b.p. 72–76° (3 mm.), $n^{27}\text{D}$ 1.4301, m.p. of 1-naphthylurethan 61–62° (reported[9] m.p. 65.5°).

The 1-naphthylurethan of an authentic sample of *n*-nonyl alcohol, m.p. 61°, did not depress the m.p. of our 1-naphthylurethan.

Synthesis of α-Ethylheptanoic Acid.—Alkylation of diethyl malonate first with *n*-amyl bromide, then with ethyl bromide by standard procedures[10] gave diethyl ethyl-*n*-amylmalonate, b.p. 129–134° (7.5 mm.), $n^{24}\text{D}$ 1.4292 (reported[11] b.p. 136.5° (10 mm.), $n^{25}\text{D}$ 1.4259) in 54% over-all yield.

Diethyl ethyl-*n*-amylmalonate, 69.5 g. (0.27 mole), was refluxed for six hours in a solution of 112 g. of potassium hydroxide in 830 ml. of ethyl alcohol. The solution was then cooled, 250 ml. of water was added, and the alcohol was removed by distillation. The basic aqueous layer was extracted with ether, then acidified with hydrochloric acid; crude ethyl-*n*-amylmalonic acid separated on cooling in an ice-bath and stirring. The crude acid was collected by filtration, and the mother liquor was twice extracted with 100-ml. portions of ether. The ether extracts were combined, the crude acid dissolved therein, and the solution was dried over anhydrous sodium sulfate. After removal of ether, the crude acid was decarboxylated by heating at 180–185° until evolution of carbon dioxide ceased. The residual product was distilled from a simple distillation flask to give 34 g. (80% yield) of crude α-ethylheptanoic acid, b.p. 110–114° (3.5 mm.), $n^{23}\text{D}$ 1.4240. Another similar run gave 73.5% yield. Fractional distillation of 34 g. of crude material gave 23.3 g. (68.5%) of pure α-ethylheptanoic acid, b.p. 121–122° (6 mm.), $n^{27}\text{D}$ 1.4255. *Anal.* Calcd. for $C_9H_{18}O_2$: C, 68.31; H, 11.46; neut. equiv., 158.2. Found: C, 68.80; H, 11.48; neut. equiv., 158.1.

Synthesis of 2-Ethylheptanol.—A solution of 15.8 g. (0.1 mole) of α-ethylheptanoic acid in 150 ml. of ether was added dropwise to a solution of 6.2 g. (0.16 mole) of lithium aluminum hydride in 200 ml. of ether at such rate as to maintain gentle reflux. After addition was complete the mixture was refluxed for an additional hour, then cooled in ice and the excess lithium aluminum hydride decomposed by the dropwise addition of 25 ml. of water. The mixture was treated with 250 ml. of 10% sulfuric acid. The aqueous layer was separated, saturated with sodium chloride, and thrice extracted with 100-ml. portions of ether. The original ether layer and the ether extracts were combined, washed with sodium carbonate solution, then with water, and dried over anhydrous sodium sulfate. The ether was removed by distillation, and the residue was fractionally distilled through the Todd column to give 9.8 g. (68% yield) of 2-ethylheptanol, b.p. 92° (5 mm.), $n^{23}\text{D}$ 1.4330. *Anal.* Calcd. for $C_9H_{20}O$: C, 74.93; H, 13.98. Found: C, 74.54; H, 13.67. The alcohol gave a 1-naphthylurethan, m.p. 43–44° after two crystallizations from petroleum ether.

Synthesis of 1-Methyl-2-ethylacrolein.—Diethyl ketone, 50 g. (0.58 mole), was condensed with 45 g. (0.75 mole) of methyl formate in the presence of 27 g. (0.5 mole) of sodium methoxide and the resulting sodium salt of the hydroxymethylene ketone was treated with methanolic hydrogen chloride according to the procedure of Royals and Brannock.[4] The reaction product (a mixture of the β-ketoacetal and methoxymethylene ketone) showed b.p. 53–58° (3.5 mm.), $n^{25}\text{D}$ 1.4260 and was obtained in 62% yield. This mixture was reduced with lithium aluminum hydride at −10° and the reduction product was hydrolyzed and dehydrated essentially as described by Seifert and Schinz.[6] The product was fractionally distilled through the Todd column to give 12.9 g. (54%) of 1-methyl-2-ethylacrolein, b.p. 77–78.5° (100 mm.), $n^{28}\text{D}$ 1.4390–1.4440, m.p. of 2,4-dinitrophenylhydrazone 158° (reported m.p. 159°[12] and 161°[13]), m.p. of semicarbazone 205° (reported[17] m.p. 207°).

