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New Synthetic Routes to Carbohydrates by the Use of Telomers of Vinylene Carbonate with Polyhalomethanes*

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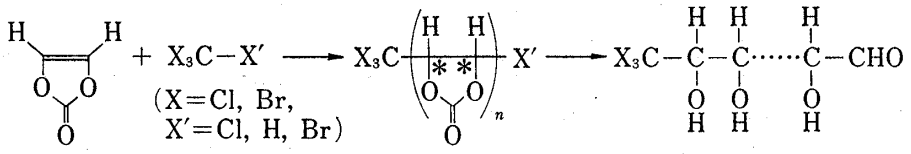
Type **2** telomers ($n=1$, 2) of vinylene carbonate **1** with polyhalomethanes, carbon tetrachloride and chloroform, were transformed to pentoses (triose) by new route involving two-step conversion of trichloromethyl groups into aldehydes, and tetroses and hexoses by smooth cyanation followed by reductive hydrolysis of trichloromethyls in analogous treatment described for pentoses. Thus DL-arabinose and DL-xylose were prepared in 44% (and 32%) and 43% (and 38%) yields from 5-chloro-5'-trichloromethyl-[4,4'-bi-1,3-dioxolane]-2,2'-dione, **3** and **4** (and 5-trichloromethyl-[4,4'-bi-1,3-dioxolane]-2,2'-dione, **5** and **6**), respectively, providing the unamiguous stereochemistry of the $n=2$ telomers **3** and **4** (and **5** and **6**) as *trans-"syn"-trans* and *trans-"anti"-trans* configurations. 4-Chloro-5-trichloromethyl-1,3-dioxolan-2-one **13** gave DL-glyceraldehyde, DL-threose and DL-erythrose. DL-Galactose and DL-altrose, and DL-idose and DL-glucose were obtained from the syn form **3**, and the anti form **4**, respectively.

Previous paper in this series described the radical telomerization of vinylene carbonate **1** with polyhalomethanes to permit a two-step synthesis of halogenated pentoses *via* the type **2** telomers stereoselectively formed,[2)] which could be served as highly potential intermediates for the novel synthesis of other type of carbohydrates as well as polyalcohols.[3)]



1 **2** : $n=1, 2, \cdots$

This short-step method is of considerable significance in the potential usefulness for stereoselective preparation of much higher monosaccharides in contrast to previously reported syntheses[4)] from simple non-carbohydrate substances involving the formose synthesis,[5)] but applicable only to the preparation of the compounds with odd number of carbon atoms. Introduction of one carbon unit to structurally characteristic telomers **2** by smooth cyanation, contrary to unsatisfactory substitution with other carbanions, opens up the route to the even carbon sugar derivatives. And conversion of the polyhalomethyl groups into the aldehydes under mild conditions would provide new method to both natural and unnatural halogen-free monosaccharides.

We report here new facile synthetic routes to triose, tetoroses, pentoses and hexoses from the low telomers (**2**, $n=1$ and $n=2$) obtained in the reaction using carbon tetrachloride and

* Dedicated to the memory of Prof. Eiji Ochiai.

1) Location: *Hongo, Bunkyo-ku, Tokyo, 113, Japan.*

2) T. Tamura, T. Kunieda, and T. Takizawa, *Tetrahedron Lett.*, **1972**, 2219; *idem.*, *J. Org. Chem.*, **39**, 38 (1974).

3) For a review of this area, T. Kunieda and T. Takizawa, *J. Syn. Org.* (Japan)., **33**, 560 (1975).

4) J. Apsimon, "The Total Synthesis of Natural Products," Vol I, Wiely, New York, N.Y., 1973, Chapter 1.

5) A. Butlew, *Compt. Rend.*, **53**, 145 (1861); *idem*, *Ann.*, **120**, 295 (1861). for a recent review, T. Mizuno, *Kagaku no Ryoiki* **26**, 762 (1973).

chloroform as telogens, and hence, the unequivocal stereochemistry of $n=2$ telomers by their chemical transformation to the authentic sugars.

Synthesis of Pentoses and Glyceraldehyde

Low telomers, $n=1$ (**13** and **14**) and $n=2$ (**3**, **4** and **5**, **6**), which were stereoselectively obtained in the telomelization of 1 with carbon tetrachloride and chloroform, were transformed into glyceraldehyde and pentoses, arabinose and xylose by the steps involving the conversion of trichloromethyl groups to aldehydes.

Photoreduction[6] under mild conditions seems to be the method of choice for selective conversion of trichloromethyl groups into dichloromethyls in such labile compounds as the telomers. Thus, the $n=2$ telomers **3**, **4**, **5**, and **6** were irradiated with high-pressure mercury lamp in tetrahydrofuran to give the dichloromethyl compounds, **7**, **8**, **9**, and **10** in high yields (Table I), respectively. Nickel carbonyl[7] is satisfactory agent for this purpose as well. Treatment of **7** and **8** with excess sodium borohydride in boiling 90% methanol smoothly afforded tetrahydroxy compounds (**11** and **12**), which were also obtained from **9** and **10** on the same treatment.

Table I. Yield of Photoreduction and Hydrolysis

Compound	Yield (%)[a]	Pentose	Yield (%)[b]
7	79	DL-arabinose	56
8	80	DL-xylose	54
9	72	DL-arabinose	44
10	79	DL-xylose	48

a) isolated yield
b) overall yield (by sugar analyzer) based on dichloromethyl compounds

Some difficulties were encountered in hydrolysis of dichloromethyl groups not activated with vicinal carbonyl or olefinic groups to the carbonyls without epimerization and repeated atempts with nucleophilic reagents like metal acetates, perchlorate, or alkoxides were unsuccessful. The most suitable reagent examined so far is silver nitrate,[8] with which model compound 1,1-dichlorooctane was hydrolyzed in aqueous methanol at 90° to octanal including small amount of acetal in 62% yield. Thus, aqueous solutions of **11** and **12** were treated with silver nitrate at 70° to give moderate yields of DL-arabinose and DL-xylose, respectively (see Table I). Simultaneous hydrolysis of protecting groups of **16** (and **9**,**10**) with silver nitrate gave only poor yields of monosaccharides indicative of the importance of intramolecular participation of hydroxyl groups. Identification of the products with authentic monosaccharides was performed by liquid chromatographic analysis which showed no contamination of practical amount of C_2-epimers, in either case.

These chemical transformations have provided the unequivocal evidence for *trans*-"*syn*"-*trans* and *trans*-"*anti*"-*trans* configurations of the $n=2$ telomers **3** and **5**, and **4** and **6**, respectively, as tentatively assigned previously.[2] Therefore, hydrolysis of the carbonate groups of the telomers **3** and **4** leads to the formation of 5,5,5-trichloro-5-deoxy-DL-lyxose and -xylose, respectively, in analogy with the $n=2$ telomers of **1** with methylene bromide as telogen.[2]

In a similar synthetic route, DL-glyceraldehyde was obtained from the $n=1$ adducts, **13**, and **14**, though in low yields.

This method comprises mild and selective reactions which would permit the general transformation of higher telomers **2** ($n\geqq3$) to heptoses, nonoses and the higher unnatural monosaccharides.

6) N. Mitsuo, T. Kunieda, and T. Takizawa, *J. Org. Chem.*, **38**, 2255 (1973).
7) T. Kunieda, T. Tamura, and T. Takizawa, *J. Chem. Soc., Chem. Commun.*, **1972**, 885.
8) *cf.* B.M. Trost and M.J. Bogdanowicz, *J. Am. Chem. Soc.*, **95**, 2038 (1973). We are indebted to Professor Trost for experimental detail of this procedure prior to the full publication.

