

Novel Synthesis of 1,4,2-Dithiazolium Salts

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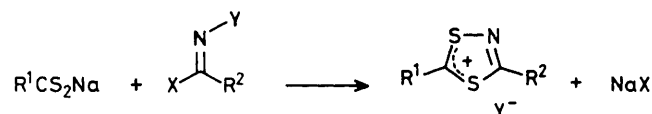
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Reaction between α -chloro-oxime *o*-sulphonates and dithiocarbamate salts gives isolable intermediates which may be cyclised with fluoroboric acid to 1,4,2-dithiazolium salts, in what is potentially a highly versatile synthetic approach to these compounds.

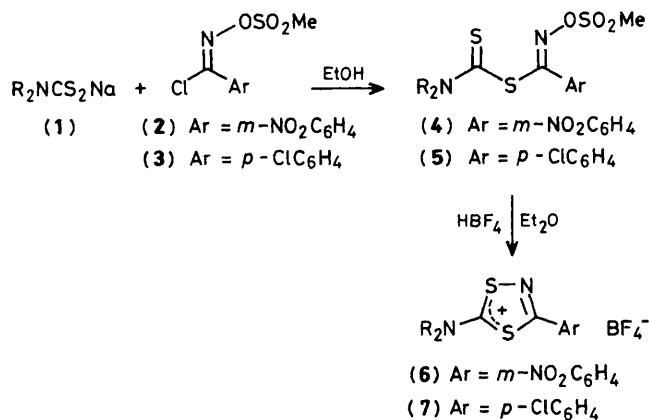
Although 1,2,4-dithiazolium salts have been known and studied for some time,¹ the 1,2,3-² and 1,3,2-compounds³ were first reported only a few years ago, while the 1,4,2-isomers were prepared for the first time only very recently by the *S*-methylation of 1,4,2-dithiazole-5-thiones.⁴ In view of the potentially rich chemistry of the 1,4,2-cations, by analogy with that of 1,3-dithiolium salts,⁵ we were interested in developing a general synthesis which would allow the widest possible range of substituents at C-5 and C-3. An attractive strategy is the reaction between a dithiocarboxylate ion and an imine derivative (Scheme 1), X and Y being good leaving groups. We now report the successful application of this

approach to the preparation of the first examples of 5-dialkyl-amino-1,4,2-dithiazolium salts.

Reaction between sodium dithiocarbamates (1) and α -chloro-oxime *O*-sulphonates (2) and (3) (prepared⁶ from hydrox-amoyl chlorides, methanesulphonyl chloride, and triethyl-



Scheme 1



a; R = Et
 b; R₂ = -[CH₂]₄-
 c; R₂ = -[CH₂]₅-
 d; R = Me

Scheme 2

amine), leads to the isolable, though rather unstable, intermediates (4) and (5), which may be cyclised to the dithiazolium salts (6) and (7) with fluoroboric acid in diethyl ether (Scheme 2). For example, a solution of the sulphonate (2) (1 g) in absolute ethanol (~50 ml) was added slowly to the dithiocarbamate (1a) (0.81 g) in the same solvent (~30 ml), and the solution stirred (25 °C; 20 h). Filtration, washing of the residue with chloroform, and evaporation of the combined filtrates gave (4a) as a yellow oil which solidified (0.869 g; 62%); δ_{H} (CDCl₃, 90 MHz), 1.30 (6H, t, *J* 7 Hz, CH₂Me), 3.23 (3H, s, SO₂Me), 3.86 (4H, q, *J* 7 Hz, CH₂Me) and 7.4–8.6 (4H, m, ArH). Treatment of (4a) in chloroform solution (20 ml) with fluoroboric acid (50% in diethyl ether; 5 ml) gave a white precipitate, which was filtered and recrystallised from methanol to give (6a) (0.85 g, 62%) as white

needles, \dagger m.p. 183 °C, *m/z* 296 (*M*⁺), δ_{H} (CD₃CN) 1.45, 1.46 (6H, 2t, *J* 7.4 Hz, Me), 3.82, 3.94 (4H, 2q, *J* 7.4 Hz, CH₂), and 7.86–8.66 (4H, m, ArH). Similarly prepared were (6b–d) and (7a–c) in (unoptimised) yields of 11–43%.

All dithiazolium salts prepared showed characteristic i.r. (Nujol) absorptions in the ranges 1580–1600, 1340–1360, and 1240–1280 cm⁻¹, and common peaks in their ¹³C n.m.r. spectra (CD₃CN, 22.5 MHz) in the ranges δ 188–195 (C-5) and 164–167 (C-3); all showed evidence (¹H and ¹³C n.m.r.) of restricted rotation about the exocyclic C–N bond.

Although our approach to 1,4,2-dithiazolium salts is not as straightforward as that of Paton, Crosby, and coworkers,⁴ we believe it to be more versatile, in that a wider range of substituents (including alkyl and aryl groups) is potentially accessible at C-5.

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References

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[†] The dithiazolium salts (6) and (7) gave satisfactory elemental analyses, and spectroscopic data consistent with their structures.