Generation of Thionitroso Compounds by Benzisothiazole Ring Opening

Marc F. Joucla and Charles W. Rees

Department of Chemistry, Imperial College of Science and Technology, London SW7 2AY, U.K.

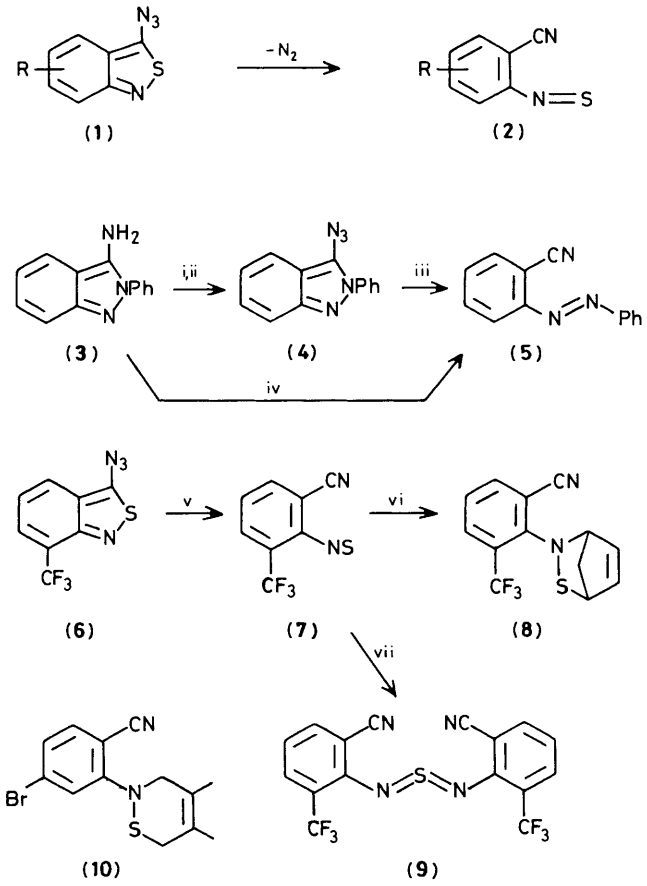
Oxidation of 3-amino-2-phenylindazole (**3**) or thermolysis of 3-azido-2-phenylindazole (**4**) gives 2-cyanoazobenzene (**5**) quantitatively; thermolysis or photolysis of 3-azido-2,1-benzisothiazoles (**1**) induces similar ring opening to give the transient 2-cyanothionitrosobenzenes (**2**).

Organic thionitroso compounds, R–N=S, still remain elusive and their chemistry is unexplored. A few thionitrosoalkanes[1] and thionitrosoarenes[2] have been generated and intercepted in Diels–Alder reactions, and unstable *N*-thionitrosamines have been isolated.[3] We now report an entirely new approach to this functional group based on the known opening of five-membered heterocyclic rings with carbene or nitrene precursors in the α-position.[4] We have extended this process to benzo derivatives of heterocyclic azides [*e.g.* (**1**) → (**2**)] where the formation of a benzene ring, as well as a cyano group, should greatly favour the loss of nitrogen and the ring opening; these two steps could be concerted or a discrete nitrene intermediate could be involved.

The idea was first tested on a reaction where the product would be stable. Thus 3-amino-2-phenylindazole[5] (**3**) was converted into the 3-azide (**4**), ν(N_3) 2120 cm^{-1}, in high yield (95%), though the azide was unstable and decomposed rapidly at 40—60 °C. On boiling in tetrachloromethane or light petroleum (b.p. 60—80 °C) for 5 min it gave a quantitative yield of 2-cyanoazobenzene (**5**), m.p. 62—63 °C (lit.,[6] m.p. 61.5—63 °C). Direct oxidation of the 3-amino compound (**3**) with lead tetra-acetate in benzene at room temperature also gave the ring-opened product (**5**) quantitatively.

