HETEROCYCLES, Vol. 57, No. 2, 2002, pp. 245-257, Received, 31st October, 2001

REACTIONS OF 5,5-DIMETHYL-4-METHYLENE-1,3-DIOXOLAN-2-ONE WITH AMINES IN THE PRESENCE OF PALLADIUM CATALYST

Min Shi,* Yu-Mei Shen, and Ya-Jun Chen

State Key Laboratory of Organometallic Chemistry,
Shanghai Institute of Organic Chemistry,
Chinese Academy of Sciences, 354 Fenglin Lu, Shanghai 200032 China
mshi@pub.sioc.ac.cn, Fax: 86-21-64166128

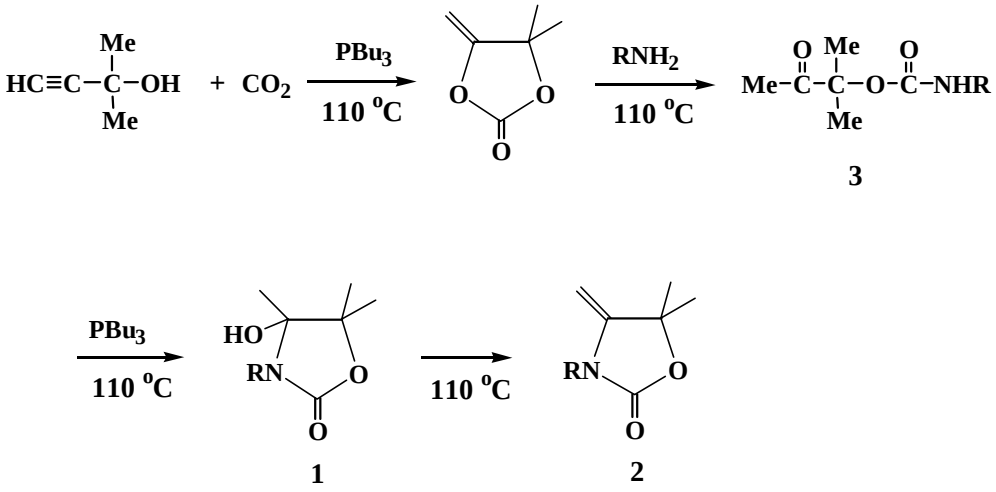
Abstract-In the reaction of 5,5-dimethyl-4-methylene-1,3-dioxolan-2-one with primary amines in the presence of Pd(0) catalyst, the 3-alkyl-4-hydroxy-4,5,5-trimethyloxazolidin-2-ones (**1**) are obtained as the major products, along with the formation of ring opened products at room temperature. On the other hand, 3-alkyl-5,5-dimethyl-4-methyloxazolidin-2-ones (**2**) are obtained as reaction products in high yields at high temperature. But in the absence of Pd(0) catalyst, the ring opened compounds alkylcarbamic acid 1,1-dimethyl-2-oxopropyl esters (**3**) are formed exclusively. In addition, in the reaction of 5,5-dimethyl-4-methylene-1,3-dioxolan-2-one with secondary amines, the ring opened compounds were obtained as the sole products. A plausible mechanism for the formation of **1** and **2** is proposed.

Introduction

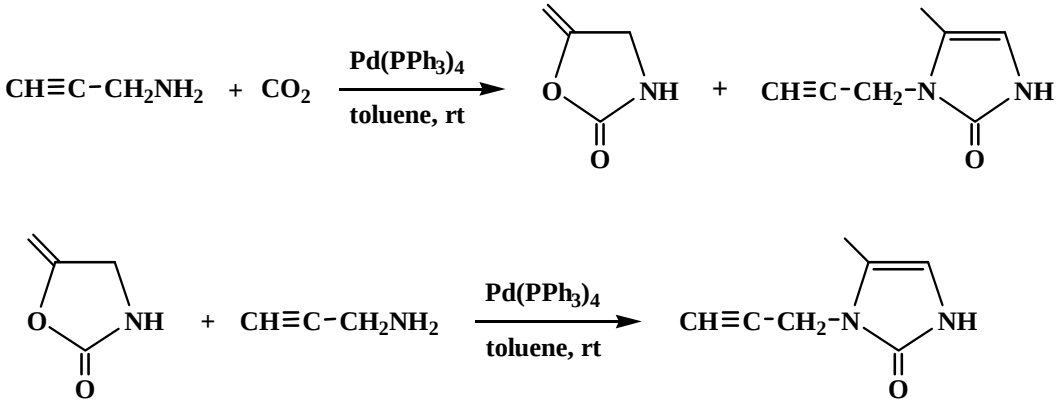
Oxazolidinones exhibit unique physical and chemical properties, accommodating a variety of applications in pharmacology (medical drugs), agriculture (pesticides, fungicides, herbicides), and chemical industry (intermediates of synthesis).[1] Oxazolidinones can be obtained from α,β-difunctional substrates such as β-amino alcohols, oxiranes and aziridines, in the presence of phosgene,[1] carbonate,[1] isocyanate[2] or carbon dioxide.[3] Recently, Dixneuf and coworkers reported that 3-alkyl-4-hydroxy-4,5,5-