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Nitrolysis of 1,3–6,8-Diendomethylene-1,3,6,8-tetrazacyclodecane

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In view of the successful nitrolysis of hexamethylenetetramine and related compounds[1] as well as 1,3-dicyclohexylimidazolidine[2] it seemed possible that conditions could be found wherein 1,3–6,8-diendomethylene-1,3,6,8-tetrazacyclodecane (I),[3] could be nitrolyzed to 1,3,6,8-tetranitro-1,3,6,8-tetrazacyclodecane (X). However we have been unsuccessful in the attempt to synthesize this compound, which might be expected to exhibit unusual explosive properties. Instead we have found that the nitrolysis of I takes quite a different course.

In contrast to hexamethylenetetramine, 1,3–6,8-diendomethylene-1,3,6,8-tetrazacyclodecane (I) is not a stable compound.[4] The yield from 1,2-diaminoethane and formaldehyde is lower than that of hexamethylenetetramine from ammonia and formaldehyde and the purity of I is not so high. A solution of I in acetic acid is unstable, and the dinitrate decomposes within an hour, whereas hexamethylenetetramine dinitrate is permanently stable. Under these circumstances it might be expected that the methods of hexamethylenetetramine nitrolysis would not be applicable to diendomethylenetetrazacyclodecane I. Indeed when I is treated with ammonium nitrate and nitric acid in acetic anhydride at 65° it seems to decompose, since 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX, II) is the only product which has been isolated.

When hexamethylenetetramine is treated at 25° with nitric acid and acetic anhydride alone nitrolysis occurs smoothly to give a good yield of 1,7-diacetoxy-2,4,6-trinitro-2,4,6-triazaheptane and bisacetoxymethylnitramide. Under these conditions a relatively small yield of impure 1,6-diacetoxy-2,5-dinitro-2,5-diazahexane (IV), is obtained from diendomethylenetetrazacyclodecane I. However a good yield of relatively pure IV is obtained when acetyl chloride is included in the system. Indeed the yield approaches the 2:1 ratio expected if nitrolytic scission has occurred at two symmetrically disposed methylene–amine linkages in the diendomethylenetetrazacyclodecane.

Although IV has been identified previously[5] by synthesis from 1,2-dinitraminoethane (III) and formalin, it has now been characterized further by conversion to the unstable nitroxy analog V, which in turn has been transformed to 1,6-dimethoxy-2,5-dinitro-2,5-diazahexane VI by known methods.[5]

Although we have not yet succeded in the preparation of tetranitrotetrazacyclodecane (X), certain controlled solvolyses can be caused to alter the nitrolysis of diendomethylenetetrazacyclodecane I. If nitric acid is added to an ethanolic solution of I, the precipitate which first forms (the mono- and/or dinitrate) redissolves when more nitric acid is added

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(9) D. W. Adamson and J. Kenner, *J. Chem. Soc.*, 842 (1934).

(10) R. Adams and R. M. Kamm in H. Gilman and A. H. Blatt, "Organic Syntheses," 2nd Ed., Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 250.

(11) A. W. Dox and E. G. Jones, THIS JOURNAL, **50**, 2033 (1928); H. A. Shonle, A. K. Ketlch and E. E. Swanson, *ibid.*, **52**, 2440 (1930); P. Karrer, B. Shibata, A. Wattstein and L. Jacubowicz, *Helv. Chim. Acta*, **13**, 1292 (1930).

(12) C. F. H. Allen, THIS JOURNAL, **52**, 2955 (1930).

(13) M. M. Backes, *Compt. rend.*, **196**, 277 (1933).

