

Photochemical Transformation of Telomers III. Photolysis of Dimethyl (2*R**,4*R**)-2-Bromo-2,4-dimethyl- 4-(2,2,2-trichloroethyl)glutarate

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ABSTRACT: The photolysis of dimethyl (2*R**,4*R**)-2-bromo-2,4-dimethyl-4-(2,2,2-trichloroethyl)glutarate was examined and reaction paths for ten products are proposed. A homolytic cleavage of the carbon–bromine bond of the substrate occurred first forming a radical intermediate and subsequent reactions yielded the products *via* decomposition of the intermediate and recombination of secondly formed radical species. Ionic lactonization of the substrate and diastereoisomerization proceeded simultaneously.

KEY WORDS Photolysis / Telomer / Methyl Methacrylate Dimer / Homolytic Cleavage / Carbon–Bromine Bond / Recombination / Diastereoisomerization / Lactonization /

The photochemistry of organic halides is characterized by cleavage of the carbon–halogen bond.^{1,2} In recent studies on the solution photoreaction of aliphatic halides,^{3–5} workers have concentrated their attention on understanding whether the products are formed from a radical species or from an ionic one.

We previously reported the photolysis of methyl 2-bromo-4,4,4-trichloro-2-methylbutyrate (**1**)⁶ obtained from the telomerization of methyl methacrylate (MMA) using bromotrichloromethane (BTCM) as a telogen.⁷ In the preceding paper,⁸ we described the effects of copper powder on the photolysis of **1**. The results indicated that the conversion of the substrate and amount of products *via* a homolytic cleavage of the carbon–bromine bond increased with the amount of copper powder added. Since there have been a few studies on the photochemistry of aliphatic

halides containing different halogen atoms,^{9,10} we had interest in the photochemistry of telomers such as **1**.

meso- and *dl*-Dimers of MMA with a head-to-head linkage, formed by recombination of the tertiary carbon radicals produced by a homolytic cleavage of the carbon–bromine bond, are interesting. Rae *et al.* reported the synthesis and characterization of the *meso*- and *dl*-isomers of tetramethyl 2,4,5,7-tetramethyloctane-2,4,5,7-tetracarboxylate and thermal degradation of its *meso*-isomer as a model to study the effects of head-to-head linkage in thermal degradation of poly(MMA).^{11,12}

We report here the photolysis of the dimer, dimethyl (2*R**,4*R**)-2-bromo-2,4-dimethyl-4-(2,2,2-trichloroethyl)glutarate (**2a**), prepared by the telomerization of MMA with BTCM. The effects of irradiation time, temperature,

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and light source on the photolysis of **2a** are examined, and path of the reaction is discussed.

EXPERIMENTAL

Materials

Dimer **2a** was prepared by the telomerization of MMA with BTCM as described previously,⁷ and purified by recrystallization from hexane before use: mp 58–59.5°C, UV_{\max} (methanol) 214 nm (ϵ 501). Commercial methanol was stored over molecular sieves 3A and distilled before use. Other solvents were purified before use by the usual methods.

Measurements

Melting points were measured with a Yamato MP-21 melting point apparatus and were uncorrected. IR spectra were recorded on a JASCO IR Report-100 spectrophotometer. UV-vis spectra were obtained on a Shimadzu UV-180 spectrophotometer. ¹H NMR spectra were recorded on a Varian VXR-300 (300 MHz) spectrometer with chloroform-*d* as a solvent and tetramethylsilane as the internal standard. ¹³C NMR spectra were recorded on the same instrument (75 MHz) with chloroform-*d* as the solvent and internal standard (δ = 76.9). Mass spectra were taken with a Hitachi M-80 spectrometer with a direct inlet probe, using the chemical ionization method at a voltage of 20 eV.

Irradiation

Photoreaction was conducted by irradiating with the following light sources: a 100 W high-pressure mercury lamp in water-cooled Pyrex well surrounded by a reaction solution, 32 W low-pressure mercury lamp in air-cooled quartz well surrounded by the solution.

Photolysis of Dimer **2a**

A solution of 5 g of **2a** in 150 ml of methanol was kept at a given temperature with stirring by a magnet under a nitrogen atmosphere, and

irradiated by the desired light for a given time. After removal of the solvent by evaporation, the residue was washed with 10% brine and chromatographed on silica gel using benzene as an eluent to separate the starting material from the products. This isolation procedure was repeated as necessary for purification of the products.

