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The First Examples of Selective Carbonylation of n-Butane and n-Pentane

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Abstract: The polyhalomethane based superelectrophilic systems allowed us to accomplish the first efficient and selective carbonylation of n-butane and n-pentane with CO. Depending on the nature of the superelectrophilic system, Me_3CCOOR or EtCH(Me)COOR (R = H, Alk) can be obtained at -20°C, 1 atm from n-butane and CO after water (or alcohol) treatment in ≈ 90% yield based on the superelectrophilic system. Pentane reacts with CO in the presence of the CBr_4•$2AlBr_3$ superacid to give a single product, $EtC(Me)_2COOR$, in almost quantitative yield.

Selective functionalization of alkanes and cycloalkanes is one of the most important and challenging problems in organic chemistry. The complexity of this task is due to the inertness of this class of compound whose reactions occur only under the action of hard reagents or under severe conditions. Therefore, no examples have been reported on the selective carbonylation of butane and pentane to date. Recently we found that polyhalomethane based superelectrophilic systems[1,2] initiate various functionalization reactions of alkanes and cycloalkanes, including selective carbonylation of propane,[3] cyclopentane,[4] cyclohexane and methylcyclopentane,[5] as well as formylation of adamantane[6] with CO in organic media under mild conditions.

This paper reports the first examples of facile, selective carbonylation of n-butane and n-pentane with CO in the presence of CX_4•$nAlBr_3$ (X = Br or Cl; n = 2 or 3) in CH_2Br_2 solution.

n-Butane reacts with an atmospheric pressure of CO in the presence of CBr_4•$2AlBr_3$ at -20°C for 0.5h to give, after treatment with water or alcohol, the pivaloyl acid **1** (or its ester) in 84% yield based on CBr_4•$2AlBr_3$ (Table 1). In addition, 2-methylbutanoic acid **2** (or its ester) is formed in 16% yield (**Scheme 1**). As before, although the yields of **1** in the reactions at 0°C are high and amount to 60-82%, the selectivity of product **1** formation strongly decreases. In some cases, at 0°C the quantities of **1** and **2** are close. This can be due to both the shift of the equilibrium $^{tert}Bu^+ \rightleftharpoons {}^{sec}Bu^+$ to the right and acceleration of the $^{tert}BuCO^+$ decarbonylation rate with temperature increase:[10]

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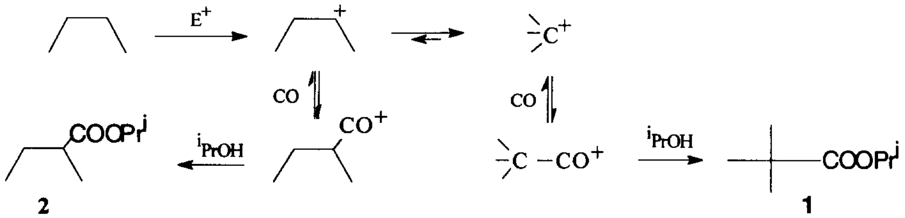


Scheme 1.

Table 1. Carbonylation of n-butane and n-pentane with CO catalyzed by polyhalomethane-AlBr$_3$ aprotic organic superacids under mild conditions.[7]

Run	Superacid	Alkane	Carbonylation conditions			Products (after ^{i}PrOH work-up),[8] mol. % based on superacid	
			T, °C	t, h	[AlBr$_3$], g/ml		
						^{tert}BuCOOPr^i (**1**)	^{sec}BuCOOPr^i (**2**)
1	CBr$_4$•2AlBr$_3$	n-Butane	-20	0.5	0.6	84	16
2	CBr$_4$•2AlBr$_3$		-20	1	0.9	68	35
3	Al$_2$Br$_6$		-20	1	0.9	0	0
4	CBr$_4$•2AlBr$_3$		0	0.5	0.6	75	58
5	CBr$_4$•3AlBr$_3$		-20	0.5	0.66	73	42
6	CBr$_4$•3AlBr$_3$		0	0.5	1.2	40	105
7	CCl$_4$•2AlBr$_3$		-20	2	0.6	11	47
8	CCl$_4$•2AlBr$_3$		0	1	0.52	35	47
9	CCl$_4$•3AlBr$_3$		-20	0.5	0.63	20	86
10	CCl$_4$•3AlBr$_3$		-20	1	1.3	28	74
						Et(Me)$_2$CCOOPr^i (**3**)*	
11	CBr$_4$•2AlBr$_3$	n-Pentane	-20	0.5	0.66	100	
12	CBr$_4$•2AlBr$_3$		0	0.5	0.66	77	
13	CCl$_4$•2AlBr$_3$		-20	1.0	0.66	15	
14	CCl$_4$•2AlBr$_3$		0	0.5	0.66	54	
15	CCl$_4$•3AlBr$_3$		-20	1.0		112	
						EtCOOH - AmCOOH mixture	
16	HF-SbF$_5$	n-Pentane	30	1		53[9]	

