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

The Thermal Decomposition of Phenyl Vinyl Ether

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In connection with a general study of the molecular rearrangements of the alpha, beta-unsaturated ethers it became necessary to examine the behavior of phenyl vinyl ether on thermal decomposition. Powell and Adams[1] have reported that the principal product of the reaction is phenol. Our results have led us to believe that although phenol plays a part in the reaction it always appears in the end-products in relatively small amounts.

A sample of phenyl vinyl ether was heated in a sealed tube as described in the reference cited, and on distillation essentially the same fractions were obtained. It was observed, however, that a large part of the high-boiling material was insoluble in aqueous alkali. In subsequent experiments the reaction mixture was extracted with alkali and then distilled under diminished pressure. From a 20-g. sample, the alkali extract never contained more than half a gram of phenol isolated as tribromophenol. The balance of the product gave on distillation a large portion of unchanged starting material and 2–6 g. of a colorless oil which boiled at 154–155° at 14 mm.; approximately an equal amount of tarry residue always remained.

The colorless oil was shown to have the empirical formula $C_{14}H_{14}O_2$. It was insoluble in aqueous alkali, but with bromine water it gave a bulky precipitate of tribromophenol, and on oxidation with nitric acid, the only product isolated was 2,4-dinitrophenol. Hydrolysis gave phenol and acetaldehyde. The physical and chemical properties seemed to correspond to acetaldehyde diphenylacetal as described by Fosse.[2] A sample was therefore prepared by his method and the compounds were found to be identical.

The tarry residue remaining after the distillation could not be induced to crystallize or sublime. The apparent molecular weight was found to be 806, although the figure is perhaps much too low, due to included impurities.

The presence of acetaldehyde diphenylacetal in the decomposition products of phenyl vinyl ether is difficult to explain, although a reasonable mechanism by which it might be formed involves the addition of phenol to the unchanged starting material. $C_6H_5OH + C_6H_5OCH{=}CH_2 \longrightarrow CH_3\text{-}CH(OC_6H_5)_2$. That hydroxy compounds add to alpha,beta-unsaturated ethers is well known, but to ensure the plausibility of the reaction in this case, a mixture of phenyl vinyl ether and phenol was heated in a sealed tube under the usual conditions of the decomposition reaction. The unexpected result was that all of the phenyl vinyl ether was destroyed; from the tarry mixture only phenol could be isolated and in greater amounts than had

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(1) Powell with Adams, THIS JOURNAL, **42**, 646 (1920).

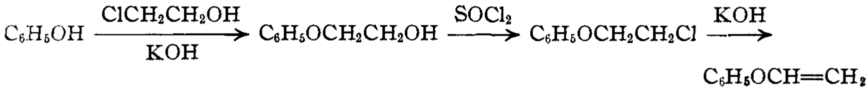
(2) Fosse, *Bull. soc. chim.*, [3] **23**, 515 (1900).

been added. This seemed to point to the instability of acetaldehyde diphenylacetal in the presence of relatively large amounts of phenol at high temperatures, a supposition which was confirmed by heating the two substances together to 260°. The result was the same as in the preceding experiment. However, by slowly adding phenol to boiling phenyl vinyl ether during a period of several hours, a smooth addition took place and the corresponding acetal was formed in 90% yield.

The origin of the phenol is not clear, although it is probably connected in some way with the polymeric material which always appears as a side product.

Experimental Part

The phenyl vinyl ether used in this work was prepared by the following set of reactions



$$C_6H_5OH \xrightarrow[KOH]{ClCH_2CH_2OH} C_6H_5OCH_2CH_2OH \xrightarrow{SOCl_2} C_6H_5OCH_2CH_2Cl \xrightarrow{KOH} C_6H_5OCH{=}CH_2$$

Although yields were not large, the nature of all reagents made the synthesis more satisfactory than others in the literature.[3]

β-Chlorophenetole.—Two moles each of potassium hydroxide, phenol and ethylene chlorohydrin, 350 cc. of water and 400 cc. of benzene were placed in a two-liter flask under a reflux condenser and boiled on a steam-bath for twelve hours. The benzene layer was separated, washed free of phenol with 5% sodium hydroxide and dried by boiling off about one-third of the benzene. It was added slowly through a dropping funnel set in a reflux condenser to 2 moles of practical grade thionyl chloride in an equal volume of benzene. The solvent was evaporated and the product was distilled at atmospheric pressure under a hood; yields were consistently 50–53%; b. p. 213–221°.

Phenyl Vinyl Ether.—This was prepared in 50% yield by twice distilling the crude β-chlorophenetole from powdered potassium hydroxide in the manner previously described by the present authors.[4] It boiled at 154–158° and redistillation gave 155–156°, the value in the literature.

Thermal Decomposition of Phenyl Vinyl Ether.—The following typical run is given in detail. All others were similarly performed with differences only in time and temperature.

Twenty-five grams of phenyl vinyl ether was sealed in a soft glass Carius tube and heated to 295–300° for three hours. The tube was allowed to cool, and on unsealing no pressure was observed. The product was clear and only slightly discolored. It was taken up in ether and extracted twice with 50-cc. portions of 5% sodium hydroxide. This extract brominated gave 0.7 g. of tribromophenol, m. p. and mixed m. p. 90–91°, indicative of about 0.3 g. of phenol. The ether solution was evaporated and distilled under diminished pressure. The first fraction was 4.5 g. of unchanged starting material which came over below 70° at 14 mm. An intermediate fraction of 3.8 g. distilled as the temperature rose steadily to 153°. The principal fraction, 8.6 g., was collected at 153–156°. A tarry residue remained.

