Selective Formation of α-Cleavage Cycloadduct of Oxirane with Heterocumulene Promoted by High-Coordinated Trialkyltin Complexes

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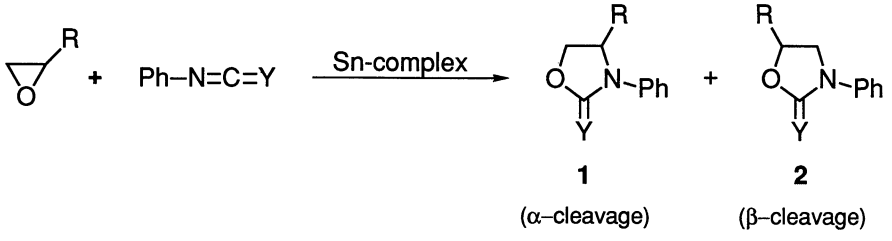
In the reaction of monosubstituted oxiranes and heterocumulenes, trialkyltin iodides coordinated by phosphine oxides effectively catalyzed the formation of heterocycles via cleavage at the substituted site in the oxirane ring, while other types of organotin complexes or noncomplexed organotin iodides promoted selective cleavage at the opposite site. A mechanistic investigation demonstrated that the coordination of phosphine oxide promotes the reverse reaction of the oxirane-ring cleavage leading to the predominant formation of α-cleavage cycloadducts.

Although the cycloaddition of monosubstituted oxiranes with heterocumulenes has been a useful method for the synthesis of five-membered heterocycles,[1-6] most reactions were reported to proceed via the cleavage of oxiranes at their nonsubstituted site (β-cleavage).[7,8] The change of the regioselectivity of oxirane-ring cleavage from β-cleavage to α-cleavage (cleavage at the substituted site) is a simple and useful tool to increase the scope of cycloaddition of oxiranes with heterocumulenes. Although many regioselective cleavages were reported in the reaction of oxiranes with nucleophiles, the effective change in cycloaddition reactions with nucleophiles has rarely been reported.[9,10] We recently reported that tetraphenylstibonium iodide was a versatile catalyst for the selective α-cleavage cycloaddition of general monosubstituted oxiranes.[11] However, the activity of this catalyst is highly dependent on the substrates used; for example, 1,2-epoxy-3-chloropropane and sulfur-containing heterocumulenes were not reactive at all. On the other hand, although some organotin halide complexes were briefly reported to catalyze β-cleavage cycloaddition, their activity and structures vary in accordance with the combination of tin halides with ligands.[12-19] These results and the high affinity of tin for sulfur compounds[20-24] prompted us to investigate a selective α-cleavage cycloaddition of oxiranes to heterocumulenes including isothiocyanates by means of complexation of organotin iodides.[25]

In this paper, we wish to report the regio-controlled cycloaddition of monosubstituted oxiranes with heterocumulenes such as isocyanates, carbodiimides and isothiocyanates. The direction of oxirane-ring cleavage is strongly dependent on the complexation mode. Trialkyltin iodides coordinated by phosphine oxides promoted α-cleavage cycloaddition, yielding 3,4-disubstituted five-membered heterocycles. On the other hand, the complex of Bu_2SnI_2 and noncomplexed organotin iodide resulted in a selective β-cleavage cycloaddition. A plausible reaction path is explainable in terms of an equilibrium in the oxirane cleavage step. The effect of complexation was demonstrated by using an intermediary adduct, while no such adduct could be detected in the Ph_4SbI catalyst system though a similar reaction path has been proposed.[26]

Results and Discussion

Cycloaddition with Isocyanates and Carbodiimides. Table 1 lists the results of cycloadditions of monosubstituted oxiranes with carbodiimides or isocyanates, noncomplexed Bu_3SnI catalyzed the selective β-cleavage addition (Entry 1). For α-cleavage addition, the addition of bases was indispensable, and the complexes



1 (α–cleavage) **2** (β–cleavage)

	Y	R
a	N-Ph	Me
b	N-Ph	Et
c	N-Ph	Ph
d	N-Ph	CH_2OPh
e	N-Ph	CH_2Cl

	Y	R
f	N-Bu^n	Et
g	O	Me
h	O	Et
i	O	*n*-Hex
j	O	Ph

Scheme 1.

Table 1. Cycloaddition of Monosubstituted Oxirane with Carbodiimide and Isocyanate

