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One-step tetrahydrofuran ring opening by saturated hydrocarbons and CO

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Selective one-pot tetrahydrofuran ring opening by saturated hydrocarbons and CO in the presence of $CX_4{\cdot}2AlBr_3$ superelectrophilic complex leading to esters $RCOO(CH_2)_4Br$ has been performed for the first time.

Alkane chemistry has been developed with a remarkable success.[1–8] Recently, effective catalytic functionalizations of saturated hydrocarbons, including methane and ethane,[8] have been performed. However, despite a considerable progress in this field of chemistry, alkanes and cycloalkanes still represent enormous resources for organic synthesis based on readily available oil raw materials.

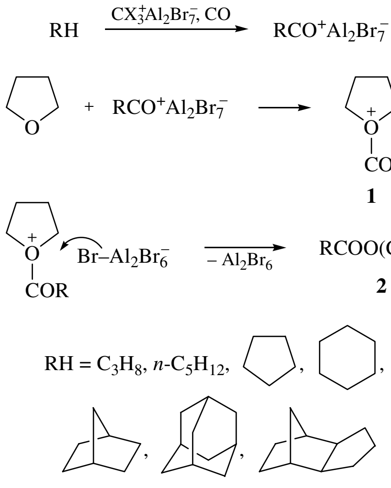
Here, we report the first example of the use of alkanes (cycloalkanes) and CO as the equivalents of acylium salts in a one-pot synthesis of esters $RCOO(CH_2)_4Br$ from tetrahydrofuran (THF) in the presence of the superelectrophilic systems $CX_4{\cdot}2AlBr_3$.

The opening of a THF ring under the action of electrophilic reagents is well known.[9,10] For example, the cleavage of a THF ring by acyl halides[10(a)–(c)] (or carboxylic acids[10(d)]) in the presence of Lewis or protic acids to give inaccessible halogen-substituted butyl esters has been reported. Our approach was based on the use of new superelectrophilic systems, which can effectively generate carbocations from saturated hydrocarbons under very mild conditions.[11] When the generation of carbocations occurs in a CO atmosphere, acylium cations are formed.[12]

Superelectrophiles based on polyhalomethanes allow the generation of acylium salts from alkanes,[13–15] mono-,[16–18] bi-[19] and tricyclanes.[19] It is of importance that the acylation can be carried out as a one-pot procedure. The one-pot acylation of aromatics and the acyldesilylation of tetraorganosilanes by saturated hydrocarbons and CO were reported.[17]

Under selected conditions, acylium salts were generated from alkanes (propane[14] and *n*-pentane[15]) and cycloalkanes (cyclopentane,[17] cyclohexane, methylcyclopentane,[18] norbornane, adamantane and trimethylenenorbornane[19]) and CO in the presence of superelectrophilic complexes $CX_4{\cdot}2AlBr_3$ (E). Then THF was introduced to the *in situ* generated acylium salt (Scheme 1).[†]

Scheme 1 includes the generation of an acylium salt from a saturated hydrocarbon and CO, the transformation of THF and the acylium salt into oxonium salt **1**, which undergoes ring opening resulting in ester **2** with the $(CH_2)_4Br$ group. In these reactions, the $\{RH–CO–CX_4{\cdot}2AlBr_3\}$ systems serve as donors of two functional groups for the substrate molecule. When the procedure is strictly followed, only one isomer is formed in each reaction. Owing to the enhanced stability of the oxonium salt against decarbonylation compared to the corresponding acylium cations, the reactions with THF proceed at 20–50 °C and give the target products in 70–90% yields with respect to E. With *n*-pentane and trimethylenenorbornane as starting compounds, the yields of esters **2** are 40–47% (Table 1). No fragmentation products due to the decarbonylation of acylium salts were formed. Since the isomerisation of carbocations under selected conditions does almost not occur, a sole isomeric ester $RCOO(CH_2)_4Br$ is formed, as a rule, in all reactions. Only in the reaction of cyclohexane, small amounts of **2** (R = 1-methylcyclopent-1-yl) are formed. In the absence of THF, the reactions of alkanes or cycloalkanes (other than adamantane) with CO give carbonyl-containing products in very poor yields, if any, even at 20 °C. Similarly to carbonylation reactions, the ring-opening reaction should be carried out under a CO atmosphere. Bromides RBr and only small amounts of esters $RCOO(CH_2)_4Br$ were formed, when the reactions with THF were carried out in the absence of CO.



