

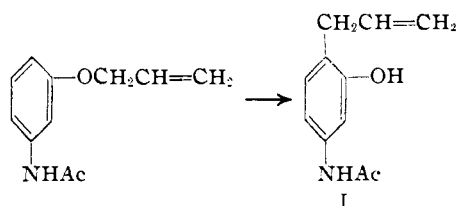
[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

**Thermal Rearrangement of *m*-Acetamidophenyl Allyl Ether**

BY RICHARD T. ARNOLD, JOHN MCCOOL AND EVERETT SCHULTZ

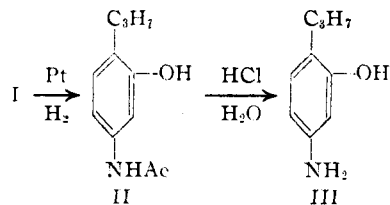
Chief interest in the Claisen thermal rearrangement of phenyl allyl ethers has centered around the mechanism of this reaction. Because of the possibility of obtaining at least two isomeric products, few *m*-substituted phenyl allyl ethers have been rearranged.

During the course of one of our researches the rearrangement of *m*-acetamidophenyl allyl ether was studied. The effect of the solvent employed was striking. No isolable material resulted when purified petroleum ether (b. p. 200–220°) was used, but the reaction proceeded smoothly in *N,N*-*d*-dimethylaniline (200°)



The formula assigned to the reaction product was assumed to be correct by analogy with observations of Hurd, Greengard and Pilgrim<sup>1</sup> who studied the thermal rearrangement of resorcinol monoallyl ether.

The rearrangement product (I) was reduced catalytically to 2-propyl-5-acetamidophenol (II) which in turn was hydrolyzed to the corresponding amine (III)



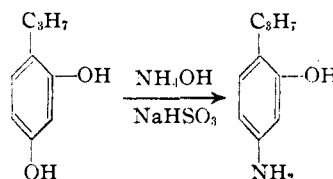
Both compounds II and III were crystalline solids melting at 173–174° and 132–132.5°, respectively.

Just as this work was completed, a paper appeared by Hartung, Minnick and Koehler<sup>2</sup> in which they described the synthesis of III

(1) Hurd, Greengard and Pilgrim, *THIS JOURNAL*, **52**, 1700 (1930).

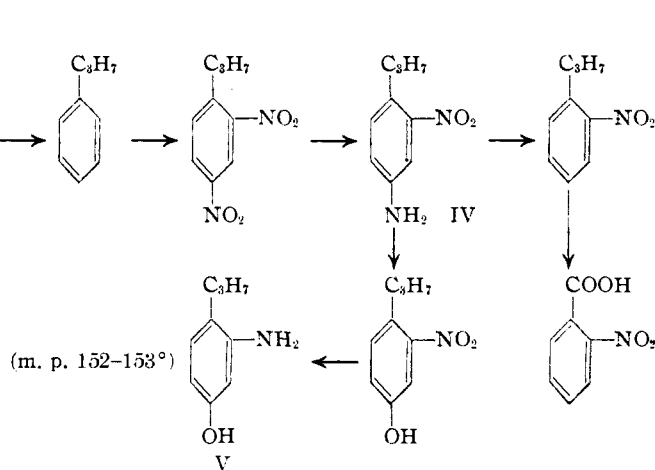
(2) Hartung, Minnick and Koehler, *ibid.*, **68**, 507 (1941).

by direct amination of *n*-propylresorcinol.



The melting point recorded for the propylamino-phenol obtained in this manner was 109–110°. All attempts to prepare a solid acetyl derivative gave an oil. No structure proofs were given.

