Studies on Telomers and Oligomers of Vinylene Carbonate. VII.1) Facile Synthesis of Trihalogenomethyl-containing Aldo-sugars and Polyalcohols

Tsuchum Matsuura, Takehisa Kunieda, and Takeo Takizawa

Faculty of Pharmaceutical Sciences, University of Tokyo

(Received May 20, 1976)

Facile routes to trichloromethyl-containing aldoses and polyalcohols from low telomers of vinylene carbonate with carbon tetrachloride are described. 3,3,3-Trichloro-3-deoxyglyceraldehyde derived from \( n = 1 \) adduct was dimerized to five-membered 1,3-dioxolane derivative preferentially, in contrast to the corresponding 3,3-dichloro compound which gave the dimer in 1,4-dioxane structure. Three-step procedure involving acetalization followed by removal of cyclic carbonate groups and subsequent deacetalization was mild and selective enough to permit the hydrolysis of \( n = 2 \) telomers to 5,5,5-trichloro-5-dioxo-DL-lyxose and -xylose in excellent yields, while acid hydrolysis under more drastic conditions (at 100—110°C) gave the rearranged 5,5,5-trichloro-3,3-dideoxy-pentosulose in dimeric form exclusively. Reduction of telomers (\( n = 1 \) and 2) and the derivatives with sodium borohydride gave polyalcohols of the type \( \text{Cl}_3\text{C}-(\text{CHOH})_n\text{H} \) (\( n = 2, 3, \) and 4), among which some compounds showed considerable sedative activities.

Keywords—telomer; trihalogenomethyl-aldoses; trihalogenomethyl-polyalcohols; vinylene carbonate; 3-deoxy-pentosone; acetalization

In connection with our research programs on the novel synthesis of carbohydrates by telomerization of vinylene carbonate,3) the present paper describes the convenient synthetic routes to polyalcohols including aldo-sugars which contain tri- (or di-) chloromethyl group at the terminal position from the low telomers of vinylene carbonate with carbon tetrachloride previously isolated4) and the preliminary results pharmacologically evaluated with some of the polyalcohols thus obtained.

Re-examination of the reported hydrolysis (with sulfuric acid4) or sodium alkoxides\( ^{a \text{al}} \) of the type 1 telomers, quite sensitive towards nucleophiles, into aldose derivatives revealed the formation of the complicating mixture of little preparative value as a consequence of the undesirable side reactions (epimerization, degradation and condensation) and showed the need for the mild and selective hydrolytic method to \( x \)-hydroxy-aldehydes, which would permit an efficient conversion from vinylene carbonate telomers to carbohydrates.

\[
\begin{align*}
\text{X}_n\text{C} & \text{H}\quad \text{H} \quad \text{O} \\
\text{O} & \text{O} \quad \text{O} \\
\text{H}_2\text{O} & \xrightarrow{1} \text{X}_n\text{C} \quad \text{H}\quad \text{H} \quad \text{O} \\
\text{O} & \text{O} \quad \text{O} \\
\text{H}_2\text{O} & \xrightarrow{2} \text{X}_n\text{C} \quad \text{H}\quad \text{H} \quad \text{O} \\
\text{O} & \text{O} \quad \text{O} \\
\text{H}_2\text{O} & \xrightarrow{3} \text{X}_n\text{C} \quad \text{H}\quad \text{H} \quad \text{O} \\
\text{O} & \text{O} \quad \text{O} \\
\end{align*}
\]

1 (X, X' = Cl, Br) 2 3

Trichloromethyl-aldoses

Chloro-substituted ethylene carbonate rings underwent the smooth and selective ring-opening merely by standing the aqueous solutions at room temperature to afford the excellent

2) Location: Hongo, Bunkyo-ku, Tokyo.
yields of crystalline $\alpha$-hydroxy-aldehydes (2) in dimeric forms. Thus, $n=1$ compound (4) gave dimeric five membered ring product (9) (80%) selectively, and the acetonide (12) as a major product in the presence of large excess of acetone, while dichloromethyl compound (5) prepared from 4$^{a, b}$ and the stereoisomeric 13a (trans-“syn”-trans)$^b$ and 13b (trans-“anti”-trans)$^b$ preferentially formed six-membered ring dimers (10 (70%), 16a (87%) and 16b) (90%), respectively.$^6$