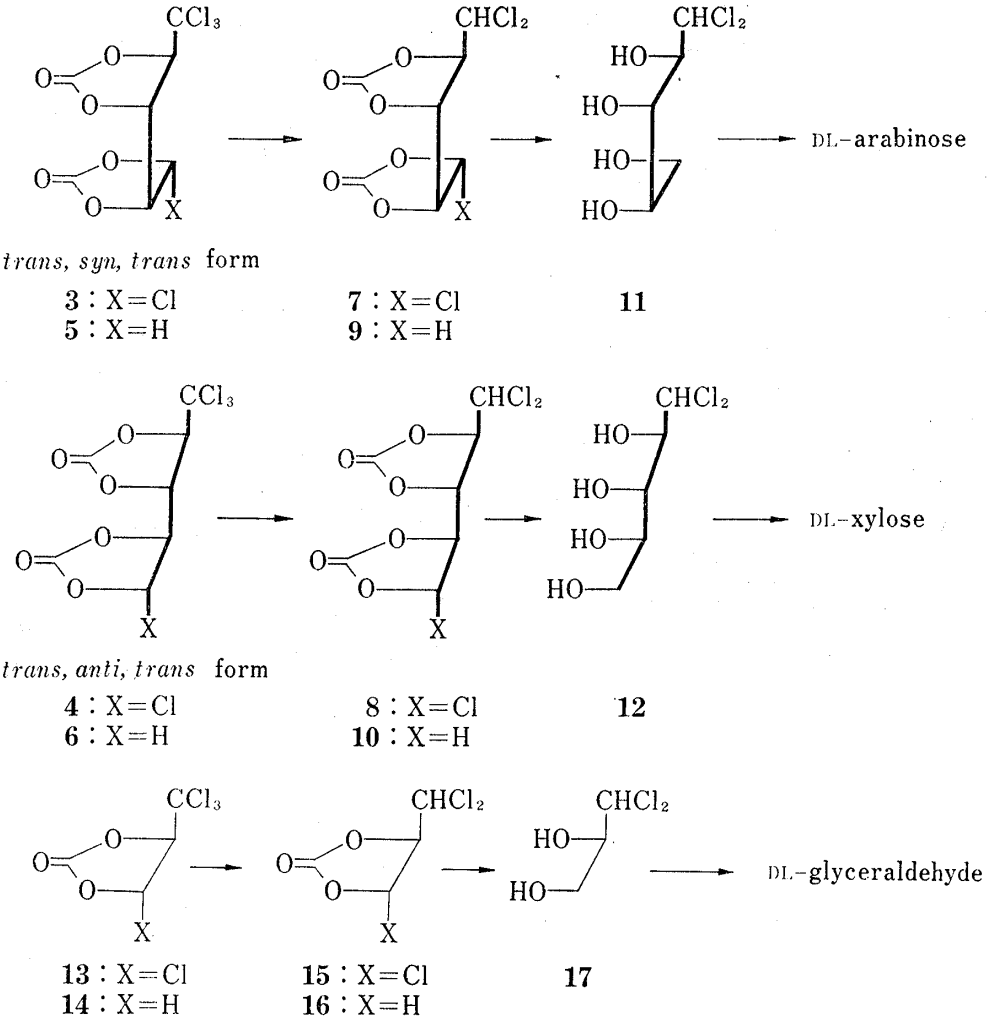


Chart 1

Synthesis of Tetroses and Hexoses

Monosaccharides with even carbon numbers were prepared from the telomers, **13**, **3**, and **4** (carbon tetrachloride as telogen) which have active secondary halogen easily substituted with cyanide in contrast to other carbanions. Treatment of **13** with sodium cyanide in dimethylformamide at room temperature afforded a 64% yield of *trans* and *cis* cyano compounds,[9] **18** and **19** (a ratio of 1.1 : 1), of which the configurational assignment was determined by nuclear magnetic resonance (NMR) spectral data (vicinal coupling constants of 4 Hz for **18** and 8 Hz for **19**).[10] Phase transfer catalysis reaction[11] was particularly useful for this nucleophilic displacement. Reaction of **13** with sodium cyanide in the presence of tetrabutyl ammonium bromide as a catalyst in aqueous methylene chloride at 0° for 2 hr gave *trans*- and *cis*-isomers in 47% and 25% yields, respectively.

trans-Nitrile (**18**) could be readily esterified with dry hydrogen chloride in absolute methanol to **20** in 90% yield, which on photoreduction afforded dichloromethyl derivative (**21**) in 72% yield. Reduction of the ester group of **21** proceeded smoothly with sodium

9) R. Kiston and N.E. Griffth, *Anal. Chem.*, **24**, 334 (1952). The intensity of the infrared absorption of the cyano groups is considerably quenched when oxygen containing groups are introduced at α-position and the cyano compounds isolated showed no absorptions characteristic of cyano groups in the region of 2200—2300 cm.

10) *cf.* L.M. Jackman and S. Sternhell, "Application of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," 2nd ed, Pergamon Press, Elmsford, N.Y., 1969, p. 280.

11) E.V. Dehlmlow, *Angew. Chem. Internat. Edit.*, **13**, 170 (1974).

borohydride to give the triol **22**, which on hydrolysis with aqueous silver nitrate, gave DL-threose in 64% yield in addition to the negligible amount of the epimer. Similar esterification of *cis*-**19** afforded a carbonate ring-cleaved product (**23**) in 72% yield, presumably owing to large steric repulsion between *cis* substituents. Irradiation of the acetate (**25**) in tetrahydrofuran gave the dichloromethyl compound (**26**) (70% yield), which was hydrolyzed to DL-erythrose in 25% yield (route a). Alternative pathway (route b) involves photoreduction of **19** as an initial step followed by esterification to a mixture of **29** and **30**, which were converted to DL-erythrose in 39% overall yield from **19**.

trans cyano compounds (**33** and **35**) prepared from the adducts (**31** and **32**) of carbon tetrabromide and methylene bromide to vinylene carbonate were similarly converted to the identical dibromide (**38**), which was smoothly methanolyzed to acetal (**39**) with the aid of silver nitrate. Borohydride reduction of the acetal followed by mild hydrolysis with an ion exchange resin (IR-120 (H^+)) gave DL-threose in 31% yield.

Fractional recrystallization of the cyanation products of **7** resulted in the isolation of *trans* and *cis* cyano compounds, **41** (J_{ab}=5 Hz)[10] and **42** (J_{ab}=6 Hz) in 7% and 24% yields, respectively, while chromatographic separation on silica gel gave cyanohydrin **43** as only isolable product (66% yield), which could be led to cis-carbonate compound (**42**) with phosgene. The cyanation products derived from **8** were fractionated by careful crystallization into *trans* and *cis* isomers, **44** (J_{ab}=4 Hz)[10] and **45** (J_{ab}=9 Hz) in 5% and 31% yields, respectively.

