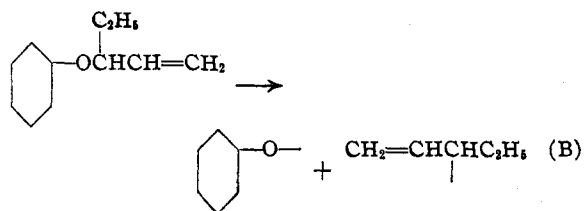
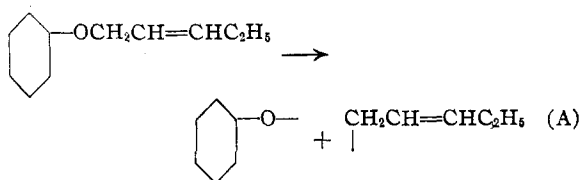


was concentrated to about 25 cc., cooled, extracted with ether, acidified with dilute sulfuric acid and allowed to stand. The solid obtained in this way was crystallized twice from water containing about 5% alcohol, using decolorizing carbon; m. p. 113–114°; yield 0.5 g. A sample of α -phenoxypropionic acid prepared from α -bromopropionic ester and sodium phenoxide according to the directions of Bischoff⁴ melted at 114–115°. (Bischoff gives 115–116°, Saarbach 112–113°.) A mixed melting point with the acid obtained by the oxidation of the ether showed no depression.

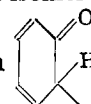
The rearrangement of this ether was carried out by boiling in diethylaniline in an atmosphere of carbon dioxide. The product (28% yield) boiled at 141–145° at 31 mm.

The phenylurethan of the rearrangement product was crystallized from petroleum ether, dilute methyl alcohol, petroleum ether and finally from dilute methyl alcohol, as colorless needles melting at 107–108.5° (Claisen gives 107–109°). The mixed melting point with the urethan of the phenol obtained by rearranging γ -ethylallyl phenyl ether was 108–109.5°.

The relation of the present results to the mechanism of the phenyl allyl ether rearrangement is not clear. It is evident, however, that the widely held formulation of Claisen must be modified. The view that rearrangement is preceded by dissociation



to yield fragments A and B, one of which isomerizes to the other before combination with



or its benzenoid isomer, leads to the prediction that the two isomeric ethers should give the same rearrangement product. The results of the present study, designed to test this hypothesis, are not in agreement with this prediction. Further work which is in progress has as its aim the accumulation of pertinent facts.

Summary

The three isomeric ethers, α -ethylallyl phenyl ether, γ -ethylallyl phenyl ether and α,γ -dimethylallyl phenyl ether have been rearranged and the structures of their rearrangement products were investigated. The first and third-named ethers rearrange in accordance with the pattern outlined by Claisen, but γ -ethylallyl phenyl ether does not, since it yields a rearrangement product identical with that obtained from α,γ -dimethylallyl phenyl ether.

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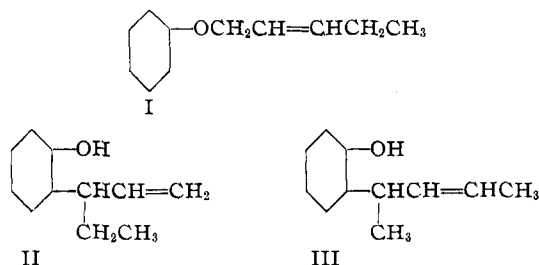
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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

The Rearrangement of Phenyl Allyl Ethers. II. Phenyl Crotyl Ether

BY WALTER M. LAUER AND HERBERT E. UNGNADE

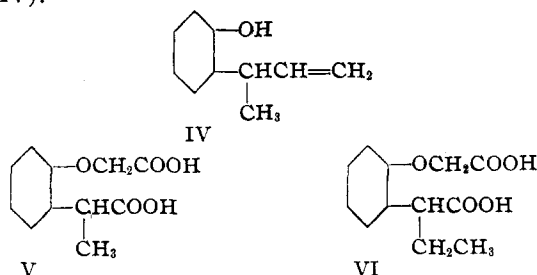
A recent study¹ of γ -ethylallyl phenyl ether (I) led to the conclusion that its rearrangement product was not the expected *o*-(α -ethylallyl)-phenol (II) but *o*-(α,γ -dimethylallyl)-phenol (III)



The present study was carried out in order to ob-

tain further evidence for the structure assigned to this rearrangement product.

According to Claisen and Tietze² phenyl crotyl ether, $\text{C}_6\text{H}_5\text{O}-\text{CH}_2-\text{CH}=\text{CHCH}_3$, when rearranged by heat yields *o*-(α -methylallyl)-phenol (IV).



(1) Lauer and Filbert, *THIS JOURNAL*, **58**, 1388 (1936).

