Polymerization of 4-Methylene-1,3-dioxolane Derivatives

Seung-Jae Lee, Jeong-Ki Park†, and Myoung-Seon Gong*

Department of Chemistry, Dankook University Cheonan, Chungnam 330-714, Korea
†Department of Chemical Engineering, Korea Advenced Institute of Science and Technology, 373-1 Kusung-dong, Yusong-Ku, Taejon 305-701, Korea
Received May 3, 1995

The 4-methylene-1,3-dioxolane derivatives, 2-[(2-methoxyethoxy)methyl]-4-methylene-1,3-dioxolane (**4a**), 4-methylene-2-phenyl-1,3-dioxolane (**4b**), 4-methylene-2-(*p*-methoxyphenyl)-1,3-dioxolane (**4c**), 4-methylene-2-[*p*-(2-methoxyethoxy) phenyl]-1,3-dioxolane (**4d**) were prepared by acetalization, followed by dehydrochlorination with potassium *tert*-butoxide (*t*-BuOK). They were readily polymerized with boron trifluoride and tungsten hexachloride. Monomer **4a** underwent 70% ring-opening polymerization with WCl_6, whereas monomers **4b** and **4c** polymerized with quantitative ring-opening to form poly(keto ether)s. Especially **4d** underwent Claisen-type isomerization to afford 2-[4-(2-methoxyethoxy)phenyl]-3(2H)-dihydrofuranone in the presence of WCl_6. Acid catalyzed mechanisms were suggested for the behaviors of polymerization and isomerization of 4-methylene-1,3-dioxolane derivatives with BF_3 and WCl_6 catalyst.

Introduction

Recently, α-methylene-1,3-dioxolane derivatives have been polymerized with various initiators such as radical,[1-9] cation[10,11] and transition metal.[12,13] The free radical polymerization of 4-methylene-2-phenyl-1,3-dioxolane was studied by Bailey *et al.*[1] Three polymerization routes are concievable for the polymerization of 4-methylene-2-phenyl-1,3-dioxolane with a radical initiator.[1] They are vinyl, ring-opening *via* double bond and elimination polymerization. We have also reported that 4-metnylene-2-phenyl-1,3-dioxolane underwent photo-initiated free radical ring-opening polymerization to form poly(keto-ether) at room temperature.[5,7]

The cationic polymerization of 4-methylene-1,3-dioxolane derivatives resulted in polymer with another mixed mode of polymerization : vinyl and ring opening *via* double bond.[10,14] Some of 4-methylene-1,3-dioxolane derivatives were reported to polymerize in the ring-opening fashion to form poly (keto-ether) by metal based catalyst such as tungsten hexachloride.[12,13]

In the course of studying 4-methylene-1,3-dioxolane derivatives with a special substituent at 2-position, it was found that they would undergo polymerization or isomerization to give polymers or other cyclization products. The modes of polymerization were dependent upon the substituent at 2-position of 4-methylene-1,3-dioxolane because of an ability of forming stable intermediate by ring-opening. An olefinic cyclic ether, 2-[4-(2-methoxyethoxy)phenyl]-4-methylene-1,3-dioxolane is of particular interest beacause they make it possible to synthesize 3(2H)-dihydrofuranone which was rarely prepared from other methods.

In this paper, we would like to report the polymerization of some 4-methylene-1,3-dioxolane derivatives and for the first time Claisen-type isomerization reaction, which was a novel route of 3-furanone, of 2-[4-(2-methoxyethoxy)phenyl)]-4-methylene-1,3-dioxolane with tungsten hexachloride or boron trifluoride. We hope that this suggestion could give us some insight for the structure of the reaction intermediate and the reaction mechanism.

Experimental

4-Methlene-2-phenyl-1,3-dioxolane (**4b**) and 4-methylene-2-(*p*-methoxyphenyl)-1,3-dioxolane (**4c**) were prepared by the method previously reported.[5] 2-Methoxyethoxyacetaldehyde diethylacetal was prepared by reacting bromoacetaldehyde diethylacetal with sodium 2-methoxyethanol in tetrahydrofuran. Methylene chloride was purified by drying with calcium hydride and distillation over sodium metal. 2-Methoxyethyl chloride, *p*-methoxybenzaldehyde, 3-chloro-1,2-propanediol, *p*-hydroxybenzaldehyde, benzaldehyde (Aldrich Chemical Co.) were used without further purification. *tert*-Butanol was purified by distillation over sodium metal. Dowex 50W (strong cation exchange resin) was used as acetalization catalyst. Tungsten hexachloride (Aldrich Chemical Co. 99+%) was purified by sublimation under vacuum. The catalyst was prepared by dissolving 0.6 g of WCl_6 in 30 g of methylene chloride (2 wt.%) in nitrogen atmosphere. Borontrifluoride etherate (Purified Grade, Aldrich Chemical Co.) was used without further purification.

