

2-(*p*-Substituted phenyl)-4-Methylene-1, 3-Dioxolane 유도체의 합성과 라디칼 중합

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(1989년 9월 25일 접수)

Syntheses and Radical Polymerization of 2-(*p*-Substituted phenyl)-4-Methylene-1,3-Dioxolane Derivatives

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(Received September 25, 1989)

요 약 : 파라 위치의 치환제가 개환 및 탈리가 동시에 일어나는 라디칼 중합에 미치는 영향을 조사하기 위하여 $-\text{CH}(\text{CH}_3)_2$ (IIa), $-\text{OCH}_3$ (IIb), $-\text{H}$ (IIc), $-\text{Cl}$ (IId), $-\text{Cl}$, 2- Cl (IIe), $-\text{CN}$ (IIf)의기가 있는 2-(*p*-substituted phenyl)-4-methylene-1, 3-dioxolane 유도체를 합성하였다. 125°C에서 라디칼 개시제로 3 몰 %의 DTBP를 사용한 중합에서 전자 주체가 치환된 단량체인 IIa와 IIb는 4~7%, 21~23%, 70~75%의 비닐, 개환, 탈리 중합이 일어났다. 반면에 전자 받개가 있는 IIe, IIf는 15~20%, 75~80%, 5%의 비닐, 개환, 탈리가 일어나 탈리에 큰 차이를 보여주었다. 즉 전자 주체기가 개환은 약간 탈리는 크게 증진시킨다. 이와 반대로 전자 받개기는 개환에 의하여 생긴 벤질 라디칼을 크게 안정화시킨다. 모든 단량체들은 태양광에 의한 비 증압 광중합을 실온에서 시킨 결과 탈리가 수반되지 않은 완전한 개환 중합이 진행되었다.

Abstract : 2-(*p*-Substituted phenyl)-4-methylene-1,3-dioxolane derivatives containing $-\text{CH}(\text{CH}_3)_2$ (IIa), $-\text{OCH}_3$ (IIb), $-\text{H}$ (IIc), $-\text{Cl}$ (IId), $-\text{Cl}$, 2- Cl (IIe), $-\text{CN}$ (IIf) groups on para position were prepared to investigate the effect of substituent on radical ring opening and elimination polymerization. When the polymerizations were carried out with 3 mole % DTBP as radical initiator at 125°C for 72h, the polymers with electron donating substituent such as isopropyl and methoxy possess the composition of 4~7 % ring intact, 21~23 % ring opening and 70~75 % elimination units. In contrast monomers IIe and IIf with electron withdrawing group polymerized to give the polymer with 15~20 % ring intact, 75~80 % ring opening and 5 % elimination units. The electron withdrawing substituent which stabilize the benzyl radical more inhibited the elimination as benzaldehyde derivatives. When the photopolymerization with sunlight was carried out at room temperature for 72 h, all the monomers underwent almost quantitative ring opening without elimination.

INTRODUCTION

Recently various olefinic cyclic ethers such as α -methylene derivatives of 1,3-dioxolane,^{1,2} tetrahydrofuran,^{3,4} spiro orthoester,⁵ spiro orthocarbonate,⁶ oxetane³ have been successfully polymerized by free radical ring-opening process.

Bailey and coworkers⁶ reported that 2-phenyl-4-methylene-1,3-dioxolane underwent free radical polymerization to give the polymers with three polymerization modes. Those were addition, ring opening, and elimination.

Endo and Hiraguri⁷ reported that 2,2-diphenyl-4-methylene-1,3-dioxolane was polymerized radically via quantitative ring opening, followed by elimination of benzophenone to form polyketone.

It was also reported that 2-phenyl-2-methoxy-4-methylene-1,3-dioxolane⁹ underwent radical polymerization to give the polymers constituted by ring opening and elimination units.

α -Methylene-1,3-dioxolane ring itself does not possess enough reactivity to polymerize by radical ring opening reaction. By introducing a phenyl group to 1,3-dioxolane ring, the polymerizability of the resulting monomer becomes enhanced, enough to show the better tendency to polymerize by ring opening with radical initiators. In the radical ring opening polymerization of 4-methylene-1,3-dioxolane derivatives, subsequent elimination reaction was occurred.

