

Scientific paper

Oxidation of Alcohols and Hydroquinones to Carbonyl Compounds Using Cetyltrimethylammonium Peroxodisulfate as a New, Selective and Regenerable Oxidant

Azade Geran Urimi, Heshmatollah Alinezhad
and Mahmood Tajbakhsh*

Department of Chemistry, Mazandaran University, Babolsar, Iran

* Corresponding author: E-mail: tajbakhsh@umz.ac.ir

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Abstract

Cetyltrimethylammonium peroxodisulfate, $(\text{CTA})_2\text{S}_2\text{O}_8$, was quantitatively prepared and used for the oxidation of various alcohols and hydroquinones to the corresponding carbonyl compounds in acetonitrile. Selective oxidation of allylic or benzylic alcohols in the presence of saturated aliphatic alcohols were achieved. This new oxidizing agent could be regenerated and reused several times and has advantages over similar oxidants in terms of the amount of used oxidant, short reaction time, simple work up, and high yield

Keywords: Cetyltrimethylammonium peroxodisulfate, oxidation, alcohols, hydroquinones.

1. Introduction

The oxidation of alcohols to the corresponding carbonyl compounds is one of the most fundamental reactions in organic synthesis.^{1,2} Many standard oxidation procedures have been available for this purpose.

The selective oxidation of allylic and benzylic alcohols is an important transformation because of the complexities in natural product structures, and many methods have been developed to accomplish this particular reaction.^{3–7} Although the various methods have some synthetic advantages individually, they still suffer from one or more drawbacks such as, low yield, harsh or delicate reaction condition, the need for large excess of oxidant and side reactions. Therefore, it is still important to develop a selective, mild and efficient method. In recent years new peroxodisulfate oxidants such as tetrakis(pyridine)silver(II) peroxodisulfate $([\text{Ag}(\text{Py})_4]\text{S}_2\text{O}_8)$,⁸ benzyltriphenylphosphonium peroxodisulfate $(\text{PhCH}_2\text{PPh}_3)_2\text{S}_2\text{O}_8$,⁹ *n*-butyltriphenyl phosphonium peroxodisulfate $(n\text{-BuPPh}_3)_2\text{S}_2\text{O}_8$,¹⁰ bis(1-benzyl-4-aza-1-azoniabicyclo [2.2.2]octane) peroxodisulfate,¹¹ and potassium peroxodisulfate,¹² have been used for oxidation of organic substrates. In connection with our ongoing program to find

new oxidizing agents,^{13,14} for organic substrates, we have found that $(\text{CTA})_2\text{S}_2\text{O}_8$ is an efficient and selective oxidant for benzylic, allylic and aliphatic alcohols and hydroquinones

$(\text{CTA})_2\text{S}_2\text{O}_8$ is easily prepared by addition of an aqueous solution of cetyltrimethylammonium chloride to a solution of potassium peroxodisulfate in water.¹⁵

2. Results and Discussion

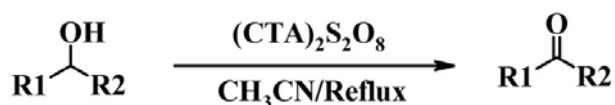
In order to find the optimum conditions for the oxidation of alcohols and hydroquinones with $(\text{CTA})_2\text{S}_2\text{O}_8$, we have chosen 4-chlorobenzylalcohol as a model substrate. We have performed the oxidation in different solvents such as hexane, acetone, THF, chloroform, dichloromethane and acetonitrile at different temperatures and different molar ratio of oxidant. The results showed that a 1:(0.8–1) molar ratio of 4-chlorobenzylalcohol to $(\text{CTA})_2\text{S}_2\text{O}_8$ in refluxing acetonitrile gave an excellent yield of 4-chlorobenzaldehyde after only 2 minutes (see Table 1, entry 1). In this procedure the oxidant is carefully added to the substrate and the mixture is refluxed until TLC analysis indicates a complete reaction.

