

Acylation of Alcohols Using Acetic Acid and Oxidation of Alcohols Using Hydrogen Peroxide in the Presence of Benzyl Triphenylphosphonium Tribromide

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Abstract: -In this study benzyl triphenylphosphonium tribromide was prepared by oxidation of bromide ion with HNO_3 in the prescnce of benzyl triphenylphosphonium chloride in H_2O as solvent.

The application of BTPTB as catalyst for direct acetylation of alcohols with acetic acid was investigated. The acetylation reaction was performed at 70°C in acetic acid. On the other hands, oxidation of benzylic alcohols was achived in high yield by BTPTB in the presence of hydrogen peroxide at 60°C in CH_3CN as solvent.

Keywords: Benzyl triphenylphosphonium tribromide, Acylation of alcohols, Oxidation alcohols, Hydrogen peroxide

1-1- An overview of tribromide salts and their use in organic reactions

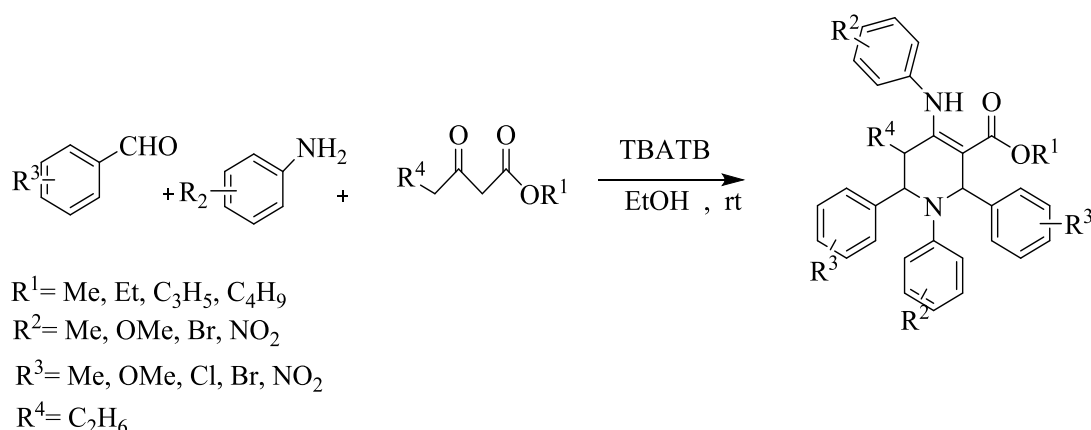
Ammonium salts and phosphonium tribromide are compounds that play the role of bromine in reactions, among these salts we can refer to tetrabutylammonium tribromide, pyridinium tribromide, etc. In this section, some of these salts and their use in organic reactions are mentioned.

1-1-1- tetrabutylammonium tribromide (TBATB)

Tetrabutylammonium tribromide is one of the salts that is widely used in organic reactions. In this section, 3 examples of reactions performed by this catalyst are mentioned.

1-1-1-1- Preparation of functionalized pipyridines

In 2010, Chadheri and co-workers reported a useful and environmentally friendly synthesis of tetrabutylammonium tribromides [1]. A wide variety of organic transformations of tetrabutylammonium tribromide have been reported by other authors [2]. One-pot multicomponent reaction, the preparation of functionalized pipyridine derivatives from the reaction of aromatic aldehydes, aromatic amines and 1,3-dicarbonyl derivatives in the presence of TBATB catalyst has been reported (Scheme 1-1).



Scheme 1-1: Preparation reaction of functionalized pypyridine in the vicinity of tetrabutylammonium tribromide TBATB

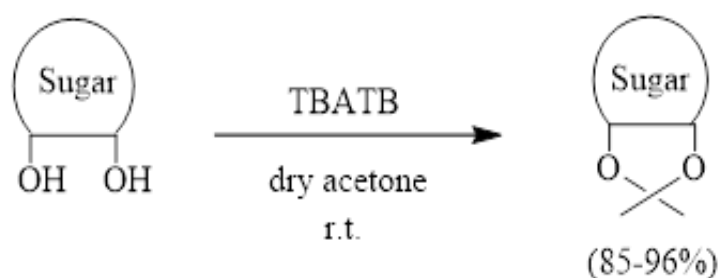
The time of these reactions is between 8-47 hours and the yield is between 24-75%. The advantages of using this method include good yield, mild reaction conditions, environmentally friendly, lack of boring separation methods and low cost.

1-1-1-2-Tetrabutylammonium tribromide (TBATB) is an effective and mild reagent for O-isopropylation of carbohydrates.

Another one of the most widely used ammonium tribromide salts is tetrabutylammonium tribromide. One of its applications is the protection of carbohydrates through O-isopropylation. A wide range of O-isopropylidene derivatives can be prepared from sugars and their derivatives by reacting with acetone at room temperature with 2 mol% of tetrabutylammonium tribromide reagent.

The O-isopropylidene acetal group is a common protecting group that is widely used in carbohydrate chemistry to prepare valuable building blocks.

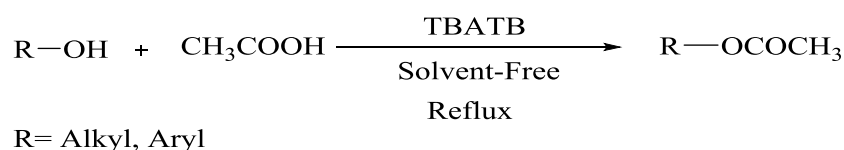
In 2010, Abuti Khan and his colleagues used this reagent for the -O-isopropylation of carbohydrates. The best result was obtained in 2 hours with an efficiency of 96%. The advantages of this method include good efficiency, low amount of catalyst, mild reaction conditions and easy separation (Scheme 1-2) [3].



Scheme 1-2:O-isopropylation of sugars

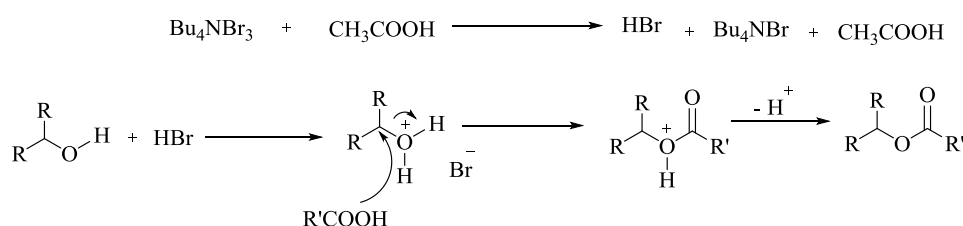
1-1-1-3- Direct condensation of carboxylic acids with alcohols

In 2006, Naik and co-workers reported the direct condensation of alcohols with carboxylic acids in the vicinity of TBATB catalyst under solvent-free reflux conditions (Scheme 1-3) [4].



Scheme 1-3: Preparation of esters in the vicinity of TBATB catalyst

The proposed mechanism for this reaction is shown in (Scheme 1-4).

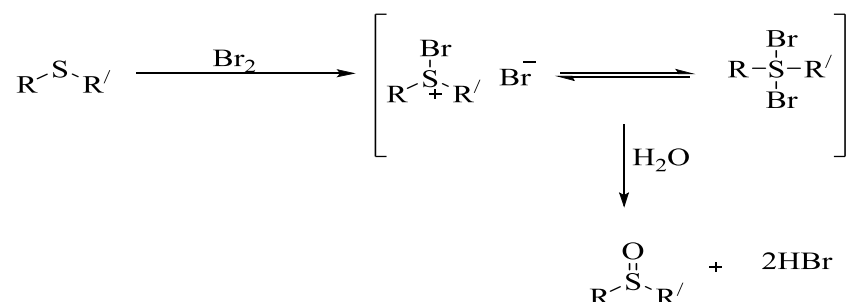


Scheme 1-4: Proposed mechanism for acetylation

In this reaction, aliphatic and aromatic alcohols with electron donating and withdrawing groups have been used in the vicinity of the TBATB catalyst under conditions of reverse distillation without solvent. that alcohols of the first type give better results in less time than alcohols of the second type. The time of these reactions is between 10-60 minutes and the yield of the products is reported between 80-95%.

1-1-2- Oxidation of sulfides to sulfoxides in the vicinity of pyridinium tribromide (PyHBr₃)

In 2006, Mr. Heshmat Ali and colleagues synthesized a variety of sulfides in the vicinity of the pyridinium tribromide (PyHBr₃) catalyst with hydrated silica gel, oxidized non-aqueous intermediates [5]. The combination of pyridinium tribromide and hydrated silica gel slowly releases molecular bromine and bromine oxidizes sulfide (Scheme 1-5) [6-9].

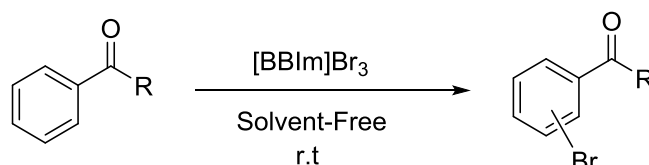


Scheme 1-5: Oxidation of sulfides to sulfoxides in the vicinity of PyHBr₃ catalyst

In this reaction, dialkyls, arylalkyls and diarylsulfides are used with silica gel in the vicinity of PyHBr_3 catalyst. The time of these reactions is between 20-150 minutes and the yield is between 43-100%. The advantages of this method are high efficiency, formation of non-aqueous intermediates and easy operation.

1-1-3- Bromination of aldehydes and ketones using 1,3-di-n-butyl-imidazolium tribromide ionic liquid ($[\text{BBIm}]\text{Br}_3$) under solvent-free conditions

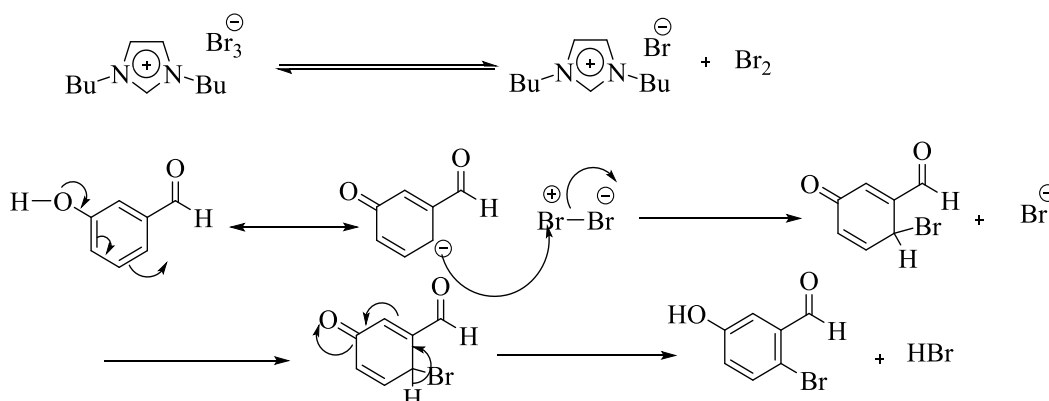
In 2011 Burikar and co-workers reported the bromination of aryl aldehydes and ketones using 1,3-di-n-butylimidazolium tribromide ($[\text{BBIm}]\text{Br}_3$) catalyst under solvent-free conditions at room temperature. (Scheme 1 -6) [10]



R= Alkyl, Aryl

Scheme 1-6: Bromination of aldehydes and ketones in the presence of 1,3-di-n-butylimidazolium tribromide ($[\text{BBIm}]\text{Br}_3$)

The proposed mechanism for the bromination of aromatic aldehydes and ketones in the vicinity of $[\text{BBIm}]\text{Br}_3$ catalyst is shown in Scheme 1-7.



