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Microwave accelerated selective and facile deprotection of allyl esters catalyzed by Montmorillonite K-10

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Carboxylic acids are regenerated from their corresponding substituted allyl esters by Montmorillonite K-10 using microwave irradiation under solvent free conditions to afford enhanced yields and reduced reaction times compared to thermal conditions.

Introduction

When a chemical reaction is to be carried out selectively at one reactive site in a multifunctional molecule, the other reactive sites must be temporarily blocked. Many protective groups have been, and are being, developed for this purpose.[1]

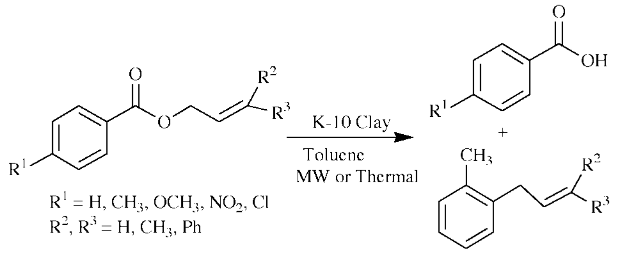
Functional group protection and deprotection strategies are essential to target-oriented synthesis in organic chemistry. Carboxylic acids can be protected as anhydrides,[2] amides[3] or esters.[4] Unsaturated esters are particularly useful as protecting groups because of their stability, the ease with which they can be obtained by reaction of the corresponding alcohol with acid chloride or alkylation of the acid with the corresponding allyl halide under base catalyzed conditions.[5] Deprotection of allyl ester can be done by using methodologies that employ $Pd(OAc)_2$,[6a] $PdCl_2(Ph_3P)_2$,[6b] $(Ph_3P)_3RhCl$,[6c] Me_2CuLi,[6d] formic acid[7] and sulfated SnO_2.[8] Reports also show only a few carboxylic acids which were protected as a but-3-en-1-yl ester and have been deprotected *via* ozonolysis[9a] and β-elimination.[9b] Recently we have reported the use of natural kaolinitic clay and EPZG for selective allyl ester deprotection.[10]

As there is a need for 'clean technology revolution', the use of solid, inorganic catalysts promises to go a long way to improve the current technology which is very inefficient or leads to unacceptable levels of waste.[11] Clays can be used as an efficient and versatile catalyst for various organic reactions. In montmorillonite clay one octahedral aluminate layer is sandwiched between two tetrahedral silicate layers.[12] This clay is non-toxic, non-corrosive, cheap and recyclable. Montmorillonite clay has both Brønsted and Lewis acidic catalytic sites available, hence its natural occurrence, as well as its ion-exchange properties allows it to function efficiently as a catalyst. Recent reports on Montmorillonite K-10 focus on some important reactions[13–18] and various transformations.[19]

Microwave assisted heterogeneous reactions[20] with various solid inorganic support have attracted research interest because of the simplicity, greater stability and rapid synthesis of a variety of organic compounds.[21] The salient features of the microwave approach along with the use of mineral supported reagents or catalysts are the enhanced reaction rates, formation of pure products in high yields and the ease of manipulation. Recently, solvent-free microwave assisted reactions[22] have gained more popularity as they provide an opportunity to work with open vessels. This avoids the risk of development of high pressure and provides a possibility of upscaling the reaction on a preparative scale and helps the induction of the reaction under 'dry conditions'.[22]

Results and discussion

Table 1 lists a variety of allyl esters which were converted to their parent acid in the presence of nucleophile, catalyst Montmorillonite K-10 by both thermal and microwave accelerated solvent free conditions. The time required for completion of the reaction by the microwave method is appreciably shorter than when using thermal conditions with mild reaction conditions. It is noted that during the course of reaction, the allyl cation formed reacts with the aromatic nucleus of toluene, 1,4-dimethoxybenzene or anisole *via* alkylation. When toluene is used as the nucleophile the product is monoalkylated at the *ortho* position and is obtained in moderate yield (Scheme 1). It is evident from Table 1 that entries 2, 4, 5, 6 and 18 are easily deprotected whereas the cinnamyl ester requires the presence of more nucleophilic aromatic species such as anisole. The presence of a methyl ester in mixed ester selectively deprotects in good yield (entry 18). It is also important to note that aryl or alkyl esters (entries 19 and 20) remain unaffected under these reaction conditions.