![Chemical structure diagram]

Chart 1

Structures of the dimers as well as their diacetates including stereochemistry were established as shown in the Charts on the basis of the nuclear magnetic resonance (NMR) spectral data (Table I). Five-membered ring structure of 9 was further demonstrated by reductive photolysis$^{b b}$ of the diacetate of 9 to give 11 which was distinctly different from the diacetate of 10 directly derived from 5. Diacetates of the dimers (10, 16a, and 16b) showed in each case the identical signals due to H$_a$ and H$_b'$ as well as those of H$_b$ and H$_b'$ in the NMR spectra, indicative of the high symmetry in the 1,4-dioxane structures.

Complete hydrolysis of the $n=2$ telomers (13a and 13b) or of the remaining cyclic carbonates of 16a and 16b under more drastic conditions (dilute hydrochloric acid at 100–110$^\circ$C in a sealed

<table>
<thead>
<tr>
<th>TABLE I. NMR Spectral Data for Dimer Derivatives</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compound</td>
</tr>
<tr>
<td>----------</td>
</tr>
<tr>
<td>9 diacetate$^a$</td>
</tr>
<tr>
<td>9 bis-methyl formate$^a$</td>
</tr>
<tr>
<td>10 diacetate$^b$</td>
</tr>
<tr>
<td>11$^a$</td>
</tr>
<tr>
<td>16a diacetate$^c$</td>
</tr>
<tr>
<td>16b diacetate$^b$</td>
</tr>
</tbody>
</table>

$^a$ CDCl$_3$, $^b$ CF$_3$COOH, $^c$ CH$_2$CN at 60 MHz


tube) resulted in the exclusive formation of unexpected compound (17) as colorless prisms (mp 138°, C_{10}H_{10}O_{8}Cl_{6}) (96%) which gave a diacetate and was assigned as the dimer of 5,5,5-trichloro-3,5-dideoxy-pentosulose\(^7\) based on the spectral data and the following reactions. Treatment of 17 with sodium borohydride and borodeuteride gave high yields of 20 and 20-1, 2-\(d_2\) (in a diastereomeric mixture), respectively, proving during the hydrolysis the rearrangement to 3-deoxy-pentosone by the Lobry de Bruyn-Alberda van Ekenstein isomerization\(^8\) of the primary products, lyxose and xylose derivatives. This monomeric structure was further confirmed by the isolation of quinoxaline derivative\(^{(21)}\) arising from the reaction with \(o\)-phenylene-diamine as well as by the reddish purple coloration of the di-oxide with nickel acetate\(^9\), though the dimeric actual structure still remains equivocal.


Efficient method for the conversion of the telomers to the aldoses involves selective protection of the aldehyde groups followed by hydrolysis with bases and subsequent deacetylation with acids. Thus, \( n=2 \) telomers (13a and 13b) were heated in methanol to give quantitative yields of dimethyl acetics (15a and 15b) characterized as \( \beta \)-nitrobenzoates. On the same treatment, the \( n=1 \) adduct (4) afforded the acetal (8) in high yield \( \text{via} \) the primary substitution product (6) whose intermediacy in this reaction could be shown by the exclusive conversion to 8 under the identical conditions and the isolation of both products (6 and 8) depending on the duration. Sodium borohydride or triethylamine was satisfactory for the cleavage of the remaining carbonate rings of 15a,b to give 18a and 18b, which, on subsequent treatment with a cation exchange resin (IR-120 H\(^+\)), gave 5-deoxy-5,5-trichloro-DL-lyxose (19a) and -xyllose (19b) in 83% and 96% overall yields from 13a and 13b, respectively. Acetylation of 19a and 19b with acetic anhydride catalyzed by sulfuric acid resulted in the preferential formation of \( \beta \)-anomers which was shown by vicinal coupling constants \( (J_{1,2}) \) of 3.5 Hz and <0.5 Hz, respectively.\(^{10} \) This mild method would provide the routes to heptoses and nonoses from higher telomers \( (n=3 \text{ and } 4) \) which were previously isolated.\(^{4} \)

