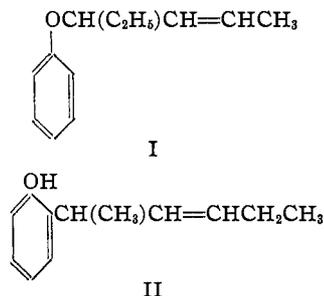


[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

The Chemistry of Vitamin E. XIX. Alkenylation of Phenol with 4-Chloro- and 4-Bromo-2-hexene; Rearrangement of the Phenyl Ether¹

BY LEE IRVIN SMITH, HERBERT E. UNGNADE, WALTER M. LAUER AND ROBERT M. LEEKLEY

α -Ethylcrotyl phenyl ether (I) was obtained by Hurd and Cohen² by action of 4-chlorohexene-2 upon an acetone solution of phenol in the presence of potassium carbonate.



When distilled under reduced pressure, the ether partially rearranged into a phenol which was regarded as *o*-(α,δ -dimethylcrotyl)-phenol, II.

Incidental to the synthesis and examination of substances related in structure to the tocopherols, we have repeated the synthesis of the ether I and have determined the structures of two of the by-products formed along with the ether I. The ether was prepared both from 4-chloro- and 4-bromohexene-2 and phenol under varied conditions. The product was always a mixture, which consisted of the ether I along with mono- and dialkenylphenols. The disubstitution product was formed in fairly large amounts when equimolecular proportions of the phenol and halide were used, but the amount of this could be diminished by using an excess of phenol. The mixture was separated readily by extracting the monoalkenylphenol with aqueous alkali, followed by extraction of the dialkenylphenol with Claisen's alkali.³ The phenyl ether which was not extracted by the alkali was purified by high vacuum distillation, for only under these conditions could it be obtained free from phenolic impurities. The ether was found to undergo rearrangement even at 100° at a measurable rate: at this temperature, 0.88% of the ether rearranged in twenty-four hours, while at 120°, rearrangement proceeded to the extent of 9.6% in twenty-

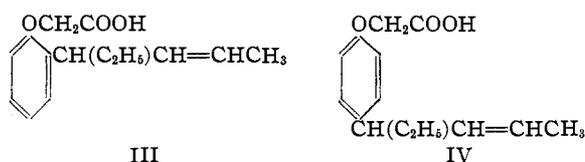
four hours. These results support the observation of Hurd and Cohen² that the ether rearranges during distillation.

In order to ascertain whether or not the various products were homogeneous, the phenyl ether, monoalkenylphenol and dialkenylphenol were ozonized. Reductive cleavage of the ozonides gave mixtures of aldehydes in each case and it therefore appears that the compounds are not pure. All of them are probably mixtures of α,γ -allylic isomers containing the following groupings



Oxidation of the ether likewise led to a mixture of phenoxy acids; a mixture also resulted on reduction to the saturated ether, the constants of which differed somewhat from those given for 3-phenoxyhexane by Hurd and McNamee.⁴ Cyclization of the mixture of monoalkenylphenols with pyridinium chloride gave an alkali-insoluble product which was a mixture, probably of isomeric chromans.

The monoalkenylphenol portion was converted to aryloxyacetic acids by reaction of their sodium salts with ethyl bromoacetate. From the mixture of aryloxyacetic acids so obtained, there was isolated, after many crystallizations, small amounts of two pure isomeric acids, C₁₄H₁₈O₃, one melting at 95.2–96° and the other at 110–110.5°. These acids both gave acetaldehyde and small amounts of formaldehyde upon ozonolysis; it appeared therefore that both contained the α -ethylcrotyl group and hence the isomerism did not lie in the nature, but rather in the position, of the side chain. If so, one acid must be the ortho compound III, and the other the para compound IV.