Entry	R	Y	Sn	Base (ratio)[a]	Time/h	Yield/%	1/2
1	Et	*N*-Ph	*n*-Bu_3SnI	—	12	82	0/100
2	Et	*N*-Ph	*n*-Bu_3SnI	*n*-Bu_3PO (1/1)	9	88	71/29
3	Et	*N*-Ph	*n*-Bu_3SnI	Et_3N (1/1)	4	79	31/69
4	Et	*N*-Ph	*n*-Bu_3SnI	*n*-Bu_3P (1/1)	5	83	55/45
5	Et	*N*-Ph	*n*-Bu_2SnI_2	*n*-Bu_3P (1/1)	1	100	41/59
6	Et	*N*-Ph	*n*-Bu_2SnI_2	Ph_3P (1/1)	1	92	0/100
7	Et	*N*-Ph	*n*-Bu_3SnCl	*n*-Bu_3PO (1/1)	36	16	0/100
8	Et	*N*-Ph	*n*-Bu_3SnI	*n*-Bu_3PO (10/1)	14	100	82/18
9	Et	*N*-Ph	*n*-Bu_3SnI	HMPA (50/1)[c]	36	61	91/9
10	Et	*N*-Ph	Me_3SnI	HMPA (50/1)[c]	10	97	89/11
11	Me	*N*-Ph	*n*-Bu_3SnI[b]	*n*-Bu_3PO (1/1)	1.5	73	82/18
12	Ph	*N*-Ph	Me_3SnI	HMPA (1/1)	23	75	94/6
13	CH_2OPh	*N*-Ph	*n*-Bu_3SnI	HMPA (50/1)[c]	29	66	73/27
14	CH_2Cl	*N*-Ph	*n*-Bu_3SnI[b]	*n*-Bu_3PO (1/1)	3	70	55/45
15	Et	*N*-Bu^n	*n*-Bu_3SnI[b]	*n*-Bu_3PO (1/1)	24	57	65/35
16	Et	O	*n*-Bu_3SnI	HMPA (50/1)[c]	2	93	24/76
17	Et	O	*n*-Bu_3SnI[b]	*n*-Bu_3PO (1/1)	1	97	62/38
18	Me	O	*n*-Bu_3SnI[b]	*n*-Bu_3PO (1/1)	1	93	46/54
19	*n*-Hex	O	*n*-Bu_3SnI[b]	*n*-Bu_3PO (1/1)	1	99	66/34
20	Ph	O	*n*-Bu_3SnI	HMPA (50/1)[c]	2	81	90/10

Sn-complex/NCY/oxirane=0.2/2/20 mmol, 50°C. a) Base/Sn ratio. b) 2 mmol. c) Sn/HMPA/NCY/oxirane=0.2/10/2/4 mmol.

investigated were the combination of tributyltin iodide and phosphine oxides such as tributylphosphine oxide and hexamethylphosphoric triamide (HMPA). These complexes predominantly gave 3,4-disubstituted oxazolidines **1** which have been obtained in small amounts by the action of conventional catalysts such as Lewis bases (triethylamine[27] and sodium ethoxide[10]), -acids ($AlCl_3$[10] and LiCl[28]) and tetraalkylammonium halides.[29,30] Moreover, the use of excess amounts of phosphine oxides gave a higher selectivity of **1** (91%), although a longer reaction time was required (Entry 9). This problem was overcome by the use of Me_3SnI (which is more active due to its high acidity) instead of Bu_3SnI (89% selectivity, Entry 10). However, the α-cleavage ability enhanced by the addition of bases, could not be explained in terms of Lewis acidity since a stronger Lewis acid, noncomplexed Bu_3SnI, is considered to cleave an oxirane ring more easily at the substituted site.[10] The formation of **1** in the case of (chloromethyl)oxirane (Entry 14) is particularly noteworthy since even the versatile catalyst Ph_4SbI could not produce it at all.

The above results strongly suggest that the complexation mode and the stability of the resulting complexes are responsible for the regio-control of oxazolidine formation. It was reported that phosphine oxides coordinate to tributyltin iodide to form five-coordinated complexes, while they form six-coordinated complexes with dibutyltin diiodide.[31-34] It is interesting that the former showed the opposite regioselectivity of the latter. The stability of the complexes also seems to be important for α-cleavage cycloaddition, since if the complexes dissociate to the original tributyltin iodide and ligands, the resulting free tributyltin iodide would promote the β-cleavage of oxiranes. Tributylphosphine oxide and HMPA are superior to either tributylphospine or triethylamine due to the higher coordination ability toward tin atoms.[35] Moreover, excess amounts of phosphine oxides disturb the dissociation of complexes, although the interaction between oxiranes and tin complexes would be weakened to reduce reactivity.

The addition of isocyanates to oxiranes was less selective than carbodiimides and suffered from the requirement of an equimolar amount of tributyltin iodide (Entries 17—19). Isocyanates perhaps were so active that catalytic control could not be enhanced.

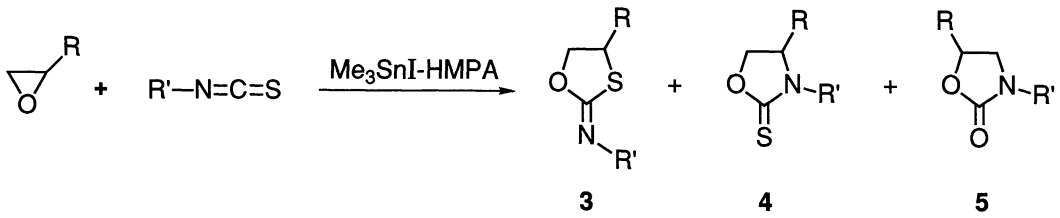
Cycloaddition of Oxirane with Isothiocyanate. The lower electrophilicity and high affinity for tin atoms prompted us to use isothiocyanates instead of carbodiimides in the cycloaddition reactions. Results are shown in Table 2. The catalyst, an Me_3SnI–HMPA system, effected a regioselective cycloaddition to give 4-substituted 2-imino-1,3-oxathiolane **3** and 3,4-disubstituted 1,3-oxazolidine-2-thione **4**. This result was very interesting since other organotin halide complexes gave β-cleavage cycloadducts, as previously reported.[7] Moreover, a large excess of HMPA was not required as was the case with the carbodiimides.