FT-IR spectra were obtained with a Midac spectrophotometer and the positions of the absorption band are reported in cm^{-1}. ^1H NMR spectra were recorded on a Varian EM 360A spectrometer and the chemical shifts are recorded in ppm from tetramethylsilane as an internal standard. ^{13}C NMR spectra were performed with a Bruker Am 300 spectrometer. Elemental analyses were obtained with a Yanaco MT-3 CHN-Analyzer. The mass spectrum was obtained on a HP 5989A mass spectrometer. The molecular ion is represented as M^+. The peaks corresponding to various fragments are reported as m/e (assignment : relative intensity). Gel-permeation chromatography (GPC) data were obtained with a Waters HPLC using three columns (μ-Stryragel 10^2, 10^3 and 10^4 Å) in tetrahydrofuran and calibrated with polystyrene standards.

2-(2-Methoxyethoxymethyl)-4-chloromethyl-1,3-dioxolane (3a). A mixture of 2-methoxyethoxyacetaldehyde diethylacetal (9.6 g, 50.0 mmol), 3-chloro-1,2-propanediol (6.0 g, 55 mmol) and 0.5 g of Dowex-50W(H^+) resin in 100 mL

of benzene was placed in a 250 mL round bottomed flask equipped with Dean-Stark separator. The reaction mixture was refluxed and the benzene was added in a 50 mL portion untill the calculated amount of ethanol was eliminated for 8 hr. The reaction mixture was cooled and filtered through the glass filter. After the solvent was evaporated and the residue was vacuum distilled to give 8.2 g of **3a**.

3a : Yield 78.0%, Bp 90℃/ 0.1 torr.; FT-IR 2890-2980 (C-H), 1380 (C-H bending), 1220-1080 (C-O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.0 (t, 1H, acetal proton), 4.1-3.9 (m, 3H, -OC$\underline{H}_2$C$\underline{H}$(CH_2Cl)O-), 3.5-3.8 (m, 6H, -OC$\underline{H}_2$C$\underline{H}_2$-OC$\underline{H}_2$-), 3.6 (s, 3H, C$\underline{H}_3$O-), 3.4-3.7 (m, 2H, -C$\underline{H}_2$Cl).

2-(2-Methoxyethoxymethyl)-4-methylene-1,3-dioxolane (4a). A mixture of 10.5 g (50.0 mmol) of 2-(2-methoxyethoxymethyl)-4-chloromethyl-1,3-dioxolane in 20 mL of *tert*-butanol was added slowly to the solution of 2.4 g (60.0 mmol) of potassium dissolved in 50 mL of *tert*-butanol at 20 ℃ under nitrogen atmosphere. After the addition was completed, the temperature was raised to 80 ℃ and the gentle refluxing was maintained for 24 hr. The excess *tert*-butanol was evaporated and 100 mL of ethyl ether was added. The resulting precipitate was removed by filtration and the residue was vacuum distilled through a column to give 6.7 g of **4a** as a colorless liquid.

4a : Yield 76.8%, Bp 78 ℃/ 0.1 torr.; FT-IR 2890-2980 (C-H), 1680 (C=C), 1380 (C-H bending), 1220-1080 (C-O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.9-5.1 (t, 1H, acetal proton), 4.2-3.8 (m, 2H, =C$\underline{H}_2$), 3.3-3.8 (m, 8H, -OC$\underline{H}_2$C$\underline{H}_2$-OC$\underline{H}_2$- and -OC$\underline{H}_2$C(=CH_2)O-), 3.6 (s, 3H, C$\underline{H}_3$O-).

***p*-(2-Methoxyethoxy)benzaldehyde (2d).** *p*-Hydroxybenzaldehyde (12.20 g, 100.0 mmol) was dissolved in ethanol (100 mL) and a solution of sodium hydroxide (4.5 g, 112.5 mmol) in water (10 mL) was added dropwise with vigorous stirring. 2-Methoxyethyl chloride (10.86 g, 120 mmol) was dropped for 30 min and the reaction mixture was refluxed for 4 days at 80 ℃ under nitrogen. After the solvent was removed by evaporation under reduced pressure, the residue was dissolved in diethyl ether and washed with water several times. The crude product, which was obtained after evaporation of solvent, was vacuum distilled to give 14.2 g of **2d**.

