of sodium (0.3 g.) in methanol (20 ml.) was added and the mixture allowed to stand overnight. After neutralization with carbon dioxide, the solution was evaporated to dryness and repeatedly extracted with light petroleum. The solvent was evaporated and the residue sublimed *in vacuo* yielding 1.1 g. (70%) of IX, m.p. 109°.

neo-Inositol (X).—The anhydroinositol IX (415 mg.) was heated on the steam-bath with 0.1 *N* sulfuric acid[18] (5 ml.) for three hours. The substance dissolved in a few minutes (with loss of acetone) and after about 30 minutes crystals began to separate. They were filtered and washed with water giving 160 mg. (52%) of *neo*-inositol. For analysis it was recrystallized from water. It decomposes and sublimes on slow heating but when dropped on a heated block it melts at 315°. It has no optical activity.

Anal. Calcd. for $C_6H_{12}O_6$: C, 40.0; H, 6.7. Found: C, 40.3; H, 7.2.

The hexaacetate, prepared by acetylation with sodium acetate and acetic anhydride, was crystallized from ethanol and melted at 253°.

(18) Heating with hydrochloric acid gives chlorodeoxyinositols as by-products; their presence can be shown by paper chromatography in acetone–water (8:2 v./v.).

Anal. Calcd. for $C_{18}H_{24}O_{12}$: C, 50.0; H, 5.6. Found: C, 50.3; H, 5.65.

The acid mother liquor of *neo*-inositol was mixed with an equal amount of ethanol resulting in a precipitate (6 mg.) which was shown by paper chromatography to consist of a mixture of *neo*- and (−)-inositols. The clear liquor was decanted and neutralized with barium carbonate and filtered; the filtrate was evaporated to dryness and the residue crystallized from aqueous ethanol to give 103 mg. (34%) of (−)-inositol which, after another crystallization, had m.p. 242–243°, $[\alpha]^{25}D$ −64.5 ± 2° (*c* 1.0, water); reported for (−)-inositol is the m.p. 246° and $[\alpha]D$ −65° (water).

Acknowledgments.—The authors wish to express their gratitude to Dr. G. Lindstedt, the Swedish Tanning Research Institute, Stockholm, and to Dr. R. H. Smith, The Rubber Research Institute of Malaya, Kuala Lumpur, for generous gifts of pinitol and quebrachitol, respectively. Financial assistance by the (Australian) Commonwealth Science Fund to one of us (N.K.M.) is gratefully acknowledged.

SYDNEY, AUSTRALIA

[CONTRIBUTION FROM THE DEPARTMENT OF AGRICULTURAL BIOCHEMISTRY, UNIVERSITY OF MINNESOTA]

Periodate Oxidation in the Synthesis of Some Partially Methylated Sugars[1]

BY G. W. HUFFMAN, BERTHA A. LEWIS, F. SMITH AND D. R. SPRIESTERSBACH

RECEIVED FEBRUARY 19, 1955

Cleavage of the carbon chain between positions C_1 and C_2 by periodate oxidation, under acid conditions to preserve the intermediate formyl group produced from C_1, has provided a means of synthesizing 2-*O*-methyl-D-arabinose, 2-*O*-methyl-D-threose and 2,5-di-*O*-methyl-D-arabinose from 3-*O*-methyl-D-glucose, 3-*O*-methyl-D-xylose and 3,6-di-*O*-methyl-D-glucose, respectively. Scission of C_1 from the hitherto unknown 3,5-di-*O*-methyl-D-glucose by periodate oxidation has yielded 2,4-di-*O*-methyl-D-arabinose. A similar oxidation of 1,2-*O*-isopropylidene-3-*O*-methyl-D-glucose followed by reduction and hydrolysis provides an additional route to 3-*O*-methyl-D-xylose.

Methylation studies applied to polysaccharides require partially methylated sugar derivatives as reference compounds. Many of these partially methylated sugars are incompletely characterized, some are known only in an impure state while others have never been synthesized. It is shown herein that oxidation of well-characterized partially methylated sugars or their derivatives with periodic acid provides a simple and convenient route for the synthesis of certain methylated sugars.

