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An Efficient Method for the Preparation of Carboxylic Esters via Mixed Anhydrides by the Promotion of a Catalytic Amount of Lewis Acid

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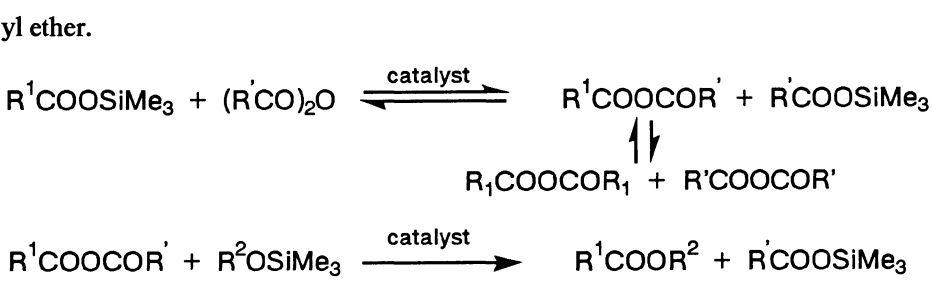
Various carboxylic esters are prepared in excellent yields by the reaction of nearly equimolar amounts of silyl derivatives of carboxylic acids and alcohols with p-trifluoromethylbenzoic anhydride in the presence of a catalytic amount of Lewis acid.

A number of esterification procedures have been reported concerning the preparation of carboxylic esters from the corresponding acids and alcohols;1) namely the condensation by heating the two reactants with catalytic amounts of protic acids or Lewis acids,2) and the coupling between activated derivatives of carboxylic acids and alcohols under basic conditions. There have been known a few methods for the effective preparation of esters from equimolar amounts of carboxylic acids and alcohols. For example, 1-alkyl-2-halopyridinium salts developed in our laboratory have been demonstrated as a useful reagent for the preparation of carboxylic esters in the coexistence of a tertiary amine.3) Further, a convenient method for the preparation of esters and lactones via mixed anhydrides under basic condition is developed by Yamaguchi et al. using 2,4,6-trichlorobenzoyl chloride as a bulky acid moiety in order to realize the chemoselectivity of the reaction.4)

Now we would like to report an efficient method for the preparation of carboxylic esters from nearly equimolar amounts of silyl derivatives of acids and alcohols under mild condition by the use of carboxylic anhydrides and a catalytic amount of Lewis acid.

In the course of our continuing studies on the exploration of new catalytic synthetic reactions using Lewis acids,5) it was postulated that the following successive reactions would lead to the formation of carboxylic esters starting from silyl derivatives of carboxylic acids and alcohols by the assistance of suitable carboxylic anhydrides; (1) the initial formation of the mixed anhydride, and (2) the alcoholysis of the formed anhydride with an alkyl silyl ether.



$$R^1COOSiMe_3 + (R'CO)_2O \xrightleftharpoons{\text{catalyst}} R^1COOCOR' + R'COOSiMe_3$$

$$R^1COOCOR' \rightleftharpoons R_1COOCOR_1 + R'COOCOR'$$

$$R^1COOCOR' + R^2OSiMe_3 \xrightarrow{\text{catalyst}} R^1COOR^2 + R'COOSiMe_3$$

When acetic acid trimethylsilylester was treated with benzoic anhydride in the presence of a catalytic amount of Lewis acid, a facile formation of the mixed anhydride and two homo anhydrides was suggested by ^1H NMR experiment. Of the three above anhydrides, the following experiments would support that the mixed anhydride is a key intermediate of the present reaction; that is 4-phenyl-2-butanol trimethylsilylether smoothly reacted with acetic acid trimethylsilylester in the presence of an active acidic species generated from $TiCl_4$ and $AgClO_4$, and benzoic anhydride in dichloromethane at -23 °C for 3h to give the corresponding ester in 58% yield, while the trimethylsilylether reacted with acetic anhydride under same condition to give the ester in 17% yield.