**Trichloromethyl-polyalcohols**

Direct action of sodium borohydride on the telomers (4, 13a and b) afforded high yields of trichloromethyl-propanediol (23) and trichloro-5-deoxy-lyxitol and -xylitol (25a and b) in a single step. On the similar treatment, \( \text{trans} \) cyano compound (26) derived from 4\(^{3} \) and \( \text{trans} \) ester (22)\(^{3} \) gave \( \text{theo}-\text{cyanohydrin} \) (27) and trichloro-4-deoxy-threitol (24) in 73—82% and 58% yields, respectively. Convenient and high-yield preparation of 23 in this route provides a potential source for carbonyl protection as an ethylene ketal\(^{11} \) which could be cleaved under neutral conditions by the familiar \( \beta,\beta,\beta \)-trichloro ether reductive elimination.\(^{12} \)

**Preliminary Pharmacological Assays\(^{13} \)**

Some of the above polyalcohols containing trichloromethyl group which was known to show sedative actions in many compounds\(^{14} \) were examined for the effects on the central nervous system of the mice. Compounds, (9, 23, 24, 25a, and 25b), had low oral toxicity \( (L_{D_{50}}>1000 \text{ mg/kg}) \) to ICR-JCL mice (male),\(^{15} \) nearly comparable to that of ethylene-carbon tetrachloride telomers.\(^{10} \) Among the compounds evaluated, 23 (100 mg/kg) showed the most promising properties as a hypnotic agent. In oral administration at the level of 100 mg/kg, 25a showed significant analgesic and little hypnotic actions, while the stereoisomer (25b) was much more active in hypnotic action than analgesic. Compounds (9 and 24) showed little biological activity in this screening tests.


\(^{11} \) T. Kunieda and T. Takizawa, unpublished observations.


\(^{13} \) For these preliminary tests, we are much indebted to Drs. T. Kobayashi and M. Mori, The Mitsubishi-Yukayakuin Research Laboratories.


\(^{15} \) Similar compound, 3,3-dichloro-2-hydroxy-2-propenal prepared from 4-dichloromethylene-5-chloro-1,3-dioxolan-2-one, showed the \( L_{D_{50}} \) value 300 mg/kg.

Experimental

All melting points (Yanaco micro melting point apparatus) are uncorrected. Infrared (IR) spectra were recorded on a JASCO-IR-S infrared spectrophotometer or JASCO-IRA-1 Grating infrared spectrophotometer, absorptions given in cm⁻¹. NMR spectra were recorded on a Hitachi R-24 spectrometer (80 MHz) using tetramethylsilane (TMS) as an internal standard. Telomers used were prepared from vinylene carbonate and carbon tetrachloride in the presence of benzoyl peroxide. ⁴

3-Deoxy-3,3,3-trichloro-3-methylglyceraldehyde, Dimer (9) ——The solution of 4 (2.4 g, 0.01 mole) in a mixture (50 ml) of acetone and water (1:1) or tetrahydrofuran (THF) and water (1:1) was stirred at room temperature for 40 hr. The organic solvent was removed under reduced pressure, and the crystalline material precipitated was collected by filtration and washed with water to give the dimer (9) (1.42 g, 80%), which was recrystallized from MeOH–CH₂Cl₂ to afford colorless prisms, mp 173—178 °C (partly sublimed). IR (Nujol) 3440, NMR (CDCl₃, 100 MHz) δ 4.25 (1H, d, J = 4 Hz), 4.46 (1H, d, J = 2 Hz), 4.65 (1H, s, OH), 5.44 (1H, s, OH), 5.64 (1H, d, J = 2 Hz), 5.66 (1H, d, 4 Hz). Anal. Calcd. for C₆H₄O₂Cl₄: C, 20.28; H, 1.89. Found: C, 20.32; H, 1.82.