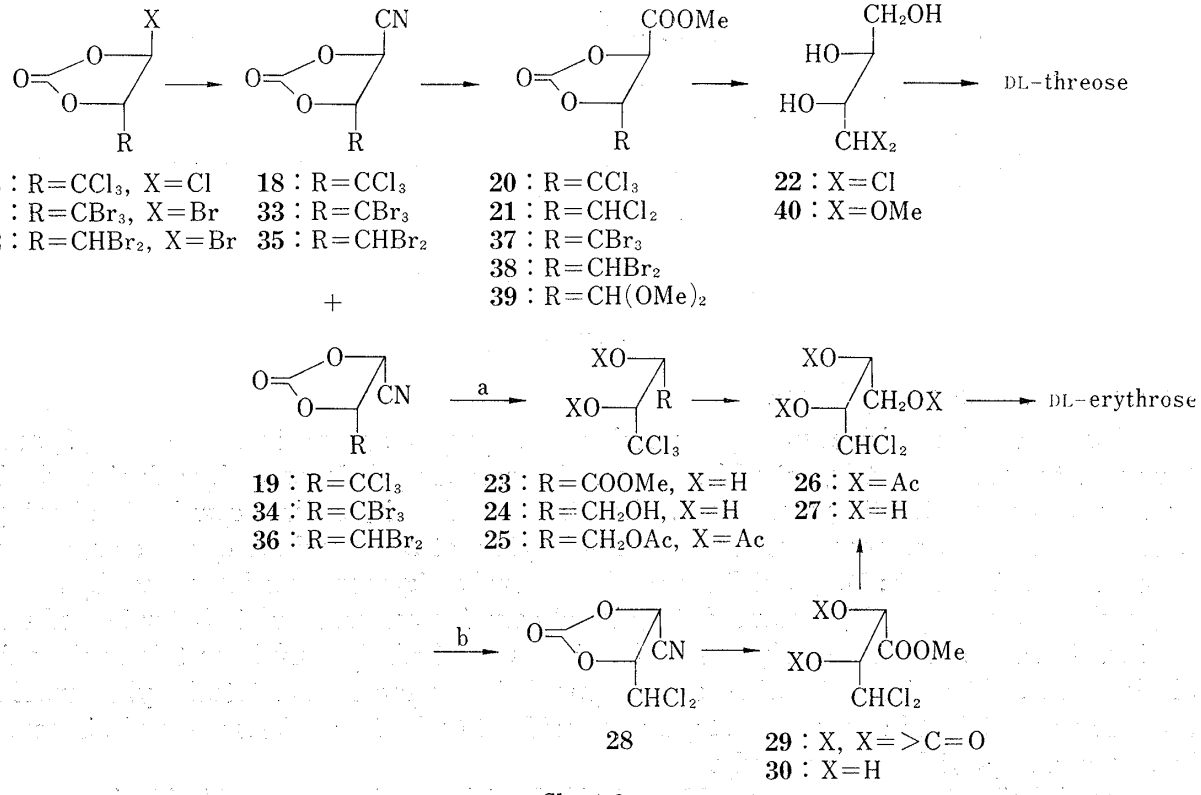


Chart 2

Esterification of *trans*-cyano compounds (**41** and **44**) proceeded smoothly to give excellent yields of **46** and **50**, which were converted to DL-galactose (49%) and DL-idose (24%) via the borohydride reduction products, **53** and **55**, respectively. Formation of appreciable amount of DL-sorbose became apparent during hydrolysis of **55**, reflecting configurational unstability of DL-idose.[12]

12) *cf.* D-Idose is well known to isomerize readily to D-sorbose, owing to conformational high instability. S. Coffey, "Rodd's Chemistry of Carbon Compounds," Vol. I Part F, Elsevier, New York, N.Y., 1967 p. 239.

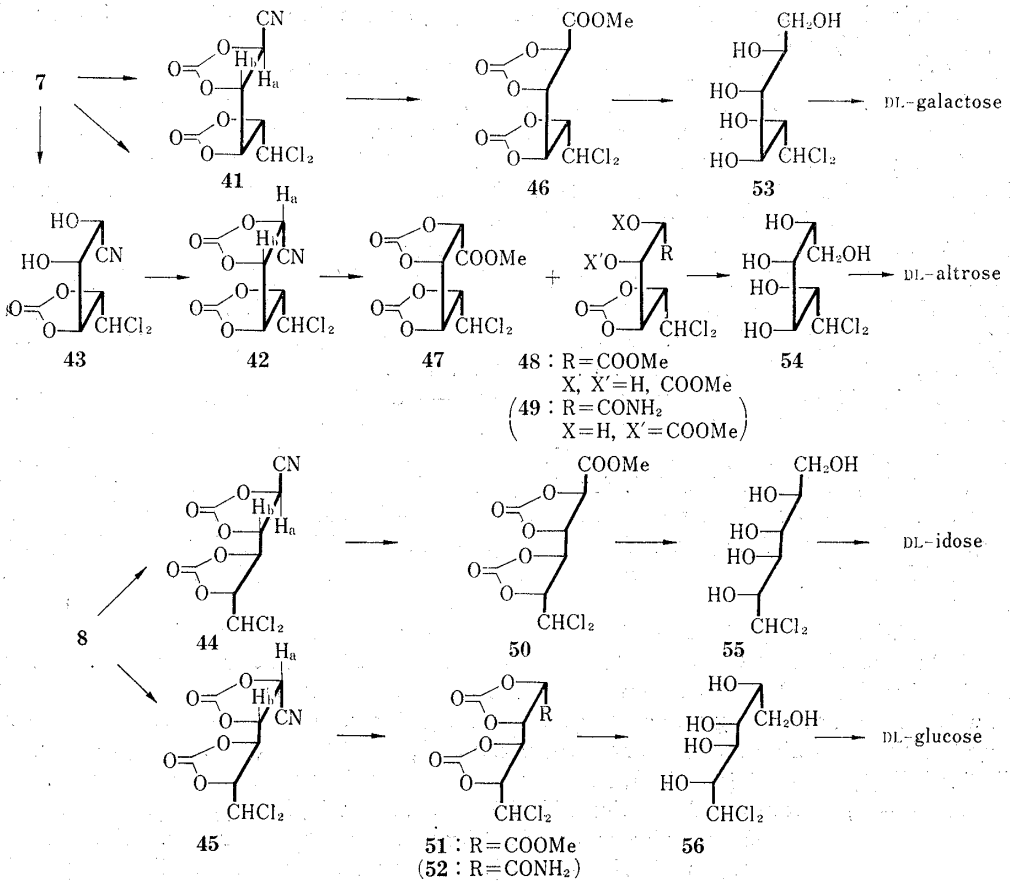


Chart 3

On the other hand, *cis*-isomers gave the complicated results toward the similar treatment with methanolic hydrogen chloride. The products derive from **42** consisted of the esters, **47** (8%) and **48** (48%) in addition to the amide (**49**) (38%), and **45** afforded the expected ester (**51**) (36%) and the amide (**52**) (27%). Reduction of the esters **48** (**47**) and **51** and subsequent hydrolysis with silver nitrate gave DL-altrose and DL-glucose in 42% and 57% yields, respectively.

Synthetic methods described here would provide the general stereoselective routes to unnatural heptoses, octoses and the higher monosaccharides from achiral simple compounds *via* the higher telomers **2** ($n \geqq 3$).

Experimental

All melting points were taken in Yanaco micro melting point apparatus and are uncorrected. Infrared (IR) spectra were determined on a JASCO Model DS-402G spectraphotometer, absorptions given in cm^{-1}. NMR spectra were recorded on a Hitachi R-24 spectrometer (60 MHz) using tetrametylsilane (TMS) as an internal standard. Sugar analyses were performed with a JEOL liquid chromatographic autoanalyzer, Model JLC-6AH. The samples dissolved in 0.13M sodium borate buffer (pH 7.5) were applied to the column of JEOL Resin LC-R-3 transformed into borate form and eluted successively with 0.13M, 0.25M and 0.35M borate buffer adjusted at pH 7.5, 9.0 and 9.6, respectively. Sugar components were detected with the orcinol-sulfuric acid method while the absorbances at 511 nm and 428 nm were automatically recorded. Yields of carbohydrates were determined by quantitative analysis of the chromatograms thus obtained.

Preparation of Telomers——Telomers were prepared from vinylene carbonate and polyhalomethanes in presence of benzoyl peroxide by the slightly modified procedure previously reported.[2] Thus, reactions of 1 and CCl_4 (mole ratio of 1: 20), $CHCl_3$ (ratio 1: 25) and CBr_4 (ratio 1: 3) gave the $n=1$ adducts **13** mp 54° (65%), **14** mp 99° (24%) and **31** mp 86° (64%), respectively. Similarly, the $n=2$ telomers **3** mp 186° and **4**

mp 156° were obtained from **1** and CCl_4 (ratio 1: 10) in 23% yield, and **5**[13] mp 152° and **6**[13] mp 186° from **1** and $CHCl_3$ (1: 20) in 8.5% yield.