Because of the discrepancy in the melting points found by these investigators and those observed in this Laboratory, it was tentatively assumed that the substance formed by the amination of propylresorcinol might be 3-amino-4-propylphenol (V). That this assumption was erroneous was indicated by an unambiguous synthesis of (V) starting with propiophenone



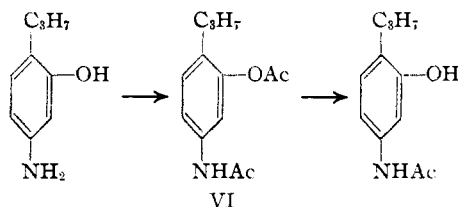
There can be little doubt concerning the structure of (V), because the orientation of the groups in the intermediate 3-nitro 4-propylaniline (IV) has been definitely established by removal of the amino group followed by oxidation to *o*-nitrobenzoic acid.<sup>3</sup>

We have now shown that the propylamino-phenol resulting from the amination of propylresorcinol is identical with that formed by reducing and hydrolyzing the rearrangement prod-

(3) Brady and Cunningham, *J. Chem. Soc.*, 121 (1935).

uct of *m*-acetamidophenyl allyl ether. The difference in melting point has been attributed to dimorphism.<sup>4</sup>

Repetition of the amination of propylresorcinol in this Laboratory gave a propylaminophenol melting at 132–132.5° which did not depress the melting point of a sample of III obtained from *m*-acetamidophenyl allyl ether. In view of the fact that the high melting form had been previously synthesized in the same laboratory, this result is easily understood. Contrary to earlier observations,<sup>2</sup> a solid was formed on treatment of the aminophenol (III) with acetic anhydride. This substance (m. p. 117–118°) proved to be a diacetate (VI) which on careful hydrolysis gave a monoacetate (m. p. 173–174°) identical with (II).



**Acknowledgment.**—The authors are grateful to Dr. M. L. Moore of the Sharp and Dohme Company for generous samples of hexyl- and propylresorcinol.

### Experimental

***m*-Acetamidophenyl Allyl Ether.**—*m*-Acetamidophenol (20 g.), allyl bromide (17 g.), potassium carbonate (18.5 g.), and acetone (100 cc.) were placed in a 500-cc. three-necked flask fitted with a mercury sealed stirrer and condenser. This mixture was refluxed for eight hours. Water was added to dissolve the inorganic salts and precipitate the allyl ether which was then dissolved in ethyl ether. After extracting the unreacted phenol, the solvent was removed. The crude solid was recrystallized from benzene-petroleum ether; yield 19.2 g.; m. p. 87–88°.

*Anal.* Calcd. for  $C_{11}H_{13}O_2N$ : C, 69.11; H, 6.80. Found: C, 68.99; H, 6.80.

**2-Allyl-5-acetamidophenylacetate.**—*m*-Acetamidophenyl allyl ether (36.5 g.) was refluxed in dimethylaniline (110 g.) for six hours in a current of hydrogen or nitrogen. The solution was cooled, an equal volume of petroleum ether (b. p. 60–68°) added, and the solid precipitate collected. This was dissolved in 160 cc. of boiling acetic acid (40%) and then crystallized. Recrystallization was carried out with acetic acid (10%); yield 32 g.; m. p. 132–133°.

*Anal.* Calcd. for  $C_{13}H_{15}O_3N$ : C, 66.95; H, 6.42. Found: C, 66.91; H, 6.12.

(4) Unfortunately the work reported by Hartung, Minnick and Koehler was carried out several years ago and no sample of III (m. p. 109–110°) was available for comparison. The authors appreciate the cooperation and suggestions furnished by Prof. Hartung.

**2-Allyl-5-acetamidophenol (I).**—On dissolving the above diacetate in dilute sodium hydroxide (10%) and carefully acidifying with dilute sulfuric acid the phenol was obtained. After recrystallization from water it melted at 160.5–162°.

*Anal.* Calcd. for  $C_{11}H_{13}O_2N$ : C, 69.11; H, 6.80. Found: C, 68.87; H, 6.80.

**2-Propyl-5-acetamidophenol (II).**—2-Allyl-5-acetamidophenyl acetate (3 g.) was dissolved in ethanol (20 cc.) and platinum oxide (0.06 g.) added. After reduction at three atmospheres, the solution was filtered, solvent removed, and the residue (1.74 g.) recrystallized from water. The solid obviously was not pure and was warmed with potassium carbonate solution to complete the hydrolysis. Recrystallization from water gave a pure material; m. p. 173.5–174°.