Diacetate: mp 109—110 °C (from n-hexane–benzene), IR (Nujol) 1770, NMR (CDCl₃) δ 2.18 (3H, s), 2.20 (3H, s), 4.75 (1H, d, J = 2 Hz), 5.82 (2H, s), 6.55 (1H, d, J = 2 Hz). Anal. Calcd. for C₁₆H₂₀O₄Cl₄: C, 27.54; H, 2.15. Found: C, 27.33; H, 2.27.

Bis-methyl formate: mp 77—78 °C (from n-hexane–ether), IR (Nujol) 1767, NMR (CDCl₃) δ 3.87 (6H, s), 4.75 (1H, d, J = 1.6 Hz), 5.64 (1H, d, J = 3.6 Hz), 5.94 (1H, d, J = 5.6 Hz), 6.44 (1H, d, J = 1.6 Hz). Mass Spectrum m/z: 467 (M⁺-1), 469, 471, 473, 475, and 395 (base). Anal. Calcd. for C₁₆H₂₂O₄Cl₄: C, 25.49; H, 2.14. Found: C, 26.23; H, 2.27. ¹⁷

2-(1-Acetoxy-2,2-dichloroethyl)-5-dichloromethyl-1,3-dioxolan-4-yl Acetate (11) ——Diacetate of 9 (170 mg, 0.587 mmole) was dissolved in THF (15 ml) and irradiated in a pyrex tube with a high pressure mercury lamp for 10 hr. The solvent was evaporated in vacuo and chromatography on silica-gel (CH₂Cl₂) followed by recrystallization from n-hexane–benzene gave 11 (106 mg, 74%), mp 87—88 °C, IR (Nujol) 1770, NMR (CDCl₃) δ 2.16 (3H, s), 2.19 (3H, s), 4.46 (1H, d, d, J = 1.5 and 5.4 Hz), 5.64 (1H, d, J = 1.5 Hz), 5.60 (1H, d, J = 3.8 Hz), 5.46 (1H, d, d, J = 3.8 and 5.4 Hz), 5.69 (1H, d, J = 5.4 Hz), 5.90 (1H, d, J = 5.4 Hz). Anal. Calcd. for C₁₆H₁₈O₄Cl₂: C, 32.46; H, 3.27. Found: C, 32.74; H, 3.34.

2,2-Dimethyl-5-trichloromethyl-1,3-dioxolan-4-ol (12) ——Adduct (4) was dissolved in a 10% aqueous acetone and worked up in the analogous manner as described for 7. Acetone (12) was obtained as an oily substance in addition to 7 and the spectral properties follow: IR (neat) 3440, NMR (CDCl₃) δ 1.56 (6H, s), 4.60 (1H, d, J = 2 Hz), 5.58 (1H, d, J = 2 Hz).

Acetate: mp 48—48.5 °C (from n-hexane–CH₂Cl₂), IR (Nujol) 1759, NMR (CDCl₃) δ 1.59 (3H, s), 1.60 (3H, s), 2.14 (3H, s), 4.76 (1H, d, J = 2 Hz), 6.45 (1H, d, J = 2 Hz). Anal. Calcd. for C₁₆H₁₄O₂Cl₄: C, 34.59; H, 3.96. Found: C, 34.31; H, 3.93.

3-Deoxy-3,3,3-trichloro-3-methylglyceraldehyde, Dimer (10) ——Compound (5) (2.0 g, 0.01 mole) prepared from 4¹⁷ was dissolved in 50% aqueous THF (50 ml) and kept at room temperature for 40 hr. The solution was concentrated in vacuo and the precipitates were collected and washed with water to give the dimer (10) as colorless crystals (1.0 g, 70%). Pure sample was obtained by recrystallization from MeOH, mp 180—185 °C (partly sublimed), IR (Nujol) 3405, Anal. Calcd. for C₂₀H₁₄O₂Cl₄: C, 25.17; H, 2.80. Found: C, 25.14; H, 2.88.

