Preparation of 5*H*-1,4,2-Dithiazoles *via* 1,3-Dipolar Cycloadditions of Nitrile Sulphides to Thiocarbonyl Compounds; the First Synthesis of a 3,5-Diaryl-1,4,2-dithiazolium Salt

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Nitrile sulphides from the thermal decomposition of 1,3,4-oxathiazol-2-ones add to thiocarbonyl compounds giving moderate to high yields of 5*H*-1,4,2-dithiazoles; an adduct from *O*-ethyl thiobenzoate has been converted into 3-(4-nitrophenyl)-5-phenyl-1,4,2-dithiazolium tetrafluoroborate.

As a follow-up to our earlier synthesis of 5-amino-1,4,2-dithiazolium salts,[1a,b] we were interested in preparing examples having 5-alkyl or -aryl substituents, since all known examples bear an amino[1a–c] or a mercapto[1d] group at this site. Variable-temperature n.m.r. and *X*-ray crystallographic studies had shown for the 5-amino compounds that the positive charge resided mostly on the exocyclic nitrogen atom;[1b] a 5-alkyl or -aryl substituent should 'force' the positive charge into the ring, thus generating a novel heteroaromatic cation. An attractive approach to such compounds (**2**) was by transformation of suitably substituted 5*H*-1,4,2-dithiazoles (**1**) (Scheme 1), where X is a potential leaving group.

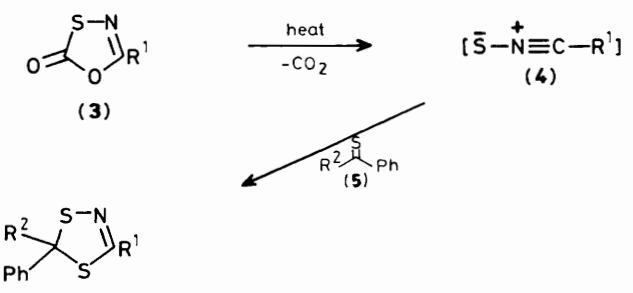
With the exception of 1,1-dioxides,[2] there appear to have been only two isolated reports of 5*H*-1,4,2-dithiazoles (**1**);[1b,3] these compounds are of interest in their own right, having an unexplored chemistry, and a potential for biological activity. A potentially very general synthetic route is the 1,3-dipolar cycloaddition reaction between a nitrile sulphide and a thiocarbonyl compound. Although nitrile sulphides have been added to carbonyl groups to give 2*H*-1,3,4-oxathiazoles,[4] and nitrile oxides have been added to carbonyl and to thiocarbonyl groups to give 5*H*-1,4,2-dioxazoles[5] and 5*H*-1,4,2-oxathiazoles,[6] respectively, this approach has apparently not been applied to the preparation of 5*H*-1,4,2-dithiazoles. We now report the successful preparation of a number of these compounds by 1,3-dipolar cycloaddition and the conversion of one of them into the first example of a 3,5-diaryl-1,4,2-dithiazolium salt.

Thermal decomposition of the oxathiazolones (**3**)[7] to the nitrile sulphides (**4**) in the presence of the thioketones (**5**)[8] gave the 5*H*-1,4,2-dithiazoles (**6**)—(**8**) in 17—65% yields (unoptimized). For example, dropwise addition of the oxathiazolone (**3b**) (0.01 mol) during 4 h to a refluxing solution of 2,2-dimethyl-1-phenylpropane-1-thione (0.01 mol) in xylene (20 ml) under N_2, followed by heating for a further 2 h, gave, after evaporation of the solvent and chromatography (SiO_2; eluant ether–light petroleum), the dithiazole (**7b**)† (25%), m.p. 78—79 °C, ν_{max} (Nujol) 1600, 1530, and 1349 cm^{-1}; δ_H ($CDCl_3$) 1.13 (9 H, s), 7.29 (5 H, s), 7.91 (2 H, m), and 8.23 (2 H, m); δ_C ($CDCl_3$) 26.6(q), 42.0(s), 92.2(s), 123.8(d), 127.5(d), 128.5(d), 129.0(d), 138.1(s), 141.8(s), 148.4(s), and 158.2(s); *m/z* 358 (M^+, 3%) and 301 (100). The dithiazoles (**6a—h**), (**7f**), and (**8b** and **f**)† were prepared similarly. A major side reaction was the production of the nitrile R^1CN together with sulphur, as has been observed previously in preparations of nitrile sulphides by this method.[6b] The dithiazoles themselves, however, were reasonably stable under the reaction conditions, compound (**6e**) for example being 55% decomposed into the nitrile, sulphur, and the ketone only after 72 h in refluxing xylene. In the ^{13}C n.m.r. spectra of the products (**6**)—(**8**), the ring C-3 signal ranged from 156.5 to 159.5 p.p.m. for R^1 = Ar, being near 150 and 172 p.p.m. for R^1 = Me and Bu^t, respectively, and the C-5 signal ranged from 81 to 92 p.p.m. depending upon R^2. Mass spectra showed the parent ion, as well as fragments corresponding to R^1–C≡N$^{+\cdot}$, $R^1CNS^{+\cdot}$, $PhCSR^{2+\cdot}$, and $PhR^2CS_2^{+\cdot}$.