Acting upon this assumption, the unsaturated

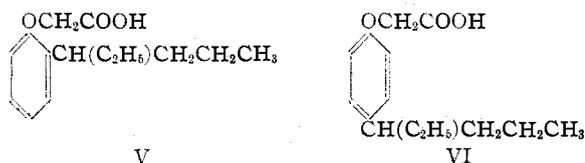
(1) Paper XVIII, THIS JOURNAL, 61, 2424 (1939).

(2) (a) Hurd and Cohen, THIS JOURNAL, 53, 1917 (1931); (b) see also Hurd and Puterbaugh, J. Org. Chem., 2, 384 (1938).

(3) Claisen, ANN., 418, 96 (1919).

(4) Hurd and McNamee, THIS JOURNAL, 54, 1648 (1932).

acids III and IV were reduced to the saturated acids, and these two saturated acids, V and VI, were synthesized.



The synthetic acids were identical with the acids obtained from the monoalkenylphenols; it follows therefore, that among the monoalkenylphenols obtained by action of a 4-halo-2-hexene and potassium carbonate upon phenol in acetone there are two which contain the α -ethylcrotyl group in the *o*- and *p*-positions, respectively, to the hydroxyl group. These results, however, are not sufficient to map the course of the reaction beyond the data given, for the acids III and IV were obtained only in small amounts and it is certain that other substances were present in the monoalkenylphenol portion of the reaction product.

The dialkenylphenol portion of the product was also a mixture. In view of the complexity of the monoalkenylphenol mixture, the dialkenylphenol portion must be very complicated indeed. No pure compounds were isolated from this mixture but because of its complex nature and because our interest lay more in the monoalkenylphenols and the cyclic compounds derived from them, not a great deal of work was done upon it. The components of the mixture were, however, all 2,6-dihexenylphenols, because the mixture was insoluble in aqueous alkali, soluble only in Claisen's alkali, was phenolic, and could not be rearranged by heating. The insolubility in aqueous alkali eliminates a 2,4-dialkenylphenol, for these are completely soluble. The constituents of the mixture, therefore, must be related as stereoisomers, or allylic isomers, or both.

All of the products obtained from the reaction between phenol and the unsaturated halides were tested by Dr. H. M. Evans for vitamin E activity.⁵ The phenyl ether I, as well as the monoalkenylphenols and the isomeric cyclic compounds derived from them, were inactive in 50-mg. doses. The dialkenylphenol, however, was active when fed at this level.

Experimental Part⁶

Hexene-2-ol-4.—The procedure given by Hurd and Cohen² was followed. 3 moles of ethylmagnesium bromide

(5) Paper XIII in this series, *J. Org. Chem.*, **4**, 376 (1939).

(6) Microanalyses by J. W. Opie and H. H. Hoehn.

being added to 2 moles of crotonaldehyde. This resulted in a decrease of secondary products. The yield was 128–133 g., b. p. 60–60.5° under 21 mm., 64–65° under 25 mm.: n_D^{20} 1.4345–1.4346.

4-Chloro-2-hexene.—The alcohol (132 g.) containing anhydrous sodium sulfate (50 g.) was cooled in ice and salt and dry hydrogen chloride was passed into it. When saturated, the mixture was allowed to stand for several hours at 0°, when it was again saturated with the gas, increasing the weight a total of 53.5 g. The mixture was allowed to stand overnight at 0°. Water was added, the oily layer was separated, washed with water, then with dilute bicarbonate and dried over potassium carbonate. Fractionation of this oil gave 111 g. of product boiling at 66–67° under 110 mm.: n_D^{20} 1.4385; n_D^{20} 1.4382 for a specimen prepared from the alcohol and phosphorus pentachloride.

