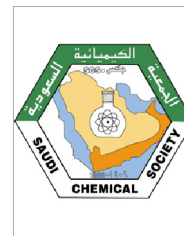




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ORIGINAL ARTICLE

Oxidation of benzylic and some aliphatic alcohols 1,2-ethylenebis(triphenylphosphonium) chlorochromate (EBTPPCC): As a new, an efficient and mild oxidant



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KEYWORDS

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Abstract 1,2-Ethylenebis(triphenylphosphonium)chlorochromate was quantitatively prepared and used for the oxidation of various benzylic and some aliphatic alcohols to their corresponding carbonyl compounds in water or acetonitrile and under microwave irradiation. This new oxidizing agent has advantages over similar oxidants in terms of the amount of used oxidant, short reaction time, simple work-up, and high yields. Furthermore, the oxidation of alcohols occurred under microwave irradiation many times and it produced the corresponding carbonyl compounds with high yields and short reaction times, when compared with the conventional method. Finally, the oxidation of different alcohols were accomplished in water under reflux condition with good yields as green chemistry.

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1. Introduction

Since the appearance of Collins reagent in 1968 (Collins et al., 1968), the development of new chromium(VI) oxidizing agent for the effective and selective oxidation of organic substrates,

in particular alcohols, has attracted a great deal of continued interest in organic synthesis. Up to now several efficient chromium(VI) reagents such as pyridinium chlorochromate (Corey and Suggs, 1975), pyridinium dichromate (Corey and Schmidt, 1975), 2,2-bipyridiniumchlorochromate (Guziec and Luzzio, 1980), 2,6-dicarboxypyridinium chlorochromate (Tajbakhsh et al., 2002; Tajbakhsh et al., 2004), 2,6-dicarboxypyridinium fluorochromate (Tajbakhsh et al., 2005a,b), tetrabutylphosphonium dichromate (Memarian et al., 2006), 1-methylimidazolium chlorochromate (Kim and Chang, 1978), 1-(benzoylamino)-3-methyl imidazolium chlorochromate (Martinez et al., 1995), ethylenebis(*N*-methylimidazolium)chlorochromate (Tajbakhsh et al., 2008), methyl triphenylphosphoniumhalo-

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chromate (Ghamamy et al., 2008), propyltriphenylphosphonium fluorotrioxochromate(VI) Javanshir et al., 2008, and tributyl ammonium chlorochromate (Ghamamy and Mazaery, 2005) have been introduced to improve the selectivity, the mildness and therefore, the effectiveness of the oxidant species, specially in the oxidation of complex and highly sensitive compounds.

The chlorochromate anion, while it combines with organophilic cation, becomes a very useful agent for the oxidation of organic compound in the nonaqueous solution. Although many chromium(VI) reagents are available for the oxidation of organic substrates, they have certain limitations such as instability, a need for an excess amount of the reagent, and poor selectivity about substrates. Therefore, there still exists a need for highly efficient and mild oxidizing agents.

Also, the microwave which enhanced organic reactions has gained popularity over the usual homogeneous and heterogeneous reactions, as they could be conducted rapidly and so, they produce pure products in quantitative yields without the use of solvents (Perreux and Loupy, 2001; Lindstroem et al., 2001).

We have found that EBTPPC is an efficient and mild oxidizing agent for the oxidation of benzylic and some aliphatic alcohols. (EBTPP)ClCrO₃ was easily prepared by the addition of an aqueous solution of 2-bromoethyl triphenylphosphonium bromide to a solution of CrO₃ and HCl in water.

2. Experimental

All the alcohols were purchased from Fluka and Merck. The reactions were monitored by TLC using Silica gel plates. The products were identified by comparison of their ¹H NMR, IR and GC spectra and physical data with those of authentic samples. ¹H NMR spectra were measured by the Bruker AC 100 MHz spectrometer with tetra methylsilane as an internal reference and DMSO-*d*₆ and also CDCl₃ as solvents. IR spectra were recorded by the Shimadzu FT-IR 8440S spectrophotometer. GC spectra were recorded by a Shimadzu 17a-GC spectrophotometer. Elemental analysis was performed on a LECO 250 instrument.

