

Oxidation of aromatic alcohols and diols with peroxodisulfate under heterogeneous conditions^{1†}

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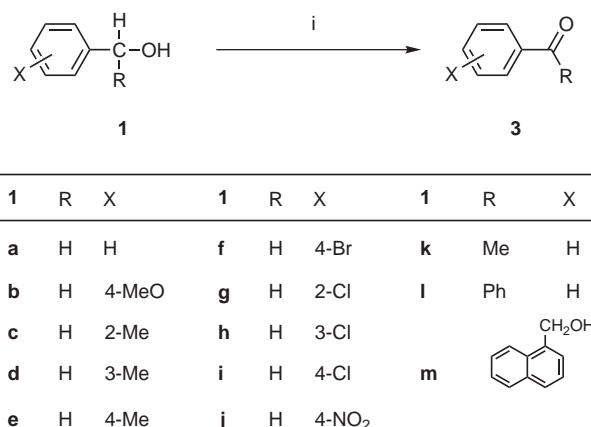
A combined use of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ as the terminal oxidant and AgNO_3 as the catalyst can effect the oxidation of aromatic alcohols and diols in hexane in the presence of montmorillonite K10 preloaded with a small amount of water, giving the corresponding carbonyl compounds in high yields under relatively mild conditions.

Keywords: aromatic alcohols and diols, peroxodisulfate

Oxidation of alcohols is one of the basic reactions and achieves extensive use in organic synthesis, for which a wide variety of reagents and reagent systems are available.² In view of practical demands and recent environmental constraint,³ the use of supported reagents and catalysts for organic synthesis has now gained general acceptance as practical, environmentally benign substitutes for conventional solution phase counterparts.^{3,4} Thus, we have recently investigated various reactions^{5,6a,b} including the oxidation of alcohols^{6a,b} in aprotic solvents in the presence of solid support materials (*in situ* generated supported reagents),^{4d} enabling selective and high-yielding reactions to be carried out under mild conditions.

Peroxodisulfate anion ($\text{S}_2\text{O}_8^{2-}$) is one of the most powerful oxidants as suggested by its large redox potential and plays an important role in the oxidations of certain functional groups, the results of which have been collected in comprehensive review articles^{7,8} such as those on alkaline peroxodisulfate oxidations known as the Elbs reaction.⁸ Although there have been mechanistic investigations into the oxidation of alcohols with peroxodisulfates,⁹ a preparative reaction has hitherto been little researched. Indeed, the only previous studies, of which we are aware, are those on the oxidation of benzyl alcohol **1a** and glycols under aqueous conditions.^{9a,b} Our attempted oxidation of **1a** was carried out with a reagent combination of ammonium peroxodisulfate, $(\text{NH}_4)_2\text{S}_2\text{O}_8$, and a catalytic amount of silver nitrate, AgNO_3 , in hexane in the presence of montmorillonite K10 preloaded with a small amount of water (moist montmorillonite; see Experimental section). Although an elevated temperature and a slightly prolonged period of time (60 °C, 2.5 h) were required to effect the reaction, the selectivity and the yield (99%; Table 1, run 1) of benzaldehyde **3a** are noteworthy as compared to those observed in the earlier oxidation (30 °C, 2 h),^{9a} since the latter gave **3a** only in moderate yield (75%, isolated as the oxime), being undesirably accompanied by appreciable amounts of over-oxidation products, benzoic acid (8%) and resin. This promising result coupled with our continued interest in the oxidation of aromatic alcohols with a variety of reagents⁶ prompted us to examine the utility of the new solid-solution biphasic system for the oxidation of a series of aromatic alcohols (Scheme 1).

In order to get information on the behaviour of peroxodisulfates in aprotic solvent and to optimise the reaction conditions for the selective formation of carbonyl compounds, some control experiments were first examined using **1a** as the



Scheme 1 i, $(\text{NH}_4)_2\text{S}_2\text{O}_8$, AgNO_3 , moist montmorillonite, hexane