By working over the second and third fractions, 8 g. of pure acetaldehyde diphenylacetal was obtained; b. p. 154–155° at 14 mm., 174–175° at 26 mm.

Anal. Calcd. for $C_{14}H_{14}O_2$: C, 78.5; H, 6.5. Found: C, 78.6, 78.6; H, 6.5, 6.6.

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(3) Wohl and Berthold, *Ber.*, **43**, 2175 (1910); v. Braun and Kirschbaum, *ibid.*, **53**, 1399 (1920).

(4) Lauer and Spielman, THIS JOURNAL, **53**, 1533 (1931).

A sample was prepared according to the directions of Fosse[2] and the boiling points were found to be the same. On cooling with solid carbon dioxide both crystallized; m. p. and mixed m. p. 9–10°.

The usual run of 20 g. of phenyl vinyl ether heated to 260–280° for twelve hours gave 0.11 g. of phenol and 2.0 g. of the acetal. In no case was the amount of phenol isolated more than one-tenth of the yield of acetal.

Addition of Phenol to Phenyl Vinyl Ether.—Eight grams of phenyl vinyl ether was heated to boiling in an atmosphere of carbon dioxide. To this was added dropwise during eight hours 5 g. of phenol in 2 g. of phenyl vinyl ether. Boiling was continued for eight hours as the temperature (thermometer in liquid) rose slowly to 210°. The product was distilled and 10.4 g. of acetaldehyde diphenylacetal was collected at 172–178° at 26 mm.

Summary

Phenyl vinyl ether has been shown to decompose at 260–300° to give phenol, acetaldehyde diphenylacetal and an unknown substance of high molecular weight.

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Isomorphism and Alternation in the Melting Points of the Normal Alcohols, Acetates, Bromides, Acids and Ethyl Esters from C_{10} to C_{18}

BY JANE DICK MEYER AND E. EMMET REID

The alternation of properties, particularly melting points, in various series has engaged the attention of many investigators.[1,2,3] When the melting points of the normal alcohols are plotted against the number of carbon atoms a decided alternation is evident in the lower members but becomes so small for the higher that the scattered data in the literature are not sufficiently accurate and consistent to show whether it exists or not.

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(1) (a) Timmermans, *Bull. soc. chim. Belg.*, **30**, 89–97; **31**, 389 (1922); **35**, 276–288 (1926); **38**, 295 (1929); (b) Deffet, *ibid.*, **40**, 385–402 (1931); (c) Cuy, THIS JOURNAL, **42**, 503 (1920); (d) Pauly, *Z. anorg. allgem. Chem.*, **119**, 271–291 (1922): (e) Piper, Chibnall, Hopkins, Pollard, Smith and Williams, *Biochem. J.*, **25**, 2072–2094 (1931); (f) Garner and Randall, *J. Chem. Soc.*, **125**, 881 (1924); (g) Garner, Madden and Rushbrooke, *ibid.*, 2491 (1926); (h) Garner and Rushbrooke, *ibid.*, 1351–1359 (1927); (i) Garner and King, *ibid.*, 1849–1861 (1929); (j) King and Garner, *ibid.*, 578–580 (1931); (k) Malkin, THIS JOURNAL, **52**, 3739 (1930); (l) Malkin, *Nature*, **127**, 126–127 (1931); (m) Malkin, *J. Chem. Soc.*, 2796–2805 (1931); (n) Piper and Malkin, *Nature*, **126**, 278 (1930); (o) Whitby, *J. Chem. Soc.*, 1458 (1926); (p) Levene, West and Van der Scheer, *J. Biol. Chem.*, **20**, 521–534 (1915); **23**, 72; (q) Levene and Taylor, *ibid.*, **59**, 905–921 (1924); (r) Shepard, Henne and Midgley, THIS JOURNAL, **53**, 1948–1958 (1931); (s) Deese, *ibid.*, **53**, 3673–3682 (1931); (t) Verkade and Coops, *Rec. trav. chim.*, **46**, 903–917 (1927); (u) Blau, *Monatsh.*, **26**, 103 (1905); (v) Krafft, *Ber.*, **15**, 1714 (1882); (w) Gascard, *Compt. rend.*, **170**, 886–888, 1326–1328 (1920); *ibid.*, **153**, 1484–1487 (1911); *Ann. chim.*, [9] **15**, 347 (1921); (x) Bleyburg and Ulrich, *Ber.*, **64**, 2504–2513 (1913).

(2) Talvitie, *Ann. Acad. Sci. Fennicae*, No. 16, **A26**, 1–94 (1927).

(3) (a) Blaise and Guerin, *Bull. soc. chim.*, [3] **29**, 1903 (1903); (b) Jeffreys, *Am. Chem. J.*, **22**, 14 (1899); (c) Slotta and Jacobi, *J. prakt. Chem.*, [2] **120**, 249 (1929); (d) Fridau, *Ann.*, **83**, 1 (1852); (e) Oskerko, *J. Russ. Phys.-Chem. Soc.*, **46**, 413 (1914); *Chem. Zentr.*, II, 1264 (1914); (f) Youtz, THIS JOURNAL, **47**, 2252 (1925); (g) Vorländer and Selke, *Z. physik. Chem.*, **129**, 435 (1927); (h) Piper and co-workers, *Biochem. J.*, **25**, 2072 (1931).