The *in situ* Generation of Thiazyl Trichloride: A Synthon for C–N–S Heterocycles

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The novel reagent $NSCl_3$ is readily generated by treatment of $(NSCl)_3$ with an excess of SO_2Cl_2; the reactions of $NSCl_3$ with methacrylonitrile or thioacetamide produce 4-cyanoisothiazole or 5-methyl-1,3,2,4-dithiazolium chloride, respectively, in good yields.

Although NSF_3 is well characterized,[1] the corresponding chloride, $NSCl_3$, is unknown. We describe here the generation and ^{14}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 $(NSCl)_3$ is in equilibrium with NSCl in solution.[2] The ^{14}N n.m.r. spectrum of $(NSCl)_3$ in chloroform at 25 °C shows two peaks at 338 and −262 p.p.m. (ref. $MeNO_2$).[3] The relative intensity of the former peak increases as the temperature is raised, so these signals are attributed to NSCl and $(NSCl)_3$, respectively. The addition of an excess of sulphuryl chloride to a solution of $(NSCl)_3$ in chloroform is accompanied by the evolution of SO_2. The ^{14}N n.m.r. spectrum of this solution shows a strong signal at −4 p.p.m., which we attribute to $NSCl_3$, in addition to much weaker signals for NSCl and $(NSCl)_3$. Since $(NSCl)_3$ is usually prepared by the action of an excess of SO_2Cl_2 on S_4N_4 or $S_3N_2Cl^+Cl^-$,[4] it is not surprising that attempts to *isolate* $NSCl_3$ have given only $(NSCl)_3$. A *solution* of $NSCl_3$ 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 $NSCl_3$ (10 mmol) obtained by the treatment of a solution of $(NSCl)_3$ (3.33 mmol) in chloroform (25 ml) with a large excess of SO_2Cl_2 (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 [$C_4H_2N_2S$, 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]; ^1H n.m.r. (200 MHz, $CDCl_3$) δ 9.22 (s, 1H), 8.70 (s, 1H); ^{13}C n.m.r. (200 MHz, $CDCl_3$) δ 157.7, 156.0, 112.4, 109.3; i.r. (Fluorolube mull) $\nu(C{\equiv}N)$ 2234s cm^{-1}; $\lambda_{max.}$(MeCN) 246 nm, ε 9.3 × 10^3 l mol^{-1} cm^{-1}. This high yield, direct preparation of (**1**; R = CN) from methacrylonitrile and $NSCl_3$ 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.[5]

Compound (**2**; R = Me, X = Cl) was prepared by the addition of thioacetamide (35.4 mmol) to a solution of $(NSCl)_3$ (11.8 mmol) in SO_2Cl_2 (*ca.* 50 ml). The reaction mixture was heated at reflux for 16 h. After removal of the excess of SO_2Cl_2, 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 ($CH_3CN_2S_2$, 20%), 78 (S_2N, 50), 73 (CH_3CNS, 25), 64 (S_2, 100), 48 (?, 80), 46 (NS, 25), 41 (CH_3CN, 5), 32 (S, 30); ^1H n.m.r. (200 MHz, $CDCl_3$), 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^{-1}.

The formation of (**2**; R = Me, X = Cl) from thioacetamide and $NSCl_3$ also involves a cyclo-condensation reaction with loss of 2 mol of HCl [equation (2)].

Several derivatives of (**2**) (R = Me, Bu^t, CF_3, or I; X = AsF_6) have been obtained recently by the cycloaddition reaction of $NS_2^+AsF_6^-$ with the corresponding nitrile and the reduction of this cation produces thermally stable radicals with interesting properties.[6–8] The advantages of the alternative route to (**2**) described here are (a) the relative ease of preparation and handling of $NSCl_3$ compared to $NS_2^+AsF_6^-$,[9,10] 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 $NSCl_3$ for the synthesis of C–N–S heterocycles. Further studies of the generality of these procedures and of the application of $NSCl_3$ in the preparation of other S–N ring systems are in progress.

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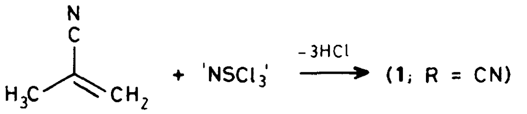
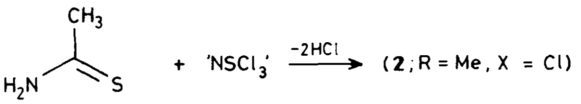
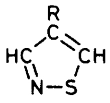


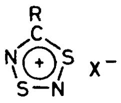
(1)



(2)



(**1**)



(**2**)

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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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