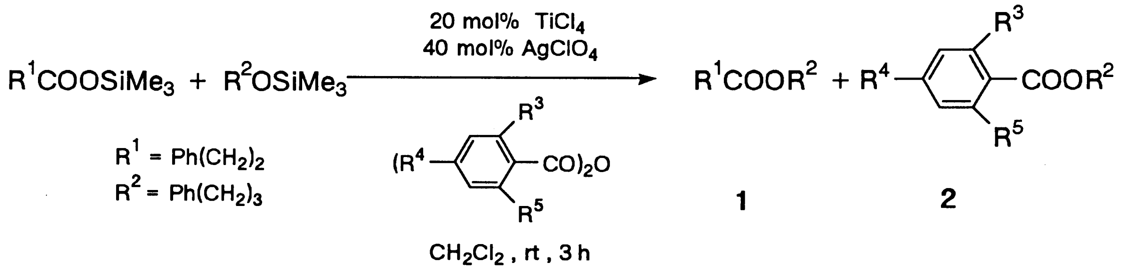


Table 1. Effect of Substituents in Aromatic Ring of Benzoic Anhydride

Entry	R^3	R^4	R^5	Yield / %	1 / 2 a)	Entry	R^3	R^4	R^5	Yield / %	1 / 2 a)
1	H	H	H	98	94 / 6	6	H	CF_3	H	91	>200 / 1
2	Cl	H	H	89	93 / 7	7	H	MeO	H	95	38 / 62
3	Cl	H	Cl	68	78 / 22	8	MeO	H	H	91	4 / 96
4	H	Cl	H	60	97 / 3	9	Me	H	H	90	36 / 64
5	H	F	H	93	98 / 2	10	Me	H	Me	97	3 / 97

a) Determined by ^{1}H-NMR.

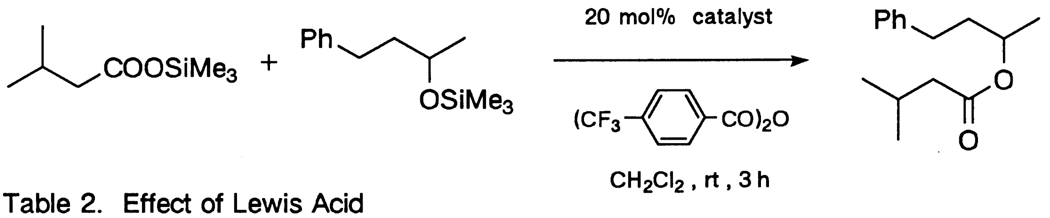


Table 2. Effect of Lewis Acid

Entry	Catalyst	Yield / %	Entry	Catalyst	Yield / %
1	$TiCl_4$	42 (1.9) a)	8	$AlCl_3 + 2AgOTf$	80
2	$TiCl_4 + 2AgClO_4$	84	9	$GaCl_3 + 2AgOTf$	83
3	$TiCl_4 + 2AgOTf$	94	10	$InCl_3 + 2AgOTf$	91
4	$ZrCl_4 + 2AgOTf$	84	11	$FeCl_3 + 2AgOTf$	81
5	$HfCl_4 + 2AgOTf$	86	12	$SnCl_2 + 2AgClO_4$	83
6	$SnCl_4 + 2AgOTf$	68 (2.1) a)	13	$Sn(OTf)_2$	95
7	$SbCl_5 + 2AgOTf$	39 (0.8) a)	14	$TrClO_4$	80

a) Yields of 4-phenyl-2-butyl p-trifluoromethylbenzoate.

Then our effort was focused on the chemoselectivity of the second step. In order to find a suitable acid moiety in the mixed anhydride, various carboxylic homo anhydrides were examined first. As described above, only in the case of benzoic anhydride, the desired reaction did proceed with high selectivity to give the corresponding esters in high yields. Next, the effect of substituents in aromatic ring of benzoic anhydrides was examined and it was found that the anhydride having an electron withdrawing group such as trifluoromethyl group at para-position gave better selectivity (Table 1). Furthermore, several Lewis acids were examined by taking the reaction of 3-methylbutyric acid trimethylsilylester and 4-phenyl-2-butanol trimethylsilylether as a model (see Table 2). It was shown there that the active metallic species generated in situ from $TiCl_4$ and silver triflate, and tin(II) triflate gave good results.

Several examples of the present esterification are demonstrated in Table 3. In every case, the reaction proceeds smoothly at room temperature in dichloromethane to give the corresponding esters in excellent yields from nearly equimolar amounts of silyl derivatives of carboxylic acids and alcohols.

