STUDIES ON SYNTHETIC USE OF ORGANOTIN HALIDE-BASE SYSTEMS

(有機スズハライド—塩基系の合成的利用に関する研究)

1987

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Preface

The work of this thesis has been performed under the guidance of Professor Haruo Matsuda at Department of Applied Fine Chemistry, Faculty of Engineering, Osaka University.

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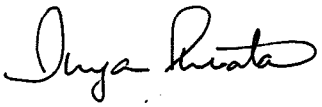


Ikuya Shibata

List of Publications

1. Reaction of Tributyltin ω-Haloalkoxides with Isocyanates or Carbodiimides. A Possibility of the Addition of an Sn-O bond across the C=O group of Isocyanate.
   Akio Baba, Hiroshi Kishiki, Ikuya Shibata, and Haruo Matsuda.
   Organometallics, **4**, 1329 (1985).

2. Novel Use of Organotin Halide-Base Complex on Organic Synthesis. Cycloaddition Reaction of Oxetane with Isocyanates.
   Akio Baba, Ikuya Shibata, Masahiro Fujiwara, and Haruo Matsuda.
   Tetrahedron Lett., **26**, 5167 (1985).

3. The Cycloaddition of Isocyanates and Carbodiimides to Oxiranes Catalyzed by Organotin Iodide-Lewis Base Complexes.
   Akio Baba, Ikuya Shibata, Kazuhiro Masuda, and Haruo Matsuda.
   Synthesis, **1985**, 1144.

4. Reaction of Tri-n-butyltin ω-Haloalkoxide ($n\text{-}Bu_3SnO(CH_2)_nX$) with Isothiocyanate.
   Akio Baba, Ikuya Shibata, Hiroki Kashiwagi, and Haruo Matsuda.
   Bull. Chem. Soc. Jpn., **59**, 341 (1986).

5. Cycloaddition Reaction of Heterocumulenes with Oxiranes Catalyzed by an Organotin Iodide-Lewis Base Complex.
Ikuya Shibata, Akio Baba, Hiroyuki Iwasaki, and Haruo Matsuda.
J. Org. Chem., **51**, 2177 (1986).

6. Regioselective Ring Cleavage of Oxiranes Catalyzed by Organotin Halide-Triphenylphosphine Complex.
Ikuya Shibata, Akio Baba, and Haruo Matsuda.
Tetrahedron Lett., **27**, 3021 (1986).

7. Control of Product in the Reaction of Tri-n-butyltin ω-Haloalkoxide ($n\text{-}Bu_3SnO(CH_2)_nX$) with Diphenylketene.
Ikuya Shibata, Akio Baba, and Haruo Matsuda.
Bull. Chem. Soc. Jpn., **59**, 4000 (1986).

8. Formation of N-Tributylstannyl-2-oxazolidone from $(Bu_3Sn)_2O$ and 2-Chloroethyl Isocyanate.
Ikuya Shibata, Akio Baba, and Haruo Matsuda.
J. Chem. Soc., Chem. Commun., **1986**, 1703.

9. Cycloaddition of Oxetanes with Heterocumulenes Catalyzed by Organotin Iodide-Lewis Base Complex.
Ikuya Shibata, Takafumi Imoto, Akio Baba, and Haruo Matsuda.
J. Heterocycl. Chem., in press.

Contents

General Introduction

Development of new synthetic reactions using organometallic compounds as reagents or catalysts has been one of the main object in organic synthesis.

Recently, numerous works on using transition metal complexes as catalysts have remarkably progressed. In contrast, as to the use of typical organometallic compounds, equimolar amounts with substrates are, in general, necessary, and their catalytic uses are hardly reported.

The readily available organotin reagents, which can be prepared readily in high yields and reasonably cheaply, are often used as valuable reagents. Their many new applications in synthetic chemistry are receiving more and more interest from synthetic chemists. However, in almost cases, equimolar amounts of organotin reagents with substrates are required. Therefore, the use of organotin reagents as catalysts is an important problem.

The main purposes of the present research are to prepare heterocyclic compounds using organotin compounds, and to develop these syntheses as catalytic reactions.

This thesis consists of four chapters. Chapter 1 deals with the preparation of heterocyclic compounds using equimolar amounts of organotin ω-haloalkoxides. The control of products and a plausible reaction mechanism are also described.

Chapter 2 refers the catalytic cycloaddition of cyclic

ethers with heterocumulenes. Organotin halide-Lewis base complexes are found to be efficient catalysts which are superior to those already reported.

In chapter 3, a new method for the regioselective ring cleavage of oxiranes, catalyzed by organotin halide-Lewis base complexes is described.

Furthermore, as applications of organotin ω-haloalkoxide-base systems in organic synthesis, chapter 4 describes the preparation of different types of heterocyclic compounds.

Chapter 1. Reaction of Tributyltin ω-Haloalkoxides ($Bu_3SnO(CH_2)_nX$) with Heterocumulenes.

1-1 Introduction.

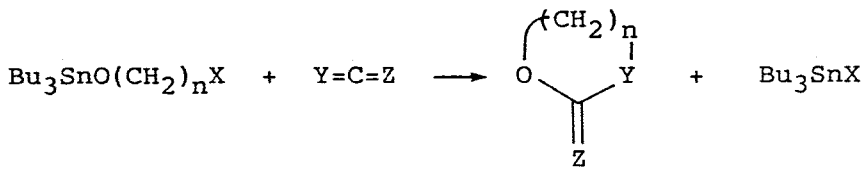
As the Sn-O bond is reactive, it is useful in organic synthesis.[1] A variety of unsaturated substrates such as RNCO, RNCS, CO_2, CS_2, RCHO have been shown to undergo insertion into the Sn-O bond.[1] These reactions have been studied so far with trialkyltin alkoxides,[2a] bis(trialkyltin) oxides,[3] trialkyltin oximates,[4] trialkyltin glycolates,[5] dialkyltin dialkoxides,[6] and tin (II) dialkoxides.[7] It has been reported that the Sn-O bond reacts exothermally with isocyanates to give N-stannylcarbamates[2-8] in all cases. Bloodworth et al. also assume the addition of the Sn-O bond across N=C group rather than across C=O group, although a possibility for rearrangement is considered[2] (eq 1).

$$R_3Sn-\underset{\displaystyle R}{\overset{}{N}}-\overset{\displaystyle O}{\overset{\|}{C}}-OR' \quad \rightleftharpoons \quad R_3Sn-O-\overset{\displaystyle N-R}{\overset{\|}{C}}-OR' \qquad (1)$$

However, no definitive evidence for the direction of the addition has been obtained as yet.

A tin atom favors bonding to halogens over oxygen such that the elimination of tin-halogen bond leads to the

Scheme 1



X= Cl, Br, I

n= 2, 3

Y=C=Z; R-N=C=O

R-N=C=N-R

R-N=C=S

$R_2C=C=O$

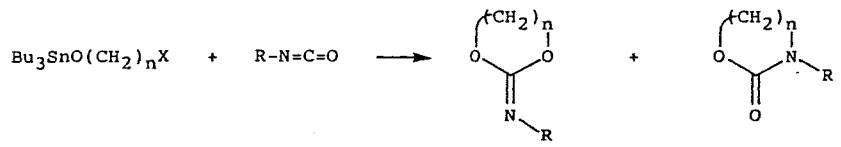
cyclization in the thermolysis of trialkyltin ω-halogeno-alkoxides ($R_3SnO(CH_2)_nX$), as described by Pommier et. al.[9]

On the basis of these facts, this chapter describes some novel reactions of $Bu_3SnO(CH_2)_nX$ with heterocumulenes to give heterocyclic compounds as shown in Scheme 1.

1-2 Reaction of $Bu_3SnO(CH_2)_nX$ with Isocyanates.

Tributyltin ω-haloalkoxides ($Bu_3SnO(CH_2)_nX$) were allowed to react with isocyanates under dry nitrogen. They reacted exothermally even at room temperature and the characteristic IR absorption band at 2275 cm^{-1} due to isocyanates immediately disappeared with the formation of a new band around 1700 cm^{-1}. After the reaction, products were readily precipitated by adding hexane. The precipitates were almost pure as confirmed by means of ^1H-

Table 1. Reaction of $Bu_3SnO(CH_2)_nX$ with RNCO.[a]



1 2

Entry	n	X	R	Solvent (ml)	Temp. (°C)	Product	Yield[b] (%)	1/2 ratio[c]
1	2	Cl	Ph	-	60	1aa, 2aa	2	
2	2	Br	Ph	-	60	"	80	25/75
3	2	I	Ph	-	60	"	89	22/78
4	2	I	Ph	-	25	"	56	20/80
5	2	Cl	Ph	PhH (15)	60	"	0	
6	2	Br	Ph	PhH (15)	60	"	50	60/40
7	2	I	Ph	PhH (15)	60	"	55	51/49
8	2	Cl	Ph	HMPA (3)	25	"	92	0/100
9	2	B	Ph	HMPA (3)	25	"	92	0/100
10	2	I	Ph	HMPA (3)	25	"	91	0/100
11	2	I	Ph	Hexane (15)	60	"	59	26/74
12	2	I	p-$CH_3C_6H_4$	Hexane (15)	60	1ab, 2ab	84	57/43
13	2	I	p-$CH_3C_6H_4$	HMPA (3)	25	2ab	81	0/100
14	2	I	p-ClC_6H_4	Hexane (15)	60	1ac, 2ac	31	37/63
15	2	I	p-ClC_6H_4	HMPA (3)	25	2ac	92	0/100
16	2	I	p-$NO_2C_6H_4$	Hexane (15)	60	1ad, 2ad	37	11/89
17	2	I	p-$NO_2C_6H_4$	HMPA (3)	25	2ad	93	0/100
18	2	I	Me	-	25	1ae, 2ae	86	92/8
19	2	I	Me	PhH (15)	60	"	84	95/5
20	2	I	Me	HMPA (3)	25	"	100	42/58
21	3	I	Ph	-	80	2ba	3	0/100
22	3	I	Ph	-	100	"	85	0/100
23	3	I	Ph	-	120	"	94	0/100
24	3	I	Ph	HMPA (3)	25	"	93	0/100
25	3	I	p-$CH_3C_6H_4$	-	100	2bb	89	0/100
26	3	I	p-ClC_6H_4	-	100	2bc	79	0/100
27	3	I	p-$NO_2C_6H_4$	-	100	2bd	75	0/100
28	3	I	Me	-	100	2be	100	0/100

[a] $Bu_3SnO(CH_2)_nX$ 10 mmol, RNCO 9 mmol, Time 1 h, [b] Based on RNCO, GLC yield.
[c] Determined by GLC and ^1H-NMR.

NMR spectra.

The results of the reactions between $Bu_3SnO(CH_2)_2X$ and isocyanates are summarized in Table 1 (Entries 1-20).

The yields and the ratio of the products were drastically changed by the solvent, the kind of halogen or the substituent on the isocyanate.

When reactions were carried out in bulk, two types of products, N-phenyl-2-dioxolanimine (**1aa**) and 3-phenyl-2-oxazolidinone (**2aa**) were obtained (entries 1-4). In benzene, although the total yield of **1aa** and **2aa** was lower, the ratio of **1aa** increased up to 60% (entries 5-7). On the other hand, the use of hexamethylphosphoric triamide (HMPA) led to quantitative formation of **2aa** even at room temperature, no **1aa** was obtained (entries 8-10).

The halogen atom in $Bu_3SnO(CH_2)_2X$ also affected the reactivity. The iodide was most effective in yielding the heterocyclic compounds (entries 3 and 7). Products were hardly obtained in the reaction with the chloride (entries 1 and 5). This order of halogen; Cl < Br < I, is the same as the order in the formation of cyclic ethers from $Bu_3SnO(CH_2)_nX$ reported by Pommier et. al.[9]

HMPA enhanced the reactivity so greatly that **2aa** was produced in 92% yield even in the case of the chloride, and that the difference of the reactivity between halides could not be observed (entries 8-10). In contrast to the effect on reactivity, the **1aa/2aa** ratio was not affected by halogen moieties.

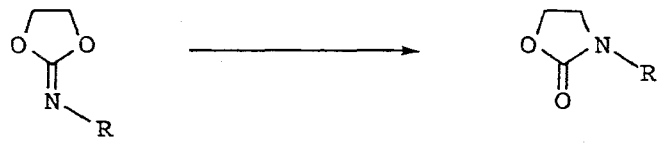
The reaction temperature did not affect the **1a/2a**

ratio. When the reaction of $Bu_3SnO(CH_2)_2I$ with phenyl isocyanate was carried out at 25°C in bulk, the yield decreased to 56%, whereas the **1aa/2aa** ratio was almost unchanged in comparison with the ratio at 60°C (entries 3 and 4).

Other aryl isocyanates also gave the corresponding heterocyclic compounds (entries 12-17). It is apparent that electron donating substituents on an aromatic ring increased both the reactivity and the ratio of **1a** in hexane solution (entries 11, 12, 14 and 16). For example, p-tolyl isocyanate gave **1ab** and **2ab** in 84% yield (**1ab/2ab** ratio=57/43) (entry 12). And p-nitrophenyl isocyanate gave them in 37% yield (**1ac/2ac**= 11/89) (entry 16). In HMPA, the exclusive formation of **2a** was observed as expected (entry 13, 15 and 17).

On the other hand, the reaction with methyl isocyanate gave noteworthy results (entries 18-20). First, its reactivity is higher than that of the aryl isocyanate and the total yield of the products was greater than 80% even in benzene (entry 19). Second, it is surprising that the reaction in benzene or in bulk resulted in the selective formation of **1ae**, which was not observed in the reaction with aryl isocyanates. Even in the reaction using HMPA as solvent, the **1ae/2ae** ratio was 42/58 (entry 20). Under the extreme conditions (150°C for 2h), only **2ae** was obtained in lower yield (27%). This may be because of the lability and facile polymerization of **1a**, which was confirmed with an authentic sample.

It is well known that 2-oxazolidinones are formed by the rearrangement of 2-dioxolanimines[14-16] (eq 2).



(2)

So in this study, the rearrangement might be considered. Actually, the formation of **2aa** was detected in 66% yield by heating **1aa** at 80°C in the presence of Bu_3SnI. However, at lower temperature (such as 60°C and 25°C), no rearrangement was observed even using any solvents listed in Table 1. Moreover, in the reaction of $Bu_3SnO(CH_2)_2I$ and PhNCO in the presence of **1aa**, neither the rearrangement of **1aa** nor the change in the yield of **2aa** were recognized.

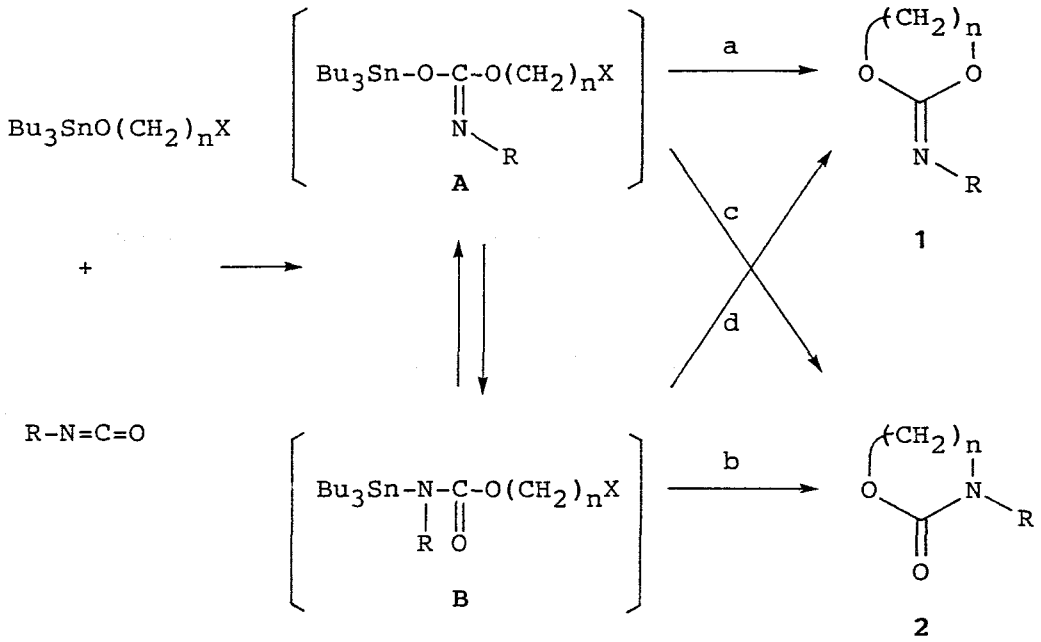
From these results, once produced **1aa** is not considered to rearrange under the reaction conditions listed in Table 1.

No intermolecular substitution was observed. It is characterized by the fact that the adduct of tributyltin methoxide and PhNCO did not react with n-propyl iodide at all.

A plausible mechanism for the reaction of $Bu_3SnO(CH_2)_2X$ with isocyanates is proposed as shown in Scheme 2.

At first, two types of adducts, **A** and **B**, are formed. The former is the adduct of Sn-O bond across the C=O group of an isocyanate and the latter is the adduct across the C=N group.[10] Although the adduct shows a strong IR absorption band around 1700 cm^{-1}, this can not be assigned with

Scheme 2



confidence to the N=C or the C=O group, because the stretching frequency in these adducts may overlap.

Of course, there is a possibility for the interconversion between **A** and **B**.

In next stage, **1a** and **2a** are produced by the intramolecular substitution in the adduct **A** and **B**, respectively (path a and b). Of course, the path c and d can be considered. However, in the reactions which have been thought to proceed via stannylcarbamates, only the formations of the compounds adding at the N atom have been

reported.[2,8,12,13] The adduct **A** can be considered to be more reactive and less stable than the adduct **B**.[11] The ratios of **1a** are larger in the higher yield reactions as shown in Table 1 (Entries 11, 12 and 16). From these facts, we may describe the reaction pathway yielding **1a** via the intermediate **A**. This fact is interesting because the evidence of the addition across the C=O group has not been reported.

In the reaction using HMPA, **2a** was produced exclusively. This fact may indicate if the equilibrium between **A** and **B** is fast and reversible the yields of **1a** and **2a** will depend on the value of the equilibrium constant and the rate constant for conversion of **A** to **1a** and **B** to **2a**. The adduct **B** may be stabilized by the co-ordination of HMPA to the tin atom as a Lewis base. This co-ordination increase the nucleophilicity of the nitrogen atom adjacent to the tin atom and accelerates the intramolecular substitution, giving **2a** predominantly.

Tributyltin γ-halopropoxides ($Bu_3SnO(CH_2)_3X$) also reacted with isocyanates (entries 21-28). The reactivity was lower than that of $Bu_3SnO(CH_2)_2X$, and high temperature was necessary to obtain heterocyclic compounds in high yields. Moreover, it is noteworthy that no 2-dioxanimine derivative (**1b**) was produced even in the reaction with MeNCO in contrast to the reaction with $Bu_3SnO(CH_2)_2X$. It may be considered that this reaction temperature is high (100°C) enough to perform the rearrangement from 2-dioxanimines (**1b**) to 2-oxazinones (**2b**), or the adduct **A** may

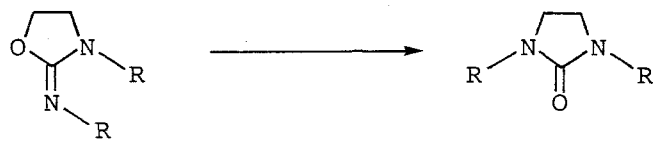
be more stabilized under the severe condition. Consequently, **2b** were obtained selectively in this case.

