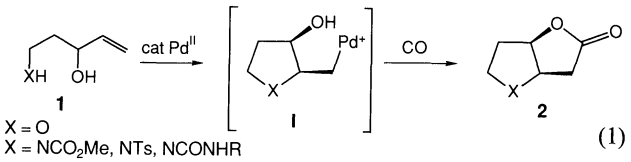
Efficient Synthesis of 2-Vinyl-γ-butyrolactones and 2-Vinyl-γ-butyrolactams by Palladium-Catalyzed Decarboxylative Carbonylation

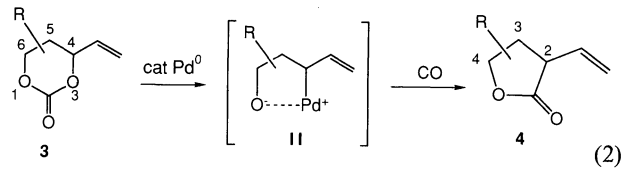
Takashi BANDO, Shuji TANAKA, Keigo FUGAMI, Zen-ichi YOSHIDA,† and Yoshinao TAMARU*
Department of Applied Chemistry, Faculty of Engineering, Nagasaki University, Bunkyo, Nagasaki 852
† Department of Synthetic Chemisty, Faculty of Engineering, Kyoto University, Sakyo, Kyoto 606
(Received August 16, 1991)

4-Vinyl-1,3-dioxan-2-ones (cyclic carbonates) undergo decarboxylation- carbonylation by the catalysis of Pd(0) species under CO (in most cases, 1 atm) to provide 2-vinyl-γ-butyrolactones in good yields. The course of the reaction of 6-vinyltetrahydro-2*H*-1,3-oxazin-2-ones (cyclic carbamates) depends on the substituent on the nitrogen atom. When it is H or Ts (and COPh), 2-vinyl-γ-butyrolactams or 6-amino-3-hexenoic acid esters are obtained. Cyclic *N*-benzylcarbamates are unreactive. *trans*-2,3-Disubstituted lactones and lactams arise stereoselectively from carbonates and carbamates, irrespective of their stereochemistry, respectively.

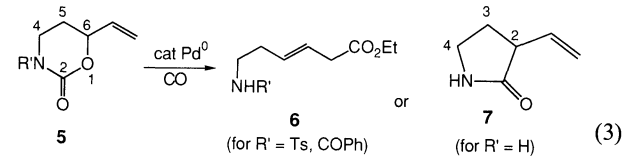
γ-Butyrolactones are versatile intermediates for the syntheses of many physiologically interesting compounds.[1] Recently, we have explored a few new synthetic methods for γ-butyrolactone derivatives as part of a study aimed at new methodologies based on the oxidizing ability of Pd(II) catalysts (e.g., Eq. 1).[2]



(1)



(2)



(3)

In this paper we describe an efficient method for the synthesis of 2-vinyl-γ-butyrolactones (**4**) and 2-vinyl-γ-butyrolactams (**7**) via Pd(0) catalyzed decarboxylative carbonylation of 4-vinyl-1,3-dioxan-2-ones (cyclic carbonates) (**3**)[3] and 6-vinyltetrahydro-2*H*-1,3-oxazin-2-ones (cyclic carbamates) (**5**), respectively (Eqs. 2 and 3). In these reactions the allylic oxygen atom plays a decisive role in determining the course of the reaction. In Eq. 1, it controls the stereochemistry on cyclization of **1** to lead to *cis*-2-palladomethyl-3-hydroxy heterocyclic intermediates **I**.[4] In Eqs. 2 and 3, the allylic oxygen serves as a leaving group to furnish an allylpalladium intermediate **II**. Carbonates **3** and carbamates **5** were readily prepared in high yields by the reaction of **1** (X=O, NH) with methyl chloroformate.

Results and Discussion

Decarboxylative Carbonylation of Carbonates 3: Synthesis of 2-Vinyl-γ-butyrolactones (4). Recently Tsuji et al.[5] have demonstrated that carbonylation of π-allylpalladium is greatly accelerated by the use of an alkyl allyl carbonate as substrate to obtain 3-alkenoic acid esters in high yields under an ambient pressure of CO. The reaction is somewhat accelerated by increasing the pressure of CO. This is in contrast to the palladium catalyzed carbonylation of other allylic esters and allylic halides, which usually requires a much higher pressure of CO (100—500 atm).[6]

During mechanistic investigation of the reaction in Eq. 1,[4d] we fortunately found that cyclic carbonates **3** cleanly undergo decarboxylative carbonylation to furnish 2-vinyl-γ-butyrolactones (4), a class of compounds of great synthetic and physiological interest (Eq. 2).[1]

Generally the reaction proceeds smoothly at ambient temperature in the presence of 3 mol% of tetrakis(triphenylphosphine)palladium(0) as a catalyst under 1 atm of CO. In order to clarify the synthetic scope, 14 kinds of cyclic carbonates **3a**—**m** were examined. Results are summarized in Table 1. Aprotic solvents, such as dioxane and tetrahydrofuran (THF), are satisfactory. In those instances where lower temperatures were required, a dioxane–THF mixed solvent (5 : 1 vol.) was used (Runs 8—10, Table 1). In a protic solvent such as dry ethanol almost no 2-vinyl-γ-butyrolactones (**4**) were produced; instead, a mixture of α-alkylidene-γ-butyrolactone (**4'**) and 6-hydroxy-3-hexenoic acid ester (**8**) was produced (cf. Run 2, Table 1).

The reaction tolerates substituents both on the ring carbons and olefinic carbons of **3**. Moreover, by substitution the reaction becomes cleaner and results in better yields. For instance, carbonates possessing substituents on the ring carbons (e.g., **3a**, **3e**, **3g**, **3h**, Table 1) or on the olefinic carbons (e.g., **3b** and **3d**) give lactones in good yields. In particular, occurrence of carbonyla-

Table 1. Palladium(0) Catalyzed Decarboxylative Carbonylation of **3**

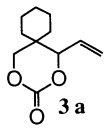
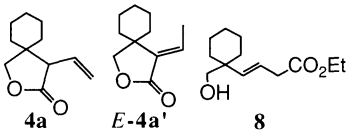
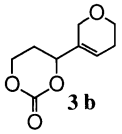
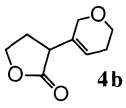
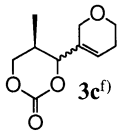
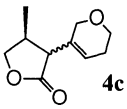
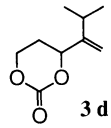
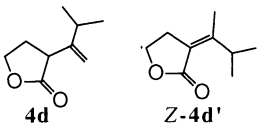
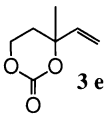
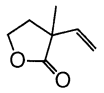
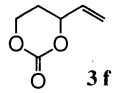
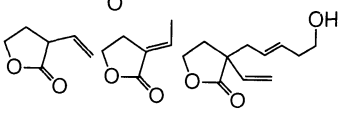
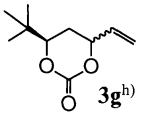
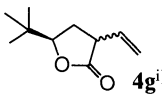
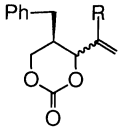
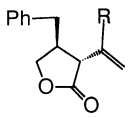
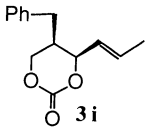
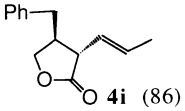
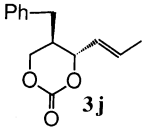
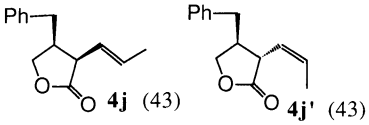
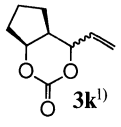
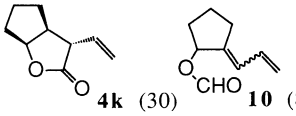
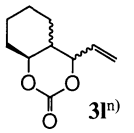
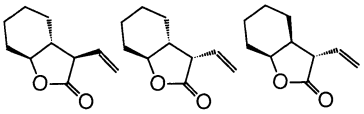
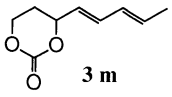
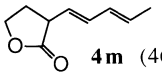
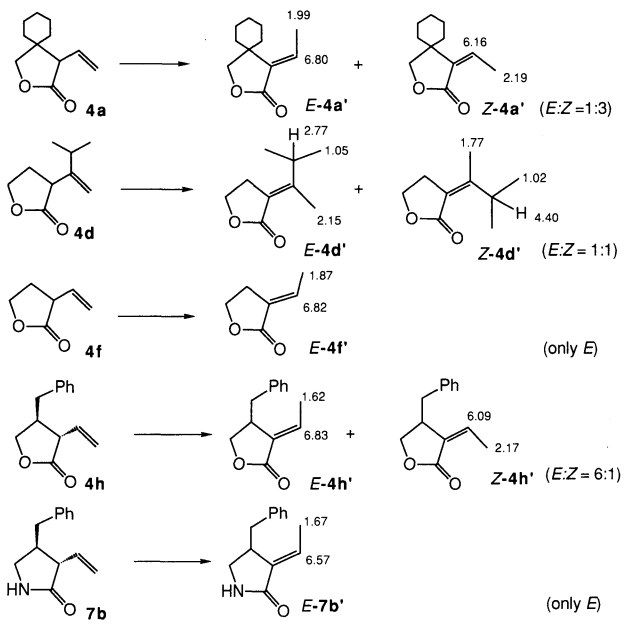
Run	Substrate **3**	Conditions[a] (temp, time, CO press.)	Product (% isolated yield)
1	 **3a**		 **4a** *E*-**4a'** **8**
2[b]		r.t., 3 h, 1 atm	(89) (0) (0)
		r.t., 24 h, 1 atm	(0) (32) (39)
3	 **3b**	r.t., 7 h, 1 atm	 **4b** (77)
4[c]	 **3c**[f]	r.t., 46 h, 1 atm	 **4c** (48)[g]
	 **3d**		 **4d** *Z*-**4d'**
5		r.t., 3 h, 1 atm	(35) (35)
6		r.t., 6 h, 45 atm	(85) (0)
7	 **3e**	r.t., 3 h, 1 atm	 **4e** (66)
	 **3f**		 **4f** *E*-**4f'** **9**
8[d]		0°C, 4 h, 1 atm	(25) (14) (9)
9[d]		0°C, 7 h, then r.t., 10 h, 45 atm	(53) (4) (0)
10[d]	 **3g**[h]	0°C, 2 h, then r.t., 4 h, 45 atm	 **4g**[i] (62)
11[e]			
	3h[j] (R=H)	r.t., 17 h, 1 atm	**4h** (R=H, 88)
12	**3h**[k] (R=Me)	r.t., 24 h, 1 atm	**4h** (R=Me, 69)
13	 **3i**	r.t., 8 h, 1 atm	 **4i** (86)
14	 **3j**	r.t., 9 h, 1 atm	 **4j** (43) **4j'** (43)
15[c]	 **3k**[l]	0°C, 3 h, then r.t., 14 h, 45 atm	 **4k** (30) **10** (8)

Table 1. (Continued)

Run	Substrate 3	Conditions[a] (temp, time, CO press.)	Product (% isolated yield)
16[m]	 **3l**[n]	r.t., 22 h, then 50 °C, 3 h, 1 atm	 **4l** (56) **4l′** (12) **4l″** (15)
17	 **3 m**	r.t., 21 h, 1 atm	 **4m** (46)

a) Usual conditions: carbonate **3** (1 mmol) and $Pd(PPh_3)_4$ (0.03 mmol) in dry dioxane (5 mL). b) In dry ethanol. c) In dry THF. d) In dioxane–THF (5:1 mL). e) $Pd(OAc)_2(PPh_3)_2$ (0.03 mmol) in place of $Pd(PPh_3)_4$. f) A mixture of *cis*-**3c**:*trans*-**3c**=1.2:1. g) A mixture of *cis*-**4c**:*trans*-**4c**=1:1.2. h) A mixture of *cis*-**3g**:*trans*-**3g**=1:1. i) A mixture of *cis*-**4g**:*trans*-**4g**=1:1. j) A mixture of *cis*-**3h** (R=H):*trans*-**3h** (R=H)=1:1.3. k) A mixture of *cis*-**3h** (R=Me):*trans*-**3h** (R=Me)=1:1. l) A mixture of *cis*-**3k**:*trans*-**3k**=1.3:1. m) In dry benzene. n) A diastereomeric mixture of 3:1:1.

tion at a tertiary carbon is very impressive (Run 7, Table 1). On the other hand, the parent compound **3f** gives an intractable mixture of products under the usual conditions (r.t., 1 atm of CO). In this case, the reaction is much improved when conducted at 0 °C (Run 8, Table 1). However, the yield of the expected **4f** is still unsatisfactory. Two major side products (*E*-**4f′** and **9**) were isolated. 2-Vinyl-γ-butyrolactone **4f** may be produced via carbonylation of alkoxypalladium **II** (R=H, Eq. 2). The alkoxypalladium intermediate **II** may also be responsible for production of these side products *E*-**4f′** and **9**, where **II** serves as a base to generate an enolate of **4f**. Protonation and alkylation of the enolate with **II** might produce *E*-**4f′** and **9**, respectively. If this were the case, these side reactions might be suppressed by prompt consumption of **II** under a higher pressure of CO. Indeed, a better result is obtained under 45 atm of CO (Run 9, Table 1).