2d : Yield 78.7%, Bp 104-106 ℃/ 0.1 torr.; FT-IR 3030 (aromatic C-H), 2870 (C-H), 1760 (C=O), 1280-1150 (C-O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 9.6 (s, 1 H, formyl H), 7.6-6.8 (2 d, 4H, aromatic protons), 3.8-4.2 (t, 4H, -OC$\underline{H}_2$C$\underline{H}_2$O-), 3.6 (s, 3H, C$\underline{H}_3$O-).

4-Chloromethyl-2-[4-(2-methoxyethoxy)phenyl]-1,3-dioxolane (3d). A mixture of 18.0 g (100 mmol) of *p*-(2-methoxyethoxy)benzaldehyde and 13.3 g (120.0 mmol) of 3-chloro-1,2-propanediol in 100 mL of toluene was heated at 80 ℃ with 0.5 g of Dowex-50W (H^+) resin in a 250 mL flask equipped with Dean-Stark separator. After the calculated amount of water was collected by azeotropic distillation for 12 hr, the ion exchange resin was removed by filtration. The mixture was washed with water by using separatory funnel and the solvent was evaporated. The crude product was purified by vacuum distillation to afford 20.2 g of **3d** as a viscous colorless liquid.

3d : Yield 74.2%, Bp 150 ℃/ 0.1 torr.; FT-IR 3045 (aromatic C-H), 2850-2960 (C-H), 1300-1105 (C-O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.4-6.9 (2 d, 4H, aromatic protons), 5.5-5.2 (d, 1H, acetal proton), 3.9-3.7 (m, 7H, -OC$\underline{H}_2$C$\underline{H}_2$O- and -OC$\underline{H}_2$C$\underline{H}$(CH_2Cl)O-), 3.6 (s, 3H, C$\underline{H}_3$O-), 3.5 (m, 2H, -C$\underline{H}_2$Cl).

4-Methylene-2-[4-(2-methoxyethoxy)phenyl]-1,3-dioxolane (4d). A solution of 13.6 g (50.0 mmol) of 4-chloromethyl-2-[4-(2-methoxyethoxy)phenyl]-1,3-dioxolane (**3c**) in 20 mL of *tert*-butanol was added slowly to the solution of 2.43 g (60.0 mmol) of potassium dissolved in 50 mL of *tert*-butanol at 20 ℃ under nitrogen atmosphere. After the addition was completed, the temperature was raised to 80 ℃ and the gentle refluxing was maintained for 24 hr. The reaction mixture was cooled and *tert*-butanol was removed by evaporation. The crude product was dissolved in 100 mL of diethyl ether and washed with distilled water. After the evaporation of ethyl ether, the resulting residue was vacuum distilled through a column to give 9.0 g of **4d** as a colorless liquid.

4d : Yield 76.0%, Bp 138 ℃/ 0.1 torr.; FT-IR (KBr) 3045 (aromatic C-H), 2850-2960 (C-H), 1680 (C=C), 1300-1105 (C-O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.3-6.8 (2 d, 4H, aromatic protons), 5.8 (s, 1H, acetal proton), 4.2-3.8 (m, 2 d, =C$\underline{H}_2$), 3.9-3.7 (m, 6H, -OC$\underline{H}_2$C$\underline{H}_2$O- and -OC$\underline{H}_2$C(=CH_2)O-), 3.6 (s, 3 H, C$\underline{H}_3$O-). Anal. Calcd for $C_{13}H_{16}O_4$: C, 68.10; H, 6.78. Found : C, 67.27; H, 6.53.

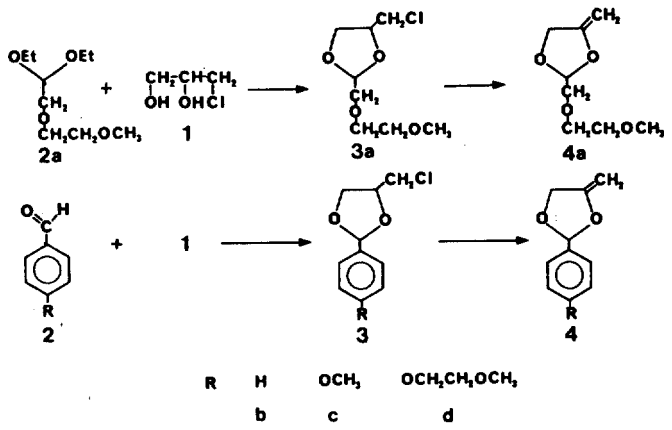
Polymerization or isomerization of 4-MDO derivatives with tungsten hexachloride. A solution of **4c** (1 g, 4.2 mmol) in 4 mL of purified methylene chloride was injected to a septum rubber capped glass ampoule in a dry nitrogen atmosphere. The ampoule was then placed in a cooler at −50 ℃ and 0.7 mL (4.0 mol%) tungsten chloride solution was introduced. After 4 hr, the mixture was quited with excess triethylamine and poured into a large amount of cold *n*-hexane. The white precipitate was collected and reprecipitated from methylene chloride into *n*-hexane. The solid product was obtained after drying under vacuum at 50 ℃ for 12 hr.