4-Bromo-2-hexene.—The alcohol (42 g.) and aqueous hydrobromic acid (250 g., 40%) were allowed to stand, with frequent shaking, for twenty-four hours. Water was added and the oil worked up as described for the chloro compound above. Fractionation under 20 mm. pressure gave 7 g. of the monobromo compound, b. p. 35–39°, and 30 g. of the dibromo compound, b. p. 90–110°. Although the yield was poor, the product, contrary to the statement of Hurd and Puterbaugh,^{2b} could be obtained this way. The procedure used for the chloride was not tried for preparation of the bromide, but in view of our success with this method generally for converting allylic alcohols to halides⁷ we believe that a good yield of the bromide could be obtained using gaseous hydrogen bromide at 0°. However, it remains to be established whether or not this bromide (and also the chloride) is a pure substance or a mixture of allylic isomers.

Phenyl α -Ethylcrotyl Ether I (and Allylic Isomer).—Phenol and potassium carbonate were placed in a flask equipped with an efficient reflux condenser. The halide was added to the cooled (0°) mixture, which was then refluxed until a negative Beilstein test was obtained. Water and petroleum ether were added, and the aqueous layer was removed and extracted with petroleum ether. The combined organic layers were extracted several times with aqueous sodium hydroxide (10%) and then with Claisen's alkali. The residual petroleum ether solution was washed with water and dried over potassium carbonate. After removal of the solvent, the ether I was distilled under high vacuum. The phenols in the aqueous alkaline extraction were precipitated by passing carbon dioxide into the solution. These were removed by ether extraction. The extracts were dried over potassium carbonate, the solvent was removed and the residue was distilled. The Claisen's alkali extracts were diluted with water, acidified with sulfuric acid and extracted with ether. After drying over sodium sulfate the ether was removed and the residue was distilled. The results of several experiments are given in Table I, and the properties of the compounds are given in Table II.

Cyclization of the Monoalkenylphenols.—The monoalkenylphenol fraction (6 g.) was refluxed with pyridinium chloride (1 g.).⁸ The initial b. p. was 222°; after sixty

(7) Paper IX in this series, *J. Org. Chem.*, **4**, 334 (1939).

(8) (a) Claisen, *Ann.*, **401**, 26 (1913); (b) Bartz, Miller and Adams, *This Journal*, **57**, 371 (1937).

TABLE I
RESULTS OF ALKENYLATION EXPERIMENTS

Phenol, g.	Halide, g.	K ₂ CO ₃ , g.	Acetone, cc.	Time, hrs.	Phenyl ether	Products, g. Mono alkenyl-phenol	Di-alkenyl-phenol
8.0	(Cl) 10	11.7	20	4	5.0 ^a
5.0	(Br) 7	7.3	16	8	6.0 ^a
183.0	(Cl) 229	268.0	200	8	60.0 ^a	45	48
94.0	(Cl) 111	140.0	150	24	47.0	22	5

^a Part of the ether was lost in these experiments by rearrangement during distillation. Thus, the 60 g. of ether in run 3 (distilled under 18 mm. pressure), was accompanied by 45 g. of high boiling material (b. p. 128–168° under 18 mm.) which contained 13 g. of alkali soluble phenol, b. p. 129–132° under 15 mm., n_D^{20} 1.5292. The alkali insoluble remainder of the 45 g. was redistilled; this gave 15 g. of the ether and 13 g. of the higher boiling, alkali insoluble, rearrangement product.

TABLE II
PROPERTIES OF ALKENYLATION PRODUCTS

Compound	B. p., °C.	ρ , mm.	n_D^{20}
Phenyl ether I ^a	103–106	13	1.5059
	116–120	18	1.5054
	34.5–35.5	10 ⁻⁵	1.5053
Monoalkenylphenols	135–137	10	1.5296
	141–144	12	1.5299
Dialkenylphenols ^b	169–170	9	1.5220
	175–179	11	1.5224
	60	10 ⁻⁶	1.5225

^a The pure phenyl ether shows 0.9 mole of active hydrogen in the Grignard machine. This is probably due to cleavage by the Grignard reagent: see Lüttringhaus, *et al.*, *Ber.*, 71, 1673 (1938). The authors are indebted to W. W. Prichard for this analysis.