1-3 Reaction of $Bu_3SnO(CH_2)_nX$ with Diphenylcarbodiimide.

Diphenylcarbodiimide also reacted with $Bu_3SnO(CH_2)_nX$ exothermally and gave the corresponding heterocyclic compounds. Table 2 shows these results.

These reactions took place under milder conditions than the reactions of the isocyanates. Thus N-pheny-3-phenyl-2-oxazolidinimine (**3a**) or N-phenyl-3-phenyl-2-oxazinimine (**3b**) were obtained in high yields at room temperature even when HMPA was not used as a solvent. These products also could be easily isolated by adding hexane after the reaction.

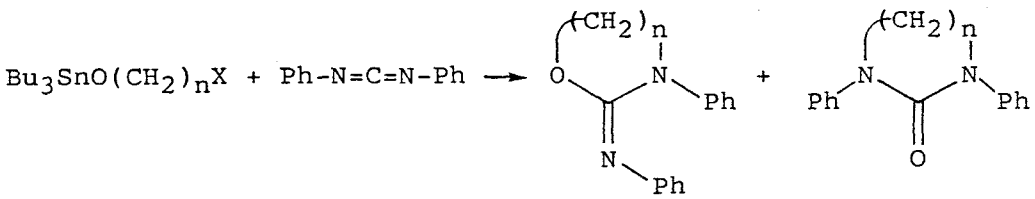
The rearrangement of 2-oxazolidinimines to 2-imidazolidinones has been proposed under severe conditions.[14]



(3)

As expected, in our experiment, 1,3-diphenyl-2-imidazolidinone (**4a**) was obtained selectively at 200°C as shown in Table 2 (entries 8 and 9). This product was formed via an **3a**, catalyzed by Bu_3SnI.

Table 2. Reaction of $Bu_3SnO(CH_2)_nX$ with PhNCNPh.[a]



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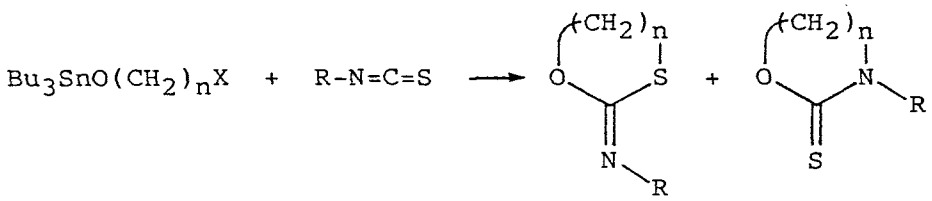
Entry	X	n	Temp. (°C)	Product	Yield[b] (%)	3/4 ratio[c]
1	Cl	2	25	**3a**	91	100/0
2	Cl	3	25	**3b**	28	100/0
3	Br	2	25	**3a**	94	100/0
4	Br	3	25	**3b**	91	100/0
5	I	2	25	**3a**	86	100/0
6	I	3	25	**3b**	86	100/0
7	Br	2	150	**3a**	87	100/0
8	Br	2	200	**3a, 4a**	84	56/44
9	I	2	200	**4a**	87	0/100

[a] $Bu_3SnO(CH_2)_nX$ 10 mmol, PhNCNPh 9 mmol, Time 1 h. [b] Based on PhNCNPh. [c] Determined by ^{1}H-NMR.

1-4 Reaction of $Bu_3SnO(CH_2)_nX$ with Isothiocyanates.

Treatment of $Bu_3SnO(CH_2)_2X$ with phenyl isothiocyanate gave a mixture of N-phenyl-2-oxathiolanimine (**5aa**) and 3-phenyl-2-oxazolidinthione (**6aa**). The proportion of these

Table 3. Reaction of $Bu_3SnO(CH_2)_nX$ with RNCS.[a]



5 6

Entry	n	X	R	Solv. (ml)	Product	Yield[b] (%)	5/6 Ratio[c]
1	2	Cl	Ph	hexane (10)	**5aa, 6aa**	43	7/93
2	"	Cl	Ph	DMF (5)	"	90[d]	49/51
3	"	Br	Ph	hexane (10)	"	68	17/83
4	"	I	Ph	hexane (10)	"	80	34/66
5	"	I	Ph	DMF (5)	"	100[d]	83/17
6	"	Br	$PhCH_2$	hexane (10)	**5ab, 6ab**	41	68/32
7	"	Br	$PhCH_2$	DMF (5)	"	91	77/23
8	"	Br	Me	hexane (10)	**5ac, 6ac**	15	20/80
9	"	Br	Me	DMF (5)	"	33	90/10
10	"	I	Me	DMF (5)	"	56	100/0
11	3	Br	Ph	hexane (10)	**6ba**	14	0/100
12	"	Br	Ph	DMF (5)	"	57	0/100
13	"	I	Ph	hexane (10)	"	73	0/100

[a] $Bu_3SnO(CH_2)_nX$ 10 mmol, RNCS 8 mmol, Temp. 40°C, Time 1 h, [b] Based on RNCO. [c] Determined by GLC. [d] 25°C.

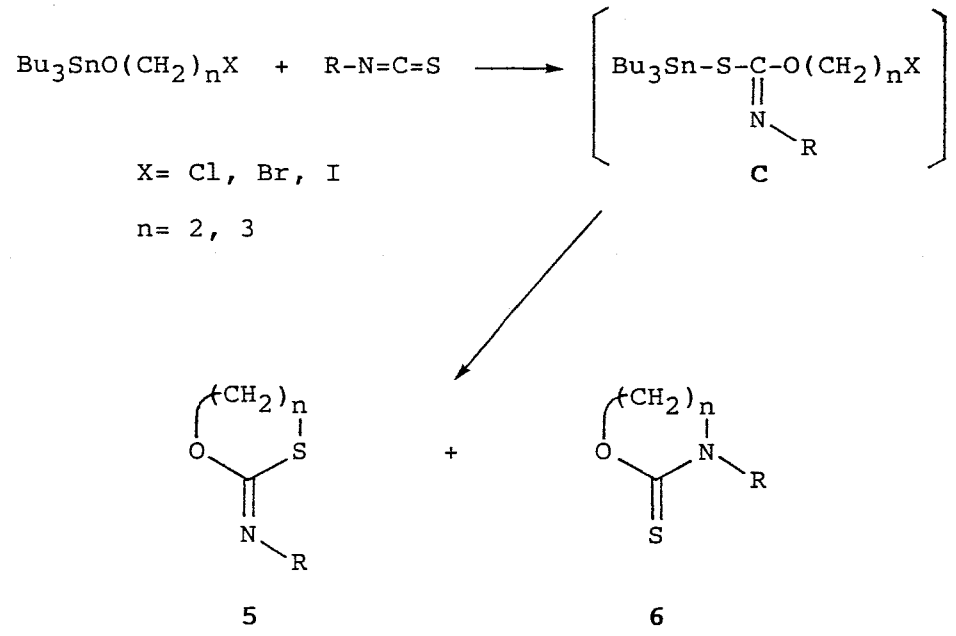
products appeared to be dependent on the nature of substrates and solvents as shown in Table 3.

The order of the reactivity of halogen species was Cl < Br < I, and the proportion of **6aa** was decreased in this order (entries 1, 3 and 4). The use of the chloride in hexane induced the predominant formation of **6aa** (entry 1). Meanwhile, DMF, when used as a solvent, accelerated the reaction, and the proportion of **5aa** was greater than in hexane (entries 2 and 5). Similar effects of DMF were observed in the reactions with alkyl isothiocyanates, although, the reactivity of which was low (entries 6-10).

At the initial stage of the reaction, the addition to isothiocyanates proceeded exothermically, and the IR absorption band of NCS immediately disappeared and the new band around 1600 cm^{-1} (C=N) was recognized.[17]

In the case of isocyanates, two types of adducts were considered. However, because of the great affinity of tin toward sulfur atoms,[1] the addition of may take place only across the C=S group of RNCS as described by Davies et al.,[2b] giving **C** as an intermediate (Scheme 3). In next stage, the intramolecular alkylation at the sulfur atom and at the nitrogen atom gives **5a** and **6a**, respectively. Although the formation of **6a** was generally predominant, DMF increased the proportion of **5a**. This is explained by the co-ordination of DMF to the tin atom in **C** as a Lewis base. The basicity of the sulfur atom adjacent to the tin is thus increased, therefore, the intramolecular S-alkylation is accelerated, giving **5** predominantly.

Scheme 3

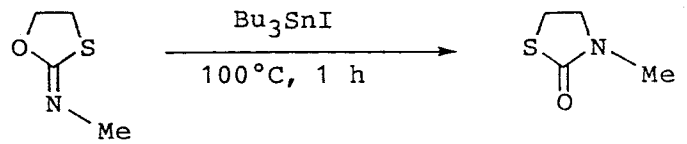


This is not the case, however, in the case of γ-halopropoxides ($Bu_3SnO(CH_2)_3X$). Compound **6b** was produced in a higher selectivity than $Bu_3SnO(CH_2)_2X$ even when DMF was used (entries 11-13).

Alternatively, the isomerization of initially formed **5** to **6** catalyzed by Bu_3SnI, which is a by-product of the reaction, can be considered. However, no isomerization was recognized by the treatment of **5ac** with an equimolar Bu_3SnI at 40°C for 1 h, and **5ac** was recovered quantitatively.

On the other hand, treatment of **5ac** with an equimolar Bu_3SnI at 100°C for 1 h induced the formation of the

2-thiazolidinone **7** in 50% yield as described by Sakai et al. (eq 4).[18]



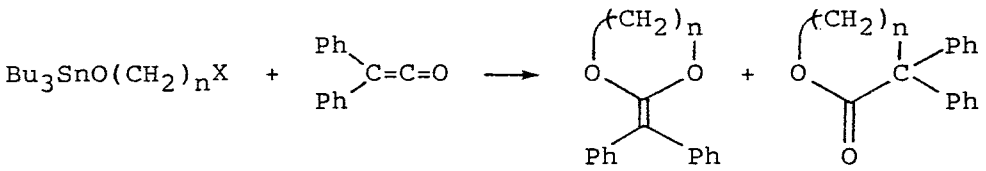
5ac **7** (4)

In this case, formation of **6ac** could not be recognized. We thus conclude that no isomerization of **5** to **6** occurred under present conditions.

1-5 Reaction of $Bu_3SnO(CH_2)_nX$ with Diphenyketene.

The results of the reactions of $Bu_3SnO(CH_2)_2X$ with diphenylketene are summarized in Table 4 (entries 1-8). The types of products and the reactivity varied with temperature, additives and the kind of halogen. γ-Butyrolactone (**9a**) was obtained in only the reactions with iodide derivative (entries 1-3), and the 1,3-dioxolane **8a** was exclusively produced from the bromide (entry 4). Moreover, the ratio of **9a** to **8a** was increased with lowering the reaction temperature, however the reaction proceeded very slowly below 60°C. The presence of Lewis bases allowed the reaction to proceed in high yields under significantly milder conditions, in addition, giving **8a** exclusively (entries 6-8).

Table 4. Reaction of $Bu_3SnO(CH_2)_nX$ with Diphenylketene.[a]



8 9

Entry	n	X	Base	Temp. (°C)	Product	Yield[b] (%)	8/9 ratio[c]
1	2	I	-	80	8a, 9a	60	40/60
2	"	I	-	100	"	52	50/50
3	"	I	-	150	"	51	85/15
4	"	Br	-	100	8a	43	100/0
5	"	Cl	-	120	"	12	100/0
6	"	I	HMPA[e]	60	"	67	100/0
7	"	Br	Et_3N[d]	40	"	78	100/0
8	"	Br	Ph_3P[d]	40	"	93	100/0
9	3	I	-	120	9b	77	0/100
10	"	I	HMPA[e]	100	8b	52	100/0

[a] $Bu_3SnO(CH_2)_nX$ 5 mmol, Ph_2CCO 4 mmol, Time 1 h. [b] Based on Ph_2CCO. [c] Determined by ^{1}H-NMR. [d] 5 mmol, [e] 3 ml.

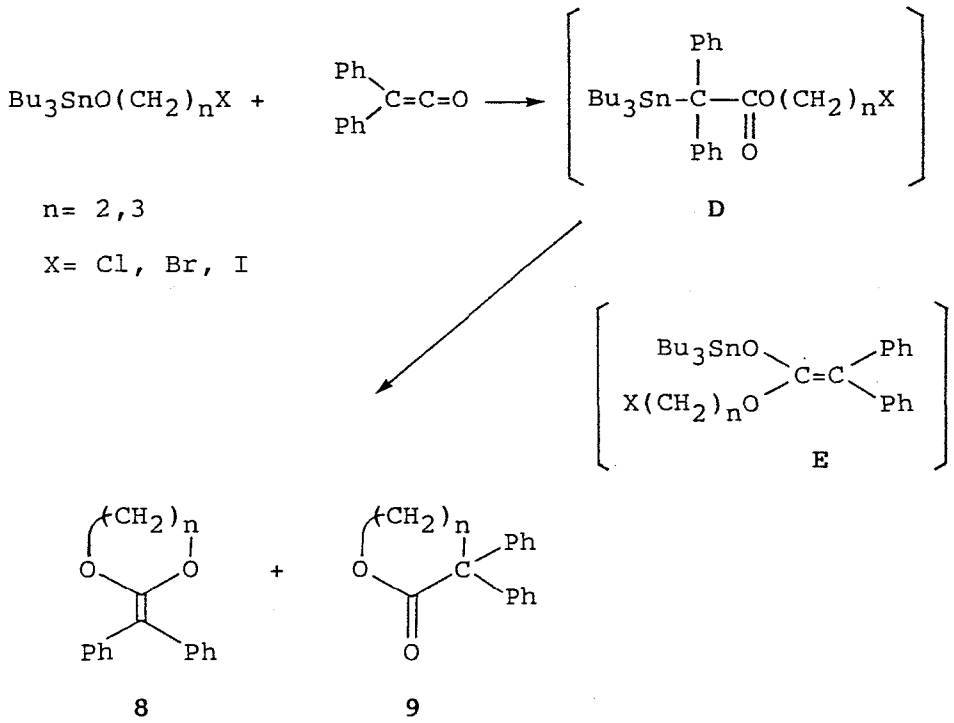
The effect of the number of methylene groups was very definitive as shown in the reaction with γ-halopropoxides ($Bu_3SnO(CH_2)_3X$). In sharp contrast to the 1,3-dioxolane formation from the reaction of $Bu_3SnO(CH_2)_2X$, δ-valerolactone (**9b**) was selectively obtained (entries 9).

Moreover, the effect of base was more remarkable, and the product was completely changed from the lactone **9b** to the 1,3-dioxane **8b** (entry 10). This drastic change is very characteristic of the reaction of diphenylketene. Thus, no change of products by the addition of bases was observed in the reaction with isocyanates or isothiocyanates.

As Bloodworth et. al have reported,[2] these reactions are thought to proceed via stannyl ester type of adduct **D** as shown in Scheme 4

Products, **8** and **9**, may be formed by intramolecular O- and C alkylations, respectively. As to the formation of **8**, stannyl enolate type of adduct **E** can be considered. However, IR spectrum showed the absorption at 1730 cm^{-1} (C=O) in the intermmediate, where no cyclization occurred. And this absorption was also observed in the case using HMPA as a solvent. From these facts, we propose D as an intermediate rather than **E**.[11] While it is unclear exactly why the remarkable alternation of products occurred, the significant effect of the number of methylene group seems to suggest an important role of the intramolecular co-ordination of the terminal halide to the tin atom. The characteristic reaction mode of diphenylketene may be rationalized by the lower ability of an intermolecular co-ordination of **D** in comparison with the adducts with an isocyanate. Namely, the nitrogen atom in the adduct of isocyanates, $Bu_3SnN(R)COO(CH_2)_nX$, can bring an intermolecular co-ordination toward another tin atom,[2a] whereas the carbon atom adjacent to Sn atom in **D** has no co-ordinative ability.

Scheme 4



1-6 Experimental Section.

General. Mps were obtained by using a Yanaco Micromelting point apparatus, which are uncorrected. IR spectra were recorded on a HITACHI 260-30 spectrometer using KBr pelets or KRS-5 cells. ^{1}H-NMR and ^{13}C-NMR spectra were performed on a JEOL Model PS-100 and on a JEOL Model FX-60 spectrometer, respectively or Hitachi RMU-6E model. Analytycal GLC was performed on a following instrument by using 2m * 3mm glass column packed with Silicone OV-1 or OV-

17 on Uniport KS (5%, 60-80 mesh); a SHIMADZU GC-3B with TCD, Herium as a carrier gas. Column chromatography was done with silica gel (Wakogel C-200). Elemental analysis were performed by the section of elemental analysis in the department of Osaka University.

Materials. Commercially available isocyanates and isothiocyanate were used without further purification. Diphenylcarbodiimide,[19] diphenylketene[20] were synthesized by a described method.

Tributyltin ω-haloalkoxides[9] were synthesized in good yield as follows. Tributyltin methoxide (0.04 mol), which was prepared as a described method by Alleston and Davies,[22] and the corresponding haloalkylacetates (n= 2,3, 0.05 mol) were stirred at room temperature for about 10 min under nitrogen, and then heated at 50°C under reduced pressure (100 mmHg) for 2 h. Additional heating for 2 h at 10^{-3} mmHg removed the unconverted starting esters, giving almost pure tributyltin ω-haloalkoxides.

Tributyltin β-chloroethoxide ($Bu_3SnO(CH_2)_2Cl$): bp 78°C (10^{-4} mmHg); IR (neat) 1070 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.90-1.80 (m, 27H), 3.50 (t, 2H), 3.90 (t, 2H).

Tributyltin β-bromoethoxide ($Bu_3SnO(CH_2)_2Br$): bp 110°C (10^{-4} mmHg); IR (neat) 1070 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.90-1.80 (m, 27H), 3.40 (t, 2H), 3.90 (t, 2H).

Tributyltin β-iodoethoxide ($Bu_3SnO(CH_2)_2I$): IR (neat) 1070 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.90-1.80 (m, 27H), 3.05 (t, 2H), 3.80 (t, 2H).

Tributyltin γ-chloro-propoxide ($Bu_3SnO(CH_2)_3Cl$): bp 80°C (10^{-4} mmHg); IR (neat) 1070 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.90-1.80 (m, 27H), 1.90 (t, 2H), 3.65 (t, 2H), 3.80 (t, 2H). Tributyltin γ-bromopropoxide ($Bu_3SnO(CH_2)_3Br$): bp 108°C (10^{-4} mmHg); IR (neat) 1070 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.90-1.80 (m, 27H), 2.00 (m, 2H), 3.50 (t, 2H), 3.80 (t, 2H). Tributyltin γ-iodopropoxide ($Bu_3SnO(CH_2)_3I$): IR (neat) 1070 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.90-1.80 (m, 27H), 1.90 (t, 2H), 3.30 (t, 2H), 3.63 (t, 2H).