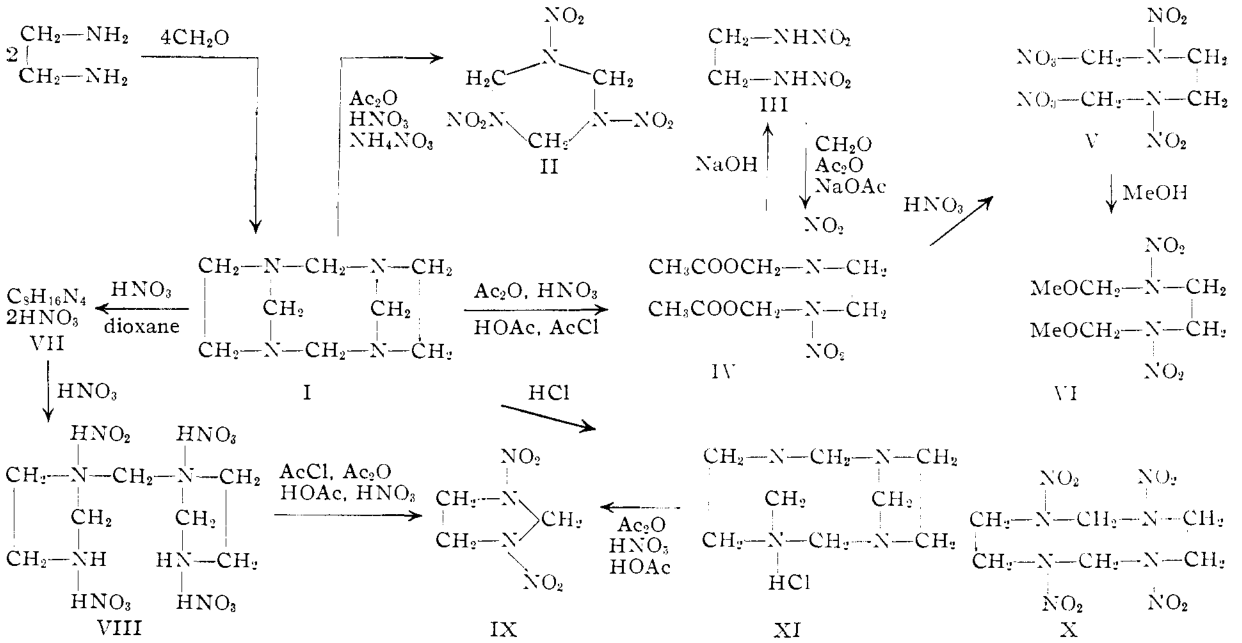
(1) H. Gilman, "Organic Chemistry," Vol. IV, John Wiley and Sons, Inc., New York, N. Y., 1953, p. 983.

(2) J. L. Boivin and G. F. Wright, *Can. J. Research*, **28**, 213 (1950).

(3) C. A. Bischoff, *Ber.*, **31**, 3248 (1898).

(4) C. A. Bischoff and F. Reinfeld, *ibid.*, **36**, 35 (1903).

(5) G. S. Myers and G. F. Wright, *Can. J. Research* **27B**, 489 (1949).



at room temperature, and a new precipitate appears. This salt cannot be purified satisfactorily, but its analysis approximates to that of methylene-bis-imidazolidine tetranitrate (VIII). Furthermore its behavior conforms with this composition since more than one equivalent of 1,3-dinitro-1,3-diazacyclopentane (IX)[6] is isolable when the salt described as VIII is nitrolyzed in acetic anhydride with a chloride catalyst.

The same product (IX) is obtained in poorer yield when diendomethylenetetrazacyclodecane monohydrochloride (XI) is treated with nitric acid and acetic anhydride in acetic acid. Because of the observable instability of this salt it is probable that it undergoes scission with demethylolation before nitrolysis occurs, and thus yields IX rather than IV.

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Experimental[7]

1,3-6,8-Diendomethylene-1,3,6,8-tetrazacyclodecane.—A solution of 2460 g. (31.5 moles) of 1,2-diaminoethane and 500 g. (12.5 moles) of sodium hydroxide in 30 l. of water was added at 20° with stirring to 5120 g. (63 mole) of 40% formalin in 3 l. of water during one-half hour. After 28 hr. at 25° the water was distilled off under 30 mm. The remainder was filtered to remove 2250 g. (90%) of crude product, m.p. 196–207° (sinters at 165°) or 196–204° when washed with two 600-ml. lots of acetone. The filtrate was used as a source of alkali in subsequent preparations.