trimethyloxazolidin-2-ones (**1**), 3-alkyl-5,5-dimethyl-4-methyloxazolidin-2-ones (**2**) or carbamic acid 1,1-dimethyl-2-oxo-propyl esters (**3**) can be prepared directly from propargyl alcohol, CO_2 and primary amines in the presence of phosphines at high temperature (110 ^{o}C) in moderate yields.[4] The reaction process was shown in Scheme 1. During our own investigations on the palladium catalyzed chemical reactions for the fixation of CO_2, we found that propargylamine could react with carbon dioxide to afford 5-methylene-2-oxazolidinone and 5-methyl-1-prop-2-ynyl-1,3-dihydroimidazol-2-one which was derived from the further reaction of 5-methylene-2-oxazolidinone with propargylamine in the presence of palladium(0) catalysts *via* a novel palladium catalyzed amination of olefin under mild reaction conditions at the same time (Scheme 2).[5] This interesting finding guided us to investigate the reaction of α-

Scheme 1



Scheme 2

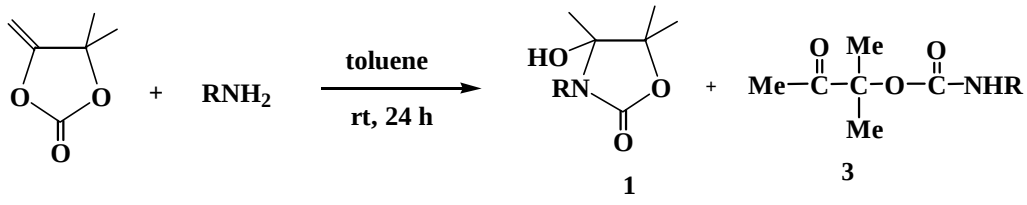


methylene cyclic carbonate, prepared from the reaction of 2-methyl-3-butyn-2-ol with CO_2 in the presence of PBu_3,[4a] with primary or secondary amines in the presence or absence of palladium catalyst. Herein, we wish to report the full detail of those investigations along with a plausible reaction mechanism for the formation of **1** and **2**.

Results and Discussion

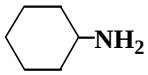
As a result, we first confirmed that, in the absence of Pd(0) catalyst, for the reaction of butylamine, cyclohexylamine or benzylamine, the ring opened addition products (**3**) became the sole products without formation of oxazolidinones (**1**) and (**2**) at room temperature (Scheme 3, Table 1). On the other hand,

Scheme 3



R= butyl, R= cyclohexyl, R= benzyl

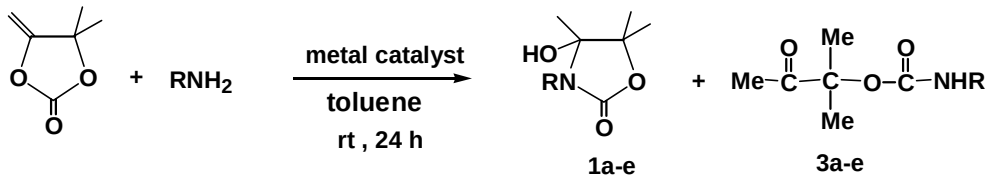
Table 1. The reaction of 4,4-dimethyl-5-methylene-2-oxo-1,3-dioxolane with primary amines in the absence of Pd(0) complex at room temperature.

entry	RNH_2	Yield (%)	
		1	**3**
1	$CH_3(CH_2)_3NH_2$	**0**	**87**
2		**0**	**70**
3	$PhCH_2NH_2$	**0**	**65**

using palladium(0) complex [$Pd(PPh_3)_4$ or $Pd_2(dba)_3$] as a catalyst, α-methylene cyclic carbonate can directly react with primary amines to give the oxazolidinones (**1**) in moderate yields at room temperature in toluene, along with the formation of the small amount of ring opened addition products (**3**) (Scheme 4). In addition, in the presence of other transition metals such as Ru, Ni, Ir or Pd(II) catalyst, the ring opened

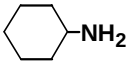
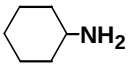
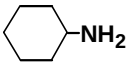
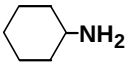
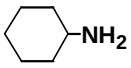
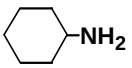
addition products (**3**) was obtained as the major product. Their yields were summarized in Table 2. This results suggested that the transition metals such as Ru, Ni, Ir or Pd(II) complex did not act as a catalyst for this reaction.

