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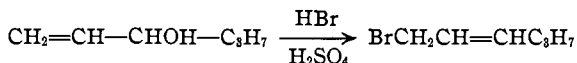
HEXYL AND HEXENYL DERIVATIVES OF PHENOL

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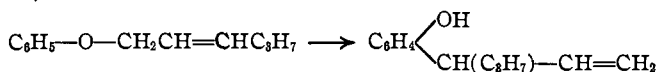
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Phenoxy-1-hexene-2 or γ -*n*-propylallyl phenyl ether, $C_6H_5-O-CH_2-CH=CH-C_3H_7$, was prepared and studied. The bromo-1-hexene-2, from which it was synthesized, was made by the action of hydrobromic acid on hexene-1-ol-3



Chloro-1-hexene-2 was also prepared and its structure established both by hydrogenation into *n*-hexyl chloride and by hydrolysis to hexene-2-ol-1.

Hydrogenation of phenoxy-1-hexene-2 gave rise to phenyl *n*-hexyl ether. The latter was also prepared from sodium phenoxide and *n*-hexyl chloride.¹ The ether was crystallized for the first time. When phenoxy-1-hexene-2 was pyrolyzed, rearrangement into a phenol, *o*-hydroxyphenyl-3-hexene-1, occurred.



For purposes of comparison, 3-phenoxyhexane and *o*-hydroxyphenyl-1-hexene-2 were synthesized.

Chloro-1-hexene-2.—This synthesis and also its proof of structure by hydrogenation were performed by Dr. Frank L. Cohen. Fourteen grams of hexene-1-ol-3,² b. p. 52–53° (20 mm.) and n_D^{16} 1.4269, was dissolved in 20 cc. of benzene and 7 g. of phosphorus trichloride was added to it dropwise. The next day the benzene layer was decanted, washed with cold water, dried over calcium chloride and distilled. The chlorohexene was collected at 35–50° and 40 mm. Redistillation at atmospheric pressure gave these fractions: 3 g., 110–118°, n_D^5 1.4630; 6 g., 120–123°, n_D^5 1.4565; 6 g., 123–129°, n_D^5 1.4520. In another run, 40 g. of the hexene-1-ol-3 was used and 34 g. of the chlorohexene was formed. A portion boiling at 42–44° (40 mm.) or 120–122° (751 mm.) was analyzed.

Anal. Calcd. for $C_6H_{11}Cl$: Cl, 29.46. Found: Cl, 30.1, 29.57.

Proof of Structure.—The chlorohexene was reduced by hydrogen, using Adams' platinum oxide catalyst. A saturated chloride was obtained, b. p. 126–127°, which was then hydrolyzed into the corresponding alcohol by refluxing with a 10% solution of sodium hydroxide. The alcohol thus obtained was converted into the dinitrobenzoate ester, m. p. 53–54°. A mixed melting point determination with known *n*-hexyl dinitrobenzoate was 53–55°. Since hydrogenation of unsaturated compounds proceeds without rearrangement, it is established that the compound studied was chloro-1-hexene-2, and not chloro-3-hexene-1.

Bromo-1-hexene-2.—Twenty grams of hexene-1-ol-3 was added to a mixture of

¹ Tronov and Ladigina, *Ber.*, **62**, 2844 (1929) used hexyl bromide; Dionneau, *Ann. chim.*, [9] **3**, 209 (1915), used magnesium on 5-iodo-1-phenoxyhexane.

² Delaby, *ibid.*, [9] **19**, 287 (1923); Bouis, *ibid.*, [10] **9**, 409 (1928).

48 g. of hydrobromic acid (48%) and 13 g. of sulfuric acid. The mixture was left overnight, then was ether-extracted, the ether solution washed with cold water, dried and distilled: yield, 23 g.; b. p. 43–45° (10 mm.), 50–53° (25 mm.); n_D^{16} 1.4770. Bouis³ prepared this halide using phosphorus tribromide and pyridine, rather than hydrobromic and sulfuric acids.

Hydrolysis of the Halides.—Ten grams of sodium hydroxide in 25 cc. of water was refluxed for two and one-half hours with 4.5 g. of bromo-1-hexene-2. The mixture was ether-extracted, the extract dried over calcium chloride and distilled *in vacuo*. Three cc. of hexene-2-ol-1 was collected at 54–57° (20 mm.); n_D^{25} 1.4490. Similarly, 4 g. of chloro-1-hexene-2 was hydrolyzed into 2 cc. of the same alcohol; n_D^{25} 1.4485. The refractive index is considerably higher than the index for hexene-1-ol-3.

