

Photochemical Transformation of Telomers I. Photolysis of Methyl 2-Bromo-4,4,4-trichloro-2-methylbutyrate

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ABSTRACT: The photochemical reaction of methyl 2-bromo-4,4,4-trichloro-2-methylbutyrate (**1**) was studied aiming at its chemical modification. The effects of irradiation time, temperature, and solvent polarity on the photolysis of **1** were investigated. The formation of ten photoproducts was confirmed, and the route of photolysis is proposed. Homolytic cleavage of the carbon-bromine bond occurred predominantly to induce different types of photoprocesses, such as disproportionation, elimination, hydrogen abstraction, recombination, and addition. The elimination reaction proceeded contrary to Saytzeff's law, and the debromine-coupling and addition reactions gave some novel dimeric telomers.

KEY WORDS Photochemical Transformation / Methyl 2-Bromo-4,4,4-trichloro-2-methylbutyrate / Photolysis / Cleavage of Carbon-Bromine Bond / Photodimerization / Head-to-Head Orientation / Diastereoisomer / Lactonization /

The photochemistry of halides has been extensively studied,^{1,2} but there have been reported few studies on the photochemical reactions of aliphatic compounds containing plural diverse halogens.³

In the previous papers,^{4,5} we reported the radical telomerization of a series of alkyl methacrylates using bromotrichloromethane (BTCM) as a telogen and the characteristics of the resulting telomers up to trimers. The resulting telomers can be utilized as "reactive oligomers" by chemical modification of their functional groups. For example, the pyrolysis and hydrolysis of the corresponding dimeric telomers easily gave γ -lactones, which are useful as unique polycondensing oligomers by carboxylation of their residual functional groups.⁶

The object of this work was to elucidate the photolysis behavior of methyl methacrylate (MMA) monomer telomerized with BTCM, that is, methyl 2-bromo-4,4,4-trichloro-2-

methylbutyrate (**1**), and to find valuable oligomers in the field of polymer science. The effects of irradiation time, temperature, and solvent polarity on the photolysis of **1** are discussed, and the route of the photolysis is considered on the basis of the structural analysis of the photoproducts.

EXPERIMENTAL

Measurements

Melting points were measured with a Yamato MP-21 melting point apparatus. Boiling points were determined during distillation. UV spectra were recorded with a Shimadzu UV-180 spectrophotometer. IR spectra were measured on a KBr plate or in KBr disks with a Hitachi 295 spectrophotometer. ¹H NMR spectra were determined with a JEOL JNM-C-60HL spectrometer (60 MHz) using Me₄Si as an internal standard. Mass spectra were taken on a Hitachi M-80 spectrom-

eter using a chemical ionization method at 20 eV of ionization energy. All isotope peaks resulting from bromine and chlorine atoms were satisfactorily detected in the mass spectra. The isotope peaks corresponding only to ^{79}Br and ^{35}Cl are treated in this paper. The determination of organic halogen was carried out by semimicro higher alcohol-metallic sodium method.⁷

Materials

Telomer **1** was prepared by the telomerization of MMA with BTCM as described in the previous paper,⁴ and purified by distillation under reduced pressure before use: a colorless liquid; bp 86.0–88.5°C (600 Pa), UV_{max} (methanol) 208 nm (ϵ 578). Commercial methanol and propanols were stored over molecular sieves 3A and distilled before use. Commercial benzene and tetrahydrofuran (THF) were dried over calcium hydride and distilled before use.

Photolysis of **1**

A prescribed solution of **1** (10 g in 150 ml) was placed in a Riko UVL-100H-100P photochemical reaction apparatus. The mixture was heated at a given temperature with stirring under a nitrogen atmosphere, and irradiated by light from a 100W high pressure immersion mercury lamp placed the Pyrex vessel for a given time. After evaporation of the reaction solvent, the residue was washed with 10% sodium chloride solution to remove the resulting hydrogen bromide, and developed on column chromatography of silica gel (Wakogel C-300) with a mixture of benzene and carbon tetrachloride (1 : 2, vol/vol) to isolate the starting material and the photoproducts. The eluting order was as follows: unreacted telomer **1** > internally unsaturated telomer **2a** > terminally unsaturated telomer **2b** \geq hydrogenated telomer **3** \geq meso-dimeric telomer **4a** > dl-dimeric telomer **4b** > syndiotactic dimeric telomer **5a** \geq isotactic dimeric telomer **5b** > other photoproducts. The overlapping fractions

were determined on the basis of ^1H NMR data.

