Photo-Claisen Rearrangement. The Photochemical Rearrangement of Allyl Phenyl Ethers[*1]

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Two years ago, Woodward and Hoffmann presented an ingenious theory in an attempt to interpret the stereochemical cours of the so-called "electrocyclic" and "sigmatropic" transformations.1) They suggested1b) that the photo-Claisen rearrangement reported to give a para-rearrangement product2) would serve as an example of the [3, 5] sigmatropic transformation. Another example of the photo-Claisen rearrangement had previously been reported to give only a para-rearrangement product.3)

Although this interpretation of the photo-Claisen rearrangement was highly attractive, the following facts seemed to us conflicting enough to warrant a thorough reinvestigation of the photo-rearrangement of allyl phenyl ethers:

(1) An eight-membered cyclic transition state these systems seems sterically impossible.

(2) γ-^{14}C-Allyl 2, 6-dimethylphenyl ether has been shown to rearrange to 4-α- and 4-γ- ^{14}C-allyl-2, 6-dimethylphenols.2)

$$(CH_3)_2C_6H_3\text{–}OCH_2CH\overset{*}{=}CH_2 \rightarrow$$

$$\overset{*}{C}H_2{=}CH\overset{*}{C}H_2\text{–}C_6H_2(CH_3)_2OH$$

(3) Several related systems, phenyl esters,4) acyl anilides,5) phenoxyacetic acid,6) and ethyl phenyl carbonate,7) have been reported to rearrange photochemically to ortho- and para-rearrangement products.

The recent publication of a communication8) dealing with an investigation closely related to ours prompts us to publish our own results.

Experimental

Materials. The allyl phenyl ethers for the photoreaction were purified by rectification until no appreciable impurity was observed by glc.

Reaction Procedure. A 5% solution of a sample in isopropyl alcohol was irradiated with an immersion-type 10W low-pressure mercury lamp (Ricoh Kagaku Sangyo Co., UVL300Q) under a nitrogen atmosphere. After irradiation, most of the solvent was removed under reduced pressure, and the residual mixture was analyzed by glc.

Identification of Products. *o*- and *p*-Allylphenols, 2-allyl-3, 5-dimethylphenol, *trans-o*- and *-p*-but-2-enylphenols, and *o*- and *p*-(1-methyl-prop-2-enyl)phenols were identified by a comparison of their retention times with those of authentic sample. 4-Allyl-3, 5-dimethylphenol was isolated from the reaction mixture by means of preparative glc and was identified spectrometrically. Two unknown peaks in the gas chromatogram of the reaction mixture from *trans*-but-2-enyl phenyl ether were tentatively assigned to *cis-o*- and *-p*-but-2-enylphenols on the basis of their having been formed by the irradiation of their trans-isomers.

Analyses. The samples were analyzed by the use of a Hitachi K-23 gas chromatograph. A 1-meter Celite-545 (60—80 mesh) column with 33% Silicon KF-54 was used. The results in the table are given as the percentage ratio of the peak area.

Results and Discussion

As shown in the table, all the compounds rearranged to give ortho- and para-rearrangement products in addition to the parent phenols of the starting ethers. Some unidentified products were also present. *trans*-But-2-enyl phenyl ether was shown to give *o*- and *p*-but-2-enyl and *o*- and *p*-(1-methylprop-2-enyl)phenols. The results are consistent with those of Schmid2) and clearly indicate that the rearrangement does not proceed

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[*1] A preliminary account of this investigation has been presented at the 19th Annual Meeting of the Chemical Society of Japan, Tokyo, March, 1966; Abstr., Vol. 3, p. 209.

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2) K. Schmid and H. Schmid, *Helv. Chim. Acta*, **36**, 687 (1953).

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4) a) H. Kopsa, *J. Org. Chem.*, **27**, 2293 (1962); b) J. C. Anderson and C. B. Resse, *J. Chem. Soc.*, **1963**, 1781; c) W. M. Horspool and P. L. Pauson, *ibid.*, **1965**, 5162; d) R. A. Finnegan and J. J. Mattice, *Tetrahedron*, **21**, 1015 (1965).