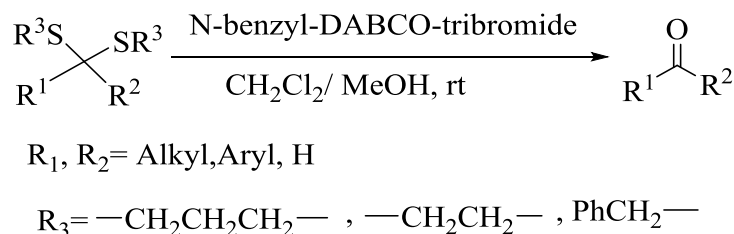
Scheme 1-7: Proposed mechanism of the bromination reaction of aldehydes and aromatic ketones in the vicinity of $[\text{BBIm}]\text{Br}_3$ catalyst

In this method, tribromides as an ionic liquid play an important role in obtaining monobromo derivatives with the final goal of their synthesis, in solvent-free and safe conditions [11,12].

Disadvantages of this method include long reaction time, halogenated solvents, harsh reaction conditions, use of expensive catalyst, average yield and difficult separation of some products. Reaction time up to 120 minutes and product yield up to 98% have been reported.

1-1-4- Use of N-benzyl dabcotribromide catalyst in the deprotection of dithioacetals

In 2005, Moghadi Moghadam and his co-workers presented a method using N-benzyl dabcotribromide catalyst as an efficient and recyclable reagent for the deprotection of dithioacetals in dichloromethane/methanol solvents at room temperature. This reaction was performed in a short time and with a better yield (Scheme 1-8) [13].



Scheme 1-8: Deprotection of dithioacetals in the vicinity of N-benzyl dabcotribromide catalyst

The advantages of this method are: high yield, short reaction time, cheap and non-toxic reagent. Therefore, the reaction time is between 3-10 minutes and the yield of the products is between 85-98%.

Protecting groups are useful tools in organic syntheses, among which, dithioacetals are of particular importance due to their stability, acidic conditions, and also as acylcarbonium equivalents in organic syntheses [14].

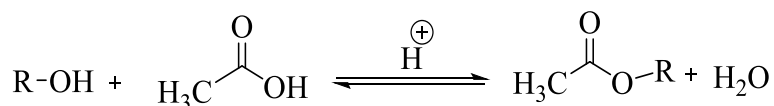
However, the main problem of thioacetals is deprotection and preparation of related carbonyl compounds [15]. From salts of heavy elements such as mercury (II) chloride [16], mercury (II) oxide, boron trifluoride-diethyl ether [17], cerium (IV) ammonium nitrate, selenium dioxide [18], silver iodine nitrate [19] and bismuth nitrate [20] can be mentioned for the deprotection of dithioacetals. These substances are very toxic and not water friendly. Recently, benzyl-triphenylphosphonium tribromide and 1-benzyl-4-aza-1-azoniabicyclo [2-2-2] octane have been used to deprotect di-thioacetals in the corresponding carbonyl compounds [21].

1-2- An overview of esterification methods of alcohols

Research on the processes related to the protection of functional groups is one of the most important issues related to organic chemistry. Protection of functional groups often requires several interconversions during the synthesis process, especially in carbohydrates and steroids [22].

Acetylation of the hydroxy group and its conversion to esters is one of the most useful methods in converting organic compounds [23]. These compounds are prepared from the reaction of alcohols with carboxylic acids such as acetic acid in acidic medium (Scheme 1-9).

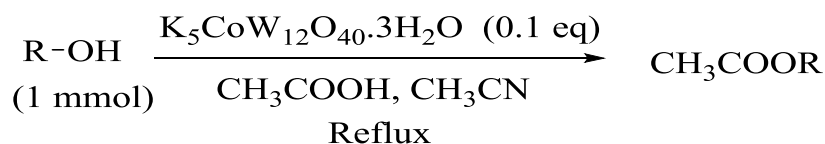
Esters are used as very useful chemicals in the pharmaceutical, food and cosmetic industry [24].

**Scheme 1-9:** Reaction of esters in the presence of acetic acid

Various methods for esterification of alcoholic compounds have been reported in different articles [25]. In this section, we review the methods reported in different articles.

1-2-1- Using potassium dodeca tungsto cobaltate.

Three water ($\text{K}_5\text{CoW}_{12}\text{O}_{40} \cdot 3\text{H}_2\text{O}$) as a catalyst
In 2001, Habibi and colleagues from potassium dodecatungstocobaltate. used three water ($\text{K}_2\text{CoW}_{12}\text{O}_{40} \cdot 3\text{H}_2\text{O}$) as a mild catalyst for the esterification of alcohols by acetic acid (Scheme 1-10) [26].



R=Alkyl, Benzyl

Scheme 1-10: Direct esterification of alcohols in the vicinity of the catalyst of dodecatungstocobaltate, three water ($\text{K}_5\text{CoW}_{12}\text{O}_{40} \cdot 3\text{H}_2\text{O}$)

Also, the said catalyst can be recovered and used for several times without losing efficiency. For example, the yield of 1-heptyl acetate produced by the reaction of 1-heptanol and acetic acid is 98% after 4 catalyst recovery times and 85% after 7 recovery times.

1-2-2- Use of triethylammonium salts as ionic liquids

Today, ionic liquids are of interest as a non-toxic catalyst to perform many reactions [27]. Many of them are used in performing esterification reactions [28,29]. In 2007, Ganeshpour and his colleagues have used ionic liquids such as triethylammonium sulfate, trimethylammonium dihydrogen phosphate, and triethylammonium tetrafluoroborate for the esterification of carboxylic acids with aliphatic alcohols (Scheme 1-11) [30].

**Scheme 1-11:** Using triethylammonium salts as ionic liquids

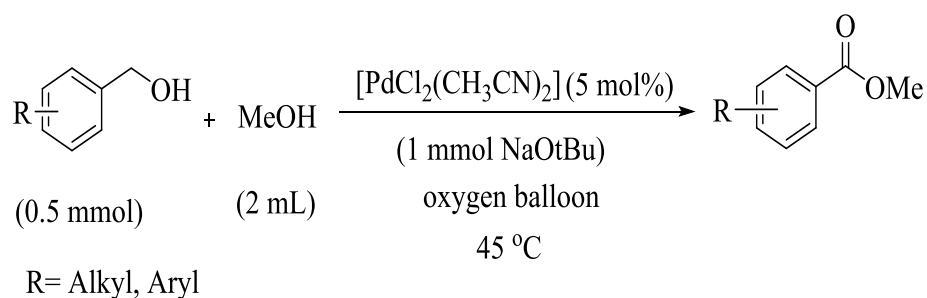
In their research, they found that the higher the acid strength of the ionic liquids, the higher the reaction efficiency. For example, after increasing the amount of

catalyst from paratoluenesulfonic acid to triethylammonium tetrafluoroborate ionic liquid, the reaction efficiency increased from 18% to 90%.

1-2-3-Direct esterification of alcohols using palladium catalys

Ester groups are one of the most important and abundant functional groups found among natural materials and polymers [31-32].

In 2011 Liu and co-workers presented the reaction of esters using alcohols in methanol solvent (Scheme 1-12).

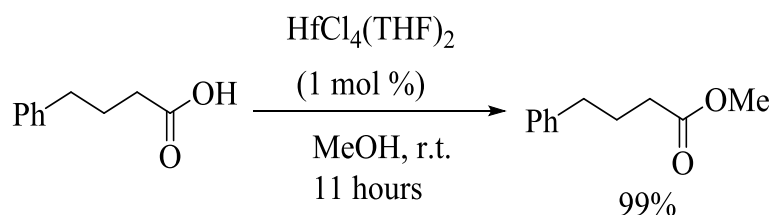


Scheme 1-12: Preparation of esters in the vicinity of Pd^{II} catalyst

In this reaction, aromatic and aliphatic alcohols are used in the vicinity of palladium aerobic catalyst at a temperature of 45 °C and methanol as a solvent. The efficiency of the products is between 60-89%.

1-2-4- direct condensation of carboxylic acids with alcohols with hafnium (IV) salt

In 2000, Ashihara reported the direct condensation of carboxylic acids with alcohols in the presence of HfCl₄ (THF)₂ catalyst (Scheme 1-13) [33].



Scheme 1-13: Direct esterification reaction of carboxylic acids with alcohols in the vicinity of HfCl₄(THF)₂ catalyst

In this reaction, aromatic and aliphatic alcohols are used in the vicinity of 1% mol of solid carbon acid catalyst in toluene solvent and at room temperature. The time of these reactions is between 5-36 hours and the yield is between 91-99%. One of the advantages of this method is the use of high strength recyclable catalyst.

1-2-5-Comparison of different heterogeneous catalysts and different alcohols for oleic acid esterification reaction

In 2008, Marchetti and co-workers reported an esterification method using oleic acid and various alcohols in the vicinity of heterogeneous catalysts (Scheme 1-14) [34].

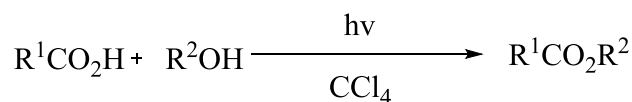


Scheme 1-14: Reaction of esters in the vicinity of heterogeneous catalysts

R and R' represent a carbon chain, where R' represents alcohols of the first type [35-40].

1-2-6- Use of esterification of carboxylic acids with alcohols in methane Perhalogens

In 2004, Riohao and co-workers synthesized esters with high selectivity from the reaction of carboxylic acids and alcohols under photocatalytic conditions using CCl_4 or $BrCCl_3$ at room temperature (Scheme 1-15) [41].



$R^1 = \text{Alkyl, Aryl}$

$R^2 = \text{MeOH, EtOH, } C_3H_7OH$

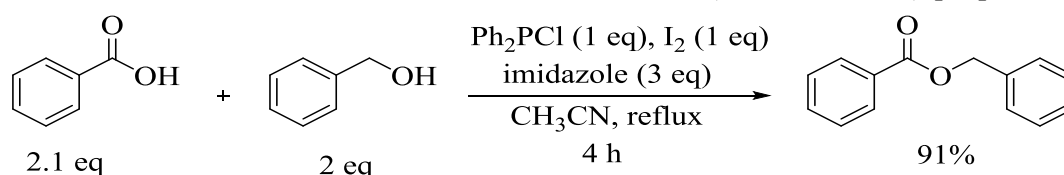
Scheme 1-15: Esterification in the vicinity of CCl_4

By studying the photochemical reactions of various organic compounds, they found that carboxylic acids are easily converted to the corresponding esters in the presence of alcohols and carbon tetrachloride [42].

They reported reaction time between 2.5-72 hours and product yield between 66-99%.