5-Chloro-5′-dichloromethyl-4,4′-bi-1,3-dioxolane-2,2′-dione (7)——According to the procedure[6] described previously, solutions of **3** (750 mg, 2.4 mmole) in tetrahydrofuran (THF) (100 ml) were irradiated in a quartz vessel without filter with a high-pressure mercury lamp for 5 hr. The solvent was removed *in vacuo* and purification of the products by chromatography on silica gel (CH_2Cl_2) followed by recrystallization from CCl_4–CH_2Cl_2 gave **7** (582 mg, 79%), mp 116°, identical with the sample[6] prepared previously, with respect to IR and NMR data and chromatographic behaviours.

5-Chloro-5′-dichloromethyl-4,4′-bi-1,3-dioxokane-2,2′-dione (8)——Analogous to the method described for **7**, irradiation of **4** (1.1 g, 3.5 mmole) for 4 hr gave **8** (780 mg, 80%) as colorless needles, which was recrystallized from CH_2Cl_2–CCl_4 to afford an analytical sample as colorless needles. mp 163°; IR (Nujol) 1840; NMR (CH_3CN) δ 6.60 (d, J=2 Hz, 1H, C_5–H), 6.20 (d, J=4 Hz, 1H, $CHCl_2$), 5.15 (m, 3H). *Anal.* Calcd. for $C_7H_5O_6Cl_3$: C, 28.85; H, 1.73. Found: C, 28.79; H, 1.66.

5-Trichloromethyl-[4,4′-bi-1,3-dioxolane]-2,2′-dione (9)——UV-irradiation of **5** (380 mg, 1.3 mmole) in THF for 8 hr afforded a colorless solid, **9** (240 mg; 72%) in the same manner as described for **7**. Recrystallization from CH_2Cl_2 gave colorless needles, mp 88°; IR (Nujol) 1800; NMR (CH_3CN) δ 6.25 (d, J=4 Hz, 1H, $CHCl_2$), 5.05 (m, 3H), 4.35 (m, 2H). *Anal.* Calcd. for $C_7H_6O_6Cl_2$: C, 32.72; H, 2.36. Found: C, 32.61; H, 2.23.

5-Trichloromethyl-[4,4′-bi-1,3-dioxolane]-2,2′-dione (10)——On the similar irradiation for 5 hr, **6** (750 mg, 2.7 mmole) gave **10** (582 mg, 79%), mp 168° from CH_2Cl_2–CCl_4; IR (Nujol) 1810; NMR (CH_3CN) δ 6.15 (d, J=4 Hz, 1H, $CHCl_2$), 5.00 (m, 3H), 4.50 (m, 2H). *Anal.* Calcd. for $C_7H_6O_6Cl_2$: C, 32.72; H, 2.36. Found: C, 32.74; H, 2.28.

Octanal and 1,1-Dimethoxyoctane——A mixture of 1,1-dichlorooctane[14] (1.85 g, 10 mmole) and silver nitrate (17 g, 100 mmole) in 90% CH_3OH (30 ml) was kept in a sealed tube at 95° overnight. The precipitate was removed by filtration and the filtrate was evaporated *in vacuo*. The resulting oil was chromatographed on silica gel with benzene as eluting solvent to give octanal (650 mg, 58%), (2,4-dinitrophenylhydrazone mp 104°, lit[15] mp 105°) and 1,1-dimethoxyoctane[16] (60 mg, 3.5%), NMR ($CDCl_3$) δ 4.35 (t, J=6 Hz, 1H, $CHCl_2$), 3.25 (s, 6H, 2×OCH_3), 0.7—1.8 (m, 15H), in addition to the unchanged material (230 mg).

DL-Arabinose——a) From **7**: A solution of **7** (900 mg, 3.2 mmole) in 95% CH_3OH (30 ml) was treated with $NaBH_4$ (468 mg, 1.2 mmole) under ice cooling for 1 hr and then at 60° for 2 hr. The reaction mixture was neutralized with an ion exchange resin (IRC-50 H^+). Removal of the solvent followed by flash evaporation with CH_3OH (3 times) gave dichloromethyl compound (**11**) (800 mg) as amorphous powder, which showed no absorption of ester groups in the IR spectrum and was used for next step without further purification. A mixture of **11** (100 mg) thus obtained and silver nitrate (830 mg, 4.9 mmole) in water (3 ml) was kept in a sealed tube at 70° overnight. The precipitate was removed by filtration and the filtrate treated with methanolic hydrogen chloride to remove excess silver ion as silver chloride. The precipitate was filtered off and the filtrate was neutralized with an ion exchange (Dowex-1 HCO_3^{-1}-form). Evaporation of the filtrate gave crude DL-arabinose as an amorphous powder which showed retention time 250 min on the liquid chromatogram (249 min for the authentic D-arabinose). Sugar analysis of this product showed a 56% overall yield of DL-arabinose from **7** with negligible amount of C-2 epimer, ribose.

b) From **9**: A mixture **9** (780 mg, 3 mmole) and $NaBH_4$ (456 mg, 12 mmole) in 90% CH_3OH (30 ml) was stirred at 60° for 2.5 hr. The reaction mixture was neutralized with an ion exchange resin (IRC-50 H^+), and evaporation of the solvent gave dichloromethyl compound (**11**) (600 mg, which showed the absence of carbonyl groups in the IR spectrum. Treatment of **11** (100 mg) with silver nitrate (830 mg, 4.9 mmole) in water (3 ml) afforded DL-arabinose in a 44% overall yield. Retention times for DL-arabinose and D-arabinose on liquid chromatograms were 220 min and 219 min, respectively.

DL-Xylose——a) From **8**: In analogy to the procedure described for DL-arabinose, **8** (1 g, 3.6 mmole) reacted with $NaBH_4$ (520 mg, 14 mmole) in 95% CH_3OH (30 ml) to give dichloromethyl compound (**12**) (700 mg), of which a part (100 mg) was hydrolyzed with silver nitrate (830 mg, 4.9 mmole) in water (3 ml) to DL-xylose with retention time 247 min (248 min for the authentic D-xylose) in a 54% overall yield based on **8**.

b) From **10**: In the same way as described for DL-arabinose, **10** (365 mg, 1.4 mmole) was treated with $NaBH_4$ (218 mg, 5.7 mmole) in 90% CH_3OH (20 ml) to give dichloromethyl compound (**12**) (326 mg) as an amorphous powder which gave DL-xylose in 48% yield based on **10**.

4-Dichloromethyl-1,3-dioxolan-2-one (16)——Analogously to the procedure described above, a solution of **14** (2 g, 9.7 mmole) in THF (100 ml) was irradiated with UV-lamp for 7 hr. Evaporation of the solvent gave **16** (1.4 g, 84%), mp 62—63° (from *n*-hexane); IR (Nujol) 1825 and 1800; NMR ($CDCl_3$) δ 6.00 (d, J=

13) Previous paper[2] erronenously reported that the n=2 telomers **5** and **6** were eluted out from the silica gel column in a reverse turn under the conditions described.
14) A.J. Hill and F. Tyson, *J. Amer. Chem. Soc.*, **50**, 172 (1928).
15) C. Morel, *Soap. Perfum. Cosmet.*, **1954**, 279.
16) S. Motoki, S. Satumabayashi, and H. Kusano, *Bull. Chem. Soc. Japan.*, **38**, 922 (1965).

3 Hz, 1H, $CHCl_2$), 5.15 (m, 1H, C_1–H), 4.55 (m, 2H, C_2–H). *Anal.* Calcd. for $C_4H_4O_3Cl_2$: C, 28.10; H, 2.36. Found: C, 28.06; H, 2.76.

3,3-Dichloro-1,2-propanediol (17)——a) A solution of **15**[6] (2 g, 9.7 mmole) in 90% CH_3OH (20 ml) was treated with $NaBH_4$ (1.8 g, 47 mmole) under ice cooling for 1 hr and then at room temperature overnight. The reaction mixture was neutralized with an ion exchange resin (IRC-50 H^+). After removal of the solvent, resulting oil was chromatographed on silica gel using CH_2Cl_2 as elution solvent to give **17** (960 mg, 81%), IR (Neat) 3320.

b) Treatment of **16** (1.6 g, 9.4 mmole) with $NaBH_4$ (1.42 g, 37 mmole) in 90% CH_3OH (10 ml) at 60° for 3 hr gave **17** (980 mg, 72%), whose IR spectrum was in accord with that of **15**. IR (Neat) 3320.

