**Addition of Carbon Tetrachloride to 1-Octene.**—This reaction was carried out as described above except that all reagents were doubled and 89.6 g of 1-octene was used in place of allyl alcohol. The mixture was heated in six 45-ml polymerization tubes. The products were 41 g (38.5%) of 1,1,1,3-tetrachlorononane,[4,11,12] bp 95–98° (1.7–2.0 mm), $n^{20}$D 1.4768, nmr ($CCl_4$) $\delta$ 3.2 (2 d, 2, $-CH_2CCl_3$), 4.2 (m, 1, -CHCl-), 1.85 (m, 2, $-CH_2CHCl-$), 1.36 (m, 8, $-CH_2-$), 0.9 (t, 3, $-CH_3$), and 5.5 g (4%) of 9,9,11-trichloro-7-heptadecene, bp 170° (2.0 mm), $n^{20}$D 1.4766, nmr ($CCl_4$) $\delta$ 0.9 (t, 3, $-CH_3$), 1.2–1.8 (m, 10, $-CH_2-$), 4 (m, 1, -CHCl-), 5.5 (d, 1, -CH=), 2.7 (d, 2, $=CClCH_2-$). *Anal.* Calcd for $C_{17}H_{31}Cl_3$: C, 59.74; H, 9.14; Cl, 31.12. Found: 59.37; H, 9.28; Cl, 31.11.

**Addition of 1,1,1,3-Tetrachloropropane to 1-Octene.**—A mixture of 42 g of 1-octene, 68 g of 1,1,1,3-tetrachloropropane, 40 ml of isopropyl alcohol, 0.9 g of $FeCl_3 \cdot 6H_2O$, 0.7 g of benzoin, and 0.5 g of diethylamine hydrochloride was refluxed at 85° for 20 hr. The mixture was washed twice with water and steam distilled. The residue was fractionated but the distillation cuts were mixtures as indicated by gas chromatography. Mass spectroscopy coupled to a gas chromatograph indicated that the three major components were 14.0% of $C_{11}H_{18}Cl_2$, 8.4% of $C_{11}H_{19}Cl_3$, and 2.8% of $C_{11}H_{20}Cl_4$.

**Registry No.**—Carbon tetrachloride, 56-23-5; ethylene, 74-85-1; 1,1,1,3-tetrachloropropane, 1070-78-6; 1,1,1,3-tetrachlorobutane, 13275-19-9; 1,1,5-trichloro-1-pentene, 2677-33-0; 1,3,5-trichloro-2-pentene, 34909-84-7; 1,1,1,5-tetrachloropentane; 2467-10-9; 1,3,3,5-tetrachloropentane, 24616-07-7, methyl methacrylate, 80-62-6; methyl 2,4,4,4-tetrachlorobutyrate, 25335-11-9; dimethyl 2,4,4,6-tetrachloroheptanedioate, 34909-87-0; allyl alcohol, 107-18-6; 2,4,4,4-tetrachlorobutan-1-ol, 3290-70-8; 2,4,4,6-tetrachloroheptane-1,7-diol, 34909-89-2; 1-octene, 111-66-0; 1,1,1,3-tetrachlorononane, 1070-27-5; 9,9,11-trichloro-7-heptadecene, 34909-90-5.

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## Deoxygenations of 2-(D-*arabino*-Tetrahydroxybutyl)pyrazine 4-*N*-Oxide and 1-*N*-Oxide

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Deoxygenations of aromatic *N*-oxides[1] have been carried out with sulfur dioxide,[2] sulfurous acid,[3] phosphorus trichloride,[4] or phosphorus oxychloride[5] or by catalytic reduction over Raney nickel[6] or palladium carbon.[7] The reactions of pyrazine 1-*N*-oxide and pyrazine 1,4-di-*N*-oxide with phosphorus oxychloride have been reported to give 2-chloropyrazine and 2,6-dichloropyrazine in 25 and 40% yield, respectively.[8]

