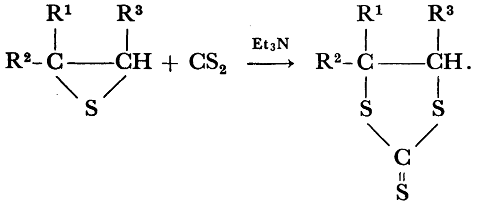
Bull. Chem. Soc. Jpn., 61, 921—925 (1988)

The Reaction of Oxiranes with Carbon Disulfide under High Pressure

Yoichi TAGUCHI,* Koshin YANAGIYA, Isao SHIBUYA, and Yasuo SUHARA
National Chemical Laboratory for Industry, Higashi, Tsukuba, Ibaraki 305
(Received August 4, 1987)

The reaction of 2,2-dimetyloxirane with carbon disulfide in the presence of triethylamine was accelerated under high pressure to give 5,5-dimethyl-1,3-oxathiolane-2-thione in a high yield, while 2-hexyloxirane under the same reaction condition formeds 4-hexyl-1,3-dithiolane-2-thione (**2b**) as the main product and 5-hexyl-1,3-oxathiolane-2-thione (**1b**) as a minor product. A feasible mechanism for this formation is that **1b** and 2-hexylthiirane (**4b**) are produced in the first stage of reaction, and that **2b** is then formed by the reaction of **1b** or **4b** with carbon disulfide. In reactions of a variety of oxiranes with carbon disulfide, 1,3-dithiolane-2-thiones were obtained in high yields under 800 MPa at 100 °C within 20 h. Concerning the effect of substituents in oxiranes, the selectivity for product **2b** is in the decreasing order; 2-phenyl->2-methyl->2-ethyl->2-hexyl->2,3-tetramethylene->2,2-dimethyl->2-(chloromethyl)-. Tertiary amines, such as *N,N*-dimethylethylamine, pyridine, and *N*-methylmorpholine, serve as good catalysts for the reaction.

There have been many reports[1—8)] that oxiranes react with carbon disulfide to form various products such as thiiranes, 1,3-dithiolane-2-thiones, and 1,3-oxathiolane-2-thiones, but these products except thiiranes have not been obtained in good yield. Many organic reactions, when conducted under high pressure, show product selectivities different from those they show under ordinary pressure,[9)] and we found that the reaction of thiiranes with carbon disulfide was accelerated under high pressure to give 1,3-dithiolane-2-thiones with high selectivity and yield:[10)]



Therefore, it is expected that acceleration by compression may be observed also with the reaction of oxiranes, and that the formation of thiiranes, which are often main products under ordinary pressure, may be suppressed by compression.

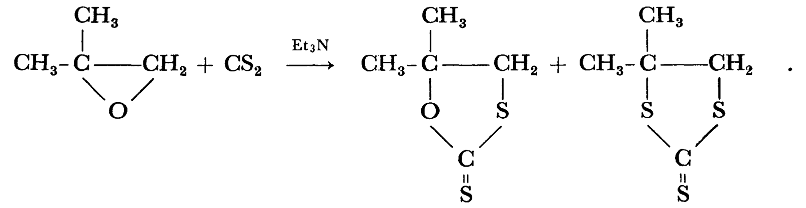
In this paper, we report that the reaction of oxiranes with carbon disulfide is also accelerated by compression to give 1,3-dithiolane-2-thiones, 1,3-oxathiolane-2-thiones, 1,3-oxathiolan-2-ones, and thiiranes, and that the proportion of these products is dependent on pressure, temperature, the amount and kind of catalyst, and substituents in oxiranes. Furthermore, formation mechanisms for these products are discussed, and the reactivity of oxiranes is compared with that of thiiranes.

Results and Discussion

A reaction of 2,2-dimethyloxirane with carbon disulfide in a sealed tube at 100 °C for 20 h gave only 4% of 4,4-dimethyl-1,3-oxathiolane-2-thione (**1a**), but, when conducted under 800 MPa, gave 68% of **1a** and 8% of 5,5-dimethyl-1,3-dithiolane-2-thione (**2a**), which verifies that this reaction is to be accelerated remarkably by compression.