DL-Glyceraldehyde——According to the method described for DL-arabinose, **17** (88 mg, 0.61 mmole) was treated with silver nitrate (1.05 g, 6.0 mmole) in water (3 ml) at 105° overnight to give DL-glyceraldehyde (5.3%) which was identical with commercial DL-glyceraldehyde dimer on the liquid chromatographic behaviors.

***trans*- and *cis*-2-Oxo-5-trichloromethyl-1,3-dioxolane-4-carbonitrile (18 and 19)**——a) A solution of **13** (30 g, 0.125 mmole) in dry DMF (30 ml) was treated with NaCN (7.35 g, 0.15 mmole) at room temperature for 24 hr. After removal of the insoluble materials by filtration, the filtrate was poured into ice-water and the mixture was extracted with benzene three times. The extracts were dried over anhydrous magnesium sulfate and evaporated *in vacuo* to leave an oil, which was chromatographed on silica gel using a mixture of *n*-hexane and benzene (3: 7) as eluting solvent to give **18** (9.8 g, 34%) and **19** (8.65 g, 30%). **18**, mp 113° (from *n*-hexane); IR (KBr) 1825 and 1805; NMR (DMSO-d_6) δ 6.40 (AB quartet, J=4 Hz). *Anal.* Calcd. for $C_5H_2O_3NCl_3$: C, 26.06; H, 0.88; N, 6.08. Found: C, 26.11; H, 0.85; N, 6.09. **19**, mp 144° (from CCl_4); IR (KBr) 1820; NMR (DMSO-d_6) δ 6.18 (AB, q, J=8 Hz). *Anal.* Calcd. for $C_5H_2O_3NCl_3$: C, 26.06; H, 0.88, N, 6.08. Found: C, 26.02; H, 1.28; N, 6.53.

b) A solution of NaCN (1.13 g, 23 mmole) in water (6 ml) was added to a solution of **13** (5 g, 21 mmole) and tetrabutyl ammonium bromide (30 mg, 0.09 mmole) in CH_2Cl_2 (50 ml) under ice cooling and the mixture was stirred at 0° for 2 hr. The CH_2Cl_2 layer was separated, washed with water (3×30 ml) and dried over anhydrous magnesium sulfate. Removal of the solvent left an oil, of which chromatography on silica gel gave **18** (2.3 g, 47%) and **19** (1.2 g, 25%), identical in all respects with the compounds described above.

Methyl *trans*-2-Oxo-5-trichloromethyl-1,3-dioxolane-4-carboxylate (20)——Dry hydrogen chloride gas was bubbled through a solution of **18** (1.25 g, 5.4 mmole) in absolute CH_3OH (10 ml) under ice cooling for 10 min. The precipitate was removed by filtration and the filtrate was evaporated *in vacuo* to leave a colorless solid. Recrystallization from *n*-hexane gave **20** as colorless needles, (1.1 g, 84%), mp 80—82°; IR (Nujol) 1835, 1815, 1745; NMR ($CDCl_3$) δ 5.25 (d, J=2 Hz, 1H, C_5–H), 5.10 (d, J=2 Hz, 1H, C_4–H), 4.92 (s, 3H, OCH_3). *Anal.* Calcd. for $C_6H_5O_5Cl_3$: C, 27.36; H, 1.90. Found: C, 27.54; H, 1.99.

Methyl *trans*-5-Dichloromethyl-2-oxo-1,3-dioxolane-4-carboxylate (21)——a) A solution of **20** (1.76 g, 6.7 mmole) in THF (100 ml) was irradiated with UV-lamp for 7 hr. Evaporation of the solvent gave an oil, which was distilled *in vacuo* to give **21** (1.21 g, 79%), bp 124° (0.4 mm); IR (Neat) 1835 and 1760; NMR ($CDCl_3$) δ 5.96 (d, J=3.2 Hz, 1H, $CHCl_2$), 5.12 (d, J=3.6 Hz, 1H, C_4–H), 5.08 (d-d, J_1=3.6 Hz, J_2=3.2 Hz, 1H, C_5–H), 3.92 (s, 3H, OCH_3). *Anal.* Calcd. for $C_6H_5O_5Cl_2$: C, 31.00; H, 2.62. Found: C, 31.10; H, 2.74.

b) A solution of **20** (2 g, 7.6 mmole) and nickel tetracarbonyl (4 ml, 25 mmole) in THF (15 ml) was stirred at 40° in a slow stream of nitrogen for 64 hr. The yellow precipitate was removed by filtration and the filtrate was evaporated *in vacuo* to leave a viscous oil, which was chromatographed on silica gel with with benzene as an eluting solvent to give a colorless oil (1.2 g, 70%), which showed identical IR spectrum (Neat) with that of **21**.

DL-Threose——$NaBH_4$ (664 mg, 17 mmole) was added to a solution of **21** (400 mg, 1.7 mmole) in 90% CH_3OH at 0° and the mixture was refluxed for 3 hr. Treatment of the mixture with IRC 50 (H^+) was followed by flash-evaporation with CH_3OH gave **22** (280 mg) as a powder, which showed the absence of carbonyl groups in the IR spectrum. The triol **22** (150 mg) was hydrolyzed with silver nitrate (1.45 g, 8.5 mmole) in water (5 ml) at 75° to DL-threose (64% yield from **21**), which gave retention time 123 min on the chromatogram (122 min for the authentic D-threose[17]).

Methyl *erythro*-2,3-Dihydroxy-4,4,4-trichlorobutyrate (23)——Dry hydrogen chloride gas was bubbled through a solution of **19** (8.68 g, 38 mmole) in absolute CH_3OH (60 ml) under ice cooling for 5 min. Evaporation of the solution left an oil, which was chromatographed on silica gel using CH_2Cl_2 as eluting solvent to give **23** (5.51 g, 62%). Recrystallization from CH_2Cl_2 gave an analytical sample of mp 134—135°; IR (Nujol) 3300 and 1760; NMR (DMSO-d_6) δ 5.15 (d, J=5 Hz, 1H), 4.45 (d, J=5 Hz, 1H), 3.80 (s, 3H, OCH_3). *Anal.* Calcd. for $C_5H_7O_4Cl_3$: C, 25.28; H, 2.51. Found: C, 25.52; H, 2.62.

DL-4,4-Dichloro-1,2,3-butanetriol, Triacetate (26)——A $NaBH_4$ (4.7 g, 0.13 mmole) was added to a solution of **23** (2.96 g, 13 mmole) in 90% CH_3OH (50 ml) and the mixture was stirred at 60° for 3 hr. Treatment with an ion exchange resin (IRC-50 H^+) followed by evaporation of the solvent gave a powder **24** (1.82 g)

17) S. Morgennlie, *Acta. Chem. Scand.*, **26**, 1709 (1972).

which showed no carbonyl absorptions in the IR spectrum. Acetylation of **24** with acetic anhydride (4 ml, 43 mmole) in pyridine (8 ml) in the usual way gave an oily product which was purified by chromatography on silica gel (CH_2Cl_2) to give the acetate **25** (680 mg, 13.4%) as a colorless oil, IR (Neat) 1740; NMR ($CDCl_3$) δ 5.80 (d, $J=3$ Hz, 1H, C_3–H), 5.65 (m, 1H, C_2–H), 4.25 (m, 2H, C_1–H), 2.20—2.05 (3s, 9H, $3\times$OAc). Solutions of the above acetate **25** (440 mg, 1.3 mmole) in THF (100 ml) were irradiated with UV-lamp for 3 hr. Evaporation of the solvent *in vacuo* gave an oil, whose purification was achieved by chromatography on silica gel (CH_2Cl_2) to give **26** (290 mg, 74%) as a colorless liquid which was partly decomposed on distillation at 88°/0.22 mm, IR (Neat) 1740; NMR ($CDCl_3$) δ 5.90 (d, $J=4$ Hz, 1H, $CHCl_2$), 5.7—5.2 (m, 2H), 4.25 (m, 2H), 2.2—2.1 (3s, 9H, $3\times$OAc).

