Stereochemistry in the Dimerization of 2,3-Epoxybutane by Trifluoromethanesulfonic Acid

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2,3-Epoxybutane (**1**) gave stereoisomeric mixtures of dioxane and dioxolane dimers when treated with catalytic amounts of trifluoromethanesulfonic acid (**2**). Six out of eight possible isomers (five dioxanes and three dioxolanes) were observed. The three dioxolane stereoisomers and three out of five dioxane stereoisomers have been assigned. Stereochemical considerations for the reaction were given on the basis of NMR analysis.

Cyclic oligomer formation frequently occurs in the cationic polymerization of heteroatom-containing cyclic monomers.[1-5] In the cationic polymerization of epoxides, the reaction conditions, especially the initiators and the solvents, have great influence on the polymerization behavior. Ethylene oxide gave quantitative amounts of dioxane when treated with superacids and their derivatives.[6] To clarify the reaction mechanism of cationic polymerization of epoxides, the reaction of 2,3-epoxybutane (**1**) with trifluoromethanesulfonic acid (**2**) was studied particularly with respect to stereochemistry in the cyclodimer formation.

Experimental Section

Proton NMR spectra were obtained with a JEOL JNM-PMX 60 spectrometer and were referenced to tetramethylsilane as an internal standard. Chromatographic data were obtained on a Yanaco G 180 gas chromatograph connected with 2-m stainless steel columns packed with Silicone GESE 30 and on a Shimadzu 7 AG gas chromatograph with a FID detector connected with a Silicone OV 101 coated glass capillary column (57 m long and 0.3 mm i.d.) operated at 65 °C with a split ratio of 50:1. All of the reactions were carried out under a dry nitrogen atmosphere. Hydrolysis of dioxolane isomers was carried out by stirring with 8% hydrochloric acid in methanol–water at room temperature for 10 h.

2,3-Epoxybutane (1). The mixture of cis and trans isomers of 1 (**1a**) was commercially supplied. *cis*-2,3-Epoxybutane (**1b**) and *trans*-2,3-epoxybutane (**1c**) were synthesized from *cis*- and *trans*-2-butene via the chlorohydrin method.[7,8] 1 was dried over calcium hydride.

Reaction of 1 with 2. 1 (1.05 g, 14.5 mmol) was reacted with **2** (45.9 mg, 0.306 mmol) in 30 mL of 1,2-dichloroethane solution at 50 °C for 20 h. The reaction was stopped with excess triethylamine, and the reaction products were analyzed on GLC. For preparative purposes, dichloromethane was used as solvent and the reaction was carried out at 30 °C for 74 h.

The gas chromatograms of the reaction products from **1a**, **1b**, and **1c** are shown in Figure 1. The peaks indicated in Figure 1 were separated by preparative gas chromatography after a coarse distillation. The peaks I from **1a**, **1b**, and **1c** in each chromatogram were identified as methyl ethyl ketone (**3**).

2,*cis*-4,*trans*-5-Trimethyl-2-ethyl-1,3-dioxolane (4a). The peaks II from **1a** and **1b** had the same NMR signals: NMR ($CDCl_3$) δ 0.94 (t, 3 H, J = 7.0 Hz, CH_3CH_2), 1.26 (d, 6 H, J = 5.5 Hz, $CH_3CHCHCH_3$), 1.34 (s, 3 H, CH_3C), 1.70 (q, 2 H, J = 7.0 Hz, CH_3CH_2), 3.65 (m, 2 H, $CH_3CHCHCH_3$). The multiplet at δ 3.65 became a singlet when decoupled from δ 1.26, and the doublet at δ 1.26 became a singlet from δ 3.65. Anal. Calcd for $C_8H_{16}O_2$: C, 66.61; H, 11.19. Found: C, 66.63; H, 11.22. On hydrolysis, this compound gave a quantitative yield of *dl*-2,3-butanediol. Based on these data, this compound was identified as 2,*cis*-4,*trans*-5-trimethyl-2-ethyl-1,3-dioxolane (**4a**).[9]

