Reactivity of Telomers IV.[†] Catalytic Reaction of *t*-Butyl 2-Bromo-4,4,4-trichloro-2-methylbutyrate with Copper Powder

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(Received May 26, 1995)

ABSTRACT: Reactions of *t*-butyl 2-bromo-4,4,4-trichloro-2-methylbutyrate (**1**) in the presence of copper powder afforded predominantly four types of products *via* a homolytic cleavage of the carbon–bromine bond. The effects of the following factors on the conversion of the substrate and composition of products were studied: activity of copper powder, contact time, concentration of the substrate, temperature of reaction, kind of solvent, and amount of copper powder added. The catalytic reaction of **1** in methanol proceeded with the formation of copper(I) bromide, whereas that in an aprotic polar solvent was exclusively accompanied by the formation of copper(II) bromide.

KEY WORDS Catalytic Reaction / Telomer / Copper Powder / Homolytic
Cleavage / Condensing Agent / Solvent Effect / Disproportionation /
Dehalogenation / Recombination / Addition /

We reported the photolysis of telomers, the mono- and di-adducts, prepared by the radical telomerization of methyl methacrylate using bromotrichloromethane (BTCM) as a telogen.^{1,2} In the previous paper,³ we described the addition effects of copper powder on the photolysis of the monoadduct. 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. To our surprise, the reaction of the monoadduct with copper powder as a Br-scavenger without irradiation led to the formation of the same products in considerable amounts.

Although the reaction of organic halides using copper powder as a condensing agent is known as “the Ullmann reaction”, in general, the reaction is adapted for the aromatic halide,

but not for the aliphatic halide.⁴ This mild and simple reaction of telomers with copper powder appeals to us synthetically, and presents an attractive and novel fact.

In the present paper, we deal with the catalytic reaction of the monoadduct; *t*-butyl 2-bromo-4,4,4-trichloro-2-methylbutyrate (**1**), obtained from the radical telomerization of *t*-butyl methacrylate with BTCM, in the presence of copper powder. The addition effects of copper powder upon the reactivity of **1** were examined under various conditions, and path of the reaction is discussed comparing to that of the photolysis of **1**.

EXPERIMENTAL

General Methods

All melting points were measured with a

[†] Revised the title of this series; “Photochemical Transformation of Telomers”.

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Yamato MP-21 melting point apparatus and were uncorrected. IR spectra were obtained on a JASCO IR Report-100 spectrophotometer. ^1H NMR spectra were recorded on a Varian VXR-300 (300 MHz) spectrometer with chloroform-*d* as the solvent and tetramethylsilane as the internal standard. ^{13}C NMR spectra were recorded on the same instrument (75 MHz) with chloroform-*d* as the solvent and internal standard ($\delta = 76.9$). 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.

Materials

Telomer **1** was prepared according to the same method as described previously,⁵ and purified by distillation *in vacuo* before use: bp 98–99°C/2 Torr, ^1H NMR δ 1.51 (9H, s, *t*-Bu), 2.17 (3H, s, Me), 3.54 (1H, d, $J = 15.2$ Hz, CH_2), and 4.22 (1H, d, $J = 15.2$ Hz, CH_2); ^{13}C NMR δ 26.1 (Me), 27.3 ($\text{C}(\text{Me})_3$), 57.4 (C), 62.5 (CH_2), 82.9 ($\text{C}(\text{Me})_3$), 95.2 (CCl_3), and 168.4 (CO). Copper powder was prepared by the reduction of cupric sulfate with zinc powder immediately before use.⁶ Commercial methanol was stored over molecular 3A sieves and distilled before use. Commercial acetonitrile was dried over phosphorus pentoxide and distilled before use. Commercial benzene, carbon tetrachloride, *N,N*-dimethylformamide (DMF), pyridine, and dimethyl sulfoxide (DMSO) were dried over calcium hydride and distilled before use. Other reagents and solvents were commercially purchased and used without further purification.