2.1. Preparation of ethylenebis(triphenylphosphonium)bromide (EBTPPB)

Three general methods were used for the preparation of EBTPPC. In one (method A) a mixture of triphenylphosphine (8.76 g, 30 mmol) and 1,2-dibromoethane (0.861 ml, 10 mmol) was stirred in DMF (10 ml) at 120–150 °C for 4 h. After cooling the mixture, water (10 ml) was added to the solution. Then the white solid¹ was produced and also, the mixture was filtered. In addition the collected filtrates was evaporated on the rotary evaporator. Finally, the crystal of ethylenebis(triphenylphosphonium)bromide were obtained.

Secondly, (methodB): a mixture of triphenylphosphine (20 mmol, 5.84 g) and 1,2-dibromoethane (10 mmol, 0.861 g) was magnetically stirred under solvent-free condition and at 150 °C for 6–7 h. After cooling the mixture, water (10 ml) was added to the solution. Then the mixture was filtered,

and so, evaporated the solvent on the rotary evaporator. Finally the white crystals of EBTPPB were collected.

Finally, the best method (Method C) is using a quantity of catalytic SbF₅, that is added to 1,2-dibromoethane for separating bromine, then triphenylphosphine was added to those in order to give EBTPPB (80%, 5.69 g). Mp: 321–323 °C.

¹H NMR, (CDCl₃), (δ, 3.4 ppm, S, CH₂), (7.76, S, aromatic hydrogens).

IR(KBr)_{nm}, 590_{nm}(w), 720_{nm}(m), 760_{nm}(S), 1150_{nm}(m), 1375_{nm}(m), 1440_{nm}(S), 1580–1640_{nm}(m), 3300_{nm}(h).

2.2. Preparation of ethylenebis(triphenylphosphonium)-chlorochromate (EBTPPCC)

To a solution of (10 mmol, 0.99 g)CrO₃ in a 100 ml beaker, hydrochloric acid 6 M (15 ml) was added over a period of 0.5 h and after that, stirring was continued for 0.5 h. A clear orange solution was obtained. Then (5 mmol, 3.56 g) ethylenebis(triphenylphosphonium)bromide in 25 ml water was added to the solution of CrO₃ in 6 N HCl. The reaction mixture was cooled to 0 °C and the yellow-orange form was collected by filtration, then it was separated and dried under vacuum for 24 h to give EBTPPCC (80.46%, 3.25 g). Mp: 319 °C.

2.3. Oxidation of alcohols: general procedure

To a solution of benzylic alcohol (1 mmol) in acetonitrile (or water), (10 ml) ethylenebis(triphenylphosphonium)chlorochromate (1 mmol, 0.823 g) was added and the mixture was magnetically stirred under reflux condition for 65–200 min. The progress of the reaction was monitored by TLC (eluent: *n*-hexane/EtoAC 5:2). After completion of the reaction, the solvent was evaporated and diethyl ether (10 ml) was added to the residue. The supernatant was decanted and the insoluble residue was washed by diethyl ether (3 × 10 ml). The combined ether extracts were concentrated under reduced pressure and the crude product was purified by column chromatography.

2.4. General procedure for the oxidation of alcohols under microwave irradiation

In microwave a mixture of an alcohol (1 mmol) and EBTPPCC (1 mmol, 0.823 g) was irradiated in closed vessel in a microwave

Table 1 Oxidation of 4-chlorobenzylalcohol using (EBTPP)ClCrO₃^a in different solvents.

Entries	Solvent	Reaction time (min)	Yield (%) ^b
1	CH ₃ CN	45	98
2	Acetone	70	80
3	THF	70	80
4	CH ₂ Cl ₃	70	56
5	CHCl ₃	70	65
6	<i>n</i> -Hexane	70	40
7	DMF	180	70
8	CH ₃ CN	90	60 ^c
9	Water	45	76