Scheme 1. DBU catalyzed isomerization of **4** and **7** and selected ^1H NMR spectral data of **4′** and **7′** (γ in ppm, $CDCl_3$).

While digressing from the main subject of this paper, it seems worthwhile to note some chemistry of alkylidene products *E*-**4a′** (Run 2, Table 1), *Z*-**4d′** (Run 5), and *E*-**4f′** (Runs 8 and 9), that are obtained as single geometric isomers. Stereoselective formation of *E*-**4f′** is expected from an A(1,3)-strain[7] between the methyl group and the carbonyl oxygen atom in the corresponding *Z* isomer (Scheme 1). However, the specific formation of *E*-**4a′** and *Z*-**4d′** is rather surprising on the basis of small differences of thermodynamic stabilities between the two possible isomers. In fact, an independent base catalyzed isomerization of **4a** (with 1,8-diazabicyclo-[5.4.0]undec-7-ene (DBU) in refluxing THF) provided the other *Z*-**4a′** isomer as a major product together with *E*-**4a′** in 3:1 ratio (Scheme 1). On the other hand, kinetic protonation of the lithium enolate, generated by treatment of **4a** with 1.2 equiv of LDA at −20 °C in THF, provided the starting **4a** as a major component (63%) together with *Z*-**4a′** and *E*-**4a′** (30%, 2:1, 2 mol dm^{-3} HCl at −78 °C). Methylation of the same enolate with methyl iodide furnished the 2-methyl derivative of **4a** exclusively (−78 °C for 8 h).[8] Judging from the product distributions observed for these two experiments, the specificity observed for isomerization of **4** to **4′** under the carbonylation conditions must be controlled by other factors: Unlike the case of lithium enolate, the enolate formed by the reaction of **4** with **II** may form a solvent separated ion pair, for the counter cation is most likely protonated **II** (Fig. 1). Accordingly, the enolate may strongly favor a sickle-form **III** over a U-form **IV**[9] in order to minimize electrostatic repulsion between the partial anionic charges on the carbonyl oxygen and methylene terminus. The structure of alkylidene products **4′**, all of which are characterized by methyl group *trans* to the carbonyl, may well be reconciled with structure **III**.

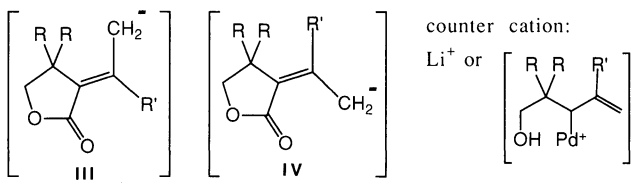
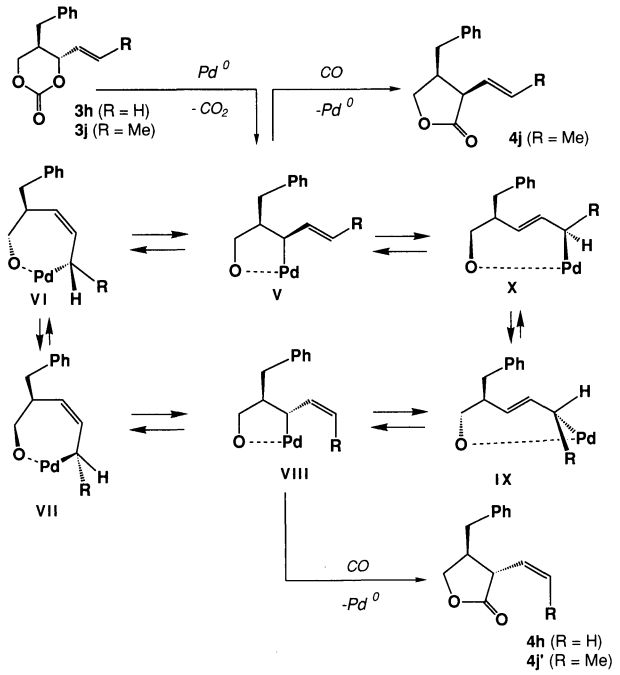


Fig. 1.

The alkoxypalladium intermediate **II** also may be responsible for formation of another type of side product, **10** (Run 15, Table 1). In this case a higher pressure of CO and a lower temperature were required for formation of the anticipated **4k**. Under the usual conditions (r.t., 1 atm of CO), only an intractable mixture of products was produced. Formation of **10** may be ascribed to the high acidity of the cyclopentyl methine proton of an intermediate **II**, which may dehydropalladate readily to yield a 2-propenylidenecyclopentyl alcohol, the presumable precursor of **10**.[10] Indeed, despite close structural similarity to **3k**, the reaction of **31** is quite normal and even under usual conditions the expected lactones (**41**, **41′**, and **41″**) are obtained in a good total yield (Run 16, Table 1).

The present decarboxylative carbonylation shows a strong tendency to provide *trans* 2,3-disubstituted lactones, irrespective of the stereochemistry of the starting carbonates (Runs 11—15, Table 1). On the other hand, 2,4-disubstituted lactone is obtained non-stereoselectively (Run 10, Table 1).

In order to clarify details of the stereochemical course of the reaction, a pair of carbonates **3i** and **3j** was examined. *cis*-Carbonate **3i** was specifically converted to *trans*-lactone **4i** with retention of geometry at the double bond. *trans*-Carbonate **3j** with an *E* double bond, on the other hand, gives a mixture of *cis*-lactone **4j** with an *E* double bond and *trans*-lactone **4j′** with a *Z* double bond. All these results indicate that the reaction involves either an inversion of configuration at the C-4 ring carbon (of the carbonate) with retention of geometry at the double bond or an isomerization of the double bond with retention of configuration of the C-4 ring carbon. That is, the stereochemistry of **4** is correlated with that of **3** by a single inversion of either the C-4 configuration or olefinic geometry. This behavior of the reaction might be rationalized by invoking an equilibrium between alkoxypalladium intermediates **V** and **VIII** (Scheme 2). In this equilibrium, inversion in configuration of the ring carbon correlates with inversion of geometry of the double bond (see below for a detailed discussion). For instance, intermediate **V**, formed from *trans*-**3h** (R=H) by addition of Pd(0) to the allylic C–O bond with an inversion of configuration,[11] might isomerize to the relatively stable isomer **VIII** (R=H) and then undergo carbonylation with retention of configuration[11] to specifically provide *trans* 2,3-disubstituted butyrolactone **4h** (R=H). On the other hand, *cis*-**3h**



Scheme 2.

might directly provide **VIII** (R=H), which is responsible for formation of **4h** (R=H, Scheme 1). In the case of **3j**, the difference in thermodynamic stabilities, between **V** and **VIII** (R=Me) may be so small that both intermediates are responsible for carbonylation, and hence give a mixture of **4j** and **4j′** in equal amounts. The specific formation of **4i** from **3i** (Run 13, Table 1) may be explained in an analogous way.

The result of Run 4 (Table 1) further seems to support the reaction sequence shown in Scheme 2. Thus, the exactly reversed *cis*/*trans* ratio in the products (as compared with the ratio of the starting carbonates) reflects that for these substrates isomerization of the double bond may be impossible and the *cis*- and *trans*-**3c** are destined to cyclize to *trans*- and *cis*-**4c**, respectively.

In order to get further support for the proposed mechanism, the effects of solvents and pressure of CO on product distributions were examined in detail by using an example with **3j** as a probe system (Table 2). Unlike many precedents,[6] this reaction is seriously retarded with an increase in pressure of CO (Runs 3 and 4, Table 2). These results imply that the rate determining step with **3j** is an oxidative addition of Pd(0) to an allylic carbonate moiety, which is suppressed by coordination of CO to Pd(0). The constant product distribution under a lower pressure of CO (Run 1) or in a more polar solvent system [dioxane–HMPA (Run 6) vs. dioxane] or less polar one (benzene, Run 5) clearly indicates that the firstly formed **V** (R=Me, Scheme 2) isomerizes to **VIII** (R=Me) very quickly and the equilibrium is established, irrespective of solvent polarity, before carbonylation of **V** and **VIII** takes place. Such a fast rotational isomerization seems to be possible only via the *cis*-oxapalladacycloheptenes

Table 2. The Reaction of **3j** under Various Conditions[a]

Run	Solvent	Pressure of CO (time)	Ratio of **4j** to **4j'**[b]
1[1]	Dioxane	0.5 atm (28 h)[1]	1:1
2	Dioxane	1 atm (9 h)	1:1
3	Dioxane	5 atm (41 h)	No reaction
4	Dioxane	45 atm (60 h)	No reaction
5	Benzene	1 atm (4 h)	1:1
6	Dioxane-HMPA[c]	1 atm (4 h)	1:1

a) Carbonate **3j** (1 mmol) and $Pd(PPh_3)_4$ (0.03 mmol) in 5 mL of a given solvent at ambient temperature. b) Based on VPC and ^1H NMR. c) Two equivalents of HMPA to **3j**.

(**VI** and **VII**), because the ring strain of the *trans* isomers (**IX** and **X**) is such that rotational isomerization through these intermediates is expected to be very slow.[12] If ionic dissociation (or elongation) of the Pd–O bond of **IX** and **X** were involved, isomerization via these intermediates might proceed readily. However, such a process involving charge separation is expected to be highly dependent on solvent polarity and may be eliminated on the basis of the constant product distributions observed for Runs 5 and 6 in Table 2.

Decarboxylative Carbonylation of Carbamates 5: Synthesis of 2-Vinyl-γ-butyrolactams (7). Compared with the synthesis of 3-alkenoic acid esters via carbonylation of allylic substrates, synthesis of 3-alkenoic acid amides via similar methodology is more rare.[5a,13] We examined the decarboxylative carbonylation of cyclic carbamates **5** (R=H and R=toluenesulfonyl) and expected to obtain γ-butyrolactam **7** (Eq. 3). However, for carbonates **5** (R=H), almost no reaction took place under the conditions established for **3** or even under forcing conditions [3 mol% $Pd(PPh_3)_4$ in dioxane at reflux for 8 h under 1 atm of CO]. The following attempts were fruitless and resulted in recovery of the starting material: 3 mol% $Pd(PPh_3)_4$ in acetonitrile at 50 °C for 1 d; $Pd(OAc)_2(PPh_3)_2$ (3 mol%) in THF at 50 °C for 18 h, in DME at reflux for 1 d, or in DMF at 100 °C for 1 d; $PdCl_2(PPh_3)_2$ (3 mol%) in dioxane at reflux for 1 d. Carbamates **5** (R=toluenesulfonyl) decomposed to give intractable mixture of products under the conditions established for **3** (at 60 °C).

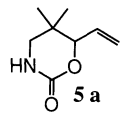
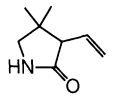
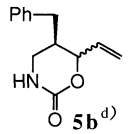
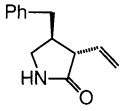
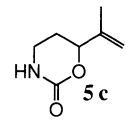
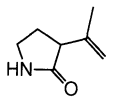
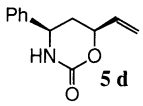
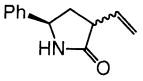
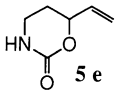
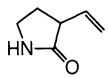
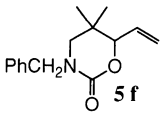
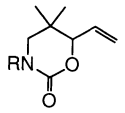
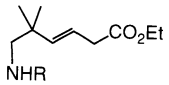
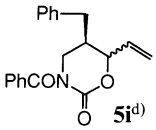
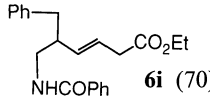
Eventually we found that the use of protic solvents, making sharp contrast to the use of aprotic solvents in the conversion of **3** to **4** discussed above, is essential for reaction. The reaction was most satisfactorily undertaken by use of $Pd(OAc)_2(PPh_3)_2$ (3 mol%) in dry ethanol at reflux. Results are summarized in Table 3 (Runs 1—7). As apparent from these data, the reactions are quite similar to those with carbonates **3** (cf. above): (1) Substitution on ring carbons or olefinic carbons as well as higher pressure of CO gives better yields. The reaction of the parent carbamate **5e** under 1 atm of CO provides an intractable mixture of products (cf. Run 7, Table 3). (2) Higher pressure of CO causes retardation of the reaction (Run 2). (3) A 5,6-disubstituted carbamate selectively produces 2,3-*trans* substituted γ-butyrolactam (Runs 3 and 4). (4) No stereoselectivity is observed for the transformation of 4,6-disubstituted carbamate (Run 6).

