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Full Paper

Aqueous Media Oxidation of Alcohols with Ammonium Persulfate

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Oxidation of series of various primary and secondary alcohols to corresponding carbonyl compounds with ammonium persulfate in aqueous media was described. No over oxidation of primary alcohols to carboxylic acids and secondary alcohols to esters was observed. Under such conditions benzoin was converted to benzoic acid.

Keywords oxidation, alcohol, aqueous media, ammonium persulfate

For economical and ecological reasons, synthetic chemists were confronted with the increasing obligation of optimizing their synthetic methods. Therefore, maximizing efficiency and minimizing costs in the production of molecules and macromolecules constitute one of the most exciting challenges for synthetic chemistry.[1-3] The ideal synthesis should produce the desired product in 100% yield and selectivity, in a safe and environmentally acceptable process.[4]

One of these acceptable processes is to run reactions in aqueous media. Organic reactions in water, without the use of any damaging organic solvents, are of great current interest, because water is an easily available, economical, safe and environmentally benign solvent.[5]

Ammonium persulfate is a clean and readily accessible oxidizing agent. It is commonly used in industry for bleaching[6] and for wastewater treatment.[7] However, only sporadic literature is available that describes its applications to organic synthesis, the oxidation of alkenes[8] and substituted aromatics,[9] cyclization[10] and deoximation under strenuous conditions using sulfuric acid.[11]

Oxidation of alcohols to carbonyl compounds is one of the most famous and important classes of organic reactions from different points of views. Therefore several methods are developed and then introduced into the chemical literatures.[12-19]

Along this line and in continuation of our program to develop methods in the green chemistry,[20-26] we have decided to investigate the oxidation of organic compounds by ammonium persulfate in the aqueous media because, very recently, the conversion of ketoximes to the corresponding carbonyl compounds with this reagent was reported by our laboratory.[26] Herein we wish to report the oxidation of another functional group by the same media and reagent. We found ammonium persulfate was capable of oxidizing a wide range of alcohols efficiently to the corresponding carbonyl compounds in 30—92 ℃ in the aqueous media. Our results and conditions are summarized in Table 1. In each case, firstly we studied the reaction at r.t. and then raised the temperature to the indicated temperature in the Table 1.

The mechanism of above transformation probably involves the cleavage of ammonium persulfate to radical anion **1** by heat. This radical abstracts a hydrogen atom from alcohol to generate radical **2**. In the next step, intermediate **3** is obtained by coupling of radicals **1** and **2**. The elimination of ammonium hydrogen sulfate from this intermediate liberates the carbonyl compound (Scheme 1).

No over oxidation of primary alcohols to carboxylic acids and secondary alcohols to esters was observed (Entries 1—11). However, it was found that if the product was not separated from the excess reagent after the reaction was over, the aldehyde would be oxidized to the corresponding carboxylic acid. Surprisingly under the same reaction conditions, the functional group of olefin can not be oxidized (Entry 3). Our tries in the conversion of benzoin to benzil led to produce of benzoic acid (Entry 12). Products were extracted by diethyl ether and vacuum evaporation of ether phase gave products that were often pure by NMR and TLC. Products containing impurities were purified by short column chromatograghy. The reaction is simple and does not require any special care or conditions to prevent overoxidation. The higher yields, ease of preparation, ease of use, safety and low cost of the reaction make this method clearly superior to the previous methods of oxidation of alcohols to the corresponding carbonyl compounds. For instance, NaOCl is a reagent that converts the alcohols to carbonyl compounds in the presence of catalyst of β-cyclodextrin in aqueous media.[19] In this

