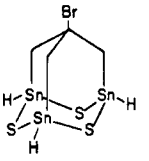
Koch and Gleicher[9] have determined the relative reactivities of bridgehead hydrogen atoms toward abstraction by trichloromethyl radical and have shown that there is a good linear relation between the heats of reaction and the rates of hydrogen abstraction. We have found that the heats of reaction given by MNDO show an equally good correlation with the experimental data (r = 0.995). Applying this relation to our data for **2** and **3** (Table IV), we conclude that **2**, and hence also **1**, should react with trichloromethyl radical about 6000 times faster than adamantane, a prediction which we hope will soon be tested by experiment.

Ducharme et al.[6] have stated that **1**, in presence of AIBN as a radical catalyst, reduces alkyl halides in a manner "similar to dehalogenations effected by tin hydrides". We accordingly calculated the energetics of the corresponding free radical chain reaction between **2** and ethyl bromide, using MNDO heats of formation; see eq 1 and 2. The

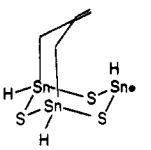
$$3 + C_2H_5Br \rightarrow 5 + C_2H_5\cdot \quad \Delta H = 27.9 \text{ kcal/mol} \quad (1)$$

$$C_2H_5\cdot + 2 \rightarrow 3 + C_2H_6 \quad \Delta H = -23.0 \text{ kcal/mol} \quad (2)$$

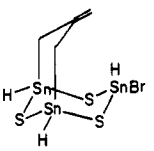
endothermicity of the first step seems too large for the reaction to occur with a reasonable chain length under other than drastic conditions. Ducharme et al. suggested that **3** may undergo intramolecular fragmentation to form the isomeric radical **6** which could then react as a normal stannyl radical with alkyl bromides, forming **7**. MNDO indeed predicts **7** to be lower in energy than **5** by 6.2 kcal/mol (Table III). We tried to check this idea by calculating **6**, but without success. All the structures studied reverted to **3** exothermically and without activation. While it is possible that rearrangement may accompany reaction with the alkyl bromide in a single concerted step, it seems likely that the activation energy for such a multibond process would be rather large. It should be noted that the only example of a reduction cited by Ducharme et al. referred to a compound (α-bromo-*p*-phenylacetophenone) where the corresponding radical must be strongly stabilized by the α-acyl group.



5



6



7

The remarkable stability of **3** can be interpreted nicely in terms of synergism between sigmaconjugation and hyperconjugation, of the kind recently invoked[10] to explain the anomeric effect and the preferred conformations of alkyl radicals. Synergism occurs in such cases when hyperconjugation involves a CX bond trans to the singly or doubly occupied AO and the stabilizing effect should be greater, the less electronegative is X. In **3**, all three C–Sn bonds are trans to the singly occupied AO. It should be noted in this connection that Hannon and Traylor[11] have shown that loss of hydride from a position β to tin in an organostannane occurs most readily when the hydrogen is antiperiplanar to the adjacent C–Sn bond, as the argument above predicts.

Acknowledgment. This work was supported by the Air Force Office of Scientific Research (Contract No. AFOSR 49620 83 C 0024) and the Robert A. Welch Foundation (Grant No. F-126). The calculations were carried out with a Digital VAX 11/780 computer purchased with grants from the National Science Foundation and The University of Texas at Austin.

Registry No. **1**, 87922-35-8; **2**, 88212-59-3; **3**, 96504-44-8; **4**, 96504-45-9; **5**, 96504-46-0; **6**, 96504-47-1; **7**, 96504-48-2; $CCl_3\cdot$, 3170-80-7; C_2H_5Br, 74-96-4; $C_2H_5\cdot$, 2025-56-1.

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(11) Hannon, S. J.; Traylor, T. G. *J. Org. Chem.* **1981**, *46*, 3645.

