Formation of *N*-Tributylstannyl Heterocycle from Bis(tributyltin) Oxide and ω-Haloalkyl Isocyanate. One-Pot Convenient Synthesis of 2-Oxazolidinones and Tetrahydro-2*H*-1,3-oxazin-2-one

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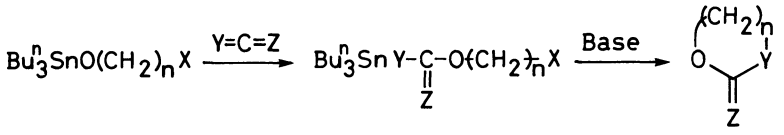
Novel types of compounds, *N*-tributylstannyl-2-oxazolidinone (**4a**) and tetrahydro-2*H*-1,3-oxazin-2-one (**4b**), are formed from the adduct of $(n\text{-Bu}_3\text{Sn})_2\text{O}$ (**1**) with ω-haloalkyl isocyanate (**2**), and the subsequent coupling reaction with alkyl halides gives a variety of *N*-substituted 2-oxazolidinones and tetrahydro-2-oxazinones in a one-pot procedure. Both the cyclization and the coupling reaction proceed quantitatively in the presence of HMPA which enhances the reactivity of the Sn–heteroatom bond by coordination.

Many organotin reagents have become widely used in organic synthesis.[1] Some important features of tin compounds are facile insertion of a heterocumulene such as an isocyanate toward a Sn–O bond,[2] and a great affinity toward a sulfur[3] or a halogen atom.[4]

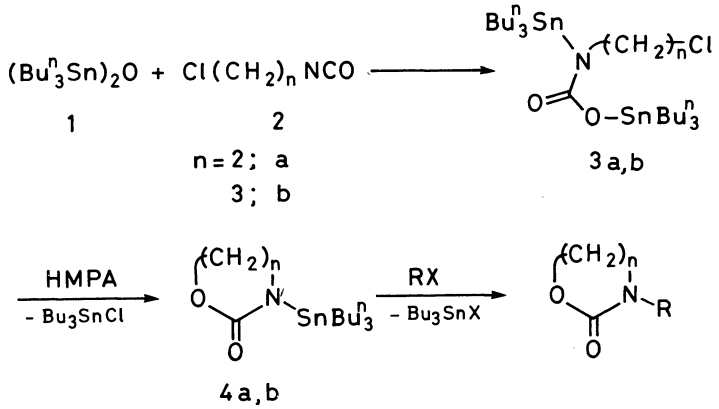
We have reported the preparation of five- and six-membered heterocyclic compounds from the adduct of tributyltin ω-haloalkoxides ($n\text{-Bu}_3\text{SnO(CH}_2)_n\text{X}$) with a heterocumulene[5] (Scheme 1), in which a Lewis base plays an important role in the cyclization.

The coordination of a base toward the Sn atom increases the basicity of the adjacent heteroatom, which induces facile cyclization.

In connection with our interest in the use of this type of cyclization, we wish to report here a convenient method for the preparations of new compounds, *N*-tributylstannyl-2-oxazolidinone (**4a**) and tetrahydro-2*H*-1,3-oxazin-2-one (**4b**), by the cyclization of the adduct (**3**), generated from $(n\text{-Bu}_3\text{Sn})_2\text{O}$ (**1**) and ω-haloalkyl isocyanate (**2**). Furthermore, the preparation of a variety of *N*-substituted 2-oxazolidinones and tetrahydro-2-oxazinones by the subsequent coupling reaction could be achieved under mild and neutral conditions (Scheme 2).[6] 2-Oxazolidinones are an important class of heterocyclic compounds which have many biological uses.[7] In particular, the use of *N*-stannyl-2-oxazolidinones and tetrahydro-2-oxazinones in organic synthesis has never been reported, although the silylated analogue is widely known as a silylating agent.[8]



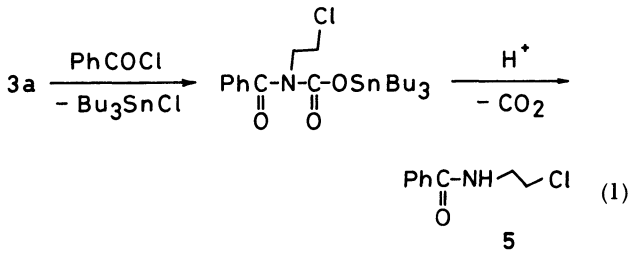
Scheme 1.



Scheme 2.

Results and Discussion

As shown in Scheme 2, *N*-tributylstannyl-2-oxazolidinone (**4a**) could be readily formed from the reaction of $(n\text{-Bu}_3\text{Sn})_2\text{O}$ (**1**) and 2-chloroethyl isocyanate (**2a**). At first, the isocyanate inserts into the Sn–O bond spontaneously to give *N*-stannylcarbamate (**3a**). This intermediate was indicated by the appearance of an IR absorption band at 1600 cm^{-1} in place of the NCO group (2280 cm^{-1}). ^1H NMR showed the multiplet peaks between δ 3.30 and 3.70 due to methylene groups adjacent the nitrogen and chloro atoms. To trap the intermediate **3a**, we tried the reaction with benzoyl chloride (Eq. 1). The *N*-acylation proceeded smoothly, and subsequent work-up gave the amide (**5**) in 98% yield, accompanied by decarboxylation.