*) In addition, small amounts of 2:1 mixture of **4** and **5** esters are formed in <1 - 7% total yield

The CCl$_4$•2AlBr$_3$ system is noticeably less active in butane carbonylation, while Al$_2$Br$_6$ in CH$_2$Br$_2$ solution is completely inert. Moreover, with CCl$_4$•2AlBr$_3$ as a superelectrophilic system, ester **2** becomes the main carbonylation product, and this tendency increases on passing from CCl$_4$•2AlBr$_3$ to CCl$_4$•3AlBr$_3$. Importantly, at -20°C in the presence of CCl$_4$•3AlBr$_3$ product **2** can be obtained in *ca.* 90% yield (together with small amounts of product **1**) (Table 1, run 9).

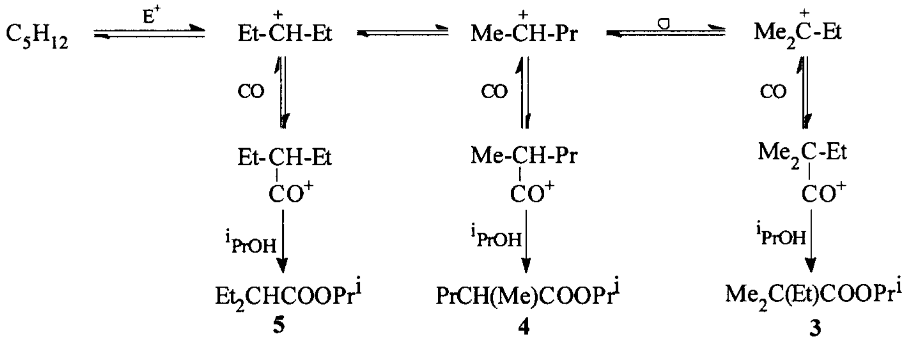
This fact is, probably, due to the increase in the decarbonylation rate of the less stable $^{tert}BuCO^+$ cation in the presence of excess of aluminum bromide. Consequently, the accumulation of the less stable $^{sec}Bu^+$ cation and finally more stable $^{sec}BuCO^+$ cation occurs.

Note that the overall yield of (**1** + **2**) mixture at 0°C reaches 1.45 mole per mole of $CBr_4{\bullet}3AlBr_3$. It means that the activity of the system is retained after reduction of the initial $CBr_4{\bullet}3AlBr_3$ complex into $CHBr_3{\bullet}3AlBr_3$.

$$
\begin{aligned}
CX_4 &\xrightarrow{nAlX_3} CX_3^+ \\
RH + CX_3^+ &\longrightarrow R^+ + CHX_3 \\
CHX_3 &\xrightarrow{nAlX_3} CHX_2^+ \\
RH + CHX_2^+ &\longrightarrow R^+ + CH_2X_2
\end{aligned}
$$

It is important that the production of **1** and **2** can be controlled in favour of the former or the latter in good yields by the nature of the superelectrophilic system.

n-Pentane also readily reacts with CO (**Scheme 2**) in the presence of $CBr_4{\bullet}2AlBr_3$ at -20°C to afford (after the reaction with ^iPrOH) $Et(Me)_2CCOOPr^i$ (**3**) as virtually a single product in almost quantitative yield (Table 1). At 0°C, somewhat lower yields of **3** are observed but still with high selectivity ($\geq$ 95%). Note that $CCl_4{\bullet}3AlBr_3$ is very effective in pentane carbonylation at -20°C (Table 1).



