

Cumulative Double Bond Systems: Thermolysis of Benzoyl Peroxide in the Presence of Bisaryliminosulphur Derivatives

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Thermal decomposition of benzoyl peroxide in the presence of bisaryliminosulphur derivatives (ArN:S:NAr) affords the corresponding azobenzene (ArN=NAr) and diphenyl disulphide. It is suggested that the products originate from a bridged thiadiazolidinyl radical (8) formed by attack of the phenyl radical at sulphur followed by intramolecular cyclization.

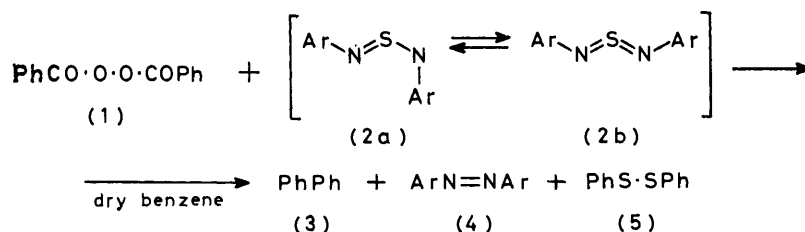
WE have recently reported the addition of aryl nitrenes¹ and aryl radicals² to *N*-sulphonylanilines (ArN=S=O). As a further step in the study of the behaviour of cumulative double bonds toward free radicals we now report the reaction of phenyl radicals bisaryliminosulphur derivatives (2).

Attention has recently been paid to the structure as well as to the reactivity of these heterocumulenes.³ The

subject in the light of theoretical⁸ interest in additions of free radicals to allenes.

The reaction of equimolar amounts of benzoyl peroxide (1) and compound (2) in boiling dry benzene under nitrogen gave biphenyl (3), azobenzene (4), and diphenyl disulphide (5) in high yields (Scheme 1).

The formation of the products can be rationalized as in Scheme 2. Thermal decomposition of the peroxide (1)



SCHEME 1 Ar = *p*-ClC₆H₄, *p*-MeO·C₆H₄, or *p*-MeC₆H₄

cis,trans-form (2a) is the only isomer present in the solid state⁴ and in the gas phase,⁵ whereas in solution in equilibrium mixture with the less stable *trans,trans*-form (2b) exists. The co-ordination properties of (2)⁶ and its reactivity with ionic species⁷ have also been investigated.

The structural similarity of allenes and bisaryliminosulphur derivatives gives further importance to our

¹ G. De Luca and G. Renzi, *Gazzetta*, in the press.

² G. De Luca, G. Renzi, M. Felici, and A. Tundo, *Tetrahedron Letters*, 1976, 75.

³ G. Leandri, V. Busetti, G. Valle, and M. Mammi, *Chem. Comm.*, 1970, 413.

⁴ J. Kuyper and K. Vrieze, *J. Organometallic Chem.*, 1975, **86**, 127.

⁵ J. R. Grunwell and W. C. Danison, jun., *Internat. J. Sulfur Chem.*, 1973, **8**, 379.

⁶ J. Kuyper and K. Vrieze, *J.C.S. Chem. Comm.*, 1976, 64; J. Kuyper, K. Vrieze, and A. Osham, *J. Organometallic Chem.*, 1974, **74**, 289.

gives benzoyloxyl radicals⁹ which, by loss of carbon dioxide, afford phenyl radicals (6). These can effect homolytic aromatic substitution of the benzene to give biphenyl (3), or react with the bisaryliminosulphur to afford the radical (7). The attack of the phenyl radical at the sulphur atom of compound (2), which in solution exists in the dipolar form ArN⁻S⁺=NAr, is suggested on the basis of the known¹⁰ nucleophilic nature of the phenyl radical; moreover the intermediate adduct (7), because

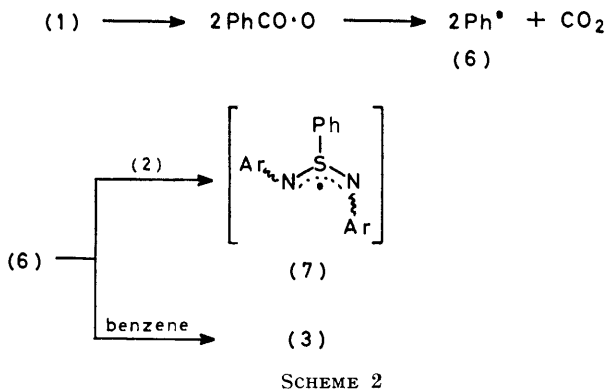
⁷ G. Kresze and W. Wucherpfennig, *Angew. Chem. Internat. Edn.*, 1967, **6**, 149; R. Cramer, *J. Org. Chem.*, 1961, **26**, 3476; T. Minami, H. Miki, H. Matsumoto, Y. Oshiro, and T. Agawa, *Tetrahedron Letters*, 1968, 3049.

⁸ P. I. Abell in 'Free Radicals,' ed. J. K. Kochi, Wiley-Interscience, New York, vol. II, 1973, p. 105.

⁹ J. K. Kochi in 'Free Radicals,' ed. J. K. Kochi, Wiley-Interscience, New York, vol. II, 1973, p. 699.

