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.; $n^{20}\text{D}$ 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., $n^{20}\text{D}$ 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.

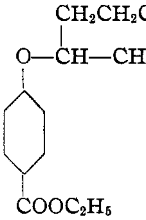
MINNEAPOLIS, MINN. RECEIVED MAY 29, 1939

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

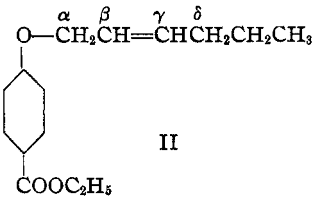
The Rearrangement of Phenyl Allyl Ethers. V. The Isomeric Ethyl *p*-(α- and γ-Propylallyloxy)-benzoates

BY WALTER M. LAUER AND ROBERT M. LEEKLEY[1,2]

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.



I



II

Several years ago, it was reported[3] 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)-

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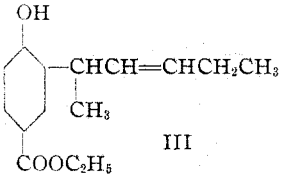
[1] Abstract of Ph.D. thesis submitted July, 1938.

[2] Shevlin Fellow, 1937–1938.

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

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

phenol involves the usual transposition from the α- to γ-carbon atom of the unsaturated chain, whereas the formation of the abnormal rearrangement product, *o*-(α,γ-dimethylallyl)-phenol, requires a migration of the aromatic residue to either the β- or δ-carbon atom. A choice between these two possibilities should be feasible in the case of II, for if a shift to the β-carbon occurs, the abnormal rearrangement product should be III, while a shift to the δ-carbon should lead to structure IV for the abnormal rearrangement product.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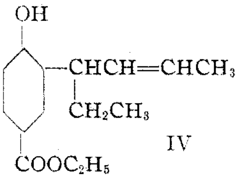
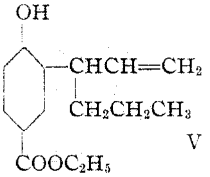
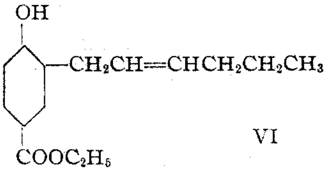

IV


V

The present work demonstrates that ethyl 3-(α-methyl-γ-ethylallyl)-4-hydroxybenzoate (III) results along with the normal rearrangement product, ethyl 3-(α-propylallyl)-4-hydroxybenzoate (V). Therefore, at least in this case, it must be concluded that a β (or ε) and not a δ shift is involved in the formation of the abnormal rearrangement product.

Ethyl *p*-(α-propylallyloxy)-benzoate (I) was obtained, along with its isomer, ethyl *p*-(γ-propylallyloxy)-benzoate (II), by the action of 3-chloro-1-hexene on ethyl *p*-hydroxybenzoate. This mixture of esters, which consisted of approximately 75% of the α-substituted allyloxy isomer, upon hydrolysis yielded the corresponding acids, which were separated by fractional crystallization. The lower melting acid, upon ozonolysis gave formaldehyde, and on esterification yielded the desired ethyl *p*-(α-propylallyloxy)-benzoate.

Rearrangement of the ester (I) produced the normal rearrangement product, ethyl 3-(γ-propylallyl)-4-hydroxybenzoate (VI).

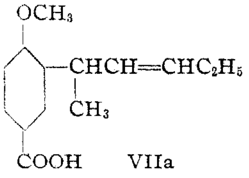

VI

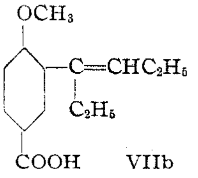
The structure of the rearrangement product (VI) was established in the following way. Methylation followed by hydrolysis yielded a 3-hexenylanisic acid, which upon ozonolysis gave butyraldehyde. Furthermore, the rearrangement product did not reduce a hot mercuric acetate solution, but did so after isomerization with a strong potassium hydroxide solution which is known to convert allylbenzenes into propenylbenzenes.

