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Synthesis of phenoxy acetic acid esters of alcohols using PNT as an activator

Sanjeev M. Reddy
Department of Chemistry,
G.M.V. Kotgyal, Dist. Nanded (M.S.) India.

Jitendra S. Pulle
Department of Chemistry,
S.G.B. College Purna (Jn.), Dist. Parbhani (M.S.), India

Abstract

A suitable method for the condensation of phenoxy acetic acid esters of alcohols explored by the activation p-methylphenoxy acetic acid and coupling with variety of alcohols, using PNT and NMM in chloroform.

Key Words: phenoxyacetic acid, alcohols, phosphonitrilic chloride, N-methyl morpholine

Introduction

Organic esters are important compounds which are widely used in the manufacturing of flavours, pharmaceuticals, plasticizers and polymers. Furthermore, these are also used as emulsifiers in the food and cosmetic industries. Different synthetic routes are available to synthesize these organic esters. Most of the esters were briefly reviewed by Yadav and Mehta. [1] The methodology for the ester synthesis most used is direct esterification of carboxylic acids with alcohols in the presence of acid catalysts. The reactions show nucleophilic attack of the alcohol on the protonated carbonyl group of the carboxylic acid [2,3] using the kinetic correlations of experimental data.

Co-ordinator
IQAC
Shri Guru Bu...
Purna (Jn) Dist. Parbhani 431...

PRINCIPAL
Shri Guru Buddhiswami Mahavidyalaya

Altiokka and Citak [4] proposed mechanism which involves the reaction of isobutanol adsorbed on the acid sides of an Amberlyst catalyst with free acetic acid from the bulk solution as the primary route for esterification. An opposite picture was proposed by Lilja et al. [5] who suggested the rate determining reaction step to the nucleophilic attack by liquid alcohol on the adsorbed carboxylic acid on Amberlyst-15.

Phosphonitrilic chloride (PNT) contains three alternative P – N subunits with six functional chlorine atoms covalently bonded to phosphorous atom. In various organic transformations, PNT has been used as dehydrating agent [6], reagent [7,8], catalyst [9-11] and as activator [12-18]. In the present work, we report the activation of phenoxy acetic acid with PNT and subsequent condensation with alcohols to give phenoxy acetic acid esters of alcohols.

The synthesis of phenoxy acetic acid esters III, by the reaction of phenoxy acetic acid I, with alcohols II, using PNT and NMM under mild conditions in good yields (Scheme 1)

I II III

Scheme 1

Experimental procedure

I. Preparation of p-methyl phenoxy acetic acid

In a round bottom flask p-cresol (1 g) and NaOH (9 mol %) were taken. Chloro acetic acid (2.5 mL) was added dropwise and little water was added in a round bottom flask. The contents of the flask were heated on water bath for 1 h, cooled and water (10 mL) was added. The contents were acidified with dilute HCl to congo-red and extracted with diethyl ether. The ethereal extract was then washed with water (10 mL). The aryloxy acetic acid obtained was then extracted by shaking with 5 % Na_2CO_3 (25 mL) solution and acidified with dilute HCl. The p-methyl phenoxy acetic acid obtained was recrystallized from ethanol.

p-Cresol Chloroacetic acid p-Methylphenoxyacetic acid

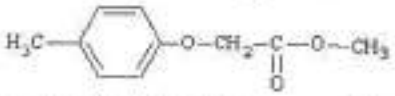
II. Preparation of phenoxy esters of alcohols

Typical procedure

PNT (0.025 mmol), NMM (1.5 mmol) and chloroform were stirred at room temperature for about 5 minutes. p-Methyl phenoxy acetic acid (1.5 mmol) was added and the reaction mixture was stirred for about 30 minutes. Methanol (5 mL) was added and stirring continued. After the completion of the reaction (monitored by TLC), the contents of the flask were washed by saturated $NaHCO_3$, then with water, dried over Na_2SO_4, filtered and evaporated in vaccum. The products obtained were purified by flash column chromatography.

Spectral analysis

The products were analysed by FTIR, ^{1}HNMR and mass spectra. The spectral data of the representative phenoxy acetic acid ester compound synthesized is given as:



p-phenoxy-4-methylphenoxyacetate

IR (cm^{-1}) : 1750 -C(=O)-O ester

1225 Ar-O-C

^{1}HNMR (ä ppm) : 2.3, s, 3H, CH_3; 3.8, s, 3H, CH_3;

4.6, s, 2H, -CH_2-; 6.8-7.2, m, 4H, Ar-H

Mass : 180 (M+)

Results and discussion

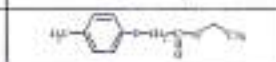
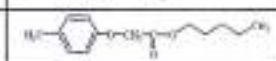
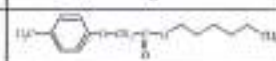
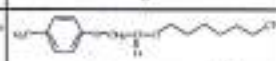
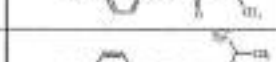
PNT was activated with NMM in chloroform which then activates p-methyl phenoxy acetic acid. The activated p-methyl phenoxy acetic acid reacts with alcohols to give the corresponding phenoxy esters of alcohols in good yields Table 1. Various alcohols reacted with p-methyl phenoxy acetic acid under mild

conditions to give corresponding esters. Primary alcohols with different chain length were reacted well to give corresponding esters. Secondary alcohol (entry 8) also reacted to give desired product but required relatively longer reaction time.

Conclusion

PNT was found to be an efficient catalyst for the condensation of p-methyl phenoxy acetic acid and a variety of alcohols to the corresponding phenoxy acetic acid esters of alcohols under mild conditions.

Table 1 : Synthesis of phenoxy acetic acid esters of alcohols using PNT/NMM

Entry	Alcohol	Phenoxyacetic acid ester	Yield (%)
1			92
2			90
4			88
4			91
5			90
6			92
7			90
8			92
9			88

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Co-ordinator IQAC
Shri Guru Buddhiswami Mahavidyalaya
Purna (Jn) Dist. Parbhani - 431511 (M.S.)

PRINCIPAL