

# Hydroxylation of Alkylphenols by Cerium(IV) in Conjunction with Hydrogen Peroxide and Sodium Dodecyl Sulphate

H. Mohindra Chawla,\* S. Kumar Sharma, K. Chakrabarty, and S. Bhanumati

Department of Chemistry, Indian Institute of Technology, Hauz Khas, New Delhi - 110 016, India

Hydroxylation of alkylphenols has been achieved by oxidation with cerium(IV) ammonium nitrate in conjunction with hydrogen peroxide in sodium dodecyl sulphate medium; concurrent oxidation of alkyl groups and subsequent decarboxylation have also been observed in some cases.

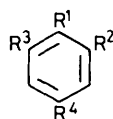
We report a procedure for hydroxylation of alkylphenols (1)–(5) by using cerium(IV) ammonium nitrate (CAN) in conjunction with hydrogen peroxide and sodium dodecyl sulphate (SDS).† In some cases the alkyl groups are also oxidized and decarboxylated on prolonged reaction; for instance 2,6-dimethylphenol (5) gave 1,4-dihydroxybenzene (7) in 70% yield while 2-methylphenol (3) gave 2-methyl-1,4-dihydroxybenzene (8) in 47% yield based upon the reactant concentration and as determined by <sup>1</sup>H n.m.r. spectroscopy.

Hydroxylation does not occur in the absence of H<sub>2</sub>O<sub>2</sub>, Ce<sup>IV</sup>, or AcOH. In the absence of SDS, the reaction gives oxidative coupling products in addition to the hydroxylated derivatives; for example (2) on treatment with Ce<sup>IV</sup>/H<sub>2</sub>O<sub>2</sub> gave (12) and (13) while (3) gave (8), (14), and (15). We have also determined that the yield of hydroxylation products is dependent upon the concentration of SDS (Figure 1, Curve A) and is highest for [SDS] = 2–4 × 10<sup>-3</sup> mol l<sup>-1</sup>. The yield of hydroxylated products remained practically constant for [SDS] = 4–6 × 10<sup>-3</sup> mol l<sup>-1</sup>, and decreased markedly in a linear fashion at higher concentrations of SDS.

Since the extent of hydroxylation was highest in the presence of 2–4 × 10<sup>-3</sup> mol l<sup>-1</sup> of SDS, the increase in yield may be due to the formation of micellar aggregates in this

concentration range.<sup>1–3</sup> This view was supported by the known value of the critical micellar concentration of SDS<sup>4</sup> and also by studying the effect of counter-ions, *e.g.* urea hydrochloride, when the yield of hydroxylated products (*e.g.* 2,6-dimethylphenol) dropped from approximately 70 to 38%, while the yield of dimeric and trimeric products increased many fold (Figure 1, Curve B). Cationic surfactants such as cetyltrimethylammonium bromide (CTAB) led to a larger concentration of oxidative coupling products (Figure 1, Curve C). No brominated product could be detected. At considerably higher concentrations of CTAB, cetyltrimethylammonium nitrate was precipitated, as shown by n.m.r. spectroscopy.

It is difficult to define yet the precise mechanism of the reaction, but our preliminary experiments indicate that the reaction involves free radicals, is devoid of distinct charged species, and occurs at the micellar interface. The micellar catalysis is probably due to radical stabilization in the hydrophobic environment.<sup>2,5</sup> This opinion is in consonance



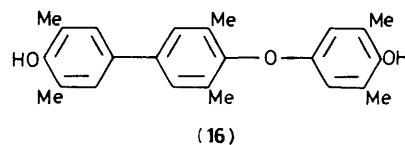
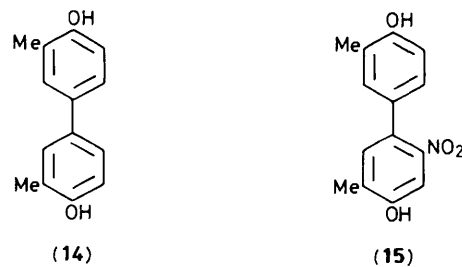
	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	R <sup>4</sup>
(1)	Me	H	H	H
(2)	OH	H	H	H
(3)	OH	Me	H	H
(4)	OH	H	H	Me
(5)	OH	Me	Me	H
(6)	OH	H	H	Me
(7)	OH	H	H	OH
(8)	OH	Me	H	OH
(9)	OH	OH	H	Me
(10)	Me	OH	H	OH
(11)	CHO	H	H	H
(12)	OH	H	H	NO <sub>2</sub>
(13)	OH	NO <sub>2</sub>	H	NO <sub>2</sub>

