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The first efficient electrophilic carbonylation of ethane with carbon monoxide

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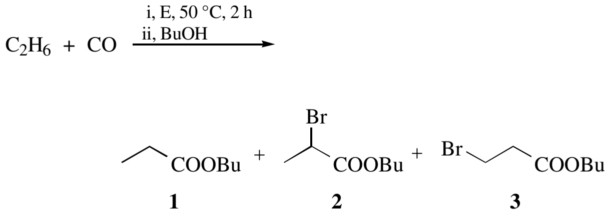
Ethane reacts with CO without solvent in the presence of polyhalomethane·2AlBr$_3$ superelectrophilic systems to form EtCOOR after alcoholysis together with small amounts of corresponding esters of 1- and 2-bromopropanoic acids.

Ethane is the second alkane to methane in both inertness and abundance in natural gas. Therefore, the development of direct methods for ethane functionalization is one of the most important problems in the chemistry of alkanes.

Among the numerous examples of electrophilic carbonylation of saturated hydrocarbons (mainly by HX–AlCl$_3$ at elevated temperature and pressure with protic superacids under ambient conditions), only a very limited number of selective reactions have been described (see refs. 1–6 and references therein). These are reactions of propane (in the presence of polyhalomethane-containing promotors)[3] and carbonylation of C$_5$–C$_6$[7] cycloalkanes, all in HF–SbF$_5$ media. The polyhalomethane-based superelectrophilic systems were found to be good initiators for selective carbonylation of propane,[8] butane and pentane,[9] as well as C$_5$–C$_6$[10] cycloalkanes in organic media. These reactions occur probably *via* the Koch–Haaf mechanism involving the generation of carbocations followed by CO trapping to give acylium cations.[11] The electrophilic carbonylation of ethane has not been reported earlier. On the contrary, catalytic carbonylation of methane, ethane, propane (nonselective) and cyclohexane in CF$_3$COOH in the presence of a Pd(OAc)$_2$ + CuCl$_2$ mixture and K$_2$S$_2$O$_8$ as an oxidant was performed.[12] These reactions were carried out at 80 °C for 20 h and required large amounts of K$_2$S$_2$O$_8$ and CF$_3$COOH. For example, 100 g of Pd(OAc)$_2$, 150 g of Cu(OAc)$_2$, 8 kg of K$_2$S$_2$O$_8$ and 17 dm^3 of trifluoroacetic acid are needed to obtain 1 kg of EtCOOH.[12]

We report the first example of the efficient electrophilic carbonylation of ethane with CO. At 50 °C, ethane reacts with CO in the presence of polyhalomethane–AlBr$_3$ superelectrophilic systems to form EtCOOBu **1** after treatment of the reaction mixture with *n*-butanol (Scheme 1).†



E = CBr$_4$·2AlBr$_3$, CCl$_4$·3AlBr$_3$, CHCl$_3$·3AlBr$_3$

Scheme 1

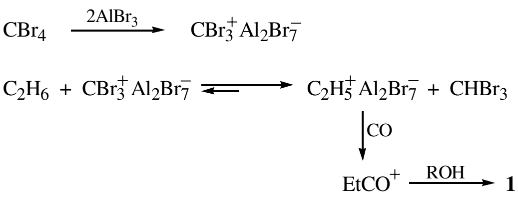
With CBr$_4$·2AlBr$_3$ superacid as a promoter, the yield of **1** is 86% on a superelectrophile basis after 2 h (Table 1). In addition, esters **2** and **3** of 1- and 2-bromopropanoic acids are formed as by-products. The overall yields of ethane carbonylation products **1**–**3** are close to quantitative values with respect to the superelectrophile. Interestingly, under similar conditions, 50–60% yields of **1** can be achieved using CCl$_4$·3AlBr$_3$ and CHCl$_3$·3AlBr$_3$, while AlBr$_3$ in CH$_2$Br$_2$ is completely inactive. In the case of CHCl$_3$·3AlBr$_3$, the ethane carbonylation occurs with a very high selectivity, although the yield of **1** is lower. The yields of **1** in the presence of the CBr$_4$·2AlBr$_3$ system strongly depend on temperature and the CO/C$_2$H$_6$ ratio (m). Higher yields of **1** were obtained at 50 °C. On going from $m = 1$ to $m = 2.2$, the yields of **1** considerably increase, while they fall down at $m = 3$ (Table 1). The yields and selectivities of formation of **1** also decrease on going from the hardest CBr$_4$·2AlBr$_3$ system to the milder CCl$_4$·3AlBr$_3$ and CHCl$_3$·3AlBr$_3$ systems.

Table 1 Carbonylation of ethane with CO initiated by polyhalomethane-based superelectrophiles (E) at 50 °C.

Run	E	P_{CO}	$P_{C_2H_6}$	CO:C$_2$H$_6$:E	t/h	Products (mol%) 1	2	3
1[a]	CBr$_4$·2AlBr$_3$	20	20	1:1:0.05	3	35	6	6
2[a]	CBr$_4$·2AlBr$_3$	45	20	2.2:1:0.05	3	66	10	4
3[a]	CBr$_4$·2AlBr$_3$	48	16	3:1:0.06	3	58	8	3
4	CBr$_4$·2AlBr$_3$	15	10	1.5:1:0.2	1	20	7	1
5	CBr$_4$·2AlBr$_3$	45	20	2.2:1:0.05	1	37	4	1
6	CBr$_4$·2AlBr$_3$	45	20	2.2:1:0.05	2	86	6	traces
7	CBr$_4$·2AlBr$_3$	48	16	3:1:0.05	3	47	6	2
8	CBr$_4$·3AlBr$_3$	45	20	2.2:1:0.05	2	82	12	2
9	CBr$_4$·AlBr$_3$	45	20	2.2:1:0.1	2	17	22	2
10	CCl$_4$·3AlBr$_3$	45	20	2.2:1:0.04	2	61	8	2
11	CCl$_4$·3AlBr$_3$	42	18	2.3:1:0.06	2	46	18	7
12	CHCl$_3$·3AlBr$_3$	42	18	2.3:1:0.06	1	50	traces	traces
13	CH$_2$Br$_2$·2AlBr$_3$	45	20	2.2:1:0.05	2	traces	0	0

[a]The reactions were carried out at 65 °C.

The proposed scheme of the ethane carbonylation involves generation of the ethyl cation followed by CO trapping to form the EtCO$^+$ cation and, finally, EtCOOR **1** (Scheme 2). An increase in both the superelectrophile strenght and the CO/C$_2$H$_6$ ratio (within a certain range) is favourable to the generation of the ethyl cation and its addition to a CO molecule. For elucidation of the mechanism of formation of bromine-containing products **2** and **3**, a further study is required.



Scheme 2

Thus, the new superelectrophilic systems allowed us to perform the efficient one-pot functionalization of ethane, which is an inert alkane.

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† *General procedure.* To form a homogeneous liquid system, a mixture of appropriate amounts of AlBr$_3$ and a polyhalomethane was heated and stirred without solvent in a 50 ml stainless steel autoclave (Parr Instrument Co.) at 80 °C for 5 min. After cooling to 50 °C, ethane and CO were supplied to the autoclave, and the reaction mixture was heated and stirred at 50 °C. After completion of the reaction, *n*-butanol was added at room temperature. The resulting mixture was poured into water, extracted, washed, dried and analysed by GC and GC–MS.

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