Reactions of oxalyl chloride with 1,2-cycloalkanediols in the presence of triethylamine

Reactions of Oxalyl Chloride with 1,2-Cycloalkanediols in the Presence of Triethylamine

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The relationship between the product patterns and the configurations of 1,2-cycloheptane- and 1,2-cyclooctanediols 9 in the cyclocondensations with oxalyl chloride in the presence of triethylamine at 0 °C has been shown analogous to that obtained for 1,2-disubstituted acyclic ethylene glycols 1: *cis*-1,2-cyclooctanediol (9f) produced the cyclic oxalate 14f as the major product, while *trans*-1,2-cycloheptanediol (9e) and *trans*-1,2-cyclooctanediol (9g) formed the cyclic carbonates 12e, g as the major products. On the other hand, the cyclic oxalates 14a—d were formed as the major products from 1,2-cyclopentane- and 1,2-cyclohexanediols regardless of the configuration. These results can be accounted for by assuming the boat-like transition states for cyclizations of the half esters of comparatively rigid five- and six-membered diols 9a—d. The cyclic oxalates 14a, c may be directly formed through the resulting tetrahedral intermediates from *cis*-diols (9a, c), and the cyclic carbonates 12a, c as the minor products after ring inversion of the tetrahedral intermediates. The tetrahedral intermediates from the *trans*-isomers 9b, d cannot undergo ring inversion, producing no traces of the cyclic carbonates 12b, d.

Key words 1,2-cycloalkanediol cyclocondensation; oxalyl chloride; cyclic oxalate ester; cyclic carbonate ester; stereocontrolled cyclization; stereoelectronic effect

We have already reported that acyclic glycols **1** generally react with oxalyl chloride in tetrahydrofuran (THF) in the presence of triethylamine at 0 °C or room temperature to form the unstable cyclic oxalate **4** together with the cyclic carbonates **2**: unsubstituted, monosubstituted, and *erythro*-1,2-disubstituted ethylene glycols produced **4** and/or the polymeric oxalates as the major products, while *threo*-1,2-disubstituted ethylene glycols and pinacol afforded **2** as the major products.[1)]

According to our proposed mechanism[1)] illustrated in Chart 1, the formation of the carbonate **2a** from pinacol (**1a**) in the presence of triethylamine is interpreted in terms of stereochemically controlled formation of the tetrahedral intermediate **6** from the initially formed *s*-trans intermediate **5**, followed successively by deprotonation and stereoelectronically controlled cleavage (the nonbonding electron pairs contributing to bond cleavage are shown as shaded lobes) of the C–C bond through **7** and **3**. The cyclic oxalate **4a** can be formed only after the conformer **7** changes into **8**. The almost exclusive formation of **2a** from pinacol (**1a**) is attributable to the large rotational barrier from **7** to **8** compared with the activation energy for the decay of **7** leading to **3**. If this is the case, the corresponding tetrahedral intermediate **11** from *trans*-1,2-cyclohexanediol (**9d**) should produce the carbonate **12d** exclusively, because it cannot undergo ring-inversion and must go through the boat form **13** for the formation of the oxalate **14d**. However, 'normal' cyclization of the *s*-trans intermediate **10** leading to **11** (course A) suffers from severe steric congestion as depicted as **10A**. In the case of the acyclic series, this steric interaction (**5A**) would be avoided by bringing the conformation close to the eclipsed form **5B**. If the cyclization of **10** takes place from the other side of the carbonyl plane as shown in **10B** (course B), the tetrahedral intermediate **15** with a boat or twist-boat conformation is formed as a result of 'abnormal' cyclization. Once **15** is formed, the exclusive formation of the cyclic oxalate **14d** is expected through **16**. Thus it is of considerable interest to study the reactions of 1,2-cycloalkanediols with oxalyl chloride in the presence of triethylamine.