^b d_{20}^{20} 0.9394; *MR* calcd., 82.31; found, 83.83. *Anal.* Calcd. for C₂₃H₂₆O: C, 83.72; H, 10.08. Found: C, 83.62; H, 9.93. The density and refractive index values of this dihexenylphenol as functions of the temperature lie closely on straight lines.

minutes the b. p. dropped to 216° and remained constant. The product boiled at 106–108° under 10 mm.; n_D^{20} 1.5225. It was insoluble in alkali.

Conversion of the Monoalkenylphenols to Aryloxyacetic Acids.—The monoalkenylphenol fraction (3.391 g.) and ethyl bromoacetate (5 cc.) were added to a solution of sodium ethoxide (0.45 g. of sodium in 20 cc. of ethanol). The mixture was refluxed for six hours. Aqueous sodium hydroxide (10 cc., 25%) was added and the mixture was refluxed for four hours longer. The alcohol was distilled out under reduced pressure and the solid residue removed and dissolved in water. Addition of acid precipitated the aryloxyacetic acids (4.340 g.). These did not reduce mercuric acetate in hot acetic acid, hence the double bond had not shifted toward the ring.

The mixture of acids was fractionally crystallized alternately from petroleum ether and from aqueous acetic acid. After many crystallizations (approximately 30) small amounts (80–100 mg.) of two pure acids were obtained. These were III and IV, melting at 110–110.5° and 95.2–96°, respectively.

Anal. Calcd. for C₁₄H₁₈O₃: C, 71.80; H, 7.69. Found (III, m. p. 110–110.5°): C, 71.93; H, 7.99. Found (IV, m. p. 95.2–96°): C, 71.84; H, 7.99.

Ozonolysis.—The acid III (20 mg.) in chloroform (60 cc.) was ozonized at 0°. The ozonide was reductively cleaved using essentially Whitmore's method⁹ and the volatile aldehyde was distilled into aqueous dimethone solutions (1%). The crude precipitate (35 mg.) was crystallized first from aqueous ethanol and then from petroleum ether. The bulk of the product was acetaldehydedimethone, m. p. 138–139°; mixed m. p. with an authentic specimen (m. p. 140–141°), 139–140°. A small amount (about 1 mg.) of formaldehydedimethone, m. p. 168–170°, also was obtained. Acid IV (20 mg.) was similarly treated; the crude dimethone weighed 35 mg. and it consisted almost entirely of acetaldehydedimethone, m. p. 138.5–139.5°; mixed m. p., 139.5–140.5°. A trace of formaldehydedimethone, m. p. 178–180°, was also obtained.

Reduction.—The pure acid III, m. p. 110–110.5° (85 mg.) was reduced in absolute ether using a platinum oxide catalyst. After removal of the catalyst, the solvent was evaporated. The crystalline residue was taken up in ether and extracted with aqueous sodium bicarbonate (10%). Acidification of the aqueous layer precipitated *o*-(3-hexyl)-phenoxyacetic acid (V). After several crystallizations from petroleum ether, the acid melted at 65–66° although not sharply. Unfortunately there was insufficient material for further purification. The synthetic acid (see below) when first obtained melted at 65°; when completely purified, it melted sharply at 75–76°. The isomeric acid IV, m. p. 95.2–96° (120 mg.) was catalytically reduced in methanol using a platinum oxide catalyst. The product, an oil, was the methyl ester of the reduced acid. This was hydrolyzed by warming it for thirty minutes with aqueous sodium hydroxide (5 cc., 10%) and ethanol (5 cc.). Acidification of the mixture produced an oil which was removed by ether extraction. The ether solution was extracted with sodium bicarbonate; acidification of the bicarbonate solution precipitated *p*-(3-hexyl)-phenoxyacetic acid (VI) which was recrystallized from petroleum ether. It melted at 81–82°; when mixed with the synthetic acid (m. p. 82–83° see below) it melted at 81–83°.

