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A novel, highly efficient azeotropic method of esterification of *p*-hydroxybenzoic acid

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ABSTRACT

p-hydroxybenzoic acid esters (Parabens) have been synthesized by azeotropic distillation technique using toluene as azeotropic agent in presence of minimum amount of concentrated sulphuric acid with corresponding alcohol. This method helps to avoid the etherification of free hydroxyl group and polycondensation of phenol containing carboxylic acid as an impurity.

KEYWORDS

Esterification;
p-hydroxybenzoic acid;
Alcohol;
Parabens;
Azeotropic distillation.

INTRODUCTION

Parabens have been attracting great interest because of their importance in synthetic organic chemistry. Parabens are associated with various biological activities viz. antifungal and antimicrobial activities[1] they have also found applications as preservative agents in foods, beverages, drugs and cosmetics[1]. The antimicrobial activity of parabens is directly dependent on the chain lenth[2,3]. Some *para*-hydroxy alkylbenzoates (parabens) are found in nature at low level in plant sources like barley, blackcurrants, peaches, carrots, onions, beans, vanilla, corn, and flax seed oil etc. Several methods for the synthesis of parabens have been reported in the literature such as *p*-TSA or $ZnCl_2$ under microwave irradiation[4], montmorillonite K10 clay[5] and ionic liquid[6]. Although these methods are suitable for certain synthetic applications but many of these methods are associated with one or more disadvantages such as long reaction time, harsh reaction conditions, unsatisfactory yields, use of expensive catalyst and tedious work-up. Consequently there is scope for further development of better yields, simple purification and separation method and easy synthetic procedure applicable to industry.

EXPERIMENTAL

General procedure

Melting points were determined in open glass capillaries and are uncorrected. ^{1}H NMR spectra were recorded at room temperature on a 400 MHz Bruker spectrometer in $CDCl_3$ using TMS as an internal standard. Reactions were monitored by TLC on aluminum sheets precoated with silica gel $60F_{254}$. *p*-hydroxybenzoic acid and alcohols were purchased from Merck, India. Alcohols were purified by distillation before use.

Typical experimental procedure for the synthesis of ethyl-4-hydroxybenzoate (3b)

A 500 mL 4-nacked round bottom flask fitted with overhead mechanical stirrer, a dropping funnel, a ther-

mometer and dean-stark with condenser. Flask was charged with 100 mL toluene, 2 mL concentrated sulphuric acid, *p*-hydroxybenzoic acid (50g, 0.362 mole) and ethanol (16.5g, 0.35 mole) and heated the reaction mixture at 95-98°C and continuously added ethanol (28.0 g, 0.6 mole) through dropping funnel within 5 h then performed azeotropic distillation with continuous removal of water formed in reaction mixture. The progress of reaction is monitored by TLC. After completion of reaction, reaction mixture was cooled to 5°C. Filtered the reaction mixture and washed with water (25mLX3) and dried in vacuo to afford the pure product in 95% yield. Product was characterized by IR, ^{1}H NMR and mass spectroscopic data.

Ethyl-4-hydroxybenzoate (3b)

Solid; m.p. 114-115°C; IR (KBr) νcm^{-1}: 3222, 2850, 3000, 1672, 1169, 1582; ^{1}H NMR (TMS) δppm: 1.2 (t, *J* = 6.8 Hz, 3H), 4.2 (q, *J* = 7.6 Hz, 2H), 6.8 (d, *J* = 8.8 Hz, 2H), 7.8 (d, *J* = 8.8 Hz, 2H), 10.3 (bs, 1H).

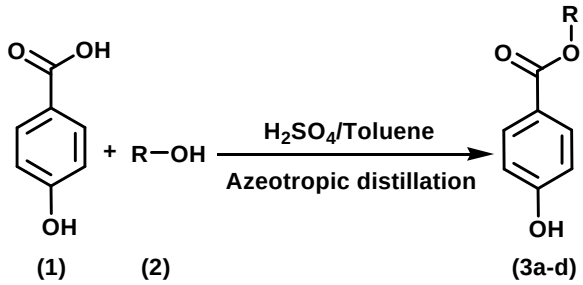
RESULTS AND DISCUSSION

Synthetic esters are generally prepared by reaction of alcohol with organic carboxylic acid in presence of catalyst such as sulphuric acid, the reaction is known as Fischer esterification. The Fischer esterification is a reversible reaction. The equilibrium is pushed to the product side by taking excess of a reactant by continuously removing the water formed in the reaction.

Herein, we report the simple and effective method for the synthesis of *p*-hydroxybenzoic acid esters (Parabens) by azeotropic distillation technique using toluene as azeotropic agent in presence of minimum amount of concentrated sulphuric acid with corresponding alcohol (Scheme 1). This method helps to avoid the etherification of free hydroxyl group and polycondensation of phenol containing carboxylic acid as an impurity. The product produced by this technique gives extremely pure and further purification is not required.

Esterification of *p*-hydroxybenzoic acid with four common alcohols was carried out under similar conditions. Results are summarized in TABLE 1. Good to excellent yields and perfect selectivity were obtained in all cases.

Azeotropic technique is seems to be more effective, efficient and economical to get highly pure compound with short reaction time and easy workup procedure. Reaction and azeotropic distillation can be carried out in same reaction vessel and as water formed in the reaction, it can be removed continuously by ternary azeotropic distillation and aqueous bottom phase separates out via phase separator. Reaction will complete within 5-6 h with minimum amount of alcohol. Recovered toluene can be used as such for next batch and corresponding alcohol can be used after purification by distillation.



Scheme 1

TABLE 1 : Efficient synthesis of parabens (3a-3d)

Entry	Alcohol	Temperature (°C)	Reaction time (h)	Product[a]	Yield (%)
1	Methanol	90-95	5	3a	94
2	Ethanol	95-98	5	3b	95
3	*n*-Propanol	90-105	6	3c	95
4	*n*-Butanol	90-105	6	3d	93

[a]**All products were characterized by IR, ^{1}H NMR and mass spectroscopic data and their mps compared with literature values**

CONCLUSIONS

In summary, a novel method for the synthesis of parabens by azeotropic distillation technique using toluene as azeotropic agent in presence of minimum amount of concentrated sulphuric acid with corresponding alcohol was developed on high yield for the first time. The main advantages of this methodology are: (1) easy synthetic procedure; (2) extremely high purity product obtained with good yields; (3) for commercial point of view, process is economical; (4) quantity of effluent is less; (5) toluene and excess alcohol can be recycled.

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