Reaction of Tributyltin ω-Haloalkoxides with Isocyanates (Typical Procedure).

All reactions were carried out under dry nitrogen. A typical procedure is described for the reaction of tributyltin β-iodoethoxide ($Bu_3SnO(CH_2)_2I$) with phenyl isocyanate.

A mixture of $Bu_3SnO(CH_2)_2I$ (4.55 g, 9.87 mmol) and phenyl isocyanate (1.05 g, 8.82 mmol) was stirred by a magnetic stirrer in a 50 ml round bottomed flask. Heat was evolved. The infrared spectrum showed disappearance of the characteristic of NCO at 2275 cm^{-1}, and the presence of a new band at 1660 cm^{-1}. After the reaction for 1h at 60°C, hexane was added on cooling, then 1.28 g (89%) of a white precipitates was obtained immediately. This was collected by filtration, washed with hexane and dried in vacuo. The precipitates turned out to be N-pheny-1,3-dioxolan-2-imine (**1aa**) (20% yield), and 3-phenyl-2-oxazolidinone (**2aa**) (69% yield). The **1aa**/**2aa** ratio was determined by ^1H-NMR spectrum. The compound **1aa** was decomposed readily to

ethylene carbonate and aniline on standing. When the reaction was carried out in a solvent, tributyltin ω-haloalkoxide, an isocyanate and a solvent were charged in this order.

N-Phenyl-1,3-dioxolan-2-imine (1aa): bp 130°C (10^{-4} mmHg) (lit.[18] 148-150 (15 mmHg)); IR (neat) 1720 cm^{-1}; ^1H NMR ($CDCl_3$) δ=4.38 (s, 4H), 6.90-7.40 (m ,5H); ^{13}C NMR ($CDCl_3$) δ=66.49, 64.73, 122.95, 123.39, 128.58, 145.41, 153.48.

N-p-Tolyl-1,3-dioxolan-2-imine (1ab): This compound was obtained as a mixture with 3-p-tolyl-2-oxazolidinone. However, this compound was labile to decompose to ethylene carbonate and p-toluidine on column chromathography, so the pure compound could not be obtained. The yield of N-p-tolyl-1,3-dioxolan-2-imine was determined by GLC or by ^1H-NMR (δ4.40)

N-p-Chlorophenyl-1,3-dioxolan-2-imine (1ac): mp 85°C; IR (KBr) 1695 cm^{-1}; ^1H NMR ($CDCl_3$) δ=4.45 (s,4H), 6.82-7.32 (m, 4H); ^{13}C NMR ($CDCl_3$) δ=64.87, 66.73, 124.56, 128.67, 144.04, 153.82; Anal. Calcd for $C_9H_8NO_2Cl$: C, 54.70; H, 4.08; N, 7.09. Found: C, 54.87; H, 4.09; N, 6.99.

N-p-Nitrophenyl-1,3-dioxolan-2-imine (1ad): This compound is labile and pure product could not be obtained. The yield was determined as ethylene carbonate by GLC or ^1H-NMR (δ4.40).

N-Methyl-1,3-dioxolan-2-imine (1ae): bp 99°C (25 mmHg) (lit.[18] 98-100°C (25mmHg)); IR (neat) 1740 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.85 (s, 3H), 4.38 (s, 4H); ^{13}C NMR ($CDCl_3$)

=32.93, 65.46, 154.41.

3-Phenyl-1,3-oxazolidin-2-one (2aa): mp 120°C (lit.[22] 118-121°C); IR (KBr) 1735 cm^{-1}; ^1H NMR ($CDCl_3$) δ=3.96 (t, 2H), 4.20 (t, 2H), 7.00-7.60 (m, 5H); ^{13}C NMR ($CDCl_3$) δ=44.13, 60.47, 117.91, 123.49, 128.97, 139.34, 154.70.

3-p-Tolyl-1,3-oxazolidin-2-one (2ab): mp 88°C (lit.[22] 90°C); IR (KBr) 1735 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.28 (s, 3H), 3.94 (t, 2H), 4.40 (t, 2H), 7.14 (d, 2H), 7.40 (d, 2H); ^{13}C NMR ($CDCl_3$) δ=22.67, 45.28, 61.28, 118.33, 129.54, 133.68, 135.80, 155.37.

3-p-Chlorophenyl-1,3-oxazolidin-2-one (2ac): m.p. 118°C (lit.[22] 116-117°C); IR (KBr) 1740 cm^{-1}; ^1H NMR ($CDCl_3$) δ=3.97 (t, 2H), 4.44 (t, 2H), 7.10-7.60 (m, 4H); ^{13}C NMR ($CDCl_3$) δ=45.11, 61.30, 119.38, 129.01, 129.21, 136.94, 155.14.

3-p-Nitrophenyl-1,3-oxazolidin-2-one (2ad): mp 155°C (lit.[22] 155° C); IR (KBr) 1750 cm^{-1}; ^1H NMR ($CDCl_3$) δ=4.14 (m, 2H), 4.51 (m, 2H), 7.80 (d, 2H), 8.20 (d, 2H); ^{13}C NMR ($CDCl_3$) δ=46.25, 63.14, 118.86, 125.96, 144.14, 146.29, 156.07.

3-Methyl-1,3-oxazolidin-2-one (2ae): bp 102°C (4 mmHg) (lit.[22] 87-90°C (1mmHg)); IR (neat) 1750 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.88 (s, 3H), 3.56 (t, 2H), 4.30 (t, 2H); ^{13}C NMR ($CDCl_3$) δ=30.63, 46.43, 61.21, 158.52.

3-Phenyl-1,3-oxazin-2-one (2ba): mp 95°C; IR (KBr) 1680 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.16 (m, 2H), 3.70 (t, 2H), 4.40 (t, 2H), 7.32 (m, 5H); ^{13}C NMR ($CDCl_3$) δ=22.26, 48.49, 66.78, 125.64, 126.42, 128.87, 142.91, 152.55; Anal. Calcd for $C_{10}H_{11}NO_2$:

C, 67.78; H, 6.26; N, 7.90. Found: C, 67.87; H, 6.29; N, 7.85.

3-p-Tolyl-1,3-oxazin-2-one (2bb): mp 127°C; IR (KBr) 1695 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.13 (m, 2H), 2.32 (s, 3H), 3.65 (t, 2H), 4.38 (t, 2H), 7.17 (s, 4H); ^{13}C NMR ($CDCl_3$) δ=20.84, 22.41, 48.78, 66.83, 125.64, 129.65, 136.45, 140.41, 152.79; Anal. Calcd for $C_{11}H_{13}NO_2$: C, 69.09; H, 6.85; N, 7.32. Found: C, 69.65; H, 6.90; N, 7.22.

3-p-Chlorophenyl-1,3-oxazin-2-one (2bc): mp 111°C; IR (KBr) 1670 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.15 (m, 2H), 3.66 (t, 2H), 4.18 (t, 2H), 7.30 (s, 4H); ^{13}C NMR ($CDCl_3$) δ=22.36, 48.58, 67.03, 127.06, 129.16, 132.04, 141.49, 152.50; Anal. Calcd for $C_{10}H_{10}NO_2Cl$: C, 56.75; H, 4.76; N, 6.62; Cl, 16.75. Found: C, 56.77; H, 4.80; N, 6.49; Cl, 16.48.

3-p-Nitrophenyl-1,3-oxazin-2-one (2bd): mp 125°C; IR (KBr) 1680 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.26 (m, 2H), 3.83 (t, 2H), 4.46 (t, 2H), 7.56 (d, 2H), 8.23 (d, 2H); ^{13}C NMR($CDCl_3$) δ=23.66, 49.65, 68.41, 125.15, 126.33, 145.86, 151.07, 152.74; Anal. Calcd for $C_{10}H_{10}N_2O_4$: C, 54.05; H, 4.54; N, 12.61. Found: C, 54.07; H, 4.52; N, 12.57.

3-Methyl-1,3-oxazin-2-one (2be): bp 103°C (2 mmHg); IR (KBr) 1680 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.08 (m, 2H), 3.00 (s, 3H), 3.36 (t, 2H), 4.28 (t, 2H); ^{13}C NMR ($CDCl_3$) δ=21.67, 36.01, 46.48, 66.00, 153.48; Anal. Calcd for $C_5H_9NO_2$: C, 52.16; H, 7.88; N, 12.17. Found: C, 51.90; H, 7.87; N, 12.00.

The Rearrangement of 1aa to 2aa.

In the presence of Bu_3SnI; In a 50 ml round bottomed flask, N-phenyl-1,3-dioxolan-2-imine (**1aa**) (0.51 g, 3.10

mmol) and Bu_3SnI (2.59 g, 6.21 mmol) were placed under nitrogen. The mixture was heated with stirring. The reaction mixture was homogeneous throughout the heating. After heating for 1 h, white precipitates were obtained by adding hexane. The solid was collected by filtration, washed with hexane and dried in vacuo (0.42 g). It contained only **1aa** and **2aa**, and the ratio was determined by ^1H-NMR.

In the presence of $Bu_3SnO(CH_2)_2I$ and PhNCO; $Bu_3SnO(CH_2)_2I$ (1.23 g, 2.67 mmol), phenyl isocyanate (0.23 g, 1.93 mmol) and N-phenyl-1,3-dioxolan-2-imine (0.32 g, 1.96 mmol) were charged in this order. The reaction was carried out at 60°C for 1 h, **1aa** (0.38 g, 2.33 mmol) and **2aa** (0.21 g, 1.29 mmol) were obtained.

Reaction of $Bu_3SnO(CH_2)_nX$ with Diphenylcarbodiimide (Typical Procedure).

$Bu_3SnO(CH_2)_2I$ (2.61 g, 5.66 mmol) and diphenylcarbodiimide (0.92 g, 4.74 mmol) were mixed in a 50 ml round bottomed flask. Heat was evolved and the mixture became white in color. After stirring for 1 h at room temperature, hexane was added on cooling, giving white precipitates 0.97 g (86%) of N-phenyl-3-phenyl-1,3-oxazolidin-2-imine (**3a**). When the reaction was carried out at 200°C, the product was 1.02 g (87%) of 1,3-diphenyl-2-imidazolidinone (**4a**).

N-Phenyl-3-phenyl-1,3-oxazolidin-2-imine (3a): mp 115°C (lit.[23] 115°C); IR (KBr) 1675 cm^{-1}; ^1H NMR ($CDCl_3$) δ=3.90

(t, 2H), 4.34 (t, 2H), 6.90-7.90 (m, 10H); ^{13}C NMR ($CDCl_3$) δ=46.43, 63.70, 118.84, 122.51, 123.00, 123.34, 128.58, 128.87, 139.83, 147.50, 149.13.

N-Phenyl-3-phenyl-1,3-oxazin-2-imine (3b): mp 106°C; IR (KBr) 1630 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.10 (m, 2H), 3.65 (t, 2H), 4.20 (t, 2H), 6.80-7.50 (m, 10H); ^{13}C NMR ($CDCl_3$) δ=23.53, 47.26, 65.85, 121.68, 123.44, 125.39, 128.33, 128.97, 144.96, 148.20, 149.46.

1,3-Diphenyl-1,3-imidazolidin-2-one (4a): mp 203°C (lit.[14] 211°C); IR (KBr) 1700 cm^{-1}; ^1H NMR ($CDCl_3$) δ=3.95 (s, 4H), 6.90-7.70 (m, 10H); ^{13}C NMR ($CDCl_3$) δ=42.08, 118.20, 123.19, 128.97, 140.22, 155.09.

Reaction of $Bu_3SnO(CH_2)_nX$ with Isothiocyanates (Typical Procedure).

$Bu_3SnO(CH_2)_2I$ (3.70 g, 10 mmol) and phenyl isothiocyanate (1.08 g, 8 mmol) were stirred under dry nitrogen on cooling, then heat was evolved about 40°C. The infra-red spectrum showed the disappearance of the characteristic absorption band of NCS at 2100 cm^{-1} and the presence of a new band around 1600 cm^{-1}. After additional 5 min, DMF (5 ml) was added and the stirring was continued for 1 h at 25°C. The addition of excess amounts of hexane on cooling induced 1.79 g of white precipitates immediately, which were filtered, washed with hexane and dried in vacuo. The precipitates contained N-phenyl-1,3-oxathiolan-2-imine (**5aa**) as a mixture with **6aa** (100%, **5aa:6aa**= 83:17, entry 5). The **5**/**6** ratio was determined by GLC. Analytically pure

sample of **5aa** was obtained by column chromatography (Silica gel, $CHCl_3$). Compound **6aa** was obtained as the major product from the reaction of $Bu_3SnO(CH_2)_2Cl$ (Table 3, entry 1).

N-Phenyl-1,3-oxathiolan-2-imine (5aa): mp 65-67°C (lit.[18] 65-65.5°C); IR (KBr) 1035, 1110, 1640 cm^{-1}; ^1H NMR ($CDCl_3$) δ=3.40 (t, 2H), 4.50 (t, 2H), 6.90-7.50 (m, 5H).

N-Benzyl-1,3-oxathiolan-2-imine (5ab): bp 113-115°C (10^{-3} mmHg); IR (neat) 1060, 1660 cm^{-1}; ^1H NMR ($CDCl_3$) δ=3.40 (t, 2H), 4.40 (t, 4H), 7.20-7.40 (m, 5H); ^{13}C NMR ($CDCl_3$) δ=31.7, 58.0, 68.8, 126.7, 127.5, 128.2, 139.4, 163.1; MS, m/e 193 (M^+).

N-Methyl-1,3-oxathiolan-2-imine (5ac): bp 66-67°C (2 mmHg) (lit.[18] 117-118°C (20 mmHg)); IR (neat) 1050, 1670 cm^{-1}; ^1H NMR ($CDCl_3$) δ=3.00 (s, 3H), 3.40 (t, 2H), 4.30 (t, 2H).

3-Phenyl-1,3-oxazolidin-2-thione (6aa): mp 97°C (lit.[24] 95.5°C); IR (KBr) 1180, 1300, 1430, 1495 cm^{-1}; ^1H NMR ($CDCl_3$) δ=4.20 (t, 2H), 4.60 (t, 2H), 7.20-7.60 (m, 5H).

3-Benzyl-1,3-oxazolidin-2-thione (6ab): mp 90-91°C; IR (KBr) 1160, 1330, 1520 cm^{-1}; ^1H NMR ($CDCl_3$) δ=3.60 (t, 2H), 4.50 (t, 2H), 4.82 (s, 2H), 7.30-7.40 (m, 5H); ^{13}C NMR ($CDCl_3$) δ=47.2, 52.0, 65.9, 128.1, 128.3, 128.8, 134.5, 188.0; MS, m/e 193 (M^+)

3-Methyl-1,3-oxazolidin-2-thione (6ac): bp 120°C (0.3 mmHg) (lit.[25] 127°C (0.4 mmHg)); IR (neat) 1180 cm^{-1}; ^1H NMR ($CDCl_3$) δ=3.21 (s, 3H), 3.82 (t, 2H), 4.52 (t, 2H).

3-Phenyl-1,3-oxazine-2-thione (6ba): mp 138-139°C; IR (KBr) 1300, 1320, 1480, 1500 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.10-2.40 (m,

2H), 3.70 (t, 2H), 4.50 (t, 2H), 7.20-7.50 (m, 5H); ^{13}C NMR ($CDCl_3$) δ=21.4, 50.7, 67.7, 126.6, 127.8, 129.4, 145.5, 187.1; MS, m/e 193 (M^+).

The Isomerization of 5.

N-Methyl-1,3-oxathiolan-2-imine **5ac** (0.56 g, 5 mmol) and Bu_3SnI (2.08 g, 5 mmol) were stirred under N_2 in a 50 ml round bottomed flask, after 1 hour at 100°C, the GLC analysis showed the disappearance of **5ac**, and 3-methyl-2-thiazolidinone **7** was formed in 50% yield, this was purified by column chromatography (silica gel, $CHCl_3$) and distillation. The spectral dara for **7** is as fpllows: bp 65°C (10^{-3} mmHg) (lit.[18] 73-75°C (0.2 mmHg)); IR (neat) 1240, 1690 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.88 (s, 3H), 3.30 (t, 2H), 3.60 (t, 2H).

Reaction of $Bu_3SnO(CH_2)_nX$ with Diphenylketene (Typical Procedure).

$Bu_3SnO(CH_2)_nX$ (2.30 g, 5 mmol) and diphenylketene (0.78 g, 4 mmol) were stirred in a 50 ml round bottomed flask, then heat was evolved about 40°C. The infrared spectrum showed disappearance of the characteristic absorption band of CCO at 2100 cm^{-1}, and the presence of the new band at 1730 cm^{-1}. After 1 hour at 80°C, addition of excess amounts of hexane on cooling induced 0.57 g (60%) of white precipitates immediately, which were collected by filtration, washed with hexane and dried in vacuo. The precipitates were turned out to 2-diphenylmethylene-1,3-dioxolane (**8a**) (24% yield) and α,α-diphenyl-γ-butyrolactone

(9a) (36% yield). The 8a/9a ratio was determined by ^{1}H-NMR spectra.

2-Diphenylmethylene-1,3-dioxolane (8a): mp 148-149°C (lit.[14] mp 149-151°C); IR (KBr) 1660 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=4.20 (s, 4H), 7.00-7.40 (m, 10H).

2-Diphenylmethylene-1,3-dioxane (8b): mp 80-81°C; IR (KBr) 1640cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.95-2.25 (m, 2H), 4.15 (t, 4H), 7.10-7.40 (s, 10H); MS, m/e 252 (M^+).

α,α-Diphenyl-γ-butyrolactone (9a): Pure sample was isolated by cloumn chromatography (Silica-gel, $CHCl_3$). mp 80-81°C (lit.[26] 77-79°C); IR (KBr) 1780 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=2.98 (t, 2H), 4.22 (t, 2H), 7.32 (s, 10H); MS, m/e 238 (M^+).

α,α-Diphenyl-δ-valerolactone (9b): mp 116°C (lit,[27] 112°C); IR (KBr) 1730 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.88 (m, 2H), 2.62 (t, 2H), 4.22 (t, 2H), 7.22 (s, 10H); MS, m/e 252 (M^+).

1-7 References and Notes.

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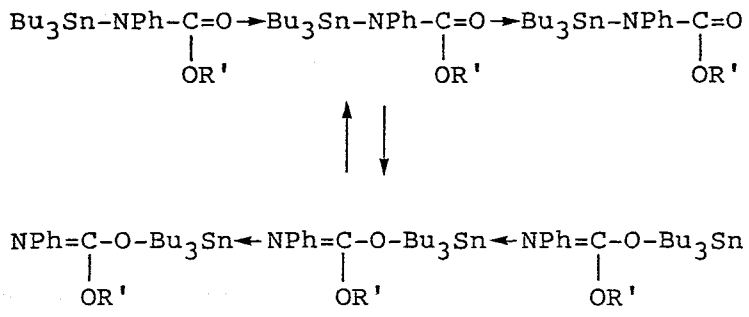

(11) In adducts of tin alkoxide and ketene, the adduct of keto type is more stable but less reactive toword carbonyl compounds than the adduct of the enol type. E. Shimada, K. Inomata, and T. Mukaiyama, Chem. Lett., **1974**, 689.