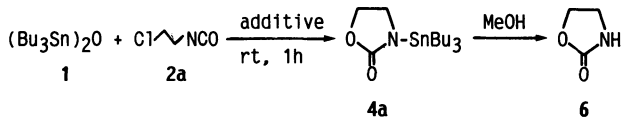


(1)

In the next stage, heating of **3a** induces the cyclization to give **4a**. IR band of the C=O group shifted to 1680 cm^{-1}, and ^1H NMR indicated the peaks of methylene groups adjacent to the nitrogen and chloro groups at δ 3.40—3.80 and 4.25—4.65, respectively. Moreover, GLC analysis showed the quantitative formation of the eliminated by-product, *n*-Bu_3SnCl.

The compound **4a** is so reactive that it was readily protonated to give 2-oxazolidinone (**6**) during work-up. Interestingly, the cyclization step is affected by additives (Table 1). Without any additives, the reaction hardly took place under the mild conditions (Entry 1), and elevated temperature (80 °C) was necessary to complete the cyclization (Entry 1, parentheses). Among the additives, the ones bearing a high coordinating ability toward a Sn atom are effective for the cyclization, and particularly, hexamethylphosphoric triamide (HMPA) was the most suitable one.[9] This coordination increases the basicity of the heteroatom adjacent to the Sn atom. Thus, the cyclization to form **4a** proceeded in high yield at room temperature in the presence of HMPA (Entry 6).

Table 1. Effect of Additive[a]



Entry	Additive	Yield of **6**/%[b]
1	—	tr (98)[c]
2	Et_3N	tr
3	Bu_3P	tr
4	DMF	73
5	Bu_3PO	62
6	HMPA	85

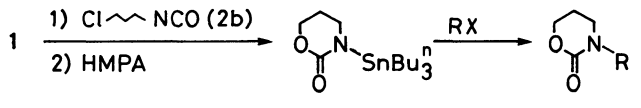
a) **1**; 5 mmol, **2a**; 5 mmol, additive 10 mmol. b) GLC yield. c) 80 °C, 1 h.

We next examined the coupling reactions of **4a** with organic halides. It is possible to carry out a one pot cyclization-coupling reaction by simply adding an acid chloride to the cyclization mixture. In this way, 3-benzoyl-2-oxazolidinone (**7**) was formed directly in 86% yield (Table 2, Entry 1). The acylation proceeded cleanly, affording the corresponding 3-acyl-2-oxazolidinones[10] (**7**—**13**). The yields are good or excellent, no side reactions were observed. Moreover, purification of the products was simple, and the by-product, *n*-Bu_3SnCl, could be removed completely by column chromatography using hexane as an eluent. With a half molar equivalent of oxalyl dichloride and adipoyl dichloride, bis(2-oxazolidinones) (**14**, **15**) were obtained, respectively (Entries 8 and 9).

Other organic halides also gave good yields. Similar to acid chlorides, the reactions with phosphoryl chlorides and a sulfonyl chloride proceeded spontaneously, and gave 3-phosphoryl- and 3-sulfonyl-2-oxazolidinones (**16**—**18**), respectively (Entries 10—12). With activated organic halides such as α-bromo carbonyl compounds, allyl and benzyl bromides, the coupling reactions proceeded at 80 °C to form **19**—**25** in high yields (Entries 13—19).

As in the cyclization reactions, HMPA was found to facilitate these coupling reactions, in contrast to the severe conditions previously reported for the alkylation of *N*-unsubstituted 2-oxazolidinone (**6**).[7a] For example, reaction of **4a** with cinnamyl bromide in the absence of HMPA at 80 °C for 1 h afforded only 31% of compound **22**; in the presence of HMPA, 73% yield was obtained (Entry 16). Apparently, HMPA enhances the reactivity of the Sn–N bond by coordination.

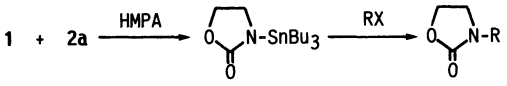
We next tried to prepare six-membered compounds, tetrahydro-2*H*-1,3-oxazin-2-one derivatives, by the analogous reactions using 3-chloropropyl isocyanate (**2b**) (Eq. 2).