Scheme 4



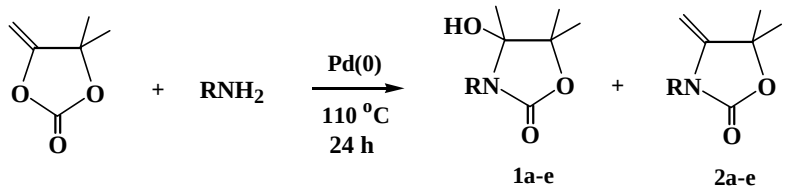
a: R= propargyl, b: R= allyl, c: R= butyl, d: R= cyclohexyl, e: R= benzyl

Table 2. The reaction of 4,4-dimethyl-5-methylene-2-oxo-1,3-dioxolane with primary amines in the presence of Pd(0) complex at room temperature.

entry	RNH_2	catalyst	Yield (%)	
			1	3
1	$CH{\equiv}CCH_2NH_2$	$Pd(PPh_3)_4$	90	trace
2	$CH_2{=}CHCH_2NH_2$	$Pd(PPh_3)_4$	85	trace
3	$CH_3(CH_2)_3NH_2$	$Pd(PPh_3)_4$	91	2
4		$Pd(PPh_3)_4$	65	20
5		$Pd_2(dba)_3$	70	17
6	$PhCH_2NH_2$	$Pd(PPh_3)_4$	83	6
7		$RhH_4(PPh_3)_3$	0	50
8		$IrCl(CO)(PPh_3)_2$	0	45
9		$NiBr_2(PPh_3)_2$	0	60
10		$Pd(OAc)_2$	0	30

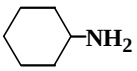
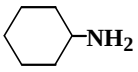
If the reaction was carried out at high temperature, the oxazolidinones (**2**) were exclusively obtained in high yields except propargylamine (Scheme5, Table 3). Obviously, **2** was derived from **1** *via* a dehydration process at higher temperature. At present, we do not understand why **1a** cannot undergo a dehydration process.

Scheme 5



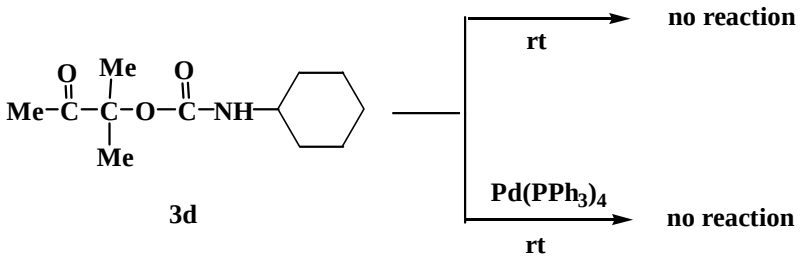
a: R= propargyl, b: R= allyl, c: R= butyl,
d: R= cyclohexyl, e: R= benzyl

Table 3. The reaction of 4,4-dimethyl-5-methylene-2-oxo-1,3-dioxolane with primary amines in the presence of Pd(0) complex at high temperature.

entry	RNH_2	catalyst	Yield (%)	
			1	2
1	$CH{\equiv}CCH_2NH_2$	$Pd(PPh_3)_4$	62	0
2	$CH_2{=}CHCH_2NH_2$	$Pd(PPh_3)_4$	0	61
3	$CH_3(CH_2)_3NH_2$	$Pd(PPh_3)_4$	0	70
4		$Pd(PPh_3)_4$	0	60
5		$Pd_2(dba)_3$	0	65
6	$PhCH_2NH_2$	$Pd(PPh_3)_4$	0	80

In order to clarify the reaction mechanism of the formation of **1** or **2** in the presence of Pd(0) complex, we carried out the reaction of cyclohexylcarbamic acid 1,1-dimethyl-2-oxo-propyl ester (**3d**) in the presence or absence of Pd(0) catalyst. In these control experiments, we confirmed that no reactions occurred at room temperature (Scheme 6). Only at higher temperature (110 ^{o}C), we found that the oxazolidinone (**2d**) was formed in 20% yield even without any catalyst and PBu_3 can raise the yield of **2d** to 76% (Scheme 7, Table 4, entry 4), but PPh_3 and $Pd(PPh_3)_4$ showed no improvement for this reaction at 110 ^{o}C (Table 4,

Scheme 6



Scheme 7

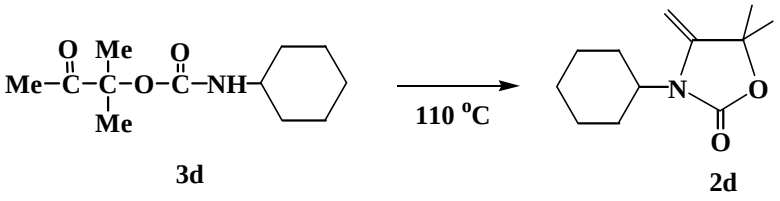


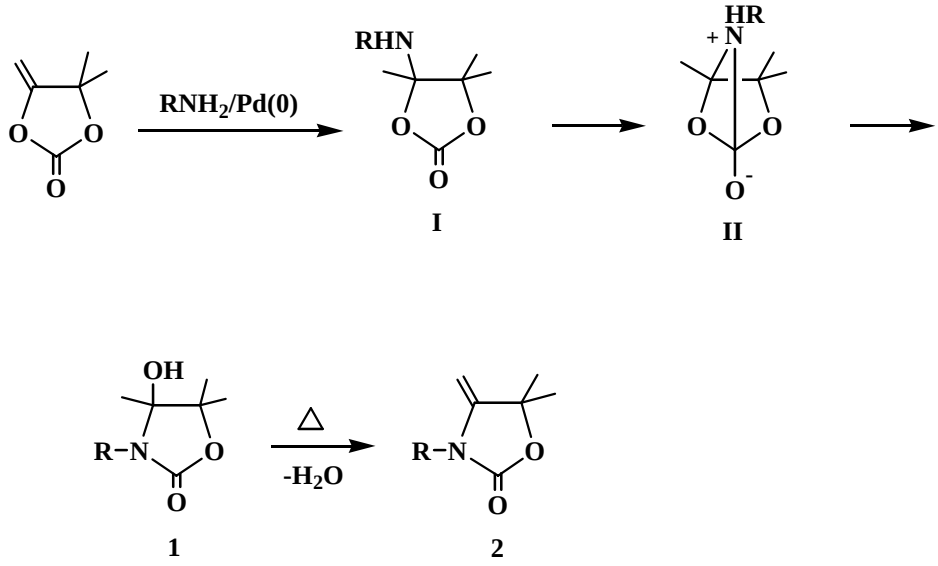
Table 4. The reaction of 3d at 110 °C.