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

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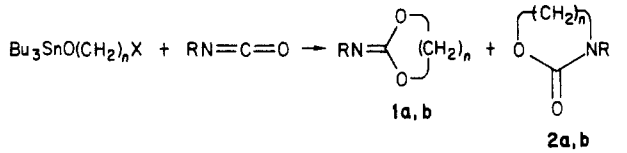
In the reaction of tributyltin ω-haloalkoxides ($Bu_3SnO(CH_2)_nX$, X = Cl, Br, I) and isocyanates, the formation of iminodioxolane derivatives was observed. These products are not obtained in the direct addition of oxiranes and isocyanates, whereas $Bu_3SnO(CH_2)_2X$ is considered to be a synthon of ethylene oxide. The yield of iminodioxolanes was affected substantially by various factors such as solvent, temperature, the halogen (X), and the substituents on the isocyanates used. In particular, the iminodioxolane was obtained exclusively in the reaction with methyl isocyanate. A possibility of the formation of these compounds via the addition of the Sn—O bond across the C=O group of an isocyanate is discussed. In addition, the formation of various heterocyclic compounds from $Bu_3SnO(CH_2)_nX$ (n = 2, 3) and isocyanates or a carbodiimide under mild conditions is reported.

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, and RCHO have been shown to undergo insertion into the Sn–O bond.[1] These reactions

0276-7333/85/2304-1329$01.50/0

Table I. Reactions between Tributyltin ω-Haloalkoxides ($Bu_3SnO(CH_2)_nX$) and Isocyanates[a]

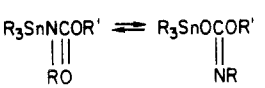


1a, b 2a, b

entry	n	X	R	solvent (mL)	temp, °C	yield,[b] %	1/2 ratio[c]
1	2	Cl	C_6H_5		60	2	
2	2	Br	C_6H_5		60	80	25/75
3	2	I	C_6H_5		60	89	22/78
4	2	I	C_6H_5		25	56	20/80
5	2	Cl	C_6H_5	PhH (15)	60	0	
6	2	Br	C_6H_5	PhH (15)	60	50	60/40
7	2	I	C_6H_5	PhH (15)	60	55	51/49
8	2	Cl	C_6H_5	HMPA (3)	25	92	0/100
9	2	Br	C_6H_5	HMPA (3)	25	92	0/100
10	2	I	C_6H_5	HMPA (3)	25	91	0/100
11	2	I	C_6H_5	hexane (15)	60	59	26/74
12	2	I	p-$CH_3C_6H_4$	hexane (15)	60	84	57/43
13	2	I	p-$CH_3C_6H_4$	HMPA (3)	25	81	0/100
14	2	I	p-ClC_6H_4	hexane (15)	60	31	37/63
15	2	I	p-ClC_6H_4	HMPA (3)	25	92	0/100
16	2	I	p-$NO_2C_6H_4$	hexane (15)	60	37	11/89
17	2	I	p-$NO_2C_6H_4$	HMPA (3)	25	93	0/100
18	2	I	CH_3		25	86	92/8
19	2	I	CH_3	PhH (15)	60	84	95/5
20	2	I	CH_3	HMPA (3)	25	100	42/58
21	3	I	C_6H_5		80	3	0/100
22	3	I	C_6H_5		100	85	0/100
23	3	I	C_6H_5		120	94	0/100
24	3	I	C_6H_5	HMPA (3)	25	93	0/100
25	3	I	p-$CH_3C_6H_4$		100	89	0/100
26	3	I	p-ClC_6H_4		100	79	0/100
27	3	I	p-$NO_2C_6H_4$		100	75	0/100
28	3	I	CH_3		100	100	0/100

[a] $Bu_3SnO(CH_2)_nX$, 10 mmol; RN=C=O, 9 mmol; time, 1 h. [b] Based on RN=C=O used unless otherwise noted. [c] Determined by GLC and ^1H NMR.