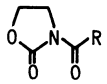
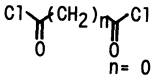
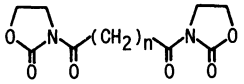
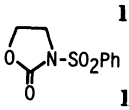
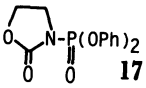
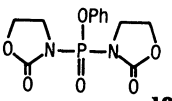
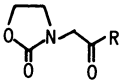
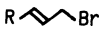
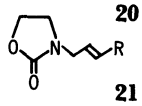
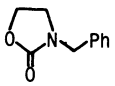
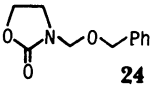
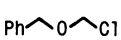
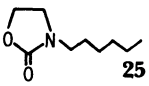
(2)

These results are shown in Table 3. Compared to the case of five-membered ring formation, the cyclization to form **4b** required severe conditions (80 °C, 1 h) for completion. Subsequent reaction with organic halides gave a variety of tetrahydro-2-oxazinone derivatives (**26**—**30**) in good yields.

Table 2. Synthesis of 2-Oxazolidinones

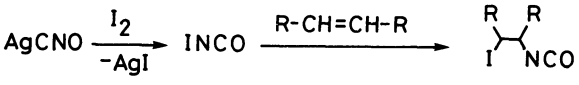


4a

Entry	RX	Conditions[a]	Product	Yield/%[a]
	RCOCl			
1	R=Ph	rt, 10 min	**7**	86
2	Me	rt, 10 min	**8**	100
3	*i*-Pr	rt, 10 min	**9**	100
4	$PhCH_2$	rt, 10 min	**10**	94
5	$PhOCH_2$	rt, 10 min	**11**	99
6	PhCH=CH	rt, 10 min	**12**	88
7	$PhCH_2O$	rt, 10 min	**13**	100
				
8	n= 0	rt, 10 min	**14**	78[c]
9	4	rt, 10 min	**15**	84[c]
				
10	$PhSO_2Cl$	rt, 10 min	**16**	80
				
11	$(PhO)_2PCl$	rt, 10 min	**17**	93
				
12	$PhOPCl_2$	rt, 10 min	**18**	100[c]
				
13	R=Ph	80°C, 15 h	**19**	76
14	EtO	80°C, 15 h	**20**	78
				
15	R=H	80°C, 15 h	**21**	81
16	Ph	80°C, 15 h	**22**	73
				
17		80°C, 15 h	**23**	60
				
18		80°C, 15 h	**24**	90
				
19		80°C, 15 h	**25**	91

a) At the coupling reaction. b) Isolated yield. c) 0.5 equiv of RX was used.

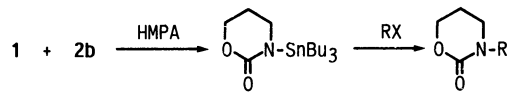
Next, the preparation of 4,5-disubstituted 2-oxazolidinones was accomplished as follows. It is reported that iodine isocyanate (INCO) derived from silver cyanate and iodine, adds to an olefin in a stereospecific manner to produce 2-iodoethyl isocyanates[11] (Eq. 3).



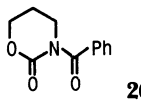
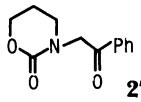
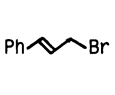
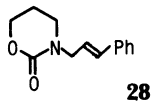
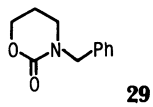
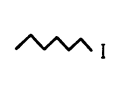
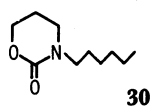
(3)

Employing these substrates, the preparation of 4,5-dialkyl-2-oxazolidinones could be achieved by the

Table 3. Synthesis of Tetrahydro-2-oxazinones

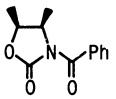
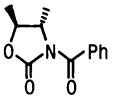
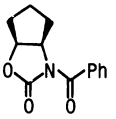
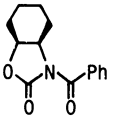
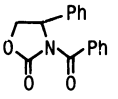


4b

Entry	RX	Condition[a]	Product	Yield/%[b]
1		rt, 10 min	 **26**	100
2		80 °C, 15 h	 **27**	72
3		80 °C, 15 h	 **28**	100
4		80 °C, 15 h	 **29**	87
5		80 °C, 15 h	 **30**	80

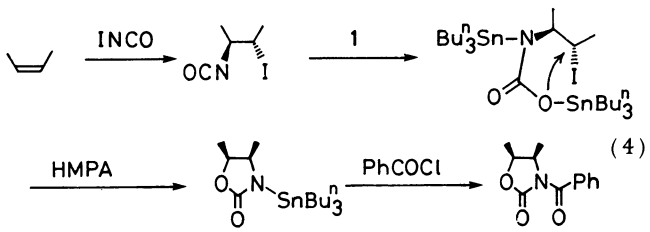
a) At the coupling reaction. b) Isolated yield.

Table 4. Synthesis of 2-Oxazolidinones from Olefins

Entry	Olefin	Product	Yield/%[a]
1		 **31**	88
2		 **32**	98
3		 **33**	66
4		 **34**	50
5		 **35**	52

a) Isolated yield.

combination with our method (Table 4). For example, as shown in Eq. 4, *cis*-2-butene afforded *threo*-iodo isocyanate which reacted with **1** to give the adduct. Next, the cyclization to form *N*-stannyl-2-oxazolidinone proceeded via backside attack of the oxygen on the terminal alkyl iodide.[12] As a result, *cis*-4,5-dimethyl-2-oxazolidinone (**31**) was prepared in 88% overall yield (Entry 1).