*Anal.* Calcd. for  $C_{11}H_{15}O_2N$ : C, 68.39; H, 7.77. Found: C, 68.44; H, 7.66.

**2-Propyl-5-aminophenol (III).**—One gram of 2-propyl-5-acetamidophenol was refluxed for fifteen minutes with 1:1 hydrochloric acid then cooled and filtered. After washing the amine hydrochloride with ether, it was dissolved in water and neutralized with sodium carbonate solution. The precipitated aminophenol (0.6 g.) was readily recrystallized from water; m. p. 132–132.5°.

*Anal.* Calcd. for  $C_9H_{13}ON$ : C, 71.52; H, 8.67. Found: C, 71.13; H, 8.46.

**Amination of Propylresorcinol.**—This reaction was carried out according to the directions of Hartung, Minnick and Koehler.<sup>2</sup> The product after recrystallization from water melted at 132–132.5°.

**2-Propyl-5-acetamidophenyl Acetate.**—2-Propyl-5-aminophenol (0.6 g.) was heated with acetic anhydride (1.0 cc.) at the boiling point for five minutes. The reaction mixture was poured into water, and after standing in an ice chest for several hours a solid crystallized. The solid on recrystallization from water and ethanol melted at 117.5–118°.

*Anal.* Calcd. for  $C_{13}H_{17}O_3N$ : C, 66.50; H, 7.24. Found: C, 66.48; H, 7.24.

**Hydrolysis of 2-Propyl-5-acetamidophenyl Acetate.**—2-Propyl-5-acetamidophenyl acetate (1.15 g.) was boiled with a solution containing sodium carbonate (20 cc. of 20%), 50 cc. of water and a little sodium hydroxide. After solution was completed, the mixture was cooled and extracted with ether. Evaporation of the solvent gave a crude residue; m. p. 165–170°. Recrystallization gave a substance melting at 173.5–174.5° which proved to be identical with the monoacetate obtained from *m*-acetamidophenyl allyl ether.

**2,4-Dinitropropylbenzene.**—This compound was prepared according to the directions of Brady and Cunningham.<sup>3</sup>

**3-Nitro-4-propylaniline.**—A modification of earlier published directions<sup>3</sup> gave good results. 2,4-Dinitropropylbenzene (12.1 g.) in ethanol (40 cc.) was added to a sulfide solution in a three-necked flask fitted with a condenser and efficient stirrer. The sulfide mixture was prepared from ethanol (36 cc.) and concentrated ammonium hydroxide (36 cc.), half of which had been previously saturated with hydrogen sulfide. The mixture was boiled for thirty minutes while being stirred violently to prevent

bumping. The precipitated sulfur was removed by filtration and washed with small portions of ethanol. Small pieces of ice were added to the alcohol solutions until crystals separated. After the slow addition of water (400 cc.) the mixture was chilled overnight. The solid formed was dissolved in concentrated hydrochloric acid (130 cc.) and then filtered. Slow addition of alkali gave an amine; 5.5 g. (54%); m. p. 59–59.5°.

**3-Nitro-4-propylphenol.**—3-Nitro-4-propylaniline (16.5 g.) was dissolved in 26 cc. of concentrated sulfuric acid and 125 cc. of water by warming on a steam cone. The hot solution was added with good stirring to a mixture of 250 cc. of water and 270 g. of ice. At 0° sodium nitrite (6.0 g. in 51 cc. of water) was added. The amine salt dissolved and the excess nitrous acid was decomposed with urea. This solution was added dropwise to a boiling solution of 152 cc. of concentrated sulfuric acid and 1500 cc. of water. The tar was removed by filtration through sand. The cooled filtrate was extracted with ether. Basic extraction of the ether layer followed by acidification and another ether extraction gave a solution which on evaporation and distillation yield the nitrophenol; 2.7 g.; m. p. 46.5–47.5°.