The acetate was recrystallized from THF to give colorless crystals, mp 245—245 °C (partly sublimed), IR (nujol) 1760, NMR (CFCl₃) δ 3.35 (6H, s), 4.35 (2H, d, d, J = 1.5 and 8 Hz), 5.54 (2H, d, J = 8 Hz), 6.47 (2H, d, J = 1.5 Hz). Anal. Calcd. for C₂₀H₁₈O₄Cl₄: C, 34.46; H, 3.27. Found: C, 34.59; H, 3.29.

3,6-Bis(2-oxo-5-trichloromethyl-1,3-dioxolan-4-yl)-1,4-dioxane-2,5-diol (16a) and (16b) ——A solution of telomer (13a) (300 mg, 0.92 mmole) in THF (10 ml) was added 2N HCl (10 ml) and the mixture was stirred at room temperature for 40 hr. The solvent was removed in vacuo, and the resulting solid was washed with water to leave a colorless solid. Recrystallization from MeOH-acetone gave 16a as colorless prisms, mp 174—175 °C, IR (Nujol) 3480 and 1790, Anal. Calcd. for C₂₅H₂₆O₄Cl₄: C, 27.53; H, 1.90. Found: C, 27.23; H, 1.78.

Diacetate: mp over 300 °C (from CH₂Cl₂-benzene), IR (Nujol) 1809, 1801 and 1770, NMR (CDCl₃) δ 4.37 (2H, d, d, J = 9 and 1 Hz), 5.19 (2H, d, d, J = 4 and 1 Hz), 5.42 (2H, d, J = 4 Hz), 6.24 (2H, d, J = 9 Hz). Anal. Calcd. for C₂₅H₂₂O₄Cl₄: C, 31.42; H, 2.29. Found: C, 31.60; H, 2.18.

b) In the same way as above, telomer 13b gave 16b (384 mg, 90%) which was recrystallized from MeOH-acetone to afford colorless crystals, mp 184—185 °C, IR (nujol) 3490 and 1815, Anal. Calcd. for C₂₅H₂₂O₄Cl₂: C, 27.53; H, 1.90. Found: C, 27.23; H, 1.78.

Diacetate: mp over 300 °C (from CH₂Cl₂), IR (Nujol) 1822 and 1763 NMR (CFCl₃) δ 2.36 (6H, s), 4.34 (2H, d, d, J = 9 and 1 Hz), 5.08 (2H, d, d, J = 4 and 1 Hz), 5.30 (2H, d, J = 4 Hz), 6.13 (2H, d, J = 9 Hz). Anal. Calcd. for C₂₅H₂₂O₄Cl₂: C, 31.42; H, 2.29. Found: C, 31.66; H, 2.34.

5,5,5-Trichloro-3,5-dideoxy-5-entulosose, Dimer (17) ——The solution of 13a (2.0 g, 6 mmole) in 50% aqueous dioxane (8 ml) was heated at 100—110 °C in a sealed tube for 10 hr. The solvent was removed in vacuo

¹⁷ In spite of extensive purification procedures and acceptable spectral data, elementary analyses showed the unsatisfactory results, which were reproducible on repeated runs.
and purification of an oily residue by chromatography on silica gel (CH₂Cl₂) gave 17 (1.32 g, 96%), which was recrystallized from ether-CH₂Cl₂ to afford colorless prisms, mp 136—138°, IR (Nujol) 3405 and 3380, NMR (CDCl₃) δ 3.50 (1H, m), 4.00 (2H, m), 5.27 (IH, s), 5.78 (1H, s). Anal. Calcd. for C₉H₁₉O₄Cl₂: C, 27.33; H, 2.27. Found: C, 27.45; H, 2.27.

Diacetate: mp 187—188° (from n-hexane-ether), IR (Nujol) 1758, NMR (CDCl₃) δ 2.15 (6H, s), 2.50 (3H, m), 3.32 (1H, q, J = 14 and 6 Hz), 4.00 (2H, m), 6.02 (1H, s), 6.37 (1H, s). Anal. Calcd. for C₁₅H₁₈O₄Cl₂: C, 32.12; H, 2.68. Found: C, 31.93; H, 2.66.

