

Oxidation of Substituted Toluenes to Benzaldehydes using Solid Peroxygen Sources Catalysed in the Presence of Bromide and Cobalt(II) Acetate

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Substituted toluenes can be selectively oxidized to the aldehydes employing solid peroxygens in the presence of cobalt(II) acetate, acetic acid and an inorganic bromide source.

The oxidation of an aromatic sidechain is an industrially important process. However, the transformation of toluenes to benzaldehydes and benzoic acids is difficult to perform. The most demanding stage is the introduction of the initial oxygen, as subsequent conversion between oxidation levels is relatively easy. The products of such oxidations are useful intermediates in such areas as agrochemical, perfumery, pharmaceutical and polymer chemicals. Traditionally, transi-

tion metal oxidants¹ such as manganese and chromium have been used in the chemical industry over many years. They have a major disadvantage in that they produce large volumes of effluent containing the spent transition metal. The oxidation of toluenes can be achieved directly using such transition metal oxidants. For example, cobalt–air has often been employed on a large scale.⁴ In particular, it is extensively used in conjunction with acetic acid and a bromide source (commonly known as the CAB system) for the production of terephthalic acid from *p*-xylene. Solvay Interlox⁷ have adapted the CAB–O₂ system and used aqueous H₂O₂ in place of air as the oxidant. There are three main advantages to employing aqueous H₂O₂. Firstly, the system can be run under milder temperature and pressure conditions typically, between 50–80 °C and 1 bar. Secondly, general purpose plant equipment can be employed. Finally, the product selectivity can be better controlled. However, the system still suffers from two main drawbacks: (i) deactivation of ‘active’ cobalt species by water means that relatively high levels of cobalt are required for good reaction; (ii) carboxylic acids are produced as side products particularly at higher conversion rates (the aldehydes often being the most desirable product).

We now report a process employing a solid peroxygen as the oxidant in the presence of catalytic quantities of cobalt(II) acetate and bromide to give a much more selective formation of aromatic aldehyde over the process which uses aqueous H₂O₂. The model substrate for the present study was 4-*tert*-butyltoluene and the solid oxidants screened in our study were: sodium perborate monohydrate (PBS-1), sodium perborate tetrahydrate (PBS-4), sodium carbonate sesquihydrate (sodium percarbonate Na₂CO₃·1.5H₂O₂) and urea hydrogen peroxide (UHP). Reactions were run in acetic acid at 45 °C. The substrate was converted to the industrially important 4-*tert*-butylbenzaldehyde as the major product and 4-*tert*-butylbenzyl bromide in small amounts, whereas when aqueous H₂O₂ (35% *m/m*) was employed the products were aldehyde and the carboxylic acid (Scheme 1).

The most effective of the solid oxidants was found to be PBS-1. There are two important factors which need to be considered when operating the system. Firstly, the mole ratio of cobalt to bromide must be controlled at about 1:1 for a high selectivity to aldehyde to be achieved. Secondly, it was important to retard dismutation of peroxide to water and oxygen via the temperature at which the reaction was carried out, addition rate and structure of the primary oxidant used, thus reducing overoxidation of aldehyde to carboxylic acid by an auto-oxidation pathway.

A range of substrates were oxidized using the PBS-1 oxidant and are tabulated below. Again it is worth noting that no over oxidation to the carboxylic acid was observed, which was in striking contrast to when aqueous H₂O₂ was the primary oxidant source.