The structure of **1a** was assigned based on IR, ^{1}H NMR, and CI-MS spectra, and the spectral data of **2a** agreed with the known data.[10)] The isomer of **1a**, 4,4-dimethyl-1,3-oxathiolane-2-thione, was not detected. Table 1 shows effects of pressure, temperature, and the kind of catalysts on the reaction. *N,N*-Dimethylethylamine, triethylamine, *N*-methylmorpholine, pyridine, and tetraethylammonium bromide are good catalysts under high pressure, and the ratio of **2a** to total yield decreases in the above-listed order (Runs 2 and 6—9). This order agrees with that of their catalytic activities for the reaction of 2,2-dimethylthiirane with carbon disulfide.[10)] Table 1 also shows that the ratio of **2a** to total yield increases at higher temperatures or in the presence of strong catalyst (Runs 2 and 6).

Table 2 shows the effect of reaction conditions on the reaction of 2-hexyloxirane with carbon disulfide:



1a **2a**

Table 1. Reaction of 2,2-Dimethyloxirane with CS_2[a]

Run No.	Catalyst	Press.	Temp	Yield/%		
		MPa	°C	**1a**	**2a**	Total
1	Et_3N	0.1[b]	100	4	—	4
2	Et_3N	800	100	68	8	76
3	Et_3N	800	70	82	2	84
4	Et_3N	800	40	54	3	57
5	Et_3N	300	40	Trace	—	Trace
6	*N*,*N*-Dimethylethylamine	800	100	67	18	85
7	*N*-Methylmorpholine	800	100	89	5	94
8	Pyridine	800	100	88	4	92
9	Et_4NBr	800	100	62	2	64

a) 2,2-Dimethyloxirane 5 mmol; CS_2 25 mmol; reaction time 20 h; catalyst 0.5 mmol. b) In a sealed glass tube.

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

Run No.	Press.	Temp	Time	Conv.	Yield/%				
	MPa	°C	h	%	**1b**	**2b**	**3b**	**4b**	Total
1	0.1[b]	100	20	52	17	1	—	7	25
2	200	100	20	94	57	27	—	—	84
3	500	100	20	100	17	59	7	—	83
4	800	100	20	100	5	71	12	1	89
5	500	40	20	47	4	10	4	22	40
6	500	70	20	100	18	26	5	3	52
7	800	40	20	100	4	10	—	24	38
8	800	70	20	100	17	53	9	6	85
9	800	100	7	100	15	63	15	—	93

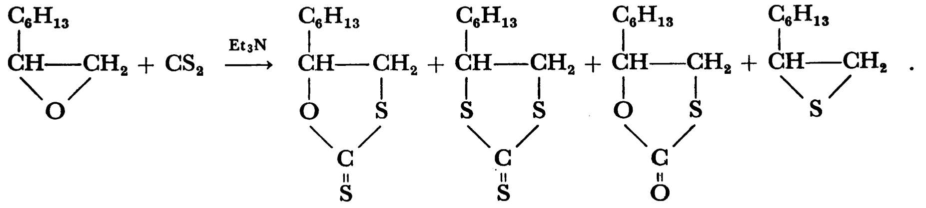
a) 2-Hexyloxirane 5 mmol; CS_2 25 mmol; Et_3N 0.5 mmol. b) In a sealed glass tube.

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

Run No.	Catalyst	Conv.	Yield/%				
		%	**1b**	**2b**	**3b**	**4b**	Total
1	*N*,*N*-Dimethylethylamine	100	5	67	13	—	85
2	Et_3N	100	5	71	12	1	89
3	*N*-Methylmorpholine	100	30	46	13	—	89
4	Pyridine	100	20	43	8	1	72
5	Et_4NBr	64	13	9	11	3	36
6	LiCl	41	9	Trace	4	1	14

a) 2-Hexyloxirane 5 mmol; CS_2 25 mmol; catalyst 0.5 mmol; pressure 800 MPa; reaction temperature 100 °C; reaction time 20 h.

This reaction under 800 MPa at 100 °C for 20 h gave 4-hexyl-1,3-dithiolane-2-thione (**2b**) as the main product, and the yield of 5-hexyl-1,3-oxathiolane-2-thione (**1b**) was only 5%, in contrast to that for the reaction of 2,2-dimethyloxirane with carbon disulfide. 5-Hexyl-1,3-oxathiolan-2-one (**3b**) and 2-hexylthiirane (**4b**) were also produced as minor products. The structures of **1b** and **3b** were assigned based on their IR, ^1H NMR, and CI-MS spectra taken after purification by column chromatography, and the spectral data



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

of **2b** and **4b** agreed with the known data.[10] The isomer of **1b**, 4-hexyl-1,3-oxathiolane-2-thione, was not detected. For this reaction, at 100 °C the yield of **2b** increased as pressure or reaction time was increased (Runs 1—4 and 7), and at 40 °C **4b** was obtained as the main product though its yield was not high (Runs 5 and 7).

