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Studies on Telomers and Oligomers of Vinylene Carbonate. V.[1] Preparation and Stereochemistry of Adducts of Vinylene Carbonate with Tribromomethyl Compounds as Potential Intermediates for Sugar-like Compounds

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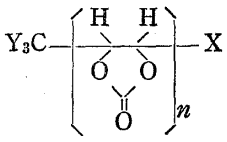
Free radical telomerization of vinylene carbonate with bromoform (and carbon tetrabromide) afforded two isomeric telomers, dibromomethylene-4,4'-bis(5-bromo-1,3-dioxolan-2-one) (**5a,b**) as two fold addition products in addition to the 1: 1 adducts. On the similar treatment, this type of products (**7a,b 9a,b**) was obtained from 5-substituted-4-tribromomethyl-1,3-dioxolan-2-ones.

A sequence of reactions involving methanolysis and reductive photolysis to give methyl 5-methoxypyranosides permitted the stereochemical assignment of **5a** and **b** as *dl* (anti)- and *meso*(*syn*)-configurations, respectively.

Preceding papers in this series[1a,d] described that free radical telomerization of vinylene carbonate in the medium of polyhalomethanes, carbon tetrachloride, chloroform and methylene bromide, resulted in the stereoselective and smooth formation of the purely separable low telomers of type **1**, which could be converted to polyhydroxylic compounds including aldo-sugars of triose to hexoses, in short routes involving mere hydrolysis under mild conditions[3] or two-step conversion of polyhalomethyl groups to formyls. This novel and facile synthesis of aldoses has shown the high potential of this type of telomerization as synthetic tools for carbohydrates.



1: $n=1,2,3\cdots$
X, Y=Cl, Br, H

On the other hand, free radical telomerization of vinylene carbonate with bromoform and tetrabromomethane showed quite different features from those with methylene bromide and polychloromethanes not to afford $n=2$ or higher telomers of type **1**, but only the "two-fold addition" products corresponding to $n=2$ telomers in addition to the $n=1$ adducts.

In this paper we report the stereochemical and mechanistic aspects on this radical addition reaction of tribromomethyl compounds to vinylene carbonate (**2**).

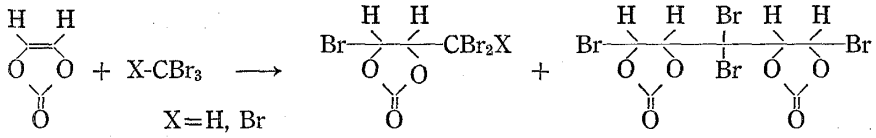
Preparation

Radical reaction of **2** with bromoform in the presence of conventional initiators such as benzoyl peroxide and azobisisobutyronitrile gave 1: 1 adducts **4** and **3**, and two stereo-isomeric dimers **5a** (mp 148°) and **5b** (mp 132°) in a ratio of 1.6: 1, of which the latter three were also formed in the use of tetrabromomethane in place of bromoform. Changes of the ratio of telogen to monomer did not result in the variation in the product composition to give no practical amounts of products corresponding to tri- or higher telomers, in sharp contrast to the telomerization with dibromomethane previously described.[1a]

1) The following papers constitute Part I—IV of this series. a) Part I: T. Tamura, T. Kunieda, and T. Takizawa, *Tetrahedron Letters*, **1972**, 2219; *idem*, *J. Org. Chem.*, **39**, 38 (1974); *b*) Part II: T. Kunieda, T. Tamura, and T. Takizawa, *Chem. Commun.*, **1972**, 885; *c*) Part III: N. Mitsuo, T. Kunieda and T. Takizawa, *J. Org. Chem.*, **38**, 2255 (1973); *d*) Part IV: H. Takahata, T. Kunieda, and T. Takizawa, *Chem. Pharm. Bull.* (Tokyo), **23**, 3017 (1975).

2) Location: *Hongo, Tokyo, 113, Japan.*

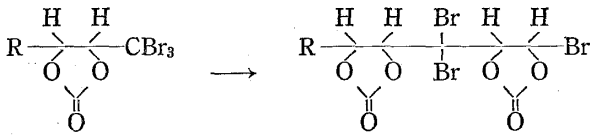
3) T. Matsuura, T. Kunieda, and T. Takizawa, *Chem. Pharm. Bull.* (Tokyo) in press.



2 **3**: X=Br; **4**: X=H **5a** : (mp 148°); **5b** : (mp 132°)

Compounds, **5a** and **b**, are apparently the "two-fold addition"[4] products which were shown by the high yield and the nearly identical isomer ratio (1.5: 1) on the separate treatment of **3** with **2** under similar conditions.

