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Stereoselective Formation of Allyl Ethers by Reaction of Epoxides with Organic Chlorides under Liquid-Solid Phase-Transfer Catalysis

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A series of *trans*-3-chloroallyl ethers and *trans*-3-thioallyl ethers were stereoselectively synthesized in one step by the reaction of 1-chloro-2,3-epoxypropane or 2,3-epoxypropyl sulfides with alkyl chlorides in the presence of solid sodium hydroxide and quaternary ammonium salt as a phase-transfer catalyst. Phase-transfer catalytic hydroxide ion-initiation followed by stereoselective isomerization of the epoxide ring through β-elimination is postulated as the important part of the reaction pathway.

Epoxy compounds have been utilized extensively in organic synthesis and industry as synthetic intermediates because of their facile preparation, and their high chemical reactivity attributable to the ring strain of the small-ring.[1,2] The reactions of various nucleophilic species with these compounds have been developed for synthetic applications.[1,3] Also, the isomerization of epoxides to allylic alcohols under the influence of strong, non-nucleophilic bases such as lithium dialkylamide attracted attention.[4] Since the formation of *trans*-3-chloroallyl alcohol through the stereoselective ring-opening of 1-chloro-2,3-epoxypropane with butyllithium was reported in 1964 (Scheme 1),[5] much work has been reported in this field,[6-9] and the crucial mechanistic point concerning the stereochemistry of β-elimination in the isomerization was indicated by deuterium-labelled experiments.[10]

Phase-transfer (PT) catalytic reaction in organic chemistry has been developed extensively in the last two decades and many synthetic techniques[11-15] have been established, which include hydroxide ion-initiated reactions due to the strong basicity of quaternary ammonium hydroxide under PT catalytic conditions. Recently, during the course of an investigation regarding the reactivity of 1-chloro-2,3-epoxypropane under PT catalytic conditions, we found a simple synthetic method for the preparation of oligoethylene glycol di-2,3-epoxypropyl ethers in good yields.[16] In this reaction, the formation of a small amount of a by-product (compound **1**) was always observed which could be isolated by fractional distillation.

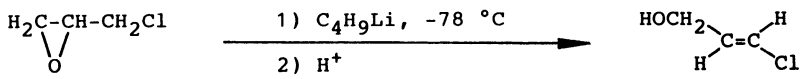
By identifying the compound **1** as *trans*-3-chloroallyl 2,3-epoxypropyl ether, a new reaction of epoxy compounds which can directly and stereoselectively afford *trans*-allyl ethers under PT catalytic conditions was disclosed. Based on the postulated reaction mechanism, we anticipated this new PT catalytic reaction would have utility for the synthesis of various kinds of *trans*-3-substituted allyl ethers.

In this paper, we report the development of this finding to the synthesis of *trans*-3-chloroallyl and *trans*-3-thioallyl ethers under PT catalytic conditions (Scheme 2).

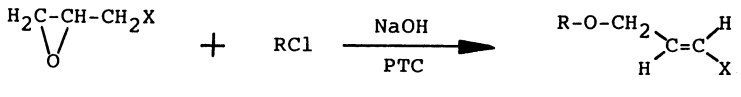
It is reported that 3-chloroallyl ethers are useful materials because of their dual functionality, and accordingly have attracted some attention.[17-22]

Results and Discussion

The structure of compound **1** was ascertained by spectral and elemental analyses. Absorptions due to the carbon-carbon double bond and ether linkages were observed in the infrared spectrum (1640 and 1110 cm^{-1}), and the presence of an epoxy ring and an olefinic moiety in trans form were confirmed from values of chemical shifts and coupling constants in the ^1H NMR. The existence of the *trans*-3-chloroallyloxy moiety was confirmed by ^1H NMR and ^{13}C NMR. Mass spectral and elemental analyses are also consist-