entry	catalyst	Yield (%)
		3d
1	none	26
2	PPh_3	27
3	$Pd(PPh_3)_4$	28
4	PBu_3	76

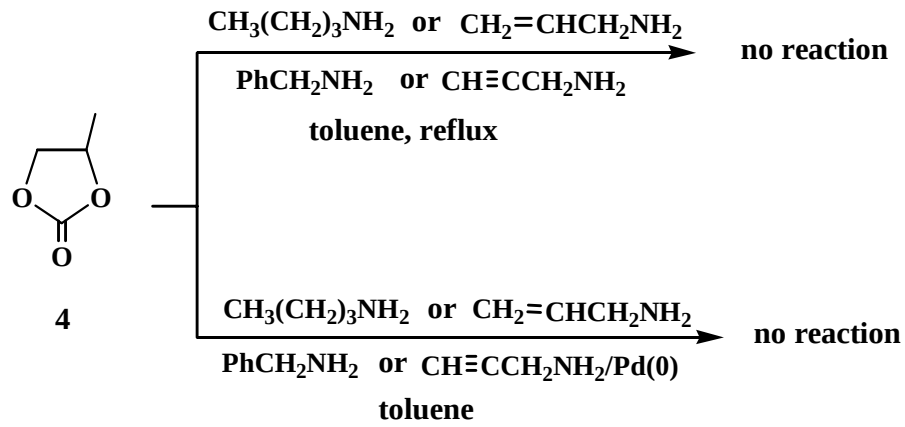
entry 2 and 3). This result suggests that PPh_3 or $Pd(PPh_3)_4$ can not promote the cyclization of **3**. The stability of **3** has been disclosed by Francis in 1976.[6] Thus, based on these results, we believe that the formation of **1** in the presence of Pd(0) catalyst under mild reaction conditions underwent different reaction route from that elucidated in Scheme 1. We proposed a new mechanism in Scheme 8 to explain the formation of **1** catalyzed by Pd(0) catalyst (Scheme 8). The first step is the intermolecular amination of olefinic moiety in α-methylene cyclic carbonate to give the intermediate (I)[5,7] which further undergo the intramolecular attacking of amino group to the carbonyl group affording the intermediate (II) and the subsequent breaking of C-O bond gave **1**. At high temperature, both dehydration of **1** and cyclization of **3** took place to afford **2**. In order to verify the mechanism shown in Scheme 8, we carried out the reaction

of 4-methyl-[1,3]dioxolan-2-one (**4**), which do not have the olefinic moiety, with butylamine, propenylamine or propargylamine under the same conditions (in the absence of catalyst or in the presence of catalyst) and found that no reaction occurred at all (Scheme 9). To the best of our knowledge, this mechanism has been never disclosed before. Recently, Buchwald and Hartwig have used very exotic ligands to effect palladium-catalyzed C-N bond formation,[8] but we have achieved this using very simple

Scheme 8



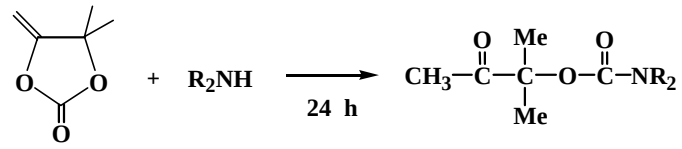
Scheme 9



[$Pd(PPh_3)_4$ or $Pd_2(dba)_3$].[5] By this new reaction mechanism we can explain the reaction shown in Scheme 4 in the presence of Pd(0) catalyst. At room temperature in the presence of Pd(0) catalyst, both reaction process elucidated in Scheme 3 and Scheme 8 take place to give the **1** and **3**, respectively. But the major reaction process is the palladium catalyzed intramolecular cyclization (Scheme 8). At high temperature,

the dehydration of **1** and cyclization of **3** occurred at the same time to exclusively afford **2**. Herein, we found a novel palladium(0) catalyzed transformation of cyclic carbonate to oxazolidinone (**1**) or (**2**) and disclose a new reaction mechanism in the presence of Pd(0) catalyst.

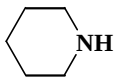
It should be emphasized here for secondary amines, only the ring opened products dialkylcarbamic acid 1,1-dimethyl-2-oxopropyl esters (**5**) were obtained under the same reaction conditions either in the presence or absence of palladium(0) catalyst (Scheme 10). Their yields were summarized in Table 5. This result suggests that, for secondary amines, owing to their high nucleophilicities, the direct attacking to the carbonyl group of α-methylene cyclic carbonat can take place to give the corresponding ring-opened products (**5**).



