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The Synthesis of 1,3-Dithiolan-2-ones on the Reaction of Oxiranes with Carbon Disulfide under High Pressure

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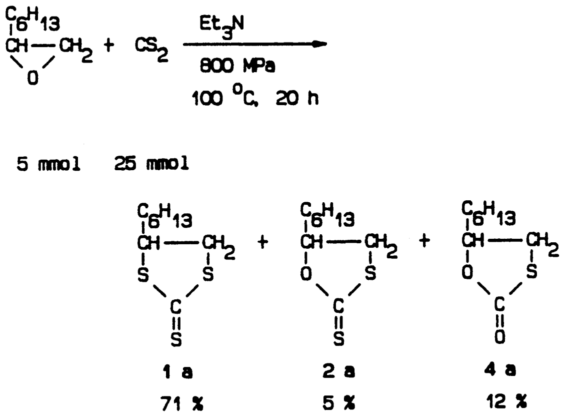
An equimolar reaction of 2-hexyloxirane with carbon disulfide in hexane was run in the presence of triethylamine under 800 MPa at 100 °C for 20 h, and gave 63% of 4-hexyl-1,3-dithiolan-2-one (**3a**), 21% of 4-hexyl-1,3-dithiolane-2-thione (**la**) and 5% of 5-hexyl-1,3-oxathiolan-2-one (**4a**). Hexane, benzene, and diisopropyl ether were good solvents for the reaction. The reaction of a variety of oxiranes with carbon disulfide produced 1,3-dithiolan-2-ones as the main products under 500 MPa at 100 °C for 20 h. Upon a reaction of 2-hexyloxirane with carbon disulfide, 5-hexyl-1,3-oxathiolane-2-thione (**2a**), and 2-hexylthiirane (**5a**) were produced during the first stage of reaction. The formation of **la** and **4a** began immediately, whereas, the formation of **3a** required a long induced period. A feasible mechanism for the formation of **3a** is proposed to be a rearrangement of **2a** in the presence of triethylamine, free from carbon disulfide.

Many organic reactions are accelerated by compression.[1,2] It has recently been reported that the reactions of many thiiranes with carbon disulfide in the presence of triethylamine under high pressure give 1,3-dithiolane-2-thiones nearly quantitatively.[3] The reactions of many oxiranes with carbon disulfide are also accelerated by compression to give 1,3-dithiolane-2-thiones (**1**) as a main product.[4] **1** is considered to be formed via 1,3-oxathiolane-2-thiones (**2**),[4] and the relative ratio of **2** to the total yield is high during the early period of the reaction. Therefore, it is expected that **2** is formed with high yield and selectivity by the choice of suitable reaction conditions. The equimolar reaction of oxiranes and carbon disulfide in a solvent was investigated under high pressure for this purpose. As a result, an interesting rearrangement was found to occur without yielding **2**.

In this paper, we report on reactions in which no **2** was obtained and 1,3-dithiolan-2-ones (**3**) were newly formed as the main products upon the reaction of oxiranes with carbon disulfide. When excess carbon disulfide was used, **3** was not found.[4] The formation of **3** is considered to include some rearrangement, since **3** can not be formed by a simple addition reaction. There have been no reports on a similar rearrangement under high pressure. The effects of the pressure, temperature, reaction time, molar ratio of reactants, the amount and kind of catalysts, and the kind of solvents have been investigated in detail with regard to the reaction of 2-hexyloxirane with carbon disulfide. The mechanism for the formation of the products is also discussed.

Results and Discussion

A reaction of 2-hexyloxirane with excess carbon disulfide at 100 °C for 20 h under 800 MPa gave 71% of 4-hexyl-1,3-dithiolane-2-thione (**1a**), 5% of 5-hexyl-1,3-oxathiolane-2-thione (**2a**) and 12% of 5-hexyl-1,3-oxathiolan-2-one (**4a**).[4] However, an equimolar reaction in hexane under the same reaction conditions gave 63% of 4-hexyl-1,3-dithiolan-2-one (**3a**), 21% of **1a** and 5% of **4a**; no **2a** was produced.



