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The first one-pot amidation of alkanes and cycloalkanes

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Abstract

Alkanes (or cycloalkanes) and CO in the presence of superelectrophilic systems $CX_4{\cdot}2AlBr_3$ (X = Cl, Br) have been applied for the first time as equivalents of acylium salts in one-pot selective syntheses of amides from amines.

Keywords: Alkanes; Cycloalkanes; Superelectrophiles; Functionalization; Amines; Amides

1. Introduction

Transformations of saturated hydrocarbons into valuable fine chemicals constitutes an important timely topic of research, stimulated by both the synthetic challenges and the substantial economic interest in the use of natural resources.[1]

This work presents the first example of the application of alkanes (cycloalkanes) and CO as the equivalents of acylium salts in the one-pot synthesis of amides from amines in the presence of the superelectrophilic systems $CX_4{\cdot}2AlBr_3$ (X = Cl, Br).

Amides represent a significant class of compounds owing to their versatility as building blocks or intermediates for the synthesis of fine chemicals.[2,3] Most possess biological activities themselves or may serve as intermediates for the synthesis of biologically active compounds.[4,5] Various routes have been elaborated for the synthesis of amides. They mainly consist of treatment of amines with activated derivatives of carboxylic acids, namely, acyl halides, anhydrides, and esters.[2–5] Amidation of alkenes or alkynes with carbon monoxide and amines, catalyzed by Pd or Co,[6,7] radical initiated the amidation of alkyl iodides,[8] as well as other methods for the syntheses of amides (see for example, Refs. 9 and 10) have also been described.

The advantage of the presented method consists in the application of saturated hydrocarbons and CO in the synthesis of amides. Our approach was based on the use of new superelectrophilic systems, which are able to generate carbocations effectively from saturated hydrocarbons under very mild conditions.[1k,11] When carbocations are prepared under a CO atmosphere, acylium cations are formed.[12]

The one-pot acylation of alcohols (see reviews[1k,11]) and aromatics, acyldesilylation of tetraorganosilanes,[13] and THF ring opening[14] by saturated hydrocarbons and CO have been reported.

The acylation of amines by {RH+CO} has been carried out as follows. Under optimized conditions, the acylium salts were generated from alkanes (propane,[15] *n*-pentane[16]) and cycloalkanes (cyclopentane,[13] norbornane, adamantane, and trimethylenenorbornane[17]) and CO in the presence of superelectrophilic complexes $CX_4{\cdot}2AlBr_3$ (E). Next, an amine was introduced to the in situ generated acylium salt. When the procedure is strictly followed, only one isomer is formed in each reaction (Scheme 1). Similar to the reported reactions,[14] the amidation of propane,

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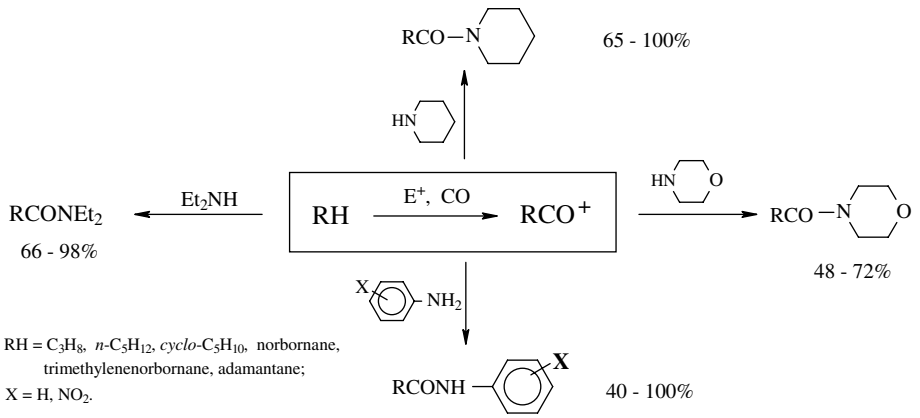


Scheme 1. One-pot amidation of alkanes and cycloalkanes.

n-pentane, cyclopentane, norbornane, adamantane, and trimethylenenorbornane resulted in amides containing isopropyl, *tert*-pentyl, cyclopentyl, 2-norbornyl, 1-adamantyl, and 2-trimethylenenorbornyl groups, respectively. Both carbonylation and acylation reactions should be carried out under a CO atmosphere.