During the course of an investigation of heterocyclic compounds derived from carbohydrates, it was shown[9] that 2-amino-2-deoxy-D-glucose oxime (**1**) reacted with glyoxal to yield 2-(D-*arabino*-tetrahydroxybutyl)pyrazine 4-*N*-oxide (**2**) identical with that derived from 2-amino-2-deoxy-D-mannose oxime and glyoxal. The present report describes an investigation of the deoxygenations of carbohydrate-derived pyrazine *N*-oxides. The deoxygenation of 2-(D-*arabino*-tetraacetoxybutyl)-pyrazine 4-*N*-oxide (**3**) with phosphorus oxychloride yields the monochloropyrazine derivative **4**. In this case, the possible substitution position of chlorine is 3 or 5 on the pyrazine ring. The nmr spectrum of the crystalline monochloro tetraacetyl derivative **4** showed two singlets at $\tau$ 1.47 and 1.54 due to the uncoupled protons at C-3 and C-6 of the pyrazine ring. Thus it may be concluded that the position of chlorination is C-5 of the pyrazine ring (Scheme I).

On the other hand, the catalytic deoxygenation of 2-(D-*arabino*-tetrahydroxybutyl)pyrazine 4-*N*-oxide (**2**) was performed in methanol with palladium/carbon at room temperature by using a slightly positive pressure of hydrogen. The deoxygenated product **6** was oxidized with potassium permanganate to yield the pyrazinemonocarboxylic acid **7**, which showed an identical infrared spectrum, paper chromatographic $R_f$ value,[10,11] and melting point with the authentic pyrazine-2-carboxylic acid. This fact shows that the 4-*N*-oxide **2** has been completely deoxygenated to 2-(D-*arabino*-tetrahydroxybutyl)pyrazine (**6**).

1-Amino-1-deoxy-D-fructose oxime (D-isoglucosamine oxime) (**9**) is an isomer of 2-amino-2-deoxy-D-glucose oxime (**1**) and can form a pyrazine 1-*N*-oxide derivative by the reaction with glyoxal. Little has been known of this sugar oxime and it was synthesized according to the procedure described by Breuer[12] from 1-amino-1-deoxy-D-fructose acetate (**8**)[13] and hydroxylamine. The condensation product **10** of this sugar oxime and glyoxal showed the identical molecular formula, ultraviolet maximum, and ultraviolet molecular absorption coefficient with those of 2-(D-*arabino*-tetrahydroxybutyl)pyrazine 4-*N*-oxide (**2**), but showed a quite different melting point and infrared spectrum from those of the latter. The deoxygenation by catalytic reduction of **10** was carried out according to the method used for the 4-*N*-oxide **2** and yielded the deoxygenated product **6**, which had identical physical constants and infrared spectrum with those of the deoxygenated product

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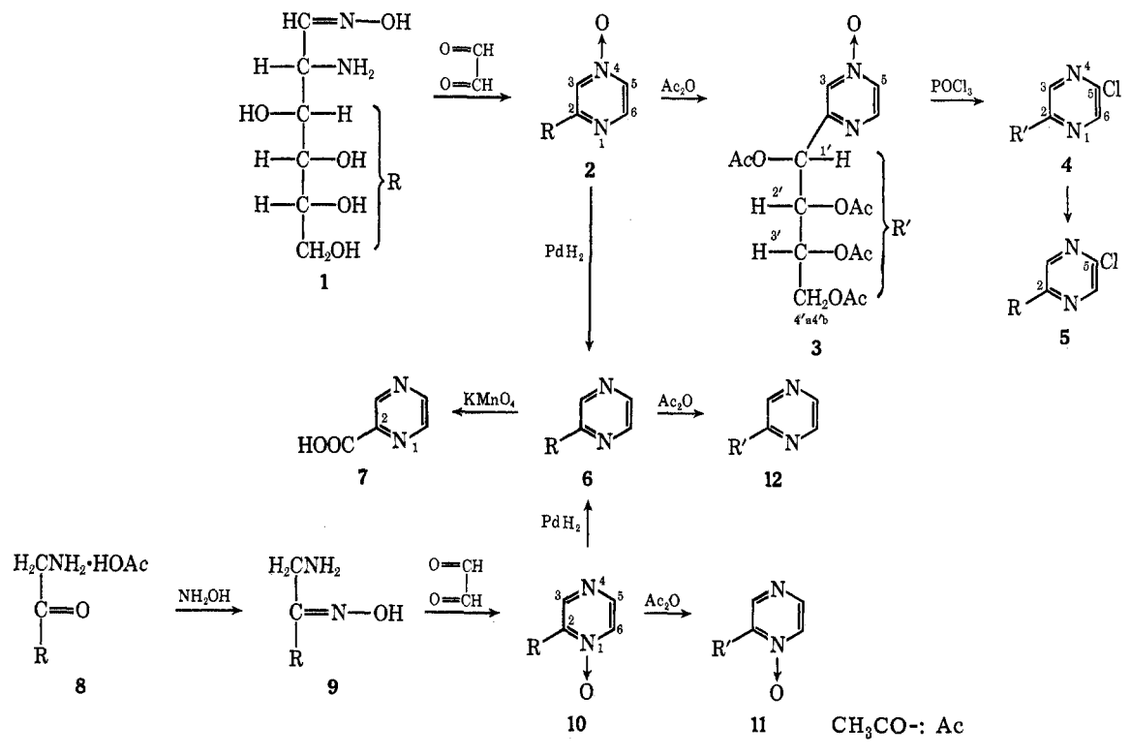
SCHEME I