2,*trans*-3,*trans*-5,*cis*-6-Tetramethyl-1,4-dioxane (5a). The peak III from **1a** gave very complex NMR peaks (lower trace of **1a**-i in Figure 2): NMR ($CDCl_3$) δ 0.93 (t, J = 7.0 Hz, CH_3CH_2), 0.96 (t, J = 7.0 Hz, CH_3CH_2), 1.12 (d, J = 6.0 Hz, $CH_3CHCHCH_3$), 1.14 (d, J = 6.0 Hz, $CH_3CHCHCH_3$), 1.17 (d, J = 6.0 Hz, $CH_3CHCHCH_3$), 1.30 (s, CH_3C), 1.40 (s, CH_3C), 1.63 (q, J = 7.0 Hz, CH_3CH_2), 1.72 (q, J = 7.0 Hz, CH_3CH_2), 3.30 (m, $CH_3CHCHCH_3$), 4.23 (m, $CH_3CHCHCH_3$), 4.28 (m, $CH_3CHCHCH_3$). The peaks at δ 0.93, 0.96, 1.30, and 1.40 seemed to be assignable to two dioxolane isomers. The peak at δ 1.12 was decoupled as a singlet from δ 3.30, and the peaks at δ 1.14 and 1.17 became a singlet when decoupled from δ 4.25. Corresponding to this, the multiplets at δ 3.30, 4.23, and 4.28 became three singlets by decoupling from δ 1.15 (upper trace of **1a**-i in Figure 2). These NMR data clearly indicated that III from **1a** was a mixture of three components and that two of these were dioxolane derivatives and one a dioxane derivative. The gas chromatogram on the capillary column was also indicative of three components in III from **1a**. In order to make the assignments clear, the mixture was hydrolyzed. The residual peak after hydrolysis (the peak III in the trace of **1a**-ii in Figure 1) was separated by preparative gas chromatography and identified as **5a**:[10] NMR ($CDCl_3$) δ 1.12 (d, 12 H, J = 6.0 Hz, $CH_3CHCHCH_3$), 3.30 (m, 4 H, $CH_3CHCHCH_3$) (bottom trace of **1a**-ii in Figure 2). The peak at δ 3.30 became a sharp singlet on decoupling from δ 1.12, and the reverse decoupling gave the same result (upper and middle traces of **1a**-ii in Figure 2). Anal. Calcd for $C_8H_{16}O_2$: C, 66.61; H, 11.19. Found: C, 66.62; H, 11.21. Mp 39.5~40.0 °C.

2,*cis*-4,*cis*-5-Trimethyl-2-ethyl-1,3-dioxolane (4b) and 2,*trans*-4,*trans*-5-Trimethyl-2-ethyl-1,3-dioxolane (4c). The peak III from **1c** was also separated: NMR ($CDCl_3$) δ 0.93 (t, J = 7.0 Hz, CH_3CH_2), 0.96 (t, J = 7.0 Hz, CH_3CH_2), 1.14 (d, J = 6.0 Hz,

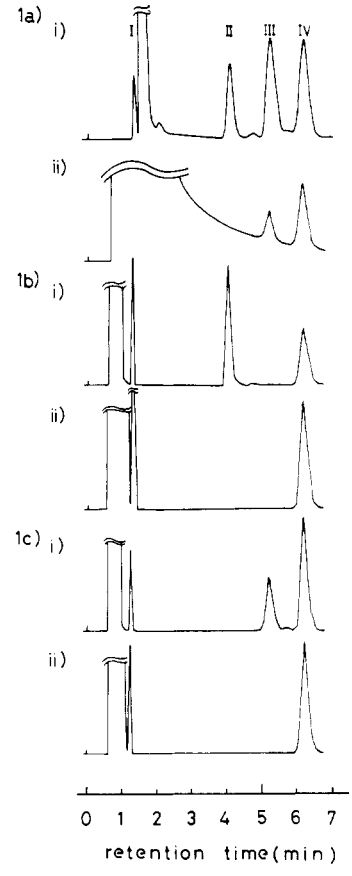

Figure 1. Gas chromatograms of products from the reaction of 1 with **2**. **1a**, **1b**, and **1c** indicate the starting monomer, respectively. Chromatograms i and ii are those of the products before and after hydrolysis, respectively. Thus, the chromatograms **1a**-i and **1a**-ii are those of the products from **1a** before and after the hydrolysis.