(4)

Similarly, the diastereoisomer, *trans*-dimethyl-2-oxazolidinone (**32**), was obtained from *trans*-2-butene (Entry 2).[13] Thus, 4,5-disubstituted 2-oxazolidinones could be easily prepared from olefins in a stereospecific manner by a one-pot reaction. The additional results obtained using other olefins are shown in Table 4.

In summary, we have demonstrated an effective and direct method for the preparation of 2-oxazolidinones and tetrahydro-2*H*-1,3-oxazin-2-ones by using organotin reagents. Our method provides several advantages in terms of mild and neutral conditions, high yields of products and operational convenience.

Experimental

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 pelletes or KRS-5 cells. ^{1}H NMR and ^{13}C NMR spectra were performed on Hitachi R-90HS spectrometer. Mass spectra were recorded on a Hitachi RMU-6E instrument. Analytical GLC was performed on Shimadzu GC-3B with TCD using a 2 m×3 mm glass column packed with Silicone OV-1 on uniport HP (5%, 60—80 mesh). Silica-gel column chromatography was used (Wakogel C-200).

Benzoyl-2-chloroethylamide (5). Under dry nitrogen, 0.53 g (5 mmol) of 2-chloroethyl isocyanate (**2a**) was added to 2.98 g (5 mmol) of bis(tributyltin) oxide (**1**). This process to form **3a** proceeded spontaneously. Next, to this solution was added 1.40 g (10 mmol) of PhCOCl at room temperature. After stirring for 10 min, the reaction mixture was chromatographed by silica-gel column, where decarboxylation occurred. Elusion with benzene gave the compound **5** which was purified by recrystallization from benzene–hexane (1:1): Mp 86—87 °C; MS *m/z* 183.5 (M^+); IR 1630 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=3.50—4.00 (m, 4H, CH_2), 6.35—6.85 (br, 1H, NH), 7.20—7.90 (m, 5H, phenyl). Calcd for $C_9H_{10}NOCl$: C, 58.86; H, 5.45; H, 7.63%. Found: C, 58.55; H, 5.41; N, 7.97%.

3-Benzoyl-2-oxazolidinone (7) (General Procedure for the Preparation of 2-Oxazolidinones): To the liquid of **3a** formed in situ was added 1.80 g (10 mmol) of HMPA. This mixture was stirred at 40 °C for 1 h, giving *N*-stannyl-2-oxazolidinone (**4a**) which was converted to **6** upon MeOH. Without HMPA, the cyclization required severe conditions (80 °C, 1 h). To this mixture containing **4a** was added 0.70 g (5 mmol) of benzoyl chloride at room temperature. After

10 min, the reaction mixture was chromatographed, and purified by recrystallization from benzene–hexane (1:1): mp 166—168 °C (lit,[14] mp 168 °C); IR (KBr) 1670, 1770 cm^{-1}; MS *m/z* 191 (M^+); ^1H NMR ($CDCl_3$) δ=3.80—4.35 (m, 2H, $C\underline{H}_2O$), 4.35—4.90 (m, 2H, $C\underline{H}_2N$), 7.10—8.00 (m, 5H, phenyl). The following compounds **8**—**18** were obtained in a similar manner by using suitable organic halides.

3-Acetyl-2-oxazolidinone (8): Mp 85 °C (lit,[7a] mp 87—87.5 °C); IR (KBr) 1690, 1780 cm^{-1}; MS *m/z* 129 (M^+); ^1H NMR ($CDCl_3$) δ=2.55 (s, 3H, $C\underline{H}_3$), 4.05 (t, *J*=8 Hz, 2H, $C\underline{H}_2N$), 4.45 (t, *J*=8 Hz, 2H, $C\underline{H}_2O$).

3-Isopropionyl-2-oxazolidinone (9): Wax, purified by Kugelrohr distillation at 100 °C/10^{-3} mmHg (1 mmHg= 133.322 Pa); IR (neat) 1700, 1780 cm^{-1}; MS *m/z* 157 (M^+); ^1H NMR ($CDCl_3$) δ=1.20 (d, *J*=7 Hz, 6H, $C\underline{H}_3$), 3.60—3.90 (m, 1H, $Me_2C\underline{H}$), 4.05 (dd, *J*=7 and 9 Hz, 2H, $C\underline{H}_2N$), 4.45 (dd, *J*=7 and 9 Hz, 2H, $C\underline{H}_2O$); Calcd for $C_7H_{11}NO_3$: C, 53.50; H, 7.01; N, 8.92%. Found: C, 53.38; H, 6.98; N, 9.04%.