5a: R= C_2H_5
5b: R= C_4H_9
5c: R_2= $(CH_2)_5$

Scheme 10

Table 5. The reaction of 4,4-dimethyl-5-methylene-2-oxo-1,3-dioxolane with secondary amines.

entry	R_2NH	Temp. [^{0}C]	Yield (%) 5
1	$(C_2H_5)_2NH$	20	85
2	$(C_4H_9)_2NH$	110	82
3		110	82

Efforts are underway to elucidate the mechanistic details of this reaction and to disclose its scope and limitations of this reaction and subsequent transformation thereof. Work in this direction is currently in progress.

EXPERIMENTAL

General. MPs were obtained with a Yanagimoto micro melting point apparatus and are uncorrected. ^{1}H NMR spectra were recorded on a Bruker AM-300 spectrometer for solution in $CDCl_3$ with tetramethylsilane (TMS) as internal standard; J-values are in Hz. MS spectra were recorded with a HP-

5989 instrument and HRMS was measured by a Finnigan MA+ mass spectrometer. Organic solvents were dried by standard methods when necessary. All of the compounds reported in this paper gave satisfactory CHN microanalyses with a Carlo-Erba 1106 analyzer. Commercially obtained reagents were used without further purification. All reactions were monitored by TLC with Huanghai GF_{254} silica gel coated plates. Flash Column Chromatography was carried out using 200-300 mesh silica gel.

General procedure for the palladium-catalyzed reactions of cyclic carbonate with primary amines. 5,5-Dimethyl-4-methylene-1,3-dioxolan-2-one (256 mg, 2.0 mmol) in toluene (10 mL), cyclohexylamine (238 mg, 2.4 mmol), and $Pd(PPh_3)_4$ (29 mg, 0.025 mmol) was added into a 50 mL round bottom flask with a magnetic stir bar. The reaction mixture was stirred at rt for 24 h. The solvent was removed under reduced pressure and the residue was purified by a silica gel column chromatograph (eluent: petroleum ether/EtOAc= 1/5) to give 4-hydroxy-4,5,5-trimethyl-3-prop-2-ynyloxazolidin-2-one (**1a**) as a white solid. **4-hydroxy-4,5,5-trimethyl-3-prop-2-ynyloxazolidin-2-one (1a)**: 329 mg, 90%; mp 100-102 ^oC (Dichloromethane/Hexane); IR ($CHCl_3$) ν_{max} 1740 cm^{-1} (C=O); ^1H NMR ($CDCl_3$, TMS, 300 MHz) δ 1.36 (s, 3H, CH_3), 1.43 (s, 3H, CH_3), 1.45 (s, 3H, CH_3), 2.25 (t, 1H, J = 2.3 Hz, CH), 3.53 (s, 1H, OH), 4.02 (dd, 1H, J = 18.3, 2.4 Hz, CH), 4.17 (dd, 1H, J = 18.3, 2.4 Hz, CH); MS (EI) m/z 184 $(MH)^+$; HRMS Calcd for $C_9H_{13}NO_3$: requires M, 183.0895. Found: 183.0902 (M^+); *Anal.* Calcd for $C_9H_{13}NO_3$: C, 59.00; H, 7.15; N, 7.65. Found: C, 58.92; H, 7.11; N, 7.64.

The Formation of 3-allyl-4-hydroxy-4,5,5-trimethyloxazolidin-2-one (1b): A colorless liquid. 316 mg, 85%; IR ($CHCl_3$) ν_{max} 1731 cm^{-1} (C=O); ^1H NMR ($CDCl_3$, TMS, 300 MHz) δ 1.32 (s, 3H, CH_3), 1.33 (s, 3H, CH_3), 1.39 (s, 3H, CH_3), 3.70 (ddd, 1H, J = 16.5, 6.1, 1.2 Hz, CH_2), 3.95 (ddd, 1H, J = 16.5, 6.1, 1.2 Hz, CH_2), 4.71 (s, 1H, OH), 5.12 (dd, 1H, J = 10.2, 1.2 Hz, CH), 5.22 (dd, 1H, J = 16.5, 1.2 Hz, CH), 5.79-5.92 (m, 1H, CH); MS (EI) m/z 186 $(MH)^+$; HRMS Calcd for $C_9H_{15}NO_3$: requires M, 185.1052. Found: 185.1021 (M^+); *Anal.* Calcd for $C_9H_{15}NO_3$: C, 58.36; H, 8.16; N, 7.56. Found: C, 58.22; H, 8.13; N, 7.51.