Preparation of Copper Powder⁶

Under bubbling of nitrogen gas, zinc powder (2.6 g, 40 mmol) in limited amount was added to saturated aqueous solution of cupric sulfate pentahydrate (10.0 g, 40 mmol) in a large test tube (i.d. 27 mm $\times$ L. 200 mm). After reddish copper powder precipitated, the supernatant solution was decanted and the residual deposit was washed with dilute

hydrochloric acid solution, followed by washing with distilled water to neutralize. The supernatant solution was decanted and replaced three times with a water-soluble solvent for the catalytic reaction of **1**. The resulting copper powder was collected by filtration as required and immersed immediately in a nonaqueous solvent for reaction of **1**.

Typical Catalytic Reaction of **1** with Copper Powder

Telomer **1** (10.2 g, 30 mmol) was placed in a three-necked round bottom flask equipped with a magnetic stirrer. Freshly-activated copper powder (40 mmol) suspended with a solvent (150 ml) was added to the flask, and the mixture was vigorously stirred at a prescribed temperature for a given time under a nitrogen atmosphere. The resulting precipitate was collected by filtration and separated by a Soxhlet extractor with benzene into halide of copper and the products. After removal of the solvent from the filtrate, the residue was chromatographed on silica gel (Wakogel C-300) using 3:1-carbon tetrachloride and benzene as an eluent to separate the starting material from the products.

Photolysis of **1**

A solution of **1** (10.2 g, 30 mmol) in 150 ml of methanol was kept at 30°C with stirring under a nitrogen atmosphere, and irradiated by a 100 W high-pressure mercury lamp *via* a water-cooled Pyrex filter for 24 h. After removal of the solvent by evaporation, the residue was worked up conventionally.

Characterization of the Products

t-Butyl 2,4,4,4-Tetrachloro-2-methylbutyrate (**2**). Colorless liquid; bp 84–86°C/2 Torr; IR (neat) 1740 cm^{-1} (C=O); ^1H NMR δ 1.51 (9H, s, *t*-Bu), 1.98 (3H, s, Me), 3.43 (1H, d, $J = 15.3$ Hz, CH_2), and 4.01 (1H, d, $J = 15.3$ Hz, CH_2); ^{13}C NMR δ 25.7 ($\text{C}(\text{Me})_3$), 27.3 (Me), 61.9 (CH_2), 65.7 (C), 83.1 ($\text{C}(\text{Me})_3$), 94.8 (CCl_3), and 168.0 (CO).

A mixture of *t*-butyl α -(2,2,2-trichloroethyl)-acrylate (**3**) and *t*-butyl 4,4,4-trichloro-2-methylbutyrate (**4**) was obtained as a colorless liquid and not separated on the column. IR (neat) 1745, 1735 (C=O), and 1630 cm⁻¹ (C=C); ¹H NMR δ 1.30 (3H, d, J =7.3 Hz, Me of **4**), 1.46 (9H, s, *t*-Bu of **4**), 1.51 (9H, s, *t*-Bu of **3**), 2.58 (1H, dd, J =15.0, 2.7 Hz, CH₂ of **4**), 2.84 (1H, m, CH of **4**), 3.45 (1H, dd, J =15.0, 8.1 Hz, CH₂ of **4**), 3.73 (2H, d, J =*ca.* 1 Hz, CH₂ of **3**), 5.93 (1H, q, J =*ca.* 1 Hz, =CH₂ of **3**), and 6.46 (1H, d, J =*ca.* 1 Hz, =CH₂ of **3**).

α -(2,2,2-Trichloroethyl)acrylic acid (**3'**). Colorless flakes (from carbon tetrachloride); mp 117–118°C; IR (KBr-disk) 3400–2400 (carboxylic OH), 1680 (carboxylic C=O), and 1625 cm⁻¹ (C=C); ¹H NMR δ 3.78 (2H, d, J =*ca.* 0.8 Hz, CH₂), 6.20 (1H, q, J =*ca.* 0.8 Hz, =CH₂), 6.75 (1H, d, J =*ca.* 0.8 Hz, =CH₂), and 10.5 (1H, broad s, COOH); ¹³C NMR δ 53.3 (CH₂), 97.5 (CCl₃), 132.7 (C or =CH₂), 135.1 (=CH₂ or C), and 171.4 (CO); MS m/z 207, 205, and 203 (M+H)⁺.