Interestingly, the electronic nature of substituents on the nitrogen atom decisively affects the course of the reaction.[14] When substituted with the electron-releasing benzyl group, no reaction takes place and the starting material **5f** is recovered under the usual reaction conditions [$Pd(OAc)_2(PPh_3)_2$ in ethanol or dioxane, Run 8, Table 3]. $Pd(PPh_3)_4$ showed no catalytic activity with **5f** in dioxane (at reflux for 44 h). $(dba)_3Pd_2C_6H_6$ and 2 equivalents of PPh_3 in ethanol (at reflux for 1 d) or in dioxane (at reflux for 11 h) also resulted in recovery of the starting material **5f**. After all of this, we have not yet been successful for the carbonylation of **5f**. On the other hand, carbamates substituted with electron-withdrawing groups on the nitrogen smoothly undergo carbonylation even at room temperature (Eq. 3 and Runs 9—11, Table 3). In these cases, however, no butyrolactams are obtained; instead, 6-amino-3-hexenoic esters **6** are isolated in good yields.[4d]

This contrasting reactivity may be rationalized by the ability of carbamates as leaving groups in combination with the nitrogen atoms as nucleophiles. Oxidative addition of Pd(0) to the allylic C–O bond may be retarded by electron-releasing substituents (e.g., for **5f** in Run 8, Table 3). Once an oxidative addition takes place, carbonylation may proceed via **V** or **VIII** (with NR′ in place of O) for the carbamates with a strong nitrogen nucleophile (R′=H, **5a**—**e**) and via **IX** or **X** (with NR′ in place of O) for the carbamates with a poor nitrogen nucleophile (R′=Ts or COPh, **5g**—**i**) to provide **7** and **6**, respectively (Scheme 2 and Table 3). The intermediacy of **IX** and **X** may be surprising in light of the mechanism proposed above for the reaction of carbonates **3**, which relies on equilibria among **V**, **VI**, **VII**, and **VIII** (vide supra). In a protic solvent, as for the reaction of **5**, however, the amide anion of the intermediates **V**—**X** may be in equilibrium with its protonated form and the Pd–NHR′ bonds may become loose. Accordingly, intermediates **IX** and **X** (with O replaced by NHTs or NHCOPh) are expected to be much more stable than their oxygen analogs. The coordination of an amine is such that intermediates **V** (and/or **VIII**) (with NH_2 in place of O) are still favored over all others and hence γ-butyrolactams **7** may be produced selectively. The production of a mixture of *E*-**4a′** and **8** (Run 2, Table 1), observed for the reaction of carbonate **3a**, may be regarded as a case that involves all of the intermediates **V**—**X** with oxygen in the structures, as shown in Scheme 2.

Structure Determination of Products. The structure of 2-alkylidene-γ-butyrolactones **4′** was determined unequivocally on the basis of the following criteria: (1) Owing to magnetic anisotropy of the carbonyl group, *syn*

Table 3. Palladium(0) Catalyzed Decarboxylative Carbonylation of **5**

Run	Substrate **5**	Conditions[a] (temp, time, CO press.)	Product (% isolated yield)
1	 **5a**	r.t., 19 h, then 78°C, 22 h, 1 atm	 **7a** (53)
2		r.t., 24 h, then 80°C, 26 h, 38 atm	**7a** (62)[b]
3		r.t., 24 h, then 60°C, 38 h, 1 atm	 **7b** (48)
4	**5b**[d]	r.t., 24 h, then 60°C, 40 h, 45 atm	**7b** (79)
5	 **5c**	r.t., 31 h, then 60°C, 38 h, 1 atm	 **7c** (42)
6	 **5d**	r.t., 18 h, then 60°C, 6 h, 30 atm	 **7d** (55)[d]
7	 **5e**	r.t., 22 h, then 60°C, 6 h, 45 atm	 **7e** (23)
8	 **5f**	r.t., 16 h, then 78°C, 77 h, 1 atm	No reaction
9	 **5g** (R=Ts)	r.t., 24 h, then 60°C, 30 h, 1 atm	 **6g** (R=Ts, 84)
10	**5h** (R=COPh)	r.t., 61 h, 1 atm	**6h** (R=COPh, 83)
11[c]	 **5i**[d]	r.t., 48 h, 1 atm	 **6i** (70)

a) Usual conditions: carbamate **5** (1 mmol) and $Pd(OAc)_2(PPh_3)_2$ (0.03 mmol) in dry ethanol (5 mL). b) Isolated yield based on 60% conversion. c) $Pd(PPh_3)_4$ (0.03 mmol) in place of $Pd(OAc)_2(PPh_3)_2$. d) A mixture of *cis*:*trans*=1:1.

protons to a carbonyl resonate at lower fields than the corresponding *anti* protons (Scheme 1).[15] (2) Protons *syn* to a carbonyl are significantly shifted downfield upon gradual doping with an europium shift reagent [$Eu(fod)_3$ in $CDCl_3$], as compared to the results with the *anti* ones. For example, in *E*-**4h′** the vinyl proton is shifted more than 2 times as large as the methyl protons. On the other hand, in *Z*-**4h′** the methyl protons show about one and a half times as large shift as the vinyl proton. Similarly the vinyl proton of *E*-**4a′** and the methyl protons of *Z*-**4a′** are shifted over 3 times and one and a half times as large as the methyl and vinyl protons of *E*-**4a′** and *Z*-**4a′**, respectively. A large NOE between methyl and C-3 methylene protons further supports the structure of *E*-**4f′**.

The isomers **4l**, **4l′**, and **4l″** were inseparable by means

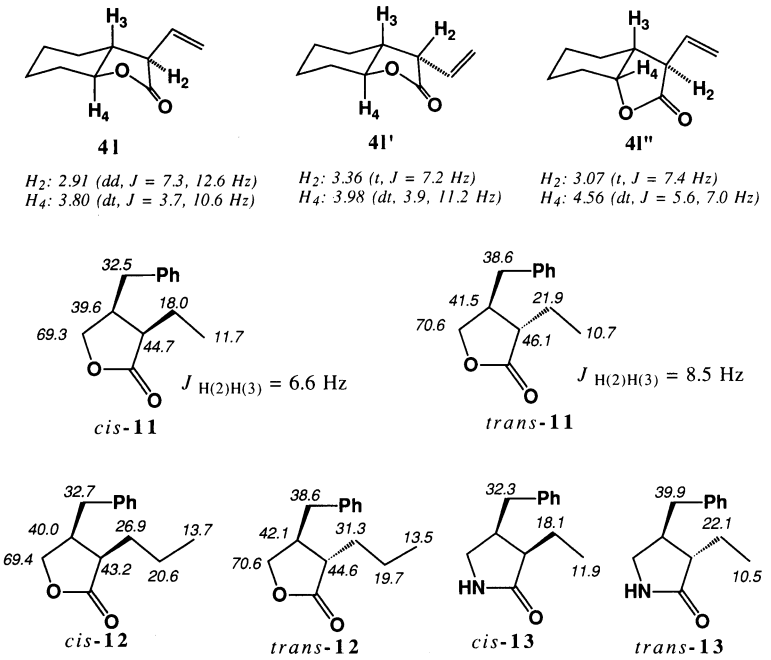


Fig. 2. Selected ^1H and ^{13}C NMR spectral data (γ in ppm, $CDCl_3$).

of column chromatography and the ^1H NMR spectrum of their mixture was very complex (Fig. 2). Fortunately, however, the H_2 and H_4 protons of these isomers appear separately (400 MHz). The *trans* junction in **4l** and **4l′** was deduced from the characteristic coupling pattern (dt, J=ca. 4 and 11 Hz) of H_4 protons. This assignment was further supported by the higher field resonances of the axial H_4 protons of **4l** and **4l′**, as compared with that of the equatorial H_4 proton of **4l″**. The stereochemistry of the vinyl groups in **4l**, **4l′**, and **4l″** was tentatively assigned by analogy with the 2,3-*trans* selectivity generally observed for other examples in this study.

The *trans* structure of **4h** (R=H) was determined as follows. Double bond isomerization of **4h** (R=H) with DBU (Scheme 1), followed by hydrogenation over Lindlar catalyst provided a stereoisomeric mixture of **11** in a 3 : 1 ratio (Fig. 2). No stereochemical information was obtained by comparison of ^1H NMR spectra of these isomers (*cis*-**11**, $J_{H(2)H(3)}$=6.6 Hz; *trans*-**11**, $J_{H(2)H(3)}$=8.5 Hz); however, their ^{13}C NMR spectra turned out to be very diagnostic. All the ring carbons of the major isomer resonate at higher fields than those of the minor isomer. Most significant differences are observed for the ethyl C-1′ and benzyl carbons, and both carbons of the major isomer resonate at 4—6 ppm higher fields than the corresponding carbons of the minor isomer. On the basis of a steric compression effect,[16] the major isomer should be assigned as *cis*-**11**. This assignment may be reconciled with stereoselectivity observed for the hydrogenation of mixture of *E*- and *Z*-**4h′**, which gives *cis*-**11** as the major product as a result of a hydrogenation from the sterically less hindered side. The ^{13}C and ^1H NMR spectra of the hydrogenation product of **4h** (R=H) were superimposable with those of *trans*-**11** in every respect.

For a 1 : 1 mixture of **4j** and **4j′** (Table 1), each isomer could be separated by means of column chromatography. The *E* structure of **4i** and **4j** and the *Z* structure of **4j′** are apparent from their olefinic vicinal coupling constants, 15.9 and 10.8 Hz, respectively. Independent hydrogenation of **4i** and **4j′** provided the same product, *trans*-**12**. Hydrogenation of **4j** provided the other isomer, *cis*-**12**. Structures of *cis*- and *trans*-**12** are apparent from comparison of ^{13}C NMR data given in Fig. 2.

Experimental

Melting points were determined in capillary tubes with a Büchi apparatus and were not corrected. Unless otherwise specified, short-path (bulb to bulb) distillation were carried out in a Kugelrohr apparatus. In these cases, boiling points refer to the oven temperature. Microanalyses were performed by the Microanalysis Center either Kyoto University or Nagasaki University. Analyses agreed with the calculated values within ±0.3%. Infrared spectra were measured with a Hitachi Model EPI-G3 grating spectrophotometer. Proton magnetic resonance spectra were determined either at 60 MHz on a JEOL JNM-PMX60 instrument, at 90 MHz on a JEOL FX90Q instrument, or at 400 MHz on a JEOL-GX400 instrument with tetramethylsilane as an internal standard. Carbon-13 NMR spectra were determined at 22.4 MHz on a JEOL FX90Q instrument with chloroform-*d* (76.92 ppm) as an internal standard. Chemical shift values were given in ppm downfield

from an internal standard. Mass spectra were measured either on a Hitachi Model RMU6C or on a JEOL D-300 instrument (high-resolution mass spectrometer). R_f values were determined over Merck Kieselgel $60F_{254}$.

Dioxane was dried and distilled from sodium under argon. Tetrahydrofuran was dried over sodium–benzophenone. Ethanol, dichloromethane, and triethylamine were dried and distilled from calcium hydride. Bis(triphenylphosphine)palladium(II) acetate[17] and $(dba)_3Pd_2C_6H_6$[18] were prepared according to the literature methods.

4-Pentene-1,3-diol and 5-Amino-1-penten-3-ol: 4-Pentene-1,3-diols[19] and 5-amino-1-pentene-3-ols[20] were prepared according to the method reported previously from our laboratories.

Separation of Diastereometers of (*E*)-2-Benzyl-4-hexene-1,3-diol: To a solution of a diastereomeric mixture of (*E*)-2-benzyl-4-hexene-1,3-diols in a large excess of 2,2-dimethoxypropane was added a catalytic amount of *p*-toluenesulfonic acid and the mixture was allowed to stand at room temperature for 2 d. After dilution with ether, the mixture was washed with aq $NaHCO_3$ and dried ($MgSO_4$). Evaporation of the solvent gave a mixture of acetonides quantitatively. The stereoisomers were separated by flash column chromatography over silica gel (benzene–ethyl acetate gradient). Each acetonide was then treated with 2 mol dm^{-3} HCl in EtOH (room temperature) to afford the diastereomerically pure diol.

***cis*-5-Benzyl-2,2-dimethyl-4-[(*E*)-1-propenyl]-1,3-dioxane:** R_f=0.74 (benzene : ethyl acetate=8 : 1); oil; IR (neat film) 2980 (m), 1670 (w), 1375 (s), 965 (s), 700 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.48 (s, 6H), 1.38—1.70 (m, 1H), 1.75 (d, J=5.6 Hz, 3H), 2.60—3.22 (m, 2H), 3.43—4.13 (m, 2H), 4.59 (dd, J=2.7, 4.6 Hz, 1H), 5.55 (dd, J=4.6, 15.2 Hz, 1H), 5.72 (dq, J=15.2, 5.6 Hz, 1H), 7.21 (s, 5H).

***trans*-5-Benzyl-2,2-dimethyl-4-[(*E*)-1-propenyl]-1,3-dioxane:** R_f=0.68 (benzene:ethyl acetate=8 : 1); oil; IR (neat film) 2990 (s), 1670 (w), 1375 (s), 1200 (s), 1100 (m), 965 (m), 700 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.39 (s, 3H), 1.46 (s, 3H), 1.74 (d, J=6.1 Hz, 3H), 1.80—2.08 (m, 1H), 2.60—2.85 (m, 2H), 3.48—3.67 (m, 2H), 4.02 (dd, J=7.6, 9.5 Hz, 1H), 5.45 (dd, J=7.6, 15.4 Hz, 1H), 5.86 (dq, J=15.4, 6.1 Hz, 1H), 6.99—7.32 (m, 5H). Found: C, 78.22; H, 9.13%. Calcd for $C_{16}H_{22}O_2$: C, 78.01; H, 9.00%.