Similar synthetic procedures were applied to the synthesis of product **4a** and **4b**. In the case of **4d**, the solid product (**5**) was purified by Kugueller distillation apparatus under vacuum.

Cationic Polymerization or isomerization reaction of 4-methylene-1,3-dioxolane derivatives with borontrifluoride etherate. A solution of **4d** (1.3 g, 5 mmol) dissolved in 4 mL of dry methylene chloride was placed in a septum rubber capped glass ampoule in a dry nitrogen atmosphere. The ampoule was immersed in a cooler at −50 ℃ and 18.65 μL (3 mol%) of borontrifluoride etherate was introduced by using micro-syringe. After the ampoule was maintained 4hr, the polymerization mixture was quenched with excess triethylamine. The polymer solution was poured into a large ammount of cold *n*-hexane. The yellow precipitate was collected and reprecipitated from methylene chloride into *n*-hexane. The solid product was obtained after drying under vacuum at 50 ℃ for 12 hr.

Other monomers **4a**, **4b** and **4c** were polymerized by similar procedures described above.

P4a : Yield 85%, FT-IR (KBr) 2850 (C-H), 1725 (C=O), 1416, 1310, 1068, 979 (C-O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.0 (m, 1H, acetal proton), 3.9-3.6 (m, -OC$\underline{H}_2$C(C$\underline{H}_2$-)O-, -C$\underline{H}_2$OC$\underline{H}_2$C$\underline{H}_2$O- and -CO-C$\underline{H}_2$O-), 3.2 (s, 3H, -OC$\underline{H}_3$), 2.2-2.8 (m, -OCH_2C(C$\underline{H}_2$-)O- and -C$\underline{H}_2$CO-); ^{13}C NMR ($CDCl_3$) 200.6 (-$\underline{C}$O-), 102.9, 102.6, 101.9 (acetal C's), 71.8, 70.8, 70.5 (-O$\underline{C}H_2$ $\underline{C}H_2$O-), 67.8 (-CO-$\underline{C}H_2$-O-), 58.9 (O$\underline{C}H_3$), 43.9 (-$\underline{C}H_2$-CO-);



Scheme 1.

Anal. Calcd for $C_8H_{14}O_4$: C, 55.17; H, 8.05. Found : C, 54.74; H, 7.49.

P4b : Yield 76%, FT-IR (KBr) 3045 (aromatic C-H), 28 80-2960 (C-H), 1735 (C=O), 1350 (C-H), 1300-1105 (C-O), 760, 710 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.2 (m, 5H, phenyl), 4.7 (m, 1H, -O-C<u>H</u>(Ph)-), 3.8 (m, 2H, -CO-C<u>H</u>$_2$-O-), 2.8 and 2.6 (m, 2H, -C<u>H</u>$_2$CO-); ^{13}C NMR ($CDCl_3$) 205.0 (-<u>C</u>O-), 139.6, 128.6, 126.6 (aromatic C's), 77.9 (-O-<u>C</u>H(Ph)-), 74.3 (-CO-<u>C</u>H$_2$-O-), 47.1 (-<u>C</u>H$_2$-CO-); Anal. Calcd for $C_{10}H_{10}O_2$: C, 74.08; H, 6.17. Found : C, 74.04; H, 6.12.

P4c : Yield 90%, FT-IR (KBr) 3012 (aromatic C-H), 2908-2832 (C-H), 1732 (C=O), 1610, 1514, 1250-1030 (C-O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.2-6.8 (2 d, 4H, aromatic protons), 4.8 (s, 1 H, -O-C<u>H</u>(Ph)O-), 3.8 (m, 2H, -CO-C<u>H</u>$_2$-O-), 3.2 (s, 3H, -OC<u>H</u>$_3$), 2.8-2.6 (m, 2H, -C<u>H</u>$_2$CO-); Anal. Calcd for $C_{11}H_{12}O_3$: C, 68.75; H, 6.25. Found : C, 68.24; H, 6.19.

