Cleavage of Alkyl Aryl Ethers with Lithium Iodide

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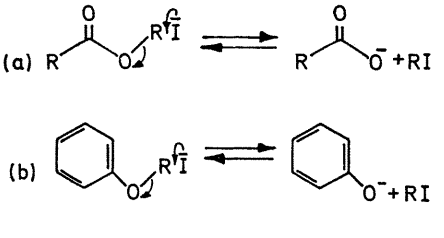
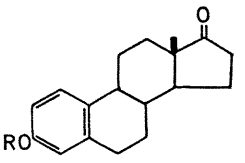
Summary Alkyl aryl ethers are cleaved by lithium iodide to yield the corresponding phenol.

THE halogenolysis of esters by iodide ion is a reaction of considerable utility, allowing the equivalent of ester hydrolysis in the presence of functions sensitive to either acid or base.[1] Examination of the mechanism (*a*) of this reaction indicates that a similar cleavage (*b*) of alkyl aryl ethers should be possible.





(1)

We find that these ethers can in fact be cleaved in this manner. Thus a solution of 2-methoxynaphthalene (1 g.) in dry 2,4,6-collidine (4 ml.) containing LiI (1·5 g. dried at 300° under nitrogen) was heated to reflux under nitrogen for 10 hr., acidified, and extracted giving an almost quantitative yield of 2-naphthol. Oestrone methyl ether (**1**; R = Me) gave oestrone (**1**, R = H) in 48 hr. Oestrone ethyl ether (**1**; R = Et) was also cleaved, although more slowly. The reaction mixture becomes mildly basic as the cleavage proceeds but may be buffered by the addition of an equivalent amount of an acid, *e.g.* benzoic acid. Alternatively, the reaction may be carried out with $LiI,3H_2O$ at 180—200° in the absence of solvent. No cleavage was observed with 17-benzyloxyandrostane and hexadecyl methyl ether.

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[1] E. Taschner and B. Liberek, *Roczniki Chem.*, 1956, **30**, 323; F. Elsinger, J. Schreiber, and A. Eschenmoser, *Helv. Chim. Acta*, 1960, **43**, 113.