General Procedure for Preparation of Cyclic Carbonate 3 (4-Vinyl-1,3-dioxan-2-one): To a solution of 4-pentene-1,3-diol (4 mmol) and triethylamine (32 mmol) in dry dichloromethane (30 ml), was added an excess amount of methyl chloroformate (24 mmol) at 0 °C. After the mixture was stirred at an ambient temperature for several h, the majority of dichloromethane was evaporated. Then, to the mixture was added 1 mol dm^{-3} HCl (12 mL) and the mixture was extracted with ethyl acetate (30 mL×2). The combined organic layers were washed with brine and dried over magnesium sulfate. After removal of the solvent, the residue was purified by flash column chromatography over silica gel (benzene–ethyl acetate gradient). Yields ranged 65—98%. For this reaction, the use of a large excess of methyl chloroformate (6 equiv) was essential. Otherwise, 3-hydroxy-4-pentenyl methyl carbonate was obtained as a major product. One typical example is shown below.

1-Vinyl-2,4-dioxaspiro[5.5]undecan-3-one (3a): To a solution of 1-[1-(hydroxymethyl)cyclohexyl]-2-propen-1-ol (1.18 g, 6.93 mmol) and triethylamine (7.73 mL, 55.4 mmol) in dry dichloromethane (30 mL) was added methyl chloroformate (3.21 mL, 41.6 mmol) at 0 °C over a 15 min period. Then the mixture was stirred at room temperature for 22 h. After standard work-up as described above, **3a** was afforded (1.33 g, 98% yield, R_f=0.41 in benzene : ethyl acetate=8 : 1) as an oil; IR (neat film) 2930 (s), 1745 (s), 1400 (m), 1105 (s), 990 (m), 770 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.10—1.87 (m, 10H), 4.06 (dd, J=1.2, 11.2 Hz, 1H), 4.37 (d, J=11.2 Hz, 1H), 4.65 (d, J=6.0 Hz, 1H), 5.27—5.53 (m, 2H), 5.90 (ddd, J=6.0, 8.8, 18.0 Hz, 1H). Found: C, 67.30; H, 8.10%. Calcd for $C_{11}H_{16}O_3$: C, 67.32; H, 8.22%.

4-(5,6-Dihydro-2*H*-pyran-3-yl)-1,3-dioxan-2-one (3b): Oil; IR (neat film) 2910 (m), 1740 (s), 1405 (s), 1245 (s), 1190 (s), 1100 (s), 960 (m), 760 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.00—2.35 (m, 4H), 3.77 (t, J=5.6 Hz, 2H), 4.11—4.25 (m, 2H), 4.34—4.55 (m, 2H), 4.86 (t, J=7.3 Hz, 1H), 5.91—6.08 (m, 1H). Found: C, 58.71; H, 6.59%. Calcd for $C_9H_{12}O_4$: C, 58.69; H, 6.57%.

5-Methyl-4-(5,6-dihydro-2*H*-pyran-3-yl)-1,3-dioxan-2-one (3c): A mixture of *cis* : *trans*=1.2 : 1.0; oil; IR (neat film) 2900 (s), 1740 (s), 1405 (s), 1200 (s), 1010 (m), 765 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.97 (d, J=6.6 Hz, 3H, Me of *cis* isomer), 1.07 (d, J=7.3 Hz, 3H, Me of *trans* isomer), 1.99—2.38 (m, 3H), 3.68—3.89 (m, 2H), 3.97—4.99 (m, 7H), 5.98 (m, 1H); ^{13}C NMR ($CDCl_3$) δ=9.4 (Me, *cis* isomer), 11.3 (Me, *trans* isomer), 24.1, 24.5, 28.4, 28.6, 63.3, 63.4, 63.6, 64.4, 80.2, 86.2, 121.2, 125.9, 131.9, 132.3, 147.6, 148.0. Found: C, 60.31; H, 7.23%. Calcd for $C_{10}H_{14}O_4$: C, 60.59; H, 7.12%.

4-(1-Isopropylvinyl)-1,3-dioxan-2-one (3d): Oil; IR (neat film) 2970 (m), 1740 (s), 1645 (w), 1405 (s), 1115 (s), 910 (m), 770 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.11 (d, J=6.8 Hz, 3H), 1.13 (d, J=6.8 Hz, 3H), 1.77—2.51 (m, 3H), 4.34—4.52 (m, 2H), 4.95 (dd, J=5.1, 8.3 Hz, 1H), 5.11—5.20 (m, 2H). Found: C, 63.48; H, 8.40%. Calcd for $C_9H_{14}O_3$: C, 63.51; H, 8.29%.

4-Methyl-4-vinyl-1,3-dioxan-2-one (3e): Oil; bp 120 °C (1 mmHg, 1 mmHg=133.322 Pa); IR (neat film) 2980 (m), 1740 (s), 1405 (m), 1276 (s), 1135 (s), 930 (m), 770 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.53 (s, 3H), 1.84—2.32 (m, 2H), 4.26—4.45 (m, 2H) 5.22—5.47 (m, 2H), 5.86 (dd, J=11.0, 16.4 Hz, 1H). Found: C, 59.20; H, 7.00%. Calcd for $C_7H_{10}O_3$: C, 59.14; H, 7.09%.

4-Vinyl-1,3-dioxan-2-one (3f): Oil; bp 130 °C (1 mmHg); IR (neat film) 2920 (w), 1740 (s), 1405 (s), 1195 (s), 1110 (s), 990 (m), 765 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.74—2.42 (m, 2H), 4.34—4.53 (m, 2H), 4.83—5.12 (m, 1H), 5.25—5.45 (m, 2H), 5.91 (ddd, J=5.9, 10.7, 16.6 Hz, 1H). Found: C, 56.04; H, 6.40%. Calcd for $C_6H_8O_3$: C, 56.24; H, 6.29%.

4-*t*-Butyl-6-vinyl-1,3-dioxan-2-one (3g): 1 : 1 Diastereomeric mixture; R_f=0.43 in benzene : ethyl acetate=8 : 1; IR (KBr disk) 2960 (m), 1745 (s), 1640 (w), 1380 (m), 1240 (s), 1200 (s), 1100 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.98 (s, 9H of one isomer), 1.00 (s, 9H of the other isomer), 1.62—2.34 (m, 2H), 4.00—4.27 (m, 1H), 4.71—5.01 (m, 1H of one isomer), 5.01—5.22 (m, 1H of the other isomer), 5.22—5.77 (m, 2H), 5.71—6.11 (m, 2H). Found: C, 65.23; H, 8.67%. Calcd for $C_{10}H_{16}O_3$: C, 65.19; H, 8.75%.

5-Benzyl-4-vinyl-1,3-dioxan-2-one (3h, R=H): A mixture of *cis* : *trans*=1.0 : 1.3; oil; IR (neat film) 2910 (m), 1740 (s), 1400 (m), 1200 (s), 1115 (s), 990 (m), 700 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.02—3.11 (m, 4H), 3.94—4.39 (m, 2H), 4.71 (t, J=6.1 Hz, 1H of *trans* isomer), 5.01 (br s, 1H of *cis* isomer), 5.31—5.62 (m, 2H), 5.70—6.19 (m, 1H), 7.07—7.46 (m, 5H). Found: C, 71.30; H, 6.50%. Calcd for $C_{13}H_{14}O_3$: C, 71.54; H, 6.47%.

5-Benzyl-4-isopropenyl-1,3-dioxan-2-one (3h, R=Me): A

mixture of *cis*:*trans*=1:1; oil; IR (neat film) 2920 (m), 2860 (m), 1750 (s), 1650 (w), 1400 (m), 1200 (s), 1130 (s), 910 (m), 700 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.72—1.87 (m, 3H, coalescing to a pair of s, 1.79 and 1.83, by irradiation at 5.15), 2.20—3.07 (m, 3H), 3.87—4.43 (m, 2H), 4.64 (d, J=7.6 Hz, 1H of *trans* isomer), 4.99 (br s, 1H of *cis* isomer), 5.07—5.38 (m, 2H), 7.04—7.43 (m, 5H); ^{13}C NMR ($CDCl_3$) δ=16.3, 18.6, 28.7, 33.5, 34.2, 34.5, 68.9, 69.2, 81.9, 86.0, 112.6, 116.6, 126.2, 126.5, 128.3, 128.5, 136.5, 137.4, 137.8, 139.2, 147.9, 148.2. Found: C, 72.60; H, 6.97%. Calcd for $C_{14}H_{16}O_3$: C, 72.39; H, 6.94%.

***cis*-5-Benzyl-4-[(*E*)-1-propenyl]-1,3-dioxan-2-one (3i):** Oil; IR (neat film) 1740 (s), 1670 (w), 1200 (s), 1100 (s), 965 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.83 (d, 3H, J=5.9 Hz), 2.17—2.99 (m, 3H), 4.02—4.40 (m, 2H), 4.92 (dd, J=2.9, 6.1 Hz), 5.59 (dd, J=6.1, 15.4 Hz, 1H), 5.92 (dq, J=15.4, 5.9 Hz) 7.05—7.42 (m, 5H); ^{13}C NMR ($CDCl_3$) δ=17.4, 30.8, 36.2, 68.5, 81.0, 123.7, 126.3, 128.2, 132.2, 137.8, 148.0.

***trans*-5-Benzyl-4-[(*E*)-1-propenyl]-1,3-dioxan-2-one (3j):** Oil; IR (neat film) 1745 (s), 1670 (w), 1200 (s), 1115 (s), 970 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.78 (d, J=6.1 Hz, 3H), 2.05—2.40 (m, 1H), 2.44 (dd, J=9.5, 13.4 Hz, 1H), 2.92 (dd, J=4.9, 13.4 Hz, 1H), 4.04 (dd, J=7.8, 11.1 Hz, 1H), 4.23 (dd, J=4.6, 11.1 Hz, 1H), 4.63 (t, J=7.6 Hz, 1H, coalescing to d, J=7.1 Hz, by irradiation at 5.49), 5.49 (ddd, J=1.0, 7.1, 15.1 Hz, 1H), 5.92 (dq, J=6.1, 15.1 Hz, 1H), 7.05—7.43 (m, 5H); ^{13}C NMR ($CDCl_3$) δ=16.9, 33.3, 36.9, 69.1, 83.1, 126.1, 126.5, 128.0, 128.2, 132.2, 136.5, 147.9. Found: C, 72.58; H, 6.78%. Calcd for $C_{14}H_{16}O_3$: C, 72.39; H, 6.94%.

5-Vinyl-2.4-dioxabicyclo[4.3.0]nonan-3-one (3k): *cis, cis* Isomer: Oil; R_f=0.52 (benzene:ethyl acetate=2:1); IR (neat film) 2955 (s), 2870 (w), 1740 (s), 1375 (m), 1200 (s), 1165 (w), 1080 (m), 765 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.63—2.23 (m, 6H), 2.23—2.60 (m, 1H), 4.89—5.15 (m, 2H), 5.23—5.56 (m, 2H), 5.85 (ddd, J=4.9, 10.0, 16.8 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ=21.9, 22.1, 33.6, 40.3, 77.5, 84.8, 117.6, 132.8, 149.2.

***trans, cis* Isomer:** Oil; R_f=0.61 (benzene:ethyl acetate=2:1); IR (neat film) 2960 (s), 1745 (s), 1370 (m), 1200 (s), 1080 (s), 940 (m), 765 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.08—2.49 (m, 11H), 4.04—4.42 (m, 1H), 4.84 (dd, J=6.1, 10.0 Hz, 1H, coalescing to d, J=10.0 Hz, by irradiation at 5.87), 5.22—5.54 (m, 1H), 5.87 (ddd, J=6.1, 10.0, 16.8 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ=19.5, 22.3, 28.0, 44.3, 81.6, 86.3, 118.3, 134.2. Found: C, 64.41; H, 7.21%. Calcd for $C_9H_{12}O_3$: C, 64.27; H, 7.19%.

5-Vinyl-2,4-dioxabicyclo[4.4.0]decan-3-one (3l): A mixture of three diastereomers (3:1:1), whose stereochemistry is unknown; oil; IR (neat film) 2910 (s), 1740 (s), 1640 (w), 1370 (m), 1195 (s), 990 (m), 765 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.85—2.35 (m, 9H), 3.89—4.31 (m, 1H), 4.31—5.24 (m, 1H of two minor isomers), 4.49 (dd, J=6.6, 10.3 Hz, 1H of a major isomer), 5.24—5.51 (m, 2H), 5.61—6.22 (m, 1H of two minor isomers), 5.80 (ddd, J=6.6, 8.8, 17.6 Hz, 1H of a major isomer); ^{13}C NMR ($CDCl_3$) δ= (major isomer) 22.9, 23.6, 25.1, 30.5, 79.6, 84.1, 118.9, 132.9, (minor isomers) 19.4, 22.8, 23.9, 24.7, 28.9, 30.9, 34.8, 39.6, 76.14, 80.8, 81.1, 116.9, 118.8, 131.4, 134.3.