1-2-7- Use of chlorodiphenylphosphine, molecular iodine and imidazole in acetonitrile solvent

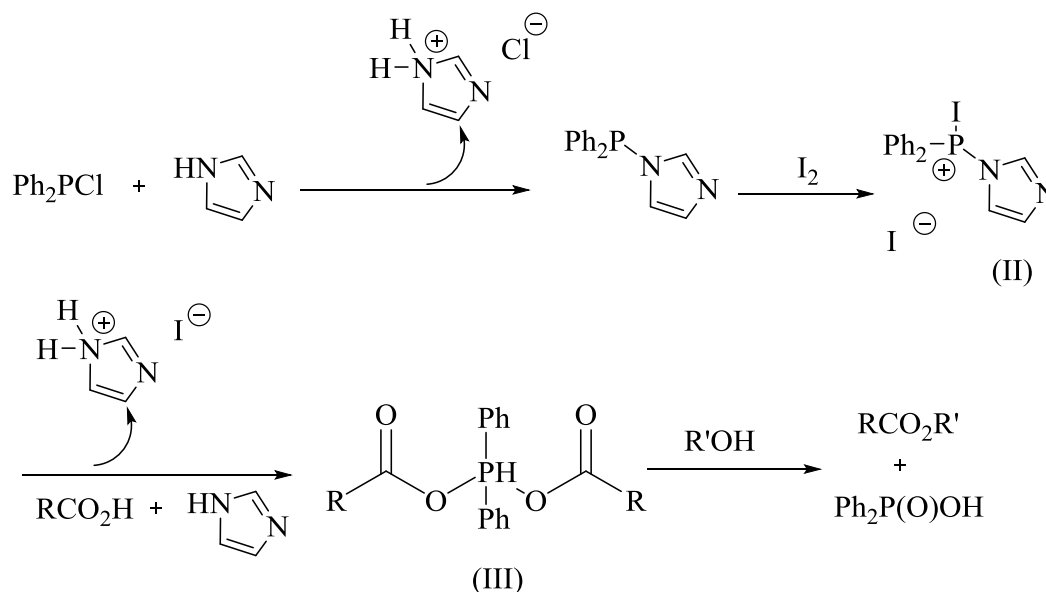
In 2010, Norouzi and his colleagues synthesized the alkyl esters of carboxylic acids, phenolics and thioesters from the reaction of carboxylic acids, phenols and thiols with chlorodiphenylphosphine in the vicinity of molecular iodine and imidazole in acetonitrile solvent and reflux distillation conditions (Scheme 1-16) [43].



Scheme 1-16: Preparation of alkyl esters of carboxylic acids, phenolic and thioesters

Electron-withdrawing groups on the benzoic acid ring, such as NO₂, give more efficiency in a short time, but electron-donating groups on the benzoic acid ring, such as CH₃, give more efficiency in a longer time.

The proposed mechanism to carry out the reaction in this method is shown in (Scheme 1-17).



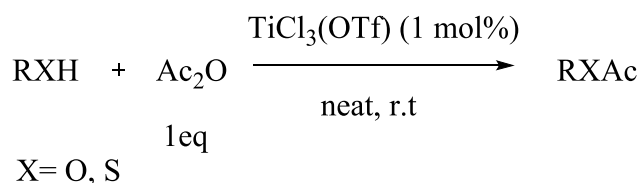
Scheme 1-17: Proposed mechanism for esterification

Imidazoles not only neutralize the released halogen acids, but also increase the reactivity of reagent systems.

In this reaction, aliphatic alcohols and benzyl alcohols have been used in the vicinity of Ph_2PCl catalyst, in acetonitrile solvent and under reverse distillation conditions. The time of these reactions is between 1-5.5 hours and the yield of the products is between 88-93%. Alcohols of the first type have less time and better efficiency than alcohols of the second type, and alcohols of the third type do not form a product. Ester reactions have also been considered in the pharmaceutical industry [44].

1-2-8- Using titanium (IV) trichlorotrifluoromethanesulfonate $\text{TiCl}_3(\text{OTf})$ as a catalyst

In 2008, Firouzabadi and his colleagues used solid titanium (IV) trichlorotrifluoromethanesulfonate (TiCl_3) as an active, non-toxic and suitable catalyst for the direct esterification of alcohols, phenols, thiols and α -hydroxyphosphonates. with acetic anhydride in the presence of organic solvents at room temperature and solvent-free conditions (Scheme 1-18) [45].



Scheme 1-18: Esterification reaction in the vicinity of $\text{TiCl}_3(\text{OTf})$ catalyst

They reported reaction times between 1-120 minutes and product yields between 77-100%. As a result, alcohols of the first, second, allylic and benzylic types were converted to the corresponding ester with high efficiency in a short period of time.

1-3- A review of oxidation methods of benzyl alcohols

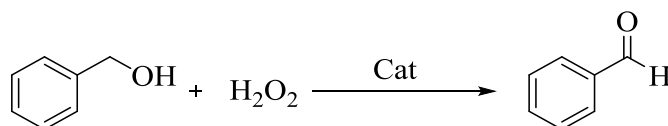
Recent research has used environmentally friendly oxidants such as oxygen to replace peroxides [46-47] and toxic heavy metals such as dichloromethane and permanganate [48-49] in organic reactions. Hydrogen peroxide is considered as an important oxidant in chemical transitions in organic reactions [50]. Hydrogen peroxide is a unique oxidant because it produces water as a byproduct. In organic reactions, hydrogen peroxide is a better oxidant than oxygen. Some oxygen/organic compounds mixtures may spontaneously ignite [51].

Another advantage of using hydrogen peroxide compared to other cheap oxidants, such as sodium perborate and many organic peroxyacids, is its high stability. The limiting factor for the use of H_2O_2 as an oxidant in organic reactions is the unavoidable presence of water in commercial hydrogen peroxides and reduction products.

Few articles have been published on the topic of oxygen utilization in catalyzed oxidation reactions.

Among the characteristics of this reagent, we can mention its extraction and use and its cheapness.

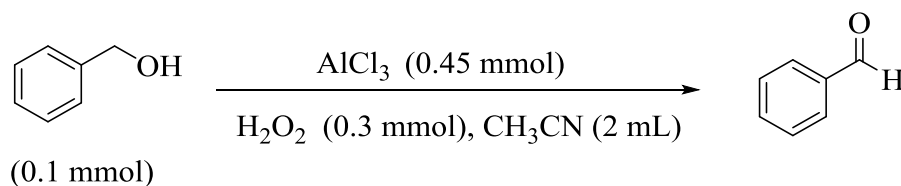
The general oxidation reaction of benzyl alcohols using hydrogen peroxide as an oxidizing agent is shown in Scheme 1-19.



Scheme 1-19: Reaction of benzyl alcohol in the presence of hydrogen peroxide
Here we review some of the articles reported in this field.

1-3-1- Oxidation of benzyl alcohols using aluminum trichloride (AlCl_3) as a catalyst

In 2008, Lee and co-workers used aluminum trichloride (AlCl_3) as an active catalyst in the oxidation of benzyl alcohols by H_2O_2 as an oxidizing agent (Scheme 1-20) [52].

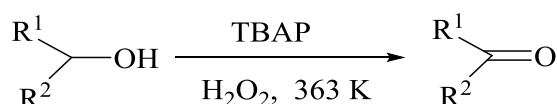


Scheme 1-20: Oxidation of benzyl alcohols using AlCl_3 as a catalyst in the vicinity of hydrogen peroxide

In this method, benzyl alcohols, benzhydrol and their derivatives were converted to aldehydes and corresponding ketones with high efficiency. For example, benzyl alcohol was converted to benzaldehyde with 95% conversion. One of the disadvantages of this method is that chain alcohols have a low percentage conversion, for example, octanol was converted to the corresponding aldehyde with a yield of 55%.

1-3-2-Oxidation of alcohols with triethyl ({2,4,6-trimethyl-3,5-bis[(triethylazaniomyl)methyl]-phenyl} methyl)azanium (tribromide) in the presence of hydrogen peroxide

In 2012, Hay and co-workers reported the oxidation of alcohols using the catalyst triethyl ({2,4,6-trimethyl-3,5-bis[(triethylazaniomyl)methyl]phenyl}methyl)azanium (tribromide) (reported TBAP) in the vicinity of hydrogen peroxide (Scheme 1-21) [53].



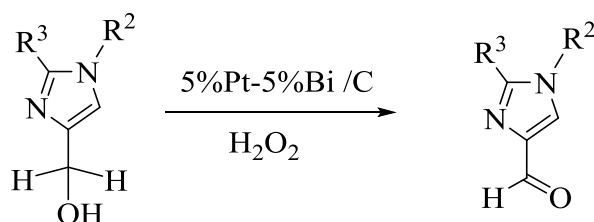
Scheme 1-21: Type (II) alcohol reaction in the presence of hydrogen peroxide

The main advantage of this method is the solvent-free conditions and that the catalysts can be prepared easily and without the use of toxic substances and used for the next cycle. Also, this catalyst can be recycled and reused without losing its activity.

The results show that the oxidation is carried out by the complex complex of TBAP and hydrogen peroxide with high percentages.

1-3-3-Oxidation of alcohols using bismuth platinum catalyst modified on carbon in the vicinity of hydrogen peroxide

A bismuth platinum-on-carbon catalyst [54-56] for the oxidation of hydroxymethylimidazoles (alcohols) to formylimidazoles (aldehydes) in the presence of hydrogen peroxide is shown in (Scheme 1-22).

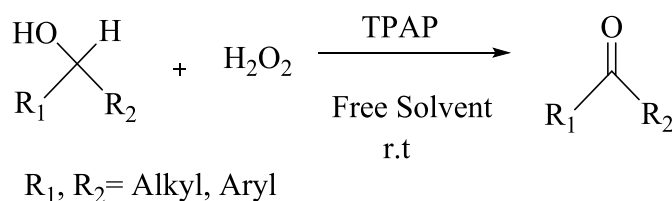


Scheme 1-22: Oxidation of hydroxymethylimidazoles

Formylimidazoles are also used in the preparation of pharmaceuticals such as diuretics and antihypertensives. In this reaction, alcohol derivatives of pyrazoles are used in the vicinity of hydrogen peroxide and at a temperature of 60 °C. The time of these reactions is between 60-90 minutes and the yield is between 67.3-100%.

1-3-4- Oxidation of alcohols using tetra-n-propylammonium perruthenate (TPAP) catalyst

Campestrini and co-workers reported the oxidation of alcohols using hydrogen peroxide by the catalyst tetra-n-propylammonium perruthenate (TPAP) with pure silica gel at room temperature and under solvent-free conditions (Scheme 1-23) [57].

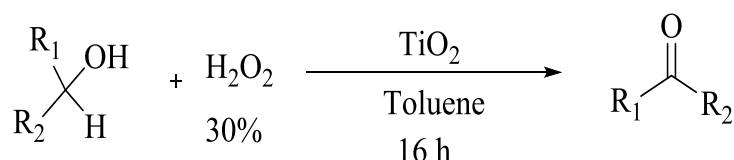


Scheme 1-23: Oxidation of alcohols using TPAP catalyst

In this method, aliphatic and aromatic alcohols are used in the vicinity of TPAP catalyst at room temperature. The efficiency of reactions is between 28-100%.

1-3-5- Oxidation of alcohols using titanium (IV) oxide (TiO₂) as a catalyst

In 2013, Nyamionda and co-workers reported the oxidation of aromatic alcohols and alkyl alcohols using titanium (IV) oxide (TiO₂) as a catalyst by 30% hydrogen peroxide (Scheme 1-24) [58].



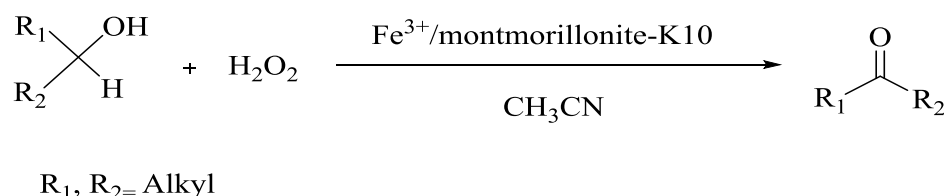
$R_1, R_2 = \text{Alkyl, Aryl}$

Scheme 1-24: Oxidation of alcohols using TiO₂ as a catalyst in the vicinity of hydrogen peroxide

Aromatic and aliphatic alcohols are involved in this reaction and the yield of products is between 35-100%.

1-3-6-Oxidation of alcohols using Fe^{3+} /montmorillonite-k10 catalyst

Oxidation of different alcohols using hydrogen peroxide by Fe^{3+} /montmorillonite-k10 catalyst in acetonitrile solvent was investigated (Scheme 1-25) [59].

