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A FACILE METHOD OF TRANSESTERIFICATION USING PHOSPHORUS YLID

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Summary: The transesterification of carboxylic esters catalyzed with phosphorus ylid under neutral and mild conditions has been investigated. The reactions of esters having an electron withdrawing group with methanol proceeded rapidly and with high yield, whereas the reverse reactions proceeded slowly or not at all.

Common alcoholysis of carboxylic esters are carried out with acidic or basic catalysts under reflux.[1-2] In cases of enolizable esters,[3] i.e., acetoacetate, and esters of strong acids,[4] i.e., oxalate and fumalate, the reactions can be achieved under neutral conditions at steam-bath temperature, but the rates are slow. Therefore, we investigated the transesterification catalyzed by the phosphorus ylids,[5] $R_3P{=}CHCH_2X$, which are obtained easily from tertiary phosphine and acrylic compound under neutral and mild conditions, and explored the scope of the reaction.

The reactions were carried out by using 1.0 mmol of ester, 100 mmol of alcohol and 0.3 mmol of triphenylphosphine and acrylonitrile at 25°C. The yields were calculated by the GLC analysis. The results of transesterification of a series of ethyl esters to methyl esters are shown in Table 1. The reactions of carboxylates having an electron withdrawing group on acyl function were very rapid. However, in case of maleate, the reaction was slow and gave the mixed ester in only 17% yield, while the reaction of fumalate was completed within an hour. This result may be attributed to the steric effect caused by two ester functions in *cis* configuration. Aromatic acid esters reacted more slowly than aliphatic

Table 1. Transesterification of ethyl esters to methyl esters

R-COOEt, R:	pKa[a]	Reaction time (hr)	R-COOMe, Yield; (%)	
EtOCO	1.27	0.25		100
EtOCOCH$_2$	2.84	1	(48)[b]	29
EtOCOCH$_2$CH$_2$	4.21	1	(18)[b]	0
cis-EtOCOCH=CH	1.94	1	(17)[b]	0
trans-EtOCOCH=CH	4.38	1		100
CH$_3$	4.76	1		12
ClCH$_2$	2.87	0.5		100
CNCH$_2$	2.47	1		100
CH$_3$CH$_2$CH$_2$	4.82	1		0
trans-C$_6$H$_5$CH=CH	4.44	24		60
C$_6$H$_5$	4.20	24		15
p-MeOC$_6$H$_4$	4.47	24		0
p-NO$_2$C$_6$H$_4$	3.43	24		71

a) pKa value of a parent acid.

b) Mixed ester.

esters.

The results of transesterification of oxalic esters with different alcoho are shown in Table 2.

The ester exchanges of higher esters, except benzyl and t-butyl esters, t give methyl esters proceeded rapidly and with high yields, whereas the reverse reactions to give higher esters proceeded slowly or not at all. t-Butyl and benzyl esters did not react with alcohols.

Table 3 shows the results of transesterification of ethyl acetate to meth acetate using the ylids derived from tertiary phosphines and acrylic compounds. The ylids derived from tributylphosphine exhibited higher pH value in methanol and greater catalytic effect than those derived from triphenylphosphine. However, the catalytic effect of the ylids did not change so much by varying o acrylic compounds.

As no reaction took place by the usage of only triphenylphosphine or acrylonitrile, it is certain that the reactions were catalyzed by the ylid formed from the two. The betaine [I][5] might react as a bifunctional cataly activating both carbonyl group and alcohol at the same time. The interactio between the phosphorus cation and the carbonyl oxygen atom increases the

Table 2. Transesterification of oxalates with different alcohols

$$R^1OCOCOOR^1 + R^2OH \longrightarrow \underset{[A]}{R^1OCOCOOR^2} + \underset{[B]}{R^2OCOCOOR^2}$$

$R^1OCOCOOR^1$ R^1:	R^2OH R^2:	Reaction time, (hr)	Yield, (%) [A]	[B]
Et	Me	15	0	100
n-Pr	Me	15	0	100
i-Pr	Me	15	0	100
$PhCH_2$	Me	60	0	0
Ph	Me	30	0	100
t-Bu	Me	60	0	0
Me	Et	60	0	100
n-Pr	Et	60	42	46
Me	n-Pr	60	59	31
Et	n-Pr	60	49	13
Me	i-Pr	420[a)]	48	9
Me	t-Bu	60	0	0
Me	Ph	60	0	0
Me	$PhCH_2$	60	0	0

a) At 80°C.

Table 3. Transesterification of ethyl acetate to methyl acetate using various catalysts for 30 min at 30°C[a)]

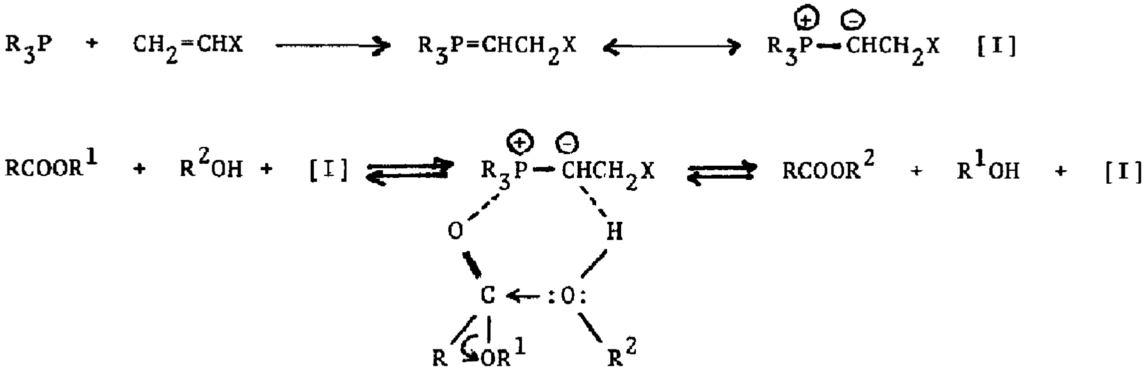
Catalyst	Yield, (%)	pH[b)]
$Ph_3P{=}CHCH_2CN$	34	9.7
$Ph_3P{=}CHCH_2COOMe$	39	9.5
$Ph_3P{=}CHCH_2COOEt$	44	9.9
$Bu_3P{=}CHCH_2CN$	94	13.0
$Bu_3P{=}CHCH_2COOMe$	93	12.4
$Bu_3P{=}CHCH_2COOEt$	83	12.7

a) 1.0 mmol of ethyl acetate, 20 mmol of methanol, and 1.0 mmol of phosphine and acrylic compound were used.

b) 10 mmol/l in methanol at 25°C.

electrophilic reactivity of the carbonyl carbon, thus enhancing reaction with doner oxygen of the alcohol. Simultaneously, the anionic part of [I] forms a hydrogen bond with the alcohol increasing its nucleophilic reactivity.

Consequently, it is concluded that the transesterification using phosphoru ylid proceeds through a six-membered intermediate shown in the following schme.



This assumption is supported by the findings that the ylid exhibiting higher pH value in methanol shows greater catalytic effect, and that the adduct formed from triphenylphosphine and diethyl azodicarboxylate shows similar catalytic effect.[6)]

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