

removal of the solvent, a drop of sulfuric acid was added and the residue distilled under atmospheric pressure. The distillate was again distilled from a drop of sulfuric acid, the second distillate was dried over calcium chloride and redistilled under 15 mm. pressure. The portion boiling at 125–130° (23 g.) was a colorless, mobile liquid, n_D^{20} 1.5223, consisting of the *p*-hexenylanisoles.

Anal. Calcd. for $C_{13}H_{18}O$: C, 82.04; H, 9.54. Found: C, 82.04; H, 9.52.

p-(3-Hexyl)-anisole (IX).—The above hexene (9.9 g.) in methanol (100 cc.) was reduced with hydrogen (45 lb. (3 atm.) pressure) in the presence of 0.2 g. of palladized calcium carbonate (5% palladium). The catalyst was removed, most of the methanol was evaporated and the residue was washed with water. The oil was separated with a little ether, dried over calcium chloride, and distilled. The hexane (5.4 g.) boiled at 125–125.5° under 15 mm., n_D^{20} 1.4988.

Anal. Calcd. for $C_{14}H_{20}O$: C, 81.18; H, 10.49. Found: C, 81.51; H, 10.12.

p-(3-Hexyl)-phenol (X).—The *p*-methoxy compound IX (16.5 g.), acetic acid (40 cc.) and constant boiling hydriodic acid (60 cc.) were refluxed for three and one-half hours. The mixture was made alkaline with aqueous sodium hydroxide (25%) and the alkaline solution was saturated with carbon dioxide to liberate the phenolic product. The mixture was extracted with ether and the ethereal solution was dried over magnesium sulfate. After removal of the ether, the residue was distilled under reduced pressure (14 mm.) from a flask with a short neck. The distillate then was redistilled. The fraction boiling at 134–145° under 14 mm. solidified to a mushy solid which melted slightly above room temperature. It was almost colorless and weighed 5 g.

Anal. Calcd. for $C_{12}H_{18}O$: C, 80.83; H, 10.18. Found: C, 80.51; H, 9.87.

p-(3-Hexyl)-phenoxyacetic Acid (VI).—Ethyl bromoacetate (5 g.) was added to a solution of the phenol X (3.56 g.) in sodium ethoxide (0.46 g. of sodium in 20 cc. of absolute

ethanol). Using the procedure described above for handling the phenol mixture, the ethereal solution of acid VI was extracted with saturated sodium bicarbonate. Acidification of the bicarbonate solution produced an oil which solidified when rubbed with a glass rod. The solid was removed and crystallized from petroleum ether, then from dilute acetic acid, and again from petroleum ether. At this point the product weighed 280 mg., but it was not analytically pure. Three more crystallizations from petroleum ether (b. p. 90–100°) gave a product which melted at 82–83°. When mixed with the acid VI (m. p. 81–82°) obtained from the monoalkenylphenol mixture the substance melted at 81–83°.

Anal. Calcd. for $C_{14}H_{20}O_3$: C, 71.19; H, 8.48. Found: C, 71.10; H, 8.63.

Summary

1. Phenol in the presence of potassium carbonate and acetone reacts with 4-chloro- and 4-bromohexene-2 to give mono- and diallylation products as well as a phenyl ether.

2. All of these products are mixtures.

3. The monoalkenylphenol portion of the reaction product contains ortho and para α -ethylcrotylphenol. These phenols were isolated as the corresponding aryloxyacetic acids, which were reduced to the 3-(*o*- and *p*-carboxymethyl)-hexanes, and the structures of these were proved by synthesis.

4. The diallylation product consisting of 2,6-diallylated phenols showed vitamin E activity in 50-mg. doses. The phenyl hexenyl ether, the mono allylated phenols, and the cyclized products derived from them, showed no vitamin E activity.

MINNEAPOLIS, MINNESOTA

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The Odor of Alkoxy Diphenyls

BY C. M. BREWSTER AND IVAN J. PUTMAN, JR.

