Silica Chloride: A Versatile Heterogeneous Catalyst for Esterification and Transesterification[1]

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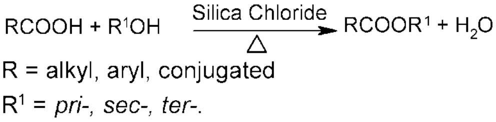
Abstract: Silica chloride has been found to be an efficient catalyst for esterification of carboxylic acids (aliphatic, aromatic and conjugated) with alcohols (primary, secondary and tertiary) as well as for transesterification of esters (by both alcoholysis and acidolysis).

Key words: esterification, transesterfication, silica chloride, alcoholysis, acidolysis

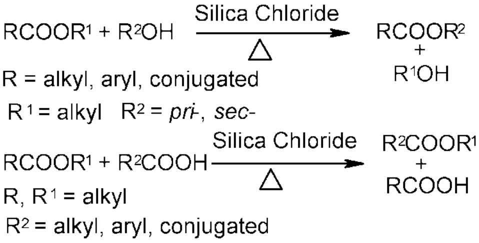
Esterification of carboxylic acids with various alcohols is one of the most important and widely applicable transformations in organic synthesis.[2] A large number of methods for esterification catalyzed by various protic and Lewis acids including solid acids, ion exchange resins, zeolite and clay are now well-known.[2,3] However, some of the reported methods are associated with certain drawbacks such as harsh reaction conditions, tedious experimental procedures, long reaction times, poor yields, complex side reactions and narrow range of applicability. Moreover, the number of suitable methods for one-step esterification of carboxylic acids with tertiary alcohols are also limited.[3c] The reagents (such as phosgene, isobutene etc.) which are generally utilized for this purpose are incompatible with harsh reaction conditions and tedious experimental procedures.

Transesterification of an ester with an alcohol (alcoholysis) or with an acid (acidolysis) can also be applied for the preparation of another ester.[4a] A variety of protic and Lewis acids, organic and inorganic bases, enzymes, and antibodies are known[3f,4] to catalyze this reaction. Recently some of the catalysts, like diphenylammonium triflate, iodine etc., have been employed for both esterification and transesterification.[5] However, the number of such catalysts are limited. Additionally, the transesterification of an ester applying both alcoholysis and acidolysis by utilizing the same catalyst is also not frequently observed. Here we report a simple and general method for esterification and transesterification using silica chloride as a heterogeneous catalyst.

During our recent work on the development of novel synthetic methodologies we have observed that silica chloride is an efficient catalyst for esterification of carboxylic acids and transesterification of esters (Schemes 1 and 2)



Scheme 1



Scheme 2

Various carboxylic acids were treated with different alcohols in the presence of silica chloride to produce the corresponding esters (Table 1). Both the aliphatic and aromatic acids can be applied for esterification and all the three types of alcohols (primary, secondary and tertiary) can be used. Different other catalysts reported[2,3] earlier were found to be active for esterification with primary and secondary alcohols but it was difficult to prepare the esters with tertiary alcohols. Even, some of the catalysts which have been reported to work for esterification with tertiary alcohols, have been studied with a very limited number of reactions.[3e,5b] Silica chloride has presently been found to be an efficient catalyst for esterification of aliphatic, aromatic and conjugated acids with tertiary alcohols (Table 1).

Transesterification of esters has also effectively been carried out using silica chloride as catalyst. Aliphatic as well as aromatic esters were equally applied (Table 2). Both the alcoholysis and acidolysis of esters could be carried out under mild reaction conditions. Thus the acid part and also the alcohol part of an ester can easily be exchanged with other acids or alcohols to generate new esters.

Trimethylsilyl chloride was also previously applied[8] for esterification of carboxylic acids but the reaction was reported with only primary alcohols. The reaction times were generally very high and the reagent was used in excess. Transesterification was also not studied with this reagent.