Thermal Lactonization of **5**

The dimeric telomers **5** were heated in the absence of solvent. The resulting lactones **7a** and **7b** were separated by column chromatography of silica gel (Wakogel C-300) with benzene as the eluent.

Characterization of the Photoproducts

Methyl β -(Trichloromethyl) methacrylate (2a). Colorless liquid; bp 65–67°C (130 Pa). This product was identical to an authentic sample.⁴

Methyl α -(2,2,2-Trichloroethyl) acrylate (2b). Colorless liquid; bp 96–97°C (800 Pa); IR (neat) 1735 (C=O) and 1630 cm^{-1} (C=C); ^1H NMR (CCl_4) δ 3.76 (2H, s, CH_2CCl_3), 3.80 (3H, s, CO_2CH_3), 6.03 (1H, m, = CH_2), and 6.53 ppm (1H, m, = CH_2); MS m/z (rel intensity) 217 (QM^+ , 48), 181 (100), and 153 (80).

Methyl 4,4,4-Trichloro-2-methylbutyrate (3). Colorless liquid (not distilled); IR (neat) 1745 cm^{-1} (C=O); ^1H NMR (CCl_4) δ 1.33 (3H, d, $J=7.2$ Hz, CH_3), 2.40–3.57 (3H, m, $\text{CHCH}_2\text{CCl}_3$), and 3.67 ppm (3H, s, CO_2CH_3); MS m/z (rel intensity) 218 (M^+ , 55), 181 (100), and 153 (87).

Dimethyl (2RS,3SR)-2,3-Dimethyl-2,3-di-(2,2,2-trichloroethyl)succinate (4a). Colorless prisms (from carbon tetrachloride); mp 102–103.5°C; IR (KBr) 1735 cm^{-1} (C=O); ^1H NMR (CCl_4) δ 1.36 (6H, s, CH_3), 3.56 (4H, s, CH_2CCl_3), and 3.73 ppm (6H, s, CO_2CH_3); MS m/z (rel intensity) 435 (QM^+ , 1), 403 (9), 399 (4), 367 (4), 363 (2), 339 (5), 218 (46), 181 (79), and 153 (100); Found: Cl, 48.82%. Calcd for $\text{C}_{12}\text{H}_{16}\text{O}_4\text{Cl}_6$: Cl, 48.68%.

Dimethyl (2RS,3RS)-2,3-Dimethyl-2,3-di-(2,2,2-trichloroethyl)succinate (4b). Colorless grains (from carbon tetrachloride); mp 120–121°C; IR (KBr) 1730 cm^{-1} (C=O); ^1H NMR (CCl_4) δ 1.49 (6H, s, CH_3), 2.90 (2H, d, $J=15.0$ Hz, CH_2CCl_3), 3.70 (6H, s, CO_2CH_3), and

3.82 ppm (2H, d, $J=15.0$ Hz, CH₂CCl₃); MS m/z (rel intensity) 435 (QM⁺, 7), 403 (56), 399 (17), 367 (26), 363 (9), 339 (27), 218 (76), 181 (66), and 153 (100); Found: Cl, 48.50%. Calcd for C₁₂H₁₆O₄Cl₆: Cl, 48.68%.

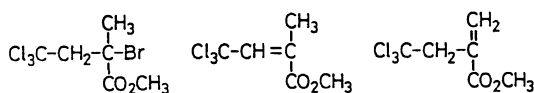
Dimethyl (2RS,4SR)-2-Bromo-4-methyl-2,4-di(2,2,2-trichloroethyl)glutarate (5a). Colorless needles (from carbon tetrachloride); mp 112.5–114°C; IR (KBr) 1755 and 1745 cm⁻¹ (C=O); ¹H NMR (CCl₄) δ 1.52 (3H, s, CH₃), 2.87 (2H, s, 2-C*CH₂4-C*), 2.95 (2H, d, $J=15.0$ Hz, CH₂CCl₃), 3.41 (2H, d, $J=15.0$ Hz, CH₂CCl₃), 3.71 (3H, s, 4-C*CO₂CH₃), and 3.83 ppm (3H, s, 2-C*CO₂CH₃); MS m/z (rel intensity) 513 (QM⁺, 0.1), 481 (7), 477 (1), 453 (13), 433 (100), 401 (32), 373 (27), 337 (45), and 181 (63); Found: Br+Cl, 56.24%. Calcd for C₁₂H₁₅O₄BrCl₆: Br+Cl, 56.72%.