Table 1 summarizes the results of the reactions of some selected 1,2-cycloalkanediols with 1.1—1.3 mol eq of oxalyl chloride in THF in the presence of triethylamine at 0 °C for 40 min. The formation of the cyclic oxalate **14b** is suggestive of the absence of the 'normal' cyclization for *trans*-1,2-cyclopentanediol (**9b**). Unfortunately, the absence of the cyclic carbonate **12b** cannot be a proof against the 'normal' cy-

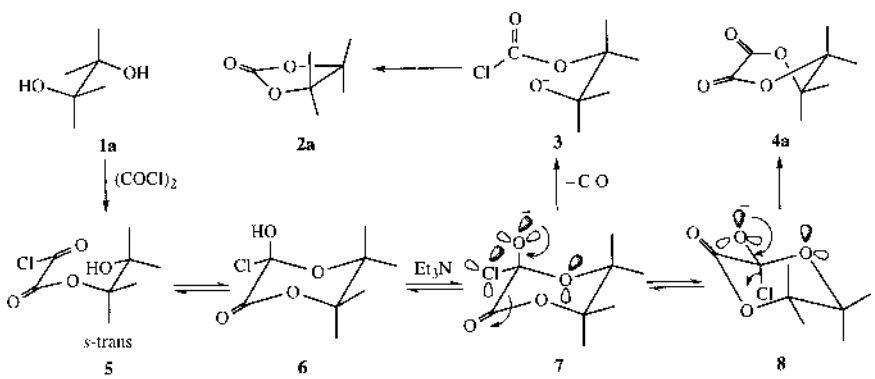

Chart 1

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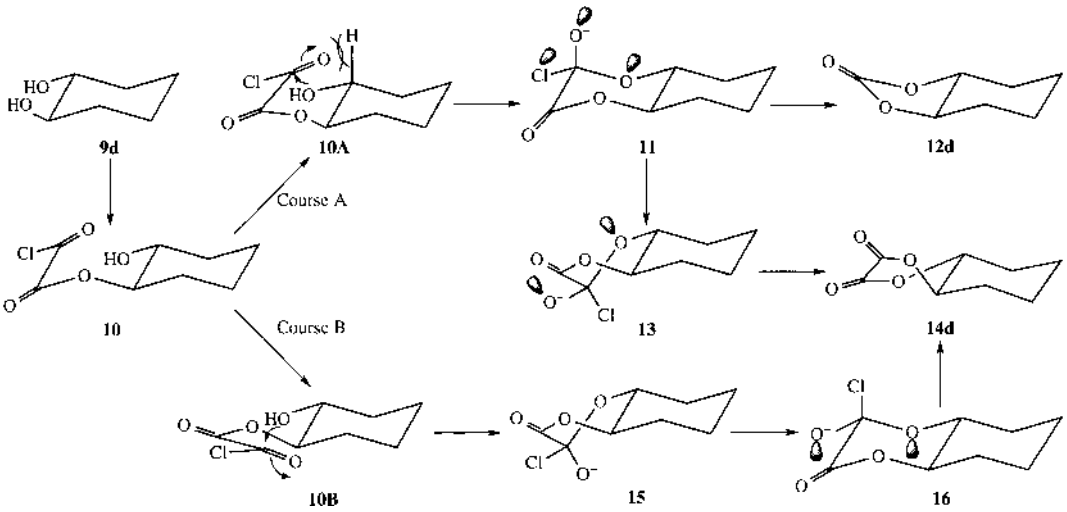

Chart 2

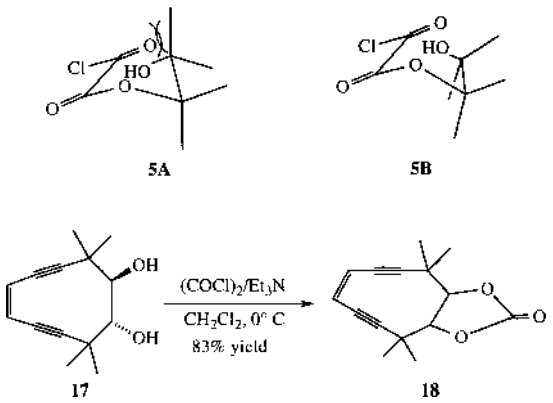

Chart 3

Table 1. Reactions of 1,2-Cycloalkanediols (**9**) with Oxalyl Chloride in THF in the Presence of Triethylamine

Substrate	Estimated yield (%)[a]			Isolated yield (%)	
	14	**12**	Polymers	**14**	**12**
cis-1,2-Cyclopentanediol (**9a**)	75	18	4	31	14
trans-1,2-Cyclopentanediol (**9b**)[b]	44	0	56	—[c]	0
cis-1,2-Cyclohexanediol (**9c**)	86	<3	11	60	0.5
trans-1,2-Cyclohexanediol (**9d**)	75	0	25	64	0
trans-1,2-Cycloheptanediol (**9e**)[b]	32	65	3	—[c]	51
cis-1,2-Cyclooctanediol (**9f**)	58	42	—[d]	26	37
trans-1,2-Cyclooctanediol (**9g**)	17	83	0	—[c]	80

a) Determined by means of ^{1}H-NMR spectroscopy. *b*) An excess (1.3 mol eq) of oxalyl chloride was used. *c*) Could not be isolated. *d*) A trace if any.