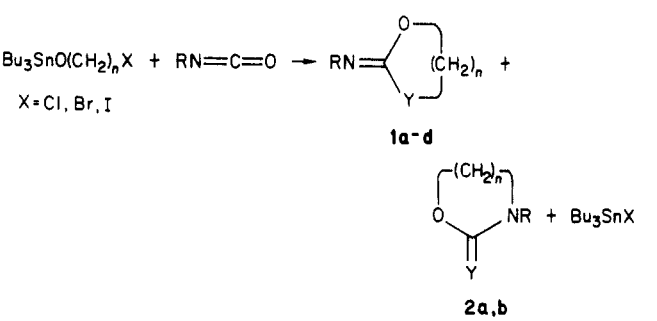
have been studied so far with trialkyltin alkoxides,[2] bis(trialkyltin) oxides,[3] trialkyltin oximates,[4] trialkyltin glycolates,[5] dialkyltin dialkoxides,[6] and tin(II) dialkoxides.[7] It has been reported that the Sn–O bond reacts exothermally with isocyanates to give *N*-stannylcarbamates[2-8] 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).



(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 cyclization in the thermolysis of trialkyltin ω-haloalkoxides ($R_3SnO(CH_2)_nX$), as described by Pommier et al.[9] On the basis of these facts,

Scheme I



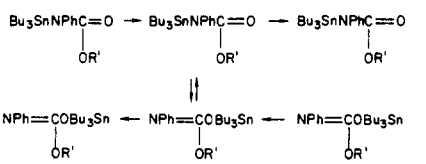
1a-d 2a,b

a, n=2, Y=O;
b, n=3, Y=O;
c, n=2, Y=N-R;
d, n=3, Y=N-R

we have studied some novel additions of $Bu_3SnO(CH_2)_nX$ to isocyanates or a carbodiimide to give heterocyclic com-

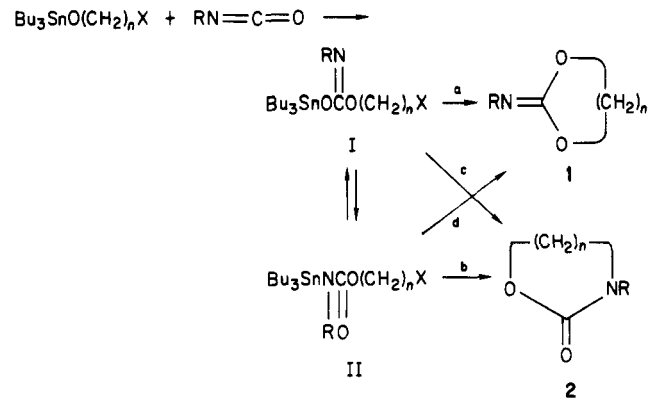
(1) See, for example: Sawyer, A. K. "Organotin Compounds", Marcel Dekker: New York, 1971; Vol. 1, pp 153.
(2) Bloodworth, A. J.; Davies, A. G. *J. Chem. Soc.* **1965**, 5238.
(3) Bloodworth, A. J.; Davies, A. G. *J. Chem. Soc.* **1965**, 6245. Davies, A. G.; Symes, W. R. *Chem. Commun.* **1965**, 25.
(4) Harrison, P. G.; Zuckerman J. J. *Inorg. Chem.* **1970**, *9*, 175.
(5) Sakai, S.; Kiyohara, Y.; Itoh, K.; Ishii, Y. *J. Org. Chem.* **1970**, *35*, 2347. Agur, D. P.; Srivastaka, G.; Mehrostra, R. C. *Ind. J. Chem.* **1974**, *12*, 1193.
(6) Davies, A. G.; Harrison, P. G. *J. Chem. Soc. C* **1967**, 1313.
(7) Harrison, P. G.; Zuckerman, J. J. *Chem. Commun.* **1969**, 321. Harrison, P. G.; Zuckerman, J. J. *Inorg. Nucl. Chem. Lett.* **1969**, *5*, 545.
(8) Davies, A. G. *Synthesis* **1969**, 56.
(9) Delmond, B.; Pommier, J. C.; Valade, J. *J. Organomet. Chem.* **1973**, *50*, 121.

(10) Of course, as Bloodworth et al. proposed, there is a possibility of a self-association in the adduct.



(11) In adducts of tin alkoxide and ketene, the adduct of keto type is more stable but less reactive toward carbonyl compounds than the adduct of the enol type. Shimada, E.; Inomata, K.; Mukaiyama, T. *Chem. Lett.* **1974**, 689.
(12) Wakeshima, I.; Suzuki, H.; Kijima, I. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 1069.