Dimethyl (2RS,4SR)-2-methyl-2,4-di(2,2,2-trichloroethyl)glutarate (6). Colorless columns (from hexane); mp 84–85.5°C; IR (KBr) 1750 and 1740 cm⁻¹ (C=O); ¹H NMR (CCl₄) δ 1.43 (3H, s, CH₃), 2.00 (2H, d, $J=5.4$ Hz, 2-C*CH₂4-C*), 2.50–3.41 (3H, m, 4-C*HCH₂CCl₃), 2.90 (1H, d, $J=15.6$ Hz, 2-

C*CH₂CCl₃), 3.49 (1H, d, $J=15.6$ Hz, 2-C*CH₂CCl₃), and 3.70 ppm (6H, s, CO₂CH₃); MS m/z (rel intensity) 434 (M⁺, 0.1), 403 (7), 375 (10), 339 (18), and 101 (100); Found: Cl, 48.43%. Calcd for C₁₂H₁₆O₄Cl₆: Cl, 48.68%.

(2RS,4RS)-2-Methyl-4-methoxycarbonyl-2,4-di(2,2,2-trichloroethyl)-4-butanolide (7a). Colorless needles (from benzene); mp 146–147.5°C; IR (KBr) 1790 and 1745 cm⁻¹ (C=O); ¹H NMR (CDCl₃) δ 1.62 (3H, s, CH₃), 2.41 (1H, d, $J=15.0$ Hz, 2-C*CH₂CCl₃), 3.27 (2H, s, 2-C*CH₂4-C*), 3.33 (1H, d, $J=15.0$ Hz, 2-C*CH₂CCl₃), 3.29 (1H, d, $J=15.6$ Hz, 4-C*CH₂CCl₃), 3.89 (3H, s, CO₂CH₃), and 3.96 ppm (1H, d, $J=15.6$ Hz, 4-C*CH₂CCl₃); MS m/z (rel intensity) 419 (QM⁺, 0.2), 383 (2), 359 (29), 295 (18), 257 (6), and 159 (100); Found: Cl, 50.26%. Calcd for C₁₁H₁₂O₄Cl₆: Cl, 50.54%.

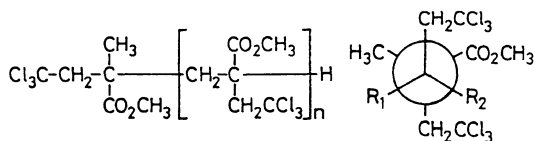
(2RS,4SR)-2-Methyl-4-methoxycarbonyl-2,4-di(2,2,2-trichloroethyl)-4-butanolide (7b). Colorless needles (from carbon tetrachloride); mp 126–127.5°C; IR (KBr) 1790 and 1765 cm⁻¹ (C=O); ¹H NMR (CDCl₃) δ 1.37 (3H, s, CH₃), 2.79 (1H, d, $J=15.0$ Hz, 2-C*CH₂CCl₃), 3.13 (1H, d, $J=15.6$ Hz, 2-C*CH₂4-C*), 3.20



1

2a

2b

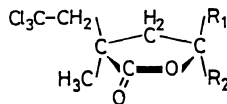
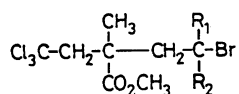


3: $n=0$

6: $n=1$

4a: R₁ = CO₂CH₃, R₂ = CH₃

4b: R₁ = CH₃, R₂ = CO₂CH₃



5a: R₁ = CO₂CH₃, R₂ = CH₂CCl₃

5b: R₁ = CH₂CCl₃, R₂ = CO₂CH₃

7a: R₁ = CO₂CH₃, R₂ = CH₂CCl₃

7b: R₁ = CH₂CCl₃, R₂ = CO₂CH₃

(1H, d, $J=15.0$ Hz, 2-C*CH₂CCl₃), 3.35 (1H, d, $J=15.6$ Hz, 4-C*CH₂CCl₃), 3.50 (1H, d, $J=15.6$ Hz, 2-C*CH₂4-C*), 3.79 (1H, d, $J=15.6$ Hz, 4-C*CH₂CCl₃), and 3.90 ppm (3H, s, CO₂CH₃); MS m/z (rel intensity) 419 (QM⁺, 0.2), 383 (1), 359 (31), 295 (18), 257 (6), and 159 (100); Found: Cl, 50.30%. Calcd for C₁₁H₁₂O₄Cl₆: Cl, 50.54%.