P4d : Yield 85%, mp 55 ℃; FT-IR 3054 (aromatic C-H), 2828-2880 (C-H), 1718 (C=O), 1250, 1125, 1060 (C-O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.4-7.2 (2 d, 4H, aromatic protons), 4.9 (m, 1H, -O-C<u>H</u>(Ph-)CH$_2$-), 3.9-3.7 (m, 6H, -OC<u>H</u>$_2$C<u>H</u>$_2$O- and -CO-C<u>H</u>$_2$O-), 3.3 (s, 3H, C<u>H</u>$_3$O-), 2.5 (m, 2H, -C<u>H</u>$_2$CO-); ^{13}C NMR ($CDCl_3$) 214.0 (-<u>C</u>O-), 158.5, 131.9, 127.0, 114.4 (aromatic C's), 78.7 (-O-<u>C</u>H(Ph)-), 71.3, 70.6 (-OC<u>H</u>$_2$C<u>H</u>$_2$O-), 67.0 (-CO-C<u>H</u>$_2$-O-), 58.8 (O<u>C</u>H$_3$), 44.2 (-<u>C</u>H$_2$-CO-); MS (EI), m/e 179 (M^++1), 178 (M^+), 120, 59, 44; Anal. Calcd for $C_{13}H_{16}O_4$: C, 68.10; H, 6.78. Found : C, 67.23; H, 6.62.

Results and Discussion

The 4-methylene-1,3-dioxolane derivatives, 2-[(2-methoxyethoxy)methyl]-4-methylene-1,3-dioxolane (**4a**), 4-methylene-2-phenyl-1,3-dioxolane (**4b**), 4-methylene-2-(*p*-methoxy-phenyl)-1,3-dioxolane (**4c**), 4-methylene-2-[*p*-(2-methoxyethoxy) phenyl]-1,3-dioxolane (**4d**) were prepared by acid catalyzed acetalization of the corresponding aldehyde with 3-chloro-1,2-propanediol, followed by dehydrochlorination with potassium *tert*-butoxide (*t*-BuOK) as indicated in Scheme 1.

4-Methylene-1,3-dioxolane monomers **4a-4d** were polymerized with a transition metal catalyst (WCl_6) or Lewis acid (BF_3) under various conditions. Model reactions were carried out to examine the activity of catalyst and the feasibility of polymerization of 1,3-dioxolane ring containing no exo-methylene group. When 2-phenyl-1,3-dioxolane and 1,3-dioxolane were polymerized with tungsten hexachloride, no polymers were obtained. Therefore, it can be deduced that tungsten hexachloride does not polymerize 1,3-dioxolane ring, lacking of exo-methylene group. This observation implies that the methylene group plays a crucial role for the polymerization of 4-methylene-1,3-dioxolanes, when tungsten hexachloride is used as a catalyst.

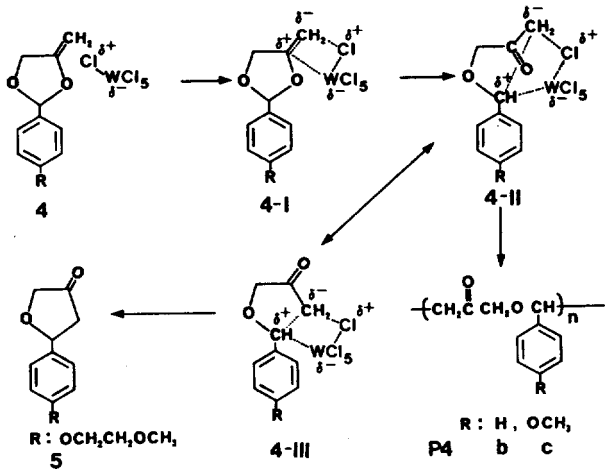
Table 1. Conditions and Results of Polymerization of 4-Methylene-1,3-dioxolane Derivatives

Monomer	Initiator in mol%	Temp. in ℃	Yield[a] in %	Mw[b]	Ring-opening Content (%)
4a	WCl_6 (4)	−50	85	4900	70
	WCl_6 (4)	25	89	6500	60
	BF_3 (3)	−50	60	3800	68
4b	WCl_6 (4)	−50	76	4200	100
	WCl_6 (4)	0	80	4500	95
	WCl_6 (4)	25	64	6400	85
	BF_3 (3)	−50	62	5200	100
4c	WCl_6 (4)	−50	90	9600	100
	WCl_6 (4)	25	75	8000	90
	BF_3 (3)	−50	82	5900	90
4d	WCl_6 (4)	−50	85	−	100[d]
	WCl_6 (4)	25	69	−	100[d]
	BF_3 (3)	−50	65	−	100[d]

[a] Yields were measured gravimetrically. [b] Weight average molecular weight were taken with a Waters HPLC using three columns (μ-Styragel 10^2, 10^3 and 10^4 Å), and calibrated with polystyrene standards in chloroform at 254 nm. [c] Ring-opening contents were determined by the integration ratios of ring-intact acetal proton and ring-opened benzyl or α-proton. [d] Isomerization product.

