

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 $C_{18}H_{18}O_3$: 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.

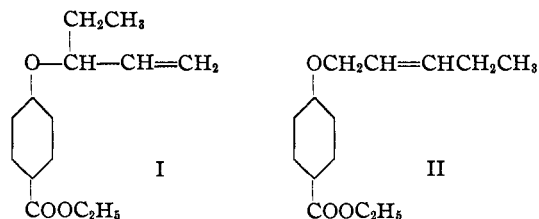
RECEIVED MAY 29, 1939

[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

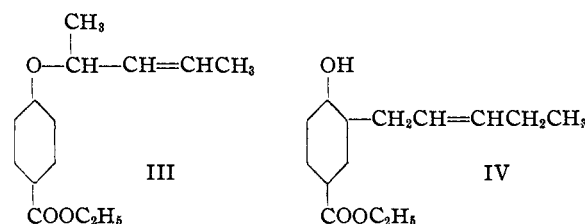
BY W. M. LAUER AND H. E. UNGNADE¹

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 series³ 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.



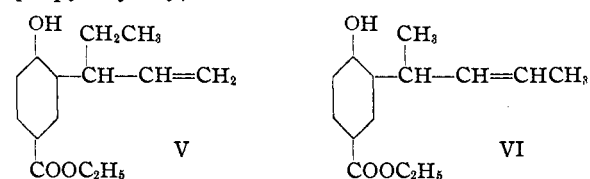
Ethyl *p*-(α -ethylallyloxy)-benzoate, I, on py-

rolysis yielded the normal rearrangement product, IV, together with a small amount of 1,3-penta-



diene and ethyl *p*-hydroxybenzoate. 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.



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

(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).

obtained in pure form by fractional crystallization. Repeated attempts to isolate the corresponding derivative of the abnormal rearrangement product, VI, were unsuccessful. However, there can be little doubt of its presence since ozonolysis of the pyrolysis product always yielded formaldimethone and acetaldimethone.

Ethyl *p*-(α,γ -dimethylallyloxy)-benzoate, III, on pyrolysis yielded 1,3-pentadiene and ethyl *p*-hydroxybenzoate, in amounts which corresponded to slightly more than 50% cleavage of the phenyl ether. Methylation of the rearrangement product, followed by hydrolysis, yielded a product which upon crystallization showed the properties of a mixture. Ozonolysis of this mixture gave acetaldimethone and a small amount of formaldimethone. If ozonolysis can be relied upon, then it must be concluded that ethyl *p*-(α,γ -dimethylallyloxy)-benzoate, III, also yields an abnormal as well as a normal rearrangement product.

Experimental

Ethyl *p*-(α -Ethylallyloxy)-benzoate (I) was prepared from 3-chloro-1-pentene (31 g., b. p. 48–48.5° at 150 mm., n_D^{20} 1.4258) and ethyl *p*-hydroxybenzoate (49.2 g.) in the presence of acetone (150 g.) and potassium carbonate (41 g.). The combined ether–petroleum ether extracts were shaken three times with aqueous sodium hydroxide (10%), dried over potassium carbonate, and distilled in a Hickman still; fraction 1, b. p. 89–90° at 0.1 mm. (11.5 g.); fraction 2, b. p. 90–95° at 0.1 mm. (2 g.); residue 2.5 g.

Hydrolysis of fraction 1 with potassium hydroxide (30 g.) in methanol (90 g.) for a period of twenty minutes gave a mixture of acids upon acidification with sulfuric acid. Fractional crystallization from benzene, petroleum ether, aqueous methanol, and aqueous ethanol finally yielded the pure *p*-(α -ethylallyloxy)-benzoic acid, m. p. 108–109°, since ozonolysis yielded formaldimethone.

Hydrolysis of fraction 2 and the residue gave only *p*-(γ -ethylallyloxy)-benzoic acid (m. p. 156.5–157.5°).

Pure *p*-(α -ethylallyloxy)-benzoic acid (1.36 g.) was converted to the ethyl ester (1.40 g.), through the silver salt. The ethyl ester gave a negative phenol test.⁴

Pyrolysis of Ethyl *p*-(α -Ethylallyloxy)-benzoate.—The ethyl *p*-(α -ethylallyloxy)-benzoate (1.40 g.) began to boil at 200° at 40 mm. After one hour of heating the boiling point remained constant at 236°.

