similarities in the behavior of sulfones and ketones in the Michael condensation pointed out. The mercuric chloride test was positive with bis-(phenylsulfonyl)-methane but negative with benzyl *p*-tolyl sulfone. The other reactions of active methylene compounds tested were not successful with these sulfones.

PHILADELPHIA, PENNA. RECEIVED JUNE 3, 1936

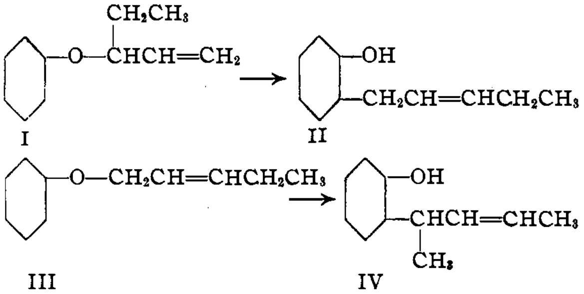
[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

The Rearrangement of Phenyl Allyl Ethers[1]

BY WALTER M. LAUER AND WILLIAM F. FILBERT

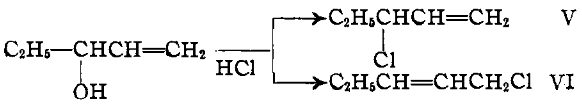
The results of Claisen's investigations dealing with the rearrangement of phenyl allyl ethers are well known. It is sufficient for our present purpose to recall that the migrating allyl group shows a preference for the ortho position and that the point of attachment of the allyl group in the cases hitherto investigated is shifted from the alpha to the gamma carbon atom. The rearrangement of a number of substituted phenyl allyl ethers has been examined,[2] but no study has been made of an isomeric pair of the type, $C_6H_5OCH(R)CH=CH_2$ and $C_6H_5OCH_2CH=CHR$. This omission presumably is due to the difficulty of obtaining the isomeric halides necessary for the usual synthesis of these ethers. Fortunately, however, Meisenheimer and Link[3] have shown that the action of hydrogen chloride on ethylvinylcarbinol leads to a mixture of $CH_3CH_2CHClCH=CH_2$ and $CH_3CH_2CH=CHCH_2Cl$, which may be separated by means of a careful fractional distillation. It was therefore considered not without interest to prepare such a pair of isomeric ethers and to study their rearrangement.

The ether I yielded the expected rearrangement product, II, but its isomer, III, quite unexpectedly, yielded IV.



The Isomeric Ethers

The two isomeric chlorides, 3-chloro-1-pentene and 1-chloro-2-pentene, were prepared by the action of gaseous hydrogen chloride upon ethylvinylcarbinol.



$$C_2H_5\underset{\displaystyle OH}{\underset{|}{C}}HCH=CH_2 \xrightarrow{HCl} \begin{cases} C_2H_5\underset{\displaystyle Cl}{\underset{|}{C}}HCH=CH_2 & \text{V} \\ C_2H_5CH=CHCH_2Cl & \text{VI} \end{cases}$$

The two isomeric ethers, I and II, were obtained from these chloropentenes by treatment with phenol and potassium carbonate in the presence of acetone. On account of the possibility of an alpha-gamma transposition, it was especially important to establish the structures of these ethers. This was accomplished by oxidation: I yielded α-phenoxybutyric acid, $C_6H_5OCH(C_2H_5)COOH$, whereas III under similar conditions gave phenoxyacetic acid, $C_6H_5OCH_2COOH$.