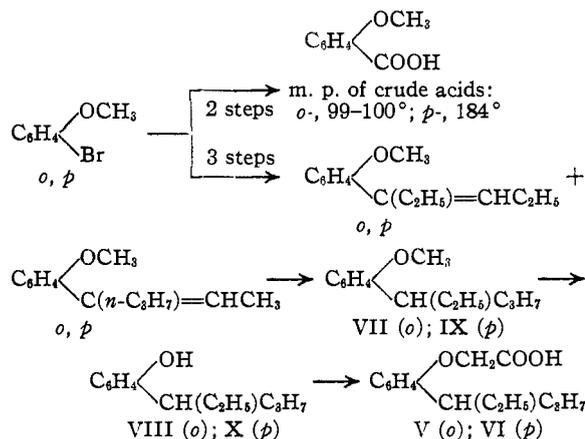
Synthesis of *o*- and *p*-(3-Hexyl)-phenoxyacetic Acids. (V and VI).—Since these acids were *o,p*-isomers, it was very important that the two bromoanisoles, *o*- and *p*-, be absolutely pure and not contaminated with each other. *o*-Bromophenol, prepared according to "Organic Syntheses"¹⁰ from phenol, was converted into *o*-bromoanisole,

(9) Whitmore, *THIS JOURNAL*, 54, 3711 (1932); 56, 180 (1934).

(10) *Org. Syntheses*, 14, 15 (1934).

but this product gave, via carbonation of the Grignard reagent, an *o*-anisic acid most of which melted at 92°, but which did not melt completely even at 105°. Recrystallization from petroleum ether did not give a product with a better m. p. Accordingly, it was decided to synthesize *o*-bromoanisole by a method involving intermediates the purity of which could be checked at each step. The routes from the bromoanisoles to the acids V and VI involved the same steps; these are shown in the chart.

SYNTHESIS OF *o*- AND *p*-(3-HEXYL)-PHENOXYACETIC ACIDS V AND VI



Ortho Series (experimental by H. E. UNGNADE)

o-Nitroanisole (150 g.) in ethanol (100 cc.) was reduced with hydrogen (1200 lb. (80 atm.) pressure) at 100° in the presence of Raney nickel. The yield of *o*-anisidine, b. p. 100–101° under 9 mm., was 102 g. This anisidine gave an acetyl derivative which, without purification, melted at 85–86°.¹¹ The anisidine was converted to *o*-bromoanisole through the Sandmeyer reaction, according to the procedure of "Organic Syntheses"¹²; the yield of *o*-bromoanisole, b. p. 214–215°, was 100 g. One gram of this material was converted to the Grignard reagent, which was then carbonated. The crude *o*-anisic acid so produced melted at 99–100°.¹³

Hexanol-3.—To a Grignard solution prepared from ethyl bromide (93.8 g.) and magnesium (20.6 g.) was added purified butyraldehyde (62 g.). The product, isolated and purified in the usual way, boiled at 132–135° and weighed 40 g.

Hexanone-3.—The hexanol (40 g.) was oxidized by dropping it, with stirring, into sodium dichromate (81.6 g.) in sulfuric acid (68 g.) and water (400 cc.) at such a rate that the temperature was maintained at 50–55°. The upper layer was separated, the aqueous layer was extracted with ether and the ether extract was combined with the organic layer. The solution was washed with sodium hydroxide solution (10%), then once with water and finally with calcium chloride solution. After drying over calcium chloride, the ether was removed and the residue frac-

tionated. The main fraction (34 g.) was hexanone-3, b. p. 121–123.5°.