The fact that no consumption of **3** was observed under

Table 2. Catalytic Cycloaddition of Monosubstituted Oxiranes with Isothiocyanates

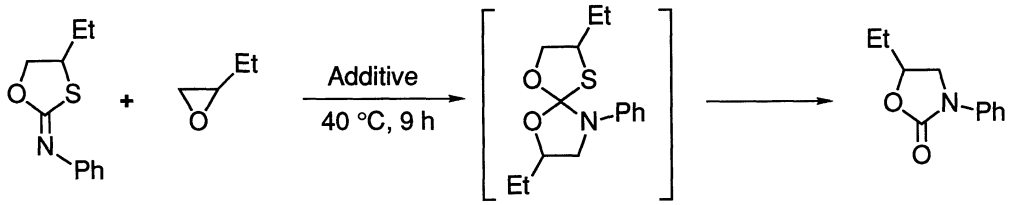
Entry	R	R′	Time/h	**3** (%)	**4** (%)	**5** (%)
1	Me	Ph	5	78	14	7
2	Et	Ph	10	56	19	5
3	Ph	Ph	5	59	18	Trace
4	Et	Me	30	16	0	51

Me_3SnI/HMPA/oxirane/NCS=0.2/0.6/10/2 mmol.



	R	R'
a	Me	Ph
b	Et	Ph
c	Ph	Ph
d	Et	Me

Scheme 2.



Me_3SnI	17 %
Me_3SnI-HMPA (1/3)	0
$AlCl_3$ (0.3 h)	86

Scheme 3.

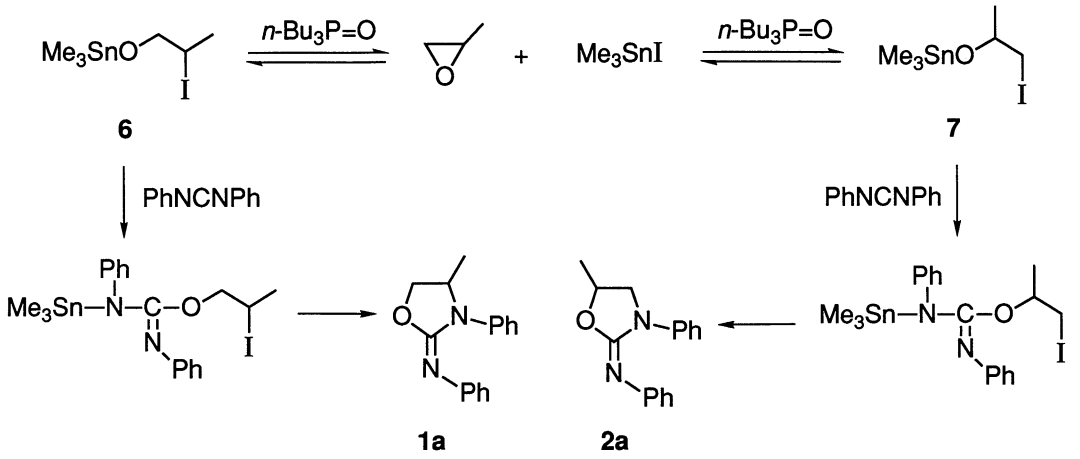
the same conditions as those used for the cycloaddition showed that there was no rearrangement of **3** to **4**.

In this type of cycloaddition, a desulfurization has often been reported,[7] which is assumed to be caused by the addition of oxirane to **3**, producing oxazolidinones **5** as depicted in Scheme 3. Consequently, the 3,5-disubstituted oxazolidinones **5** would probably not be produced via a β-cleavage of the oxirane ring. This type of rearrangement was confirmed as follows. Strong Lewis acids such as $AlCl_3$ readily caused this transformation in an 86% yield, while no oxazolidinone formation was promoted by the Me_3SnI complex. This result may be ascribed to the low acidity of Me_3SnI coordinated by HMPA. Although methyl isothiocyanate gave **5** in a 51% yield, this side reaction was observed only minimally with the addition of phenyl isothiocyanate.

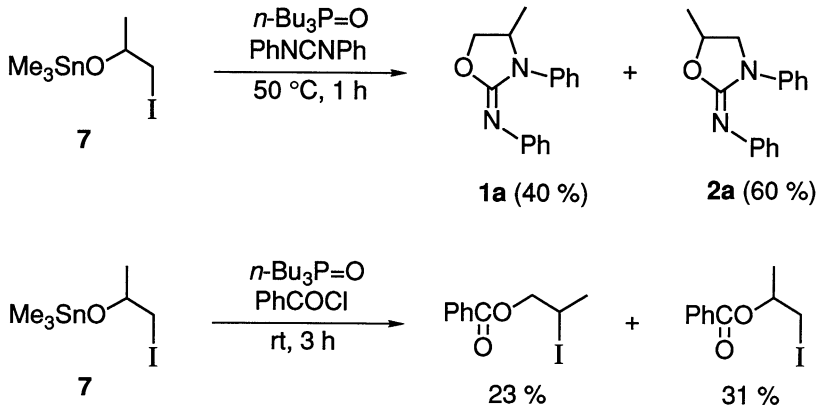
Reaction Mechanism. The reaction path way to 3,4- and 3,5-disubstituted five-membered heterocycles is illustrated in Scheme 4 and is exemplified by the addition of methyloxirane to diphenylcarbodiimide.