17 was also obtained from 13b and therefore the mixture of 13a and 13b was routinely used for the preparation.

5,5,5-Trichloro-1,2,4-pentanetriol (20)—To a cooled solution of 17 (100 mg, 0.23 mmole) in 85% aqueous MeOH (10 ml) was added NaBH₄ (40 mg, 1.03 mmole) and the mixture was refluxed for 3 hr. The solution was neutralized with an ion exchange resin (Amberlite IR-120 H⁺) and the resin was filtered off. Removal of the solvent followed by flash evaporation with MeOH (3 times) gave a colorless solid which was recrystallized from MeOH-acetone to give 20 as colorless needles (70 mg, 67%), mp 132—134°, IR (Nujol) 3320 and 3185, NMR (D₂O) δ 1.80 (2H, m), 3.40 (2H, t), 3.75 (1H, m), 4.30 (1H, d, J = 9 and 2 Hz). Anal. Calcd. for C₆H₁₂O₄Cl₂: C, 26.87; H, 4.06. Found: C, 27.14; H, 4.09.

5,5,5-Trichloro-1,2,4-pentanetriol-1,2-diacetate (20-diacetate) In the same procedure as described for 20, reduction of 17 (60 mg, 0.14 mmole) with NaBD₄ (0.2 g, 4.9 mmole) gave 20-diacetate (41 mg, 66%), which was recrystallized from MeOH-CH₂Cl₂ to afford colorless prisms, mp 128—130°, IR (Nujol) 3300, NMR (D₂O) δ 1.80 (2H, m), 3.50 (1H, d, J = 7 Hz), 4.30 (1H, d, J = 9 and 2 Hz).

α-Trichloromethyl-2-quinoxalinemethanol (21)—The mixture of 17 (1.0 g, 2.27 mmole) and α-phenylene diamine (0.49 g, 4.54 mmole) in 30 ml of ethanol was refluxed for 4 hr and the solvent was removed in vacuo. Purification of the product by chromatography on silica gel (CH₂Cl₂) followed by recrystallization from CHCl₃ gave 21 (0.7 g, 52%) as colorless needles, mp 105—106°, IR (Nujol) 3360 and 1560. NMR (CDCl₃) δ 5.53 (2H, m), 4.76 (1H, d, J = 3 and 9 Hz), 7.57—8.09 (4H, m), 8.71 (1H, s). Anal. Calcd. for C₁₅H₁₁Cl₃O₂: C, 45.28; H, 3.09; N, 9.61. Found: C, 45.35; H, 3.04; N, 9.71.

4-(1-Hydroxy-2,2-dimethoxyethyl)-5-trichloromethyl-1,3-dioxolan-2-one (15a) and (15b)—A methanolic solution (50 ml) of 13a (2.5 g, 7.8 mmole) was refluxed in the presence of catalytic amount of p-toluene sulfonic acid for 65 hr. The solvent was removed in vacuo and the residue was chromatographed on silica-gel (CH₂Cl₂) to give 15a (2.37 g, quantitatively) as a colorless viscous oil. IR (neat) 3480 and 1822.

p-Nitrobenzoate: mp 107—108° (from n-hexane-ether), IR (Nujol) 1822, 1740, and 1603. NMR (CDCl₃) δ 5.51 (6H, s), 4.78 (1H, d, J = 5.5 Hz; acetal proton), 5.15 (1H, m), 5.41—5.51 (2H, m), 8.25 (4H, s). Anal. Calcd. for C₁₅H₁₁O₅N₂Cl₂: C, 39.28; H, 3.07; N, 3.05. Found: C, 39.35; H, 3.00; N, 2.96.

b) In the same procedure as described for the methanalysis to 15a, telomer (13b) (1.42 g, 4.36 mmole) gave the acetate (15b) (1.345 g, quantitatively) as a colorless viscous oil. IR (neat) 3480 and 1820.