Cleavage of 1,2-glycols by periodic acid,[2] a reaction which proceeds rapidly to completion unless the glycol is of the fixed *trans* type,[3,4] has been utilized previously both for structural studies of simple and complex carbohydrates[5–7] and for synthetic purposes.[8]

Certain partially methylated sugars, when subjected to oxidation with periodic acid, do not consume the expected quantity of periodate.[9–11] This incomplete oxidation has been attributed to an intermediate stable formyl ester formed by preferential cleavage of the carbon chain between C_1 and C_2 without rupture of the acetal linkage. Support for this theory was forthcoming from the observation that oxidation of 3-*O*-methyl-D-glucose with periodic acid gave the well-defined 4-*O*-formyl 2-*O*-methyl-D-arabinose.[12]

By utilizing the stability of the intermediate formyl ester produced by periodate cleavage of the glycol grouping at C_1 and C_2, the following methylated sugars have been prepared: 2-*O*-methyl-D-arabinose, 2-*O*-methyl-D-threose and 2,5-di-*O*-methyl-D-arabinose from 3-*O*-methyl-D-glucose, 3-*O*-methyl-D-xylose and 3,6-di-*O*-methyl-D-glucose, respectively.

Whereas the formyl esters of some sugars were stable at room temperature, that formed from 3-*O*-methyl-D-glucose underwent hydrolysis and further cleavage of the carbon chain occurred unless the periodate oxidation was carried out in the cold. The intermediate formyl esters are sensitive to alkaline reagents for treatment of them momentarily

(1) Paper No. 3320, Scientific Journal Series, Minnesota Agricultural Experiment Station, University of Minnesota, St. Paul, Minnesota.

(2) L. Malaprade, *Bull. soc. chim.*, **43**, 683 (1928); *Compt. rend.*, **186**, 382 (1928).

(3) R. J. Dimler, H. A. Davis and G. E. Hilbert, THIS JOURNAL, **68**, 1377 (1946).

(4) B. H. Alexander, R. J. Dimler and C. L. Mehltretter, *ibid.*, **73**, 4658 (1951).

(5) E. L. Jackson and C. S. Hudson, *ibid.*, **59**, 994 (1937).

(6) M. Abdel-Akher, J. K. Cadotte, Bertha A. Lewis, R. Montgomery, F. Smith and J. W. Van Cleve, *Nature*, **171**, 474 (1953).

(7) M. Abdel-Akher, J. K. Hamilton, R. Montgomery and F. Smith, THIS JOURNAL, **74**, 4970 (1952).

(8) (a) J. C. Sowden, *ibid.*, **72**, 808 (1950); (b) **73**, 5496 (1951).

(9) T. G. Halsall, E. L. Hirst and J. K. N. Jones, *J. Chem. Soc.*, 1427 (1947).

(10) K. H. Meyer and P. Rathgeb, *Helv. Chim. Acta*, **32**, 1102 (1949).

(11) G. D. Greville and D. H. Northcote, *J. Chem. Soc.*, 1945 (1952).

(12) G. R. Barker and D. C. C. Smith, *Chemistry and Industry*, 1035 (1952).

with dilute alkali readily effected saponification and liberated the free sugars.

By periodate oxidation 2,4-di-*O*-methyl-D-arabinose has been obtained from 3,5-di-*O*-methyl-D-glucose. Similarly oxidation of 1,2-*O*-isopropylidene-3-*O*-methyl-D-glucofuranose followed by reduction of the aldehydic group generated at C_5 with sodium borohydride furnished 1,2-*O*-isopropylidene-3-*O*-methyl-D-xylofuranose from which 3-*O*-methyl-D-xylose was derived by hydrolysis. This procedure is similar to that used previously for the preparation of 1-C^{14}-D-xylose from 1,2-*O*-isopropylidene-1-C^{14}-D-glucose.[8b]

The previously unknown 3,5-di-*O*-methyl-D-glucose was synthesized by tritylation of 1,2-*O*-isopropylidene-3-*O*-methyl-D-glucofuranose and subsequent methylation followed by removal of the trityl and isopropylidene groups. As a result of the steric protection provided by the trityl group it was difficult to introduce a methyl group into the OH group at C_5 and subsequent removal of the isopropylidene and trityl groups after the methylation gave a mixture of 3,5-di-*O*-methyl-D-glucose and 3-*O*-methyl-D-glucose.