The preparation of *1-chloro-2-pentene* (VI) and *3-chloro-1-pentene* (V) was carried out as follows. Ninety-nine grams (1.15 moles) of freshly distilled ethylvinylcarbinol was saturated with dry hydrogen chloride at 0°. After standing for three hours in an ice box, the reaction mixture was again saturated at 0°. This process was then repeated after standing overnight. The total gain in weight was 62 g. Finally after standing for twenty-four hours in an ice box, the lower aqueous layer was separated and the mixed chlorides were placed over anhydrous potassium carbonate for two weeks. The mixture was filtered and then fractionally distilled using a 60-cm. Widmer column. Refractionation gave the following results: (1) $C_2H_5CHClCH=CH_2$, b. p. 50–50.2° (150 mm.), 42.1 g.; (2) intermediate, b. p. 50.2–62° (149 mm.), 2.1 g.; (3) $C_2H_5CH=CHCH_2Cl$, b. p. 62° (149 mm.) to 63.2° (146 mm.), 43.5 g.; (4) residue 3.7 g.

γ-Ethylallyl Phenyl Ether (III).—A mixture of 18.8 g. of phenol (0.2 mole), 20.9 g. of 1-chloro-2-pentene (0.2 mole), 29.0 g. (0.21 mole) of anhydrous potassium carbonate and 20 cc. of acetone, combined in the order named, was placed in a 200-cc. round-bottomed flask. The reaction mixture was refluxed on the steam-bath for eighteen hours, cooled, taken up in water and 25 cc. of ether added. After separating the aqueous layer, it was again extracted with ether. The combined ether extract was then shaken twice with 15–20 cc. of 20% sodium hydroxide. After drying

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[1] Abstract of a thesis submitted to the Graduate Faculty of the University of Minnesota by William F. Filbert for the degree of Doctor of Philosophy, August, 1934.

[2] For an excellent discussion see Hurd, "The Pyrolysis of Carbon Compounds," Chemical Catalog Co., Inc., N. Y., 1929, p. 214 *et seq.*; also Hurd *et al.*, THIS JOURNAL, **52**, 1700, 3356 (1930); **53**, 1068, 1917 (1931); **54**, 1648 (1932).

[3] Meisenheimer and Link, *Ann.*, **479**, 211 (1930).

the ether solution over magnesium sulfate, it was concentrated and then subjected to distillation at reduced pressure; yield 18.6 g. (57%); b. p. 118.6° (20 mm.); d^{20}_{20} 0.9566. Analysis by use of the Grignard machine showed the presence of a negligibly small amount of active hydrogen.

α-Ethylallyl Phenyl Ether (I).—In a 500-cc. flask fitted with a condenser the reagents were placed in the following order and amounts: 28.2 g. of phenol (0.3 mole), 43.5 g. of anhydrous potassium carbonate (0.31 mole), 40 cc. of acetone, and 31.4 g. of 3-chloro-1-pentene (0.3 mole). After standing at room temperature for eighteen hours, the mixture was heated for nine hours and then allowed to stand overnight. Sufficient water to dissolve the precipitate was added and the solution was then extracted several times with ether. The combined ether extracts, after washing with two 25-cc. portions of 20% sodium hydroxide followed by 25 cc. of water, were dried over anhydrous magnesium sulfate. Distillation under reduced pressure using a Widmer column gave the following fractions: (1) chloropentene; (2) b. p. 103–115° (18.5 mm.); (3) b. p. 115–118° (18 mm.). Fraction 2 redistilled yielded 5.6 g. of α-ethylallyl phenyl ether, b. p. 92–93° (15 mm.); d^{20}_{20} 0.9465. Likewise fraction 3 gave 9.9 g. of the isomer γ-ethylallyl phenyl ether; b. p. 116–117° (17 mm.); d^{20}_{20} 0.9567.

Oxidation of the isomeric ethers was accomplished by means of potassium permanganate in aqueous acetone solution.

(a) **γ-Ethylallyl Phenyl Ether.**—One and two-tenths grams of III, dissolved in aqueous acetone, was treated with 3.2 g. of potassium permanganate dissolved in a small amount of water. After standing overnight, the solution became almost colorless. The reaction mixture was filtered and the solution acidified. About one-half of the solvent was then distilled off to remove most of the acetone. The solution was extracted twice with ether. The ether extract, washed with a small amount of water, then was extracted twice with a 5% solution of sodium carbonate. Acidification of the carbonate solution with dilute sulfuric acid precipitated 0.32 g. of phenoxyacetic acid; melting point and mixed melting point with an authentic specimen of phenoxyacetic acid 98–99.5°.