In order to investigate the effect of substituent on the para position of phenyl group in radical ring opening and elimination polymerization, we have synthesized 2-(*p*-substituted phenyl)-4-methylene-1,3-dioxolane derivatives and polymerized them radically.

EXPERIMENTAL

Materials: Chlorobenzene and benzene were purified by consecutive washing with sulfuric acid, water, aqueous sodium hydroxide, and water, and dried over calcium chloride and distilled from calcium hydride. *p*-Substituted benzaldehyde derivatives and 3-chloro-1, 2-propanediol (Aldrich

Chemical Co.) were used without further purification. *t*-Butanol was purified by distillation from sodium. Dowex 50W (strong cation exchange resin) were used as acetalization catalyst.

Methods: NMR spectra were recorded with a T-60A Varian nuclear magnetic resonance spectrometer. The infrared spectra were obtained by a Perkin-Elmer Model 1310 spectrometer. Size exclusion chromatography was carried out with two columns (Waters μ -styrogel 10³ and 10⁴ Å), calibrated with polystyrene standards, chloroform as eluent at 254nm.

Representative Syntheses of 2-(*p*-substituted phenyl)-4-Chloromethyl-1,3-Dioxolane Derivatives (I_a-I_f)

A mixture of 13.1 g (0.10 mole) of *p*-cyanobenzaldehyde and 14.3 g (0.13 mole) of 3-chloro-1, 2-propanediol in 100 mL of toluene was heated at 80°C with 0.5 g of Dowex-50W(H⁺) resin in a 250mL flask equipped with Dean-Stark separator. After the calculated amount of water was collected by azeotropic distillation for 12h, the ion exchange resin was removed by filtration. The mixture was washed with water and the solvent was evaporated. The crude product was purified by vacuum distillation to obtain 17.8 g of I_f (80% yield, bp: 130°C / 0.1 torr).

Preparation of 2-(*p*-cyanophenyl)-4-Methylene-1, 3-Dioxolane

A solution of 22.3 g (0.10 mole) of I_f in 20 mL of *t*-butanol was added slowly to the mixture of 50mL of *t*-butanol and 5.0 g (0.13 mole) of potassium at 20°C under nitrogen atmosphere. After the addition was completed, the temperature was raised to 80°C and the gentle refluxing was maintained for 24h. The *t*-butanol was evaporated and 100mL of ethyl ether was added. The resulting precipitate was removed by filtration. The residue was vacuum distilled through a column to give 13.8 g of monomer II_f (73% yield, bp: 112°C / 0.1 torr.)

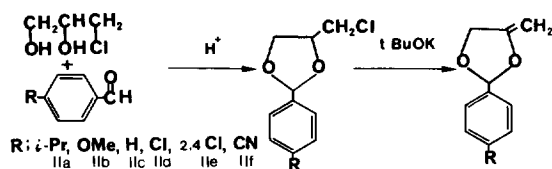
Representative Radical Polymerization of Monomers (II_a-II_f)

In a polymerization tube placed a solution of monomer II_f (0.5 g, 2.6 mmole) and DTBP (0.0114

g, 3 mole % of II_f) in 1.5 mL of chlorobenzene. The tube was then placed in oil bath and kept at 120°C for 72h. After the tube was opened, the polymer was purified by precipitation into petroleum ether. The polymer was further reprecipitated from dichloromethane into petroleum ether. White polymer was finally obtained. (0.19 g, 72 % yield)

RESULTS AND DISCUSSION

Synthesis: 2-(p-Substituted phenyl)-4-methylene-1, 3-dioxolane derivatives (II_a - II_f) were prepared by acetalization of p-substituted benzaldehyde with 3-chloro-1, 2-propanediol, followed by dehydrochlorination of chloromethyl derivative (I_a - I_f) with potassium t-butoxide. The data are collected in Table 1 and Table 2.



