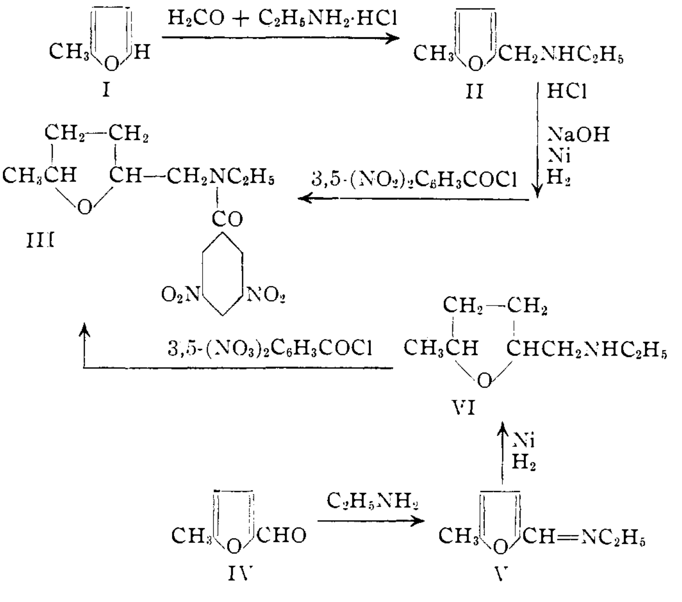

5-Methylfurfural (IV) was condensed with ethylamine to give the imino (V) derivative. Reduction of V with hydrogen and Raney nickel gave N-ethyl 5-methyltetrahydrofurfurylamine (VI) in 56% over-all yield. The crystalline 3,5-dinitrobenzoate (III) of VI was identical with that prepared from II.

N-Ethyl-5-methyltetrahydrofurfurylamine.—(A) 5-methylfurfural[3] (51.8 g., 0.47 mole) and 64.3 g. (0.47 mole) of 33% $EtNH_2$ were mixed with cooling in a 200-cc. Erlenmeyer flask. After the strong heating had subsided the reaction was allowed to stand at room temperature for one hour with occasional shaking. At the end of this time the upper organic layer was separated and washed once with 100 cc. of water.

The crude imine was hydrogenated directly, using 4 g. of Raney nickel catalyst and an initial hydrogen pressure of 1700 lb. Distillation of the product gave 43.8 g. of colorless oil, b. p. 92–95° (50 mm.). This represents a 56% over-all yield from 5-methylfurfural. Calcd. for $C_8H_{17}NO$: N, 9.8. Found: N, 9.6.

(B) Twenty-five grams of N-ethyl-5-methylfurfurylamine, prepared as described previously, was hydrogenated using 2 g. of Raney nickel catalyst and an initial hydrogen pressure of 1800 lb. Distillation of the product yielded 23 g. (90%) of colorless oil, b. p. 67–70° (20 mm.). Calcd. for $C_8H_{17}NO$: N, 9.8. Found: N, 9.8.

A purified sample of the tetrahydro amine had the physical constants: n^{25}_D 1.4387; d^{25}_4 0.887.

N-Ethyl-5-methyltetrahydrofurfurylamine Hydrochloride.—The salt was prepared as described previously. It crystallized as buff plates from acetone, m. p., 98–99°.

Anal. Calcd. for $C_8H_{18}NOCl$: N, 7.8; Cl, 19.8. Found: N, 7.7; Cl, 19.6.

N-Ethyl-N-5-methyltetrahydrofurfuryl 3,5 Dinitrobenzamide.—The 3,5-dinitrobenzoates of both the amines from (A) and (B), prepared according to Shriner and Fuson,[4] separated as colorless needles from alcohol. The melting points from (A): 89–89.5°; from (B) 87–88°; a mixture of the two, 87–88°. *Anal.* Calcd. for $C_{15}H_{19}N_3O_4$: N, 12.5. Found: N, from (A), 12.6; from (B), 12.2.

Summary

The synthesis of seventeen new furfuryl amines has been accomplished by condensing 2-methylfuran with formaldehyde and various substituted ammonium chlorides. The reaction takes place at the free *alpha* position on the furan nucleus.

The structure of these compounds has been demonstrated in one instance by the identity of the properties and mixed melting point of the product with those of a sample prepared by an alternative and unambiguous method.

AMES, IOWA RECEIVED MARCH 4, 1946

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[3] Rinkes, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 393.