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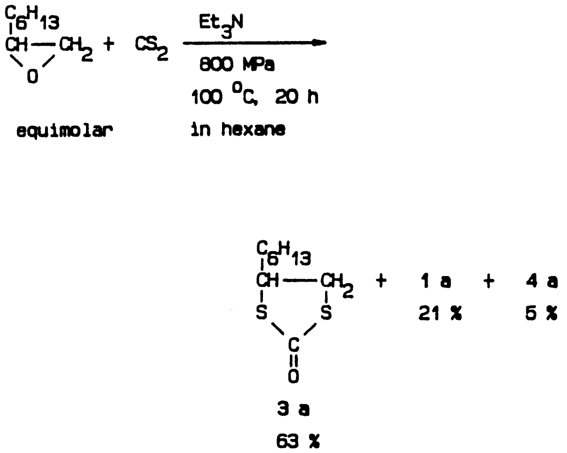

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Table 1 shows the effects of pressure, temperature, and reaction time on the reaction. The reaction under ordinary pressure gave no products (Run 1); this fact shows that this reaction can be remarkably accelerated by compression. At a pressure higher than 500 MPa, **3a** was the main product and none of **2a** was produced unexpectedly (Runs 3—7). Under 200 MPa, both products **2a** and **3a** were obtained and 29% of 2-

Table 1. Reaction of 2-Hexyloxirane with CS_2[a)]

Run	Press.	Temp	Time	Conv.	Yield/%					
	MPa	°C	h	%	**1a**	**2a**	**3a**	**4a**	**5a**	Total
1	0.1[b)]	100	20	19	—	—	—	—	—	—
2	200	100	20	95	18	19	12	2	29	80
3	500	70	20	100	12	—	55	4	15	86
4	500	100	20	100	16	—	68	5	—	89
5	800	70	20	100	12	—	33	1	25	71
6	800	100	7	100	13	—	44	—	8	65
7	800	100	20	100	21	—	63	5	—	89

a) 2-Hexyloxirane 5 mmol; CS_2 5 mmol; Et_3N 0.5 mmol; hexane 3 ml. b) In a sealed glass tube.

Table 2. Effect of Solvents on the Reaction of 2-Hexyloxilane with CS_2[a)]

Run	Press.	Solvent	Conv.	Yield/%					
	MPa		%	**1a**	**2a**	**3a**	**4a**	**5a**	Total
1	500	Hexane	100	16	—	68	5	—	89
2	500	Benzene	100	17	4	72	5	—	98
3	500	IPE	100	16	—	70	5	—	91
4	500	CH_3CN	100	25	—	43	—	—	68
5	800	$CHCl_3$	100	16	—	31	4	11	62
6	500	Acetone	100	14	—	3	—	1	18
7	500	DMF	91	10	1	1	—	6	18

a) 2-Hexyloxilane 5 mmol; CS_2 5 mmol; Et_3N 0.5 mmol; reaction time 20 h; reaction temperature 100 °C.

Table 3. Effect of Various Catalysts on the Reaction of 2-Hexyloxirane with CS_2[a)]

Run	Catalyst	Press.	Temp	Time	Conv.	Yield/%					
		MPa	°C	h	%	**1a**	**2a**	**3a**	**4a**	**5a**	Total
1	*N*-Methylmorpholine	200	100	20	17	—	2	—	—	8	10
2	*N*-Methylmorpholine	500	70	20	81	4	31	—	1	4	40
3	*N*-Methylmorpholine	800	70	20	100	18	48	—	5	10	81
4	*N*-Methylmorpholine	800	100	7	100	16	—	60	1	14	91
5	Pyridine	200	100	20	33	2	14	—	—	7	23
6	Tributylamine	800	100	20	100	29	—	54	5	—	88
7	2,6-Dimethylpyridine	800	100	20	74	6	26	—	4	—	36

a) 2-Hexyloxirane 5 mmol; CS_2 5 mmol; catalyst 0.5 mmol; hexane 3 ml.