3-Phenylacetyl-2-oxazolidinone (10): Mp 55—56 °C; IR (KBr) 1690, 1760 cm^{-1}; MS *m/z* 205 (M^+); ^1H NMR ($CDCl_3$) δ=3.95 (t, *J*=8 Hz, 2H, $C\underline{H}_2N$), 4.10—4.60 (m, 4H, $C\underline{H}_2O$ and $PhC\underline{H}_2$), 6.90—7.60 (m, 5H, phenyl); Calcd for $C_{11}H_{11}NO_3$: C, 64.39; H, 5.37; N, 6.83%. Found: C, 64.18; H, 5.07; N, 6.88%.

3-Phenoxyacetyl-2-oxazolidinone (11): Mp 93—95 °C; IR (KBr) 1720, 1790 cm^{-1}; MS *m/z* 221 (M^+); ^1H NMR ($CDCl_3$) δ=4.05 (t, *J*=8 Hz, 2H, $C\underline{H}_2N$), 4.50 (t, *J*=8 Hz, 2H, $C\underline{H}_2O$), 5.25 (s, 2H, $PhOCH_2$), 6.80—7.50 (m, 5H, phenyl); Calcd for $C_{11}H_{11}O_4N$: C, 59.72; H, 4.98; N, 6.33%. Found: C, 59.66; H, 4.93; N, 6.32%.

3-Cinnamoyl-2-oxazolidinone (12): Mp 148—149 °C; IR (KBr) 1620, 1770 cm^{-1}; MS *m/z* 217 (M^+); ^1H NMR ($CDCl_3$) δ=4.00—4.30 (m, 2H, $C\underline{H}_2N$), 4.30—4.60 (m, 2H, $C\underline{H}_2O$), 7.20—8.00 (m, 7H, phenyl and $C\underline{H}_2$=CH-Ph); Calcd for $C_{12}H_{11}NO_3$: C, 66.36; H, 5.07; N, 6.45%. Found: C, 66.24; H, 4.95; N, 6.55%.

3-Benzyloxycarbonyl-2-oxazolidinone (13): Mp 98—100 °C (lit,[7a] mp 101—102 °C); IR (KBr) 1800 cm^{-1}; MS *m/z* 221 (M^+); ^1H NMR ($CDCl_3$) δ=3.80—4.20 (m, 2H, $C\underline{H}_2N$), 4.30—4.60 (m, 2H, $C\underline{H}_2O$), 5.30 (s, 2H, $PhC\underline{H}_2$), 7.20—7.70 (m, 5H, phenyl).

3,3′-Oxalylbis(2-oxazolidinone) (14). The compounds **14** and **15** were prepared by using 0.5 equiv of acyl chlorides: mp 234—236 °C (lit,[7a] mp 238 °C); IR (KBr) 1710, 1790 cm^{-1}; MS *m/z* 228 (M^+); ^1H NMR ($CDCl_3$) δ=4.00—4.50 (m, 4H, $C\underline{H}_2N$), 4.50—4.90 (m, 4H, $C\underline{H}_2O$).

3,3′-Adipoylbis(2-oxazolidinone) (15): Mp 138 °C (lit,[7a] mp 138 °C); IR (KBr) 1710, 1780 cm^{-1}; MS *m/z* 284 (M^+); ^1H NMR ($CDCl_3$) δ=1.70—2.00 (m, 4H, $COCH_2C\underline{H}_2$), 2.96 (t, *J*=7 Hz, 4H, $COC\underline{H}_2$), 4.01 (t, *J*=7 Hz, 4H, $C\underline{H}_2N$), 4.32 (t, *J*=7 Hz, 4H, $C\underline{H}_2O$).

3-Phenylsulfonyl-2-oxazolidinone (16): Mp 136—138 °C (lit,[15] mp 130—135 °C); IR (KBr) 1770 cm^{-1}; MS *m/z* 227 (M^+); ^1H NMR ($CDCl_3$) δ=3.90—4.30 (m, 2H, $C\underline{H}_2N$), 4.30—4.60 (m, 2H, $C\underline{H}_2O$), 7.40—8.20 (m, 5H, phenyl).

3-Diphenyloxyphosphinyl-2-oxazolidinone (17): Mp 94—95 °C; IR (KBr) 1770 cm^{-1}; MS *m/z* 319 (M^+); ^1H NMR ($CDCl_3$) δ=3.84 (t, *J*=8 Hz, 2H, $C\underline{H}_2N$), 4.33 (t, *J*=8 Hz, 2H, $C\underline{H}_2O$), 7.20—7.40 (m, 10H, phenyl); Calcd for $C_{15}H_{14}NO_5P$: C, 56.43; H, 4.39; N, 4.39%. Found: C, 56.57; H, 4.44; N, 4.49%.

3,3′-Phenoxyphosphinylidenebis(2-oxazolidinone) (18). This compound was prepared by using 0.5 equiv of phenyl phosphorodichloridate: mp 158 °C; IR (KBr) 1770 cm^{-1}; MS *m/z* 312 (M^+); ^1H NMR ($CDCl_3$) δ=4.00—4.30 (m, 4H, $C\underline{H}_2N$), 4.40—4.70 (m, 4H, $C\underline{H}_2O$), 7.20—7.50 (m, 5H, phenyl); Calcd for $C_{12}H_{13}N_2O_6P$: C, 46.15; H, 4.17; N, 8.97%. Found: C, 45.99; H, 4.20; N, 8.89%.