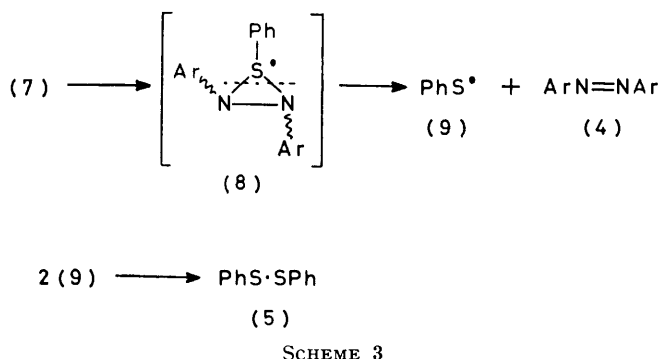
¹⁰ A. Clerici, F. Minisci, and O. Porta, *Gazzetta*, 1973, **103**, 171.

of the delocalization of the free electron, is presumably more stable than the one obtainable by interaction of the phenyl radical with the nitrogen atom. This function



of the sulphur as an electron acceptor finds support from previous research.¹¹

The intermediate (7) can cyclize to form the thiadiazolindinyl radical (8). The geometry of the bridged radical (8) is analogous to that proposed for the intermediate in the reactions of phenyl¹² and methyl¹³ radicals with episulphides. Fragmentation of (8) should afford azobenzene (4) and the phenylthio radical (9), which by dimerization gives diphenyl disulphide (5) (Scheme 3).



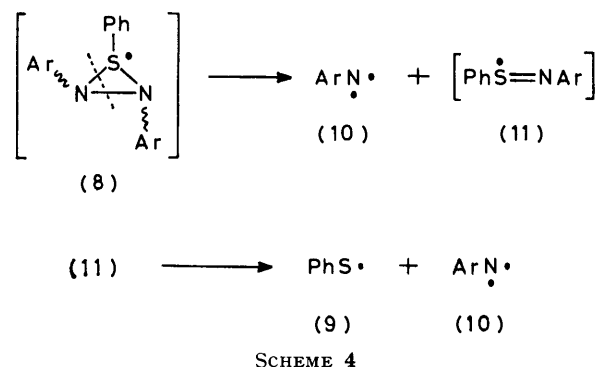
Scheme 4 summarizes a different fragmentation path open to the radical (8) which would also explain the formation of the reaction products. The resulting arylnitrene triplet (10) will dimerize, as previously established,¹⁴ to the azo-derivative.

The relevance of this alternative mechanism has been investigated by means of crossover experiments. Phenyl radicals were generated in the presence of equimolar quantities of bis-*p*-chloro- and -*p*-methoxy-phenylimino-

sulphur derivatives; the main products were *pp'*-dichloro- and *pp'*-dimethoxy-azobenzene, whereas the *p*-chloro-*p'*-methoxyazobenzene was formed only in low yield. This last compound must originate from intermolecular combination of free *p*-chloro- and *p*-methoxyphenyl nitrenes, thus indicating that the mechanism in Scheme 4 does operate, if only to a minor extent.

Supporting evidence for intermediate aryl nitrenes is the isolation of small quantities of carbazole from thermolysis of the peroxide (1) in the presence of bis-*o*-biphenyliminosulphur.

Thus the desulphurization of compounds (2) occurs mainly intramolecularly, as suggested in Schemes 2 and 3.



Similar results have been obtained by Leandri¹⁵ and others¹³ for reactions of bisaryliminosulphur derivatives with zinc or alumina.

EXPERIMENTAL

Bisaryliminosulphur derivatives were prepared according to established procedures.^{4,16}

Reaction Conditions.—For example bis-*p*-chlorophenyliminosulphur (380 mg, 1.34 mmol) and benzoyl peroxide (325 mg, 1.34 mmol) in dry benzene were boiled under nitrogen for 72 h. After cooling 5% sodium hydrogen carbonate solution was added. The organic phase was dried (Na₂SO₄), concentrated, and analysed (a) by column chromatography [SiO₂; light petroleum-ether; products identified by i.r. (Nujol or KBr) and mass spectra and by mixed m.p. with authentic samples when solid] and (b) by g.l.c. [Perkin-Elmer F11; silicone gum rubber E301 on Chromosorb G AW-DMCS (2 m × 1/8 in)]. The following products were identified: biphenyl (84 mg) diphenyl disulphide (67 mg), and *pp'*-dichloroazobenzene (135 mg).

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¹² J. K. Weseman, R. Williamson, J. L. Greene, jun., and P. B. Shevlin, *J.C.S. Chem. Comm.*, 1973, 901.

¹³ E. Jakubowski, M. G. Ahmed, E. M. Lown, H. S. Sandhu, R. K. Gosavi, and O. P. Strausz, *J. Amer. Chem. Soc.*, 1972, **94**, 4094.

¹⁴ R. A. Abramovitch, 'Organic Reactive Intermediates,' ed. S. P. McManus, Academic Press, New York-London, 1973, ch. 3, p. 169.

¹⁵ G. Leandri and P. Rebora, *Gazzetta*, 1957, **87**, 503.

¹⁶ H. H. Horhold and J. Beck, *J. prakt. Chem.*, 1969, 621; R. Mayer and U. Pleiss, *Internat. J. Sulfur Chem.*, 1973, **8**, 285.