Formation and Reactions of 1,4,2-Dithiazolium Cations

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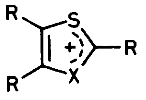
3-Aryl-5-methylthio-1,4,2-dithiazolium salts, prepared by treatment of the corresponding 1,4,2-dithiazole-5-thiones with dimethyl sulphate, react with aniline and with active methylene compounds to form, respectively, 5-phenylimino- and 5-alkylidene-1,4,2-dithiazoles.

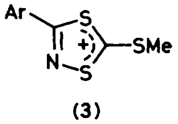
The chemistries of 1,3-dithiolium and 1,3-oxathiolium cations, (**1**) and (**2**), have been the subject of extensive investigation.[1] Particular attention has been paid to their reactions with nucleophilies which tend to take place at the 2-position. We now report the first examples of the analogous 1,4,2-dithiazolium system.

3-Aryl-5-methylthio-1,4,2-dithiazolium salts (**3**) were prepared by methylation of 3-aryl-1,4,2-dithiazole-5-thiones (**4**), which are readily available[2] from the corresponding thioamide and trichloromethanesulphenyl chloride. The synthetic method is illustrated for 3-*p*-methoxyphenyl-5-methylthio-1,4,2-dithiazolium tetrafluoroborate (**3a**). A mixture of (**4a**)

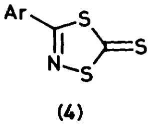


(1) X = S

(2) X = O

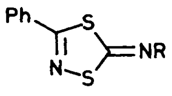


(3)



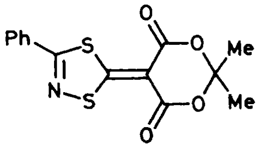
(4)

a; Ar = p - $MeOC_6H_4$
b; Ar = Ph
c; Ar = p - MeC_6H_4
d; Ar = p - ClC_6H_4

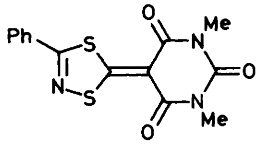


(5)

a; R = Ph
b; R = CO_2Et



(6)



(7)

(2.0 g) and dimethyl sulphate (6 ml) was heated at 80—100 °C until a homogenous liquid was obtained (*ca.* 10 min). After cooling 40% fluoroboric acid (2 ml) was added, followed by diethyl ether (5 ml). The resulting precipitate was filtered, dried, and recrystallised from acetic acid to give (**3a**) (2.64 g, 93%) as an orange solid,† m.p. 128—131 °C (decomp.); δ_H [$(CD_3)_2CO$, 80 MHz] 8.13 (d, 2H, J 9 Hz, ArH), 7.24 (d, 2H, J 9 Hz, ArH), 3.98 (s, 3H, OMe), and 3.48 (s, 3H, SMe); m/z (fast atom bombardment) 256 (M^+). Other aryldithiazolethiones reacted similarly. From (**3b**—**d**) the following were prepared: (**4b**), 71%, m.p. 137—138 °C, m/z 226 (M^+); (**4c**), 24%, m.p. 117 °C, m/z 240 (M^+); (**4d**), 46%, m.p. 139—141 °C, m/z 262, 260 (M^+).

The reactions of the dithiazolium salts with some nucleophiles were also studied. A solution of (**3b**) (0.50 g, 1.60 mmol) in acetic acid (10 ml) was treated with aniline (0.30 g, 3.22 mmol). The mixture was heated for 5 min at *ca.* 50 °C, poured into cold water (150 ml) and extracted with diethyl ether. Removal of the solvent yielded an orange solid from which was obtained 3-phenyl-5-phenylimino-1,4,2-dithiazole (**5a**) (0.19 g, 43%),† m.p. 72—74 °C, m/z 270 (M^+), 135 ($PhCNS^+$), 103 ($PhCN^+$). Few 5-amino-1,4,2-diathiazoles are known, the only previous examples being *N*-ethoxycarbonyl derivatives such as (**5b**), formed directly from the corresponding dithiazolethiones and ethyl azidoformate.[2]

Having established that the methylthio group in (**3**) could be displaced by an amine, their reactivity towards the carbon nucleophiles Meldrum's acid[3] and *N,N*-dimethylbarbituric acid was examined. Triethylamine (0.55 g, 5.4 mmol) was addded to a solution of (**3b**) (1.50 g, 4.8 mmol) and Meldrum's acid (0.69 g, 4.8 mmol) in nitromethane and the mixture heated at 80 °C for 15 min. Addition to cold water and extraction with dichloromethane afforded the 5-alkylidenedithiazole (**6**) (0.82 g, 53%) as a white solid, m.p. 222 °C (from ethanol); δ_H ($CDCl_3$, 80 MHz) 7.4—8.1 (m, 5H, PhH) and 1.77 (s, 6H, Me); m/z 321 (M^+). *N,N*-Dimethylbarbituric acid reacted similarly yielding (**7**) (89%), m.p. 246—248 °C; δ_H ($CDCl_3$, 80 MHz) 7.4—8.1 (m, 5H, PhH) and 3.43 (s, 6H, Me); m/z 333 (M^+).

The reactions of 1,4,2-dithiazolium cations with nucleophiles closely parallel those of 1,3-dithiolium ions which also take place at the carbon adjacent to both sulphur atoms.

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References

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3 H. McNab, *Chem. Soc. Rev.*, 1978, **7**, 345.

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† All new compounds gave satisfactory elemental analyses.