The Formation of 3-butyl-4-hydroxy-4,5,5-trimethyloxazolidin-2-one (1c): A colorless liquid. 366 mg, 91%; IR ($CHCl_3$) ν_{max} 1729 cm^{-1} (C=O); ^1H NMR ($CDCl_3$, TMS, 300 MHz) δ 0.85 (t, 3H, J = 7.3 Hz, CH_3), 1.17-1.27 (m, 2H, CH_2), 1.29 (s, 3H, CH_3), 1.35 (s, 3H, CH_3), 1.40 (s, 3H, CH_3), 1.43-1.56 (m, 2H, CH_2), 3.01-3.20 (m, 2H, CH_2), 4.82 (s, 1H, OH); MS (EI) m/z 202 $(MH)^+$; HRMS Calcd for $C_{10}H_{19}NO_3$: requires M, 201.1365. Found: 201.1387 (M^+); *Anal.* Calcd for $C_{10}H_{19}NO_3$: C, 59.68; H, 9.52; N, 6.96. Found: C, 59.52; H, 9.47; N, 6.88.

The Formation of 3-cyclohexyl-4-hydroxy-4,5,5-trimethyloxazolidin-2-one (1d): A white solid. 295 mg, 95%; mp 121-123 ^{o}C (Dichloromethane/Hexane); IR ($CHCl_3$) ν_{max} 1724 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$, TMS, 300 MHz) δ 1.20-1.50 (m, 4H, CH_2), 1.32 (s, 3H, CH_3), 1.39 (s, 3H, CH_3), 1.42 (s, 3H, CH_3), 1.56-1.80 (m, 2H, CH_2), 1.80-2.0 (m, 2H, CH_2), 2.0-2.30 (m, 2H, CH_2), 2.40 (s, 1H, OH), 3.15-3.24 (m, 1H, CH); MS (EI) m/z 227 (M^+); HRMS Calcd for $C_{12}H_{21}NO_3$: requires M, 227.1521. Found: 227.1515 (M^+); *Anal.* Calcd for $C_{12}H_{21}NO_3$: C, 63.41; H, 9.31; N, 6.16. Found: C, 63.22; H, 9.28; N, 6.14.

The Formation of 3-benzyl-4-hydroxy-4,5,5-trimethyloxazolidin-2-one (1e): A white solid. 390 mg, 83%; mp 132-134 ^{o}C (Dichloromethane/Hexane); IR ($CHCl_3$) ν_{max} 1731 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$, TMS, 300 MHz) δ 1.20 (s, 3H, CH_3), 1.34 (s, 3H, CH_3), 1.44 (s, 3H, CH_3), 4.30 (d, 1H, J = 16.1 Hz, CH_2), 4.48 (d, 1H, J = 0.6 Hz, OH), 4.69 (d, 1H, J = 16.1 Hz, CH_2), 7.25-7.31 (m, 5H, Ar); MS (EI) m/z 235 (M^+); HRMS Calcd for $C_{13}H_{17}NO_3$: requires M, 235.1208. Found: 235.1219 (M^+); *Anal.* Calcd for $C_{13}H_{17}NO_3$: C, 66.36; H, 7.28; N, 5.95. Found: C, 66.22; H, 7.23; N, 5.91.

The Formation of 3-allyl-5,5-dimethyl-4-methyleneoxazolidin-2-one (2b): A colorless liquid. 204 mg, 61%; IR ($CHCl_3$) ν_{max} 1758 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$, TMS, 300 MHz) δ 1.39 (s, 6H, $2CH_3$), 3.91 (d, 1H, J = 2.9 Hz, CH), 3.95-3.99 (m, 3H, CH and CH_2), 5.05 (dd, 1H, J = 4.2, 1.0 Hz, CH), 5.11 (t, 1H, J = 1.0 Hz, CH), 5.58-5.68 (m, 1H, CH); MS (EI) m/z 167 (M^+); HRMS Calcd for $C_9H_{13}NO_2$: requires M, 167.0946. Found: 167.0949 (M^+); *Anal.* Calcd for $C_9H_{13}NO_2$: C, 64.65; H, 7.84; N, 8.38. Found: C, 64.41; H, 7.73; N, 8.36.

The Formation of 3-butyl-5,5-dimethyl-4-methyleneoxazolidin-2-one (2c): A colorless liquid. 256 mg, 70%; IR ($CHCl_3$) ν_{max} 1716 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$, TMS, 300 MHz) δ 0.95 (t, 3H, J = 7.3 Hz, CH_3), 1.39 (m, 2H, CH_2), 1.50 (s, 6H, $2CH_3$), 1.60 (m, 2H, CH_2), 3.45 (t, 2H, J = 7.3, CH_2), 3.99 (d, 1H, J = 2.9 Hz, CH), 4.09 (d, 1H, J = 2.9 Hz, CH); MS (EI) m/z 183 (M^+); HRMS Calcd for $C_{10}H_{17}NO_2$: requires M, 183.1259. Found: 183.1270 (M^+); *Anal.* Calcd for $C_{10}H_{17}NO_2$: C, 65.54; H, 9.35; N, 7.64. Found: C, 65.47; H, 9.13; N, 7.45.

