

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

Ikuya SHIBATA,* Kenji NAKAMURA, Akio BABA, and Haruo MATSUDA
Department of Applied Chemistry, Faculty of Engineering, Osaka University,
2-1 Yamadaoka, Suita, Osaka 565
(Received September 30, 1988)

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.

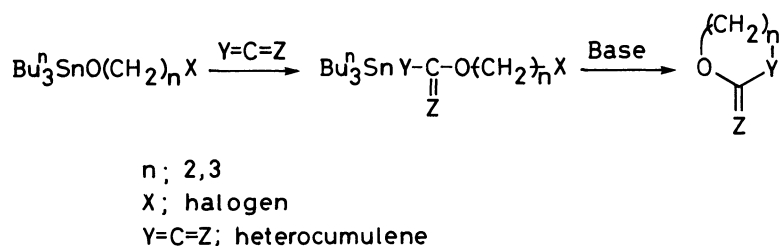
Many organotin reagents have become widely used in organic synthesis.¹ Some important features of tin compounds are facile insertion of a heterocumulene such as an isocyanate toward a Sn–O bond,² and a great affinity toward a sulfur³ or a halogen atom.⁴

We have reported the preparation of five- and six-membered heterocyclic compounds from the adduct of tributyltin ω -haloalkoxides ($n\text{-Bu}_3\text{SnO}(\text{CH}_2)_n\text{X}$) with a heterocumulene⁵ (Scheme 1), in which a Lewis base plays an important role in the cyclization.

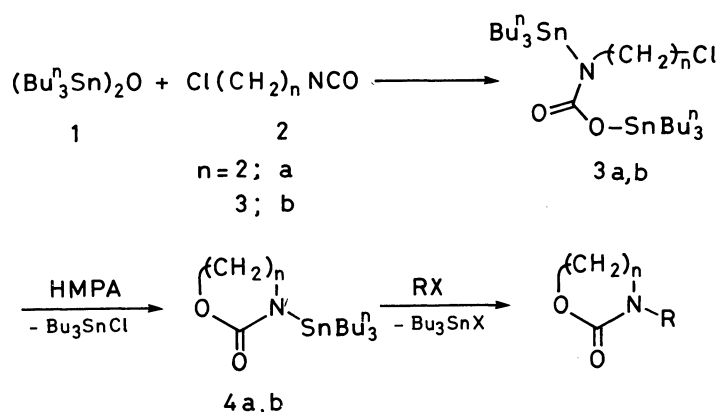
The coordination of a base toward the Sn atom increases the basicity of the adjacent heteroatom, which induces facile cyclization.

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

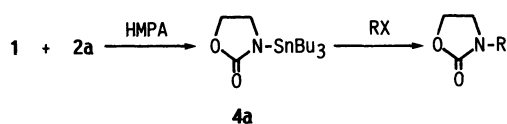


Scheme 1.



Scheme 2.

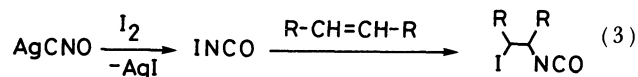
Table 2. Synthesis of 2-Oxazolidinones



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>i</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 ₂ O	rt, 10 min	13	100
8	$n = 0$	rt, 10 min	14	78 ^{c)}
9	4	rt, 10 min	15	84 ^{c)}
10	PhSO ₂ Cl	rt, 10 min	16	80
11	(PhO) ₂ PCl	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	Ph-Br	80°C, 15 h	23	60
18	Ph-CH ₂ -O-CH ₂ -Cl	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 isocyanates¹¹⁾ (Eq. 3).



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

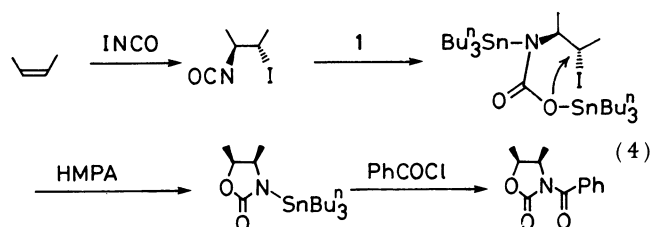
Table 3. Synthesis of Tetrahydro-2-oxazinones

$1 + 2b \xrightarrow{\text{HMPA}} \text{4b} \xrightarrow{\text{RX}} \text{Product}$

Entry	RX	Condition ^{a)}	Product	Yield/% ^{b)}
1		rt, 10 min		100
2		80 °C, 15 h		72
3		80 °C, 15 h		100
4		80 °C, 15 h		87
5		80 °C, 15 h		80

a) At the coupling reaction. b) 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).