4-[(1*E*,3*E*)-1,3-Pentadienyl]-1,3-dioxan-2-one (3m): Oil; IR (neat film) 2910 (s), 1740 (s), 1655 (m), 1405 (s), 1245 (s), 1190 (s), 1105 (s), 990 (s), 765 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.77 (d, J=5.9 Hz, 3H), 1.93—2.33 (m, 2H), 4.26—4.57 (m, 2H), 4.97 (pseudo dd, J=5.9, 12.5 Hz, 1H), 5.28—6.55 (m, 4H). Found: C, 64.41; H, 7.15%. Calcd for $C_9H_{12}O_3$: C, 64.27; H, 7.19%.

General Procedure for Decarboxylative Carbonylation of Cyclic Carbonate 3: Into a flask containing $Pd(PPh_3)_4$ (0.03 mmol), equipped with a rubber balloon filled with CO, was introduced a solution of carbonate **3** (1 mmol) in 5 mL of dry dioxane via a syringe. The mixture was stirred for the period of time and at the temperature indicated in Tables 1 and 2. Progress of the reaction was monitored with TLC. After evaporation of solvent, the residue was directly subjected to column chromatography over silica gel (benzene–ethyl acetate gradient). One typical example is as follows.

4-Vinyl-2-oxaspiro[4.5]decan-3-one (4a, Run 1, Table 1): Into a flask containing $Pd(PPh_3)_4$ (14.2 mg, 0.012 mmol)), equipped with a rubber balloon filled with CO, was introduced a solution of **3a** (80.4 mg, 0.410 mmol) in 2 mL of dry dioxane via a syringe. The mixture was stirred at room temperature for 3 h. The reaction was followed by means of TLC (**3a**, R_f=0.41; **4a**, R_f=0.65 in benzene:ethyl acetate=8:1). After evaporation of the solvent, the residue was directly subjected to column chromatography over silica gel (benzene–ethyl acetate gradient) to give **4a** as an oil (65.7 mg, 0.364 mmol, 89% yield); bp 130 °C (2 mmHg); IR (neat film) 2925 (s), 1775 (s), 1640 (w), 1140 (s), 1015 (s), 925 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.02—1.78 (m, 10H), 2.90 (d, J=8.0 Hz, 1H), 3.92 (d, J=8.8 Hz, 1H), 4.26 (d, J=8.8 Hz, 1H), 5.13—5.45 (m, 2H), 5.75 (ddd, J=8.0, 10.4, 16.4 Hz, 1H). Found: C, 73.54; H, 9.07%. Calcd for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95%.

(*E*)-4-Ethylidene-2-oxaspiro[4.5]decan-3-one (*E*-4a'): IR (neat film) 2910 (s), 2840 (m), 1740 (s), 1670 (m), 1220 (s), 960 (m), 735 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.04—2.12 (m, 10H), 1.98 (d, J=7.7 Hz, 3H), 4.13 (s, 2H), 6.82 (q, J=7.7 Hz, 1H). Found: C, 73.35; H, 9.11%. Calcd for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95%.

Ethyl (*E*)-4-[1-(Hydroxymethyl)cyclohexyl]-3-butenoate (8): Oil; bp 130 °C (2 mmHg); IR (neat film) 3450 (br s) 1735 (s), 1450 (m), 1370 (m), 1160 (m), 1030 (s), 970 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.16—1.78 (m, 10 H), 1.26 (t, J=7.1 Hz, 3H), 3.10 (d, J=5.9 Hz, 2H), 3.31 (s, 2H), 4.15 (q, J=7.1 Hz, 2H), 5.36 (d, J=16.2 Hz, 1H), 5.62 (dt, J=5.9, 16.2 Hz, 1H). Found: C, 68.94; H, 10.07. Calcd for $C_{13}H_{22}O_3$: C, 68.99; H, 9.80%.

2-(5,6-Dihydro-2*H*-pyran-3-yl)-γ-butyrolactone (4b): Oil; bp 160 °C (2 mmHg); IR (neat film) 2850 (m), 1770 (s), 1380 (m), 1160 (s), 1030 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.00—2.57 (m, 4H), 3.11 (t, J=9.0 Hz, 1H), 3.77 (t, J=5.6 Hz, 2H), 4.07—4.47 (m, 4H), 5.73—5.88 (m, 1H). Found: C, 64.36; H, 7.15%. Calcd for $C_9H_{12}O_3$: C, 64.27; H, 7.19%.

***cis*- and *trans*-2-(5,6-Dihydro-2*H*-pyran-3-yl)-3-methyl-γ-butyrolactone (4c):** A mixture of *cis*:*trans*=1:1.2; oil; bp 160 °C (2 mmHg); IR (neat film) 2940 (s), 1765 (s), 1380 (m), 1150 (s), 1105 (s), 1010 (s), 690 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.02 (d, J=6.8 Hz, 3H, Me of *trans* isomer), 1.14 (d, J=6.3 Hz, 3H, Me of *cis* isomer), 2.08—2.37 (m, 2H), 2.45—3.14 (m, 3H), 3.63—4.19 (m, 5H), 4.19—4.54 (m, 1H), 5.70—5.95 (m, 1H); ^{13}C NMR ($CDCl_3$) δ=13.6 (Me, *cis* isomer), 15.8 (Me, *trans* isomer), 25.0, 25.1, 33.9, 35.3, 47.0, 52.1, 63.8, 65.7, 67.3, 72.4, 72.6, 123.4, 124.2. Found: C, 65.89; H, 7.84%. Calcd for $C_{10}H_{14}O_3$: C, 65.91; H, 7.74%.

2-(1-Isopropylvinyl)-γ-butyrolactone (4d): R_f=0.58 (benzene:ethyl acetate=8:1); oil; bp 120 °C (9 mmHg); IR (neat film) 2950 (m), 1765 (s), 1640 (w), 1460 (m), 1370 (m), 1150 (s), 1020 (s), 950 (w), 900 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.11 (d, J=6.6 Hz, 6H), 2.07—2.71 (m, 3H), 3.23 (t, J=8.8 Hz, 1H), 4.19—4.48 (m, 2H), 4.99 (d, J=12.2 Hz, 1H), 5.00 (d,

J=12.2 Hz, 1H). Found: C, 69.85; H, 9.31%. Calcd for $C_9H_{14}O_2$: C, 70.10; H, 9.15%.

(*Z*)-2-(1,2-Dimethylpropylidene)-γ-butyrolactone (*Z*-4d'): R_f=0.64 (benzene : ethyl acetate=8 : 1); oil; IR (neat film) 2960 (m), 1750 (m), 1740 (s), 1460 (m), 1370 (m), 1200 (s), 1065 (s), 1035 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.02 (d, J=6.8 Hz, 6H), 1.77 (t, J=1.7 Hz, 3H), 2.84 (pseudo dd, J=1.7, 7.6 Hz, 2H), 4.29 (t, J=7.6 Hz, 2H), 4.40 (septet, J=6.8 Hz, 1H). Found: C, 69.98; H, 9.20%. Calcd for $C_9H_{14}O_2$: C, 70.10; H, 9.15%.

2-Methyl-2-vinyl-γ-butyrolactone (4e): Oil; bp 120 °C (16 mmHg); IR (neat film) 2980 (m), 1770 (s), 1640 (w), 1380 (m), 1185 (s), 1090 (s), 1030 (s), 930 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.36 (s, 3H), 1.95—2.52 (m, 2H), 4.13—4.38 (m, 2H), 5.07—5.31 (m, 2H), 5.89 (dd, J=10.0, 17.8 Hz, 1H). Found: C, 66.75; H, 8.08%. Calcd for $C_7H_{10}O_2$: C, 66.65; H, 7.99%.

2-Vinyl-γ-butyrolactone (4f): Oil; bp 110 °C (16 mmHg); IR (neat film) 2910 (w), 1765 (s), 1640 (w), 1375 (m), 1170 (m), 930 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=2.03—2.67 (m, 3H), 3.10—3.43 (m, 1H), 4.07—4.45 (m, 2H), 5.12—5.38 (m, 2H), 5.94 (ddd, J=5.9, 9.3, 17.8 Hz, 1H). Found: C, 64.22; H, 7.29%. Calcd for $C_6H_8O_2$: C. 64.27; H, 7.19%.

(*E*)-2-Ethylidene-γ-butyrolactone (*E*-4f'): Oil; IR (neat film) 2900 (m), 1750 (s), 1675 (m), 1370 (m), 1215 (s), 1130 (s), 1030 (s), 710 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ=1.87 (dt, J=7.1, 2.0 Hz, 3H), 2.85—2.91 (m, 2H), 4.38 (t, J=7.6 Hz, 2H), 6.78—6.85 (m, 1H).

2-[(2*E*)-5-Hydroxy-2-pentenyl]-2-vinyl-γ-butyrolactone (9): Oil; IR (neat film) 3100—3700 (br s), 2920 (s), 1760 (s), 1640 (w), 1375 (m), 1180 (s), 1030 (s), 930 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.69 (br s, 1H), 2.15—2.42 (m, 4H, 1'-H_2 and 4'-H_2), 2.23 (t, J=7.1 Hz, 2H), 3.64 (t, J=6.1 Hz, 2H, 5'-H_2), 4.25 (pseudo dt, J=2.0, 7.3 Hz, 2 H, 4-H_2), 5.07—5.32 (m, 2H), 5.42—5.60 (m, 2H), 5.89 (dd, J=10.5, 17.1 Hz); MS m/z (rel intensity, %) 166 (2), 112 (100), 67 (13), 55 (8). HRMS Found: m/z 166.0988. Calcd for $C_{11}H_{16}O_3$—CH_2O: M, 166.0994.

2-Vinyl-4-*t*-butyl-γ-butyrolactone (4g): Mixture of *cis* : *trans*=1 : 1; oil; bp 100 °C (4 mmHg); IR (neat film) 2950 (s), 1760 (s), 1640 (w), 1480 (w), 1365 (w), 1180 (s), 1000 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.96 (s, 9H of one isomer), 0.97 (s, 9H of the other isomer), 1.77—2.50 (m, 2H), 3.16—3.51 (m, 1H), 4.10 (pseudo t, J=5.3 Hz, 1H of one isomer), 4.22 (pseudo t, J=7.3 Hz, 1H of the other isomer), 4.39—5.10 (m, 2H), 5.70—6.21 (m, 1H); ^{13}C NMR ($CDCl_3$) δ=24.8 (Me of both isomers), 28.6, 29.6, 33.1, 33.8, 44.2, 44.7, 85.8, 86.0, 117.2, 117.7, 133.0, 133.3. Found: C, 71.59; H, 9.87%. Calcd for $C_{10}H_{16}O_2$: C, 71.39, H, 9.59%.

***trans*-3-Benzyl-2-vinyl-γ-butyrolactone (4h, R=H):** Oil; bp 160 °C (2 mmHg); IR (neat film) 2900 (m), 1770 (s), 1640 (w), 1015 (s), 925 (m), 700 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=2.50—3.11 (m, 4H), 3.93 (dd, J=8.1, 9.3 Hz, 1H), 4.26 (dd, J=6.6, 9.3 Hz, 1H), 5.17—5.43 (m, 2H), 5.80 (ddd, J=6.6, 10.7, 15.9 Hz, 1H), 7.05—7.44 (m, 5H); ^{13}C NMR ($CDCl_3$) δ=37.3, 43.2, 49.4, 70.9, 119.7, 126.7, 128.6, 131.6, 137.5, 176.3. Found: C, 77.08, H, 6.99%. Calcd for $C_{13}H_{14}O_2$: C, 77.20; H, 6.98%.

***trans*-3-Benzyl-2-isopropenyl-γ-butyrolactone (4h, R=Me):** Oil; bp 180 °C (2 mmHg); IR (neat film) 2910 (m), 1765 (s), 1640 (m), 1374 (m), 1150 (s), 1015 (s), 900 (s), 700 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.78 (dd, J=0.7, 1.5 Hz, 3H), 2.45—3.08 (m, 4H), 3.93 (pseudo t, J=9.5 Hz, 1H), 4.26 (dd, J=6.7, 9.4 Hz, 1H), 4.90—5.11 (m, 2H), 7.05—7.42 (m, 5H); ^{13}C NMR ($CDCl_3$) δ=19.6 (Me), 37.7, 41.6, 53.6, 70.9, 116.1, 126.6, 128.5, 137.6, 138.5. Found: C, 77.55; H, 7.46%. Calcd for $C_{14}H_{16}O_2$: C, 77.75; H, 7.46%.

***trans*-3-Benzyl-2-[(*E*)-1-propenyl]-γ-butyrolactone (4i):** Oil; IR (neat film) 2910 (m), 1765 (s), 1455 (m), 1240 (m), 1160 (s), 1015 (s), 695 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.75 (d, J=6.1 Hz, 3H), 2.49—3.13 (m, 4H), 3.92 (dd, J=8.8, 9.0 Hz, 1H), 4.27 (dd, J=6.3, 9.0 Hz, 1H), 5.36 (dd, J=7.1, 15.9 Hz, 1H), 5.72 (dq, J=15.9, 6.1 Hz, 1H), 7.04—7.43 (m, 2H); ^{13}C NMR ($CDCl_3$) δ=18.10 (q, C-3'), 37.60 (t, benzyl), 43.88 (d, C-3), 49.08 (d, C-2), 71.12 (t, C-4), 124.60 (d), 126.84 (d), 128.35 (d), 128.73 (d), 131.54 (d), 137.86 (s), 177.31 (d); MS m/z (rel intensity, %) 216 (M, 8), 185 (17), 143 (15), 125 (M—$PhCH_2$, 32), 91 ($PhCH_2$, 32), 81 (100). HRMS Found: m/z 216.1143. Calcd for $C_{14}H_{16}O_2$: M, 216.1149. Found: C, 77.52; H, 7.54%. Calcd for $C_{14}H_{16}O_2$: C, 77.75; H, 7.46%.

