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ORGANIC SYNTHESES WITHOUT SOLVENT: BASE-CATALYSED ESTER INTERCHANGE

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Summary: Ester interchange of methyl or ethyl carboxylic esters by primary or secondary alcohols is carried out effectively when solid-liquid phase transfer catalysis (PTC) is achieved in the absence of added organic solvent. Vinyl and isopropenyl acetates undergo ester interchange, even in the absence of PTC catalyst, with primary alcohols and phenols.

The important ester interchange reaction (1,2) has been hardly studied under phase transfer catalysis (PTC) conditions (3-5).

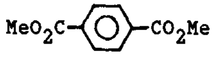
$$RCO_2Me \text{ (or Et)} + R'OH \rightleftharpoons RCO_2R' + MeOH \text{ (or EtOH)}$$

Solid-liquid PTC *without added solvent* is an efficient method for anionic activation (6,7) and furthermore the absence of any solvent allows the reaction to be performed under vacuum; the alcohol (methanol or ethanol) generated is therefore continuously removed and the reaction results in a complete shift of the transesterification equilibrium. In the usual PTC methods, the presence of an organic solvent would made it difficult to work under vacuum (8).

Pure methyl or ethyl esters are allowed to react with a molecular amount of an alcohol, in the presence of less than one equivalent of solid K_2CO_3 and of a catalytic amount of quaternary ammonium salt. The reaction is performed under ≃20 torr in a closed evacuated vessel containing P_2O_5 (method A), or directly under the vacuum of a water-pump (method B) (9).

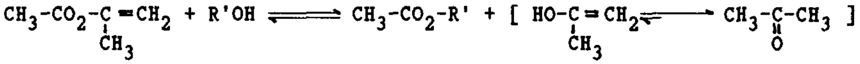
Yields are excellent (Table 1) with primary, lower with secondary alcohols. Neither tertiary alcohols, nor phenol react on these conditions.

TABLE 1: Transesterification of esters or diesters (10 mmol[a]) with ROH (10 mmol[a]) in presence of solid K_2CO_3 (method A: 5 mmol[a]; method B: 2 mmol[a]) and Aliquat ($MeN^+Oct_3\ Cl^-$ essentially) or NBu_4HSO_4 (method A: 0,5 mmol[a]; method B: 0,2 mmol[a]).

Esters or diesters	R	Method	Temp.	Time (h)	Yields (%) Aliquat	Yields (%) NBu_4HSO_4
$PhCO_2Me$	$nC_4H_9-\underset{C_2H_5}{CH}-CH_2-$	A	RT[b]	8	100	21
		B	55°C	3	99	10
$PhCO_2Me$	$nC_6H_{13}-\underset{CH_3}{CH}-$	A	RT[b]	72	24	75
		B	70°C	10	13	72
$CH_3(CH_2)_{16}CO_2Me$	$nC_8H_{17}-$	B	55°C	2	59	97
$O{=}C(OEt)_2$	$nC_8H_{17}-$	A	RT[b]	24	78 + 11[c]	
	$nC_4H_9-\underset{C_2H_5}{CH}-CH_2-$	A	RT[b]	24	100	
		B	70°C	2	99 + traces[c]	

a) Twofold amount for diesters b) RT: room temperature c) monotransesterification product

Isopropenyl acetate has been described as allowing ester interchange in solution with acid (10,11) or under enzymatic (12) catalysis. The driving force of the reaction consists in the formation of the unstable enolic form of acetone, inducing the complete shift of the transesterification equilibrium.



$$CH_3\text{-}CO_2\text{-}\underset{CH_3}{C}{=}CH_2 + R'OH \rightleftharpoons CH_3\text{-}CO_2\text{-}R' + [\ HO\text{-}\underset{CH_3}{C}{=}CH_2 \rightleftharpoons CH_3\text{-}\underset{\overset{\|}{O}}{C}\text{-}CH_3\ ]$$

This reaction is very easily achieved by solid-liquid PTC without solvent . In fact, this reaction is so easy in these "dry" heterogeneous conditions, that it is even possible to carry it out *without any PTC catalyst* and at *atmospheric pressure* (Table 2).

TABLE 2: Transesterification of isopropenyl acetate (10 mmol) with 1-octanol and phenol (10 mmol) in presence of solid K_2CO_3 (2 mmol) [and Aliquat (0,2 mmol)].

R'OH	Temp.	Time (h)	Yields (%)
$nC_8H_{17}OH$	70°C	2	65^a
	70°C	2	74^b
	70°C	24	91^b
PhOH	70°C	0,5	$100^{a\ or\ b}$
	RT	24	$\geqslant 98^{a\ or\ b}$

a) without Aliquat b) in the presence of Aliquat

Yields are again excellent with primary, but very poor with secondary alcohols. Tertiary alcohols fail to react, but *phenols* give rise to good yields of phenolic esters which, to our knowledge, have been prepared by transesterification only once, namely from trimethylsilyl esters (13). Vinyl acetate reacts similarly, but gives rise to lower yields.

These results constitute a new illustration of the high efficacy of organic syntheses under solid-liquid PTC conditions in the absence of solvent.

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