The same type of isomeric products **7a** and **b**, and **9a** and **b** was obtained in the isomer ratio of 1: 1 each by the similar treatments of *trans*-**6** and *trans*-**8**, respectively, which were conveniently prepared from **3** by cyanation of secondary bromine using phase transfer



3: R=Br; **6**: R=CN, *trans*; **8**: R=$COOCH_3$, *trans* **5a, b**: R=Br; **7a, b**: R=CN; **9a, b**: R=$COOCH_3$

catalyst,[5] tetrabutylammonium bromide, and the esterification of **6** thus formed. Attempted synthesis of 1: 1 products of *cis*-**8** and **2** was unsuccessful resulting in the recovery of most starting materials. This method on appropriate modifications would provide the new synthetic routes to uronic acids as well as α-hydroxy-aldehydes.

Reaction Pathway

In contrast to the general observation on bromoform with the tendency towards exclusive bromine transfer,[6] hydrogen[6a] and bromine would be equally abstracted from telogen by

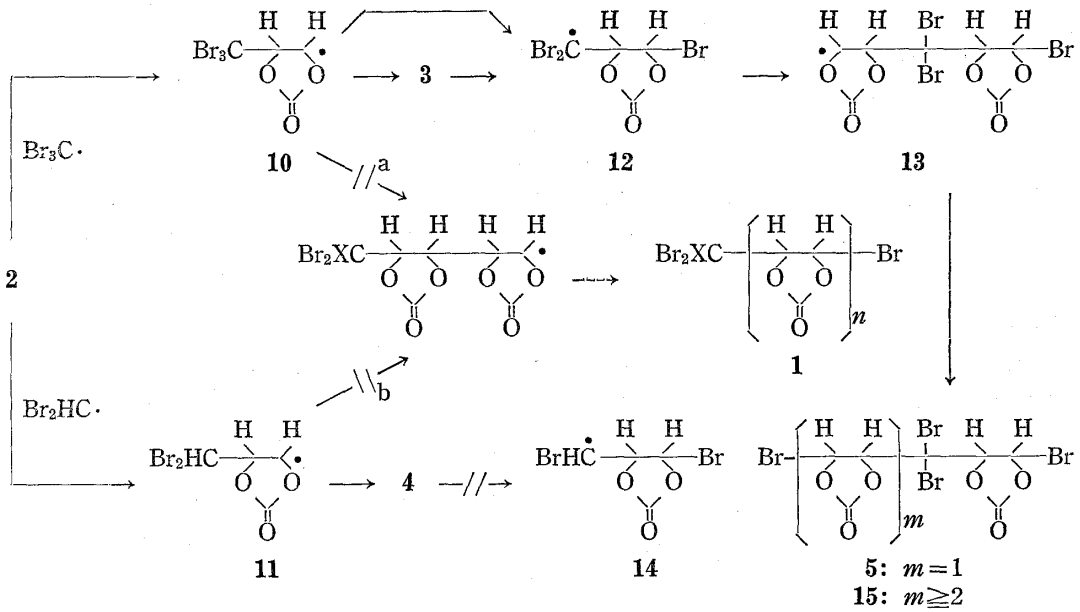


Chart 1

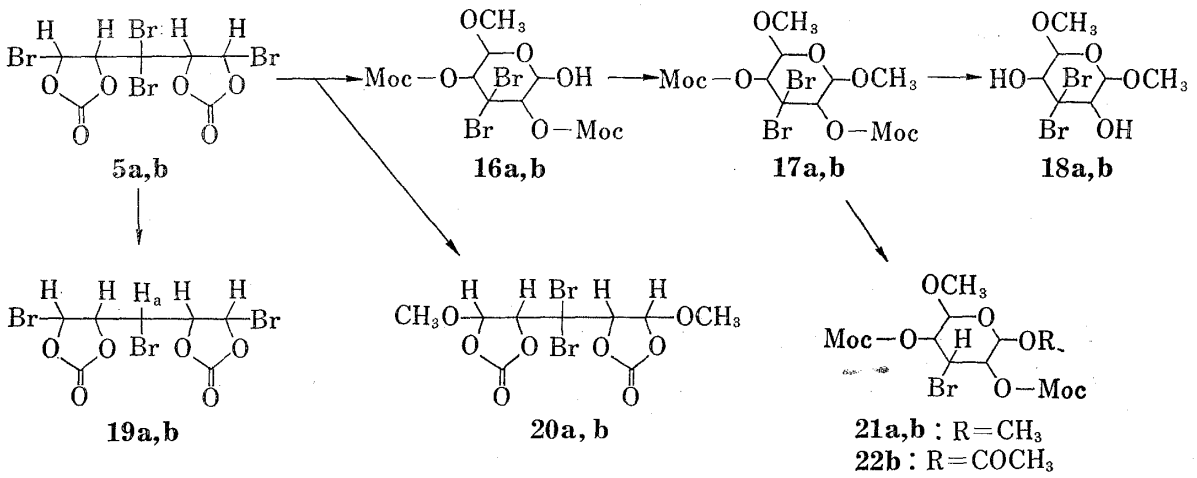
4) *cf.* R. Kh. Freidlina and E.C. Chukovskaya, *Synthesis*, **1974**, 477.
5) E.V. Dehlmlow, *Angew. Chem. Internat. Edit.*, **13**, 170 (1974).
6) C.M. Starks, "Free Radical Telomerization," Academic Press, New York, 1974 p. 133; *a*) Hydrogen abstraction may be supported by the formation of appreciable amounts of benzoic acid in the use of benzoylperoxide as a radical initiator.