Monomers were quite stable in air on standing at room temperature and in moisture but polymerized even with sunlight within 5 days. This may involve reaction with double bond by radical, rather than oxygen bond by trace of cation.

Polymerization: Polymerization of monomers (II_a - II_f) were carried out various radical initiators such as 2, 2'-azobis-isobutyronitrile (AIBN), benzoyl-peroxide (BPO), di-t-butylperoxide (DTBP). The conditions and results of radical polymerization are summarized in Table 3.

In the case of polymerization with AIBN, the yield of polymer was very low for most monomers. The polymer obtained in Exp. No. 1 possess composition of 25 % ring intact, 50 % ring opening, and 25 % elimination units. When the monomer II_a was polymerized at 85°C over a period of 72h with 3 mole % BPO as initiator, the extent of elimination increased to 47 % in Exp. No. 2.

When the polymerization was carried out at 125°C using DTBP as the initiator, the white solid polymer was isolated after purification. The elimination reaction is more prevailing at higher temperature compared with AIBN and BPO. In the NMR spectra, all the polymers show three

Table 1. Preparation of 2-(p-Substituted phenyl)-4-chloromethyl-1, 3-dioxolane Derivatives

Compound (-R)	bp °C / 0.1torr	Yield (%)	NMR(CDCl ₃ , ppm)
-CH(CH ₂) ₃ I_a	112	85	7.3(m, 4H, aromatic), 5.75(d, 1H, benzylic) 4.6-4.2(m, 3H, -OCH ₂ , -CH-O-), 3.6(m, 2H, -CH ₂ Cl) 2.9(m, 1H, methine), 1.2(d, 6H, two methyl)
-OCH ₃ I_b	120	87	6.5-7.2(m, 4H, aromatic), 5.6(d, 1H, benzylic) 4.4-3.7(m, 3H, -OCH ₂ -CH-O-), 3.6(s, 3H, -OCH ₃) 3.1-3.5(m, 3H-OCH ₂ -CH-O-)
-H I_c	105	88	7.2(s, 5H, aromatic), 5.8(d, 1H, benzylic) 4.0-4.2(m, 3H, -OCH ₂ -CH-O-), 3.5(m, 2H, -CH ₂ Cl)
-Cl I_d	110	83	7.3(s, 4H, aromatic), 6.7-6.0(d, 1H, benzylic) 3.8-4.6(m, 3H, -OCH ₂ -CH-O-), 3.6(m, 2H, -CH ₂ Cl)
-Cl, 2-Cl I_e	124	79	7.7-7.0(m, 3H, aromatic), 6.0(d, 1H, benzylic) 3.8-4.6(m, 3H, -OCH ₂ -CH-O-), 3.3-3.8(m, 2H, -CH ₂ Cl)
-CN I_f	130	80	7.6(s, 4H, aromatic), 5.7-6.0(d, 1H, benzylic) 3.9-4.6(m, 3H, -OCH ₂ -CH-O-), 3.4-3.8(m, 2H, -CH ₂ Cl)

Table 2. Preparation of 2-(p-substituted phenyl)-4-Methylene-1, 3-Dioxolane Derivatives