Characterization of the Products

Dimethyl (2*R**,4*S**)-2-Bromo-2,4-dimethyl-4-(2,2,2-trichloroethyl)glutarate (**2b**),⁷ methyl α -(2,2,2-trichloroethyl)acrylate (**3**),⁶ dimethyl 2,4-dimethyl-4-(2,2,2-trichloroethyl)-2-pentenedioate (**4a**),⁷ and dimethyl 2-methyl-4-methylene-2-(2,2,2-trichloroethyl)glutarate (**4b**)⁷ were identified by comparison of their ¹H NMR spectra with those of authentic samples.

Dimethyl (2*R**,4*R**)-2,4-Dimethyl-2-(2,2,2-trichloroethyl)glutarate (**5**). Colorless viscous liquid; IR (neat) 1740 cm⁻¹ (C=O); ¹H NMR δ 1.19 (3H, d, J = 7.1 Hz, 4-C*Me), 1.43 (3H, s, 2-C*Me), 1.50 (1H, dd, J = 14.5, 7.5 Hz, 3-CH₂), 2.34 (1H, dd, J = 14.5, 9.2 Hz, 3-CH₂), 2.61 (1H, m, 4-C*H), 2.91 (1H, d, J = 15.3 Hz, Cl₃CCH₂), 3.58 (1H, d, J = 15.3 Hz, Cl₃CCH₂), 3.67 (3H, s, 5-CO₂Me), and 3.68 (3H, s, 1-CO₂Me); ¹³C NMR δ 19.9 (2-C*Me), 20.0 (4-C*Me), 35.0 (4-C*), 43.8 (3-CH₂), 46.2 (2-C*), 51.7 (1-CO₂Me), 52.1 (5-CO₂Me), 60.6 (Cl₃CCH₂), 96.8 (CCl₃), 175.1 (1-CO₂Me), and 176.6 (5-CO₂Me); MS m/z 323, 321, and 319 (M + H)⁺.

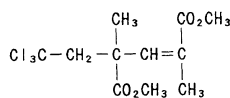
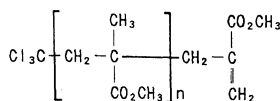
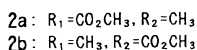
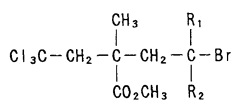
Dimethyl (2*R**,4*R**,5*S**,7*S**)-2,4,5,7-Tetramethyl-4,5-dimethoxycarbonyl-2,7-(2,2,2-trichloroethyl)octanedioate (**6a**). mp 204–206°C (dec.) (CCl₄); IR (KBr-disk) 1735 and 1710 cm⁻¹ (CO); ¹H NMR δ 1.05 (6H, s, 4,5-C*Me), 1.32 (6H, s, 2,7-C*Me), 2.20 (2H, d, J = 14.3 Hz, 3,6-CH₂), 2.32 (2H, d, J = 14.3 Hz, 3,6-CH₂), 2.90 (2H, d, J = 15.3 Hz, Cl₃CCH₂ × 2), 3.45 (2H, d, J = 15.3 Hz, Cl₃CCH₂ × 2), 3.68 (6H, s, 4,5-C*CO₂Me), and 3.68 (6H, s, 1,8-CO₂Me); ¹³C NMR δ 14.8 (4,5-C*Me), 17.6 (2,7-C*Me), 43.3 (3,6-CH₂), 46.2 (2,7-C*), 51.8 (4,5-C*), 52.0 (4,5-C*CO₂Me), 52.3

(1,8-CO₂Me), 64.3 (Cl₃CCH₂ × 2), 96.2 (CCl₃ × 2), 174.8 (4,5-C*CO₂Me), and 176.3 (1,8-CO₂Me); MS *m/z* 643, 641, 639, 637, and 635 (M + H)⁺. Found: C, 41.83%; H, 4.95%. Calcd for C₂₂H₃₂O₈Cl₆: C, 41.47%; H, 5.06%.

