at 9 mm.; $n^{20}D$ 1.5602; 62.7% yield). A trace (0.38 g.) of material remained in the original solvent layer; from the alkaline solution by acidification and extraction was isolated 0.63 g. of a gum.

To the dry Solution B (5.00 g.) was added 10 ml. of triethylamine. The ether was removed by slow distillation, the residue was heated under reflux for three hours, and then acidified with dilute hydrochloric acid. Only a trace was alkali-soluble. The methylbenzofuran weighed 2.34 g. (b.p. 75–77° at 12 mm.; $n^{20}D$ 1.5629; 59% yield).

B. **From *o*-Allenylphenyl Acetate (V).**—To a solution prepared by dissolving 2.3 g. of sodium in 70 ml. of absolute methanol was added 6.33 g. of the freshly distilled acetate. The color changed to deep amber and the mixture became warmer. It was heated under reflux for 11 hours and the bulk of the solvent was removed by distillation. The odor of methyl acetate was unmistakable. The residue was acidified and extracted with ether. Two rough fractionations gave a total of 3.88 g. of 2-methylbenzofuran (b.p. 77–80° at 14 mm.; $n^{20}D$ 1.5583; 81% yield). The residue (0.47 g.) was not characterized.

An attempt to transmetallate 2-methylbenzofuran by heating with ethylmagnesium bromide failed; the starting material was recovered after treatment of the mixture with acetyl chloride.

Reaction of 2-(Chloromethyl)-benzofuran with Alkali Cyanides.—Five grams of the chloride was heated under reflux for two hours with 4.9 g. of powdered sodium cyanide in 50 ml. of reagent acetone. An equal volume of water was added and heating continued for six hours. The product did not crystallize from hexane. It was hydrolyzed by heating with 10 g. of potassium hydroxide in aqueous ethanol. The 2-benzofurylacetic acid,[18] m.p. 99.5–100.5°, weighed 1.27 g. (24%) after recrystallization from hexane. The neutral fraction contained 2-benzofurylcarbinol (about 0.8 g.) isolated as the phenylurethan.

The chloride (5.0 g.) was heated under reflux with mechanical stirring for seven hours with 6.5 g. of potassium cyanide in 25 ml. of acetone and 25 ml. of purified dioxane. All but 10 ml. of the solvents was removed by distillation, and water was added to the residue. After extraction into ether, distillation of this solvent, and addition of petroleum ether (70–90°) and benzene, 0.70 g. of light tan crystals separated. Recrystallization produced fine white needles, m.p. 161.8–162.4°. The compound resisted attempted hydrolysis with alcoholic alkali and has not been identified.

Anal. Found: C, 80.17; H, 4.95; N, 3.22.

The residue from distillation of the benzene–petroleum ether filtrate above did not crystallize. Distillation yielded, after a small forerun of unchanged chloride, a total of 1.25 g. boiling at 95–110° (0.5 mm., principally at 105–110°). 2-Benzofurylacetonitrile formed colorless needles from hexane, m.p. 58.5–59.7°.

Anal. Calcd. for $C_{10}H_7NO$: C, 76.42; H, 4.49. Found: C, 76.53; H, 4.33

The nitrile was hydrolyzed to 2-benzofurylacetic acid by alcoholic alkali.

Ultraviolet Absorption Spectra.—The measurements for Fig. 1 were made on a Beckman model DU spectrophotometer. Samples of easily polymerizable materials were freshly distilled and the measurements were completed within a few hours. The *o*-allenylphenol from 1.67 g. of chloride was made up to 100 ml. with ether. Evaporation at the aspirator of a 10-ml. aliquot left 0.1523 g.; although some impurities are undoubtedly included in this figure, it was the only available basis for the calculation of extinction coefficients. A 2-ml. aliquot of this solution was diluted to 25 ml. with 95% ethanol, and 2 ml. of that mixture again made up to 25 ml. with ethanol. Solutions of *o*-propenylphenol and *o*-allylphenol were prepared similarly. The other spectra were determined with ethanol as the solvent.

EUGENE, OREGON

RECEIVED MARCH 12, 1951

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[18] Reichstein and Reichstein, *Helv. Chim. Acta*, **13**, 1275 (1930), reported a constant of 98–99° for the compound, obtained by a more indirect method, which, however, was not open to the possibility of rearrangement.