Monomer (-R)	bp °C / 0.1 torr	Yield (%)	NMR(CDCl ₃ , ppm)	IR(cm ⁻¹) ^a
-CH(CH ₂) ₃ II _a	87	77	7.2(m, 4H, aromatic), 6.0(s, 1H, benzylic) 3.8-4.3(m, 2H, -C=CH ₂), 4.5(m, 2H, -O-CH ₂ -) 2.8(m, 1H, methine), 1.1(d, 6H, two methyl)	vinyl(C=C) 1675, ether(C-O) 1075
-OCH ₃ II _b	97	75	6.5-7.5(m, 4H, aromatic), 5.7(s, 1H, benzylic) 4.3(m, 2H, -O-CH ₂ -), 3.5-4.1(m, 2H, -C=CH ₂) 3.4(s, 3H, -OCH ₃)	vinyl(C=C) 1680, ether(C-O) 1080
-H II _c	77	76	7.3(s, 5H, aromatic), 6.0(s, 1H, benzylic) 4.5(m, 2H, -OCH ₂ -CH-O-), 3.8(m, 2H, -C=CH ₂)	vinyl(C=C) 1680, ether(C-O) 1065
-Cl II _d	80	73	7.25(s, 4H, aromatic), 5.93(s, 1H, benzylic) 4.4(m, 2H, -OCH ₂ -), 3.6-4.3(m, 2H, -C=CH ₂)	vinyl(C=C) 1685, ether(C-O) 1085, (C-Cl) 740(br)
-Cl, 2-Cl II _e	104	71	7.1-7.6(m, 3H, aromatic), 6.3(s, 1H, benzylic) 4.6(m, 2H, -O-CH ₂ -), 3.8-4.5(m, 2H, -C=CH ₂)	vinyl(C=C) 1680, ether(C-O) 1080, (C-Cl) 750(br)
-CN II _f	112	73	7.5(s, 4H, aromatic), 6.0(s, 1H, benzylic) 4.5(s, 2H, -OCH ₂ -), 3.8-4.5(m, 2H, -C=CH ₂)	vinyl(C=C) 1685, ether(C-O) 1080, (-CN) 2235(sp)

a br:broad, sp:sharp

Table 3. Conditions and Radical and Characteristics of Photopolymerization of 4-Methylene-1, 3-Dioxolane (II_a-II_f)

Exp. No.	Monomer ^a	Initiator (mole %)	Temp. (°C)	Yield ^b (%)	M _w ^c	Composition of Polymer in % ^d		
						RI	RO	E
1	II _a	AIBN, 3	65	22	—	25	50	25
2	II _a	BPO, 3	85	37	—	16	37	47
3	II _a	DTBP, 3	125	10 ^e	7200	4	21	75
				38				
4	II _a	hν	25	76	2100	0	100	0
5	II _b	DTBP, 3	125	13 ^e	6700	7	23	70
6	II _c	DTBP, 3	125	57	5200	20	57	23
7	II _c	hν	25	94	2400	0	100	0
8	II _d	DTBP, 3	125	78	4800	30	65	5
9	II _e	DTBP, 3	125	69	5100	20	75	5
10	II _e	hν	25	96	2700	0	100	0
11	II _f	DTBP, 3	125	72	7230	15	80	5

^aVolume of chlorobenzene in mL per g of monomer was 3 mL^bYields of powdery polymer were measured gravimetrically^cWeight-average molecular weight were determined by GPC(waters 10³ and 10⁴ Å) with polystyrene as standard.^dRI:ring intact, RO:ring opening, E:elimination. The values for RI, RO and E were determined by integration ratios of benzyl protons at 5.7 ppm and phenyl peak at 7.2 ppm. The degree of elimination was measured by the ratio of the increase of carbonyl peak at 2.7 ppm and decrease of phenyl peak at 7.2 ppm.^eYields of insoluble polymers.

modes of polymerization. The broad multiplet peak at 5.6~6.0 ppm indicates the presence of benzyl proton in the ring, which can be interpreted only by assuming that some of monomer undergo addition polymerization. On the other hand, benzyl proton of the polymer formed by ring opening exhibited multiplet peaks at 4.5~5.0 ppm in Fig. 1-a. It was noteworthy that the NMR peaks around 2.7ppm increase and other peaks involving phenyl peak around 7.2 ppm decrease. This fact

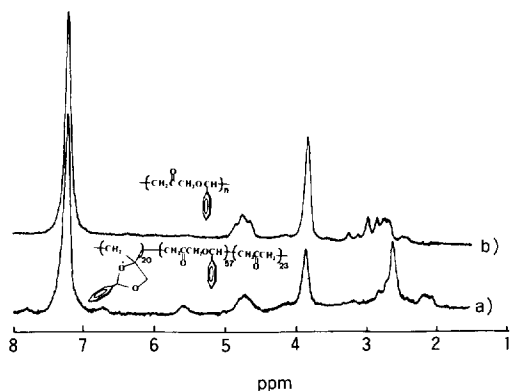


Fig. 1. Superimposed ^1H -NMR spectra of polymers obtained from (a) radical polymerization of II_c initiated by 3 mole % DTBP at 125°C , 1 g of II_c in 3 mL of chlorobenzene (b) photoinitiation of II_c with sunlight without sensitizer in neat at 25°C .