The 3,5-di-*O*-methyl-D-glucose was characterized, after oxidation with bromine, as the crystalline amide of 3,5-di-*O*-methyl-D-gluconic acid. The structure was further confirmed by periodate oxidation of the dimethylglucose. The 2,4-di-*O*-methyl-D-arabinose so formed which was identified as its anilide proved to be identical with a specimen previously obtained by methylation and hydrolysis of 3-*O*-(D-galactopyranosyl)-D-arabopyranose.[13]

Experimental

A. 3,5-Di-*O*-methyl-D-glucose.—1,2:5,6-Di-*O*-isopropylidene-3-*O*-methyl-D-glucofuranose (29 g.) obtained by methylation of 1,2:5,6-di-*O*-isopropylidene-D-glucose[14] was converted to 1,2-*O*-isopropylidene-3-*O*-methyl-D-glucofuranose, $n^{25}D$ 1.4680, in 91% yield by hydrolyzing with aqueous acetic acid.[15] To a solution of 1,2-*O*-isopropylidene-3-*O*-methyl-D-glucofuranose (6.2 g.) in dry pyridine (50 ml.) was added triphenylmethyl chloride (8.2 g.) and the solution was kept at room temperature in a desiccator over phosphorus pentoxide for 2 days. Water was added to the pyridine solution to incipient turbidity and after one hour the solution was poured into water with stirring. The 1,2-*O*-isopropylidene-3-*O*-methyl-6-*O*-trityl-D-glucofuranose which separated as an oil was extracted with chloroform; the chloroform solution was washed with water, dried over anhydrous magnesium sulfate and concentrated *in vacuo* to a sirup (7 g.) which failed to crystallize. The trityl derivative was dissolved in acetone (40 ml.) and methylated by stirring with powdered sodium hydroxide (1.8 g.) for 0.5 hours after which methyl sulfate (2.1 ml.) was added dropwise over a period of 1.5 hours at 40–45°. After the addition of methyl sulfate the bath temperature was maintained at 50° for 1.5 hours. The reaction mixture was cooled, diluted with water and extracted with chloroform. The chloroform extract was washed until free from alkali, dried over calcium chloride and concentrated *in vacuo* to a sirup. The incompletely methylated sirup (4 g.) was subjected to two Purdie methylations by dissolving in acetone (5 ml.) and methyl iodide (15 ml.) and adding silver oxide (5 g.) to the refluxing solution over a period of 3–4 hours. The cooled solution was filtered and the residue washed with methanol. The combined filtrate and washings were concentrated *in vacuo* to a sirup which was dissolved in chloroform, washed three times with water, dried over magnesium sulfate and concentrated to a sirup. The sirup, which was a mixture of 1,2-*O*-isopropylidene-3,5-di-*O*-methyl-6-*O*-trityl-D-glucofuranose and 1,2-*O*-isopropylidene-3-*O*-methyl-6-*O*-trityl-D-glucofuranose, was converted to the free methylated sugars[16] by treating for 1 minute an ice-cold solution of the sirupy mixture in glacial acetic acid (12 ml.) with a cold solution (3 ml.) of glacial acetic acid saturated with hydrogen bromide. Ice-cold water (25 ml.) was added, the precipitated trityl bromide filtered off and the solution heated at 80° for 1.5 hours. The bromide ions were precipitated with silver oxide, the solution was filtered and saturated with hydrogen sulfide, filtered and concentrated *in vacuo* to a sirup. The 3,5-di-*O*-methyl-D-glucose (0.98 g.), obtained pure by separation from 3-*O*-methyl-D-glucose on a hydrocellulose–cellulose column[17] using methyl ethyl ketone–water azeotrope as the developing solvent, showed $[\alpha]^{24}D$ −21.3° in water (*c* 3.0) and R_f, 0.33 (methyl ethyl ketone–water). *Anal.* Calcd. for $C_8H_{16}O_6$: $-OCH_3$, 29.8. Found: $-OCH_3$, 30.4.

3,5-Di-*O*-methyl-D-gluconamide.—A solution of 3,5-di-*O*-methyl-D-glucose (0.090 g.) in water (1 ml.) was oxidized with bromine (0.1 ml.) at room temperature for 4 days. The solution was aerated to remove excess bromine, neutralized with silver oxide, filtered, saturated with hydrogen sulfide, filtered and concentrated *in vacuo* to a sirup. The sirup was heated *in vacuo* (0.005 mm.) at 100° for 3 hours to convert the 3,5-di-*O*-methyl-D-gluconic acid to the γ-lactone (0.074 g.). The crystalline 3,5-di-*O*-methyl-D-gluconamide, obtained by treating the lactone with methanolic ammonia for 2 days at 5° followed by concentration *in vacuo*, had m.p. 150–152° and $[\alpha]^{23}D$ +29.0° in methanol (*c* 0.7), after recrystallization from ethanol. *Anal.* Calcd. for $C_8H_{17}O_6N$: C, 43.1; H, 7.7; N, 6.3. Found: C, 42.9; H, 7.8; N, 5.9.