the initiator-derived radicals, resulting in the initial formation of two kinds of radicals, tribromomethyl and dibromomethyl radicals, which attack the double bond of **2** to leave the intermediate radicals, **10** and **11**, respectively (Chart 1). Radical species thus formed would much prefer to react by bromine abstraction from telogen to give 1:1 adducts, **3** and **4**, rather than by addition to **2** which leads to type **1** telomers, as might be rationalized on the assumption of π-bond dissociation energy of nearly 65 kcal/mol, which is intermediate between bond dissociation energies (D) of Br_2HC-Br (D, 55.5 kcal/mol) and BrH_2C-Br (D, 69.5 kcal/mol).[7] Thus, the formation of type **1** telomers ($n \geqq 2$) *via* the routes a and b, as well as the transformation of **13** to **15**, was prevented, while the routes to 1:1 adducts ($n=1$), $n=2$ and higher telomers of type **1** were competitively allowed in the case of methylene bromide. Dimers **5** and not **15** would be formed by "two-fold" addition involving the intermediate free radicals **12** derived from **3** (and **10**), while the corresponding dimers could not be obtained from **4** which would not give the radicals **14** under the reaction conditions employed.

Stereochemistry (Methanolysis and Photo-reduction)

Radical addition of polyhalomethyl compounds to vinylene carbonate proceeds exclusively in *trans*-fashion to give *trans*- 4,5-disubstituted-1,3-dioxolan-2-ones, as demonstrated previously on the basis of their nuclear magnetic resonance (NMR) spectral data.[1a] This is the case for the products described above. There still remains ambiguity about the stereochemistry of the carbon skeleton of isomeric "two-fold addition" products **5a** and **b**, for which two configurations, *meso* (*trans-syn-trans*)-and *dl* (*trans-anti-trans*)-forms, may be anticipated. The following reactions were undertaken to make unambiguous assignment of the dimeric structures.

Compounds **5a** and **5b**, quite sensitive towards nucleophiles, underwent the smooth methanolysis simply by standing the alcoholic solutions at room temperature to afford cyclic hemiacetals, **16a** (73%) and **16b** (84%) as major products, respectively, in addition to substitution products, **20a** (9%) and **20b** (5%), which did not give **16a, b** under the same conditions (Chart 2). Six-membered ring structures of **16a, b** were confirmed on the basis of the NMR



a series: *anti*-form (*dl*-), *b* series: *syn*-form (*meso*-), (Moc=CH_3OCO-)

Chart 2

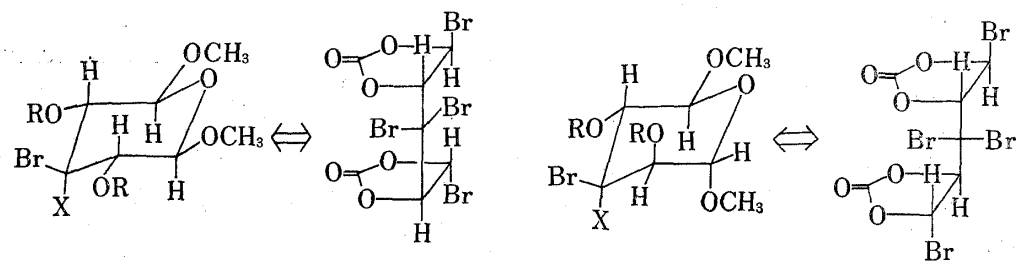
data of their derivatives as well as the chemical reactions as follows. Treatment of **16a** and **b** with methyl iodide in the presence of silver oxide gave the methylation products **17a** (28%) and **17b** (33%), respectively, as the sole isolable crystalline isomers, which could be hydrolyzed with ammonia to **18a** and **b**. On the treatment with aqueous tetrahydrofuran, **5a** was easily hydrolyzed to the unstable dialdehyde which was successively treated with ethanol to give 6-ethoxy-4,4-dibromotetrahydropyran-2,3,5-triol characterized as the triacetate.