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.

Table 4. Synthesis of 2-Oxazolidinones from Olefins

Entry	Olefin	Product	Yield/% ^{a)}
1			88
2			98
3			66
4			50
5			52

a) Isolated yield.

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 pellets or KRS-5 cells. ¹H NMR and ¹³C 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. Elution 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; ¹H NMR (CDCl₃) δ=3.50–4.00 (m, 4H, CH₂), 6.35–6.85 (br, 1H, NH), 7.20–7.90 (m, 5H, phenyl). Calcd for C₉H₁₀NOCl: C, 58.86; H, 5.45; N, 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 (CDCl₃) δ=3.80–4.35 (m, 2H, CH₂O), 4.35–4.90 (m, 2H, CH₂N), 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 (CDCl₃) δ=2.55 (s, 3H, CH₃), 4.05 (t, *J*=8 Hz, 2H, CH₂N), 4.45 (t, *J*=8 Hz, 2H, CH₂O).

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 (CDCl₃) δ=1.20 (d, *J*=7 Hz, 6H, CH₃), 3.60–3.90 (m, 1H, Me₂CH), 4.05 (dd, *J*=7 and 9 Hz, 2H, CH₂N), 4.45 (dd, *J*=7 and 9 Hz, 2H, CH₂O); Calcd for C₇H₁₁NO₃: 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 (CDCl₃) δ=3.95 (t, *J*=8 Hz, 2H, CH₂N), 4.10–4.60 (m, 4H, CH₂O and PhCH₂), 6.90–7.60 (m, 5H, phenyl); Calcd for C₁₁H₁₁NO₃: 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 (CDCl₃) δ=4.05 (t, *J*=8 Hz, 2H, CH₂N), 4.50 (t, *J*=8 Hz, 2H, CH₂O), 5.25 (s, 2H, PhOCH₂), 6.80–7.50 (m, 5H, phenyl); Calcd for C₁₁H₁₁O₄N: 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 (CDCl₃) δ=4.00–4.30 (m, 2H, CH₂N), 4.30–4.60 (m, 2H, CH₂O), 7.20–8.00 (m, 7H, phenyl and CH₂=CH–Ph); Calcd for C₁₂H₁₁NO₃: C, 66.36; H, 5.07; N, 6.45%. Found: C, 66.24; H, 4.95; N, 6.55%.

3-Benzoyloxycarbonyl-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 (CDCl₃) δ=3.80–4.20 (m, 2H, CH₂N), 4.30–4.60 (m, 2H, CH₂O), 5.30 (s, 2H, PhCH₂), 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 (CDCl₃) δ=4.00–4.50 (m, 4H, CH₂N), 4.50–4.90 (m, 4H, CH₂O).

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 (CDCl₃) δ=1.70–2.00 (m, 4H, COCH₂CH₂), 2.96 (t, *J*=7 Hz, 4H, COCH₂), 4.01 (t, *J*=7 Hz, 4H, CH₂N), 4.32 (t, *J*=7 Hz, 4H, CH₂O).

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 (CDCl₃) δ=3.90–4.30 (m, 2H, CH₂N), 4.30–4.60 (m, 2H, CH₂O), 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 (CDCl₃) δ=3.84 (t, *J*=8 Hz, 2H, CH₂N), 4.33 (t, *J*=8 Hz, 2H, CH₂O), 7.20–7.40 (m, 10H, phenyl); Calcd for C₁₅H₁₄NO₅P: 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

