

## The *in situ* Generation of Thiaryl Trichloride: A Synthron for C–N–S Heterocycles

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The novel reagent NSCl<sub>3</sub> is readily generated by treatment of (NSCl)<sub>3</sub> with an excess of SO<sub>2</sub>Cl<sub>2</sub>; the reactions of NSCl<sub>3</sub> with methacrylonitrile or thioacetamide produce 4-cyanoisothiazole or 5-methyl-1,3,2,4-dithiazolium chloride, respectively, in good yields.

Although NSF<sub>3</sub> is well characterized,<sup>1</sup> the corresponding chloride, NSCl<sub>3</sub>, is unknown. We describe here the generation and <sup>14</sup>N n.m.r. spectroscopic characterization of this thermally unstable compound and its use as an *in situ* reagent for high yield, direct syntheses of 4-cyanoisothiazole (**1**; R = CN) and 5-methyl-1,3,2,4-dithiazolium chloride (**2**; R = Me, X = Cl).

I.r. studies indicate that (NSCl)<sub>3</sub> is in equilibrium with NSCl in solution.<sup>2</sup> The <sup>14</sup>N n.m.r. spectrum of (NSCl)<sub>3</sub> in chloroform at 25 °C shows two peaks at 338 and -262 p.p.m. (ref. MeNO<sub>2</sub>).<sup>3</sup> The relative intensity of the former peak increases as the temperature is raised, so these signals are attributed to NSCl and (NSCl)<sub>3</sub>, respectively. The addition of an excess of sulphuryl chloride to a solution of (NSCl)<sub>3</sub> in chloroform is accompanied by the evolution of SO<sub>2</sub>. The <sup>14</sup>N n.m.r. spectrum of this solution shows a strong signal at -4 p.p.m., which we attribute to NSCl<sub>3</sub>, in addition to much weaker signals for NSCl and (NSCl)<sub>3</sub>. Since (NSCl)<sub>3</sub> is usually prepared by the action of an excess of SO<sub>2</sub>Cl<sub>2</sub> on S<sub>4</sub>N<sub>4</sub> or S<sub>3</sub>N<sub>2</sub>Cl<sup>+</sup>Cl<sup>-</sup>,<sup>4</sup> it is not surprising that attempts to isolate NSCl<sub>3</sub> have given only (NSCl)<sub>3</sub>. A solution of NSCl<sub>3</sub> in chloroform or sulphuryl chloride is, however, a useful reagent for the synthesis of cyclic S–N compounds as illustrated by the following two examples.

Compound (**1**; R = CN) was prepared by the addition of methacrylonitrile (10 mmol) to a solution of NSCl<sub>3</sub> (10 mmol) obtained by the treatment of a solution of (NSCl)<sub>3</sub> (3.33 mmol) in chloroform (25 ml) with a large excess of SO<sub>2</sub>Cl<sub>2</sub> (10 ml). The reaction mixture was heated at reflux for 16 h and, after the removal of volatile materials *in vacuo* (**1**; R = CN) (7.8 mmol) was obtained in 78% yield as air-stable, white crystals by sublimation of the orange-red residue under a static vacuum of 0.1 Torr at 50 °C:† m.p. 95 °C; *m/z* (electron impact, 70 eV) 110 [C<sub>4</sub>H<sub>2</sub>N<sub>2</sub>S, 100%], 83 [HC(S)CCN, 80], 59 [HCSN, 50], 56 [CC(S)H, 15], 51 [?, 15], 45 [HCS, 30], 38 [CCN, 20], 32 [S, 25]; <sup>1</sup>H n.m.r. (200 MHz, CDCl<sub>3</sub>) δ 9.22 (s, 1H), 8.70 (s, 1H); <sup>13</sup>C n.m.r. (200 MHz, CDCl<sub>3</sub>) δ 157.7, 156.0, 112.4, 109.3; i.r. (Fluorolube mull) ν(C≡N) 2234s cm<sup>-1</sup>; λ<sub>max</sub>(MeCN) 246 nm, ε 9.3 × 10<sup>3</sup> l mol<sup>-1</sup> cm<sup>-1</sup>. This high yield, direct preparation of (**1**; R = CN) from methacrylonitrile and NSCl<sub>3</sub> formally involves a cyclo-condensation reaction with loss of 3 mol of HCl [equation (1)] and compares favourably with the usual four-step synthesis of 4-cyanoisothiazoles from the parent ring system.<sup>5</sup>

