A New Method for the Synthesis of *tert*-Alkyl Chlorides from *tert*-Alcohols

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Tert-Alkyl chlorides **5** are prepared in good yield from the corresponding alcohols **1** in a facile two step synthesis. The method involves treatment of the corresponding crude oxalyl monochloride alkyl ester **2** with *N*-hydroxy-pyridine-2-thione sodium salt **3** in tetrachloromethane at reflux to give the bright yellow *N*-(alkoxyoxalyloxy)pyridine-2-thiones **4** which undergo decomposition to the chlorides **5** in good yield. The reaction is conveniently monitored by the loss of colour from the mixed anhydride.

We have recently reported novel free radical chain reactions for the reductive deoxygenation of *tert*-alcohols[1,2] and for the formation of quaternary carbon centres from *tert*-alcohols.[3,2] These reactions have the advantages of being little susceptible to steric hindrance and of avoiding rearrangement-prone carbocation intermediates. We now wish to report an extension of this methodology, related to our Hunsdiecker procedure[4,5] for the formation of *tert*-chlorides from *tert*-alcohols. *tert*-Alkyl chlorides have recently been employed as precursors for quaternary carbon centres by reaction with alkyl titanium,[6] or alkyl aluminium[7] reagents. We were therefore of the opinion that a new, mild and neutral method for the elaboration of *tert*-alkyl chlorides would find use in organic synthesis.

Thus *tert*-alcohols **1** were converted into the corresponding oxalyl monochloride alkyl ester **2** by treatment with excess oxalyl chloride in benzene. Crude **2** is then added to a suspension

of *N*-hydroxypyridine-2-thione sodium salt **(3)** in tetrachloromethane, at reflux under nitrogen, giving the bright yellow *N*-(alkoxyoxalyloxy)pyridine-2-thiones **4** which underwent decomposition, presumably *via* an autoinitiated free radical chain mechanism leading to the chlorides **5** in good overall yield (Table).

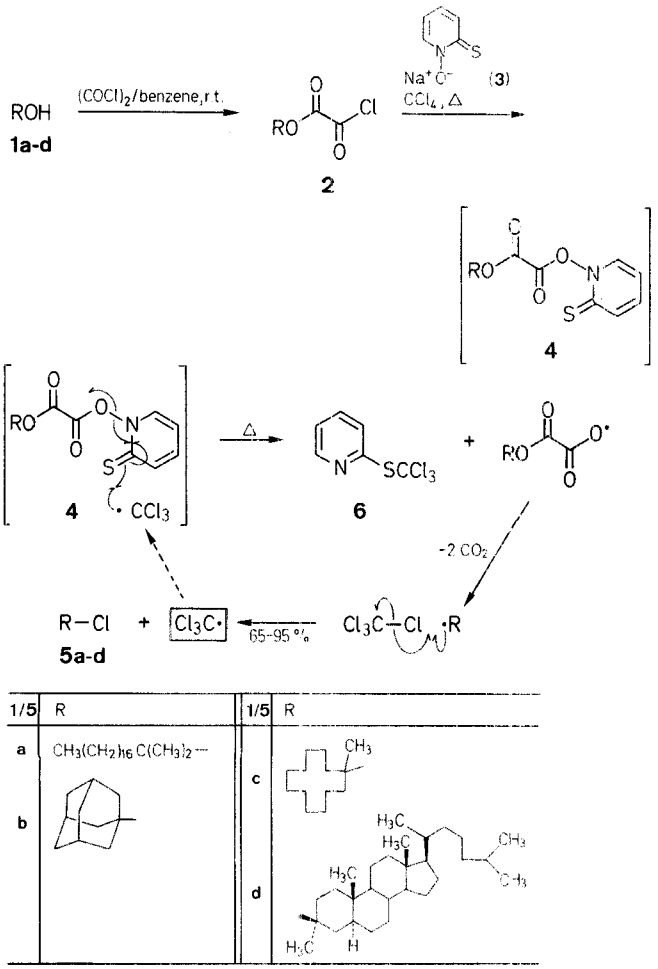

Table. Alkyl Chlorides Prepared

Product	Yield (%)	Yield of Sulphide **6** (%)	m.p. (°C)	Lit. m.p. (°C)	NMR ($CDCl_3$/TMS) δ(ppm)[e]
5a	85	70	19	19.6[8]	0.9 (t, 3H); 1.3 (m, 32H); 1.7 (s, 3H)
5b	65	70	165[a]	165[a,5]	1.65 (m, 6H); 2.1 (m, 9H)
5c	65	73	40–42	76[9]	1.4 (m, 18H); 1.65 (s, 3H); 1.7 (m, 4H)
5d ($\alpha+\beta$)	95[b]	70	155[c]	148[10]	3-α-Cl: 0.65 (s, 3H, 18-CH_3); 0.74 (s, 3H, 19-CH_3)[d]; 0.80 (d, 6H, J = 8 Hz, 26-, 27-CH_3); 0.84 (d, 3H, J = 8 Hz, 21-CH_3)

