

An eco-friendly method for the synthesis of aryl and alkyl esters of carboxylic acids using acid activated Indian bentonite

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Esterification of various carboxylic acids with phenol and alcohols has been achieved using acid activated Indian bentonite (AAIB) as catalyst. The catalyst is versatile, and the reaction is found to work well for primary, secondary and tertiary alcohols. The yields are very good under specific reaction conditions.

The esterification of carboxylic acids is one of the most important transformations in organic synthesis¹. A variety of methods are available for converting a carboxylic acid into its alkyl or aryl ester. The simplest and industrially most important esterification process is the acid catalysed reaction between the carboxylic acid and alcohol or phenol. The simplicity of this method, vast available information and its well-studied mechanism have led one to assume that the field is mature. This is not quite true. The reaction conditions do not fulfil the "green chemistry" norms.

This esterification in the case of phenols is difficult in general. The reaction of acid halides with phenols in presence of a base like pyridine is regarded as one of the best methods to prepare phenolic esters². Other methods used for the preparation of aryl esters involve the use of thallium salts of phenol with acid chlorides³, use of ultrasound in the absence of base or catalyst⁴ and tetrabutylammoniumhydrogensulphate as phase transfer catalyst for sterically hindered phenols⁵. Since these methods use acid chlorides, undesirable products like HCl and SO₂ are released during their preparation.

The lipase catalysed esterification of cresols⁶, esterification in fluorous media⁷, conversion of carboxylic acids to their corresponding methyl esters using CBr₄/CH₃OH under the influence of ultra-violet radiation⁸ and using boron trichloride⁹ or diphenylammonium triflate (DPAT) as catalyst with equimolar amounts of carboxylic acids and alcohols¹⁰ have been reported. Silicon tetrachloride¹¹, Fe³⁺-K10 montmorillonite clay^{12,13}, solid acidic catalysts¹⁴⁻¹⁶ and zeolites¹⁷ have been used for

esterification reactions. The esterification of carboxylic acids with alcohols in the presence of di-*t*-butyl dicarbonate¹⁸ and the direct esterification of aldehydes and alcohols with pyridinium hydrobromide perbromide in water at room temperature¹⁹ have also been reported. Very few of these are environmentally safer, the clays and zeolites being particularly so. Recently, esterification of succinic anhydride with *p*-cresol and dicarboxylic acids to diesters has been reported over cation exchanged montmorillonite clay catalysts^{20,21}.

We have used acid activated Indian bentonite (AAIB) as catalyst for the synthesis of several esters of various carboxylic acids. The catalyst is also effective in the synthesis of *p*-cresyl esters of various carboxylic acids²². The catalyst used here can be prepared²³ easily. It can be safely handled, non-corrosive, environmentally friendly and is recovered by simple filtration, regenerated by washing with water and then can be reused. This method allows a wide range of carboxylic acids and alcohols to be incorporated into the industrially important esters.

Results and discussion

Various carboxylic acids and phenol were refluxed in the presence of AAIB in toluene and *o*-xylene to produce the corresponding esters. The results compiled in Table 1 indicate that phenyl esters of the carboxylic acids can be obtained in 65-86% yield after a reaction period of 6 h in *o*-xylene and 8 h in toluene. The esterification of acetic acid with phenol gave lower yield in toluene after 8 h, which we attribute to the relatively lower boiling point of acetic acid making it unavailable on the catalyst for reaction with phenol.

Table 2 shows the results of esterification of various carboxylic acids with different alcohols. The yields of esters in entries 1, 2, 8, 11, 12, 14 and 19 are poor. Increase in the molar ratio of carboxylic acid to alcohol, improved the yield of isopropyl myristate (entry 3) in the reaction of myristic acid with isopropyl alcohol. How-

Table 1. Synthesis of phenyl esters of various carboxylic acids catalysed by acid activated Indian bentonite (Amount of catalyst = 500 mg, molar ratio [acid : phenol] = 1 : 2 [5 : 10 mmol])

Sl. no.	Carboxylic acid	Solvent	Time (h)	Yield (%) ^a	Stretching of C=O (cm ⁻¹)
1.	Acetic acid	Toluene	8	09	1766
2.	Propionic acid	Toluene	8	79	1762
3.	<i>n</i> -Butyric acid	Toluene	8	82	1759
4.	<i>n</i> -Hexanoic acid	<i>o</i> -Xylene	6	78	1761
5.	<i>n</i> -Octanoic acid	<i>o</i> -Xylene	6	83	1761
6.	<i>n</i> -Decanoic acid	<i>o</i> -Xylene	6	80	1761
7.	Lauric acid	<i>o</i> -Xylene	6	79	1762
8.	Myristic acid	<i>o</i> -Xylene	6	76	1751
9.	Palmitic acid	<i>o</i> -Xylene	6	86	1759
10.	Stearic acid	<i>o</i> -Xylene	6	76 ^b , 81	1759
11.	Benzoic acid	Toluene	8	80	1738
12.	Cinnamic acid	Toluene	8	84	1735
13.	Phenylacetic acid	Toluene	8	65	1751

^aIsolated yields, ^bcatalyst = *p*-toluenesulphonic acid.

