in vacuo and the residue was triturated with several portions of dry ether then maintained at 1 mm., leaving 0.75 g. (52%) of a hygroscopic, nitroprusside-positive foam which darkened on standing; λ_{max}^{film} 3.0 (OH, NH), 3.90 (SH), and 6.0–6.1 μ (amide C═O).

Anal. Calcd. for $C_{11}H_{19}NO_6S$: C, 47.6; H, 6.91; N, 5.05; S, 11.6. Found: C, 45.7; H, 6.93; N, 5.60; S, 11.8.

6-Acetamido-1,2,3,4-tetra-O-acetyl-6-deoxy-L-idothiapyranose (XII).—The mercaptide (XIV), 4.23 g. (5.40 mmoles), suspended in 40 ml. of 0.1 *N* hydrochloric acid, was treated with hydrogen sulfide as described for the preparation of IX. After the filtration through Celite, the filtrate was stirred at room temperature for 1.5 hr., then neutralized, and evaporated, yielding 0.75 g. of a foam that gave a positive reducing sugar test and a positive nitroprusside test; its infrared spectrum indicated the presence of the isopropylidene group, however. The foam was stirred in 0.1 *N* hydrochloric acid overnight, then neutralized, and evaporated, giving 0.53 g. of a glass whose n.m.r. spectrum in deuterium oxide showed the presence of about 60–70% of the original isopropylidene group. Finally, the material in 20 ml. of 0.5 *N* hydrochloric acid was stirred at 40–45° for 3.5 hr., then neutralized, and evaporated, yielding 0.41 g. of sirup whose n.m.r. spectrum showed the essential absence of the isopropylidene group.

The sirup, 0.35 g., was treated with 5 ml. of dry pyridine and the solution was decanted from some insoluble material, chilled to 0°, and 5 ml. of acetic anhydride was added. The mixture was maintained at 5° for 18 hr. and at room temperature for 2 hr., then was poured into 50 ml. of ice–water. The solution was neutralized with solid sodium carbonate, and extracted with two 20-ml. portions of dichloromethane; the extracts were washed with 20 ml. of water and dried. Evaporation left 0.26 g. of yellow sirup which crystallized on standing. It was recrystallized three times from benzene–petroleum ether (b.p. 30–60°), affording 0.065 g. of crystals, m.p. 165–166°; $[\alpha]^{24}$ +54.5° (1%); λ_{max}^{Nujol} 2.99, 3.02 and 6.42 (NH), and 5.68 (O-acetyl C═O), 6.02 μ (amide C═O); there was no appreciable absorption near 5.90 μ, suggestive of an S-acetyl carbonyl, nor near 7.40 μ, suggestive of the methyl group of the S-acetate. The n.m.r. spectrum showed absorptions at γ 2.71 (benzene solvent, 0.36 protons), 3.85 (C-1 doublet, J = 3.5 c.p.s.), 7.83, 7.91, 7.96, and 8.01 (CH_3CO protons totaling 15 protons).

Anal. Calcd. for $C_{16}H_{23}NO_9S \cdot 0.06C_6H_6$: C, 47.9; H, 5.74; N, 3.42; S, 7.84. Found: C, 48.1; H, 5.87; N, 3.45; S, 7.60.

The mother liquors from the recrystallizations were combined and evaporated *in vacuo* leaving a sirup, $[\alpha]^{25}$ −29.5° (1.1%), whose infrared spectrum was similar to that of the crystalline solid and demonstrated the same functional groups.

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2-Deoxy Sugars. VII. 2-Deoxy-D-allose (2-Deoxy-D-*ribo*-hexose) *via* the Fischer–Sowden Nitromethane Synthesis[1]

W. WERNER ZORBACH[2] AND ABRAHAM P. OLLAPALLY[3]

Department of Chemistry, Georgetown University, Washington 7, D. C.