Table 3 shows the effect of various catalysts on the reaction. Lithium chloride has no catalytic activity for the reaction of thiiranes with carbon disulfide,[10] but it has a little catalytic activity for the reaction of 2-hexyloxirane (Run 6). A dependence similar to that indicated by the results in Table 1 was observed with respect to the ratio of **2b** to total yield, that is, the ratio decreased in the order; triethylamine≥*N*,*N*-dimethylethylamine>pyridine≥*N*-methylmorpholine>tetraethylammonium bromide>lithium chloride. As a result, it is suggested that **1b** is formed as the main product in the first stage and then converted into **2b** as reaction proceeds.

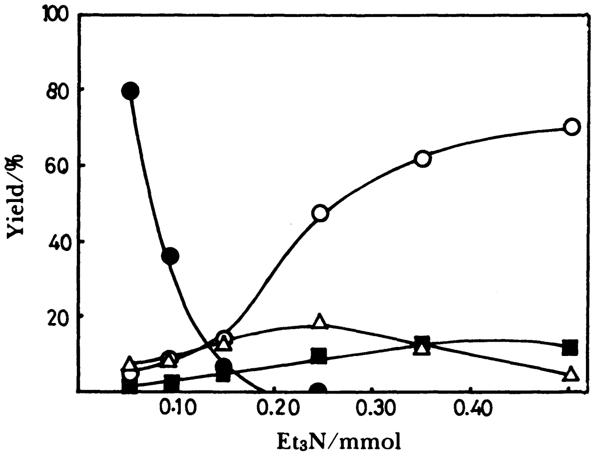
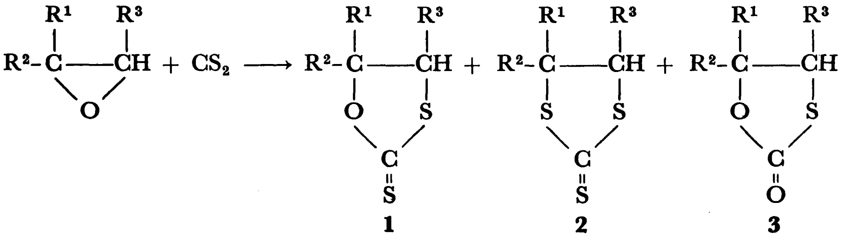


Fig. 1. Effect of amount of Et_3N on the reaction of 2-hexyloxirane with CS_2; reaction temperature: 100 °C, reaction time: 20 h, pressure: 800 MPa, 2-hexyloxirane: 5 mmol. CS_2: 25 mmol.
—△—: **1b**. —○—:**2b**, —■—: **3b**, —●—: 2-hexyloxirane.

Figure 1 shows the relation between products and the amount of triethylamine used as a catalyst for the reaction. As the rate of the reaction of thiiranes with carbon disulfide is proportional to the amount of triethylamine catalyst,[10] it is considered that the rate of the reaction of 2-hexyloxirane is proportional to the amount of triethylamine in the range 0.05—0.50 mmol. In the first stage **1b** was formed as the main product but its yield was not so much increased as reaction proceeded. On the other hand, the yield of **2b** increased as reaction proceeded even after 2-hexyloxirane was consumed completely. This fact also supports the suggestion that **2b** is formed as a result of the conversion of **1b**.

Table 4 shows products and yields for the reaction of various oxiranes with carbon disulfide. Two kinds of reaction conditions were used for comparison of reactivities of oxiranes. The conditions of Method A (catalyst *N*-methylmorpholine, 800 MPa, 70 °C, 20 h) is milder than that of Method B (catalyst triethylamine, 800 MPa, 100 °C, 20 h). 2-Phenyloxirane reacted with carbon disulfide to give 4-phenyl-1,3-dithiolane-2-thione with high selectivity even by

Table 4. Reaction of Various Oxiranes with CS_2[a)]

