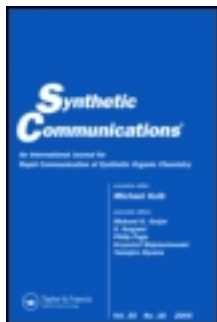


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A NEW SIMPLIFIED METHOD FOR ESTERIFICATION OF SECONDARY AND TERTIARY ALCOHOLS

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Abstract: Esters of secondary and tertiary alcohols have been synthesized in the absence of solvent and catalyst and only under the effect of temperature with high yields.

Esters represent a family of organic molecules of great interest, widely used in numerous applications. Consequently, the synthesis of esters has been the subject of much previous work.

The usual methods involve condensation of an alcohol with a carboxylic acid in the presence of a mineral acid. This synthetic approach results in good yields with primary alcohols, limited yields with secondary alcohols and poor yields with tertiary ones. Other procedures take advantage of the reactivity of alcohol functions towards anhydrides. Such synthetic routes classically call for an appropriate solvent and a basic catalyst (1-6).

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We would like to put forth a new way to prepare esters starting from anhydrides, secondary and even tertiary alcohols, characterized by the absence of solvent and catalyst. We feel these conditions are very attractive from the industrial point of view (7,8).

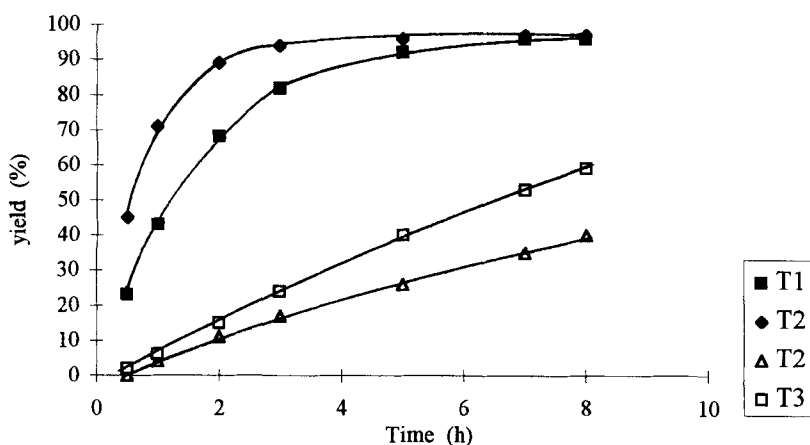
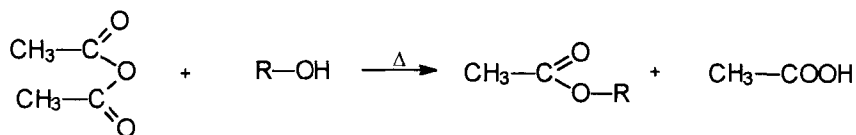


Figure: Esterification of acetic anhydride

R = (CH₃)₂CH- (-◆- and -■-)



R = (CH₃)₃C- (-□- and -△-)

T1 = 75°C - T2 = 90°C - T3 = 105°C

Figure shows that the reaction proceeds favorably, even in the presence of a tertiary alcohol. This result may be attributed to the special behaviour of reactions carried out without solvent. These conditions prove to be even more favorable for similar reactions with secondary alcohols, as expected (the yields are higher despite a lower reaction temperature).

These first results are confirmed by those obtained by reacting the same alcohols with anhydrides of various structures (table). Only cyclic anhydrides failed to give the expected monoester in the presence of tertiary alcohol.

Table: Esterification of alcohols with various anhydrides.

R ₁	R ₂	Time (h)	Yield (%)
CH ₃ -	(CH ₃) ₂ CH-	3	94
	(CH ₃) ₃ C-	8	59
CH ₃ -CH ₂ -	(CH ₃) ₂ CH-	3	95
	(CH ₃) ₃ C-	7	75
	(CH ₃) ₂ CH-	1.5	95 ^a
	(CH ₃) ₃ C-	8	0 ^b
	(CH ₃) ₂ CH-	5	91 ^a
	(CH ₃) ₃ C-	8	0 ^b

R₂ = (CH₃)₂CH- : T_{bath} = 90°C

R₂ = (CH₃)₃C- : T_{bath} = 105°C

a : formation of monoester

b : formation of diacid

EXPERIMENTAL PART

All products used were of commercial origin and used without further purification.

In a round bottom flask equipped with a condenser, the anhydride and alcohol are introduced in a molar ratio [alcohol] / [anhydride] = 3. The reaction mixture is heated under agitation during the time indicated in table.

Esters obtained from acetic and propionic anhydrides are purified by straight forward distillation except 2-propanol acetate which is purified by chromatography on a silica column, using hexane-ether mixture as eluant, and distillation. Their physico-chemical characteristics conform to litterature values and similar to commercial products.

The purification of the monoester produced by condensing, maleic anhydride with 2-propanol was carried out by extraction. This allows for elimination of remaining unreacted anhydride as a water soluble diacid, followed by distillation (B.P. = 105°C under P = 50mmHg and M.P. = 48.3 °C). ¹H NMR in deuterated DMSO confirms the structure of the product :

δ 1.19 - 1.22 (d, 6H, 2CH₃) 4.93 - 4.99 (heptet, 1H, CH)
 6.39 (s, 2H, CH).

Anal. Found (Calcd). C₇H₁₀O₄: %C 52.278 (53.164), %H 6.484 (6.329).

The monoester resulting from the reaction of phthalic anhydride with 2-propanol was isolated by precipitation, according to the procedure described in the litterature (9), and was recrystallized from a petroleum ether-toluene mixture (90/10). The melting point of the compound is 79.5°C. The ¹H NMR in deuterated DMSO solution shows the following features :

δ 1.27 - 1.30 (d, 6H, 2CH₃) 5.06 - 5.13 (heptet, 1H, CH)
 7.60 - 7.72 (m, 4H, CHarom.).

Anal. Found (Calcd). C₁₁H₁₂O₄: %C 63.118 (63.461), %H 5.755 (5.769).

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