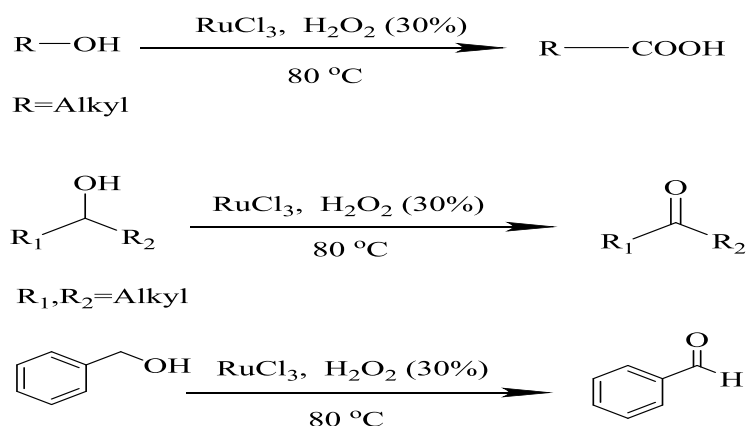


Scheme 1-25: Oxidation of alcohols using Fe^{3+} /montmorillonite-k10 catalyst in the vicinity of hydrogen peroxide

The advantages of this method include short reaction time, easy separation of some products, high yield. In this method, aliphatic and aromatic alcohols are used using hydrogen peroxide in the presence of montmorillonite k10 catalyst in acetonitrile solvent. The efficiency of the products is between 92-100%.

1-3-7- Oxidation of alcohols using ruthenium trichloride (RuCl_3) catalyst

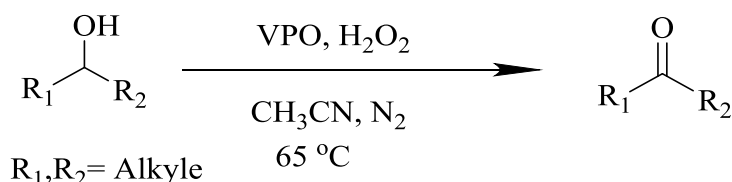
Oxidation of alcohols using hydrogen peroxide is performed by RuCl_3 ruthenium trichloride catalyst under phase transition conditions. In this method, alcohols of the second type are converted to ketones (100%), benzylic alcohol of the first type is converted to aldehyde (95-100%) and alcohols Aliphatics of the first type are converted to carboxylic acid (60-70%) and the reaction took place at 80°C , and the role of phase transfer is the transfer of H_2O_2 and RuCl_3 to the organic phase, as well as the preservation of the catalyst metal in the oxide state (Scheme 1-26) [60].



Scheme 1-26: Oxidation of alcohols using RuCl_3 catalyst in the vicinity of hydrogen peroxide

1-3-8- Oxidation of alcohols using hydrogen peroxide by vanadium phosphorus oxide catalyst

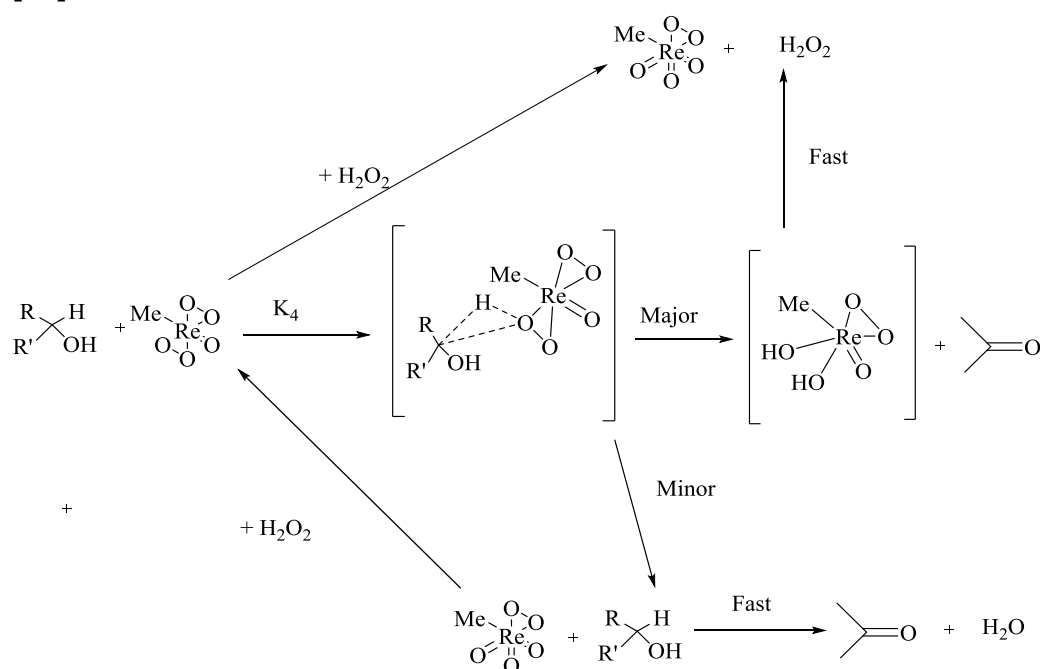
In 2013, Nyamionda and co-workers reported vanadium phosphorus oxide (VPO), which is an effective catalyst for liquid phase oxidation of alcohols using hydrogen peroxide in acetonitrile solvent at 65 °C under nitrogen atmosphere (Scheme 1-27) [61].



Scheme 1-27: Oxidation of alcohols using hydrogen peroxide by VPO catalyst

1-3-9- Oxidation of alcohols using hydrogen peroxide by methyltrioxornium catalyst

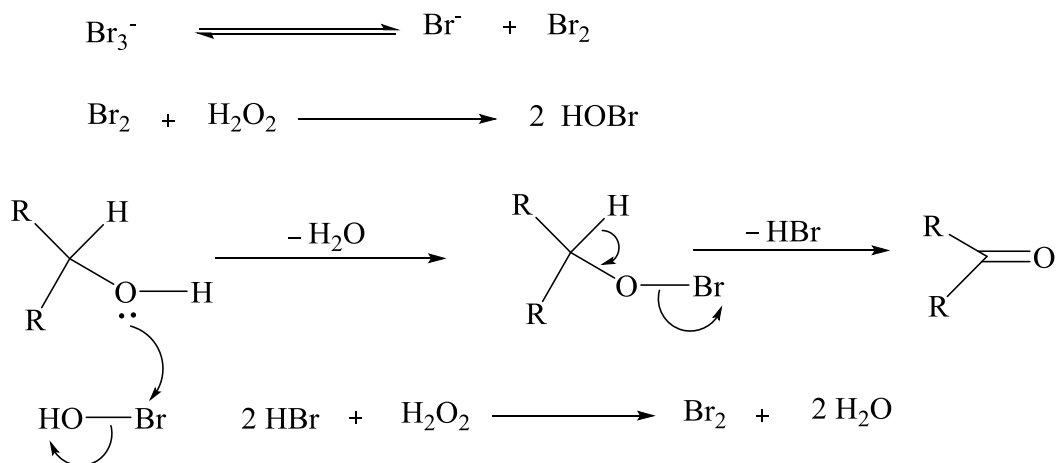
Oxidation of alcohols using hydrogen peroxide (30%) to oxidize alkenes, hydroxyamines and halides through the addition of a small amount of methyltrioxornium (MTO) catalyst by different mechanisms is shown in (Scheme 1-28) is [62].



Scheme 1-28: Proposed mechanism for the oxidation of alcohols using MTO catalyst in the presence of hydrogen peroxide

1-3-10- Oxidation of alcohols using quaternary ammonium tribromide salt by hydrogen peroxide

In 2013 Mr. Day and co-workers reported a stable quaternary ammonium salt of tribromide prepared by oxidation of ammonium bromide by persulfate as a catalyst for the oxidation of alcohols (Scheme 1-29) [63].



Scheme 1-29: Proposed mechanism for the role of Br_3 as a catalyst in the oxidation reaction of alcohols

The time of these reactions is between 1-62 hours and the yield is between 72-97%. One of the advantages of this method is the use of a high-strength recyclable catalyst.

1-4-research goal

According to the catalysts mentioned in the previous sections for organic transformations such as esterification of alcohols and oxidation of benzyl alcohols in the vicinity of H_2O_2 , which is usually an H^+ generating acid or a Lewis acid, in this project we intend to benzyl tri Phenylphosphonium tribromide (BTPTB) was prepared by using the oxidation of bromide ion with HNO_3 and as a mild catalyst to create Br_2 necessary to catalyze reactions such as the direct esterification of alcohols using acetic acid and also the oxidation of benzyl alcohols in Use the proximity of hydrogen peroxide as a suitable oxidant. Various factors in this reaction, such as the type of solvent, the amount of catalyst, and the type of temperature will be investigated.

Experimental part

1-2- public section

The chemicals used in this research were purchased from Merck, Germany. Some solvents were purchased from Merck, Germany, and some from domestic companies. The progress of the reactions was monitored by thin layer chromatography (TLC) using Merck 60 F_{254} silica gel plates, and the compounds were observed by ultraviolet (UV) light irradiation or by impregnation with iodine vapors. Ethyl acetate and n-hexane solvents were used for TLC. The prepared products were separated and purified by TLC plates. Melting points were

determined by electrothermal device 9100. Infrared (IR) spectra were recorded by Perkin Elmer RXI spectrophotometer in the form of KBr tablets.

2-2- Preparation of benzyltriphenylphosphonium chloride reagent

Benzyl chloride (1.26 g, 10 mmol) was added to a 20 ml round-bottom flask containing triphenylphosphine (1.31 g, 5 mmol), and the flask was placed in an oil bath with a temperature of 120 °C for half an hour. It was stirred, then the obtained mixture was cooled to room temperature, and 5 mL of diethyl ether solvent was added to it, and it was filtered through a funnel and washed twice with diethyl ether (5 mL), the precipitate was completely dried. As a result, benzyltriphenylphosphonium chloride salt was obtained with 89% yield and melting point of 337 °C.

2-3- Preparation of benzyltriphenylphosphonium tribromide reagent (BTPTB) through the oxidation of bromide ion by nitric acid

Benzyltriphenylphosphonium chloride (3 g, 7.72 mmol) was dissolved in a 50 ml flask containing 10 mL of distilled water, and a solution of KBr (2.57 g, 23.16 mmol) in 5 mL of distilled water was added to it. It was stirred at room temperature by a magnetic stirrer. Then concentrated nitric acid (3.7 mL) was added drop by drop until a yellow-orange precipitate was formed. The obtained mixture was stirred for 50 minutes, then the resulting precipitate was filtered with filter paper and washed with distilled water (3x10 mL). The yellow-orange precipitate separated in oven was completely dried and the benzyl triphenylphosphonium tribromide salt was obtained with a yield of 89%, and a melting point of 112 °C [64, 65].

2-4-Direct acetylation of alcohols

2-4-1- General method of direct esterification of alcohols using BTPTB catalyst

In a 20 ml round bottom flask containing benzyl alcohol derivative (1 mmol) and acetic acid (1.5 mL), the amount of catalyst (0.03 g, 0.06 mmol) was added. The reaction was placed in a reflux distillation mode in an oil bath with a temperature of 70 °C. The progress of the reaction was checked by TLC in the solvents of n-hexane and ethyl acetate in ratios of 1:3 and the complete reaction time was recorded. After the completion of the reaction, the reaction mixture was poured into a funnel with ethyl acetate (4 mL) and washed with saturated sodium bicarbonate solution (2 x 3 mL). After separating the organic phase from the aqueous phase, the organic phase by Sodium sulfate was dried without water. The final product was obtained after evaporation using a rotary evaporator.

2-4-2- Preparation of 2,4-dichlorobenzyl acetate derivative using BTPTB catalyst

In a 25 ml round bottom flask containing 2,4-dichlorobenzyl alcohol (1 mmol), acetic acid (1.5 mL) and the amount of BTPTB catalyst (0.03 g, 0.06 mmol) were added and the mixture The reaction was subjected to reflux distillation.