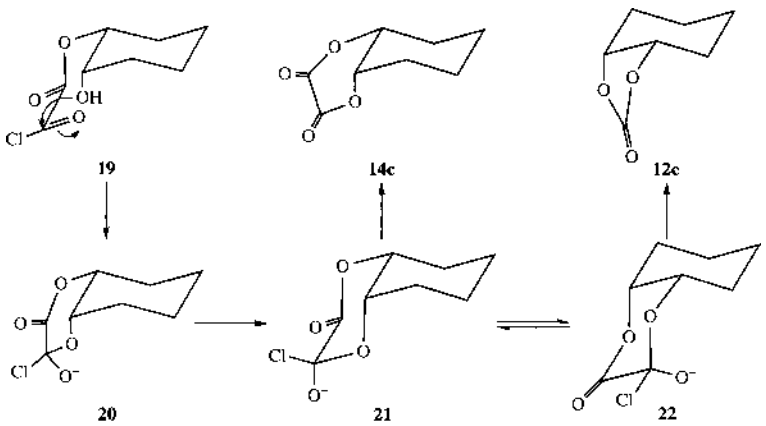

Chart 4

clization because there is always a very limited possibility of the formation of the hitherto unknown highly strained **12b**.[2] However, the product ratio determined by ^{1}H-NMR spectroscopy for the reaction of *trans*-1,2-cyclohexanediol (**9d**) shows that the cyclic oxalate **14d** was formed in 75% yield with no trace of the cyclic carbonate **12d**, verifying that the 'normal' cyclization is prohibited for **9d**. On the contrary, *trans*-1,2-cycloheptanediol (**9e**) and *trans*-1,2-cyclooctanediol (**9g**) afforded the cyclic carbonates **12e**, **g** in 65 and 83% yields, respectively. These results were anticipated because the 'normal' cyclization is possible for the more flexible **9e**, **g**, and the resulting intermediates (type **11**) are not allowed to undergo ring inversion. A closely related case to the reaction of **9e**, **g** has been reported for **17** by Nicolaou *et al.*[3] without any comment on the mechanism of the formation of the cyclic carbonate **18** as shown in Chart 3.

cis-1,2-Cycloalkanediols **9a**, **c**, **f** produced the oxalates **14** predominantly, analogous to the results obtained for acyclic *erythro*-glycols.[1)] It is natural to consider that the reaction with *cis*-1,2-cyclooctanediol (**9f**) proceeded in a manner similar to that of the acyclic glycols. However, the cyclization mode for the five- and six-membered ring *cis*-glycols **9a**, **c** must be the same as that for the *trans* isomers **9b**, **d**. According to the hypothetical sequence exemplified for the reaction of **9c** in Chart 4, the oxalate **14c** is directly formed from the intermediate **21**, and the carbonate **12c** after a conformational change into **22** in contrast to the case of the acyclic glycols (Chart 2).

In conclusion, we have reported that the relationship between the product patterns and the configurations of the cyclic glycols **9** in the reactions with oxalyl chloride in the presence of triethylamine is basically the same as that obtained for 1,2-disubstituted acyclic ethylene glycols **1**.[1)] However, the five- and six-membered ring glycols **9b**, **d** with trans configuration are exceptions. Reactions of these compounds presumably proceeded through boat-like transition states, leading to the formation of the cyclic oxalates **14b**, **d** with a complete absence of the cyclic carbonates. Although the five- and six-membered ring glycols **9a**, **c** with cis configuration are also considered to undergo cyclization through boat-like transition states, ring-inversion of the tetrahedral intermediates is possible in these cases, and the cyclic carbonates **12a**, **c** were formed as minor products.