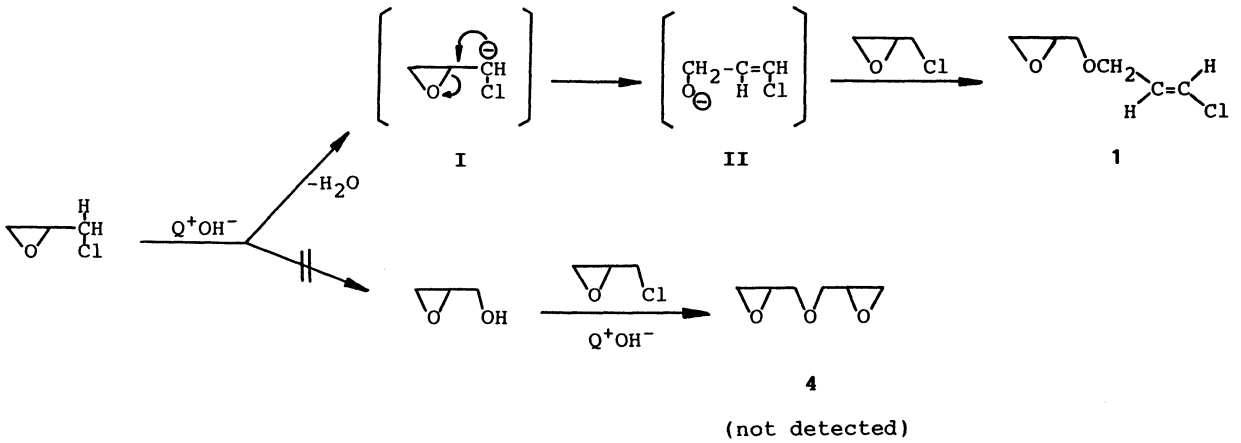
Scheme 1.



X: Cl-, ⟨○⟩-S-, n-C_8H_{17}S- Yield: 22-85%

R: ⟨△⟩, ⟨○⟩-CH_2-, CH_2=C(-CH_3)-CH_2-, n-C_8H_{17}-

Scheme 2.



Scheme 3.

ent with this structure. This structure was separately confirmed by the reaction of 1,3-dichloropropene (34% cis, 66% trans) with 2,3-epoxy-1-propanol, which afforded a mixture of about 30% *cis*- and 70% *trans*-3-chloroallyl 2,3-epoxypropyl ethers (**1'**and **1**, respectively) (The cis : trans ratios of raw chlorides and products were estimated by ^{1}H NMR). Compound **1** was synthesized easily in one step from 1-chloro-2,3-epoxypropane in the presence of solid sodium hydroxide under the PT catalytic conditions as described in the experimental section. The proposed mechanism for the formation of **1** is represented in Scheme 3.

It is rational to consider that the reaction is initiated by the abstraction of a proton geminal to the chlorine atom from 1-chloro-2,3-epoxypropane with a hydroxide ion paired with the PT catalyst ammonium ion (Q^+OH^-). The carbanion **I** thus generated rearranges stereoselectively with ring-opening to the more stable and more nucleophilic alkoxide **II**,[4,23] which then reacts with another 1-chloro-2,3-epoxypropane molecule to afford **1**. Of course, the concerted route leading to **II** directly from proton abstraction can not be excluded. In the presence of alcohol, the hydroxide ion of Q^+OH^- gives mainly alkoxide, which further forms the alkyl 2,3-epoxy-1-propyl ethers by the nucleophilic substitution reaction.[16] However, in the absence of alcohol, owing to its poor nucleophilicity, the hydroxide ion acts as a base and gives a 1-chloro-2,3-epoxypropane anion **I** rather than 2,3-epoxy-1-propanol by the nucleophilic substitution reaction. This can be deduced from the fact that di-2,3-epoxypropyl ether was not detected (lower route in Scheme 3).

The above mechanism was supported by the formation of benzyl and 2-methylallyl *trans*-3-chloroallyl ethers (**2** and **3**) via the reaction of 1-chloro-2,3-epoxypropane in the presence of 2-methylallyl chloride or benzyl chloride, respectively (Table 1). The reaction of 1-chloro-2,3-epoxypropane with benzyl chloride (2 : 1 molar ratio) afforded **2** in 50% yield based on benzyl chloride together with **1** (22% based on 1-chloro-2,3-epoxypropane); reaction with 2-methylallyl chloride (2 : 1 molar ratio) gave **3** in 27% yield based on 2-methylallyl chloride together with **1** (15% based on 1-chloro-2,3-epoxypropane). Accordingly, this procedure using liquid-solid PT catalysis may lead to a general synthetic method for the preparation of *trans*-3-chloroallyl ethers.