[a] Sealed tube.
[b] 3: 1, α-Cl, β-Cl.
[c] 3α-Cl, after recrystallisation.
[d] In the 3β-Cl, 19-CH_3 resonates at δ = 0.72 ppm.
[e] Jeol PMX 60 SI and/or Varian XL 200.

The reactions were conveniently monitored by the disappearence of the bright yellow colour of the *N*-(alkyloxyoxalyloxy)pyridine-2-thiones **4**. Pure chlorides were readily isolated by simple filtration of the reaction mixture, evaporation of the solvent and filtration on silica. We have previously adequately demonstrated the compatibility of closely related systems with a whole range of functional groups.[1–5]

We next attempted the conversion of *tert*-alcohols into *tert*-alkyl bromides by simply replacing tetrachloromethane with bromotrichloromethane as solvent. Unfortunately we were only able to isolate the products of elimination. The isolation of trichloromethyl pyridyl sulphide **(6)** in good yield from these experiments implied that the bromides had been formed and that these had undergone base promoted elimination with the pyridyl sulphide as base. We were unable to prevent this elimination even by carrying out the reaction photochemically at room temperature. Application of the procedure to the bridgehead *tert*-alcohol 1-adamantanol gave 1-bromoadamantane[5] and trichloromethyl pyridyl sulphide **(6)** in 65 and 75% yields respectively.

During the course of this investigation we discovered that the treatment of tris-1-adamantanylmethanol[11] with oxalyl chloride in benzene gave, directly, the previously unknown tris-1-adamantanylmethyl chloride. It is unclear at this stage whether this is due to the action of hydrogen chloride on the alcohol or to a decomposition of this particular oxalyl monochloride alkyl ester. Simple oxalyl monochloride alkyl esters are reported[12] to be stable to at least 150 °C, and treatment with pyridine at 100 °C is usually required for their conversion to alkyl chlorides.

Formation of *tert*-Alkyl Chlorides 5 from *tert*-Alcohols 1; General Procedure:

Freshly distilled oxalyl chloride (1 ml, 11 mmol) is added at room temperature to a stirred solution of the alcohol (1 mmol) in dry benzene (5–10 ml), and the mixture stirred overnight at room temperature. After evaporation of the volatiles the crude reaction mixture is taken up in tetrachloromethane (5 ml) and added dropwise to a stirred suspension of *N*-hydroxypyridine-2-thione sodium salt (0.17 g, 1.1 mmol) in tetrachloromethane at reflux. After decolourisation of the thus formed bright yellow solution, the cooled reaction mixture is filtered on celite and evaporated to dryness. Filtration through a short silica gel column gives the pure chlorides (eluant 40–60 petroleum ether) and subsequently trichloromethyl pyridyl sulphide **(6)** (eluent dichloromethane), whose spectra are identical to those of an authentic sample.

Tris-1-adamantanylmethyl Chloride

Tris-1-adamantanyl methanol (100 mg; 0.23 mmol) is added to a stirred solution of freshly distilled oxalyl chloride (0.64 g, 5 mmol) in dry benzene (5 ml) at room temperature. After standing overnight at room temperature removal excess oxalyl chloride gives the crude chloride which is recrystallized from benzene; yield: 97 mg (93 %): m.p. 227 °C.

^{1}H-NMR (200 MHz, C_6D_6/TMS): δ = 1.58 ppm (45 H s).

^{13}C-NMR (C_6D_6/TMS): δ = 30.2, 31.2, 38.3, 39.4, 53.3 ppm.

MS (70 eV): *m/e* = 416 (M – HCl), 135, 93, 79.

$C_{31}H_{45}Cl$ (453.1) calc. C 82.17 H 10.01 Cl 7.82
found 82.12 9.89 7.35

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