Table 1. Oxidation of 4-chlorobenzylalcohol using $(\text{CTA})_2\text{S}_2\text{O}_8^a$

| Entries | Solvent | Reaction Time (min) | yield (%) ^b |
|---------|---------------------------------|---------------------|------------------------|
| 1 | CH ₃ CN | 2 | 97 |
| 2 | Acetone | 10 | 90 |
| 3 | THF | 60 | 75 |
| 4 | CH ₂ Cl ₂ | 60 | 50 |
| 5 | CHCl ₃ | 60 | 30 |
| 6 | <i>n</i> -Hexane | 60 | 10 |

^a 1:1 molar ratio of substrate to oxidant at reflux temperature of solvents ^b Yields refer to isolated products.

In order to show the applicability and generality of this method, we have examined the reaction of benzylic, allylic and aliphatic alcohols with $(\text{CTA})_2\text{S}_2\text{O}_8$ in refluxing acetonitrile (Scheme 1). The results are shown in the Table 2.



R1= Alkyl, Aryl, Vinyl

R2= Alkyl, Allyl, H

Scheme 1

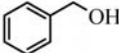
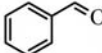
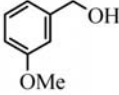
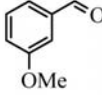
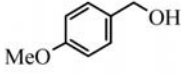
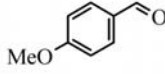
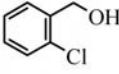
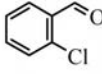
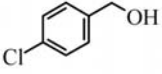
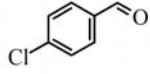
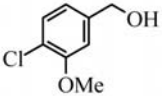
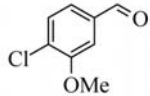
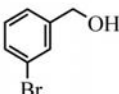
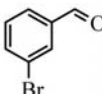
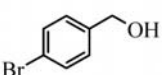
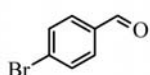
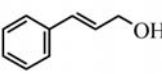
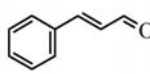
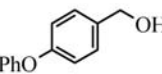
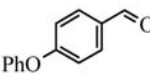
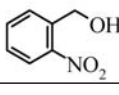
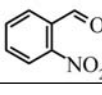
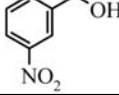
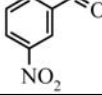
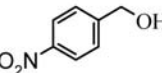
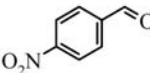
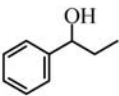
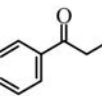
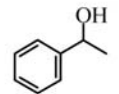
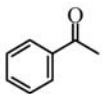
As indicated in the Table 2, benzylic alcohols with different substituents at the phenyl ring when treated with $(\text{CTA})_2\text{S}_2\text{O}_8$ in refluxing acetonitrile afforded the corresponding aldehydes (Table 2, entries 1–10) and ketones (Table 2, entries 14–16) in excellent yields and short reaction time. Benzoin under the reaction conditions required a longer reaction time and gave a lower yield (Table 2, entry 17). Benzylic alcohols bearing a strongly electron withdrawing group such as NO₂ gave lower yield and required also a longer reaction time (Table 2, entries 11–13). Primary and secondary aliphatic, as well as allylic alcohols needed longer reaction time and afforded the corresponding aldehydes and ketones in lower yield and higher molar ratio of oxidant did not improve the yield of the reaction (Table 2, entries 18–23).

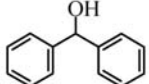
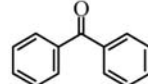
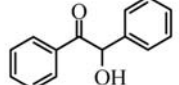
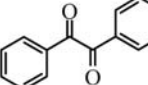
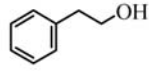
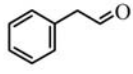
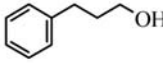
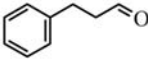


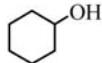
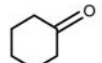
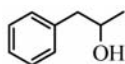
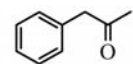
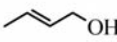
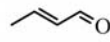
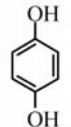
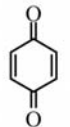
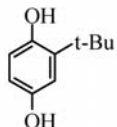
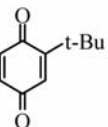
Similarly, hydroquinones gave the corresponding benzoquinones in excellent yields under the same reaction conditions (Table 2, entries 24 and 25). No significant side reactions, such as overoxidation to the respective carboxylic acids or oxidation of double bonds were observed.