The progress of the reaction was checked by TLC in a solution of ethyl acetate and n-hexane with a ratio of 1 to 3. After the completion of the reaction (10 min), the reaction mixture was poured into a separatory funnel with ethyl acetate (4 mL) and washed with saturated sodium bicarbonate solution (2 x 3 mL). After separation, the organic phase was dried by anhydrous sodium sulfate and 2,4-dichlorobenzylacetate was obtained in the amount of 179 mg (yield 95%) after evaporation of the solvent by a rotary evaporator.

2-5- Oxidation of alcohols in the presence of hydrogen peroxide

2-5-1- General method of oxidation of alcohols using BTPTB catalyst

To a 25 ml round bottom flask containing benzyl alcohol derivative (1 mmol) and acetonitrile solvent (5 mL), hydrogen peroxide (0.4 mL) and amount of BTPTB catalyst (0.17 g, 0.3 mmol) were added and The flask was placed in an oil bath at a temperature of 60 °C. The reaction mixture was stirred by a magnetic stirrer. The progress of the reaction was checked by TLC in a mixture of ethyl acetate and n-hexane with a ratio of 1 to 6.

After the completion of the reaction, the reaction mixture was poured into the separating funnel with ethyl acetate (4 mL) and washed with saturated sodium bicarbonate solution (2 x 3 mL). After separating the organic phase from the aqueous phase, the organic phase was dried using anhydrous sodium sulfate. The final product was obtained after evaporation of the solvent using a rotary evaporator.

2-5-2-Preparation of 4-chlorobenzaldehyde derivative (6f) using BTPTB catalyst

A 25 ml round bottom flask containing 4-chlorobenzyl alcohol (1 mmol) and acetonitrile solvent (5 mL), hydrogen peroxide (0.4 mL) and amount (0.17 g, 0.3 mmol) of BTPTB catalyst were added. And it was stirred in an oil bath at a temperature of 60 °C. The progress of the reaction was checked by TLC in a mixture of ethyl acetate and n-hexane with a ratio of 1 to 6.

After the completion of the reaction, the reaction mixture was poured into a separatory funnel with ethyl acetate (4 mL) and washed with saturated sodium bicarbonate solution (2 x 3 mL). After separating the organic phase from the aqueous phase, the organic phase was dried using anhydrous sodium sulfate. 4-Chlorobenzaldehyde was obtained after evaporation of the solvent using a rotary evaporator, in the amount of 182.5 mg (90% yield).

1-3- Preparation of benzyltriphenylphosphonium tribromide (BTPTB) reagents

Bromine is a molecule that is widely used as a reagent for bromination and oxidation of organic compounds. Since liquid bromine is a toxic and dangerous compound and there are problems such as transporting and weighing it, many attempts have been made by organic chemists to replace it with another suitable reagent. Tribromides are more suitable than liquid bromine because they are solid, so they are easy to store, transport and maintain. Recently, the application and use of methods of producing tribromides without the use of bromine have been expanded and in these methods, an oxidant is usually used to produce Br_2 from Br^- in the medium and to prepare tribromides without removing bromine from the reaction medium. Recently, working has been developed on the use of methods for the production of tribromides without the use of bromine. In this project, we plan to prepare benzyltriphenylphosphonium tribromide (BTPTB) salts by using bromide ion oxidation by concentrated nitric acid (HNO_3) in aqueous medium and introduce the use of the resulting salt in the direct esterification of alcohols in Check the proximity of acetic acid and the oxidation of benzyl alcohols to aldehydes.

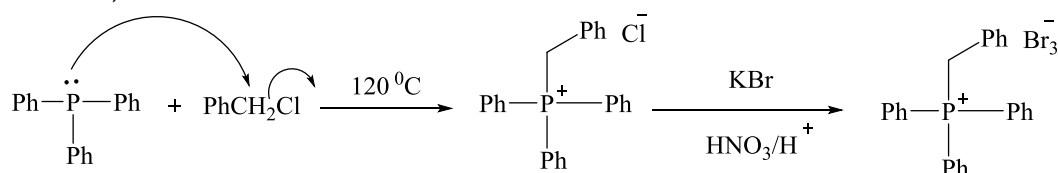
The preparation of benzyltriphenylphosphonium tribromide reagent is done in two steps:

First step: First, from the reaction of triphenylphosphine and benzyl chloride, benzyltriphenylphosphonium chloride salt is obtained.

Second stage: benzyltriphenylphosphonium tribromide salt is formed from the oxidation of benzyltriphenylphosphonium chloride salt in the vicinity of bromide ion and HNO_3 .

In this method, bromide ion is oxidized to tribromide by HNO_3

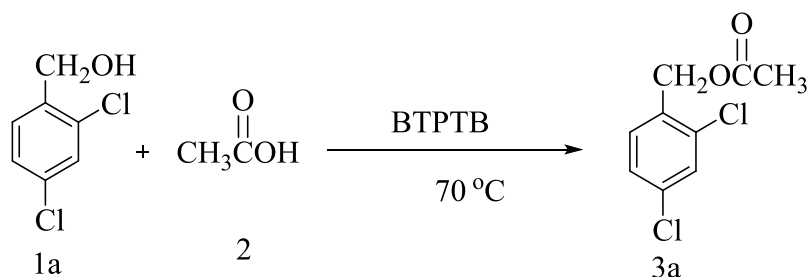
(Scheme 3-1).



Scheme 3-1: Preparation of benzyltriphenylphosphonium tribromide reagent

3-2-Direct esterification of alcohols by acetic acid in the vicinity of BTPTB

Various methods for direct esterification of alcohols have been reported. Among the methods of direct esterification of alcohols is acetylation, which is often done using acetic anhydride in solvent-free conditions. In this section, direct esterification of alcohols using acetic acid was performed by BTPTB catalyst. Among the alcohols, 2,4-dichlorobenzyl alcohol was chosen as a model (Scheme 3-2).



Scheme 3-2: Direct esterification of 2,4-dichlorobenzyl alcohol by acetic acid in the vicinity of BTPTB

To optimize the conditions, things like the amount of catalyst and the effect of temperature were investigated. The following are reviewed.

3-2-1- Investigating the amount of catalyst and the effect of temperature used in the esterification of alcohols

To investigate the effect of temperature and amount of catalyst, the reaction of 1 mmol of 2,4-dichlorobenzyl alcohol with 1.5 ml of acetic acid was investigated under different conditions and the results are shown in Table 3-1.

Table 3-1: Investigating the amount of catalyst and the effect of temperature in the preparation of 2,4-dichlorobenzylacetol

conversion percentage	time (minutes)	Temperature (°C)	Amount of catalyst (mmol)	Row
80	120	70	-	1
90	30	70	0.02	2
90	20	70	0.04	3
95	10	70	0.06	4
10	30	25	0.06	5
90	40	50	0.06	6
95	6	100	0.06	7

1: The reaction was investigated using 1 mmol of 2,4-dichlorobenzyl alcohol and 1.5 ml of acetic acid.

2: Progress of the reaction was followed by TLC

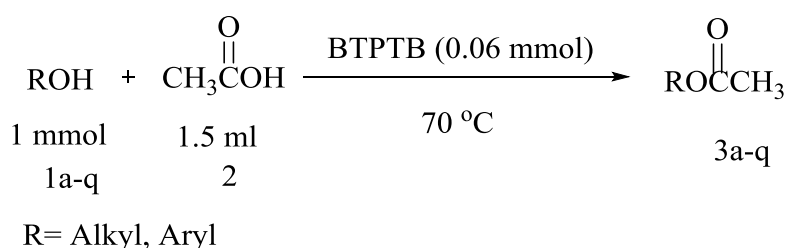
According to the results of table 3-1 in rows 1 to 4, to investigate the effect of BTPTB catalyst amount on the reaction speed of 2,4-dichlorobenzyl acetate preparation, different amounts of catalyst were used at 70 degrees Celsius. It was observed that using 0.06 mmol of BTPTB catalyst, the reaction of acetic acid with 1 mmol of alcohol was carried out after 10 minutes with 95% conversion to 2,4-dichlorobenzyl acetate.

Using amounts of 0.02 and 0.04 mmol of catalyst, the reaction was performed in times higher than 10 minutes, so in order to achieve shorter times, 0.06 mmol of catalyst was selected.

In order to achieve the best temperature in rows 5 to 7, a reaction mixture in the vicinity of 0.06 mmol of BTPTB catalyst was placed in a round-bottom flask and in an oil bath with temperatures of 50, 70 and 100 °C and room temperature given.

At temperatures below 70 °C, the reaction time is long, and at room temperature, the product yield is less than 50%, while at 70 and 100 °C, the product yield is 95%, and the reaction time is 10 and 6 minutes, respectively. Considering the preference of using a lower temperature in this method, 70 degrees Celsius was chosen as the optimal temperature.



Therefore, the optimal conditions for the preparation of esters are as follows: alcohol 1 mmol, acetic acid 1.5 ml and catalyst in the amount of 0.06 mmol, temperature 70 degrees Celsius (Scheme 3-3).

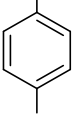
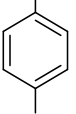
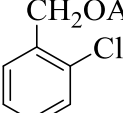
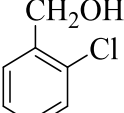
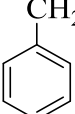
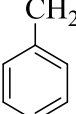
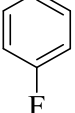
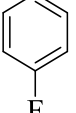
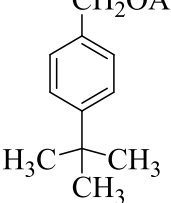
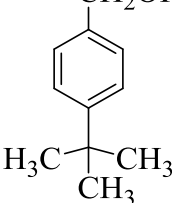
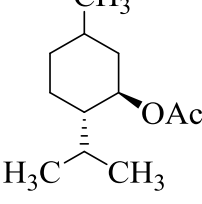
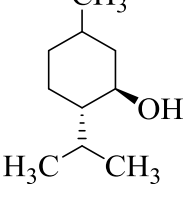
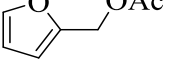
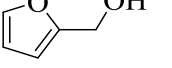
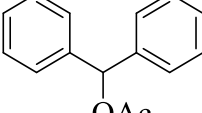
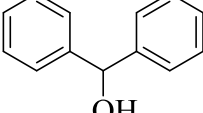


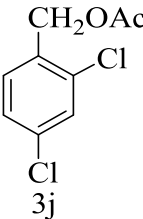
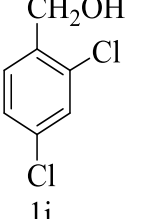
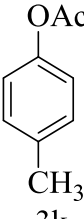
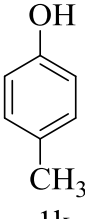
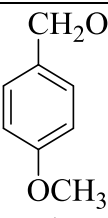
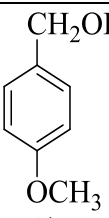
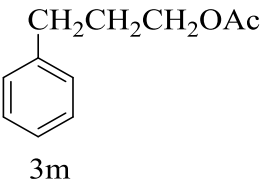
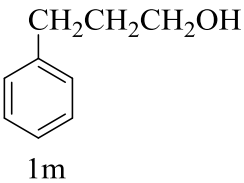
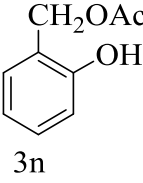
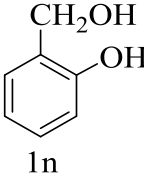
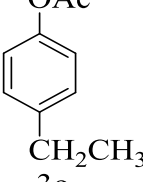
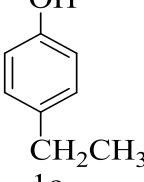
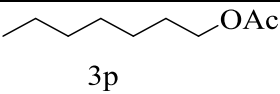
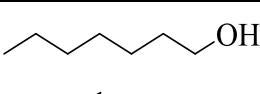
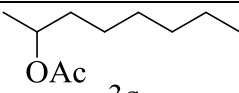
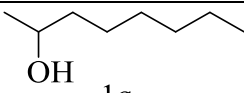
Scheme 3-3: Direct esterification of alcohols with acetic acid in the vicinity of BTPTB catalyst

In this way, based on the above optimal conditions, the reaction of the preparation of esters with various derivatives of alcohols was investigated, which led to the formation of products with good yield. The results are shown in table (3-2).

