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Acetylation of alcohols by acetic acid and alcohol oxidation with hydrogen peroxide adjacent to benzyl triphenylphosphonium

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Abstract

In this project, benzyl triibromide (BTPTB) was synthesized by ion-bromide oxidation and HNO3 in the vicinity of benzyl terphenylphosphonium chloride. The use of BTPTB as a catalyst for direct acetylation of alcohols with acetic acid was investigated. Acylation reaction was performed at 70 ° C in acetic acid solvent. On the other hand, the oxidation of high-efficiency benzyl alcohol (BTPTB) in the presence of hydrogen peroxide at 60 ° C in CH3CN solvent was performed. Also, BTPTB was prepared by ion-bromide oxidation by HNO3 and its application in reactions including direct steering of alcohols using acetic acid and alcohol oxidation using hydrogen peroxide was investigated. Sterilization of alcohols was carried out using acetic acid at 70 ° C. Under these conditions, different alcohols were studied and it was found that they converted to the corresponding esters with proper efficiency.

Keywords: Benzyl trifenylphosphonium, Alcohol sterilization, Oxidation of Alcohols, Hydrogen Peroxide

1.Introduction

Ammonium and phosphonium trifluoric salts are compounds that play the role of bromine in reactions. These salts include tetrabutyl ammonium trifluoride, pyridine trifemide. Tetrabothillammonium trifluoride is one of the salts that is used extensively in organic reactions. One of the most commonly used salts of ammonium trifluoride is tetrabutylammonium trifluoride. Its uses protect carbohydrates through O-isopropylation. A wide range of O-isopropylidine derivatives can be prepared from their sugars and derivatives in reaction with acetone at room temperature with 2% of tetrabutylammonium trifluoride reagent.

Khan et al. used this reagent for O-isopropylation of carbohydrates in 2010. The best result was obtained at 96% yield over 2 hours. The advantages of this method are good yield, low catalysts, mild reaction conditions, and easy separation [1]. In 2006, Naik et al. reported a direct condensation of alcohols with

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carboxylic acids in the vicinity of the TBATB catalyst under distilled and non-solvent conditions [2]. In 2011, Borikar et al. Reported on the deposition of ariylaldehydes and ketones using a 3,1-d-n-butyllimidazolium tri-bromide catalyst ([BBIm] Br_3) in solvent-free and room temperature conditions. [3].

The stabilization of the hydroxy group and its conversion to esters is one of the most useful methods for converting organic compounds [4]. These compounds are prepared from the reaction of alcohols with carboxylic acid such as acetic acid in an acidic environment. In 2011, Liu et al. provided the reaction of esters using alcohol in a methanol solvent. Objects in 2000 reported direct concentration of carboxylic acid with adjuvants of catalytic $HfCl_4$ $(THF)_2$ [5]. In 2010, Nowrouzi et al. Combined the reaction of carboxylic acid, phenols and thiols with chloro-triphenylphosphine in the presence of molecular iodine and isadazole in acetonitrile, and the conditions for the distillation of carboxylic acid, phenol and thioserides [6]. Recent research has shown that ecological oxidants such as oxygen are used to replace peroxides [7] and harmful heavy metals such as dichloromethane and progamate [8-9] in organic reactions. Hydrogen peroxide is considered as an important oxidizing agent in chemical transfer in organic reactions [10].

Hydrogen peroxide is unique because of the production of water as a byproduct of a single oxidizing agent. In organic reactions, hydrogen peroxide is better oxidised than oxygen, some of the oxygen / organic compounds may spontaneously ignite [11]. In 2013, Niamonda et al. reported the oxidation of aromatic alcohols and alcoholic alcohols using titanium (IV) oxide (TiO2) as a catalyst with 30% hydrogen peroxide. Also, in 2016, De et al. Reported a stable four-dimensional aluminum salt prepared by phosphorus with ammonium oxide oxidation as oxidizing alcohol catalysts [12].