The first step, cleavage of the oxirane ring, appears to be a key step for regio-control of this addition. The cleavage of methyloxirane by trimethyltin iodide (Me_3SnI) in the presence of $Bu_3P{=}O$ proceeded readily at room temperature. However, the identification of the resulting adducts and the ratio of **6** and **7** could not be determined by NMR, though the predominant formation of **7** was indicated. This result suggested that the predominant formation of the α-cleavage adduct was not due to the selective α-cleavage of oxiranes at the first step. On the other hand, in the absence of $Bu_3P{=}O$, the addition of Me_3SnI to methyloxirane was exothermic and resulted in the quantitative formation of a distillable trimethyltin 2-iodopropoxide, and the resulting propoxide was added to diphenylcarbodiimide, forming **2a** quantitatively when reacted at 50 °C for 1 h. This selective formation of **2a** indicates that methyloxirane would be cleaved at the β-site to give **7**. On the other hand, surprisingly, in the presence of $Bu_3P{=}O$, this propoxide **7** gave **1a** in a 40% yield together with **2a** (60%) as shown in Scheme 5. This result seemed to suppose the transformation of the 3,5-disubstituted product by the complex $Bu_3P{=}O$ and Me_3SnI, but this idea was proved false by the fact that no consumption of **2a** by the complex was observed even under far more drastic conditions (80 °C, 3 h). A similar result was observed in the reaction with benzoyl chloride (Scheme 5).

Next, the transformation of 2-iodoisopropoxide **7** to 2-iodoisopropoxide **6** will be considered. The isolation of **6** from the mixture of **7** and $Bu_3P{=}O$ was attempted. The distillation of the adduct, however, was failed, and methyloxirane was regenerated in a 78% yield. The methyloxirane was thought to be generated from **7** by the



Scheme 4.



Scheme 5.

action of $Bu_3P{=}O$ during distillation. This result strongly suggested that facile equilibrium between **7** and the starting substrates was promoted by $Bu_3P{=}O$. Moreover, although the oxirane ring is subject to cleavage at the β-site even in the presence of $Bu_3P{=}O$, the participation of **6** is apparently plausible from the results shown in Scheme 5 in spite of the lack of visual evidence such as NMR spectra.

On the basis of the above results, the reaction mechanism for the predominant formation of 3,4-disubstituted cycloadducts can be explainable in terms of the equilibrium of the addition of oxirane and Me_3SnI as shown in Scheme 4. At first, the cleavage of oxirane results in the formation of **6** and **7**. Diphenylcarbodiimide adds electrophilically to both tin iodoalkoxides, where the alkoxide **6** would preferentially react because of the higher reactivity of a primary alkoxide over a secondary one (**7**). The addition is followed by the cyclization into 3,4-disubstituted oxazolidine **1a**. In the presence of $Bu_3P{=}O$, a facile transformation of **7** to **6** leads to the predominant formation of **1a**. The coordination of bases accelerates the addition of heterocumulenes to tin ω-haloalkoxides as already reported.[7,16,36-39] On the other hand, an isocyanate, a higher reactive heterocumulene, can readily react even with the secondary alkoxide **7**, and the selective formation of 3,4-disubstituted oxazolidinones is difficult. The lower electrophilicity of isothiocyanate, of course, results in a selective α-cleavage cycloaddition.

Conclusion

The complexes of organotin iodides with Lewis bases controlled the regiospecific addition of monosubstituted oxirane to heterocumulenes. The coordination of appropriate bases has some notable potentials: Activation of the addition, specification of the regioselectivity, and limitation of side reactions.

Experimental

Apparatus and Materials. Melting points are uncorrected. IR spectra were recorded on a Hitachi 260-30 spectrophotometer. ^1H NMR and ^{13}C NMR spectra were measured on a Hitachi R-90H or a JEOL JNM-GSX-400 spectrometer. Mass spectra were obtained with a JEOL JMS-DS303

spectrometer. Microanalyses were recorded on a JEOL JMS-DX303 spectrometer (data software processing, JMS-DA 5000). Analytical GLC was performed on a Shimadzu GC-8A using a 2 m×3 mm glass column packed with Silicone OV-1 on Uniport HP (5%, 60—80 mesh). Short-path distillations of products were carried out in a Kugelrohr apparatus.

All oxiranes were freshly distilled from CaH_2. All Lewis bases were purified by general procedures. Isothiocyanates and PhNCO were obtained from commercial sources and used without further purification. PhNCNPh,[40] BuNCNPh,[41] and organotin iodides[42,43] were prepared according to the described methods.

