1,3-Dipolar Cycloadditions of Nitrile Sulphides to 1,4-Quinones: a Route to Novel Isothiazolonaphthoquinones and Bis-(isothiazolo)benzoquinones

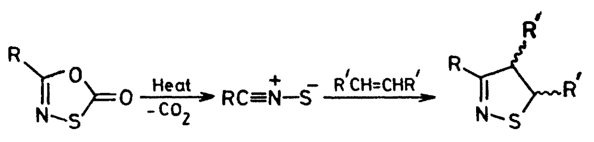
By R MICHAEL PATON* and JOHN F ROSS
(*Department of Chemistry, University of Edinburgh, West Mains Road, Edinburgh* EH9 3JJ)

and JOHN CROSBY*
(*Imperial Chemical Industries Ltd , Organics Division, PO Box* 42, *Hexagon House, Blackley, Manchester* M9 3DA)

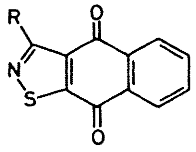
Summary Nitrile sulphides, generated by thermolysis of 1,3,4-oxathiazol-2-ones, react with 1,4-naphthoquinone and 1,4-benzoquinone to yield the isothiazoloquinones (**4**)—(**6**)

WHILE the 1,3-dipolar cycloaddition reactions of nitrile sulphides (**1**) with alkynes and nitriles are well known and provide convenient routes to isothiazoles[1] and 1,2,4-thiadiazoles,[2] the corresponding process for alkene dipolarophiles yielding isothiazolines (**2**) has received much less attention [3,4] Alkenes employed have been restricted to those suitably activated (*e g* dimethyl fumarate), and no cycloadduct was isolated from the reaction of (**1a**), generated by thermolysis of the oxathiazolone (**3a**), with 1,4-naphthoquinone [4] Formation of the dithiin (**7**) was, however, claimed as evidence for a transient labile adduct in this latter case We now report that nitrile sulphides generated in the presence of excess of 1,4-naphthoquinone (NQ) and 1,4-benzoquinone (BQ) *do* yield adducts the corresponding isothiazolonaphthoquinones (**4**) and bis-(isothiazolo)benzoquinones (**5** and **6**)

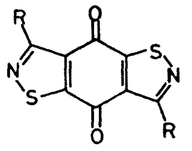
A solution of (**3a**) (56 mmol) and NQ (168 mmol) in xylene (250 ml) was heated under reflux until h p l c analysis showed complete consumption of (**3a**) (after *ca* 12 h) The reaction mixture was worked-up to give the



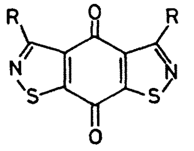
(3) (1) (2)



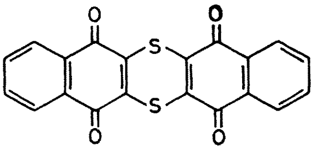
(4)



(5)



(6)



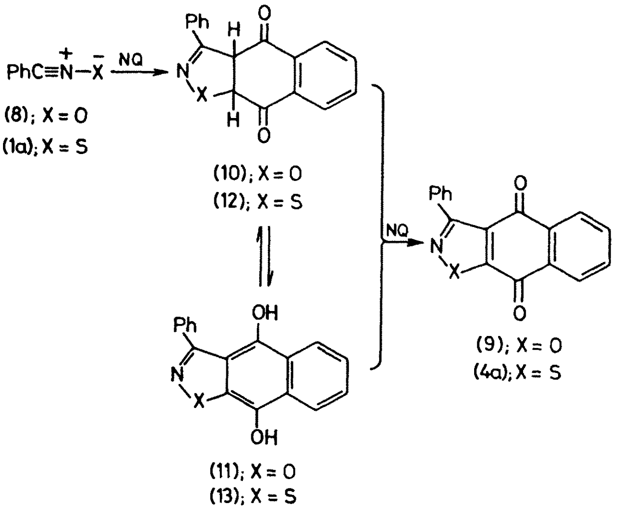
(7)

a; R = Ph
b; R = 4-$MeOC_6H_4$
c; R = Me

dithiin (**7**) (1·3 mmol),[4] benzonitrile (63%)†, and 3-phenylisothiazolonaphthoquinone (**4a**) (36%) as an orange solid, m.p. 217—219 °C. Similarly, (**3b**) and NQ after 5 h gave (**4b**) (42%, m.p. 228—229 °C) and 4-methoxybenzonitrile (52%), and (**4c**) (32%, m.p. 147—149 °C) was obtained from (**3c**) and NQ after 4 h.

Thermolysis of a mixture of (**3b**) and BQ (1 : 4) under similar conditions led to the formation of (**5b**)(33%, m.p. 214—215 °C), with some (**6b**) (1%, m.p. 269—271 °C) as co-product. Likewise, (**3c**) with BQ gave (**5c**) (19%, m.p. 221—222 °C).

In these reactions nitrile sulphides closely parallel the behaviour of nitrile oxides.[5] Benzonitrile oxide (**8**) with NQ yields (**9**), presumably *via* 1,3-dipolar cycloaddition of (**8**) to the alkenic double bond of NQ to form a tautomeric mixture of the isoxazolinoquinone (**10**) and the isoxazolodihydroxynaphthalene (**11**), with (**9**) being formed by subsequent oxidation by excess of NQ. Similar behaviour in the case of nitrile sulphide (**1a**) would lead to the observed compound (**4a**) *via* (**12**) and (**13**).



(*Received*, 8*th September* 1980; *Com.* 973.)

---

† Nitrile by-products are frequently observed and have been attributed[2] to fragmentation of the nitrile sulphide competing with the cycloaddition process.

[1] R. K. Howe, T. A. Gruner, L. G. Carter, L. L. Black, and J. E. Franz, *J. Org. Chem.*, 1978, **43**, 3736 and references therein.
[2] R. K. Howe and J. E. Franz, *J. Org. Chem.*, 1974, **39**, 962.
[3] R. K. Howe and J. E. Franz, *J. Org. Chem.*, 1978, **43**, 3742 and references therein.
[4] J. E. Franz and L. L. Black, *Tetrahedron Lett.*, 1970, 1381.
[5] C. Grundmann and P. Grünanger, 'The Nitrile Oxides,' Springer-Verlag, West Berlin and Heidelberg, 1971, p. 122.