3-Phenacyl-2-oxazolidinone (19). The coupling reaction of **4a** formed in situ with phenacyl bromide was performed at 80 °C for 15 h. The following compounds **20**—**25** were obtained in a similar manner using suitable organic halides: mp 105—108 °C; IR (KBr) 1700, 1750 cm^{-1}; MS *m/z* 205 (M^+): ^1H NMR ($CDCl_3$) δ=3.73 (dd, *J*=7 and 9 Hz, 2H, $C\underline{H}_2N$), 4.45 (dd, *J*=7 and 9 Hz, 2H, $C\underline{H}_2O$), 4.70 (s, 2H, $PhCOC\underline{H}_2$), 7.20—8.30 (m, 5H, phenyl); Calcd for $C_{11}H_{11}NO_3$; C, 64.38; H, 5.40; N, 6.83%. Found: C, 64.54; H, 5.29; N, 6.66%.

3-Ethoxycarbonylmethyl-2-oxazolidinone (20): Wax, purified by Kugelrohr distillation at 100 °C/10^{-3} mmHg; IR (neat) 1740, 1760 cm^{-1}; MS *m/z* 173 (M^+); ^1H NMR ($CDCl_3$) δ=1.29 (t, *J*=7 Hz, 3H, $C\underline{H}_3$), 3.70 (dd, *J*=7 and 9 Hz, 2H, $C\underline{H}_2N$), 4.02 (s, 2H, $C\underline{H}_2COOEt$), 4.10—4.50 (m, 4H, $C\underline{H}_2Me$ and $C\underline{H}_2O$); Calcd for $C_7H_{11}NO_4$: C, 48.55; H, 6.36; N, 8.09%. Found: C, 48.75; H, 6.47; N, 7.99%.

3-Allyl-2-oxazolidinone (21): Wax, purified by Kugelrohr distillation at 100 °C/10^{-3} mmHg (lit,[16] bp 123—125 °C/0.7 mmHg); IR (neat) 1750 cm^{-1}; MS *m/z* 127 (M^+); ^1H NMR ($CDCl_3$) δ=3.51 (dd, *J*=7 and 9 Hz, 2H, $C\underline{H}_2N$), 3.90 (d, *J*=6 Hz, 2H, $NC\underline{H}_2CH$=CH_2), 4.34 (dd, *J*=7 and 9 Hz, 2H, $C\underline{H}_2O$), 5.10—6.10 (m, 3H, $C\underline{H}$=$C\underline{H}_2$).

3-Cinnamyl-2-oxazolidinone (22): Mp 69 °C; IR (KBr) 1740 cm^{-1}; MS *m/z* 203 (M^+); ^1H NMR ($CDCl_3$) δ=3.62 (dd, *J*=7 and 9 Hz, 2H, $C\underline{H}_2N$), 4.08 (d, *J*=7 Hz, 2H, $C\underline{H}_2CH$=CHPh), 4.38 (dd, *J*=7 and 9 Hz, 2H, $C\underline{H}_2O$), 6.00—6.70 (m, 2H, $C\underline{H}$=$C\underline{H}$Ph), 7.20—7.60 (m, 5H, phenyl); Calcd for $C_{12}H_{13}NO_2$: C, 70.94; H, 6.40; N, 6.90%. Found: C, 70.78; H, 6.46; N, 6.66%.

3-Benzyl-2-oxazolidinone (23): Mp 77—78 °C (lit,[7a] mp 79—80 °C); IR (KBr) 1750 cm^{-1}; MS *m/z* 177 (M^+); ^1H NMR ($CDCl_3$) δ=3.40 (dd, *J*=7 and 9 Hz, 2H, $C\underline{H}_2N$), 4.28 (dd, *J*=7 and 9 Hz, 2H, $C\underline{H}_2O$), 4.41 (s, 2H, $PhC\underline{H}_2$), 7.40—7.60 (m, 5H, phenyl).

3-Benzyloxymethyl-2-oxazolidinone (24): Wax, purified by Kugelrohr distillation at 150 °C/10^{-3} mmHg; IR (neat) 1760 cm^{-1}; MS *m/z* 207 (M^+); ^1H NMR ($CDCl_3$) δ=3.62 (dd, *J*=7 and 9 Hz, 2H, $C\underline{H}_2N$), 4.25 (dd, *J*=7 and 9 Hz, $C\underline{H}_2O$), 4.56 (s, 2H, $C\underline{H}_2Ph$), 4.83 (s, 2H, $NC\underline{H}_2O$), 7.30—7.50 (m, 5H, phenyl); Calcd for $C_{11}H_{13}NO_3$:C, 63.77; H, 6.28; N, 6.76%. Found: C, 63.37; H, 6.41; N, 6.86%.