The presence of the base peak at *m/z* 301 in the mass spectrum of compound (**7b**) suggested that the 3,5-diaryl-1,4,2-dithiazolium cation might be quite stable. A compound of type (**1**) was thus sought having a group X = OEt which might readily be solvolysed to yield the cation as in Scheme 1. Reaction between the oxathiazolone (**3b**) and *O*-ethyl thiobenzoate gave the bright yellow ethoxy compound (**9b**)† (10%) [m.p. 140—141 °C; ν_{max} (Nujol) 1595, 1524, 1350, and 1064 cm^{-1} (C–O); δ_H ($CDCl_3$) 1.33 (3 H, t), 3.51 (2 H, q), 7.2 (3 H, m), 7.7 (2 H, m), 7.81 (2 H, m), and 8.13 (2 H, m); δ_C ($CDCl_3$) 14.7(q), 60.9(t), 116.0(s), 124.0(d), 127.9(d), 128.1(d), 128.8(d), 128.9(d), 137.9(s), 138.4(s), 148.6(s), and 156.2(s); *m/z* 346 (M^+, 8%) 301 ($M^+ - OEt$, 5)], together with much 4-nitrobenzonitrile (90%). Treatment of (**9b**) overnight with 48% HBF_4 in ether followed by dilution with anhydrous

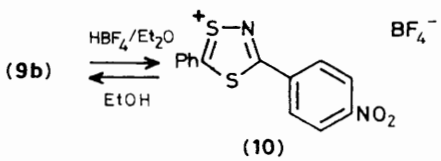
(**1**) (**2**)

Scheme 1



(**6**) R^2 = Ph **a**; R^1 = Ph **e**; R^1 = 4-MeC_6H_4
(**7**) R^2 = Bu^t **b**; R^1 = 4-$NO_2C_6H_4$ **f**; R^1 = 4-$MeOC_6H_4$
(**8**) R^2 = Me **c**; R^1 = 4-ClC_6H_4 **g**; R^1 = Me
(**9**) R^2 = OEt **d**; R^1 = 4-FC_6H_4 **h**; R^1 = Bu^t

Scheme 2



(**9b**) (**10**)

Scheme 3

† Satisfactory microanalytical data were obtained for new compounds.

ether (Scheme 3) gave a pale yellow precipitate of 3-(4-nitrophenyl)-5-phenyl-1,4,2-dithiazolium tetrafluoroborate (**10**)† (87%), which decomposed with darkening above 140 °C; ν_{max} (Nujol) 1605, 1590, 1510, 1460, 1353, 1285, 1080, 1050 (BF_4^-), 857, and 780 cm^{-1}; δ_H (CD_3CN) 7.69 (2 H, m) 7.89 (2 H, m), 8.04 (2 H, m), and 8.29 (3 H, m); δ_C (CF_3CO_2H) 127.3(d), 132.3(d), 132.5(d), 133.5(d), 136.3(s), 136.5(s), 142.8(d), 153.4(s), 182.6(s), and 221.9(s); *m/z* 301 (M^+, 17%), 180 (M^+−PhCS, 29), 153 ($PhCS_2^{+\cdot}$, 25), 148 (M^+ − $PhCS_2$, 31), and 121 ($PhCS^+$, 50) (fragments containing one fluorine atom were also observed; these included the base peak). Recrystallisation from ethanol converted the salt (**10**) back into the 5*H*-1,4,2-dithiazole (**9b**).

In view of the possible variation in both R^1 and the nature of the thiocarbonyl compound, this promises to be a very general synthetic route to 5*H*-1,4,2-dithiazoles, and to a number of derived 1,4,2-dithiazolium salts.

We thank the University of Hong Kong for a research grant (for K.F.W.).

Received, 22nd February 1988; Com. 8/00666K

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