RESULTS AND DISCUSSION

Photolysis Behavior of Methyl 2-Bromo-4,4,4-trichloro-2-methylbutyrate (1)

Table I shows the effect of irradiation time on the photolysis of **1** in methanol at 30°C. The conversion yield of **1** and the production yields of all photoproducts increased gradually with irradiation time. The dimeric photoproducts **5a** and **5b** combined in a head-to-tail orientation may be particularly difficult with respect to their formation at an early stage in the photoreaction. Table II shows the effect of temperature on the photolysis of **1** in primary alcohols for 24 h. The conversion yield of **1**

increased linearly with increasing photoreaction temperature, and all of the photoproducts, except **5a** and **5b**, increased roughly in proportion to the product yield. The head-to-tail telomers **5a** and **5b** tended to be transformed into other photoproducts under heating. Table III shows the effect of solvent polarity on the photolysis of **1** at 30°C for 24 h. This irradiation light is passed through a Pyrex glass, and the UV spectra of **1** suggests that the effective wavelength is mainly 313 nm. However, as shown in Table III, the molar absorptivity (ϵ) of the solvent at 313 nm has no positive correlation with the conversion yield. In spite of the enhancement of the conversion yield, the photolysis of **1** in 2-propanol was similar in the distribution of photoproducts to that in methanol. On the other hand, the photoreactivity of **1** was very poor in benzene, and the photodimerization was not observed. On the contrary, though THF itself underwent photodeterioration, the photolysis of **1** in THF was rapid and gave appreciably the photodimeric products **4a** and **4b** combined in a

Table I. Effect of irradiation time on the photolysis of **1**^a

Time h	Conversion %	Product yield/%							
		2a	2b	3	4a	4b	5a	5b	Others
6	13	Trace	5	3	2	2	—	—	—
24	44	1	14	5	4	5	2	1	12
48	62	2	19	8	6	7	4	3	13
72	79	3	24	9	7	8	9	5	14

^a Carried out in methanol at 30°C.

Table II. Effect of temperature on the photolysis of **1**^a

Temp °C	Conversion %	Product yield/%							
		2a	2b	3	4a	4b	5a	5b	Others
30	44	1	14	5	4	5	2	1	12
60	68	3	21	12	10	12	Trace	Trace	10
90 ^b	88	2	19	13	15	16	—	—	23

^a Carried out in methanol for 24 h.

^b Carried out in 1-propanol.

Table III. Effect of solvent on the photolysis of **1**^a

Solvent	$\epsilon_{313} \times 10$	Conv. %	Product yield/%							
			2a	2b	3	4a	4b	5a	5b	Others
Methanol	8.64	44	1	14	5	4	5	2	1	12
2-Propanol	8.37	66	—	18	8	7	8	2	1	22
Benzene	13.20	15	—	8	3	—	—	—	—	4
THF	9.17	89	—	18	7	11	14	—	—	39

