[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

The Pyrolysis of Allyl-*p*-phenetidine

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The predominating type of pyrolytic decomposition followed by the allylanilines has been shown[1] to differ from that encountered in the simpler allyl phenyl ethers. The allylanilines formed propylene, the corresponding primary amine and tarry material rather than products of allyl group migration from nitrogen to the aromatic nucleus. This behavior in some respects resembles that of 2,4-dimethyl-6-propylphenyl allyl ether,[2] which gave allene, diallyl, propylxylenol and resinous material. Previous work[1] on allylaniline, diallylaniline and diallyl-*p*-phenetidine has been extended to include allyl-*p*-phenetidine.

In connection with the proposed mechanism for the thermal decomposition of allylanilines, it is important to know if hydrogen is evolved at reflux temperatures. None was present in the gases from the diallylanilines, but some was found when allylaniline was heated at 600–700°. While allylaniline did not decompose at its reflux temperature (218°) it has been found that allyl-*p*-phenetidine is slowly decomposed on refluxing at 270°. Per mole of allyl-*p*-phenetidine, 0.465 mole of *p*-phenetidine was found, the loss in weight corresponded to 0.40 mole of propylene, resin equivalent to 0.447 mole was formed, and material equivalent to 0.10 mole was unidentified. No hydrogen was present. A search for 6-ethoxyquinoline and 6-ethoxytetrahydroquinoline failed to disclose either. At higher temperatures allylaniline gave some quinoline; this effect is extensive in the presence of lead dioxide.[3]

The most probable mechanism for these data is the one previously set forth wherein the initial step was formation of radicals

$$\mathrm{ArNHC_3H_5} \longrightarrow \mathrm{ArNH—} + \mathrm{C_3H_5—}$$

but instead of assuming that these radicals undergo disproportionation it is proposed that they become hydrogenated to *p*-phenetidine and propylene, respectively, by collision with neighboring undecomposed molecules. The latter molecules would thus be converted into an acroleinanil, $\mathrm{ArN{=}CHCH{=}CH_2}$, which is regarded as the forerunner of the resinous material. The absence of hydrogen as a reaction product makes it appear certain that molecular hydrogen plays no part in the reaction mechanism. It might be argued, for example, that molecules of $\mathrm{ArNHC_3H_5}$ changed first into $\mathrm{H_2} + \mathrm{ArN{=}CHCH{=}CH_2}$ with the hydrogen thus formed splitting another molecule of allyl-*p*-phenetidine into phenetidine and propylene. Three facts eliminate this possibility. Molecular hydrogen is sufficiently inert to escape partly as such but none is found. The mechanism would fail with the tertiary amines, diallylaniline and diallyl-*p*-phenetidine, which have been found actually to pyrolyze more readily than does allyl-*p*-phenetidine itself. Again, when hydrogen is removed from an allylaniline, especially by the aid of lead dioxide,[3] the product is related to quinoline and not a resin.

Experimental

Allyl-*p*-phenetidine.—Allyl-*p*-phenetidine was prepared by the general method of Hepp.[4] Allyl bromide was added to the reaction product of sodium on phenacetin; the thick oil resulting was hydrolyzed by sodium hydroxide in alcohol. Steam distillation of the product, followed by vacuum fractionation with a nitrogen leak gave allyl-*p*-phenetidine free from *p*-phenetidine. The yield was 31%; 37% if recovered *p*-phenetidine was taken into account.

The compound boils at 134.5° at 10 mm., 140° at 15 mm., and with decomposition at 265° at 745 mm. pressure. It shows d^{20}_4 1.0096; $n^{20}\mathrm{D}$ 1.5493.

Anal. Calcd. for $\mathrm{C_{11}H_{15}ON}$: C, 74.52; H, 8.53. Found: C, 74.55; H, 8.48.

Allyl-*p*-toluenesulfon-*p*-phenetidine.—Allyl-*p*-phenetidine was treated with 1.5 equivalents of *p*-toluenesulfonyl chloride and 5 equivalents of 2 *N* potassium hydroxide. The usual treatment gave crude alkali-insoluble material in a yield of 86% of the calculated amount. Crystallization from methyl alcohol and water accompanied by treatment with bone black gave the derivative in white needles melting at 81°.

An identical product was obtained by treating *p*-toluenesulfone-*p*-phenetidide[1] with an excess of allyl bromide in *N* potassium hydroxide solution at room temperature. Considering a small proportion of the starting material recovered unchanged, the yield was 99.5%.

Anal. Calcd. for $\mathrm{C_{18}H_{21}O_3NS}$: C, 65.21; H, 6.39. Found: C, 65.49; H, 6.37.