7) C. Walling, "Free Radicals in Solution", John Wiley & Sons, Inc., 1957, p. 50.

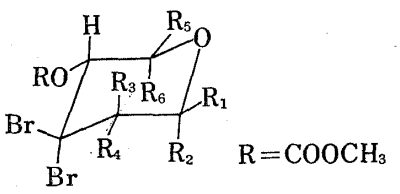
In the virtually same way as described for the selective conversion of trichloromethyl groups to dichloromethyls,[1c] **17a** and **b** underwent the smooth photolytic reduction on ultraviolet (UV)-irradiation of the tetrahydrofuran solutions to give excellent yields of **21a** and **b**, whose NMR spectra showed the stereoselective formation of axial protons, though there is no distinction between axial and equatorial protons newly generated in the former compound, since conformational change ($^4C_1 \rightleftarrows {}^1C_4$) gives the identical conformer.

Compounds, **19a**, **b** and **22b** were similarly prepared from the corresponding *gem*-dibromo compounds in high yields by this mild and general photolytic route. This kind of selective reduction has a precedent in the use of nickel carbonyl.[1b]

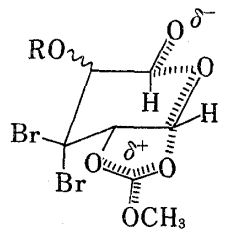
NMR data for certain compounds summarized in Table I permit the stereochemical assignment to telomers **5a** and **b**. The NMR spectra of **17b** and **18b** showed an AB pattern signal due to methine protons with the coupling constant, J_{vic}=7.5 Hz, which is in good accord with $J_{axial-axial}$ values in pyranose rings,[8] strongly indicative of the all equatrial-substituted structure **23** with a symmetrical plane in the molecule. Therefore, this stereochemistry, which was further substantiated by the NMR data of **21b**, makes it possible to assign *meso*(*syn*)-configuration to the isomer **5b**. NMR spectrum of **19b** showing a clear-cut triplet signal due to Ha-proton, in contrast to that of **19a** which shows doublet-doublet peaks (J=8.0 Hz, J'=2.0 Hz), is consistent with this configurational assignment.



23 **5b** **24** **5a**



25: $R_1=R_4=R_5=H$, $R_2=R_6=OCH_3$, $R_3=OR$
26: $R_2=R_4=R_5=H$, $R_1=R_6=OCH_3$, $R_3=OR$
27: $R_1=R_3=R_6=H$, $R_2=R_5=OCH_3$, $R_4=OR$



28: R=COOCH$_3$

As for compounds **17a** and **18a**, among the possible structures of **24** to **27** (including their $^4C_1$-conformers), isomers **25** and **26** could be precluded on the basis of NMR data indicating 1,2-diaxial protons ($J_{1,2}$=7.0 Hz) and two 1,5-protons in the relationship between axial (δ, 4.70) and equatorial (δ, 5.29) positions, and structure **27** could not account for the doublet-doublet signals due to H-3 showing J=8.0 and 3.0 Hz attributable to diaxial and axial-equatorial couplings, in the NMR spectrum of the photolysis product **21a**. Thus, structure **24** is satisfactorily compatible with the spectral data of isomer **17a** and hence *dl*-configuration (*trans-anti-trans*) was assigned to telomer **5a**.

8) R.U. Lemieux, R.K. Kuluing, H.J. Bernstein, and W.G. Schneider, *J. Am. Chem. Soc.*, **80**, 6098 (1958); For reviews: L.D. Hall, *Advances in Carbohyd. Chem.*, **19**, 51 (1964); S.J. Angyal, *Angew. Chem.*, **81** 172 (1969) *etc.*

A plausible mechanism for the selective formation of six-membered tetrahydro-pyran structures may involve solvolysis of **5a** and **b** to the intermediary bis(methoxycarbonyloxy)-dialdehydes followed by cyclization to **16a** and **b** through the transition states like **28**, in which effective participation of neighboring methoxycarbonyl group is anticipated. This mechanism also shows the formation of **16a** as an isomeric mixture and the exclusive formation of an isomer **16b** from **5a** and **b**, respectively.

Conversion of the above products to sugar-like compounds including cyclitols and uronic acids will be the subject of the separate paper.

