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O.N. Chupakhin on his 70th Anniversary

Synthesis of Esters in the Presence of Chlorosilanes

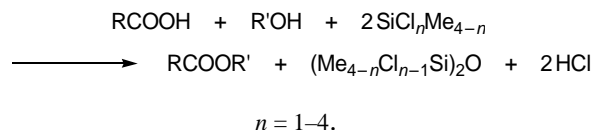
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Abstract—Esterification of various carboxylic acids with primary alcohols in the presence of chloro(methyl)-silanes provides a simple and convenient synthetic route to esters.

Carboxylic acid esters constitute an important class of organic compounds; they are involved in a number of chemical reactions [1]. Nacao *et al.* [2] used chlorosilanes to convert carboxylic acids into the corresponding esters. The reactions were carried out with 0.5 equiv of chlorosilane. However, the scheme given below shows that 2 equiv of chlorosilane is required to complete the process. By reaction of oleic acid with ethanol under the conditions described in [2] we obtained only 16% of ethyl oleate.



In the present work we compared for the first time the reactivity of chlorosilanes and examined the effect of the carboxylic acid and alcohol structure on the esterification process. As a result, we developed a simple and convenient procedure for the synthesis of a number of esters. The reactions were performed by heating a mixture of the reactants for 1–1.5 h at the boiling point. The molar ratio carboxylic acid–chlorosilane–alcohol was 1:3.5:5. This reactant ratio allowed us to use even water-containing alcohols, e.g., rectified ethanol. The products were isolated by distillation. In reactions with anhydrous alcohols, the amount of chlorosilane can be reduced, but it should be no less than 2 equiv, otherwise the yield decreases.

The effect of chlorosilane nature was examined in the synthesis of ethyl benzoate as an example. The yields of ethyl benzoate were 50, 68, 72, and 86%,

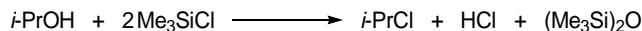
respectively, in the presence of SiCl_4 , SiCl_3Me , SiCl_2Me_2 , and SiClMe_3 . It is seen that the yield of ethyl benzoate depends on the number of chlorine atoms in the chlorosilane. The highest yield was obtained with chlorotrimethylsilane, while in the case of tetrachlorosilane the yield was the lowest. These findings indicate that intermediate product is not benzoyl chloride (in this case, tetrachlorosilane would be the most efficient) but the corresponding silyl ester.

Table contains the results of esterification of various carboxylic acids with lower alcohols in the presence of chlorotrimethylsilane. Here, the alcohol structure was crucial. The esterification of benzoic acid was successful only with unbranched alcohols: no respective ester was obtained in the reaction with 2-propanol. Presumably, the latter reacted with chlorotrimethylsilane to afford isopropyl chloride which was detected in the distillate. The same factor is likely to be

Synthesis of esters RCOOR' in the presence of chlorotrimethylsilane

R	R'	Yield, %
$\text{CH}_3(\text{CH}_2)_{10}$	C_2H_5	72
$\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7$	C_2H_5	57
$\text{C}_6\text{H}_9(\text{CH}_3)_2\text{C}$	C_2H_5	73
C_6H_5	CH_3	71
C_6H_5	C_2H_5	86
C_6H_5	C_4H_9	76
C_6H_5	<i>iso</i> - C_3H_7	0
$\text{C}_6\text{H}_5\text{CH}_2$	C_2H_5	93
3-Indenyl	C_2H_5	50

responsible for decrease in the yield of esters in going from chlorotrimethylsilane to tetrachlorosilane.



Our results show that almost any carboxylic acid can be subjected to esterification under the above conditions. The proposed procedure is most convenient for the preparation of methyl esters, for in this case removal of water from the reaction mixture as azeotrope is impossible. The procedure is easy, and the reaction occurs at a fairly high rate. Chlorotrimethylsilane can readily be recovered by isolation of hexamethyldisiloxane from the distillate and its subsequent transformation into the former [3].

The reaction of carboxylic acids with alcohols in the presence of chlorotrimethylsilane can be regarded as a convenient preparative route to the corresponding esters. Their yields are fairly high, and chlorotrimethylsilane is an accessible reagent.

EXPERIMENTAL

The purity of the products was checked by GLC on a Shimadzu GC-14A instrument using an HP-5 quartz capillary column (25 m×0.25 mm, stationary phase

SE-54); flame-ionization detector; carrier gas nitrogen, split ratio 1:100; oven temperature programming from 100°C (3 min) at a rate of 10 deg/min; injector temperature 230°C; detector temperature 250°C; sample volume 1 μl. The chromatograms were recorded using a Chromatopack C-RbA automatic integrator.

A mixture of 0.1 mol of carboxylic acid, 0.35 mol of chlorosilane, and 0.5 mol of the corresponding alcohol was heated for 1–1.5 h until appreciable evolution of hydrogen chloride was no longer observed. Volatile products were removed under atmospheric pressure, and the residue was distilled in a vacuum. The products were identified by comparing their physical constants with those reported in the literature.

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