(2) Claisen and Tietze, *Ber.*, **59**, 2344 (1926).

Consequently, oxidation of the aryloxyacetic acid derived from the rearrangement product of phenyl crotyl ether should yield the dibasic acid V. Such a series of transformations has already been described for the rearrangement product of γ -ethylallyl phenyl ether (I) and on the basis of its composition it was concluded that the structure of the dibasic acid was V rather than VI. The present work describes the rearrangement of phenyl crotyl ether and the conversion of its rearrangement product to the dibasic acid and demonstrates the fact that it is identical with the one previously obtained. This supplies additional evidence that III rather than II represents the correct structure for the rearrangement product of γ -ethylallyl phenyl ether.

The work of Claisen and Tietze² has shown that direct alkenylation of phenol with crotyl bromide leads to a product differing from that obtained by the indirect method which involves ether formation with subsequent rearrangement. The formation of the dibasic acid V here described incidentally furnishes independent confirmatory evidence pointing to IV, the accepted structure of the rearrangement product of phenyl crotyl ether.

Experimental

Methylvinylcarbinol was prepared by the action of methylmagnesium iodide on acrolein.

Crotyl bromide was obtained from methylvinylcarbinol by treatment with 45% hydrobromic acid according to the procedure of Claisen.^{2,3} The directions of Claisen were followed for the preparation and rearrangement of *phenyl crotyl ether*. The rearrangement product was converted to the phenylurethan which melted at 88.5–89° (Claisen gives 89.5–90.5° as the melting point of this compound). The phenylurethan of the rearrangement product was analyzed.

Anal. Calcd. for $C_{17}H_{17}O_2N$: C, 76.38; H, 6.40. Found: C, 76.29; H, 6.45.

Oxidation of Phenyl Crotyl Ether.—Phenyl crotyl ether (1.2 g.) was dissolved in aqueous acetone. A concentrated aqueous solution containing 3.2 g. of potassium permanganate was added and the mixture allowed to stand overnight. The manganese dioxide was filtered off and the filtrate was then acidified with dilute sulfuric acid. The solution

was concentrated to one-half its original volume and then subjected to extraction with ether. The ether extract was washed with water and then extracted with 5% sodium carbonate. Acidification of the carbonate solution followed by cooling yielded 0.32 g. of *phenoxyacetic acid*. The melting point and mixed melting point with an authentic sample of phenoxyacetic acid was 97–98°.

The aryloxyacetic acid of the rearrangement product was prepared in accordance with the method of Koelsch.⁴ One gram of the *o*-(α -methylallyl)-phenol (IV) was mixed with 3.5 cc. of 33% sodium hydroxide. To this mixture 2.5 cc. of 50% monochloroacetic acid was added slowly with shaking. After heating in a test-tube on the steam-bath for one hour, the solution was acidified with dilute sulfuric acid. The mixture was then extracted with ether and the ether extract washed with water. The product was then extracted with dilute sodium carbonate and after acidification was crystallized from water; m. p. 120–120.5°.

Anal. Calcd. for $C_{12}H_{14}O_3$: C, 69.87; H, 6.84. Found: C, 69.66; H, 6.74.

Oxidation of *o*-(α -Methylallyl)-phenoxyacetic Acid.—The oxidation was accomplished by dissolving the *o*-(α -methylallyl)-phenoxyacetic acid (1.033 g.) in 50 cc. of water containing sufficient acetone to form a homogeneous solution. Potassium permanganate (2.7 g. in 100 cc. water, ca. 8% excess) was added dropwise to the cooled solution and the reaction mixture allowed to stand overnight. After filtration, the filtrate was acidified with dilute sulfuric acid and extracted with one 50-cc. and two 25-cc. portions of ether. The combined ether extracts were dried over magnesium sulfate and then allowed to evaporate spontaneously. The residual oil insoluble in petroleum ether did not solidify at –15°. The oil, dissolved in benzene, was heated on the steam-bath for several hours. After standing overnight, the white crystalline product was collected; m. p. 170–171°; mixed with a sample of the product obtained¹ by the oxidation of *o*-(α , γ -dimethylallyl)-phenoxyacetic acid it melted at 170–171°.

Anal. Calcd. for $C_{11}H_{12}O_6$: C, 58.90; H, 5.40. Found: C, 59.16; H, 5.56.

Summary

Evidence is presented which confirms *o*-(α , γ -dimethylallyl)-phenol and *o*-(α -methylallyl)-phenol as the structures of the rearrangement products of γ -ethylallyl phenyl ether and γ -methylallyl phenyl ether, respectively.

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(3) Young and Winstein, *THIS JOURNAL*, **57**, 2013 (1935).

(4) Koelsch, *ibid.*, **53**, 304 (1933).