Reaction of Oxirane with Carbodiimide. Diphenylcarbodiimide (2 mmol) was added to a solution of Me_3SnI (2 mmol) and Bu_3PO (2 mmol) in ethyloxirane (20 mmol) under dry nitrogen. The mixture was stirred at 50 °C until the infrared absorption of N=C=N (2150 cm^{-1}) disappeared, and the yields of **1b** (82%) and **2b** (18%) were determined by GLC. The products were isolated by column chromatography on silica gel, giving **1b** (eluted by chloroform; 399 mg, 75%) and **2b** (eluted by benzene; 69 mg, 13%).

4-Methyl-3-phenyl-2-phenylimino-1,3-oxazolidine (1a):[11] Mp 89 °C; IR (KBr) 1680 cm^{-1} (C=N).

5-Methyl-3-phenyl-2-phenylimino-1,3-oxazolidine (2a):[44] Mp 72—73 °C; IR (KBr) 1670 cm^{-1} (C=N); ^1H NMR ($CDCl_3$) δ=1.45 (3H, d, J=6.0 Hz), 3.55 (1H, dd, J=7.0 and 8.0 Hz), 4.05 (1H, t, J=8.0 Hz), 4.50—4.90 (1H, m), and 6.90—7.80 (10H, m); MS m/z 252 (M^+).

4-Ethyl-3-phenyl-2-phenylimino-1,3-oxazolidine (1b): Bp 200 °C/0.01 mmHg (1 mmHg=133.322 Pa); IR 1680 cm^{-1} (C=N); ^1H NMR ($CDCl_3$) δ=0.92 (3H, t, J=6.9 Hz), 1.40—1.97 (2H, m), 3.90—4.58 (3H, m), and 6.57—7.97 (10H, m); ^{13}C NMR ($CDCl_3$) δ=8.41 (q), 24.51 (t), 58.42 (d), 68.60 (t), 122.14 (d), 122.45 (d), 123.30 (d), 124.15 (d), 128.36 (d), 128.85 (d), 138.31 (s), 146.72 (s), and 147.45 (s); MS m/z 266 (M^+). Found: C, 76.53; H, 6.87; N, 10.50%. Calcd for $C_{17}H_{18}ON_2$: C, 76.67; H, 6.81; N, 10.52%.

5-Ethyl-3-phenyl-2-phenylimino-1,3-oxazolidine (2b): Bp 170 °C/0.01 mmHg; IR 1680 cm^{-1} (C=N); ^1H NMR ($CDCl_3$) δ=0.97 (3H, t, J=6.8 Hz), 1.35—1.95 (2H, m), 3.52 (1H, dd, J=6.8 and 8.1 Hz), 3.92 (1H, t, J=8.1 Hz), 4.15—4.70 (1H, m), and 6.60—8.23 (10H, m); ^{13}C NMR ($CDCl_3$) δ=8.78 (q), 27.44 (t), 50.74 (t), 76.16 (d), 119.34 (d), 122.82 (d), 123.30 (d), 124.03 (d), 129.03 (d), 139.34 (d), 140.44 (s), 148.05 (s), and 148.79 (s); MS m/z 266 (M^+). Found: C, 76.75; H, 6.72; N, 10.51%. Calcd for $C_{17}H_{18}ON_2$: C, 76.67; H, 6.81; N, 10.52%.

3,4-Diphenyl-2-phenylimino-1,3-oxazolidine (1c):[11] Mp 122 °C; IR (KBr) 1680 cm^{-1} (C=N).

3,5-Diphenyl-2-phenylimino-1,3-oxazolidine (2c):[11] Mp 111—113 °C; IR (KBr) 1680 cm^{-1} (C=N).

4-Phenoxymethyl-3-phenyl-2-phenylimino-1,3-oxazolidine (1d): Mp 77—79 °C; IR (KBr) 1675 cm^{-1} (C=N); ^1H NMR ($CDCl_3$) δ=3.83—4.27 (2H, m), 4.27—4.86 (3H, m), and 6.32—7.85 (15H, m); ^{13}C NMR ($CDCl_3$) δ=56.86 (d), 66.16 (t), 67.44 (t), 114.49 (d), 121.50 (d), 122.11 (d), 122.32 (d), 123.24 (d), 124.46 (d), 128.36 (d), 129.03 (d), 129.46 (d), 138.12 (s), 147.17 (s), 149.74 (s), and 157.97 (s); MS m/z 344 (M^+). Found: C, 76.59; H, 5.71; N, 8.29%. Calcd for $C_{22}H_{20}O_2N_2$: C, 76.72; H, 5.85; N, 8.31%.

5-Phenoxymethyl-3-phenyl-2-phenylimino-1,3-oxazolidine (2d): Mp 105—106 °C; IR (KBr) 1690 cm^{-1} (C=N); ^1H NMR ($CDCl_3$) δ=3.70—4.01 (4H, m), 4.48—4.81 (1H, m), and 6.64—8.10 (15H, m); ^{13}C NMR ($CDCl_3$) δ=48.52 (t), 67.92 (t), 72.79 (d), 114.81 (d), 118.83 (d), 121.70 (d), 122.43 (d), 122.98 (d), 123.41 (d), 128.53 (d), 128.83 (d), 129.63 (d), 139.69 (s), 147.19 (s), 148.19 (s), and 158.16 (s); MS m/z 344 (M^+). Found: C, 76.68; H, 5.70; N, 8.08%. Calcd for $C_{22}H_{20}O_2N_2$: C, 76.72; H, 5.85; N, 8.31%.