Pyrolysis of Allyl-*p*-phenetidine by Refluxing.—Several runs were made with the same general results. The following experiment may be taken as representative.

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(1) Carnahan and Hurd, THIS JOURNAL, **52**, 4586 (1930).

(2) Claisen and Tietze, *Ann.*, **449**, 94 (1926).

(3) Koenigs, *Ber.*, **12**, 453 (1879).

(4) Hepp, *ibid.*, **10**, 327 (1877).

A 70.8-g. (0.4 mole) sample was placed in a 125-cc. flask to which was sealed 75 cm. of 1 cm. inside diameter tubing to serve as an air condenser. A thermometer rested on the bottom of the flask and extended into the condenser. Through a 15-cm. tube sealed to the flask nitrogen could be passed into the apparatus. Provision was made for the collection of gaseous products over water. The flask was heated in a fused salt bath to maintain a reflux about 15 cm. above the liquid level. The refluxing was continued for one hundred twenty hours with the temperature of the liquid in the flask averaging 270°.

During the pyrolysis gas was slowly evolved. Analysis showed 93.0% soluble in 85% sulfuric acid, 1.4% oxygen, 5.6% nitrogen. Passed through a solution of dry bromine in dry carbon tetrachloride, the gas formed propylene bromide, n^{20}_D 1.5181. The amount of gas over water was 965 cc. at 21° and 740 mm. equivalent to 0.035 mole propylene. The small amount collected is partly owing to the fairly high solubility of propylene in water (44.6 cc. per 100 cc. of water) and the long time of contact. The loss of weight in this experiment was 7.3 g. If this loss is considered to be represented by propylene evolved, it would correspond to 0.174 mole or 0.44 mole of propylene per mole of allyl-*p*-phenetidine. Another experiment in which the loss of weight of the refluxed material was ascertained quantitatively indicated 0.404 mole of propylene per mole of the amine.

Liquid products of the pyrolysis were poured while hot into a 200-cc. balloon flask with a side-neck carrying a nitrogen leak. Distillation through a 1.5 × 38 cm. packed column was carried out at 9 mm. pressure. The first fraction was colorless, boiled at 114–116°, and weighed 20.5 g. The second fraction was also colorless, boiled at 116–130°, and weighed 5.05 g. Both these fractions gave *p*-toluenesulfone-*p*-phenetidide,[1] m. p. 108°, in yields as high as obtained from pure *p*-phenetidine. Melting points in mixture with an authentic specimen of the derivative were unchanged.

When distillation through the column became impossible, the procedure was continued in a Claisen flask. The deep yellow liquid collected through the range 160–235° at 19 mm. weighed 6.75 g. Of this liquid, 40% was soluble in 3 *N* hydrochloric acid. In the soluble portion attempts were made to identify 6-ethoxyquinoline[5] (b. p. 290–292°) and 6-ethoxytetrahydroquinoline[6] (b. p. 164–166° at 17 mm.). On account of their high boiling points, these compounds should be present in this fraction rather than one composed predominantly of *p*-phenetidine. The procedures of Soun and Benirschke[6] were followed in the preparation of 6-ethoxyquinoline and 6-ethoxytetrahydroquinoline. The methiodide of the former melted at 193–194°, that of the latter at 208–209°. A search for the two compounds in the acid-soluble material above as well as in the intermediate (116–130° at 9 mm.) fraction did not disclose either of them.

The non-basic material was not further investigated. Possibly it may represent a lower stage of polymerization than the resin itself.

The residue from the distillation procedures was a dark brown brittle resin weighing 31.25 g., m. p. 68–88°.

The resin was soluble in ether, acetone, benzene, xylene and concentrated sulfuric acid, giving in each case a solution with a green-blue fluorescence. This phenomenon may indicate the presence of nitrogen rings in the resin since certain salts of 6-ethoxyquinoline and quinine exhibit fluorescence. On long boiling with 3 *N* hydrochloric acid about 6% of the resin dissolved. No simple water-insoluble material such as *p*-phenetidine was produced by boiling 5.0 g. of the resin with 25 cc. of 25% hydrochloric acid for twenty-seven hours. Likewise, boiling for twelve hours with 60% sulfuric acid effected no decomposition.

Summary

1. Allyl-*p*-phenetidine and allyl-*p*-toluenesulfon-*p*-phenetidide have been prepared and characterized.

2. Allyl-*p*-phenetidine has been found to decompose on refluxing at atmospheric pressure into *p*-phenetidine, propylene and resinous material. The initial step of this process appears to be a splitting into radicals at the carbon-to-nitrogen bond.

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[5] Grimaux, *Bull. soc. chim.*, [3] **15**, 23 (1896).

[6] Sonn and Benirschke, *Ber.*, **54**, 1732 (1921).