5) D. Elad, D. V. Rao and V. I. Stenberg, *J. Org. Chem.*, **30**, 3252 (1965).

6) D. P. Kelly and J. T. Pinhey, *Tetrahedron Letters*, **1964**, 3427.

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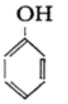
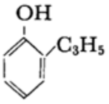
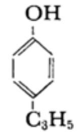
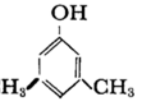
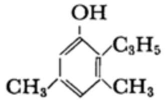
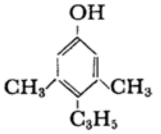
TABLE 1. ANALYSES OF PRODUCTS

(1) Allyl phenyl ether

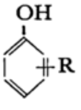
Time of irradiation (hr)	Starting material			
12	84.2%	2.3%	7.3%	6.3%
24	68.6	4.9	14.3	12.3
48	39.6	10.2	26.8	23.4

(2) Allyl 3,5-dimethylphenyl ether

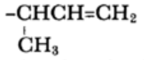
Time of irradiation (hr)	Starting material			
12	81.5%	3.9%	8.8%	5.8%
24	67.5	7.3	15.2	10.0
48	36.5	14.7	29.4	19.4

(3) *trans*-But-2-enyl phenyl ether

Time of irradiation (hr)	Starting material	Phenols (%)						
		I	*o*-II	*p*-II	*o*-III	*o*-IV	*p*-III	*p*-IV
24	77.3%	3.7	3.6	3.7	4.7	1.2	4.6	1.2
48	53.3%	8.6	6.6	6.9	9.1	3.4	8.3	3.8



(I) R = -H

(II) 
$-\underset{CH_3}{CH}CH{=}CH_2$

(III) $-CH_2CH{=}CHCH_2$ (*trans*)

(IV) $-CH_2CH{=}CHCH_2$ (*cis*)

via a cyclic process, but probably involves a radical or an ionic recombination of two fragments.

The products do not seem to undergo further rearrangement; in each case, the ortho/para ratio of the products[*3] was unchanged during the irradiation. In fact, as has been reported by Kelly *et al.*,8) these phenols are quite stable to any irradiation except for trans-cis isomerisation.

In the rearrangement of but-2-enyl phenyl ethers, the ratio of (1-methylprop-2-enyl)phenols to but-2-enylphenols was about 0.6. Although some steric factors may be responsible for the observed ratio, this value strongly suggests that the reaction mechanism is a radical process. If the reaction proceeded through an ionic path, the fragmentation would lead to a phenoxide anion and an allyl cation, and from the reported data of the SN1 reaction of crotyl and methylallyl substrates, the ratio would be expected to be about 0.1—0.2.9)

The ortho/para ratio of the products is 1.1 for allyl phenyl ether, 1.5 for allyl 3,5-dimethylphenyl ether, and 1.0 for but-2-enyl phenyl ether, showing in each case a slight preference for the attack on the para-position. Although somewhat different results have been previously reported,8) the discrepancy may be ascribed to the differences in the experimental conditions. Steric factors seem to be operative in the rearrangement of allyl 3,5-dimethylphenyl ether.

To ascertain whether the rearrangement is intra- or inter-molecular, a mixed solution of allyl 3,5-dimethylphenyl ether and *trans*-but-2-enyl phenyl ether, each 5% in isopropyl alcohol, was irradiated. The products were analyzed both as free phenols and as their methyl ethers. Other than the rearrangement products expected for each component separately, no trace of crossed products could be detected, a clear indication of the intramolecular nature of the reaction. The mechanism of the photo-Fries rearrangement has been suggested4a) to be a radical recombination within a solvent cage. Arenesulfonyl anilides have also been shown to rearrange photochemically *via* an intramolecular process.10) Thus, as in the preceding cases, the photo-rearrangement of allyl phenyl ethers can most consistently be interpreted by a radical recombination mechanism within a solvent cage.

[*3] Although the ratio of the peak area was used for the isomer ratio without calibration throughout the discussion, the error seems to be small, as was found to be the case with *o*- and *p*-allylphenols.

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