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Condensation of nitromethane with D-ribose (**1**) leads to a sirupy mixture of the nitrohexitols (**2** and **3**), which on acetylation yielded the corresponding epimeric acetylated derivatives **4** and **5**, the latter of which was crystalline. Both **4** and **5** were separately deacetylated by acid hydrolysis to regenerate the nitrohexitols (**2** and **3**), each of which underwent the Nef reaction to give D-allose (**6**) and D-altrose (**7**), respectively, thus establishing the structure of the crystalline acetylated nitrohexitol (**5**) as 2,3,4,5,6-penta-*O*-acetyl-1-deoxy-1-nitro-D-altritol. Elimination of a molecule of acetic acid from **5** gave the acetylated nitrohexene (**8**), which underwent reduction of the double bond to give the sirupy 3,4,5,6-tetra-*O*-acetyl-1,2-dideoxy-1-nitro-D-*ribo*-hexitol (**9**). Alkaline hydrolysis of **9**, followed by the Nef reaction, gave 2-deoxy-D-allose (2-deoxy-D-*ribo*-hexose) (**11**) in 20% yield. Alternately, the acetylated deoxynitrohexitol (**9**) could be deacetylated by aqueous acid giving crystalline 1,2-dideoxy-1-nitro-D-*ribo*-hexitol (**10**), which underwent the Nef reaction to give 2-deoxy-D-allose (**11**) in 38% yield. Yields of **11** by both the alkaline and acid procedure are based on the hexene (**8**).

2-Deoxy-D-allose (2-deoxy-D-*ribo*-hexose) (**11**) has not been reported to occur naturally, but may be obtained by the hydrolysis of methyl 4,6-*O*-benzylidene-2-deoxy-α-D-*ribo*-hexoside[4] for which an improved preparation in four steps, starting with methyl α-D-glucopyranoside, has been reported.[5] Our interest in preparing both cardenolides[6] and nucleosides containing as the carbohydrate component 2-deoxy-D-allopyranose (2-deoxy-D-*ribo*-hexopyranose) prompted us to investigate an alternate and perhaps more economical procedure for synthesizing the hexose (**11**).

In a variation of their nitromethane synthesis for lengthening the carbon chain of aldoses, Sowden and Fischer described[7] a general method for producing 2-deoxy sugars, and were successful in converting D-arabinose to 2-deoxy-D-*arabino*-hexose (2-deoxyglucose). In the same paper D-ribose (**1**) was treated similarly; in this case, however, the synthesis was not carried beyond the preparation and isolation of the intermediary 3,4,5,6-tetra-*O*-acetyl-1-nitro-D-*ribo*-hexene-1 (**8**). Our own work, which is presently described, is concerned with a re-examination of the conversion of D-ribose (**1**) to the acetylated hexene (**8**) as well as with the transformation of the latter to 2-deoxy-D-allose (**11**).

Condensation of D-ribose (**1**) with nitromethane and removal of the sodium from the sodium salts of the nitro alcohols by an ion-exchange resin gave a sirupy mixture of the free, epimeric nitro alcohols **2** and **3**, from which neither epimer could be obtained in crystalline form. Whereas Sowden and Fischer, on acetylating the sirup containing **2** and **3**, obtained only a sirupy mixture of the acetylated nitro alcohols **4** and **5**[7] we were able to secure crystalline 2,3,4,5,6-penta-*O*-acetyl-1-deoxy-1-nitro-D-altritol (**5**) in 19% yield based on D-ribose (**1**). In an effort to determine

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(2) To whom all inquiries regarding this paper should be addressed.

(3) This work was taken from a dissertation to be submitted to the Graduate School of Georgetown University in partial fulfillment of the degree of Doctor of Philosophy in Chemistry.

(4) W. W. Zorbach and T. A. Payne, *J. Am. Chem. Soc.*, **80**, 5564 (1958).

(5) D. A. Prins, *ibid.*, **70**, 3955 (1948).

(6) W. W. Zorbach and W. Buhler, *Ann. Chem.*, **670**, 116 (1963).

(7) J. C. Sowden and H. O. L. Fischer, *J. Am. Chem. Soc.*, **69**, 1048 (1947).

