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The oxidation of aromatic aldehydes by magnesium monoperoxyphthalate and urea–hydrogen peroxide

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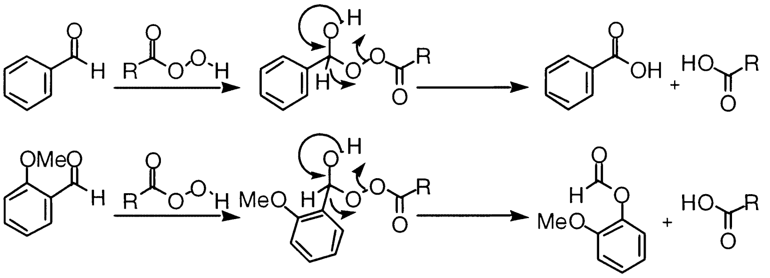
Abstract—Magnesium monoperoxyphthalate and urea–hydrogen peroxide–acetic anhydride are effective reagents in the oxidation of benzaldehyde to benzoic acid and *o*- and *p*-methoxybenzaldehyde to the corresponding phenols. On the other hand, aromatic aldehydes, including the isomeric methoxybenzaldehydes, are oxidised to the corresponding benzoic acid derivatives in good to excellent yields by the hydroperoxide anion generated from urea–hydrogen peroxide. © 2001 Elsevier Science Ltd. All rights reserved.

The oxidation of aldehydes to carboxylic acids has been studied on many occasions.[1] The recent reports on the catalytic oxidative esterification of aldehydes using hydrogen peroxide in the presence of catalytic vanadium pentoxide[2] and the biphasic oxidation of aldehydes to carboxylic acids using aqueous hydrogen peroxide[3] prompt this report of our similar studies using magnesium monoperoxyphthalate (MMPP) and urea–hydrogen peroxide (UHP).[4] Hydrogen peroxide has been used as the source of the active oxygen in the oxidation of aromatic aldehydes in the presence of sulfuric acid,[5] and the high temperature slow decomposition of the perhydrate derived from dodecanal was shown to give dodecanoic acid.[6] The interaction of hydrogen peroxide with formic acid is known to give performic acid and this combination has been used to oxidise methoxy and methyl substituted benzene derivatives to phenols and quinones,[7] as well as benzaldehyde derivatives to the related benzoic acids.[8] We showed previously that the Baeyer–Villiger reaction proceeds efficiently for a number of ketones using either MMPP,[9] or trifluoroperoxyacetic acid, the latter reagent being generated by the interaction of UHP with trifluoroacetic anhydride in the presence of disodium hydrogen phosphate.[10] In this communication we report the oxidation of benzaldehyde and substituted derivatives to the related carboxylic acids using MMPP and UHP–acetic anhydride, Baeyer–Villiger (Dakin) reactions of *o*- and *p*-methoxybenzaldehydes that lead to phenolic products and high yield oxidation reactions using UHP in the presence of aqueous sodium hydroxide.

The oxidation of an aldehyde to an ester in alcoholic solution presumably proceeds by oxidation of the hemi-acetal. In the absence of hemi-acetal formation it is clear that the outcome of oxidation reactions that involve aldehydes depends crucially on the migratory aptitude of either hydride ion or the other functional group (Scheme 1). The evidence in the literature shows that, at present, no reagent system is perfect. The oxidation of benzaldehyde and substituted derivatives



Scheme 1.

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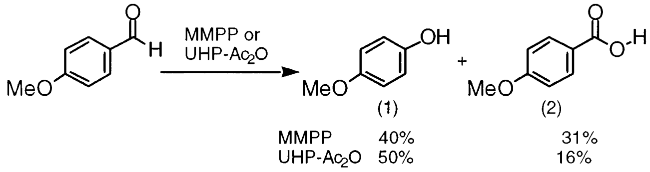


(1)

provide good substrates for a comparison of the various available methods. Thus, the oxidation of 4-methoxybenzaldehyde using the system hydrogen peroxide–boric acid–sulfuric acid gave 4-methoxyphenol in 97% yield,[11] and using *m*-chloroperoxybenzoic acid in 92% yield.[12] On the other hand, the oxidation of 4-methoxybenzaldehyde under two-phase conditions using methyltrioctylammonium tetrakis(oxodiperoxotungstato)phosphate gave the corresponding benzoic acid in only 6% yield together with a low yield of 4-methoxyphenol.[13] In our hands, 2-methoxybenzaldehyde gave 2-methoxyphenol in 81% yield using MMPP and in 64% yield using UHP–acetic anhydride, the phenol being isolated as a result of hydrolysis of the formate ester during work-up.