Scheme 1

The structures of esters $RCOO(CH_2)_4Br$ were proved by ^1H and ^{13}C NMR, GC and GC-MS.[‡]

Table 1 One-pot synthesis of esters $RCOO(CH_2)_4Br$ from saturated hydrocarbons (RH), CO and THF in the presence of superelectrophiles (E).[a]

Run no.	RH	T/°C for ring opening	*t*/h for ring opening	Yield (%) based on E[b]
1	Propane	50	2	70
2	*n*-Pentane	50	2	40
3	Cyclopentane	–8	24	17
4	Cyclopentane	20	24	75
5	Cyclopentane	50	2	70
6[c]	Cyclohexane	50	2	90
7	Norbornane	20	24	73
8[d]	Adamantane	20	12	29
9[d]	Adamantane	50	2	78
10	Trimethylenenorbornane	50	2	47

[a] E = $CX_4{\cdot}2AlBr_3$ (solvent, CH_2X_2; X = Br, Cl); [$AlBr_3$]. [b] Yields are given according to GC data. [c] Additionally, **2** (R = 1-methylcyclopent-1-yl) was formed in 10% yield. [d] [$AlBr_3$] = 0.04 g cm^{-3}.

[†] *Conditions for the* in situ *generation of acylium salts (carbonylation stage) under atmospheric CO pressure.*[14–19] E = $CX_4{\cdot}2AlBr_3$ in CH_2X_2 solution (X = Br, Cl; [$AlBr_3$] = 0.46 g cm^{-3}). [RH]:[E] molar ratio, temperature and reaction time: for *n*-pentane or cyclopentane, 10:1, –20 °C, 1 h; for norbornane, 1:1, –20 °C, 1 h; for cyclohexane, 1:1, 0 °C, 1 h; for trimethylenenorbornane, 1:1, 10 °C, 2 h; for adamantane, 1:1, 0 °C, 3 h (in this case, [$AlBr_3$] = 0.04 g cm^{-3}). Generation of isopropylcarboxonium salt was performed under propane–CO (3:2) gas atmosphere, P = 1 atm, –20 °C, 2 h.

Conditions for THF ring opening reactions. After the formation of an acylium salt, an excess of THF was added to the reaction mixture. Then the reaction mixture was left to warm up room temperature or heated at 50 °C (Table 1). At 50 °C, the reactions of THF with acylium salts generated from propane, pentane or cyclopentane were carried out under refluxing. When the reaction was over, ether was added to the reaction mixture under cooling. Then water (or alcohol) was added dropwise. After ether extraction, washing organic layer with water, drying with $MgSO_4$, products were analysed by GC and GC-MS. For NMR studies, ether and light products were removed from ether extracts.

In conclusion, the use of the polyhalomethane-based superelectrophilic systems allows us to accomplish one-pot THF ring opening under the action of saturated hydrocarbons and CO as the equivalents of acylium salts. These reactions occur selectively to give esters $RCOO(CH_2)_4Br$ in high or moderate yields. Although THF ring opening by acyl halides in the presence of Lewis acids was described about 70 years ago, only ester **2** with R = Pr^i [ref. 10(*d*)] was prepared earlier. It is noteworthy that, apart from the obvious availability of saturated hydrocarbons and CO compared to traditional acylating systems, some acids and their derivatives such as RCOOH, RCOCl, where R = norbornane, trimethylenenorbornane, adamantane cannot be easily synthesised. Thus, the use of saturated hydrocarbons + CO instead of traditional systems is of special interest.

