

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

The Rearrangement of Phenyl Allyl Ethers. IV. An Examination of the Pyrolysis Product of Phenyl Allyl Ether for Evidence of Para Rearrangement

BY WALTER M. LAUER AND ROBERT M. LEEKLEY

The para rearrangement of phenyl allyl ethers, while not as common as ortho rearrangement, has nevertheless been observed. For example, Claisen and Eisleb¹ obtained methyl 2-hydroxy-3-methyl-5-allylbenzoate by heating methyl 2-allyloxy-3-methylbenzoate and recently Mumm and his co-workers² have studied the para rearrangement of substituted allyl ethers of this same methyl *o*-cresotinate. That para rearrangement is not confined to cases in which both ortho positions are blocked becomes apparent from a study by Staudinger of the rearrangement of γ,γ -dimethylallyl *o*-anisyl ether. The rearrangement product upon methylation and subsequent degradation yielded veratric acid.

In view of these facts it was considered advisable to reexamine the pyrolysis of phenyl allyl ether for evidence of para rearrangement. The results of this study show that no appreciable amount of *p*-allylphenol is formed.

Although Claisen has shown conclusively that the product obtained by the pyrolysis of allyl phenyl ether is *o*-allylphenol, the methods which were used were such that a small amount of *p*-allylphenol in the rearrangement product might have escaped detection. In the present investigation a method sufficiently sensitive for the detection of even a small amount of *p*-allylphenol was used. *o*-Allylphenol and *p*-allylphenol are not easy to separate, but the corresponding hydroxybenzaldehydes are easily separated, since salicylaldehyde forms a copper derivative but *p*-hydroxybenzaldehyde does not. If a mixture of the two aldehydes is treated with a solution of copper acetate, the salicylaldehyde is precipitated as the copper derivative and the *p*-hydroxybenzaldehyde may be removed by extraction with ether. This method was tested with known mixtures of the two aldehydes, and in one of these tests seventy milligrams of *p*-hydroxybenzaldehyde was recovered from a mixture that contained 10 g. of salicylaldehyde and 100 mg. of *p*-hydroxybenzaldehyde. The rearrangement product obtained by the pyrolysis of allyl phenyl ether was

converted to the corresponding hydroxybenzaldehyde by isomerization with potassium hydroxide followed by ozonolysis.

No trace of *p*-hydroxybenzaldehyde could be found in the salicylaldehyde produced from the rearrangement product. It was therefore concluded that if any *p*-allylphenol was formed by the rearrangement of allyl phenyl ether, it must be in very small amount.

This conclusion was confirmed in other ways. A sample of *o*-allylphenol which had been prepared by the decarboxylation of 3-allyl-4-hydroxybenzoic acid was compared with one prepared by the rearrangement of allyl phenyl ether. There were no significant differences in refractive indices or in melting points of the crude phenylurethans between the two samples.

Experimental

o-Allylphenol (b. p. 110–113° at 23 mm.; n_{20}^D 1.5453) prepared by the rearrangement of allyl phenyl ether, was isomerized to *o*-propenylphenol by means of methyl alcoholic potassium hydroxide according to the procedure of Claisen.³ Completeness of isomerization was established by means of a quantitative determination of the $-\text{CH}=\text{CHCH}_3$ group using mercuric acetate.

The ozonide, prepared in ethyl acetate from 14 g. of propenylphenol was decomposed by reductive cleavage according to the method of Hahn and Wassmuth.⁴ Acetaldehyde was identified as one of the cleavage products by means of its dimethone (m. p. 138.5–140°).

The residue, after removal of the ethyl acetate and the acetaldehyde, was shaken with a saturated solution of sodium bisulfite. The bisulfite addition product, washed with ether, was decomposed with dilute sulfuric acid. Extraction with ether, followed by removal of the ether, yielded a residue which was treated with copper acetate. The copper derivative of salicylaldehyde weighed 7.86 g. and the residue of ether-soluble material weighed 301 mg. The ether solutions of the several components indifferent to the copper acetate treatment were combined. Salicylic acid was identified, but no phenylhydrazone precipitated after treatment with phenylhydrazine hydrochloride and sodium acetate, even though the addition of a small amount of *p*-hydroxybenzaldehyde produced an immediate precipitate.

Separation of Salicylaldehyde and *p*-Hydroxybenzaldehyde.—A mixture containing salicylaldehyde (10 g.) and *p*-hydroxybenzaldehyde (0.1 g.) was shaken for three

(1) Claisen and Eisleb, *Ann.*, **401**, 21 (1913).

(2) Mumm and Möller, *Ber.*, **70**, 2214 (1937).

(3) Claisen *Ann.*, **418**, 69 (1919).