The Formation of 3-cyclohexyl-5,5-dimethyl-4-methyleneoxazolidin-2-one (2d): A white solid. 251 mg, 60%; mp 48-50 ^{o}C (Dichloromethane/Hexane); IR ($CHCl_3$) ν_{max} 1758 cm^{-1} and 1669 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$, TMS, 300 MHz) δ 1.19-1.57 (m, 4H, CH_2), 1.50 (s, 6H, $2CH_3$), 1.50-1.80 (m, 2H, CH_2), 1.80-1.95 (m, 2H, CH_2), 2.0-2.20 (m, 2H, CH_2), 3.51-3.62 (m, 1H, CH), 3.98 (d, 1H, J = 2.9 Hz, CH),

4.20 (d, 1H, J = 2.9 Hz, CH); MS (EI) m/z 209 (M^+); HRMS Calcd for $C_{12}H_{19}NO_2$: requires M, 209.1416. Found: 209.1404 (M^+); *Anal.* Calcd for $C_{12}H_{19}NO_2$: C, 68.87; H, 9.15; N, 6.69. Found: C, 68.77; H, 9.10; N, 6.41.

The Formation of 3-benzyl-5,5-dimethyl-4-methyleneoxazolidin-2-one (2e): A colorless liquid. 347 mg, 80%; IR ($CHCl_3$) ν_{max} 1749 cm^{-1} and 1679 cm^{-1} (C=O); ^1H NMR ($CDCl_3$, TMS, 300 MHz) δ 1.51 (s, 6H, $2CH_3$), 3.96 (d, 1H, J = 2.9 Hz, CH), 4.03 (d, 1H, J = 2.9 Hz, CH), 4.64 (s, 2H, $=CH_2$), 7.24-7.36 (m, 5H, Ar); MS (EI) m/z 217 (M^+); HRMS Calcd for $C_{13}H_{15}NO_2$: requires M, 217.1103. Found: 217.1072 (M^+); *Anal.* Calcd for $C_{13}H_{15}NO_2$: C, 71.87; H, 6.96; N, 6.45. Found: C, 71.77; H, 6.86; N, 6.40.

The Formation of 1,1-dimethyl-2-oxopropyl butylcarbamate (3c): A colorless liquid. 350 mg, 87%; IR ($CHCl_3$) ν_{max} 1716 cm^{-1} (C=O); ^1H NMR ($CDCl_3$, TMS, 300 MHz) δ 0.91 (t, 3H, J = 6.3 Hz, CH_3), 1.22-1.57 (m, 4H, $2CH_2$), 1.40 (s, 6H, $2CH_3$), 2.15 (s, 3H, CH_3), 3.16 (q, 2H, J = 6.3 Hz, CH_2), 4.74 (s, 1H, NH); MS (EI) m/z 201 (M^+); HRMS Calcd for $C_{10}H_{19}NO_3$: requires M, 201.1365. Found: 201.1361 (M^+); *Anal.* Calcd for $C_{10}H_{19}NO_3$: C, 59.68; H, 9.52; N, 6.96. Found: C, 59.56; H, 9.56; N, 6.80.

The Formation of 1,1-dimethyl-2-oxopropyl cyclohexylcarbamate (3d): A white solid. 318 mg, 70%; mp 104-106 ^oC (Dichloromethane/Hexane); IR ($CHCl_3$) ν_{max} 1713 cm^{-1} (C=O); ^1H NMR ($CDCl_3$, TMS, 300 MHz) δ 1.08-1.52 (m, 6H, CH_2), 1.44 (s, 6H, $2CH_3$), 1.52-1.80 (m, 2H, CH_2), 1.82-2.0 (m, 2H, CH_2), 2.15 (s, 3H, CH_3), 3.43-3.45 (m, 1H, CH), 4.66 (s, 1H, NH); MS (EI) m/z 184 (M^+-43); HRMS Calcd for $C_{12}H_{21}NO_3$: requires M, 227.1521. Found: 227.1529 (M^+); *Anal.* Calcd for $C_{12}H_{21}NO_3$: C, 63.41; H, 9.31; N, 6.16. Found: C, 63.36; H, 9.23; N, 6.11.

The Formation of 1,1-dimethyl-2-oxopropyl benzylcarbamate (3e): A white solid. 307 mg, 65%; mp 102-104 ^oC (Dichloromethane/Hexane); IR ($CHCl_3$) ν_{max} 1714 cm^{-1} (C=O); ^1H NMR ($CDCl_3$, TMS, 300 MHz) δ 1.47 (s, 6H, $2CH_3$), 2.09 (s, 3H, CH_3), 4.36 (d, 2H, J = 6.0 Hz, CH_2), 5.10 (s, 1H, NH), 7.27-7.35 (m, 5H, Ar); MS (EI) m/z 236 $(MH)^+$; HRMS Calcd for $C_{13}H_{15}NO_2$: requires (M-H_2O), 217.1103. Found: 217.1095 (M^+-H_2O); *Anal.* Calcd for $C_{13}H_{17}NO_3$: C, 66.36; H, 7.28; N, 5.95. Found: C, 66.22; H, 7.21; N, 5.87.

The Formation of 1,1-dimethyl-2-oxopropyl *N,N*-diethylcarbamate (5a): A colorless liquid. 342 mg, 85%; IR ($CHCl_3$) ν_{max} 1716 cm^{-1} and 1696 cm^{-1} (C=O); ^1H NMR ($CDCl_3$, TMS, 300 MHz) δ 1.10-1.16 (m, 6H, $2CH_3$), 1.46 (s, 6H, $2CH_3$), 2.13 (s, 3H, CH_3), 3.29 (d, 4H, J = 6.5 Hz, $2CH_2$); MS (EI) m/z 158

(M^+-43); HRMS Calcd for $C_8H_{16}NO_2$: requires (M-43), 158.1181. Found: 158.1189 (M^+-43); *Anal.* Calcd for $C_{10}H_{19}NO_3$: C, 59.68; H, 9.52; N, 6.96. Found: C, 59.62; H, 9.45; N, 6.87.