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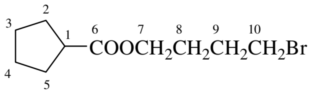
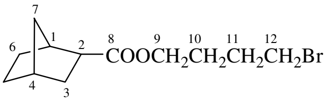
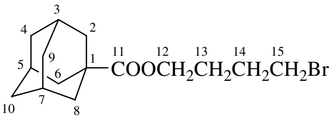
‡ *Selected spectral data.*



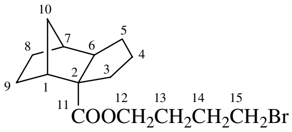
^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.49–1.98 (m, 13H, H^1–H^5, H^8–H^9), 3.41 (t, 2H, H^{10}, *J* 6.6 Hz), 4.05 (t, 2H, H^7, *J* 6.4 Hz). ^{13}C NMR (400 MHz, $CDCl_3$, calculated[20] δ value is given in square brackets) δ: 25.62 [26.16] (C^3, C^4), 27.19 [28.88] (C^8), 29.16 [29.42] (C^9), 29.84 [30.00] (C^2, C^5), 33.95 [33.20] (C^{10}), 43.66 [44.83] (C^1), 63.07 [65.07] (C^7), 176.90 [175.89] (C^6). MS, *m*/*z* (I_{rel}, %): 169 $[M - Br]^+$ (4), 153, 151 $[M - C_5H_9]^+$ (0.7), 141 $[M - Br - C_2H_4]^+$ (0.9), 137, 135 $[(CH_2)_4Br]^+$ (66), 136, 134 $[CH_2{=}CH(CH_2)_3Br]^+$ (15), 115 $[C_5H_9COOH_2]^+$ (72), 114 $[C_5H_9COOH]^+$ (6), 109, 107 $[(CH_2)_2Br]^+$ (3), 97 $[C_5H_9CO]^+$ (77), 69 $[C_5H_9]^+$ (100).



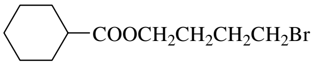
^{1}H NMR, δ: 1.16 (m, 2H, H^6), 1.43 (m, 2H, H^5), 1.52 (m, 2H, H^7), 1.78 (m, 2H, H^{10}), 1.93 (m, 2H, H^{11}), 2.29 (m, 1H, H^2), 2.30 (m, 1H, H^4), 2.47 (m, 2H, H^1), 3.43 (m, 2H, H^{12}, *J* 6.6 Hz), 4.07 (m, 2H, H^9, *J* 6.4 Hz). ^{13}C NMR, δ: 27.28 [25.40] (C^5), 28.50 [28.88] (C^{10}), 29.22 [29.42] (C^{11}), 29.36 [29.70] (C^6), 33.05 [32.60] (C^3), 34.01 [33.20] (C^{12}), 35.89 [37.80] (C^4), 36.37 [40.70] (C^7), 40.82 [41.10] (C^1), 46.37 [47.43] (C^2), 63.15 [65.07] (C^9), 175.99 [171.97] (C^8). MS, m/z (I_{rel}, %): 209, 207 $[M - 67]^+$ (5), 195 $[M - Br]^+$ (2), 141 $[C_7H_{11}COOH_2]^+$ (38), 137, 135 $[(CH_2)_4Br]^+$ (49), 136, 134 $[CH_2{=}CH(CH_2)_3Br]^+$ (7), 123 $[C_7H_{11}CO]^+$ (28), 95 $[C_7H_{11}]^+$ (100), 67 $[C_5H_7]^+$ (36).