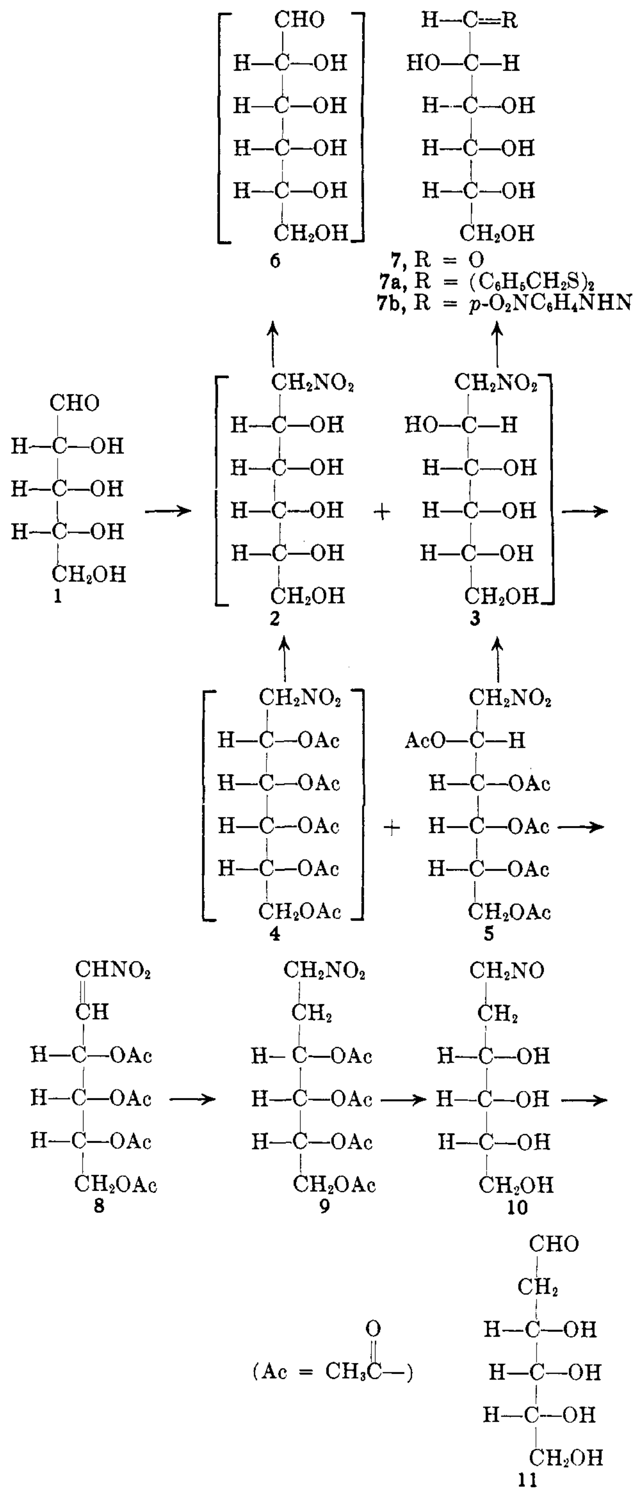
whether **5** had the *allo* or *altro* configuration, we considered means for deacetylating the material prior to conversion *via* the Nef reaction[8] to either D-allose (**6**) or D-altrose (**7**). Attempts to deacetylate **5** in methanol using either ammonia or small amounts of sodium methoxide failed, but when the material was refluxed with 1 *N* hydrochloric acid, deacetylation took place as evidenced by conversion of the resulting sirupy nitro alcohol to D-altrose (**7**). Under these conditions **7** was the sole carbohydrate product as disclosed by paper chromatograms, and was further characterized by conversion to the known dibenzyl dithioacetal (**7a**)[9] and to its *p*-nitrophenylhydrazone (**7b**), not hitherto described. When the acetylated nitro alcohol **5** was deacetylated under more acidic conditions and then subjected to the Nef reaction, a small amount of another carbohydrate material appeared on the chromatograms along with D-altrose (**7**). The artifact is most likely D-ribose (**1**), because it has an R_f value coincident with that of authentic **1** and gives the same coloration as does D-ribose when treated with aniline hydrogen phthalate reagent.[10]