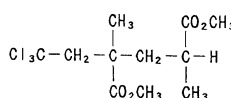
Dimethyl (2R,4R*,5R*,7R*)-2,4,5,7-Tetramethyl-4,5-dimethoxycarbonyl-2,7-(2,2,2-trichloroethyl)octanedioate (6b)*. mp 152–156°C (dec.) (CCl₄); IR (KBr-disk) 1730 and 1720 cm⁻¹ (CO); ¹H NMR δ 0.97 (6H, s, 4,5-C*Me), 1.32 (6H, s, 2,7-C*Me), 2.17 (2H, d, *J* = 13.9 Hz, 3,6-CH₂), 2.64 (2H, d, *J* = 13.9 Hz, 3,6-CH₂), 2.90 (2H, d, *J* = 15.3 Hz, Cl₃CCH₂ × 2), 3.51 (2H, d, *J* = 15.3 Hz, Cl₃CCH₂ × 2), 3.66 (6H, s, 4,5-C*CO₂Me), and 3.69 (6H, s,

1,8-CO₂Me); ¹³C NMR δ 15.1 (4,5-C*Me), 17.7 (2,7-C*Me), 42.4 (3,6-CH₂), 46.2 (2,7-C*), 51.0 (4,5-C*), 51.9 (1,8-C*CO₂Me), 52.2 (4,5-CO₂Me), 64.2 (Cl₃CCH₂ × 2), 96.3 (CCl₃ × 2), 174.4 (4,5-C*CO₂Me), and 176.1 (1,8-CO₂Me); MS *m/z* 643, 641, 639, 637, and 635 (M + H)⁺. Found: C, 41.53%; H, 4.93%. Calcd for C₂₂H₃₂O₈Cl₆: C, 41.47%; H, 5.06%.

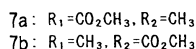
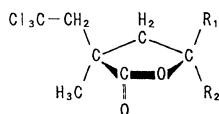
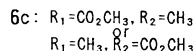
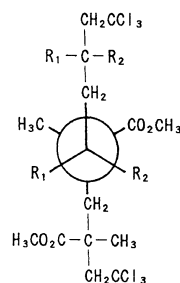
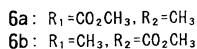
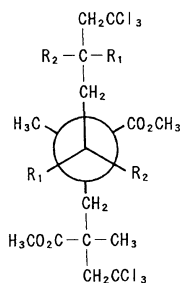
Dimethyl (2R,4R*,5S*,7R*)- or (2R*,4R*,5R*,7S*)-2,4,5,7-Tetramethyl-4,5-dimethoxycarbonyl-2,7-(2,2,2-trichloroethyl)octanedioate (6c)*. mp 175–178°C (dec.) (CCl₄); IR (KBr-disk) 1740 and 1730 cm⁻¹ (CO); ¹H NMR δ 0.94 (3H, s, 5-C*Me), 1.14 (3H, s, 4-C*Me), 1.32 (3H, s, 2-C*Me), 1.52 (3H, s,



4a



5



7-C*Me), 2.16 (1H, d, $J=13.9$ Hz, 6-CH₂), 2.27 (1H, d, $J=14.2$ Hz, 3-CH₂), 2.35 (1H, d, $J=14.2$ Hz, 3-CH₂), 2.79 (1H, d, $J=13.9$ Hz, 6-CH₂), 2.90 (1H, d, $J=15.3$ Hz, 2-C*CH₂CCl₃), 2.96 (1H, d, $J=15.3$ Hz, 7-C*CH₂CCl₃), 3.51 (1H, d, $J=15.3$ Hz, 2-C*CH₂CCl₃), 3.66 (1H, d, $J=15.3$ Hz, 7-C*CH₂CCl₃), 3.66 (3H, s, 1-CO₂Me), 3.67 (3H, s, 8-CO₂Me), 3.69 (3H, s, 5-C*CO₂Me), and 3.70 (3H, s, 4-C*CO₂Me); ¹³C NMR δ 14.9 (5-C*Me), 17.5 (4-C*Me), 17.6 (2-C*Me), 20.7 (7-C*Me), 42.5 (3-CH₂), 42.7 (6-CH₂), 46.2 (2,7-C*), 51.2 (4-C*), 51.8 (5-C*CO₂Me), 51.9 (5-C*), 52.0 (8-CO₂Me), 52.2 (4-C*CO₂Me, 1-CO₂Me), 61.2 (7-C*CH₂CCl₃), 64.2 (2-C*CH₂CCl₃), 96.3 (2-C*CH₂CCl₃), 96.8 (7-C*CH₂CCl₃), 173.6 (4-C*CO₂Me), 174.9 (5-C*CO₂Me), 175.2 (8-CO₂Me), and 176.1 (1-CO₂Me); MS m/z 643, 641, 639, 637, and 635 (M+H)⁺. Found: C, 41.41%; H, 4.91%. Calcd for C₂₂H₃₂O₈Cl₆: C, 41.47%; H, 5.06%.