3-(*o*-Methoxyphenyl)-3-hexanol and *o*-Hexenylanisoles.—*o*-Bromoanisole (56 g.) was converted into the Grignard reagent, and to this was added hexanone-3 (30 g.) in ether. The product was isolated in the usual way, but the carbinol was not purified. Instead, it was distilled at atmospheric pressure with sulfuric acid (2 drops). The distillate was washed with sodium carbonate, then with water, and dried over calcium chloride. Fractionation gave 40 g. of a mixture of *o*-hexenylanisoles boiling at 120–125° under 14 mm.

***o*-(3-Hexyl)-anisole, (VII).**—The unsaturated anisole mixture (40 g.) was reduced in methanol (100 cc.) by hydrogen (42 lb. (3 atm.) pressure) in the presence of a platinum oxide catalyst. The product (37 g.) boiled at 104–105° under 9 mm.

Anal. Calcd. for C₁₃H₂₀O: C, 81.42; H, 10.41; *MR* calcd., 60.3. Found: C, 81.38; H, 10.77. *n*_D²⁰ 1.4975–1.4976; *d*₄²⁰ 0.9242; *MR* found, 60.8.

***o*-(3-Hexyl)-phenol, (VIII).**—The methoxy compound VII (10 g.), hydriodic acid (32 g., d. 1.50), acetic acid (70 cc.) and acetic anhydride (5 cc.) were refluxed for two hours. The mixture became homogeneous after an hour and a half. The cooled mixture was made alkaline with aqueous sodium hydroxide, and the phenol was liberated by passing a stream of carbon dioxide into the alkaline solution. The mixture was extracted with ether, the extract was thoroughly washed with water and dried over magnesium sulfate. After removal of the ether, the residue was distilled. The phenol VIII (5 g.) boiled at 109–111° under 10 mm. It was colorless, possessed a faint aromatic odor and was fairly soluble in 5% aqueous alkali.

Anal. Calcd. for C₁₂H₁₈O: C, 80.89; H, 10.18; *MR* calcd., 55.8. Found: C, 80.27, 80.10; H, 9.55, 10.22; *n*_D²⁰ 1.5099; *d*₄²⁰ 0.9531; *MR* found, 55.8.

***o*-(3-Hexyl)-phenoxyacetic Acid (V).**—Ethyl bromoacetate (5 cc.) was added to a solution of the phenol VIII (3.56 g.) in sodium ethoxide (0.46 g. of sodium in 20 cc. of absolute ethanol). Following the procedure described above for the phenol mixture, the acid V (m. p. 65° after one crystallization) was isolated. Crystallized several times from petroleum ether, it melted at 75–76°.

Anal. Calcd. for C₁₁H₂₀O₃: C, 71.19; H, 8.48; neut. equiv., 236. Found: C, 70.81; H, 8.69; neut. equiv., 239.

Para Series (experimental by R. M. LEEKLEY)

***p*-Bromophenol** was prepared according to "Organic Syntheses"¹² (p. 123) and was converted to *p*-bromoanisole by a procedure also given in "Organic Syntheses"¹² (p. 50). A small amount of the *p*-bromoanisole was converted to the Grignard reagent and the latter was carbonated. The crude *p*-anisic acid so obtained melted at 184°.¹⁴

3-(*p*-Methoxyphenyl)-3-hexanol and *p*-Hexenylanisoles.—*p*-Bromoanisole (40 g.) (0.25 mole) in ether (150 cc.) was converted into the Grignard reagent, and to this was added hexanone-3 (20 g., 0.20 mole) in ether (50 cc.). The product was isolated in the usual way and, after re-

(11) Kaufmann, *Ber.*, **42**, 3482 (1909), gives the m. p. as 87–88° after purification.

(12) "Organic Syntheses." Coll. Vol. I, John Wiley & Sons, Inc., New York, N. Y., 1932, p. 131.

(13) Claisen, *Ann.*, **418**, 87 (1919), gives the m. p. as 100–101° after purification.

(14) Oppenheim and Pfaff, *Ber.*, **8**, 893 (1875).

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 $C_{18}H_{26}O$: 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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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE STATE COLLEGE OF WASHINGTON]

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).