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(17) The intermediate **A** may also exist in the presence of DMF, because the IR absorption around 1600 cm^{-1} (C=N) was confirmed even in the presence of bases.

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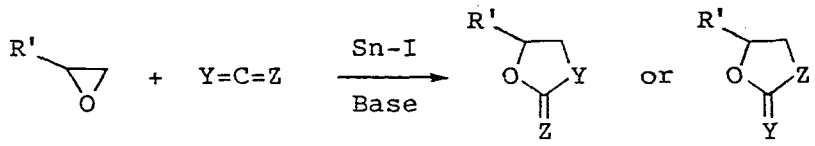
Chapter 2 Cycloaddition Reaction of Cyclic Ethers with Heterocumulenes Catalyzed by Organotin Halide-Lewis Base Complex.

2-1 Introduction.

Oxiranes are useful intermediates in organic synthesis because of their easy accessibility and high reactivity being accompanied with their ring opening.[1] In particular, oxiranes react with heterocumulenes in a fashion of the 1,3-cycloaddition, giving five-membered heterocyclic compounds,[2] and a number of catalysts have been developed with varying degrees of success. However, in the reactions using these catalysts, vigorous reaction temperatures and sometimes, reactive polar solvents are required,[2] and so they are accompanied by undesirable reactions such as the trimerization of isocyanates and addition to solvents.

As described in chapter 1, heterocyclic compounds were obtained from the equimolar reactions of tributyltin ω-haloalkoxides ($Bu_3SnO(CH_2)_nX$, n= 2, 3, X= halogen) with heterocumulenes. This type of tin reagent can be regarded as an adduct of oxirane or oxetane with Bu_3SnX.[3] Of importance is that the addition of Lewis bases significantly accelerates this reaction. A facile complex formation of organotin halides with Lewis bases is widely known. These facts led to investigate whether complexes of organotin halides and Lewis bases can be employed as excellent

Scheme 5



Y=C=Z; R-N=C=O

R-N=C=S

R-N=C=N-R"

$R_2C=C=O$

catalysts for the cycloaddition of cyclic ethers with heterocumulenes. Although the structures and stabilities have been intensively investigated,[4] these complexes are not used extensively in organic synthesis.[5] On the basis of these facts, this chapter describes the cycloaddition of cyclic ethers with heterocumulenes, catalyzed by organotin halide-Lewis base complexes (Scheme 5).

2-2 Cycloaddition of Oxiranes with Heterocumulenes.

2-2-1 Cycloaddition of Oxiranes with Isocyanates.

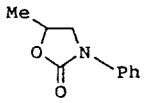
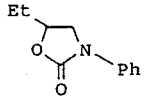
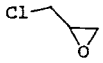
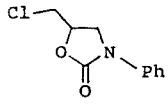
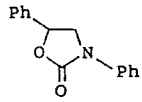
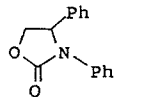
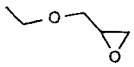
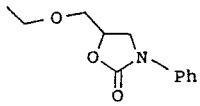
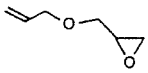
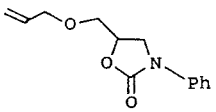
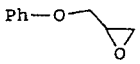
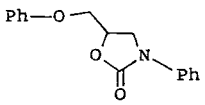
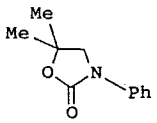
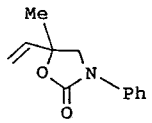
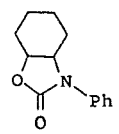
Initially, the catalytic activity of in situ generated organotin halide-Lewis base complexes (10 mol %) was investigated in terms of the cycloaddition of propylene oxide with PhNCO. Table 5 shows these results (entries 1-

10). The organotin iodide alone had low activity (entry 1), but satisfactory results were obtained by complexation with Lewis bases. The cycloaddition was performed under very mild conditions (40°C, 2h) to yield 5-methyl-3-phenyl-2-oxazolidinone **10** in excellent yields. This is remarkable because very severe conditions are necessary using previous catalysts such as lithium halides,[6] quaternary ammonium salts,[7] Lewis bases[8] and Lewis acids.[9] . Even the current method of choice uses LiBr-Bu_3PO or LiBr-HMPA as a catalyst at above 80°C.[6e,f]

One disturbing side reaction using these catalysts is the trimerization of isocyanates. This trimerization proceeds so smoothly in the presence of Lewis bases[10] that dropwise addition is necessary to depress it when using the LiCl-DMF[6c,d] or the LiBr-Bu_3PO[6e,f] system as a catalyst. Without dropwise addition of the isocyanate, we observed that LiBr-HMPA gave **10** in only 34% yield at 40°C for 2 h and that the rest of isocyanate was converted to its trimer, as was confirmed by IR spectra (1700 cm^{-1} C=O). In contrast with these systems, our catalysts are very effective toward the cycloaddition, and the trimerization of PhNCO is no longer a problem. Therefore, the dropwise addition of PhNCO is not necessary.

The combination of organotin halides and Lewis bases is very important. Tributyltin iodide (Bu_3SnI) was more effective with Ph_3PO than with Ph_3P, whereas, this order was reversed in the case of dibutyltin diiodide (Bu_2SnI_2) (entries 2, 3, 8 and 9). Reaction proceeded more smoothly

Table 5. Cycloaddition of Oxiranes with PhNCO.[a]

Entry	Oxirane	Cat. System	Product	Yield (%)[b]
1		Bu_3SnI	 10	tr.
2		Bu_3SnI-Ph_3P		73
3		Bu_3SnI-Ph_3PO		96
4		Bu_3SnI-Et_3N		34
5		Bu_3SnI-DBU		41
6		Bu_3SnCl-Ph_3P		10
7		Bu_3SnBr-Ph_3P		35
8		Bu_2SnI_2-Ph_3P		94
9		Bu_2SnI_2-Ph_3PO		76
10		Bu_2SnI_2-Et_3N		69
11		Bu_3SnI-Ph_3P	 11	97
12		Bu_3SnI-Ph_3PO		100
13		Bu_3SnI-Ph_3P	 12	39
14		Bu_3SnI-Ph_3PO		90
15		Bu_3SnI-Ph_3P	 13a +  13b	tr.
16		Bu_3SnI-Ph_3PO		58 (37:63)[c]
17		Bu_3SnI-Ph_3PO	 14	100
18		Bu_3SnI-Ph_3PO	 15	89
19		Bu_3SnI-Ph_3PO	 16	88
20		Bu_3SnI-Ph_3PO	 17	12
21		Bu_2SnI_2-Ph_3P		13
22		Me_2SnI_2-HMPA		100
23		Bu_3SnI-Ph_3PO	 18	9
24		Me_2SnI_2-HMPA		22
25		Bu_3SnI-Ph_3PO	 19	tr.
26		Me_2SnI_2-HMPA		tr. (70)[d]

[a] PhNCO 10 mmol, Oxirane 50 mmol, Tin halide 1 mmol, Base 1 mmol, Temp. 40°C, Time 2 h.

[b] Based on PhNCO, GLC yield. [c] Determined by GLC. [d] PhNCO was added dropwise at 80°C.

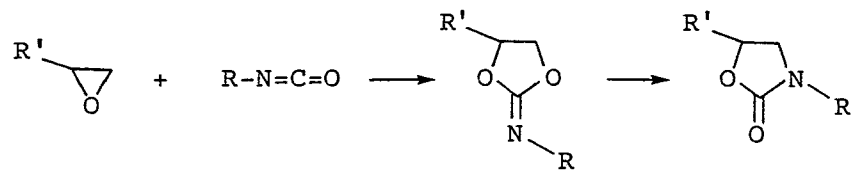
when catalyzed by the iodide than the chloride or the bromide (entries 2, 6 and 7). Strong Lewis bases such as Et_3N and DBU were unfavorable (entries 4, 5 and 10).

Table 5 shows the results of the cycloaddition of oxiranes with PhNCO to yield 2-oxazolidinones **11-19** (Table 5, entries 11-26), in which PhNCO was added at once. The reactivity of monosubstituted oxiranes could be compared by using Bu_3SnI-Ph_3P as a catalyst, which is less effective than Bu_3SnI-Ph_3PO and Bu_2SnI_2-Ph_3P. Butylene oxide, with an electron-donating substituent, was very reactive (entry 11), whereas, epichlorohydrin, with an electron-withdrawing one, showed relatively poor reactivity (entry 13), and styrene oxide hardly reacted (entry 15). However, an active complex, Bu_3SnI-Ph_3PO, afforded good yields of 2-oxazolidinones **11-16** from the cycloaddition of various monosubstituted oxiranes with PhNCO (entries 11-19). Reactions of aliphatic oxiranes proceeded via the regioselective cleavage at the unsubstituted carbon-oxygen bond of the oxirane (β-cleavage), giving 5-substituted-2-oxazolidinones only. On the other hand, styrene oxide gave 4-substituted-2-oxazolidinone **13b** as a mixture with 5-substituted isomer **13a** (entries 15 and 16). Disubstituted oxiranes showed poor reactivity in comparison with monosubstituted oxiranes. For instance, isobutylene oxide gave low yields of **17** (entries 20 and 21). However, the complex Me_2SnI_2-HMPA led to **17** in a quantitative yield (entry 22). This complex has a significant catalytic activity in comparison with other complexes mentioned above.

Cyclohexene oxide did not gave **19** at all under the same conditions (entries 25 and 26), however, compound **19** could be obtained in 70% yield by adding PhNCO dropwise at 80°C in order to depress the trimerization of PhNCO (entry 26 in parenthesis). Isoprene oxide gave **18** in a poor yield even when Me_2SnI_2-HMPA was used as a catalyst (entry 24).

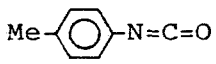
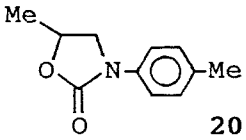
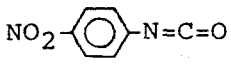
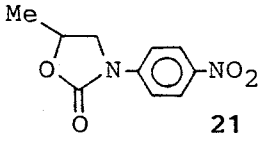
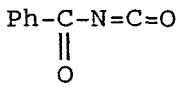
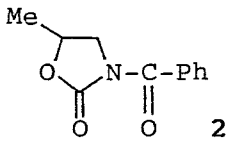
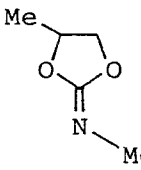
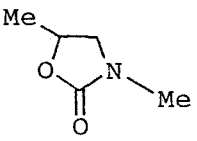
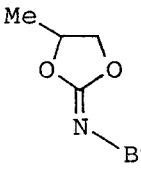
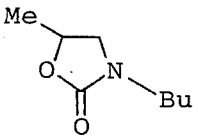
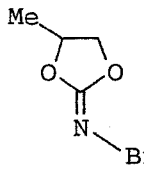
Other isocyanates also yielded cycloadducts with propylene oxide when catalyzed by Bu_3SnI-Ph_3PO (Table 6). Aromatic- and benzoyl isocyanates gave the corresponding 2-oxazolidinones **20-22** (entries 1-3). An electron-withdrawing substituent on the aromatic ring of an isocyanate decreased the reactivity. For example, p-nitrophenyl isocyanate gave **21** in 21% yield (entry 2), although p-tolyl isocyanate gave **20** in a quantitative yield (entry 1).

On the other hand, the formation of 2-dioxolanimines, **23**, **25** and **27** in the reaction of propylene oxide with aliphatic isocyanates, such as MeNCO, BuNCO and $PhCH_2NCO$, is very noteworthy (entries 4-6). 2-Dioxolanimines have not been isolated in the reactions activated by previous catalysts,[11] although they are considered as a precursor in the formation of 2-oxazolidinones[6b,12] (eq 5).



(5)

Table 6. Cycloaddition of Propylene Oxide with RNCO.[a]

Entry	R-N=C=O	Product	Yield (%)[b]
1		 **20**	100
2		 **21**	21
3		 **22**	85
4	Me-N=C=O	 **23**  **24**	100 (89/11)[c]
5	Bu-N=C=O	 **25**  **26**	100 (74/26)[c]
6	$PhCH_2$-N=C=O	 **27**	57

[a]Isocyanate 10 mmol, Propylene oxide 50 mmol, Bu_3SnI 1 mmol, Ph_3PO 1 mmol, Temp. 40°C, Time 2 h. [b]Based on RNCO, GLC yield. [c]Determined by GLC.

Table 7. Cycloaddition of Propylene Oxide with MeNCO.[a]

Entry	Additive	Yield (%)[b]	23/24[c]
1	Bu_3SnI	100	44/56
2	Bu_3SnI-Ph_3P	100	62/38
3	Bu_3SnI-Bu_3P	90	88/12
4	Bu_3SnI-Ph_3PO	93	94/6

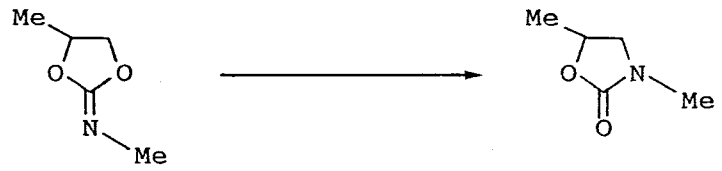
[a]MeNCO 5 mmol, Propylene oxide 50 mmol, Bu_3SnI 5 mmol, Base 5 mmol, Temp. 25° C, Time 1 h. [b]Based on MeNCO, GLC yield. [c]Determined by GLC.

In the stoichiometric reaction of propylene oxide with MeNCO in the presence of an equimolar amount of Bu_3SnI, a mixture of 2-dioxolanimine **23** and 2-oxazolidinone **24** was obtained (Table 7, entry 1), the addition of Lewis bases lowered the proportion of **24** (entries 2-4).

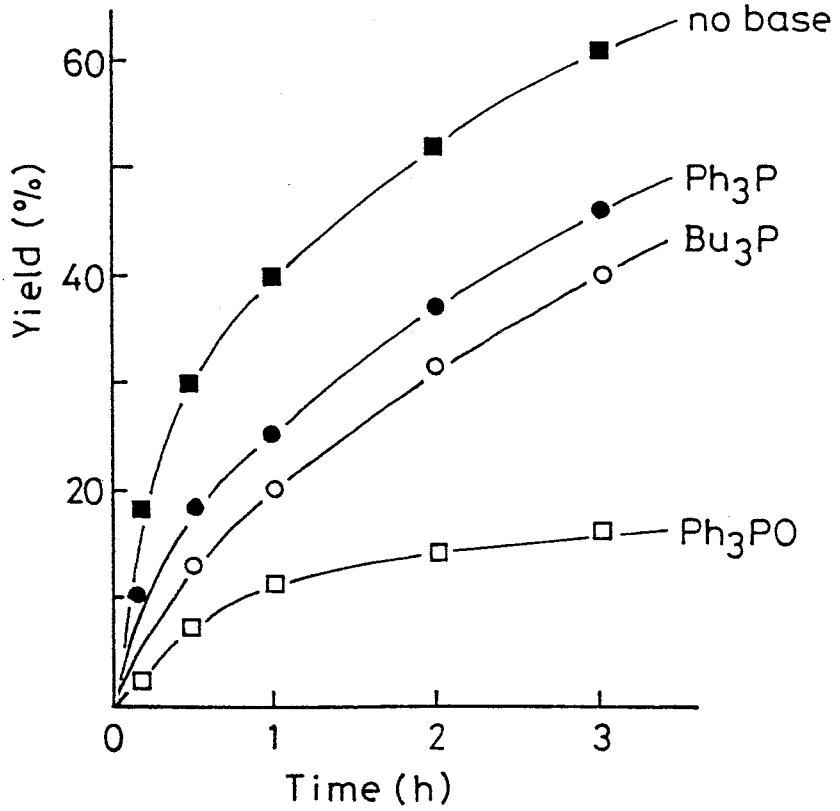
In these reactions, compound **24** may be formed by the isomerization of **23**. Authentic compound **23** is transformed into **24** in 61% yield after 3 hours upon treatment with an equimolar amount of Bu_3SnI (Fig. 1). It is noteworthy that the isomerization was depressed by adding bases, especially Ph_3PO.

Contrary to the N-alkyl-2-dioxolanimines above mentioned, we confirmed that no isomerization of N-phenyl-2-dioxolanimine **28** to the corresponding N-phenyl-2-oxazolidinone **10** takes place in the presence of an equimolar

Figure 1. The Isomerization of 23 to 24.

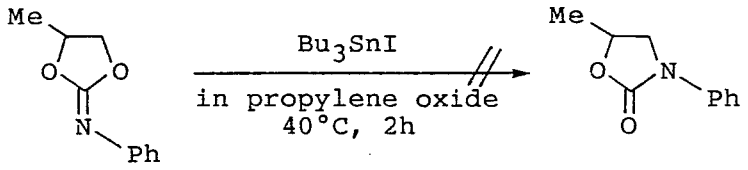


23 24



23 5 mmol, Bu_3SnI 5 mmol, Base 5 mmol, Propylene oxide 50 mmol, Temp. 25°C.

amount of Bu_3SnI and an excess of propylene oxide under conditions similar to those noted in Table 5 (eq 6).



28 10 (6)

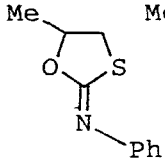
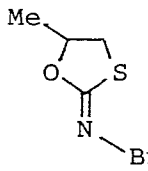
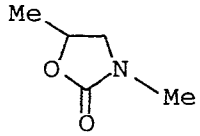
A higher reaction temperature is necessary to achieve this isomerization, as described in chapter 1.

From these facts, in the catalytic cycloaddition (Table 6), it appears that N-alkyl-2-dioxolanimines, **23**, **25** and **27**, are formed first and then N-alkyl-2-oxazolidinones, **24**, **26** may be formed via the isomerization. On the other hand, N-aryl-2-oxazolidinones are thought to be formed directly, and not via the isomerization of the corresponding 2-dioxolanimines.

2-2-2 Cycloaddition of Oxirane with Isothiocyanates.

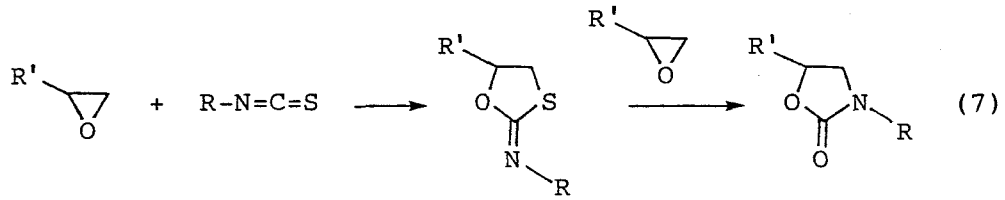
Isothiocyanates reacted with propylene oxide across the C=S group catalyzed by organotin halide-Lewis base complexes to yield 2-oxathiolanimines (Table 8). This is noteworthy, because in the cycloaddition of oxiranes with isothiocyanates, 2-oxathiolanimines are detected only when using activated isothiocyanates such as acetyl- and benzoyl isothiocyanates.[13] Aromatic- and aliphatic isothiocyanates

Table 8. Cycloaddition of Propylene Oxide with RNCS.[a]

Entry	R-N=C=S	Cat. System	Time (h)	Product	Yield[b] (%)
1	Ph-N=C=S	Bu_3SnI-Ph_3PO	2		9
2		"	24	**29** **10**	88 (72/28)[c]
3		Me_2SnI_2-HMPA	2		100 (100:0)[c]
4	$PhCH_2N=C=S$	"	2	 **30**	59
5	Me-N=C=S	"	2	 **24**	tr.
6		"	30		75

[a]Isothiocyanate 10 mmol, Propylene oxide 50 mmol, Tin halide 1 mmol, Base 1 mmol, temp. 40°C. [b]Based on RNCS, GLC yield. [c]Determined by GLC.

usually do not give 2-oxathiolanimines[14] because of the facile conversion to 2-oxazolidinones in the presence of oxiranes[15] (eq 7).



