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AN EFFICIENT AND GENERAL METHOD FOR ESTER HYDROLYSIS ON THE SURFACE OF SILICA GEL CATALYZED BY INDIUM TRIIODIDE UNDER MICROWAVE IRRADIATION

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ABSTRACT : Carboxylic esters are hydrolyzed to the corresponding carboxylic acids in high yields through a simple microwave assisted operation on the surface of silica gel moistened with few drops of water in presence of indium triiodide.

Ester hydrolysis is one of the most common reactions in organic synthesis and is usually accomplished by heating the ester in either aqueous acid or base.[1] The acidic and basic methods, though satisfactory usually, sometimes pose problems for substrates containing either acid or base sensitive groups. Rearrangements and isomerization of double bonds[2] under acidic hydrolysis are also observed. Thus, a number of methods involving deprotection of esters under neutral condition have been developed.[3] However, most of these methods are substrate-specific and thus lack general applicability. Recently, we have

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introduced a transesterification process under catalysis of indium triiodide[4] and envisioned its application for ester hydrolysis by replacement of alcohol with water.

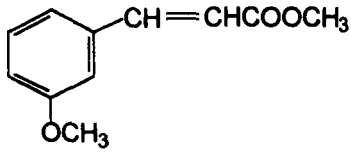
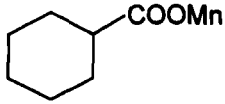
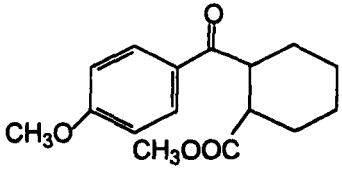
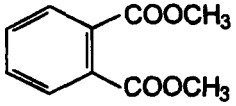
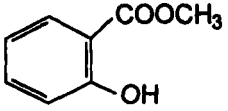
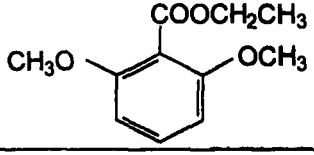
Although, methyl phenylacetate and benzyl acetate underwent hydrolysis under reflux in water in presence of indium triiodide, many other esters remained unaffected. However, we have discovered an effective hydrolysis of carboxylic esters on the surface of moist silica gel impregnated with indium triiodide under microwave irradiation.

$$RCOOR^1 \xrightarrow[MW]{SiO_2 / InI_3 / H_2O} RCOOH$$

In a typical experimental procedure, the carboxylic ester was added to moist silica gel impregnated with indium triiodide and the whole mass was then irradiated under microwave in a domestic microwave oven at 480 W for a certain period of time as required to complete the reaction (TLC). The reaction mixture was then eluted with ether and the ether extract, after usual work-up, furnished the carboxylic acid.

A wide range of structurally varied carboxylic esters underwent hydrolysis by this procedure to produce the corresponding carboxylic acids in high yields. The results are summarized in Table 1. As shown in Table 1, this procedure is effective for aliphatic, alicyclic and aromatic esters. The considerably sterically hindered esters (entries 5,6,13) and diester are also hydrolysed to the corresponding acids without any difficulty. The reaction condition is tolerant to ketone, hydroxyl, methoxyl and C=C moieties.

Table1:Microwave Assisted Hydrolysis of Carboxylic Esters by $InI_3/SiO_2/H_2O$

Entry	Carboxylic Ester	Reaction Time (mins)	Yield (%)a
1	$PhCH_2COOCH_3$	25	92
2	CH_3COOCH_2Ph	35	93
3	$CH_3(CH_2)_{16}COOCH_3$	32	90
4	$PhCOOCH_2Ph$	15	92
5	$(Ph)_2CHCOOCH_3$	90	70
6	$(Ph)_2C(CH_3)COOCH_3$	80	75
7		53	88
8		25	87
9	$PhCH_2COOMn$	37	88
10		45	83
11		45	89
12		60	85
13		32	87

a Yields refer to those of pure isolated products. Mn denotes l-menthyl

Conventional heating in THF makes the hydrolytic process very slow and incomplete even after prolonged period of 12-15 hours. Microwave heating on silica gel surface without indium triiodide also does not lead to satisfactory result, the progress of reaction being only marginal.

In conclusion, this procedure on the surface of moist silica gel impregnated with indium triiodide provides a very efficient, novel and general method for hydrolysis of esters under semi-neutral condition. We believe, this will find significant applications in the field of organic synthesis.

General Experimental Procedure. Representative Example: To a THF solution of indium triiodide, prepared by heating indium (115 mg, 1 mmol) and iodine (379 mg, 1.5 mmol) under reflux in THF (3 ml) following a reported procedure,[5] was added silica gel (HF 254, 2 g) and the mixture was stirred for 15 minutes for uniform mixing. THF was then stripped off under reduced pressure to furnish 'silica gel impregnated with InI_3'. Now methyl phenylacetate (2 mmol, 300 mg) was added into the bed of silica gel impregnated with InI_3 under stirring followed by a few drops of H_2O. The whole solid mass was then irradiated by microwave in a domestic microwave oven (BPL, India) at 480 W for 25 minutes (silica gel bed was moistened with a few drops of H_2O every five minutes). The reaction mixture was then eluted with ether and the ether extract after being washed with sodium thiosulfate solution, brine and dried over Na_2SO_4, was evaporated to leave the crude phenylacetic acid which was purified by column chromatography to furnish the pure product (251 mg, 92%), mp 78^0C; IR (KBr) 1710 cm^{-1} ; ^{1}H NMR ($CDCl_3$) δ 3.65 (3 H, s), 7.5 (5 H, s), 8.3 (1 H, broad).

The carboxylic acids obtained are all known compounds and are easily identified by their spectral data and melting points.

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