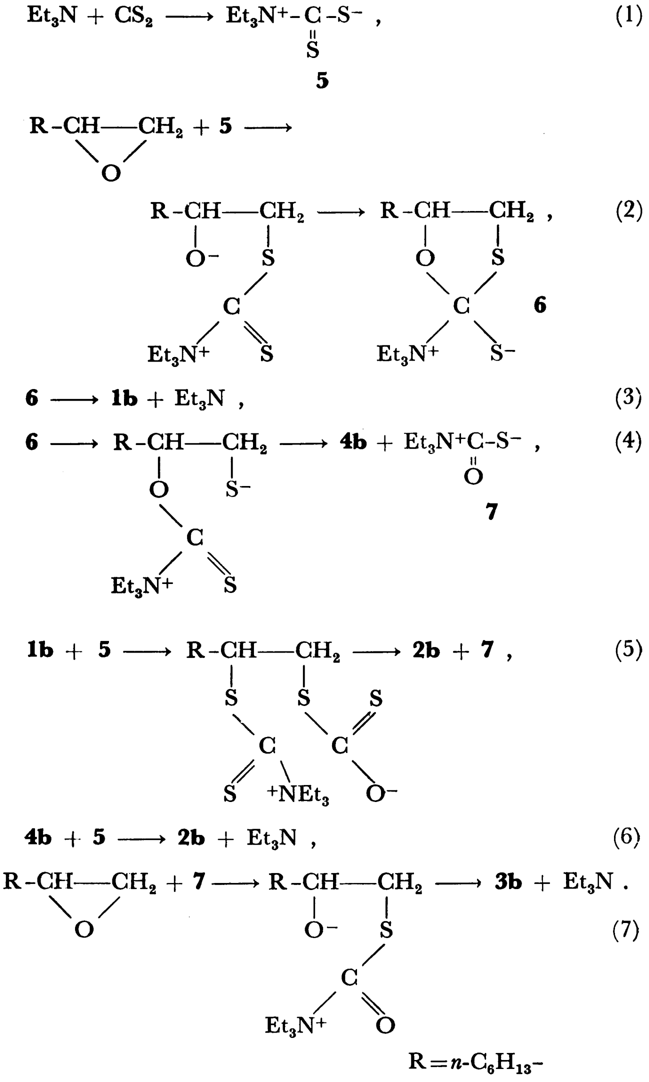


Run No.	Epoxide			Method	Yield/%			
	R^1	R^2	R^3		1	2	3	Total
1	CH_3	H	H	A[b)]	9	41	9	59
2	CH_3	H	H	B[c)]	—	83	7	90
3	C_2H_5	H	H	A	20	37	9	66
4	C_2H_5	H	H	B	5	68	17	90
5	C_6H_{13}	H	H	B	28	27	12	67
6	C_6H_5	H	H	A	—	86	—	86
7	C_6H_5	H	H	B	—	93	—	93
8	H	$(CH_2)_4$		A	54	36	6	96
9	H	$(CH_2)_4$		B	6	76	5	87
10	CH_3	CH_3	H	B	82	2	—	84
11	$ClCH_2$	H	H	B	35	—	16	51

a) Epoxide 5 mmol; CS_2 25 mmol; pressure 800 MPa; reaction time 20 h. b) *N*-Methylmorpholine 0.5 mmol; reaction temperature 70 °C. c) Et_3N 0.5 mmol; reaction temperature 100 °C.

Method A. 2-(Chloromethyl)oxirane reacted with carbon disulfide to give **1** and **3** with low yields. This might be due to lowered catalytic activity caused by an interaction between chlorine atom and triethylamine. A similar low reactivity has been observed with the reaction of thiiranes with carbon disulfide.[10] For the series of these oxiranes, the ratio of **2** to total yield is in the decreasing sequence: 2-phenyl->2-methyl->2-ethyl->2-hexyl->2,3-tetramethylene->2,2-dimethyl->2-(chloromethyl)-.

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



Reaction 1, the first step of adduct **5** formation from carbon disulfide and triethylamine, is followed by Reaction 2, consisting successively of the addition of **5** to 2-hexyloxirane and the ring closure yielding **6**. Reaction 3 is the elimination of triethylamine from **6** to give **1b**. The two carbon atoms of the oxirane ring can be attacked by **5**, but in practice, only product **1b** was formed selectively, which product may be considered to have been produced by an selective attack of **5** at the less-hindered carbon atom of the oxirane ring. It is well-known that nucleophilic attack in the presence of base will occur at sterically less-hindered sites.[11] Thus, the formation of **1b** conforms to this rule on. In addition, part of **6** also is converted to **4b** and adduct **7** (Reaction 4). This conversion is similar in mechanism to the reaction of oxiranes with thiourea to produce thiiranes.[12] At such a low temperature as 40 °C a considerable amount of **4b** was formed (Runs 5 and 7, Table 2), which phenomenon suggests that the formation of **4b** proceeds faster than that of **1b**.