(7)

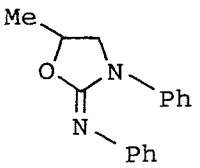
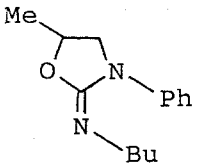
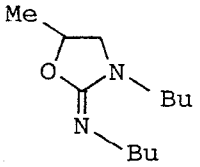
With the organotin halide-Lewis base complex as catalysts, isothiocyanates showed lower reactivity in comparison with isocyanates. For example, PhNCS reacted with propylene oxide to give 2-oxathiolanimine **29** in 9% yield when catalyzed by Bu_3SnI-Ph_3PO at 40°C for 2 h (entry 1),[16] although PhNCO gave **10** quantitatively (Table 5, entry 3). A prolonged reaction time (24 h) was necessary to achieve a higher yield (entry 2). In this case, 2-oxazolidinone **10** was formed as a by-product.

However, complex Me_2SnI_2-HMPA showed a greater catalytic activity to yield 2-oxathiolanimine **29** in a quantitative yield at 40°C for 2 h (entry 3). This complex is so active that the cycloaddition is complete under mild conditions before the isomerization of **29** to **10** takes place. N-Benzyl-2-oxathiolanimine **30** was also obtained from the cycloaddition of propylene oxide with $PhCH_2NCS$ (entry 4), although the reactivity was lower than PhNCS. In the case of MeNCS, the reactivity was much lower, and N-methyl-2-oxathiolanimine could not be isolated, and only **24**, the converted product, was obtained (entry 6).

2-2-3 Cycloaddition of Oxirane with Carbodiimides.

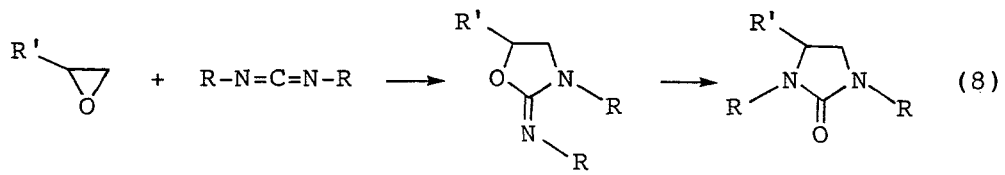
The cycloaddition of propylene oxide with carbodiimides yielded 2-oxazolidinimines (Table 9). In the reaction of PhNCNPh, the complex Bu_2SnI_2-Ph_3P was most effective, affording **31** in high yield (entry 4).

Table 9. Cycloaddition of Propylene Oxide with RNCNR'.[a]

Entry	R-N=C=N-R	Cat. System	Product		Yield (%)[b]
1	Ph-N=C=N-Ph	Bu_3SnI		31	44
2		$Bu_3SnI-Ph_3P$			57
3		$Bu_3SnI-Ph_3PO$			80
4		$Bu_2SnI_2-Ph_3P$			92
5	Bu-N=C=N-Ph	$Bu_2SnI_2-Ph_3P$		32	100
6	Bu-N=C=N-Bu	$Bu_3SnI-Ph_3P$		33	9
7		$Bu_2SnI_2-Ph_3P$			85

[a]RNCNR' 10 mmol, Propylene oxide 50 mmol, Tin halide 1 mmol, Base 1 mmol, Temp. 40°C, Time 2 h. [b]Based on RNCNR', GLC yield.

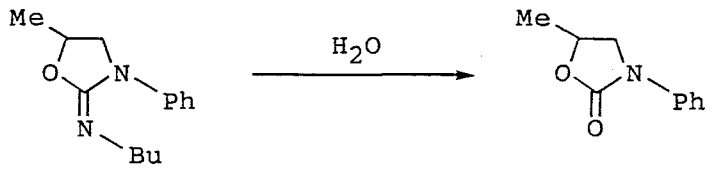
From earlier observations, 2-imidazolidinones are major products under severe conditions using several catalysts,[17] and they are considered to be formed by isomerization of 2-oxazolidinimines[18] (eq 8).



(8)

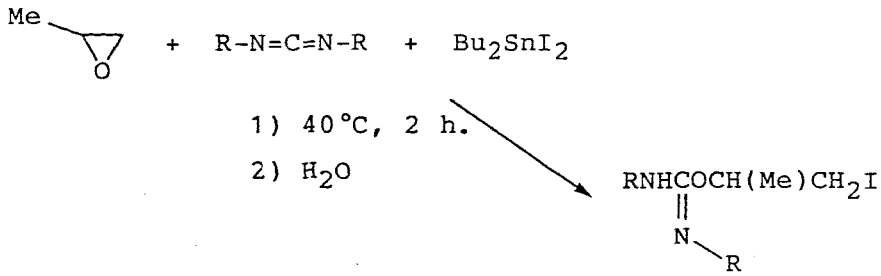
These results indicate that the catalytic activity oforganotin halide-Lewis base complexes is very high, and hence the reaction conditions are mild enough to trap the intermediate quantitatively without the isomerization.

In the reaction with an unsymmetrical carbodiimide such as BuNCNPh, the cycloaddition took place selectively across the Ph-N=C group of BuNCNPh rather than the Bu-N=C group to yield 3-phenyl-2-oxazolidin-N-butylimine (32) (entry 5). Structural evidence was afforded by hydrolysis to give 2-oxazolidinone **10** (eq 9).



32 **10** (9)

Aliphatic carbodiimides were less reactive than PhNCNPh. The cycloaddition of BuNCNBu gave 33 in 9% yield when catalyzed by Bu_3SnI-Ph_3P (entry 6), although compound 31 was obtained from PhNCNPh in 57% yield under the same conditions (entry 2). However, Bu_2SnI_2-Ph_3P was more active, affording 33 in 85% yield (entry 7). Other bulky carbodiimides such as diisopropyl- and dicyclohexyl-carbodiimide did not give cycloadducts. Treatment of these carbodiimides with an equimolar amount of Bu_2SnI_2 and propylene oxide followed by hydrolysis gave acyclic iminocarbamate adducts (eq 10).



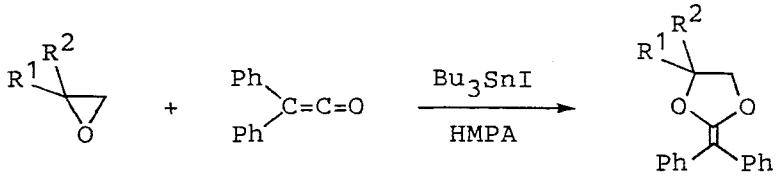
(10)

R = isopropyl	34	64 %
cyclohexyl	35	56 %

2-2-4 Cycloaddition of Oxiranes with Diphenylketene.

As shown in Table 10, cycloaddition proceeded under very mild conditions using Bu_3SnI-HMPA as a catalyst, and a

Table 10. Cycloaddition of Oxiranes with Ph_2CCO.[a]



Entry	R^1	R^2	Product	Yield (%)[b]
1	Me	H	**36**	100
2	Et	H	**37**	93
3	Me	Me	**38**	73
4	CH_2Cl	H	**39**	88
5	$PhOCH_2$	H	**40**	82
6	Ph	H	**41**	94

[a]Ph_2CCO 5 mmol, Oxirane 25 mmol, Bu_3SnI 1 mmol, HMPA 1 mmol, Temp. 40°C, Time 1 h, [b]Based on Ph_2CCO.

variety of 1,3-dioxolanes (**36-41**) were obtained in good to excellent yields. These reactions generally requires very severe conditions (ca. 200°C) using LiCl as a catalyst.[17]

2-2-5 A Plausible Catalytic Cycle.

As described in chapter 1, organotin β-haloethoxides can be regard as the synthon of oxiranes. The features of the reaction using $Bu_3SnO(CH_2)_2X$ are similar with the direct addition of oxiranes with heterocumulenes such that the cycloaddition may proceed via an organotin β-haloethoxides.

Accordingly, the following mechanism can be proposed (Scheme 6).

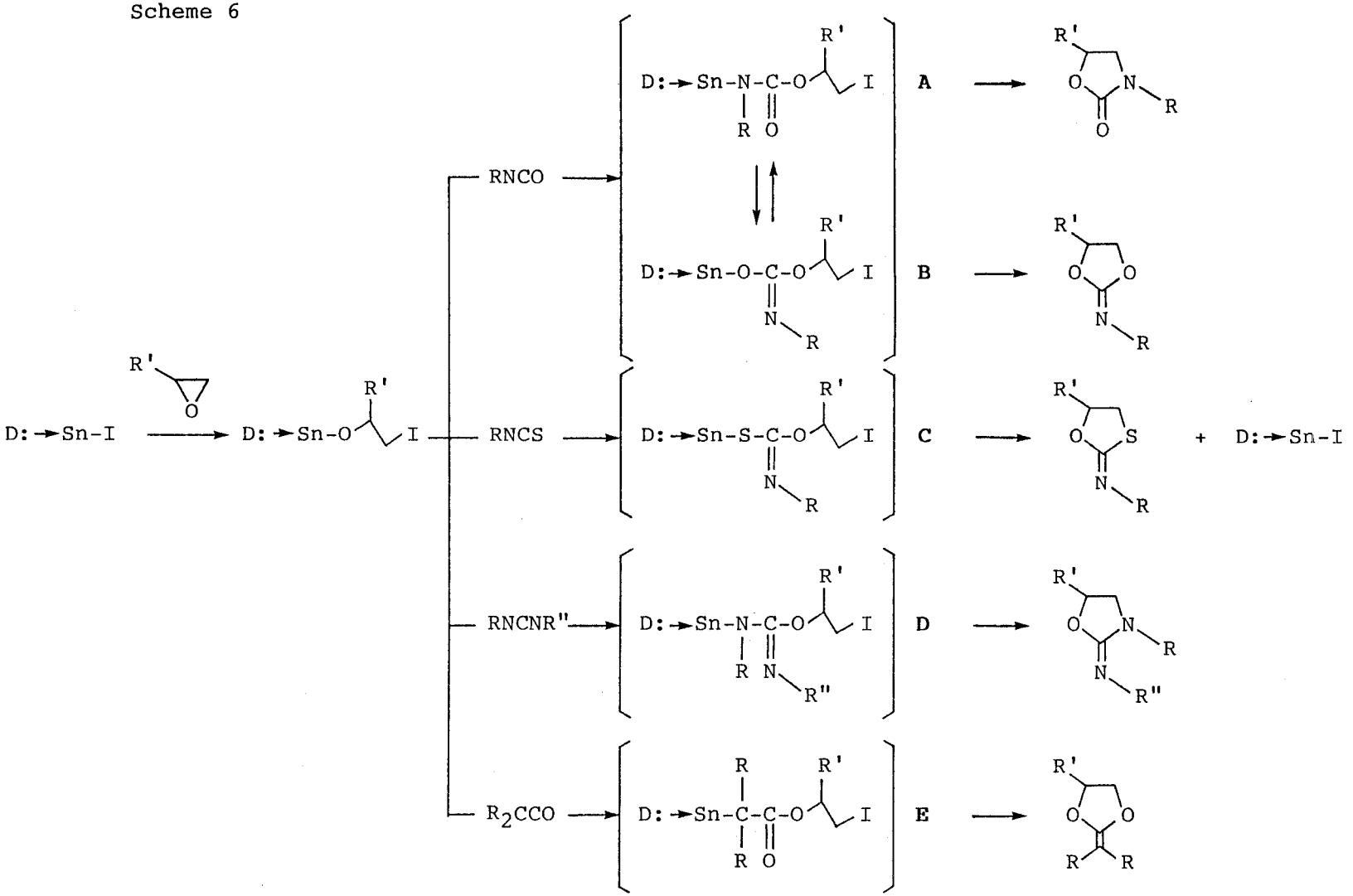
(1) Initially, an organotin β-iodoalkoxide is formed via the cleavage of an oxirane by the tin-halogen bond.

(2) This is followed by the addition of the Sn-O bond to heterocumulenes to yield intermediates **A-E.**

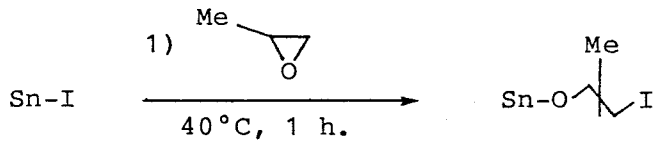
(3) The intramolecular alkylation produces five-membered heterocyclic compounds.

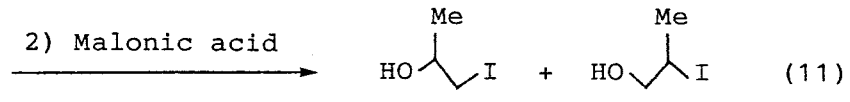
In this catalytic cycle, step 2 and step 3 are consistent with the reaction path described in chapter 1. So, step 1 is important for the completion of this catalytic cycle. Organotin halides are effective for ring opening of oxiranes, such as the polymerization of oxiranes[19] and the formation of halohydrins.[20] Fiorenza et al. have reported that Me_3SnI cleaves propylene oxide to give trimethyltin β-iodoalkoxide (Me_3SnOCH_2CHMeI).[20b] They have reported cleavage at the hindered MeCH-O bond (α-cleavage) rather

Scheme 6


D:→Sn-I
R'
O
D:→Sn-O
R'
I
RNCO
RNCS
RNCNR"
R2CCO
D:→Sn-N-C-O
R
O
R'
I
A
B
C
D
E
D:→Sn-O-C-O
N
R
D:→Sn-S-C-O
D:→Sn-C-C-O
R"
S
+
D:→Sn-I

than at the CH_2-O bond (β-cleavage) of propylene oxide. Contrary to this fact, in this study, the heterocyclic compounds obtained are 5-substituted ones only, which are formed via β-cleavage of oxiranes. Actually, we confirmed that treatment of Bu_3SnI with propylene oxide followed by destannylation with malonic acid afforded 1-methyl-2-iodoethanol **42a** selectively, and especially, addition of Ph_3PO increased the yield (eq 11).





(11)

42a **42b**

Bu_3SnI	47 %	0 %
Bu_3SnI-Ph_3PO	77 %	0 %

This fact indicates that the reaction proceeds via an organotin β-iodoethoxide which is formed by the regiospecific β-cleavage of oxiranes (Step 1). In the case of styrene oxide, because of the stabilization of a positive charge by conjugative electron release from the π-orbital of an aromatic substituent,[21] β-cleavage may accompany α-cleavage, giving 4-phenyl-2-oxazolidinone **13b** along with the 5-phenyl-isomer **13a**.

The types of products are determined in step 2. In the case of isocyanates, two types of intermediates, **A** and **B**, can be considered, and the features were interpreted in chapter 1. In the case of isothiocyanates, 2-oxathiolanimines are obtained via intramolecular S-alkylation in the intermmediate **C**. The order of the reactivity of RNCS in the cycloaddition was R= aryl- > benzyl- > alkyl, which is consistent with the order of reactivity in the addition of the Sn-O bond to RNCS as described by Sakai et al.[15] As for carbodiimides, intermediate **D** is proposed. This was trapped as destannylated compounds, **34** and **35**, in the reaction of diisopropyl- or dicyclohexylcarbodiimide. In this case, bulky substituents on the nitrogen atom may prevent the intramolecular cyclization. The addition of the Sn-O bond occurs across the Aryl-N=C group rather than the Alkyl-N=C group in the reaction of BuNCNPh. Finally, the reaction with ketene addords the stannylester type of intermmediate **E**, as explained in 1-5.

In next stage of step 3, Lewis bases play an important role. The co-ordination of a base to the tin atom increases the basicity of the adjacent hetero atom, and hence the intramolecular alkylation is accelerated, giving heterocyclic compounds. The Sn-I bond is formed in this step.

In conclusion, organotin halide-Lewis base complexes are efficient catalysts for cycloaddition of oxiranes with heterocumulenes under mild and neutral conditions.

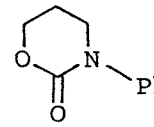
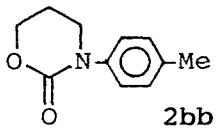
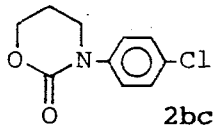
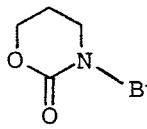
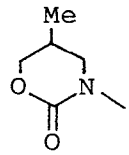
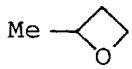
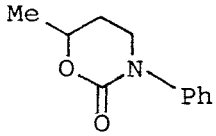
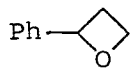
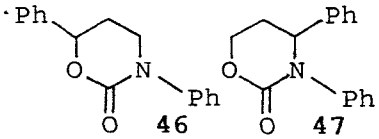
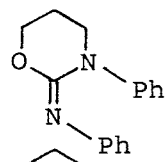
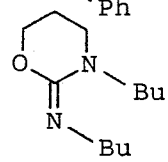
2-3 Cycloaddition of Oxetanes with Heterocumulenes.

Cycloaddition of oxetanes with heterocumulenes can be considered as a useful method for preparation of six-membered heterocyclic compounds. However, few examples are reported on this type of cycloaddition because of the lower reactivity of oxetanes for ring opening in comparison with oxiranes. Only one patent reported the reaction of oxetane with carbodiimides in the presence of triethylamine.[22] In fact, equimolar amounts of the complex of Bu_2SnI_2 with Ph_3PO was necessary to achieve the cycloaddition of oxetane with PhNCO, where 69% yield of 3-phenyl-2-oxazinone (**2ba**) was achieved at 40°C for 3 h. This is the first example of the cycloaddition of oxetanes with isocyanates. However, when a catalytic amount of this tin complex was used, desired 2-oxazinones were scarcely obtained. This might be due to the trimerization of isocyanates.[10] Accordingly, it is necessary to develop more effective tin complexes for completing this catalytic reaction without trimerization of isocyanates.

Fortunately, the catalytic activity was increased by the selection of the combination between organotin iodides and Lewis bases. Among the catalysts examined in the reaction of oxetane with PhNCO, the most effective catalyst was the complex of diphenyltin diiodide (Ph_2SnI_2) with HMPA, which afforded 77% yield of 2-oxazinone (**2ba**) at 80°C for 1 h.