Amines of various types (aliphatic, cyclic, and aromatic) were readily acylated with saturated hydrocarbons and CO in the presence of the above superelectrophiles to give amides in good or moderate yields (Table 1). The structures of the amides were proved by ^{1}H and ^{13}C NMR, GC and GC–MS and in some cases by elemental analysis.

Although half the amides described in this Letter had been prepared earlier,[18–27] their NMR and MS-spectra were reported for a few compounds only. To the best of our knowledge, amides **3**–**5**, **8**, **11**, **13**–**15**, and **20** are new compounds.

In conclusion, the use of the polyhalomethane-based superelectrophilic systems have allowed us to use saturated hydrocarbons and CO as equivalents of acylium salts in the one-pot synthesis of amides from amines. These reactions give amides selectively in high or moderate yields. It is noteworthy that, apart from the obvious availability of saturated hydrocarbons compared to traditional acylating systems, some acids and their derivatives cannot be easily synthesized. Thus, the application of saturated hydrocarbons and CO instead of traditional systems is of interest.

2. Experimental

2.1. Conditions for the in situ generation of acylium salts under atmospheric CO pressure (carbonylation stage)[13,15–17]

$E = CX_4{\cdot}2AlBr_3$ 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, 0.5–1 h, X = Br; for norbornane = 1:1, −20 °C, 1 h or 0 °C, 1 h, X = Cl; 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 the isopropylcarboxonium salt was performed under a propane/CO (3:2) gas atmosphere, $P = 1$ atm, −20 °C, 2 h.

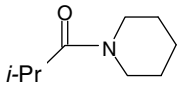
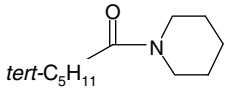
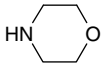
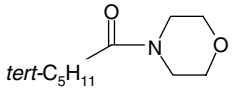
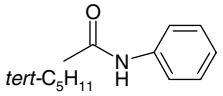
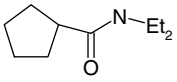
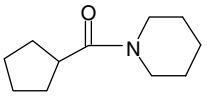
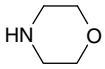
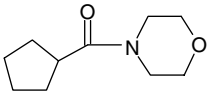
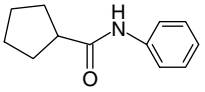
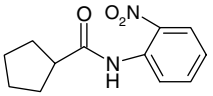
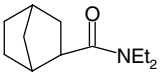
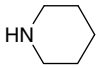
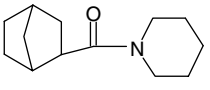
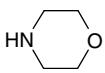
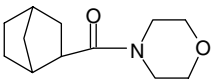
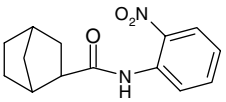
2.2. Conditions for the acylation reactions

When the formation of an acylium salt was over, an amine ([1–4]):[E] was added to the reaction mixture at the same temperature. Then the temperature of the reaction mixture was allowed to warm to 20 °C. After 0.5 h, ether was added to the reaction mixture under cooling. The reactions of the in situ generated RCO^+ with *o*-nitroaniline were carried out at 0 °C for 4 h (R = *cyclo*-C_5H_9) and at 35 °C for 1 h (R = C_7H_{11}, norbornyl). Then water was added dropwise. After ether or $CHCl_3$ extraction, washing the organic layer with water and drying with $MgSO_4$, the products were analyzed by GC and GC–MS methods. The structures of the amides were proved by ^{1}H and ^{13}C NMR, GC and GC–MS, and in some cases by elemental analysis.

Typical procedures:

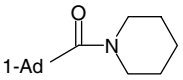
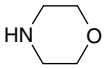
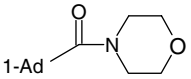
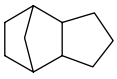
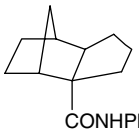
- A solution of tetrabromomethane (0.49 g, 1.48 mmol) and anhydrous aluminum bromide (0.68 g, 2.5 mmol) in anhydrous CH_2Br_2 (2 ml) was stirred at −20 °C under a C_3H_8/CO (3:2) gas atmosphere, $P = 1$ atm for 2 h. Then piperidine 0.42 g (4.9 mol) was added under the same conditions. The reaction mixture was left to warm up to 0 °C. Then ether and water were carefully added to the reaction mixture under cooling. After ether extraction, washing the organic layer with water, and drying with $MgSO_4$, the products were analyzed by GC and GC–MS and NMR methods. Yield of amide (**1**) was 0.16 g (70%). Spectra are presented in Supplementary data.
- To a stirred solution of tetrabromomethane (0.82 g, 2.47 mmol) and aluminum bromide (1.33 g, 4.99 mmol) in anhydrous CH_2Br_2 (2.5 ml), pentane (2.7 ml, 24.9 mmol) was added at −20 °C under atmospheric