B. 2,4-Di-*O*-methyl-D-arabinose.—3,5-Di-*O*-methyl-D-glucose (0.187 g.) was oxidized with 0.1 *N* periodic acid (50 ml.) at 5° for 3 hours at which time the periodate consumption was constant at 0.96 mole periodate per mole of sugar. The solution was treated with dilute barium hydroxide until slightly alkaline and the excess alkali was neutralized with carbon dioxide. After filtering the solution it was concentrated *in vacuo* to dryness and the residue extracted with absolute ethanol. The sirup obtained by removal of the ethanol was deionized by passing an aqueous solution of it over Amberlite IR-120[18] and Duolite A-4[19] ion-exchange resins. Concentration of the aqueous solution yielded chromatographically pure 2,4-di-*O*-methyl-D-arabinose in 90% yield, $[\alpha]^{21}D$ −108° in methanol (*c* 2.4)[20]; R_f, 0.26 (methyl ethyl ketone–water). The 2,4-di-*O*-methyl-D-arabinose (0.072 g.) was converted to the anilide by refluxing in ethanol (3 ml.) containing aniline (80 mg.) for 2.5 hours. On concentration of the solution *in vacuo*, the anilide crystallized spontaneously. Recrystallization from ethyl acetate yielded 2,4-di-*O*-methyl-D-arabinose anilide[13] (yield 0.071 g.), $[\alpha]^{21}D$ +30° in methanol (*c* 1.0) changing in 19 hours to −58°, m.p. and mixed m.p. 139–142°.[13] *Anal.* Calcd. for $C_{13}H_{19}O_4N$: C, 61.7; H, 7.6. Found: C, 61.7; H, 7.7.

C. 3-*O*-Methyl-D-xylose.—When 1,2-*O*-isopropylidene-3-*O*-methyl-D-glucofuranose (2.01 g.) was treated with 0.1 *N* periodic acid (250 ml.) at room temperature, the periodate consumption reached a constant value of 1.02 moles per mole of sugar in 5 hours. The barium salts precipitated upon neutralization with barium carbonate were removed by centrifugation and sodium borohydride (0.3 g.) was added to effect reduction of the aldehydic group formed at C_5; little or no change in rotation occurred during the reduction. The aqueous solution was extracted six times with chloroform, the chloroform extract was washed with water, dried over magnesium sulfate, and concentrated *in vacuo* to give 1,2-*O*-isopropylidene-3-*O*-methyl-D-xylofuranose as a colorless liquid (1.45 g.). The 3-*O*-methyl-D-xylose was obtained from the latter by heating a solution of it in water

(13) F. Smith, *J. Chem. Soc.*, 744 (1939).

(14) W. L. Glen, G. S. Myers and G. A. Grant, *ibid.*, 2568 (1951).

(15) K. Freudenberg, W. Dürr and H. v. Hochstetter, *Ber.*, **61**, 1735 (1928).

(16) *Cf.* P. A. Levene and A. L. Raymond, *J. Biol. Chem.*, **102**, 331 (1933).

(17) J. D. Geerdes, Bertha A. Lewis, Rex Montgomery and Fred Smith, *Anal. Chem.*, **26**, 264 (1954).

(18) A product of Rohm and Haas Co., Philadelphia, Pa.

(19) A product of Chemical Process Co., Redwood City, Calif.

(20) A rotation of $[\alpha]D$ −37.8° (methanol) has been quoted erroneously for this compound (R. A. Laidlaw and E. G. V. Percival, *Advances in Carbohydrate Chem.*, **7**, 30 (1952)).