(4) Hahn and Wassmuth, *Ber.*, **67**, 696 (1934).

hours with ether (50 ml.) and a saturated aqueous copper acetate solution (150 ml.). After the mixture had been allowed to stand overnight, it was filtered. The precipitate, washed with ether, weighed 9.65 g. The filtrate was extracted, first with the ether that had been used to wash the precipitate, and then twice with fresh ether. The combined ether extracts were concentrated to 50 ml. and then shaken with more of the saturated copper acetate solution (100 ml.). The precipitate after washing with ether weighed 2.1 g. The filtrate was again extracted with ether and the extract treated with copper acetate as before. This time 0.7 g. of copper derivative was obtained, making a total of 12.45 g. (99.5%). The filtrate from the last crop of copper derivative was extracted with ether. The ether extract yielded 71 mg. (71%) of pure *p*-hydroxybenzaldehyde (m. p. 115–116.5°) after suitable treatment.

Pyrolysis of Ethyl *p*-Allyloxybenzoate.—One-half hour at 230–250° converted the ethyl *p*-allyloxybenzoate to ethyl 3-allyl-4-hydroxybenzoate (m. p. 77–78° after crystallization from benzene), in 89% yield.

Hydrolysis and Decarboxylation of Ethyl 3-Allyl-4-hydroxybenzoate.—Hydrolysis was accomplished by boiling for three hours with 2 *N* sodium hydroxide. Crystallization from a mixture of ether and petroleum ether yielded the acid of m. p. 127–128°; yield 85%. Decarboxylation of the acid (8 g.) by heating with quinoline (10 g.) yielded *o*-allylphenol (b. p. 93–94° at 8 mm.; n_D^{20} 1.5450).

Pyrolysis of *p*-Allyloxybenzoic Acid.—*p*-Allyloxybenzoic acid (m. p. 162–163°, Claisen reported 162°) was obtained by the hydrolysis of its ethyl ester. This acid (10 g.) was heated with quinoline (10 g.) and a trace of copper powder for eight hours at 200–210°. The pyrolysis product was dissolved in a mixture of ether and petroleum ether (1:2), extracted three times with dilute sulfuric acid, once

with water, and five times with aqueous sodium hydroxide (10%). The alkaline extract was acidified and then extracted with ether. The ether extract yielded on distillation a 60% yield of *o*-allylphenol (b. p. 97–98° at 11 mm., n_D^{20} 1.5452).

Phenylurethan of *o*-Allylphenol.—This derivative was prepared from each of the three samples of *o*-allylphenol in exactly the same way. A mixture of the phenol (340 mg.), phenyl isocyanate (240 mg.) and a trace of dry pyridine was heated for one hour at 100°. The phenylurethan was extracted from diphenylurea with boiling petroleum ether (b. p. 90–100°). The phenylurethan obtained from the petroleum ether was then placed in a vacuum desiccator. The melting point of the derivative was taken without further purification.

The melting points of the phenylurethans were as follows: (1) from *o*-allylphenol prepared by decarboxylation of 3-allyl-4-hydroxybenzoic acid, m. p. 103.5–104.5°; (2) from *o*-allylphenol obtained by the pyrolysis of allylphenyl ether, m. p. 103.5–104.5°; (3) from *o*-allylphenol obtained by the pyrolysis of *p*-allyloxybenzoic acid, m. p. 104–105°. One crystallization of the phenylurethans was sufficient to raise the melting point to 106–107° (Claisen reported 106.5° as the m. p. of the pure compound) in each case.

Summary

The pyrolysis product of allyl phenyl ether was examined for evidence of para rearrangement. The rearrangement of this ether proceeds without the formation of any appreciable amount of *p*-allylphenol, however.

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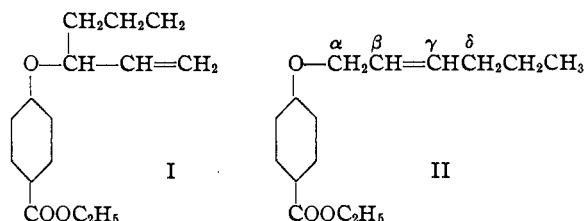
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The Rearrangement of Phenyl Allyl Ethers. V. The Isomeric Ethyl *p*-(α - and γ -Propylallyloxy)-benzoates

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The substituted allyl ethers of ethyl *p*-hydroxybenzoate lend themselves admirably to rearrangement studies since both the ethers and their rearrangement products are converted to solid acids by hydrolysis. This circumstance makes possible a more precise study of the nature of the rearrangement products. Furthermore, since the para position is blocked by the carbethoxyl group the possibility of para rearrangement is eliminated. In view of these facts, the isomeric ethers, ethyl *p*-(α -propylallyloxy)-benzoate (I) and ethyl *p*-(γ -propylallyloxy)-benzoate (II) were chosen for investigation.



Several years ago, it was reported³ that rearrangement of γ -ethylallyl phenyl ether leads to *o*-(α , γ -dimethylallyl)-phenol. That *o*-(α -ethylallyl)-phenol was also formed during this rearrangement was demonstrated by Hurd and Pollack.⁴ The formation of *o*-(α -ethylallyl)-

(1) Abstract of Ph.D. thesis submitted July, 1938.

(2) Shevlin Fellow, 1937–1938.

(3) Lauer and Filbert, *THIS JOURNAL*, **58**, 1389 (1936).

(4) Hurd and Pollack, *J. Org. Chem.*, **3**, 550 (1939).