DL-Erythrose——a) From **26**: To a solution of **26** (86 mg, 0.29 mmole) in absolute methanol (10 ml) was added 2 ml of a freshly prepared solution of sodium methoxide (0.5 g of sodium dissolved in 100 ml of methanol) with stirring at room temperature for 30 min. The mixture was neutralized with an ion exchange resin IR-120 (H^+) and evaporation of the solvent gave **27** (50 mg) as an amorphous powder. According to the method described the above, **27** was treated with the silver nitrate (486 mg, 2.9 mmole) in water (3 ml) to give DL-erythrose (28% overall yield from **26**). The retention times of DL-erythrose and D-erythrose[17] showed 132 min and 130 min, respectively.

b) From **29**: $NaBH_4$ (317 mg, 8.3 mmole) was added to a solution of **29** (170 mg, 0.74 mmole) in 90% methanol (10 ml). The mixture was refluxed for 3 hr to give **27** (190 mg) as an amorphous powder. Similarly, **27** was treated with silver nitrate (1.4 g, 8.2 mmole) in water (3 ml) to give DL-erythrose (65% overall yield from **29**). The retention times of DL-erythrose and D-erythrose[17] showed 80 min and 77 min, respectively.

***cis*-5-Dichloromethyl-2-oxo-1,3-dioxolane-4-carbonitrile** (**28**)——A solution of **19** (1.7 g, 7.4 mmole) in THF (100 ml) was irradiated with UV-lamp for 45 hr. Evaporation of the solvent *in vacuo* gave **28** (1.13 g, 78%) as an oil, which was homogeneous on thin-layer chromatography (TLC) plate and used for next procedure without further purification. IR (Neat) 1820; NMR ($CDCl_3$) δ 5.95 (d, $J=6$ Hz, 1H, $CHCl_2$), 5.55 (d, $J=8$ Hz, 1H, C_4–H), 5.10 (d-d, $J_1=8$ Hz, $J_2=6$ Hz, 1H, C_5–H).

Methyl 5-Dichloromethyl-2-oxo-1,3-dioxolane-4-carboxylate (**29**) **and Methyl 4,4-Dichloro-2,3-dihydroxybutyrate** (**30**)——Dry hydrogen chloride gas was gently bubbled through a solution of **28** (760 mg, 3.9 mmole) in absolute CH_3OH (15 ml) under ice cooling for 5 min. Evaporation of solution left an oily residue which was chromatographed on silica gel using CH_2Cl_2 as eluting solvent to give **29** (285 mg, 32%) as colorless needles, mp 120° (from CCl_4) in addition to an oily product **30** (320 mg, 41%). Spectral data are as follows. **29** IR (Nujol) 1800 and 1750; NMR ($CDCl_3$) δ 6.05 (q, 1H, $CHCl_2$), 5.20 (m, 2H), 5.87 (s, 3H, OCH_3). *Anal.* Calcd. for $C_6H_6O_5Cl_2$: C, 31.46; H, 2.64. Found: C, 31.73; H, 2.58. **30** IR (Neat) 3320 and 1750; NMR (CH_3CN) δ 5.90 (d, $J=5$ Hz, 1H, $CHCl_2$), 4.25 (m, 2H), 3.80 (s, 3H, OCH_3).

***trans*- and *cis*-5-Tribromethyl-2-oxo-1,3-dioxolane-4-carbonitrile** (**33 and 34**)——A solution of **31** (39 g, 93 mmole) in dry DMF (40 ml) was treated with sodium cyanide (10 g, 0.2 mmole) at room temperature for 30 hr. After removal of the precipitate by filtration, the filtrate was poured onto ice-water and the mixture was extracted with benzene for three times. The extracts were dried over anhydrous magnesium sulfate and evaporated *in vacuo* to leave an oil, which was chromatographed on silica gel using a mixture of *n*-hexane and benzene (1: 1) as eluting solvent to give **33** (9.4 g, 28%) and **34** (8.2 g, 24%). Recrystallization of **33** from *n*-hexane gave pure trans isomer of mp 111° as colorless needles, IR (KBr) 1820; NMR ($CDCl_3$) δ 5.34 (d, $J=4$ Hz, 1H), 5.18 (d, $J=4$ Hz, 1H). *Anal.* Calcd. for $C_5H_2O_3NBr_3$: C, 16.75; N, 3.84. Found: C, 16.89; N, 3.75. Recrystallization from CCl_4 gave *cis* isomer of mp 198°; IR (KBr) 1810; NMR (CH_3CN) δ 5.90 (d, $J=8$ Hz, 1H), 5.60 (d, $J=8$ Hz, 1H). *Anal.* Calcd. for $C_5H_2O_3NBr_3$: C, 16.75; N, 3.84. Found: C, 16.71; N, 3.71.

***trans*- and *cis*-5-Dibromomethyl-2-oxo-1,3-dioxolane-4-carbonitrile** (**35 and 36**)——A solution of **32** (10 g, 29 mmole) in DMF (5 ml) was treated with NaCN (2.1 g, 44 momle) at room temperature overnight. The reaction mixture was worked up in analogy to the procedure described for **31** to give **35** (1.6 g, 18%) and **36** (3.8 g, 45%). **35** IR (Neat) 1830; NMR ($CDCl_3$) δ 5.87 (d, $J=3$ Hz, 1H, $CHBr_2$), 5.26 (d, $J=4$ Hz, 1H, C_4–H), 5.15 (m, 1H, C_5–H). **36** mp 140°; IR (KBr) 1810; NMR (CH_3CN) δ 6.10 (d, $J=4$ Hz, 1H, $CHBr_2$), 5.66 (d, $J=9$ Hz, 1H, C_4–H), 5.30 (d–d, $J_1=9$ Hz, $J_2=4$ Hz, 1H, C_5–H). *Anal.* Calcd. for $C_5H_3O_3NBr_2$: C, 21.08; H, 1.06; N, 4.92. Found: C, 21.05; H, 1.01; N, 4.85.

Methyl *trans*-5-Tribromomethyl-2-oxo-1,3-dioxolane-4-carboxylate (**37**)——Dry hydrogen chloride gas was bubbled through a solution of **33** (9 g, 25 mmole) in absolute CH_3OH (50 ml) under ice cooling for 30 min. The precipitate was removed by filtration and the filtrate was evaporated *in vacuo* to leave a colorless solid **37** (8.9 g, 91%), which was recrystallized from *n*-hexane to show mp 84—86°; IR (KBr) 1820 and 1750; NMR ($CDCl_3$) δ 5.22 (d, $J=4$ Hz, 1H), 4.98 (d, $J=4$ Hz, 1H), 3.88 (s, 3H, OCH_3). *Anal.* Calcd. for $C_6H_5O_5Br_3$: C, 18.14; H, 1.26. Found: C, 18.30; H, 1.30.

Methyl *trans*-5-Dibromomethyl-2-oxo-1,3-dioxolane-4-carboxylate (**38**)——a) Analogously to the method described for **7**, a solution of **37** (2.7 g, 6.8 mmole) in THF (100 ml) was irradiated with UV-lamp for 4.5 hr. Evaporation of the solvent followed by chromatography on silica gel (benzene) gave **38** (1.27 g, 58%) as an oil. IR (Neat) 1845 and 1760; NMR ($CDCl_3$) δ 5.84 (d, $J=1$ Hz, 1H, $CHBr_2$), 5.06 (m, 2H), 3.90 (s, 3H, OCH_3).

b) A solution of **37** (6.1 g, 15 mmole) and nickel tetracarbonyl (6 ml, 38 mmole) in THF (30 ml) was stirred at 40° in a slow stream of nitrogen for 2.5 hr. The red precipitate was removed by filtration and the

filtrate was evaporated *in vacuo* to leave an oil, which was chromatographed on silica gel (benzene) to give a colorless oil (3.1 g, 63%), identical with **38** obtained above.

c) In the similar procedure described for **37** *trans*-cyano compound (**35**) (377 mg, 1.3 mmole) was esterified with dry hydrogen chloride gas in absolute CH_3OH (20 ml) to give **38** (300 mg, 71%), which gave identical IR spectrum with that of **38**.