This reaction did not proceed in the absence of PT catalyst, and the raw material, 1-chloro-2,3-epoxypropane, was recovered almost quantitatively.

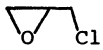
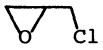
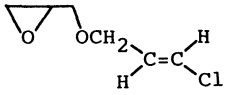
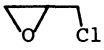
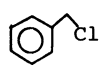
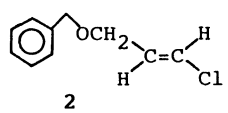
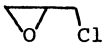
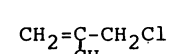
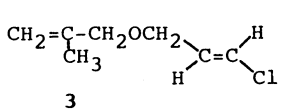
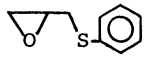
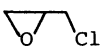
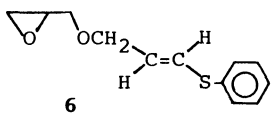
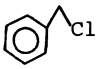
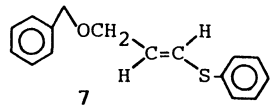
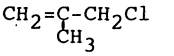
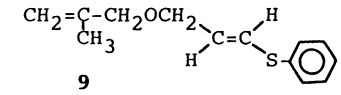
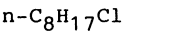
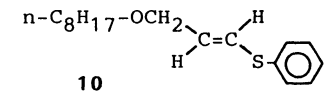
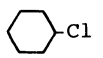
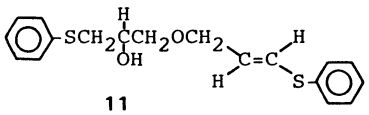
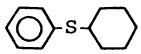
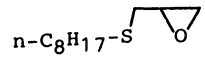
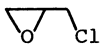
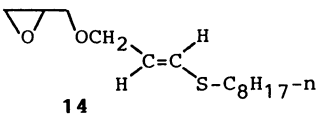
In the case of 1-bromo-2,3-epoxypropane, the corresponding *trans*-3-bromoallyl ether was obtained in low yield (about 6%) under the same PT catalytic conditions as those for 1-chloro-2,3-epoxypropane. The major product was light brownish powder which is probably a polymeric substance.

So far as we know, the direct synthesis of *trans*-3-chloroallyl ethers from 1-chloro-2,3-epoxypropane is not recorded in the literature. Although 1-chloro-2,3-epoxypropane is usually reactive to nucleophiles under basic conditions, di-2,3-epoxypropyl ether (**4**) could not be detected in the products of the present reactions. On the other hand, in a separate reaction, it was confirmed that 2,3-epoxy-1-propanol gives di-2,3-epoxypropyl ether (**4**) in 23% yield by the reaction with 1-chloro-2,3-epoxypropane under the same reaction conditions. From these facts, this reaction can be considered to reveal an interesting phenomenon based on the strong basicity and weak nucleophilicity of Q^+OH^-.

This epoxide ring-opening reaction was also applied to 2,3-epoxypropyl sulfide **5**, **13** affording the corresponding *trans*-3-thioallyl ethers. The results of the reaction of phenyl and alkyl 2,3-epoxypropyl sulfide with various chlorides are shown in Table 1.

Although the reaction conditions were not optimized, it is clear that the yield of *trans*-3-thioallyl ethers decreased with less reactive chlorides. The yield of the corresponding octyl ether **10** from octyl chloride was relatively low (22%) compared with more reactive chlorides, such as 2,3-epoxypropyl (**6**, 85%), 2-methylallyl (**9**, 80%) or benzyl chloride (**7**, 73%). Although the reactivity of benzyl chloride toward S_N2 reactions is usually