The acetylated nitroaltritol (**5**) readily lost 1 mole of acetic acid by refluxing with sodium bicarbonate in benzene[11] to give the known acetylated nitrohexene (**8**)[7] in 59% yield. In order to increase the total yield of the hexene (**8**) we turned to an examination of the filtrate which remained after exhaustive removal of the crystalline acetylated nitroaltritol (**5**) from the sirupy acetylation mixture. The filtrate was reduced to a sirup and was deacetylated under the same conditions given for **5** (*vide supra*), and without further purification was subjected to the Nef reaction. Paper chromatograms disclosed a single carbohydrate material, having an R_f value the same as that for authentic D-allose (**6**), demonstrating for practical purposes a complete separation of **4** from **5**. Unfortunately, repeated attempts to secure additional, crystalline hexene (**8**) from the sirupy acetylated nitroallitol (**4**) failed.

Hydrogenation of the nitrohexene (**8**) using freshly prepared palladium black[12] gave the acetylated 2-deoxynitrohexitol (**9**) which could not be obtained in crystalline form. Without further purification the sirupy material was treated with excess sodium hydroxide and the resulting solution was added to moderately concentrated sulfuric acid, giving 2-deoxy-D-allose (2-deoxy-D-*ribo*-hexose) (**11**) in 20% yield based on the hexene (**8**) (see Chart I).

Alternately, the acetylated hexitol (**9**) was deacetylated employing 1 *N* hydrochloric acid and, under these conditions, the intermediary nitrohexitol (**10**), not isolable through the alkaline procedure, was secured in crystalline form in 79% yield (based on **8**). To our knowledge this is the first reported instance in which a 2-deoxynitrohexitol has been isolated in crystalline form. In a separate experiment **9** was deacetylated in the same manner and the resulting crude hexitol (**10**), without further purification, was subjected to the Nef reaction giving 2-deoxy-D-allose (**11**) in 38% yield based on the hexene (**8**) demonstrating the superiority of this method for converting an acetylated nitro alcohol to the corresponding aldose.

Chart I



The acid-catalyzed deacetylation of the three acetylated nitro alcohols **4**, **5**, and **9** appears to take place smoothly without bringing about other changes in the molecule. It is to be noted that, whereas the epimeric nitro alcohols **2** and **3** could not be separated by fractional crystallization, the acetylated derivatives **4**

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[8] J. U. Nef, *Ann. Chem.*, **280**, 263 (1894).

[9] N. K. Richtmyer and C. S. Hudson, *J. Am. Chem. Soc.*, **57**, 1720 (1935).

[10] S. M. Partridge, *Nature*, **164**, 443 (1949). The author states that the reagent gives a bright red coloration with pentoses whereas, with hexoses and hexuronic acids, varying shades of brown and green are obtained. In our hands, D-ribose (**1**) gave a distinctly red coloration, while the color developed by both D-allose (**6**) and D-altrose (**7**) was brown.

[11] E. Schmidt and G. Rutz, *Ber.*, **61**, 2142 (1928).

[12] J. Tausz and N. von Putnoky, *ibid.*, **52**, 1576 (1919).

and **5** were readily separated and, through acid hydrolysis, a resolution of **2** and **3** was effected. This procedure may have considerable utility in selected cases of the nitromethane synthesis of aldoses where not only a resolution of the epimeric nitro alcohols arising from the nitromethane condensation cannot be effected, but also where separation of the epimeric aldoses at the end may be beset by difficulties.