Scheme 1

Experimental

IR spectra were recorded in chloroform on a Perkin-Elmer 137-E spectrometer. The ^1H NMR spectra were recorded on a Bruker 200 MHz instrument and the chemical shifts were reported with Me_4Si as an internal standard. The mass spectra were recorded on Finnigan MAT-1020-B 70 eV mass spectrometer. Microwave reactions were carried out in an IBF made domestic microwave oven operating at its full power at 1000 MHz. Catalyst Montmorillonite K-10 and all chemicals were obtained from Aldrich Chemicals.

General procedure

To a mixture of the allyl ester (10 mmol), 1,4-dimethoxybenzene or anisole (15 mmol) or toluene (15 ml, in the case of thermal reactions) and catalyst Montmorillonite K-10 clay (10% w/w) were added in a glass test tube and mixed thoroughly followed by irradiation in a microwave oven or heating with stirring under reflux in an oil bath (toluene 15 ml as solvent).

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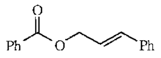
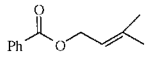
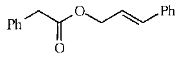
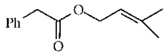
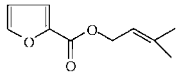
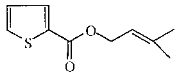
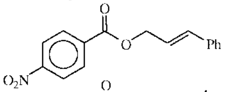
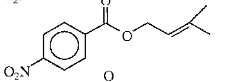
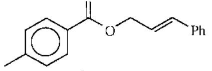
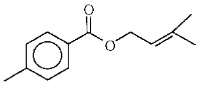
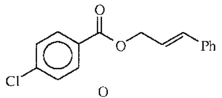
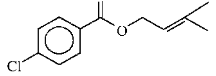
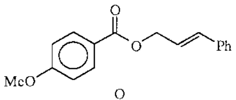
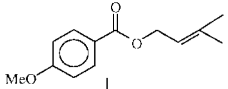
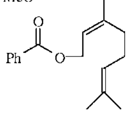
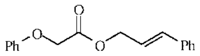
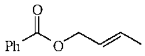
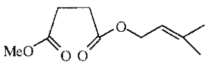
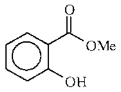
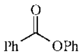
Table 1 Deprotection of allyl esters catalysed by Montmorillonite K-10

		Thermal		Microwave	
Entry	Allyl esters	Time/h	Yield (%)[a]	Time/ min	Yield (%)[a]
1		6	94	20	96
2		5	94[b]	20	98
3		8.5	80	20	85
4		8.5	90[b]	20	97
5		14	60[b,c]	20	70[c]
6		14	62[b,c]	10	70[c]
7		10	87	10	92
8		10	85	10	90
9		8	92	20	97
10		8.5	90	20	95
11		8.5	92	20	95
12		8	90	20	97
13		10	85	10	90
14		10	87	10	92
15		15	87	20	97
16		9	80	20	85
17		10	47	20	60[c]
18		20	67[b,c]	20	72[c]
19		20	0	20	0
20		20	0	20	0

[a] Isolated yield characterized by mp, IR, ^{1}H NMR and MS. [b] Yields without the addition of nucleophile. [c] Essentially only the starting material remained.

The reaction was monitored by TLC. After the completion of the reaction, this mixture was cooled to room temperature and the catalyst was separated by filtration. The reaction mixture was concentrated to remove excess toluene under vacuum. The reaction mixture was diluted with chloroform and washed with 1 M NaOH (3–4 times). The aqueous layer was separated and acidified with dilute HCl. The acidified aqueous layer was extracted with organic solvent to obtain the corresponding acid in pure form. The chloroform layer was washed with brine, dried and concentrated to get crude alkylated product, which was purified by column chromatography over silica gel. Pure monoalkylated product was obtained in moderate yield.

In conclusion, the present method provides a useful alternative for deprotection of allyl esters. The notable advantages of this methodology are mild and solvent free conditions, short reaction time (10 to 20 min), chemoselectivity and its environmental friendly conditions. We believe this will serve as a useful addition to modern organic synthetic methodologies.

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