4-Chloromethyl-3-phenyl-2-phenylimino-1,3-oxazolidine (1e): Due to its thermal instability **1e** was purified by column chromatography: IR 1680 cm^{-1} (C=N); ^1H NMR ($CDCl_3$) δ=3.50—3.82 (2H, m), 4.28—4.77 (3H, m), and 6.58—7.80 (10H, m); ^{13}C NMR ($CDCl_3$) δ=42.93 (t), 58.17 (d), 67.32 (t), 122.51 (d), 123.18 (d), 124.95 (d), 128.42 (d), 129.15 (d), 137.45 (s), 146.90 (s), and 149.40 (s); MS m/z 286 (M^+). Found: C, 66.94; H, 5.22; N, 9.71; Cl, 12.58%. Calcd for $C_{16}H_{15}ON_2Cl$: C, 67.01; H, 5.27; N, 9.77; Cl, 12.36%.

5-Chloromethyl-3-phenyl-2-phenylimino-1,3-oxazolidine (2e): Mp 86—88 °C; IR (KBr) 1690 cm^{-1} (C=N); ^1H NMR ($CDCl_3$) δ=3.75 (2H, d, J=5.8 Hz), 3.90—4.35 (2H, m), 4.70—5.00 (1H, m), and 6.90—7.90 (10H, m); ^{13}C NMR ($CDCl_3$) δ=44.51 (t), 49.26 (t), 73.26 (d), 122.22 (d), 122.51 (d), 123.39 (d), 124.22 (d), 128.43 (d), 128.91 (d), 138.26 (s), 147.61 (s), and 150.15 (s); MS m/z 286 (M^+). Found: C, 66.77; H, 5.25; N, 9.80; Cl, 12.63%. Calcd for $C_{16}H_{15}ON_2Cl$: C, 67.01; H, 5.27; N, 9.77; Cl, 12.36%.

2-Butylimino-4-ethyl-3-phenyl-1,3-oxazolidine (1f): Mp 190 °C/0.01 mmHg; IR 1675 cm^{-1} (C=N); ^1H NMR ($CDCl_3$) δ=0.80—1.03 (6H, m), 1.26—1.86 (6H, m), 3.27 (2H, t, J=6.5 Hz), 3.99—4.46 (3H, m), and 6.94—7.72 (5H, m); ^{13}C NMR ($CDCl_3$) δ=7.77 (q), 13.54 (q), 20.15 (t), 23.66 (t), 33.51 (t), 45.86 (t), 57.29 (d), 67.11 (t), 120.16 (d), 121.96 (d), 127.97 (d), 138.85 (s), and 149.67 (s); MS m/z 246 (M^+). Found: C, 72.95; H, 9.05; N, 11.36%. Calcd for $C_{15}H_{12}ON_2$: C, 73.13; H, 9.00; N, 11.37%.

2-Butylimino-5-ethyl-3-phenyl-1,3-oxazolidine (2f): Bp 120 °C/0.01 mmHg; IR 1670 cm^{-1} (C=N); ^1H NMR ($CDCl_3$) δ=0.88—1.19 (6H, m), 1.23—1.95 (6H, m), 3.31 (2H, t, J=6.7 Hz), 3.51 (1H, dd, J=8.2 and 6.9 Hz), 3.94 (1H, t, J=8.0 Hz), 4.32—4.61 (1H, m), and 6.89—7.73 (5H, m); ^{13}C NMR ($CDCl_3$) δ=8.84 (q), 13.93 (q), 20.85 (t), 27.50 (t), 33.90 (t), 46.37 (t), 50.89 (t), 75.28 (d), 117.60 (d), 121.38 (d), 128.33 (d), 140.44 (s), and 149.19 (s); MS m/z 246 (M^+). Found: C, 73.48; H, 8.95; N, 11.32%. Calcd for $C_{15}H_{12}ON_2$: C, 73.13; H, 9.00; N, 11.37%.

Reaction of Oxirane with Isocyanate. As a typical procedure, phenyl isocyanate (2 mmol) was added dropwise to a solution of Bu_3SnI (2 mmol) and Bu_3PO (2 mmol) in methyloxirane (20 mmol) for 1 h with stirring at 50 °C under dry nitrogen. Following addition, the formation and the yields of two products, α-cleavage cycloadduct **1g** (43%) and β-cleavage cycloadduct **2g** (50%), were monitored by GLC. The excess oxirane was removed in vacuo, and the mixture was subjected to isolation by column chromatography on silica gel, giving viscous **1g** (eluted by chloroform; 135 mg, 38%) and crystalline **2g** (eluted by benzene; 152 mg, 43%).

4-Methyl-3-phenyl-1,3-oxazolidin-2-one (1g):[11] Mp 51 °C; IR (KBr) 1740 cm^{-1} (C=O).