phosphorodichloride: mp 158 °C; IR (KBr) 1770 cm⁻¹; MS *m/z* 312 (M⁺); ¹H NMR (CDCl₃) δ=4.00–4.30 (m, 4H, CH₂N), 4.40–4.70 (m, 4H, CH₂O), 7.20–7.50 (m, 5H, phenyl); Calcd for C₁₂H₁₃N₂O₆P: 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 (CDCl₃) δ=3.73 (dd, *J*=7 and 9 Hz, 2H, CH₂N), 4.45 (dd, *J*=7 and 9 Hz, 2H, CH₂O), 4.70 (s, 2H, PhCOCH₂), 7.20–8.30 (m, 5H, phenyl); Calcd for C₁₁H₁₁NO₃: 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 (CDCl₃) δ=1.29 (t, *J*=7 Hz, 3H, CH₃), 3.70 (dd, *J*=7 and 9 Hz, 2H, CH₂N), 4.02 (s, 2H, CH₂COOEt), 4.10–4.50 (m, 4H, CH₂Me and CH₂O); Calcd for C₇H₁₁NO₄: 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 (CDCl₃) δ=3.51 (dd, *J*=7 and 9 Hz, 2H, CH₂N), 3.90 (d, *J*=6 Hz, 2H, NCH₂CH=CH₂), 4.34 (dd, *J*=7 and 9 Hz, 2H, CH₂O), 5.10–6.10 (m, 3H, CH=CH₂).

3-Cinnamyl-2-oxazolidinone (22): Mp 69 °C; IR (KBr) 1740 cm⁻¹; MS *m/z* 203 (M⁺); ¹H NMR (CDCl₃) δ=3.62 (dd, *J*=7 and 9 Hz, 2H, CH₂N), 4.08 (d, *J*=7 Hz, 2H, CH₂CH=CHPh), 4.38 (dd, *J*=7 and 9 Hz, 2H, CH₂O), 6.00–6.70 (m, 2H, CH=CHPh), 7.20–7.60 (m, 5H, phenyl); Calcd for C₁₂H₁₃NO₂: 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 (CDCl₃) δ=3.40 (dd, *J*=7 and 9 Hz, 2H, CH₂N), 4.28 (dd, *J*=7 and 9 Hz, 2H, CH₂O), 4.41 (s, 2H, PhCH₂), 7.40–7.60 (m, 5H, phenyl).

3-Benzoyloxymethyl-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 (CDCl₃) δ=3.62 (dd, *J*=7 and 9 Hz, 2H, CH₂N), 4.25 (dd, *J*=7 and 9 Hz, CH₂O), 4.56 (s, 2H, CH₂Ph), 4.83 (s, 2H, NCH₂O), 7.30–7.50 (m, 5H, phenyl); Calcd for C₁₁H₁₃NO₃: 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 (CDCl₃) δ=0.80–1.90 (m, 11H, NCH₂C₅H₁₁), 3.28 (t, *J*=7 Hz, 2H, CH₂C₅H₁₁), 3.58 (dd, *J*=7 and 9 Hz, 2H, CH₂N), 4.33 (dd, *J*=7 and 9 Hz, 2H, CH₂O).

3-Benzoyltetrahydro-2H-1,3-oxazin-2-one (26) (General Procedure for the Preparation of Tetrahydro-2H-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-2H-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^+); ^1H NMR (CDCl_3) δ =2.00–2.40 (m, 2H, CH_2), 3.91 (t, J =6 Hz, 2H, CH_2N), 4.43 (t, J =5 Hz, 2H, CH_2O), 7.20–8.20 (m, 5H, phenyl); Calcd for $\text{C}_{11}\text{H}_{11}\text{NO}_3$: C, 64.39; H, 5.37; N, 6.83%. Found: C, 64.11; H, 5.43; N, 6.84%.

3-Phenacyltetrahydro-2H-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^+); ^1H NMR (CDCl_3) δ =2.16 (m, 2H, CH_2), 3.43 (t, J =6 Hz, 2H, CH_2N), 4.41 (t, J =5 Hz, CH_2O), 4.82 (s, 2H, PhCOCH_2), 7.20–8.00 (m, 5H, phenyl); Calcd for $\text{C}_{12}\text{H}_{13}\text{NO}_3$: C, 65.75; H, 5.94; N, 6.39%. Found: C, 65.55; H, 5.91; N, 6.45%.

3-Cinnamyltetrahydro-2H-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^+); ^1H NMR (CDCl_3) δ =1.90–2.00 (m, 2H, CH_2), 3.32 (t, J =6 Hz, 2H, CH_2N), 4.11 (d, J =6 Hz, 2H, $\text{CH}_2\text{CH}=\text{CHPh}$), 4.26 (t, J =5 Hz, 2H, CH_2O), 6.00–6.70 (m, 2H, $\text{CH}=\text{CHPh}$), 7.10–7.60 (m, 5H, phenyl); Calcd for $\text{C}_{13}\text{H}_{15}\text{NO}_2$: C, 71.89; H, 6.91; N, 6.45%. Found: C, 71.65; H, 7.08; N, 6.34%.