(b) **α-Ethylallyl Phenyl Ether.**—A 1-g. sample of (I) oxidized in the manner described in (a) yielded an oil which finally crystallized; melting point after two crystallizations from water 80–82°. α-Phenoxybutyric acid prepared according to the directions of Bischoff[4] did not cause any lowering of the melting point when mixed with this oxidation product.

The Rearrangement Products.—The convenient technique of Claisen, which involves heating of the ether in diethylaniline, was adopted after it had been shown that the same rearrangement products were obtained in the absence of diethylaniline. That α-ethylallyl phenyl ether (I) gave *o*-(γ-ethylallyl)-phenol (II) upon rearrangement is indicated by the fact that ozonolysis of the methyl ether of II led to the formation of propionaldehyde. The direct nuclear alkenylation of phenol with 1-chloro-2-pentene, VI, also gave a product which was identical with that obtained by the rearrangement of I. Apparently, this α-monosubstituted allyl phenyl ether follows the rearrangement pattern outlined by Claisen.

The rearrangement of **3-phenoxy-1-pentene (I)** was carried out by boiling 5.6 g. of this ether with one-half its weight of diethylaniline in an atmosphere of carbon dioxide. The temperature of the boiling mixture rose from 201 to 225° in three and one-half hours. After cooling, the reaction mixture was taken up in ether and petroleum ether, extracted twice with dilute sulfuric acid to remove the amine, and then three times with 20% sodium hydroxide to remove the phenol. The alkaline solution was acidified with hydrochloric acid and extracted with three 15-cc. portions of ether. After drying with anhydrous magnesium sulfate, the ether solution was concentrated and the residue distilled at reduced pressure. About 1 cc. of higher boiling material remained; yield 4.7 g. (83%); b. p. 131–132.5° (16 mm.); d^{20}_{20} 0.988.

The phenylurethan was prepared by the action of phenyl isocyanate on the phenol dissolved in petroleum ether, in the presence of potassium carbonate. After crystallization from petroleum ether and dilute methyl alcohol, it melted at 67–68°.

Anal. Calcd. for $C_{18}H_{19}O_2N$: C, 76.85; H, 6.81. Found: C, 76.65; H, 6.61.

The aryloxyacetic acid was prepared from 1 g. of the phenol by the method of Koelsch[5] giving 0.78 g. of *o*-(2-pentenyl)-phenoxyacetic acid. After crystallization from dilute methyl alcohol, it melted at 108.5–110°.

The methyl ether of the rearrangement product (II) was obtained in 88% yield by treating the phenol with methyl iodide in the presence of a methyl alcohol solution of sodium methoxide; b. p. 143–145° (35 mm.); d^{20}_{20} 0.9586. *Ozonolysis* of this methyl ether was carried out using ethyl bromide as solvent. Decomposition of the ozonide was accomplished in a manner similar to that used by Whitmore.[6] The steam distillate contained some brown oil, which was probably a polymer of homoanisaldehyde; it failed to give a semicarbazone. The remainder of the steam distillate was treated with methone (dimethylhydroresorcinol).[7] The precipitated derivative, recrystallized once from alcohol, had a melting point of 120–165°. By washing with cold acetone, a small residue of formaldimethone was obtained. This could have resulted only by deep-seated decomposition of the molecule. The solution from which this mixture of derivatives had been filtered was treated with more methone. The precipitate was crystallized from alcohol, then carbon tetrachloride and finally from dilute acetone; colorless plates, m. p. 152.5–153°. A mixed melting point with propionaldimethone showed no depression.

Anal. Calcd. for $C_{19}H_{28}O_4$ (propionaldimethone): C, 71.2; H, 8.81. Found: C, 71.1; H, 8.62.

