in chloride ion was taken as an indication of the extent of reaction. The results were reproducible to within 2%. The data thus obtained are plotted in Fig. 1.

One mole each of the two isomers was hydrolyzed for two hours under conditions similar to those for the smaller runs. The low boiling dichloride gave the low boiling chloroalcohol (α-3-chloro-2-propen-1-ol) and the high boiling dichloride gave the high boiling (beta) chloroalcohol.

Catalytic Hydrolysis of 3-Chloro-2-propen-1-ol.—The low and high boiling isomers of 3-chloro-2-propen-1-ol were subjected to a sixty-minute regular catalytic hydrolysis to ascertain the extent of hydrolysis of the vinyl chlorine. The results are in Table I.

Acid and Basic Hydrolysis of 1,3-Dichloropropene.—The two dichlorides were also hydrolyzed using a 1% sodium hydroxide solution and a 1.5% hydrochloric acid solution to give a comparison of the extent of reaction in thirty minutes with cuprous chloride catalyzed acid hydrolysis. All conditions were similar to those for the catalytic hydrolysis except for the hydrolyzing medium. The results are in Table I.

Acknowledgment.—This research was financed in part by a grant from the University of Texas Research Institute, Project No. 76. The authors wish to express their appreciation.

Summary

1. 1,3-Dichloropropene has been hydrolyzed by the use of a hydrochloric acid solution of cuprous chloride; the low boiling (alpha) isomer hydrolyzed more slowly than the high boiling (beta) isomer.

2. From this fact it was concluded that the effect of the cuprous chloride–chloride ion complex is through the double bond, that the action of the complex is the rate controlling step, and that the configuration of the isomer directly affects this rate of reaction.

3. The *trans* structure has been assigned to the low boiling (alpha) isomer of 1,3-dichloropropene and the *cis* structure assigned to the high boiling (beta) isomer.

AUSTIN, TEXAS

RECEIVED APRIL 1, 1946

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

The Reaction of 2-Methylfuran with Formaldehyde and Substituted Ammonium Chlorides[1]

BY R. F. HOLDREN AND R. M. HIXON

Recent work in this Laboratory had made 2-methylfuran readily available.[2] It was observed that this compound undergoes the Mannich reaction when treated with formaldehyde and substituted ammonium chlorides. Preparation of several substituted furfuryl amines by this reaction is reported herein.

Materials.—The ethyl and dimethylamine hydrochlorides were of Eastman Kodak Co. White Label grade and were used without further purification. Isopropylamine was prepared by catalytic hydrogenation of 2-nitropropane, Eastman practical grade. The octyl-, dodecyl- and octadecylamines were supplied through the courtesy of the Chemical Division of Armour and Company. The morpholine and piperidine were of Eastman practical, the other amines were of Eastman white label grade. All the amines were converted into hydrochlorides by adding the calculated amount of hydrochloric acid, evaporating to dryness and recrystallizing from ether–ethanol.

Procedure.—The details of the reaction of 2-methylfuran with formaldehyde and ethylamine hydrochloride will illustrate the general procedure followed.

(A) To a solution of 163 g. (2 moles) of ethylamine hydrochloride in 162 g. of 37% formaldehyde (2 moles) at 30° in a flask equipped with a dropping funnel, stirrer and reflux condenser, 82 g. (1 mole) of 2-methylfuran was added dropwise during one hour. Stirring was continued until heat evolution ceased. The mixture was cooled to room temperature and neutralized with 81 g. of sodium hydroxide dissolved in 160 cc. of water. The top, organic layer was separated and the water solution extracted once with 100 cc. of ether. The combined ether and amine layer was washed with two 50-cc. portions of water and dried over sodium sulfate.

The ether was removed and the residue distilled under reduced pressure, giving a colorless oil, b. p. 71° (17 mm.), yield, 36.9 g. or 25.9%.

(B) An alternate procedure, which was used only in the case of the ethyl derivative, was to keep the reaction mixture cooled to 30–35° while adding the 2-methylfuran. The yield of secondary amine was increased to 44.6% by this method.

The hydrochlorides of the amines were prepared by adding the calculated quantity of cold, concentrated hydrochloric acid to a solution of 3–5 cc. of the amine in 20 cc. of anhydrous ether cooled to 0°. Crystallization could be induced, if the hydrochloride separated as an oil, by evaporating a solution of it in 100 cc. of acetone to 25 cc. and pouring this slowly into 100 cc. of boiling ether. In some cases recrystallization from acetone–alcohol mixtures is practical.