The crude product was crystallized from acetone (13.5 ml./g., 54% recovery), m.p. 204–216°, from dioxane (5 ml./g., 80% recovery), m.p. 198–211° or from 1:1 ethanol–acetone (5 ml./g., 50% recovery), m.p. 207–213°. Long boiling in these solvents should be avoided because of decomposition. The amine is very soluble in water, methanol, ethanol, butanol and chloroform but is little soluble in benzene or diethyl ether. It decomposes to 1,2-diaminoethane and formaldehyde when heated for 5 min. at 60° in acetic acid.

1,6-Diacetoxy-2,5-dinitro-2,5-diazahexane.—A mixture of 1.42 ml. (0.02 mole) of acetyl chloride, 77.6 ml. (0.8 mole) of acetic anhydride and 50 ml. of acetic acid was stirred and chilled at 0° while 16.6 ml. (0.40 mole) of absolute nitric acid was added at a rate such that temperature did not exceed 12°. Then 16.8 g. (0.1 mole) of finely-ground 1,3-6,8-diendomethylene-1,3,6,8-tetrazacyclodecane was added at a rate such that a temperature of 5–10° was maintained (17 min.). After 10 hr. subsequently at 0° the system was poured into 600 g. of ice and 100 ml. of 30% aqueous sodium hydroxide was added.

After 12 hr. the solidified crystals were filtered at 0°, 38 g. (65%), m.p. 64–71°, and crystallized from hot acetone (1.5 ml./g., recovery 55%) with Darco, m.p. 82.2–82.7°. After a subsequent crystallization (m.p. 83°) this product was identified by mixture melting point with an authentic sample.[6] The molecular weight, determined ebullioscopically in benzene, was observed as 304; calcd. 294.

When this experiment was repeated under conditions identical with those described above except for exclusion of acetyl chloride, the 30% crude yield obtained was so gummy that a melting point could not be obtained. However, identity of the product was demonstrated by mixture melting point after crystallization from acetone.

1,6-Dimethoxy-2,5-dinitro-2,5-diazahexane.—To 10 g. (0.23 mole) of half-frozen 99% nitric acid was added 0.5 g. (0.0017 mole) of diacetoxydinitrodiazahexane during 10 sec. The system was then warmed and maintained at 25° during 6 min., after which it was chilled to −75° and 50 ml. of water was added during 5 min. The white solid, filtered and washed with methanol and ether, weighed 0.4 g. (78%) and melted at 67–70°, somewhat lower than the m.p. reported by Woodcock.[8] Since this dinitroxydinitrodiazahexane was very unstable it was converted at once to the dimethoxy analog by agitation with a tenfold excess (5 ml., 0.13 mole) of methanol during 3 min. After 2 hr. the solution was boiled, then cooled and 5 ml. of water was added. Evaporation precipitated 0.21 g. (62%), m.p. 78–79°. After repeated crystallization from carbon tetrachloride (85% recovery) it melted at 80.1–80.3° (Woodcock reports m.p. of 79–80°).

Anal. Calcd. for $C_6H_{14}N_4O_6$: C, 30.4; H, 5.93; N, 23.6. Found: C, 30.4; H, 5.87; N, 23.6.

Monohydrochloride of 1,3-6,8-Diendomethylene-1,3,6,8-tetrazacyclodecane.—A solution of 0.06 g. (0.0014 mole) of hydrogen chloride in 15 ml. of anhydrous ether was added with stirring to 0.5 g. (0.003 mole) of the base in 25 ml. of acetone during 10 min. at −8°. The white precipitate was filtered off, dry ether washed, and dried at once at 0° (20 mm.) during 20 min. and then at −70° (1.5 mm.) for an hour, m.p. 96–100°. Since the salt decomposes at once even at low temperature it was analyzed without delay.

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[6] L. Goodman, THIS JOURNAL, **75**, 3019 (1953).

[7] Melting points have been corrected against known standards

[8] D. Woodcock, *J. Chem. Soc.*, 1635 (1949).

Anal. Calcd. for $C_8H_{17}ClN_4$: C, 47.1; H, 7.94; N, 27.6. Found: C, 46.7; H, 8.30; N, 27.4.