γ -*n*-Propylallyl Phenyl Ether (Phenoxy-1-hexene-2)

(a) **From Bromo-1-hexene-2 (or Chloro-1-hexene-2) and Sodium Phenoxide in Alcohol.**—Three grams of sodium was dissolved in 75 cc. of absolute alcohol, after which 9.5 g. of phenol was added. To the sodium phenoxide solution thus prepared, 16 g. of bromo- (or chloro-) 1-hexene-2 was added. Cooling under the tap was necessary to control the reaction. The mixture was left overnight, after which 120 cc. of water was added. It was ether extracted, the extract washed with dilute alkali and then with water, dried and distilled. Eleven grams of a fraction, b. p. 125–128° (12 mm.), was obtained. Mr. M. P. Puterbaugh has confirmed these directions.

Anal. Calcd. for $C_{12}H_{18}O$: C, 81.75; H, 9.15. Found: C, 81.8; H, 9.0.

(b) **From Bromo-1-hexene-2, Phenol and Potassium Carbonate.**—Sixteen grams of the bromide was added to a solution of 9.5 g. of phenol in 75 cc. of dry ether. Into it was added 15 g. of dry potassium carbonate and 30 cc. of dry acetone. The mixture was refluxed for two hours. It was left overnight and worked up as before; yield, 14 cc. Mr. Puterbaugh also tested this method and obtained a 25.5 g. (57%) yield, using 41 g. of the bromide, 23.5 g. of phenol, 34.5 g. of potassium carbonate and 50 cc. of acetone (no ether). These constants characterized the phenoxy-1-hexene-2: b. p. 105–107° at 4–5 mm., d_4^{20} 0.9408, n_D^{15} 1.5130, n_D^{20} 1.5109. The corresponding reaction between chloro-1-hexene-2, phenol and potassium carbonate (or pyridine) failed. Most of the chloride was recovered after five hours of refluxing.

Ortho γ -*n*-Propylallylphenol (*o*-Hydroxyphenyl-1-hexene-2).—Five grams of phenol was dissolved in 100 cc. of dry ether⁴ at 5° and 1.5 g. of sodium ribbon was inserted. After the first violent reaction, the mixture was heated till the sodium was consumed. Then 5 g. of chloro-1-hexene-2 was added, the mixture refluxed for six hours, filtered, and 50 cc. of ether added. It was washed with water, dried, the ether evaporated and the residue distilled at 20 mm. After collecting a small amount of phenol at 80°, the temperature rose rapidly to 144°. A viscous, colorless liquid (3–4 cc.) was obtained; n_D^{25} 1.5250. This *o*-propylallylphenol was insoluble in sodium bicarbonate solution but soluble in 5% potassium hydroxide solution.

Anal. (Zerewitinoff). Calcd. for $C_6H_{11}C_6H_4OH$: OH, 1.00. Found: OH, 0.98.

New Syntheses of Phenyl *n*-Hexyl Ether (1-Phenoxyhexane)

(a) **From Phenoxy-1-hexene-2.**—Three cc. of the compound was hydrogenated catalytically using 0.2 g. of the Adams' platinum oxide catalyst, 25 cc. of alcohol and

³ Bouis, *Ann. chim.*, [10] 9, 421 (1928).

⁴ Similar C-alkylations, using ether instead of alcohol, which promotes O-alkylation, have been studied by Claisen, *Z. angew. Chem.*, 36, 478 (1923); Claisen and others, *Ann.*, 442, 210 (1925).

hydrogen. Reduction was rapid and reaction ceased when the calculated quantity of hydrogen had been absorbed. After filtration and distillation (b. p. 126–130° (12 mm.)) of the filtrate, 2.5 cc. of phenyl hexyl ether was collected.

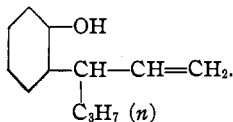
(b) From *n*-Hexyl Chloride (Williamson Synthesis).—Hexyl alcohol was synthesized from *n*-butylmagnesium bromide and ethylene oxide. After conversion to hexyl chloride, 8 g. of it was added to a solution of sodium phenoxide (2 g. of sodium, 6.5 g. of phenol) in absolute alcohol (75 cc.). The mixture was left for a day and then refluxed for two hours. Some alcohol was evaporated off, then water was added and the mixture ether extracted, the extract washed with dilute alkali, dried and distilled. Three cc. of phenyl hexyl ether was obtained, b. p. 125–128° at 11 mm.

Physical Properties.—Following a redistillation, the phenyl hexyl ether from either (a) or (b) gave these constants: n_D^{25} 1.4889, d_4^{25} 0.918. By strong cooling, it solidified readily to fine, hard crystals; m. p. -19° .

3-Phenoxyhexane, $C_6H_5-O-CH(C_2H_5)-CH_2CH_2CH_3$.—3-Hexanol, prepared from *n*-butyraldehyde and ethylmagnesium bromide, was converted into 3-bromohexane by the action of 48% hydrobromic acid and sulfuric acid. Ten grams of the bromide was heated for four hours in absolute alcohol (60 cc.) with sodium phenoxide (6 g. of phenol, 2 g. of sodium). The details were similar to the Williamson synthesis of 1-phenoxyhexane. Four cc. of the ether was obtained: b. p. 129–132° (12 mm.); d_4^{25} 0.923; n_D^{25} 1.4893. The melting point of -35 to -33.5° was obtained on crystals obtained by cooling the liquid to -78° . The bulb of a corrected toluene thermometer was immersed in the melting crystals.