p-Nitrobenzoate: mp 127—128° (from n-hexane-ether), IR (Nujol) 1810, 1745, and 1607. NMR (CDCl₃) δ 3.40 (3H, s), 3.55 (3H, s), 4.75 (1H, d, J = 6.5 Hz; acetal proton), 4.85 (1H, d, J = 4 Hz), 5.22 (1H, d, J = 4 and 1.8 Hz), 5.50 (1H, d, d, J = 6.5 and 1.8 Hz), 8.31 (4H, s). Anal. Calcd. for C₁₅H₁₁O₅N₂Cl₂: C, 39.28; H, 3.07; N, 3.05. Found: C, 39.39; H, 3.13; N, 3.13.

5-Deoxy-5,5,5-trichloro-di-L-xlyose (19a)—The mixture of 15a (2.62 g, 8.4 mmole) and NaBH₄ (1.08 g, 28 mmole) in 80% aqueous MeOH (50 ml) was refluxed for 1 hr and neutralized with a cation exchange resin (Amberlite IR 120 H⁺). Another portion of the resin was added and the mixture was stirred at room temperature overnight. Removal of the solvent followed by flash evaporation with MeOH (3 times) gave crude xlyose (19a) (1.5 g, 82%) as an oil, whose IR spectrum (neat) showed band at 3400 and no absorption in the carbonyl region.

Triacetate (1,2-cis Isomer): mp 105—106° (from n-hexane-ether), IR (Nujol) 1765, NMR (CDCl₃) δ 2.08 (3H, s), 2.10 (3H, s), 2.12 (3H, s), 4.86 (1H, d, J = 5 Hz), 5.05 (1H, d, d, J = 5 and 5 Hz), 5.35 (1H, d, J = 3.5 and 5 Hz), 6.44 (1H, d, J = 3.5 Hz). Anal. Calcd. for C₁₅H₁₁O₅Cl₂: C, 36.32; H, 3.61. Found: C, 36.47; H, 3.44.

5-Deoxy-5,5,5-trichloro-ni-xlylose (19b)—The acetate (15b) (0.93 g, 3 mmole) in the same manner as described for 19a gave crude product of 19b (0.89 g, 86%) as viscous oil, which showed the absence of carbonyl functions in the IR spectrum. IR (neat) 3500.

1.1-Dimethoxy-3,3,3-trichloro-2-propanol (8)—Adduct (4) (1.2 g, 5 mmole) was dissolved in 25 ml of absolute MeOH and it was refluxed in the presence of catalytic amount of TsOH for 50 hr. Removal of the solvent followed by chromatography on silica-gel (CH₂Cl₂) gave 8 (1.11 g, 99%) as an oil. Further purification by distillation gave a viscous oil, bp 72—73°C/1 mm, IR (neat) 3480, NMR (CDCl₃) δ 3.40 (3H, s), 3.53 (3H, s), 4.08 (1H, d, J = 2 Hz), 4.75 (1H, d, J = 2 Hz). Anal. Calcd. for C₁₅H₁₁O₅Cl₂: C, 26.84; H, 4.03. Found: C, 26.94; H, 4.20.

b) A methanolic solution (50 ml) of 4 (7 g, 29 mmole) and TsOH (catalytic amounts) was refluxed for 10 hr. Working up as above gave 6 (2 g, 29%) and 8 (2.5 g, 38%) as oily products which were identified with the authentic samples.
c) A methanolic solution (15 ml) of 6 (1.13 g, 4.8 mmole) was treated in the same way as above to give 8 (1.1 g, quantitatively), whose IR and NMR spectra were identical with those of 8 prepared from 4.

4-Methoxy-5-trichloromethyl-1,3-dioxolan-2-one (6)—Compound 4 (6.0 g, 0.025 mole) was treated with NaOH (1.0 g, 0.025 mole) in absolute MeOH (60 ml) under ice-cooling for 7 hr. The methanol was removed in vacuo and acetone was added. Precipitates were filtered off. Evaporation of the filtrate followed by chromatography on silica gel (benzene) gave 6 (2.9 g, 50%) in addition to 7 (0.1 g, 2.2%). Spectral data were following: IR (neat) 1828, NMR (CDCl₃) δ 3.60 (3H, s), 4.75 (1H, d, J = 2 Hz), 5.50 (1H, d, J = 2 Hz).