Results and conditions of polymerization or isomerization of various 4-methylene-1,3-dioxolane derivatives were summarized in Table 1 along with molecular weight data of resulting polymers. When the 4-methylene-1,3-dioxolane, 2-methyl- and 2,2-dimethyl-4-methylene-1,3-dioxolane were polymerized with cationic catalysts such as BF_3 and $AlCl_3$, the ring-opening content was dependent upon the substituent at 2-position of 1,3-dioxolane ring and experimental conditions.[10] The stablility of cationic intermediates formed by ring-opening is responsible for the ring-opening content in the course of polymerization. In the case of the alkyl group, which could form the primary cationic intermediate if ring opening occurred, the extent of ring opening was within 70%.[10,14]

When the polymerization of **4a** was carried out with tungsten hexachloride at −50 ℃, the viscous liquid polymer was obtained after precipitation of polymerization mixture into *n*-hexane. The polymer showed peaks at 110-100 ppm attributable to ring-intact acetal carbon as well as 201 ppm attributable to ring-opened carbonyl carbon in its ^{13}C NMR spectrum. In ^1H NMR spectrum, a broad multiplet peak at 5.4 ppm corresponding to the acetal protons in the 1,3-dioxolane ring, which was shown in monomer **4a**, indicated that some of the ring had not opened. This observation is also consistent with the presence of a carbonyl absorption band at 1735 cm^{-1} with medium intensity and strong C-O absorption band around 1200 cm^{-1} in an IR spectrum of polymer **P4a**. This



Scheme 2.

spectral analysis It shows 70% ring-opening (30% ring intact) content, which is comparable to the previously reported result obtained from 2-benzyl-4-methylene-1,3-dioxolane.[13]

When the monomer **4b** was polymerized at −50 ℃ in the presence of tungsten hexachloride (5 mol%) as an initiator, the powdery polymer was formed after precipitation of methylene chloride solution into cold *n*-hexane. Monomer **4b** was completely ring-opened by tungsten hexachloride. It is reasoned that the formation of the stable benzyl intermediate **4-II** during ring-opening might make it even more prone to ring open than **4a** as illustrated in Scheme 2. It has been already reported that **4b** undergoes quantitative ring-opening to give the poly(keto-ethers).[12] The phenyl substituent at 2-position in 1,3-dioxolane ring can provide a sufficient driving force by forming stable benzyl intermediate to ring open the 4-methylene-1,3-dioxolane derivatives. It was also found that the amount of ring-opening was varied by the polymerization temperature, that is, the lower extent of ring-opening at higher temperature was obseved for the polymerization of the **4b**.

Monomer **4c** was also polymerized easily in the presence of WCl_6 to give a powdery polymer in 90% yield. The spectral data also showed that the polymerization proceeded by a clean ring-opening mode at −50 ℃. Under the same polymerization conditions, the polymerizability and yield of **4c** were higher than those of monomer **4b**. The results is attributable to the methoxy group as an electron donating group. It was also expected that monomer **4c** underwent polymerization with less than quantitative ring-opening at higher temperature in Table 1. The methoxy substituent at *para*-position in **4c** make it possible that the ring-opening is favored by forming more stable resonance intermediate **4c-II** as shown in Scheme 2. From these results, the following mechanism is suggested for the polymerization of 4-methylene-1,3-dioxolane derivatives, though the chemical pathways not clearly elucidated. However a cationic mechanism is adopted for an interpretation of the polymerization of 4-methylene-1,3-dioxolane derivatives since the chemical structure of polymers obtained from boron trifluoride is identical to that of the polymer from tungsten hexachloride.

Monomers **4a-4c** were also polymerized easily in the presence of boron trifluoride even at −50 ℃ to give viscous

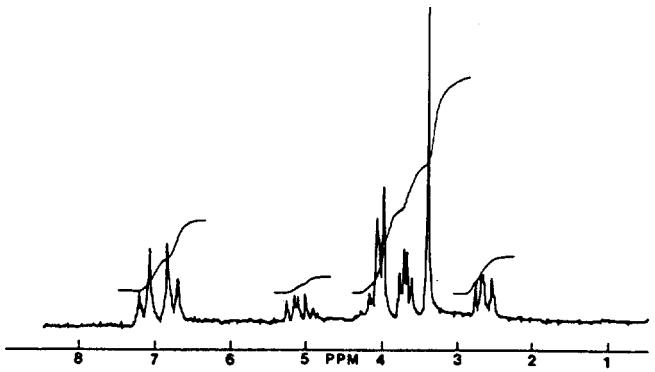


Figure 1. ^{1}H NMR spectra of 2-[4-(2-methoxyethoxy)phenyl]-3(2H)-dihydrofuranone obtained from a tungsten hexachloride catalyzed isomerization reaction of **4d**.