Table I. NMR Spectral Data for Methyl 5-Methoxypyranosides (2,6-Dimethoxytetrahydropyrans)

Compounds	H-1	H-2	H-3	H-4	H-5	OCH_3-1	$OCOCH_3$-2	$OCOCH_3$-4	OCH_3-5
17a[a]	4.70 (d, J=7.0)	5.09 (d, J=7.0)	—	5.42 (s)	5.29 (s)	3.60 (s)	3.89 (s) or 3.91 (s)	3.91 (s) or 3.89 (s)	3.55 (s)
17b[a]	4.70 (d, J=7.5)	5.04 (d, J=7.5)	—	5.04 (d, J=7.5)	4.70 (d, J=7.5)	3.53 (s)	3.90 (s)	3.90 (s)	3.53 (s)
18a[b]	4.52 (d, J=7.0)	3.90 (d, J=7.0)	—	4.25 (s)	5.19 (s)	3.58 (s)	—	—	3.58 (s)
18b[b]	4.55 (d, J=7.5)	3.64 (d, J=7.5)	—	3.64 (s)	4.55 (s)	3.51 (s)	—	—	3.51 (s)
21a[a]	4.47 (d, J=8.0)	5.02 (d.d, J=8.0, J'=10.0)	4.13 (d.d, J=8.0, J'=3.0)	5.27 (d, J=3)	4.64 (s)	3.52 (s) or 3.54 (s)	3.84 (s)	3.84 (s)	3.52 (s) or 3.54 (s)
21b[a]	4.49 (d, J=7.0)	5.02 (d.d, J=10.2, J'=7.0)	4.03 (t, J=10.2)	5.02 (d.d, J=10.2, J'=7.0)	4.49 (d, J=7.0)	3.54 (s)	3.87 (s)	3.87 (s)	3.54 (s)

a) in $CDCl_3$ *b*) in CH_3CN. Chemical shifts (δ) and coupling constants (J) are given in ppm and Hz, respectively.

Experimental[9]

Dibromomethylene-4,4′-bis(5-bromo-1,3-dioxolan-2-one) (5a,b)——a) In the virtually same procedure as described in previous paper,[1a] radical addition of $CHBr_3$ to **2** (mole ratio of 4: 1) gave **3** and **4** as 1: 1 adducts and **5a** (mp 147—148°, 11%) and **5b** (mp 131—132°, 7%) as n=2 products, which were all identical with the authentic specimens with regard to the IR and NMR spectral data.[1a]

b) Analogously for the procedure above, a solution of **2** and CBr_4 in benzene was refluxed under N_2 gas for 70 hr in addition of benzoyl peroxide (BPO) at 3 hr intervals. Reaction in a ratio of 3: 1 of **2** to CBr_4 gave **3** and **5a,b** in 39% and 11%, respectively and the mole ratio of 1: 2 gave 58% and 3% yields.

c) A solution of **2** (14 g, 0.16 mmol) and **3** (68 g, 0.16 mol) in benzene was refluxed for 60 hr in the same way as described above. Purification of the products by chromatography on silica gel gave **5a** (28 g, 35%) and **5b** (19 g, 24%) in addition to the unchanged material 3 (10 g), which gave a corrected total yield of 67% for **5a,b**.

5-Tribromo-2-oxo-1,3-dioxolane-4-carbonitrile (6)——An aqueous solution (15 ml) of sodium cyanide (5.5 g, 0.11 mole) was added into the solution of **3** (43 g, 0.1 mol) and tetrabutylammonium bromide (0.2 g) in methylene chloride (200 ml), and the mixture was vigorously stirred at room temperature for 8 hr. The mixture was poured onto ice-water and it extracted with methylene chloride. The extracts were dried (Mg-

9) Melting points were determined on a hot plate using Yanaco micro melting point apparatus and are uncorrected. The spectrometers, JASCO-IRS, and Hitachi R-24 (60 MHz) or JEOL PS-100 (100 MHz) were used for IR (in Nujol mull) and NMR (tetramethylsilane as internal standard) spectral data, respectively.

SO_4) and evaporated *in vacuo* to leave an oil which was chromatographed on silica gel (*n*-hexane–benzene, 1: 1) to give *trans*-cyano derivative **6** (16.5 g, 45%) and *cis*-isomer (7.0 g, 21%), which were identical with the authentic samples prepared separately.[10]

5′-Bromo-dibromomethylene-4,4′-bis(2-oxo-1,3-dioxolane)-5-carbonitrile (7a,b)——In analogous manner to that for the preparation of **5a,b** from **2** (and **3**), a solution of **2** (1.73 g, 20 mmole) and **6** (2.47 g, 6.8 mmole) in benzene (50 ml) was refluxed gently under N_2 while BPO (0.3 g) was added every 3 hr. After 40 hr, the benzene was removed *in vacuo* and separation of the isomeric products was achieved by chromatography on silica gel (CH_2Cl_2) to give **7a** (0.21 g, 10%) and **7b** (0.19 g, 8%) in addition to **6** (130 mg). Products were recrystallized from CH_2Cl_2–*n*-hexane.

