benzylidene-D-mannitol, 1,6-didesoxy-2,3,4,5-dibenzylidene-D-mannitol and the known 1,6-didesoxy-D-mannitol of Micheel.

BETHESDA, MARYLAND RECEIVED APRIL 30, 1943

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF TEXAS]

Tertiary Alkyl Primary Amines, $RR'R''CNH_2$. III[1]

BY HENRY R. HENZE AND THOMAS R. THOMPSON[2]

It has been demonstrated that carbinamines result from interaction of allylmagnesium bromide and α-alkoxyalkyl cyanides,[3,4] alkyl cyanides,[4] an aralkyl cyanide,[4] alkenyl cyanides,[4] and keto nitriles.[5] Because of the more satisfactory yields of amines obtained in use of α-alkoxyalkyl cyanides, we have continued our utilization of alkoxyacetonitriles and have extended the investigation to include both α- and β-substituted ethoxypropionitriles.

It is of interest to note that β-ethoxypropionitrile reacts, essentially as do α-ethoxypropionitrile and α-alkoxyacetonitriles, with two equivalents of allylmagnesium bromide to form the diallyl-2-ethoxyethylcarbinamine. However, in contrast to the behavior of the α-alkoxynitriles, β-ethoxypropionitrile does not react with propylmagnesium bromide to form an adduct capable of further interaction with allylmagnesium bromide. Nor does this β-alkoxynitrile react smoothly with propylmagnesium bromide to yield the anticipated ketone.

Ability of an adduct, formed initially by interaction of an α-alkoxynitrile with an alkylmagnesium bromide, to react further with the allyl Grignard reagent has been again demonstrated utilizing the adducts produced from *n*-propoxyacetonitrile and isoamoxyacetonitrile, respectively, with methylmagnesium bromide.

All of the allylcarbinamines prepared in this study were reduced catalytically to the corresponding *n*-propyl analogs. Both types of amines are but sparingly soluble in water but readily form picrates and other salts. Unsaturation in the allylcarbinamines can be tested for satisfactorily by mixing acetone solutions of the amine and potassium permanganate. However, chloroform solutions of bromine are decolorized with virtually the same rapidity by both the allyl and propyl amines.

Through the courtesy of Eli Lilly and Company, four of these carbinamines have been tested for possible effect upon blood pressure. The methylisoamoxymethyl-allyl and *n*-propyl carbinamines and the methyl-*n*-propoxymethyl-allyl and *n*-propyl carbinamines were tested by injection into the vein of a pitted cat. Their action seems to be comparable to that of less complex aliphatic amines in lowering blood pressure instead of raising it.

Experimental

α-Ethoxypropionitrile.—α-Chloroethyl ethyl ether[6] (140 g.) was added to 112 g. of dry cuprous cyanide suspended in 200 cc. of anhydrous benzene and the mixture was stirred for two hours before being warmed on the steam-bath for four hours. Distillation and refractionation of the product produced 65 g. (51% yield) of α-ethoxypropionitrile[7]; b. p. 129–130° (751 mm.); d^{20}_4 0.8743; n^{22}_{D} 1.3890.

β-Ethoxypropionitrile.—Ethylene cyanohydrin was prepared from ethylene chlorohydrin and sodium cyanide[8] and was converted into β-chloropropionitrile[9] by reaction with thionyl chloride in chloroform solution. The chloronitrile was obtained in 60% yield, b. p. 175° (747 mm.)[10]; $d^{20}_4$1. 1573; n^{20}_{D} 1.4360; *MR* calcd. 20.67; *MR* found 20.22.

Twenty-three grams of freshly cut sodium was added in portions to 350 cc. of ethanol and gently warmed until solution was complete. With cooling in an ice-bath and vigorous stirring, 73.5 g. of β-chloropropionitrile was added slowly. After the initial reaction had subsided, the mixture was warmed for two hours on the steam-bath. Excess sodium ethylate was decomposed by addition of 5 cc. of water and saturation with carbon dioxide. Inorganic material was removed by centrifugation. The alcohol was distilled and the residue upon fractionation yielded 46.6 g.

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(1) From the Ph.D. dissertation of T. R. Thompson, June, 1942. Presented before the Division of Organic Chemistry at the 105th meeting of the American Chemical Society at Detroit, Michigan, April 12–16, 1943.