^a Carried out at 30°C for 24 h.**Table IV.** Isomer ratios of photolysates

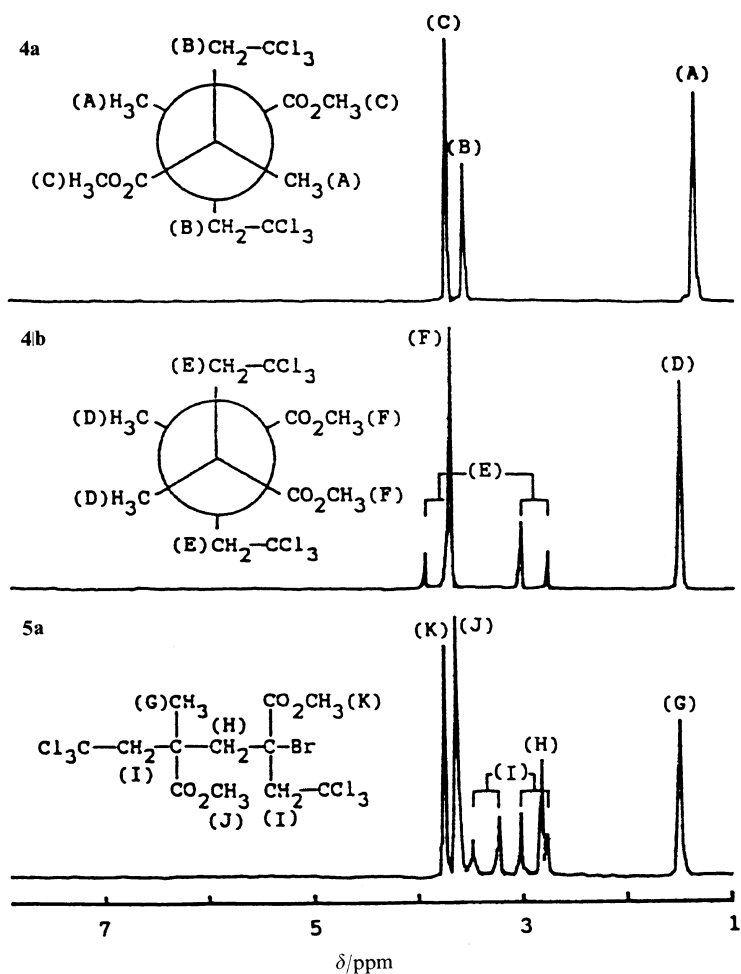
Solvent	Temp °C	Time h	%		%		%	
			2a	2b	4a	4b	5a	5b
Methanol	30	6	12	88	51	49	—	—
		24	3	97	42	58	60	40
		48	8	92	49	51	59	41
		72	10	90	48	52	65	35
	60	24	12	88	44	56	—	—
1-Propanol	90		8	92	48	52	—	—
2-Propanol	30		0	100	47	53	58	42
Benzene			0	100	—	—	—	—
THF			0	100	44	56	—	—

head-to-head orientation, while **5a** and **5b** were entirely absent.

Structure and Isomer Ratios of the Photoproducts

The photoproducts can be classified roughly into monomeric and dimeric components. Their structures were determined on the basis of ¹H NMR, IR, and MS spectra. Table IV shows the isomer ratios of photoproducts under each photoreaction condition. The two structural isomers **2a** and **2b** differ in the position of unsaturation. The internally unsaturated isomer **2a** was identical with the ionic elimination product of **1** with triethylamine.⁴ The production ratio of **2b** was much greater than that of **2a** regardless of the photoreaction conditions. Figure 1 shows the ¹H NMR spectra of the two symmetrical diastereoisomers **4a** and **4b**. In spite of the dimeric compounds, a couple of methyl protons (A), (D) and methyl ester protons (C), (F) appeared

as a singlet, respectively. However, because of difference in the magnetic environment about a couple of methylene groups, the corresponding protons of **4a** and **4b** exhibited contrasting signals. That is, the geminal methylene protons (B) of *meso*-form **4a** resonated as a singlet owing to equivalence, whereas those protons (E) of *dl*-form **4b**, as an AB pattern of doublet-doublet owing to nonequivalence. As a general rule, the *dl*-form **4b** was produced slightly more than the *meso*-form **4a** as shown in Table IV. Though it was difficult to fractionate the two diastereoisomers **5a** and **5b** by column chromatography of silica gel, the partial resolution of **5a** was successful by fractional crystallization from carbon tetrachloride. On the basis of the ¹H NMR spectrum of **5a** as shown in Figure 1, the dimeric photoproduct **5a** may be taken as an unsymmetrical head-to-tail telomer. The photoradiation of **5a** in methanol at 60°C for 6 h afforded lactone **7a** in ca. 10% yield. Furthermore, the thermal lacto-