***cis*-3-Benzyl-2-[(*E*)-1-propenyl]-γ-butyrolactone (4j):** Oil; IR (neat film) 2910 (m), 1770 (s), 1660 (w), 1450 (m), 1160 (s), 1020 (s), 700 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.79 (d, J=5.6 Hz, 3H), 2.30—3.05 (m, 3H), 3.35 (pseudo t, J=7.3 Hz, coalescing to d, J=7.3 Hz, by irradiation at 5.47), 3.91—4.27 (m, 2H), 5.47 (dd, J=8.0, 15.4 Hz, 1H), 5.77 (dq, J=15.4, 5.6 Hz, 1H), 7.06—7.25 (m, 2H); ^{13}C NMR ($CDCl_3$) δ=18.0 (Me), 34.0 (benzyl), 42.1 (C-3), 47.2 (C-2), 70.2 (C-4), 121.7, 126.5, 128.6, 132.4, 138.8, 177.1; MS m/z (rel intensity, %) 216 (M, 11), 187 (7), 171 (4), 157 (7), 143 (20), 132 (23), 117 (14), 91 ($PhCH_2$, 100), 81 (80). HRMS Found: m/z 216.1142. Calcd for $C_{14}H_{16}O_2$: M, 216.1149.

***trans*-3-Benzyl-2-[(*Z*)-1-propenyl]-γ-butyrolactone (4j'):** Mp 98—103 °C (benzene–hexane, contaminated with a small amount of **4j**); IR (KBr disk) 2960 (m), 1760 (s), 1600 (w), 1440 (m), 1160 (s), 1010 (s), 705 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.69 (dd, J=2.0, 6.8 Hz, 3H), 2.41—3.05 (m, 3H), 3.27 (pseudo t, J=9.0 Hz, 1H, coalescing to d, J=9.3 Hz, by irradiation at 5.29), 3.95 (pseudo t, J=8.8 Hz, 1H), 4.32 (dd, J=7.0, 8.8 Hz, 1H), 5.29 (ddd, J=2.0, 9.0, 10.8 Hz, 1H), 5.85 (dq, J=10.8, 6.8 Hz, 1H), 7.3 (m, 5H); ^{13}C NMR ($CDCl_3$) δ=13.2 (Me), 37.8 (benzyl), 44.5 and 45.0 (C-2 and C-3), 71.1 (C-4), 124.2, 126.8, 128.6, 128.7, 130.4, 176.5. Found: C, 77.48; H, 7.46%. Calcd for $C_{14}H_{16}O_2$: C, 77.75; H, 7.46%.

***trans*-4-Vinyl-2-oxabicyclo[3.3.0]octan-3-one (4k):** Oil; bp 120 °C (2 mmHg); IR (neat film) 2950 (s), 1760 (s), 1640 (w), 1180 (s), 985 (s), 930 (w) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ=1.42—2.27 (m, 6H), 2.75—2.80 (m, 1H, C_3H), 3.01—3.04 (m, 1H, C_2H, coalescing to d, J=3.9 Hz, by irradiation at 5.90), 4.97—4.99 (m, 1H, C_4H, coalescing to d, J=6.3 Hz, by irradiation at 2.00, coalescing to dd, J=1.8, 5.6 Hz, by irradiation at 2.78), 5.22—5.31 (m, 2H), 5.89 (ddd, J=6.7, 10.3, 17.2 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ=23.2, 32.1, 33.0, 44.4, 51.5, 84.5, 117.1, 133.3. Found: C, 71.26; H, 7.93%. Calcd for $C_9H_{12}O_2$: C, 71.03; H, 7.95%.

2-(Propenylidene)cyclopentyl Formate (10): Oil; IR (neat film) 2940 (m), 2720 (m), 1725 (s), 1600 (m), 1410 (w), 1005 (s), 955 (m), 900 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.73 (pseudo quintet, J=6.8 Hz, 2H), 2.15 (pseudo q, J=6.8 Hz, 2H), 2.46 (pseudo t, J=6.8 Hz, 2H), 4.90—5.35 (m, 2H), 5.71 (dt, J=6.8, 14.6 Hz, 1H, coalescing to d, J=14.6 Hz, by irradiation at 2.15), 6.00—7.05 (m, 2H); ^{13}C NMR ($CDCl_3$) δ=21.4, 31.6, 43.0, 201.9; MS m/z (rel intensity, %) 124 (15), 105 (18), 80 (100), 57 (21). HRMS Found: m/z 124.0879. Calcd for $C_9H_{12}O_2$—CO: M, 124.0888.

9-Vinyl-7-oxabicyclo[4.3.0]nonan-8-one: Mixture of **4l**, **4l'**, and **4l''** in a ratio of 14 : 3 : 4; oil; bp 120 °C (2 mmHg);

^{1}H NMR ($CDCl_3$, 400 MHz) δ=1.22—2.07 (m, 8 H), 2.22—2.29 (m, 1H of **4l** and **4l′**, C_3H), 2.37 (pseudo quintet, *J*=6.1 Hz, 1H of **4l″**, C_3H), 2.91 (dd, *J*=7.3, 12.6 Hz, 1H of **4l**, coalescing to d, *J*=12.6 Hz, by irradiation at 5.82, C_2H), 3.07 (t, *J*=7.4 Hz, 1H of **4l″**, coalescing to d, *J*=7.4 Hz, by irradiation at 5.82, C_2H), 3.26 (t, *J*=7.2 Hz, 1H of **4l′**, coalescing to d, *J*=7.2 Hz, by irradiation at 5.82, C_2H), 3.80 (dt, *J*=3.7, 10.6 Hz, 1H of **4l**), 3.98 (dt, *J*=3.9, 11.2 Hz, 1H of **4l′**), 4.56 (dt, *J*=5.6, 7.0 Hz, 1H of **4l″**), 5.22—5.34 (m, 2 H), 5.72—5.86 (m, 1H of **4l′** and **4l″**), 5.81 (ddd, *J*=7.3, 10.5, 17.2 Hz, 1H of **4l**); ^{13}C NMR ($CDCl_3$) δ= (**4l**) 23.9, 25.1, 30.1, 50.0, 50.3, 82.5, 118.8, 132.1, 175.8; δ= (**4l′** and **4l″**) 20.8, 21.4, 23.8, 24.8, 25.6, 27.3, 28.3, 30.4, 40.3, 48.0, 49.0, 49.3, 81.8, 118.5, 119.3, 128.3, 131.9, 174.4, 176.2. Found: C, 72.25; H, 8.60%. Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49%.

2-[(1-*E*,3*E*)-1,3-Pentadienyl]-γ-butyrolactone (4m): Oil; bp 120 °C (2 mmHg); IR (neat film) 2900 (m), 1765 (s), 1655 (w), 1370 (m), 1145 (s), 1020 (s), 990 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.75 (d, *J*=5.6 Hz, 3H), 1.98—2.74 (m, 2H), 3.07—3.43 (m, 1H), 4.08—4.52 (m, 2H), 5.39—6.47 (m, 4H); MS *m*/*z* (rel intensity, %) 152 (86), 108 (8), 93 (100), 91 (15), 79 (36), 77 (24). HRMS Found: *m*/*z* 152.0819. Calcd for $C_9H_{12}O_2$: M, 152.0836. Found: C, 70.39; H, 8.10%. Calcd for $C_9H_{12}O_2$: C, 71.03; H, 7.95%.

General Procedure for Hydrogenation of Unsaturated Lactone: Into a flask containing Lindlar catalyst (about half the weight of the unsaturated lactone), equipped with a rubber balloon filled with hydrogen, was introduced a solution of unsaturated lactone (0.5 mmol) in 5 mL of dry benzene via a syringe. The mixture was stirred overnight at an ambient temperature and then filtered through cellulose powder. Evaporation of the solvent gave colorless oil, which was directly subjected to column chromatography over silica gel (benzene–ethyl acetate gradient).

***trans*-3-Benzyl-2-ethyl-γ-butyrolactone (*trans*-11):** Oil; R_f=0.61 (benzene : ethyl acetate=8 : 1); IR (neat film) 2960 (m), 1770 (s), 1455 (m), 1170 (s), 1020 (s), 705 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ=0.99 (t, *J*=7.5 Hz, 3 H), 1.65—1.73 (m, 2H), 2.27 (dt, *J*=8.5, 6.0 Hz, 1H, coalescing to d, *J*=8.5 Hz, by irradiation at 1.69), 2.53—2.64 (m, 1H), 2.69 (dd, *J*=9.0, 13.6 Hz, 1H of benzyl protons), 2.93 (dd, *J*=5.9, 13.6 Hz, 1H of benzyl protons), 3.90 (dd, *J*=7.8, 9.2 Hz, 1H), 4.23 (dd, *J*=7.4, 9.2 Hz, 1H), 7.13—7.27 (m, 5H); ^{13}C NMR ($CDCl_3$) δ=10.7 (C-2′), 21.9 (C-1′), 38.6 (benzyl), 41.5 (C-3), 46.1 (C-2), 70.6 (C-4), 126.5, 128.4, 138.0; MS *m*/*z* (rel intensity, %) 204 (M, 6), 176 (12), 113 (M−$PhCH_2$, 19), 91 ($PhCH_2$, 100), 85 (22). HRMS Found: *m*/*z* 204.1158. Calcd for $C_{13}H_{16}O_2$: M, 204.1150. Found: C, 76.57; H, 7.93%. Calcd for $C_{13}H_{16}O_2$: C, 76.44; H, 7.90%.

***cis*-3-Benzyl-2-ethyl-γ-butyrolactone (*cis*-11):** Oil; R_f=0.65 (benzene : ethyl acetate=8 : 1); IR (neat film) 2930 (m), 1775 (s), 1450 (m), 1170 (s), 1030 (m), 705 (s) cm^{-1}: ^{1}H NMR ($CDCl_3$, 400 MHz) δ=1.13 (t, *J*=7.5 Hz, 3H), 1.57—1.71 (m, 1H of CH_2CH_3), 1.97 (pseudo heptet, *J*=7.0 Hz, 1H of CH_2CH_3), 2.36 (dd, *J*=11.7, 13.6 Hz, 1H of benzyl protons), 2.59 (dt, *J*=6.6, 8.9 Hz, 1H), 2.76—2.85 (m, 1H), 2.88 (dd, *J*=4.5, 13.6 Hz, 1H of benzyl protons), 4.03 (pseudo d, 2H, *J*=4.0 Hz, 2H), 7.13—7.36 (m, 5H); ^{13}C NMR ($CDCl_3$) δ=11.7 (C-2′), 18.0 (C-1′), 32.5 (benzyl), 39.6 (C-3), 44.7 (C-2), 69.2 (C-4).

***trans*-3-Benzyl-2-propyl-γ-butyrolactone (*trans*-12):** Oil; IR (neat film) 2970 (m), 1780 (s), 1455 (m), 1170 (s), 1025 (s), 710 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.90 (t, *J*=7.1 Hz, 3H), 1.18—1.81 (m, 4H), 2.16—2.45 (m, 1H, C_2H), 2.45—3.12 (m, 3 H), 3.89 (dd, *J*=6.8, 9.3 Hz, 1H), 4.23 (dd, *J*=6.6, 9.3 Hz, 1H), 7.04—7.45 (m, 5H); ^{13}C NMR ($CDCl_3$) δ=13.5 (Me), 19.7 (C-2′), 31.3 (C-1′), 38.6 (benzyl), 42.1 (C-3), 44.6 (C-2), 70.6 (C-4), 126.48, 128.4, 137.8; MS *m*/*z* (rel intensity, %) 218 (M, 5), 176 (51), 127 (M−$PhCH_2$, 11), 91 ($PhCH_2$, 100), 85 (62). HRMS Found: *m*/*z* 218.1307. Calcd for $C_{14}H_{18}O_2$: M, 218.1307.

***cis*-3-Benzyl-2-propyl-γ-butyrolactone (*cis*-12):** Oil; IR (neat film) 2960 (m), 1775 (s), 1455 (m), 1170 (s), 1020 (m), 705 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.00 (t, *J*=7.1 Hz, 3H), 1.23—1.84 (m, 4H), 2.13—3.04 (m, 4H), 4.02 (pseudo d, *J*=3.4 Hz, 2H), 7.06—7.43 (m, 5H); ^{13}C NMR ($CDCl_3$) δ=13.7 (Me), 20.6 (C-2′), 26.7 (C-1′), 32.7 (benzyl), 40.0 (C-3), 43.2 (C-2), 69.4 (C-4). Found: C, 77.00; H, 8.18%. Calcd for $C_{14}H_{18}O_2$: C, 77.03; H, 8.31%.

General Procedure for Preparation of Cyclic Carbamate 5 (6-Vinyltetrahydro-2*H*-1,3-oxazin-2-one): The title compound was prepared according to the following two step reactions.