In a study of the osmophoric properties of ethers it seemed of interest to examine alkyloxy ethers of the hydroxy-diphenyls, as few compounds of this class have been prepared or studied, and the substitution of a phenyl radical for a nuclear hydrogen atom might be expected to weaken the strong odor of the mononuclear phenolic ethers.

Durrans¹ in his extensive survey of the odors of organic compounds stated that while etheri-

fication nearly always produces compounds of pleasant aromatic odor, the replacement of the hydroxyl hydrogen by an alkyl group may or may not strengthen the odor. In methyl *p*-tolyl ether, for example, the odor is strengthened, but in eugenol methyl ether the introduction of the same alkyl group markedly weakens the odor. We have found little difference in intensity of odor between the alkyl ethers and the unsubstituted phenols in the present series of compounds.

(1) Durrans, *Perf. Ess. Oils Rec.*, **10**, 104–136 (1919).

The most unusual fact in connection with the odor of these ethers is that in each case the ortho compound is stronger in odor than the para, although even with the ortho ethers the odor is faint, whether examined at room temperature or heated to 100°. This is contrary to the results summarized by Durrans, who found that in most instances the para ether has the stronger odor.

Unsaturation in the substituted alkyl group does not seem to be of great importance; a slight strengthening of odor was noted in the allyl ethers, without appreciable change in character.

There is no marked difference in procedure in making the ethers described in this paper, except that the reactions take place more slowly and with greater difficulty than in forming the mono-nuclear ethers,² which is to be expected from the greater molecular weight. When a third phenyl group is introduced, as in the benzyl ether of *p*-hydroxydiphenyl, the reactivity is increased since the radical has the effect of an alkyl group.

Experimental

2-Diphenyl-propyl Ether.—A mixture of 15 g. of *o*-hydroxydiphenyl and 3.8 g. of sodium hydroxide was refluxed on a water-bath with 85 cc. of acetone³ for one hour. Fifteen grams of propyl bromide was added in small portions, and the mixture gently refluxed for six hours. Soon after addition of the propyl bromide a granular precipitate of sodium bromide began to separate. At the end of the reaction the solvent was removed by distillation, and the yellow liquid dissolved in ether, washed twice with water, and the ether solution dried with sodium sulfate. The ether solution was refluxed with activated carbon for one hour, filtered, the ether distilled off and the residual oil fractionated *in vacuo*. The water-white liquid has a faint aromatic odor, b. p. 303°; yield from 15 g. of the phenol, 17 g.

Anal. Calcd. for C₁₅H₁₆O: C, 84.85; H, 7.60. Found: C, 84.48, 84.52; H, 7.65, 7.67.

The methyl ether of *o*-hydroxydiphenyl was prepared by the same method, using methyl iodide as the halide. The colorless oil has a faint, slightly pungent fruity-aromatic odor; b. p. 288°. Borsche and Scholten⁴ used methyl sulfate; they give the b. p. as 274°; yield from 10 g. of the phenol, 9 g.

The ethyl ether of *o*-hydroxydiphenyl was prepared easily by the method which we used for the propyl ether; the halide used was ethyl bromide. Hönigschmid⁵ used a

(2) We obtained only small yields when alcohol was used as solvent, although with mononuclear phenolic ethers this solvent is quite satisfactory.

(3) Claisen and Eisleb [*Ann.*, **401**, 29 (1913)] recommended the use of acetone as solvent in the preparation of ethers. If a higher boiling point solvent is necessary, methyl ethyl ketone is to be preferred.

(4) Borsche and Scholten, *Ber.*, **50**, 601 (1917).

(5) Hönigschmid, *Monatsh.*, **22**, 569 (1901).

somewhat different procedure; our simpler method gives an equally pure product, m. p. 34°. The odor of the crystals is faint and aromatic, resembling that of the methyl ether, but somewhat sweeter and more flower-like; yield from 10 g. of the phenol, 9 g.