[CONTRIBUTION FROM POLYCHEMICALS DEPARTMENT, EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS & CO., INC.]

Synthesis of 3-Amino-1,2-propanediol and 2,3-Diamino-1-propanol

BY R. C. SCHREYER

Synthesis of 3-amino-1,2-propanediol and 2,3-diamino-1-propanol from methoxyacetaldehyde and hydrogen cyanide involving no halogen containing compounds has been described. A number of substituted propionitriles and propylamines have been reported.

Syntheses of 3-amino-1,2-propanediol and 2,3-diamino-1-propanol were desired which involved no halogen containing compounds. 3-Amino-1,2-propanediol has been prepared by amination of hydroxypropylene oxide[1] or 3-chloro-1,2-propanediol[2] with aqueous ammonia. Abderhalden and Eichwald[3] have reported the synthesis of 2,3-diamino-1-propanol by amination of β,γ-dibromopropyl methyl ether followed by cleavage with hydrogen bromide.

In this investigation methoxyacetaldehyde–water azeotrope, obtained by the air oxidation of methoxyethanol over silver, was the starting material for the syntheses of the desired intermediates. 3-Methoxy-2-hydroxypropionitrile (I) was formed by treatment of methoxyacetaldehyde with hydrogen cyanide. Attempts to hydrogenate the cyanhydrin directly to 3-methoxy-2-hydroxypropylamine (IV) were not successful due to decomposition. The hydroxyl group of the cyanhydrin was protected by reaction with ethylal and a trace of acid to form 3-methoxy-2-ethoxymethoxypropionitrile (II). Hydrogenation of (II) to (III) then proceeded in high yields. The ethoxymethoxy group was removed by processing with ethanol in presence of acid to give (IV). 3-Amino-1,2-propanediol (V) was obtained by cleavage of the ether linkage with hydrochloric acid.

2,3-Diamino-1-propanol (VIII) was obtained by amination of (I) to 3-methoxy-2-aminopropionitrile (VI) followed by hydrogenation to 3-methoxypropylenediamine (VII) and cleavage of the ether linkage.

Acknowledgments.—The assistance of H. R. Stephens and A. J. Beattie in the preparation of some of the compounds reported is gratefully acknowledged.

Experimental

3-Methoxy-2-hydroxypropionitrile.—Hydrogen cyanide (290 ml.) was added portionwise to a stirred mixture of 515 g. of methoxyacetaldehyde–water azeotrope (13% H_2O) and 1 g. of pyridine, maintaining the temperature at 50–60°. The addition time was 2 hours. The mixture was cooled

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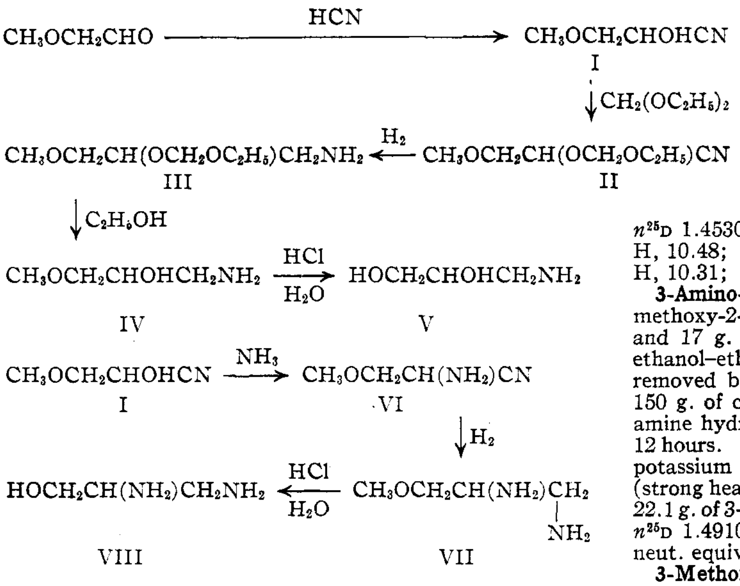
[1] L. Smith and T. Nilsson, *J. prakt. Chem.*, **162**, 63 (1943).