The small amount of material which collected in the trap was treated with bromine at the temperature of liquid air. The reaction mixture was then allowed to come to room temperature and the excess bromine removed under diminished pressure. The crystalline product weighed 200 mg. and was identified as 1,2,3,4-tetrabromopentane (m. p. 113–114°, yield 8.6%). A petroleum ether (b. p. 60–68°) solution of the main rearrangement product was shaken with aqueous sodium hydroxide (5%). The alkaline solution after acidification with dilute sulfuric acid

was extracted with ether. Evaporation of the ether yielded a residue which was heated with a sodium hydroxide solution (5%) for one hour. Acidification gave 0.86 g. of rearrangement product, melting at 101–102° after crystallization from petroleum ether.

The rearrangement product, dissolved in alcoholic sodium ethoxide, was methylated with dimethyl sulfate (1.1 g.), and then converted to the methoxy acid (0.65 g.). Two crystallizations from dilute methyl alcohol and one from petroleum ether yielded a pure product (m. p. 117–117.5°, 200 mg.). The 3-(γ -ethylallyl)-4-methoxybenzoic acid obtained in this manner did not reduce mercuric acetate nor did it give a positive phenol test.

Anal. Calcd. for $C_{13}H_{16}O_3$: C, 70.90; H, 7.27. Found: C, 70.73; H, 7.62.

Ozonolysis of 3-(γ -Ethylallyl)-4-methoxybenzoic acid.—One hundred and ten milligrams in ethyl bromide (60 ml.) at 0°, followed by reductive cleavage, gave a dimethone (110 mg.) which proved to be propionaldimethone (m. p. and mixed m. p. 151–151.5°). The dimethone was converted to its anhydride by heating with glacial acetic acid containing a small amount of sulfuric acid. After one crystallization from petroleum ether, the anhydride melted at 139–140°. Mixed with the anhydride obtained from an authentic specimen of propionaldimethone, the melting point showed no change.

Ethyl *p*-(γ -ethylallyloxy)-benzoate (II) was obtained by refluxing a mixture consisting of *p*-hydroxybenzoic ester (61.6 g.), potassium carbonate (64 g.), acetone (200 ml.) and 1-chloro-2-pentene (40 g.). The major portion of the acetone was removed under diminished pressure and water in sufficient quantity to dissolve the solids was then added. Extraction with an ether–petroleum ether mixture gave an extract, which in turn was extracted three times with aqueous sodium hydroxide, and dried. Distillation in a Hickman still yielded pure ethyl *p*-(γ -ethylallyloxy)-benzoate (b. p. 108–109° at 0.1 mm.; freezing point 34.1°; 41 g.).

Anal. Calcd. for $C_{14}H_{18}O_3$: C, 71.75; H, 7.75. Found: C, 71.64; H, 7.61.

Hydrolysis of the phenyl ether (20 g.) gave a practically quantitative yield of *p*-(γ -ethylallyloxy)-benzoic acid (m. p. 157–158°).

Anal. Calcd. for $C_{12}H_{14}O_3$: C, 69.87; H, 6.84. Found: C, 69.53; H, 6.79.

Reduction of *p*-(γ -ethylallyloxy)-benzoic acid with hydrogen and platinum oxide in methanol yielded *p*-(*n*-amyloxy)-benzoic acid (m. p. 123–124°). Admixing with an authentic specimen of this saturated acid produced no change in the melting point.

Ozonolysis of *p*-(γ -ethylallyloxy)-benzoic acid at 0° in ethyl bromide and ethyl acetate, followed by decomposition of the ozonide, yielded propionaldimethone (m. p. and mixed m. p. 149–150°). Conversion of the dimethone to its anhydride by heating in glacial acetic acid containing sulfuric acid gave a product which after crystallization from petroleum ether melted at 140–141°. An authentic specimen of propionaldimethone produced an anhydride melting at the same temperature.

Pyrolysis of ethyl *p*-(γ -ethylallyloxy)-benzoate (40.5 g.) was carried out at a pressure of 40 mm. The temperature

(4) Folin and Ciocalteu, *J. Biol. Chem.*, **73**, 627 (1929).

rose from 195 to 233° and then remained constant. The liquid air trap collected pentadiene (0.13 g., 13.3% yield), which on bromination yielded 1,2,3,4-tetrabromopentane (m. p. 113.5–114.5°).

The main product was shaken with aqueous sodium hydroxide and low-boiling petroleum ether. The alkaline solution on acidification gave a solid product (39.88 g.), which showed a negative test with mercuric acetate. All attempts to separate this mixture of phenols failed. Similarly, attempts to separate the products of hydrolysis were unsuccessful.

Methylation of the Pyrolysis Product.—The mixture of phenols (38 g.), dissolved in sodium methoxide, was treated with dimethyl sulfate (48 g.). After most of the methanol was distilled off the residue was refluxed with aqueous potassium hydroxide (10%). Acidification produced the methoxy acids.

