Tetrahedron Letters No.48, pp. 5953-5956, 1966. Pergamon Press Ltd.
Printed in Great Britain.

THE PHOTOCHEMICAL REARRANGEMENT OF ARYL ETHERS

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(Received 6 September 1966; in revised form 3 October 1966)

Aryloxyacetic acids have recently been shown[2] to rearrange on photolysis to give o-hydroxyarylacetic acids and p-hydroxyarylacetic acids. In all examples studied where both ortho and para positions were unsubstituted the major rearrangement product was the o-isomer. These results prompted us to re-examine the photolysis of allyl phenyl ether, benzyl phenyl ether and diphenyl ether, which had been reported[3] to give phenol and the p-substituted phenol only.

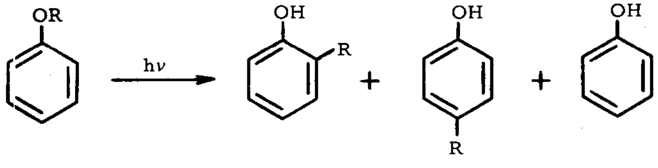
We have found that these three ethers in dilute ethanol solution rearrange when irradiated through quartz with light from a high pressure mercury arc to give both the o-substituted phenol and the p-substituted phenol, the former being the major product in each case. Benzyl phenyl ether and allyl phenyl ether rearranged at very much faster rates than diphenyl ether. In all the irradiations some phenol was produced. Product yields and reaction times are given in the table.

TABLE

Yield (%)*

Aryl Ether	Reaction time (hr.)	Recovered Ether	Phenol II	Phenol III
Ia	8	3	18	14
Ib	6	91	3	1
Ic	5	40	23	13
Id	13	7	22	16

*Yields were determined by g.l.c. of the volatile fraction from each reaction. The products were isolated by preparative g.l.c.

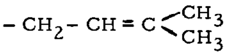


I II III

a; R = $-CH_2Ph$

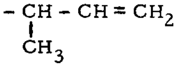
b; R = $-Ph$

c; R = $-CH_2-CH=CH_2$

d; R = 

$-CH_2-CH=C\begin{matrix}CH_3\\CH_3\end{matrix}$

e; R = $-CH_2-CH=CH-CH_3$

f; R = 

$-\underset{\displaystyle CH_3}{CH}-CH=CH_2$

The o-phenylphenol (IIb) and p-phenylphenol (IIIb) were identified by comparison with authentic samples, o-benzylphenol (IIa) and o-allylphenol (IIc) were identified as their phenylurethane derivatives while p-benzylphenol (IIIa) and p-allylphenol (IIIc) were characterised as the benzoate and 3,5-dinitrobenzoate respectively.

An examination of the scope and mechanism of the rearrangement of allyl aryl ethers has been undertaken and we report here some preliminary results. Under the same conditions as above 3-methylbut-2-enylphenyl ether (Id) rearranges at about the same rate as (Ic) to yield o-(3-methylbut-2-enyl)phenol (IId) and p-(3-methylbut-2-enyl)phenol (IIId). Both (IId) and (IIId) were isolated by preparative g.l.c. and identified by their infrared and p.m.r. spectra. In addition, the relatively high yield of p-allylphenol in the photolysis of allyl phenyl ether, compared with the thermal rearrangement[4], is not due to the further rearrangement of o-allylphenol, since irradiation of o-allylphenol produces no p-allylphenol. Thus the rearrangement does not proceed by way of six-membered cyclic transitions tates.

The rearrangement of (Id) on photolysis contrasts with the absence of rearranged products when this ether is subjected to the usual conditions of the Claisen rearrangement[4,5]. However, certain substituted 3-methylbut-2-enyl phenyl ethers have been shown to yield rearranged products on pyrolysis[6].

Finally, the photolysis of trans-but-2-enyl phenyl ether (Ie) was investigated. A g.l.c. study of the mixture showed it to consist of o-(but-2-enyl)phenol (IIe; 8% cis and 10% trans), o-(1-methylprop-2-enyl)phenol (IIf; 10%), p-(but-2-enyl)phenol (IIIe; 8% cis and 8% trans) and p-(1-methylprop-2-enyl)phenol (IIIf; 7%).

These results indicate that the photochemical rearrangement of allyl phenyl ethers probably proceeds by homolysis (or heterolysis) of the excited ether to give two stabilised radicals (or ions) which recombine to give *o*- and *p*-allyl phenols. It would appear that steric factors influence which carbon of the allylic radical (or ion) couples to the aromatic ring. We are at present investigating whether the rearrangement is inter- or intra-molecular.

References

1. Present Address, Department of Organic Chemistry, University of Melbourne.
2. D. P. Kelly and J. T. Pinhey, *Tetrahedron Letters*, 1964, 3427.
3. M. S. Kharasch, G. Stampa and W. Nudenberg, *Science*, 1952, **116**, 309.
4. D. S. Tarbell, *Organic Reactions*, 1944, **2**, 1.
5. This has been confirmed in the present work.
6. A. Jefferson and F. Scheinmann, *Chem. Comm.*, 1966, 239; and references therein.