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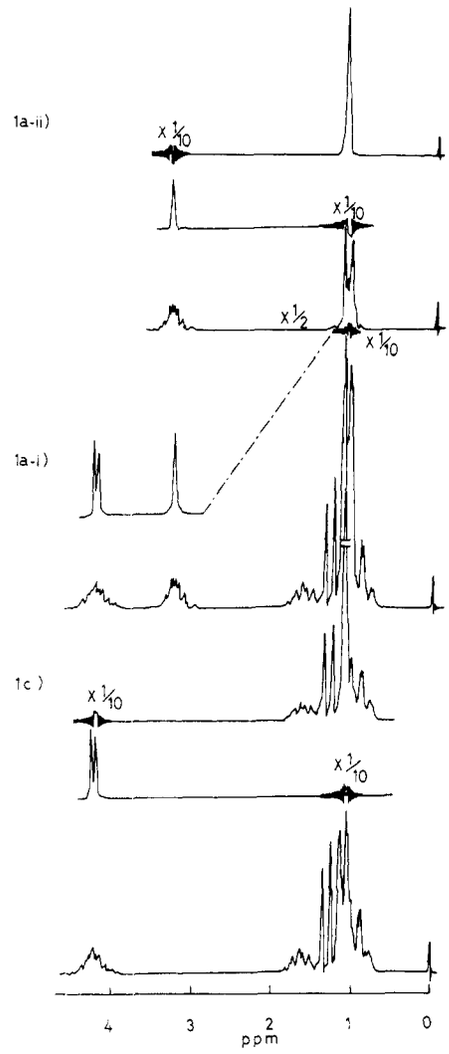


Figure 2. ^{1}H NMR spectra of the third product III in Figure 1 from **1a** and **1c**. **1a** and **1c** indicate the starting monomers, and i and ii indicate the spectra before and after hydrolysis.

$CH_3CHCHCH_3$), 1.17 (d, J = 6.0 Hz, $CH_3CHCHCH_3$), 1.30 (s, CH_3C), 1.40 (s, CH_3C), 1.63 (q, J = 7.0 Hz, CH_3CH_2), 1.72 (q, J = 7.0 Hz, CH_3CH_2), 4.23 (m, $CH_3CHCHCH_3$), 4.28 (m, $CH_3CHCHCH_3$). The peaks at δ 4.23 and 4.28 were decoupled to two singlets on irradiation at δ 1.15, and the peaks at δ 1.14 and 1.17 became a singlet on decoupling from δ 4.25. It was apparent that two dioxolane isomers were contained in peak III from **1c**. The gas chromatographic result on the capillary column also suggested this. By considering the difference in shielding effect between methyl and ethyl groups, the signals at δ 0.93, 1.14, 1.40, 1.63, and 4.28 were assigned to **4b** and those at δ 0.96, 1.17, 1.30, 1.72, and 4.23 to **4c**.[7] When the signals of **5a** were subtracted from the signals of III from **1a**, the residual signals were quite similar to those of III from **1c**, and consequently the three components in III from **1a** were deduced to be **5a, 4b,** and **4c**.

***2,cis-3,trans-5,cis-6*-Tetramethyl-1,4-dioxane (5b).** The peaks IV from **1b** and **1c** gave identical NMR signals (bottom trace of **1b** and **1c** in Figure 3): NMR ($CDCl_3$) δ 1.05 (d, 6 H, J = 6.0 Hz, CH_3CH), 1.13 (d, 3 H, J = 7.0 Hz, CH_3CH), 1.26 (d, 3 H, J = 7.0 Hz, CH_3CH), 3.05 ~4.10 (m, 4 H, CH_3CH). The peak at δ 1.26 was decoupled to a singlet when irradiated at δ 3.83 (top trace of **1b** and **1c** in Figure 3). Corresponding to this, the multiplet at δ 3.05~4.10 was converted into four doublets located at δ 3.36 (J = 9.0 Hz), 3.59 (J = 9.0 Hz), 3.79 (J = 3.0 Hz), and 3.96 (J = 3.0 Hz) when decoupled from δ 1.26 (middle trace of **1b** and **1c** in Figure 3). The two coupling constants 9.0 and 3.0 Hz correspond to the values of J_{aa} and J_{ae}, respectively. Anal. Calcd for $C_8H_{16}O_2$: C, 66.61; H, 11.19. Found: C, 66.59; H, 11.17. Based on these data, the peaks IV from **1b** and **1c** were assigned as **5b**.[10]

***2,trans-3,cis-5,trans*-6-Tetramethyl-1,4-dioxane (5c).** The differences in NMR spectra between IV from **1a** and **1b** or **1c** in Figure 3 are in two points (bottom trace of **1a** in Figure 3). (1) A new doublet appeared at δ 1.25 (d, J = 6.0 Hz, CH_3CH). (2) Corresponding to this, two quartets were superimposed on the multiplet at δ 3.05~4.10. The