Di-t-butyl (2*R**,3*S**)-2,3-Dimethyl-2,3-di(2,2,2-trichloroethyl)succinate (**5a**). Colorless columns (from hexane); mp 118–119.5°C (dec.); IR (KBr-disk) 1710 cm⁻¹ (C=O); ¹H NMR δ 1.41 (6H, s, Me $\times$ 2), 1.51 (18H, s, *t*-Bu $\times$ 2), 3.55 (2H, d, J =15.0 Hz, CH₂ $\times$ 2), and 3.74 (2H, d, J =15.0 Hz, CH₂ $\times$ 2); ¹³C

NMR δ 15.9 (Me $\times$ 2), 27.6 (C(Me)₃ $\times$ 2), 52.6 (C $\times$ 2), 55.0 (CH₂ $\times$ 2), 82.8 (C(Me)₃ $\times$ 2), 97.7 (CCl₃ $\times$ 2), and 171.3 (CO $\times$ 2); MS m/z 527, 525, 523, 521, and 519 (M+H)⁺. Found: C, 41.48%; H, 5.27%. Calcd for C₁₈H₂₈O₄Cl₆: C, 41.49%; H, 5.42%.

Di-t-butyl (2*R**,3*R**)-2,3-Dimethyl-2,3-di(2,2,2-trichloroethyl)succinate (**5b**). Colorless needles (from hexane); mp 182–183°C (dec.); IR (KBr-disk) 1710 cm⁻¹ (C=O); ¹H NMR δ 1.52 (6H + 18H, s, Me $\times$ 2, *t*-Bu $\times$ 2), 3.08 (2H, d, J =15.4 Hz, CH₂ $\times$ 2), and 3.88 (2H, d, J =15.4 Hz, CH₂ $\times$ 2); ¹³C NMR δ 16.0 (Me $\times$ 2), 27.7 (C(Me)₃ $\times$ 2), 53.0 (C $\times$ 2), 55.8 (CH₂ $\times$ 2), 82.7 (C(Me)₃ $\times$ 2), 97.6 (CCl₃ $\times$ 2), and 171.1 (CO $\times$ 2); MS m/z 527, 525, 523, 521, and 519 (M+H)⁺. Found: C, 40.91%; H, 5.18%. Calcd for C₁₈H₂₈O₄Cl₆: C, 41.49%; H, 5.42%.

Di-t-butyl (2*R**,4*S**)-2-methyl-2,4-di(2,2,2-trichloroethyl)glutarate (**6a**). Colorless columns (from hexane); mp 101.5–102.5°C; IR (KBr-disk) 1720 cm⁻¹ (C=O); ¹H NMR δ 1.46 (3H, s, Me), 1.49 (9H, s, *t*-Bu), 1.49 (9H, s, *t*-Bu), 1.82 (1H, dd, J =14.2, 3.7 Hz, 3-CH₂), 2.00 (1H, dd, J =14.2, 8.3 Hz, 3-CH₂), 2.72 (1H, dd, J =14.9, 2.8 Hz, 4-C*CH₂), 2.85 (1H, m, 4-C*H), 2.92 (1H, J =15.3 Hz, 2-C*CH₂), 3.25 (1H, dd, J =14.9, 8.6 Hz, 4-C*CH₂), and 3.53 (1H, J =15.3 Hz, 2-C*CH₂); ¹³C NMR δ 19.0 (Me), 27.7 (C(Me)₃), 27.8 (C(Me)₃), 40.7 (4-C*), 44.5 (3-C), 47.6 (2-C*), 58.3 (4-C*CH₂), 61.0 (2-C*CH₂), 81.8 (C(Me)₃ $\times$ 2), 96.9 (2-C*CH₂CCl₃), 97.7 (4-C*CH₂CCl₃), 173.6 (CO), and 173.8 (CO); MS m/z 527, 525, 523, 521, and 519 (M+H)⁺. Found: C, 41.44%; H, 5.34%. Calcd for C₁₈H₂₈O₄Cl₆: C, 41.49%; H, 5.42%.