In this study, according to the catalysts mentioned for organic transformations, such as alcohol starchation and oxidation of alkali alcohol in the vicinity of H_2O_2, which is usually used from an H_2+ generator, BTPTB using ion-bromide oxidation with HNO_3 and stearing of alcohols using acetic acid were prepared. Also, the oxidation of basic alcohol in the vicinity of hydrogen peroxide as an appropriate oxidizer was carried out. Furthermore, various factors in this reaction such as solvent type, catalyst content and temperature investigated.

2. Materials and methods

2.1. Materials

The chemicals used in this study were purchased from the German Mercantile Company. Some solvents were purchased from the German corporation and some domestic companies. The reaction progresses were controlled by thin layer chromatography (TLC) using 60 F_{254} silica gel plates and the compounds were observed by ultraviolet light (UV) or by iodine iodization. Ethyl acetate and n-hexane solvents were used for TLC. Compounds prepared by TLC plates were isolated and purified. The melting points were recorded by the Perkin Elmer RXI spectrophotometer as a KBr tablet.

2.2. Preparation of benzyl trifenylphosphonium chloride

A 20 ml thin-walled balloon containing trifenylphosphine (50mmol, 1 / 31g), benzyl chloride (10mmol1, / 26g) was added and stirred at 120 ° C for half an hour, then mixed and cooled to reach to the room temperature. 5 ml of dimethyl ether solvent was added and washed with a funnel twice with dimethyl

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ether (5 ml) and dried completely. As a result, the benzyl trifenyl-phosphonium chloride salt yielded 89%, and the melting point was 337 ° C.

2.3. oxidation of alcohol using a BTPTB catalyst

A 25 ml balloon containing the benzyl alcohol (1 mmol) and acetonitrile (5 ml), hydrogen peroxide (0/4 mL), and amount (0.3 mmol 0, / 17 g) of the BTPTB catalyst was prepared and mixed at 60 ° C. by magnetic stirrer. The progression of TLC reaction in a mixture of ethyl acetate and n-hexane solvents was investigated with a ratio of 1 to 6.

3.Discussion and results

3.1. Preparation of benzyl trifenylphosphonium trifluoride (BTPTB) reactors

Preparation of benzyl triphenylphosphonium trifluoride was performed in two steps: First Step is the reaction of trifenylphosphine and benzyl chloride as the benzyl trifenylphosphonium chloride salt. The second step is the oxidation of benzyl trifenylphosphonium chloride salt in the vicinity of ion bromide and HNO_3 salt of benzyl trifenylphosphonium tribromide. In this method, the ion bromide is oxidized by HNO_3 to the tris (Fig. 1).

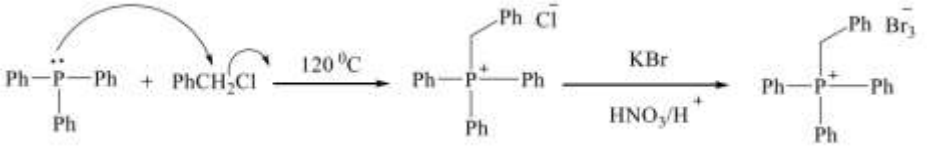


Figure 1: Preparation of benzyl triphenylphosphonium trifluoride reagent

3.2. The direct sterilization of alcohol by acetic acid in the vicinity of the BTPTB

Various methods have been reported for the direct sterilization of alcohols. One of the methods for direct sterilization of alcohols is acetylation, which is often carried out using solventless anhydride stearate. In this section, direct stearization of the alcohols using acetic acid was performed by the catalyst BTPTB. As a model, 4,2-dichlorobenzyl alcohol was selected as an alcohol (Fig. 2).