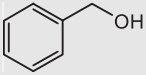
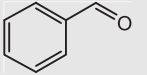
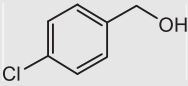
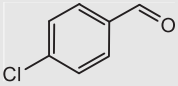
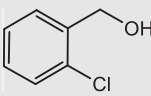
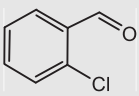
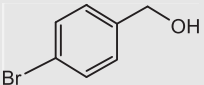
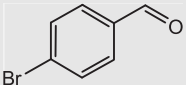
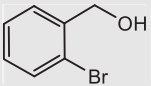
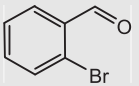
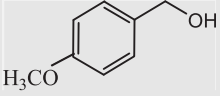
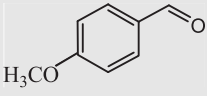
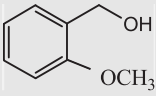
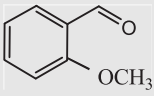
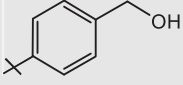
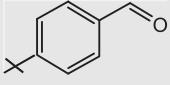
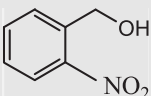
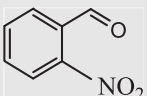
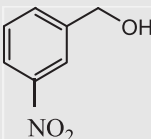
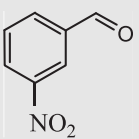
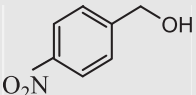
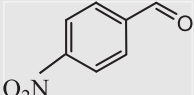
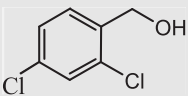
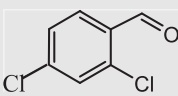
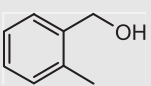
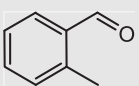
^a 1:1 Molar ratio of substrate to oxidant at reflux temperature of solvents.

^b Yields refer to isolated products.

^c Yields at room temperature.

¹ Ethylenebis(triphenylphosphonium)bromide are carefully dissolved in water, but the unreacted products as additional triphenylphosphines and so, 1,2-dibromoethane were produced the white solid.

Table 2 Oxidation of various alcohols using ethylenebis(triphenylphosphonium)ClCrO₃ in the various conditions.

Entries	Substrate	Product	Yield (%) ^a (Time)		
			Acetonitrile	MW ^b	Water
1			96 (80 min)	100 (3.5 min)	73 (90 min)
2			98 (45 min)	98 (3 min)	76 (45 min)
3			90 (120 min)	99 (5 min)	80 (135 min)
4			98 (80 min)	100 (4 min)	80 (80 min)
5			88 (160 min)	100 (6 min)	80 (150 min)
6			80 (150 min)	85 (4 min)	78 (180 min)
7			78 (180 min)	90 (9 min)	80 (200 min)
8			95 (45 min)	95 (3 min)	90 (60 min)
9			66 (400 min)	95 (12 min)	57 (420 min)
10			69 (320 min)	98 (8.5 min)	67 (350 min)
11			63 (400 min)	90 (10 min)	60 (420 min)
12			95 (40 min)	100 (5 min)	73 (40 min)
13			95 (30 min)	95 (2 min)	75 (40 min)

(continued on next page)

Table 2 (continued)

Entries	Substrate	Product	Yield (%) ^a (Time)		
			Acetonitrile	MW ^b	Water
14			95 (120 min)	100 (5 min)	80 (120 min)
15			80 (450 min)	90 (7 min)	75 (420 min)
16			75 (360 min)	85 (20 min)	85 (20 min)
17			68 (400 min)	78 (18 min)	65 (420 min)
18			65 (430 min)	70 (20 min)	65 (480 min)

The mole ratio of substrate to the oxidant: 1:1.5, under reflux condition.

^a Yield refers to isolated products; all products were identified by comparing IR, NMR, and TLC with those of authentic samples.

^b Activation by domestic microwave oven (operating at 2.45 GHz, 1 W). The final temperature of the reactions after irradiation depending on the reaction time varies between 120 and 160 °C.

oven (operating at 1000 W) for 3–9 min, and work-up was continued as mentioned above to get the corresponding aldehyde or ketone (Table 2).