Table 1
One-pot synthesis of amides from alkanes (cycloalkanes), CO and amines in the presence of superelectrophiles (E)[a]

Entry	RH	Amine	Product		Yield (%)[b]
1	C_3H_8			(**1**)	70
2		Et_2NH	*i*-$PrCONEt_2$	(**2**)	69
3	*n*-C_5H_{12}	Et_2NH	*tert*-$C_5H_{11}CONEt_2$	(**3**)	66
4				(**4**)	80
5				(**5**)	69
6		$PhNH_2$		(**6**)	54
7		Et_2NH		(**7**)	77
8				(**8**)	100[c]
9				(**9**)	66
10		$PhNH_2$		(**10**)	40
11		*o*-$NH_2C_6H_4NO_2$		(**11**)	100
12		Et_2NH		(**12**)	98
13				(**13**)	96
14				(**14**)	72
15[d]		*o*-$NH_2C_6H_4NO_2$		(**15**)	75

(*continued on next page*)

Table 1 (*continued*)

Entry	RH	Amine	Product		Yield (%)[b]
16		Et_2NH	1-AdCONEt$_2$	(**16**)	77
17				(**17**)	65
18				(**18**)	48
19		$PhNH_2$	1-AdCONHPh	(**19**)	60
20		$PhNH_2$		(**20**)	76

[a] E = CX_4·2$AlBr_3$ (solvent CH_2X_2; X = Br, Cl). E = CBr_4·2$AlBr_3$ (runs 1–11) and CCl_4·2$AlBr_3$ (runs 12–20); solvent CH_2X_2 (X = Br, Cl).
[b] Yields are given accordingly to GC.
[c] 56% yield was obtained in reaction **8** with CBr_4·1.5$AlBr_3$.
[d] The reactions with *o*-nitroaniline were carried out at 0 °C for 4 h (run 11) and at 35 °C for 1 h (run 15).

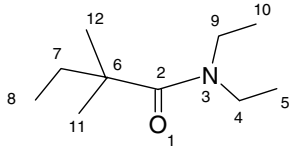
CO pressure. The mixture was stirred for 0.5 h and then morpholine (0.65 g, 7.5 mmol) was added under the same conditions. After stirring for 30 min at −20 °C, the reaction mixture was allowed to warm up to 20 °C. All procedures were carried out under a CO atmosphere. Similar to the protocol described for (**1**), 0.32 g (69%) of amide (**5**) was prepared. Spectral data are given below.

- To a stirred solution of tetrachloromethane (0.3 g, 1.95 mmol) and aluminum bromide (1.06 g, 3.97 mmol) in anhydrous CH_2Br_2 (2 ml), norbornane (0.266 g, 1.95 mmol) was added at 0 °C under atmospheric CO pressure. The mixture was stirred for 1 h and then piperidine (0.68 g, 8 mmol) was added under the same conditions. After stirring for 30 min at 0 °C, the reaction mixture was allowed to warm up to 20 °C. All procedures were carried out under a CO atmosphere. After usual workup, 0.46 g (96%) of amide (**13**) was obtained. Spectral data for (**13**) are given below.
- To a stirred solution of tetrachloromethane (0.75 g, 4.88 mmol) and aluminum bromide (2.6 g, 9.75 mmol) in anhydrous CH_2Br_2 (5.2 ml), trimethylenenorbornane (0.66 g, 4.85 mmol) was added at 10 °C under atmospheric CO pressure. The mixture was stirred for 2 h and then aniline (1.5 ml) was added under the same conditions. After stirring for 30 min at 10 °C, the reaction mixture was allowed to warm up to 20 °C. All procedures were carried out under a CO atmosphere. After workup of water and extraction with $CHCl_3$, the organic extract was washed with 5% HCl, then by $NaHCO_3$ aqueous solution, organic solution was dried over $MgSO_4$, and 0.46 g (96%) of amide (**20**) was obtained. Data for (**20**) are presented below.

Spectra for amides 1, 2, 4, 6, 7, 9–12, 14–19 are given in Supplementary data.