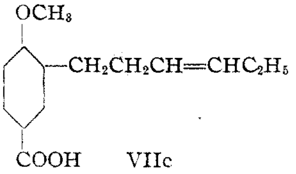
Ethyl *p*-(γ-propylallyloxy)-benzoate (II) was prepared from 1-chloro-2-hexene and ethyl *p*-hydroxybenzoate. This reaction occurred without an α-γ-transposition since a freezing point curve indicated that the product did not consist of a mixture of esters. Hydrolysis of the ester yielded *p*-(γ-propylallyloxy)-benzoic acid, which was in turn reduced to *p*-(*n*-hexyloxy)-benzoic acid. The saturated acid, which was obtained in the above manner, was found to be identical with a sample prepared from *n*-hexyl bromide and ethyl *p*-hydroxybenzoate.

A mixture of rearrangement products was obtained by the pyrolysis of ethyl *p*-(γ-propylallyloxy)-benzoate. This mixture was methylated and then hydrolyzed to produce two 3-hexenylanisic acids, which were separated by fractional crystallization.

The lower melting acid was shown to be 3-(α-methyl-γ-ethylallyl)-4-methoxybenzoic acid, VIIa. The structure was proved in the following way. Ozonolysis produced propionaldehyde. There are only three possible 3-hexenylanisic acids which contain a continuous six-carbon chain from which propionaldehyde could be formed. These three compounds possess the structures, VIIa, VIIb and VIIc.


VIIa


VIIb


VIIc

Of these three structures VIIb was eliminated since the acid did not reduce mercuric acetate. If structure VIIc were the correct one, 3-(*n*-hexyl)-anisic acid would be formed by catalytic reduction. Actually, the hexylanisic acid which was formed by reduction was not identical with the sample prepared by the reduction of 3-(γ-propylallyl)-anisic acid. Therefore the lower melting of the two 3-hexenylanisic acids which were derived from the rearrangement products was 3-(α-methyl-γ-ethylallyl)-4-methoxybenzoic acid, VIIa.

The higher melting isomeric 3-hexenylanisic acid was 3-(α-propylallyl)-4-methoxybenzoic acid, since ozonolysis produced formaldehyde.

The rearrangement of ethyl p-(γ-propylallyloxy)-benzoate (II), therefore, leads to two rearrangement products. In order to estimate the relative amounts of these two products, the original mixture of pyrolysis products was ozonized. The dimethones of the volatile aldehydes were separated by fractional crystallization. On the basis of this rather inaccurate method it was estimated that the ratio of abnormal to normal rearrangement product was approximately two to one.

Experimental

p-(α-Propylallyloxy)-benzoic Acid.—A solution of ethyl p-hydroxybenzoate (55 g.) in acetone (200 ml.) was placed in a flask fitted with a reflux condenser, a dropping funnel and a mercury-sealed stirrer. Anhydrous potassium carbonate (50 g.) was then added and the reaction mixture was refluxed gently on the steam-bath while 3-chloro-1-hexene (39.5 g.; b. p. 63–64° at 110 mm.; $n^{20}\text{D}$ 1.4310) was added. The reaction mixture was heated under reflux with stirring for twelve hours. After this period most of the acetone was removed by distillation. Enough water to dissolve the salt was added and the product was extracted with ether (150 ml. total). Petroleum ether (100 ml.) was then added to the ether extract and the acidic components were removed by extraction with four portions of aqueous sodium hydroxide (5%). After most of the solvent had been removed by distillation, the product was heated on the steam-bath under diminished pressure for several hours. During this time 3-chloro-1-hexene (13 g.) distilled. The residue which did not distil at 12 mm. at the temperature of the steam-bath was distilled in a Hickman still. Three fractions were collected (b. p. 105–106° at approx. 0.05 mm.) and their refractive indices determined: (1) $n^{20}\text{D}$ 1.5150; (2) $n^{20}\text{D}$ 1.5162; (3) $n^{20}\text{D}$ 1.5173. The drift in the refractive index was considered to be an indication that the product was not a single compound.