Experimental

All melting points were determined using a Kofler hot stage. Unless otherwise indicated, all paper chromatograms were carried out by an ascending technique, employing butanol–pyridine–water (6:4:3). Reducing, carbohydrate materials were detected with aniline hydrogen phthalate reagent.[10]

2,3,4,5,6-Penta-*O*-acetyl-1-deoxy-1-nitro-D-altritol (**5**).—The condensation of nitromethane with 50 g. (0.33 mole) of D-ribose (**1**) and deionization of the resulting sodium salts to give 44.5 g. (63%) of a sirupy mixture of the nitrohexitols (**2** and **3**) was carried out under essentially the same conditions given[7] by Sowden and Fischer for D-arabinose. Acetylation of the 44.5 g. of sirup was accomplished by dissolving it in 445 ml. of acetic anhydride, followed by the addition of 6 drops of concentrated sulfuric acid. After heating in a boiling water bath for 3.5 hr., the mixture was added over a period of 45 min. to 3 l. of ice–water containing crushed ice, and was then set aside in a refrigerator overnight. The supernatant liquid was decanted from the semisolid mass that had collected on the bottom and, after rinsing with cold water, the material was dissolved in 300 ml. of chloroform and was transferred to a separatory funnel. After shaking with 100 ml. of water, the chloroform extract was dried over anhydrous sodium sulfate, filtered, and evaporated *in vacuo*. The sirupy residue was further dried under a reduced pressure of 0.1 mm. at 40°, giving 82.5 g. of crude, noncrystalline **4** and **5**. The sirup was redissolved in 275 ml. of chloroform and was repeatedly decolorized with Darco G-60 until a pale, amber-colored solution was obtained. The solution was then evaporated to a thin sirup whereupon the bulk of the mass crystallized. Seed crystals were taken, and the material was redissolved in a minimum amount of absolute ethanol at 50°. After seeding, crystallization began without delay and, after standing overnight, there was obtained 23.7 g. of crude product, melting at 125–129°. By carefully working up the liquors an additional 3.0 g. of material was secured, bringing the total yield to 26.7 g. (30%). Recrystallization from absolute ethanol gave pure 2,3,4,5,6-penta-*O*-acetyl-1-deoxy-1-nitro-D-altritol (**5**), m.p. 132–133°, $[\alpha]^{24}_{\mathrm{D}}$ +47.2°.(*c* 1.00, $CHCl_3$).

Anal. Calcd. for $C_{16}H_{23}O_{12}N$: C, 45.59; H, 5.50; N, 3.32. Found: C, 45.41; H, 5.61; N, 3.35.

Conversion of 2,3,4,5,6-Penta-*O*-acetyl-1-deoxy-1-nitro-D-altritol (**5**) **to D-altrose** (**7**).—To 1.57 g. (3.7 mmoles) of **5** was added 26 ml. of 1 *N* hydrochloric acid and the mixture was refluxed for 75 min. After cooling and diluting with water to 40 ml., the mixture was neutralized with an excess of silver carbonate. Decolorization and evaporation of the filtrate gave 649 mg. (82%) of sirupy nitroaltritol (**3**) which was treated in turn with 5 ml. of 2 *N* sodium hydroxide and 8 ml. of 40% (v./v.) aqueous sulfuric acid. The material was worked up by essentially the same procedure given[7] for 2-deoxy-D-*arabino*-hexose and in this manner there was obtained 524 mg. (78%) of sirupy D-altrose (**7**). When chromatographed on paper, the material gave a single spot, coincident in position (R_f 0.45) with authentic **7**.

D-Altrose Dibenzyl Dithioacetal (**7a**).—The entire sirupy material obtained in the preceding preparation was treated with 1.25 ml. of toluenethiol and 0.9 ml. of concentrated hydrochloric acid. After stirring for 7 hr. a little crushed ice was added, with stirring continued for an additional 3 hr. The solid which had formed was filtered by suction and was washed with a small quantity each of ethanol and dry ether. The material was dissolved in 4 ml. of hot, absolute ethanol and the solution was poured into 100 ml. of water heated to 95°. After standing for 4 hr., the separated crystals were filtered and washed and, after drying for 2 days in a vacuum desiccator over potassium hydroxide, there was obtained pure D-altrose dibenzyl dithioacetal (**7a**), m.p. 121–122°, $[\alpha]^{23}_{\mathrm{D}}$ +37.3° (*c* 1.00, pyridine). For comparison purposes, a sample of **7a** was prepared from authentic D-altrose by a method described[9] by Richtmyer and Hudson, and had m.p. 121–122° and $[\alpha]^{20}_{\mathrm{D}}$ +38.9°.