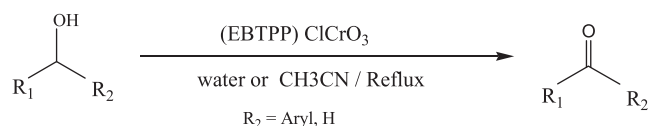
3. Results and discussion

We have synthesized ethylenebis(triphenylphosphonium)chlorochromate (EBTPCC) and studied its oxidizing properties for alcohols under different reaction conditions. This compound is easily and cheaply prepared from triphenylphosphine and 1,2-dibromoethane followed by treatment with CrO₃ in the presence of HCl with high yield. It is completely soluble in DMF, acetone and acetonitrile, and insoluble in methylenechloride, *n*-hexane and diethyl ether. One more advantage of EBTPCC in the comparison of the PCC and similar Cr(VI) reagents that is much less hygroscopic and also, is not decomposition at room temperature. The chromium content of the reagent and the calculated results are in very good agreement. A wide variety of alcohols such as benzylic, allylic and aliphatic were treated with 1 equivalent of EBTPCC in refluxing CH₃CN. In order to find the optimum condition for the oxidation of benzylic alcohols with (EBTPP)ClCrO₃, we have chosen 4-chlorobenzyl alcohol as a model substrate. We have accomplished the oxidation in the different solvents such as *n*-hexane, acetone, DMF, THF, chloroform, dichloromethane and also acetonitrile under reflux and room temperatures and with different molar ratios of oxidants. The results are shown in Table 1.

In order to show the applicability and generality of this method, we have examined the reaction of benzylic and aliphatic alcohols with (EBTPP)ClCrO₃ in refluxing acetonitrile and water (Scheme 1). The results are shown in Table 2.

As shown in Table 2, benzylic alcohols were oxidized to the corresponding aldehydes or ketones with good to excellent yields (Table 2, entries 1–15). No significant byproducts, such as over oxidation to the respective carboxylic acids, were observed. The oxidation of allylic alcohols was somewhat slower. Thus cinnamyl alcohol has been required 7.30 h, for completion of the reaction (Table 2, entry 15). It is an evidence from Table 2 which was shown the exception for all the nitro benzyl alcohols (Table 2, entries 9–11). The selectivity of this reagent was indicated by oxidation of benzylic alcohols in the presence of aliphatic primary and secondary alcohols. The treatment of 1-propanol or 2-propanol and also cyclohexanol under refluxing acetonitrile in the presence of EBTPCC were oxidized to the corresponding carbonyl compounds in 6–8 h (Table 2, entries 15–18).

Generally the rings had electron releasing groups which were reactive toward an electrophile and this oxidant. On the

**Scheme 1**

contrary the rings contained electron withdrawing groups which were unreactive toward this reagent. The functional groups such as nitro were also unreactive to this reagent and electrophiles (Table 2, entry 9–11).

The effect of halogen substituent upon an aromatic ring is the predominance regarded as being an electron donating group via resonance of π charge to the ring. It is observed experimentally that in the presence of halogens they greatly activate the aromatic ring toward this reagent and an electrophilic attack (Table 2, entries 2–5).

We have also conducted these oxidation reactions under microwave irradiation and refluxing water. When we carried out the oxidation reaction under microwave irradiation, oxidation of benzylic alcohols occurred in an even much shorter time 3–12 min, with excellent yields (Table 2); all reactions produced better yields in comparison to conventional conditions. In addition reactions in water produced good yields in comparison to some organic solvent but the yield was less than refluxing acetonitrile (Table 2). Also, those aliphatic alcohols were remained unchanged (Table 2, entries 16–18). However, water is too important in the green chemistry.

4. Conclusion

In conclusion, we have shown that EBTTPCC is an efficient and inexpensive reagent for the selective oxidation of benzylic alcohols. Allylic and benzylic alcohols under microwave irradiation are oxidized in a much shorter reaction time in comparison to refluxing in the acetonitrile. Over oxidation to the corresponding carboxylic acid was not observed at all. Interestingly, the α,β -unsaturated alcohols underwent oxidation very efficiently without an effect on the olefinic bond and the reaction is an essentially chemoselective. Furthermore, functional groups such as nitro were also inert to this reagent and no byproduct was observed.

Acknowledgements

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