(2) Research Assistant, University of Texas Research Institute, 1941–1942; present address: General Aniline and Film Corp., Binghamton, N. Y.

(3) Allen and Henze, THIS JOURNAL, **61**, 1790 (1939).

(4) Henze, Allen and Leslie, *ibid.*, **65**, 87 (1943).

(5) Rehberg with Henze, *ibid.*, **63**, 2785 (1941).

(6) Henze and Murchison, *ibid.*, **53**, 4077 (1931).

(7) Gauthier [*Ann. chim. phys.*, (8) **16**, 313 (1909)] reported b. p. 129–130° (730 mm.); d^{16}_4 0.878; n^{16} 1.390.

(8) "Organic Syntheses," John Wiley and Sons, Inc., New York, 1923, Vol. III, p. 57. Our material b. p. 220–221° (746 mm.); d^{20}_4 1.0554; n^{20}_{D} 1.4247; γ^{20} 49.42 dynes/sq. cm.; *MR* calcd. 17.34; *MR* found 17.19; *P* calcd. 179.0; *P* found 178.4.

(9) Chapman and Stephen, *J. Chem. Soc.*, **127**, 888 (1925).

(10) Henry [*Chem. Zentr.*, **69**, II, 22 (1898)] reported b. p. 174–176°; $d^{18.5}$ 1.1443.

(57.5%); b. p. 78° (25 mm.)[11]; d^{20}_4 0.9139; n^{20}_D 1.4061; *MR* calcd. 26.69; *MR* found 26.62.

Diallyl-1-ethoxy-ethylcarbinamine.—Allylmagnesium bromide was prepared according to Gilman and McGlumphy[12] and its condensation with 44 g. of α-ethoxypropionitrile was carried out according to the method of Allen and Henze.[3] The greenish-brown oily adduct was decomposed by addition of a cold, saturated solution of ammonium chloride. Fractionation separated 28 g. (35% yield) of liquid boiling at 104–107° (25 mm.) from 25 g. of higher boiling products and residue. Redistillation yielded 20 g.; b. p. 70° (5 mm.); b. p. (in capillary) 198.0–198.5° (751.7 mm.); d^{20}_4 0.8783; n^{20}_D 1.4555; *MR* calcd. 57.13; *MR* found 56.95.

Anal. Calcd. for $C_{11}H_{21}NO$: N, 7.64. Found: N, 7.75.

One gram of carbinamine was dissolved in 15 cc. of water saturated with sulfur dioxide and treated with a saturated solution of picric acid. The yellow precipitate (1.5 g. or 85% yield) was crystallized from 25% alcohol in the form of glistening yellow needles. This picrate melts at 103° (cor.).

Anal. Calcd. for $C_{17}H_{24}N_4O_8$: N, 13.59. Found: N, 13.71.

Diallyl-2-ethoxyethylcarbinamine.—From 25 g. of β-ethoxypropionitrile and allylmagnesium bromide was obtained 31.8 g. of brown oil which was distilled under diminished pressure to yield 15 g. (33% yield) of material boiling at 108° (13 mm.) and 15 g. of tarry residue. Upon redistillation, 14 g. was collected; b. p. 95° (5 mm.); d^{20}_4 0.8803; n^{20}_D 1.4594; *MR* calcd. 57.13; *MR* found 56.94.

Anal. Calcd. for $C_{11}H_{21}NO$: N, 7.64. Found: N, 7.64.

The carbinamine readily yielded a picrate (85%); m. p. 91° (cor.).

Anal. Calcd. for $C_{17}H_{24}N_4O_8$: N, 13.59. Found: N, 13.49.

1-Ethoxyethyldi-*n*-propylcarbinamine.—Fourteen and one-half grams of diallyl-1-ethoxyethylcarbinamine was dissolved in 50 cc. of acetone and hydrogenated in the presence of 0.1 g. of the Adams catalyst; reaction was complete after vigorous shaking for eight hours at room temperature with hydrogen under 70 cm. pressure. Fourteen grams (94.5% yield) of liquid remained after removal of the solvent. Eighty-one per cent. of the theoretical amount of the saturated carbinamine distilled at 56° (2 mm.); d^{20}_4 0.8463; n^{20}_D 1.4347; *MR* calcd. 58.06; *MR* found 57.72.