D-Altrose *p*-Nitrophenylhydrazone (**7b**). **A. From Authentic D-Altrose** (**7**).—To a mixture of 500 mg. (2.8 mmoles) of D-altrose (**7**) in 5 ml. of methanol was added 425 mg. of *p*-nitrophenylhydrazine. After refluxing for 1.5 hr. the mixture was cooled to room temperature and an additional 3 ml. of methanol was added. The separated material was filtered by suction and was washed with 5 ml. of methanol, giving 757 mg. (91%) of yellow needles, m.p. 186–188°. Recrystallization from absolute ethanol gave pure hydrazone (**7b**), m.p.188–190°.

Anal. Calcd. for $C_{12}H_{17}O_7N_3$: C, 45.74; H, 5.39; N, 13.33. Found: C, 45.81; H, 5.63; N, 13.35.

B. From D-Altrose (**7**) **Prepared from the Acetylated Nitroaltritol** (**5**).—A sample of 1.57 g. of **5** was deacetylated with 1 *N* hydrochloric acid and subjected to the Nef reaction in the same manner given previously (*vide supra*), resulting in 488 mg. of sirupy D-altrose (**7**) which was dissolved in 5 ml. of methanol. To this solution was added 390 mg. of *p*-nitrophenylhydrazine and the mixture was refluxed for 1.5 hr. After refrigerating for 6 hr. the separated material was filtered and amounted to 200 mg., m.p. 145–148°. Two recrystallizations from absolute ethanol gave pure D-altrose *p*-nitrophenylhydrazone (**7b**), m.p. 188–190°. No depression in the melting point was observed when admixed with a specimen of **7b** obtained in the preceding preparation.

Formation of D-Allose (**6**).—After removal of the crystalline acetylated nitroaltritol (**5**) from the acetylation mixture containing both **4** and **5**, the combined filtrates were evaporated *in vacuo* and the residue was dried under high vacuum. A portion of the sirup weighing 1.19 g. was deacetylated and the resulting sirupy nitroallitol (**2**) was subjected to the Nef reaction in the same manner as that described for converting **5** to D-altrose (**7**). The D-allose (**6**) thus formed did not crystallize, but when chromatographed on paper gave a single spot coincident in position with a sample of authentic **6** (R_f 0.35). The hexose (**6**) was not further characterized.

3,4,5,6-Tetra-*O*-acetyl-1-nitro-D-*ribo*-hexene-1 (**8**).—To a solution of 12.0 g. (0.029 mole) of the acetylated nitroaltritol (**5**), m.p. 125–129°, in 240 ml. of dry benzene was added 12 g. of sodium bicarbonate. After refluxing for 2.5 hr., the reaction mixture was filtered by suction and the filtrate was evaporated to dryness *in vacuo*. The residue was dissolved in dry ether and was decolorized with Darco G-60. After filtering, the solution was boiled down to a small volume and was allowed to stand overnight, giving 6.1 g. (59%) of pure **8**, m.p. 86–87°, $[\alpha]^{25}_{\mathrm{D}}$ +17.1°[7] (*c* 1.00 $CHCl_3$).