Anal. Calcd. for $C_{12}H_{18}O$: C, 80.9; H, 10.1. Found: C, 81.0, 80.97; H, 9.90, 9.98.

Pyrolysis of γ -*n*-Propylallyl Phenyl Ether.—Three cc. of the ether was placed in a



side-arm test-tube which was heated uniformly by a bath. Rearrangement,⁶ as evidenced by an exothermic reaction, occurred at 210–215°. When the temperature of the liquid reached 292°, 1.5 cc. of liquid distilled which, after redistillation at 12 mm., gave n_D^{25} 1.5244. The phenol dissolved in dilute alkali and analysis confirmed the presence of one hydroxyl.

Presumably it was *o*-hydroxyphenyl-3-hexene-1.

Anal. (Zerewitinoff). Calcd. for $C_{12}H_{18}OH$: OH, 1.00. Found: OH, 0.97.

In duplicating this pyrolysis with a 20-g. sample of the ether, Mr. M. P. Puterbaugh identified ordinary phenol as well as the higher phenol. The 2 g. of phenol was collected at 80–85° at 6–7 mm. and it solidified in the receiver. There was 2 g. of an intermediate fraction (b. p. 85–120°), following which 8 g. (a 40% yield) of hydroxyphenyl-3-hexene-1 distilled at 120–122° (7 mm.). Index of refraction data on this fraction were n_D^{16} 1.5275, n_D^{20} 1.5255. Zerewitinoff analysis for hydroxyl gave a value of 0.98. About 4 g. of a fourth fraction was collected at 7 mm. between 135–165°.

Summary

Chloro-1-hexene-2 and bromo-1-hexene-2 were synthesized and their structures established by hydrolysis into hexene-2-ol-1. Hydrogenation of the chloride yielded *n*-hexyl chloride. Phenoxy-1-hexene-2, on reduction, yielded phenyl *n*-hexyl ether. The latter was also made by the Williamson reaction, as was 3-phenoxyhexane. Above 215°, phenoxy-1-hexene-2 rearranged into *o*-hydroxyphenyl-3-hexene-1, a phenol resembling the isomeric

⁶ Compare Hurd and Cohen, *THIS JOURNAL*, 53, 1917 (1931).

o-hydroxyphenyl-1-hexene-2, which was synthesized for purposes of comparison. The physical properties of these compounds were determined.

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[COMMUNICATION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

THE USE OF NICKEL AS A CATALYST FOR HYDROGENATION. II

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A study of the preparation of nickel catalysts¹ indicated that in general sodium bicarbonate was to be preferred to sodium carbonate or potassium hydroxide as a precipitant in the preparation of nickel catalysts. This was true because the resulting catalysts were somewhat more active and less sensitive to variations in the procedure of preparation. More recently it has become evident that ammonium carbonate is in general the most satisfactory precipitant.

Procedure Recommended for the Preparation of a Nickel Catalyst.—Fifty-eight grams of Baker and Adamson or Mallinckrodt c. p. nickel nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), dissolved in 80 ml. of distilled water, was ground for thirty to sixty minutes in a mortar with 50 g. of acid washed kieselguhr (*ex* Johns-Manville "Filter-Cel") until the mixture was apparently homogeneous and flowed as freely as a heavy lubricating oil. It was then slowly added to a solution prepared from 34 g. of Mallinckrodt c. p. ammonium carbonate, monohydrate ($(\text{NH}_4)_2\text{CO}_3 \cdot \text{H}_2\text{O}$) and 200 ml. of distilled water. The resulting mixture was filtered with suction, washed with 100 ml. of water in two portions, and dried overnight at 110° . The yield was 66 g. Just before use, 2 to 6 g. of the product so obtained was reduced for one hour at 450° in a stream of hydrogen which passed over the catalyst at a rate of 10 to 15 ml. per minute. The catalyst was then cooled to room temperature and transferred in a stream of hydrogen to the reaction vessel, which had been filled with carbon dioxide.

Time of Reduction, Nickel Content and Activity of Catalysts.—Some years ago the time and temperature for the reduction of nickel on a kieselguhr support in this Laboratory was rather arbitrarily set as one hour at 450° , since this gave a catalyst of good activity. Diwoy in this Laboratory observed that for certain rather inactive preparations the catalyst was more active if a higher temperature or a longer time was used in the reduction of the nickel oxide. On the basis of this observation it seemed desirable to ascertain the optimum conditions for the reduction of various types of nickel catalysts. Armstrong and Hilditch² showed that the activity of

¹ Adkins and Covert, *J. Phys. Chem.*, **35**, 1684–1691 (1931).

² Armstrong and Hilditch, *Proc. Roy. Soc. (London)*, **99A**, 490–495 (1921).