After the secondary amines had been removed from the reaction mixture, *n*-alkyldi-(5-methylfurfuryl)-amines were isolated by distillation. In the direct preparation of the compound derived from ethylamine a yield of 74% was realized if the temperature was controlled at 30–40°. If the reaction was allowed to heat to reflux the yield was only 43%.

Results.—The data regarding the compounds thus prepared are collected in the tables. Little attempt was made to find optimum conditions for the reactions. In one or two cases it was observed that higher yields were obtained by cooling the reaction mixture instead of allowing reflux temperatures to be reached. The acid-labile furan nucleus was polymerized by the hydrochlorides at the higher temperatures with resulting decrease in yield.

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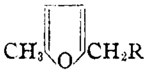
[1] From a thesis submitted by R. F. Holdren to the Graduate Faculty of Iowa State College in partial fulfillment of the requirements for the degree of Doctor of Philosophy. Supported in part by a grant from Quaker Oats Company to the Industrial Science Research Institute of Iowa State College.

[2] Burnette, *Iowa State Coll. J. Sci.*, **19**, 9 (1944).

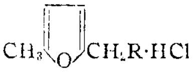
TABLE I

COMPOUNDS OF TYPE  $CH_3C_4H_2OCH_2R$

R	Moles of 2-methylfuran	Yield, %	Physical constants B. p., °C.	Mm.	d^{25}_4	n^{25}	Formula	Nitrogen, % Calcd.	Found
$-NHCH_2CH_3$	1.00	25.9	71-76	17	0.944	1.4689	$C_8H_{13}NO$	10.1	10.2
$-NH(CH_2)_3CH_3$	0.600	21.0	110-115	22	0.921	1.4659	$C_{10}H_{17}NO$	8.4	8.3
$-NH(CH_2)_7CH_3$	0.775	31.6	115-118	2	0.901	1.4671	$C_{14}H_{25}NO$	6.3	6.1
$-NH(CH_2)_{11}CH_3$	0.500	15.0	135	2	0.888	1.4678	$C_{18}H_{33}NO$	5.0	4.9
$-NH(CH_2)_{17}CH_3$	0.250	33.6	195-197	2	[a]	[a]	$C_{24}H_{45}NO$	3.9	4.0
$-N(CH_3)_2$	1.00	64.7	68-70	25	0.921	1.4620	$C_8H_{13}NO$	10.1	10.2
$-NHCH(CH_3)_2$	0.421	22.2	82-83	20	0.923	1.4630	$C_9H_{15}NO$	9.1	9.2
$-NHCH_2CH{=}CH_2$	1.00	12.6	93	21	0.959	1.4832	$C_9H_{13}NO$	9.3	9.1
$-NHCH_2CH_2OH$	0.500	42.2	100-102	3	1.082	1.5020	$C_8H_{13}NO_2$	9.0	8.9
$-NC_4H_8O$	1.00	78.5	133	20	1.057	1.4961	$C_{10}H_{15}NO_2$	7.7	7.7
$-NC_5H_{10}$	0.536	77.6	88-89	6	0.981	1.4950	$C_{11}H_{17}NO$	7.8	7.9[b]
$-NHCH_2C_6H_5$	0.900	34.6	104-108	1	1.042	1.5411	$C_{13}H_{15}NO$	7.0	7.1
$-NHC_6H_{11}$	1.00	52.8	75-77	1	0.984	1.4960	$C_{12}H_{19}NO$	7.2	7.4

[a] Solid, m. p. 27-28°. [b] By Dumas method, other nitrogen analyses by Kjeldahl.

