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Facile Deprotection of Aromatic *tert*-Butyl and Allylic Esters Under Microwave Irradiation Conditions

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ABSTRACT

A simple and efficient method for the deprotection of *tert*-butyl and allylic esters is described, which occurs under microwave irradiation with *p*-toluenesulfonic acid in solvent-free conditions.

Key Words: Deprotection; Esters; Microwave; Solvent-free.

INTRODUCTION

Protection of carboxylic acids into carboxylic esters are fundamental procedures in numerous organic synthesis. Among others, transformation of carboxylic acids to *tert*-butyl, allyl, and prenyl (3-methylbut-2-enyl) esters

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received much attention due to their ease of preparation and high stabilities.^[1] A variety of useful methods for deprotection of *tert*-butyl esters have been reported. For example, deprotection of *tert*-butyl esters can be efficiently mediated by use of various reagents, such as trifluoroacetic acid,^[2] nitric acid,^[3] and ZnBr₂,^[4] in dichloromethane solvent. On the other hand, the reported methods for deprotection of allylic esters still remain far less in comparison with those of *tert*-butyl esters. Recently, several efficient methods for deprotection of allylic esters have been developed using reagents such as palladium(II) acetate,^[5,6] iodine,^[7] sulfated tin oxide,^[8] and K-10 clay.^[9] However, generally these methods make use of toxic and expensive reagents and performed for extended period of times, which limit their practical utilities.

Recently, microwave promoted organic synthesis coupled with solventfree conditions utilized in wide variety of organic synthesis.^[10] In connection with our program on the development of microwave accelerated organic synthetic method, we wanted to effect deprotection of carboxylic esters in solvent-free conditions. In this paper, we describe the efficient microwave promoted deprotection of *tert*-butyl and allylic esters by treatment with *p*-toluenesulfonic acid (Sch. 1).

Treatment of aromatic *tert*-butyl esters with *p*-toluenesulfonic acid monohydrate (2.0 equiv.) under microwave irradiation for 3-4 min smoothly furnished carboxylic acids in high yields. When we also tested several aromatic allyl and prenyl esters under the same conditions, their corresponding carboxylic acids were produced in very good yields. The results are summarized in Table 1. As shown in Table 1, it seems like that the electron density in aromatic ring did not much affect the efficiency of the present method. On examination of different protic organic acids (trifluoroacetic acid, trifluoromethanesulfonic acid, and chlorosulfonic acid) for the present method, we found *p*-toluenesulfonic acid as the reagent of choice in terms of yields and cleanness of reactions.

In summary, a simple, efficient, and rapid method for the deprotection of aromatic *tert*-butyl and allylic esters has been developed by combination of *p*-toluenesulfonic acid and microwave irradiation in solvent-free conditions.



Scheme 1.

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Deprotection of tert-Butyl and Allylic Esters

Substrate	Deprotection yield (%) ^a			
	R = t-butyl	R = allyl	R = prenyl	
COOR	96	97	82	
	93	90	80	
	92	82	80	
	86	86	84	
	73	70	90	
	80	72	84	

Table 1.	Yields in	deprotection	of aromatic	carboxylic	esters.
		acproceenon	01 41011444		

^aIsolated yield.

The application of the present method to other carboxylic esters is currently underway.

EXPERIMENTAL

A commercial domestic microwave oven (Samsung RE-50M) with 700 W power output was used for all reactions. ¹H NMR spectra were obtained on a Varian Gemini 2000–300 MHz spectrometer. Infrared (IR) spectra were recorded on Jasco FT-IR 5300 spectrophotometer.

General Procedure

A mixture of carboxylic ester (1.0 mmol) and *p*-toluenesulfonic acid monohydrate (0.380 g, 2.0 mmol), was placed in a 50 mL of glass tube. The reaction mixture was inserted in an alumina bath inside a domestic microwave oven and irradiated (700 W) six to eight times for a period of 30 sec with 10-sec intervals. After completion of the reaction, the product was dissolved in ethyl ether (30 mL) and extracted with aqueous 10% sodium carbonate solution (2×30 mL). The aqueous layer was neutralized with dilute HCl and the product was extracted with ethyl ether (2×20 mL). The combined organic layer was dried with sodium sulfate and evaporated to give the carboxylic acid.

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