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LETTERS TO THE EDITOR

Catalytic Synthesis of Polyfluoroalkyl Chloroformates

A. I. Rakhimov, L. A. Butkovskaya, and A. V. Baklanov

Volgograd State Technical University
pr. Lenina 28, Volgograd, 300131 Russia
e-mail:organic@vstu.ru

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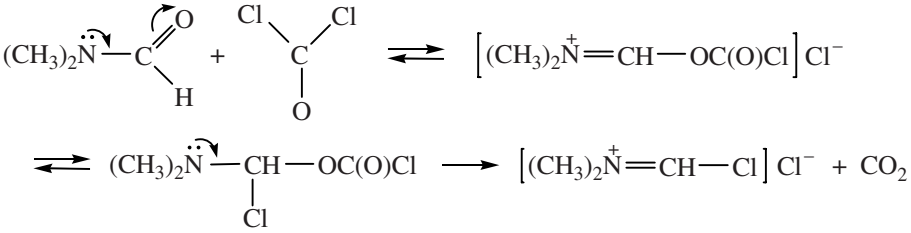
The aliphatic alcohols eagerly react with phosgen even at low temperatures. When the alcohol excess is avoided and the alcohol is added to phosgen alkyl chloroformates R–O–C(O)Cl are formed in high yields.

The noncatalysed reaction with phenols and polyfluoroalcohols R_FOH due to their low nucleophilicity proceeds significantly slower, and the target products are formed in low yields. For example, when polyfluorinated alcohols are reacted with phosgen at 4–12°C for 3 h the corresponding chloroformates R_F–O–C(O)Cl are formed in 43–68% yield [1]. We have found that for accelerating this reaction and improving yield of the fluorine-containing chloroformates the nitrogen-containing catalysts can be used, in particular, N,N-disubstituted amides.

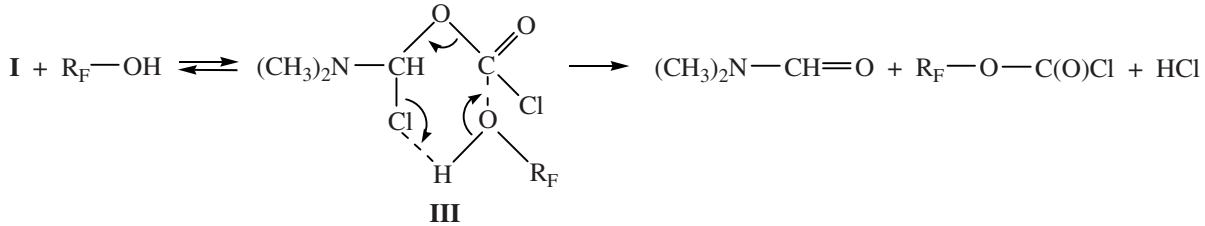
According to modern views [2] on the mechanism of the reaction of N,N-disubstituted amides with Lewis acids (including phosgen) a highly reactive intermediate **I** is formed in the first step that loosing CO_2 converts to chloromethylenedimethyliminium chloride **II**.



I **II**

If the treatment with phosgen is carried out under the constant presence in the reaction mixture of polyfluorinated alcohol the intermediate **I** reacts with it without CO_2 elimination to form complex **III** whose subsequent transformation leads to the formation of chloroformate and hydrogen chloride and to the regeneration of the catalyst.

We have found that *N,N*-dimethylformamide exhibits the highest catalytic effect in the synthesis of poly-



III

fluorinated alkyl chloroformates [$R_f = X(CF_2)_nCH_2$, X = H or F, n = 1, 2, 4,6].

The treatment with phosgen of polyfluorinated alcohols in the presence of DMF increased the yield of polyfluorinated chloroformates to 90%, and therewith the phosgen consumption decreased three times and the use of diethyl ether as solvent was unnecessary. The smallest amount of DMF exhibiting the noticeable catalytic effect is 0.01 mol/mol of alcohol. Under these conditions the yield of polufluorinated chloroformate is 70%. At the DMF content 0.05 mol/mol of alcohol the yield increases to 86%, and when the amount of catalyst is 0.07 mol/mol of alcohol the 90% yield of chloroformate is achieved. Further increase in the DMF content does not affect the yield of the target product. The optimal reaction conditions are as follows: the alcohol : phosgen : catalyst ratio 1:1.2:0.05, the starting reaction temperature 0°C, the final reaction temperature 90°C, the reaction time 2.5 h.

It cannot be excluded that high catalytic activity of DMF is due to its ability to form stable associates with polyfluorinated alcohols [3] resulting in the polarization of O–H bond of the alcohol that facilitates the nucleophilic substitution of chlorine in phosgen with polyfluoroalkoxy group.

1,1,3-Trihydroperfluoropropyl chloroformate (X = H, *n* = 2). A mixture of 33.0 g of 1,1,3-trihydroperfluoropropanol and 0.57 g of DMF was cooled to 0°C and 14.85 g of liquid phosgen was added to it. After that the reaction mixture was heated to 90°C and the additional 14.85 g of gaseous phosgene was passed through it in the course of 2.5 h. The target product, 43.8 g (93%), was formed, bp 35°C (32 mm Hg), n_D^{20} 1.3520, d_4^{20} 1.5179. The other chloroformates were prepared analogously.

1,1-Dihydroperfluoropropyl chloroformate (X = F, *n* = 1). Yield 90%, bp 40°C (165 mm Hg), n_D^{20} 1.3210, d_4^{20} 1.4896.

1,1,5-Trihydroperfluoropentyl chloroformate (X = H, *n* = 4). Yield 90%, bp 50°C (11 mm Hg), n_D^{20} 1.3376, d_4^{20} 1.6475.

1.1-Dihydroperfluoropentyl chloroformate (X = F, *n* = 4). Yield 88%, bp 36°C (15 mm Hg), n_D^{20} 1.3182, d_4^{20} 1.6200.

1,1-Dihydroperfluoroheptyl chloroformate (X = F, *n* = 6). Yield 88%, bp 59°C (13 mm Hg), n_D^{20} 1.3188, d_4^{20} 1.7105.

1,1,7-Trihydroperfluoroheptyl chloroformate (X = H, *n* = 6). Yield 87%, bp 63°C (3 mm Hg), n_D^{20} 1.3338, d_4^{20} 1.7240.

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