of the 4-*N*-oxide **2**. Therefore, it can be concluded that the condensation product **10** is 2-(D-*arabino*-tetrahydroxybutyl)pyrazine 1-*N*-oxide.

Tetra-*O*-acetates **11** and **12** of the 1-*N*-oxide **10** and the deoxygenated product **6** were prepared with acetic anhydride and pyridine. Nmr studies on these materials (**4**, **11**, **12**) showed identical patterns in the region $\tau$ 3.4–5.8 with that of **3**.[9] The finding indicates that the deoxygenation conditions do not alter the conformation and configuration of these tetrahydroxybutyl side chains.

## Experimental Section[14]

**2-(D-*arabino*-Tetraacetoxybutyl)-5-chloropyrazine (4).**—To 15 ml of phosphorus oxychloride, 5.7 g of 2-(D-*arabino*-tetraacetoxybutyl)pyrazine 4-*N*-oxide (**3**)[9] was added portionwise with stirring. After refluxing for 10 min, the solution was poured into ice water (200 g), and an aqueous solution of sodium hydroxide was added to make pH 9.0. The mixture was extracted several times with chloroform, and the combined extracts were washed with water, dried with sodium sulfate, and concentrated *in vacuo* to a syrup. It was dissolved with a little ether, and petroleum ether (bp 30–70°) was added to give crystals. They were recrystallized from ethyl acetate by adding ether and petroleum ether successively, giving 2.7 g (44.8%) of **4**: mp 72°; $[\alpha]^{25}D$ −7.8° (after 48 hr) (*c* 1.0, methanol); uv max (methanol) 210 and 276 m$\mu$; nmr ($CDCl_3$) $\tau$ 8.06, 7.94, 7.90, 7.78 (s, 3 H, AcO-1′, AcO-2′, AcO-3′, and AcO-4′), 5.74 (m, 2 H, $J_{4'a4'b}$ = 12.5 Hz, H-4′), 4.72 (m, 1 H, $J_{3'4'a}$ = 3.0 Hz, $J_{3'4'b}$ = 4.0 Hz, H-3′), 4.35 (q, 1 H, $J_{2'3'}$ = 9.0 Hz, H-2′), 3.89 (d, 1 H, $J_{1'2'}$ = 2.5 Hz, H-1′), 1.54, 1.47 (s, 1 H, H-3 and H-6).

*Anal.* Calcd for $C_{16}H_{19}N_2O_8Cl$: C, 47.71; H, 4.76; N, 6.96; Cl, 8.80. Found: C, 47.56; H, 4.75; N, 6.89; Cl 8.70.