Conversion of the Hexene (**8**) **to 2-Deoxy-D-allose** (**11**) (**Alkaline Procedure**).[7]—To a solution of 1 g. (2.8 mmoles) of the acetylated nitrohexene (**8**) in 105 ml. of absolute ethanol was added 0.11 g. of palladium black.[12] Hydrogenation was carried out in a Parr Hydrogenator (Series 3910) and was complete in 30 min. as evidenced by the uptake of 1 mole of hydrogen. After filtering the catalyst, the filtrate was evaporated *in vacuo*, giving 0.98 g. of a sirup from which crystalline material could not be obtained. Without further purification the sirup was dissolved in 35 ml. of 1 *N* sodium hydroxide and was allowed to stand for 1 hr. The solution was then added slowly with stirring to 12 ml. of 40% (v./v.) aqueous sulfuric acid and was neutralized with an excess of freshly prepared barium carbonate. The barium salts were removed by centrifugation and the combined, filtered decantate and washings was further deionized with Rexyn RG501(H-OH) ion-exchange resin (Fisher Scientific Co.). After filtering and washing, the filtrate was evaporated *in vacuo* at 50° and was dried under high vacuum for 1 hr. at the same temperature. The residue was dissolved in 3 ml. of absolute ethanol giving crude, crystalline material, which, when recrystallized twice from absolute ethanol, gave 90 mg. (20%) of pure 2-deoxy-D-allose (**11**), m.p. 140–142°, $[\alpha]^{24}_{\mathrm{D}}$ +57.5° (*c* 1.175, water). No depression in the melting point was observed when **11** was admixed with an authentic specimen.

1,2-Dideoxy-1-nitro-D-*ribo*-hexitol (**10**).—One gram (2.8 mmoles) of the hexene (**8**) was reduced in the same manner as described in the preceding preparation. To the resulting sirup was added 27 ml. of 1 *N* hydrochloric acid and the mixture was heated in a boiling water bath for 75 min. After diluting to 35 ml. with water and adding an excess of silver carbonate, the solution was filtered. The filtrate was further deionized using Rexyn RG501 (H-OH) ion-exchange resin and, after filtering, was evaporated *in vacuo* at 50° giving 506 mg. (93% based on **8**) of material melting at 88–94°. In a subsequent experiment the crude material was decolorized once with Darco G-60 and was recrystallized twice from absolute ethanol giving pure **10**, m.p. 106–107°, $[\alpha]^{24}\text{D}$ +4.5° (*c* 0.10, water).

Anal. Calcd. for $C_6H_{13}O_6N$: C, 36.44; H, 6.71; N, 7.17. Found: C, 36.94; H, 6.50; N, 7.07.

Conversion of the Deoxynitrohexitol (10) to 2-Deoxy-D-allose (11).—The 506 mg. (2.6 mmoles) of crude hexitol (**10**) obtained in the preceding preparation was dissolved in 4 ml. of 2 *N* sodium hydroxide and the solution was added without delay to 4 ml. of a stirred, 40% (v./v.) aqueous solution of sulfuric acid. The product was worked up in the same manner as given for the preparation of **11** by the alkaline procedure (*vide supra*). After decolorizing with Darco G-60, the material was recrystallized once from absolute ethanol giving 170 mg. (40%) of 2-deoxy-D-allose (**11**), melting at 130–133°. Two additional recrystallizations raised the melting point of **11** to 140–142°.

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The Disproportionation of Some Chlorofluoroalkyl Nitroso Compounds[1]

D. E. O'CONNOR AND PAUL TARRANT

Department of Chemistry, University of Florida, Gainesville, Florida

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Fluorochloroalkyl nitroso compounds have been shown to disproportionate into nitro and chloro derivatives with the evolution of some nitrogen. A kinetic study of the decomposition of α- and β-chloro nitroso compounds has been made and a mechanism postulated.