Nitrate Salts from 1,3–6,8-Diendomethylene-1,3,6,8-tetrazacyclodecane. A. With Six Equivalents of Acid.—A solution of 90 ml. of 70% nitric acid (1.5 moles) in 150 ml. of absolute ethanol was added with vigorous stirring to a solution of 42 g. (0.25 mole) of the base in 400 ml. of ethanol. As the addition proceeded a thick yellow slurry came down. When the temperature was allowed to rise to 17° the slurry dissolved and a fine white powder precipitated. After complete addition the system was shaken for 15 min., then filtered and the solid washed with ether and vacuum-dried, 80 g., m.p. 140–141°. Essentially the same yield (m.p. 143.8°) was obtained when anhydrous reagents were used. This salt is unstable and decomposes, especially in presence of moisture, with evolution of formaldehyde. When heated to 95° for 1 hr. on a watchglass it was converted to 94% of the theoretical yield of 1,2-diaminoethane dinitrate. A satisfactory analysis of the compound could not be obtained. The formula most closely approaches that of methylene-bis-imidazolidine tetranitrate.

Anal. Calcd. for $C_7H_{20}N_8O_{12}$: C, 20.5; H, 4.93; HNO_3, 61.7. Found: C, 19.8; H, 5.12; HNO_3, 60.7.

B. With Two Equivalents of Nitric Acid.—A solution of 16 ml. (0.25 mole) of 70% nitric acid in 100 ml. of dioxane was added at 0° with vigorous stirring to 21 g. (0.125 mole) of I in 110 ml. of dioxane. A fine white solid precipitated as the acid solution was added. This was filtered, washed with acetone and with ether and dried at 10° (0.1 mm.) for 15 min., m.p. 15–19°. Calcd. for $C_8H_{18}N_6O_6$: HNO_3, 42.8. Found (Treadwell, ferrous sulfate): HNO_3, 44.0. When this compound (which decomposed slowly to a tar even over phosphorus pentoxide) was treated with nitric acid in ethanol it formed a mixture of 1,2-diaminoethane dinitrate and the salt obtained by procedure A.

1,3-Dinitro-1,3-diazacyclopentane. A. From the Hydrochloride.—A mixture of 1 ml. (0.02 mole) of 98% nitric acid and 2.5 g. (0.02 mole) of 95% acetic anhydride was prepared at −35°. To this solution at −35° during 10 min. was added 1 g. (0.005 mole) of diendomethylenetetrazacyclodecane monohydrochloride. After gradual warming to 0° during 7 hr. the system was poured into 25 g. of ice. The precipitated oil had solidified after one day and was filtered, 1.0 g. (60% on 1:2 basis), m.p. 124–127°. This crude product was heated with 10 ml. of 70% nitric acid for 4 min., then 25 ml. of water was added and the system cooled, 0.60 g., m.p. 134–134.8°.

Anal. Calcd. for $C_3H_6N_4O_4$: C, 22.2; H, 3.73; N, 34.6. Found: C, 22.5; H, 3.80; N, 34.3.

B. From the Tetranitrate.—A solution of 0.42 g. (0.0054 mole) of acetyl chloride, 0.48 ml. (0.0108 mole) of 98% nitric acid, 78.4 g. (0.73 mole) of acetic anhydride and 30 ml. (0.53 mole) of acetic acid was prepared at 2°. To this stirred system was added 22.6 g. (0.054 mole) of freshly prepared and finely ground tetranitrate salt during a 13-minute period at 4°. The thick slurry was allowed to warm to 25° during 30 min. and then was stirred for 15 hr. The system was then filtered to remove 9.2 g., m.p. 128–130° after washing with acetic acid. The filtrate and washings were poured into 150 g. of ice. The solid which separated was filtered off and water-washed, 4.8 g., m.p. 126–128°, m.m.p. with first crop not depressed. The total dry product, 14 g. (73% on 1:2 basis) was crystallized from 350 ml. of 95% ethanol, m.p. 130°. A mixture melting point with the product of procedure A was not lowered.

The molecular weight, determined ebullioscopically in benzene, averaged 155; calcd. 162. The solubility in 100 ml. of aqueous solution was found to be 0.1 g. at 20°, 0.3 g. at 44°, 0.6 g. at 60°, 1.5 g. at 80° and 4.7 g. at 100°. After boiling the compound for 60 hr. in 1% sulfuric acid 17% was decomposed to 1,2-dinitraminoethane. Dinitrodiazacyclopentane forms a eutectic, m.p. 70.5°, with 14% of trinitrotoluene. The substance is comparable with tetryl in explosive properties, since its figure of insensitiveness is 0.78 that of picric acid, while its power (Trauzl) is 1.36 that of picric acid. It decomposes without ignition at 205° but ignites at once when it is dropped on a surface at 350°. In hot 50% sulfuric acid the substance decomposes rapidly to give a quantitative yield of gas (1:2 basis) which is 94% nitrous oxide and 6% nitrogen.

