Reaction of $N(SCl)_2^+$ Salts with Tin(II) Chloride: A New Preparative Route to Salts of the SNS^+ Cation

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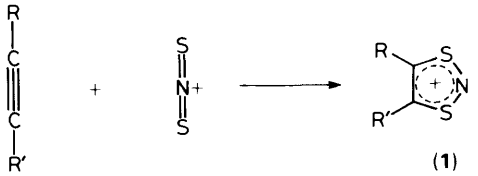
The salts SNS^+X^- (X = $AlCl_4$ or $SbCl_6$) have been isolated (>70% yield) from $N(SCl)_2^+X^-$ by reduction with anhydrous tin(II) chloride in liquid SO_2 or CH_2Cl_2.

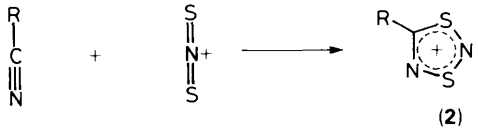
The SNS^+ salts have been found to react with a variety of unsaturated organic groups, including RCCR′ and RCN, to give heterocyclic cations (**1**) and (**2**) respectively in high yield (typically ≥ 90%). Reduction of these materials has led to a variety of novel free-radical analogues.[1–4] However the hazardous nature of the AsF_6^- salt preparation[5] (involving S_4N_4 and AsF_5) and also the low solubility of the readily prepared $SbCl_6^-$ salt[6] has limited further exploitation of such cycloaddition reactions.

We now report a novel route to two SNS^+ reagents, which occurs in high yield, and should potentially lead to a wide variety of other SNS^+ salts. The reaction of $SnCl_2$ with readily available[6,7] $N(SCl)_2^+X^-$ (X = $AlCl_4$ or $SbCl_6$) in liquid SO_2 or CH_2Cl_2 produced $SnCl_4$ and SNS^+X^-. The yield of isolated product was maximized using solvents in which the SNS^+X^- product was least soluble (CH_2Cl_2 for $SNS^+AlCl_4^-$ and SO_2 for $SNS^+SbCl_6^-$).

The suitability of these salts as synthons for heterocyclic ring systems is presently being investigated and we may anticipate similar preparations of analogous salts.



(1)



(2)

Experimental

Moisture-sensitive materials were handled under nitrogen in a Vacuum Atmospheres Corporation glove-box (HE43-2) fitted with an HE-493 Dri-Train. Infra-red spectra were recorded as Nujol mulls between KBr or CsI plates using Perkin-Elmer 577 and 457 grating spectrophotometers.

Tin(II) chloride was recrystallized from acetone before use. Sulphur dioxide was distilled off P_4O_{10} and stored over CaH_2 before use.

Preparation of $S_2N^+AlCl_4^-$.—The salt $N(SCl)_2^+AlCl_4^-$ (0.318 g, 1 mmol) and $SnCl_2$ (0.190 g, 1 mmol) were placed with a magnetic flea in one leg of a two-limbed reaction vessel and CH_2Cl_2 (5 cm^3) was syringed in. The reaction mixture was stirred at room temperature for 24 h to give a yellow precipitate of $S_2N^+AlCl_4^-$ and a quantity of highly soluble red by-product which was readily removed by filtration. The product was extracted in a sealed extractor[8] with CH_2Cl_2 for 24 h to remove any traces of $SnCl_4$ and minor side-products (mostly $S_3N_2^+$ $AlCl_4^-$). The overall yield of $S_2N^+AlCl_4^-$ (0.213 g) was 86% (Found: Al, 10.85; N, 5.40. Calc. for $S_2N^+AlCl_4^-$: Al, 10.95; N, 5.65%). I.r.: 1 494s, 470s br, and 380s cm^{-1}.

Preparation of $S_2N^+SbCl_6^-$.—This salt was prepared similarly from $N(SCl)_2^+SbCl_6^-$ (1.460 g, 3.02 mmol) and $SnCl_2$ (0.574 g, 3.02 mmol) but in liquid SO_2 (*ca.* 5 cm^3). The reaction mixture was stirred for 36 h to produce highly insoluble S_2N^+ $SbCl_6^-$ under a red solution. The red solubles were filtered off and the yellow product washed with SO_2 by back-condensation before exhaustive extraction with SO_2 in a sealed extractor.[8] The overall yield of purified $S_2N^+SbCl_6^-$ (0.874 g) was 70% (Found: Cl, 52.00; N, 3.40; S, 15.35; Sb, 29.70. Calc. for $S_2N^+SbCl_6^-$: Cl, 51.55; N, 3.40; S, 15.50; Sb, 29.55%). I.r.: 1 480s, 376vs, and 345vs cm^{-1}.

Acknowledgements

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