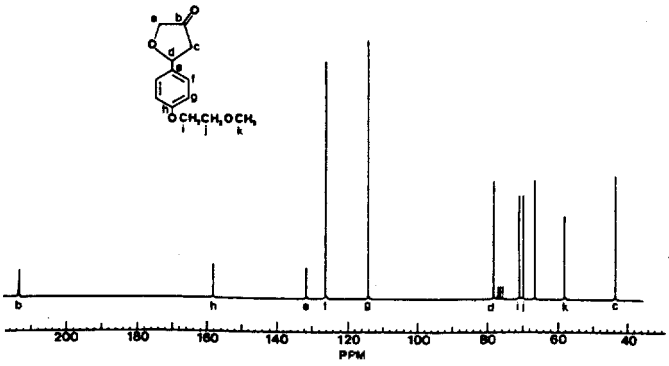
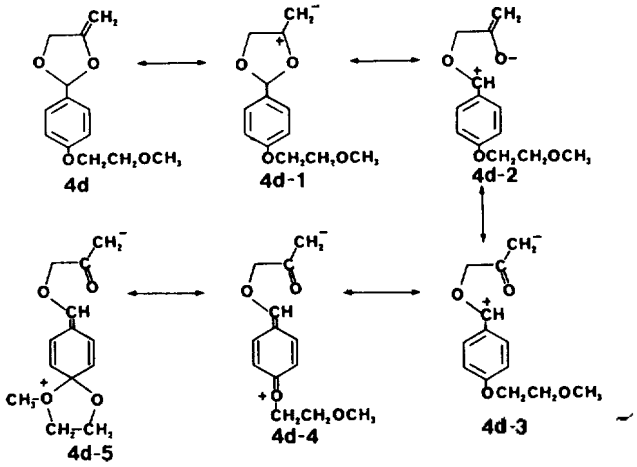


Figure 2. ^{13}C NMR spectra of 2-[4-(2-methoxyethoxy)phenyl]-3(2H)-dihydrofuranone obtained from a tungsten hexachloride catalyzed isomerization reaction of **4d**.

or white powdery polymers. The yields were lower than those obtained from tungsten hexachloride. On the other hand the ring-opening content and chemical structure of polymers were comparable to those of polymers obtained with tungsten hexachloride.

Most of polymers were soluble in common organic solvents such as chloroform, tetrahydrofuran, acetone, ethanol and benzene. They are partially soluble in methanol and insoluble in pentane and hexane. The polymers have a weight average molecular weight Mw in the range of 3800-8000 and molecular weight distribution was in the range of 2-3. In the case of polymer **P4a**, the liquid phase at room temperature might be due to the flexible methoxyethoxy group as a side chain by lowering melting temperature.

When the polymerization of monomer **4d** was performed with 4 mol% of tungsten hexachloride at both −50 ℃ and 25 ℃ for 8 hr, no polymers were obtained. Meanwhile, the precipitated solid product was crystallized from 1,2-dichloroethane to give a slightly yellow crystal. This observation implies that **4d** completely didn't undergo polymerization at all. It was found that the major portion of the monomer underwent a Claisen rearrangement to form an 3(2H)-dihydrofuranone derivative. The possible modes of reaction of **4d** were characterized by various spectroscopies. An IR spectrum of the product obtained from **4d** shows a strong absorption band at 1735 cm^{-1} indicating the presence of the car-



Scheme 3.

bonyl group. In the ^1H NMR spectrum, the absence of a peak at 5.8 ppm assignable to the acetal proton of 1,3-dioxolane ring and the presence of a multiplet peak at 4.9 ppm corresponding to ring opened benzyl proton indicated that the monomer **4d** undergoes ring-opening and then isomerizes with WCl_6 at -50 ℃ as shown in Figure 1. ^{13}C NMR spectrum of polymer also shows no peak around 103 ppm corresponding to the ring-intact acetal carbon, and a peak at 214 ppm assignable to carbonyl carbon indicating that **4d** undergoes quantitative ring-opening as shown in Figure 2. Moreover, the mass spectrum and elemental analysis were consistent with the assigned ring-opened isomerization product. In the case of monomer **4d** possessing substituted phenyl group with long 2-methoxyethoxy group at para position, the possible resonance structures were shown in Scheme 3. Since the stability of these cationic intermediates increased, intra molecular reaction or isomerization occured rather than polymerization. The release of ring strain of 1,3-dioxolane ring and formation of the relatively stable carbonyl group are strong driving forces for the ring-opening, and the relative stability of the resulting ring-opened species **4-II** is also a factor. This result can be interpreted in terms of the relative stabilities of initially formed species **4d-I** and its rearranged species **4d-II** and **4d-III** in Scheme 2. As illustrated in Scheme 3, the initially formed species **4d-1** and **4d-2** easily rearranged to the more stable species **4d-3** which is overstabilized by the resonance form **4d-4**, **4d-5** and the actual reactive species, thus coupling takes place cleanly to form 2-[4-(2-methoxyethoxy)phenyl]-3(2H)-dihydrofuranone (**5**).