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Table 1 Esterification of Carboxylic Acids with Alcohols

Entry	Acid	Alcohol	Time (h)	Isolated Yield[a] (%)	Ref.
1	$PhCH_2CO_2H$	MeOH	5	96	[6]
2	$PhCH_2CO_2H$	EtOH	5	94	[6]
3	$4\text{-}OHC_6H_4CH_2CO_2H$	EtOH	6	95	[6]
4	$PhCH_2CO_2H$	$PhCH_2OH$	8	86	[7]
5	$CH_3(CH_2)_{16}CO_2H$	MeOH	5	94	[6]
6	$CH_3(CH_2)_{16}CO_2H$	EtOH	6	96	[6]
7	$PhCO_2H$	MeOH	5	95	[6]
8	$4\text{-}OHC_6H_4CO_2H$	MeOH	5	93	[6]
9	$3\text{-}ClC_6H_4CO_2H$	MeOH	5	97	[6]
10	$3\text{-}ClC_6H_4CO_2H$	EtOH	6	95	[6]
11	$2\text{-}CO_2HC_6H_4CH_2CO_2H$	MeOH	7	93	[6]
12	$PhCH{=}CHCO_2H$	MeOH	5	94	[6]
13	$PhCH{=}CHCO_2H$	BuOH	7	93	[6]
14	$CH_3(CH_2)_7CH{=}CH(CH_2)_7CO_2H$	MeOH	7	94	[6]
15	$C_6H_4CH_2CO_2H$	*i*-PrOH	6	93	[6]
16	$4\text{-}OHC_6H_4CH_2CO_2H$	*i*-PrOH	7	92	[7]
17	$CH_3(CH_2)_{16}CO_2H$	*i*-PrOH	7	93	[5b]
18	$4\text{-}OHC_6H_4CO_2H$	*i*-PrOH	6	92	[6]
19	$PhCH{=}CHCO_2H$	*i*-PrOH	7	93	[6]
20	$PhCH_2CO_2H$	*t*-BuOH	10	79	-
21	$4\text{-}OHC_6H_4CO_2H$	*t*-BuOH	9	82	[6]
22	$3\text{-}ClC_6H_4CO_2H$	*t*-BuOH	8	85	-
23	$PhCH{=}CHCO_2H$	*t*-BuOH	9	83	[6]

[a] The structures of all the esters were settled from their spectral (^1H NMR and MS) data.

The present catalyst, silica chloride can easily be prepared[9] from silica gel (finer than 200 mesh) and thionyl chloride, and should be properly activated. Both the ingredients are inexpensive and readily available. The catalyst is heterogeneous and can easily be handled and removed from the reaction mixture by simple filtration. The recovered catalyst, however, when applied again under the present experimental conditions has been found to decrease the yields of esters (isolated yields: 26–38% only). With different acids, alcohols and esters silica chloride was verified to be effective for both esterification and transesterification. Only a few catalysts like diphenylammonium triflate,[5a] iodine,[5b] silica supported sodium hydrogen sulfate[7] and distannoxanes[10] are known to possess the capacity to catalyze both these reactions.

In summary, silica chloride can be applied as a versatile catalyst for esterification of carboxylic acids (aliphatic, aromatic and conjugated) with primary, secondary and tertiary alcohols as well as for transesterfication of esters by both alcoholysis and acidolysis. The catalyst is heterogeneous, inexpensive, non-hazardous and convenient to handle. We feel the present procedure of esterification and transesterification can be applied for both academic and industrial purposes.

The spectra were run on the following instruments: ^1H NMR: Varian Gemini 200 MHz and EIMS: VG Micromass 7070 H (70 eV). The carboxylic acids and alcohols were obtained commercially.