Table 4. Effects of the Amount of Triethylamine and Molar Ratio of Reactants[a)]

Run	Press.	Et_3N	CS_2	Conv.	Yield/%					
	MPa	mmol	oxirane	%	**1a**	**2a**	**3a**	**4a**	**5a**	Total
1	500	0.05	1	58	1	19	—	—	6	26
2	500	0.10	1	95	20	28	13	5	11	77
3	500	0.15	1	97	16	16	39	5	17	93
4	500	0.25	1	98	16	1	63	7	7	94
5	500	0.50	1	100	16	—	68	5	—	89
6	500	1.00	1	100	20	—	66	7	—	93
7	500	6.00	1	100	24	—	60	1	—	85
8	800	0.50	1.5	100	66	3	16	9	—	94
9	800	0.50	0.5	100	1	—	3	3	—	7

a) 2-Hexyloxirane 5 mmol; hexane 3 ml; reaction time 20 h; reaction temperature 100 °C.

hexylthiirane (**5a**) was also formed (Run 2).

Table 2 shows the effect of solvents. **3a** was formed in high yields in hexane, benzene, and diisopropyl ether (IPE); however, in polar solvents, such as acetone and *N*,*N*-dimethylformamide (DMF), the yield of **3a** decreased.

Table 3 shows the effect of catalysts. When *N*-methylmorpholine was used as a catalyst under 800 MPa at 100 °C, **3a** was obtained as the main product (Run 4), but under lower pressure or at a lower

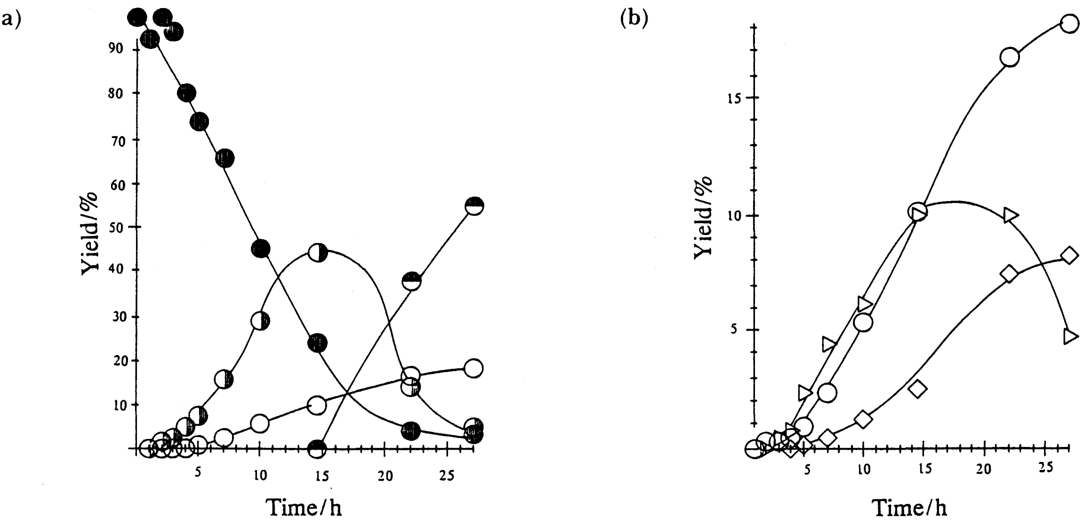


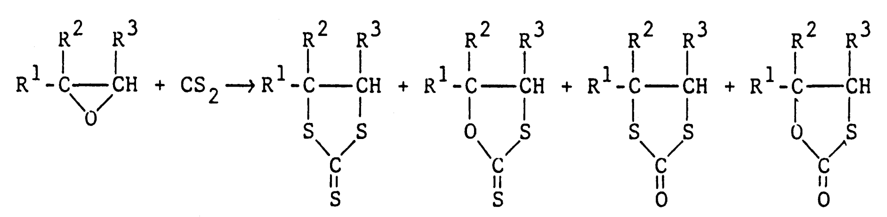
Fig. 1. Relation of the yields of products and reaction time on the reaction of 2-hexyloxirane with CS_2. Reaction temperature: 70 °C, pressure: 300 MPa, 2-hexyloxirane: 50 mmol, CS_2: 50 mmol, Et_3N: 5 mmol, heptane: 30 ml, tetradecane: 0.50 g.
—●—: 2-hexyloxirane, —○—: **1a**, —◑—: **2a**, —◒—: **3a**, —◇—: **4a**, —▷—: **5a**.

temperature **3a** was not formed (Runs 1—3).