(1) *N*-Methoxycarbonyl-5-amino-1-penten-3-ol. To a solution of 5-amino-1-pentene-3-ol (10 mmol) and triethylamine (12 mmol) in dry dichloromethane (20 mL) was added methyl chloroformate (12 mmol) at 0 °C over 5 min period. Then the solution was stirred at room temperature for several hours. After evaporation of the solvent, 10 mL of water and 2 mol dm^{-3} HCl (2 mL) were added and the mixture was extracted with ethyl acetate (30 mL×2). The combined organic layer was washed with brine and dried over magnesium sulfate. Evaporation of the solvent afforded the title compound, pure enough for direct use in the next step.

(2) 6-Vinyltetrahydro-2*H*-1,3-oxazin-2-one (5). To a dry THF (20 mL) solution of crude *N*-methoxycarbonyl-5-amino-1-penten-3-ol (10 mmol) was added sodium hydride (12 mmol) portionwise with cooling in a water bath. The mixture was stirred at room temperature for several hours. After evaporation of the majority of the solvent, the mixture was diluted with ethyl acetate, washed with brine, and then dried over $MgSO_4$. After evaporation of the solvent, carbamate **5** was isolated by means of column chromatography over silica gel and/or recrystallization.

5,5-Dimethyl-6-vinyltetrahydro-2*H*-1,3-oxazin-2-one (5a): Mp 99—101 °C (benzene–hexane); IR (KBr disk) 3230 (s), 1690 (s), 1490 (m), 1415 (m), 1290 (s), 1130 (s), 1045 (m), 1005 (m), 960 (m), 750 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.02 (s, 6H), 2.88—3.22 (m, 2H), 4.40 (d, *J*=6.0 Hz, 1H), 5.25—5.51 (m, 2H), 5.86 (ddd, *J*=6.0, 9.0, 18.0 Hz, 1H), 6.22 (br s, 1H, NH); ^{13}C NMR ($CDCl_3$) δ=18.9, 23.2, 30.4, 51.1, 84.8, 119.0, 134.6, 154.1. Found: C, 61.88; H, 8.30; N, 9.30%. Calcd for $C_8H_{13}NO_2$: C, 61.91; H, 8.44; N, 9.03%.

5-Benzyl-6-vinyltetrahydro-2*H*-1,3-oxazin-2-one (5b): Mixture of *cis* : *trans*=1 : 1; oil; IR (neat film) 3250 (br s), 2920 (m), 1700 (s), 1485 (s), 1270 (m), 1110 (m), 700 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=2.24—3.40 (m, 5H), 4.57 (t, *J*=6.1 Hz, 1H of *trans* isomer), 4.82 (br s, 1H of *cis* isomer), 5.25—5.62 (m, 2H), 5.68—6.19 (m, 2 H), 7.01—7.44 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ=32.3, 35.1, 35.8, 36.3, 41.2, 41.8, 78.9, 80.5. Found: C, 71.61; H, 6.71; N, 6.60%. Calcd for $C_{13}H_{15}NO_2$: C, 71.87; H, 6.96; N, 6.45%.

6-Isopropenyltetrahydro-2*H*-1,3-oxazin-2-one (5c): Mp 118—120 °C (benzene–hexane); IR (KBr disk) 3300 (s), 2980 (m), 1660 (s), 1480 (s), 1295 (s), 1140 (s), 920 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.80 (s, 3H), 1.89—2.13 (m, 2H), 3.25—3.48 (m, 2H), 4.69 (dd, *J*=4.9, 7.8 Hz, 1H), 4.95—5.12 (m, 2H), 5.80 (br s, 1H, NH). Found: C, 59.50; H, 7.93; N, 9.78%. Calcd for

$C_7H_{11}NO_2$: C, 59.56; H, 7.85; N, 9.92%.

***cis*-4-Phenyl-6-vinyltetrahydro-2*H*-1,3-oxazin-2-one (5d):** IR (neat film) 3210 (s), 1695 (s), 1400 (s), 1300 (s), 1040 (s), 930 (m), 755 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.61—2.44 (m, 2H), 4.64 (dd, J=4.9, 11.5 Hz, 1H), 4.75—5.01 (m, 1H), 5.11—5.55 (m, 2H), 5.93 (ddd, J=5.4, 10.0, 16.8 Hz, 1H), 7.36 (s, 5H); ^{13}C NMR ($CDCl_3$) δ=36.6, 55.0, 76.8, 117.0, 125.7, 128.0, 128.7, 134.0, 140.4. Found: C, 71.01; H, 6.58; N, 6.77%. Calcd for $C_{12}H_{13}NO_2$: C, 70.92; H, 6.44; N, 6.89%.

6-Vinyltetrahydro-2*H*-1,3-oxazin-2-one (5e): Mp 59—61 °C (benzene–hexane); IR (KBr disk) 3300 (br), 2980 (m), 1700 (s), 1300 (s), 1140 (m), 940 (m), 775 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.59—2.28 (m, 2H), 3.26—3.48 (m, 2H), 4.67—4.93 (m, 1H), 5.18—5.54 (m, 2H), 5.92 (ddd, J=4.9, 10.3, 17.1 Hz, 1H), 6.27 (br s, 1H, NH). Found: C, 56.91; H, 7.04; N, 11.11%. Calcd for $C_6H_9NO_2$: C, 56.68; H, 7.14; N, 11.02%.

3-Benzyl-5,5-dimethyl-6-vinyltetrahydro-2*H*-1,3-oxazin-2-one (5f): To a solution of **5a** (767 mg, 4.94 mmol) in dry THF (10 mL) was added sodium hydride (60% assay in mineral oil, 240 mg, 6.0 mmol) under water bath cooling, and the mixture was stirred for 1 h. Then benzyl bromide (0.71 mL, 6.0 mmol) was added, and the mixture was stirred at room temperature for 1 d. After neutralization with 1 mol dm^{-3} HCl, the mixture was extracted with ethyl acetate (30 mL×2). The combined extracts were washed with brine and dried over magnesium sulfate. Evaporation of the solvent followed by purification by means of column chromatography over silica gel gave **5f** in 87% yield: Oil; IR (neat film) 2960 (m, 1690 (s), 1485 (m), 1255 (m), 1200 (m), 1100 (m), 1010 (m), 700 (s) cm^{-1}; ^1H NMR ($CDCl_3$) =0.91 (s, 3H), 0.94 (s, 3H), 2.79 (d, J=11.7 Hz, 1H), 2.99 (d, J=11.7 Hz, 1H), 4.38 (d, J=5.4 Hz, 1H), 4.48 (d, J=14.9 Hz, 1H), 4.66 (d, J=14.9 Hz, 1H), 5.24—5.51 (m, 2H), 5.81 (ddd, J=5.4, 8.9, 16.8 Hz, 1H), 7.31 (s, 5H). Found: C, 73.30; H, 7.98; N, 5.60%. Calcd for $C_{15}H_{19}NO_2$: C, 73.44; H, 7.81; N, 5.71%.

5,5-Dimethyl-3-tosyl-6-vinyltetrahydro-2*H*-1,3-oxazin-2-one (5g): This was obtained in 80% yield according to a procedure similar to the preparation of **5f**; mp 87.5—89.5 °C (benzene–hexane); IR (KBr disk) 2960 (s), 1720 (s), 1340 (m), 1160 (s), 920 (m), 750 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.96 (s, 3H), 1.06 (s, 3H), 2.43 (s, 3H), 3.54 (d, J=12.0 Hz, 1H), 3.80 (d, J=12.0 Hz, 1H), 4.42 (d, J=5.9 Hz, 1H), 5.19—5.44 (m, 2H), 5.87 (ddd, J=5.9, 8.5, 17.8 Hz, 1H), 7.90 (d, J=8.5 Hz, 2H), 8.31 (d, J=8.5 Hz, 2H). Found: C, 58.41; H, 6.30; N, 4.51; S, 10.61%. Calcd for $C_{15}H_{19}NO_4S$: C, 58.23; H, 6.19; N, 4.53; S, 10.36%.

3-Benzoyl-5,5-dimethyl-6-vinyltetrahydro-2*H*-1,3-oxazin-2-one (5h): This was obtained in 64% yield according to a procedure similar to the preparation of **5f**; IR (KBr disk) 2980 (m), 1730 (s), 1690 (s), 1410 (m), 1300 (m), 1200 (m), 990 (m), 810 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.11 (s, 3H), 1.13 (s, 3H), 3.51, (d, J=12.7 Hz, 1H), 3.76 (d, J=12.7 Hz, 1H), 4.58 (d, J=6.1 Hz, 1H), 5.32—5.59 (m, 2H), 5.91 (ddd, J=6.1, 9.0, 17.8 Hz, 1H), 7.29—7.70 (m, 5H). Found: C, 69.18; H, 6.68; N, 5.31%. Calcd for $C_{15}H_{17}NO_3$: C, 69.48; H, 6.61; N, 5.41%.

3-Benzoyl-5-benzyl-6-vinyltetrahydro-2*H*-1,3-oxazin-2-one (5i): Mixture of *cis*:*trans*=1:1; oil; IR (neat film) 2940 (m), 1735 (s), 1690 (s), 1400 (m), 1290 (s), 1165 (s), 695 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.23—3.16 (m, 3H), 3.42—4.11 (m, 2H), 4.71 (t, J=6.6 Hz, 1H of *trans* isomer), 4.88—5.03 (m, 1H of *cis* isomer), 5.36—5.69 (m, 2 H), 5.77—6.31 (m, 1H), 7.10—7.65 (m, 10H); ^{13}C NMR ($CDCl_3$) δ=33.1, 35.6, 37.0, 38.0, 45.1, 45.5, 80.1, 81.9, 119.4, 120.0, 127.5, 127.6, 128.5, 128.6, 130.8, 131.2, 133.7, 137.0, 137.3, 150.4, 150.7, 172.5. Found: C, 74.88; H, 5.99; N, 4.13%. Calcd for $C_{20}H_{19}NO_3$: C, 74.75; H, 5.96; N, 4.36%.

General Procedure for Decarboxylative Carbonylation of Cyclic Carbamate 5: Into a flask containing $Pd(OAc)_2(PPh_3)_2$ (0.03 mmol), equipped with a rubber balloon filled with CO, was introduced a solution of a carbamate **5** (1 mmol) in 5 mL of dry ethanol via a syringe. The mixture was stirred for the period of time and at the temperature indicated in Table 3. After evaporation of the solvent, the residue was directly subjected to column chromatography over silica gel (benzene–ethyl acetate gradient). One typical example is given below.

3-Benzyl-2-vinyl-γ-butyrolactam (7b): Reacted were $Pd(OAc)_2(PPh_3)_2$ (16.8 mg, 0.024 mmol), CO, and **5b** (162 mg, 0.746 mmol) in 4 mL of dry ethanol. The mixture was stirred for 24 h at room temperature, then 38 h at 60 °C. It is rather difficult to follow the reaction by TLC (**5b**, R_f=0.50; **7b**, R_f=0.45 in ethyl acetate). The reaction was followed more accurately by examining a small aliquot of the reaction mixture by means of ^1H NMR. After evaporation of the solvent, the residue was directly subjected to column chromatography over silica gel (benzene–ethyl acetate gradient) to afford **7b** in 48% yield; mp 66—67 °C (benzene–hexane); IR (KBr disk) 3200 (br), 2880 (m), 1700 (s), 1645 (w), 1495 (s), 1455 (s), 1280 (s), 985 (s), 930 (s), 760 (s), 710 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.38—3.41 (m, 4H), 5.10—5.36 (m, 2H), 5.80 (ddd, J=7.1, 8.5, 18.6 Hz, 1H), 6.44 (br s, 1H, NH), 7.06—7.39 (m, 5H); ^{13}C NMR ($CDCl_3$) δ=38.9, 42.9, 45.7, 51.5, 118.2, 126.2, 128.3, 128.6, 131.1, 138.8, 177.4. Found: C, 77.49; H, 7.50; N, 6.83%. Calcd for $C_{13}H_{15}NO$: C, 77.58; H, 7.51; N, 6.96%.

3,3-Dimethyl-2-vinyl-γ-butyrolactam (7a): Mp 116—118 °C (benzene–hexane); IR (KBr disk) 3200 (s), 2960 (m), 1690 (s), 1365 (m), 1130 (m), 925 (s), 790 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.03 (s, 3H), 1.15 (s, 3H), 2.72 (d, J=8.5 Hz, 1H), 2.96—3.23 (m, 2H), 5.10—5.42 (m, 2H), 5.87 (ddd, J=8.5, 10.5, 16.1 Hz, 1H), 6.37 (br, 1H, NH); ^{13}C NMR ($CDCl_3$) δ=22.6, 26.4, 40.4, 54.2, 57.6, 120.6, 131.2, 178.1; MS m/z (rel intensity, %) 139 (M, 50), 124 (7), 96 (38), 84 (75), 82 (34), 81 (100), 72 (15). HRMS Found: m/z 139.0998. Calcd for $C_8H_{13}NO$: M, 139.0997. Found: C, 67.89; H, 9.62; N, 9.89%. Calcd for $C_8H_{13}NO$: C, 69.03; H, 9.41; N, 10.06%.