(2*R**,4*S**)-(7a) and (2*R**,4*R**)-4-Methoxycarbonyl-2,4-dimethyl-2-(2,2,2-trichloroeth-

yl)-4-butanolide (7b) were identified by comparison of ¹H NMR spectra with those of authentic samples.⁷

Lactonization of Dimer 2a

A solution of 50 mg of 2a in 1.5 ml of a solvent was heated at 60°C for a given time in a sealed tube under irradiation-free. The yield of lactone was determined from ¹H NMR data of the reaction mixture.

RESULTS AND DISCUSSION

Photolysis Behavior of Dimer 2a

Table I shows the effects of irradiation time on the photolysis of 2a in methanol using the high-pressure mercury lamp. The irradiation light passed through a Pyrex glass. The UV spectrum of 2a shows that the light of wavelengths around 310 nm is effective. The substrate decreased with reaction time and almost disappeared after 72 h. The photoproducts 4a, 4b, 5, 6a, and 6b were comparable to those obtained in the photolysis of homologous

Table I. Effects of irradiation time on the photolysis of 2a^a

Time h	Conversion %	Product composition/% ^b										
		2b	3	4a	4b	5	6a	6b	6c	7a	7b	Others ^c
6	32	6	—	3	35	6	*	*	*	—	*	<50
24	79	6	—	3	19	—	4	*	*	11	7	<50
72	99	*	1	—	48	—	2	2	*	5	7	<35

^a Irradiated by a high-pressure mercury lamp in MeOH at 30°C.

^b *, trace.

^c Collected as mixed components adsorbed strongly on the column.

Table II. Effects of temperature on the photolysis of 2a (1)^a

Temp °C	Conversion %	Product composition/% ^b										
		2b	3	4a	4b	5	6a	6b	6c	7a	7b	Others ^b
0	37	11	—	5	57	5	5	5	5	—	—	7
30	79	6	—	3	19	—	4	*	*	11	7	<50
60	98	—	—	—	26	—	—	—	—	38	—	36

^a Irradiated by a high-pressure mercury lamp in MeOH for 24 h.

^b See Table I.

telomer **1** as reported previously.⁶ Terminal olefin **4b** was the main product. The formation of diastereoisomer **2b** was confirmed at the earlier stage of the photolysis of **2a**, whereas two lactones **7a** and **7b** were formed appreciably at a later stage. Terminal olefin **3** and diastereotetramer **6c** were isolated as noteworthy products.

Table II shows the effects of temperature on the photoirradiated reaction of **2a** in methanol

using the high-pressure mercury lamp. The rate of reaction and steric selectivity in products increased with temperature. In the reaction at 0°C, the formation of all products except **3**, **7a**, and **7b** was confirmed and that of unidentified products was suppressed. Diastereoisomer **2b** and terminal olefin **4b** formed notably. Terminal olefin **4b** and *cis* lactone **7a** formed predominantly in the reaction at 60°C. The effects of temperature on the photolysis of **2a**

Table III. Effects of temperature on the photolysis of **2a** (2)^a

Temp ^b °C	Conversion %	Product composition/% ^c										
		2b	3	4a	4b	5	6a	6b	6c	7a	7b	Others ^c
30	100	*	—	5	56	9	4	*	*	—	—	<26
60	100	—	—	3	29	11	4	*	*	9	—	<44

^a Irradiated by a low-pressure mercury lamp in MeOH.

^b Time, 5 h (30°C); 2 h (60°C).

^c See Table I.