Scheme II



pounds as shown in Scheme I.

From these results, $Bu_3SnO(CH_2)_nX$ can be considered as the synthon of cyclic ethers. However, no iminodioxolanes (**1a**) were detected in the reaction of oxiranes and isocyanates, which is assumed to be the precursor of the oxazolidinone (**2a**).[16-18] In addition, the formation of **1a** is interesting because it may suggest the presence of the imidate-type intermediate I (Scheme II).

Results and Discussion

Tributyltin ω-haloalkoxides ($Bu_3SnO(CH_2)_nX$) were allowed to react with heterocumulenes 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}. The reaction products were readily precipitated by adding hexane. The precipitates were almost pure as confirmed by means of their ^1H NMR spectra. The results of the reactions between $Bu_3SnO(CH_2)_2X$ and isocyanates are summarized in Table I (entries 1–20).

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

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

The halogen atom in $Bu_3SnO(CH_2)_2X$ aslo affected the reactivity. The iodide was most effective in yielding the heterocyclic compounds (entries 3 and 7). Practically no products were 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]

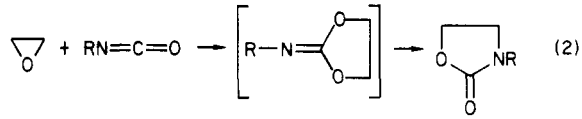
HMPA enhanced the reactivity so greatly that **2a** was produced in 92% yield even in the case of the chloride, and no difference in reactivity between halides could be observed (entries 8–10). In contrast to this effect on reactivity, the **1a**/**2a** ratio was not affected by halogen moieties.

The reaction temperature did not affect **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 **1a**/**2a** 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 the aromatic ring increased both the reactivity and the proportion of **1a** in hexane solution (entries 11, 12, 14, and 16). For example, *p*-tolyl isocyanate gave **1a** and **2a** in 84% yield (**1a**/**2a** ratio = 57/43) (entry 12) and *p*-nitrophenyl isocyanate in 37% yield (**1a**/**2a** ratio = 11/89) (entry 16). In HMPA, exclusive formation of **2a** was observed, as expected (entries 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 isocyanates 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 **1a**, which was not observed in the reaction with aryl isocyanates. Even in the reaction using HMPA as solvent, the **1a**/**2a** ratio was 42/58 (entry 20). Under more extreme conditions (150 °C for 2 h), only **2a** was obtained in lower yield (27%). This may be because of the liability and facile polymerization of **1a**, which was confirmed with an authentic sample.

It is well-known that oxazolidinones are formed by the 1,3-cycloaddition reaction of isocyanates with oxiranes promoted by various catalysts.[14-16] Although no iminodioxolanes can be detected in these reactions because of the severe conditions, the formation of oxazolidinones is explained by assuming the rearrangement of iminodioxolanes[16-18] (eq 2).



(2)

So in our study, such a rearrangement might be considered. Actually, the formation of oxazolidinone was detected in 66% yield on heating 2-(phenylimino)-1,3-dioxolane at 80 °C in the presence of Bu_3SnI. However, at lower temperature (such as 60 and 25 °C), no rearrangement was observed even using the solvents listed in Table I. Moreover, in the reaction of $Bu_3SnO(CH_2)_2I$ and phenyl isocyanate in the presence of 2-(phenylimino)-1,3-dioxolane, neither rearrangement of the iminodioxolane nor a change in the yield of oxazolidinone were observed.

From these results, **1a** is not considered to rearrange under the reaction conditions listed in Table I once it has been formed.

No intermolecular substitution was observed. The adduct of tributyltin methoxide and phenyl isocyanate did not react with *n*-propyl iodide at all.

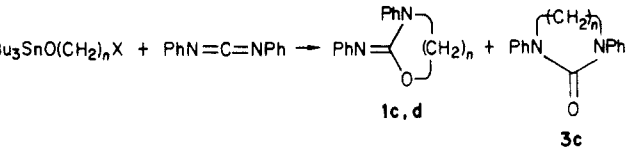
A plausible path for the reaction of $Bu_3SnO(CH_2)_2X$ and isocyanates is shown in Scheme II.