7a: mp 154—155°, IR 1830 cm^{-1}, NMR ($CDCl_3$), δ 5.20 (1H, d, J=4.0 Hz), 5.22 (1H, d, J=2.0 Hz), 5.40 1H, d, J=4.0 Hz), 6.65 (1H, d, J=2.0 Hz). *Anal.* Calcd. for $C_5H_4O_6NBr_3$: C, 21.33; H, 0.89; N, 3.11. Found: C, 21.58; H, 1.04; N 3.03.

7b: mp 135—137°, IR 1830 cm^{-1}, NMR ($CDCl_3$), δ 5.28 (1H, d, J=3.5 Hz), 5.40 (1H, d, J=2.5 Hz), 5.45 (1H, d, J=3.5 Hz), 6.59 (1H, d, J=2.5 Hz). *Anal.* Calcd. for $C_5H_4O_6NBr_3$: C, 21.33; H, 0.89; N, 3.11. Found: C, 21.46; H, 0.98; N, 3.07.

Methyl 5′-Bromo-dibromomethylene-4,4′-bis(2-oxo-1,3-dioxolane)-5-carboxylate (9a,b)——Analogously to the procedure described for **7a,b**, the mixture of **2** (15.5 g, 0.18 mol) and **8** (25 g, 0.06 mol) prepared from **6**, in benzene (150 ml) was refluxed in the presence of BPO for 74 hr. Purification of the isomeric products by chromatography on silica gel (CH_2Cl_2) gave **9a** (9.1 g, 34%) and **9b** (8.5 g, 33%).

9a: mp 148—149° from CCl_4, IR 1820, 1760 cm^{-1}, NMR ($CDCl_3$), δ 3.96 (3H, s), 5.15 (1H, d, J=4.0 Hz), 5.24 (1H, d, J=4.0 Hz), 5.40 (1H, d, J=2.0 Hz), 6.69 (1H, d, J=2.0 Hz). *Anal.* Calcd. for $C_9H_7O_8Br_3$: C, 22.36; H, 1.45. Found: C, 22.39; H, 1.39.

9b: amorphous powder, IR 1840, 1750 cm^{-1}, NMR ($CDCl_3$), δ 3.89 (3H, s), 5.12 (2H, s), 5.34 (1H, d, J= 2.4 Hz), 6.61 (1H, d, J=2.4 Hz). 5′-Methoxy compound which was readily prepared on treatment of **9b** with dry methanol: mp 152—154° from CH_2Cl_2–*n*-hexane. *Anal.* Calcd. for $C_{10}H_{10}O_9Br_2$: C, 27.65; H, 2.30. Found: C, 27.71; H, 2.06.

3,5-Bis(methoxycarbonyloxy)-4,4-dibromo-6-methoxytetrahydro-2-pyranol (16a,b) and Dibromomethylene-4,4′-bis(5-methoxy-1,3-dioxolan-2-one) (20a,b)——a) From **5a**: A solution of **5a** (3 g, 6 mmol) in dry methanol (50 ml) was stirred at room temperature overnight. Removal of the solvent *in vacuo* gave oily products which were separated by chromatography on silica gel (CH_2Cl_2) to give crystalline **20a** (0.22 g, 9%) and **16a** (1.95 g, 73%) using CH_2Cl_2 and a mixture of CH_2Cl_2 and acetone (98: 2) as eluting solvents, respectively.

20a: mp 181—183° from CCl_4 as colorless needles, IR 1815 cm^{-1}, NMR ($CDCl_3$) δ 3.64 (6H, s), 4.73 (2H, d, J=2.0 Hz), 5.59 (2H, d, J=2.0 Hz). *Anal.* Calcd. for $C_9H_{10}O_8Br_2$: C, 26.60; H, 2.46. Found: C, 26.69; H, 2.21.

16a: an amorphous powder, IR 3300, 1765 cm^{-1}. **16a** Acetate: mp 150—175° from *n*-hexane-CH_2Cl_2 as colorless prisms, presumably as a diastereomeric mixture, IR 1765 cm^{-1}, NMR ($CDCl_3$) δ 2.12 (3H, s), 3.51 and 3.53 (3H), 3.88 (6H, s), 4.7—5.5 (3H, m), 5.90 (0.4 H, d, J=7.0 Hz), 6.11 (0.2 H, d, J=5.0 Hz), 6.55 (0.4 H, s). *Anal.* Calcd. for $C_{12}H_{16}O_{10}Br_2$: C, 30.00; H, 3.33. Found: C, 30.15; H, 3.33. **16a** Benzoate; mp 232—234° from CH_2Cl_2–acetone, IR 1760, 1735 cm^{-1}. *Anal.* Calcd. for $C_{17}H_{18}O_{10}Br_2$: C, 37.64; H, 3.32. Found: C, 37.62; H, 3.30.

b) From **5b**: Analogously to the procedure for **5a**, treatment of **5b** (5.3 g, 10.5 ml) with dry methanol (50 ml) gave **20b** (0.45 g, 7%) and **16b** (3.4 g, 84%).