Table 2 Transesterification of Carboxylic Esters with Alcohols or Acids

Entry	Ester	Alcohol/Acid	Time (h)	Isolated Yield[a] (%)	Ref.
1	$PhCH_2CO_2Me$	EtOH	8	91	6
2	$PhCH_2CO_2Me$	*i*-PrOH	9	90	6
3	$4\text{-}OHC_6H_4CH_2CO_2Et$	*i*-PrOH	12	83	7
4	$CH_3(CH_2)_{16}CO_2Me$	BuOH	11	89	6
5	$CH_3(CH_2)_{16}CO_2Pr$	MeOH	10	86	6
6	$CH_3(CH_2)_{16}CO_2Me$	*i*-PrOH	9	82	5b
7	$PhCO_2Me$	BuOH	10	76	6
8	$4\text{-}OHC_6H_4CO_2Me$	*i*-PrOH	12	82	6
9	$3\text{-}ClC_6H_4CO_2Me$	EtOH	9	85	6
10	$PhCH{=}CHCO_2Me$	BuOH	10	86	6
11	$PhCH{=}CHCO_2Et$	BuOH	12	88	6
12	$PhCH{=}CHCO_2Pr$	MeOH	11	86	6
13	$CH_3(CH_2)_7CH{=}CH(CH_2)_7CO_2Me$	EtOH	9	85	6
14	EtOAc	$PhCH_2CO_2H$	7	94	6
15	EtOAc	$4\text{-}OHC_6H_4CH_2CO_2H$	7	92	6
16	EtOAc	$CH_3(CH_2)_{16}CO_2H$	6	93	6
17	EtOAc	$4\text{-}OHC_6H_4CO_2H$	11	79	6
18	EtOAc	$3\text{-}ClC_6H_4CO_2H$	10	83	6
19	EtOAc	$CH_3(CH_2)_7CH{=}CH(CH_2)_7CO_2H$	9	82	6
20	EtOAc	$PhCH{=}CHCO_2H$	11	80	6

[a] The structures of all the products were settled from their spectral (^{1}H NMR and MS) data.

Esterification of Acids; Ethyl 2-Phenylacetate; Typical Procedure

To a solution of phenyl acetic acid (136 mg, 1 mmol) in EtOH (10 mL) was added silica chloride (150 mg). The mixture was refluxed and the progress of the reaction was monitored by TLC. After 5 h, the mixture was filtered and the concentrated filtrate was subjected to column chromatography over silica gel using hexane–EtOAc (9:1) as eluent to yield ethyl 2-phenylacetate (154 mg, 94%).

Transesterification of Esters (Alcoholysis); Isopropyl 2-Phenylacetate; Typical Procedure

To a solution of methyl 2-phenylacetate (150 mg, 1 mmol) in *i*-PrOH (10 mL) was added silica chloride (150 mg). The mixture was refluxed for 10 h and filtered. The filtrate was concentrated and the residue was purified by column chromatography over silica gel using hexane–EtOAc (8:2) as eluent to obtain pure isopropyl 2-phenylacetate (178 mg, 90%).

Transesterification of Esters (Acidolysis); Ethyl 4-Hydroxybenzoate; Typical Procedure

4-Hydroxybenzoic acid (138 mg, 1 mmol) was dissolved in EtOAc (10 mL). Silica chloride (150 mg) was added, and the mixture was refluxed for 12 h and filtered. The filtrate was concentrated and the residue was purified by column chromatography over silica gel using hexane–EtOAc (8:2) as eluent to give ethyl 4-hydroxybenzoate (131 mg, 79%).

The spectral (^{1}H NMR and MS) and analytical data of the unknown esters are given below.

tert-Butyl 2-Phenylacetate (entry 20, Table 1)

^{1}H NMR ($CDCl_3$): $\delta = 7.36–7.17$ (m, 5 H), 3.43 (s, 2 H), 1.42 (s, 9 H).

EI-MS: $m/z = 192$ (M^+), 119, 91.

Anal. Calcd for $C_{12}H_{16}O_2$: C, 75.00; H, 8.33. Found: C, 74.96; H, 8.27.

tert-Butyl 3-Chlorobenzoate (entry 22, Table 1)

^{1}H NMR ($CDCl_3$): $\delta = 7.94$ (t, 1 H, $J = 2.4$ Hz), 7.83 (dd, 1 H, $J = 8.0, 2.4$ Hz), 7.48 (dd, 1 H, $J = 8.0, 2.4$ Hz), 7.35 (1 H, t, $J = 8.0$ Hz), 1.58 (s, 9 H).

EI-MS: $m/z = 212$ (M^+), 157, 139.

Anal. Calcd for $C_{11}H_{13}ClO_2$: C, 62.26; H, 6.13. Found: C, 62.35; H, 6.19.

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