In order to determine the chemoselectivity, the oxidation reaction was carried out with a mixture of allylic (or benzylic) and saturated alcohol under the reaction conditions and the results are shown in Table 3.

When benzylic alcohol, allylic alcohol or *t*-butylhydroquinone were treated with one equivalent of

Table 2. The oxidation of various benzylic, allylic and aliphatic alcohols, and hydroquinones using cetyltrimethylammonium peroxodisulfate in acetonitrile under reflux condition.

| Entry | Substrate | Product | Time (min) | Yield (%) ^{a, b} |
|-------|---|---|------------|---------------------------|
| 1 |  |  | 2 | 95 |
| 2 |  |  | 10 | 95 |
| 3 |  |  | 2 | 95 |
| 4 |  |  | 10 | 95 |
| 5 |  |  | 2 | 97 |
| 6 |  |  | 10 | 95 |
| 7 |  |  | 3 | 95 |
| 8 |  |  | 7 | 95 |
| 9 |  |  | 7 | 95 |
| 10 |  |  | 10 | 95 |
| 11 |  |  | 30 | 50 |
| 12 |  |  | 30 | 60 |
| 13 |  |  | 30 | 60 |
| 14 |  |  | 9 | 95 |
| 15 |  |  | 10 | 95 |

| Entry | Substrate | Product | Time (min) | Yield (%) ^{a, b} |
|-------|---|---|------------|---------------------------|
| 16 |  |  | 10 | 95 |
| 17 |  |  | 30 | 60 |
| 18 |  |  | 60 | 60 |
| 19 |  |  | 60 | 60 |
| 20 |  |  | 60 | 40 |
| 21 |  |  | 60 | 50 |
| 22 |  |  | 60 | 80 |
| 23 |  |  | 60 | 60 |
| 24 |  |  | 5 | 95 |
| 25 |  |  | 15 | 95 |




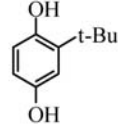
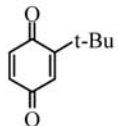
^a Products were characterized by their physical constants, spectral characteristics (IR, ¹H NMR, GC), and comparison with authentic samples.

^b Yield of isolated pure carbonyl compounds.

(CTA)₂S₂O₈ in refluxing acetonitrile for appropriate time, aliphatic alcohols remained unchanged (see Table 3).

In order to show the drawbacks and advantages of this method we have compared the oxidation of benzyl and *p*-methoxybenzyl alcohols with some reagents reported in the literature (Table 4). As shown in this table, among the peroxodisulfate reagents, (Table 4, entries 1–5), (CTA)₂S₂O₈ has the advantage of reusability and selectivity between aliphatic and benzylic alcohols (Table 4, entry 1). The polymer-supported peroxodisulfate (P-S₂O₈) showed selectivity only between benzylic alcohols and hydroquinones (Table 4, entry 3). 3,6-Bis (triphenylphosphonium)-cyclohexene peroxodisulfate (BT-

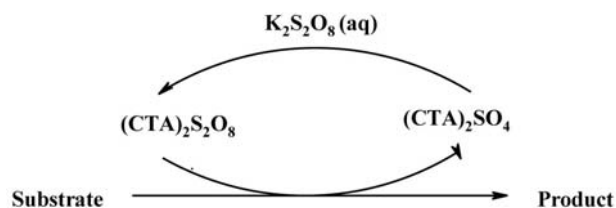
Table 3. The chemoselective oxidation of allylic and benzylic alcohols with (CTA)₂S₂O₈.

| Entry | Substrates pair | Product | Time (min) | Yield (%) ^a |
|-------|---|---|------------|------------------------|
| 1 | PhCH ₂ OH Ph(CH ₂) ₂ OH | PhCHO | 4 | 95% |
| 2 | Ph-CH=CH-OH Ph(CH ₂) ₃ OH | Ph-CH=CH-O | 10 | 95% |
| 3 |   |  | 12 | 94% |
| 4 |  (CH ₂) ₃ OH |  | 15 | 94% |

^a Yield determined by ¹H NMR

PCP) oxidizes only benzylic alcohols and does not have any effect on the aliphatic alcohols (Table 4, entry 5). The other reagents can not be regenerated and no selectivity between alcohols was reported for them (Table 4, entries 6–11).