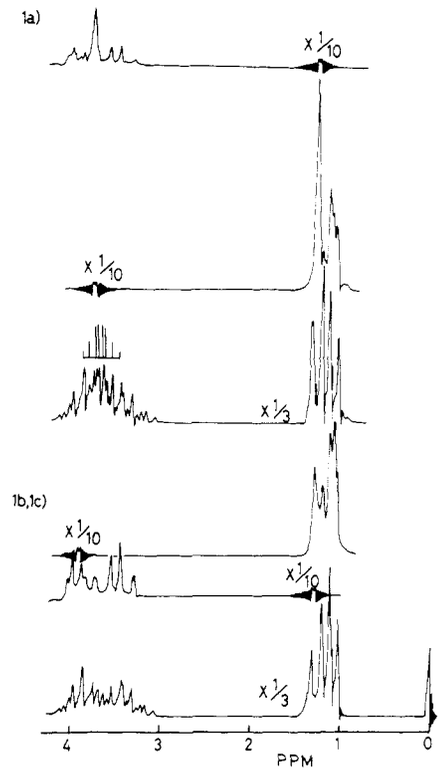


Figure 3. ^{1}H NMR spectra of the fourth product IV in Figure 1. **1a, 1b,** and **1c** indicate the starting monomers.

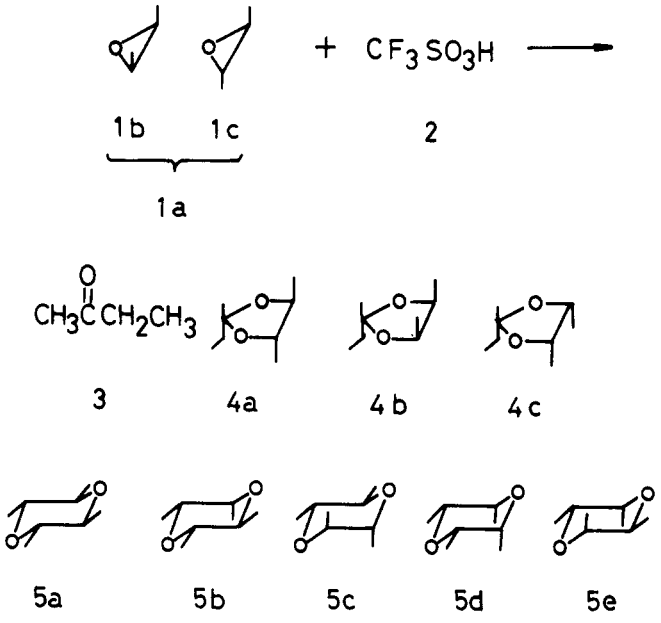
chromatographic result on the capillary column indicated that IV from **1a** was a mixture of two components. These two components were not changed by hydrolysis. This indicated that the two components were dioxanes. The NMR signals were separated by the use of a shift reagent. In the spectrum with 20 mol % of Eu(fod)$_3$-d_{27}, the methyl signals were separated into five doublets at δ 1.65 (3 H, J = 7.0 Hz), 1.95 (3 H, J = 6.0 Hz), 2.13 (3 H, J = 6.0 Hz), 2.29 (12 H, J = 6.0 Hz), and 2.80 (3 H, J = 7.0 Hz) and the methine into four multiplets at δ 4.74 (1 H), 5.13 (1 H), 5.47 (1 H), and 6.04 (1 H) and an octet at δ 5.64 (4 H), although the separation of the central four peaks of the octet was not good enough. The four doublets at δ 1.65, 1.95, 2.13, and 2.80 and the four multiplets were assigned to **5b**. When the signal of IV from **1b (5b)** was subtracted from that of IV from **1a** in Figure 3, the remaining signals were a doublet at δ 1.25 (12 H, J = 6.0 Hz, CH_3CH) and an octet at δ 3.66 (4 H, CH_3CH). The octet was decoupled to a singlet by irradiation at δ 1.25 (top trace of **1a** in Figure 3) and the doublet at δ 1.25 to a singlet by irradiation at δ 3.66 (middle trace of **1a** in Figure 3). These results indicated that this dioxane was highly symmetrical. By analyzing the spectrum as an $X_3AA'X'_3$ type, J_{HH} was determined to be 6.6 Hz, compatible with $\frac{1}{2}(|J_{aa} + J_{ee}|)$, namely, trans coupling. Thus, the dioxane has axial–axial and equatorial–equatorial couplings. From these data, the dioxane was assigned as **5c** out of three possible dioxanes (**5c, 5d,** and **5e**) in which two axial methyls are present in the ring.

Results and Discussion

The possible five dioxane and three dioxolane isomers are shown in Scheme I.