3-Hexyl-2-oxazolidinone (25): Wax, purified by Kugelrohr distillation at 100 °C/10^{-3} mmHg (lit,[7a] bp 176 °C/1 mmHg); IR (neat) 1740 cm^{-1}; MS *m/z* 171 (M^+); ^1H NMR ($CDCl_3$) δ=0.80—1.90 (m, 11H, $NCH_2C_5\underline{H}_{11}$), 3.28 (t, *J*=7 Hz, 2H, $C\underline{H}_2C_5H_{11}$), 3.58 (dd, *J*=7 and 9 Hz, 2H, $C\underline{H}_2N$), 4.33 (dd, *J*=7 and 9 Hz, 2H, $C\underline{H}_2O$).

3-Benzoyltetrahydro-2*H*-1,3-oxazin-2-one (26) (General Procedure for the Preparation of Tetrahydro-2*H*-1,3-oxazin-2-ones). To a neat liquid of 2.98 g (5 mmol) of **1** was added 0.60 g (5 mmol) of 3-chloropropyl isocyanate (**2b**). After 10 min, 1.80 g (10 mmol) of HMPA was added to this reaction mixture, and heated at 80 °C for 1 h, where *N*-stannyltetrahydro-2*H*-1,3-oxazin-2-one (**4b**) was formed. Next, 0.70 g (5 mmol) of benzoyl chloride was added to this solution, and stirred at room temperature for 10 min. The product **26** was obtained by column chromatography: mp

87 °C; IR (KBr) 1680, 1720 cm^{-1}; MS *m/z* 205 (M^+); ^{1}H NMR ($CDCl_3$) δ=2.00—2.40 (m, 2H, $C\underline{H}_2$), 3.91 (t, *J*=6 Hz, 2H, $C\underline{H}_2N$), 4.43 (t, *J*=5 Hz, 2H, $C\underline{H}_2O$), 7.20—8.20 (m, 5H, phenyl); Calcd for $C_{11}H_{11}NO_3$: C, 64.39; H, 5.37; N, 6.83%. Found: C, 64.11; H, 5.43; N, 6.84%.

3-Phenacyltetrahydro-2*H*-1,3-oxazin-2-one (27). The coupling reaction of **4b** with organic halides to form **27—30** was performed at 80 °C for 15 h: mp 93 °C; IR (KBr) 1680, 1700 cm^{-1}; MS *m/z* 219 (M^+); ^{1}H NMR ($CDCl_3$) δ=2.16 (m, 2H, $C\underline{H}_2$), 3.43 (t, *J*=6 Hz, 2H, $C\underline{H}_2N$), 4.41 (t, *J*=5 Hz, $C\underline{H}_2O$), 4.82 (s, 2H, $PhCOC\underline{H}_2$), 7.20—8.00 (m, 5H, phenyl); Calcd for $C_{12}H_{13}NO_3$: C, 65.75; H, 5.94; N, 6.39%. Found: C, 65.55; H, 5.91; N, 6.45%.

3-Cinnamyltetrahydro-2*H*-1,3-oxazin-2-one (28): Wax, purified by Kugelrohr distillation at 150 °C/10^{-3} mmHg; IR (neat) 1690 cm^{-1}; MS *m/z* 217 (M^+); ^{1}H NMR ($CDCl_3$) δ=1.90—2.00 (m, 2H, $C\underline{H}_2$), 3.32 (t, *J*=6 Hz, 2H, $C\underline{H}_2N$), 4.11 (d, *J*=6 Hz, 2H, $C\underline{H}_2CH$=CHPh), 4.26 (t, *J*=5 Hz, 2H, $C\underline{H}_2O$), 6.00—6.70 (m, 2H, $C\underline{H}$=$C\underline{H}$Ph), 7.10—7.60 (m, 5H, phenyl); Calcd for $C_{13}H_{15}NO_2$: C, 71.89; H, 6.91; N, 6.45%. Found: C, 71.65; H, 7.08; N, 6.34%.

3-Benzyltetrahydro-2*H*-1,3-oxazin-2-one (29): Mp 35 °C; IR (KBr) 1690 cm^{-1}; MS *m/z* 191 (M^+); ^{1}H NMR ($CDCl_3$) δ=2.03 (m, 2H, $C\underline{H}_2$), 3.21 (t, *J*=6 Hz, 2H, $C\underline{H}_2N$), 4.25 (t, *J*=5 Hz, 2H, $C\underline{H}_2O$), 4.55 (s, 2H, $PhC\underline{H}_2$), 7.20—7.30 (m, 5H, phenyl); Calcd for $C_{11}H_{13}NO_2$: C, 69.11; H, 6.81; N, 7.33%. Found: C, 68.93; H, 6.83; N, 7.34%.