Experimental

General Notes All melting points were determined using a Yamato MP-1 or Büchi model 530 capillary melting point apparatus and values are corrected. Spectra reported herein were recorded on a JEOL JMS-SX102A mass spectrometer, a Hitachi model 320 UV spectrophotometer, a Shimadzu FTIR-8100 or a FTIR-8400 IR spectrophotometer, a JEOL JNM-EX-270 or a JEOL JNM-GSX-500 NMR spectrometer (measured in $CDCl_3$ at 25 °C with tetramethylsilane as an internal standard). Elemental analyses and MS measurements were performed by Dr. M. Takani and her associates at Kanazawa University. The following abbreviations are used: br=broad, m=multiplet.

***cis*-Tetrahydro-4*H*-cyclopenta-1,3-dioxol-2-one (12a)** A 2.0 M solution of phosgene in toluene (1.1 ml, 2.2 mmol) was added to a solution of **9a** (204 mg, 2 mmol) and pyridine (0.71 ml, 8.8 mmol) in dry toluene (20 ml), and the mixture was stirred at 0 °C for 15 min. The resulting mixture was diluted with toluene (10 ml), washed successively with water, 5% aqueous citric acid, water, and saturated aqueous sodium bicarbonate (10 ml each). The organic layer was dried over magnesium sulfate and concentrated *in vacuo*, leaving a colorless oil (176 mg). The washings were combined, brought to pH 5 by addition of 10% hydrochloric acid, saturated with sodium chloride, and extracted with benzene (3×10 ml). The extracts were dried over magnesium sulfate and concentrated *in vacuo*, leaving a colorless oil (47 mg). The crude products were combined and purified by flash chromatography [hexane–ethyl acetate (3 : 2, v/v)] to give **12a** as a colorless solid (174 mg, 68%), mp 29—29.5 °C (lit.[4)] mp 34—36 °C). MS *m/z*: 128 (M^+). IR ν_{max}^{Nujol} cm^{-1}: 1800 (C=O). ^{1}H-NMR δ: 1.57—1.90 (4H), 2.06—2.24 (2H) [m each, $(CH_2)_3$], 5.11 (2H, m, two CH's). ^{13}C-NMR δ: 21.5, 33.1 (CH_2), 81.8 (CH), 155.4 (C=O).

***cis*-Hexahydro-1,3-benzodioxol-2-one (12c)** A 2.0 M solution of phosgene in toluene (1.1 ml, 2.2 mmol) was added to a solution of **9c** (232 mg, 2 mmol) and triethylamine (1.26 ml, 9 mmol) in dry THF (24 ml), and the mixture was stirred at 0 °C for 20 min. The resulting precipitate was filtered off, and the filtrate was concentrated *in vacuo.* The residue was purified by flash chromatography [hexane–ethyl acetate (3 : 2, v/v)] to give **12c** as a semi-solid (110 mg, 39%) (lit.[5)] mp 38—39 °C). IR ν_{max}^{Nujol} cm^{-1}: 1775 (C=O). ^{1}H-NMR δ: 1.35—1.53 (2H), 1.55—1.72 (2H), 1.82—1.95 (4H) [m each, $(CH_2)_4$], 4.68 (2H, m, two CH's). ^{13}C-NMR δ: 19.1, 26.7 (CH_2), 75.7 (CH), 155.3 (C=O).

(±)-*trans*-Hexahydro-1,3-benzodioxol-2-one (12d) This compound was obtained in 69% yield from **9d** (349 mg, 3 mmol) in a manner similar to that employed for the preparation of **12c**. Recrystallization from hexane–ether (2 : 1, v/v) afforded **12d** as colorless prisms, mp 53—54.5 °C (lit.[5)] mp 53—54 °C). IR ν_{max}^{Nujol} cm^{-1}: 1792 (C=O). ^{1}H-NMR δ: 1.31—1.52, 1.6—1.8, 1.84—2.03, 2.21—2.35 [2H each, m, $(CH_2)_4$], 4.02 (2H, m, two CH's). ^{13}C-NMR δ: 23.1, 28.2 (CH_2), 83.5 (CH), 155.0 (C=O).