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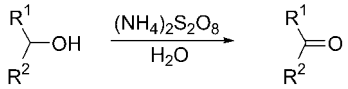
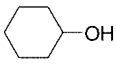
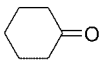
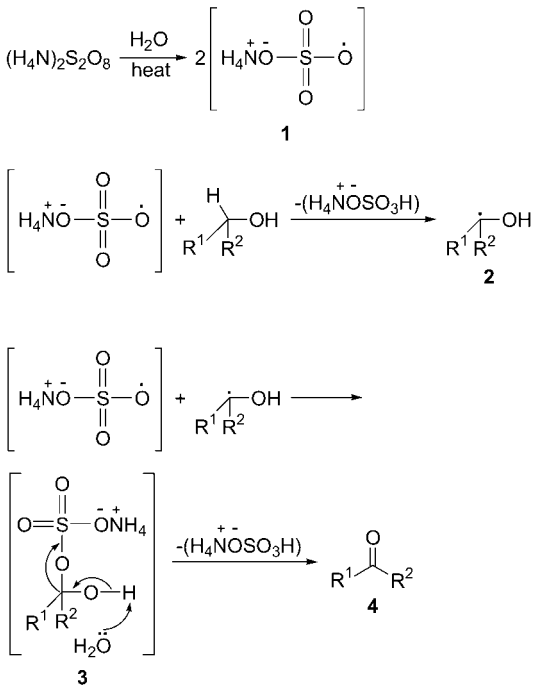
Table 1 Oxidation of alcohols with ammonium persulfate



Entry	Substrate	Product	Time/h	Temperature/℃	Yields[a] (%)	m.p. (℃) or b.p. (℃)/kPa	
						Found	Reported[27]
1	$PhCHOHCH_2CH_3$	$PhCOCH_2CH_3$	1.5	80	83	217—221/101	214—218/101
2	$PhCHOHCH_3$	$PhCOCH_3$	1.5	80	89	204—205/101	202/101
3	$PhCH=CHCH_2OH$	$PhCH=CHCHO$	1.0	85	99	128—129/101	127/101
4	$PhCH_2OH$	PhCHO	2.0	60	85	180—182/101	179/101
5	$2\text{-}ClC_6H_4CH_2OH$	$2\text{-}ClC_6H_4CHO$	1.0	60	80	210/101	208/101
6	$CH_3(CH_2)_3OH$	$CH_3(CH_2)_2CHO$	2.0	30	88	78—79/101	75—77/101
7	$CH_3(CH_2)_4OH$	$CH_3(CH_2)_3CHO$	1.0	50	88	102/101	102/101
8	$4\text{-}ClC_6H_4CH_2OH$	$4\text{-}ClC_6H_4CHO$	1.0	80	98	45—47	46
9	$4\text{-}BrC_6H_4CH_2OH$	$4\text{-}BrC_6H_4CHO$	1.5	80	95	45—57	55—58
10	$4\text{-}NO_2C_6H_4CH_2OH$	$4\text{-}NO_2C_6H_4CHO$	1.0	80	90	103—105	106
11			2.0	75	87	156—158/101	156/101
12	PhCH(OH)COPh	$PhCO_2H$	0.50	80	92	119—122	121—123

[a] Yields refer to isolated products.

Scheme 1



method cyclohexanol was oxidized to cyclohexanone at 50 ℃ within 5 h in 30% yield, while in our present method, the yield of cyclohexanone product was 85% for 2 h reaction time, at 75 ℃ without using any catalyst.

In conclusion, in this study we introduced a new methodology for the aqueous oxidation of primary and secondary alcohols in the absence of organic solvent. Since the reaction was conducted in the aqueous media, the work-up of the reaction mixture was easy. The advantages such as availability of the reagent, mild reaction conditions and high yields of products will make this method a practical useful method to oxidation of alcohols to carbonyl compounds.

Experimental

All yields refer to isolated products. Chemicals were purchased from Aldrich, Fluka, Merck and Riedel de Haen AG chemical companies. Thin layer chromatography (TLC) was carried out using glass sheets precoated with silica gel 60F. Melting points were determined on an Electro thermal Gallen Kamp apparatus and uncorrected. ^{1}H NMR spectra were recorded on a JEOL EX-90A (90 MHz) spectrophotometer. IR spectra were obtained using a Shimadzu IR-435 spectrometer. The purity of products was determined by GC and ^{1}H NMR spectroscopy and comparison with reported physical data in the literature.

