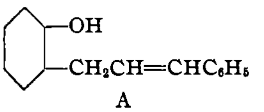
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

Observations on the Rearrangement of Allyl Aryl Ethers

BY CHARLES D. HURD AND LOUIS SCHMERLING[1]

In studying the cinnamyl derivatives of phenol, Claisen[2] found that the *o*-cinnamylphenol obtained by direct alkylation was different from the product obtained by pyrolysis of cinnamyl phenyl ether. To the former he assigned structure (A) and to the latter (B). Although this conclusion is not doubted from a qualitative standpoint, it has never been established whether or not (B) was formed exclusively or whether it was admixed to a small extent with (A). Since this is a matter of considerable importance in regard to the mechanism of rearrangement of allyl aryl ethers, it was decided to study this and other related questions.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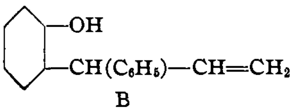

B

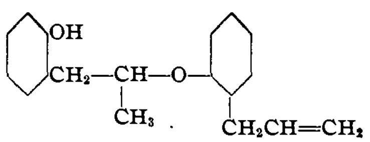
Accordingly, Claisen's two compounds were synthesized and subjected to ozonolysis. The ozonide from (A) should yield benzaldehyde but no formaldehyde on hydrolysis, whereas that from (B) should yield formaldehyde and no benzaldehyde. This was found to be the case, thus confirming Claisen's conclusion.

To determine whether the allyl aryl ether rearrangement is intra- or intermolecular, a mixture of cinnamyl phenyl ether, $C_6H_5{-}O{-}CH_2CH{=}CHC_6H_5$, and allyl β-naphthyl ether, $C_{10}H_7{-}O{-}CH_2CH{=}CH_2$ was heated. If intermolecular, some *o*-allylphenol should be formed. Since this is relatively low boiling (104° at 14 mm.) compared to 1-allyl-2-naphthol (177° at 12 mm.) or *o*-(α-phenylallyl)-phenol (190° at 13 mm.), its isolation from the reaction mixture would be accomplished easily. 1-Allyl-2-naphthol and *o*-(α-phenylallyl)-phenol were found but no *o*-allylphenol.

Similar evidence for the intramolecular nature of this rearrangement was obtained by studying a mixture of allyl β-naphthyl ether and 2-hexenyl phenyl ether.

In connection with this work, some of the hexenylresorcinols were synthesized. Resorcinol hexenyl monoether, $HOC_6H_4OCH_2CH{=}CHC_3H_7$, was isolated for the first time. It was insoluble in alkali and was stable at 100°.

The rearrangement of allyl phenyl ether into *o*-allylphenol was also studied. Claisen[3] obtained an 80% yield on heating at the reflux temperature for six hours. Our yields were only about half. The bulk of the product was a polymer from which a dimer and trimer were separated by distilling the tar from a molecular still. The dimer was soluble in dilute alkali, was unsaturated toward bromine, was unaffected[4] by hot formic acid, and had a molecular refraction of 80.5. These data are in harmony with *o*-(2-(*o*-allylphenoxy)-propyl)-phenol



which has a calculated molecular refraction of 81.1.

Experimental Part

Cinnamyl Phenyl Ether.—A mixture of cinnamyl bromide (80 g.), acetone (200 cc.), phenol (50 g.) and potassium carbonate (75 g.) was refluxed for four hours, then 200 cc. of water was added. The ether separated and solidified. It was washed with dilute alkali and water, and the yield was 78 g. or 92%. It melted at 67°. This is preferable to Claisen and Tietze's[5] method wherein sodium phenoxide reacted with cinnamyl bromide in methanol.

o-(α-Phenylallyl)-phenol.—The rearrangement of cinnamyl phenyl ether by refluxing for four hours in diethylaniline was performed essentially as described by Claisen and Tietze. The reaction product boiled at 186–189° (18 mm.); phenylurethan, m. p. 93–94° (Claisen and Tietze reported 91°).

o-Cinnamylphenol (m. p. 55°, phenylurethan, m. p. 132°) was prepared according to Claisen's directions.[6] The essential feature of this synthesis was the gradual addition of cinnamyl bromide in benzene to a suspension of an equivalent quantity of sodium phenoxide in benzene followed by refluxing for five hours. Likewise, Claisen's directions[7] were followed in the preparation of allyl β-naphthyl ether, namely, the heating of a mixture of 0.1 molar quantities of β-naphthol, allyl bromide and potassium carbonate in 200 cc. of acetone. The refractive index at 25° was found to be 1.600. The synthesis of hexenyl phenyl ether (from 0.1 molar quantities of 1-bromo-2-

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[1] Parke, Davis and Company Fellow, 1933–1935.

