The Photoisomerization of Alkyl Phenyl Ethers to Alkylphenols

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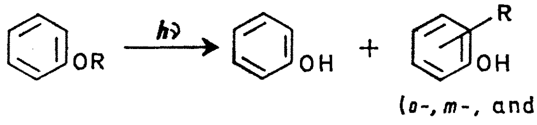
Summary Photolysis of alkyl phenyl ethers in the wavelength region 200—250 nm yields the isomeric alkylphenols.

THE irradiation of methanol—or cyclohexane—solutions of alkyl phenyl ethers with a 450 w Hanovia medium-pressure mercury lamp in a Vycor or quartz immersion well, yields, after 24—48 h, phenol plus a mixture of all three alkylphenols isomeric with the starting ether. The total yields of phenolic products are low, 2% or less, when the Vycor well is used, and higher when the quartz well is used (see Table).



Irradiation of anisole through a Corex filter for 48 h produces no phenolic material. Thus the cleavage and rearrangement of these ethers must result from absorption of radiation of wavelengths lower than 250 nm.

No polyalkylated phenols have been detected, but a yellow, presumably polymeric, substance precipitates on prolonged irradiation, particularly in hydrocarbon solvents. In addition, some soluble yellow material is formed. This has not been characterized as yet, but may be a fulvene derivative as reported by Bryce-Smith.[1]

The phenols were separated by preparative gas chromatography, following base extraction of the photolysate, and were identified by i.r. and n.m.r. spectroscopy.

For the following reasons it is felt that the cleavage of the ethers to phenol is probably the homolytic process noted by Porter[2] in the flash photolysis of anisole.

(i) Methane is formed in the anisole photolysis.

(ii) The yield of phenol, in contrast to that of the alkylphenols, appears to be dependent on solvent. Solvent studies are, however, incomplete at this time.

Yields and compositions of phenolic photoproducts (*quartz well*; *solvent*: *methanol*)

Starting ether	Absolute yields of photoproducts (%) Phenol	*o*-Isomer	*m*-Isomer	*p*-Isomer
PhOMe	2·81	2·38	0·28	1·61
PhOEt	2·85	2·19	0·44	1·97
$PhOPr^i$	9·10	2·06	0·77	2·32
$PhOBu^t$	41·3	7·40	1·11	9·81

(iii) The absolute yield of phenol (see Table) increases as the alkoxy-group on the starting ether is changed from MeO to Bu^tO, exhibiting the classic pattern attributed to the increasing stabilization of a carbonium ion or radical by an increase in substitution at the α-carbon.

On the other hand, in the case of methyl-, ethyl-, and isopropyl-phenyl ethers, the yields of alkylated phenols remain relatively constant, within experimental error. Furthermore, in a "crossover" experiment, *o*-methylanisole was mixed with phenetole and irradiated. After 24 h, gas chromatography revealed no phenolic products other than those formed in the irradiation of the two ethers separately. For these reasons, we favour either a caged-radical pathway or one involving a valence tautomer of benzene for the isomerization of the simple alkyl phenyl ethers. Some support is lent to the latter choice by Havinga's observation[3] of the photochemical 1–2 scrambling of ring hydrogens in tritiated anisole, presumably *via* a benzvalene intermediate.

An analogous photoisomerization of phenyl ether, phenyl benzyl ether, and phenyl allyl ether was first reported by Kharasch,[4] and subsequently re-studied and extended by Pinhey[5] and Schmid[6] to other ethers of the phenyl allyl type. Pinhey, in particular, presents compelling evidence for a free-radical mechanism in the rearrangement of *trans*-but-2-enyl phenyl ether.[5a]

It may well be that t-butyl phenyl ether is also isomerizing *via* free radicals, in view of the sizable increase in the yields of the *o*- and *p*-alkyl phenols relative to that of the *m*-isomer in this case.

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