Di-t-butyl (2*R**,4*R**)-2-methyl-2,4-di(2,2,2-trichloroethyl)glutarate (**6b**). Colorless columns (from hexane); mp 80–83.5°C; IR (KBr-disk) 1715 cm⁻¹ (C=O); ¹H NMR δ 1.48 (9H, s, *t*-Bu), 1.49 (3H, s, Me), 1.49 (9H, s, *t*-Bu), 1.73 (1H, dd, J =14.5, 5.0 Hz, 3-CH₂), 2.06 (1H, dd, J =14.5, 6.5 Hz, 3-CH₂), 2.75 (1H, dd, J =15.0, 2.5 Hz, 4-C*CH₂), 2.88 (1H,

$J = 15.3$ Hz, $2\text{-C}^*\text{CH}_2$), 2.90 (1H, m, $4\text{-C}^*\text{H}$), 3.30 (1H, $J = 15.0$, 8.6 Hz, $4\text{-C}^*\text{CH}_2$), and 3.66 (1H, $J = 15.3$ Hz, $2\text{-C}^*\text{CH}_2$); ^{13}C NMR δ 20.4 (Me), 27.7 ($\text{C}(\text{Me})_3$), 27.8 ($\text{C}(\text{Me})_3$), 40.4 (4-C^*), 44.2 (3-C), 47.6 (2-C^*), 57.9 ($4\text{-C}^*\text{CH}_2$), 59.5 ($2\text{-C}^*\text{CH}_2$), 81.7 ($\text{C}(\text{Me})_3$), 81.8 ($\text{C}(\text{Me})_3$), 97.1 ($2\text{-C}^*\text{CH}_2\text{CCl}_3$), 97.8 ($4\text{-C}^*\text{CH}_2\text{CCl}_3$), 173.4 (CO), and 173.7 (CO); MS m/z 527, 525, 523, 521, and 519 ($\text{M} + \text{H}$)⁺. Found: C, 41.42%; H, 5.29%. Calcd for $\text{C}_{18}\text{H}_{28}\text{O}_4\text{Cl}_6$: C, 41.49%; H, 5.42%.

(2*R**, 4*R**)-2-Methyl-4-*t*-butoxycarbonyl-2,4-di(2,2,2-trichloroethyl)-4-butanolide (**7a**). Colorless grains (from carbon tetrachloride); mp 174–176°C; IR (KBr-disk) 1780 and 1735 cm^{-1} (C=O); ^1H NMR δ 1.51 (9H, s, *t*-Bu), 1.59 (3H, s, Me), 2.32 (1H, d, $J = 14.9$ Hz, 3-CH₂), 3.20 (1H, d, $J = 15.6$ Hz, $2\text{-C}^*\text{CH}_2$), 3.25 (1H, d, $J = 14.9$ Hz, 3-CH₂), 3.32 (1H, d, $J = 15.6$ Hz, $2\text{-C}^*\text{CH}_2$), 3.33 (1H, d, $J = 15.5$ Hz, $4\text{-C}^*\text{CH}_2$), and 3.95 (1H, d, $J = 15.5$ Hz, $4\text{-C}^*\text{CH}_2$); ^{13}C NMR δ 26.0 (Me), 27.6 ($\text{C}(\text{Me})_3$), 42.6 (3-C), 43.8 (2-C^*), 59.1 ($4\text{-C}^*\text{CH}_2$), 59.2 ($2\text{-C}^*\text{CH}_2$), 80.5 (4-C^*), 84.3 ($\text{C}(\text{Me})_3$), 93.9 ($4\text{-C}^*\text{CH}_2\text{CCl}_3$), 95.9 ($2\text{-C}^*\text{CH}_2\text{CCl}_3$), 169.4 ($4\text{-C}^*\text{CO}$), and 177.9 (1-CO); MS m/z 469, 467, 465, 463, and 461 ($\text{M} + \text{H}$)⁺. Found: C, 36.08%; H, 3.83%. Calcd for $\text{C}_{14}\text{H}_{18}\text{O}_4\text{Cl}_6$: C, 36.32%; H, 3.92%.