[2] Claisen, *Ber.*, **58**, 279 (1925).

[3] Claisen, *Ann.*, **418**, 79 (1919).

[4] Semmler, *Ber.*, **41**, 2185 (1908) found that this is characteristic of compounds with allyl side-chains, whereas those with propenyl side-chains are resinified [to dimers, Glichtich, *Bull. soc. chim.*, **35**, 1160 (1924)].

[5] Claisen and Tietze, *Ber.*, **58**, 279 (1925).

[6] Claisen, Kremers, Roth and Tietze, *Ann.*, **442**, 234 (1925).

[7] Claisen, *Ber.*, **45**, 3158 (1912).

hexene, phenol, potassium carbonate and 200 cc. of acetone) and its pyrolysis to *o*-(α-*n*-propylallyl)-phenol followed the directions of Hurd and McNamee.[8]

Pyrolysis of Mixtures of Ethers.—A mixture of 7.5 g. of allyl β-naphthyl ether and 4.5 g. of cinnamyl phenyl ether was heated under a reflux condenser for four hours by a bath at 240°. An exothermic rearrangement was observed. The volume of the alkali-soluble portion was 3 cc. The only low-boiling material collected during distillation at 15 mm. was one drop of phenol. There was no evidence for *o*-allylphenol. One cc. of 1-allyl-2-naphthol was collected at 160–180°; $n^{20}\text{D}$ 1.6170. It solidified on seeding with a crystal of 1-allyl-2-naphthol. At 180–190° there was obtained about 0.3 cc. of *o*-(phenylallyl)-phenol.

A mixture of 4.2 g. of allyl β-naphthyl ether and 4 g. of 2-hexenyl phenyl ether was heated similarly for six hours at a bath temperature of 250°. An exothermic reaction was noticed at 224° (temperature of mixture itself).

On working up the product (by alkali extraction and vacuum distillation) there was obtained 0.4 cc. of phenol which solidified and melted at 30°; bromination yielded tribromophenol, m. p. 96°. About 0.5 cc. of *o*-hexenylphenol, $n^{22}\text{D}$ 1.5250, was collected at 128–148° (18 mm.), and 1.1 cc. of 1-allyl-2-naphthol, $n^{16}\text{D}$ 1.6167, at 165–180°. The latter solidified. After crystallization from 50% alcohol it melted at 55°. No *o*-allylphenol, b. p. 104 (14 mm.), was observed.

Ozonolysis of *o*-Cinnamylphenol and *o*-(α-Phenylallyl)-phenol.—A 3% ozone stream was conducted through a solution of 3 g. of *o*-cinnamylphenol in 100 cc. of carbon tetrachloride for four hours. Some of the ozonide separated but the bulk of it was soluble. The solvent was removed under reduced pressure and the residual ozonide hydrolyzed with water. The aqueous layer (even on boiling) was free from any odor of formaldehyde. Also, formaldehyde was proved absent by the resorcinol ring test. The water-insoluble oil was taken up in ether, washed with dilute sodium bicarbonate and dilute sodium carbonate and evaporated. The residual benzaldehyde weighed 0.75 g.; its phenylhydrazone melted correctly at 155°.

Four grams of the isomeric *o*-(α-phenylallyl)-phenol, ozonized as before, yielded an oily ozonide which was hydrolyzed by shaking it with water and zinc dust. Formaldehyde was present in quantity as indicated by the strong odor and by the resorcinol ring test. The viscous, insoluble oil was taken up in ether and washed with sodium bicarbonate solution. Acidification of the wash solution gave no water-insoluble (benzoic) acid. The ether layer was then washed with sodium carbonate solution before evaporating the ether. The residue, a thick oil, gave no phenylhydrazone and yielded no benzoic acid on oxidation with potassium permanganate.

Resorcinol 2-Hexenyl Monoether.—Resorcinol (16.5 g.) was converted to its sodium salt by interaction with the calculated amount of sodium ethoxide in 400 cc. of absolute alcohol. This solution was added with stirring during three hours into 49 g. of 1-bromo-2-hexene. Stirring was continued overnight and then the solution was refluxed for two hours. The alcohol was removed and the residue extracted with carbon tetrachloride (125 cc.). The extract was washed with water to remove unreacted resorcinol. Then the solution was extracted with a 10% solution of sodium hydroxide. This process removed hexenylresorcinol but did not dissolve resorcinol hexenyl monoether or diether. From the alkaline extract by acidification, ether extraction and distillation in a Hickman still[9] at 100° and 0.001 mm. was obtained 6 cc. of 4-hexenylresorcinol,[10] $n^{22}\text{D}$ 1.5398.