[4] Shriner and Fuson, "The Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1940, p. 147.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

Vinyl Ethyl Ether and Other Vinyl Ethers

BY CHARLES D. HURD AND DONALD G. BOTTERON[1]

The preparation of vinyl ethers by the action of solid potassium hydroxide on 2-bromoethyl alkyl ethers is known, illustrations[2] being vinyl allyl ether and vinyl γ-ethylallyl ether. No such synthesis of simple vinyl alkyl ethers from 1-chloroethyl alkyl ethers has been reported, however, although 2,2-dichlorovinyl ethyl ether has been prepared from ethyl 1,2,2-trichloroethyl ether by the action of heat[3] and by the action of 50% potassium hydroxide.[4]

When mixed with pyridine and distilled, 1-chloroethyl ethyl ether yielded vinyl ethyl ether: $CH_3CHClOC_2H_5 + C_5H_5N \rightarrow CH_2{=}CHOC_2H_5 + C_5H_5NHCl$. No vinyl ethyl ether was obtained when solid potassium hydroxide, solid sodium hydroxide, dibutylamine, or dimethylaniline was used as the base. Hydrolysis was en-

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[1] Research associate, 1941–1943. This investigation was sponsored by Pittsburgh Plate Glass Company.

[2] Hurd and Pollack, THIS JOURNAL, **60**, 1905 (1938); *J. Org. Chem.* **3**, 550 (1939).

[3] Oddo and Mameli, *Gazz. chim. ital.*, **33**, II, 373 (1904); *Chem. Zentr.*, **75**, I, 920 (1904).

[4] Godefroy, *Compt. rend.*, **102**, 869 (1886).

countered when the solid hydroxides were used since both ethyl alcohol and acetaldehyde were obtained together with unchanged chloro ether.

Attempts to adapt this reaction to the bis-1-chloroethyl ethers of ethylene glycol or diethylene glycol gave none of the anticipated vinyl ethers. In these cases, bases promoted acetal formation, ethylene acetal being obtained in 78% yield by reaction of ethanediol bis-1-chloroethyl ether with pyridine, and 3-oxapentamethylene acetal (or 2-methyl-1,3,6-trioxacyclooctane) being formed by heating a mixture of 2-(1-chloroethoxy)-ethyl ether and quinoline.

Two experiments were performed with vinyl 2-hydroxyethyl ether. The first was hydrogenation. The vinyl ether hydrogenated readily in the presence of a platinum catalyst, yielding cellosolve. In the second experiment the compound, in the form of its sodium derivative, underwent reaction with allyl bromide to yield vinyl 2-allyloxyethyl ether, $CH_2{=}CHCH_2OCH_2CH_2OCH{=}CH_2$.

Experimental

1-Chloroethyl ethyl ether was prepared from paraldehyde, ethanol and hydrogen chloride.[5] Vinyl 2-hydroxyethyl ether was obtained by reaction of sodium on ethylene bromoacetal.[6]

Vinyl Ethyl Ether.—Twenty-four grams (0.22 mole) of 1-chloroethyl ethyl ether was added to 40 ml. (0.5 mole) of pyridine at room temperature. From the mixture was obtained 14 ml. of distillate before the vapor temperature reached 100°. This was redistilled through a 12-cm. Vigreux column to yield 6.8 g. (0.1 mole, 43%) of vinyl ethyl ether, b. p. 35–40°, $n^{21}\text{D}$ 1.3737. Values reported[7] for carefully purified material: b. p. 35.72 and $n^{20}\text{D}$ 1.3768. Wislicenus[8] found that ethyl vinyl ether polymerizes in the presence of iodine. Our material was found to react vigorously when added to a crystal of iodine.

Ethanediol Bis-1-chloroethyl Ether.—A mixture of 80 ml. of paraldehyde and 42 ml. of ethylene glycol was saturated with dry hydrogen chloride at 0°. The upper layer was dried over sodium sulfate, then fourteen hours at −10° over drierite, and then was distilled. The portion boiling above 85° (20 mm.) was redistilled; yield, 25.2 g. (18%) of b. p. 92–94° (15 mm.), $n^{20}\text{D}$ 1.4498, density 1.149 at 23.5°.

Anal. Calcd. for $C_6H_{12}Cl_2O_2$: Cl, 38.0. Found: Cl, 35.3.