test substrate. Independent reactions in the absence and the presence of commercial and predried (350 °C, 6 h) montmorillonite K10, but otherwise under the same conditions of run 1 showed that **1a** was recovered unchanged in every case. On the other hand, in the presence of moist montmorillonite the reaction ran smoothly to 100% conversion and gave **3a** in essentially quantitative yield (run 1), suggesting clearly that moist montmorillonite catalyses the reaction. It is likely that crystal lattices of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ and AgNO_3 may be penetrated and then broken up by water to generate highly dispersed active species over the high-surface area of the clay,¹⁰ enabling the oxidation to occur under the reaction conditions. The reaction without adding AgNO_3 was sluggish, and led to low conversion of **1a** (34%) and poor yield of **3a** (11%), suggesting that Ag^{2+} species and/or sulfate anion radical ($\text{SO}_4^{\cdot-}$), generated from the reaction of $\text{S}_2\text{O}_8^{2-}$ and AgNO_3 ,⁷ could be the real oxidant. Thus, moist montmorillonite and AgNO_3 are indispensable for the oxidation to occur at a reasonable rate. Of inorganic solid supports tested (aluminas, silica gels and clays), montmorillonite K10 was found to be the most effective for the present reaction. Another comparative study showed that $(\text{NH}_4)_2\text{S}_2\text{O}_8$ is more active than sodium and potassium salts as suggested by the conversions of **1a** under the conditions of run 1 (100, 61 and 11%, respectively).

Based on the preliminary experiments, oxidations of aromatic alcohols **1** were examined using catalytic amount of AgNO_3 (5 mol% with respect to **1**), $(\text{NH}_4)_2\text{S}_2\text{O}_8$ and moist montmorillonite. The reaction can easily be performed by efficiently stirring the heterogeneous mixture with **1** in hexane

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† This is a Short Paper, there is therefore no corresponding material in *J. Chem. Research (M)*.

Table 1 Oxidation of aromatic alcohols and diols^a

Run	Substrate	(NH ₄) ₂ S ₂ O ₈ mmol	t (h)	Product	(%) ^b
1	1a	2.5	2.5	3a^c	99
2	1b	2.5	0.5	3b^d	94
3	1c	2.5	2.5	3c^e	95
4	1d	2.5	2.5	3d^f	96
5†	1e	2.5	2.5	3e^g	86
6	1f	4.0	3.0	3f^{h,i}	99
7	1g	5.0	3.0	3g^j	90
8	1h	5.0	3.0	3h^k	93
9	1i	4.0	3.0	3i^{l,m}	92
10	1j	5.0	6.0	3j^{n,o}	90
11	1k	2.5	2.5	3k^p	93
12	1l	2.5	2.5	3l^{q,r}	91
13	1m	2.5	2.5	3m^{†,s}	92
14	2a	2.5	1.0	3a^c	82
15	2b	2.5	2.5	3a^c	94
16	2c	2.5	2.5	3l^{q,r}	quant.

a) Under argon, at 60 °C; substrate 1 mmol, AgNO₃ 0.05 mmol, moist montmorillonite 1 g, hexane 10 ml. b) Isolated yield. c) NMR, *Ref.* 13, pp. 103; IR, *Ref.* 14, pp. 2522. d) NMR, *Ref.* 13, pp. 109; IR, *Ref.* 14, pp. 2529. e) NMR, *Ref.* 13, pp. 103; IR, *Ref.* 14, pp. 2522. f) NMR, *Ref.* 13, pp. 106; IR, *Ref.* 14, pp. 2525. g) NMR, *Ref.* 13, pp. 108; IR, *Ref.* 14, pp. 2527. h) Mp 57–58 °C (lit., 59–60 °C; *Ref.* 12, pp. 930) i) NMR, *Ref.* 13, pp. 109; IR, *Ref.* 14, pp. 2529. j) NMR, *Ref.* 13, pp. 104; IR, *Ref.* 14, pp. 2523. k) NMR, *Ref.* 13, pp. 106; IR, *Ref.* 14, pp. 2525. l) M.p. 45–46 °C (lit., 47 °C; *Ref.* 12, pp. 1282). m) NMR, *Ref.* 13, pp. 109; IR, *Ref.* 14, pp. 2529. n) M.p. 104–105 °C (lit., 106 °C; *Ref.* 12, pp. 4749). o) NMR, *Ref.* 13, pp. 111; IR, *Ref.* 14, pp. 2532. p) NMR, *Ref.* 13, pp. 7; IR, *Ref.* 14, pp. 2366. q) Mp 47–48 °C (lit., 48.5–49 °C; *Ref.* 12, pp. 637). r) NMR, *Ref.* 13, pp. 61; IR, *Ref.* 14, pp. 2451. s) NMR, *Ref.* 13, pp. 131; IR, *Ref.* 14, pp. 2564.

† *p*-Formylbenzyl alcohol (*p*-OHCC₆H₄CH₂OH; *ca* 6% by GC) was formed.