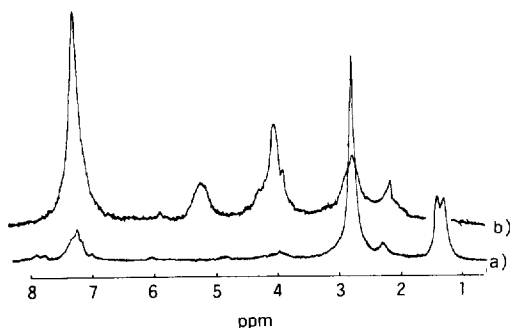
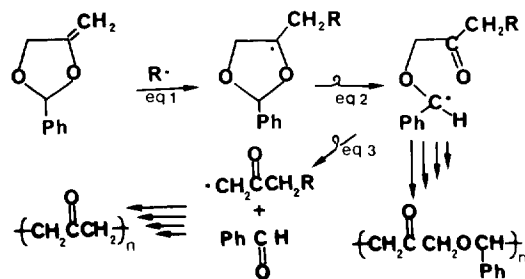


Fig. 2. Superimposed ^1H -NMR spectra of polymers obtained from radical polymerization of (a) 2-(p-isopropyl phenyl)-4-methylene-1,3-dioxolane (II_a) and (b) 2-(2,4-dichlorophenyl)-4-methylene-1,3-dioxolane (II_e) initiated by 3 mole % DTBP at 125°C , 1 g of monomer in 3 mL of chlorobenzene.



implies that the phenyl group is eliminated as benzaldehyde derivatives during polymerization in Figure 1-a and 2-a. From these results, the following mechanism is proposed.

The electron donating group such as isopropyl and methoxy of para position on the benzene ring enhanced the elimination than electron withdrawing group as shown in Table 3. In the case of monomers II_a and II_b , the amount of polymers with electron donating substituent were rather small than those of electron withdrawing monomers II_d , II_e and II_f , which ascribe to forming benzaldehyde derivatives as elimination product. Moreover these polymers partially consisted of insoluble polymer due to cross-linking of the carbonyl group formed by elimination. The low composition of elimination unit shown in Figure 2-b indicates that the electron withdrawing substituent stabilized the benzyl radical more effective than electron donating group. The elimination compound was benzaldehyde derivatives, but isolated as benzoic acids after oxidation in air on standing for 2 days. They were verified by NMR, IR and GC.

When the photopolymerization with sunlight without sensitizer was carried at room temperature for 72 h, the white solid polymer were obtained in good yield. As shown in Figure 3., the IR spectrum of the resulting polymer exhibits a strong absorption band at 1730cm^{-1} ascribed to the carbonyl group. In the NMR spectra, the absence of a peak at 5.6-6.0 ppm showed that 4-methylene-1,3-dioxolane derivatives had undergone almost quantitative ring opening without elimination as indicated in Figure 1-b.

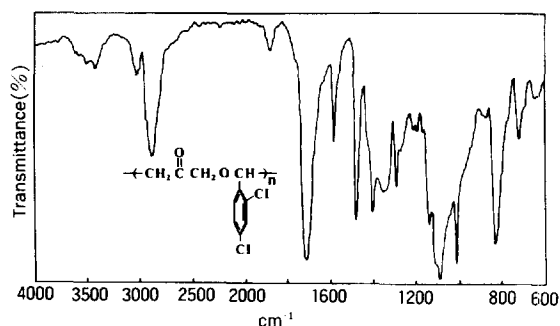


Fig. 3. Infrared spectrum of polymers obtained from photopolymerization of II_e with sunlight without sensitizer at room temperature.

The present studies were supported by the Basic Science Research Institute Program, Ministry of Education, 1988.

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