**2-(D-*arabino*-Tetrahydroxybutyl)-5-chloropyrazine (5).**—To a solution of 2.7 g of the tetra-*O*-acetate **4** in 100 ml of methanol, ammonia gas was passed through with cooling with ice water. After keeping overnight at room temperature, the reaction mixture was concentrated to separate a crystalline substance which was washed with ethahol, acetone, and ether. Recrystallization from water gave 900 mg (57.6%) of **5**: mp 172–173°; $[\alpha]^{15}D$ −70.0°, (after 48 hr) (*c* 1.0, water); ir (Nujol) 3280 $cm^{-1}$ (OH); uv max (water) 277 m$\mu$.

*Anal.* Calcd for $C_8H_{11}N_2O_4Cl$: C, 40.95; H, 4.78; N, 11.97; Cl, 15.11. Found: C, 40.71; H, 4.82; N, 11.86; Cl, 14.89.

**2-(D-*arabino*-Tetrahydroxybutyl)pyrazine (6).**—A suspension of 2 g (0.01 mol) of **2**[9] and 0.5 g of palladium/carbon in methanol was stirred for 60 hr at room temperature under a slightly positive pressure of hydrogen until the 4-*N*-oxide **2** was almost dissolved in methanol. After separation of the catalyst and the unchanged **2**, the methanolic solution was concentrated *in vacuo*, and the residue, 1.5 g (81.0%), mp 166–169°, was recrystallized from water to give 1.0 g (54.2%) of **6**: mp 168–170°; $[\alpha]^{14}D$ −66.7° (after 24 hr) (*c* 1.0, water); ir (Nujol) 3350 (OH) and 840 $cm^{-1}$; uv max (water) 266 m$\mu$.

*Anal.* Calcd for $C_8H_{12}N_2O_4$: C, 47.99; H, 6.04; N, 14.00. Found: C, 47.74; H, 6.06; N, 13.95.

**2-(D-*arabino*-Tetrahydroxybutyl)pyrazine 1-*N*-Oxide (10).**—1-Amino-1-deoxy-D-fructose acetate (**8**) was obtained in 89% yield according to the method of Kuhn and Haas,[13] mp 136° (lit.[13] mp 137°). To the solution of 24 g (0.1 mol) of this acetate **8** in 1 *N* sodium methoxide (100 ml), a methanolic solution of hydroxylamine (0.15 mol) was added, and the mixture was kept overnight at room temperature. Concentration of the reaction mixture *in vacuo* and the addition of ethanol (*ca.* 400 ml) afforded an amorphous mass (**9**). It was dissolved in 100 ml of water, and 14 g (0.1 mol) of a 40% aqueous solution of glyoxal was added. The reaction solution was kept overnight at room temperature and passed through a column of Amberlite IR-120 ($H^+$) (100 ml). After the pH of washings became almost neutral, the adsorbed 1-*N*-oxide **10** was eluted with water (1.5 l.). The effluent was concentrated *in vacuo*, and the white crystalline substance formed was collected by filtration and washed with water–ethanol (1:1, v/v) to give 6.0 g of **10**. Recrystallization from water gave 5 g (23.1%): mp 197° (melt), 206° dec; $[\alpha]^{14}D$ 144.3° (after 24 hr) (*c* 1.0, water); ir (Nujol) 3350 (OH) 1610, and 1210 $cm^{-1}$ (N→O); uv max (water) 218 m$\mu$ ($\epsilon$ 11,000), 265 (12,000).

*Anal.* Calcd for $C_8H_{12}N_2O_5$: C, 44.44; H, 5.60; N, 12.96. Found: C, 44.15; H, 5.40; N, 12.88.

**Deoxygenation of 2-(D-*arabino*-Tetrahydroxybutyl)pyrazine 1-*N*-Oxide (10).**—The deoxygenation of the 1-*N*-oxide **10** (2.0 g) was carried out according to the method described above, and 1.6 g

(14) Ultraviolet and 60-MHz nmr spectra were recorded with a Hitachi Perkin-Elmer 139 uv-visible spectrophotometer and a Varian Model A-60 spectrometer, respectively. Tetramethylsilane ($\tau$ 10.00) was used as the internal reference standard for nmr spectra. Melting points are not corrected. Pyridine–isoamyl alcohol–water (40:35:30, v/v) and Toyo Roshi No. 50 filter paper were used for descending paper chromatography.