At first, two types of adducts, I and II, are formed. The former is the adduct of the Sn—O bond across the C=O group of the 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 cannot be assigned with 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 I and II.

In the next stage, **1a**, and **2a** are produced by intramolecular substitution in adducts I and II, respectively (paths a and b). Of course, the paths c and d can be considered.

(13) Bloodworth, A. J.; Davies, A. G. *J. Chem. Soc.* **1965**, 6858.
(14) Dyen, M. E.; Swern, D. *Chem. Rev.* **1967**, *67*, 197.
(15) Braun, D.; Weinert, J. *Liebigs Ann. Chem.* **1979**, 200.
(16) Gulbins, K.; Hamann, K. *Chem. Ber.* **1961**, *94*, 3287.
(17) Gulbins, K.; Hamann, K. *Angew. Chem.* **1961**, *73*, 434.
(18) Mukaiyama, T.; Fujisawa, T. *J. Org. Chem.* **1962**, *27*, 3337.

Table II. Reactions between Tributyltin ω-Haloalkoxides ($Bu_3SnO(CH_2)_nX$) and Diphenylcarbodiimide[a]



1c, d **3c**

X	n	temp, °C	yield,[b] %	1/3 ratio[c]
Cl	2	25	91	100/0
Cl	3	25	28	100/0
Br	2	25	94	100/0
Br	3	25	91	100/0
I	2	25	86	100/0
I	3	25	86	100/0
Br	2	150	87	100/0
Br	2	200	84	56/44
I	2	200	87	0/100

[a] $Bu_3SnO(CH_2)_nX$, 100 mmol; PhN=C=NPh, 9 mmol; time, 1 h. [b] Based on PhN=C=NPh used unless otherwise noted. [c] Determined by ^1H NMR.

However, in reactions which have been thought to proceed via stannylcarbamates, only the formation of the compounds adding at the N atom have been reported.[2,8,12,13] Adduct I can be considered to be more reactive and less stable than adduct II.[11] The ratios of **1a** are larger in the higher yield reactions as shown in Table I (entries 11, 12, and 16). From these facts, we may describe the reaction pathway as yielding **1a** via intermediate I. This is of interest because evidence for the addition across the C=O group has not been reported.

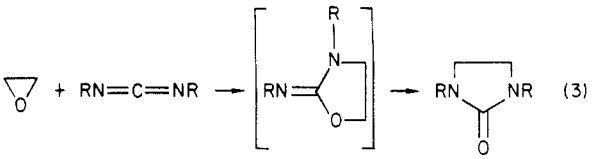
In the reaction using HMPA, **2a** was produced exclusively. If the equilibrium between I and II is fast and reversible, the yields of **1a** and **2a** will depend on the value of the equilibrium constant and the rate constant for conversion of I to **1a** and II to **2a**. Adduct II may be stabilized by coordination of HMPA to the tin atom as a Lewis base. This coordination increases 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 iminodioxane derivative (**1b**) was produced even in the reaction with methyl isocyanate, 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 cause the rearrangement from iminodioxanes (**1b**) to oxazinones (**2b**), or that adduct II may be more stable under the severe reaction conditions. Consequently, **2b** was obtained selectively in this case.

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

These reactions took place under conditions milder than those used in reactions of the isocyanates. 2-(Phenylimino)-3-phenyloxazolidine (**1c**) or 2-(phenylimino)-3-phenyloazine (**1d**) were obtained in high yield at room temperature even when HMPA was not used as a solvent. These products also could be easily isolated by adding hexane to the reaction mixture.

It was already reported that the reactions of oxiranes with carbodiimides give imidazolidinones without the formation of iminooxazolidines at high temperature around 200 °C[16] (eq 3).



(3)

The rearrangement of iminooxazolidines (**1c**) to imidazolidinones (**3c**) has been proposed under these conditions.

As expected, in our experiment, 1,3-diphenyl-2-imidazolidinone (**3c**) was obtained selectively at 200 °C as shown in Table II. This product was formed via an iminooxazolidine catalyzed by Bu_3SnI.