20b: mp 159—161° from CCl_4 as colorless needles, IR 1815 cm^{-1}, NMR ($CDCl_3$) δ 3.64 (6H, s), 4.70 (2H, d, J=2.0 Hz), 5.57 (2H, d, J=2.0 Hz). *Anal.* Calcd. for $C_9H_{10}O_8Br_2$: C, 26.60; H, 2.46. Found: C, 26.51; H, 2.39.

16b: mp 160—161° from CH_2Cl_2 as colorless prisms, IR 3300, 1765 cm^{-1}, NMR ($CDCl_3$) δ 3.52 (3H, s), 3.90 (6H, s), 4.70 (1H, d, J=7.0 Hz), 5.01 (2H, s), 5.04 (1H, d, J=7.0 Hz). *Anal.* Calcd. for $C_{10}H_{14}O_9Br_2$: C, 27.40; H, 3.20. Found: C, 27.53; H, 3.11.

Acetate: mp 198—199° from CH_2Cl_2–*n*-hexane as colorless needles, IR 1760 cm^{-1}, NMR ($CDCl_3$) δ 2.14 (3H, s), 3.52 (3H, s), 3.91 (6H, s), 4.77 (1H, d, J=7.5 Hz), 5.07 (1H, d, J=7.5 Hz), 5.21 (1H, d, J=8.0 Hz), 5.92 (1H, d, J=8.0 Hz). *Anal.* Calcd. for $C_{12}H_{16}O_{10}Br_2 \cdot H_2O$: C, 28.92; H, 3.61. Found: C, 28.93; H, 3.52.

2,6-Dimethoxy-3,5-bis(methoxycarbonyloxy)-4,4-dibromotetrahydropyran (17a,b)——a) From **16a**: A solution of **16a** (1 g, 2.3 mmol) in absolute methanol (30 ml) was treated with methyl iodide (44 mmol) and Ag_2O (10 mmol) in a sealed bottle at 40° for 10 hr with vigorous shaking. The insoluble materials were removed by filtration and the filtrate was evaporated *in vacuo* to leave a solid which was recrystallized from methanol–CH_2Cl_2 to give **17a** (285 mg, 28%) as colorless needles, mp 204—206°, IR 1760 cm^{-1}. *Anal.* Calcd. for $C_{11}H_{16}O_9Br_2$: C, 29.20; H, 3.54. Found: C, 29.16; H, 3.52.

b) From **16b**: Methyl ether **17b** was prepared from **16b** (2 g, 4.4 mmol) and methyl iodide (12 g, 88 mmol) in the presence of Ag_2O (20 mmol) in a similar treatment as above. Recrystallization from CH_3OH–

10) Treatment of **3** with NaCN in DMF gave *trans*- and *cis*-products in a ratio of 1.1: 1.[1d]

CH_2Cl_2 gave **17b** (0.67 g, 33%) as colorless needles, mp 169—171°, IR 1760 cm^{-1}. *Anal.* Calcd. for $C_{11}H_{16}O_9Br_2$: C, 29.20; H, 3.54. Found: C, 29.31; H, 3.50.

2,6-Dimethoxy-4,4-dibromotetrahydro-3,5-pyranediol (18a,b)——a) From **17a**: An aqueous ammonia (28%, 1.5 ml) was added to a solution of **17a** (0.82 g, 1.8 mmol) in tetrahydrofuran (30 ml) and the mixture was vigorously stirred at room temperature overnight. Removal of the solvent *in vacuo* gave oily products which were purified by preparative layer chromatography on silica gel (CH_2Cl_2–acetone, 98: 2) to give **18a** (43 mg, 6.3%) in addition to half-hydrolyzed product, 2,6-dimethoxy-4,4-dibromo-5-(methoxycarbonyloxy)-tetrahydro-3-pyranol (120 mg, 18%, mp 123—136°, IR 3450, 1760 cm^{-1}), presumably in isomeric mixture based on the spectral data.

18a: mp 142—144° (decomp.) from CH_2Cl_2, IR 3430 (br). *Anal.* Calcd. for $C_7H_{12}O_5Br_2$: C, 25.00; H, 3.57. Found: C, 24.56; H, 3.81.

b) From **17b**: In contrast to the above findings, isomer **17b** (0.3 g, 0.67 mmol) was nearly quantitatively hydrolyzed to **18b** (0.23 g, 95%) on treatment with aqueous ammonia as above. Recrystallization from CH_2Cl_2 afforded colorless prisms, mp 126—128° (decomp.), IR 3400 cm^{-1}. *Anal.* Calcd. for $C_7H_{12}O_5Br_2$: C, 25.00; H, 3.57. Found: C, 25.13; H, 3.57.