Table 3-2: Acetylation of alcohols and phenols through the reaction between 1 mmol of alcohol or phenol and 1.5 ml of acetic acid in the vicinity of 0.06 mmol of BTPTB catalyst at a temperature of 70 degrees Celsius

Returns	time (minutes)	the product	Alcohol/phenol	Row
93	10	CH_2OAc  3a	CH_2OH  1a	1

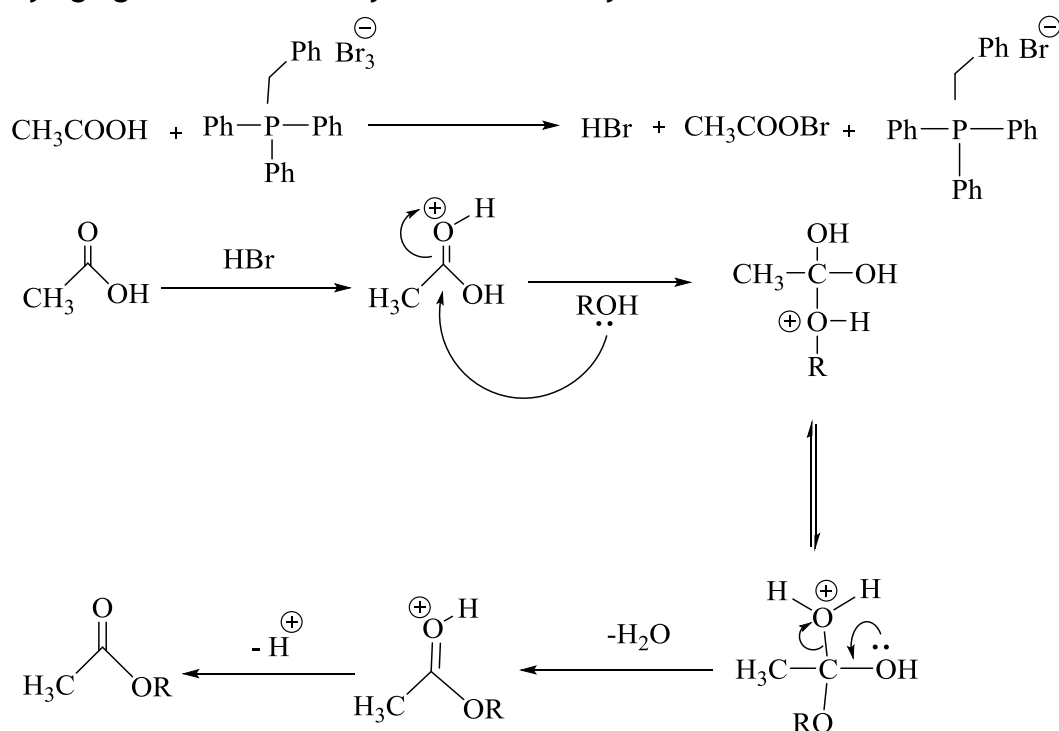
85	12	CH_2OAc  Cl 3b	CH_2OH  Cl 1b	2
85	12	CH_2OAc  3c	CH_2OH  1c	3
50	50	CH_2OAc  NO_2 3d	CH_2OH  NO_2 1d	4
83	13	CH_2OAc  F 3e	CH_2OH  F 1e	5
80	15	CH_2OAc  H_3C CH_3 3f	CH_2OH  H_3C CH_3 1f	6
86	3	CH_3  OAc H_3C CH_3 3g	CH_3  OH H_3C CH_3 1g	7
60	10	 OAc 3h	 OH 1h	8
90	5	 OAc 3i	 OH 1i	9

95	10	 <p>3j</p>	 <p>1j</p>	10
80	5	 <p>3k</p>	 <p>1k</p>	11
88	22	 <p>3l</p>	 <p>1l</p>	12
90	45	 <p>3m</p>	 <p>1m</p>	13
90	20	 <p>3n</p>	 <p>1n</p>	14
70	5	 <p>3o</p>	 <p>1o</p>	15
85	23	 <p>3p</p>	 <p>1p</p>	16
75	50	 <p>3q</p>	 <p>1q</p>	17

Esters are compounds that are sensitive to an acidic environment and in an acidic environment they turn into raw materials very quickly, therefore, the acidic environment must be neutralized immediately after the reaction is complete. For this purpose, in the extraction stage, saturated sodium bicarbonate was added to the reaction mixture.

In this method, alcohols of the first type such as heptanol are converted to the corresponding ester in a short period of time and with high efficiency due to the lack of steric hindrance compared to the second type alcohols. Alcohols of the second type, such as 2-octanol, have a lower speed due to more steric hindrance, but they have good efficiency.

The proposed mechanism of esterification of alcohols using acetic acid as an esterifying agent in the vicinity of BTPTB catalyst is shown in Scheme 3-4.



Scheme 3-4: Proposed mechanism of esterification in the vicinity of BTPTB catalyst

IR spectrum was used to identify esters. As an example, in the IR spectrum of benzyl acetate (spectrum 3-1, page 64) and 4-methoxybenzyl acetate (spectrum 3-2, page 65), the presence of a C-O stretching band at 1242 and an ester C=O stretching band at 1741 indicates the formation of an ester. It is relevant.

3-2-2- Comparison of BTPTB catalyst efficiency with a number of reported catalysts in direct esterification of alcohols. In order to check the effectiveness of BTPTB catalyst in the process of direct esterification of alcohols, we compared the reaction of preparing benzyl acetate

using acetic acid in the vicinity of BTPTB with the similar process in the vicinity of some reported catalysts. The results are reported in Table 3-3.

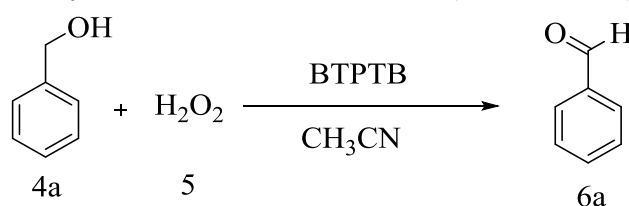
Table 3-3: Comparison of the preparation of esterification of benzyl alcohol with acetic acid in the presence of BTPTB with the same process in the presence of some catalysts reported for this process

Referenc e	Return s	time (minutes)	Conditions	SOLVEN T	the catalyst	Ro w
(66)	80	1h	60C°	MeOH	Fe-PILLC.	1
(67)	100	3h	room temperatur e	Solvent free	SBA-15	2
(31)	74	2h	45C°	MeOH	[PdCl ₂ (CH ₃ CN) ₂]]	3
(45)	10	25	room temperatur e	Solvent free	TiCl ₃ (OTF)	4
-	93	10	70C°	Acetic acid	BTPTB	5

3-3-Oxidation of alcohols by BTPTB catalyst

Various methods have been used to oxidize alcohols. In most of these methods, transition metals that pollute the environment have been used. Recently, the use of metal-free organic oxidants such as H₂O₂ has become common.

In this section, the oxidation of benzyl alcohols by hydrogen peroxide in the vicinity of BTPTB catalyst is investigated. Benzyl alcohol was used to obtain optimal conditions. The reaction of benzyl alcohol with H₂O₂ was carried out in the presence of BTPTB catalyst in acetonitrile solvent (Scheme 3-5).



Scheme 3-5: Oxidation of benzyl alcohol, in the vicinity of BTPTB catalyst

To check the optimal conditions, changes in the amount of H₂O₂, the amount of catalyst, the effect of temperature, and the effect of the role of the solvent were used. It should be noted that this reaction proceeds slowly at room temperature and it is necessary to use reverse distillation conditions.

3-3-1-Investigating the amount of hydrogen peroxide, the amount of catalyst, the effect of solvent and the effect of temperature in the oxidation reaction of alcohols

In order to optimize the reaction, things like hydrogen peroxide amount, catalyst amount, solvent effect and temperature effect were investigated. The mentioned items are checked in the table below.

Table 3-4: Investigation of the amount of catalyst, the amount of hydrogen peroxide, the effect of solvent and the effect of temperature in the preparation of aldehydes

conversion percentage	time (minutes)	temperature (Degree)	SOLVENT	Amount of catalyst (mmol)	Amount of H ₂ O ₂ (mL)	ROW
75	85	60	CH ₃ CN	0.2	0.2	1
75	75	60	CH ₃ CN	0.2	0.3	2
80	50	60	CH ₃ CN	0.2	0.4	3
80	40	60	CH ₃ CN	0.2	0.5	4
20	300	60	CH ₃ CN	-	0.4	5
85	60	60	CH ₃ CN	0.1	0.4	6
85	60	60	CH ₃ CN	0.15	0.4	7
90	40	60	CH ₃ CN	0.3	0.4	8
30	120	r.t	CH ₃ CN	0.3	0.4	9
80	60	40	CH ₃ CN	0.3	0.4	10
90	35	80	CH ₃ CN	0.3	0.4	11
85	60	60	CH ₃ CO ₂ Et	0.3	0.4	12
65	95	Reflux	(C ₂ H ₅) ₂ O	0.3	0.4	13
85	50	60	THF	0.3	0.4	14
65	60	Reflux	CH ₂ Cl ₂	0.3	0.4	15
20	60	60	Solvent Free	0.3	0.4	16

1: Reaction using 1 mmol of benzyl alcohol in 5 mL of solvent and under different conditions

2: Percent conversion obtained via TLC

According to the results of table 3-4 in rows 1 to 4, the effect of the amount of hydrogen peroxide in the vicinity of the BTPTB catalyst at a temperature of 60 degrees Celsius in acetonitrile solvent was investigated.

It can be seen in rows 1 to 2 that 0.2 and 0.3 ml of hydrogen peroxide were used, the efficiency of the products is 75% and the times are 85 and 75 minutes respectively. In the third row, 0.4 ml of hydrogen peroxide was used and it was

observed that the reaction time was shortened, as a result, the amount of 0.4 ml of hydrogen peroxide was chosen as optimal.

Also, using 0.5 ml of hydrogen peroxide after 40 minutes from the start of the reaction, the desired product was obtained with an efficiency of 80%, but the preference of using smaller amounts of the raw material made the amount of 0.4 ml of hydrogen peroxide be chosen.

In rows 5 to 9, to investigate the effect of the BTPTB catalyst amount on the reaction rate of benzaldehyde preparation, different amounts of the catalyst were used at 60°C and in acetonitrile solvent.

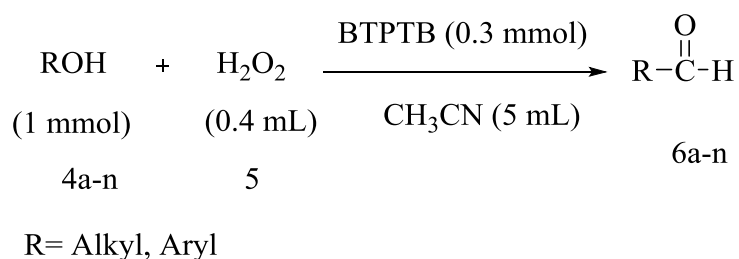
It was observed that by using the amount of 0.3 mmol of reaction catalyst after 40 minutes, the product was obtained with 90% conversion. By using less than 0.3 mmol of catalyst, the reaction time is longer and the yield of the products is lower than 90%. Therefore, in order to achieve shorter times, the amount of 0.3 mmol of the catalyst was chosen.

