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ONE-POT SYNTHESIS OF ω-CHLOROESTERS VIA THE REACTION OF ACID CHLORIDES WITH TETRAHYDROFURAN IN THE PRESENCE OF TRICHLOROBORANE

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ABSTRACT

The reaction of acid chlorides with tetrahydrofuran in the presence of trichloroborane produces ω -chloroesters in excellent yields.

Key Words: Boron trichloride; Ether cleavage; Chloroesters; Ester formation

The exothermic formation of addition complexes from ethers is a well known phenomenon.^[1] Thermal decomposition of these complexes often leads to the formation of α,ω -dihaloalkanes (Eq. 1). Aluminum,^[1]

$$\bigvee_{O} + Mx_n \longrightarrow \bigvee_{O} \xrightarrow{\Delta} X (CH_2)_4 X$$
(1)

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boron,^[2] and silicon^[3] reagents have all been employed in these cleavage reactions.^[4] Ethers can also be converted to their corresponding esters in the presence of acylating reagents and it has been shown that such transformations can be achieved in presence of transition metals^[5] and organo-lanthanide^[6] complexes.

Our continued interest in boron halide induced cleavage reactions of ethers and geminal diacetates,^[7] lactones,^[8] and esters^[9] as well as our use of acid chlorides for preparing ketones^[10] prompted us to report a simple one-pot synthesis of ω -chloroesters via the reaction of acid chlorides with tetra-hydrofuran in the presence of trichloroborane (Eq. 2).

Tetrahydrofuran readily reacts with either aromatic or aliphatic acid chlorides in the presence of trichloroborane to yield ω -chloroesters. The results are summarized in the Table 1.

We carried out a study to determine reaction conditions leading to maximum yields and found that a reaction temperature of 65° C results in a convenient reaction time of 3 h. A shorter time results in incomplete reaction and recovery of starting material whereas a longer time leads to the formation of higher homologs of the desired chloroesters (8–20%).

Although, no mechanistic study has been carried out, the reaction presumably occurs via the formation of a boron ether complex followed by nucleophilic attack of a chloride ion. Cyclic amines and acyclic ethers do not lead to the desired cleavage products.

EXPERIMENTAL

All reactions were performed in oven-dried glassware under a nitrogen atmosphere with magnetic stirring. Air and moisture sensitive compounds were introduced via syringe through a rubber septum.THF was dried and distilled prior to use. Products were purified by flash chromatography using 230–400 mesh ASTM 60 Å silica gel. All ¹H and ¹³C NMR spectra were recorded on a 250 MHz spectrometer in CDCl₃ solution, chemical shifts are given in ppm (δ) relative to TMS. All GC/MS data were obtained using a Hewlett Packard 6890 series GC system equipped with a 5973 Mass Selective Detector or a Hewlett Packard 5890 Series GC system equipped with a 5970 Mass Selective Detector.

Benzoic Acid 4-Chlorobutyl Ester:^[6] ¹H NMR (CDCl₃/TMS) δ 1.81–1.86 (m, 4H), 3.48–3.53 (t, 2H), 4.23–4.27 (t, 2H), 7.31–7.37 (t,

1998

Table 1. Reaction of Acid Chlorides with THF in the Presence of Trichloroborane^a



^aBoron trichloride (1 mmol) added to the acid chloride (3 mmol) in THF and the mixture refluxed for 3 h.

^bThe products exhibited physical and spectral data in accord with literature values. ^cIsolated yield.

2H), 7.43–7.49 (t, 1H), 7.94–7.97 (d, 2H); 13 C NMR (CDCl₃) δ 25.98, 29.07, 44.28, 63.87, 128.16, 129.31, 130.04, 132.74, 166.22; GC/MS (EI) *m/z* (relative intensity) 215 (3), 213 (M⁺, 2), 212 (5), 177 (18), 122 (68), 105 (100), 77 (71), 51 (23).

4-Methylbenzoic acid 4-Chlorobutyl Ester:^{[6] 1}H NMR (CDCl₃/TMS) δ 1.81–1.86 (m, 4H), 2.30 (s, 3H), 3.48–3.53 (t, 2H), 4.21–4.26 (t, 2H), 7.12–7.15 (d, 2H), 7.81–7.85 (d, 2H); ¹³C NMR (CDCl₃) δ 21.48, 26.06, 29.16, 44.37, 63.75, 127.37, 128.95, 129.43, 143.45, 166.40; GC/MS (EI) *m/z* (relative intensity) 229 (3) 227 (M⁺, 2) 226 (5), 191 (10), 136 (75), 119 (100), 91 (49), 65 (19), 55 (11).

Isobutyric Acid 4-Chlorobutyl Ester:^[11] ¹H NMR (CDCl₃/TMS) δ 1.08–1.11 (d, 6H), 1.69–1.81 (m, 4H), 2.42–2.50 (m, 1H), 3.48–3.53 (t, 2H), 4.00–4.06 (t, 2H); ¹³C NMR (CDCl₃) δ 18.87, 26.02, 29.08, 33.90, 44.36, 63.26, 176.95; GC/MS (EI) *m*/*z* (relative intensity) 181 (3), 179 (M⁺, 5), 143 (19), 134 (25), 91 (100), 85 (22), 71 (73), 55 (64).

Trichloroacetic Acid 4-Chlorobutyl Ester:^[12] ¹H NMR (CDCl₃/TMS) δ 1.64–1.81 (m, 4H), 3.49–3.54 (t, 2H), 4.02–4.08 (t, 2H); ¹³C NMR (CDCl₃) δ 26.15, 29.45, 44.55, 61.90, 89.10, 164.25; GC/MS (EI) m/z (relative intensity) 257 (2), 255 (M⁺,5), 223 (11), 165 (13), 149 (29), 1233 (24), 91 (100), 71 (48), 55 (67).

2,2-Dimethylpropionic Acid 4-Chlorobutyl Ester:^[13] ¹H NMR (CDCl₃/TMS) δ 1.31 (s, 9H), 1.67–1.87 (m, 4H), 3.47–3.53 (t, 2H), 4.03–4.09 (t, 2H); ¹³C NMR (CDCl₃) δ 25.87, 26.49, 29.00, 41.60, 44.40, 63.45, 176.05; GC/MS (EI) *m*/*z* (relative intensity) 195 (3), 193 (M⁺, 6) 156 (38), 135 (29), 119 (17), 91 (100), 71 (42), 55 (59).

Undecenoic Acid 4-Chlorobutyl Ester: ¹H NMR (CDCl₃/TMS) δ 1.30– 1.64 (m, 12H), 1.76–1.88 (m, 4H), 1.99–2.07 (q, 2H), 2.26–2.32 (t, 2H), 3.54– 3.58 (6, 2H), 4.08–4.12 (t, 2H), 4.89–5.02 (dd, 2H), 5.78–5.81 (m, 1H); ¹³C NMR (CDCl₃) δ 24.82, 25.99, 28.75, 28.91, 29.06, 33.64, 34.13, 44.25, 63.17, 114.00, 138.94, 173.56; GC/MS (EI) *m/z* (relative intensity) 275 (M⁺, 2), 241 (3), 163 (10), 134 (20), 91 (100), 71 (27), 55 (71).

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