Fraction 1 was hydrolyzed with methyl alcoholic potassium hydroxide (25%). The substituted benzoic acid, crystallized twice from a mixture of benzene and petroleum ether, melted at 138–139°. It was shown to be p-(γ-propylallyloxy)-benzoic acid.

The mother liquor from the first crystallization was evaporated to dryness and the residue crystallized from petroleum ether alone. Recrystallization from dilute methyl alcohol yielded a solid of m. p. 76–77°, which proved to be p-(α-propylallyloxy)-benzoic acid. This compound showed unusual behavior when melted. If the melted sample was chilled, it immediately solidified to an allotropic form, melting at 35–38°, which could again be transformed to the higher melting variety.

Anal. Calcd. for $C_{13}H_{16}O_3$: C, 70.91; H, 7.27. Found: C, 71.14; H, 7.80.

Ozonolysis of p-(α-Propylallyloxy)-benzoic Acid.—The ozonide, prepared in ethyl bromide solution from the acid (230 mg.), was decomposed according to the method of Whitmore.[5] Formaldimethone (150 mg.; m. p. 187–188.5°) was obtained.

Ethyl p-(α-Propylallyloxy)-benzoate.—The dried (at 60°) silver salt, was converted to the ethyl ester by means of ethyl iodide in dry ether. The ester (b. p. 95–97° at 0.5 mm., $n^{20}\text{D}$ 1.5130) was distilled in a Hickman still.

Anal. Calcd. for $C_{15}H_{20}O_3$: C, 72.53; H, 8.12. Found: C, 72.76; H, 8.21.

Pyrolysis of Ethyl p-(α-Propylallyloxy)-benzoate.—The ester (9.1 g.) began to boil at 220° under 40 mm. pressure, but as the rearrangement proceeded the temperature of the liquid rose gradually to 246°. Further heating was not accompanied by any boiling point increase.

The rearrangement product was dissolved in petroleum ether (40 ml.) and extracted with aqueous sodium hydroxide (5%). The alkaline extract was acidified with dilute sulfuric acid and the phenolic product was extracted with ether. Evaporation of the ether extract produced a solid which upon crystallization from petroleum ether melted at 75–76.5°.

Anal. Calcd. for $C_{15}H_{20}O_3$: C, 72.53; H, 8.12. Found: C, 72.49; H, 8.08.

This rearrangement product, ethyl 3-(γ-propylallyl)-4-hydroxybenzoate did not reduce mercuric acetate in glacial acetic acid.

3-(γ-Propylallyl)-4-methoxybenzoic Acid.—Ethyl 3-(γ-propylallyl)-4-hydroxybenzoate (920 mg.) was added to a solution of sodium methoxide (25 ml. of methyl alcohol containing 200 mg. of metallic sodium). Dimethyl sulfate (2 ml.) was then added and the reaction mixture was refluxed for forty-five minutes. The reaction mixture was again refluxed after the addition of aqueous sodium hydroxide (20 ml., 20%). Dilution of the reaction mixture with water (100 ml.) followed by acidification with dilute sulfuric acid yielded the solid acid (650 mg.); m. p. 107–108°, after crystallization from dilute methyl alcohol. This compound did not reduce a hot solution of mercuric acetate in glacial acetic acid.

Anal. Calcd. for $C_{14}H_{18}O_3$: C, 71.75; H, 7.75. Found: C, 71.73; H, 7.89.

Ozonolysis of 3-(γ-propylallyl)-4-methoxybenzoic acid produced butyraldehyde which was identified as the dimethone (m. p. 131.5–133.5°).

3-Hexyl-4-methoxybenzoic Acid.—The saturated acid (m. p. 113.5–114°) was prepared from 3-(γ-propylallyl)-4-methoxybenzoic acid by catalytic reduction using a palladium (on calcium carbonate) catalyst.

Anal. Calcd. for $C_{14}H_{20}O_3$: C, 71.14; H, 8.54. Found: C, 70.95; H, 8.68.

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[5] Whitmore, THIS JOURNAL, **54**, 3711 (1932); **56**, 180 (1934).