Reaction with Pyridine.—A mixture of 25 g. of the ether and 24 ml. of pyridine was distilled. Most of the distillate (12.8 g.) was collected at 50–95° leaving a residue of pyridine hydrochloride in the flask. Redistillation yielded 9.2 g. (78% yield) of ethylene acetal, b. p. 82–85°, $n^{20}\text{D}$ 1.4054. Reported constants for pure ethylene acetal are these: b. p. 82.5°, $n^{20}\text{D}$ 1.4022.

2-(1-Chloroethoxy)-ethyl Ether, $O(CH_2CH_2OCHClCH_3)_2$.—The general procedure was the same as in the last preparation except that attempted distillation of the ether at 20 mm. caused resinification. The crude ether was prepared by saturating a mixture of 70 ml. each of diethylene glycol and paraldehyde with hydrogen chloride at 0°. The mixture remained in a single phase, but it layered out after shaking it with three portions of sodium sulfate. The upper, water-insoluble layer (48 g., 41 ml.) was kept over drierite.

3-Oxapentamethylene Acetal.—A mixture of 37 g. of the crude chloro ether and 52 ml. of quinoline was distilled under diminished pressure. The distillate of 3-oxapentamethylene acetal, b. p. 45–50° (10 mm.), weighed 9.6 g.; density, 1.069 at 23°, $n^{20}\text{D}$ 1.4375.

Anal. (by T. S. Ma). Calcd. for $C_6H_{12}O_3$: C, 54.52; H, 9.16. Found: C, 55.04; H, 9.21.

Hydrogenation of Vinyl 2-Hydroxyethyl Ether.—One-tenth mole of this ether (8.8 g.) in 150 ml. of ethanol was reduced with hydrogen in the presence of 35 mg. of platinum oxide catalyst. Pressure drop on the gage was from 30 to 23 lb. In a parallel hydrogenation of 0.1 mole of indene the drop was from 30 to 22.4 lb. The product of the first experiment was filtered, distilled, and twice fractionated (g., °C., $n^{20}\text{D}$): 1.25, 110–134°, 1.4024; 5.22, 134–140°, 1.4068; 0.64, 140–190°, 1.4068; residue, 0.5 g. The refractive index ($n^{20}\text{D}$) of a sample of cellosolve, b. p. 135°, was 1.4070.

Vinyl 2-Allyloxyethyl Ether.—Vinyl 2-hydroxyethyl ether was prepared from 83.5 g. (0.5 mole) of 2-(bromomethyl)-dioxolane in three volumes of dry ether with 23 g. (1 mole) of sodium. After a reaction period of about five hours, 60.5 g. (0.5 mole) of allyl bromide was added. Solids were filtered off after ten hours, a little pyrogallol was added to the filtrate which was concentrated and distilled; yield 17.4 g. (27%), collected at 90–100° (120 mm.). Redistillation gave a fraction, b. p. 92–94° (120 mm.), which was not quite pure (*anal.*: C, 64.3; H, 9.02%). The fraction contained vinyl 2-hydroxyethyl ether. This was removed by extracting twice with 15-ml. portions of water, then ether-extracting the aqueous extracts four times. The organic layer, combined with the ether extracts, was dried. Distillation gave a pure fraction at 99–100° (135 mm.); $n^{20}\text{D}$ 1.4340; density 0.9128 at 20°.

Anal. (by T. S. Ma). Calcd. for $C_7H_{12}O_2$: C, 65.59; H, 9.44. Found: C, 65.77; H, 9.24.

Summary

Vinyl ethyl ether may be made by interaction of 1-chloroethyl ethyl ether and pyridine, but a different type of reaction is encountered with bis-1-chloroethyl ethers of ethylene glycol or diethylene glycol. Ethylene acetal and 3-oxapentamethylene acetal are formed, respectively, the last being new.

Vinyl 2-hydroxyethyl ether yields cellosolve on hydrogenation and it gives rise to vinyl 2-allyloxyethyl ether on reaction with allyl bromide.

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[5] Henze and Murchison, THIS JOURNAL, **53**, 4077 (1931).

[6] Hill and Pidgeon, *ibid.*, **50**, 2718 (1928).

[7] Dolliver, Gresham, Kistiakowsky, Smith and Vaughan, *ibid.*, **60**, 441 (1938).

[8] Wislicenus, *Ann.*, **192**, 106 (1878).