Table 1. Reactions of Epoxides with Organic Chlorides

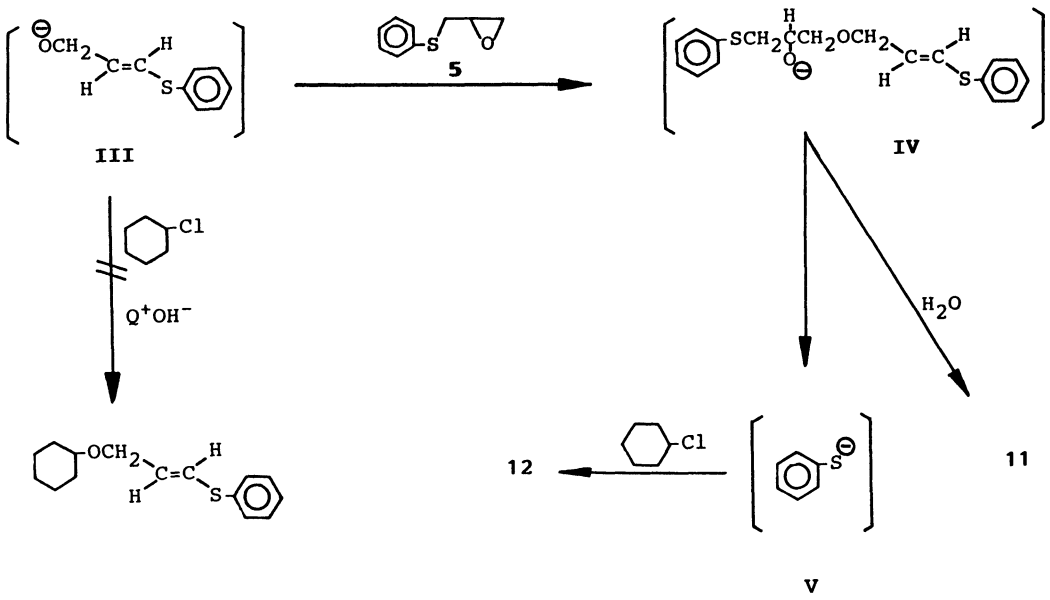
Starting Material		Time	Temp	Product	Yield[a]
Epoxide	Chloride	h	°C		%
		3	70	 **1**	38
		0.75	70	 **2**	50
		0.75	90	 **3**	27
 **5**		2	70	 **6**	85
5		2	90	 **7**	73
5		2	90	 **9**	80
5		2	100	 **10**	22
5		2	100	 **11**	20
				and  **12**	9
 **13**		2	90	 **14**	33

a) Isolated yield.

higher than that of 2-methylallyl chloride, the yield from the former was a little less than that from the latter. Apparently a competitive reaction occurred forming dibenzyl ether by the nucleophilic displacement to form benzyl alcohol under the PT catalytic alkaline conditions in the reaction using benzyl chloride. No noticeable competitive reaction occurred in the case of 2-methylallyl chloride.

In the case of a secondary chloride, cyclohexyl chloride, which has the poorest reactivity among the chlorides used, the major products obtained were *trans*-1,7-bis(phenylthio)-4-oxa-6-hepten-2-ol (**11**) and cyclohexyl phenyl sulfide (**12**) rather than the corresponding cyclohexyl *trans*-3-(octylthio)allyl ether.

It is difficult to deduce the reaction path to **12**, since the formation of the expected oxirane compound **6** or its derivatives has not been confirmed. However, from the fact that the reaction of **11** with cyclohexyl chloride in the presence of solid sodium hydroxide and PT catalyst afforded **12**, it may be reasonable to consider that the nucleophilic attack by certain species (including **III**) on **5** may give rise to the formation of a stable



Scheme 4.

benzenethiolate ion (**V**) and **6** (when **III** included) by the intramolecular displacement reaction. The resulting **V** then further reacts with cyclohexyl chloride to produce **12**, as proposed in Scheme 4.