3-(1-Hexenyl)-4-hydroxybenzoic Acid.—Ethyl 3-(γ-propylallyl)-4-hydroxybenzoate (1.75 g.) was heated for one hour at 155–160° with potassium hydroxide (4 g.) and water (2 ml.). The reaction mixture was then dissolved in water and acidified. Ether extraction yielded the crude product (1.2 g.) which after several crystallizations from benzene melted at 134–135°.

Anal. Calcd. for $C_{13}H_{16}O_3$: C, 70.91; H, 7.27. Found: C, 70.57; H, 7.65.

A precipitate was formed when a few drops of a solution of mercuric acetate in glacial acetic acid were heated with several crystals of 3-(1-hexenyl)-4-hydroxybenzoic acid.

Ethyl *p*-(γ-Propylallyloxy)-benzoate.—Ethyl *p*-hydroxybenzoate (55 g.) dissolved in acetone (200 ml.), was placed in a flask fitted with a dropping funnel, a reflux condenser, and a stirrer. Anhydrous potassium carbonate (50 g.) was added and the reaction mixture was refluxed gently while 1-chloro-2-hexene (39.5 g.) was added slowly through the dropping funnel. After the reaction mixture was stirred under reflux for twelve hours, most of the acetone was distilled off. Enough water to dissolve the salt was added and the resultant solution was extracted with ether. Petroleum ether was added to the ether extract and acidic impurities were removed from the non-aqueous extract with sodium hydroxide (5%). Distillation using a Hickman still yielded a pure product (45 g., b. p. 115–116° at 0.2 mm., n^{20}D 1.5197, m. p. 14.1°).

Anal. Calcd. for $C_{15}H_{20}O_3$: C, 72.53; H, 8.12. Found: C, 72.78; H, 8.13.

***p*-(γ-Propylallyloxy)-benzoic Acid.**—Hydrolysis of the ester (twenty-five minutes with 5 ml. of 25% methyl alcoholic potassium hydroxide) yielded the salt, which was dissolved in water and converted to the free acid with dilute sulfuric acid. Crystallization from benzene and petroleum ether gave a product which melted at 139.5–140.5°. It was identical with the *p*-(γ-propylallyloxy)-benzoic acid which was obtained as a side-product in the preparation of *p*-(α-propylallyloxy)-benzoic acid.

Anal. Calcd. for $C_{13}H_{16}O_3$: C, 70.91; H, 7.27. Found: C, 70.64; H, 7.17.

The reduction product, ***p*-hexyloxybenzoic acid** melted at 104.5–106.5°.

p-Hexyloxybenzoic acid was also prepared by the action of *n*-hexyl bromide on a solution of ethyl *p*-hydroxybenzoate in alcoholic sodium ethoxide. After hydrolysis with methyl alcoholic potassium hydroxide and acidification with dilute sulfuric acid, the acid was obtained. Purification yielded a product (m. p. 105.5–107°) which was identical with that obtained by the reduction of the *p*-(γ-propylallyloxy)-benzoic acid.

Anal. Calcd. for $C_{13}H_{18}O_3$: C, 70.23; H, 8.17. Found: C, 70.28; H, 8.16.

Pyrolysis of Ethyl *p*-(γ-Propylallyloxy)-benzoate.—The ester (56 g.) was heated to boiling (213–241°) at 40 mm. pressure for a period of one and one-half hours. A petroleum ether (b. p. 60–68°) solution of the rearrangement products was extracted with sodium hydroxide (5%). The alkaline solution was then acidified with dilute sulfuric acid and extracted with ether. Distillation of the ether extract yielded a colorless, viscous oil (53 g., n^{20}D 1.5367, b. p. 183–188° at 5 mm.). This oil did not reduce a hot solution of mercuric acetate in acetic acid. On standing for about one month, a sample of the pyrolysis product partially solidified. The mixture of isomeric phenols was analyzed.

Anal. Calcd. for $C_{15}H_{20}O_3$: C, 72.53; H, 8.12. Found: C, 72.61; H, 8.11.

Ozonolysis of the pyrolysis product yielded formaldehyde and propionaldehyde, identified as formaldimethone and propionaldimethone, respectively.