^{1}H NMR, δ: 4.07 (t, 2H, H^{12}, ^{3}*J* 6.4 Hz), 3.43 (t, 2H, H^{15}, ^{3}*J* 6.8 Hz), 1.65–2.35 (m, 19H, H^2–H^{10}, H^{13}, H^{14}). ^{13}C NMR, δ: 27.27 [28.88] (C^{13}), 27.82 [28.56] (C^3, C^5, C^7), 29.27 [29.42] (C^{14}), 33.01 [33.20] (C^{15}), 36.38 [36.96] (C^4, C^9, C^{10}), 38.47 [38.85] (C^1), 38.74 [38.70] (C^2, C^6, C^8), 62.95 [65.53] (C^{12}), 177.57 [176.47] (C^{11}). MS, *m*/*z* (I_{rel}, %): 316, 314 $[M]^+$ (0.2), 235 $[M - Br]^+$ (3), 203, 201 (0.1), 181 $[C_{10}H_{15}COOH_2]^+$ (20), 180 $[C_{10}H_{15}COOH]^+$ (3), 179 $[C_{10}H_{15}COO]^+$ (11), 163 $[C_{10}H_{15}CO]^+$ (2), 137 $[(CH_2)_4Br]^+$ (4), 136 $[C_{10}H_{16}]^+$ $[CH_2{=}CH(CH_2)_3Br]^+$, 135 $[C_{10}H_{15}]^+$, $[(CH_2)_4Br]^+$ (100), 134 $[CH_2{=}CH(CH_2)_3Br]^+$ (2), 107 (5), 105 (2), 93 (15), 81 (5), 80 (3), 79 (19), 77 (6), 67 $[C_5H_7]^+$ (7).



^{1}H NMR, δ: 4.08 (t, 2H, H^{12}, ^{3}*J* 6.4 Hz), 3.43 (t, 2H, H^{15}, ^{3}*J* 6.0 Hz), 0.99–2.04 (m, ^{19}H, H^1, H^3–H^{10}, H^{13}, H^{14}). ^{13}C NMR, δ: 25.60 [22.88] (C^9), 25.86 [22.59] (C^4), 27.29 [26.01] (C^5), 27.52 [27.62] (C^8), 29.33 [28.88] (C^{13}), 32.74 [29.42] (C^{14}), 33.02 [33.20] (C^{15}), 34.13 [33.85] (C^3), 37.97 [37.12] (C^{10}), 41.47 [38.67] (C^1), 43.91 [43.43] (C^7), 49.47 [46.43] (C^6), 62.60 [57.31] (C^2), 63.12 [64.05] (C^{12}), 177.51 [176.11] (C^{11}). MS, *m*/*z* (I_{rel}, %): 316, 314 $[M]^+$ (0.1), 249, 247 $[M - 67]^+$ (1), 235 $[M - Br]^+$ (1), 203, 201 (1), 181, 179, $[M - C_{10}H_{15}]^+$ (6), 180, $[C_{10}H_{15}COOH]^+$ (3), 163 $[C_{10}H_{15}CO]^+$ (25), 162 $[C_{10}H_{14}CO]^+$ (19), 137, $[(CH_2)_4Br]^+$ (11), 135 $[C_{10}H_{15}]^+$, $[(CH_2)_4Br]^+$ (100), 136 $[CH_2{=}CH(CH_2)_2Br]^+$, $[C_{10}H_{16}]^+$ (61), 134 $[CH_2{=}CH(CH_2)_2Br]^+$ (20), 121, 119 $[CH_2{=}CHCHBr]^+$, 112 (15), 106 (7), 105 (9), 104 (6), 95, 93 $[CH_2Br]$ (15, 16), 81 (7), 80 (7), 79 (20), 68 (13), 67 (55), 66(18), 55 (60).



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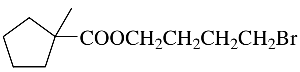

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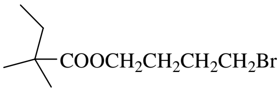

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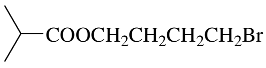

MS, *m*/*z* (I_{rel}, %): 181, 179 $[M - C_3H_7]^+$ (0.3), 143 $[M - Br]^+$ (14), 137, 135 $[(CH_2)_4Br]^+$ (7), 136, 134 $[CH_2{=}CH(CH_2)_3Br]^+$ (16), 115 $[C_3H_7COO(CH_2)_2]^+$ (1), 109, 107 $[(CH_2)_2Br]^+$ (3), 109, 107 $[CH_2CH_2Br]^+$ (3), 108, 106 $[CHCH_2Br]^+$ (1), 101 $[C_3H_7COOCH_2]^+$ (2), 95, 93 $[CH_2Br]^+$, (1), 89 $[C_3H_7COOH_2]^+$ (61), 85 (16), 73 (3), 71 $[C_3H_7CO]^+$ (76), 55 (100).

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