In rows 9 to 12, different temperatures were used to investigate the effect of temperature in the reaction of preparing benzaldehyde in acetonitrile solvent.

It was observed that at a temperature of 40 degrees Celsius, after 60 minutes, the product was obtained with 80% conversion. By using a reaction temperature of 80°C, after 35 minutes, the product was produced with a yield of 90%, therefore, in order to achieve shorter times and a lower temperature, 60°C was used as the optimal temperature in the reaction for the preparation of benzaldehyde.

In rows 13 to 17, the effect of solvent in the oxidation reaction of benzyl alcohol was investigated. According to the results obtained in Table 3-4, by comparing different solvents with each other, it was observed that when acetonitrile solvent is used at a temperature of 60 degrees Celsius, the reaction time is shorter and the yield of the product is higher compared to others. Solvents reported in the table. Therefore, the optimal reaction conditions for the preparation of benzaldehyde from 1 mmol of benzyl alcohol are as follows: reaction with 0.4 mL of hydrogen peroxide in the vicinity of 0.3 mmol of BTPTB catalyst in 5 mL of acetonitrile solvent at a temperature of 60 °C became.

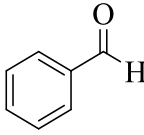
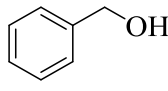
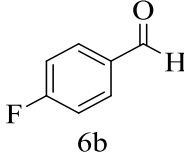
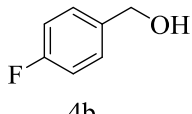
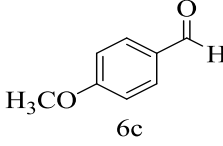
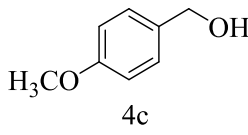
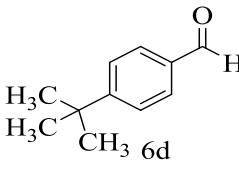
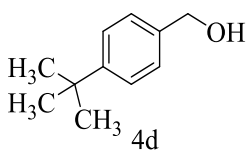
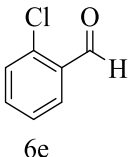
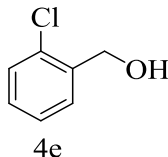
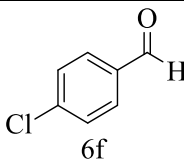
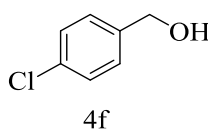
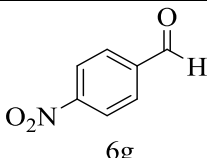
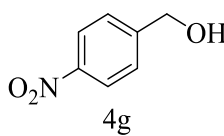
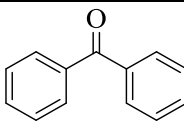
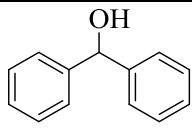
Therefore, in general, the optimal conditions for the oxidation of alcohols are summarized in scheme 3-6.

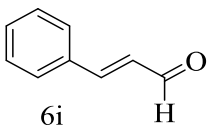
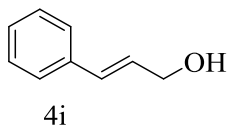
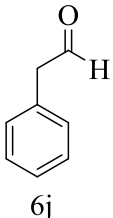
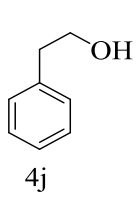
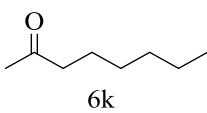
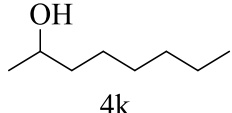
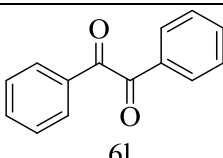
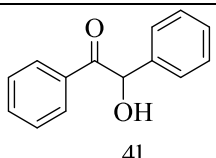
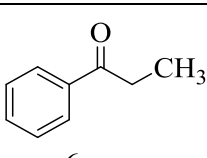
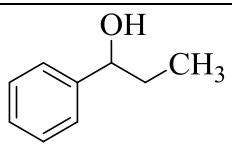


Scheme 3-6: Optimum conditions for the oxidation of alcohols

different alcohols in the above conditions leads to the formation of the corresponding products with different percentages. The results are reported in Table 3-5.

Table 3-5: Oxidation of alcohols (1 mmol) using 0.3 mmol of BTPTB in the vicinity of 0.4 ml of hydrogen peroxide in 5 ml of acetonitrile at a temperature of 60 degrees Celsius.

Percentage conversion	Reaction time (minutes)	the product	Alcohol derivative	ROW
90	40	 6a	 4a	1
75	90	 6b	 4b	2
95	95	 6c	 4c	3
93	75	 6d	 4d	4
88	150	 6e	 4e	5
90	45	 6f	 4f	6
72	120	 6g	 4g	7
95	210	 6h	 4h	8

50	210	 6i	 4i	9
85	35	 6j	 4j	10
75	300	 6k	 4k	11
-	15	 6l	 4l	12
89	40	 6n	 4n	13

1: Reaction efficiency is measured after separation and extraction.

According to Table 3-5, benzyl alcohols are oxidized faster than aliphatic alcohols, and the type of group on the aromatic ring did not affect the reaction rate in terms of electron withdrawal or acceptance.

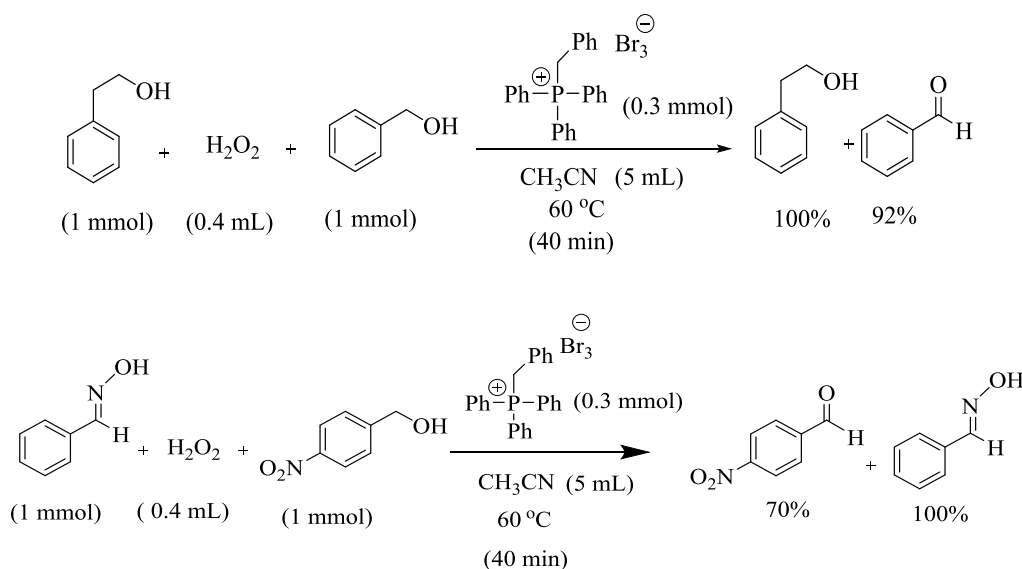
IR spectrum is used to identify aldehydes. For example, the IR spectrum of 4-chlorobenzaldehyde (6f), (spectrum 3-3, page 66), 4-nitrobenzaldehyde (6g), (spectrum 3-6, page 67), the presence of a strong stretching band, respectively in They showed the area of 1701 cm^{-1} and 1693 cm^{-1} , which indicates the formation of carbonyl aldehyde group, and the removal of OH group in the area of 3400 cm^{-1} confirms the oxidation of the corresponding alcohol.

And also the creation of two C-H stretching bands in the area of 2735 cm^{-1} and 12816 cm^{-1} is evidence of the formation of aldehyde.

3-3-2- Competitive reaction in the oxidation of benzylic and non-benzylic alcohols

To check the selectivity of these reagents and considering the greater tendency of benzyl alcohols in the oxidation reaction, competitive reactions between benzyl alcohols and non-benzyl alcohols were carried out under optimal conditions, the

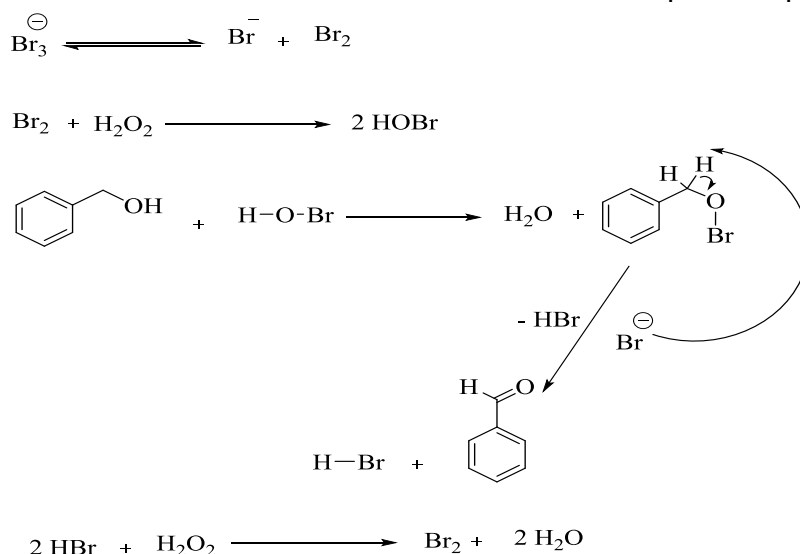
results of which are shown in scheme 3-7. Investigations showed that benzyl alcohols are converted into corresponding aldehydes in the presence of hydrogen peroxide, while non-benzyl alcohols remain intact. As an example, the reaction of benzyl alcohol and 2-phenylethanol or 3-phenylpropanol with hydrogen peroxide and using BTPTB catalyst in acetonitrile solvent was investigated. After 40 minutes, the benzyl alcohol was converted to the corresponding aldehyde. while 2-phenylethanol or 3-phenylpropanol remained intact. On the other hand, the deprotection of oximes was also investigated simultaneously with the oxidation of benzyl alcohol in a competitive reaction, in which the oxime remained intact, while the benzyl alcohol was completely oxidized to benzaldehyde with a yield of 70%.



Scheme 3-7: Oxidation of alcohols using H₂O₂, BTPTB

3-3-3- Mechanism of oxidation of alcohols by BTPTB and H₂O₂

The proposed mechanism for the oxidation of benzyl alcohols using hydrogen peroxide in the vicinity of the BTPTB catalyst is shown in Scheme 3-8. As can be seen, the role of H₂O₂ is to produce Br₂ to oxidize alcohol, and it seems that Br₂ is the main oxidizer.



Scheme 3-8: Proposed mechanism of benzyl alcohol oxidation using hydrogen peroxide in the vicinity of BTPTB catalyst

3-3-4- Comparison of the efficiency of BTPTB catalyst with a number of reported catalysts in the preparation of benzaldehyde

To check the efficiency of BTPTB catalyst in the oxidation of alcohols, in comparison with some reported catalysts, the reaction of benzaldehyde was selected as a model reaction and compared with the mentioned catalysts. The results are shown in Table 3-6.