Table 2. Synthesis of esters of various carboxylic acids catalysed by acid activated Indian bentonite (Amount of catalyst = 500 mg, molar ratio [acid : alcohol] = 1 : 2 [5 : 10 mmol], solvent : toluene)

Sl. no.	Carboxylic acid	Alcohol	Time (h)	Yield (%) ^a	Stretching of C=O (cm ⁻¹)
1.	Stearic acid	2-Propanol	8	13	1738
2.	Palmitic acid	2-Propanol	8	20	1739
3.	Myristic acid	2-Propanol	8	15, 43 ^b	1738
4.	Phenylacetic acid	2-Propanol	8	68	1737
5.	Stearic acid	1-Butanol	8	63	1739
6.	Palmitic acid	1-Butanol	8	70	1739
7.	Palmitic acid	2-Methyl-1-propanol	8	72	1739
8.	Palmitic acid	2-Methyl-2-propanol	8	14	1739
9.	Myristic acid	1-Butanol	8	74	1739
10.	<i>n</i> -Decanoic acid	1-Butanol	8	85	1739
11.	<i>n</i> -Hexanoic acid	1-Butanol	8	22	1738
12.	Propionic acid	1-Butanol	8	11	1740
13.	Phenylacetic acid	1-Butanol	8	73	1737
14.	Salicylic acid	1-Butanol	8	21	1676
15.	Palmitic acid	2-Ethoxyethanol	8	86	1740
16.	<i>n</i> -Octanoic acid	2-Ethoxyethanol	8	76	1740
17.	Propionic acid	2-Ethoxyethanol	8	73	1741
18.	Phenylacetic acid	2-Ethoxyethanol	8	87	1740
19.	Salicylic acid	2-Ethoxyethanol	8	21	1742
20.	Oleic acid	2-Ethoxyethanol	8	87	1740

^aIsolated yields, ^bmolar ratio (acid : alcohol) = 1 : 4 [5 : 20 mmol].

ever, in the remaining reactions the yields of esters were good, being 63–87%. The lower yields of esters in the case of 2-propanol and 2-methyl-2-propanol are likely to be due to competitive dehydration over esterification, since secondary and tertiary alcohols undergo elimination more easily than primary alcohols²⁴. The gaseous products formed in our experiments also gave positive test for unsaturation. The cause for lower yields of salicylic acid esters (entry 14 and 19) with different alcohols is probably the intramolecular hydrogen bonding which could retard the esterification process.

In summary, the acid activated Indian bentonite is developed as a good catalyst for the esterification of carboxylic acids with phenol and alcohols. The catalyst is heterogeneous, inexpensive and non-hazardous. The products are usually obtained in pure form after simple work up. The advantages are the ease of operation, simplicity in work up and the reusability of the catalyst. It is needless to say that the locally available highly cost effective clay can be processed as catalyst for esterification of carboxylic acids to prepare aryl as well as alkyl esters.

Experimental

All acids (except myristic acid, which was procured from Merk-Schuchardt, Germany) and solvents were purchased from S.d. fine-chem Ltd., India. All solvents were distilled prior to use. The IR spectra of the products were recorded on a Nicolet Avatar 320 FT-IR spectrometer. The purity of the compounds was checked by TLC and was satisfactory.

General procedure : In a typical experiment (Scheme 1) 5 mmol of carboxylic acid and 10 mmol of phenol or alcohol were dissolved in dry *o*-xylene or toluene (30 mL) to which 500 mg of the catalyst was added. The resultant mixture was refluxed for 6 or 8 h with azeotropic removal of water. After cooling the reaction mixture, the catalyst was filtered off and washed with the solvent (10 mL). The unreacted starting compounds were removed by washing the filtrate with 5% NaOH [with saturated NaHCO₃ solution in salicylic acid reactions] (4 × 10

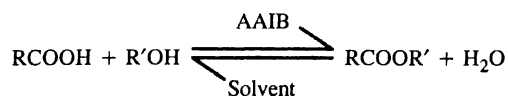
mL) followed by water (2 × 10 mL) and saturated NaCl (2 × 10 mL) and the organic layer was dried over anhydrous Na₂SO₄. The solvent was removed under reduced pressure and the product was purified by passing through a silica gel (100–200 mesh) column using benzene-petroleum ether (1 : 5) as eluant or recrystallising from ethanol.

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R = alkyl, aryl, conjugated

R' = C₆H₅, primary, secondary, tertiary

Scheme 1

Vijayakumar *et al.* : An eco-friendly method for the synthesis of aryl and alkyl esters *etc.*

and references cited therein.

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