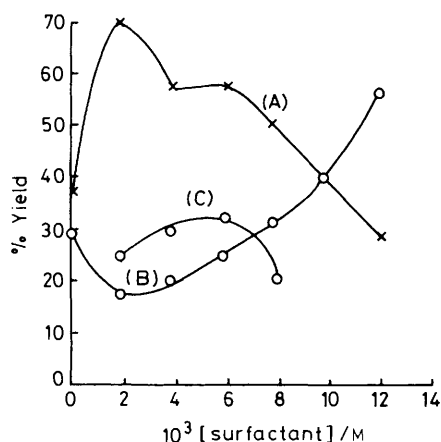
† In a typical procedure, a saturated solution (at 30 °C) of cerium(IV) ammonium nitrate (10 mM) in acetic acid (20 ml) was added in drops to a suspension of the alkyl-phenol (10 mM) in aqueous SDS (≈10<sup>-3</sup> M), and the mixture left at room temperature for 2 h. Hydrogen peroxide (30%; 10 mM) was added in drops, and the reaction followed by t.l.c. The mixture was stirred for 2 h when the reaction was *ca.* 80% complete, and then poured on crushed ice (100 g), and extracted with ethyl acetate and benzene (each 5 × 30 ml). Concentration under reduced pressure and flash chromatography over silica gel using light petroleum, benzene, and ethyl acetate as eluants gave the products, the yields of which (Table 1) were determined by <sup>1</sup>H n.m.r. spectroscopy. The yields at different concentrations of SDS were determined by u.v. measurements at 295 nm from a standard calibration curve and also by <sup>1</sup>H n.m.r. spectroscopy.

Table 1. Hydroxylation of alkylphenols.

Substrate	Hydroxy products, <sup>b</sup> % yield <sup>a</sup>	Additional products, <sup>c</sup> % yield <sup>a</sup>
(1)	(6), 37	(11), 30
(2)	(7), 22	(12), (13), 30, 15
(3)	(8), 47	(14), <sup>e</sup> (15), <sup>e</sup> 20, 15
(4)	(9), (10), 52 <sup>d</sup>	
(5)	(7), 70	(16), <sup>e</sup> 12

<sup>a</sup> Unoptimized isolated yields; <sup>1</sup>H n.m.r. studies of the product mixture showed yields to be roughly 10% higher than the isolated yields. <sup>b</sup> All compounds were identified by their spectroscopic, chemical, and analytical data. <sup>c</sup> Formed in the absence of SDS. <sup>d</sup> Combined yield. <sup>e</sup> New compound: m.p. (*t*/°C): (14) 154; (15) 176; (16) 173.





**Figure 1.** % Yield vs. [SDS], (A) and (B), or [CTAB], (C). (A), yield of hydroxylation product; (B), yield of dimers and trimers; (C), yield of oxidative coupling products.

with earlier reports.<sup>5</sup> Of the two possible radicals, hydroxyl and peroxy, the former seems to be more likely, although the latter cannot be ruled out unambiguously. This is supported by the comparative instability of peroxyacetate and plausible single electron transfer from the organic substrate to the  $Ce^{IV}$  to yield  $Ce^{III}$  which can generate hydroxyl radicals from  $H_2O_2$  while being reoxidised to  $Ce^{IV}$ . The increase in yield of hydroxylated products may also be due to recycling of the metal redox system.<sup>6</sup> The dealkylation observed in the case of 2,6-dimethylphenol and 4-methylphenol also supports the above view since their methyl groups may be oxidised to aldehyde or carboxylic acid, followed by decarbonylation or decarboxylation by a free radical mechanism as envisaged earlier.<sup>7,8</sup> Although an unambiguous mechanism by which such micellar effects operate is not yet clear,  $Ce^{IV}/AcOH/H_2O_2$  in *ca.*  $2-4 \times 10^{-3} \text{ mol l}^{-1}$  of SDS can be suggested as a

reagent for aromatic hydroxylations. Despite the fact that CAN mediated reactions have been extensively studied, this is the first report of oxidation of organic substrates with cerium(IV) in conjunction with hydrogen peroxide. The survival of hydroxy products in the presence of cerium(IV) is also interesting because they would be expected to undergo further oxidation to quinones;<sup>9</sup> this indicates the complexity of the mechanism.

K. C. and S. K. S. thank the Council of Scientific and Industrial Research, New Delhi, for the award of Senior Research Fellowships.

Received, 6th February 1987; ‡ Com. 159

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‡ Received in revised form 11th September 1987.