*Anal.* Calcd. for  $C_9H_{11}O_2N$ : C, 59.70; H, 6.13. Found: C, 59.48; H, 6.43.

**3-Amino-4-propylphenol.**—3-Nitro-4-propylphenol (4.0 g.) was dissolved in ethanol (50 cc.) and reduced with platinum at room temperature. Careful removal of the solvent followed by recrystallization from toluene-petroleum ether and finally hot water gave a white solid; m. p. 152–153°. Attempts to acetylate this material gave oils.

*Anal.* Calcd. for  $C_9H_{13}ON$ : C, 71.52; H, 8.67. Found: C, 71.30; H, 8.94.

### Summary

1. It has been shown that *m*-acetamidophenyl allyl ether on thermal rearrangement gives 2-allyl-5-acetamidophenol.

2. 2-Allyl-5-acetamidophenol has been converted to 2-propyl-5-aminophenol which is identical with the product formed from propylresorcinol by direct amination.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NORTHWESTERN UNIVERSITY]

## The Action of Hydrogen Fluoride, Sulfuric Acid and Phosphoric Acid on Optically Active 2-Butanol

BY ROBERT L. BURWELL, JR.

In the absence of suitable catalysts, alcohols are strongly resistant to configurational change. Thus, those fractions of *d*-active amyl alcohol<sup>1</sup> and *l*-2-butanol<sup>2</sup> which escape decomposition at elevated temperatures are unchanged in rotation.

Catalytic racemizations of alcohols have been little studied. Frankland and Price<sup>3</sup> investigated the racemization of the *d*-active amyl alcohol by sodium alcoholate in a sealed tube at 200°. Burwell<sup>2</sup> investigated the heterogeneous catalytic racemization of *l*-2-butanol in the presence of zinc chromite, chromium oxide and copper.

In this paper the racemizing action of hydrogen fluoride, sulfuric acid and phosphoric acid on optically active 2-butanol is reported. This reaction gains interest from its interrelations with the dehydrating and alkylating reactions which are known to be effected by the same catalysts.

### Experimental

**Materials and Technique.**—Compositions of sulfuric acid solutions were determined by density measurements. Density vs. composition tables of the "International Crit-

ical Tables" were employed. The composition of the concentrated sulfuric acid was determined in this way by a weight dilution.

100% phosphoric acid was prepared by heating Baker and Adamson 85% phosphoric acid to constant weight at 160°. The liquid anhydrous hydrogen fluoride was supplied by the Harshaw Chemical Company.

2-Butanol was resolved by the method of Viditz.<sup>4</sup> The product of the first crystallization was employed in this research without further resolution: *l*-2-butanol,  $\alpha^{20}_D$  -4.14°; *d*-2-butanol,  $\alpha^{20}_D$  +5.80°.

The active alcohol after a preliminary treatment with anhydrous potassium carbonate was dried by distillation in a small bore vacuum-jacketed column with a double internal nichrome spiral 50 cm. in length. A 50-cc. still pot was heated internally with a coil of no. 30 B. and S. gage nichrome wire. The column gave twenty-five theoretical plates as determined by the methylcyclohexane-*n*-heptane method.<sup>5</sup>

It was not found possible to fractionate commercial 2-butanol to such purity that solutions could be prepared with concentrated sulfuric acid which would remain colorless for several hours. This could readily be done, however, with the active 2-butanols (which, of course, had undergone further purification during their resolution).

The activity of the alcohol was measured in a 1-dm. semi-micro polarimeter tube. The rotation of the alcohol is

(1) Von Weber, *Z. physik. Chem.*, **179A**, 295 (1937).

(2) Burwell, *THIS JOURNAL*, **59**, 1609 (1937).

(3) Frankland and Price, *J. Chem. Soc.*, **71**, 255 (1897).

(4) Viditz, *Biochem. Z.*, **259**, 294 (1933).

(5) Beatty and Calingaert, *Ind. Eng. Chem.*, **26**, 504 (1934).