Anal. (Zerewitinoff) Calcd. for C_6H_{11}-$C_6H_3(OH)_2$: OH, 2.00. Found: OH, 1.99.

The alkali-insoluble portion was freed from the carbon tetrachloride and distilled in the Hickman still (100°, 0.001 mm.). Five fractions totaling 12.5 cc. were collected, all possessing nearly identical $n^{23}\text{D}$ values of 1.5210. All five fractions were alkali-insoluble. Analysis proved this material to be resorcinol hexenyl monoether.

Anal. (Zerewitinoff) Calcd. for HO-C_6H_4-OC_6H_{11}: OH, 1.00. Found: OH, 1.00, 0.97.

The residue in the Hickman still contained resorcinol hexenyl diether. It was volatilized by raising the temperature of the still to 160° with an air-bath. Five grams of the diether[10] was collected, $n^{23}\text{D}$ 1.5160.

Polymers of *o*-Allylphenol.—Allyl phenyl ether, b. p. 112–113° (34 mm.), $n^{21}\text{D}$ 1.5208, $n^{26}\text{D}$ 1.5190, was prepared in 82% yields according to Claisen's[11] directions. This ether (67 g.) was heated by a bath at 210–240° to maintain refluxing for five and a half hours. The temperature of the liquid rose from 190 to 220°. On working it up according to Claisen's directions there was obtained 23 g. of *o*-allylphenol (a 42% yield), and 3 g. of α-methylcumarane. A considerable quantity of dark, viscous tar remained in the distilling flask.

This tar was distilled from a Hickman still at 0.01 mm. With a bath temperature of 145° two 1-cc. fractions were collected which appeared to be a mixture of diallylphenol[12] and triallylphenol. The bath temperature was then raised to 245°, whereupon 10.5 cc. of an apparently uniform product, the dimer, distilled. The next 0.5-cc. fraction, collected at a bath temperature of 270°, set to a clear amber glass on cooling. Its molecular weight (calcd. for $C_{27}H_{30}O_3$, 402; found, 384) indicated that it was chiefly the trimer of *o*-allylphenol.

Properties of the Dimer.—The dimer was a liquid, $n^{21}\text{D}$ 1.5825, d^{25}_{25} 1.11, easily soluble in 10% sodium hydroxide but almost insoluble in 20% alkali. The acetyl and benzoyl derivatives were oils. The substance absorbed bromine (in carbon tetrachloride) without the evolution of hydrogen bromide, and it was unaffected when heated with concentrated formic acid.[13] The molecular weight, determined cryoscopically in benzene, was satisfactory for the dimer.

Mol. wt. Calcd. for $C_{18}H_{20}O_2$, 268. Found: mol. wt., 270.

Summary

It was established by ozonolysis that the product of rearrangement of cinnamyl phenyl ether is

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[8] Hurd and McNamee. THIS JOURNAL, **54**, 1648 (1932).

(9) For set-up, see Hurd and Parrish, *ibid.*, **57**, 1732 (1935).

(10) Hurd and McNamee, *ibid.*, **59**, 104 (1937).

(11) Claisen, *Ann.*, **418**, 78 (1919).

(12) Similar findings have been established in unpublished work with W. A. Yarnall.

(13) Semmler, *Ber.*, **41**, 2185 (1908).

o-(α-phenylallyl)-phenol, unadmixed with any *o*-cinnamylphenol. Similarly, *o*-cinnamylphenol, prepared by direct alkylation of phenol, was free from *o*-(α-phenylallyl)-phenol.

Study of the rearrangement behavior of mixtures of allyl β-naphthyl ether with cinnamyl phenyl ether or 2-hexenyl phenyl ether showed that the rearrangement of allyl aryl ethers is intramolecular.

Resorcinol 2-hexenyl monoether and other hexenylresorcinols were prepared.

By use of a molecular still the polymeric products formed during pyrolysis of phenyl allyl ether were separated into a dimer and trimer of *o*-allylphenol. Considerable evidence supports *o*-(2-(*o*-allylphenoxy)-propyl)-phenol as the structure of the dimer.