In any reaction of 1-chloro-2,3-epoxypropane with phenyl 2,3-epoxypropyl ether, alkyl 2,3-epoxypropyl ether, 1,2-epoxytetradecane or *N*-benzyl-*N*-methyl-2,3-epoxypropylamine, the corresponding allyl ethers could not be obtained. In these cases, only *trans*-3-chloroallyl 2,3-epoxypropyl ether (**1**) was isolated, and the 2,3-epoxypropyl compounds were recovered almost quantitatively, although it has been reported that 1,2-epoxyalkane afforded the corresponding allylic alcohol by the reaction with butyllithium.[4)]

Experimental

^{1}H NMR spectra were recorded on a JEOL JNM-PS-100 instrument in $CDCl_3$ with Me_4Si as internal standard. ^{13}C NMR spectra were obtained on a JEOL JNM-FX-60S Fourier transform spectrometer operating at 15.04 MHz with $CDCl_3$ as solvent. Mass spectra were measured on a Hitachi RMU-6E spectrometer. Infrared spectra were obtained on a Hitachi 260-10 spectrometer.

The reagents were all of reagent grade and were used without further purification. Evaporative distillation was performed from bulb to bulb using a glass tube oven model GTO-250RS.

Preparation of *trans*-3-Chloroallyl 2,3-Epoxypropyl Ether (1): Into a solution of 1-chloro-2,3-epoxypropane (92.5 g, 1.0 mol) and tetrabutylammonium hydrogensulfate (8.3 g, 0.025 mol) in dioxane (50 ml), sodium hydroxide (32 g, 0.8 mol, pellet) was carefully added maintaining the temperature between 70—80 °C over a period of 30 min with efficient stirring. Stirring was continued for an additional 2.5 h at 70 °C. The solid material was removed by filtration through a short column filled with silica gel. Product **1** was isolated by fractional distillation at reduced pressure as a colorless oil, 28.2 g, yield 38%; bp 110—111 °C/30 Torr (1 Torr= 133.322 Pa). The purity of the product was ascertained by GLC (5% Silicone SE-30 on Celite 545, 1m) as one peak. ^{1}H NMR ($CDCl_3$) δ=2.50—2.70 (m, 1H), 2.70—2.85 (m, 1H), 3.00—3.25 (m, 1H), 3.30—3.50 (m, 1H), 3.64—3.90 (m, 1H), 3.95—4.15 (d, 2H), 5.90—6.15 (m, J=14 Hz, 1H), 6.20—6.40 (m, J=14 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ=43.0, 50.0, 68.4, 70.4, 120.0, 129.5; MS *m/z* (rel intensity) 148 (M^+), 91 (65), 75 (100), 57 (78), 39 (47), 31 (45), 29 (63); IR (liquid film) 2875, 1640, 1110, 930, 800 cm^{-1}. Found: C, 48.51; H, 6.20; Cl, 23.58%. Calcd for $C_6H_9ClO_2$: C, 48.50; H, 6.10; Cl, 23.86%.

Alternative Synthesis of 1 as a Mixture with 1′: Into a Mixture of 1,3-dichloropropene (about 34% cis, 66% trans estimated by ^{1}H NMR) (7.7 g, 0.07 mol), sodium hydroxide (6 g, 0.15 mol, pellet), tetrabutylammonium hydrogensulfate (0.85 g, 0.0025 mol) in dioxane (15 ml), 2,3-epoxy-1-propanol (3.7 g, 0.05 mol) was added dropwise at 30 °C, and stirred at 40 °C for 2 h. After the workup, the mixture of **1** and **1′** was isolated by Kugelrohr distillation at reduced pressure as a colorless oil, 3.9 g, yield 53%; bp 110 °C/30 Torr. The spectral data are the same as **1** expect for ^{1}H NMR ($CDCl_3$) δ=3.90—4.10 (d, 1.2H, *trans*-OCH_2CH=$CHCl$, 70%), 4.10—4.30 (m, 0.8H, *cis*-OCH_2CH=$CHCl$, 30%).

***trans*-3-Chloroallyl Benzyl Ether (2):** A mixture of benzyl chloride (12.7 g, 0.1 mol) and 1-chloro-2,3-epoxypropane (18.4 g, 0.2 mol) was treated with sodium hydroxide under the PT catalytic conditions similar to the procedure for **1**. After the workup, compound **2** was isolated as a colorless oil by distillation at reduced pressure, 9.1 g, yield 50%, together with **1** (3.3 g, 22%); bp 55—56 °C/0.08 Torr. ^{1}H NMR ($CDCl_3$) δ=3.90—4.08 (d, 2H), 4.50 (s, 2H), 5.90—6.20 (m, J=14 Hz, 1H), 6.20—6.36 (d, J=14 Hz, 1H), 7.32 (s, H); MS *m/z* (rel intensity) 182 (M^+), 92 (48), 91 (100), 79 (12), 77 (12), 65 (10); IR (liquid film) 2850, 1640, 1450, 1350, 1110, 930, 800, 730, 700 cm^{-1}. Found: C, 65.72; H, 6.23; Cl, 19,13%. Calcd for $C_{10}H_{11}ClO$: C, 65.78; H, 6.07; Cl, 19.41%.