(±)-*trans*-Hexahydro-4*H*-cyclohepta-1,3-dioxol-2-one (12e) A solution of triphosgene (223 mg, 0.751 mmol) in dichloromethane (5 ml) was added to a solution of **9e**[6)] (131 mg, 1.01 mmol) and pyridine (0.8 ml) in dichloromethane (10 ml), and the mixture was stirred at 0 °C for 30 min. The resulting solution was diluted with chloroform (5 ml), washed successively with water, 5% aqueous citric acid, and saturated aqueous sodium bicarbonate (5 ml each), dried over magnesium sulfate, and concentrated *in vacuo* to leave a colorless oil. Flash chromatography [hexane–ethyl acetate (3 : 1, v/v)] of this product afforded a colorless solid, which was recrystallized from hexane–ethyl acetate (15 : 2, v/v), providing **12e** (76 mg, 48%) as colorless prisms, mp 79—79.5 °C (lit.[4)] mp 76—78 °C). IR ν_{max}^{Nujol} cm^{-1}: 1823 (C=O). ^{1}H-NMR δ: 1.51 (2H), 1.69 (6H), 2.32 (2H) [m each, $(CH_2)_5$], 4.38 (2H, m, two CH's); ^{13}C-NMR δ: 24.2, 24.4, 28.7 (CH_2), 82.8 (CH), 154.9 (C=O).

***cis*-Octahydrocycloocta-1,3-dioxol-2-one (12f)** A 2.0 M solution of phosgene in toluene (1.7 ml, 3.4 mmol) was added to a solution of **9f** (433 mg, 3 mmol) and pyridine (1.10 ml, 13.6 mmol) in dry toluene (30 ml), and the mixture was stirred at 0 °C for 1 h. Toluene (10 ml) was added to the resulting mixture, and the whole was washed successively with water, 5% aqueous citric acid, and saturated aqueous sodium bicarbonate (15 ml each), dried over magnesium sulfate, and concentrated *in vacuo*, leaving crude **12f** (511 mg). This was recrystallized from hexane to give **12f** (392 mg, 77%) as colorless prisms, mp 101.5—102.5 °C (lit.[7)] mp 99—101 °C). MS *m/z*: 170 (M^+). IR ν_{max}^{Nujol} cm^{-1}: 1806 (C=O). ^{1}H-NMR δ: 1.15—1.62 (6H), 1.63—1.83 (2H), 1.92—2.15 (4H) [m each, $(CH_2)_6$], 4.70 (2H, m, two CH's). ^{13}C-NMR δ: 25.1, 25.9, 27.0 (CH_2), 81.1 (CH), 154.1 (C=O).

(±)-*trans*-Octahydrocycloocta-1,3-dioxol-2-one (12g) The diol **9g** (85% purity, 480 mg) was treated in a manner similar to that described for the preparation of **12f**, and the crude product that was obtained was purified by flash chromatography [hexane–ethyl acetate (5 : 2, v/v)] to afford **12g** (353 mg), mp 75—77 °C. This was recrystallized from hexane to give **12g** as colorless prisms, mp 76.5—78.5 °C (lit.[8)] mp 79—81 °C). MS *m/z*: 170 (M^+). IR ν_{max}^{Nujol} cm^{-1}: 1796 (C=O). ^{1}H-NMR δ: 1.14—1.35 (2H), 1.38—1.60 (2H), 1.60—1.95 (6H), 2.26 (2H) [m each, $(CH_2)_6$], 4.54 (2H, m, two CH's). ^{13}C-NMR δ: 22.0, 26.9, 33.3 (CH_2), 82.9 (CH), 154.1 (C=O).

Reactions of 1,2-Cycloalkanediols (9) with Oxalyl Chloride A solution of oxalyl chloride (1.1 mol eq) in THF (10 ml per mmol of **9**) was added dropwise to a solution of **9** and triethylamine (5 mol eq) in THF (100 ml per mmol of **9**) over a period of 30 min at 0 °C under nitrogen, and the mixture was stirred at 0 °C for a further 10 min. The product ratios were determined by means of ^{1}H-NMR spectroscopy on the basis of the relative areas of the methine signals. The results are summarized in Table 1.