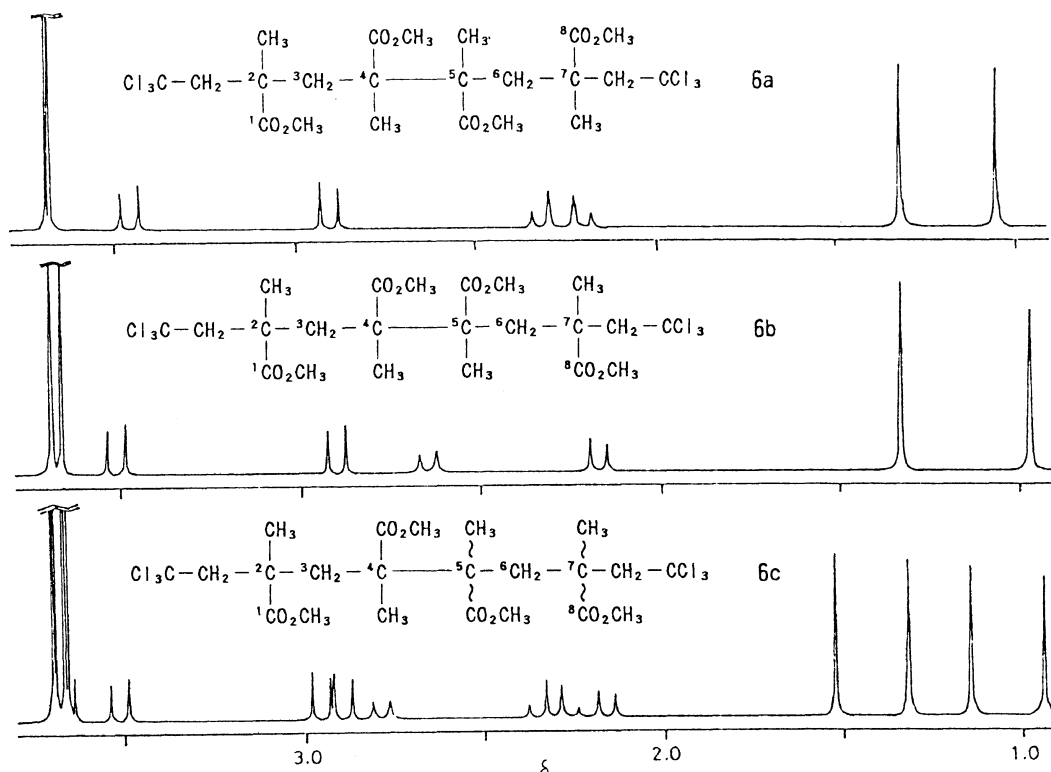


Figure 1. ¹H NMR spectra of the diastereotetramers.

using the low-pressure mercury lamp were also investigated. The results are summarized in Table III. The light of shorter wavelength almost completed the reaction within 5 h at 30°C and 2 h at 60°C, respectively. In the reaction at 30°C, the formation of terminal olefin **4b** predominated and lactones **7a** and **7b** were not detected.

Structures of the Diastereotetramers

Three diastereoisomers consisting of four MMA monomer units were isolated in the photoreaction. These diastereoisomers were endcapped with two trichloromethyl groups at both ends. The structures of the diastereotetramers were confirmed by IR, MS, NMR spectra, and elemental analysis data. Figure 1 shows the ^1H NMR spectra of the three diastereotetramers **6a**, **6b**, and **6c**. NMR signals for ^1H and ^{13}C were assigned on the basis of 2D-NMR: ^1H - ^1H and ^{13}C - ^1H (normal and long-range) COSY. Both ^1H and ^{13}C NMR spectrum of **6a** were similar to that of **6b** except for signals of 3,6-methylene protons. The isomeric structure of **6a** and **6b** was determined by comparing NMR spectra with those of the analogous diastereodimers, namely dimethyl ($2R^*,3S^*$)- and ($2R^*,3R^*$)-2,3-dimethyl-2,3-di(2,2,2-trichloroethyl)succinates, prepared by the photolysis of **1**.⁶ Because of differences in the magnetic environment around the 3,6-methylene groups, the geminal methylene protons of *meso*-form **6a** resonated as a close AB pattern of doublet-doublet ($\Delta\delta=0.12$), whereas those of *dl*-form **6b**, as a distant AB pattern of doublet-doublet ($\Delta\delta=0.47$). Judging from the NMR spectra shown in Figure 1, the tetramer **6c** seems to be a diastereoisomer consisting of either the $2R^*,4R^*,5S^*,7R^*$ - or $2R^*,4R^*,5R^*,7S^*$ -configuration.

Stability of Dimer **2a** in the Dark

As reported in the previous paper,¹³ heating of neat **2a** and **2b** in the absence of solvent results quantitatively in stereoselective lactonization (**2a**→**7a**; **2b**→**7b**) by a S_Ni cyclization.