[2] Girdler Corp., French Patent 808,024, Jan. 27, 1937.

[3] E. Abderhalden and E. Eichwald, *Ber.*, **49**, 2101 (1916).



$$CH_3OCH_2CHO \xrightarrow{HCN} \underset{I}{CH_3OCH_2CHOHCN}$$

$$\underset{I}{CH_3OCH_2CHOHCN} \xrightarrow{CH_2(OC_2H_5)_2} \underset{II}{CH_3OCH_2CH(OCH_2OC_2H_5)CN} \xrightarrow{H_2} \underset{III}{CH_3OCH_2CH(OCH_2OC_2H_5)CH_2NH_2}$$

$$\underset{III}{CH_3OCH_2CH(OCH_2OC_2H_5)CH_2NH_2} \xrightarrow{C_2H_5OH} \underset{IV}{CH_3OCH_2CHOHCH_2NH_2} \xrightarrow[H_2O]{HCl} \underset{V}{HOCH_2CHOHCH_2NH_2}$$

$$\underset{I}{CH_3OCH_2CHOHCN} \xrightarrow{NH_3} \underset{VI}{CH_3OCH_2CH(NH_2)CN} \xrightarrow{H_2} \underset{VII}{CH_3OCH_2CH(NH_2)CH_2NH_2} \xrightarrow[H_2O]{HCl} \underset{VIII}{HOCH_2CH(NH_2)CH_2NH_2}$$

to room temperature and acidified with a few drops of H_3PO_4. Vacuum distillation gave 557 g. of 3-methoxy-2-hydroxypropionitrile, b.p. 86–90° (3–4 mm.), $n^{25}D$ 1.4240 (91% yield). Calcd. for $C_4H_7O_2N$: N, 13.85. Found: N, 13.89.

3-Methoxy-2-ethoxymethoxypropylamine.—3-Methoxy-2-hydroxypropionitrile (101 g.), 254 g. of ethylal, and 0.5 g. of H_2SO_4 were refluxed for one-half hour. The ethanol–ethylal azeotrope followed by excess ethylal was removed by distillation. Vacuum distillation of the residue gave 151.8 g. of 3-methoxy-2-ethoxymethoxypropionitrile, b.p. 86–87° (6 mm.), $n^{25}D$ 1.4140 (95% yield). Calcd. for $C_7H_{13}O_3N$: N, 8.79. Found: N, 8.98.

3-Methoxy-2-ethoxymethoxypropylamine.—A charge of 70.4 g. of 3-methoxy-2-ethoxymethoxypropionitrile, 102 g. of ammonia, and 30 g. of Raney nickel was hydrogenated at 108–125° and 450–700 atmospheres pressure in a stainless steel autoclave for one hour. A pressure drop of 400 atmospheres was noted. Vacuum distillation of the discharged product gave 65 g. of 3-methoxy-2-ethoxymethoxypropylamine, b.p. 68–71° (3 mm.), $n^{25}D$ 1.4280 (90% yield). Calcd. for $C_7H_{17}O_3N$: C, 51.53; H, 10.43; N, 8.59; neut. equiv., 163. Found: C, 51.37; H, 10.58; N, 8.38; neut. equiv., 160.

3-Methoxy-2-hydroxypropylamine.—A mixture of 45.1 g. of 3-methoxy-2-ethoxymethoxypropylamine, 150 g. of ethanol, and 22 g. of HCl (g) was refluxed for 15 minutes. The ethanol–ethylal azeotrope followed by excess ethanol was removed by distillation. The mixture was then neutralized with 60% potassium hydroxide. Vacuum distillation of the neutral solution gave 25.8 g. of 3-methoxy-2-hydroxypropylamine, b.p. 75–77° (2–3 mm.), $n^{25}D$ 1.4530 (88% yield). Calcd. for $C_4H_{11}O_2N$: C, 45.71; H, 10.48; N, 13.3; neut. equiv., 105. Found: C, 45.48; H, 10.31; N, 13.04; neut. equiv., 110.