Reaction of *cis*-1,2-Cyclopentanediol (9a) Compound **9a** (238 mg, 2.33 mmol), which had been dried over a mixture of molecular sieves 4A and 3A at 45 °C for 2 d, was treated with oxalyl chloride as described above. The resulting mixture was found to contain *cis*-tetrahydro-5*H*-cyclopenta-1,4-dioxin-2,3-dione (**14a**), **12a**, the oxalate polymers, and **9a** (75 : 18 : 4 : 4). It was concentrated to dryness *in vacuo*, and the residue was washed with ether (50 and 20 ml). The combined washings were concentrated, and the residue was submitted to Kugelrohr distillation. The distillate obtained below 170 °C and at 0.1—0.6 mmHg was purified by flash chromatography [dichloromethane–ethyl acetate (15 : 1, v/v)], giving **12a** (41 mg, 14%), mp 29—30 °C, which was identical (by comparison of the IR spectra) with the authentic specimen prepared above. The distillate obtained at higher temperature was dissolved in ether (20 ml), and the insoluble solid was removed by filtration. The ethereal solution was concentrated and the resulting solid was recrystallized from dry ether, giving **14a** (113 mg, 31%), mp 75—76 °C. Further recrystallization from ether afforded an analytical sample of **14a** as colorless prisms, mp 76.5—78 °C. MS *m/z*: 157 (M^++1). IR ν_{max}^{Nujol} cm^{-1}: 1771, 1755 (C=O). ^{1}H-NMR δ: 1.79—1.90 (1H, m), 2.00—2.31 (5H, m) [$(CH_2)_3$], 4.99 (2H, m, two CH's). ^{13}C-NMR δ: 19.3, 28.8 (CH_2), 80.1 (CH), 151.9 (C=O). *Anal.* Calcd for $C_7H_8O_4$: C, 53.85; H, 5.16. Found: C, 53.76; H, 5.21. This sample was found to be decomposed after storage at −20 °C for two months.

Reaction of (±)-*trans*-1,2-Cyclopentanediol (9b) The reaction mixture was filtered, and the filtrate was concentrated *in vacuo*, leaving a brown oil. This was found to be composed of (±)-*trans*-tetrahydro-5*H*-cyclopenta-1,4-dioxin-2,3-dione (**14b**) [δ 4.71 (m)] and the oxalate polymers [δ 5.27 (m)]. This material was unstable to purification.

Reaction of *cis*-1,2-Cyclohexanediol (9c) The reaction mixture obtained from **9c** (232 mg, 2 mmol) was filtered, and the insoluble solid was washed with THF (40 ml). The combined filtrate and washings were concentrated to dryness *in vacuo.* The resulting mixture of *cis*-hexahydro-1,4-benzodioxin-2,3-dione (**14c**), **12c**, and the oxalate polymers was submitted to Kugelrohr distillation. The forerun (30 mg) was applied to flash chromatography [hexane–ethyl acetate (3 : 2, v/v)] to afford **12c** (1.3 mg, 0.5%) as a colorless oil, which was identical (by comparison of the ^{1}H-NMR spectra) with an authentic specimen. The distillate (231 mg) obtained at 140—200 °C and 0.8 mmHg was dissolved in hot ether. The insoluble solid was removed by filtration. The ethereal solution was concentrated to afford crude **14c** (204 mg, 60%), mp 81.5—83 °C. Recrystallization of this product from carbon tetrachloride afforded an analytical sample of **14c** as colorless prisms, mp 84—85 °C (lit.[9] mp 84—84.5 °C). MS *m*/*z*: 171 ($M^+ + 1$). IR ν_{max}^{Nujol} cm^{-1}: 1771, 1755 (C=O). ^{1}H-NMR δ: 1.52 (2H, m), 1.77 (2H, m), 1.97 (4H, br) [$(CH_2)_4$], 4.80 (2H, br, two CH's). ^{13}C-NMR δ: 21.0, 28.5 (CH_2), 76.7 (CH), 153.3 (C=O). *Anal.* Calcd for $C_8H_{10}O_4$: C, 56.47; H, 5.92. Found: C, 56.28; H, 5.95.