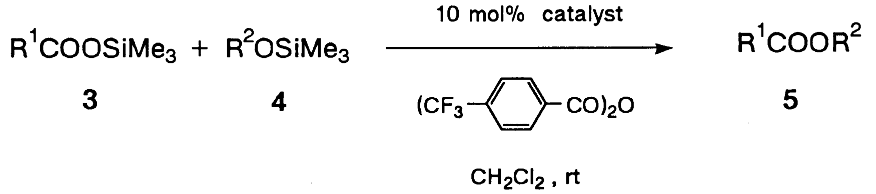


Table 3. Esterification by the Promotion of a Catalytic Amount of Lewis Acid[a]

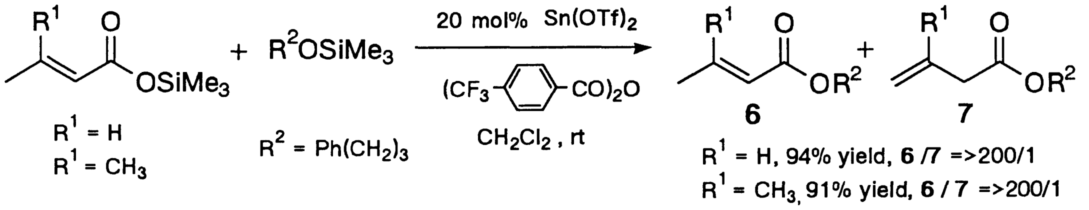
R^1	R^2	Yield / %[b] cat. A[c]	 cat. A[d]	 cat.B[d]
Me	$Ph(CH_2)_3$	90	96	96
^{i}Pr	$Ph(CH_2)_3$	90	99	99
^{i}Bu	$Ph(CH_2)_3$	93	99	99
^{t}Bu	$Ph(CH_2)_3$	91[e]	97[e]	97
$Ph(CH_2)_2$	$Ph(CH_2)_3$	92[f]	98	95
Me	$Ph(CH_2)_2CHCH_3$	91	95	95
^{i}Pr	$Ph(CH_2)_2CHCH_3$	91	99	99
^{i}Bu	$Ph(CH_2)_2CHCH_3$	96	99	99
^{t}Bu	$Ph(CH_2)_2CHCH_3$	89	99	93
$Ph(CH_2)_2$	$Ph(CH_2)_2CHCH_3$	94	98	97

a) cat A: 10 mol% of $Sn(OTf)_2$; cat B: 10 mol% of $TiCl_4$ and 20 mol% of AgOTf
b) The yields were determined by isolation. c) **3** / **4** = 1.0. d) **3** / **4** = 1.1,
e) 3-Phenyl-1-propyl p-trifluoromethylbenzoate (0.9 %) was also formed.
f) When 1 mol% of $Sn(OTf)_2$ was used, yield of **5** was 92%.

A typical experimental procedure is described for the reaction of 2-methylpropionic acid trimethylsilylester and 3-phenyl-1-propanol trimethylsilylether in the presence of a catalytic amount of tin(II) triflate; to the suspention of $Sn(OTf)_2$ (0.02 mmol) in dichloromethane (2.0 ml), the mixture of p-trifluoromethylbenzoic anhydride (0.2 mmol) and 2-methylpropionic acid trimethylsilylester (0.22 mmol) in dichloromethane (1.0 ml) and the solution of 3-phenyl-1-propanol trimethylsilylether (0.2 mmol) in dichloromethane (0.5 ml) were successively added. The reaction mixture was stirred for 3 h at rt, and then quenched with sat. $NaHCO_3$. After usual work up, the crude product was purified by preparative TLC on silica gel to afford 3-phenylpropyl 2-methylpropionate (99% yield) with an excellent selectivity (>200/1).

Esterification of crotonic acid or senecioic acid is a base sensitive reaction leading to the rearrangement of olefinic double bond to form the ester 7 even under weakly basic conditions.[6] So, the esterification between equimolar amounts of crotonic acid and alcohol has been carried out by the use of DCC or thionyl chloride.

It is also noted that the present method was successfully applied to the synthesis of crotonic acid ester or senecioic acid ester from equimolar amounts of silyl derivatives of carboxylic acid and alcohol under mild condition. When 20 mol% of $Sn(OTf)_2$ was employed in the present experiment, no rearranged product was isolated at all and the desired ester was obtained in 94% yield or 91% yield, respectively.



Further investigation concerning the scope of the present reaction is now in progress. We are grateful to Dr. Shū Kobayashi for valuable discussion and suggestions.

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