(2*R**, 4*S**)-2-Methyl-4-*t*-butoxycarbonyl-2,4-di(2,2,2-trichloroethyl)-4-butanolide (**7b**). Colorless grains (from carbon tetrachloride); mp 128–129°C; IR (KBr-disk) 1775 and

1745 cm^{-1} (C=O); ^1H NMR δ 1.43 (3H, s, Me), 1.53 (9H, s, *t*-Bu), 2.64 (1H, d, $J = 14.0$ Hz, 3-CH₂), 3.16 (1H, d, $J = 15.6$ Hz, $2\text{-C}^*\text{CH}_2$), 3.17 (1H, d, $J = 14.0$ Hz, 3-CH₂), 3.33 (1H, d, $J = 15.4$ Hz, $4\text{-C}^*\text{CH}_2$), 3.41 (1H, d, $J = 15.6$ Hz, $2\text{-C}^*\text{CH}_2$), and 3.79 (1H, d, $J = 15.4$ Hz, $4\text{-C}^*\text{CH}_2$); ^{13}C NMR δ 25.4 (Me), 27.6 ($\text{C}(\text{Me})_3$), 43.0 (3-C), 43.3 (2-C^*), 59.9 ($2\text{-C}^*\text{CH}_2$), 60.6 ($4\text{-C}^*\text{CH}_2$), 81.2 (4-C^*), 84.4 ($\text{C}(\text{Me})_3$), 93.9 ($4\text{-C}^*\text{CH}_2\text{CCl}_3$), 96.0 ($2\text{-C}^*\text{CH}_2\text{CCl}_3$), 169.3 ($4\text{-C}^*\text{CO}$), and 177.9 (1-CO); MS m/z 469, 467, 465, 463, and 461 ($\text{M} + \text{H}$)⁺. Found: C, 36.82%; H, 3.91%. Calcd for $\text{C}_{14}\text{H}_{18}\text{O}_4\text{Cl}_6$: C, 36.32%; H, 3.92%.

RESULTS AND DISCUSSION

Catalytic Reaction of Telomer **1** with Copper Powder

Table I shows the effects of contact time with copper powder on the catalytic reaction of **1** in methanol at 30°C. Extension of the contact time accelerated the consumption of substrate. Though terminal olefin **3**, H-substituted compound **4**, symmetrical dimers **5a**, **5b**, and unsymmetrical dimers **6a**, **6b** were always obtained as major products with the formation of copper(I) bromide, the amounts of **6a**, **6b** increased, whereas that of **4** decreased with time. Fresh copper powder was superior to commercial powder in the conversion of **1** due to surface activity and available surface area of the copper powder. The high concentration

Table I. Catalytic reactions of **1** with Cu powder (1)^a

Time	Conversion	Product composition/%						
h	%	3	4	5a	5b	6a	6b	Others ^b
24	18 ^c	27	39	11	10	2	3	8
	51	24	35	10	12	4	8	7
	98 ^d	21	25	10	8	2	3	31
48	89	25	27	10	10	9	12	7
	97 ^c	18	29	12	8	12	10	11

^a Stirred in MeOH (150 ml) at 30°C: **1**, 30 mmol; Cu, 40 mmol. ^b Collected as mixed components adsorbed strongly on the column. ^c Used commercial Cu powder. ^d Stirred at 60°C. ^e **1**, 90 mmol; Cu, 120 mmol.

of the substrate contributed to increase in the conversion of **1**.

The effects of temperature on the catalytic reaction of **1** in methanol for 24 h are shown in Table I. The elevation of temperature enhanced the consumption of substrate and formation of unidentified other products collected as mixed components adsorbed strongly on the silica gel column.

Table II shows the effects of solvent on the catalytic reaction of **1** at 30°C for 24 h. In spite of the enhancement of the conversion of **1**, the catalytic reaction in acetonitrile was inferior in yields of the major products to methanol. The reactivity of **1** was very poor in a nonpolar solvent such as benzene or carbon tetrachloride. The reaction of **1** in an aprotic polar solvent, such as pyridine, DMF, or DMSO, proceeded rapidly with change from reddish suspension to greenish solution and was approximately complete within 1 h. However, the formation of symmetrical dimers **5a**, **5b** was unexpectedly suppressed and the preferential formation of oligomer part corresponding to others was confirmed by gel-permeation chromatography (GPC). The catalytic reaction of **1** in pyridine gave noteworthy Cl-substituted compound **2**, which was produced

appreciably at -30°C.