Thus, by utilizing these methods, heterocyclic compounds can be obtained easily in excellent yield under mild conditions. In particular, iminodioxolanes and oxazolidines have been considered as the precursors of the cycloadducts in the reaction of oxiranes with isocyanates and with carbodiimides, respectively.

Experimental Section

General Data. Melting points were obtained by using a Yanaco micromelting point apparatus and are uncorrected. IR spectra were recorded on a Hitachi 260-30 spectrometer using KBr pellets or KRS-5 cells. ^1H NMR and ^{13}C NMR spectra were performed on a JEOL Model PS-100 and on a JEOL Model FX-60 spectrometer, respectively. Analytical GLC was performed on the following instrument by using 2 m × 3 mm glass column packed with Silicone OV-1 on Uniport KS (5%, 60–80 mesh): a Shimadzu GC-3B with TCD and as a carrier gas. Column chromatography was done with silica gel (Wakogel C-200). Elemental analyses were performed by the section on elemental analysis in our department.

Materials. Commercial isocyanates were used without further purification. Diphenylcarbodiimide was synthesized by a described method.[19] Tributyltin ω-haloalkoxides[9] were synthesized in good yield as follows. Tributyltin methoxide (0.04 mol), which was prepared as described by Alleston and Davies,[20] and the corresponding haloalkyl acetates (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^{-4} mmHg removed the unconverted starting esters, giving almost pure tributyltin ω-haloalkoxide.

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, 27 H), 3.50 (t, 2 H), 3.90 (t, 2 H).

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, 27 H), 3.40 (t, 2 H), 3.90 (t, 2 H).

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

Tributyltin γ-chloropropoxdide ($Bu_3SnO(CH_2)_3Cl$): bp 80 °C (10^{-4} mmHg); IR (neat) 1070 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.90–1.80 (m, 27 H), 1.90 (t, 2 H), 3.65 (t, 2 H), 3.80 (t, 2 H).

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, 27 H), 2.00 (m, 2 H), 3.50 (t, 2 H), 3.80 (t, 2 H).

Tributyltin γ-iodopropoxide ($Bu_3SnO(CH_2)_3I$): IR (neat) 1070 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.90–1.80 (m, 27 H), 1.90 (t, 2 H), 3.30 (t, 2 H), 3.63 (t, 2 H).

Reactions between Tributyltin ω-Haloalkoxides and Isocyanates. 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 the disappearance of the characteristic ν(NCO) at 2275 cm^{-1} and the presence of a new band at 1660 cm^{-1}. After the reaction mixture had been heated for 1 h at 60 °C, hexane

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was added on cooling. Then 1.28 g (89%) of a white precipitate was obtained immediately. This was collected by filtration, washed with hexane, and dried in vacuo. The precipitate was a mixture of 2-(phenylimino)-1,3-dioxolane (**1a**) (20% yield) and 3-phenyl-2-oxazolidinone (**2a**) (69% yield). The **1a**/**2a** ratio was determined by ^{1}H NMR spectroscopy. Compound **1a** decomposed readily to ethylene carbonate and aniline on standing. When the reaction was carried out in a solvent, tributyltin ω-haloalkoxide, an isocyanate, and solvent were given off in this order.

Reactions between Tributyltin ω-Haloalkoxides and Diphenylcarbodiimide. A typical procedure is described for the reaction between tributyltin β-iodoethoxide ($Bu_3SnO(CH_2)_2I$) and diphenylcarbodiimide. $Bu_3SnO(CH_2)_2I$ (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 the mixture was stirred for 1 h at room temperature, hexane was added on cooling, giving a white precipitate, 0.97 g (86%) of 2-(phenylimino)-3-phenyloxazolidine (**1c**). When the reaction was carried out at 200 °C, the product was 1.02 g (87%) of 1,3-diphenyl-2-imidazolidinone (**3c**).

The Rearrangement of 1a to 2a. In the Presence of Bu_3SnI. In a 50-mL round-bottomed flask, 2-(phenylimino)-1,3-dioxolane (**1a**) (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 the mixture was heated for 1 h, a white precipitate was obtained by adding hexane. The solid was collected by filtration, washed with hexane, and dried in vacuo (0.42 g). It contained only **1a** and **2a**, and the ratio was determined by ^{1}H NMR.