Reaction of (±)-*trans*-1,2-Cyclohexanediol (9d) The precipitate that separated from the reaction mixture obtained from **9d** (349 mg, 3 mmol) was removed by filtration and washed with THF (30 ml). The combined filtrate and washings were concentrated to dryness *in vacuo* to give a mixture of (±)-*trans*-hexahydro-1,4-benzodioxin-2,3-dione (**14d**) and the oxalate polymers. This was submitted to Kugelrohr distillation. The distillate (667 mg) obtained at 170—200 °C and 0.8—0.9 mmHg was dissolved in hot ether. The insoluble solid was removed by filtration. The ethereal solution was concentrated to afford crude **14d** (328 mg, 64%), mp 102—103.5 °C. Recrystallization of this product from toluene afforded an analytical sample of **14d** as colorless prisms, mp 110—113 °C (lit.[9] mp 111—112 °C). MS *m*/*z*: 171 ($M^+ + 1$). UV $\lambda_{max}^{CH_3CN}$ nm (ε): 269 (56). IR ν_{max}^{Nujol} cm^{-1}: 1786, 1759 (C=O); $\nu_{max}^{CHCl_3}$ cm^{-1}: 1782 (C=O). ^{1}H-NMR δ: 1.37, 1.58. 1.91, 2.30 [2H each, m, $(CH_2)_4$], 4.45 (2H, m, two CH's). ^{13}C-NMR δ: 22.7, 29.2 (CH_2), 80.0 (CH), 153.6 (C=O). *Anal.* Calcd for $C_8H_{10}O_4$: C, 56.47; H, 5.92. Found: C, 56.61; H, 5.84.

Reaction of (±)-*trans*-1,2-Cycloheptanediol (9e) The insoluble solid that separated from the reaction mixture obtained from **9e**[6] (260 mg, 2 mmol) was removed by filtration, and the filtrate was concentrated to dryness *in vacuo* to give a mixture of (±)-*trans*-hexahydro-5*H*-cyclohepta-1,4-dioxin-2,3-dione (**14e**), **12e**, and the oxalate polymers. The mixture was submitted to flash chromatography [hexane–ethyl acetate (3 : 1, v/v)] to afford crude **12e** (159 mg, 51%). Recrystallization of this sample from hexane–ethyl acetate (5 : 1, v/v) afforded **12e**, mp 79—79.5 °C, which was identical (by comparison of the IR and ^{1}H-NMR spectra) with an authentic sample.

Reaction of *cis*-1,2-Cyclooctanediol (9f) The precipitate that separated from the reaction mixture obtained from **9f** (288 mg, 2 mmol) was removed by filtration and washed with THF (50 ml). The combined filtrate and washings were concentrated to dryness *in vacuo* to give a mixture of *cis*-octahydrocycloocta-1,4-dioxin-2,3-dione (**14f**) and **12f**. The residue was triturated with ether (15 ml), and the insoluble solid was removed by filtration. The ethereal solution was kept in a refrigerator overnight, and the precipitate that separated was collected by filtration, giving crude **14f** (102 mg, 26%), mp 72.5—75 °C. On the other hand, the solid that remained undissolved in ether at room temperature was extracted with boiling ether (2×10 ml), and the extracts were combined with the mother liquor from which crude **14f** was obtained. The mixture was concentrated and applied to flash chromatography [hexane–ethyl acetate (3 : 1, v/v)], giving **12f** (126 mg, 37%), mp 98.5—99.5 °C, which was identical (by comparison of the IR spectra) with an authentic specimen. Recrystallization of crude **14f** from carbon tetrachloride afforded an analytical sample as colorless prisms, mp 76—77 °C. MS *m*/*z*: 199 ($M^+ + 1$). UV $\lambda_{max}^{CH_3CN}$ nm (ε): 273 (56). IR ν_{max}^{Nujol} cm^{-1}: 1761, 1748 (C=O); $\nu_{max}^{CHCl_3}$ cm^{-1}: 1782, 1763 (C=O). ^{1}H-NMR δ: 1.55 (2H), 1.65 (4H), 1.81 (2H), 2.03 (2H), 2.16 (2H) [m each, $(CH_2)_6$], 4.89 (2H, m, two CH's). ^{13}C-NMR δ: 22.5, 25.3, 27.4 (CH_2), 79.6 (CH), 153.2 (C=O). *Anal.* Calcd for $C_{10}H_{14}O_4$: C, 60.60; H, 7.12. Found: C, 60.55; H, 7.02.

Reaction of (±)-*trans*-1,2-Cyclooctanediol (9g) The precipitate was removed from the reaction mixture obtained from **9g** (288 mg, 2 mmol) by filtration and washed with THF (30 ml). The combined filtrate and washings were concentrated to dryness *in vacuo* to provide a mixture of (±)-*trans*-octahydrocycloocta-1,4-dioxin-2,3-dione (**14g**) and **12g**. Flash chromatography [hexane–ethyl acetate (5 : 2, v/v)] of this product gave **12g** (272 mg, 80%), mp 69—72 °C, which was identical (by comparison of the IR spectra) with an authentic specimen.

References and Notes

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