The residue from the steam distillation of the ozonide

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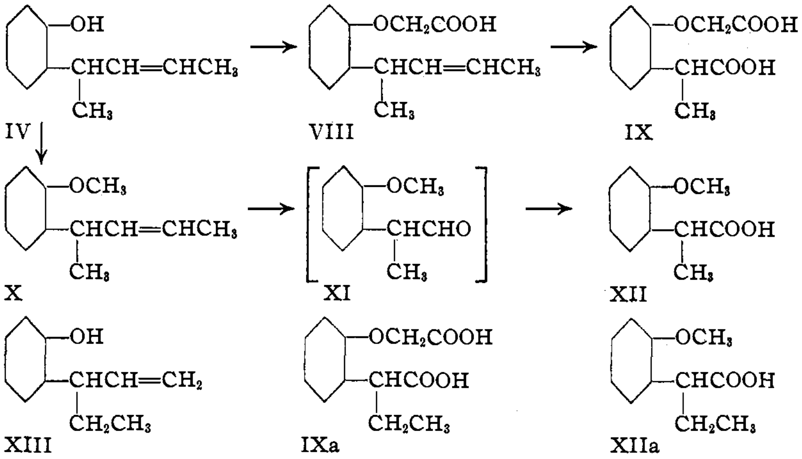
[4] Bischoff, *Ber.*, **33**, 931 (1900); see also Luchmann, *ibid.*, **29**, 1421 (1896).

[5] Koelsch, THIS JOURNAL, **53**, 304 (1931).

[6] Whitmore *et al.*, *ibid.*, **54**, 3711 (1932); **56**, 180 (1934).

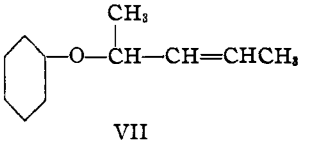
[7] Klein and Linser, *Mikrochemie*, Pregl Festschrift, 204 (1929).



was made alkaline, the precipitated zinc hydroxide filtered off, the filtrate acidified and then extracted with ether. Evaporation of the ether left an oil which finally solidified. This was dissolved in dilute sodium hydroxide and treated with charcoal. By acidification, extraction with ether and evaporation, there was obtained a solid, which when twice crystallized from water showed a melting point of 121–123°. This corresponds to the melting point of *o*-methoxyphenylacetic acid.

Direct nuclear alkylation of phenol with 1-chloro-2-pentene (VI) yielded a product which was identical with that obtained by the rearrangement of I. Sodium (4.6 g.) was dissolved in a solution of phenol (18.8 g.) in benzene (75 cc.). 1-Chloro-2-pentene (20.9 g.) in 25 cc. of benzene was then added and the mixture refluxed on the steam-bath for twelve hours. After standing for twenty-four hours the sodium chloride was dissolved in water, petroleum ether was added and the layers were separated. The petroleum ether–benzene solution was extracted with five portions of Claisen's alkali and then with one portion of water. The alkaline solution was then acidified and extracted with ether. After drying with magnesium sulfate, the ether solution was concentrated and the residue distilled at reduced pressure. A liquid (13.5 g.) boiling at 146°(29)–145° (21 mm.) was obtained. This gave an aryloxyacetic acid that was identical with the one already described.

The rearrangement of γ-ethylallyl phenyl ether (III) led to a product which is identical with that produced by the rearrangement of α,γ-dimethylallyl phenyl ether (VII).



VII

The structures of these isomeric ethers were also established by means of oxidation; VII yielded α-phenoxypropionic acid whereas III gave phenoxyacetic acid. That the rearrangement products of these isomeric ethers are identical is shown by the fact that they gave identical phenylurethans. Structure IV is assigned to this rearrangement product. The transformations outlined in the following diagram will make the reason for this choice clear.

The alternative structure XIII leads to IXa and XIIa, compounds differing in composition from IX and XII.