Anal. Calcd. for $C_{11}H_{25}NO$: N, 7.48. Found: N, 7.55.

The picrate was formed in 87% yield in the usual manner, and it melted at 110.5° (cor.).

Anal. Calcd. for $C_{17}H_{28}N_4O_8$: N, 13.46. Found: N, 13.51.

2-Ethoxyethyldi-*n*-propylcarbinamine.—Seven and one-half grams of the corresponding diallylcarbinamine was reduced in four hours and yielded 7 g. (93%); b. p. 100° (10 mm.); d^{20}_4 0.8490; n^{20}_D 1.4380; *MR* calcd. 58.06; *MR* found 57.88.

Anal. Calcd. for $C_{11}H_{25}NO$: N, 7.48. Found: N, 7.65.

A picrate was obtained in 63% yield and melts at 99.5° (cor.).

Anal. Calcd. for $C_{17}H_{28}N_4O_8$: N, 13.46. Found: N, 13.38.

Allyl-1-ethoxyethyl-*n*-propylcarbinamine.—This compound was obtained according to the method of Allen and Henze[3]; a Grignard reagent was prepared from 43 g. of *n*-propyl bromide and treated with 25 g. of α-ethoxypropionitrile; to the adduct was added the Grignard reagent formed from 40 g. of allyl bromide. The greenish-brown viscous oil was decomposed by the addition of cold, saturated ammonium chloride solution. Removal of solvent left 31.8 g. of liquid residue. Fractional distillation of the latter under reduced pressure, followed by redistillation of the fractions of lower and higher boiling points yielded 3 g. of material boiling at 45–50° (3 mm.) and 18.5 g. of product boiling at 78° (3 mm.).

The latter product, which gave a positive qualitative test for nitrogen, was basic to moist litmus, and decolorized a solution of bromine in acetic acid, proved to be the desired carbinamine, and represented 40% of the theoretical yield; d^{20}_4 0.8630; n^{20}_D 1.4450; *MR* calcd. 57.60; *MR* found 57.30.

Anal. Calcd. for $C_{11}H_{23}NO$: N, 7.56. Found: N, 7.71.

A picrate was obtained and melted at 103° (cor.).

Anal. Calcd. for $C_{11}H_{25}NO$: N, 13.53. Found: N, 13.59.

The lower boiling material was redistilled at 163–165° (758 mm.); n^{20}_D 1.4135. It formed a semicarbazone which melts at 124.5° (cor.). This derivative is identical with the semicarbazone formed from 1-ethoxyethyl *n*-propyl ketone.

Anal. Calcd. for $C_9H_{19}N_3O_2$: C, 53.70; H, 9.52. Found: C, 53.58; H, 9.39.

Allyl-2-ethoxyethyl-*n*-propylcarbinamine.—The preparation of this amine was attempted using 18.6 g. of β-ethoxypropionitrile, the Grignard reagent prepared from 27.8 g. of propyl bromide and, subsequently, the magnesium reagent from 32.7 g. of allyl bromide. Upon decomposition of the reaction product with ammonium chloride solution, about 1 g. of an orange-colored solid was formed. The solid did not melt below 310°, contained nitrogen, and burned with a luminous flame to leave a residue containing magnesium. The solid also was partially soluble in a solution containing sulfurous acid, the filtrate of which gave a solid picrate. The latter resisted attempts at purification by the usual means, and exploded on heating in a melting point tube.

Distillation of the original ether layer from the ammonium chloride treatment yielded 4 g. of liquid; b. p. 60–71° (3 mm.) and 5 g. of tarry residue. Redistillation of the liquid gave 2 g.; b. p. 220–224° (748 mm.); d^{20}_4 0.8820; n^{20}_D 1.4599; N, found 7.62; picrate, m. p. 91° (cor.). This picrate melted unchanged when mixed with an authentic sample of the picrate of diallyl-2-ethoxyethylcarbinamine.

1-Ethoxyethyldi-*n*-propylcarbinol.—Twenty-five grams of α-ethoxypropionitrile was added to the Grignard re-

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[11] Kilpi [*Z. physik. Chem.*, **86**, 672 (1914)] reported b. p. 171.3–171.5° (757 mm.); d^{15}_4 0.9285; d^{25}_4 0.9189.