5-Methyl-3-phenyl-1,3-oxazolidin-2-one (2g):[5] Mp 81 °C; IR (KBr) 1740 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ=1.52 (3H, d, J=6.0 Hz), 3.60 (1H, t, J=7.5 Hz), 4.10 (1H, t, J=8.0 Hz), 4.62—4.96 (1H, m), and 7.00—7.60 (5H, m); MS m/z 177 (M^+).

The following compounds were obtained in a similar manner.

4-Ethyl-3-phenyl-1,3-oxazolidin-2-one (1h):[11] Bp 120 °C/

0.1 mmHg; IR 1750 cm^{-1} (C=O).

5-Ethyl-3-phenyl-1,3-oxazolidin-2-one (2h):[7] Bp 124 °C/1.5 mmHg; IR 1750 cm^{-1} (C=O).

4-Hexyl-3-phenyl-1,3-oxazolidin-2-one (1i): Bp 170 °C/0.01 mmHg; IR 1750 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ=0.68—1.97 (13H, m), 4.02—4.21 (1H, m), 4.21—4.65 (2H, m), and 6.88—7.79 (5H, m); MS m/z 247 (M^+). Found: C, 72.66; H, 8.66; N, 5.71%. Calcd for $C_{15}H_{21}NO_2$: C, 72.84; H, 8.56; N, 5.67%.

5-Hexyl-3-phenyl-1,3-oxazolidin-2-one (2i): Mp 63 °C; IR 1750 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ=0.41—2.37 (13H, m), 3.65 (1H, t, J=8.1 Hz), 4.07 (1H, t, J=8.1 Hz), 4.46—5.00 (1H, m), and 6.52—7.87 (5H, m); MS m/z 247 (M^+). Found: C, 72.89; H, 8.52; N, 5.61%. Calcd for $C_{15}H_{21}NO_2$: C, 72.84; H, 8.56; N, 5.67%.

3,4-Phenyl-1,3-oxazolidin-2-one (1j):[11] Mp 79 °C; IR 1750 cm^{-1} (C=O).

3,5-Phenyl-1,3-oxazolidin-2-one (2j):[11] Mp 130 °C; IR 1740 cm^{-1} (C=O).

Reaction of Oxirane with Isothiocyanate. PhNCS (2 mmol) was added to a solution of Me_3SnI (0.2 mmol), HMPA (0.6 mmol) and ethyloxirane (10 mmol) under dry nitrogen. The mixture was stirred at 40 °C (5 h) until the infrared absorption of N=C=S disappeared, and the yields of the products, **3a** (78%), **4a** (14%) and **5a** (=**2a**) (7%) were monitored by GLC. The products, **3a** (271 mg, 70%), **4a** (46 mg, 12%) and **5a** (21 mg 6%) were subjected to isolation by TLC, and identified as follows.

4-Methyl-2-phenylimino-1,3-oxathiolane (3a): Oil; IR 1650 cm^{-1} (C=N); ^1H NMR ($CDCl_3$) δ=1.38 (3H, d, J=6.4 Hz), 3.74—4.09 (2H, m), 4.36—4.51 (1H, m), and 6.68—7.46 (5H, m); ^{13}C NMR ($CDCl_3$) δ=18.81 (q), 43.05 (d), 75.52 (t), 120.98 (d), 123.88 (d), 128.76 (d), 148.88 (s), and 168.67 (s); MS m/z 193 (M^+). HRMS. Found: m/z 193.0559. Calcd for $C_{10}H_{11}ONS$: M, 193.0562.

4-Methyl-3-phenyl-1,3-oxazolidine-2-thione (4a): Oil; IR 1180 cm^{-1} (C=S); ^1H NMR ($CDCl_3$) δ=1.28 (3H, d, J=6.4 Hz), 4.23 (1H, t, J=8.2 Hz), 4.45—4.58 (1H, m), 4.83 (1H, t, J=8.7 Hz), and 7.36—7.50 (5H, m); ^{13}C NMR ($CDCl_3$) δ=18.29 (q), 58.65 (d), 73.38 (t), 127.01 (d), 128.32 (d), 129.46 (d), 137.04 (s), and 187.76 (s); MS m/z 193 (M^+). HRMS. Found: m/z 193.0573. Calcd for $C_{10}H_{11}ONS$: M, 193.0562.

4-Ethyl-2-phenylimino-1,3-oxathiolane (3b): Isolated by column chromatography eluted by benzene and purified by distillation. Bp 104—106 °C/0.01 mmHg; IR 1650 cm^{-1} (C=N); ^1H NMR ($CDCl_3$) δ=0.93 (3H, t, J=7.3 Hz), 1.55—2.00 (2H, m), 3.60—3.95 (1H, m), 4.10 (1H, dd, J=9.2 and 5.9 Hz), 4.44 (1H, dd, J=9.2 and 5.9 Hz), and 6.85—7.33 (5H, m); ^{13}C NMR ($CDCl_3$) δ=12.20 (q), 27.07 (t), 50.49 (d), 73.97 (t), 121.20 (d), 124.06 (d), 128.94 (d), 149.13 (s), and 163.24 (s); MS m/z 207 (M^+). HRMS. Found: m/z 207.0707. Calcd for $C_{11}H_{13}ONS$: M, 207.0719.