As described in 2-2, similar catalytic cycle may be also applied in the case of oxetanes, involving the

Table 11. Cycloaddition of Oxetanes with Heterocumulenes.[a]

Entry	Substrate	Temp. (°C)	Time (h)	Product	Yield[b] (%)
1	 Ph-N=C=O	80	1	 **2ba**	77
2	 p-Tol-N=C=O	80	1	 **2bb**	100
3	 p-ClC_6H_4N=C=O	80	3	 **2bc**	46
4	 Bu-N=C=O	80	3	 **43**	63
5	 Ph-N=C=O	80	3	 **44**	68
6	 Ph-N=C=O	80	3	 **45**	100
7	 Ph-N=C=O	80	3	 **46** **47**	66 (63/37)[c]
8	 Ph-N=C=N-Ph	40	1	 **3b**	93
9	 Bu-N=C=N-Bu	40	1	 **48**	91

[a]Heterocumulene 10 mmol, Oxetane 15 mmol, Ph_2SnI_2 1 mmol, HMPA 1mmol, [b]Based on Heterocumulene. [c]Determined by GLC.

formation of an organotin γ-iodoalkoxide followed by the insertion of an isocyanate. However, the ring cleavage of oxetane and the regeneration of catalyst are considerable ploblems because the reactivity of oxetanes is lower than that of oxiranes. The choice of the combination of organotin iodide and Lewis base, therefore, is more significant in comparison with the reaction of oxiranes.

Table 11 shows the yields of various heterocycles prepared from the cycloaddition of oxetanes with isocyanates or carbodiimides, catalyzed by Ph_2SnI_2-HMPA complex. As to isocyanates, the one bearing an electron donating substituent, p-tolyl isocyanate, showed the highest reactivity, and yielded **2bb** quantitatively (entry 2). The reaction of substituted oxetanes includes a problem of the regioselectivity in the ring cleavage. In the reaction of 2-methyloxirane, the cleavage occurred regioselectively to form 6-methyl-2-oxazinone **45** as a sole product. This may be because of the ability of the tin complex to promote the cleavage at the unhindered C-O bond, and similar phenomena was also observed in 2-2-1. The 2-oxazinone **45** was confirmed by the comparison of ^{1}H-NMR spectra with that of the 4-methyl isomer.[23] On the other hand, 2-phenyloxetane gave both of the isomers, **46** and **47**. This is because of the stabilization of a positive charge by conjugative electron release from the π-orbital of an aromatic substituent as described in 2-2-1.

Next, we tried the cycloaddition of oxetane with carbodiimides (entry 8 and 9). The reactivity of

carbodiimides was higher than that of isocyanates, and the reactions were clean and gave exellent yields. Thus, 2-oxazinimine derivatives, **3b** and **48**, were obtained almost quantitatively even at 40°C for 1 h.

In conclusion, the catalytic cycloaddition of oxetanes with isocyanates or carbodiimides was achieved by using Ph_2SnI_2-HMPA complex as a catalyst, and offers a convenient and useful methods for the preparation of six membered heterocycles.

2-4 Experimental Section.

Materials. All oxiranes were freshly distilled from CaH_2. All Lewis bases were purified by general procedures. PhCONCO,[24] $PhCH_2NCO$,[25] BuNCNBu,[26] BuNCNPh[26] and PhNCNPh[27] were prepared according to described methods. Other isocyanates and isothiocyanates were commercial ones and used without further purification. Organotin iodides, Bu_3SnI, Bu_2SnI_2 and Me_2SnI_2, were produced according to described methods.[28]

Cycloaddition of Oxiranes with Isocyanate (Typical Procedure).

To a solution of Bu_3SnI (0.42 g, 1 mmol) and Ph_3PO (0.27 g, 1 mmol) in propylene oxide (2.90 g, 50 mmol) was added PhNCO (1.19 g, 10 mmol) with stirring under dry nitrogen. The resulting mixture was stirred at 40°C for 2 h, and the yield of **10** was monitored by GLC (1.70 g, 96%). The reaction mixture no longer contained the isocyanate.

The excess propylene oxide was removed in vacuo and the residue was subjected to purification by column chromatography on silica gel. Compound **10** (1.65 g, 93%) was obtained as white needles, which were recrystallized from benzene-hexane:

5-Methyl-3-phenyl-1,3-oxazolidin-2-one (10): mp 78-80°C (lit.[2b] 80-82°C); IR (KBr) 1740 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.50 (d, 3H), 3.60 (dd, 1H), 4.10 (t, 1H), 4.60-4.95 (m, 1H), 7.00-7.60 (m, 5H); MS, m/e 177 (M^+).

5-Ethyl-3-phenyl-1,3-oxazolidin-2-one (11): bp 124°C (1.5 mmHg); IR (neat) 1750 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.98 (t, 3H), 1.50-1.90 (m, 2 H), 3.50 (dd, 1 H), 3.95 (t, 1H), 4.30-4.65 (m, 1H), 7.00-7.60 (m, 5H); ^{13}C NMR ($CDCl_3$) δ=8.3 (q), 27.5 (t), 49.6 (t), 73.9 (d), 117.8 (d), 123.4 (d), 128.6 (d), 138.2 (s), 154.7 (s); MS, m/e 191 (M^+): Anal. Calcd for $C_{11}H_{13}O_2N$: C, 69.09; H, 6.85; N, 7.33. Found: C, 68.69; H, 6.77; N, 7.47.

5-Chloromethyl-3-phenyl-1,3-oxazolidin-2-one (12): mp 98-100°C (lit.[2b] 103°C); IR (KBr) 1740 cm^{-1}; ^1H NMR ($CDCl_3$) δ=3.78 (d, 2H), 3.80-4.30 (m, 2H), 4.70-5.00 (m, 1H), 7.00-7.60 (m, 5H); MS, m/e 211.5 (M^+).

Compounds **13a** and **13b** were identified by comparison with the authentic data.[6d]

3,5-Diphenyl-1,3-oxazolidin-2-one (13a): mp 130°C (lit.[6d] 128-129°C); IR (KBr) 1740cm^{-1}; ^1H NMR ($CDCl_3$) δ=3.90 (dd, 1H), 4.30 (t, 1H), 5.60 (dd, 1H), 7.10-7.60 (m, 10H); MS, m/e 239 (M^+).

3,4-Diphenyl-1,3-oxazolidine-2-one (13b): mp 79°C (lit.[6d] 78-79°C); IR (KBr) 1750 cm^{-1}; ^1H NMR ($CDCl_3$) δ=4.15 (dd, 1H), 4.75 (t, 1H), 5.40 (dd, 1H), 7.00-7.50 (m, 10H); MS, m/e 239 (M^+).

5-Ethoxymethyl-3-phenyl-1,3-oxazolidin-2-one (14): bp 124°C (1.5 mmHg); IR (neat) 1750 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.18 (t, 3H), 3.40-3.65 (m, 4H), 3.70-4.10 (m, 2H), 4.55-4.85 (m, 1H), 7.00-7.60 (m, 5H); ^{13}C NMR ($CDCl_3$) δ=14,7 (q), 46.8 (t), 66.9 (t), 70.3 (t), 71.3 (d), 117.9 (d), 123.6 (d), 128.7 (d), 138.1 (s), 154.5 (s); MS, m/e 221 (M^+); Anal. Calcd for $C_{12}H_{15}O_3N$: C, 65.14; H, 6.83; N, 6.33. Found: C, 64.96; H, 6.72; N, 6.03.

5-Allyloxymethyl-3-phenyl-1,3-oxazolidin-2-one (15): bp 159°C (10^{-3} mmHg) (lit.[2b] 176°C (0.06 mmHg)); IR (neat) 1750 cm^{-1}; ^1H NMR ($CDCl_3$) δ=3.60 (d, 2H), 3.70-4.10 (m, 4H), 4.50-4.90 (m, 1H), 5.00-5.40 (m, 2H), 5.60-6.10 (m, 1H), 7.00-7.60 (m, 5H); MS, m/e 233 (M^+).

3-Phenyl-5-phenoxymethyl-1,3-oxazolidin-2-one (16): mp 139°C (lit.[2b] 137-138°C); IR (KBr) 1740 cm^{-1}; ^1H NMR ($CDCl_3$) δ=3.95-4.30 (m, 4H), 4.90-5.10 (m, 1H), 6.80-7.65 (m, 10H); MS, m/e 269 (M^+).

5,5-Dimethyl-3-phenyl-1,3-oxazolidin-2-one (17): mp 94-95°C (lit.[32] mp 98-99.5°C); IR (KBr) 1740 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.50 (s, 6H), 3.75 (s, 2H), 7.00-7.60 (m, 5H); MS, m/e 191 (M^+).

5-Methyl-3-phenyl-5-vinyl-1,3-oxazolidin-2-one (18): bp 83°C (10^{-3} mmHg); IR (neat) 1750 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.60 (s, 3 H), 3.75 (d, 1H), 3.90 (d, 1H), 5.15-5.60 (m, 2H),

5.80-6.20 (dd, 1H), 7.00-7.60 (m, 5H); ^{13}C NMR ($CDCl_3$) δ=25.7 (q), 56.4 (t), 77.9 (s), 115.1 (t), 118.5 (d), 124.1 (d), 129.1 (d), 138.7 (s), 139.1 (d), 154.3 (s); MS, m/e 203 (M^+).

4,5-Hexahydrobenzo-3-phenyl-1,3-oxazolidin-2-one (19): mp 93-94°C; IR (KBr) 1740 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.05-2.30 (m, 8H), 4.15-4.40 (m, 1H), 4.55-4.80 (m, 1H), 7.00-7.60 (m, 5H); ^{13}C NMR ($CDCl_3$) δ=19.1 (t), 19.9 (t), 26.0 (t), 26.6 (t), 55.9 (d), 73.2 (d), 120.9 (d), 124.6 (d), 129.1 (d), 137.2 (s), 155.9 (s); MS, m/e 217 (M^+); Anal. Calcd for $C_{13}H_{15}O_2N$: C, 71.87; H, 6.96; N, 6.45. Found: C, 71.45; H,6.93; N, 6.36.

5-Methyl-3-p-tolyl-1,3-oxazolidin-2-one (20): mp 65-66°C (lit.[2b] mp 67.5°C); IR (KBr) 1740 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.52 (d, 3H), 2.30 (s, 3H), 3.58 (dd, 1H), 4.08 (t, 1H), 4.60-5.00 (m, 1H), 7.00-7.80 (m, 4H); MS, m/e 191 (M^+).

5-Methyl-3-p-nitrophenyl-1,3-oxazolidin-2-one (21): mp 131°C; IR (KBr) 1750 cm^{-1}; ^1H NMR (DMSO-d_6) δ=1.45 (d, 3H), 3.79 (dd, 1H), 4.28 (t, 1H), 4.85-5.00 (m, 1H), 7.60-8.40 (m, 4H); ^{13}C NMR (DMSO-d_6) δ=20.0 (q), 50.9 (t), 70.2 (d), 117.6 (d), 124.8 (d), 142.2 (s), 144.4 (s), 154.1 (s); MS, m/e 222 (M^+).

3-Benzoyl-5-methyl-1,3-oxazolidin-2-one (22): mp 105-106°C (lit.[2b] 111°C); IR (KBr) 1790, 1680 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.50 (d, 3H), 3.70 (dd, 1H), 4.18 (t, 1H), 4.60-4.90 (m, 1H), 7.20-8.20 (m, 5H); MS m/e 205 (M^+).

N,4-Dimethyl-1,3-dioxolan-2-imine (23). In a similar manner described above, compound 23 was prepared in 86% GLC yield

as a mixture with **24** (**23**:**24** = 89:11). Purification was accomplished by distillation: bp 45-48°C (1 mmHg); IR (neat) 1690 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.40 (d, 3H), 2.85 (s, 3H), 3.75-4.00 (m, 1H), 4.30-4.90 (m, 2H); MS, m/e 115 (M^+); Anal. Calcd for $C_5H_9O_2N$: C, 52.16; H, 7.88; N, 12.17. Found: C, 51.89; H, 8.04; N, 12.42.

N-Butyl-4-methyl-1,3-dioxolan-2-imine (**25**): bp 82-84°C (1 mmHg); IR (neat) 1720 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.90 (t, 3H), 1.20-1.60 (m, 7H), 3.15 (t, 2H), 3.70-4.00 (m, 1H), 4.20-4.85 (m, 2H); MS, m/e 157 (M^+); Anal. Calcd for $C_8H_{15}O_2N$: C, 61.12; H, 9.62; N, 8.91. Found: C, 60.89; H, 9.69; N, 8.83.

N-Benzyl-4-methyl-1,3-dioxolan-2-imine (**27**): bp 135°C (1 mmHg); IR (neat) 1750 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.35 (d, 3H), 2.92 (dd, 1H), 3.47 (t, 1H), 4.40 (s, 2H), 4.40-4.80 (m, 1H), 7.20-7.40 (m, 5H); ^{13}C NMR ($CDCl_3$) δ=20.6 (q), 48.2 (t), 50.7 (t), 70.1 (d), 127.5 (d), 128.1 (d), 128.9 (d), 135.9 (s), 158.2 (s); MS, m/e 191 (M^+).

3,5-Dimethyl-1,3-oxazolidin-2-one (**24**). A mixture of **23** (0.57 g, 5 mmol) and Bu_3SnI (2.10 g, 5 mmol) was stirred under dry nitrogen at room temperature. After 24 h, the compound **23** was completely transformed to **24** (100% yield by GLC). Purification was performed by column chromatography on SiO_2 with $CHCl_3$: bp 94-96°C (5 mmHg) (lit.[2b] 92°C (1.5 mmHg)); IR (neat) 1740 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.40 (d, 3H), 2.82 (s, 3H), 3.10 (t, 1H), 3.65 (t, 1H), 4.50-4.70 (m, 1H); MS, m/e 115 (M^+).

3-Butyl-5-methyl-1,3-oxazolidin-2-one (**26**). This compound was also obtained by the transformation of **25**: bp 93-95°C

(3 mmHg); IR (neat) 1740 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.80-1.70 (m, 10H), 3.00-3.40 (m, 3H), 3.65 (t, 1H), 4.45-4.80 (m, 1H); ^{13}C NMR ($CDCl_3$) δ=13.4 (q), 19.5 (q), 20.4 (t), 29.1 (t), 43.4 (t), 51.0 (t), 69.7 (d), 157.9 (s); MS, m/e 157 (M^+).

Cycloaddition of Propylene Oxide with Isothiocyanates (Typical Procedure).

To a mixture of Me_2SnI_2 (0.40 g, 1 mmol) and HMPA (0.18 g, 1 mmol) in propylene oxide (2.90 g, 50 mmol) was added PhNCS (1.35 g, 10 mmol) with stirring under dry nitrogen. The resulting mixture was stirred at 40°C for 2 h. The disappearance of characteristic band of PhNCS at 2100 cm^{-1} was observed in IR spectra. The yield of product was determined by GLC (1.93 g, 100%). Excess propylene oxide was removed in vacuo, and the residual high viscosity oil was chromatographed, yielding 1.90 g (98%) of **29** as a colourless clear wax.

N-Phenyl-5-methyl-1,3-oxathiolan-2-imine (29): IR (neat) 1660 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.45 (d, 3H), 2.95 (dd, 1H), 3.30 (dd, 1H), 4.50-4.90 (m, 1H), 6.95-7.60 (m, 5H); ^{13}C NMR ($CDCl_3$) δ=18.7 (q), 37.3 (t), 78.4 (d), 121.0 (d), 123.8 (d), 128.7 (d), 148.7 (s), 163.6 (s); MS, m/e 193 (M^+).
N-Benzyl-5-methyl-1,3-oxathiolan-2-imine (30): IR (neat) 1660 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.45 (d, 3H), 3.00 (dd, 1H), 3.35 (dd, 1H), 4.40 (s, 2H), 4.50-4.80 (m, 1H), 7.20-7.40 (s, 5H); ^{13}C NMR ($CDCl_3$) δ=19.0 (q), 37.7 (t), 57.3 (t), 77.6 (d), 126.6 (d), 127.4 (d), 128.2 (d), 139.5 (s), 162.5

(s); MS, m/e 207 (M^+).

Cycloaddition od Propylene Oxide with Carbodiimides (Typical Procedure).

To the solution of Bu_3SnI (0.42 g, 1 mmol) and Ph_3PO (0.27 g, 1 mmol) in propylene oxide (2.90 g, 50 mmol) was added PhNCNPh (1.94 g, 10 mmol) with stirring under dry nitrogen. The resulting mixture was stirred at 40°C for 2 h. IR spectra showed the disappearance of characteristic band of PhNCNPh at 2150 cm^{-1}. The yield of product was monitored by GLC (2.52 g, 100%). Excess of propylene oxide was removed in vacuo and the residue was chromatographed, yielding **31** (2.14 g, 85%) as white needles, which were purified by recrystallization from benzene-hexane:

N-Phenyl-3-phenyl-5-methyl-1,3-oxazolidin-2-imine (31): mp 72-73°C (lit.[17] 76-77°C); IR (KBr) 1670 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.45 (d, 3H), 3.55 (dd, 1H), 4.05 (t, 1H), 4.50-4.90 (m, 1H), 6.90-7.80 (m, 10H); MS, m/e 252 (M^+).

N-Butyl-3-phenyl-5-methyl-1,3-oxazolidin-2-imine (32): bp 90°C (2 mmHg); IR (neat) 1700 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.95-1.70 (m, 10H), 3.30 (t, 2H), 3.45 (t, 1H), 3.95 (t, 1H), 4.50-4.80 (m, 1H), 6.80-7.80 (m, 5H); ^{13}C NMR ($CDCl_3$) δ=14.0 (q), 20.1 (q), 20.6 (t), 34.0 (t), 46.5 (t),52.9 (t), 70.9 (d), 118.0 (d), 121.8 (d), 128.6 (d), 140.7 (s), 149.5 (s); MS, m/e 232 (M^+).

N,3-Dibuthyl-5-methyl-1,3-oxazolidin-2-imine (33): bp 68°C (2 mmHg); IR (neat) 1700 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.80-1.70 (m, 17H), 2.95-3.50 (m, 5H), 3.65 (t, 1H), 4.60-4.90 (m, 1H);

^{13}C NMR ($CDCl_3$) δ=13.8 (q, 2C), 19.9 (q), 20.2 (t, 2C), 29.2 (t, 2C), 33.4 (t), 45.3 (t), 53.2 (t), 73.6 (d), 155.5 (s); MS, m/e 212 (M^+).

β-Iodoisopropyl-N,N'-diisopropylcarbamamimidate (34): mp 128°C; IR (KBr) 1680 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.20-1.70 (m, 15H), 3.45 (t, 1H), 4.00-4.30 (m, 2H), 4.90-5.10 (m, 1H), 5.20-5.50 (m, 1H), 7.50 (br, 1H); Anal. Calcd for $C_{10}H_{21}ON_2I$: C, 38.47; H, 6.78; N, 8.97. Found: C, 38.15; H, 6.72; N, 8.92.