Table 4 shows the relation between the yields of the products and the amount of triethylamine used as a catalyst on the reaction. Since the rate of the reaction of thiiranes with carbon disulfide is proportional to the amount of triethylamine catalyst,[3] it is considered that the rate of the reaction of 2-hexyloxirane is proportional to the amount of triethylamine in the range of 0.05—0.50 mmol. When 0.05 mmol of triethylamine was used, **2a** was formed as the main product and **3a** was not formed (Run 1); also, none of **2a** was detected and **3a** was given as the main product when 0.50 mmol of triethylamine was used (Run 5). As a result, it is suggested that **3a** is formed by the conversion of **2a**. When a slight excess of carbon disulfide was used, **1a** was obtained as the main product and the yield of **3a** decreased (Run 8). This shows that the ratio of products depends upon the molar ratios of oxiranes and carbon disulfide; but when the ratio of carbon disulfide was reduced, the polymerization of 2-hexyloxirane proceeded preferentially (Run 9).

Figure 1 shows the relation between the yields of the products and the reaction time on the reaction in heptane under 300 MPa at 70 °C. During the initial stage, **2a** was formed as the main product, and no **3a** was formed. **3a** was first detected at 22 h after starting ; **2a**

Table 5. Reaction of Various Oxiranes with CS_2[a)]



1 **2** **3** **4**

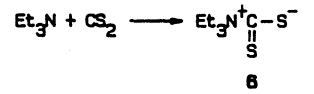
Run	Product R¹	R²	R³	Solvent	Et_3N mmol	Yield/% 1	2	3	4	Total
1	CH_3	H	H	Hexane	0.50	44	—	22	—	66
2	CH_3	H	H	Benzene	0.10	17	31	34	5	87
3	C_2H_5	H	H	Hexane	0.50	24	—	47	5	76
4	CH_3	CH_3	H	Hexane	0.50	4	54	30	—	88
5	Ph	H	H	Hexane	0.50	Trace	—	Trace	—	Trace
6	Ph	H	H	Hexane	0.05	48	—	9	—	57
7	Ph	H	H	Benzene	0.05	29	—	36	—	65
8	H	$(CH_2)_4$		Hexane	0.50	31	15	—	11	46
9	H	$(CH_2)_4$		Benzene	0.10	27	—	10	4	41

a) Oxirane 5 mmol; CS_2 5 mmol; Et_3N 0.5 mmol; pressure 500 MPa; reaction temperature 100 °C; reaction time 20 h.

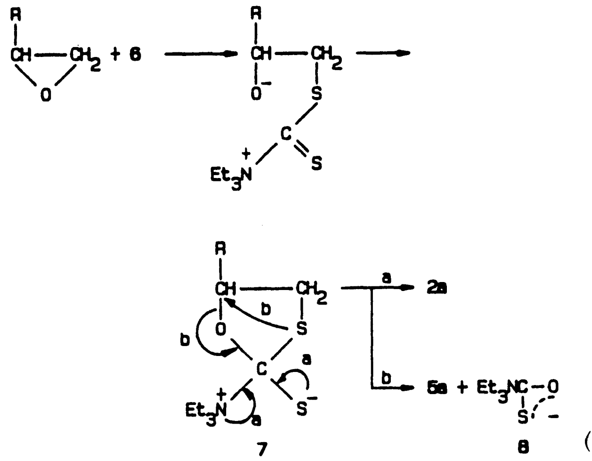
was reduced greatly. These phenomena verify that **2a** changes to **3a**, and that the formation of **3a** has a long induced period. In contrast to the production of **3a**, **1a** and **4a** were already detected at an early time, and increased as the reaction proceeded. The formation mechanisms of **1a** and **4a** are considered to be the same mechanisms as mentioned previously.[4)]

Table 5 shows the products and yields for the reactions of various oxiranes with carbon disulfide. 2-Phenyloxirane and 2-methyloxirane which produce **1** easily upon reacting with excess carbon disulfide,[4)] produced **3** as the main product under suitable reaction conditions (Runs 2 and 7). 2,2-Dimethyloxirane, which gave **2** as the main product on the reaction with excess carbon disulfide, also gave **2** as the main product, though **3** was obtained with 30% yield (Run 4).