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A Note on the Synthesis of Glycosides[1]

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During investigations into the correlation of the structure of glycosides[2] attempts were made to develop simplified procedures for the synthesis of certain methyl glycosides. In a previous communication the use of insoluble acid catalysts such as cation exchange resins for the preparation of methyl glycosides was described.[3] This paper is concerned with two other procedures that were investigated.

Treatment of acetyl glycosyl halides with methanolic magnesium methoxide leads directly to the formation of the corresponding glycoside The reaction proceeds rapidly since it is carried out in a homogeneous system.[4] Deacetylation proceeds at the same time. If the methyl glycoside does not separate from the reaction mixture it can be separated from magnesium bromide by reacetylation. This method was used for the synthesis of methyl β-D-glucopyranoside and methyl β-lactoside.[5]

The preparation of methyl glycosides by the Fischer method[6,7] can be simplified in certain cases by adding an inert solvent such as ethylene dichloride[8] to cause the methyl glycoside to crystallize directly from the reaction mixture. This avoids neutralization and concentration according to the customary procedure.[6,7] Methyl α-D-mannopyranoside and methyl β-L-arabopyranoside were made by this method.

Experimental

A. 1. Methyl 2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranoside.—To a solution of 2,3,4,6-tetra-*O*-acetyl α-D-glucosyl bromide (crude reaction product prepared in the usual way[9] or by the simplified method[10,11] from 20 g. of D-glucose pentaacetate in absolute methanol (200 ml.)) was added a methanolic solution of magnesium methoxide prepared by dissolving 1.0 g. of magnesium filings in absolute methanol (100 ml.).

After standing overnight the reaction mixture was evaporated to dryness *in vacuo*. In order to eliminate the magnesium bromide the residue was dissolved in acetic anhydride (100 ml.), fused sodium acetate (5.0 g.) was added and the mixture was refluxed for 10–20 minutes. The cooled reaction mixture was then poured with stirring into water (1000 ml.). When the excess acetic anhydride had decomposed the aqueous mixture was extracted twice with chloroform, the chloroform extract was washed with water, dried ($CaCl_2$) and concentrated to a small volume *in vacuo*. Petroleum ether (b.p. 30–60°) was added until turbidity was reached and the product allowed to crystallize (yield 7.2

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(1) Paper No. 3294, Scientific Journal Series, Minnesota Agricultural Experiment Station, University of Minnesota, St. Paul, Minn. From a thesis presented to the graduate faculty of the University of Minnesota in partial fulfillment of the requirements for the degree of Doctor of Philosophy by John W. Van Cleve, 1951.

(2) F. Smith and J. W. Van Cleve, THIS JOURNAL, **75**, 3091 (1955).

(3) J. E. Cadotte, F. Smith and D. Spriestersbach, *ibid.*, **74**, 1501 (1952).

(4) *Cf.* W. Koenigs and E. Knorr, *Ber.*, **34**, 957 (1901).

(5) *Cf.* F. Smith and J. W. Van Cleve, THIS JOURNAL, **74**, 1912 (1952).

(6) E. Fischer, *Ber.*, **26**, 2400 (1893); **28**, 1145 (1895).

(7) E. Bourquelot, *Ann. chim.*, **3**, 298 (1915).

(8) *Cf.* R. O. Clinton and S. C. Laskowski, THIS JOURNAL, **70**, 3135 (1948).

(9) F. J. Bates and Associates, "Polarimetry, Saccharimetry and the Sugars," U. S. Govt. Printing Office, Washington, D. C., 1942, p. 500; *cf.* B. Helferich and E. Günther, *Ber.*, **64**, 1279 (1931).

(10) M. Barczai-Martos and F. Korozy, *Nature*, **165**, 369 (1950).

(11) P. G. Scheurer and F. Smith, THIS JOURNAL, **76**, 3224 (1954).