In the presence of $Bu_3SnO(CH_2)_2I$ and phenyl isocyanate, $Bu_3SnO(CH_2)_2I$ (1.23 g, 2.67 mmol), phenyl isocyanate (0.23 g, 1.93 mmol), and 2-(phenylimino)-1,3-dioxolane (0.32 g, 1.96 mmol) were given off in this order. The reaction was carried out at 60 °C for 1 h: **1a** (0.38 g, 2.33 mmol) and **2a** (0.21 g, 1.29 mmol) were obtained.

2-(Phenylimino)-1,3-dioxolane: bp 130 °C (10^{-4} mmHg) (lit.[21] bp 148–150 °C (15 mmHg); IR (neat) 1720 cm^{-1}; ^{1}H NMR ($CDCl_3$) 4.38 (s, 4 H), 6.90–7.40 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 66.49, 64.73, 122.95, 123.39, 128.58, 145.41, 153.48.

2-(*p*-Tolylimino)-1,3-dioxolane. This compound was obtained as a mixture with 3-*p*-tolyl-2-oxazolidinone. However, this compound was labile and decomposed to ethylene carbonate and *p*-toluidine on column chromatography, so the pure compound could not be obtained. The yield of 2-(*p*-tolylimino)-1,3-dioxolane was determined by GLC or by ^{1}H NMR (δ 4.40).

2-((*p*-Chlorophenyl)imino)-1,3-dioxolane: mp 85 °C; IR (KBr) 1695 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.45 (s, 4 H), 6.82–7.32 (m, 4 H); ^{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.

2-((*p*-Nitrophenyl)imino)-1,3-dioxolane. This compound is labile, and pure product could not be obtained. The yield was determined as ethylene carbonate by GLC or ^{1}H NMR (δ 4.40).

2-(Methylimino)-1,3-dioxolane: bp 99 °C (25 mmHg) (lit.[21] bp 98–100 °C (25 mmHg)); IR (neat) 1740 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.85 (s, 3 H), 4.38 (s, 4 H); ^{13}C NMR ($CDCl_3$) δ 32.93, 65.46, 154.41.

3-Phenyl-2-oxazolidinone: mp 120 °C (lit.[14] mp 118–121 °C); IR (KBr) 1735 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.96 (t, 2 H), 4.20 (t, 2 H), 7.00–7.60 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 44.13, 60.47, 117.91, 123.49, 128.97, 139.34, 154.70.

3-*p*-Tolyl-2-oxazolidinone: mp 88 °C (lit.[14] mp 90 °C); IR (KBr) 1735 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.28 (s, 3 H), 3.94 (t, 2 H), 4.40 (t, 2 H), 7.14 (d, 2 H), 7.40 (d, 2 H); ^{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)-2-oxazolidinone: mp 118 °C (lit.[14] mp 116–117 °C); IR (KBr) 1740 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.97 (t, 2 H), 4.44 (t, 2 H), 7.10–7.60 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ 45.11, 61.30, 119.38, 129.01, 129.21, 136.94, 155.14.

3-(*p*-Nitrophenyl)-2-oxazolidinone: mp 155 °C (lit.[14] mp 155 °C); IR (KBr) 1750 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.14 (m, 2 H), 4.51 (m, 2 H), 7.80 (d, 2 H), 8.20 (d, 2 H); ^{13}C NMR ($CDCl_3$) δ 46.25, 63.14, 118.86, 125.96, 144.14, 146.29, 156.07.

3-Methyl-2-oxazolidinone: bp 102 °C (4 mmHg) lit.[14] bp 87–90 °C (1 mmHg); IR(neat) 1750 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.88 (s, 3 H), 3.56 (t, 2 H), 4.30 (t, 2 H); ^{13}C NMR ($CDCl_3$) δ 30.63, 46.43, 61.21, 158.52.