4-Ethyl-3-phenyl-1,3-oxazolidine-2-thione (4b): Isolated and purified in a similar manner as above. Bp 84—85 °C/0.01 mmHg; IR 1180 cm^{-1} (C=S); ^1H NMR ($CDCl_3$) δ=0.79 (3H, t, J=7.4 Hz), 1.40—1.70 (2H, m), 4.17—4.45 (2H, m), 4.57—4.71 (1H, m), and 7.20—7.54 (5H, m); ^{13}C NMR ($CDCl_3$) δ=8.14 (q), 24.85 (t), 63.48 (d), 71.19 (t), 126.68 (d), 128.03 (d), 129.19 (d), 137.11 (s), and 187.54 (s); MS m/z 207 (M^+). HRMS. Found: m/z 207.0720. Calcd for $C_{11}H_{13}ONS$: M, 207.0719.

4-Phenyl-2-phenylimino-1,3-oxathiolane-2-imine (3c): Mp 85—86 °C; IR (KBr) 1680 cm^{-1} (C=N); ^1H NMR ($CDCl_3$) δ=4.40 (1H, dd, J=7.8 and 8.8 Hz), 4.71 (1H, dd, J=6.3 and 8.8 Hz), 4.97 (1H, t, J=6.8 Hz), and 6.70—7.35 (10H, m); ^{13}C NMR ($CDCl_3$) δ=52.08 (d), 75.55 (t), 121.17 (d), 124.25 (d), 127.36 (d), 128.64 (d), 129.00 (d), 136.38 (s), and 148.88 (s); MS m/z 255 (M^+). HRMS. Found: m/z 255.0708. Calcd for $C_{15}H_{13}ONS$: M, 255.0719.

3,4-Diphenyl-1,3-oxazolidine-2-thione (4c): Mp 106—107 °C; IR (KBr) 1180 cm^{-1} (C=S); ^1H NMR ($CDCl_3$) δ=4.51 (1H, dd, J=6.8 and 9.0 Hz), 5.00 (1H, t, J=9.0 Hz), 5.41 (1H, dd, J=6.8 and 9.0 Hz), and 7.07—7.30 (5H, m); ^{13}C NMR ($CDCl_3$) δ=67.04 (d), 74.12 (t), 126.26 (d), 126.99 (d), 128.88 (d), 129.09 (d), 136.75 (s), 137.36 (s), and 187.57 (s); MS m/z 255 (M^+). HRMS. Found: m/z 255.0723. Calcd for $C_{15}H_{13}ONS$: M, 255.0719.

4-Ethyl-2-Methylimino-1,3-oxathiolane (3d): Bp 78 °C/2 mmHg; IR 1650 cm^{-1} (C=N); ^1H NMR ($CDCl_3$) δ=1.05 (3H, t, J=7.5 Hz), 1.62—1.90 (2H, m), 3.05 (3H, s), 3.51—3.78 (1H, m), 3.89—4.20 (1H, m), and 4.40 (1H, dd, J=9.5 and 6.8 Hz); ^{13}C NMR ($CDCl_3$) δ=12.08 (q), 27.08 (t), 50.19 (d), 65.59 (q), 73.09 (t), and 162.67 (s); MS m/z 145 (M^+); HRMS. Found: m/z 145.0558. Calcd for $C_6H_{11}ONS$: M, 145.0562.

5-Ethyl-3-methyl-1,3-oxazolidin-2-one (5d): Bp 70 °C/2 mmHg; IR 1750 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ=0.99 (3H, t, J=7.3 Hz), 1.50—1.88 (2H, m), 2.90 (3H, s), 3.16 (1H, dd, J=7.1 and 8.5 Hz), 3.61 (1H, t, J=8.5 Hz), and 4.27—4.51 (1H, m); ^{13}C NMR ($CDCl_3$) δ=8.64 (q), 27.82 (t), 30.83 (q), 51.69 (t), 74.28 (d), and 158.22 (s); MS m/z 129 (M^+).HRMS. Found: m/z 129.0804. Calcd for $C_6H_{11}O_2N$: M, 129.0790.

Reaction of Methyloxirane with Me_3SnI. The mixture of Me_3SnI (10 mmol) and methyloxirane (4 ml) was stirred for 1 h at room temperature under dry nitrogen. The excess oxirane was removed in vacuo, and **7** was isolated by distillation (bp 53 °C/0.1 mmHg; 2.13 *g*, 61%). ^1H NMR ($CDCl_3$) δ=0.47 (9H, s), 1.27 (3H, d, J=6.0 Hz), 3.18 (2H, d, J=5.3 Hz), 3.60—3.98 (1H, m); ^{13}C NMR ($CDCl_3$) δ=−2.44 (q), 21.22 (q), 51.59 (t), 69.21 (d).

Transformation of 3b to 5b (=2b). **3b** (1 mmol) was added to a solution of $AlCl_3$ (0.1 mmol) and ethyloxirane (5 mmol), and the mixture was stirred at 40 °C under dry nitrogen (0.3 h). The formation and the yield of **5b** (86%) was determined by GLC. **5b** (292 mg, 77%) was isolated by silica gel column treatment (eluted by benzene). The spectrum data of **5b** were the same as those of **2b**.

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