***trans*-3-Chloroallyl 2-Methylallyl Ether (3):** By the same procedure as used for the benzyl ether **2**, the 2-methylallyl ether **3** was obtained as a colorless oil in 27% yield (4.0 g) together with **1** (2.2 g, 15%) from the reaction of 2-methylallyl chloride (9 g, 0.1 mol) and 1-chloro-2,3-

epoxypropane (18.4 g, 0.2 mol); bp 75—76 °C/30 Torr. ^{1}H NMR ($CDCl_3$) δ=1.74 (s, 3H), 3.85—4.04 (t, 4H), 4.84—5.00 (m, 2H), 5.90—6.15 (m, J=14 Hz, 1H), 6.15—6.35 (d, J=14 Hz, 1H); MS m/z (rel intensity) 146 (M^+), 75 (100), 56 (56), 55 (93), 43 (59), 41 (85), 39 (89); IR (liquid film) 2925, 2860, 1642, 1450, 1120 cm^{-1}. Found: C, 56,98; H, 7.72; Cl, 23.91%. Calcd for $C_7H_{11}ClO$: C, 57.38; H, 7.56; Cl, 24.21%.

Di-2,3-epoxypropyl Ether (4): Into a mixture of 1-chloro-2,3-epoxypropane (13.8 g, 0.15 mol), tetrabutylammonium hydrogensulfate (0.85 g, 5% based on 2,3-epoxy-1-propanol) and potassium hydroxide (5.6 g, 0.1 mol, pellet), 2,3-epoxy-1-propanol (3.7 g, 0.05 mol) was added at 40 °C over 30 min with rapid stirring. Stirring was continued for an additional 30 min at 40 °C. The solid material was removed by filtration. Compound **4** was isolated by Kugelrohr distillation at reduced pressure as a colorless liquid, 1.5 g, yield 23%; bp 100 °C/30 Torr. ^{1}H NMR ($CDCl_3$) δ=2.54—2.70 (m, 2H), 2.70—2.90 (m, 2H), 3.04—3.28 (m, 2H), 3.28—3.60 (m, 2H), 3.70—4.00 (m, 2H); MS m/z (rel intensity) 130 (M^+), 57 (66), 31 (72), 29 (100); IR (liquid film) 2950, 1280, 1120, 940, 880, 780 cm^{-1}.

Phenyl 2,3-Epoxypropyl Sulfide (5): Benzenethiol (11 g, 0.1 mol) in dioxane (50 ml) was added to a suspension of 1-chloro-2,3-epoxypropane (27.7 g, 0.3 mol), sodium hydroxide (12 g, 0.3 mol, pellet) in dioxane (50 ml) at room temperature over 20 min with stirring. Stirring was continued for another 4 h. The solid material was removed by filtration, and compound **5** was isolated by Kugelrohr distillation at reduced pressure as a colorless liquid, 16.2 g, yield 98%; bp 90 °C/0.02 Torr. ^{1}H NMR ($CDCl_3$) δ=2.40—2.56 (m, 1H), 2.65—3.25 (m, 4H), 7.16—7.50 (m, 5H); MS m/z (rel intensity) 166 (M^+), 123 (50), 110 (100). Found: C, 64.66; H, 6.09; S, 19.44%. Calcd for $C_9H_{10}OS$: C, 65.03; H, 6.06; S, 19.28%.