The effects of additive amounts of copper powder are shown in Table II. High conversion of substrate (30 mmol) on the catalytic reaction of **1** in DMF at 30°C for 1 h was maintained in spite of the decrease in added amounts from 40 mmol to 20 mmol. However, the formation of oligomer part corresponding to others was suppressed, whereas identified products were predominantly obtained. The catalytic reaction of **1** in an aprotic polar solvent proceeded with the formation of copper(II) bromide, and the formation of other products *via* a homolytic cleavage of the carbon-chlorine bond seemed to be induced by excessive copper powder. This anticipation was supported by the following experimental finding: Though **3** and **4** have no carbon-bromine bonds, the catalytic reaction of a mixture of them (**3**:**4**=31:69, 30 mmol) with copper powder (40 mmol) in DMF at 30°C for 24 h showed a 73% conversion yield with the formation of copper chlorides. Formation of the unidentified oligomer similar to that obtained in the reaction of **1** was confirmed by GPC.

Structural Analysis of the Products

The identified products were monomeric and

Table II. Catalytic reactions of **1** with Cu powder (2)^a

Solvent	Convsn. %	Product composition/% ^b							
		2	3	4	5a	5b	6a	6b	Others ^c
MeOH	51	—	24	35	10	12	4	8	7
MeCN	58	—	17	17	9	10	—	—	47
PhH	2	—	—	—	—	—	—	—	*
CCl ₄	1	—	—	—	—	—	—	—	*
C ₃ H ₅ N	36 ^d	28	8	17	3	3	—	—	41
	79 ^e	35	8	18	1	1	*	*	37
	98 ^f	12	7	13	2	2	*	*	64
DMF ^h	83 ^{f,g}	—	30	27	7	7	4	5	20
	100 ^f	—	23	21	*	*	2	3	51
DMSO ⁱ	100 ^f	—	3	*	*	1	3	5	88

^a Stirred at 30°C for 24 h: **1**, 30 mmol; Cu, 40 mmol; solvent, 150 ml. ^b *, trace. ^c See Table I. ^d Stirred at -30°C for 1 h.

^e Stirred at -30° for 24 h. ^f Reaction time, 1 h. ^g Cu, 20 mmol. ^h DMF, *N,N*-dimethylformamide. ⁱ DMSO, dimethyl sulfoxide.

dimeric components. Their structures were confirmed by IR, MS, FT-NMR spectra, and elemental analysis data. The Cl-substituted product **2** resembled substrate **1** closely in

chemical and spectroscopic properties, but the quaternary carbon signal of **2** in the ^{13}C NMR spectrum resonated in a lower magnetic field than that of **1** on account of the "heavy

Figure 1. ^1H NMR spectra of the two diastereodimers.

halogen" effect; $\delta=65.7$ (**2**) and 57.4 (**1**). Though the attempted separation of a mixture of **3** and **4** by chromatography and fractional distillation was unsuccessful, they were easily distinguished by ^1H NMR spectroscopy. Figure 1 shows the ^1H NMR spectra of the two symmetrical **5a**, **5b** and the two unsymmetrical diastereodimers **6a**, **6b**. 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 spectra of **5a** were similar to that of **5b** except for signals of the methylene protons. The isomeric structures of **5a** and **5b** were determined by comparing NMR spectra with those of the analogous diastereoisomers, namely dimethyl ($2R^*,3S^*$) and ($2R^*,3R^*$)-2,3-dimethyl-2,3-di(2,2,2-trichloroethyl)succinates, prepared by the photolysis of methyl 2-bromo-4,4,4-trichloro-2-methylbutyrate.¹ Because of differences in the magnetic environment around the methylene group, the geminal methylene protons of *meso*-form **5a** resonated as a AB pattern of doublet-doublet ($\Delta\delta=0.19$), whereas those of *dl*-form **5b**, as a AX pattern of doublet-doublet ($\Delta\delta=0.79$). Both ^1H and ^{13}C NMR spectra of **6a** were similar to that of **6b** except for signals of three couples of methylene protons. The isomeric structure of **6a** and **6b** was determined by comparing NMR spectra with those of the analogous diastereoisomers, namely dimethyl ($2R^*,4S^*$)- and ($2R^*,4R^*$)-2-methyl-2,4-di(2,2,2-trichloroethyl)glutarates, prepared by the photolysis of methyl 2-bromo-4,4,4-tri-