In Figure 1, four distinct peaks from GLC of the reaction of **1a** with **2** at 50 °C in dichloroethane are shown together with those from **1b** and **1c**. In each chromatogram, the first peak was methyl ethyl ketone (**3**) and the second peak was 2,*cis*-4,*trans*-5-trimethyl-2-ethyl-1,3-dioxolane (**4a**). By comparing **1a, 1b,** and **1c** in Figure 1, it is apparent that **4a** (II from **1a** and **1b**) is formed from **1b**. In the NMR signal of the third peak III from **1a**, three different singlets were observed in the methine region when decoupled from the methyl signal, indicating three different products in the third peak. These three peaks were assigned as 2,*cis*-4,*cis*-5-trimethyl-2-ethyl-1,3-dioxolane (**4b**), 2,*trans*-4,*trans*-5-trimethyl-2-ethyl-1,3-dioxolane (**4c**), and 2,*trans*-3,*trans*-5,*cis*-6-tetramethyl-

Scheme I



1,4-dioxane (**5a**). No third peak was observed from **1b**. In the third peak III from **1c**, only **4b** and **4c** were observed but no **5a**, which clearly indicates that **5a** was formed from the cross reaction between **1b** and **1c** and that **4b** and **4c** were formed from **1c**. The peaks IV from **1b** and **1c** were identified to be 2,*cis*-3,*trans*-5,*cis*-6-tetramethyl-1,4-dioxane (**5b**). The peak IV from **1a** also contained **5c**, and it was concluded that **5c** was formed from the cross reaction of **1b** and **1c**. The stereochemistry of the reaction of 1 with **2** is summarized in Table I.

In the cationic polymerization of epoxides by trifluoromethanesulfonic acid derivatives, it is well established that there is an equilibrium between oxonium species having sulfonate anion as a counterion and covalent sulfonate ester growing species[6] and that in the oxonium ion intermediate the stereochemistry on ring opening is inversion. However, the stereochemistry on growing species by trifluoromethanesulfonic acid derivatives has not been studied yet.

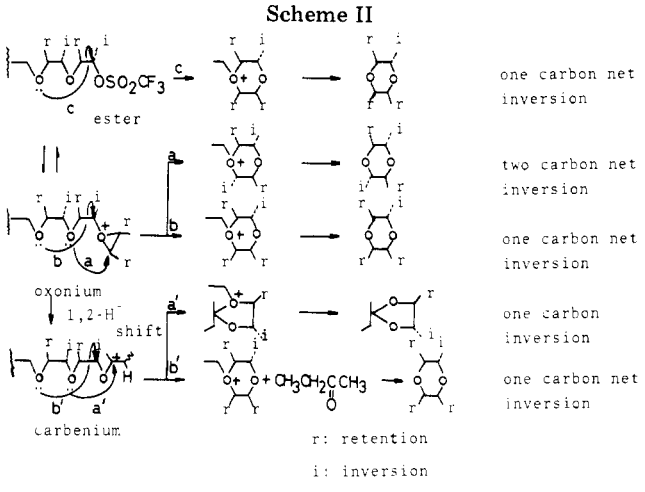
It is also well established that the distribution of cyclic oligomers is determined thermodynamically, according to the Jacobson–Stockmayer theory,[11] in the equilibrated polymerization system. In this study, the total yield of **3**, **4**, and **5** was 70% at 50 °C after 20 h of reaction in 1,2-dichloroethane and the rest was unidentified oligomers ($M_r < 600$). It would be reasonable to consider that the dimers were formed by a back-biting reaction of the growing end. Considering the oxonium ion, covalent ester species, and carbenium ion as intermediates, the formation of dioxanes, dioxolanes, and **3** can be illustrated in Scheme II.

The stereochemistry of **5** in Table I can be explained by 1 carbon net inversion, indicating the paths b, b′, c, or all of

Table I. Stereochemistry of Dimers

monomer	dioxolane	dioxane
1a	4a 4b 4c	5a 5b 5c
1b	4a	5b
1c	4b 4c	5b

Scheme II



these. The direct attack of the oxygen lone pair on the ring carbon of the oxonium intermediate, which would be difficult because of the stereochemical requirement, can be excluded on the basis of the stereochemistry of dioxane products.

Registry No.—**1b**, 1758-33-4; **1c**, 21490-63-1; **2**, 1493-13-6; **3**, 78-93-3; **4a**, 68408-41-3; **4b**, 68408-42-4; **4c**, 68408-43-5; **5a**, 42464-59-5; **5b**, 42464-58-4; **5c**, 42464-22-2.

References and Notes

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