Reduction to gem-Trichloro Polyalcohols (23, 24, 25a, 25b)—3,3,3-Trichloro-1,2-propanediol (23) provides the typical procedure as follows. To an aqueous methanolic solution of 4 (2.6 g, 10.8 mmole) was added NaBH₄ (0.5 g, 13.2 mmole) under ice-cooling and the mixture was stirred during the first 30 min and then refluxed for 45 min. After the neutralization with an ion exchange resin (Amberlite IR 120 H⁺) followed by removal of the precipitates with the aid of acetone, flash evaporation of the residue with MeOH (3 times) gave 23 (1.62 g, 83.5%), mp 85—84° (from CH₂Cl₂—acetone) (lit. 190 mp 83°), IR (Nujol) 3440, NMR (D₂O) δ 3.75 (1H, d, d), 4.20 (1H, m), 4.20 (1H, m). Anal. Calcd. for C₃H₂OCl₂: C, 20.07; H, 2.81. Found: C, 20.41; H, 2.81.

4-Deoxy-4,4,4-trichloro-δ-threitol (24) was analogously prepared from trans-ester (22) (3.6 g, 13.6 mmole) in 58% yield and recrystallized from CH₂Cl₂—acetone as colorless crystals, mp 103—104°, IR (Nujol) 3440 and 3280. Anal. Calcd. for C₃H₂OCl₂: C, 22.92; H, 3.37. Found: C, 22.84; H, 3.28.

5-Deoxy-5,5,5-trichloro-δ-lyxitol (25a) was similarly prepared by reduction of telomer (13a) (0.652 g, 2 mmole) in 78% yield (0.374 g). Recrystallization from MeOH—CH₂Cl₂ gave 25a as colorless needles, mp 151—152°, IR (Nujol) 3380, 3280, and 3180. Anal. Calcd. for C₃H₂OCl₂: C, 25.05; H, 3.76. Found: C, 24.87; H, 3.72.

5-Deoxy-5,5,5-trichloro-δ-xylitol (25b) was obtained in 85% yield (0.325 g) from telomer (13b) (0.52 g, 1.6 mmole) in the same procedure as for 25a, mp 125—128° (from MeOH—acetone), IR (Nujol) 3380, 3300, and 3240. Anal. Calcd. for C₃H₂OCl₂: C, 25.05; H, 3.76. Found: C, 25.33; H, 3.79.

4,4,4-Trichloro-2,3-dihydroxybutyronitrile (27)—a) trans-Nitrile (26) (1.5 g, 6.5 mmole) was treated with NaBH₄ (0.6 g, 0.015 mole) in 90% aqueous MeOH (30 ml) at room temperature for 1 hr. The reaction mixture was worked up in the usual way to give a mixture of the products as a solid. Separation by chromatography on silica gel (CH₂Cl₂—acetone 10%) gave cyanohydrin (27) (0.97 g, 73%) in addition to 23 (0.3 g, 25%). Recrystallization of 27 from CH₂Cl₂ gave an analytical sample of mp 80°, IR (Nujol) 3380, NMR (CH₂CN) δ 4.42 (1H, d, J = 2.8 Hz), 5.14 (1H, d, J = 2.8 Hz). Anal. Calcd. for C₃H₂OCl₂N: C, 23.49; H, 1.97; N, 6.85. Found: C, 23.03; H, 2.05; N, 6.84.

b) A solution of 26 (0.5 g, 2.16 mmole) in acetone (3 ml) and water (10 ml) was refluxed in the presence of a catalytic amount of conc. HCl for 3 hr. Removal of the solvent followed by chromatography on silica gel (CH₂Cl₂—acetone 10%) gave 27 (0.364 g, 82%) which was identical with the compound prepared above.