

Photodecomposition of Benzoisothiazoles

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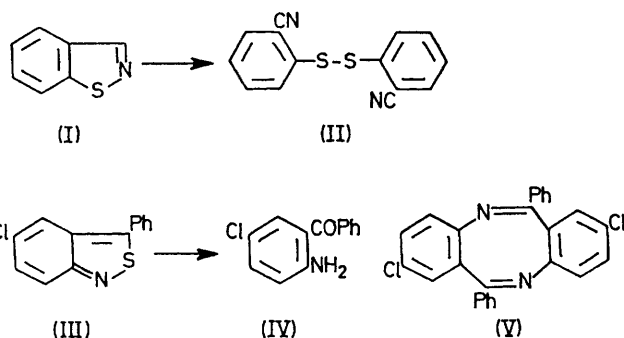
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Summary Photodecomposition of benzo[*d*]- and benzo[*c*]-isothiazoles produced not transposition products but ring-opened or dimerized products in sharp contrast with the oxygen and nitrogen analogues.

THE photo-induced transposition reactions of isothiazoles are well documented.¹ We now report the behaviour of benzo[*d*]- and benzo[*c*]-isothiazoles upon irradiation.



Irradiation of compound (I) in ether with a medium-pressure mercury arc for 7 h gave the disulphide (II) (12%). No benzothiazole, the transposition product, was detected by g.l.c. of the reaction mixture, in contrast to the cases of

† Structures were deduced on the basis of i.r., n.m.r. (220 MHz), and mass spectra, and confirmed by comparison of i.r. spectra with standard ones.

¹ M. Ohashi, A. Iio, and T. Yonezawa, *Chem. Comm.*, 1970, 1148; J. P. Cateau, A. Lablache-Combiere, and A. Pollet, *ibid.*, 1969, 1018; G. Vernin, J.-C. Poite, J. Metzger, J.-P. Aune, and H. J. M. Dou, *Bull. Soc. chim. France*, 1971, 1103; L. Lablache-Combiere and A. Pollet, *Tetrahedron*, 1972, **28**, 3141.

² H. Göth and H. Schmidt, *Chimia (Switz.)*, 1966, **20**, 148.

³ H. Tiefenthaler, W. Dorscheln, H. Göth, and H. Schmidt, *Helv. Chim. Acta*, 1967, **50**, 2244.

⁴ O. Aki, Y. Nakagawa, and K. Sirakawa, *Chem. Pharm. Bull. (Japan)*, 1972, **20**, 2372.

⁵ M. Ogata, H. Kano, and H. Matsumoto, *Chem. Comm.*, 1968, 397; *Tetrahedron*, 1969, **25**, 5205; M. A. Berwick, *J. Amer. Chem. Soc.*, 1971, **93**, 5780.

⁶ H. Labhart, W. Heinzelmann, and J. P. Dubois, *Pure Appl. Chem.*, 1970, **24**, 495; see also ref. 3.

⁷ E. J. Bowen, *Adv. Photochem.*, 1963, **1**, 23.

benzo[*d*]isoxazole² and 1*H*-indazole,³ the oxygen and nitrogen analogues. Photo-induced S-N bond cleavage was also observed with 4-phenylisothiazole, irradiation of which in ether gave 2-cyano-2-phenylvinyl disulphide as the major product.

Irradiation of compound (III),⁴ a benzo[*c*]isothiazole, in MeOH with a Pyrex-filtered medium-pressure mercury arc gave the benzophenone (IV)† (31%). Irradiation of (III) in MeCN gave the dibenzodiazocine (V)† (39%), along with 8% of (IV). These observations are also in contrast to those with other benzoazoles; *i.e.*, anthranil gave 3*H*-azepine⁵ and 2-alkylindazoles gave 1-alkylbenzimidazoles.⁶

Berwick reported that photolysis of 3-methylantranil gave 3*H*-azepines and 2-aminoacetophenone *via* the S₁ and T₁ states, respectively.⁵ On this basis the formation of (IV) may be accounted for in terms of decomposition of the triplet state of (III) followed by hydrogen abstraction from the solvent and air oxidation of the initially formed thione group into carbonyl. The course of the reaction to the dimerization product (V) is not clear. However, since the fluorescence of (III) (418 nm) displayed self-quenching with a half quenching concentration of *ca.* 2 × 10⁻⁸M, (V) cannot be formed *via* an excimer as in the case of anthracene⁷ but through bimolecular association in the ground state.

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