[12] Gilman and McGlumphy, *Bull. soc. chim.*, **43**, 1322 (1928).

agent prepared from 76 g. of *n*-propyl bromide and 15.2 g. of magnesium turnings in diethyl ether. About one-half of this ether was removed by gentle warming and was replaced by di-*n*-butyl ether, then the remainder of the ethyl ether was replaced by the butyl homolog and the mixture was heated for four hours. A brown oil separated and was decomposed with saturated ammonium chloride solution. Distillation gave 19 g. of product boiling 38–75° (2 mm.) and 2 g. of residue.

By redistillation at atmospheric pressure, the larger fraction yielded two portions; one of b. p. 163–164° (759 mm.) was identified as 1-ethoxyethyl *n*-propyl ketone (yield 10 g. or 28%) through formation of its semicarbazone; the other portion of b. p. 203–205° (759 mm.) is presumably 1-ethoxyethyldi-*n*-propylcarbinol; 2.0 g., $d^{20}{}_4$ 0.8650; $n^{20}{}_D$ 1.4245; *MR* calcd. 56.17; *MR* found 55.56.

Anal. Calcd. for $C_{11}H_{24}O_2$: C, 70.16; H, 12.85. Found: C, 70.07; H, 12.75.

In another experiment, the propylmagnesium bromide was prepared in di-*n*-butyl ether, diluted with dry toluene and α-ethoxypropionitrile in toluene was added to the hot solution of the Grignard reagent. After ten hours of heating, decomposition of the adduct yielded the ketone and a larger amount of residue, but no trace of carbinamine.

In still another experiment, the *n*-propylmagnesium bromide in ether solution was dropped from a graduated buret into an ether solution of the α-ethoxynitrile. The reaction was vigorous, causing refluxing of the ether during the addition of the first molecular proportion of the reagent. Further addition of another equivalent resulted if at all, in only very feeble reaction. There was obtained 1-ethoxyethyl-*n*-propyl ketone in 50% yield, but no evidence of carbinamine.

In contrast, *n*-propylmagnesium bromide was formed from 27.8 g. of *n*-propyl bromide and added to 18.6 g. of β-ethoxypropionitrile in ether solution. After stirring and warming, the mixture was treated with cold, saturated ammonium chloride solution, but without apparent liberation of heat. There was obtained 12 g. of an orange-colored solid which had the same properties as those of the 1 g. of orange material secured previously. Five grams of the β-ethoxypropionitrile was recovered, but no evidence of formation of a ketone or carbinamine was found.

Allylmethyl-*n*-propoxymethylcarbinamine.—Chloromethyl *n*-propyl ether[13] was converted into *n*-propoxyacetonitrile[14] using benzene as a diluent. To an ether solution of methylmagnesium iodide, prepared from 79.2 g. of methyl iodide and 12.2 g. of magnesium turnings, was added 50 g. of *n*-propoxyacetonitrile during the course of an hour, and the mixture was heated on a steam-bath for one hour. The mixture was stirred vigorously while being cooled in order to keep in suspension the white solid which formed. There was then added a solution of allylmagnesium bromide produced by interaction of 79 g. of allyl bromide, 46.8 g. of magnesium and 500 cc. of anhydrous ether. Heat was evolved during the addition and after three hours of stirring over a steam-bath, the white solid was transformed into a gray oil. Decomposition was accomplished by addition of a saturated solution of ammonium chloride and the ether layer was separated and extracted with 10% hydrochloric acid; the acid extract was made basic with 10% sodium hydroxide solution, and extracted with ether. On distillation of the dried extract, there was obtained 49 g. of liquid boiling at 100–110° (90–100 mm.) and 6 g. of tarry residue. Fractional distillation gave 40 g. (51% yield) of allylmethyl-*n*-propoxymethylcarbinamine; b. p. 100° (100 mm.); $d^{20}{}_4$ 0.8439; $n^{20}{}_D$ 1.4330; *MR* calcd. 48.36; *MR* found 48.35.

Anal. Calcd. for $C_9H_{19}NO$: N, 8.91. Found: N, 9.01.

A picrate was obtained in 91% yield. Recrystallized from a mixture of benzene and petroleum ether it melted at 110° (cor.).

Anal. Calcd. for $C_{15}H_{22}N_4O_7$: N, 14.50. Found: N, 14.60.