β-Iodoisopropyl-N,N'-dicyclohexylcarbamimidate (35): mp 209-211°C; IR (KBr) 1670 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.00-2.10 (m, 24H), 3.42 (dd, 1H), 3.50-3.90 (m, 1H), 4.15 (t, 1H), 4.60-5.00 (m, 1H), 5.15-5.50 (m, 1H); Anal. Calcd for $C_{16}H_{29}ON_2I$: C, 48.98; H, 7.45; N, 7.14. Found: C, 48.79; H, 7.29; N, 6.82.

Cycloaddition of Oxiranes with Diphenylketene (Typical Procedure).

To a solution of Bu_3SnI (0.42 g, 1 mmol) and HMPA (0.18 g, 1 mmol) in propylene oxide (1.45 g, 25 mmol) was added diphenylketene (0.97 g, 5 mmol) with stirring under dry nitrogen. The resulting mixture was stirred at 40°C for 2 h and the yield was monitored by GLC. Diphenylketene was no longer detected, which was confirmed by the disappearance of IR absorption band of ketene (2100 cm^{-1}). Excess amounts of hexane was added on cooling to the reaction mixture, then 1.12 g (89%) of white precipitates were obtained immediately. This was collected by filtration,

washed with hexane and dried in vacuo. The precipitates was 2-diphenylmethylene-4-methyl-1,3-dioxolane (36). Compounds 37 and 38 were isolated by a similar method. Compounds 39, 40 and 41 were isolated by distillation from the reaction mixture.

2-Diphenylmethylene-4-methyl-1,3-dioxolane (36): mp 88-89°C; IR (KBr) 1660 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.42 (d, 1H), 3.82 (t, 1H), 4.38 (dd, 1H), 4.70 (m, 1H), 7.00-1.40 (m, 10H); MS, m/e 252 (M^+).

2-Diphenylmethylene-4-ethyl-1,3-dioxolane (37): mp 57-58°C; IR (KBr) 1660 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.00 (t, 3H), 1.50-1.90 (m, 2H), 3.90 (t, 1H), 4.30 (t, 1H), 4.30-4.60 (m, 1H), 7.00-7.40 (m, 10H); MS, m/e 266 (M^+).

2-Diphenylmethylene-4,4-dimethyl-1,3-dioxolane (38): mp 98-100°C; IR (KBr) 1660 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.15 (s, 3H), 1.45 (s, 3H), 4.00 (d, 2H), 7.00-7.40 (m, 10H); MS, m/e 266 (M^+).

2-Diphenylmethylene-4-chloromethyl-1,3-dioxolane (39): bp 142°C (10^{-3} mmHg); IR (KBr) 1660 cm^{-1}; ^1H NMR ($CDCl_3$) δ=3.60 (d, 2H), 4.30 (t, 2H), 4.60-4.80 (m, 1H), 7.00-7.60 (m, 10H); MS, m/e 286.5 (M^+).

2-Diphenylmethylene-4-phenoxymethyl-1,3-dioxolane (40): bp 140°C (10^{-3} mmHg) (lit.[17] 220-260°C (0.8 mmHg)); IR (neat) 1660 cm^{-1}; ^1H NMR ($CDCl_3$) δ=4.10 (d, 2H), 4.30 (dd, 2H), 4.70-5.00 (m, 1H), 6.70-7.40 (m, 15H); MS, m/e 344 (M^+)

2-Diphenylmethylene-4-phenyl-1,3-dioxolane (41): bp 132°C (10^{-3} mmHg) (lit,[17] bp 225-230°C (0.8 mmHg)); IR (neat) 1660 cm^{-1}; ^1H NMR ($CDCl_3$) δ=4.10 (t, 1H), 4.60 (t, 1H), 5.50 (t,

1H), 7.00-7.40 (m, 15H); MS, m/e 314 (M^+).

1-Iodo-2-propanol (42a). The solution of Bu_3SnI (2.10 g, 5 mmol) and Ph_3PO (1.35 g, 5mmol) in propylene oxide (2.90 g, 50 mmol) was stirred under dry nitrogen at 40°C for 1 h. Malonic acid (0.38 g, 2.5mmol) was added[20b] to the reaction mixture and the stirring was continued for 2 h. GLC analysis showed the formation of 1-iodo-2-propanol (42a, 0.72 g, 77%), which was purified by distillation. Spectral data of 42a were identical with the authentic sample derived from the iodation of 1-chloro-2-propanol: bp 60°C (10 mmHg); IR (neat) 3350, 1050 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.30 (d, 3H), 3.20-3.40 (m, 3H), 3.60-3.90 (m, 1H).

Cycloaddition of Oxetanes with Isocyanates (Typical Procedure).

The reactions were performed in a sealed tube. To a solution of Ph_2SnI_2 (0.52 g, 1 mmol) and HMPA (0.18 g, 1 mmol) in oxetane (15 mmol) was added an isocyanate (10 mmol) with sirring under dry nitrogen. The tube was sealed and heated at 80°C for the time indicated in Table 11. After the reaction, the resulting mixture was chromathographed on silica gel with chloroform as eluent. The yields of products were determined by GLC based on isocyanates used.

3-Butyl-1,3-oxazine-2-one (43): bp 81-82°C (0.01 mmHg); IR (neat) 1680 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.80-1.90 (m, 7H), 1.90-2.30 (m, 2H), 3.20-3.60 (m, 4H), 4.25 (t, 2H); MS, m/e 157 (M^+).

5-Methyl-3-phenyl-1,3-oxazin-2-one (44): mp 92°C; IR (KBr) 1680 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.10 (d, 3H), 2.20-2.60 (m, 1H), 3.20-3.90 (m, 2H), 3.90-4.50 (m, 2H), 7.20-7.60 (m, 5H); MS, m/e 191 (M^+); Anal. Calcd for $C_{11}H_{13}NO_2$: C, 69.09; H, 6.85; N, 7.32. Found: C. 69.07; H, 6.79; N, 7.19.

6-Methyl-3-phenyl-1,3-oxazin-2-one (45): mp 78-79°C; IR (KBr) 1685 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.50 (d, 3H), 2.00-2.30 (m, 2H), 3.50-3.90 (m, 2H), 4.40-4.80 (m, 1H), 7.20-7.80 (m, 5H); MS, m/e 191 (M^+); Anal. Calcd for $C_{11}H_{13}NO_2$: C, 69.09; H, 6.85; N, 7.32. Found: C, 68.97; H, 6.70; N, 7.45.

Compounds **46** and **47** were separated by column chromathography.

3,4-Diphenyl-1,3-oxazin-2-one (46): mp 143-144°C; IR (KBr) 1680 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.00-2.80 (m, 2H), 4.30-4.50 (m, 2H), 5.00-5.20 (m, 1H), 7.20-7.60 (m, 10H); MS, m/e 253 (M^+); Anal. Calcd. for $C_{16}H_{15}NO_2$: C, 75.87; H, 5.97; N, 5.53. Found: C, 75.64; H, 5.86; N, 5.83.

3,6-Diphenyl-1,3-oxazin-2-one (47): mp 196-197°C, IR (KBr) 1680 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.00-2.50 (m, 2H), 3.50-4.00 (m, 2H), 5.40-5.60 (m, 1H), 7.00-7.60 (m, 10H); MS, m/e 253 (M^+); Anal. Calcd. for $C_{16}H_{15}NO_2$: C, 75.87; H, 5.97; N, 5.53. Found: C, 75.68; H, 5.88; N, 5.51.

Cycloaddition of Oxetane with Carbodiimides (Typical Procedure).

To a solution of Ph_2SnI_2 (0.52 g, 1 mmol) and HMPA (0.18 g, 1 mmol) in oxetane (15 mmol) was added a carbodiimide (10 mmol). The mixture was stirred for an hour at 40°C in a 30 ml round bottomed flask under dry

nitrogen. The compound **3b** was isolated as precipitates by adding a large amount of hexane to the reaction mixture, and purified by recrystalization from benzene-hexane. The compound **48** was isolated by column chromathography, and purified by distillation. The yields were determined by GLC based on carbodiimides used.

N-Phenyl-3-phenyl-1,3-oxazine-2-imine (48): bp 65 (0.1 mmHg); IR (neat) 1660 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.80-1.80 (m, 14H), 1.80-2.20 (m, 2H), 3.00-3.50 (m, 6H), 4.10 (t, 2H); MS, m/e 212 (M^+); Anal. Calcd for $C_{12}H_{24}N_2O$: C, 67.44; H, 11.43; N, 13.01. Found: C, 67.88; H, 11.39; N, 13.19.

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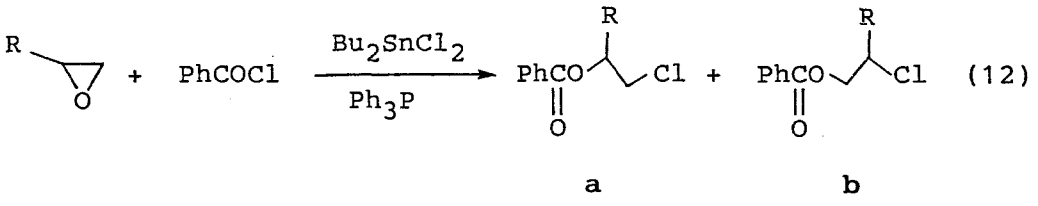
Chapter 3 Regioselective Ring Cleavage of Oxiranes Catalyzed by Organotin Halide-Lewis Base Complex.

3-1 Introduction.

Regioselective ring cleavage of oxiranes is a subject of current interest due to the wide application in organic synthesis.[1] Although a variety of reagents are useful, the exploration of new catalysts must be studied because of the general importance of this cleavage reaction. In chapter 2, it was revealed that organotin halides, when complexed with Lewis bases, played as efficient catalysts for cycloaddition of heterocumulenes with oxiranes. In the course of these studies, this organotin halide complex was found to be effective for regioselective ring cleavage of oxiranes producing organotin β-haloethoxides.[2,3]

Thus, this chapter describes the formation of vicinal chloroesters[4] from the reaction of oxiranes with acid chlorides in the presence of catalytic amounts of Bu_2SnCl_2 and Ph_3P (eq 12). In addition, this method has several advantages in terms of neutral and mild reaction conditions, stability of the catalyst and high regioselectivity.

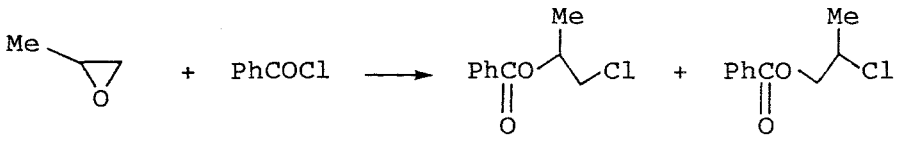


(12)

3-2 Results and Discussion.

Table 12 shows the results of the reaction of propylene oxide with benzoyl chloride to produce β-chloroester (**49**). Organotin chlorides alone have low catalytic activities, and cleavages are not regiospecific (entries 1-3). Triphenylphosphine has also no catalytic activity (entry 4). On the contrary, the complexed catalyst, Bu_2SnCl_2-Ph_3P gave **49** quantitatively via regioselective cleavage at the less-substituted carbon (β-cleavage) (entry 5).

Table 12. Reaction of Propylene Oxide with Benzoyl Chloride.[a]

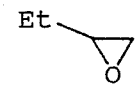
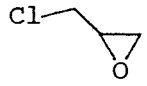
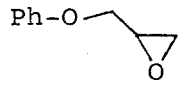
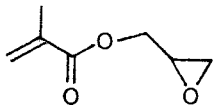
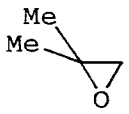
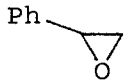
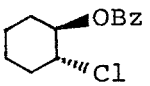
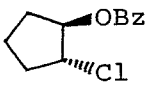


49a **49b**

Entry	Cat. System	Time (h)	Yield[b] (%)	Ratio[c] a/b
1	Bu_2SnCl_2	24	13	46/54
2	Me_2SnCl_2	5	23	46/54
3	$SnCl_2$	5	55	43/57
4	Ph_3P	24	0	
5	Bu_2SnCl_2-Ph_3P	1	100	94/6

[a]Propylene oxide 50 mmol, PhCOCl 10 mmol, Catalyst 1 mmol, Benzene 5 ml, Temp. 60°C. [b]Based on PhCOCl, GLC yields. [c]Determined by ^{1}H-NMR.

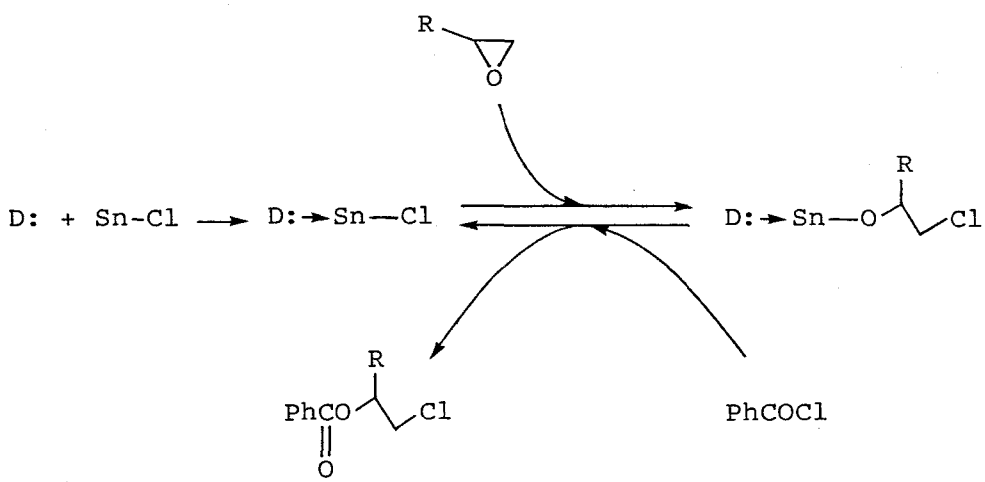
Table 13. Reaction of Oxiranes and Acid Chlorides.[a]

Entry	Oxirane	Cat. System	Time (h)	Product	Yield[b] (%)	Ratio[c] a/b
1		Bu_2SnCl_2-Ph_3P	1	**50a, 50b**	100	94/6
2		"	1	**51a**	100	100/0
3		"	1	**52a**	100	100/0
4		"	1	**53a**	100	100/0
5		"	6	**54a, 54b**	56	43/57
6		Bu_2SnCl_2	24	**55b**	63	0/100
7		Bu_2SnCl_2-Ph_3P	4	**55a, 55b**	90	33/67
8		Bu_3SnCl-DBU	24	"	98	45/55
9		Bu_2SnCl_2-Ph_3P	1	**56**	100	
10		"	6	**57**	76	

[a]Oxirane 10 mmol, PhCOCl 10 mmol, Tin chloride 1 mmol, Base 1 mmol, Benzene 5 ml, Temp. 60°C. [b]Based on PhCOCl, GLC yield. [c]Determined by ^{1}H-NMR.

Moreover, as shown in Table 13, exclusive formations of type a compounds (**50-53**) were achieved for the reactions of butylene oxide (entry 1), epichlorohydrin (entry 2), glycidyl ether (entry 3) and glycidyl ester (entries 4). Thus, the presence of certain functional group, such as ether, vinyl ester and halogen moieties can be tolerated in this reaction system. Generally, isobutylene oxide and styrene oxide favors α-cleavage because of the electronic effect. In fact, only **55b** was formed without bases (entry 6), however, the ratio of **55a** was increased by the addition of bases (entries 7 and 8) in the reaction of styrene oxide. The tin complexes have a property to promote β-cleavage of oxiranes. Using cyclohexene oxide, or cyclopentene oxide, the oxirane bridge was cleaved quite stereoselectively leading only to trans-chloroester, **56** and **57**, resulting from the usual anti-opening of the ring (entries 9 and 10).

Scheme 7



The course of the overall reaction can be interpreted as follows (Scheme 7). In the Bu_2SnCl_2 complex, the halogen is activated by the co-ordination of a Lewes base toward a tin atom, and the positive tin atom attack the oxirane oxygen. This is followed by a nucleophilic attack by the halide ion which has been formed in situ at the less substituted carbon atom of the stannylated oxirane ring, and an organotin β-haloalkoxide is formed. The addition of benzoyl chloride finally accomplishes a rapid esterification, accompanied by the regeneration of the catalyst.

In summary, the organotin halide-Lewis base complexes proved to be a highly practical and effective catalyst for regioselective ring cleavage of oxiranes with acid chlorides.

3-3 Experimental Section.

Ring Cleavage of Oxiranes with Benzoyl Chloride (Typical Procedure).

Oxirane (10 mmol) and benzoyl chloride (1.40 g, 10 mmol) were successively added to a stirred solution of Bu_2SnCl_2 (0.31 g, 1 mmol) and Ph_3P (0.26 g, 1 mmol) in benzene (5 ml), the reaction mixture was stirred at 60°C. The formation of product was monitored by GLC analysis. After the reaction, the solutuion was concentrated under reduced pressure and the residue was chromatographed (Silica gel, eluted by benzene) to give vicinal chlorobenzoates. The regioselectivity was determined by ^{1}H-NMR spectra.

Table 14. Spectral Data of β-Chloroesters.

Compound No.	IR (cm^{-1})	^1H NMR (ppm)
49a	1730	1.45 (d, 3H), 3.65 (d, 2H), 5.10-5.50 (m, 1H), 7.10-8.20 (m,5H).
49b	1730	1.55 (d, 3H), 4.10-4.50 (m, 3H), 7.10-8.20 (m, 5H).
50a	1730	1.00 (t, 3H), 1.70-2.10 (m, 2H), 3.75 (d, 2H), 5.10-5.40 (m, 1H), 7.20-8.30 (m, 5H).
50b	1730	1.00 (t, 3H), 1.70-2.10 (m, 2H), 4.30-4.70 (m, 3H), 7.20-8.30 (m, 5H).
51a	1730	3.85 (d, 4H), 5.20-5.60 (m, 1H), 7.00-8.20 (m, 5H).
52a	1720	3.90 (d, 2H), 4.20 (d, 2H), 5.40-5.70 (m, 1H), 6.80-8.20 (m, 10H).
53a	1730	1.90 (s, 3H), 3.80 (dd, 2H), 4.60 (dd, 2H), 5.20-5.70 (m, 2H), 6.00-6.30 (m, 1H),7.20-8.20 (m, 5H).
54a	1730	1.60 (s, 6H), 3.90 (s, 2H), 7.20-8.20 (m, 5H).
54b	1730	1.60 (s, 6H), 4.40 (s, 2H), 7.20-8.20 (m, 5H).
55a	1720	3.60-4.00 (m, 2H), 6.00-6.40 (m, 1H), 7.00-8.20 (m, 10H).
55b	1720	4.50-4.70 (m, 10H), 5.00-5.30 (m, 1H), 7.00-8.20 (m, 10H).
56	1720	1.20-2.60 (m, 10H), 3.90-4.30 (m, 1H), 4.90-5.30 (m, 1H), 7.30-8.30 (m, 5H).
57	1730	1.20-2.80 (m, 8H), 4.20-4.50 (m, 1H), 5.25-5.55 (m, 1H), 7.20-8.30 (m, 5H).

3-4 References and Notes.