Methyl *trans*-5-Dimethoxymethyl-2-oxo-1,3-dioxolane-4-carboxylate (**39**)——A mixture of **38** (2 g, 6.3 mmole) and silver nitrate (11 g, 65 mmole) in absolute CH_3OH (50 ml) was kept in a sealed tube at 108° overnight. The precipitates formed were removed by filtration and the filtrate was evaporated *in vacuo* to leave an oil, which was chromatographed on silica gel with CH_2Cl_2 as eluting solvent to give **39** (786 mg, 65%) in addition to an unchanged material **38** (660 mg). **39** IR (Neat) 1830 and 1760; NMR ($CDCl_3$) δ 5.00 (d, J=4 Hz, 1H, C_5–H), 4.4—4.7 (m, 2H), 3.78 (s, 3H, $COOCH_3$), 3.45 (2s, 6H, $2\times OCH_3$).

DL-Threose——A mixture of **39** (400 mg, 1.9 mmole) and $NaBH_4$ (620 mg, 19 mmole) in 90% CH_3OH (20 ml) was kept at 60° for 2.5 hr and neutralized with an ion exchange resin (IRC-50 H^+). Evaporation of the solvent followed by treatment with an ion exchange resin (IR-120 H^+) in 66% CH_3OH (15 ml) at 60° for 6 hr and then at room temperature overnight. After removal of the resin by filtration. the filtrate was evaporated *in vacuo* to give DL-threose as a powder (31% overall yield from **39**). The retention times of DL-threose and the authentic D-threose showed 140 min and 146 min, respectively, on the liquid chromatogram.

***trans*- and *cis*-5′-Dichloromethyl-2,2′-dioxo-[4,4′-bi-1,3-dioxolane]-5-carbonitrile (41 and 42)**——A solution of **7** (5.2 g, 21 mmole) in dry DMF (10 ml) was treated with NaCN (1.02 g, 21 mmole) at room temperature for three days. After removal of the insoluble materials by filtration, the filtrate was poured into ice-water and the mixture was extracted with CH_2Cl_2 for three times. The extracts were dried over anhydrous $MgSO_4$ and evaporated *in vacuo* to leave colorless crystals, which were fractionated by careful crystallization from CH_2Cl_2 to give **41** (0.4 g, 7%) and **42** (1.4 g, 24%). **41**, mp 188°; IR (KBr) 1835 and 1810: NMR (CH_3CN) δ 6.25 (d, J=3 Hz, 1H, $CHCl_2$), 5.55 (d, J=5 Hz, 1H, C_5–H), 5.15 (m, 3H). *Anal.* Calcd. for $C_8H_5O_6NCl_2$: C, 34.07; H, 1.79; N, 4.97. Found: C, 34.04; H, 1.70; N, 5.03. **42**, mp 125°; IR (Nujol) 1830 and 1810; NMR (CH_3CN) δ 6.25 (d, J=3 Hz, 1H, $CHCl_2$). 5.85 (d-d, J_1=6 Hz, J_2=1 Hz, 1H, C_5–H), 5.35 (m, 3H). *Anal.* Calcd. for $C_8H_5O_6NCl_2$: C. 34.07; H, 1.79; N, 4.97. Found: C, 34.08; H, 1.80; N, 5.04.

***cis*-5-Dichloromethyl-*α,β*-dihydroxy-2-oxo-1,3-dioxolane-4-propionitrile (43)**——In a similar procedure described for **41** and **42**, **7** (3.23 g, 11 mole) was treated with NaCN (830 mg, 17 mmole) in dry DMF (15 ml) and crude product was purified by chromatography on silica gel using a mixture of CH_2Cl_2 and acetone (1 : 0.05) as eluting solvent to afford a solid, which was recrystallized from CH_2Cl_2 to give **43** (1.9 g, 66%) as colorless needles, mp 133—135°; IR (KBr) 3400 and 1790; NMR (CH_3CN) δ 6.15 (d, J=3 Hz, 1H, $CHCl_2$), 5.10 (t, J=3 Hz, 1H, C_β–H), 4.82 (t, J=3 Hz, 1H, C_4–H), 4.55 (d, J=6 Hz, 1H, C_α–H), 4.14 (d-d, J_1=6 Hz, J_2= 3 Hz, 1H, C_β–H). *Anal.* Calcd. for $C_7H_7O_5NCl_2$: C, 32.83; H, 2.76; N, 5.48. Found: C, 32.83; H, 2.74; N, 5.31.

42 from 43——A solution of dry pyridine (1.3 ml, 16 mmole) in CH_2Cl_2 (20 ml) was added dropwise to a mixture of **43** (790 mg, 3.1 mmole) and phosgene (1.3 g, 13 mmole) in CH_2Cl_2 (20 ml) under ice cooling and the mixture was stirred at room temperature overnight. After removal of the precipitate by filtration, the filtrate was evaporated *in vacuo* to give **42** (490 mg, 56%) as colorless needles, which was identical in all respects with the sample **42** prepared above.

***trans*- and *cis*-5′-Dichloromethyl-2,2′-dioxo-[4,4′-bi-1,3-dioxolane]-5-carbonitrile (44 and 45)**——A solution of **8** (9 g, 32 mmole) in dry DMF (15 ml) was treated with NaCN (1.76 g, 36 mmole) at room temperature overnight. The insoluble materials were removed by filtration and the filtrate was poured onto ice-water. The products separated were extracted with CH_2Cl_2 and the extracted were dried over anhydrous $MgSO_4$. Removal of the solvent by evaporation *in vacuo* afforded colorless crystals, which were fractionally recrystallized from CH_2Cl_2 to give **44** mp 195° (0.8 g, 5%) and **45** mp 215—217° (2.5 g, 31%) as colorless solids. **44**, IR (KBr) 1820; NMR (CH_3CN) δ 6.25 (d, J=4 Hz, 1H, $CHCl_2$), 5.60 (d, J=4 Hz, 1H, C_5–H), 5.25 (m, 3H). *Anal.* Calcd. for $C_8H_5O_6NCl_2$: C, 34.07; H, 1.97; N, 4.97. Found: C, 33.78; H, 1.73; N, 4.95. **45**, IR (KBr) 1810; NMR (CH_3CN) δ 6.18 (d, J=3 Hz, 1H, $CHCl_2$), 5.75 (d, J=9 Hz, 1H, C_5–H), 5.1—5.4 (m, 3H). *Anal.* Calcd. for $C_8H_5O_6NCl_2$: C, 34.07; H, 1.97; N, 4.97. Found: C, 34.00; H, 1.70; N, 4.89.

Methyl *trans*-5′-Dichloromethyl-2,2′-dioxo-4,4′-bi-1,3-dioxolane-5-carboxylate (46)——Dry hydrogen chloride gas was moderately bubbled through a solution of **41** (190 mg, 0.7 mmole) in absolute methanol (10 ml) under ice cooling for 2 min. The precipitate was removed by filtrat and the filtrate was evaporated *in vacuo* to leave a colorless solid, which was recrystallized from CH_2Cl_2 to give **46** (190 mg, 90%) as colorless needles, mp 132°; IR (KBr) 1820, 1770 and 1760; NMR (CH_3CN) δ 6.25 (d, J=3 Hz, 1H, $CHCl_2$), 5.10 (m, 4H), 3.85 (s, 3H, OCH_3). *Anal.* Calcd. for $C_9H_8O_8Cl_2$: C, 34.31; H, 2.57. Found: C, 33.86; H, 2.47.