The rearrangement of γ-ethylallyl phenyl ether (III) was carried out in a small flask fitted with an air condenser. Eight and eight-tenths grams of the ether and one-half its weight of diethylaniline were heated to the boiling point in an atmosphere of carbon dioxide. The temperature rose from 220 to 235° in a period of one and three-quarter hours, after which no further increase of the boiling temperature was noted. After cooling the reaction mixture was taken up in petroleum ether and ether, the solution extracted twice with dilute sulfuric acid to remove the diethylaniline, then three times with 20% sodium hydroxide to remove the phenol. The alkaline solution was acidified with hydrochloric acid and extracted with ether. The ether solution, after drying over magnesium sulfate, was concentrated on the steam-bath and the residual oil distilled at reduced pressure; b. p. 125–127° (16 mm.); d^{20}_{20} 0.9915; yield 7.8 g. (88%).

The phenylurethan, recrystallized three times from petroleum ether and twice from dilute methyl alcohol, melted at 108.5–109.5°.

Anal. Calcd. for $C_{18}H_{19}O_2N$: C, 76.85; H, 6.81. Found: C, 76.80; H, 6.66.

The aryloxyacetic acid (VIII), crystallized from a benzene–petroleum ether mixture and twice from dilute methyl alcohol, melted at 128–130°.

Anal. Calcd. for $C_{13}H_{16}O_3$: C, 70.87; H, 7.33. Found: C, 70.84; H, 7.44.

Oxidation of the Aryloxyacetic Acid (VIII ⟶ IX).—One gram of the aryloxyacetic acid was dissolved in 50 cc. of water containing enough acetone to form a homogeneous solution. To it was added, dropwise and with shaking, a solution of 2.7 g. of potassium permanganate in 100 cc. of water. It was necessary to cool the reaction mixture during the reaction. After standing overnight, the reaction mixture was filtered. The filtrate acidified with dilute sulfuric acid, was extracted with ether. The ether solution, dried over magnesium sulfate, was evaporated slowly. The residual oil was dissolved in benzene and crystallized from this solvent, m. p. 170–171°.

Anal. Calcd. for $C_{12}H_{14}O_5$(IXa): C, 60.5; H, 5.88. Calcd. for $C_{11}H_{12}O_5$(IX): C, 58.9; H, 5.38. Found: C, 59.02; H, 5.39.

Methylation of the Rearrangement Product (IV ⟶ X).—This conversion was brought about by means of (a) methyl iodide and sodium methoxide or (b) dimethyl sulfate. A typical experiment using methyl iodide will be described. To a cooled solution of sodium methoxide prepared in a 200-cc. round-bottomed flask from 0.96 g. of sodium and 30 cc. of methanol there was added 6.8 g. of the *o*-(α,γ-dimethylallyl)-phenol, IV, followed by 5.95 g. of methyl iodide. The reaction mixture was heated for four hours on the steam-bath and then allowed to stand overnight. The alcohol was removed by distillation. Enough water was added to dissolve the sodium iodide, and the oily layer was extracted with ether. The ethereal solution, after washing with dilute sodium hydroxide and drying over anhydrous sodium sulfate, was concentrated on the steam-bath. The residual oil was distilled at reduced pressure collecting the fraction boiling at 134–137° (35 mm.); practically all of it distilled in the range 135–136° (35 mm.) and almost no residue was left; yield 6.5 g. (88%); d^{20}_{20} 0.9633.

Ozonolysis of *o*-(α,γ-Dimethylallyl)-anisole (X).—Two different procedures were used. (a) The anisole (6.2 g.) was dissolved in 50 cc. of ethyl bromide and ozonized by passing a stream of ozonized oxygen (7.5% by weight of ozone) at the rate of 10.6 liters per hour, through the solution in a suitable absorption bottle immersed in an ice–salt mixture. After two and one-half hours (65% excess) the ozonization was discontinued and the solution allowed to stand overnight.