TABLE II

HYDROCHLORIDE SALTS  $CH_3C_4H_2OCH_2R{\cdot}HCl$

R	M. p. (uncor.), °C.	Formula	Nitrogen, % Calcd.	Found	Chlorine, % Calcd.	Found
$-NHCH_2CH_3$	138-139	$C_8H_{14}NOCl$	8.0	8.0	20.2	20.0
$-NH(CH_2)_3CH_3$	169-170	$C_{10}H_{18}NOCl$	6.9	6.8	17.4	17.2
$-NH(CH_2)_7CH_3$	145-146	$C_{14}H_{26}NOCl$	5.4	5.0	13.7	13.6
$-NH(CH_2)_{11}CH_3$	147-148	$C_{18}H_{34}NOCl$	4.4	4.5	[a]	
$-NH(CH_2)_{17}CH_3$	105-107	$C_{24}H_{46}NOCl$	3.5	3.7	[a]	
$-N(CH_3)_2$	158-158.5	$C_8H_{14}NOCl$	8.0	8.0	20.2	20.0
$-NHCH(CH_3)_2$	138-139	$C_9H_{16}NOCl$	7.4	7.3	18.8	18.5
$-NHCH_2CH{=}CH_2$	90-91	$C_9H_{14}NOCl$	7.5	7.3	19.0	18.8
$-NHCH_2CH_2OH$	79-79.5	$C_8H_{14}NO_2Cl$	7.3	7.3	18.6	18.2
$-NC_4H_8O$	202-204 dec.	$C_{10}H_{16}NO_2Cl$	6.4	6.5	16.3	15.9
$-NC_5H_{10}$	147-148	$C_{11}H_{18}NOCl$	6.5	6.5[b]	16.5	16.3
$-NHCH_2C_6H_5$	178-180 dec.	$C_{13}H_{16}NOCl$	5.9	5.9	15.0	15.3
$-NHC_6H_{11}$	167-168	$C_{12}H_{20}NOCl$	6.1	6.1	15.5	15.3

[a] Hydrochlorides were too insoluble for analysis by soluble chlorine method. [b] By Dumas method, other nitrogen analyses by Kjeldahl.

TABLE III

COMPOUNDS OF THE TYPE  $(CH_3C_4H_2OCH_2)_2N-R$

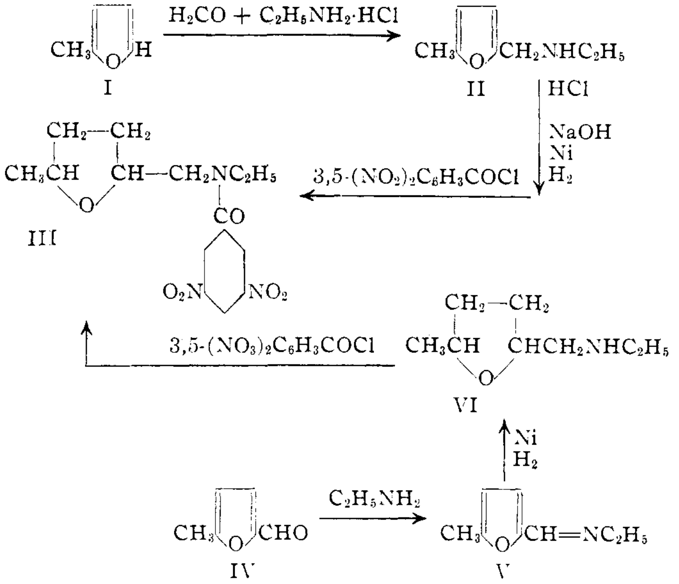
R	Yield, %	Physical constants B. p., °C.	Mm.	d^{25}_4	n^{25}	Formula	Nitrogen, % Calcd.	Found
$-CH_2CH_3$[a]	43.4	127-130	6	1.018	1.5000	$C_{14}H_{19}NO_2$	6.0	6.2
$-(CH_2)_7CH_3$[b]	35.0	150-153	1	0.947	1.4840	$C_{20}H_{31}NO_2$	4.4	4.5
$-CH_2C_6H_5$[c]	33.4	138-141	1	1.069	1.5440	$C_{19}H_{21}NO_2$	4.7	4.8[d]

[a] Hydrochloride: m. p. 151-152. Calcd. for $C_{14}H_{20}NO_2Cl$: N, 5.2; Cl, 13.1. Found: N, 5.3; Cl, 13.1. [b] Hydrochloride and picrate were uncrystallizable oils. Acid oxalate: m. p. 202-203° dec. Calcd. for $C_{22}H_{33}NO_6$: N, 3.4. Found: N, 3.5. [c] Hydrochloride: m. p. 154-156° dec. Calcd. for $C_{19}H_{22}NO_2Cl$: N, 4.2; Cl, 10.7. Found: N, 4.5; Cl, 10.2. [d] By Dumas method, other nitrogen analysis by Kjeldahl.

Only resinous products were obtained when NH_4Cl, $C_6H_5NH_2{\cdot}HCl$ and $C_6H_5NHCH_3{\cdot}HCl$ were used. As would be expected, no simple products could be isolated on attempted reaction of $NH_2OH{\cdot}HCl$ and $C_6H_5NHNH_2{\cdot}HCl$.

Discussion.—The reaction took place at the free *alpha* position in the furan nucleus. This was indicated by the fact that 2,5-dimethylfuran did not react under similar conditions.

Proof of the structure of the amine formed in the case of ethylamine hydrochloride was furnished by the reactions shown in the sequence:



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 $C_{15}H_{19}N_3O_5$: 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).