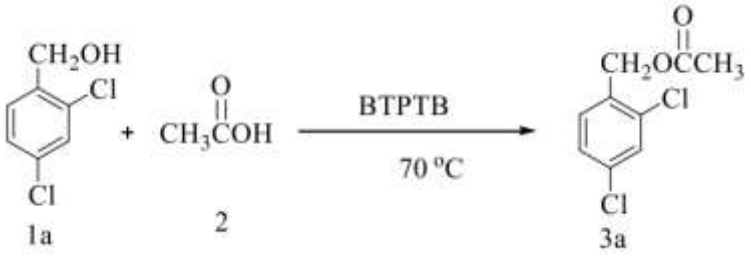


Figure 2: Direct Steriodination of 4,2-Dichlorobenzyl alcohol by acetic acid in the vicinity of BTPTB

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3.2.1. Amount of catalyst and the effect of temperature

To investigate the effect of temperature and amount of catalyst, a reaction of one millimol of 4,2-dichlorobenzyl alcohol with 1.5 milliliters of acetic acid was investigated in different conditions, and the results are presented in Table 1.

Table 1: Catalysts and Temperature Effects in the Preparation of 4,2-diclorobenzyl acetate

Num.	Convert (%)	Time (min)	Temp. ©	the catalyst amount (mmol)
1	80	120	70	–
2	90	30	70	0.02
3	90	20	70	0.04
4	95	10	70	0.06
5	10	30	25	0.06
6	90	40	50	0.06
7	95	6	100	0.06

According to the Table 1 in number 1 to 4, to evaluate the effect of BTPTB catalyst on the reaction rate of 2,4-dichlorobenzyl acetate, various catalysts at 70 ° C were used. It was observed that using a 0.06 millimole of BTPTB catalyst, acetic acid reaction with 1 millimol of alcohol was performed in 10 minutes with 95% conversion to 4,2-dichlorobenzyl acetate. In order to achieve the best temperature in rows 5-7, a mixture of reaction in the vicinity of 0.06 millimoles of BTPTB catalyst in a balloon washed and given in an oil bath at 50, 70 and 100 degrees Celsius and room temperature.

3.2.2. Comparison of the efficiency of the BTPTB catalyst with a number of reported catalysts

In order to evaluate the efficiency of the BTPTB catalyst in the process of direct alcohol sterilization, we compared the reaction of benzyl acetate using acetic acid in the vicinity of BTPTB with a similar process in the vicinity of some of the reported catalysts. Results are reported in Table 2.

Table 2- evaluate the efficiency of the BTPTB catalyst in the process of direct alcohol sterilization

Num.	Efficiency	Time (min)	Solvent	the catalyst	Refferenc
1	80	**60**	**MeOH**	Fe-PILLC	13
2	100	**180**	-	SBA-15	14
3	74	**120**	MeOH	$[PdCl_2(CH_3CN)_2]$	15
4	100	25	-	$TiCl_3$ (OFT)	16
5	93	10	Acetic Acid	BTPTB	–

3.3. Oxidation of alcohol by catalyst BTPTB

the oxidation of alkaline alcohol by hydrogen peroxide in the vicinity of the catalyst BTPTB was investigated. Benzyl alcohol was used to obtain optimal conditions. Benzyl alcohol reaction with H_2O_2 was carried out in the vicinity of the BTPTB catalyst in the acetonitrile solvent (Fig. 3).

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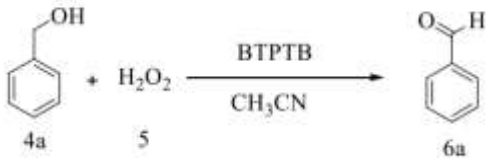


Figure 3: Benzyl alcohol oxidation, adjacent to the BTPTB catalyst

3.3.1. Effect of hydrogen peroxide, catalyst value, solvent and temperature

To optimize the reaction, a number of investigations were carried out to determine the amount of hydrogen peroxide, catalysts, solvent effect and temperature effect. The following are discussed in the table 3.