Compound (**2**; R = Me, X = Cl) was prepared by the addition of thioacetamide (35.4 mmol) to a solution of

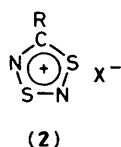
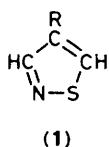
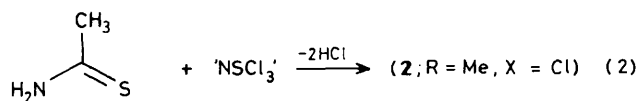
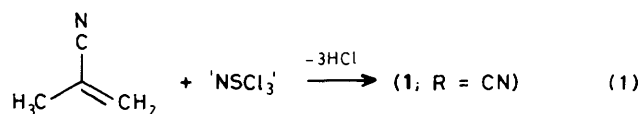
(NSCl)<sub>3</sub> (11.8 mmol) in SO<sub>2</sub>Cl<sub>2</sub> (ca. 50 ml). The reaction mixture was heated at reflux for 16 h. After removal of the excess of SO<sub>2</sub>Cl<sub>2</sub>, the addition of acetonitrile (15 ml) gave (**2**; R = Me, X = Cl) as an orange solid (18.6 mmol). Diethyl ether (50 ml) was added to the filtrate to produce a further 3.8 mmol of (**2**). The total yield was 63%:† m.p. 199 °C; *m/z* (electron impact 70 eV) 119 (CH<sub>3</sub>CN<sub>2</sub>S<sub>2</sub>, 20%), 78 (S<sub>2</sub>N, 50), 73 (CH<sub>3</sub>CNS, 25), 64 (S<sub>2</sub>, 100), 48 (? , 80), 46 (NS, 25), 41 (CH<sub>3</sub>CN, 5), 32 (S, 30); <sup>1</sup>H n.m.r. (200 MHz, CDCl<sub>3</sub>) δ 1.22 (s); i.r. (Nujol and Fluorolube mulls) 2960m, 2929s, 2956m, 1407s, 1373vs, 1350m, 1052vs, 857vs, 816vs, 794vs, 761s, 676m, 542s, 535m, 516m, 370m cm<sup>-1</sup>.

The formation of (**2**; R = Me, X = Cl) from thioacetamide and NSCl<sub>3</sub> also involves a cyclo-condensation reaction with loss of 2 mol of HCl [equation (2)].

Several derivatives of (**2**) (R = Me, Bu<sup>t</sup>, CF<sub>3</sub>, or I; X = AsF<sub>6</sub>) have been obtained recently by the cycloaddition reaction of NS<sub>2</sub><sup>+</sup>AsF<sub>6</sub><sup>-</sup> with the corresponding nitrile and the reduction of this cation produces thermally stable radicals with interesting properties.<sup>6–8</sup> The advantages of the alternative route to (**2**) described here are (a) the relative ease of preparation and handling of NSCl<sub>3</sub> compared to NS<sub>2</sub><sup>+</sup>AsF<sub>6</sub><sup>-</sup>,<sup>9,10</sup> and (b) the high solubility of (**2**; R = Me, X = Cl) in organic solvents, suggesting that this product contains a covalent S–Cl bond.

These two examples demonstrate the potential utility of the reagent NSCl<sub>3</sub> for the synthesis of C–N–S heterocycles. Further studies of the generality of these procedures and of the application of NSCl<sub>3</sub> in the preparation of other S–N ring systems are in progress.

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† Analytical data and, in the case of (**1**; R = CN), the high resolution mass spectrum confirmed the elemental composition of new compounds.

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