3-Hexyltetrahydro-2*H*-1,3-oxazin-2-one (30): Wax, purified by Kugelrohr distillation at 100 °C/10^{-3} mmHg; IR (neat) 1690 cm^{-1}; MS *m/z* 185 (M^+); ^{1}H NMR ($CDCl_3$) δ=0.80—1.90 (m, 11H, $NCH_2C_5\underline{H}_{11}$), 1.90—2.20 (m, 2H, $C\underline{H}_2$), 3.30 (m, 4H, $C\underline{H}_2N$ and $NC\underline{H}_2C_5H_{11}$), 4.23 (t, *J*=5 Hz, 2H, $C\underline{H}_2O$); Calcd for $C_{10}H_{19}NO_2$: C, 64.86; H, 10.27; N, 7.57%. Found: C, 64.97; H, 9.96; N, 7.68%.

3-Benzoyl-*cis*-4,5-dimethyl-2-oxazolidinone (31). *cis*-2-Butene (0.56 g, 10 mmol) was added to AgNCO (1.50 g, 10 mmol) in 5 ml of ether at −10 °C. The mixture was stirred vigorously while I_2 (2.54 g, 10 mmol) was added. Stirring was continued for 3 h. The slurry was filtered, and concentration of the solution gave a mobile brown liquid. To this liquid was added **1** (5.96 g, 10 mmol) at room temperature. After 10 min, HMPA (3.60 g, 20 mmol) was added to this reaction mixture, and heated at 40 °C for 1 h. Moreover, the addition of benzoyl chloride (1.40 g, 10 mmol) at room temperature and stirring for 10 min gave **31**. Mp 78 °C; IR (KBr) 1670, 1780 cm^{-1}; MS *m/z* 219 (M^+); ^{1}H NMR ($CDCl_3$) δ=1.39 (d, *J*=6.5 Hz, 3H, $NCHC\underline{H}_3$), 1.46 (d, *J*=6.5 Hz, 3H, $OCHC\underline{H}_3$), 4.50—5.00 (m, homodecoupling *J*=8 Hz, 2H, $C\underline{H}$), 7.20—7.90 (m, 5H, phenyl); ^{13}C NMR ($CDCl_3$) δ=13.2, 14.8, 54.9, 74.7, 127.9, 128.8, 132.2, 133.6, 153.0, 169.9; Calcd for $C_{12}H_{13}NO_3$: C, 65.75; H, 5.94; N, 6.39%. Found: C, 65.46; H, 5.94; N, 6.42%.

3-Benzoyl-*trans*-4,5-dimethyl-2-oxazolidinone (32): Mp 47 °C; IR (KBr) 1680, 1780 cm^{-1}; MS *m/z* 219 (M^+); ^{1}H NMR ($CDCl_3$) δ=1.46 (d, *J*=6 Hz, 3H, $NCHC\underline{H}_3$), 1.53 (d, *J*=6 Hz, 3H, $OCHC\underline{H}_3$), 4.00—4.50 (m, homodecoupling *J*=6 Hz, 2H, $C\underline{H}$), 7.20—7.90 (m, 5H, phenyl); ^{13}C NMR ($CDCl_3$) δ=17.8, 19.3, 58.2, 77.9, 128.0, 128.4, 129.2, 132.5, 162.7, 186.1; Calcd for $C_{12}H_{13}NO_3$: C, 65.75; H, 5.94; N, 6.39%. Found: C, 65.91; H, 6.03; N, 6.23%.

3-Benzoylhexahydro-2*H*-cyclopentoxazol-2-one (33): Mp 127 °C; IR (KBr) 1670, 1760 cm^{-1}; MS *m/z* 231 (M^+); ^{1}H NMR ($CDCl_3$) δ=1.80—2.30 (m, 6H, $(C\underline{H}_2)_3$), 4.80—5.20 (m, 2H, $C\underline{H}$), 7.20—7.80 (m, 5H, phenyl); Calcd for $C_{13}H_{13}NO_3$: C, 67.53; H, 5.63; N, 6.06%. Found: C, 67.20; H, 5.55; N, 6.08%.

3-Benzoylhexahydrobenzoxazol-2(3*H*)-one (34): Mp 112 °C (lit,[17] mp 114—115 °C); IR (KBr) 1670, 1690 cm^{-1}; MS *m/z* 245 (M^+); ^{1}H NMR ($CDCl_3$) δ=1.20—2.50 (m, 8H, $(C\underline{H}_2)_4$), 4.20—4.50 (m, 1H, $C\underline{H}N$), 4.50—4.80 (m, 1H, $C\underline{H}O$), 7.20—7.80 (m, 5H, phenyl).

3-Benzoyl-4-phenyl-2-oxazolidinone (35): Mp 167 °C; IR (KBr) 1680, 1790 cm^{-1}; MS *m/z* 267 (M^+); ^{1}H NMR ($CDCl_3$) δ=4.32 (dd, *J*=7 and 9 Hz, 1H, $C\underline{H}_2O$), 4.78 (t, 1H, *J*=9 Hz, $C\underline{H}_2O$), 5.64 (dd, *J*=7 and 9 Hz, 1H, $C\underline{H}N$), 7.20—7.80 (m, 10H, phenyl); Calcd for $C_{16}H_{13}NO_3$: C, 71.91; H, 4.87; N, 5.24%. Found: C, 71.80; H, 4.92; N, 5.19%.

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