Hydroxylation of Toluene and Xylenes with *t*-Butyl Hydroperoxide-Aluminum Chloride

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Although extensive studies of the oxidation reactions of various organic compounds with hydroperoxides have been carried out, the oxidation of an unactivated aromatic nucleus by hydroperoxides has been neglected. Hamilton *et al.*[1] have, however, reported on the hydroxylation of aromatic compounds by hydrogen peroxide in the presence of ferric ion and catecol. They showed that the use of alkyl hydroperoxides, such as ethyl and *t*-butyl hydroperoxides, instead of hydrogen peroxide was ineffective in the hydroxylation in the catalytic system. We wish to report here our preliminary results of a synthetically-useful method for introducing a hydroxy group directly into the aromatic nucleus of simple methylbenzenes, using *t*-butyl hydroperoxide in the presence of aluminum chloride.

In a typical experiment, a solution of 0.05 mol of the peroxide in 30 m*l* of toluene was added to a stirred mixture of 0.1 mol of aluminum chloride and 90 m*l* of toluene at −20°C over a half hour period. After having been stirred for an aditional 2 hr at this temperature, the reaction mixture was poured into ice cold hydrochloric acid. After the usual working-up, cresols (*o*- : *m*- : *p*-=56 : 8 : 36) were obtained in a 76 mol% yield, accompanied by *t*-butyltoluenes (*m*- : *p*-=65 : 35) in a 78 mol% yield.

An electrophilic mechanism for this hydroxylation is predicted by the cresol-isomer distribution and by the necessity that aluminum chloride be present.[2] The rates of this hydroxylation of methylbenzenes relative to benzene obtained by the competitive method[3] were *m*-xylene : *p*-xylene: *o*-xylene : toluene: benzene=136.6: 63.5: 62.1: 13.8: 1.0. The relative rates in our system with methylbenzenes were somewhat higher than those from electrophilic oxygenation with diiospropyl peroxydicarbonate - aluminum chloride[4] ($K_{\text{toluene}}/K_{\text{benzene}}=9.6$), and with di-*t*-butyl peroxide-aluminum chloride[5] ($K_{\text{toluene}}/K_{\text{benzene}}=10.4$). Our results suggest, therefore, that the oxidizing agent is an electrophile which exhibits a high substrate selectivity.

Information was obtained concerning the nature of the oxidizing species by carrying out the reaction of *n*-butyl hydroperoxide with toluene in the presence of aluminum chloride at −20°C for 2 hr. In this case, the oxygenation products were obtained not as phenolic metarials but as alkyl aryl ethers, namely, *n*-butyl tolyl ethers (10 mol%). This indicates that the oxidizing agent is not the hydroxy group but the alkoxy group.

On the basis of the experimental findings, the following electrophilic substitution process may be proposed for the title reaction, where the *t*-butyl oxonium ion (I) is the oxidizing agent. Since *t*-butyl hydroperoxide is prone to dissociate essentially in the form of $t\text{-BuOO}^{\delta-}\text{–}H^{\delta+}$, alumium chloride may initially co-ordinate with the peroxide at the oxygen ($\delta-$) to cause the heterolytic fission of the O–O bond. I attacks the aromatic substrate to form, presumably, a *t*-butyl aryl ether (II). The free phenol should arise from the subsequent dealkylation of II under the present reaction conditions,[6] followed by treatment with hydrochloric acid:

$$t\text{-BuOOH} + AlCl_3 \longrightarrow \underset{\text{(I)}}{t\text{-BuO}^+} + [AlCl_3(OH)]^-$$

$$\text{I} + \text{ArH} \longrightarrow \underset{\text{(II)}}{\text{ArOBu-}t} + H^+$$

$$\text{II} + \text{ArH} + AlCl_3 \longrightarrow \text{ArOAlCl}_2 + \text{ArBu-}t + HCl$$

$$\text{ArOAlCl}_2 \xrightarrow[H^+]{H_2O} \text{ArOH} + \text{HOAlCl}_2$$

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[1] G. A. Hamilton, J. W. Hanifin, Jr., and J. P. Friedman, *J. Amer. Chem. Soc.*, **88**, 5269 (1966).

[2] The yield of phenols was dependent on the ratio of aluminum chloride to peroxide, at least a 2 : 1 molar ratio being required for good results.

[3] a) The relative rates were determined by gas-liquid chromatography. b) The relative rates of xylene *vs.* toluene were *m*-xylene : *p*-xylene : *o*-xylene=9.9 : 4.6 : 4.5.

[4] P. Kovacic and S. T. Morneweck, *J. Amer. Chem. Soc.*, **87**, 1566(1965).

[5] S. Hashimoto, W. Koike and T. Murachi, *Kogyo Kagaku Zasshi*, **72**, 2015 (1969).

[6] *t*-Butyl phenyl ether underwent rapid decomposition in toluene at −20°C in the presence of aluminum chloride. The essentially quantitative dealkylation yielded phenol and *t*-butyltoluenes. However, *n*-butyl phenyl ether did not decompose under the condition.