chloro-2-methylbutyrate.^{1,3} Because of differences in the magnetic environment around the central methylene group (d), the geminal methylene protons of **6a** resonated as a ABX pattern of double doublet-double doublet ($\Delta\delta=0.18$), whereas those of **6b**, as a ABX pattern of double doublet-double doublet ($\Delta\delta=0.33$).

Comparison of Catalytic Reactions with the Photolysis of **1**

For this comparison, the reaction of **1** with photoirradiation was examined under stirring in methanol at 30°C for 24 h. In spite of slight increase in the consumption of substrate, the photolysis of **1** was inferior in yields of compounds **3**–**6** to this reaction as shown in Table III. The photolysis of **1** proceeded complicately to afford large amounts of unidentified other products. Carboxylic acid **3'** and two lactones **7a**, **7b** were isolated as noteworthy products and unsymmetrical dimers **6a**, **6b** were not detected. In our previous study,¹ dimethyl ($2R^*,4S^*$)- and ($2R^*,4R^*$)-2-bromo-4-methyl-2,4-di(2,2,2-trichloroethyl)glutarates, prepared by the photolysis of methyl 2-bromo-4,4,4-trichloro-2-methylbutyrate, underwent thermal cyclization to produce homologous lactones. The isomeric structures of **7a** and **7b** were determined by comparing NMR spectra with those of the analogous lactones, ($2R^*,4R^*$)- and ($2R^*,4S^*$)-2-methyl-4-methoxycarbonyl-2,4-di(2,2,2-trichloroethyl)-4-butanolides.

Table III. Comparison of catalytic reaction with photoreaction of **1**^a

Type of reaction	Convsn.	Product composition/%									
	%	3	3'	4	5a	5b	6a	6b	7a	7b	Others ^b
Cu powder	51	24	—	35	10	12	4	8	—	—	7
Photo irradiation	58	17	7	5	2	3	—	—	2	2	62 ^c

^a Stirred in MeOH at 30°C for 24 h. ^b See Table I. ^c A mixture of carboxylic acids from **4**, **5a**, and **5b** was present at a ratio of ca. 40 wt%.

Reaction Pathway of Telomer **1** with Copper Powder

The reaction of **1** in the presence of copper powder can be explained by the routes in Scheme 1. At the initial stage, homolytic cleavage of carbon-bromine bond occurs preferentially. The formation of copper(I) bromide predominated in methanol, whereas that of copper(II) bromide prevails in an aprotic polar solvent. The resulting bromides were identified by comparing solubility in such solvents as water, aqueous ammonia, and acetone with an authentic sample. The resulting tertiary carbon radical (A) as a transient intermediate would lead to each product.

Scheme 1. Initial course of the reactions of **1** with Cu powder.

Products **3** and **4** may be formed through disproportionation between two (A) radicals. When a hydrogen atom on the carbon atoms adjacent to the radical is released, the formation of two olefins is possible. This radical elimination proceeds at variance with Saytzeff's law, and the terminal olefin **3** is produced without forming 1,2-disubstituted olefin. Two types of dimerization occur *via* the monomeric intermediate (A); recombination of two (A) radicals and addition of (A) to the initial product **3**. The coupling reaction leads to two diastereoisomers **5a** and **5b** combined in a head-to-head orientation, while the addition reaction results in two diastereoisomers **6a** and **6b** combined in a head-to-tail orientation. It seems that diastereoisomers **6a** and **6b** form *via* the H-abstraction from the solvent or the monomeric intermediate (A) by dimeric intermediate (B). Further research on the formation path of **2** is still underway.

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