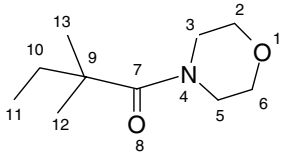
Selected spectral data:

$Me_2C(Et)CONEt_2$ **3**



NMR: ^{1}H: 0.65 (t, 3H, $^3J_{HH}$ = 7.5, $^8CH_3$); 0.92 (t, 6H, $^3J_{HH}$ = 7.0, $^{5,10}CH_3$); 1.03 (s, 6H, $^{11,12}CH_3$); 1.40 (q, 2H, $^3J_{HH}$ = 7.5, $^7CH_2$); 3.18 (br s, $^{4,9}CH_2$). ^{13}C: 8.9 (^{8}C), 12.88 (^{5,10}C); 26.22 (^{11,12}C); 32.8 (^{4,9}C); 40.9 (^{7}C); 42.4 (^{6}C); 174.9 (^{2}C). MS: 171, M^+ (14); 156, M^+-CH_3 (8); 143, $M^+-C_2H_4$ (3); 142, $M^+-C_2H_5$(4); 129, $M^+-C_3H_6$ (7); 128, $M^+-C_3H_7$ (2); 115, $M^+-C_4H_8$ (4); 114, $M^+-C_4H_9$ (3); 102, $M^+-C_6H_9$ (12); 101 (7); 100, NEt_2CO^+ (100); 95 (1); 86 (4); 72, NEt_2^+ (57); 71, $C_5H_{11}^+$ (69); 70 (13); 69 (6); 58 (30); 56 (18); 55, (21); 54 (4); 53 (5).

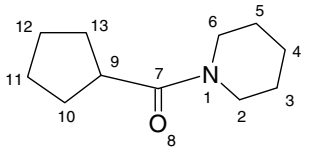
$Me_2C(Et)CONC_4H_8O$ **5**



NMR: ^{1}H: 0.82 (t, 3H, $^3J_{HH}$ = 7.4, $^{11}CH_3$); 1.17 (s, 6H, $^{12,13}CH_3$); 1.54 (q, 2H, $^3J_{HH}$ = 7.3, $^{10}CH_2$); 3.58 (m, 8H, $^{2,3,5,6}CH_2$). ^{13}C: 8.99 (^{11}C); 26.0 (^{12,13}C); 32.7 (^{10}C); 42.40 (^{9}C); 45.15 (^{3,5}C); 66.44 (^{2,6}C); 175.06 (^{7}C). MS: 185, M^+ (25); 170, M^+-CH_3(14); 157, $M^+-C_2H_4$ (14); 156, $M^+-C_2H_5$ (3); 145 (17); 144, M-$C_3H_5^+$ (4); 129, $M^+-C_4H_8$

(10); 128, $M^+-C_4H_9$ (5); 117 (2); 116, $M^+-C_5H_9$ (36); 114, $M^+-C_5H_{11}$ (10); 113, $M^+-C_4H_8O$ (75); 100, (2); 99, $C_5H_{11}CO^+$ (3); 98 (1); 95 (2); 88 (9); 87, $C_4H_9NO^+$ (24); 86, $C_4H_8NO^+$ (30); 85 (4); 84 (2); 83 (8); 72, $C_4H_8O^+$ (13); 71, (100); 69, $C_5H_9^+$ (12); 68 (8); 67 (15); 68 (1); 67 (1); 59 (2); 58 (4); 57 (44); 56 (25); 55 (28); 54 (4); 53 (4).

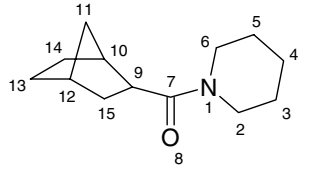
cyclo-$C_5H_9CONC_5H_{10}$ **8**



NMR: ^{1}H: 1.3–1.7 (m, 14H, $^{3\text{–}5,10\text{–}13}CH_2$); 2.74 (quin, $^3J_{HH} = 8$, ^9CH); 3.35 (m, 4H, $^{2,6}CH_2$).