(1) See for example, (a) C. H. Behrens and K. B. Sharpless, Aldrichimica Acta., **16**, 67 (1983); (b) A. S. Rao, S. K. Paknikar and J. G. Kirtane, Tetrahedron, **39**, 2323 (1983); (c) J. G. Smith, Synthesis, **1984**, 629.

(2) Fiorenza et al. reported the ring cleavage promoted by Me_3SnX (X= halogen) to produce organotin β-haloalkoxides; M. Fiorenza, A. Ricci, M. Taddei and D. Tassi, Synthesis, **1983**, 640.

(3) Although facile cleavages of oxiranes by organotin halides is scarcely reported,[2] a similar cleavage by organosilyl halides have been extensively investigated; G. C. Andrews, T. C. Crawford and L. G. Contillo, Jr., Tetrahedron Lett., **39**, 3803 (1981) and references cited therein.

(4) Oxiranes were reported to be cleaved by acetyl chlorides in the presence of chromyl chloride. However, satisfactory results were not obtained in its regioselectivity; J. E. Backwell, M. W. Young and K. B. Sharpless, Tetrahedron Lett., **40**, 3523 (1977).

Chapter 4 Synthetic Application of Organotin ω-Haloalkoxides.

4-1 Introduction.

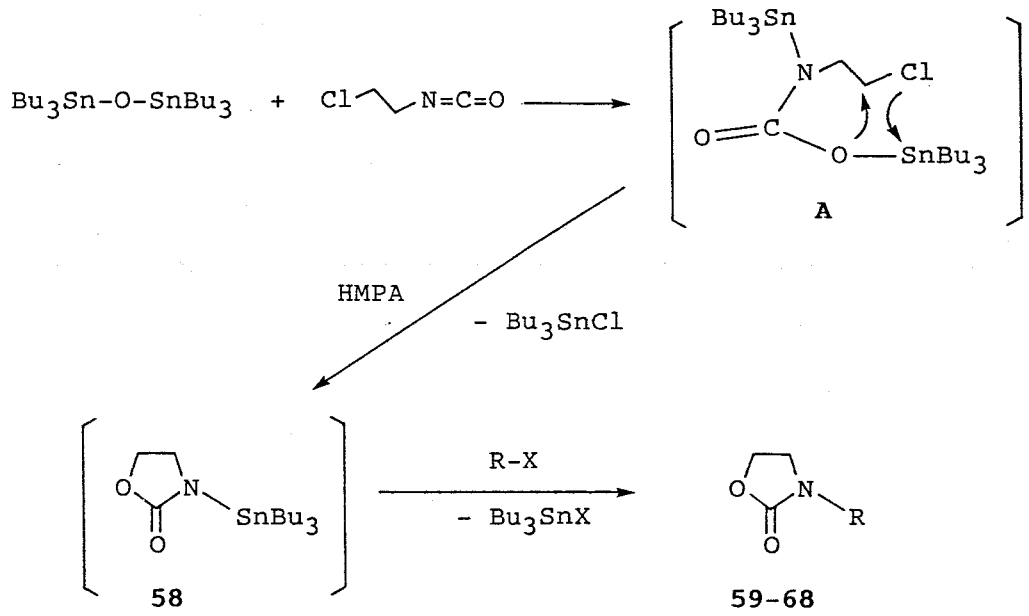
As described in chapter 1, owing to the high reactivity of the Sn-O bond and the affinity of Sn atom toward the terminal halogen, a variety of five- and six membered heterocyclic compounds were readily produced under mild conditions. The enhancement observed on adding Lewis bases to these cyclizations is explained in terms of the co-ordination to the Sn atom. In connection with the interest on the use of this types of organotin ω-halogeno compounds, this chapter describes the synthetic application of organotin ω-haloalkoxides.

4-2 Formation of N-Tributylstannyl-2-oxazolidinone.

As shown in Scheme 8, β-Halogeno-N-stannylcarbamate (**A**) could be readily formed from the reaction of $(Bu_3Sn)_2O$ with 2-chloroethyl isocyanate. The cyclization of **A** proceeds easily in the presence of HMPA, and N-Tributylstannyl-2-oxazolidinone (**58**) is formed. Although, N-Trimethylsilyl-2-oxazolidinone is widely used as a silylating agent,[1] the formation of the N-Stannylated analogue has not been reported so far.

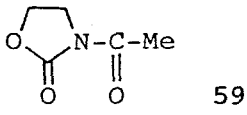
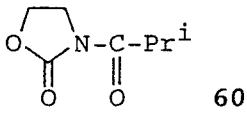
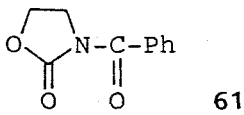
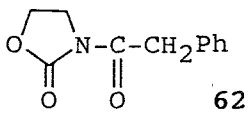
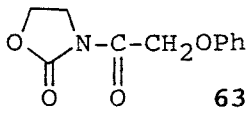
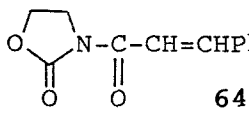
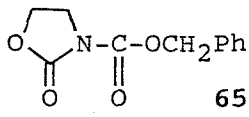
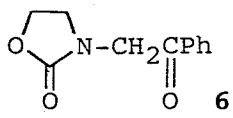
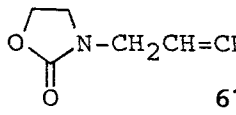
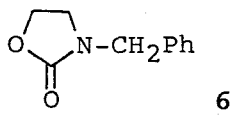
The compound **58** is so labile that it was readily hydrolyzed by the ordinal work-up for isolation, and 2-oxazolidinone was obtained quantitatively, which showed the

Scheme 8



IR band at 1720 cm^{-1} (C=O). As shown in Table 15, reactions of **(58)** with equimolar amounts of acid chlorides completed clearly at room temperature, yielding the corresponding N-acyl-2-oxazolidinones **(59-65)** (entries 1-7). The use of HMPA is essential. Otherwise, the cyclization hardly occurred, and **61** was obtained in only 5% yield. This important role of HMPA may be explained in terms of the co-ordination to the Sn atom in the stannylcarbamate **(A)**. This co-ordination increases the basicity of the oxygen atom adjacent to the Sn and accelerates the intramolecular alkylation.

Table 15. Reaction of 58 with Electrophiles.[a]

Entry	Electrophiles	Conditions	Product	Yield (%)[b]
1	MeCOCl	r.t. 10min	 59	100
2	^{i}PrCOCl	"	 60	100
3	PhCOCl	"	 61	86
4	$PhCH_2COCl$	"	 62	94
5	$PhOCH_2COCl$	"	 63	99
6	PhCH=CHCOCl	"	 64	88
7	$PhCH_2OCOCl$	"	 65	100
8	$PhCOCH_2Br$	80°C, 15 h	 66	76
9	CH_2=$CHCH_2Br$	"	 67	81
10	$PhCH_2Br$	"	 68	60

[a]$(Bu_3Sn)_2O$ 10 mmol, Cl⟨⟩NCO 10 mmol, Electrophiles 10 mmol, HMPA 4 ml. [b]Based on electrophiles.

When phenacyl-, allyl- and benzyl bromides were used as electrophiles, although the reaction conditions (80°C, 15 h) were not so mild as the case of acid chlorides, the corresponding 2-oxazolidinones (**66-68**) were obtained (76, 81 and 60%, respectively) (entries 8-10). In general, the N-alkylation of 2-oxazolidinone must be carried out in strong alkaline media.[2] Thus activation of the nitrogen through stannylation is effective, and similar activation has also been reported for some heterocycles.[3]

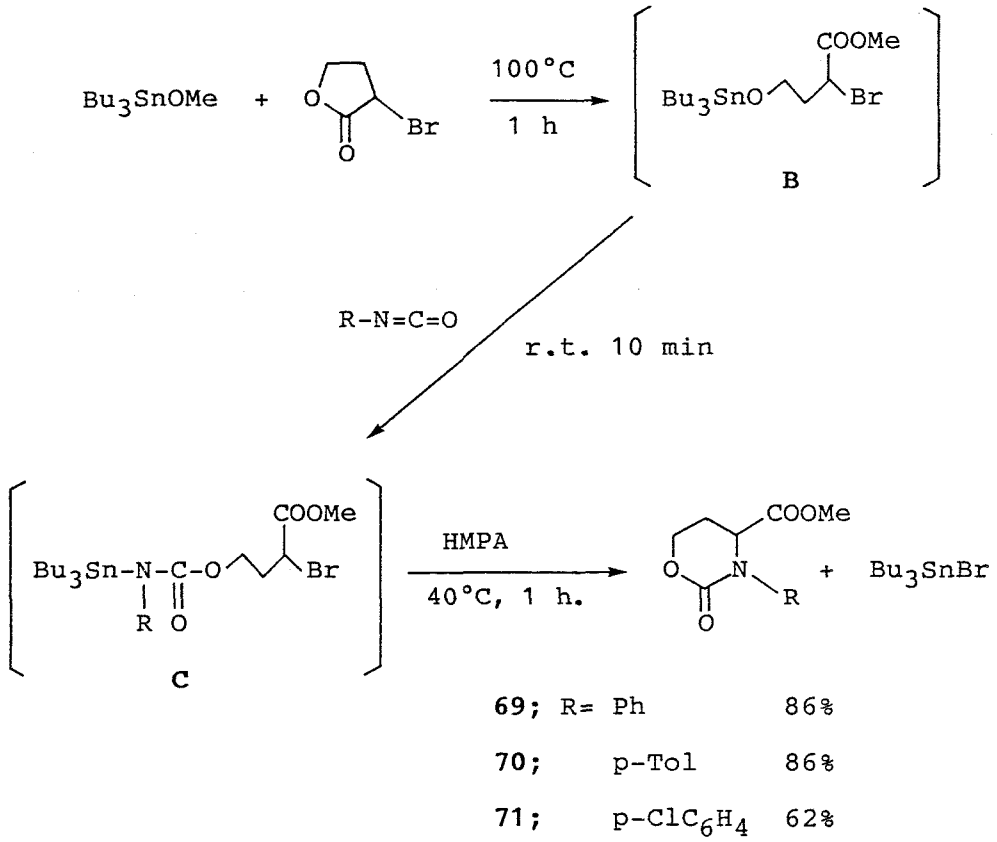
In conclusion, this method has several advantages in terms of mild and neutral conditions, high yields of products and operational convenience.

4-3 Synthesis of 2-Oxazinones via the Cleavage of Halolactone Promoted by Organotin Alkoxide.

Lactons are known to be cleavaged by organotin alkoxides to afford γ-ketosubstituted alkoxyalkyltin compounds. This regioselective ring-opening reactions for lactones is well interpreted in terms of HSAB principle.[4] Namely, organotin alkoxides act as "hard" nucleophiles, giving the adduct through acyl-oxygen bond cleavage. This formation of organotin alkoxides lead to investigate the further use for the preparation of six-membered heterocyclic compounds, as shown in Scheme 9.

This reaction proceeds via an tributyltin γ-bromoalkoxide (**B**) generated from the cleavage of the halolactone by the Sn-O bond. The formed **B**, without isolation, reacts with an isocyanate spontaneously, and gave

Scheme 9



the adduct **C**. This intermmediate is cyclized smoothly in the presence of HMPA, and 2-oxazinone is obtained, accompanied by the formation of Bu_3SnBr. From this reaction, 2-oxazinones (**69-71**) were obtained, respectively. In these cases, without HMPA, **69** was scarcely obtained under the same conditions.

4-4 Experimental Section.

Formation of N-Tributylstannyl-2-oxazolidinone (Typical Procedure).

2-Chloroethyl isocyanate (10 mmol) was added slowly to Bis(tributyltin) oxide (10 mmol) under dry nitrogen. Then heat was evolved, and a β-halogeno-N-stannylcarbamate was formed, which was confirmed by the appearance of IR absorption band at 1600 cm^{-1} in place of the disappearance of NCO group (2280 cm^{-1}). Next, HMPA (4 ml) was added, and heating at 40°C for 1 h induced the cyclization, to form N-tributylstannyl-2-oxazolidinone (58). IR spectra showed the appearance at 1770 cm^{-1} (C=O). Furthermore, the reactions with electrophiles were carried out without the isolation of 58, under the conditions listed in Table 15.

The products (59-68) were isolated by column chromatography. The yields and spectral data of the compounds obtaind are as follows.

3-Acetyl-1,3-oxazolidin-2-one (59): mp 54-55°C; IR (KBr) 1690, 1780 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.55 (s, 3H), 3.90-4.30 (m, 2H), 4.30-4.60 (m, 2H); MS, m/e 129 (M^+).

3-Isobutyryl-1,3-oxazolidin-2-one (60): wax; IR (neat) 1700, 1780 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.20 (d, 6H), 3.60-3.90 (m, 1H), 3.90-4.20 (m, 2H), 4.40-4.60 (m, 2H); MS, m/e 157 (M^+).

3-Benzoyl-1,3-oxazolidin-2-one (61): mp 166-168°C; IR (KBr) 1670, 1770 cm^{-1}; ^1H NMR ($CDCl_3$) δ=3.80-4.35 (m, 2H), 4.35-4.90 (m, 2H), 7.10-8.00 (m, 5H); MS, m/e 191 (M^+).

3-Phenylacetyl-1,3-oxazolidin-2-one (62): mp 55-56°C; IR (KBr) 1690, 1760 cm^{-1}; ^1H NMR ($CDCl_3$) δ=3.60-4.10 (m, 2H), 4.10-4.60 (m, 4H), 6.90-7.60 (m, 5H); MS, m/e 205 (M^+).

3-Phenoxyacetyl-1,3-oxazolidin-2-one (63): mp 93-95°C; IR (KBr) 1720, 1800 cm^{-1}; ^1H NMR ($CDCl_3$) δ=4.05 (t, 2H), 4.50 (t, 2H), 5.25 (s, 2H), 6.80-7.50 (m, 5H); MS, m/e 221 (M^+).

3-Cinnamoyl-1,3-oxazolidin-2-one (64): mp 148-149°C; IR (KBr) 1620, 1770 cm^{-1}; ^1H NMR ($CDCl_3$) δ=4.00-4.30 (m, 2H), 4.30-4.60 (m, 2H), 7.00-8.00 (m, 7H); MS, m/e 217 (M^+).

3-Carbobenzoxy-1,3-oxazolidin-2-one (65): mp 98-100°C; IR (KBr) 1800 cm^{-1}; ^1H NMR ($CDCl_3$) δ=3.80-4.20 (m, 2H), 4.20-4.60 (m, 2H), 5.30 (s, 2H), 7.20-7.60 (m, 5H); MS, m/e 221 (M^+).

3-Phenacyl-1,3-oxazolidin-2-one (66): mp 105-108°C; IR (KBr) 1700, 1750 cm^{-1}; ^1H NMR ($CDCl_3$) δ=3.50-3.90 (m, 2H), 4.30-4.60 (m, 2H), 4.70 (s, 2H), 7.20-8.30 (m, 5H); MS, m/e 205 (M^+).

3-Allyl-1,3-oxazolidin-2-one (67): wax; IR (neat) 1750 cm^{-1} ^1H NMR ($CDCl_3$) δ=3.40-3.70 (m, 2H), 3.80-4.00 (m, 2H), 4.20-4.40 (m, 2H), 5.10-5.50 (m, 2H) 5.50-6.00 (m, 1H); MS, m/e 127 (M^+).

3-Benzyl-1,3-oxazolidin-2-one (68): mp 77-78°C; IR (KBr) 1750 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ=3.40 (dd, 2H), 4.25 (dd, 2H), 4.30(s, 2H), 7.40-7.60 (m, 5H); MS, m/e 177 (M^+).

Conversion of Halolactone to 2-Oxazinones (Typical Procedure).

A mixture of Bu_3SnOMe (10 mmol) and α-bromo-γ-

butyrolactone (10 mmol) was heated at 100°C for 1 h under dry nitrogen. After cooling down to room temperature, to this reaction mixture was added 10 mmol of an isocyanate. This reaction proceeds smoothly. After 10 min, HMPA (10 mmol) was added and heating was continued at 80°C for 1 h. The products are isolated by column chromathography on silica gel eluted with chloroform, and are purified by recrystalization from benzene-hexane.

3-Phenyl-4-carbomethoxy-1,3-oxazin-2-one (69): mp 113-114°C; IR (KBr) 1680, 1740 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=2.30 (m, 2H), 3.67 (s, 3H), 4.30-4.60 (m, 3H), 7.20-7.40 (m, 5H); ^{13}C NMR ($CDCl_3$) δ=25.5, 52.6, 60.5, 64.0, 127.0, 127.4, 129.1, 141.7, 151.9, 170.7; MS, m/e 235 (M^+).

3-p-Tolyl-4-carbomethoxy-1,3-oxazin-2-one (70): mp 69-71°C; 1700, 1740 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=2.33 (s, 3H), 2.30-2.60 (m, 2H); 3.71 (s, 3H); 4.34-4.55 (m, 3H), 7.15-7.40 (m, 4H); ^{13}C NMR ($CDCl_3$) δ=21.1, 25.5, 52.7, 60.7, 64.1, 126.9, 129.9, 137.5, 139.3, 152.2, 171.0; MS, m/e 249 (M^+).

3-p-Chlorophenyl-4-carbomethoxy-1,3-oxazin-2-one (71): 84-86°C; IR (KBr) 1690, 1740 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=2.40-2.60 (m, 2H), 3.72 (s, 3H), 4.35-4.55 (m, 3H), 7.15-7.40 (m, 4H); ^{13}C NMR ($CDCl_3$) δ=25.7, 52.9, 60.6, 64.2, 128.6, 129.4, 133.3, 140.2, 152.0, 170.6; MS, m/e 270 (M^+).

4-5 References and Notes.

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Conclusion

The purpose of this research was to develop new synthetic reaction using organotin halide-base systems.

The important results mentioned in each chapter of these reactions are summarized as follows.

In chapter 1, the reaction of organotin ω-haloalkoxides with heterocumulenes leading to 5- or 6-membered heterocyclic compounds is described. The reactivity and compounds are controlled by the substrate and reaction conditions. It is further revealed that basic solvents, such as HMPA, play an important role to carry out these reaction in high yields under mild conditions.

In chapter 2, it is found that organotin halide-Lewis base complexes are characteristically effective catalysts for cycloaddition of cyclic ethers with heterocumulenes. Various heterocyclic compounds are obtained in high yields under neutral and mild conditions. Moreover, several new types of heterocyclic compounds which have not been obtained with conventional catalysts can be isolated.

In chapter 3, the organotin halide-Lewis base complexes have proved to be highly practical and effective catalysts for chemo- and regioselective ring cleavage of oxiranes with acid chlorides.

In chapter 4, as an application of organotin ω-haloalkoxides, a new method for synthesis of N-substituted-2-oxazolidinones via N-stannyl-2-oxazolidinone is described.

Furthermore, a convenient one-pot synthesis of 2-oxazinone derivatives is developed using the regioselective ring cleavage of a halolactone promoted by an organotin alkoxide.

In summary, the co-ordination of Lewis base towards a tin atom increases the nucleophilicity of polar substituents, such as heteroatoms or halogens, adjacent to the tin atom. Hence, the intramolecular substitution or ring opening of cyclic ethers is accelerated. I believe that several important features obtained through the present investigation would develop a new area in synthetic chemistry.