In an ealier report, 3(2H)-dihydrofuranone was prepared by Michael addition of α-hydroxyesters into α,β-unsaturated carbonyl compounds in the presence of the base catalyst.[15] Another method of preparation of 3(2H)-dihydrofuranone was acid catalyzed intramolecular cyclization of α′-hydroxy-α,β-unsaturated carbonyl compound.[16] It was also reported that mercury catalyzed hydration of alkynic diols produced 2,2,4,4-tetrasubstituted 3(2H)-dihydrofuranone in high conversion.[17] In spite of the usefulness of these methods in organic synthesis, the limited or particular chemical structure of reactants could be a major drawback for the most this type organic reaction. This rearrangement, one of the Claisen-type rearrangement, has turned to be effectively catalyzed by tungsten hexachloride and it could be successfully applied for the formation of 3(2H)-dihydrofuranone in organic synthesis.

Tungsten hexachloride is an effective catalyst for the selective polymerization of 4-methylene-1,3-dioxolane derivatives. However, only a few of systematic studies have been executed to elucidate the catalytic pathway and the reaction mechanism for the polymerization of 4-methylene-1,3-dioxolane has not been clarified thus far. The substituent at 2-position has related with ring-opening. This indicates that the polymerization does not proceed in concerted mechanism for the polymerization of 4-methylene-1,3-dioxolane derivetives by tungsten hexachloride. The mode of polymerization and the structural feature of polymers obtained from tungsten hexachloride were analogous to those obtained from cationic polymerization with boron trifluoride. Further work on the detailed mechanism of polymerization is now in progress and will be presented in the furture.

Acknowledgment. This work has been supported by the Korea Science and Engineering Foundation (NL 03171, KOSEF 93-0300-10-01-3), 1994.

References

1. Pan, C. Y.; Wu, Z.; Bailey, W. J. *J. Polym. Sci. Part C, Polym. Lett.* **1987**, *25*, 243.
2. Endo, T.; Hiraguri, Y. *J. Am. Chem. Soc.* **1987**, *109*, 3779.
3. Endo, T.; Hiraguri, Y. *J. Polym. Sci. Part C, Polym. Lett.* **1989**, *27*, 4403.
4. Gong, M. S.; Cho, I.; Chang, S.-I. *Makromol. Chem. Rapid Commun.* **1989**, *10*, 201.
5. Gong, M. S.; Cho, I.; Kim, B. G.; Kim, C. B.; Park, Y. C. *Makromol. Chem. Rapid Commun.* **1991**, *12*, 141.
6. Yoon, D. H.; Park, Y. C.; Kim, C. B.; Yang, J. K.; Gong, M. S. *Polymer (Korea)* **1990**, *14*, 82.
7. Kim, B. G.; Park, M. G.; Gong, M. S. *Polymer (Korea)* **1991**, *15*, 201.
8. Sugiyama, J.; Yokozawa, T.; Endo, T. *J. Am. Chem. Soc.* **1993**, *115*, 2041.
9. Sugiyama, J.; Yokozawa, T.; Endo, T. *Macromolecules* **1994**, *27*, 5536.
10. Goodman, M.; Abe, A. *J. Polym. Sci. Part A: Polym. Chem.* **1964**, *2*, 3471.
11. Park, J. K.; Yokozawa, T.; Endo, T. *J. Polym. Sci. Part A: Polym. Chem.* **1993**, *31*, 1141.
12. Gong, M. S.; Kim, T. M.; Kim, Y. *Makromol. Chem. Rapid Commun.* **1994**, *15*, 639.
13. Gong, M. S.; Kim, T. M.; Park, J. K. *Polymer (Korea)* **1994**, *18*, 651.
14. Ivin, K. J.; Saegusa, T. *Ring-opning Polymerization, Vol 1*; Elsevier Applied Sci. Publishers: 1984.
15. Moshfegh, A.; Fallab, S.; Erlenmeyer, H. *Helv. Chim. Acta* **1957**, *40*, 1157.
16. Nazarov, I. N.; Elizarova, A. N. *Bull. Acad. Sci. USSR, Div. Chem. Sci.* **1948**, 107.
17. Bennett, G. B.; Houlihan, W. J.; Mason, R. B.; Engstron, R. G. *J. Med. Chem.* **1976**, *19*, 709.