(84.6%) of crude crystalline substance was obtained, which was recrystallized from water to give 1.1 g (59.3%) of **6**. This compound gave an identical ir spectrum and uv absorption pattern with those of **6** derived from 4-*N*-oxide **2**, mp 167–170°, $[\alpha]^{14}D$ −65.4° (after 24 hr) (*c* 1.0, water).

*Anal.* Calcd for $C_8H_{12}N_2O_4$: C, 47.99; H, 6.04; N, 14.00. Found: C, 48.25; H, 6.25; N, 14.20.

**Pyrazine-2-carboxylic Acid (7).**—To a solution of 2.2 g of **6** in 400 ml of water, 6.0 g of potassium permanganate was added in small portions with stirring at 90° for 5 hr. After addition of a small volume of methanol for digesting the excess of potassium permanganate, the precipitate was filtered off and washed with hot water. The filtrate and washings were combined and passed through a column of Amberlite IR-120 ($H^+$). Concentration of this effluent *in vacuo* and recrystallization of the residue from water yielded 760 mg (55.8%), mp 225° dec, ir (Nujol) 1710 $cm^{-1}$ (C=O).

*Anal.* Calcd for $C_5H_4N_2O_2$: C, 48.39; H, 3.25; N, 22.28. Found: C, 48.40; H, 3.49; N, 22.28.

**2-(D-*arabino*-Tetraacetoxybutyl)pyrazine 1-*N*-Oxide (11).**—A mixture of **10** (3 g), acetic anhydride (50 ml), and pyridine (50 ml) was kept for 15 hr at room temperature and poured into ice water. The mixture was extracted with chloroform and the extract was treated as described for **3**.[9] The crystals from the chloroform extract were washed with ether and recrystallized with ethanol to give 4.1 g (76.8%) of **11**: mp 97°; $[\alpha]^{15}D$ −30.5° (*c* 1.0, methanol); ir (Nujol) 1745 (C=O), 1600, 1310 $cm^{-1}$ (N→O); uv max (methanol) 224, 269 mμ; nmr ($CDCl_3$) τ 8.80, 7.95, 7.88, 7.78 (s, 3 H, AcO-1′, AcO-2′, AcO-3′, and AcO-4′), 5.74 (m, 2 H, $J_{4'a4'b}$ = 12.5 Hz, H-4′), 4.66 (m, 1 H, $J_{3'4'a}$ = 3.0, $J_{3'4'b}$ = 4.5 Hz, H-3′), 4.24 (q, 1 H, $J_{2'3'}$ = 9.0 Hz, H-2′), 3.43 (d, 1 H, $J_{1'2'}$ = 2.5 Hz, H-1′), 1.89 (q, 1 H, H-6 or H-5), 1.57–1.64 (m, 2 H, H-5 or 6 and H-3).

*Anal.* Calcd for $C_{16}H_{20}N_2O_9$: C, 49.98; H, 5.24; N, 7.29. Found: C, 49.70; H, 5.13; N, 7.18.

**2-(D-*arabino*-Tetraacetoxybutyl)pyrazine (12).**—A mixture of **6** (500 mg), pyridine (20 ml), and acetic anhydride (20 ml) was kept at 37° for 20 hr. From the reaction mixture tetra-*O*-acetate was extracted with chloroform and the extract was treated as described for **3**[9] to give 600 mg (61.5%) of **12**: mp 110–111°; $[\alpha]^{15}D$ −1.22° (after 48 hr) (*c* 1.0 methanol); ir (Nujol) 1740 mμ (C=O); nmr ($CDCl_3$) τ 8.11, 7.97, 7.90, 7.78 (s, 3 H, AcO-1′, AcO-2′, AcO-3′, and AcO-4′), 5.74 (m, 2 H, $J_{4'a4'b}$ = 12.0 Hz, H-4′), 4.71 (m, 1 H, $J_{3'4'a}$ = 2.5, $J_{3'4'b}$ = 4.0 Hz, H-3′), 4.31 (m, 1 H, $J_{2'3'}$ = 9.0 Hz, H-2′), 3.84 (d, 1 H, $J_{1'2'}$ = 2.5 Hz, H-1′), 1.43–1.50 (m, 3 H, H-3, 5, or 6).