Table 3- the amount of hydrogen peroxide, catalysts, solvent and temperature effect

Num.	Convert (%)	Time (min)	Temp. C	Solvent	Katalyst)mmol(	H_2O_2)mL(
1	75	85	60	CH_3CN	0.2	0.2
2	75	75	60	CH_3CN	0.2	0.3
3	80	50	60	CH_3CN	0.2	0.4
4	80	40	60	CH_3CN	0.2	0.5
5	20	300	60	CH_3CN	–	0.4
6	85	60	60	CH_3CN	0.1	0.4
7	85	60	60	CH_3CN	0.15	0.4
8	90	40	60	CH_3CN	0.3	0.4
9	30	120	r.t	CH_3CN	0.3	0.4
10	80	60	40	CH_3CN	0.3	0.4
11	90	30	80	CH_3CN	0.3	0.4
12	85	60	60	CH_3CO_2Et	0.3	0.4
13	65	95	Reflux	$(C_2H_5)_2O$	0.3	0.4
14	85	50	60	THF	0.3	0.4
15	65	600	Reflux	CH_2Cl_2	0.3	0.4
16	20	60	60	Solvent Free	0.3	0.4

According to the results of Table 3 in number 1 to 4, the effect of hydrogen peroxide in the vicinity of the BTPTB catalyst at a temperature of 60 ° C in an acetonitrile solvent was investigated. It can be seen that, in numbers 1 to 2, 0.2 and 0.3 milliliters of hydrogen peroxide were used, the efficiencies of the products were 75% and the time was 85 and 75 minutes, respectively. In the third number, 0.4 milliliters of hydrogen peroxide were used and observed that the reaction time was shortened as a result of 0.4 milliliters of hydrogen peroxide as optimal.

Also, the use of 0.5 milliliters of hydrogen peroxide after 40 minutes from the beginning of the reaction, the product was obtained with a yield of 80%, but the preferred use of lower amounts of raw material resulted in the selection of 0.4 milliliters of hydrogen peroxide. In number 5 to 9, the effect of the BTPTB

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catalyst on the reaction rate of benzaldehyde was used from various catalysts at 60 ° C and in acetonitrile solvent.

It was observed that using a 0.3 millimol of reaction catalyst after 40 minutes, the product was obtained with a conversion of 90%. In numbers 9 to 12, the reaction temperature of benzaldehyde was used in acetonitrile solvent at different temperatures. It was observed that at 40 ° C the reaction after 60 minutes of the product was obtained by converting to 80%. Using a temperature of 80 ° C, the reaction was made after a period of 35 minutes with a yield of 90%, so to achieve shorter times and temperatures below 60 ° C as the optimum temperature in the reaction Preparation of benzaldehyde was used.

In number 13 to 17, the effect of solvent in the reaction of benzyl alcohol oxidation was investigated. Different solvents were compared when the acetonitrile solvent was used at a temperature of 60 ° C. The reaction time was shorter and the product yield was higher Compared with other solvents reported in the table. Thus, optimal conditions for the reaction of benzaldehyde from 1 mmol of benzyl alcohol are as follows: reaction with 0.4 milliliters of hydrogen peroxide in the vicinity of 0.3 millimoles of BTPTB catalyst in 5 mL of acetonitrile at 60 ° C Selected. Therefore, in general optimal conditions for the oxidation of alcohol are summarized in Fig. 4.

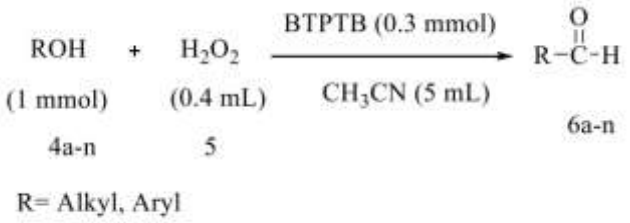


Figure 4: Optimal conditions for alcohol oxidation

4. Conclusion

Tritium salts, due to their high efficiency and ease of use, have great application in the synthesis of organic reactions. In this project, BTPTB was prepared by ion-bromide oxidation by HNO_3 and its application in reactions including direct stearing of alcohols using acetic acid and alcohol oxidation using hydrogen peroxide was investigated. Sterilization of alcohols was carried out using acetic acid at 70 ° C. Under these conditions, different alcohols were studied and it was found that they converted to the corresponding esters with proper efficiency. The oxidation of alcohol in the vicinity of H_2O_2, was used at 60 ° C, and alkaline alcohols converted to the appropriate aldehydes with suitable efficiency.

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