The preparation of nitroso compounds by the addition of nitrosyl chloride to fluoroolefins usually results in the formation of some nitro and chloro derivatives of the olefin.

$$CF_2{=}CFCl \xrightarrow{NOCl} CF_2ClCFClNO + CF_2ClCFClNO_2 + CF_2ClCFCl_2 \quad (1)$$

For example, the addition of nitrosyl chloride to tetrafluoroethylene at 100° yielded a mixture of 1-chloro-2-nitrotetrafluoroethane and 1,2-dichlorotetrafluoroethane, but no nitroso compound.[2] It was postulated that the nitroso compound was formed initially and was subsequently oxidized by nitrosyl chloride to the nitro compound. Under milder conditions using catalysis, these two reactants yield primarily 1-chloro-2-nitrosotetrafluoroethane, but some of the corresponding nitro and chloro compounds are also obtained.[3] In this laboratory it was observed that certain fluorochloroalkyl nitroso compounds decomposed slowly on standing at room temperature. Furthermore, attempts to carry out reactions of these nitroso compounds with other materials by heating resulted in the formation of the corresponding nitro and chloro compounds[4] and very little else. Our observations suggested that disproportionation was occurring approximately according to the following equation.

$$2RNO \longrightarrow RNO_2 + RCl + 0.5N_2 \quad (2)$$

Equation 2 obviously does not balance and does not account completely for the products of the reaction, but it does describe the gross features of it. Our study was undertaken to learn more about this interesting reaction.

The only other data concerning the disproportionation of fluoroalkyl nitroso compounds have been obtained with perfluoroalkyl nitroso compounds. Haszeldine and co-workers have investigated rather thoroughly the reactions of nitrosotrifluoromethane, the thermal reactions of which follow quite different courses under different conditions. Irradiation of nitrosotrifluoromethane with ultraviolet light yields a dimer, $(CF_3)_2$-NONO,[5] while heating nitrosotrifluoromethane over activated charcoal yields a mixture of nitrotrifluoromethane and hexafluoroazoxymethane[6] analogous to the reaction Bamberger reported for nitrosobenzene.[7] However, when nitrosotrifluoromethane is heated alone, a 48% yield of nitrotrifluoromethane is obtained along with the products of reaction of trifluoromethyl radicals with glass.[8] This last reaction was run under conditions similar to our experiments, the major difference being that theirs was a gas-phase reaction while ours was carried out in the liquid phase.

Andreades[9] has found that nitrosopentafluoroethane undergoes the following reaction when heated.

$$\begin{tikzcd} C_2F_5NO \arrow[r] & CF_3CF_2N{=}CFCF_3 + C_2F_5NO_2 + C_2F_5ONO \arrow[d, shift left] \\ & CF_3COF + NOF \arrow[u, shift left] \end{tikzcd} \quad (3)$$

We postulate that the course of the thermal disproportionation of fluorochloroalkyl nitroso compounds is that shown in eq. 4, 5, and 6. Our arguments are based on the products of the reaction, the effect of added reagents (NO and NOCl), and the relative thermal stabilities of four chlorofluoroalkyl nitroso compounds.

The relative thermal stabilities of 1,2-dichloro-1-nitrosotrifluoroethane (I), 1,1-dichloro-1-nitrosotrifluoroethane (II), 1-chloro-1-nitrosotetrafluoroethane (III), and 1-chloro-2-nitrosotetrafluoroethane (IV) at 78.2° were measured. Compounds I and IV were made by

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[1] Presented at the 140th National Meeting of the American Chemical Society, Chicago, Ill., Sept., 1961.

[2] R. N. Haszeldine, *J. Chem. Soc.*, 2075 (1953).

[3] J. D. Park, A. P. Stefani, and J. R. Lacher, *J. Org. Chem.*, **26**, 4017 (1961).

[4] Throughout this paper the term chloro compound refers to the chlorofluorocarbon obtained by replacement of the nitroso group by chlorine.

[5] R. N. Haszeldine and B. J. H. Mattinson, *J. Chem. Soc.*, 1741 (1957).

[6] J. Jander and R. N. Haszeldine, *ibid.*, 919 (1954).

[7] E. Bamberger, *Ber.*, **33**, 1939 (1900).

[8] D. A. Barr, R. N. Haszeldine, and C. J. Willis, *J. Chem. Soc.*, 1351 (1961).

[9] S. Andreades, 2nd International Fluorine Symposium, Estes Park, Colo., July 17–20, 1962.