*Anal.* Calcd for $C_{16}H_{20}N_2O_8$: C, 52.17; H, 5.47; N, 7.61. Found: C, 52.13; H, 5.41; N, 7.51.

**Registry No.**—**2**, 21537-56-4; **4**, 34546-42-4; **5**, 34546-43-5; **6**, 34546-44-6; **7**, 98-97-5; **10**, 34546-45-7; **11**, 34546-46-8; **12**, 34546-47-9.

## Decarboxylation of Some Thallium(III) Carboxylates. A Mass Spectral Study

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Many heavy metal alkyl and aryl derivatives have been prepared by decarboxylation of the appropriate carboxylates.[3] The photolysis of primary, secondary, and tertiary carboxylic acids in the presence of thallium(III) has been studied, and the products are thallium(I) carboxylates and organic compounds derived from the radical R·.[4] No other such studies have been reported. Observation of the fragmentation of thallium(III) carboxylates in the mass spectrometer would shed some light on the nature of decarboxylation reactions.

### Results and Discussion

**Thallium(III) Acetate.**—The ion of highest *m/e* value found in the mass spectrum of thallium(III) acetate is the molecular ion, $(CH_3COO)_3Tl^+$. It is clear that one of the major fragmentation pathways from the molecular ion is *via* successive loss of acetate groups and that this is substantiated by the observation of the appropriate metastable peaks (Table I).

TABLE I
MONOISOTOPIC MASS SPECTRA OF $(RCOO)_3Tl$ (R = $CH_3$ AND $C_6H_5$)

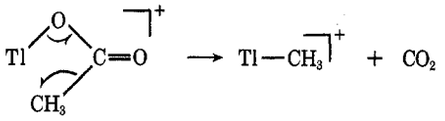
| | R = $CH_3$ | | R = $C_6H_5$ | |
|---|---|---|---|---|
| Ion | *m/e* | Rel intensity | *m/e* | Rel intensity |
| $(RCOO)_3Tl^+$ | 382 | 0.1 | 568 | *a* |
| $(RCOO)_2TlH^+$ | 324 | 1.3 | | |
| $(RCOO)_2Tl^+$ | 323 | 51 | 447 | 0.1 |
| $(RCOO)Tl(R)(H)^+$ | 280 | 0.1 | | |
| $(RCOO)TlR^+$ | 279 | 0.2 | 403 | 0.2 |
| $R_2Tl^+$ | | | 359 | 0.2 |
| $(RCOO)Tl^+$ | 264 | 0.8 | 326 | 8.6 |
| $RTl^+$ | 220 | 0.4 | 282 | 19 |
| $TlCO_2^+$ | 249 | 6.2 | 249 | 6.4 |
| $TlO^+$ | 221 | 0.2 | | |
| $Tl^+$ | 205 | 100 | 205 | 100 |

Metastable Transitions

| Process | *m/e* Obsd | *m/e* Calcd | Neutral fragment lost |
|---|---|---|---|
| | R = $CH_3$ | | |
| 323 → 264 | ~216 | 215.8 | $CH_3COO$ |
| 264 → 205 | 159.2 | 159.2 | $CH_3COO$ |
| | R = $C_6H_5$[b] | | |
| 326 → 282 | 243.9 | 243.9 | $CO_2$ |
| 403 → 205 | 104.3 | 104.3 | $C_6H_5COOC_6H_5$ |

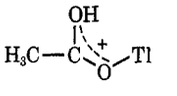
[a] Not observed. [b] Miscellaneous unassigned peak: ~174.

The formation of methylthallium species is probably associated with a rearrangement of the type



However, the possibility of thermal decarboxylation at the heated ion source cannot be ruled out, but seems less likely. It has previously been shown that the reverse reaction, *i.e.*, the insertion of carbon dioxide into the thallium–carbon bonds of trimethylthallium, does not occur at all at room temperature.[5]

Also present in the spectrum are the ions $(CH_3COO)_2TlH^+$ and $(CH_3COO)Tl(CH_3)H^+$, which are probably thallium hydride species, but the possibility of other structures such as



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