An equimolar reaction of 2-hexyloxirane with carbon disulfide in the presence of triethylamine seems to proceed as follows:



$$\mathrm{Et_3N} + \mathrm{CS_2} \longrightarrow \mathrm{Et_3\overset{+}{N}}\underset{\underset{\displaystyle S}{\|}}{C}\mathrm{-S^-} \quad (3)$$



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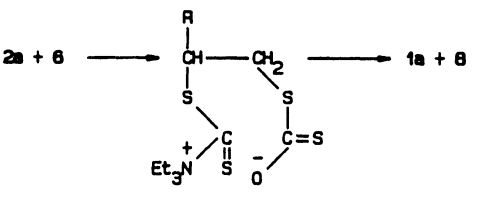

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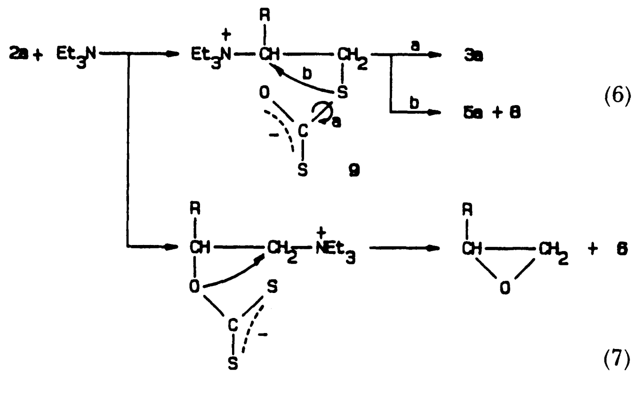

(6)

(7)

Adduct **6** attacks 2-hexyloxirane to give **2a** and **5a** (Eq. 4). **1a** is obtained through a reaction of **2a** with **6**, as mentioned previously (Eq. 5). When carbon disulfide is almost consumed and free triethylamine is present without producing **6** with carbon disulfide, **2a** reacts with triethylamine to give adduct **9**. **3a** is formed by a rotation of the C–S bond of **9**. A similar rotation has been reported regarding the isomerization of *N*-phenyl-1,3-dioxolan-2-imine.[5)] To confirm this mechanism, **2a** in hexane was heated at 100 °C in the presence of triethylamine under 800 MPa for 20 h to form **3a** as the main product (Eq. 8). In contrast, a similar reaction in carbon disulfide gave **1a** as the main product; **3a** was not obtained (Eq. 9). It is considered that the reaction of Eq. 7 is also achieved, because the formations of **1a** and **4a** in Eq. 8 need 2-hexyloxirane and **6**.

$$\mathbf{2a} \xrightarrow[\text{800 MPa, 100 °C}]{\text{Et}_3\text{N, Hexane}} \underset{9\%}{\mathbf{1a}} + \underset{18\%}{\mathbf{2a}} + \underset{52\%}{\mathbf{3a}} + \underset{6\%}{\mathbf{4a}} + \underset{15\%}{\mathbf{5a}} \quad (8)$$

$$\mathbf{2a} + \mathrm{CS_2} \xrightarrow[\text{800 MPa, 100 °C}]{\text{Et}_3\text{N}} \underset{73\%}{\mathbf{1a}} + \underset{7\%}{\mathbf{2a}} + \underset{9\%}{\mathbf{4a}} + \underset{2\%}{\mathbf{5a}} \quad (9)$$

Of Eqs. 3—7, it has been reported[3,4)] that the compression have an accelerating effect on reactions in Eqs. 3—5. The reactions of Eqs. 6 and 7 seem to also be accelerated by compression since a rearrangement of **2a** did not occur under ordinary pressure under similar reaction conditions to Eq. 8.

Some products[6—9)] which are derived from **3** are known to be accricides, fungicides, or insecticides. Though various synthetic methods of 1,3-dithiolan-2-one have been reported,[10—14)] the materials used for its derivatives are rather inaccessible. Synthesis of its derivatives by reactions of oxirane with carbon disulfide under high pressure have the advantage since many kinds of oxiranes may be obtained commercially.

Experimental

Apparatus. The apparatus used for the reaction under high pressure was the same as that described previously.[15)]

Measurement. GLC was carried out using a JEOL 20KF chromatograph with 20% SE-30 columns. ^{1}H NMR spectra were measured with a Hitachi R-40 spectrometer. Mass spectra were measured with a JEOL D-300 GC-MS spectrometer by the CI (chemical ion) method with isobutane. IR spectra were obtained with a JASCO A-302 spectrophotometer.