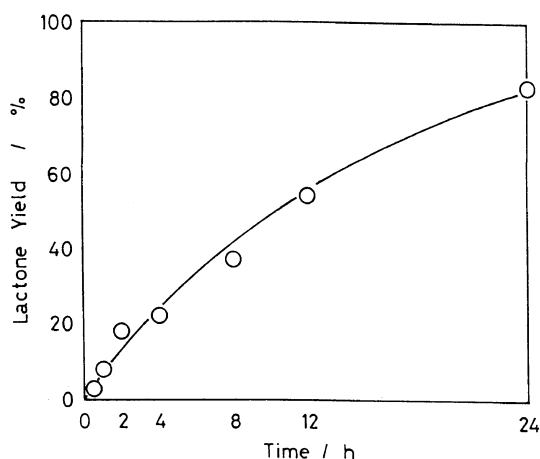


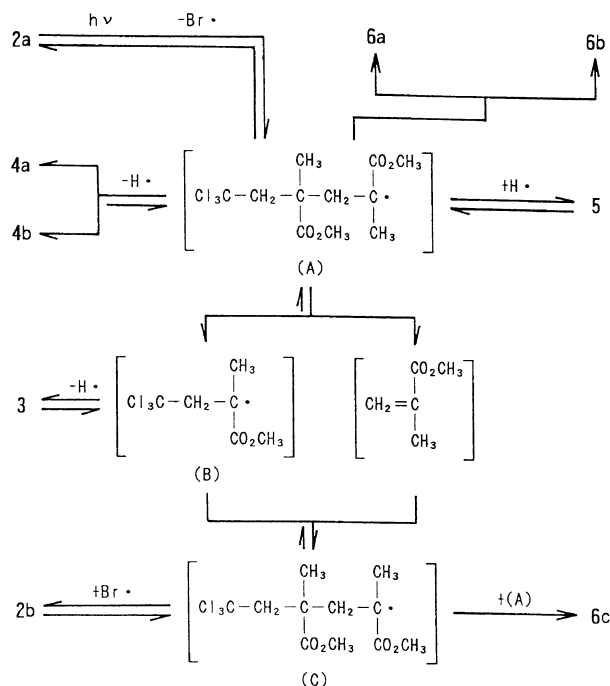
Figure 2. Time-conversion plots of the lactonization of **2a** in methanol at 60°C in the dark.

The thermal stability of **2a** in some solvents was examined in the dark. The conversion of **2a** into **7a** took place in an alkyl alcohol such as methyl, ethyl, 1-propyl, 2-propyl, or *t*-butyl alcohol at 60°C, and the lactone yield increased with decrease in the degree of branching of alkyl chains in the alcohols. The transformation of **2a** was difficult in benzene at 60°C. Although the lactonization of **2a** in methanol at 60°C proceeded as shown in Figure 2, the substrate was stable at 0°C.

Photolysis Pathway of Dimer **2a**

The photolysis of **2a** can be explained by the routes shown in Scheme 1. At the initial stage, the homolytic cleavage of carbon-bromine bond occurs preferentially. The resulting tertiary carbon radical (A) as a transient intermediate would lead to each product. When a hydrogen atom on the carbon atoms adjacent to the radical is released, the formation of two olefins and hydrogen bromide is possible. This radical elimination proceeds at variance with Saytzeff's rule, and the terminal olefin **4b** is produced in preference to the 1,2-disubstituted olefin **4a**. Another product is H-substituted compound **5**, which may be formed through hydrogen abstraction from the solvent. Products **4a** or **4b**, and **5** may also be formed

Photolysis of $\alpha,\alpha,\alpha,\omega$ -Tetrahalogenated MMA Dimer



Scheme 1. Photolysis pathway of **2a**.

through a disproportionation between two (A) radicals. A recombination of two (A) radicals leads to tetramers **6a** and **6b**. Although the photolysis of **2a**, as described above, is very similar to that of **1**; the dissociation of radical (A) into monomeric radical (B) and MMA monomer and their subsequent recombination occurs to form (A) or (C). The presence of radical (B) is evident by the formation of terminal olefin **3**. It seems that the diastereoisomer **2b** forms *via* the Br-abstraction by radical (C), and tetramer **6c** *via* the combination of radical (C) with radical (A). The ionic lactonization of **2a** and **2b** proceeds simultaneously in this photoprocess.

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