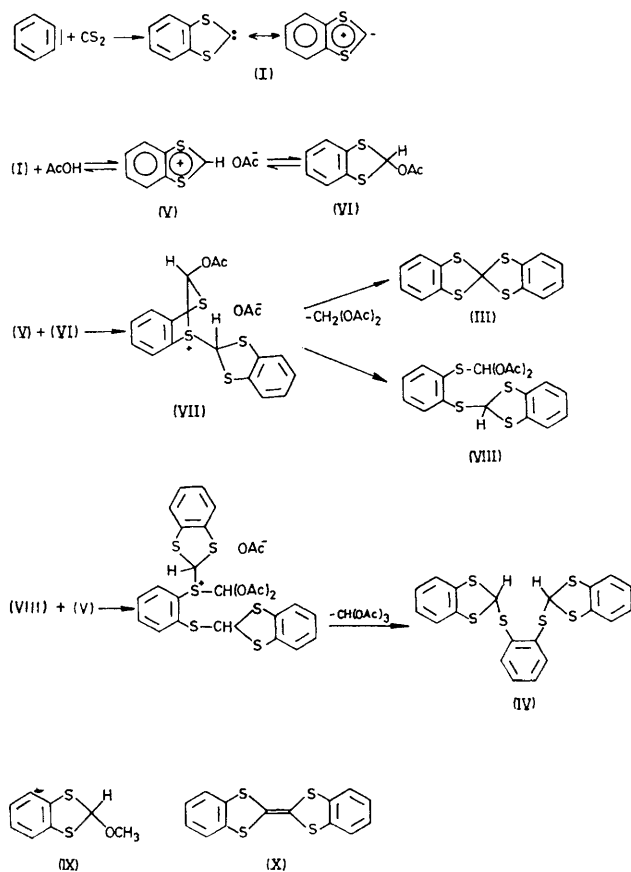
Summary Benzyne generated by oxidation of 1-aminobenzotriazole with lead tetra-acetate reacts with carbon disulphide to give products explicable in terms of the transient formation of benzo-1,3-dithiolium carbene (I).

FIELDS and MEYERSON have suggested that the transient formation of benzo-1,3-dithiolium carbene (I) from carbon disulphide and benzyne generated from phthalic anhydride at 700° in the vapour phase occurs because a product corresponding to the dimer of (I) was indicated by mass spectrometry.¹ We report evidence for the formation of (I) from benzyne and carbon disulphide in the liquid phase.

Oxidation of 1-aminobenzotriazole (II) with a slight excess of lead tetra-acetate² in a mixture of carbon disulphide and methylene dichloride afforded (III) (6%) m.p. 120°, (IV) (67%) m.p. 131—131.5°, and a small amount of two unidentified compounds. Oxidation carried out in carbon disulphide alone gave a higher yield (86%) of (IV) and a trace amount of (III). The identity of (III) and (IV) was established by mixed m.p. determination with an authentic sample† and by comparison with reported melting points.³ Benzyne generated by oxidation of 1-aminobenzotriazole (II) reacts with carbon disulphide to give resonance-stabilized, and hence nucleophilic, benzo-1,3-dithiolium carbene (I) in a manner similar to the reaction of carbon disulphide with acetylenes having at least one electron-attracting substituent.⁴ The intervention of acetic acid formed as a result of oxidation of (II) by lead tetra-acetate, results in an equilibration between (I), (V), and (VI) as was observed with 1,3-dithiolium carbene itself.^{4a} Electrophilic attack of the benzo-1,3-dithiolium ion (V) on the sulphur atom of (VI) produces the sulphonium ion (VII) which either gives the spiro-compound (III) with loss of diacetoxymethane or rearranges to (VIII). Finally, electrophilic attack of (V) on the sulphur atom attached to the diacetoxymethyl group of (VIII) followed by elimination of triacetoxymethane affords the product (IV). This reaction scheme is in agreement with the formation of (IV) from benzo-1,3-dithiolium perchlorate reported by Buza and his co-workers.³

Further evidence for the formation of (I) was obtained by oxidation of (II) in an equal volume of carbon disulphide and methanol, which afforded (IX) (78%)‡ by irreversible addition of methanol to (I). This result also suggests that carbon disulphide is more reactive than methanol towards benzyne because no anisole is formed.

When oxidation was carried out in a mixture of carbon disulphide and pyridine to suppress the protonation to (I) by acetic acid, nearly half of (II) was recovered unchanged



along with intractable tars. In this case, the primary product, *e.g.*, (X) formed by the dimerization of (I), must be oxidized by lead tetra-acetate in preference to (II).

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† Compound (III) was supplied by Prof. R. Huisgen of the University of Munich. See also R. Huisgen and V. Weberndörfer, *Experientia*, 1966, **17**, 566 and V. Weberndörfer, Ph.D. Thesis, University of Munich, 1964.

‡ Satisfactory elemental analysis and supporting spectral data were obtained for this compound.

¹ E. K. Fields and S. Meyerson, *Tetrahedron Letters*, 1970, 629.

² C. D. Campbell and C. W. Rees, *J. Chem. Soc. (C)*, 1969, 742.

³ D. Buza, A. Gryff-Keller, and S. Szymanski, *Roczniki Chem.*, 1970, **44**, 2319; D. Buza and S. Szymanski, *ibid.*, 1971, **45**, 501.

⁴ (a) H. D. Hartzler, *J. Amer. Chem. Soc.*, 1970, **92**, 1412; (b) D. L. Coffen, *Tetrahedron Letters*, 1970, 2633.