To regenerate the reagent, on completion of the reaction, the solvent was evaporated and residual was washed with ether. The solid material was dissolved in DMSO and treated with freshly prepared aqueous K₂S₂O₈ to give cetyltrimethylammonium peroxodisulfate quantitatively (Scheme 2).



Scheme 2

3. Experimental

All the alcohols and hydroquinones were purchased from Fluka and Merck. The reactions were monitored by TLC using silica gel plates. The products were purified by flash column chromatography on silica gel (Merck; 230–400 mesh) and 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 at 90 MHz with a JEOL JNMEX 90 spectrometer with tetramethylsilane as an internal reference and DMSO-d₆ as solvent. IR spectra were recorded with a Pye-unicam SP 1100 spectrophotometer. GC spectra were recorded with a

Table 4. Oxidation of alcohols using (CTA)₂S₂O₈ in comparison with other oxidants

| Entry | Substrate | Reagent | Ratio of oxidant: substrate | Time | Conditions | Yield (%) | Reuse | Selectivity | Ref |
|-------|---|---|-----------------------------|--------|------------------------------|-----------|-------|-------------|-----|
| 1 | PhCH ₂ OH | CTAP ^a | 1:1 | 2 min | CH ₃ CN/reflux | 95 | + | + | – |
| | <i>p</i> -MeOC ₆ H ₄ CH ₂ OH | | | 2 min | | 95 | | | |
| 2 | PhCH ₂ OH | ATPPD ^b | 1.15:1 | 20 min | CH ₃ CN/reflux | 95 | – | – | 13a |
| | <i>p</i> -MeOC ₆ H ₄ CH ₂ OH | | | 15 min | | 92 | | | |
| 3 | PhCH ₂ OH | P-S ₂ O ₈ ^c | 1:1 | 15 min | Water/reflux | 93 | + | + | 13b |
| | <i>p</i> -MeOC ₆ H ₄ CH ₂ OH | | | 15 min | | 95 | | | |
| 4 | PhCH ₂ OH | NTPPPODS ^d | 0.5:1 | 2 min | CHCl ₃ /reflux | 98 | + | – | 13c |
| | <i>p</i> -MeOC ₆ H ₄ CH ₂ OH | | | 2 min | | 95 | | | |
| 5 | PhCH ₂ OH | BTPCP ^e | 1:1 | 9 min | CH ₃ CN/reflux | 92 | + | + | 13d |
| | <i>p</i> -MeOC ₆ H ₄ CH ₂ OH | | | 7 min | | 95 | | | |
| 6 | PhCH ₂ OH | 2,6-DCPCC ^f | 1:1 | 8 min | CH ₃ CN/r.t. | 97 | – | – | 15b |
| | <i>p</i> -MeOC ₆ H ₄ CH ₂ OH | | | 9 min | | 87 | | | |
| 7 | PhCH ₂ OH | O-Xy... ^g | 1:1 | 4 min | Solvent-free/r.t. | 98 | – | – | 15c |
| | <i>p</i> -MeOC ₆ H ₄ CH ₂ OH | | | 5 min | | 98 | | | |
| 8 | PhCH ₂ OH | 2,6-DCPFC ^h | 1:1 | 4 min | Solvent-free/r.t. | 92 | – | – | 15e |
| | <i>p</i> -MeOC ₆ H ₄ CH ₂ OH | | | 5 min | | 90 | | | |
| 9 | PhCH ₂ OH | <i>n</i> -BTTPDC ⁱ | 1:1 | 45 min | CHCl ₃ /reflux | 100 | – | – | 16 |
| | <i>p</i> -MeOC ₆ H ₄ CH ₂ OH | | | 45 min | | 95 | | | |
| 10 | PhCH ₂ OH | MnO ₂ ^j | 12.2:1 | 48 h | Solvent-free/r.t. | 77 | – | – | 17 |
| | <i>p</i> -MeOC ₆ H ₄ CH ₂ OH | | | 48 h | | 83 | | | |
| 11 | PhCH ₂ OH | PCC/H ₅ IO ₆ ^k | 1.7:5.15:5 | 2 h | CH ₃ CN/0°C- r.t. | 72 | – | – | 18 |
| | <i>p</i> -MeOC ₆ H ₄ CH ₂ OH | | | 2 h | | 96 | | | |