3-Amino-1,2-propanediol.—A charge of 47.5 g. of 3-methoxy-2-ethoxymethoxypropylamine, 100 g. of ethanol, and 17 g. of HCl (g) was refluxed for 15 minutes. The ethanol–ethylal azeotrope followed by excess ethanol was removed by distillation. A solution of 75 g. of H_2O and 150 g. of concentrated hydrochloric acid was added to the amine hydrochloride and the resulting mixture refluxed for 12 hours. The mixture was cooled and neutralized with 60% potassium hydroxide. Vacuum distillation of the solution (strong heating necessary to drive out amine from salt) gave 22.1 g. of 3-amino-1,2-propanediol, b.p. 110–115° (1–2 mm.), $n^{25}D$ 1.4910 (yield 83%). Calcd. for $C_3H_9O_2N$: N, 15.38; neut. equiv., 91. Found: N, 14.94; neut. equiv., 91.5.

3-Methoxy-2-aminopropionitrile.—A charge of 119 g. of ammonia and 40 g. of 3-methoxy-2-hydroxypropionitrile was heated in a stainless steel autoclave at 48–65° for one hour. The discharged product was flashed distilled under vacuum and then redistilled under vacuum to give 15 g. of 3-methoxy-2-aminopropionitrile, b.p. 75–77° (1–2 mm.), $n^{25}D$ 1.4390 (yield 37%). Calcd. for $C_4H_8ON_2$: neut. equiv., 100. Found: neut. equiv., 99.9.

3-Methoxypropylenediamine.—A mixture of 10 g. of 3-methoxy-2-aminopropionitrile, 85 g. of ammonia and 30 g. of Raney nickel was hydrogenated at 100–152° and 325–700 atmospheres pressure for 1.5 hours. Vacuum distillation of the product gave 8.3 g. of 3-methoxy-1,2-propylenediamine, b.p. 46–48° (3–4 mm.), $n^{25}D$ 1.4505. Calcd. for $C_4H_{12}ON_2$: neut. equiv., 52. Found: neut. equiv., 56.

2,3-Diamino-1-propanol.—A charge of 13.5 g. of 3-methoxy-1,2-propylenediamine, 150 g. of concentrated hydrochloric acid and 100 g. of water was refluxed at 105–110° for 14 hours. The mixture was cooled and neutralized with 60% potassium hydroxide. The potassium chloride was filtered off and the filtrate vacuum distilled. A 50% yield of 2,3-diamino-1-propanol, 3.2 g., b.p. 108–110° (1–2 mm.), $n^{25}D$ 1.4935. Calcd. for $C_3H_{10}ON_2$: neut. equiv., 45. Found: neut. equiv., 47.5.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF DE PAUL UNIVERSITY]

The Pyrolysis of Phenyl Phthalate[1]

BY ROBERT P. ZELINSKI AND HARRY M. ANDERSEN[2]

The pyrolysis of phenyl phthalate at temperatures of 400, 600, 800 and 1000° has been studied. Qualitative and quantitative data concerning the products have been obtained, but a satisfactory degradation sequence has not been found.

As part of a study of the effect of temperature on the nature and amounts of the products obtained from the pyrolysis of some common plasticizers,[3] the pyrolysis of phenyl phthalate has been investigated. The literature appears to contain no report of the degradation of this ester although the pyrolysis of some alkyl phthalates has been studied.[3,4]

The experiments described in this investigation were carried out at temperatures of 400, 600, 800 and 1000° with the rate of introduction of phenyl phthalate at approximately 0.5 g./min. Sillimanite tubes were used as reaction chambers.

As expected, under comparative conditions phenyl phthalate was much less resistant to decomposition than methyl phthalate,[3] two-fifths

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[1] This work was performed with the aid of U. S. Navy funds under Subcontract 1, Contract 10431, a prime contract with the Hercules Powder Company, Allegheny Ballistics Laboratory.

[2] Taken in part from a thesis presented by Harry M. Andersen to the Graduate School of De Paul University in partial fulfillment of the requirements for the degree, Master of Science, 1950.

[3] R. P. Zelinski, J. T. Ziedlecki and A. L. Anderson, THIS JOURNAL, **72**, 5503 (1950).

[4] (a) N. Nagel and R. Abelsdorff, *Wiss. Veroffentlich Siemens-Konzern*, **5**, 193 (1926); *C. A.*, **21**, 1642 (1927); (b) H. Meyer and A. Hofmann, *Monatsh.*, **39**, 109 (1948).