Decomposition was accomplished in a manner similar to that used by Whitmore.[6] The apparatus consisted of a 100-cc. separatory funnel attached by a rubber stopper to a small Claisen flask which contained 60 cc. of water, 2.3 g. of zinc dust, a trace of silver from silver nitrate and a few milligrams of hydroquinone. The distilling flask was attached to a condenser connected by an adapter to a suction flask which, in turn, was connected to a tube reaching to the bottom of a 50-cc. distilling flask containing 45 cc. of methone reagent. The solution of the ozonide was transferred to the separatory funnel and the ethyl bromide was removed as completely as possible by applying suction. A viscous yellow oil remained, which was dropped into the boiling water contained in the distilling flask. Slow distillation took place and a white precipitate appeared in the methone reagent. After all of the ozonide had been added, water was slowly dropped in while the distillation continued until about 75 cc. of distillate had been collected.

There separated, as the bottom layer of the distillate, an oil weighing 2.9 g. This was treated with semicarbazide hydrochloride in the usual way. After twenty-four hours the precipitate was filtered off, crystallized twice from 95% ethyl alcohol and once from 60% alcohol as white needles of m. p. 162.2–162.6°.

Anal. Calcd. for $C_{11}H_{15}O_2N_3$: C, 59.70; H, 6.84. $C_{12}H_{17}O_2N_3$: C, 61.28; H, 7.23. Found: C, 59.91, 60.19; H, 6.79, 6.85.

A mixed melting point with *o*-methoxypropiophenone semicarbazone (m. p. 154–156°) gave a lowering of 25°.

The semicarbazone isolated as a product of ozonolysis was heated on the steam-bath with a small amount of aqueous oxalic acid. The droplet of oil which separated after a few minutes, was washed by decantation with water. It was then treated with 2,4-dinitrophenylhydrazine according to the directions of Allen.[8] The precipitate, after crystallizing from 95% alcohol, melted at 123–125°.

Anal. Calcd. for $C_{16}H_{16}O_5N_4$: C, 55.79; H, 4.69. $C_{17}H_{18}O_5N_4$: C, 56.96; H, 5.07. Found: C, 55.9; H, 4.80.

The distillate was treated with methone solution after separation of the above-mentioned oil. The ether extract left an oil which partially crystallized on standing. The crystals, washed once with cold alcohol, melted at 184–186°. Mixed melting point with formaldimethone showed no depression. The solution in the methone trap after decomposition of the ozonide was filtered. The precipitate melted at 136–137.5°. When mixed with a sample of acetaldimethone of m. p. 139–140°, the melting point was 137–139°.

Decomposition of the ozonide therefore furnished evidence of the formation of formaldehyde, acetaldehyde and a carbonyl compound of composition $C_{10}H_{12}O_2$. The occurrence of formaldehyde along with acetaldehyde is perhaps indicative of deep-seated changes.[9]

(b) The procedure similar to that of Hahn and Wassmuth[10] was also used. The anisole (4.8 g.) was dissolved in 60 cc. of ethyl acetate and the ozonolysis was carried out at a temperature of −10 to −15° using a mixture of air and oxygen containing 1.4% ozone by weight. A 25% excess of ozone was used. After standing overnight, the ozonide solution was subjected to catalytic hydrogenation using 0.2 g. of a 5% palladium–calcium carbonate catalyst which had been reduced in 20 cc. of ethyl acetate. After no further pressure drop, it was assumed that the reduction of the ozonide had been accomplished, and the catalyst was removed by filtration. Water was then added and the ethyl acetate was removed under reduced pressure. Since we were not successful in obtaining satisfactory aldehyde derivatives at this stage, the small amount of oil which separated out was brought into solution with acetone and the solution was subjected to oxidation by the addition of an acetone solution of potassium permanganate. The precipitated manganese dioxide was separated by filtration, the filtrate concentrated to a volume of 15 cc., cooled, acidified with hydrochloric acid and extracted with ether. The ether extract yielded an oil which solidified on cooling. After crystallization with the addition of norite it melted at 100–101°.