It was confirmed that the reaction of **1b** with carbon disulfide in the presence of triethylamine under 800 MPa gave 71% of **2b**. There are two possible mechanisms for the formation of **2b** from **1b**. One involves initial thermal dissociation of **1b** into **4b** and carbonyl sulfide; it has been reported that the reaction of oxiranes with carbon disulfide followed by pyrolysis will produce thiiranes.[7,8] However, it is questionable that the reaction in which one molecule (**1b**) decomposes into two molecules (**4b** and carbonyl sulfide) should be accelerated by compression, considering that **1b** can be stably distilled in vacuo above 100 °C. The other mechanism involves the attack of **5** at the 5-position carbon of **1b** followed by the elimination of **7** (Reaction 5). The 5-position of **1a** is expected to be hindered sterically, and consequently, **1a** is obtained as a main product even by Method B (Run 10, Table 4). This phenomenon supports the latter mechanism, so that Reaction 5 is more likely for the formation of **2b**. It is known that a carbon atom adjacent to a phenyl group is liable to be attacked by nucleophilic reagents,[13] and this liability can be responsible for the reaction in which phenyloxirane affords 4-phenyl-1,3-dithiolane-2-thione dominantly (Runs 6 and 7, Table 4). It has been reported that Reaction 6 is accelerated by compression,[10] and **3b** is considered to be derived via the reaction of 2-hexyloxirane with **7**, Reaction **7**, similar to Reaction 6.

Of Reactions 1—7, the compression is considered to have an accelerating effect on Reactions 1, 2, and 5—7, and the reason why **2b** is obtained as the main product under high pressure is considered to be connected with the acceleration of Reaction 5 by compression. Similarly, in the reaction of a variety of oxiranes with carbon disulfide under high pressure, 1,3-dithiolane-2-thiones can be obtained in high yields.

Experimental

Apparatus. The apparatus used for the reaction under high pressure was the same as that described previously.[13]

Measurement. GLC was carried out by a JEOL 20KF chromatograph with 20% SE-30 columns. ^1H 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. The typical procedure is as follows: A homogeneous mixture of 2-hexyloxirane (5 mmol), carbon disulfide (25 mmol), and *N*-methylmorpholine (0.5 mmol) in a sealed Teflon tube was compressed to 800 MPa, heated at 70 °C, and maintained for 20 h in a high-pressure equipment. The resulting mixture was subjected to evaporation and the residue was distilled with a Kugelrohr. The distillate, a mixture of **1b**—**3b** 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 **2b** and **4b** agreed with the known data.[10] **1b**: IR 1189 and 1048 cm^{-1}; ^1H NMR $\delta=0.89$ (t, 3H, CH_3), 1.32 (s, 8H, C_4H_8), 1.73—2.30 (m, 2H, CH_2), 3.35—3.80 (m, 2H, CH_2), and 4.95—5.35(m, 1H, CH); QM^+ 205. **3b**: IR 1736 cm^{-1}; ^1H NMR $\delta=0.89$ (t, 3H, CH_3), 1.33 (s, 8H, C_4H_8), 1.65—2.25 (m, 2H, CH_2), 3.13—3.68 (m, 2H, CH_2), and 4.55—4.85 (m, 1H, CH); QM^+ 189.

2-Methyloxirane, 2-ethyloxirane, 2,2-dimethyloxirane, 2,3-tetramethyleneoxirane, 2-phenyloxirane, and 2-chloromethyloxirane were treated with carbon disulfide similarly to 2-hexyloxirane. The spectral data of 1,3-dithiolane-2-thione derivatives and 5-methyl-1,3-oxathiolane-2-thione from these reactions agreed with the known data.[10,15] The spectral data of the other products of these reactions are as follows:

5-Methyl-1,3-oxathiolan-2-one: IR 1729 cm^{-1}; ^1H NMR $\delta=1.53$ (d, 3H,CH_3), 3.10—3.73 (m, 2H, CH_2), and 4.63—5.05 (m, 1H, CH); QM^+ 119.

5-Methyl-1,3-oxathiolane-2-thione: IR 1188 cm^{-1}; ^1H NMR $\delta=1.09$ (t, 3H, CH_3), 1.53—2.20 (m, 2H, CH_2), 3.50—3.74 (m, 2H, CH_2), and 4.90—5.28 (m, 1H, CH); QM^+ 149.

