A more probable course would involve the replacement of hydrogen in the corresponding oximes and could arise as follows.

$$(CF_3CHF)_2Hg \xrightarrow{NOCl} CF_3CHFNO \rightleftharpoons CF_3CF{=}NOH$$

$$\downarrow Cl_2 \text{ or } NOCl$$

$$CF_3CFClNO$$

$$CF_2{=}CHF + NOCl \longrightarrow CF_2ClCHFNO \rightleftharpoons CF_2ClCF{=}NOH$$

$$\downarrow Cl_2 \text{ or } NOCl$$

$$CF_2ClCFClNO$$

In every reaction of a fluoroalkylmercury compound with nitrosyl chloride that took place, except with bisheptafluoroisopropylmercury, some of the corresponding dichlorofluoroalkane was obtained. These

$$(CF_3CFCl)_2Hg \xrightarrow{NOCl} CF_3CFCl_2\ (5\%)$$

$$(CF_3CCl_2)_2Hg \xrightarrow{NOCl} CF_3CCl_3\ (37\%)$$

compounds could arise either from the displacement of mercury by chlorine or from the decomposition of the resulting α-chloronitroso compound by a free-radical process.[9] Since the last step of the reaction is essentially irreversible, the extent to which the more highly chlorinated product is formed depends on the stability of the free radical. These are $CF_3CCl_2\cdot$ > $CF_3CFCl\cdot$ > $(CF_3)_2CF\cdot$. Since the bisheptafluoroisopropylmercury gave no chloride in the presence of nitrosyl chloride and the other compounds gave polychlorides in amounts proportional to the radical stabilities, the radical process probably operates in this reaction.

$$CF_3CCl_2NO \longrightarrow CF_3CCl_2\cdot \xrightarrow[NOCl]{Cl_2 \text{ or}} CF_3CCl_3$$

Experimental[10]

Reactions of Alkylmercury Compounds with Nitrosyl Chloride.—The general procedure used in preparing the nitroso compounds is as follows. Dimethylformamide and the mercury alkyl were added to a 250-ml., three-necked flask, fitted with a magnetic stirrer, a gas inlet tube, and a take-off leading to a Dry Ice–acetone-cooled condenser. Nitrosyl chloride was bubbled into the solution until it was dark red. The reaction proceeded very slowly, normally requiring from 3 to 4 days. More nitrosyl chloride was added from time to time when the color of the solution had changed from dark red to green. Most of the nitroso compound passed into the Dry Ice trap as it was formed. The flask was swept with nitrogen at the end of the reaction. The product was washed twice with sodium bicarbonate to remove oxides of nitrogen and was then purified by passing it through a preparative scale vapor phase chromatographic column. The 2.5 cm. × 250 cm. column was packed with Celite with dinonyl phthalate used as the liquid phase and was operated at room temperature. This operation was necessary because the boiling point of the major impurity is very nearly the same as that of the nitroso compound. The results are shown in Table I.

TABLE I

PRODUCTS FROM THE REACTION OF FLUOROALKYLMERCURY COMPOUNDS WITH NITROSYL CHLORIDE

Mercury compound formula	Mole	Products, %	
$(CF_3CFCl)_2Hg$	0.095	$CF_3CFClNO$,[a] 79	CF_3CFCl_2,[b] 5
$[(CF_3)_2CF]_2Hg$	0.037	$(CF_3)_2CFNO$, 64	
$(CF_3CHF)_2Hg$	0.057	$CF_3CFClNO$,[c] 14	CF_3CFCl_2[b] CF_3CHFCl[d]
$(CF_3CCl_2)_2Hg$	0.10	CF_3CCl_2NO,[e] 28	CF_3CCl_3,[b] 14

[a] The n.m.r. F^{19} spectrum confirmed the structure $CF_3CFClNO$ which had a b.p. of −5° determined isoteniscopically. *Anal.* Calcd. for C_2ONClF_4: N, 8.46; Cl, 21.43; mol. wt., 165.5. Found: N, 7.65; Cl, 20.63; mol. wt., 165. [b] Identified by comparison of its infrared spectrum with an authentic sample and by its n.m.r. spectrum. [c] The boiling point of this material is −5° and its infrared spectrum was found to be identical with that of an authentic sample of $CF_3CFClNO$. [d] Identified by its n.m.r. and infrared spectra. [e] B.p. 36°, determined isoteniscopically. *Anal.* Calcd. for $C_2ONCl_2F_3$: Cl, 38.96. Found: Cl, 38.60.

