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A mild and efficient method for esterification and transesterification catalyzed by iodine†

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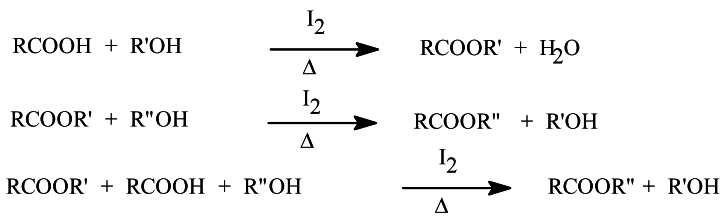
Abstract—Iodine, was found to be a practical and useful Lewis acid catalyst for the esterification of carboxylic acids with alcohols. The high catalytic activity of iodine can be used for the transesterification of esters by different alcohols including tertiary alcohols and sterically hindered primary and secondary alcohols. The method presented is especially effective for simultaneous esterification and transesterification reactions. © 2002 Published by Elsevier Science Ltd.

Esterification of carboxylic acids and transesterification of esters have wide academic as well as industrial applications. A number of useful and reliable esterification methods catalyzed by a variety of acids, ion exchange resins, zeolites, solid acid catalysts, etc., have been reported in the literature.[1–11] Recent developments include variation and improvements of well established procedures and the discovery and application of new reagents. Transesterifications are catalyzed by alkali metal hydroxides and alkoxides in appropriate alcohols and also by tin, calcium or titanium compounds.[12] Environmental considerations limit the applicability of many, otherwise useful catalysts commercially. There are not many reagents available for commercial applications that can accomplish both esterification and transesterification reactions under mild conditions. Recent methods are those using diphenyl ammonium triflate and a clay catalyst.[13] During the course of our search for a facile, practical and versatile catalyst for simultaneous esterification and transesterification reactions for the preparation of methyl esters as biodiesel from low grade vegetable oils, we observed that granular iodine can accomplish both reactions in a highly efficient manner. Reagents based on iodine reported in recent years for transesterification reactions are indium triodide,[14] iodotrimethyl silane–iodine,[15] etc.

To our knowledge, reports with molecular iodine alone have not appeared so far. Here we wish to report our results on reactions involving iodine/alcohol for their usefulness in esterification, transesterification and simultaneous esterification and transesterification reactions (Scheme 1).

In a typical experimental procedure, the ester or acid was refluxed or heated to a certain predetermined temperature with the desired alcohol in the presence of iodine. The reaction was monitored either by TLC or GC and after completion, the excess alcohol was removed and the residue was extracted with ether. The ether extract, after being washed with sodium thiosulfate and subsequently with distilled water, was evaporated to furnish the product. The esterification of



Scheme 1.

Keywords: esterification; transesterification; iodine.

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different acids such as saturated, unsaturated, hydroxy and dicarboxylic acids with a variety of alcohols proceeded in high yields and the results are summarized in Table 1. It was found that the esterification reaction proceeds smoothly with primary, secondary and tertiary aliphatic alcohols with the reactivity of the alcohols decreasing in the order primary>secondary> tertiary. The yields of the products also showed a trend in the same order as that of the reactivity. Esters of tertiary alcohols which are otherwise difficult to prepare are obtained in moderate yields (entry 12) but required longer reaction times and increased amounts of catalyst. In cases where a carboxylic acid group is directly attached to an aromatic ring, such as benzoic acid, there was no reaction. Wax esters, i.e. esters of long chain carboxylic acids with long chain alcohols, which are generally prepared via acyl chlorides, are also easily prepared by this method. Butyl lactate, a valuable intermediate for the production of butyl acrylate, is prepared in an efficient manner by esterification of commercial lactic acid (88%) with butanol even in the presence of high amounts of water (12%) in the lactic acid. Although esterification reactions are highly sensitive to the presence of trace amounts of moisture, the reaction catalyzed by iodine appears tolerant of high amounts of water in the reaction system.

The results obtained in transesterification reactions are summarized in Table 2. Transformations of esters from lower to higher homologues and vice versa were

Table 1. Esterification of carboxylic acids with alcohols using iodine

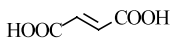
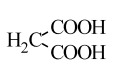
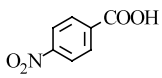
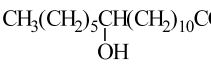
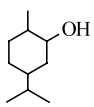
Entry	Carboxylic acid	Alcohol	Time (h)	Yield (%)
1	H_2C=CHCOOH	CH_3OH	12	95
2		CH_3OH	15	93
3	$CH_3CHOHCOOH$	$CH_3(CH_2)_3OH$	20	95
4	C_6H_5CH=CHCOOH	CH_3OH	15	78
5	$C_6H_5CH_2COOH$	CH_3OH	10	95
6		CH_3OH	15	94
7	$HOOC(CH_2)_8COOH$	CH_3OH	12	92
8	C_6H_5COOH	CH_3OH	20	No reaction
9		CH_3OH	20	No reaction
10	$CH_3(CH_2)_{16}COOH$	CH_3OH	4	98
11	$CH_3(CH_2)_{16}COOH$	$(CH_3)_2CHOH$	4	98
12	$CH_3(CH_2)_{16}COOH$	$(CH_3)_3C$-OH	20	56
13	$CH_3(CH_2)_{16}COOH$	$C_6H_5CH_2OH$	12	90
14	$CH_3(CH_2)_{16}COOH$	$CH_3(CH_2)_{16}CH_2OH$	10	89
15		$CH_3(CH_2)_3OH$	15	95
16	$CH_3(CH_2)_7CH$=$CH(CH_2)_7COOH$	CH_3OH	8	95
17	$CH_3(CH_2)_{16}COOH$		10	85
18	$CH_3(CH_2)_{16}COOH$		12	78