^a Cetyltrimethylammonium peroxodisulfate^b Allyltriphenylphosphonium peroxodisulfate^c Polymer- supported peroxodisulfate^d α -Naphthyltriphenylphosphonium peroxodisulfate^e 3,6-Bis(Triphenylphosphonium)-cyclohexene peroxodisulfate^f 2,6-Dicarboxypyridinium chlorochromate^g O-Xylylenebis (triphenylphosphonium peroxy monosulfate)^h 2,6-Dicarboxypyridinium fluorochromateⁱ *n*-Butyltriphenylphosphonium dichromate^j Manganese dioxide^k Pyridinium chlorochromate (2 mol%), H₅IO₆ (1.05 equiv)

Varian CP 3800 spectrophotometer. Elemental analysis were performed on a LECO 250 instrument.

3. 1. Preparation of Cetyltrimethylammonium Peroxodisulfate

To a solution of hexadecyl trimethylammonium bromide (3.7 g, 10 mmol) in 75 mL of water K₂S₂O₈ (1.3 g, 5 mmol) in 100 mL of water was added dropwise and the reaction mixture was stirred for 20 min at room temperature. A white solid was formed. The precipitate was filtered, washed with cold distilled water (50 mL) and dried in a desiccator under vacuum over calcium chloride to afford a white powder. The yield of (CTA)₂S₂O₈ was 92% and decomposes at 125 °C to a light brown material.

3. 2. General Procedure for Conversion of Alcohols and Hydroquinones to the Corresponding Carbonyl Compounds

To a solution of substrate (1 mmol) in MeCN (15 mL), was added (CTA)₂S₂O₈ (0.76 g, 1 mmol) and the mixture was magnetically stirred under reflux conditions

for 2–60 min. The progress of the reaction was monitored by TLC (eluent: *n*-hexane-EtOAc, 10:1). The reaction mixture was cooled to room temperature and filtered. The solid material was washed with MeCN (20 mL). The filtrates were combined and the solvent was evaporated. The resulting crude material was purified by chromatography using silica-gel and an appropriate eluent (*n*-hexane-EtOAc, 17:3). The pure carbonyl compounds were obtained in 40–97% yields (Tables 2 and 3).

3. 3. Regeneration of Cetyltrimethylammonium Peroxodisulfate

After completion of the reaction, the solvent was evaporated and residual was washed with MeCN and diethyl ether (2 × 10 mL). The solid was dissolved in DM-SO (5 mL) and added dropwise to a freshly prepared aqueous solution of potassium peroxodisulfate. The mixture was stirred at room temperature for 20 min. Then, the solid material was separated by filtration, repeatedly washed with water to remove the free peroxodisulfate, and dried in a vacuum desiccator over calcium chloride to obtain the regenerated reagent.

4. Acknowledgment

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Povzetek

Pripravili smo cetiltrimetilamonijev peroksidisulfat, (CTA)2S2O8, v kvantitativnih količinah in ga uporabili za oksidacijo različnih alkoholov in hidrokinonov v ustrezne karbonilne spojine v acetonitrilu kot topilu. Z oksidantom smo dosegli selektivno oksidacijo alilnih in benzilnih alkoholov v prisotnosti nasičenih alifatskih alkoholov. Pripravljeni novi oksidant kot reagent je mogoče regenerirati in večkrat uporabiti, in ima vrsto prednosti pred podobnimi tovrstnimi oksidanti kot so, majhne količine potrebne za reakcijo, kratek reakcijski čas, enostavna izolacija in visoki izkoristki.