3-Benzyltetrahydro-2H-1,3-oxazin-2-one (29): Mp 35 °C; IR (KBr) 1690 cm^{-1} ; MS m/z 191 (M^+); ^1H NMR (CDCl_3) δ =2.03 (m, 2H, CH_2), 3.21 (t, J =6 Hz, 2H, CH_2N), 4.25 (t, J =5 Hz, 2H, CH_2O), 4.55 (s, 2H, PhCH_2), 7.20–7.30 (m, 5H, phenyl); Calcd for $\text{C}_{11}\text{H}_{13}\text{NO}_2$: C, 69.11; H, 6.81; N, 7.33%. Found: C, 68.93; H, 6.83; N, 7.34%.

3-Hexyltetrahydro-2H-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^+); ^1H NMR (CDCl_3) δ =0.80–1.90 (m, 11H, $\text{NCH}_2\text{C}_5\text{H}_{11}$), 1.90–2.20 (m, 2H, CH_2), 3.30 (m, 4H, CH_2N and $\text{NCH}_2\text{C}_5\text{H}_{11}$), 4.23 (t, J =5 Hz, 2H, CH_2O); Calcd for $\text{C}_{10}\text{H}_{19}\text{NO}_2$: 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^+); ^1H NMR (CDCl_3) δ =1.39 (d, J =6.5 Hz, 3H, NCHCH_3), 1.46 (d, J =6.5 Hz, 3H, OCHCH_3), 4.50–5.00 (m, homodecoupling J =8 Hz, 2H, CH), 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 $\text{C}_{12}\text{H}_{13}\text{NO}_3$: 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^+); ^1H NMR (CDCl_3) δ =1.46 (d, J =6 Hz, 3H, NCHCH_3), 1.53 (d, J =6 Hz, 3H, OCHCH_3), 4.00–4.50 (m, homodecoupling J =6 Hz, 2H, CH), 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 $\text{C}_{12}\text{H}_{13}\text{NO}_3$: C, 65.75; H, 5.94; N, 6.39%. Found: C, 65.91; H, 6.03; N, 6.23%.

3-Benzoylhexahydro-2H-cyclopentoxazol-2-one (33): Mp 127 °C; IR (KBr) 1670, 1760 cm^{-1} ; MS m/z 231 (M^+); ^1H NMR (CDCl_3) δ =1.80–2.30 (m, 6H, $(\text{CH}_2)_3$), 4.80–5.20

(m, 2H, CH), 7.20–7.80 (m, 5H, phenyl); Calcd for $\text{C}_{13}\text{H}_{13}\text{NO}_3$: C, 67.53; H, 5.63; N, 6.06%. Found: C, 67.20; H, 5.55; N, 6.08%.

3-Benzoylhexahydrobenzoxazol-2(3H)-one (34): Mp 112 °C (lit.¹⁷ mp 114–115 °C); IR (KBr) 1670, 1690 cm^{-1} ; MS m/z 245 (M^+); ^1H NMR (CDCl_3) δ =1.20–2.50 (m, 8H, $(\text{CH}_2)_4$), 4.20–4.50 (m, 1H, CHN), 4.50–4.80 (m, 1H, CHO), 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^+); ^1H NMR (CDCl_3) δ =4.32 (dd, J =7 and 9 Hz, 1H, CH_2O), 4.78 (t, 1H, J =9 Hz, CH_2O), 5.64 (dd, J =7 and 9 Hz, 1H, CHN), 7.20–7.80 (m, 10H, phenyl); Calcd for $\text{C}_{16}\text{H}_{13}\text{NO}_3$: C, 71.91; H, 4.87; N, 5.24%. Found: C, 71.80; H, 4.92; N, 5.19%.

This work was supported by the Grant-in-Aid for Scientific Research No. 62550613 from the Ministry of Education, Science and Culture.