Anal. Calcd. for $C_{10}H_{12}O_3$ (XII): C, 66.6; H, 6.72; OCH_3, 17.2. $C_{11}H_{14}O_3$ (XIIa): C, 68.0; H, 7.27; OCH_3, 16.0. Found: C, 66.7; H, 6.71; OCH_3, 17.45.

α,γ-Dimethylallyl phenyl ether (VII) was prepared in accordance with the directions of Claisen.[11] The structure of this compound was established by oxidation as follows. A 2-g. sample was dissolved in a small amount of aqueous acetone and to the solution was added a saturated potassium permanganate solution in 2% excess. The reaction mixture was cooled during the addition. After standing overnight, the manganese dioxide was filtered off and washed with water and acetone. The alkaline filtrate

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(8) C. F. H. Allen, THIS JOURNAL, **52**, 2955 (1930).

(9) See for example, Clemo and MacDonald, *J. Chem. Soc.*, 1294 (1935).

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

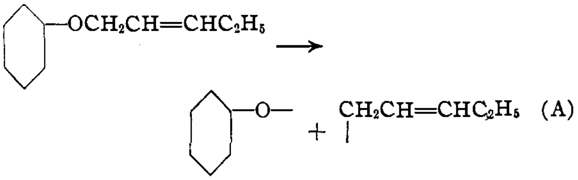
(11) L. Claisen *et al.*, *Z. angew. Chem.*, **36**, 478 (1923); *Ann.*, **442**, 210 (1925).

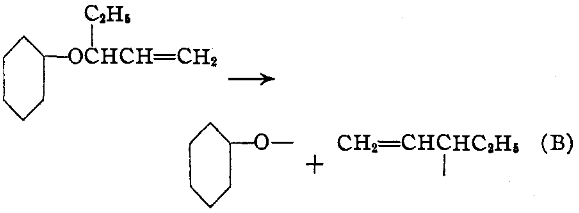
was concentrated to about 25 cc., cooled, extracted with ether, acidified with dilute sulfuric acid and allowed to stand. The solid obtained in this way was crystallized twice from water containing about 5% alcohol, using decolorizing carbon; m. p. 113–114°; yield 0.5 g. A sample of α-phenoxypropionic acid prepared from α-bromopropionic ester and sodium phenoxide according to the directions of Bischoff[4] 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.

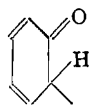
The rearrangement of this ether was carried out by boiling in diethylaniline in an atmosphere of carbon dioxide. The product (28% yield) boiled at 141–145° at 31 mm.

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.

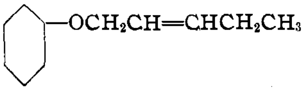
MINNEAPOLIS, MINN. RECEIVED MARCH 27, 1936

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

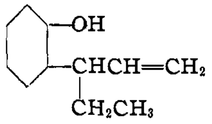
The Rearrangement of Phenyl Allyl Ethers. II. Phenyl Crotyl Ether

BY WALTER M. LAUER AND HERBERT E. UNGNADE

A recent study[1] 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)



I



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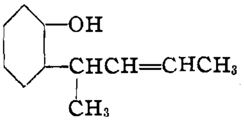
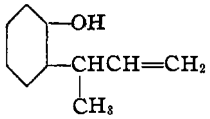


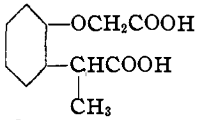
III

The present study was carried out in order to obtain further evidence for the structure assigned to this rearrangement product.

According to Claisen and Tietze[2] phenyl crotyl ether, $C_6H_5O—CH_2—CH=CHCH_3$, when rearranged by heat yields *o*-(α-methylallyl)-phenol (IV).



IV



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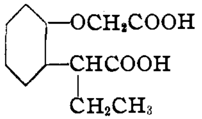

VI

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

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