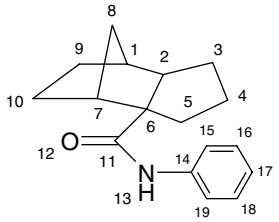
^{13}C: 24.17 (^{3,4,5}C); 25.51 (^{11,12}C); 29.61 (^{10,13}C); 40.49 (^{9}C); 65.37 (^{2,6}C); 173.65 (^{7}C). MS: 181, M^+ (52); 153, $M^+-C_2H_4$ (15); 152, $M^+-C_2H_5$ (8); 141 (16); 140, $M^+-C_3H_5$ (98); 139 (2); 138, $M^+-C_3H_7$ (17); 124, $M^+-C_4H_9$ (2); 114 (5); 113 (5); 112, $M^+-C_5H_9$ (36); 111 (2); 110 (3); 98 (2); 97, $C_5H_9CO^+$ (6); 96 (5); 95 (3); 86 (13); 85 (27); 84, $C_5H_{10}N^+$ (58); 83 (9); 82 (4), 70 (15); 69, $C_5H_9^+$ (100); 68 (10); 67 (14); 66 (2); 65 (3); 58 (2); 57 (8); 56 (23); 55 (30); 54 (7); 53 (8).

2-$C_7H_{11}CONC_5H_{10}$ **13**



NMR: ^{1}H: 1.34–1.53 (m, 12H, $^{3\text{–}5,11,13,14}CH_2$); 1.78 (m, 1H, $^{15}CH_2$); 2.18 (m, 1H, ^{12}CH); 2.27 (m, 2H, ^{10}CH, $^{15}CH_2$); 3.34 (m, 3H, ^9CH, $^{2,6}CH_2$); 3.48 (m, 2H, $^{2,6}CH_2$). ^{13}C: 24.41 (^{4}C); 25.36 (^{5}C); 26.19 (^{3}C); 28.66 (^{14}C); 29.17 (^{13}C); 34.70 (^{15}C); 35.67 (^{12}C); 36.47 (^{11}C); 40.24 (^{10}C); 42.52 (^{2}C); 43.93 (^{9}C); 46.06 (^{6}C); 173.33 (^{7}C). MS: 207, M^+ (26); 192, M^+–Me (1); 179, $M^+-C_2H_4$ (5); 1, M-$C_5H_7^+$ (100); 138 (6); 127 (6); 123 (2); 122 (3); 113, M^+-$C_7H_{10}^+$ (3); 112, M^+-$C_7H_{11}^+$ (27); 110 (1); 98 (1); 96 (4); 95 (42); 94 (2); 93 (6); 91 (3); 84, $C_5H_{10}N^+$ (28); 83 (9); 82 (3); 81 (3); 79 (6); 77 (4); 70 (3); 69 (17); 68 (4); 67, $C_5H_7^+$ (16); 66 (7); 65 (5); 57 (3); 56 (11); 55 (18); 54 (3).

2-$C_{10}H_{15}CONHC_6H_5$ **20**



NMR: ^{1}H: 1.2–1.7 (m, 12H, $^{3\text{–}5,8\text{–}10}CH_2$); 2.03 (t, 2H, $^3J_{HH} = 7.7$, $^{1,2}CH_2$); 2.52 (m, 1H, ^7CH); 7.06 (t, 1H, $^3J_{HH} = 7.7$, ^{17}CH); 7.15 (br s, 1H, ^{13}NH); 7.30 (t, 2H, $^3J_{HH} = 7.7$, $^{16,18}CH$); 7.51 (d, 2H, $^3J_{HH} = 7.7$, $^{15,19}CH$). ^{13}C: 25.27 (^{9}C); 26.09 (^{10}C); 27.63 (^{3}C); 32.84 (^{5}C); 35.03 (^{4}C); 38.83 (^{8}C); 41.61 (^{1}C); 44.55 (^{7}C); 48.89 (^{2}C); 64.17 (^{6}C); 119.61 (^{15,19}C); 123.77 (^{17}C); 128.86 (^{16,18}C); 138.27 (^{14}C); 175.40 (^{11}C). MS: 255, M^+ (26); 187, $M^+-C_5H_8$ (52); 163, $M^+-C_6H_5NH$; 136 (13); 135, Ad^+, (100); 121, $C_9H_{13}^+$, (14); 120, $M^+-C_{10}H_{15}$ (7); 119, $M^+-C_{10}H_{16}$ (7); 107, $C_8H_{11}^+$, 94 (12); 93, $C_6H_5NH_2^+$, (65); 91, $C_6H_5N^+$ (20); 83 (25); 81 (8); 79 (23); 77 (20); 67 (20); 65 (11). Yield = 89%, mp 138–139°, elemental analysis calc. for $C_{17}H_{21}ON$ ($M = 255.36$): C, 79.96; H, 8.29; N, 5.48; found C, 79.92; H, 8.36; N, 5.49.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2007.12.070.

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