The dried ether extract containing the acid-insoluble material yielded on distillation 11 g. of a liquid boiling at 50–55° (25 mm.), and 3 g. of tarry residue. Redistillation of the liquid yielded no sharply boiling fractions; however, there was obtained 3.8 g. boiling at 145–150° (753 mm.); $d^{20}{}_4$ 0.8899; $n^{20}{}_D$ 1.4112. Although impure, this fraction must be principally methyl *n*-propoxymethyl ketone,[15] as it formed a semicarbazone, m. p. 75° (cor.), after recrystallization from either diluted alcohol or a benzene-petroleum ether mixture.

Anal. Calcd. for $C_7H_{15}N_3O_2$: N, 24.26. Found: N, 24.02.

Methyl-*n*-propoxymethyl-*n*-propylcarbinamine.—Fourteen and one-half grams of allylmethyl-*n*-propoxymethylcarbinamine in 75 cc. of ethyl alcohol was reduced in the presence of 50 mg. of the Adams catalyst with hydrogen under 60 cm. pressure. The reduction was complete in two hours and yielded 13 g. (90%); b. p. 105–106° (100 mm.); $d^{20}{}_4$ 0.8300; $n^{20}{}_D$ 1.4221; *MR* calcd. 48.83; *MR* found 48.69.

Anal. Calcd. for $C_9H_{21}NO$: C, 67.86; H, 13.29; N, 8.80. Found: C, 67.61; H, 13.43; N, 8.92.

A picrate was obtained in 87% yield, following recrystallization from benzene–petroleum ether, and melted at 95° (cor.).

Anal. Calcd. for $C_{15}H_{24}N_4O_8$: N, 14.43. Found: N, 14.51.

Allylmethylisoamoxymethylcarbinamine.—Isoamyl chloromethyl ether[13] was converted into isoamoxyacetonitrile.[14] A solution of 64 g. of the latter in 50 cc. of anhydrous ether was added to one prepared from interaction of 50 g. of methyl bromide, 12.2 g. of magnesium turnings and 300 cc. of ether. A white solid formed and was kept in suspension by vigorous stirring during an hour of heating over a steam-bath. After cooling, there was added a solution of allylmagnesium bromide, prepared from 69 g. of allyl bromide in 500 cc. of anhydrous ether and 46.8 g. of magnesium turnings. There was no vigorous ebullition of the solvent during this addition but the suspended white solid was transformed into a light green oil. The mixture was warmed for four hours before being treated with ammonium chloride solution.

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(13) Favre, *Bull. soc. chim.*, [3] **11**, 881 (1894).

(14) Gauthier [*Ann. chim. phys.*, [8] **16**, 308 (1909)] reported b. p. 147–148° (735 mm.); n^{20} 1.401; we found b. p. 150–152° (752 mm.); $n^{20}{}_D$ 1.3970.

(15) Gauthier, *ibid.*, 319, reported b. p. 145° (732 mm.).

The ether solution of acid-soluble material gave 67 g. of liquid boiling at 100–110° (35 mm.). Fractionation resulted in 60 g. (65% yield) of allylmethylisoamoxymethylcarbinamine; b. p. 89–90° (8 mm.); d^{20}_4 0.8383; n^{20}_D 1.4355; *MR* calcd. 57.60; *MR* found 57.74.

Anal. Calcd. for $C_{11}H_{23}NO$: N, 7.56. Found: N, 7.60.

A picrate was obtained in 92% yield and melted at 104° (cor.) after recrystallization from benzene–petroleum ether mixture.

Anal. Calcd. for $C_{17}H_{26}N_4O_8$: N, 13.52. Found: N, 13.61.

From the ether solution of acid-insoluble material was obtained 14.3 g. of a liquid boiling at 60–106° (35 mm.). No sharply boiling fractions could be observed on redistillation; however, a 2-g. fraction, b. p. 65–85° (26 mm.), gave on treatment with 3,5-dinitrobenzoyl chloride a small yield of 3,5-dinitrobenzoyl ester which melted at 61° (cor.). This ester proved to be isoamyl 3,5-dinitrobenzoate.

Anal. Calcd. for $C_{12}H_{14}N_2O_6$: N, 9.93. Found: N, 9.80.