‡ 1-Naphthaldehyde.

under an inert atmosphere to exclude any influence of autoxidation. Simple work-up (filtration, thorough washing of the filter cake and evaporation of the solvent), followed by a single chromatography gave the product with satisfactory purity. The results are presented in Table 1. Oxidations of a benzyl alcohol series have been investigated by changing substituents on the benzene ring (runs 1–10). The reactions afforded the benzaldehydes in high yield under selected conditions, irrespective of electronic property of the substituents (runs 1, 2, 5, 6, 9 and 10) and their positions on the benzene ring (runs 3–5 and 7–9). In the case of *p*-methylbenzyl alcohol (run 5), *p*-formylbenzyl alcohol (*p*-OHCC₆H₄CH₂OH) was formed as the by-product, which might be attributed to the susceptibility of the methyl group towards S₂O₈²⁻/metal ion system.¹¹ Secondary alcohols (runs 11 and 12) and the naphthalene-methanol (run 13) were readily converted to the carbonyl compounds. The present S₂O₈-based system is also useful for the oxidative carbon–carbon bond cleavage of 1,2-diols, styrene glycol **2a**, hydrobenzoin **2b** and benzopinacol **2c**, into the carbonyl compounds (runs 14–16). It might be interesting to note that an aqueous S₂O₈²⁻/Ag⁺ system fails to oxidise water-insoluble diols, *e.g.* **2c**,^{9b} but the present reaction gave benzophenone **3l** in quantitative yield (run 16).

Summing up, the oxidation of aromatic alcohols and diols by a combination of (NH₄)₂S₂O₈ and AgNO₃ catalyst in hexane can easily be achieved with the aid of moist montmorillonite under the relatively mild conditions. The reaction is characterised by high selectivity and yield of the products and simple procedure; the latter aspect is in marked contrast to the conventional method^{9a} being accompanied by laborious work-up of the product from the aqueous reaction mixture. In view of the easy accessibility and reaction performance, we are now looking for an alternative synthetic reaction using the new biphasic system.

Experimental

General: Commercial (NH₄)₂S₂O₈ (Wako) and AgNO₃ (Kojima Chemical, Japan) were used as received. Alcohols and diols are

commercial chemicals, most of which were used as received from suppliers, but impure materials were purified by distillation or recrystallisation prior to use. Hexane was dried (CaCl₂), distilled, and stored over molecular sieves. Melting points were determined on a Yanagimoto MP-S3 melting point apparatus and are uncorrected. Mass spectra were determined on a JEOL SX-102A mass spectrometer coupled to a Hewlett Packard GC5890 Series II GC apparatus via a heated capillary column. GLC was performed on a Shimadzu GC-14B instrument equipped with a FID through a 2 m×5 mm diameter glass column packed with 5% PEG-20M on Chromosorb WAW-DMCS, and interfaced with a Shimadzu Chromatopac C-R6A integrator, with temperature programming. Moist montmorillonite (water content; 17 wt %) was prepared by adding deionised water (0.2 g) to commercial montmorillonite K10 (Aldrich; 1 g) in several portions, followed by vigorous shaking of the mixture on every addition for a few min until a free-flowing powder was obtained, 1.0 g of which was immediately used for the oxidation.

Oxidation procedure: The following procedure for benzhydrol **1l** is representative. A 30 ml, two-necked, round bottom flask, equipped with a 1.5 cm long Teflon-coated stirrer bar, a 25 cm long condenser, and a glass gas-inlet tubing connected to an argon-filled balloon, was arranged in order to perform the reaction under inert atmosphere by linking the top of the condenser to a liquid paraffin trap via a flexible silicone rubber tubing. In the flask were placed **1l** (1 mmol), (NH₄)₂S₂O₈ (2.5 mmol) and AgNO₃ (0.05 mmol; 5 mol% with respect to **1l**), hexane (10 ml) and freshly prepared moist montmorillonite (1 g), and the flask was then deaerated by gently passing a stream of dry argon throughout the system. The flask was kept at 60 °C in a thermostated oil-bath while efficient stirring was continued in order to ensure smooth reaction and to attain reproducible results. After 2.5 h, the cooled mixture was transferred onto a sintered glass funnel, and the filter cake was washed thoroughly with portions of dry ether (in total 50 ml). Rotary evaporation of the combined solvent, followed by chromatography on a silica gel column (Merck silica gel 60, hexane-AcOEt), gave benzophenone **3l** (0.166 g, 91% yield based on the starting **1l**): mp 47–48 °C (lit.¹² m.p. 48.5–49 °C); calcd. for C₁₃H₁₀O, C 85.69, H 5.53, found C 85.06, H 5.53.

Oxidations of the other alcohols and the diols **2a–c** were carried out as above, the reaction conditions of which (concentration of the peroxydisulfate salt and reaction time) were determined on the basis of reactivity of the substrates and the yields of the carbonyl compounds. The products thus obtained were identified by the comparison of NMR,¹³ MS and IR¹⁴ spectra with those of authentic samples.

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