(50 ml.) with Dowex 50[21] cation-exchange resin (1 g.) on a boiling water-bath for 4 hours. Removal of the resin and concentration of the solution gave crystalline 3-*O*-methyl-D-xylose which had m.p. 102–103° and $[\alpha]^{22}D$ +15.5° in water (*c* 2.0), after recrystallization from ethyl acetate (yield 0.9 g.).[8b]

D. 2-*O*-Methyl-D-threose.—When 3-*O*-methyl-D-xylose (0.213 g.) was oxidized with 0.1 *N* periodic acid (50 ml.) at 5°, the periodate consumption reached 1.05 moles periodate per mole of sugar in 6 hours and remained constant at this value for 3 hours. The reaction mixture was neutralized ($Ba(OH)_2$) and worked up in the usual way yielding chromatographically pure 2-*O*-methyl-D-threose (yield 65%), R_t, 0.58 (methyl ethyl ketone–water azeotrope), $[\alpha]^{23}D$ −28° in water (*c* 2.0).

Characterization of 2-*O*-Methyl-D-threose. (a) Conversion to D-Threosazone (D-Erythrosazone).—A solution of 2-*O*-methyl-D-threose (0.014 g.) in water (1.5 ml.) and acetic acid (0.2 ml.) was treated with phenylhydrazine (0.15 g.) at 80° for 1.5 hours. On cooling the yellow crystalline threose (erythrose) phenylosazone separated, m.p. and mixed m.p. 165–170°[22] after recrystallization from benzene.

(b) Formation of 2-*O*-Methyl-D-threonamide.—A solution of 2-*O*-methyl-D-threose (0.050 g.) in water (1 ml.) was oxidized with bromine (0.1 ml.) at room temperature for 48 hours at which time a chromatogram (methyl ethyl ketone–water) revealed that no 2-*O*-methyl-D-threose remained unoxidized. The 2-*O*-methyl-D-threono-γ-lactone isolated in the manner described above for 3,5-di-*O*-methyl-D-gluconoγ-lactone was distilled, b.p. 85–90° (bath temp.), 0.005 mm., $[\alpha]^{23}D$ −79.2° in methanol (*c* 0.5). Treatment of the lactone with methanolic ammonia for 2 days at 5° followed by removal of solvent furnished 2-*O*-methyl-D-threonamide, m.p. 105–106°, $[\alpha]^{22}D$ −94° in methanol (*c* 1) (after recrystallization from ethanol–petroleum ether). Values of m.p. 105–107°, $[\alpha]^{21}D$ +97.8° in methanol have been reported for 2-*O*-methyl-L-threonamide and for 2-*O*-methyl-L-threono-γ-lactone a rotation of $[\alpha]D$ +78.8° in methanol is recorded.[23] *Anal.* Calcd. for $C_5H_{11}O_4N$: N, 9.4. Found: N, 9.5.

E. 2,5-Di-*O*-methyl-D-arabinose.—Crystalline 3,6-di-*O*-methyl-D-glucose, m.p. 122°, $[\alpha]^{20}D$ +62.7° in water (*c* 1), (0.5 g.), prepared according to the method of Bell[24] was oxidized with 0.1 *N* periodic acid (100 ml.) at 20°. In 3 hours the consumption of periodate reached 1 mole per mole of di-*O*-methylglucose and it remained constant for 2 hours. The sirupy 2,5-di-*O*-methyl-D-arabinose (yield 87%), isolated as described above, showed $[\alpha]^{21}D$ +21°[25] in water (*c* 2.0). *Anal.* Calcd. for $C_7H_{14}O_5$: $-OCH_3$, 34.8. Found: $-OCH_3$, 34.6.

2,5-Di-*O*-methyl-D-arabono-γ-lactone.—Oxidation of 2,5-di-*O*-methyl-D-arabinose (0.03 g.) with bromine (0.1 ml.) in water (1 ml.) for 60 hours in the usual way gave 2,5-di-*O*-methyl-D-arabono-γ-lactone, b.p. (bath temp.) 105° (0.001 mm.), m.p. 58–59° and $[\alpha]^{20}D$ +59.6° in water (*c* 1.0) after recrystallization from ether–petroleum ether. These constants agree with those (m.p. 60°, $[\alpha]D$ −60° in water) reported for the L-isomer.[26]

F. 2-*O*-Methyl-D-arabinose.[12]—Crystalline 3-*O*-methyl-D-glucose (0.500 g.) obtained by hydrolysis of 1,2:5,6-di-*O*-isopropylidene-3-*O*-methyl-D-glucofuranose[14] was oxidized with 0.1 *N* periodic acid (100 ml.) at 5°. In 5 hours the periodate consumption reached 1.05 moles periodate per mole of sugar and it remained constant for 2 hours. Isolation in the usual manner yielded 2-*O*-methyl-D-arabinose (yield 85%) $[\alpha]^{23}D$ −87° in water (*c* 2.5), which was shown by chromatography to contain a trace of 3-*O*-methyl-D-glucose.