3-Phenyl-1,3-oxazinone: mp 95 °C; IR (KBr) 1680 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.16 (m, 2 H), 3.70 (t, 2 H), 4.40 (t, 2 H), 7.32 (m, 5 H); ^{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-oxazinone: mp 127 °C; IR (KBr) 1695 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.13 (m, 2 H), 2.32 (s, 3 H), 3.65 (t, 2 H), 4.38 (t, 2 H), 7.17 (s, 4 H); ^{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*-Clorophenyl)-1,3-oxazinone: mp 111 °C; IR (KBr) 1670 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.15 (m, 2 H), 3.66 (t, 2 H), 4.18 (t, 2 H), 7.30 (s, 4 H); ^{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-oxazinone: mp 125 °C; IR (KBr) 1680 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.26 (m, 2 H), 3.83 (t, 2 H), 4.46 (t, 2 H), 7.56 (d, 2 H), 8.23 (d, 2 H); ^{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-oxazinone: bp 103 °C (2 mmHg); IR (KBr) 1680 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.08 (m, 2 H), 3.00 (s, 3 H), 3.36 (t, 2 H), 4.28 (t, 2 H); ^{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.

2-(Phenylimino)-3-phenyloxazolidine: mp 115 °C (lit.[22] mp 115 °C); IR (KBr) 1675 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.90 (t, 2 H), 4.34 (t, 2 H), 6.90–7.90 (m, 10 H); ^{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.

2-(Phenylimino)-3-phenyloxazine: mp 106 °C; IR (KBr) 1630 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.10 (m, 2 H), 3.65 (t, 2 H), 4.20 (t, 2 H), 6.80–7.50 (m, 10 H); ^{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-2-imidazolidinone: mp 203 °C (lit.[16] mp 211 °C); IR (KBr) 1700 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.95 (s, 4 H), 6.90–7.70 (m, 10 H); ^{13}C NMR ($CDCl_3$) δ 42.08, 118.20, 123.19, 128.97, 140.22, 155.09.

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Registry No. **1a** (R = C_6H_5), 14678-39-8; **1a** (R = *p*-$CH_3C_6H_4$), 96690-04-9; **1a** (R = *p*-ClC_6H_4), 92819-22-2; **1a** (R = *p*-$NO_2C_6H_4$), 93168-13-9; **1a** (R = CH_3), 65658-11-9; **1c** (R = C_6H_5), 5679-75-4; **1d** (R = C_6H_5), 24066-67-9; **2a** (R = C_6H_5), 703-56-0; **2a** (R = *p*-$CH_3C_6H_4$), 5198-46-9; **2a** (R = *p*-ClC_6H_4), 5198-49-2; **2a** (R = *p*-$NO_2C_6H_4$), 5198-52-7; **2a** (R = CH_3), 19836-78-3; **2b** (R = C_6H_5), 56535-86-5; **2b** (R = *p*-$CH_3C_6H_4$), 61308-51-8; **2b** (R = *p*-ClC_6H_4), 61308-50-7; **2b** (R = *p*-$NO_2C_6H_4$), 96690-05-0; **2b** (R = CH_3), 96690-06-1; **3c**, 728-24-5; $Bu_3SnO(CH_2)_2Cl$, 35952-59-1; $CH_3COO(CH_2)_2Cl$, 542-58-5; $Bu_3SnO(CH_2)_2Br$, 35952-72-8; $CH_3COO(CH_2)_2Br$, 927-68-4; $Bu_3SnO(CH_2)_2I$, 96690-03-8; $CH_3COO(CH_2)_2I$, 627-10-1; $Bu_3SnO(CH_2)_3Cl$, 40894-18-6; $CH_3COO(CH_2)_3Cl$, 628-09-1; $Bu_3SnO(CH_2)_3Br$, 40894-08-4; $CH_3COO(CH_2)_3Br$, 592-33-6; $Bu_3SnO(CH_2)_3I$, 93912-82-4; $CH_3COO(CH_2)_3I$, 62116-24-9; C_6H_5NCO, 103-71-9; *p*-$CH_3C_6H_4NCO$, 622-58-2; *p*-ClC_6H_4NCO, 104-12-1; *p*-$NO_2C_6H_4NCO$, 100-28-7; CH_3NCO, 624-83-9; PhN=C=NPh, 622-16-2; Bu_3SnOCH_3, 1067-52-3; Bu_3SnI, 7342-47-4.

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