Methyl *trans*-5′-Dichloromethyl-2,2′-dioxo-[4,4′-bi-1,3-dioxolane]-5-carboxylate (50)——Analogously to the procedure for **46**, **44** (100 mg, 0.39 mmole) was treated with dry hydrogen chloride gas in absolute CH_3OH (10 ml) for 2 min to give **50** (100 mg, 90%). After recrystallization from CH_2Cl_2, it showed mp 123°; IR (KBr) 1820, 1790 and 1740; NMR (CH_3CN) δ 6.20 (d, J=2.5 Hz, 1H, $CHCl_2$), 5.1—5.2 (m, 4H), 3.80 (s, 3H, OCH_3). *Anal.* Calcd. for $C_9H_8O_8Cl_2$: C, 34.31; H, 2.57. Found: C, 34.44; H, 2.49.

Methyl *cis*-5′-Dichloromethyl-2,2′-dioxo-[4,4′-bi-1,3-dioxolane]-5-carboxylate (47, 48 and 49)——Into a cooled solution of **42** (1.52 g, 5.0 mmole) in absolute CH_3OH (20 ml) was bubbled dry hydrogen chloride gas for 5 min and the solvent was removed *in vacuo* to leave an oil, which was carefully chromatographed on silica gel using CH_2Cl_2 as eluting solvent. Three products, **47** (270 mg, 18%), **48** (790 mg, 48%) and **49** (480 mg, 30%) were obtained in pure forms and physical and spectral data are as follows. **47**, mp 107° (from CH_2Cl_2); IR (Nujol) 1840 and 1760; NMR (CH_3CN) δ 6.15 (d, J=3 Hz, 1H, $CHCl_2$), 5.20 (m, 4H), 3.80 (s, 3H, OCH_3). *Anal.* Calcd. for $C_9H_8O_8Cl_2$: C, 34.31; H, 2.57. Found: C, 34.03; H, 2.62. **48** (oil), IR (Neat) 3500, 1830 and 1770; NMR (CH_3CN D_2O) δ 6.20 (q, 1H, $CHCl_2$), 5.20 (m, 3H), 4.96 (d, J=6 Hz), 4.80 (d-d, J_1=6 Hz, J_2=4 Hz), 4.56 (d, J=4 Hz), 4.32 (t, J=4 Hz), 3.80 (4s, 6H, OCH_3). **49**, mp 156°; IR (KBr) 3500, 3400, 1830, 1810, 1745, 1665 and 1575; NMR (CH_3CN) 6.4—7.2 (m, 2H, NH_2), 6.20 (d, J=2 Hz, 1H, $CHCl_2$), 5.20 (m, 2H), 4.90 (d-d, J_1=6 Hz, J_2=4 Hz, 1H), 4.45 (b-d, 1H). *Anal.* Calcd. for $C_9H_{11}O_8NCl_2$: C, 32.53; H, 3.31; N, 4.22. Found: C, 32.56; H, 3.25; N, 4.13.

Methyl *cis*-5′-Dichloromethyl-2,2′-dioxo-[4,4′-bi-1,3-dioxolane]-5-carboxylate (51) and *cis*-5′-Dichloromethyl-2,2′-dioxo-[4,4′-bi-1,3-dioxolane]-5-amide (52)——In analogous way to the procedure for **47**, treatment of **45** (940 mg, 3.5 mmole) with dry hydrogen chloride gas in absolute CH_3OH (15 ml) for 5 min gave **51** (375 mg, 36%) in addition to the amide **52** (264 mg, 27%). **51**, mp 153° (from CH_2Cl_2); IR (KBr) 1790 and 1770; NMR (CH_3CN) δ 6.15 (d, J=3 Hz, 1H, $CHCl_2$), 5.1—5.4 (m, 4H), 3.80 (s, 3H, OCH_3). *Anal.* Calcd. for $C_9H_8O_8Cl_2$: C, 34.31; H, 2.57. Found: C, 34.08; H, 2.47. **52**, mp 229° (from CH_2Cl_2); IR (KBr) 3440, 3320, 3240, 3200, 1830, 1800 and 1695; NMR (CH_3CN) δ 6.2—7.2 (b, 2H, NH_2), 6.20 (d, J=3 Hz, 1H, $CHCl_2$), 5.1—5.4 (m, 4H). *Anal.* Calcd. for $C_8H_7O_7NCl_2$: C, 32.26; H, 2.36; N, 4.67. Found: C, 31.97; H, 2.23; N, 4.72.

DL-Galactose——A mixture of **46** (31 mg, 0.1 mmole) and $NaBH_4$ (38 mg, 1 mmole) in 90% CH_3OH (15 ml) was stirred at 60° for 3 hr. The reaction mixture was neutralized with an ion exchange resin (IRC-50 H^+) and removal of the solvent *in vacuo* gave the dichloromethyl compound **53** (21 mg) which gave the pentaacetate, mp 139° as colorless needles in the usual way using acetic anhydride in pyridine. An aqueous solution (3 ml) of **53** (21 mg) was treated with silver nitrate (231 mg, 1.3 mmole) at 75° overnight to give DL-galactose (49% overall yield from **46**). DL-Galactose and D-galactose showed on liquid chromatogram respective retention time of 188 min and 184 min, which had the agreement within the experimental error.

DL-Idose——A solution of **50** (100 mg, 0.32 mmole) in 90% CH_3OH (20 ml) was treated with $NaBH_4$ (122 mg, 3.2 mmole) at 60° for 3 hr and neutralization with cation exchange resin (IRC-50 H^+) followed by removal of the solvent and repeated flash evaporation with CH_3OH gave the dichloride **55** (60 mg) as a colorless solid, which was treated with silver nitrate (540 mg, 3.2 mmole) in water (3 ml) at 70° overnight. After neutralization, $NaBH_4$ (50 mg, 1.3 mmole) was added to the solvent treated and at room temperature overnight. The mixture was neutralized with an ion exchange resin (IR-120 H^+) and evaporation of the filtrate gave a mixture of DL-iditol and DL-glucitol as an oil. Gas chromatographic analysis[18] of two products showed retention time (7 min and 7.2 min) identical with those of D-iditol and D-glucitol and a 24% conversion yield based on **50**.

DL-Altrose——According to the same procedure as described for **53**, **48** (120 mg, 0.38 mmole) was reduced with $NaBH_4$ (144 mg, 3.8 mmole) to the dichloro alcohol **54** (80 mg), which was treated with silver nitrate (580 mg, 3.4 mmole) in water (3 ml) at 70° to afford DL-altrose (42% overall yield from **48**). DL-Altrose and the authentic D-altrose[19] showed on the liquid chromatogram retention time, 189 min and 190 min, respectively.

DL-Glucose——In an analogous manner for **53**, treatment of **51** (160 mg, 0.51 mmole) with $NaBH_4$ (190 mg, 5.1 mmole) gave the dichloride **56** (120 mg) as amorphous powder, which was hydrolyzed with silver nitrate (87 mg, 5 mmole) in water (3 ml) at 70° to DL-glucose in 57% yield based on **51**. DL-Glucose and the authentic D-glucose showed on the liquid chromatogram retention times of 194 min and 184 min, respectively.

Acknowledgement We thank the Takeda Science Foundation for a grant that aided in the purchase of the automatic sugar analyzer employed.

18) T. Imanari, Y. Arakawa, and Z. Tamura, *Chem. Pharm. Bull.* (Tokyo), **17**, 1967 (1969). The sample (100—500 μg) was treated with 0.1 ml of AcOEt and 0.1 ml of trifluoroacetic anhydride for 30 min at room temperature and two μl of reaction mixture was analyzed by gas chromatography (Simadzu GC-1c) with column (2% XF-1105) at 140° using hydrogen as carrier gas. We are much indebted to Dr. T. Imanari at this Faculty for performing gas chromatographic analysis of this sample.

19) R.L. Whiter and M.L. Wolform, "Method in Carbohydrate Chemistry," Vol. I, Academic Press, New York, N.Y. 1962, p. 102, 114.