The Formation of 1,1-dimethyl-2-oxopropyl *N,N*-dibutylcarbamate (5b): A colorless liquid. 351 mg, 82%; IR ($CHCl_3$) ν_{max} 1714 cm^{-1} and 1682 cm^{-1} (C=O); ^1H NMR ($CDCl_3$, TMS, 300 MHz) δ 0.60-0.70 (m, 6H, $3CH_3$), 1.00-1.08 (m, 4H, $2CH_2$), 1.10 (s, 6H, $2CH_3$), 1.21-1.33 (m, 4H, $2CH_2$), 1.80 (s, 3H, CH_3), 2.91-2.30 (m, 4H, $2CH_2$); MS (EI) m/z 214 (M^+-43); HRMS Calcd for $C_{12}H_{24}NO_2$: requires (M-43), 214.1807. Found: 214.1778 (M^+ -43); *Anal.* Calcd for $C_{14}H_{27}NO_3$: C, 65.33; H, 10.57; N, 5.44. Found: C, 65.21; H, 10.45; N, 5.34.

The Formation of 1',1'-dimethyl-2-oxopropyl piperidyl-1-carbonate (5c): A colorless liquid. 349 mg, 82%; IR ($CHCl_3$) ν_{max} 1714 cm^{-1} and 1682 cm^{-1} (C=O); ^1H NMR ($CDCl_3$, TMS, 300 MHz) δ 1.12 (s, 6H, $2CH_3$), 1.18-1.30 (m, 6H, $3CH_2$), 1.78 (s, 3H, CH_3), 3.08-3.13 (m, 4H, $2CH_2$); MS (EI) m/z 170 (M^+-43); HRMS Calcd for $C_9H_{16}NO_2$: requires (M-43), 170.1181. Found: 170.1185 (M^+-43); *Anal.* Calcd for $C_{11}H_{19}NO_3$: C, 61.95; H, 8.98; N, 6.57. Found: C, 61.87; H, 8.90; N, 6.54.

ACKNOWLEDGEMENTS

We thank the State Key Project of Basic Research (Project 973) (No. G2000048007) and the National Natural Science Foundation of China for financial support (20025206). We also thank the Inoue Photochirogenesis Project (ERATO, JST) for chemical reagents.

REFERENCES

1. (a) P. Adama and F. A. Baron, *Chem. Rev*., 1965, **65**, 567. (b) A. Mateen, S. Chapalamadugu, B. Kashar, A. R. Batthi, and G. R. Chaudry, *Biol. Degrad. Biorem. Toxic. Chem.*, 1994, 198. (c) Y. Y. Wigfield, *Food Sci. Technol*. (*N. Y*.) 1996. **77** (Handbook of Food Analysis, Vol. 2) 1501. (d) M. E. Dyen and D. Swern, *Chem. Rev*., 1967, **67**, 197.
2. B. M. Trost and A. R. Sudhakar, *J. Am. Chem. Soc*., 1988, **110**, 7933.
3. (a) N. Saito, K. Hatakeda, S. Ito, T. Asano, and T. Toda, *Bull. Chem. Soc., Jpn.* 1986, **59**, 1629. (b) K. Soga, S. Hosoda, H. Nakamura, and S. Ikeda, *J. Chem. Soc., Chem. Commun*., 1976, **16**, 617. (c) P. Dimroth, H. Pasedach, and E. Schefezik, *Ger. Patent*, 1964, DBP 1151507.
4. (a) J. Fournier, C. Bruneau, and P. H. Dixneuf, *Tetrahedron Lett*., 1990, **31**, 1721. (b) J. Fournier, C. Bruneau, and P. H. Dixneuf, *Tetrahedron Lett*., 1990, **31**, 1721.

5. M. Shi and Y.-M. Shen, *J. Org. Chem*., 2002, in press.

6. T. Francis and M. P. Thorne, *Can. J. Chem*., 1976, **54**, 24.

7. The references of catalytic amination of olefins with palladium catalyst. (a) A. L. Seligson and W. C. Trogler, *Organometallics*, 1993, **12**, 744. (b) P. J. Harrington, L. S. Hegedus, and K. F. McDaniel, *J. Am. Chem. Soc*., 1987, **109**, 4335. (c) Y. Yokoyama, T. Matsumoto, and Y. Murakami, *J. Org. Chem*., 1995, **60**, 148.

8. (a) B. C. Hamann and J. F. Hartwig, *J. Am. Chem. Soc*., 1998, **120**, 3694. (b) G. Mann, J. F. Hartig, F. M. S. Driver, and C. Fernandez-Rivas, *J. Am. Chem. Soc*., 1998, **120**, 827. (c) D. W. Old, J. P. Wolfe, and S. L. Buchwald, *J. Am. Chem. Soc*., 1998, **120**, 9722.