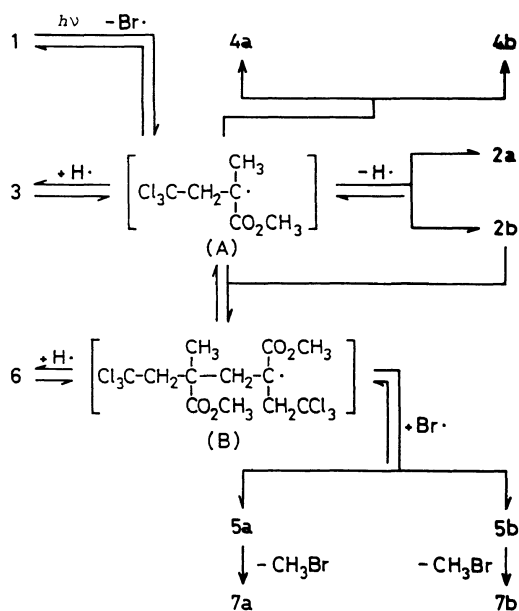
Figure 1. ^1H NMR spectra of photodimeric products.Table V. Thermal lactonization of **5**^a

Sample	Production ratio of lactone/%	
	7a	7b
5a	100	0
(5a + 5b) ^b	47	53

^a Heated at 150°C for 2 h.^b A mixture of 47:53.

nizations of **5a** and **5b** were carried out to give positive proof of the configurational assignment of **5a** and **5b**. The results are shown in Table V. The unchanged **5** was not detected.

The head-to-tail telomer **5a** gave only lactone **7a**, whereas the mixture of **5a** and **5b** (47:53) gave two lactones **7a** and **7b** in the ratio of 47:53. In the previous investigation,⁵ it was proved that the pyrolysis of the *syndiotactic* and *isotactic* MMA dimers telomerized with BTCM leads to different lactones by a S_N1 mechanism. The same lactonization of two diastereoisomers **5a** and **5b** was consistent with this assignment of configurations. As shown in Table IV, the *syndiotactic* **5a** was produced in preference to the *isotactic* **5b** in an approximate ratio of 60:40.



Scheme 1. Photolysis pathway of 1.

Photolysis Pathway of Methyl 2-Bromo-4,4,4-trichloro-2-methylbutyrate (1)

The photolysis of **1** is explained in terms of a series of routes as shown in Scheme 1. At the initial stage, the homolytic cleavage of carbon-bromine bond occurs preferentially. The resulting telomeric radical (A) as a transient intermediate would lead to each photoproduct. When a hydrogen atom on the carbon atoms adjacent to the radical part is released, the formation of two kinds of unsaturated telomers and hydrogen bromide is possible. This radical elimination proceeds against Saytzeff's law, and the terminally unsaturated telomer **2b** is produced in preference to the internally unsaturated telomer **2a**. Another monomeric photoproduct is the saturated telomer **3**, which may be formed through hydrogen abstraction from the reaction solvent. Furthermore, the two unsaturated telomers **2a** or **2b**, and the hydrogenated telomer **3** may be also formed through a disproportionation of two (A) radicals. On the other hand, two types of dimerization occurs *via* the monomeric intermediate (A); one is a recombination of two

(A) radicals, the other a addition of (A) to the initial product **2b**. The coupling reaction leads to two diastereoisomers **4a** and **4b** combined in a head-to-head orientation, while the addition reaction results in two diastereoisomers **5a** and **5b** combined in a head-to-tail orientation *via* the dimeric intermediate (B). On the photolysis of **1** at higher reaction temperature or in THF, the head-to-tail telomers **5a** and **5b** tend to change into other photoproducts such as **6**, **7a**, and **7b**.

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REFERENCES

- P. G. Sammes, in "Chemistry of the Carbon-Halogen Bond," S. Patai, Ed., Wiley, New York, N. Y., 1973, Chapter 11.
- V. Enev, I. Petkov, L. Markova, and P. Markov, *J. Photochem.*, **39**, 333 (1987).
- S. Walia, P. Dureja, and S. K. Mukerjee,

- Tetrahedron*, **43**, 2493 (1987).
4. T. Kimura, T. Kodaira, and M. Hamashima, *Polym. J.*, **15**, 293 (1983).
 5. T. Kimura and M. Hamashima, *Polym. J.*, **18**, 21 (1986).
 6. T. Kimura, M. Kishimoto, and M. Hamashima, *Polym. Prepr., Jpn.*, **34**, 255 (1985).
 7. Y. Yano, K. Izawa, H. Iwata, K. Ichikawa, and W. Kimura, *Bunseki Kagaku*, **10**, 1358 (1961).