Reaction of Oxiranes with Carbon Disulfide. A typical procedure is as follows: A homogeneous mixture of 2-hexyloxirane (5 mmol), carbon disulfide (5 mmol), and triethylamine (0.5 mmol) in a sealed Teflon tube was compressed to 800 MPa, heated at 100 °C, and maintained for 20 h in a high-pressure apparatus. The resulting mixture was subjected to evaporation and the residue was distilled with a Kugelrohr. The distillate was separated by column chromatography on silica gel using a mixture of hexane and chloroform (7 : 3 v/v) as an eluent. The spectral data of **1a** and **4a** agreed with the known data.[3,4)] The structure of **3a** was identified by a comparison of ^{1}H NMR and IR spectra of **3a** with those of **1a**, **2a**, **4a**, and 1,3-dithiolan-2-one.[10] **3a**: IR 1642 cm^{-1} ; ^{1}H NMR δ=0.89 (t, 3H, CH_3), 1.31 (s, 8H, $(CH_2)_4$), 1.65—2.10 (m, 2H, CH_2), 3.24—3.86 (m, 2H, CH_2), and 3.91—4.37 (m, 1H, CH); QM$^+$ 205.

2-Methyloxirane, 2-ethyloxirane, 2,2-dimethyloxirane, 2,3-tetramethyleneoxirane, and 2-phenyloxirane were treated with carbon disulfide similarly to 2-hexyloxirane. The spectral data of **1**, **2**, and **4** from these reactions agreed with the known data.[3,4] The spectral data of the other products of these reactions are as follows:

4-Methyl-1,3-dithiolan-2-one: IR 1642 cm^{-1}; ^{1}H NMR δ=1.60 (d, J=6.3 Hz, 3H, CH_3), 3.22—3.53 (dd, J=7.2 and 11.7 Hz, 1H, one proton of CH_2), 3.58—3.85 (dd, J=4.5 and 11.7 Hz, 1H, one proton of CH_2), and 4.00—4.42 (m, 1H, CH); QM$^+$ 135.

4-Ethyl-1,3-dithiolan-2-one: IR 1642 cm^{-1}; ^{1}H NMR δ= 1.06 (t, 3H, CH_3), 1.93 (quin, 2H, CH_2), 3.30—3.56 (dd, J=7.2 and 11.7 Hz, 1H, one proton of CH_2), 3.60—3.87 (dd, J=5.4 and 11.7 Hz, 1H, one proton of CH_2), and 3.89—4.22 (m, 1H, CH); QM$^+$ 149.

4,4-Dimethyl-1,3-dithiolan-2-one: IR 1643 cm^{-1}; ^{1}H NMR δ=1.70 (s, 6H, $2CH_3$), and 3.47 (s, 2H, CH_2); QM$^+$ 149.

4,5-Tetramethylene-1,3-dithiolan-2-one: IR 1624 cm^{-1}; ^{1}H NMR δ=1.2—2.3 (m, 8H, $4CH_2$), and 3.70—3.95 (m, 2H, 2CH); QM$^+$ 175.

4-Phenyl-1,3-dithiolan-2-one: IR 1651 cm^{-1}; ^{1}H NMR δ=3.71 (d, J=9 Hz, 2H, CH_2), 5.23 (t, 1H, CH), and 7.10—7.70 (m, 5H, C_6H_5); QM$^+$ 197.

Rearrangement of 2a in Hexane. A homogeneous mixture of **2a** (43.1 mg), triethylamine (4.0 mg), tetradecane (7.3 mg), and hexane (0.3 ml) in a sealed Teflon tube was compressed to 800 MPa, heated at 100 °C, and maintained for 20 h in a high-pressure equipment. The GLC analysis using tetradecane as a standard showed that 52% of **3a** was obtained.

Reaction of 2a with Carbon Disulfide. A homogeneous mixture of **2a** (43.3 mg), carbon disulfide (200 mg), triethylamine (3.8 mg), and tetradecane (5.9 mg) in a sealed tube was compressed to 800 MPa, heated at 100 °C, and maintained for 20 h in a high-pressure apparatus. A GLC analysis using tetradecane as a standard showed that 71% of **1a** was obtained.

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