3,4-*O*-Isopropylidene-2-*O*-methyl-D-arabinose.—To a solution of 2-*O*-methyl-D-arabinose (0.90 g.) in acetone (60 ml.) was added sulfuric acid (0.25 ml.). After 12 hours, the solution was neutralized with gaseous ammonia, filtered and concentrated *in vacuo* to a sirup which upon distillation in high vacuum gave crystalline 3,4-*O*-isopropylidene-2-*O*-methyl-D-arabinose (0.76 g.), m.p. 121° and $[\alpha]^{23}D$ −121° in methanol (*c* 3.0) after recrystallization from acetone–ether–petroleum ether. The values reported for 3,4-*O*-isopropylidene-2-*O*-methyl-L-arabinose[27] are m.p. 116–118° and $[\alpha]^{18}D$ +124.5° in methanol. *Anal.* Calcd. for $C_9H_{16}O_5$: C, 52.9; H, 7.9. Found: C, 53.0; H, 8.1.

Treatment of the 3,4-*O*-isopropylidene-2-*O*-methyl-D-arabinose with ethanolic aniline in the usual way yielded the corresponding anilide m.p. 135° (after recrystallization from ethanol).

(21) A product of Dow Chemical Co., Midland, Michigan.

(22) R. C. Hockett, THIS JOURNAL, **57**, 2260 (1935).

(23) R. Gätzi and T. Reichstein, *Helv. Chim. Acta*, **20**, 1298 (1937).

(24) D. J. Bell, *J. Chem. Soc.*, 1553 (1936).

(25) A rotation of $[\alpha]D$ +60° (water) has erroneously been quoted for 2,5-di-*O*-methyl-L-arabinose (R. A. Laidlaw and E. G. V. Percival, *Advances in Carbohydrate Chem.*, **7**, 31 (1952)).

(26) F. Smith, *J. Chem. Soc.*, 1035 (1940).

(27) Mary Ann Oldham and J. Honeyman, *ibid.*, 986 (1946).

St. Paul, Minnesota

[Contribution from the Department of Biochemistry, University of California, Berkeley]

The Degradation of Ketoses by the Disulfone Method[1]

By D. L. MacDonald and Hermann O. L. Fischer

Received March 7, 1955

The method of degrading aldoses utilizing the disulfones derived from the mercaptals has been applied to two ketoses, namely, D-fructose and *myo*inosose-2. The degradation proceeds in the anticipated manner, with the splitting of the carbon chain on both sides of the carbon atom bearing the two sulfone groups.

Up to the present, there have been described several methods for the opening of the cyclohexane ring of the inositols. The methods used lead to the production of either dialdehydes or dicarboxylic acids and they have been used frequently for the determination of the configuration of various inositols. For instance, in the determination of the configuration of *myo*inositol, Dangschat[2] cleaved a tetraacetyl *myo*inositol with lead tetraacetate to produce a dialdehyde which was oxidized subsequently to a dicarboxylic acid. More recently, Ballou and Fischer[3] have prepared derivatives of D-*manno*-hexodialdose by oxidation of diisopropylidene-D-inositol with lead tetraacetate. Another method of opening the ring was utilized by Posternak in his studies on cyclitols; for instance,[4] by oxidation of *myo*-inosose-2 with alkaline permanganate, he obtained hexaric acids, a knowledge of the structure of which enabled him to deduce the configuration of *myo*inositol.

Recently, we have described a method of degrading aldose sugars and in the present communication it is shown that it can be utilized as another means

(1) This work was supported by a grant from the Eli Lilly Company, and a preliminary report of the work appeared in Abstracts Papers, *Am. Chem. Soc.*, **126**, 9D (1954).

(2) G. Dangschat, *Naturwissenschaften*, **30**, 146 (1942).

(3) C. E. Ballou and H. O. L. Fischer, THIS JOURNAL, **75**, 3673 (1953).

(4) T. Posternak, *Helv. Chim. Acta*, **25**, 746 (1942).