Nonclassical Oxidation of Cymenes

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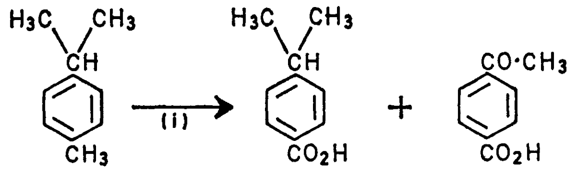
Summary Cobalt(III) ion-catalysed co-oxidation of *p*-cymene and butane affords predominantly *p*-isopropylbenzoic acid, contrary to the prediction based on the classical free-radical mechanism.

THE oxidation of *p*-cymene has been studied by many investigators under a variety of experimental conditions. Major products normally formed are *p*-toluic and terephthalic acids. *p*-Acetobenzoic, *p*-isopropylbenzoic, and α-hydroxy-*p*-isopropylbenzoic acids, and *p*-methylacetophenone were also formed in varying amounts.[1] Bourns *et al.* have identified the primary products of *p*-cymene oxidation as tertiary and primary hydroperoxides in a 4 to 1 ratio.[2] Even in anodic oxidation of *p*-cymene in methanol by electron transfer, the reactivity of the isopropyl group as compared with the methyl was 2 to 1.[3]

We find that co-oxidation of *p*-cymene and butane affords *p*-isopropylbenzoic acid (I) and *p*-acetobenzoic acid (II) in yields of 90 and 10%, respectively, when the reaction is carried out employing a large concentration of Co^{3+} ions (initially added as 5% cobaltous acetate tetrahydrate in acetic acid solvent). The products were fully characterized by their physical properties, gas chromatography, and i.r. and n.m.r. spectroscopy; also oxidized under similar conditions were: an isomeric mixture of s-butyltoluenes to s-butylbenzoic acids (89%), *p*-t-butyltoluene to *p*-t-butylbenzoic acid (95%), and *p*-ethyltoluene to *p*-ethylbenzoic acid (68%). Butane is oxidized to acetic acid. Oxidation of the methyl group in preference to other alkyl groups on the same benzene ring is surprising and cannot be rationalized on the basis of the classical free-radical mechanism.



(I) (II)

(i) $Co(OAc)_2$, $4H_2O/HOAc$;
$n\text{-}C_4H_{10}$.
100°, 20 atm. O_2; 1·5 h

Mechanistic studies to be published later in detail suggest the operation of an electron transfer mechanism with radical cation intermediates.

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[3] T. Shono and Y. Matsumura, *J. Org. Chem.*, 1970, **35**, 4157.