We then turned to 2,1-benzisothiazoles as precursors for the thionitrosoarenes. 3-Amino-7-trifluoromethyl-2,1-benzisothiazole[7] was converted, as before, into the slightly unstable 3-azide (**6**) (65%), m.p. 75—76 °C, decomp., ν(N_3) 2105 cm^{-1}. Photolysis of (**6**) in diethyl ether at room temperature through Pyrex with a 450 W high pressure Hg lamp was complete in less than 2 h; a nitrile, ν(CN) 2225 cm^{-1}, was formed which gave the *m/z* value (216) expected for the thionitroso compound (**7**), but this could not be isolated pure and after some hours it had transformed into 2-cyano-6-trifluoromethylaniline. When this photolysis was repeated in the presence of an excess of cyclopentadiene a minor amount of the same aniline was formed but the major product was the cycloadduct (**8**) (60%), an oil, ν(CN) 2220 cm^{-1}. A similar cycloadduct was formed with 1-methoxycyclohexa-1,3-diene. The azide (**6**) decomposed slowly in low boiling solvents but rapidly at 180 °C in *o*-dichlorobenzene to give the sulphurdiimide (**9**) (58%) as yellow crystals, m.p. 110—111 °C. This is the product of dimerisation of the thionitroso compound with loss of sulphur; the exactly analogous formation of dimethylsulphurdi-imide from thionitrosomethane, spontaneously and in high yield at room temperature, has already been reported.[1]

3-Amino-6-bromo-2,1-benzisothiazole[7] was converted, as before, into the thermally unstable 3-azide, m.p. 62—64 °C,



Reagents and conditions: i, $NaNO_2$, HCl; ii, NaN_3; iii, 60—80 °C; iv, $Pb(OAc)_4$, C_6H_6; v + vi, *hv*, Et_2O–cyclopentadiene; v + vii, 180 °C in *o*-dichlorobenzene.

decomp., $\nu(N_3)$ 2110 cm^{-1}, which on rapid dissolution and heating in neat 2,3-dimethylbuta-1,3-diene (69 °C) gave the cycloadduct (**10**) as an oil, $\nu(CN)$ 2218 cm^{-1}.

The fact that we observe the same reactions in the decomposition of azidoisothiazoles as those reported from very different precursors[2] lends good support to the existence of thionitroso compounds as discrete, though as yet unisolated, intermediates. Our process appears to be a general one capable of much structural variation.

We thank the Royal Society and the Centre National de la Recherche Scientifique for support of M. F. J., on leave of absence from the University of Rennes, and Dr. D. R. Waring, Kodak Ltd, Kirby, for a generous gift of the aminobenzisothiazoles.

Received, 11th January 1984; Com. 040

References

1 Y. Hata and M. Watanabe, *J. Org. Chem.*, 1980, **45**, 1691.
2 P. Tavs, *Angew. Chem., Int. Ed. Engl.*, 1966, **5**, 1048; F. A. Davis and E. B. Skibo, *J. Org. Chem.*, 1976, **41**, 1333; C. L. Pedersen, C. Lohse, and M. Poliakoff, *Acta Chem. Scand., Sect. B*, 1978, **32**, 625; R. Mayer, G. Domschke, S. Bleisch, and A. Bartl, *Tetrahedron Lett.*, 1978, 4003.
3 W. J. Middleton, *J. Am. Chem. Soc.*, 1966, **88**, 3842.
4 For representative examples, see P. A. S. Smith, G. J. W. Breen, M. K. Hajek, and D. V. C. Awang, *J. Org. Chem.*, 1970, **35**, 2215; P. A. S. Smith and H. Dounchis, *ibid.*, 1973, **38**, 2958; S-I. Hayashi, M. Nair, D. J. Houser, and H. Schechter, *Tetrahedron Lett.*, 1979, 2961.
5 M. W. Partridge and M. F. G. Stevens, *J. Chem. Soc.*, 1964, 3663.
6 P. V. Roling, *J. Org. Chem.*, 1975, **40**, 2421.
7 J. Gray and D. R. Waring, *J. Heterocycl. Chem.*, 1980, **17**, 65; for a review of 2,1-benzisothiazoles, see M. Davis, *Adv. Heterocycl. Chem.*, 1972, **14**, 63.