**Short Communication**

**Synthesis of 1,3-Dithiolan-2-ylum and 1,3-Dithian-2-ylum Tetrafluoroborate Salts**

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The 1,3-dithian-2-ylum thiocarbocation has become an important cationic formyl equivalent synthone. The synthetic potential of the 1,3-dithiolan-2-ylum thiocarbocation, however, has not been explored, presumably because no satisfactory preparation of its salts has been reported, but the usefulness of the synthetic equivalent 2-ethoxy-1,3-dithiolanes has been demonstrated. Because of the potential importance of 1,3-dithiolan-2-ylum and 1,3-dithian-2-ylum thiocarbocations as cationic formyl equivalents, we have worked out a simple and effective method for the preparation of their tetrafluoroborate salts. Our procedure represents an extension of our previously reported method for the preparation of 2-substituted 1,3-dithiolan-2-ylum and 1,3-dithiolan-2-ylum salts. Treatment of the dithiol and an acid chloride with ethereal tetrafluoroboric acid leads to the formation and precipitation of the 2-substituted salts. These have many synthetic applications. Since formyl chloride is not available, we have investigated other reagents and found that triethyl orthoformate is an equivalent reagent for the formation of the desired thiocarbocations. The tetrafluoroborate salts 2a and 2b were precipitated in 76
and 98% yield respectively from a solution of the dithiol and triethyl orthoformate in 54% HBF₄·Et₂O; lower concentrations of tetrafluoroboric acid gave lower yields of 2. In dichloromethane solution, variable and low yields of 2 were obtained. Compound 2b has previously been prepared by hydride abstraction from 1,3-dithiane by trityl tetrafluoroborate.²

The intermediates in our synthesis were probably 2-ethoxy-1,3-dithiolane and 2-ethoxy-1,3-dithiane respectively, which were cleaved by the strong acid to the thiocarbocations by analogy to the in situ generation of a 1,3-dithiolan-2-ylium salt from 2-methylthio-1,3-dithiolane.⁶ We have also explored selective cleavage of 2-alkylthio substituents for the preparation of the desired thiocarbocations. Thus, addition of tetrafluoroboric acid to 2,2′-(ethane-1,2-dithio)di-1,3-dithiolane 3a or 2,2′-(propane-1,3-dithio)di-1,3-dithiane 3b in dichloromethane precipitated the respective salts 2a and 2b in high yields. In trifluoroacetic acid, however, ¹H NMR spectra were recorded without any cleavage reaction in 3. The dimeric intermediates 3 were readily available from ethane-1,2-dithiol and triethyl orthoformate in AcOH/BF₃·Et₂O or from propane-1,3-dithiol and triethyl orthoformate in CHCl₃/HCl.¹⁵,¹⁶

**Experimental**

**General procedure for the preparation of 2a and 2b from diethiols.** A solution of triethyl orthoformate (10 mmol) in ethereal HBF₄ (54%, 5 ml) was added dropwise with stirring to a solution of 1,2-ethanediethiol or 1,3-propanediethiol in ethereal HBF₄ (54%) at −20°C. The resultant mixture was stirred at this temperature for 5 min before the cooling bath was removed, and the stirring was continued for 30 min at ambient temperature. Dry ether (70 ml) was then added, the precipitated product isolated by filtration and washed with dry ether. The product was necessarily stored under anhydrous conditions.

**1,3-Dithiolan-2-ylium tetrafluoroborate 2a.** Yield 76%. ¹H NMR (CD₃CN): δ 4.35 (4H, s), 11.1 (H-2, s). ¹³C NMR (CD₃CN): δ 45.2 (C-4,5), 219.6 (C-2).

**References**