3-(α-Propylallyl)-4-methoxybenzoic Acid and 3-(α-Methyl-γ-ethylallyl)-4-methoxybenzoic Acid.—The rearrangement product (26 g.) of ethyl *p*-(γ-propylallyloxy)-benzoate was dissolved in a solution of sodium ethoxide, and methylated with dimethyl sulfate. A mixture of hexenylanisic acids (m. p. 104–114°) was obtained in almost quantitative yield.

The two hexenylanisic acids were separated by fractional crystallization. Dilute methyl alcohol, dilute acetic acid and petroleum ether were used as solvents, but petroleum ether was found to be the most suitable for purification of the higher melting isomer. The higher melting (m. p. 142.5–143.5°) component, **3-(α-propylallyl)-4-methoxybenzoic acid,** was obtained in pure form after twenty-one crystallizations. This product did not reduce a hot mercuric acetate solution.

Pure **3-(α-methyl-γ-ethylallyl)-4-methoxybenzoic acid** was isolated from the petroleum ether mother liquors. The mother liquors richest in the more soluble fraction were evaporated to dryness and the residues combined and recrystallized from dilute acetic acid until there was no further change in melting point (m. p. 113–114°). 3-(α-Methyl-γ-ethylallyl)-4-methoxybenzoic acid did not reduce mercuric acetate.

Anal. Calcd. for $C_{14}H_{18}O_3$: C, 71.75; H, 7.75. Found: C, 71.45; H, 8.00.

Ozonolysis of 3-(α-methyl-γ-ethylallyl)-4-methoxybenzoic acid, yielded propionaldehyde, which was identified as the dimethone (m. p. 153.5–154.5°; m. p. reported 155°)[6] and its anhydride (m. p. 142–143°; m. p. (Vorlander) 142–143°; m. p. (Klein and Linser) 148°).[7]

Ozonolysis of 3-(α-propylallyl)-4-methoxybenzoic acid yielded formaldehyde which was identified as formaldimethone (m. p. 188–189°).

3-(1-Methylamyl)-4-methoxybenzoic acid (m. p. 125–126°) was prepared by the catalytic reduction of 3-(α-methyl-γ-ethylallyl)-4-methoxybenzoic acid using a palladium catalyst (on calcium carbonate).

Anal. Calcd. for $C_{14}H_{20}O_3$: C, 71.14; H, 8.54. Found: C, 70.85; H, 8.86.

3-(1-Ethylbutyl)-4-methoxybenzoic acid (m. p. 145–146°) was obtained by the catalytic reduction of 3-(α-propylallyl)-4-methoxybenzoic acid.

Anal. Calcd. for $C_{14}H_{20}O_3$: C, 71.14; H, 8.54. Found: C, 70.94; H, 8.70.

Hydrolysis of Rearrangement Product of Ethyl *p*-(γ-propylallyloxy)-benzoate.—A solution of sodium hydroxide (5.3 g.) and the rearrangement product (13.1 g.)

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(6) (a) Klein and Linser, *Mikrochemie*, Pregl Festschrift, 204, 1929; (b) Kao and Yen. *Science Repts. Natl. Tsing Hua Univ.*, Series A, **1**, 185 (1932).

(7) Vorländer, *Z. anal. Chem.*, **77**, 251 (1929); ref. 6b.

in water (100 ml.) was refluxed for one hour. Acidification produced an oil which finally solidified. The higher melting isomer, 3-(α-propylallyl)-4-hydroxybenzoic acid (m. p. 133–134°), was obtained in pure form by a series of crystallizations from benzene and petroleum ether.

Anal. Calcd. for $C_{13}H_{16}O_3$: C, 70.91; H, 7.27. Found: C, 71.01; H, 7.15.

All attempts to isolate the more soluble isomer in pure form were unsuccessful.

Methylation of 3-(α-propylallyl)-4-hydroxybenzoic acid with dimethyl sulfate gave a 97% yield of 3-(α-propylallyl)-4-methoxybenzoic acid (m. p. 142–143°).

