Novel Synthesis of 1,4,2-Dithiazolium Salts

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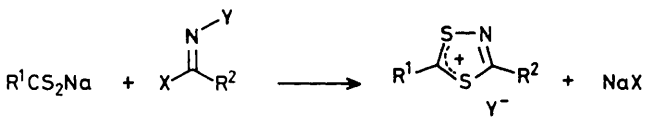
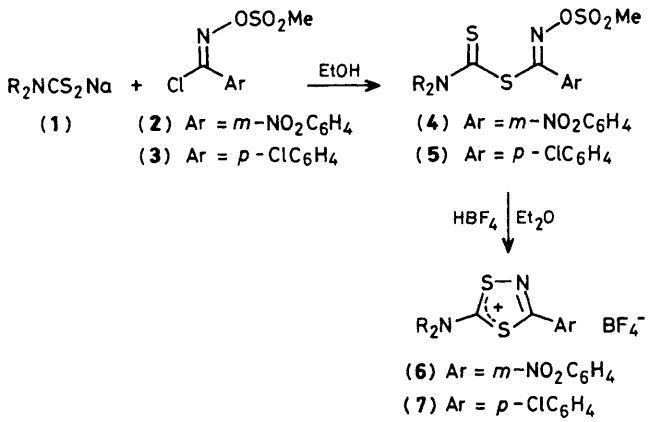
Reaction between α-chloro-oxime *o*-sulphonates and dithiocarbamate salts gives isolable intermediates which may be cyclised with fluoroboric acid to 1,4,2-dithiazolium salts, in what is potentially a highly versatile synthetic approach to these compounds.

Although 1,2,4-dithiazolium salts have been known and studied for some time,[1] the 1,2,3-[2] and 1,3,2-compounds[3] 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-dialkylamino-1,4,2-dithiazolium salts.

Reaction between sodium dithiocarbamates (**1**) and α-chloro-oxime *O*-sulphonates (**2**) and (**3**) (prepared[6] from hydroxamoyl chlorides, methanesulphonyl chloride, and triethyl-



Scheme 1



a; R = Et
b; R_2 = $-[CH_2]_4-$
c; R_2 = $-[CH_2]_5-$
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 ($CDCl_3$, 90 MHz), 1.30 (6H, t, *J* 7 Hz, CH_2*Me*), 3.23 (3H, s, SO_2Me), 3.86 (4H, q, *J* 7 Hz, CH_2Me) 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,† m.p. 183 °C, *m/z* 296 (M^+), δ_H (CD_3CN) 1.45, 1.46 (6H, 2t, *J* 7.4 Hz, Me), 3.82, 3.94 (4H, 2q, *J* 7.4 Hz, CH_2), 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 1 580—1 600, 1 340—1 360, and 1 240—1 280 cm^{-1}, and common peaks in their ^{13}C n.m.r. spectra (CD_3CN, 22.5 MHz) in the ranges δ 188—195 (C-5) and 164—167 (C-3); all showed evidence (^1H and ^{13}C 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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† The dithiazolium salts (**6**) and (**7**) gave satisfactory elemental analyses, and spectroscopic data consistent with their structures.