2-Diphenyl-isopropyl Ether.—Ten grams of *o*-hydroxydiphenyl and 2.5 g. of sodium hydroxide were refluxed in 75 cc. of acetone for one hour, then 15 g. of isopropyl bromide was added in small portions, and the reaction mixture gently boiled for six hours. To determine the progress of the reaction, a few drops were removed, the solvent evaporated, the residue shaken with dilute sodium hydroxide and ligroin, and the alkaline layer acidified. The product when refined and fractionated *in vacuo* was a water-white liquid of faint aromatic odor, b. p. 315–317°, with slight decomposition at this temperature; yield from 10 g. of the phenol, 10 g.

Anal. Calcd. for C₁₅H₁₆O: C, 84.86; H, 7.60. Found: C, 84.72; H, 8.13.

2-Diphenyl-allyl Ether.—Following the procedure for the propyl ether, allyl bromide was used and almost immediately after the addition of the first portion the solution became cloudy and sodium bromide began to separate. After three hours of refluxing the reaction was complete. The product when purified and fractionated *in vacuo* gave a colorless liquid which has the same pleasant odor as the propyl ether; slightly stronger, but weaker than the ethyl ether. The boiling point is 312°, with slight darkening which begins about 280°. There is no marked change or further decomposition even when the ether is held for one hour at a temperature above 280°. Auwers and Wittig⁶ obtained a less stable ether from *o*-hydroxydiphenyl, sodium ethylate and allyl bromide, for when heated to 250° they obtained a green colored oil with bluish fluorescence, and proved that their ether had undergone the Claisen shift. From 12 g. of the phenol we obtained a yield of 13 g. of the ether.

Anal. Calcd. for C₁₅H₁₄O: C, 85.67; H, 6.72. Found: C, 85.39; H, 6.79.

2-Diphenyl-benzyl Ether.—When benzyl chloride was condensed similarly, the yield was about 25%, even after refluxing the mixture for six hours. The unchanged benzyl chloride was distilled off, and the residue washed repeatedly with 25% aqueous sodium hydroxide to remove unchanged *o*-hydroxydiphenyl. The pale yellow liquid was dissolved in ether and refluxed with activated carbon; the filtrate was deep orange but on evaporation of the ether and continued drying at 55°, it became light yellow again. It is a nearly colorless, viscous liquid which boils with slight decomposition at 324°; yield, from 12 g. of the phenol, 4 g. At room temperature the compound is practically odorless, but when heated to 100° it has a pleasant nut-like odor.

Anal. Calcd. for C₁₉H₁₈O: C, 87.65; H, 6.20. Found: C, 87.46; H, 6.26.

4-Diphenyl-ethyl Ether.—The reaction mixture was prepared and refluxed as for the ortho compound; changes in appearance during the reaction were the same. Acidification of the filtrate gave no precipitate of *p*-hydroxydiphenyl; the yield was nearly quantitative; minute white

(6) Auwers and Wittig, *J. prakt. Chem.*, **108**, 99–112 (1924).

leaflets from alcohol, m. p. 76°. The compound is odorless; yield from 12 g. of the phenol, 11 g.

Anal. Calcd. for C₁₄H₁₄O: C, 84.58; H, 7.36. Found: C, 84.26; H, 7.16.

The methyl ether of *p*-hydroxydiphenyl, first prepared by Werner,⁷ was obtained in nearly quantitative yield, using methyl iodide as the halide, m. p. 90°. The very minute water-white granular crystals have no odor.

4-Diphenyl-propyl Ether.—Propyl bromide was condensed with *p*-hydroxydiphenyl as in the preparation of the ortho ether. The product when purified and crystallized from alcohol gave white leaflets, m. p. 76–77°. It is difficultly soluble in petroleum ether; yield from 10 g. of the phenol, 9 g., odorless.

Anal. Calcd. for C₁₈H₁₈O: C, 84.85; H, 7.60. Found: C, 84.62, 84.71; H, 7.55, 7.60.