Table 3-6: Preparation of benzaldehyde in different conditions

Reference	Returns (%)	time (minutes)	Conditions	the catalyst	ROW
54	99	90	60°C	Pt-Bi/C (5 mol %)	1
58	100	16h	environment temperature	TiO ₂	2
60	95	90	80°C	RuCl ₃	3
63	97	6h	60°C	BTMTB ¹	4
61	97	90	65°C	VPO ²	5
-	90	40	60°C	BTPTB	6

1-Benzyltrimethylammonium tribromide

2- Vanadium Phosphorus Oxide

By comparing the results of benzyl alcohol oxidation reaction in terms of efficiency and reaction time, it seems that the used method has better efficiency in reaction time compared to other methods reported in Table 3-6.

3-4-Conclusion

Due to their high efficiency and ease of use, tribromide salts are widely used in the synthesis of organic reactions. In this project, BTPTB was prepared from the oxidation of bromide ion by HNO_3 and its use in reactions including direct esterification of alcohols using acetic acid and oxidation of alcohols using hydrogen peroxide was investigated.

Esterification (acetylation) of alcohols was done using acetic acid at a temperature of 70°C . In these conditions, various alcohols were investigated and it was found that they are converted into the corresponding esters with a suitable efficiency.

Another application of BTPTB salt that was investigated in this project is the oxidation of alcohols in the vicinity of H_2O_2 . In this reaction, acetonitrile solvent was used at a temperature of 60°C . Benzyl alcohols were converted to the corresponding aldehydes in good yield.

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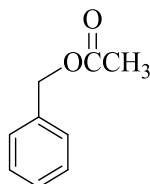
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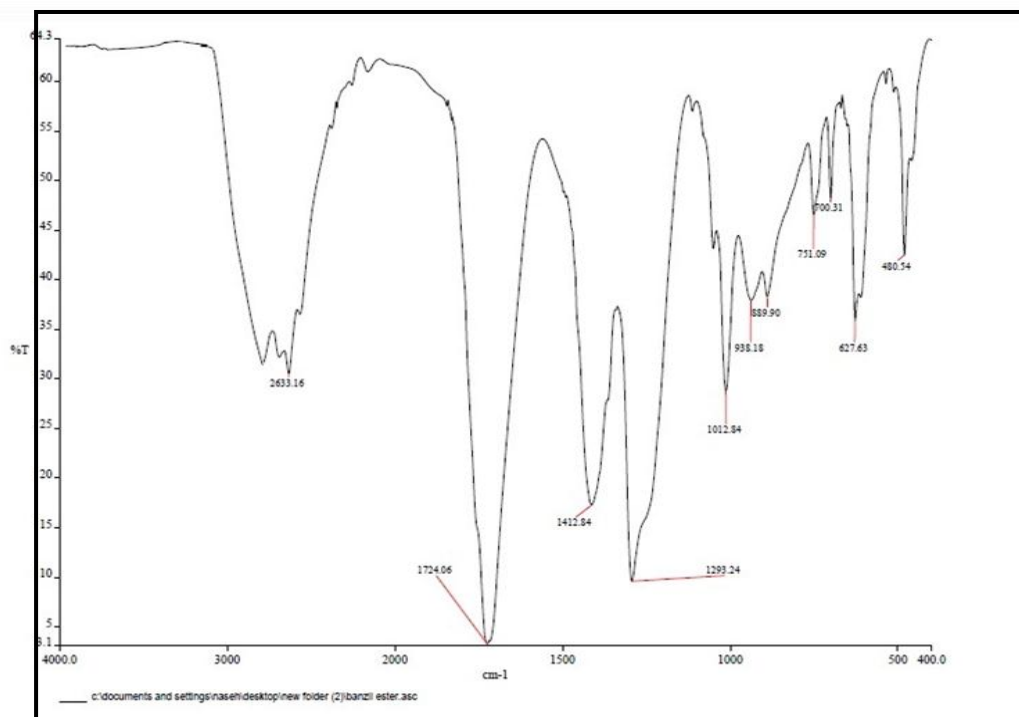
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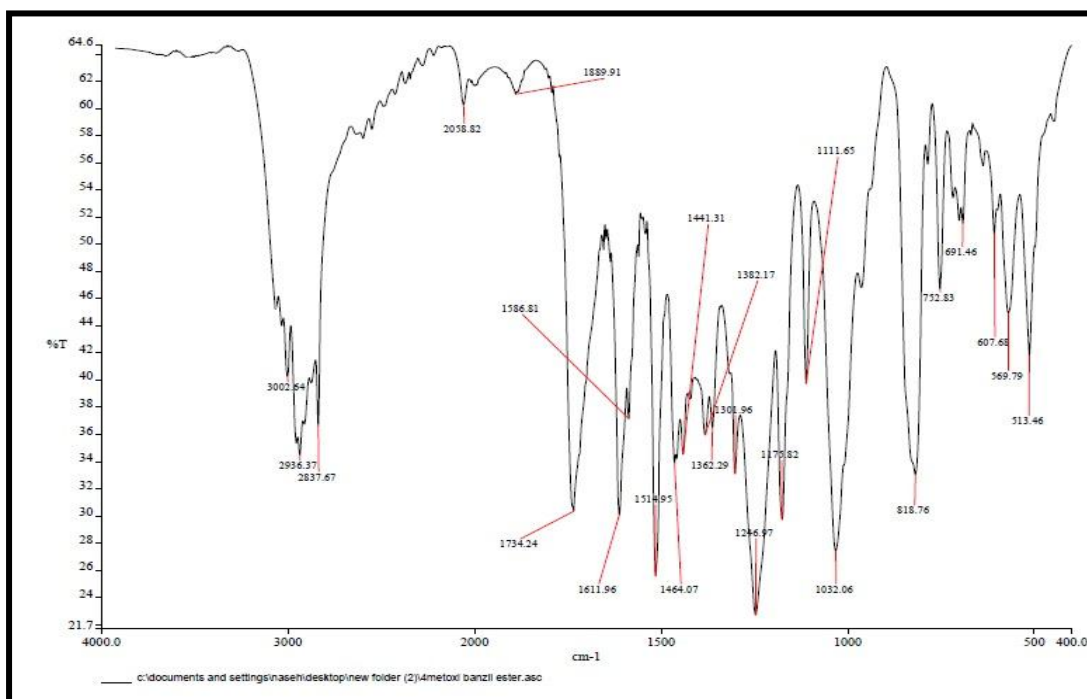
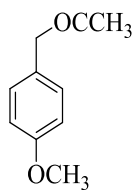
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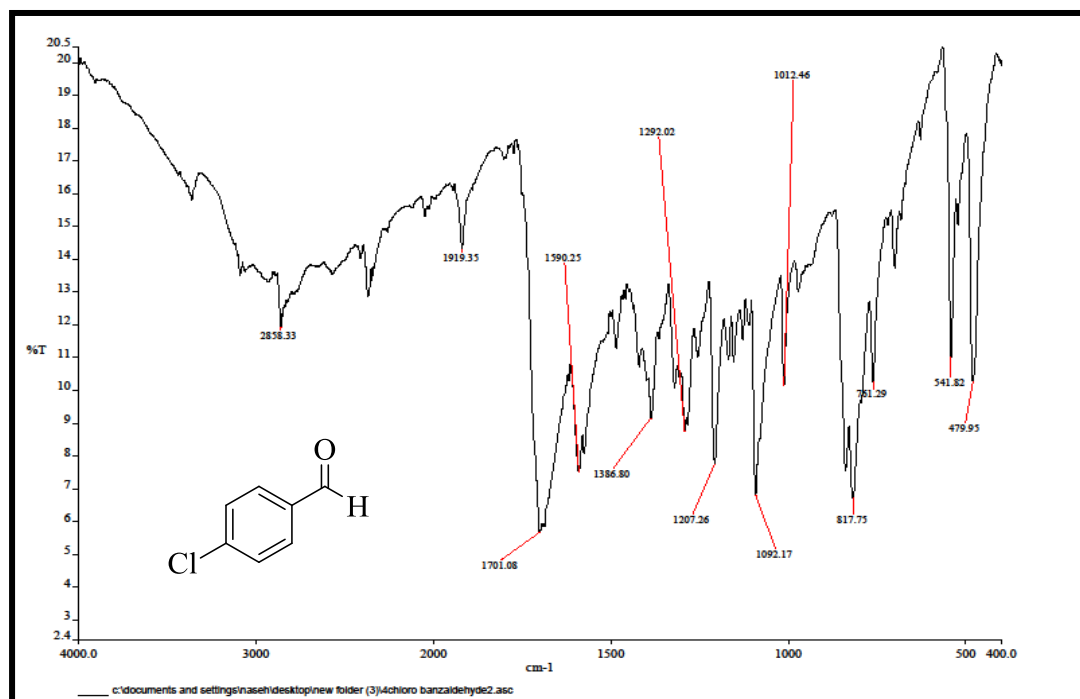




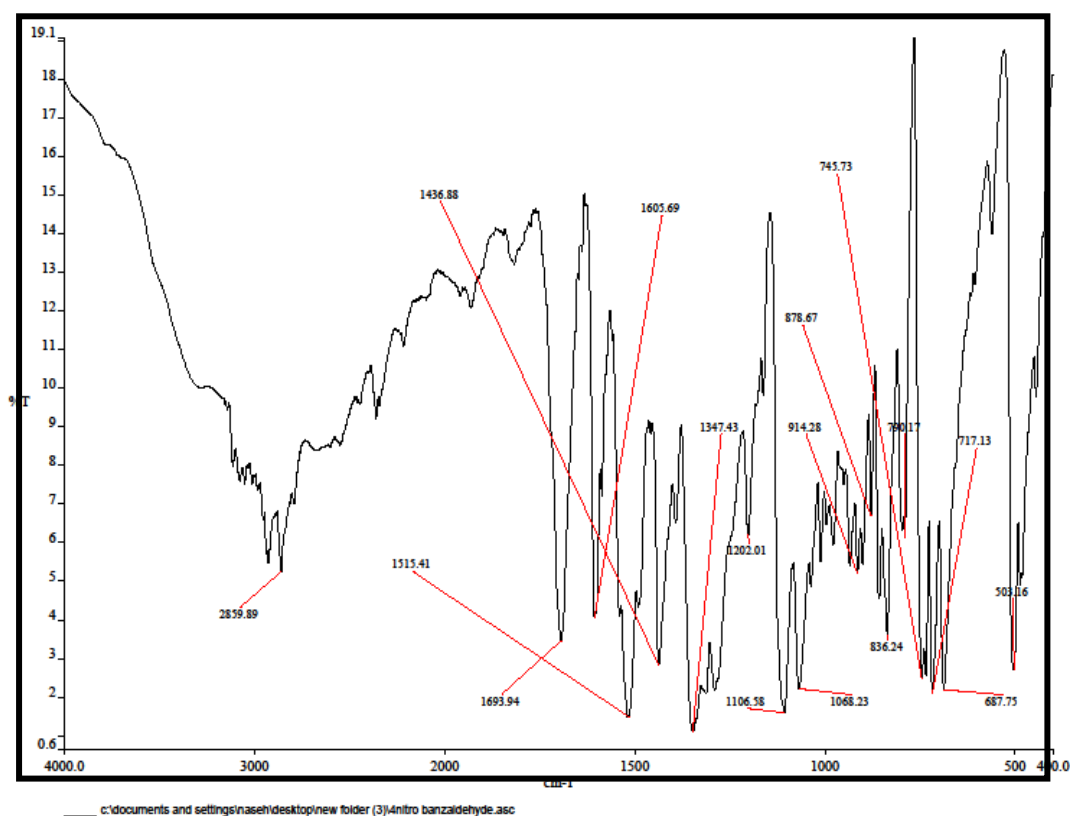
Spectrum 3-1: IR compound of benzyl acetate



Spectrum 3-2: IR compound of 4-methoxybenzyl acetate



Spectrum 3-3: IR compound of 4-chlorobenzaldehyde



Spectrum 3-4: IR compound of 4-nitrobenzaldehyde

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