Anal. Calcd. for $C_{14}H_{18}O_3$: C, 71.75; H, 7.75. Found: C, 71.45; H, 7.55.

Summary

The rearrangement of the isomeric ethyl *p*-(α- and γ-propylallyloxy)-benzoates has been investigated, with the following results.

Ethyl α-propylallyloxybenzoate undergoes rearrangement to form ethyl 3-(γ-propylallyl)-4-hydroxybenzoate, whereas ethyl γ-propylallyloxybenzoate gives two rearrangement products, namely, ethyl 3-(α-propylallyl)-4-hydroxybenzoate and ethyl 3-(α-methyl-γ-ethylallyl)-4-hydroxybenzoate.

The formation of this latter rearrangement product constitutes an additional example of an abnormal phenyl allyl ether rearrangement and supplies evidence for the view that in the case of an abnormal rearrangement, the aromatic residue becomes attached to the β-carbon atom, while the normal rearrangement leads to a transposition of the aromatic residue to the γ-carbon atom.

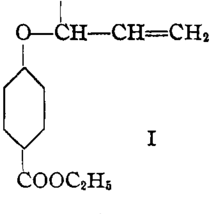
MINNEAPOLIS, MINN. RECEIVED MAY 29, 1939

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

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

BY W. M. LAUER AND H. E. UNGNADE[1]

Certain phenyl allyl ethers upon rearrangement lead to products which one would not expect on the basis of the rearrangement pattern outlined by Claisen. Such so-called abnormal rearrangement was first observed several years ago in the case of γ-ethylallyl phenyl ether.[2] The preceding paper in this series[3] furnishes an additional example, namely, ethyl *p*-(γ-propylallyloxy)-benzoate. Since in this latter case it was possible to effect a separation of derivatives of the normal and abnormal rearrangement products, a similar study of the behavior of the lower homolog, ethyl *p*-(γ-ethylallyloxy)-benzoate, II, was undertaken. The isomeric compounds, ethyl *p*-(α-ethylallyloxy)-benzoate, I, and ethyl *p*-(α,γ-dimethylallyloxy)-benzoate, III, were also prepared and investigated.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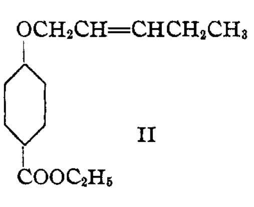
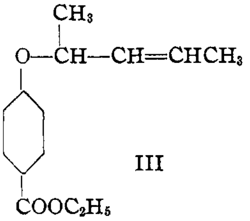
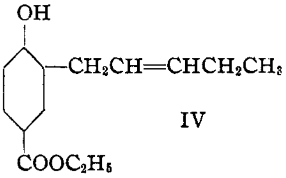

II

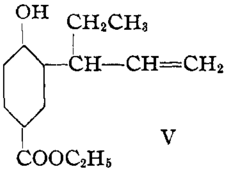
Ethyl *p*-(α-ethylallyloxy)-benzoate, I, on pyrolysis yielded the normal rearrangement product, IV, together with a small amount of 1,3-pentadiene and ethyl *p*-hydroxybenzoate.

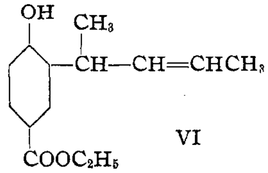

III


IV

That the rearrangement product is the normal one is indicated by the fact that the corresponding substituted anisic acid yielded propionaldimethone on ozonolysis.

Ethyl *p*-(γ-ethylallyloxy)-benzoate, II, gave both normal and abnormal rearrangement products, V and VI, thus paralleling the behavior of the previously reported case of ethyl *p*-(γ-propylallyloxy)-benzoate.


V


VI

3-(α-Ethylallyl)-4-methoxybenzoic acid, derived from the normal rearrangement product, V, was

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[1] Abstract of Ph.D. thesis submitted November, 1938

[2] Lauer and Filbert, THIS JOURNAL, **58**, 1388 (1936).

[3] Lauer and Leekley, *ibid.*, **61**, 3043 (1939).