Preparation of *trans*-1-Phenylthio-6,7-epoxy-4-oxahept-1-ene (6): A suspension of phenyl 2,3-epoxypropyl sulfide (**5**) (8.3 g, 0.05 mol), 1-chloro-2,3-epoxypropane (9.2 g, 0.1 mol), sodium hydroxide (6.0 g, 0.15 mol, pellet) and tetrabutylammonium hydrogensulfate (0.85 g, 5% based on **5**) in dioxane (20 ml) was stirred rapidly at 70 °C for 2 h. After separation of the solid material by filtration, compound **6** was isolated by Kugelrohr distillation at reduced pressure as a colorless oil, 9.4 g, yield 85%; bp 100 °C/0.05 Torr. ^{1}H NMR ($CDCl_3$) δ=2.52—2.70 (m, 1H), 2.70—2.85 (m, 1H), 3.00—3.24 (m, 1H), 3.24—3.36 (m, 1H), 3.36—3.88 (m, 1H), 3.88—4.40 (m, 2H), 5.68—6.10 (m, J=15 Hz, 1H), 6.30—6.56 (m, J=15 Hz, 1H), 7.10—7.50 (m, 5H); MS m/z (rel intensity) 222 (M^+), 113 (100), 57 (100); IR (liquid film) 2900, 1650, 1580, 1475, 1430, 1100, 640, 580 cm^{-1}. Found: C, 64.48; H, 6.39; S, 14.17%. Calcd for $C_{12}H_{14}O_2S$: C, 64.84; H, 6.35; S, 14.42%.

Compound **1** was also obtained in yield of 24% (1.7 g).

***trans*-1-Phenyl-5-phenylthio-2-oxapent-4-ene (7):** A mixture of **5** (8.3 g, 0.05 mol) and benzyl chloride (12.6 g, 0.1 mol) was treated with sodium hydroxide under the PT catalytic conditions in dioxane similar to the procedure for **6** at 90 °C for 2 h. After the workup, product **7** was isolated by Kugelrohr distillation at reduced pressure as a colorless liquid, 9.0 g, yield 73%; bp 135 °C/0.03 Torr. ^{1}H NMR ($CDCl_3$) δ=3.95—4.25 (m, 2H), 4.48 (s, 2H), 5.70—6.04 (m, J=15 Hz, 1H), 6.30—6.62 (m, J=15 Hz, 1H), 7.28 (s, 10H); MS m/z (rel intensity) 256 (M^+), 165 (30), 137 (50), 91 (100); IR (liquid film) 3050, 2860, 1600, 1500, 1120, 760, 720 cm^{-1}. Found: C, 74.67; H, 6.55; S, 12.52%. Calcd for $C_{16}H_{16}OS$: C, 74.96; H, 6.29; S, 12.51%.

In this reaction, dibenzyl ether **8** was also obtained as a by-product in 62% yield (6.3 g) based on benzyl chloride (0.1 mol).

***trans*-6-Methyl-1-phenylthio-4-oxahept-1,6-diene (9):** By the same procedure as used for **6**, the corresponding compound **9** was obtained in 80% yield (8.8 g) from phenyl 2,3-epoxypropyl sulfide (8.3 g, 0.05 mol) and 2-methylallyl chloride (9.05 g, 0.1 mol); bp 100 °C/0.02 Torr. ^{1}H NMR ($CDCl_3$) δ=1.76 (s, 3H), 3.60—4.24 (m, 4H), 4.90—5.10 (m, 2H), 5.75—6.10 (m, J=15 Hz, 1H), 6.30—6.56 (m, J=15 Hz, 1H), 7.10—7.50 (m, 5H); MS m/z (rel intensity) 220 (M^+), 111 (42), 109 (33), 55 (100); IR (liquid film) 2900, 1670, 1600, 1120, 910, 750, 700 cm^{-1}. Found: C, 70.62; H, 7.40; S, 14.34%. Calcd for $C_{13}H_{16}OS$: C, 70.87; H, 7.32; S, 14.45%.