4-Diphenyl-isopropyl Ether.—Isopropyl bromide was used as the halide. The reaction in acetone took place more slowly than in the case of the ortho ether. Dull white needles were obtained from slow evaporation of an alcoholic solution, and hexagonal leaflets from more concentrated solutions; m. p. 73°, odorless; yield from 10 g. of the phenol, 4 g.

Anal. Calcd. for C₁₈H₁₈O: C, 84.85; H, 7.60. Found: C, 84.51; H, 7.66.

4-Diphenyl-allyl Ether.—Large transparent leaflets from alcohol; m. p. 86–87°, odorless; yield from 12 g. of the phenol, 14 g. The melted crystals show a slight darkening when heated to 290°, but there is no further

decomposition when maintained at or above this temperature for one hour.

Anal. Calcd. for C₁₈H₁₈O: C, 85.67; H, 6.72. Found: C, 85.43; H, 6.79.

4-Diphenyl-*n*-butyl Ether.—Butyl bromide was used as the halide. The filtrate on acidification gave negligible quantities of unchanged *p*-hydroxydiphenyl; large white leaflets from alcohol; m. p. 74–75°, odorless; yield from 10 g. of the phenol, 13 g.

Anal. Calcd. for C₁₈H₁₈O: C, 85.67; H, 6.72. Found: C, 85.43; H, 6.79.

4-Diphenyl-benzyl Ether.—Using benzyl chloride as halide, the odorless ether was obtained in nearly quantitative yield; from 12 g. of the phenol, 18 g. of the ether was prepared; heavy white plates from alcohol, m. p. 136°.

Anal. Calcd. for C₁₉H₁₈O: C, 87.45; H, 6.20. Found: C, 87.35, 87.65; H, 6.25; 6.20.

We were not successful in preparing the *s*-butyl, *t*-butyl or *n*-amyl ether by this method using acetone as solvent, nor by trials with copper as catalyst, nor with benzene as solvent. However, preliminary trials with reagents heated in sealed tubes have been attended with some success and will be reported on later.

Summary

Several new alkyl ethers of *o*- and *p*-hydroxydiphenyls have been prepared by a simplified method. The ortho ethers possess a fragrant odor, but the para ethers are odorless.

PULLMAN, WASHINGTON

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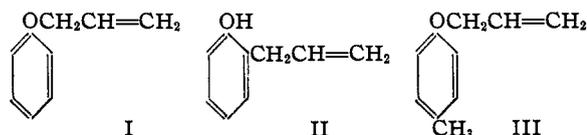
(7) Werner, *Ann.*, **322**, 167 (1902).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF ROCHESTER]

The Claisen Rearrangement. I. A Kinetic Study of the Rearrangement of Allyl *p*-Tolyl Ether in Diphenyl Ether Solution

BY JOHN F. KINCAID AND D. S. TARBELL

The rearrangement of allyl aryl ethers, illustrated by the conversion of allyl phenyl ether (I) to *o*-allylphenol (II), has been investigated ex-



tensively since its discovery by Claisen,¹ and numerous features of the reaction mechanism have been established. The object of our work is to make a kinetic study of the rearrangement of allyl ethers of various types to obtain further information about the Claisen rearrangement. We wish to report a study of the kinetics of the rearrangement of allyl *p*-tolyl ether (III) in di-

phenyl ether solution at 214.7, 200.6, and 185.8°. At the second temperature the effect of acids, bases, and oxygen on the rate was studied, and the rate of the rearrangement of the pure liquid allyl *p*-tolyl ether was measured at the two lower temperatures.

Experimental

Preparation of Materials

Allyl *p*-tolyl ether was prepared by the method of Hurd and Yarnall,² using Eastman redistilled *p*-cresol, allyl bromide, and sodium hydroxide in aqueous acetone solution. The reaction mixture was worked up by the procedure referred to, and in addition the ether was washed several times with sodium hydroxide solution to remove unreacted cresol. The product was distilled through a modified Widmer vacuum-jacketed column at 4 mm. and

(1) Claisen, *Ber.*, **45**, 3157 (1912).

(2) Hurd and Yarnall, *This Journal*, **59**, 1686 (1937).