A Novel Synthesis of 1,3,4-Oxathiazoles Using Nitrile Sulphides

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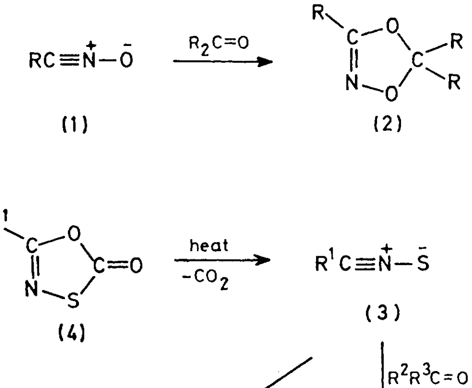
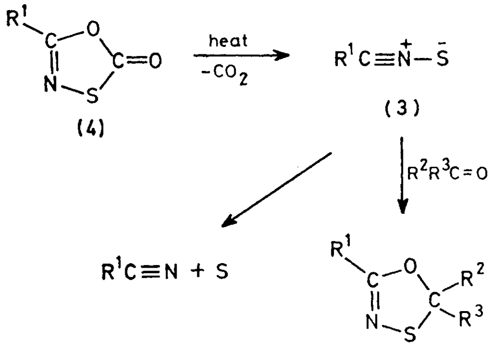
Summary Nitrile sulphides, generated by thermolysis of 1,3,4-oxathiazol-2-ones, undergo 1,3-dipolar cycloaddition to activated carbonyl groups yielding 1,3,4-oxathiazoles.

WHILE the 1,3-dipolar cycloaddition of nitrile oxides (**1**) to carbonyl compounds has proved an effective means[1] of preparing 1,3,4-dioxazoles (**2**), the corresponding reaction for nitrile sulphides (**3**) has not yet been reported. We find that (**3**) generated *in situ* by the thermal decarboxylation of 1,3,4-oxathiazol-2-ones (**4**),[2] react with chloral, hexachloroacetone, and ααα-trifluoroacetophenone, in which the carbonyl groups are activated by electron-withdrawing substituents, to produce 1,3,4-oxathiazoles (**5**), a rare class of heterocycles accessible only with difficulty by other routes.[3]

The oxathiazoles (**5**) were prepared by heating under reflux solutions of (**4**) (0·01 mol) and the carbonyl compound ($R^2R^3C{=}O$) (0·05 mol) in xylene (50 ml) until h.p.l.c. analysis† showed complete consumption of (**4**). Removal of the solvent and excess of $R^2R^3C{=}O$ afforded (**5**), sulphur, and the corresponding nitrile, which could be separated by



(1) (2)



(4) (3) (5)

TABLE. 1,3,4-Oxathiazoles (**5**) produced by reaction of (**4**) with activated carbonyl compounds.

R^1	R^2	R^3	Reaction time/h	% Yield[a]	M.p. (b.p., mmHg)/°C
Ph	CCl_3	H	26	59	67—8
Ph	CCl_3	CCl_3	8	54	53—4
4-$MeOC_6H_4$	CCl_3	H	5	76	82—3
4-$MeOC_6H_4$	CCl_3	CCl_3	5	57	87—8
4-$MeOC_6H_4$	CF_3	Ph	4	28[b]	86—7
4-ClC_6H_4	CCl_3	CCl_3	28	35[c]	104—5
4-ClC_6H_4	CF_3	Ph	12·5	18[d]	77
Me	CCl_3	H	5	62	49·5—50
Me	CCl_3	CCl_3	6	56	70
Pr^n	CCl_3	CCl_3	5	44	(135,0·003)

[a] All the adducts, which are new compounds, gave satisfactory elemental analyses and have spectroscopic properties consistent with their structures. [b] 59% 4-Methoxybenzonitrile by-product. [c] 58% 4-Chlorobenzonitrile by-product. [d] 65% 4-Chlorobenzonitrile by-product.

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† 25% Water deactivated alumina, eluted with 80% hexane–20% methylene chloride (25% water saturated).

distillation and/or recrystallisation. The oxathiazoles prepared in this manner are listed in the Table, together with the reaction times and yields of isolated products. The formation of nitrile and sulphur by-products is a common feature of nitrile sulphide reactions and has been attributed[2] to fragmentation of (**3**) competing with the cycloaddition process.

These results extend the range of known nitrile sulphide cycloadditions, previously restricted to reactions with alkyne,[4] alkene[5] and nitrile[2] dipolarophiles, and suggest yet further scope for heterocycle synthesis.

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[1] C. Grundmann and P. Grünanger, 'The Nitrile Oxides,' Springer-Verlag, West Berlin and Heidelberg, 1971, pp. 120—3.

[2] R. K. Howe and J. E. Franz, *J. Org. Chem.*, 1974, **39**, 962.

[3] *E.g.* E. M. Burgess and H. R. Penton, *J. Amer. Chem. Soc.*, 1973, **95**, 279.

[4] R. K. Howe, T. A. Gruner, L. G. Carter, L. L. Black, and J. E. Franz, *J. Org. Chem.*, 1978, **43**, 3736.

[5] J. R. Grunwell and S. L. Dye, *Tetrahedron Letters*, 1975, 1739; R. K. Howe and J. E. Franz, *J. Org. Chem.*, 1978, **43**, 3742; R. M. Paton, J. F. Ross, and J. Crosby, unpublished observations.