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PROPANOLYSIS OF ESTERS USING CHLOROTRIMETHYLSILANE

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Abstract: *A variety of methyl esters are converted into the corresponding propyl esters upon treatment with 1-propanol and chlorotrimethylsilane. Among them acyclic aliphatic esters have the best conversion rate.*

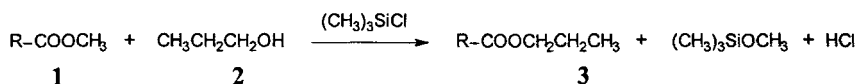
The alcoholysis of esters is a useful reaction in organic chemistry that is quite frequently employed in industrial processes to prepare compounds such as surfactants, cosmetic, flavours and monomers in the manufacture of polymers; in carbohydrate chemistry and in fat analysis, and many methods including either acid or base catalysis have been investigated.^{1,2,3}

To date, chlorotrimethylsilane has been used as a catalyst for esterifying acids, acylating alcohols in fairly good yields and removing selectively the N-t-butyloxycarbonyl group in solid phase peptide synthesis.^{4,5,6} Also, in combination with sodium iodide, it has been used for the cleavage of esters, lactones, carbamates and ethers.⁷ Recently, Jong Gun et al.⁸ introduced either sodium

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nitrite or t-butyl nitrite in combination with chlorotrimethylsilane as a catalyst for the alcoholysis of primary amides, and Dabkowski et al.⁹ have proposed chlorotrimethylsilane as an activator in nucleotide synthesis.¹⁰

We wish to report some preliminary results concerning the alcoholysis of methyl esters with 1-propanol using chlorotrimethylsilane (CTMS) which was added to a stirred mixture of methyl ester **1** and 1-propanol (**2**). The reaction mixture was stirred either at 25 °C for 6 h or under gentle reflux for 2h. After a standard work-up, the residue was weighed and redissolved in hexane and the solution was analysed by both GLC and GLC/MS (Table 1) to determine the conversion yield to propyl ester **3**.



The reaction works well with acyclic aliphatic esters in both assayed conditions (Table 1), although yields are moderate or poor with the two methyl esters presenting the shortest chain (R= propyl and pentyl), probably due to ester losses during the removal of the excess 1-propanol from the reaction mixture. Conversion of methyl cyclohexanecarboxylate to the corresponding propyl ester was only moderate in both tested conditions, though reflux increased the percentage of conversion in this case. Contrarily, aromatic esters convey a very low percentage of conversion and refluxing doesn't improve very much the results.

Table - 1

Chlorotrimethylsilane catalysed alcoholysis of methyl esters

R	Conversion ^a %		Yield ^b %	
	Room Temperature	Reflux	Room Temperature	Reflux
C ₆ H ₅ -	19	35	47	68
CH ₃ CH ₂ CH ₂ -	100	100	52	25
CH ₃ CH ₂ CH ₂ CH ₂ CH ₂ -	93	93	73	79
C ₆ H ₁₁ -	70	85	80	89
CH ₃ (CH ₂) ₁₀ -	81	89	97	98
CH ₃ CH ₂ CH=CHCH ₂ CH=CHCH ₂ CH=CH(CH ₂) ₇ -	97	97	99	100
CH ₃ (CH ₂) ₁₂ -	94	94	94	86
CH ₃ (CH ₂) ₇ CH=CH(CH ₂) ₇ -	96	96	93	96
CH ₃ (CH ₂) ₁₄ -	94	95	95	94
<i>o</i> -HO-C ₆ H ₄ -	2	6	86	74
CH ₃ (CH ₂) ₁₆ -	93	94	95	95

^a % Conversion was calculated by GC analysis. ^b Yields were calculated assuming a 100% conversion to the corresponding propyl ester

Yields are similar to the ones described by Olah et al.¹⁰ by using iodotrimethylsilane/iodine in chloroform. However, our method is shorter and easier because it avoids the use of mercury to destroy iodine.

In summary, chlorotrimethylsilane can be said to be an efficient reagent for the alcoholysis of acyclic aliphatic acids, whereas cyclic aliphatic and aromatic acids are less reactive in the assayed conditions.

General experimental procedure: One millilitre of (CH₃)₃SiCl is added to a round-bottom glass flask loaded with a mixture of methyl ester (1.5 mmol) and 5 ml of 1-propanol. The flask is closed with a glass-stopper or equipped with a

reflux condenser and a drying tube, and the reaction mixture is stirred at 25 °C for 6 h or under gentle reflux for 2h respectively. The reaction mixture is then diluted with 5 ml of diethyl ether, transferred to a separatory funnel and washed with 10 ml of saturated sodium bicarbonate solution followed by 10 ml of brine. The organic solution is then dried with anhydrous magnesium sulphate and evaporated to dryness. The residue is weighed. After a standard work-up the residue is redissolved in hexane and the solution is analysed by both GLC and GLC/MS to identify the product and determine the conversion yield.

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