(10) Analyses were by Galbraith Laboratories, Knoxville, Tenn.

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1-Deoxy-1-(methylnitrosamino)pentitols[1]

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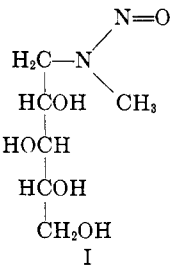
The synthesis of 1,4-dideoxy-1,4-bis(methylnitrosamino)erythritol and the corresponding 1,6-disubstituted mannitol has recently been reported.[3a] Interest in this type of compound is due to the postulate[3b] that alkyl N-nitroso compounds are metabolized to diazoalkanes which can alkylate essential cell constituents and result in an altered metabolic pattern.

The isolation of a small proportion of 1-deoxy-1-(methylnitrosamino)-D-xylitol during the synthesis of the 1,4-anhydrides of D-iditol and D-gulitol[4] led to the present study. The synthesis of the anhydrides involved nitrous acid deamination of the 1-amino-1-deoxyalditols derived from the condensation of nitromethane[5] with D-xylose. The nitrosamine (I) is the



I

product expected from the treatment of a methylglycamine (1-deoxy-1-methylaminoalditol) with nitrous acid[6] and the methylglycamine could have arisen from the condensation of nitromethane, or a reduction product thereof, with D-xylose so as to have resulted in the

(1) Supported by a grant from the Atlas Chemical Industries, Wilmington, Del.

(2) Department of Biochemistry, State University of Iowa, Iowa City, Iowa.

(3) (a) F. Berger, S. S. Brown, C. L. Leese, G. M. Timmis, and R. Wade, *J. Chem. Soc.*, 846 (1963); (b) D. F. Heath, *Nature*, **192**, 170 (1961).

(4) R. Barker, *J. Org. Chem.*, **29**, 869 (1964).

(5) J. C. Sowden and H. O. L. Fischer, *J. Am. Chem. Soc.*, **69**, 1963 (1947).

(6) A. I. Vogel, "Practical Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1957, p. 426.

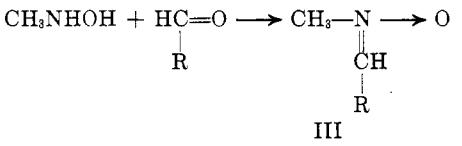
formation of a new C–N bond rather than the usual C–C bond.

The reductive amination of reducing sugars in the presence of amines,[7] ammonia,[8] and hydrazine[9] has been reported, as has the reduction of sugar oximes.[10] Since, in the preparation from which I was isolated,[4] a reduction was performed in which one would expect there to be small amounts of reducing sugar (D-xylose) and nitromethane as contaminants, a mixture of D-xylose and nitromethane was hydrogenated over platinum black in an aqueous acetic acid medium. The product of the hydrogenation was treated with nitrous acid and from that reaction I was isolated in high yield (70–80% based on D-xylose).

Similar yields of the corresponding products from D-ribose, D-lyxose, and D-arabinose were obtained using the same procedure.

Nitromethane does not appear to condense with reducing sugars under acidic conditions; therefore, the condensation probably involves a reduction product of nitromethane which is formed *in situ*. The final reduction product of nitromethane, methylamine, under the conditions used in the reduction does not give an appreciable yield of 1-deoxy-1-methylamino-D-xylitol (II). The yield of II after a greatly extended period of reduction was less than 20%. This finding is interpreted as indicating that a different condensation product is formed and reduced in the two cases.

The product of the second step in the reduction of nitromethane is probably methylhydroxylamine. Under acidic conditions the latter would condense with an aldehyde to form a nitrone (III) which on further reduction would form a methylamine derivative such as II.



III

In support of this hypothesis is the finding that, whereas a mixture of hydroxylamine and D-xylose is reduced to give a high yield of a basic nitrogenous derivative which can be deaminated with nitrous acid with the formation of 1,4-anhydro-D-xylitol, the substitution of ammonia for hydroxylamine gives essentially no condensation product.

The nitroso compounds derived from the pentoses are readily crystallizable, slightly yellow compounds. They consume 3 molar equiv. of periodate with the release of 2 molar equiv. of formic acid and 1 of formaldehyde. They give a typical Liebermann nitroso test. They have absorption maxima at 292 mμ and molar extinction coefficients of 27 ± 1. They can be reduced readily over platinum to the corresponding secondary amine.