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[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE JOHNS HOPKINS UNIVERSITY]

A Series of N-Methyl Amides[1]

BY G. F. D'ALELIO[2] AND E. EMMET REID

In order to bring out the analogies of the N-monomethyl amides to the acids we have prepared the series from the normal acids, formic to stearic. Although some of these are recorded in the literature the data on all except the acetyl are fragmentary. We have compared a number of preparation methods which have been proposed for N-alkyl amides and have investigated some of their reactions. The physical properties of our compounds are given in Tables I and II and their melting points, along with those of the corresponding acids are plotted in Fig. 1. Using Swietoslawski's[3] values for the other elements the average value for the atomic refraction of nitro-

TABLE I

PHYSICAL PROPERTIES AND ANALYSES OF THE N-METHYL AMIDES

No.	B. p. °C.	Press., mm.	M. p. amide, °C.	M. p. acid, °C.	Diff.	Nitrogen, % Found	Nitrogen, % Calcd.
1	131.0	90	− 5.4	8.4	−13.8	23.64	23.72
2	140.5	90	28.0	16.6	11.4	19.05	19.17
3	146.0	90	−43.0	−20.8	−22.2	16.03	15.90
4	156.0	90	− 5.2	− 5,5	− 0.3	13.81	13.86
5	169.0	90	−25.5	−34.0	8.5	12.09	12.17
6	183.0	90	13.6	− 3.9	17.5	10.78	10.85
7	151.0	15	14.0	− 8.9	22.9	9.67	9.79
8	161.5	15	38.9	16.3	22.6	8.84	8.91
9	175.0	15	39.1	12.3	26.8	8.11	8.18
10	...	..	57.3	32.0	25.3	7.54	7.56
11	...	..	56.0	27.8	28.2	6.99	7.03
12	...	..	68.4	43.2	25.2	6.60	6.57
13	...	..	68.2	41.5	26.7	6.05	6.12
14	...	..	78.4	53.9	24.5	5.74	5.81
15	...	..	78.3	52.3	26.0	5.43	5.48
16	...	..	85.5	61.8	23.7	5.17	5.20
17	...	..	84.8	60.7	24.1	4.87	4.94
18	...	..	92.1	68.8	23.3	4.62	4.71

TABLE II

PHYSICAL PROPERTIES OF THE N-METHYL AMIDES OF THE LOWER ACIDS

No. of C atoms in acid	n^{25}_{D}	d^0_4	d^{25}_4	d^{35}_4	Mol. ref. Found	Mol. ref. Calcd.
1	1.4300	1.0114	0.9961	...	15.23	15.30
2	1.4301[a]	...	.9571	0.9481	20.51	19.91
3	1.4345	0.9508	.9304	...	24.64	24.51
4	1.4365	.9308	.9108	...	29.05	29.11
5	1.4401	.9239	.9033	...	33.61	33.72
6	1.4431	...	.8925	.8849	37.77	38.32
7	1.4450[b]	...	.8869	.8795	42.99	42.99

[a] The values for N-methyl acetamide were determined also over the following range of temperatures, n^t_{D} where $t = 35$, 1.4253; 33, 1.4263; 32, 1.4268; 31, 1.4272; 30, 1.4277; 29, 1.4282; 28, 1.4286; 27, 1.4290; 26, 1.4294.
[b] Franchimont and Klobbie, *Rec. trav. chim.*, **6**, 247 (1887), give sp. gr. 0.895 at 15° or 0.894^{15}_4. Their product had m. p. 9° and b. p. 265.6–266.5° at 758 mm.

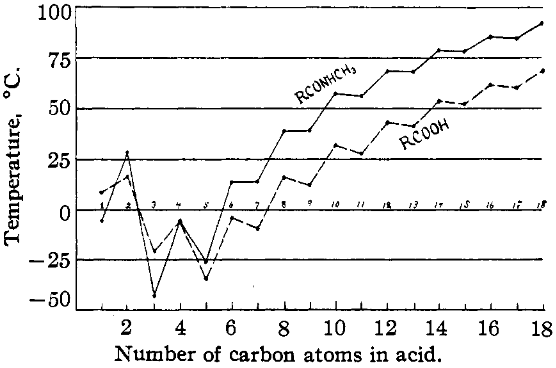

Fig. 1.—Melting points of acids and of their N-methyl amides.

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[1] From a part of the Ph.D. dissertation of G. F. D'Alelio, June, 1935.

[2] The Charles J. O'Malley Fellow of Boston College.

[3] Swietoslawski, THIS JOURNAL, **42**, 1945 (1920).