***trans*-1-Phenylthio-4-oxadodec-1-ene (10):** By the same procedure as used for **6**, the corresponding compound **10** was obtained in 22% yield (3.1 g) from phenyl 2,3-epoxypropyl sulfide (8.3 g, 0.05 mol) and octyl chloride (14.9 g, 0.1 mol); bp 120 °C/0.05 Torr. ^{1}H NMR ($CDCl_3$) δ=0.80—1.04 (t, 3H), 1.20—1.80 (m, 12H), 3.36—3.60 (m, 2H), 3.95—4.26 (m, 2H), 5.75—6.08 (m, J=15 Hz, 1H), 6.34—6.60 (m, J=15 Hz, 1H), 7.20—7.50 (m, 5H); MS m/z (rel intensity) 278 (M^+), 169 (28), 71 (45), 57 (100); IR (liquid film) 2950, 2875, 1590, 1480, 1100, 740, 700 cm^{-1}.

***trans*-1,7-Bis(phenylthio)-4-oxa-6-hepten-2-ol (11):** After treating phenyl 2,3-epoxypropyl sulfide (8.3 g, 0.05 mol) with cyclohexyl chloride (11.8 g, 0.1 mol) at 100 °C for 2 h under PT catalytic conditions, solid materials were removed by filtration through a short column filled with silica gel, and the reaction mixture was separated by Kugelrohr distillation at reduced pressure. Compound **11** as a colorless oil, 1.7 g, yield 20%; bp 180 °C/0.05 Torr, and phenyl cyclohexyl sulfide (**12**) as a colorless liquid, 0.85 g, yield 9%; bp 60 °C/0.05 Torr, were isolated respectively. Spectral analysis for **11**: ^{1}H NMR ($CDCl_3$) δ=2.80—3.10 (m, 3H), 3.40—3.70 (m, 2H), 3.70—4.10 (m, 2H), 4.10—4.30 (m, 1H), 5.70—6.00 (m, J=15 Hz, 1H), 6.30-6.50 (m, J=15 Hz, 1H), 7.10—7.60 (m, 10H); MS m/z (rel intensity) 332 (M^+), 167 (100), 149 (83), 123 (100); IR (liquid film) 3500, 2900, 1600, 1500, 1460, 1100, 1040, 760, 700 cm^{-1}. Found: C, 64.66; H, 6.09; S, 19.02%. Calcd for $C_{18}H_{20}O_2S_2$: C, 65.03; H, 6.06; S, 19.29%. Spectral analysis for **12**: ^{1}H NMR ($CDCl_3$) δ=1.00—2.10 (m, 10H), 3.00—3.20 (m, 1H), 7.10—7.60 (m, 5H); MS m/z (rel intensity) 192 (M^+), 110 (100), 55 (24). IR (liquid film) 2975, 1600, 1460, 700 cm^{-1}.

Octyl 2,3-Epoxypropyl Sulfide (13): The experimental procedure was similar to the preparation of **5** under the reaction conditions of 50 °C for 3 h. Yield 84%; bp 80 °C/0.03 Torr. ^{1}H NMR ($CDCl_3$) δ=0.80—1.00 (t, 3H), 1.16—1.80 (m, 12H), 2.50—2.90 (m, 6H), 3.00—3.24 (m, 1H); MS m/z (rel intensity) 202 (M^+), 146 (70), 112 (100), 84 (65), 83 (70), 70 (86), 69 (65), 56 (86), 55 (70); IR (liquid film) 2950, 1470, 840 cm^{-1}. Found: C, 65.10; H, 10.94; S, 15.59%. Calcd for $C_{11}H_{22}OS$: C, 65.29; H, 10.96; S, 15.84%.

***trans*-1,2-Epoxy-4-oxa-8-thiohexadec-6-ene (14):** The reaction conditions were similar to those for **6**. Yield 33%; bp 100 °C/0.05 Torr. ^{1}H NMR ($CDCl_3$) δ=0.76—1.04 (t, 3H), 1.16—1.86 (m, 12H), 2.30—2.86 (m, 4H), 3.00—3.80 (m, 3H), 3.96—4.20 (m, 2H), 5.42—5.76 (m, J=15 Hz, 1H), 6.04—6.40 (m, J=15 Hz, 1H); MS m/z (rel intensity) 258 (M^+), 145 (55), 113 (100), 57 (100), 55 (73), 31 (68); IR (liquid film) 2950, 1620, 1470, 1120, 950, 860 cm^{-1}.

Compound **1** was also obtained in 14% yield based on 1-chloro-2,3-epoxypropane.

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