References

- 1) For reviews see: A. K. Sawyer, "Organotin Compounds," Marcel Dekker New York (1971); E. Negishi "Organometallics in Organic Synthesis," Wiley, New York (1980), Vol. 1, p. 394; A. G. Davies and P. J. Smith, "Comprehensive Organometallic Chemistry," Pergamon, Oxford (1982), Vol. 2, p. 519; M. Pereyre, P. J. Quintard, and A. Rahm, "Tin in Organic Synthesis," Butterworth, London (1987).
- 2) A. J. Bloodworth and A. G. Davies, *J. Chem. Soc.*, **1965**, 5238; A. J. Bloodworth, A. G. Davies, and S. C. Vasishtha, *J. Chem. Soc. C*, **1967**, 1309.
- 3) S. Sakai, Y. Asai, Y. Kiyohara, K. Itoh, and Y. Ishii, *Organomet. Chem. Synth.*, **1**, 45 (1970); S. Sakai, Y. Fujimura, and Y. Ishii, *J. Organomet. Chem.*, **50**, 113 (1973); S. Sakai, H. Niimi, Y. Kobayashi, and Y. Ishii, *Bull. Chem. Soc. Jpn.*, **50**, 3271 (1977).
- 4) B. Delmond, J. C. Pommier, and J. Valade, *J. Organomet. Chem.*, **35**, 91 (1972); B. Delmond, J. C. Pommier, and J. Valade, *J. Organomet. Chem.*, **47**, 337 (1973).
- 5) A. Baba, H. Kishiki, I. Shibata, and H. Matsuda, *Organometallics*, **4**, 1329 (1985); A. Baba, I. Shibata, H. Kashiwagi, and H. Matsuda, *Bull. Chem. Soc. Jpn.*, **59**, 341 (1986); I. Shibata, A. Baba, and H. Matsuda, *Bull. Chem. Soc. Jpn.*, **59**, 4000 (1986).
- 6) A part of study on this cyclization-coupling reaction has been published as a communication: I. Shibata, A. Baba, and H. Matsuda, *J. Chem. Soc., Chem. Commun.*, **1986**, 1703.
- 7) For reviews see: a) M. E. Dyen, and D. Swern, *Chem. Rev.*, **67**, 197 (1967); b) V. A. Pankrotov, T. M. Frenkel, and A. M. Fainleib, *Usp. Khim. Zh. (Russ. Ed)*, **52**, 1018 (1983).
- 8) For example: C. Palomo, *Synthesis*, **1981**, 809; A. Arrieta and C. Palomo, *ibid.*, **1982**, 1050; J. M. Aizpurua, C. Palomo, and A. L. Palomo, *Can. J. Chem.*, **62**, 336 (1984).
- 9) HMPA acts as an efficient ligand to organotin compounds bearing an electron withdrawing group. T. F. Bolles and R. S. Drago, *J. Am. Chem. Soc.*, **88**, 5730 (1966).
- 10) *N*-Acyl-2-oxazolidinones are known versatile key reagents in organic synthesis. For example; a) D. A. Evans, *Aldrichimica Acta*, **15**, 23 (1982). b) K. Narasaka, M. Inoue, and N. Okada, *Chem. Lett.*, **1986**, 1109.
- 11) A. Hassner, R. P. Hoblitt, C. Heathcock, J. E. Kropp,

and M. Lorber, *J. Am. Chem. Soc.*, **92**, 1326 (1970).

12) Sn-O bond has been reported to cause the backside attack toward the alkyl halides.⁴⁾

13) The diastereoisomers, **31** and **32**, were confirmed by the coupling constant between the ring protons obtained by decoupling of the methyl protons. It has been reported that the value of cis isomer is larger than that of trans isomer: B. D. Harris, K. L. Bhat, and M. Joullie, *Tetrahedron Lett.*, **28**,

2837 (1987); D. J. Kempf, *J. Org. Chem.*, **51**, 3921, (1986).

14) O. Tsuge, T. Itoh, and K. Sakai, *Nippon Kagaku Zasshi*, **90**, 1031 (1969).

15) J. W. McFarland and R. W. Houser, *J. Org. Chem.*, **33**, 340 (1968).

16) J. S. Pierce, *J. Am. Chem. Soc.*, **50**, 241 (1928).

17) D. Ben-Ishai, *J. Am. Chem. Soc.*, **78**, 4962 (1956).