5-Ethyl-1,3-oxathiolan-2-one: IR 1718 cm^{-1}; ^1H NMR $\delta=1.09$ (t, 3H, CH_3), 1.28—2.12 (m, 2H, CH_2), 3.08—3.60 (m, 2H, CH_2), and 4.40—4.76 (m, 1H, CH); QM^+: 133.

1a: IR 1252, 1127, 1198, and 1086 cm^{-1}; ^1H NMR $\delta=1.67$ (s, 6H, $2CH_3$), and 3.48 (s, 2H, CH_2); QM^+ 149. Found: C, 40.66; H, 5.43%. Calcd for $C_5H_8OS_2$: C, 40.51; H, 5.44%.

4,5-Tetramethylene-1,3-oxathiolane-2-thione: IR 1179 and 1041 cm^{-1}, ^1H NMR $\delta=1.00$—2.65 (m, CH_2, C_4H_8), 3.54—4.00 (m, 1H, CH), and 4.13—4.65 (m, 1H, CH); QM^+ 175.

4,5-Tetramethylene-1,3-oxathiolan-2-one: IR: 1736 cm^{-1}; ^1H NMR $\delta=1.16$—2.56 (m, 8H, C_4H_8) and 3.46—3.85 (m, 1H, CH); QM^+ 158.

5-Chloromethyl-1,3-oxathiolane-2-thione: IR: 1175 and 1035 cm^{-1}; ^1H NMR $\delta=3.62$—4.08 (m, 4H, $2CH_2$) and 5.16—5.32 (m, 1H, CH); QM^+ 169.

5-Chloromethyl-1,3-oxathiolane-2-one: IR 1739 cm^{-1}; ^1H NMR $\delta=3.24$—4.04 (m, 4H, $2CH_2$) and 4.72—5.10 (m, 1H, CH); QM^+ 153.

Reaction of 1b with Carbon Disulfide. A homogeneous mixture of **1b** (43.3 mg), carbon disulfide (200 mg), triethylamine (3.8 mg), and tetradecane (5.9 mg) 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 71% of **2b** was obtained.

References

1) Ethylene-Plastique S. A., Brit. Patent 1135800 (1968); *Chem. Abstr.*, **70**, 47278g (1969). Ethylene-Plastique S. A., Fr. Patent 1505715 (1967); *Chem. Abstr.*, **70**, 19908u (1969).

2) Thiokol Chemical Corp., Brit. Patent 1092610 (1967); *Chem. Abstr.*, **68**, 21823q (1968).

3) J. A. Durden. Jr., H. A. Stansbury. Jr., and W. H. Catlette, *J. Am. Chem. Soc.*, **82**, 3082 (1960).

4) V. S. Etlis, L. N. Grobov, and G. A. Razuvaev, *Dokl. Akad. Nauk SSSR*, **140**, 623 (1961); *Chem. Abstr.*, **56**, 11528d (1962).

5) Ethylene-Plastique S. A., Fr. Patent 1515077 (1968); *Chem. Abstr.*, **70**, 96782a (1969).

6) G. A. Razuvaev and V. S. Etlis, *Zh. Obshch. Khim.*, **33**, 1366 (1963); *Chem. Abstr.*, **59**, 9827b (1963).

7) Rohm and Haas Co., U. S. Patent 3409635 (1968); *Chem. Abstr.*, **70**, 20047u (1969).

8) Esso Research and Engineering Co., U. S. Patent 3687976 (1972); *Chem. Abstr.*, **77**, 152831z (1972).

9) K. Matsumoto and A. Sera, *Synthesis*, **1985**, 999.

10) Y. Taguchi, K. Yanagiya, I. Shibuya, and Y. Suhara, *Bull. Chem. Soc. Jpn.*, **60**, 727 (1987).

11) J. G. Smith, *Synthesis*, **1984**, 630.

12) M. Sander, *Chem. Revs.*, **66**, 297 (1966).

13) Y. Taguchi and Y. Suhara, *Bull. Chem. Soc. Jpn.*, **59**, 2321 (1986).

14) M. Kurabayashi, K. Yanagiya, and M. Yasumoto, *Bull. Chem. Soc. Jpn.*, **44**, 3413 (1971).

15) N. Adachi, Y. Kido, and K. Shibata, *J. Polym. Sci., Polym. Chem. Ed.*, **15**, 937 (1977).