In addition to the above, there was collected a 6.5-g. fraction which boiled at 90–104° (26 mm.) and formed a solid semicarbazone in good yield. This derivative was quite soluble in water but crystallized well from petroleum ether; m. p. 60° (cor.). Presumably, it is the semicarbazone of methyl isoamoxymethyl ketone.

Anal. Calcd. for $C_9H_{19}N_3O_2$: N, 20.88. Found: N, 21.05.

Methylisoamoxymethyl-*n*-propylcarbinamine.—In preparation of this amine, 25.6 g. of allylmethylisoamoxymethylcarbamine in 100 cc. of ethyl alcohol was reduced in the presence of 0.1 g. of Adams catalyst and hydrogen under 70 cm. pressure. The yield was 23.1 g. (90%); b. p. 97° (8 mm.); d^{20}_4 0.8264; n^{20}_D 1.4280; *MR* calcd. 58.06; *MR* found 58.30.

Anal. Calcd. for $C_{11}H_{25}NO$: C, 70.53; H, 13.45; N, 7.48. Found: C, 70.39; H, 13.50; N, 7.57.

The picrate was recrystallized from benzene–petroleum ether (93% yield) and then melted at 86° (cor.).

Anal. Calcd. for $C_{17}H_{28}N_4O_8$: N, 13.46. Found: N, 13.60.

Summary

1. The two isomeric ethoxypropionitriles have been shown capable of reaction with two equivalents of allylmagnesium bromide to form the corresponding diallylethoxyethylcarbinamines. The latter are reduced readily by catalytic hydrogenation to the di-*n*-propylethoxyethylcarbinamines.

2. Although 1-ethoxypropionitrile and *n*-propylmagnesium bromide interact to yield an adduct with which allylmagnesium bromide reacts to yield allyl-1-ethoxyethyl-*n*-propylcarbinamine, the isomeric 2-ethoxypropionitrile does not evidence a similar behavior. The lesser activity of 2-ethoxypropionitrile is shown further by its failure to react smoothly with *n*-propylmagnesium bromide to yield an anticipated ketone.

3. The adducts formed from two additional alkoxyacetonitriles, by interaction with methylmagnesium halides, also react with allylmagnesium bromide to yield carbinamines.

4. These carbinamines lower blood pressure in a pitted cat but not to a useful degree.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, IOWA STATE COLLEGE]

The Production of Acetylmethylcarbinol by the Action of *Acetobacter suboxydans* upon 2,3-Butylene Glycol[1]

BY E. I. FULMER, L. A. UNDERKOFLER AND A. C. BANTZ

Previous communications from these laboratories have presented data on the production of keto-compounds by the action of *Acetobacter suboxydans* upon sorbitol,[2] glycerol,[3] erythritol,[4] mannitol[5] and *i*-inositol.[6] The present paper deals with the production of acetylmethylcarbinol by the action of this organism upon 2,3-butylene glycol.

Kling[7] obtained a 50% yield of acetylmethylcarbinol after a thirty-three day fermentation of 2,3-butylene glycol by *Mycoderma aceti*. Visser't Hooft[8] reported a 77% yield of the carbinol from the glycol by the action of *Acetobacter suboxydans*. Both workers used the butylene glycol obtained by the fermentative action of *Aerobacter aerogenes* and assumed that they were dealing only with

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[1] This work was supported by a grant from the Industrial Science Research funds of the Iowa State College for studies on the fermentative utilization of agricultural products.

[2] E. I. Fulmer, J. W. Dunning, J. F. Guymon and L. A. Underkofler, THIS JOURNAL, **58**, 1012 (1936).

[3] L. A. Underkofler and E. I. Fulmer, *ibid.*, **59**, 301 (1937).

[4] R. L. Whistler and L. A. Underkofler, *ibid.*, **60**, 2507 (1938).

[5] E. I. Fulmer, J. W. Dunning and L. A. Underkofler, *Iowa State Coll. J. Sci.*, **13**, 279 (1939).

[6] J. W. Dunning, E. I. Fulmer and L. A. Underkofler, *ibid.*, **15**, 39 (1940).

[7] A. Kling, *Ann. chim.*, [8] **5**, 471 (1905).

[8] F. visser't Hooft, "Biochemische onderzoekingen over het Geslacht Acetobacter," Thesis, Delft, 1925.