Scheme 2.

Highly selective formation of **3** indicates that the equilibrium $^{sec}Am^+ \rightleftharpoons {}^{tert}Am^+$ is almost completely shifted to the right. By contrast, in a $HF\text{-}SbF_5$ medium, pentane reacts with CO to form a complex mixture of carboxylic acids in overall yield of ca. 50%[9] (run 16).[11]

Note that the previously described electrophilic transformations of butane with CO[12] or $^{tert}BuCOCl$[13] in the presence of a large excess of aluminum chloride and a hydride donor, leading to the formation of ^iPrCOMe and $BuCOBu^i$ ketones, do not occur under our conditions. .The capability of polyhalomethane based superacids to perform, at -20°C, selective carbonylation of n-butane and particularly n-pentane into tertiary carboxylic acids (or their esters) after water (or alcohol) treatment is probably due to the capability of these very strong superelectrophilic systems to initiate rapid generation of butyl and amyl cations[1] and their isomerization into stable tertiary R^+. As a result, the accumulation of the most stable $^{tert}R^+$ and then $^{tert}RCO^+$ (R = Bu, Am) cations occurs. Importantly, these tert-acylium cations are formed under the conditions in which they are rather stable to decarbonylation.[10,14]

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7. The solution of polyhalomethane and aluminum bromide in methylene bromide was frozen down to -20°C, a ten-fold excess of liquid n-butane was condensed into the solution and then the reaction flask was filled with gaseous CO. The mixture was allowed to reach reaction temperature and stirred vigorously under slightly excessive pressure of CO. Then, an excess of ^iPrOH (~5ml / g $AlBr_3$) was carefully added, reaction mixture was left to warm up to room temperature and then stirred during additional 30 min. After water workup and extraction with ether, reaction products were analyzed by GC and GC-MS with undecanone-2 as internal standard.
8. **1**, ^1H NMR: 1.15 (9H, s), 1.20 (6H, d, J = 6.3), 4.92 (1H, sept, J = 6.3); MS (m/z, (I_{rel}, %)): 144 (2), 129 (5), 103 (35), 101 (5), 87 (25), 85 (62), 71 (6), 59 (51), 57 (100), 56 (43); **2**, ^1H NMR: 0.89 (3H, t, J = 7.4), 1.09 (3H, d, J = 7.0), 1.21 (6H, d, J = 6.3), 1.43 (1H, m), 1.63 (1H, m), 2.29 (1H, m), 4.96 (1H, sept, J = 6.3); MS: 144 (1), 129 (5), 116 (22), 103 (43), 102 (14), 87 (19), 85 (76), 74 (45), 59 (30), 57 (100), 56 (48); **3**, MS: 158 (4), 143 (13), 130(47), 117 (56), 99 (82), 88 (71), 87 (39), 73 (20), 72 (70), 71, (100), 59 (53).
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11. Hogeveen[10] et al. showed that tertiary and secondary butylacylium cations interconvert much more slowly than the homologous pentyl cations. Indeed, the activation barrier for the transformation of the $^sBu^+$ into the $^tBu^+$ is 15.4 kcal/mol, while the relative value for transformaton of the $^iPrCH^+Me$ into the $^tC_5H_{11}^+$ amounts to only 2 kcal/mol. In addition (at 300K) K = i-BuH/n-BuH is 4.5, while K = i-AmylH/n-AmylH is 13.0.[15] The observed difference in butane and pentane carbonylation can be realized as follows. The rapid equilibrium $^sAmyl^+ \rightleftharpoons {}^tAmyl^+$ is reached and the $^tAmyl^+$ is practically the sole cation in the reaction mixture when pentane is treated with the superelectrophile system. In the case of butane carbonylation the corresponding equilibrium is not reached. In this context, the formation of $Me_3C_6H_2C(Et)Me_2$ as a sole product was observed by us when the reaction mixture was treated with mesitylene instead of alcohol. On the contrary, the work up of butane carbonylation products with arenes (instead of alcohols) led to BuCOAr containing predominantly the secondary butyl group.
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