Repeated crystallization yielded only one pure fraction, which proved to be 3-(α -ethylallyl)-4-methoxybenzoic acid (m. p. 164.5–165.5°).

Anal. Calcd. for $C_{13}H_{16}O_3$: C, 70.91; H, 7.27. Found: C, 70.84; H, 7.52.

Many impure fractions possessing a crystal form differing from that of 3-(α -ethylallyl)-4-methoxybenzoic acid were obtained, but, unfortunately, only 3-(α -ethylallyl)-4-methoxybenzoic acid was obtained in pure form.

Ozonolysis of a sample (500 mg.) of 3-(α -ethylallyl)-4-methoxybenzoic acid gave formaldimethone (m. p. 186–188°, 200 mg.), but ozonolysis studies on the mixture of pyrolysis products always yielded formaldimethone and acetaldimethone, which were separated and identified. Pyrolysis therefore yielded both 3-(α -ethylallyl)-4-methoxybenzoic and 3-(α,γ -dimethylallyl)-4-methoxybenzoic acid.

Ethyl p -(α,γ -Dimethylallyloxy)-benzoate, III.—4-Chloro-2-pentene (23.5 g.) was added slowly to a mixture of potassium carbonate (35 g.), ethyl p -hydroxybenzoate (37.5 g.) and acetone (150 g.) and then refluxed for nine hours. Ether extraction of the aqueous solution yielded the ethyl ester of p -(α,γ -dimethylallyloxy)-benzoic acid (b. p. 108–114° at 0.1 mm.; 16.5 g.).

Anal. Calcd. for $C_{14}H_{18}O_3$: C, 71.75; H, 7.75. Found: C, 71.77; H, 7.75.

Hydrolysis of the ester III (3 g.) gave p -(α,γ -dimethylallyloxy)-benzoic acid (melting point 131–132°; 2 g.).

Anal. Calcd. for $C_{12}H_{14}O_3$: C, 69.87; H, 6.84. Found: C, 69.97; H, 7.04.

Ozonolysis of ethyl p -(α,γ -dimethylallyloxy)-benzoate (400 mg.) followed by reductive cleavage yielded acetaldimethone (300 mg.).

Pyrolysis of the ether, III (10 g.), at 40 mm. pressure

was carried out between the temperatures of 208 and 223° for a period of one hour. Penta-1,3-diene (b. p. 41–42°, 1.4 g., 58.5% yield) collected in the liquid air trap. Bromination of this diene yielded 1,2,3,4-tetrabromopentane (m. p. 113–114°).

Anal. Calcd. for $C_5H_8Br_4$: C, 15.47; H, 2.08. Found: C, 15.49; H, 2.14.

The maleic anhydride addition product (m. p. 61–62°) was also prepared.

The liquid pyrolysis product was treated with aqueous sodium hydroxide (5%) and petroleum ether. The petroleum ether solution yielded only a small amount of a pale yellow oil which was not investigated. The aqueous alkaline layer was acidified and extracted with ethyl ether. The ether extract yielded p -hydroxybenzoic acid (2.7 g.) identified as the ethyl ester (m. p. 115°), and an oil (4.4 g.) which did not crystallize. The oil was saponified. **Methylation** with dimethyl sulfate followed by saponification with aqueous sodium hydroxide (10%) yielded an acid upon acidification with dilute sulfuric acid. After four crystallizations the melting range was 128–132°, and it was concluded that the product was a mixture. The mixture was analyzed.

Anal. Calcd. for $C_{13}H_{16}O_3$: C, 70.90; H, 7.27. Found: C, 70.73; H, 7.62.

The mixture (100 mg., m. p. 128–132°) obtained by methylation was ozonized at 0° in ethyl bromide. Reductive cleavage yielded volatile aldehydes which were converted to their dimethones (150 mg.). After five crystallizations two pure dimethones were obtained, namely, formaldimethone and acetaldimethone, although the amount of formaldimethone was very small (7 mg.).

Summary

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

Ethyl α -ethylallyloxy-benzoate yields ethyl 3-(γ -ethylallyl)-4-hydroxybenzoate upon rearrangement, whereas ethyl γ -ethylallyloxybenzoate gives two rearrangement products, namely, ethyl 3-(α -ethylallyl)-4-hydroxybenzoate and ethyl 3-(α,γ -dimethylallyl)-4-hydroxybenzoate.

A study of the rearrangement of ethyl α,γ -dimethylallyloxybenzoate has furnished some evidence that the normal rearrangement product may be accompanied by an abnormal one.

MINNEAPOLIS, MINNESOTA

RECEIVED MAY 29, 1939