Typical experimental procedures

2-Methoxybenzaldehyde (1.14 g, 8.4 mmol) was added to a solution of MMPP (4.9 g, 10 mmol) in methanol (60 mL) and the mixture was stirred at room temperature for 19 h. Addition of a slight excess of aqueous potassium hydroxide followed by acidification after 1 h and extraction into dichloromethane followed by drying ($MgSO_4$), evaporation and distillation gave 2-methoxyphenol (0.847 g, 81%) (bp 112°C at 20 mm, lit.[14] bp 106.5 at 24 mm); δ_H ($CDCl_3$, 60 MHz) 3.85 (s, 3H), 5.83 (br. s, 1H), and 6.83 (m, 4H) ppm.

Acetic anhydride (2.05 g, 20 mmol) was added dropwise to a stirred mixture of UHP (7.7 g, 82 mmol), 2-methoxybenzaldehyde (1.30 g, 9.6 mmol) and disodium hydrogenphosphate (10.1 g, 75 mmol) in dichloromethane (30 mL) at 0°C. The mixture was then stirred at room temperature for 22 h. Work-up as above gave 2-methoxyphenol (0.768 g, 64%) (bp 149°C at 40 mm, lit.[14] bp 106.5 at 24 mm).

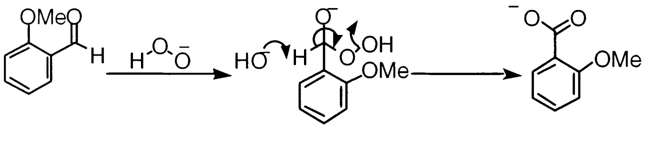
4-Methoxybenzaldehyde gave mixtures of 4-methoxyphenol (**1**) and 4-methoxybenzoic acid (**2**), the reactions, shown in Eq. (1), with MMPP [(**1**) 40%; (**2**) 31%] and UHP–acetic anhydride [(**1**) 50%; (**2**) 16%].

As expected, benzaldehyde was oxidised to benzoic acid efficiently using either MMPP (81% yield) or UHP–acetic anhydride (74%) and 3-methoxybenzaldehyde gave 3-methoxybenzoic acid in 71% yield using MMPP.

The yields reported for the oxidation of benzaldehyde derivatives using aqueous hydrogen peroxide and methyl-*n*-octylammonium bisulfate varied from excellent (4-nitrobenzaldehyde to 4-nitrobenzoic acid 88%) to poor (4-methoxybenzaldehyde to 4-methoxybenzoic acid 6%).[3] It is of interest to note that the epoxidation of the α,β-unsaturated ketone isophorone proceeded in good yield (68%) using UHP in methanol in the presence of 6 M aqueous sodium hydroxide.[10] Similarly, we found that pulegone and α-ionone gave the expected epoxides in 50 and 61% yields, respectively. The epoxidation of β-methyl-β-nitrostyrene provided interesting results that varied with the concentration of the aqueous sodium hydroxide used. When the reaction was carried out using UHP in methanol and 2 M aqueous sodium hydroxide the epoxide was obtained in 96% yield, while a reaction carried out in the presence of 6 M aqueous sodium hydroxide resulted in the formation of benzoic acid which was isolated in 73% yield. The oxidation of aliphatic aldehydes to the corresponding carboxylic acids using hydrogen peroxide in aqueous sodium hydroxide solution has been reported previously.[15] We assumed that with an aromatic aldehyde, removal of a proton from the presumed intermediate would occur at a faster rate in the presence of hydroxide ion than aryl group migration and that the oxidation of methoxy-substituted benzaldehyde derivatives would proceed efficiently to the related benzoic acid derivatives using that protocol (Scheme 2). The results of the oxidation of benzaldehyde and methoxy-substituted derivatives are shown in Table 1.

Typical experimental procedure

Aqueous sodium hydroxide (3.1 mL, 6 M) was added dropwise to a stirred solution of UHP (8.1 g, 87 mmol) and 2-methoxybenzaldehyde (1.36 g, 10 mmol) in methanol (40 mL) at room temperature. The mixture was then heated at 65°C for 1 h, acidified with hydro-



Scheme 2.

Table 1. UHP–aq. NaOH oxidation of benzaldehyde and methoxybenzaldehydes to benzoic acid and derivatives

Aldehyde (mmol)	UHP (mmol)	Time (min)	% Yield of carboxylic acid
Benzaldehyde (11.5)	87	55	94
2-Methoxybenzaldehyde (10)	87	60	90
3-Methoxybenzaldehyde (12)	88	60	95
4-Methoxybenzaldehyde (11)	87	60	72
3,4-Dimethoxybenzaldehyde (11)	87	60	63

chloric acid to give 2-methoxybenzoic acid (1.37 g, 90%), mp 100–101.5°C (from water), lit.[16] mp 101.5°C.

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