6-Ethoxy-4,4-dibromo-tetrahydro-2,3,5-pyrantriol Triacetate——A solution of **5a** (1.0 g, 2 mmole) in tetrahydrofuran (20 ml) containing water (10 ml) was kept at room temperature overnight, then neutralized with $NaHCO_3$ and evaporated *in vacuo*. The resulting products were extracted with ethanol and the ethanol was removed *in vacuo* to give an oil which was acetylated with acetic anhydride (2.4 g) in pyridine (5 ml) to give triacetate (160 mg, 15%). Recrystallization from CH_2Cl_2–*n*-hexane gave colorless crystals, mp 140—141°, IR 1760 cm^{-1}. NMR ($CDCl_3$) δ 1.22 (3H, t, J=7.8 Hz), 2.10 (3H, s), 2.22 (3H, s), 2.25 (3H, s), 3.80 (2H, q, J=7.8 Hz), 4.78 (1H, d, J=8.0 Hz), 5.35 (1H, d, J=8.0 Hz), 5.68 (1H, bs), 6.49 (1H, bs). *Anal.* Calcd. for $C_{13}H_{18}O_8Br_2$: C, 33.77; H, 3.90. Found: C, 33.81; H, 3.82.

2,6-Dimethoxy-3,5-bis(methoxycarbonyloxy)-4-bromotetrahydropyran (21a,b)——a) From **17a**: A solution of **17a** (110 mg, 0.25 mmol) in tetrahydrofuran (30 ml) was irradiated with a high-pressure Hg lamp at room temperature for 7 hr. Evaporation of the solvent gave a solid which was recrystallized from CH_2Cl_2–*n*-hexane to give **21a** (68 mg, 75%) as colorless crystals, mp 157—160°, IR 1770, 1755 cm^{-1}. *Anal.* Calcd. for $C_{11}H_{17}O_9Br$: C, 35.39; H, 4.56. Found: C, 35.18; H, 4.53.

b) From **17b**: Analogously to the method described for **17a**, **17b** (0.2 g, 0.44 mmol) was reductively photolyzed to **21b** which was recrystallized from CH_2Cl_2–*n*-hexane to give colorless crystals (143 mg, 89%), mp 160—162°, IR 1760 cm^{-1}. *Anal.* Calcd. for $C_{11}H_{17}O_9Br$: C, 35.39; H, 4.56. Found: C, 35.19; H, 4.55.

Bromomethylene-4,4′-bis(5-bromo-1,3-dioxolan-2-one) (19a,b) and 2-Acetoxy-3,5-bis(methoxycarbonyloxy)-4-bromo-6-methoxytetrahydropyran (22b)——Compounds, **19a** **19b**, and **22b**, were prepared from the corresponding *gem*-dibromo compounds **5a**, **5b**, and **16b** acetate, by reductive photolysis in the similar way as above.

19a[11]: mp 143—145° from *n*-hexane–CH_2Cl_2, 71% yield, IR 1840, 1820 cm^{-1} (broad). NMR (CH_2CN) δ 4.61 (1H, d, d, J=8.0 Hz, J'=2.0 Hz), 5.26 (1H, d, d, J=8.0 Hz, J'=2.0 Hz), 5.40 (1H, t, J=2.0 Hz), 6.61 (1H, d, J=2.0 Hz), 6.68 (1H, d, J=2.0 Hz). *Anal.* Calcd. for $C_7H_5O_6Br_3$: C, 19.76; H, 1.18. Found: C, 19.80; H, 1.15.

19b: mp 145—147° from *n*-hexane–CH_2Cl_2, 62% yield, IR 1860, 1830 cm^{-1} (broad). NMR (CH_3CN) δ 4.58 (1H, t, J=7.0 Hz), 5.37 (2H, d, d, J=7.0 Hz, J'=2.0 Hz), 6.72 (2H, d, J=2.0 Hz). *Anal.* Calcd. for $C_7H_5O_6Br_3$: C, 19.76; H, 1.18. Found: C, 20.08; H, 1.24.

22b: mp 149—150° from *n*-hexane–CH_2Cl_2, 93% yield, IR 1760 cm^{-1}, NMR ($CDCl_3$) δ 2.12 (3H, s), 3.45 (3H, s), 3.83 (6H, s), 4.02 (1H, t, J=10.0 Hz), 4.57 (1H, d, J=7.5 Hz), 5.00 (1H, q, J=7.5 Hz, J'=10.0 Hz), 5.10 (1H, q, J=7.5 Hz, J'=10.0 Hz), 5.73 (1H, d, J=7.5 Hz). *Anal.* Calcd. for $C_{12}H_{17}O_{10}Br$: C, 35.91; H, 4.24. Found: C, 36.02; H, 4.24.

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