Table 2. Transesterification of carboxylic acid esters with alcohols using iodine

Entry	Carboxylic acid ester	Alcohol	Time (h)	Yield (%)
1	$C_6H_5CH{=}CHCOOCH_3$	$CH_3(CH_2)_3OH$	20	88
2	$C_6H_5CH{=}CHCOOCH_3$	$CH_3(CH_2)_2OH$	20	91
3	$C_6H_5CH{=}CHCOO(CH_2)_2CH_3$	CH_3OH	20	89
4	$C_6H_5COOCH_3$	$CH_3(CH_2)_3OH$	20	56
5	$CH_3CHOHCOOCH_3$	$CH_3(CH_2)_3CH(C_2H_5)CH_2OH$	15	92
6	$CH_3CHOHCOO(CH_2)_3CH_3$	CH_3OH	15	90
7	$CH_3(CH_2)_{16}COOCH_3$	$CH_3(CH_2)_3OH$	15	85
8	$CH_3(CH_2)_{16}COOCH_3$	$(CH_3)_2CHOH$	20	72
9	$CH_3(CH_2)_{16}COO(CH_2)_3CH_3$	CH_3OH	20	82
10	$CH_3(CH_2)_{16}COOCH_3$	$C_6H_5CH_2OH$	20	No reaction
11	$CH_3(CH_2)_{16}COOCH_3$	$(CH_3)_3COH$	20	45
12	$CH_3(CH_2)_5CH(OH)(CH_2)_{10}COOCH_3$	$CH_3(CH_2)_6OH$	20	90
13	$CH_3(CH_2)_5CH(OH)(CH_2)_{10}COO(CH_2)_3CH_3$	CH_3OH	20	89
14	$CH_3(CH_2)_7CH{=}CH(CH_2)_7COOCH_3$	$CH_3(CH_2)_3OH$	20	90
15	$H_2C{=}CH(CH_2)_8COOCH_3$	$CH_3(CH_2)_3OH$	20	92
16	Castor oil	CH_3OH	20	90
17	Peanut oil	CH_3OH	20	94
18	Coconut oil	CH_3OH	20	92
19	Jatropha oil	CH_3OH	20	90

achieved efficiently using this procedure. Transesterification of a methyl ester to a *t*-butyl ester (entry 11) which is normally problematic is achieved with this reagent but transesterification with benzyl alcohol did not proceed. While esterification of benzoic acid was not achieved with this reagent, the transesterification of methyl benzoate to butyl benzoate was accomplished with ease.

Vegetable oils were smoothly transesterified with methanol (Table 2, entries 16 to 19). These esters are presently gaining prominence as biodiesel. Vegetable oils containing free carboxylic acids are conventionally converted to esters in two steps: first, the free carboxylic acids are converted to esters in the presence of an acid catalyst and in the second step, the acylglycerols are transesterified employing a basic catalyst. Using the protocol described in this communication *Jatropha curcas* seed oil containing 5–10% of free fatty acids could be converted to methyl esters in a one-step reaction (Table 2, entry 19).

The present procedure with iodine/alcohol provides a very efficient method for esterification and transesterification reactions. The notable advantages of this method are: operational simplicity, the ready availability and non-toxic nature of the reagent, general applicability, mild reaction conditions and high yields. While esterification and transesterification reactions are highly sensitive to moisture, special precautions need not be taken to exclude moisture or air from the system with this catalyst. With the reported method, simultaneous esterification and transesterification reactions can be

carried out in a highly efficient manner. Very few catalysts are known which catalyze esterification and transesterification reactions and iodine is one such catalyst which accomplishes both.

Experimental

General: The carboxylic acids and carboxylic esters were obtained commercially or prepared from the corresponding acids by standard methods. The esters and alcohols were distilled before use. Iodine (LOBA Chem, India) crystals was used as obtained.

General procedure for esterification: Stearic acid (5 g, 17.6 mmol), methanol (10 ml) and iodine (50 mg,), were refluxed for the specified time. The progress of the reaction was monitored by TLC. After the reaction, excess alcohol was removed under reduced pressure and the residue was extracted with diethyl ether. The ether extract was washed with a solution of sodium thiosulfate and subsequently with distilled water, dried over anhydrous sodium sulfate and concentrated in vacuo to yield the crude product, which was purified by column chromatography (hexane:ether, 9:1) to give the desired carboxylic ester (5.1 g, 98%).

General procedure for transesterification: Methyl stearate (5 g, 16.6 mmol), butanol (10 ml) and iodine (100 mg) were refluxed for the specified time. The progress of the reaction was monitored by GC. After the reaction, excess alcohol was removed under reduced pressure and the residue was extracted with diethyl ether. The ether extract was washed with a solution of sodium thiosulfate and subsequently with distilled water, dried over anhydrous sodium sulfate and concentrated in vacuo to yield the crude product, which was purified by column chromatography (hexane:ether, 9:1) and further analyzed by GC (conversion 85%).

General procedure for simultaneous esterification and transesterification: Jatropha oil (5 g), methanol (10 ml) and iodine (50 mg), were refluxed for the specified time. The progress of the reaction was monitored by TLC. After the reaction, excess alcohol was removed under reduced pressure and the residue was extracted with diethyl ether. The ether extract was washed with a solution of sodium thiosulfate and subsequently with distilled water, dried over anhydrous sodium sulfate and concentrated in vacuo to yield the crude product, which was purified by column chromatography (hexane:ether, 9:1) to give the desired carboxylic ester (4.6 g, 90%).

These procedures were followed for the esterification and transesterification of all the substrates listed in Tables 1 and 2. All the products are known compounds and are easily identified by comparison of their physical properties with those of authentic samples.[16]

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