General procedure

In a 50 mL round bottomed flask, alcohol (1.0 mmol) was added to ammonium persulfate (1.5 mmol) that was dissolved in 10 mL of water and the mixture was well stirred at indicated temperature for the designated time (Table 1). After completion of the reaction (monitored by TLC) the product was extracted into 20 mL of ether and dried over anhydrous magnesium sulfate. The solvent was removed by evaporation under reduced pressure to yield the product.

Propiophenone (Table 1, Entry 1): IR (KBr) *v*: 3090, 2950, 2860, 1695, 1587, 762, cm^{-1}; ^{1}H NMR ($CDCl_3$) δ: 1.25 (t, J=7.0 Hz, 3H), 2.88 (q, J=7.0 Hz, 2H), 7.35—7.70 (m, 5H).

Acetophenone (Table 1, Entry 2): IR (KBr) *v*: 3090, 2910, 1685, 1610, 1155 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ: 2.45

(s, 3H), 7.45—7.90 (m, 5H).

Cinamaldehyde (Table 1, Entry 3): IR (KBr) *v*: 3070, 2960, 2870, 1698, 750, 697 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 6.60 (d, J=15.9 Hz, 1H), 6.80 (dd, J=7.0, 15.9 Hz, 1H), 7.34—7.60 (m, 5H), 9.81 (d, J=7.0, 15.9 Hz, 1H).

Benzaldehyde (Table 1, Entry 4): IR (KBr) *v*: 3069, 2817, 2735, 1699, 1660, 1586, 831, 745, 682 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 7.5—8.2 (m, 5H), 9.95 (s, 1H).

2-Chlorobenzaldehyde (Table 1, Entry 5): IR (KBr) *v*: 3045, 2880, 2780, 1700, 1610, 1580, 760, 692 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 7.2—8.0 (m, 5H), 9.95 (s, 1H).

Butanal (Table 1, Entry 6): IR (KBr) *v*: 2980, 2865, 2745, 1730, 1108 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 1.01 (t, J=6.9 Hz, 3H), 1.55—1.85 (m, 2H), 2.30—2.60 (m, 2H), 9.80 (t, J=2 Hz, 1H).

Valeraldehyde (Table 1, Entry 7): IR (KBr) *v*: 2980, 2880, 2730, 1730, 1470, 110 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 1.00 (t, J=6.9 Hz, 3H), 1.20—1.75 (m, 4H), 2.35—2.55 (m, 2H), 9.77 (t, J=2.1 Hz, 1H).

4-Chlorobenzaldehyd (Table 1, Entry 8): IR (KBr) *v*: 3050, 2890, 2760, 1700, 1585, 865 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 7.60 (d, J=7.2 Hz, 2H), 7.82 (d, J=7.2 Hz, 2H), 9.99 (s, 1H).

4-Bromobenzaldehyde (Table 1, Entry 9): IR (KBr) *v*: 3050, 2905, 2880, 2775, 1705, 1595, 850 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 7.40 (d, J=6.2 Hz, 2H), 7.70 (d, J=6.2 Hz, 2H), 9.91 (s, 1H).

4-Nitrobenzaldehyde (Table 1, Entry 10): IR (KBr) *v*: 3048, 2960, 2760, 1710, 1600, 1560, 820, 735 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 8.10 (d, J=8.2 Hz, 2H), 8.58 (d, J=8.2 Hz, 2H), 10.2 (s, 1H).

Cyclohexanone (Table 1, Entry 11): IR (KBr) *v*: 2960, 1715, 1440, 1230 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 1.80—2.10 (m, 6H), 2.35—2.42 (m, 4H).

Benzoic acid (Table 1, Entry 12): IR (KBr) *v*: 3000—2500 (br), 1695, 1600, 1590, 1456, 1130, 690 cm^{-1}; ^1H NMR ($CDCl_3$) δ: 7.41—8.10 (m, 5H), 12.10 (s, 1H).

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