Preliminary testing data from the Cancer Chemotherapy National Service Center indicates that the compounds described here are neither carcinostatic nor toxic.

(7) F. Kagen, M. A. Rebenstorf, and R. V. Heinzehman, *J. Am. Chem. Soc.*, **79**, 3541 (1957).

(8) F. W. Holly, E. W. Peel, R. Mozingo, and K. Folkers, *ibid.*, **72**, 5416 (1950).

(9) R. U. Lemieux, U. S. Patent 2,830,983 (1958); *Chem. Abstr.*, **52**, 14,668 (1958).

(10) L. Maquenne and E. Roux, *Compt. rend.*, **132**, 980 (1901).

Experimental[11]

1-Deoxy-1-(methylnitrosamino)-D-xylitol.[12]—To a solution of 10 g. (66 mmoles) of D-xylose and 10 ml. (185 mmoles) of nitromethane in 200 ml. of 25% aqueous acetic acid in a pressure bottle was added 1 g. of platinum oxide. The air in the system was displaced with hydrogen to a pressure of 30 lb.[13] and the bottle was shaken vigorously. The hydrogen uptake was complete in 24 hr. at which time 14.0 l. (0.60 mole) had been taken up. The catalyst was removed by filtration and washed with water. The combined filtrates were concentrated to dryness *in vacuo* at 60°. The residue was taken up in water and passed over a column containing 200 ml. of IR 120 (H^+). The column was washed until the eluate was neutral. Concentration of this acidic eluate gave 1.1 g. of a mixture of D-xylose and xylitol (determined by chromatography).

The column was then eluted at the rate of 5 ml. per minute[14] with 11.2% aqueous ammonia. The first 300 ml. of alkaline eluate was collected and concentrated *in vacuo* at 40° to give 8.6 g. of a slightly yellow sirup which was dissolved in 200 ml. of 25% aqueous acetic acid and 7 g. of sodium nitrite added. After 4 hr. the reaction was boiled to remove the excess nitrous acid, and then concentrated at 60° *in vacuo*. The residue was taken up in water, and after deionization with IR 120 (H^+) and IR 45 a pale yellow solution was obtained. Concentration *in vacuo* gave 8.0 g. of crystalline material which was taken up in hot isopropyl alcohol (50 ml). On cooling 7.4 g. of pale yellow crystals was obtained with m.p. 120–121°. A second crop of 0.8 g. was obtained from the mother liquors. Recrystallization from the same solvent gave 6.3 g. of material, m.p. 121–122°, $[\alpha]_D$ −16.5° (*c* 3, water), and mol. wt. 193 ± 2 (by osmometry).

Anal. Calcd. for $C_6H_{14}N_2O_5$ (194.2): C, 37.1; H, 7.28; N, 14.45. Found: C, 36.9; H, 7.39; N, 14.19.

Similar yields were obtained when D-xylose, D-arabinose, and D-ribose were used instead of D-xylose. The product from the D-ribose preparation was recrystallized from ethyl acetate containing a small proportion of methanol.

The derivatives had the properties shown in Table I.

TABLE I

1-Deoxy-1-(methylnitrosamino)-	M.p., °C.	$[\alpha]^{25}D$ (*c* 3, water)	Analysis, % C	H	N
D-ribitol	85–87	−17.2°	37.0	7.46	14.20
D-lyxitol	102–103	+ 3.7°	36.9	7.18	14.41
D-arabitol	142–144	+16.5°	37.1	7.19	14.63

(11) Melting points are corrected. Paper chromatograms (descending) were run on Whatman 31 with butanone–water (25:2 v./v.).

(12) The assumption is made that the configuration of the starting material is retained in the product.

(13) The reaction proceeds equally well at atmospheric pressure.

(14) The column must be eluted slowly to allow time for the heat of reaction of the ammonia with the resin to dissipate.

The Assignment of Configurations to Three Aminodeoxyheptulosans by Proton Magnetic Resonance

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In a recent communication,[1] the syntheses of three stereoisomeric 2,7-anhydro-4-nitro-4-deoxy-β-D-heptulopyranoses and of their reduction products, the corresponding amine hydrochlorides, was described. On the basis of experiences derived from analogous syntheses, it was assumed that the new compounds bear

(1) H. H. Baer, *J. Org. Chem.*, **28**, 1287 (1963).