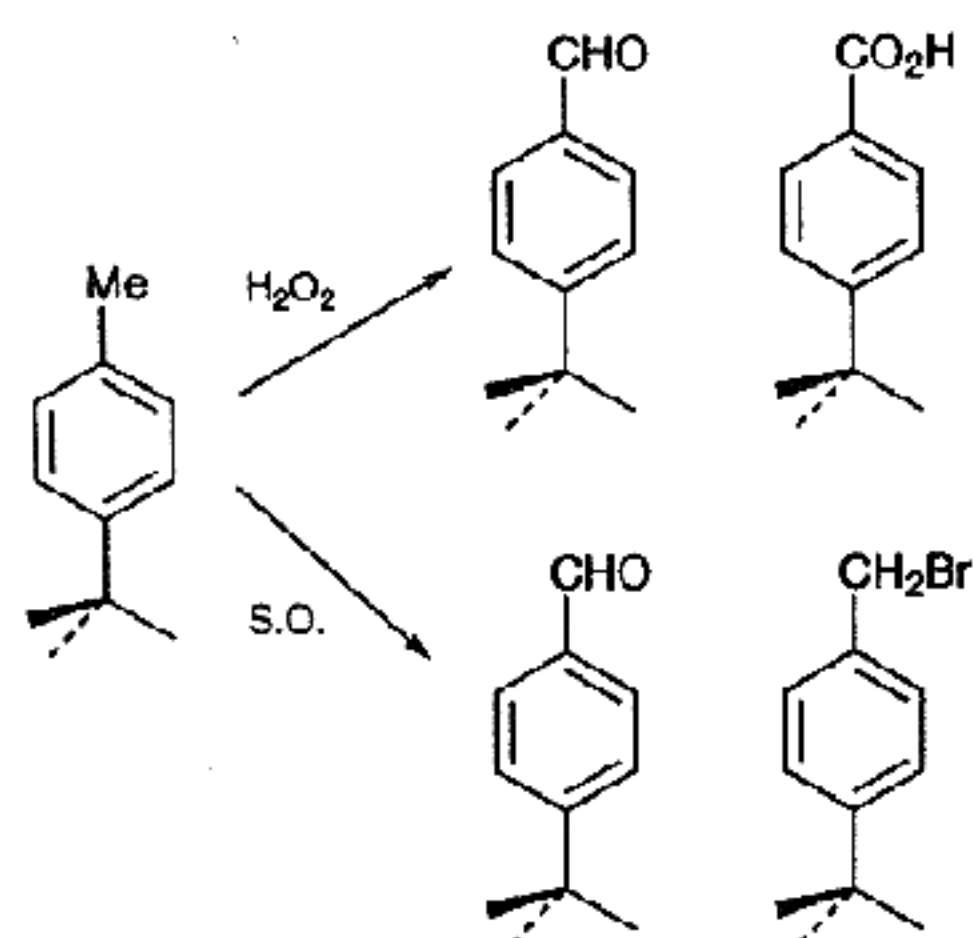
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Techniques used: GC and HPLC

Table The sidechain oxidation of substituted toluenes using PBS-1 in the cobalt(II)–acetic acid–bromide system^a

Substrate	Oxidant	Products	Selectivity (%)
4- <i>tert</i> -Butyltoluene	H ₂ O ₂	Aldehyde	40.5
		Carboxylic acid	20.5
	PBS-1	Aldehyde	75.6
4-Methoxytoluene	H ₂ O ₂	Aldehyde	45.0
		Carboxylic acid	39.0
	PBS-1	Aldehyde	71.4
Diphenylmethane	H ₂ O ₂	Benzophenone	79.1
	PBS-1	Benzophenone	80.3
<i>p</i> -Xylene	H ₂ O ₂	Aldehyde	52.9
		Carboxylic acid	14.0
	PBS-1	Aldehyde	75.5

^aReactions were run in acetic acid (50 g) at 45 °C over 3 h. Substrate (33 mmol), cobalt(II) acetate tetrahydrate (2 mmol), PBS-1 (0.05 mol) or H₂O₂ (35% *m/m*, 0.05 mol) and NaBr (5 mmol) were the other key components. The reaction was analysed by GC and HPLC against an anisole internal standard. Selectivity was expressed as (% yield of product/% conversion of substrate) × 100. Conversion was expressed as [1-(final mass of substrate/initial mass of substrate)] × 100.



S.O. = PCS, PBS-1, PBS-4, UHP
Other components = AcOH, NaBr, Co(OAc)₂

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Fig. 1: The effect of temperature on 4-*tert*-butyltoluene conversion and 4-*tert*-butylbenzaldehyde selectivity using the CAB/PBS-1 system

Table 1: The sidechain oxidation of 4-*tert*-butyltoluene using the CAB system in the presence of primary oxidants

Table 2: The structure of the primary oxidants employed in the sidechain oxidation of substituted toluenes catalysed *via* the CAB system

Table 3: The effect of mole ratio of Co:Br and oxidant:substrate on the sidechain oxidation of 4-*tert*-butyltoluene using the CAB system with PBS-1

Table 4: The sidechain oxidation of 4-*tert*-butyltoluene, benzylalcohol and 4-*tert*-butylbenzaldehyde using the CAB system with aqueous H₂O₂

Table 5: The sidechain oxidation of substituted toluenes using the CAB/PBS-1 system as the primary oxidant

Scheme 2: Proposed auto oxidation mechanism of alkylbenzenes using the CAB-O₂ system

Scheme 3: An alternative mechanism for the auto oxidation of alkylbenzenes using the CAB-O₂ system

Scheme 4: Products formed during sidechain oxidation of 4-*tert*-butyltoluene using the CAB system in the presence of solid peroxygen sources and aqueous H₂O₂

Scheme 5: Possible equilibria existing when perborates are added to acetic acid

Scheme 6: Initial electron transfer mechanism from arene to cobalt(III)

Scheme 7: Oxidation of benzyl alcohols to benzaldehydes *via* the *in situ* formation of diatomic bromine

Scheme 8: Possible mechanisms operating during the sidechain oxidation of substituted toluenes employing the CAB-peroxygen system

Scheme 9: Possible involvement of solvent during the oxidation of substituted toluenes using the CAB-peroxygen system

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