2-Isopropenyl-γ-butyrolactam (7c): Mp 38—42 °C (benzene–hexane); bp 150 °C (1 mmHg); IR (KBr disk) 3230 (br s), 2950 (m), 1680 (s), 1370 (s), 1280 (s), 1070 (m), 905 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.79 (s, 3H), 1.94—2.51 (m, 2 H), 3.11 (t, J=8.6 Hz, 1H), 3.36 (t, J=6.1 Hz, 2H), 4.87—5.01 (m, 2H), 6.86 (br 1H, NH); ^{13}C NMR ($CDCl_3$) δ=19.6, 26.6, 40.5, 49.1, 113.8, 142.0, 178.2; MS m/z (rel intensity, %) 125 (M, 97), 96 (5), 84 (15), 69 (39), 67 (100). HRMS Found: m/z 125.0857. Calcd for $C_7H_{11}NO$: M, 125.0841. Found: C, 66.90; H, 8.92; N, 11.04%. Calcd for $C_7H_{11}NO$: C, 67.17; H, 8.86; N, 11.19%.

4-Phenyl-2-vinyl-γ-butyrolactam (7d): Two diastereomers were separated by column chromatography:

One Isomer: R_f=0.58 (benzene–ethyl acetate, 1:1); mp 76—78 °C (benzene–hexane); IR (KBr disk) 3230 (br s), 1690 (s), 1460 (m), 1120 (m), 930 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.88 (ddd, J=9.0, 10.7, 12.7 Hz, 1H), 2.75 (ddd, J=6.6, 8.3, 12.7 Hz, 1H), 3.24 (pseudo q, J=8.9 Hz, 1H), 4.69 (dd, J=6.3, 8.8 Hz, 1H), 5.06—5.32 (m, 2H), 5.99 (ddd, J=6.3, 9.0, 18.1 Hz, 1H), 7.34 (s, 5H); ^{13}C NMR ($CDCl_3$) δ=38.1, 46.2, 56.4, 117.3, 125.8, 128.0, 128.8, 131.8, 134.9; MS m/z (rel intensity, %) 187 (M,

32), 144 (79), 129 (100), 105 (15).

The Other Isomer: R_f=0.68 (benzene–ethyl acetate, 1 : 1; mp 146—148 °C (benzene–hexane); IR (KBr disk) 3250 (s), 1700 (m), 1660 (s), 1455 (m), 1030 (m), 925 (s), 750 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.22 (ddd, J=5.1, 9.0, 12.9 Hz, 1H), 2.55 (dt, J=7.3, 12.9 Hz, 1H), 3.25 (pseudo q, J=7.1 Hz, 1H), 4.76 (dd, J=5.1, 8.1 Hz, 1H), 5.10—5.38 (m, 2H), 5.95 (ddd, J=6.6, 9.5, 17.8 Hz, 1H), 7.32 (s, 5H); ^{13}C NMR ($CDCl_3$) δ=37.2, 44.3, 55.8, 117.1, 125.4, 127.8, 128.9, 134.6; MS m/z (rel intensity, %) 187 (M, 36), 144 (72), 129 (100), 105 (13). HRMS Found: m/z 187.1002. Calcd for $C_{12}H_{13}NO$: M, 187.0997. Found: C, 76.33; H, 6.92; N, 7.45%. Calcd for $C_{12}H_{13}NO$: C, 76.98; H, 7.00; N, 7.48%.

2-Vinyl-γ-butyrolactam (7e): Oil IR (neat film) 3280 (br s), 2900 (m), 1700 (s), 1450 (w), 1285 (m), 1065 (m), 920 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.51—2.57 (m, 2H), 3.07 (pseudo q, J=8.0 Hz, 1H), 3.24—3.48 (m, 2H), 5.08—5.34 (m, 2H), 5.92 (ddd, J=6.6, 9.8, 17.6 Hz, 1H), 7.26 (br s, 1H); MS m/z (rel intensity, %) 111 (M, 100), 84 (34), 82 (70). HRMS Found: m/z 111.0688. Calcd for C_6H_9NO: M, 111.0684.

Ethyl *N*-Tosyl-5,5-dimethyl-6-amino-3-hexenoate (6g): Oil; bp 220 °C (1 mmHg); IR (neat film) 3280 (m), 2960 (s), 1735 (s), 1330 (s), 1160 (s), 1095 (m), 660 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.00 (s, 6H), 1.27 (t, J=7.1 Hz, 3H), 2.42 (s, 3H), 2.72 (d, J=6.6 Hz, 2H, coalescing to s by irradiation at 4.54; coalescing to s by addition of D_2O), 2.98 (d, J=6.1 Hz, 2H, coalescing to s by irradiation at 5.56), 4.15 (q, J=7.1 Hz, 2H), 4.54 (t, J=6.1 Hz, 1H, NH), 5.32 (d, J=15.9 Hz, 1H), 5.56 (dt, J=15.9, 6.1 Hz, 1H), 7.29 (d, J=9.0 Hz, 2H), 7.73 (d, J=9.0 Hz, 2H); MS m/z (rel intensity, %) 294 (M−EtO, 28), 250 (5), 184 (M−Ts, 83), 155 (Ts, 100), 91 ($PhCH_2$, 72). Found: C, 60.35; H, 7.48; N, 4.16; S, 9.46%. Calcd for $C_{17}H_{25}NO_4S$: C, 60.15; H, 7.42; N, 4.13; S, 9.44%.

Ethyl 6-Benzoylamino-5,5-dimethyl-3-hexenoate (6h): Oil; bp 200 °C (1 mmHg); IR (neat film) 3350 (br s), 2980 (s), 1735 (s), 1640 (s), 1540 (s), 1300 (s), 1180 (s), 1030 (m), 970 (m), 710 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.10 (s, 6H), 1.23 (t, J=7.1 Hz, 3H), 3.02—3.29 (m, 2H, coalescing to s by irradiation at 5.57), 3.35 (d, J=6.1 Hz, 2H, coalescing to s by irradiation at 6.33), 4.13 (q, J=7.1 Hz, 2H), 5.51—5.63 (m, 2H), 6.33 (br, 1H, NH), 7.32—7.53 (m, 3H), 7.72—7.88 (m, 2H). Found: C, 70.26; H, 7.89; N, 4.82%. Calcd for $C_{17}H_{23}NO_3$: C, 70.56; H, 8.01; N, 4.84%.

Ethyl 6-Benzoylamino-5-benzyl-3-hexenoate (6i): Oil; IR (neat film) 3300 (br, s) 2930 (m), 1735 (s), 1640 (s), 1535 (s), 1290 (s), 1180 (s), 1030 (m), 965 (m), 700 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.20 (t, J=7.1 Hz, 3H), 2.50—3.36 (m, 3H), 2.72 (m, 2H), 3.01 (d, J=5.6 Hz, 2H, coalescing to s by irradiation at 5.54), 3.52—3.90 (m, 2H), 4.08 (q, J=7.1 Hz, 2H), 5.28—5.80 (m, 2H), 6.32 (br, 1H, NH), 7.03—7.52 (m, 8H), 7.63—7.84 (m, 2H). Found: C, 75.30; H, 7.15; N, 4.10%. Calcd for $C_{22}H_{25}NO_3$: C, 75.19; H, 7.17; N, 3.99%.

***trans*-3-Benzyl-2-ethyl-γ-butyrolactam (*trans*-13):** This was obtained by the hydrogenation of **7b** according to a similar procedure for hydrogenation of unsaturated lactones, described above; oil IR (neat film) 3250 (br s), 2930 (s), 1695 (s), 1495 (m), 1455 (m), 1280 (m), 1070 (m), 700 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.95 (t, J=6.8 Hz, 3 H), 1.46—1.83 (m, 2H), 2.10 (pseudo q, J=6.3 Hz, 1H, coalescing to d, J=6.8 Hz, by irradiation at 1.63), 2.31—3.41 (m, 5H), 5.89 (br s, 1H, NH), 7.07—7.39 (m, 5H); ^{13}C NMR ($CDCl_3$) δ=10.7, 22.2, 40.1, 40.7, 45.7, 47.8, 126.1, 128.2, 128.4, 139.0, 179.9; MS m/z (rel intensity, %) 203 (M, 13), 175 (15) 112 (26), 91 ($PhCH_2$, 72), 84 (100). HRMS Found: m/z 203.1324. Calcd for $C_{13}H_{17}NO$: M, 203.1310. Found: C, 76.99; H, 8.45; N, 6.71%. Calcd for $C_{13}H_{17}NO$: C, 76.81; H, 8.43; N, 6.89%.

Partial financial supports from the Ministry of Education, Science and Culture, Yamada Science Foundation, and Ciba-Geigy Foundation are gratefully acknowledged. The authors also thank Dr. Makoto Hojo (Tsukuba University) for partial experimental assistance and Mr. Yushichiro Ohama (Nagasaki University) for NMR measurement (400 MHz).

References

1) H. M. R. Hoffmann and J. Rabe, *Angew. Chem., Int. Ed. Engl.*, **24**, 94 (1985).

2) a) Y. Tamaru and Z. Yoshida, *J. Organomet. Chem.*, **334**, 213 (1987); b) Y. Tamaru, M. Hojo, and Z. Yoshida, *J. Org. Chem.*, **56**, 1099 (1991).

3) Y. Tamaru, T. Bando, M. Hojo, and Z. Yoshida, *Tetrahedron Lett.*, **28**, 3497 (1987).

4) Y. Tamaru, T. Kobayashi, S. Kawamura, H. Ochiai, M. Hojo, and Z. Yoshida, *Tetrahedron Lett.*, **26**, 3207 (1985); b) Y. Tamaru, T. Kobayashi, S. Kawamura, H. Ochiai, and Z. Yoshida, *ibid.*, **26**, 4479 (1985); c) Y. Tamaru, H. Higashimura, K. Naka, M. Hojo, and Z. Yoshida, *Angew. Chem., Int. Ed. Engl.*, **24**, 1045 (1985); d) Y. Tamaru, M. Hojo, and Z. Yoshida, *J. Org. Chem.*, **53**, 5731 (1988).

5) a) J. Tsuji, K. Sato, and H. Okumoto, *Teterahedron Lett.*, **23**, 5189 (1982). b) J. Tsuji, K. Sato, and H. Okumoto, *J. Org. Chem.*, **49**, 1341 (1984).

6) a) W. T. Dent, R. Long, and G. H. Whitfield, *J. Chem. Soc.*, **1964**, 1588; b) J. Tsuji, J. Kiji, S. Imamura, and M. Morikawa, *J. Am. Chem. Soc.*, **86**, 4350 (1964); c) D. Medema, R. van Helden, and C. F. Kohll, *Inorg. Chim. Acta*, **3**, 255 (1969).

7) F. Johnson, *Chem. Rev.*, **68**, 375 (1968).

8) For the regio- and stereoselective protonation and alkylation of conjugate ester enolates, see a) A. S. Kende and B. H. Toder, *J. Org. Chem.*, **47**, 163 (1982); b) Y. Ikeda and H. Yamamoto, *Teterahedron Lett.*, **25**, 5181 (1984).

9) For the stereochemistry of pentadienyl anions, see a) W. Oppolzer and R. L. Snowden, *Teterahedron Lett.*, **17**, 4187 (1976); b) S. R. Wilson and D. T. Mao, *J. Am. Chem. Soc.*, **100**, 6289 (1978); c) S. R. Wilson and R. N. Misra, *J. Org. Chem.*, **45**, 5079 (1980).

10) For a similar isomerization of alkoxypalladium, see T. Fujinami, T. Suzuki, M. Kamiya, S. Fukuzawa, and S. Sakai, *Chem. Lett.*, **1985**, 199.

11) R. F. Heck, "Palladium Reagents in Organic Syntheses," Academic Press, London (1985). See, also H. Kurosawa, S. Ogoshi, Y. Kawasaki, S. Murai, M. Miyoshi, and I. Ikeda, *J. Am. Chem. Soc.*, **112**, 2813 (1990).

12) a) J. A. Marshall, T. R. Konicek, and K. E. Flynn, *J. Am. Chem. Soc.*, **102**, 3287 (1980); b) U. H. Andrews, J. E. Baldwin, and M. W. Grayston, *J. Org. Chem.*, **47**, 287 (1982); c) R. Isaksson, J. Roschester, J. Sandstrom, and L.-G. Wistrand, *J. Am. Chem. Soc.*, **107**, 4074 (1985).

13) S. Murahashi and Y. Imada, *Chem. Lett.*, **1985**, 1477.

14) For a palladium(0)-catalyzed reaction of *N*-alkyl and *N,N*-dialkyl substituted allyl carbamates, see I. Minami, Y. Ohashi, I. Shimizu, and J. Tsuji, *Tetrahedron Lett.*, **26**, 2449

(1985).
15) A. Gaudemer, "Determination of Configuration by NMR Spectroscopy," in "Stereochemistry," ed by H. B. Kagan, Georg Thieme, Stuttgart (1977), Vol. 1.
16) G. C. Levy, R. L. Lichter, and G. L. Nelson, "Carbon-13 Nuclear Magnetic Resonance Spectroscopy," 2nd ed, John Wiley & Sons, New York (1980).
17) H. Yoshimoto and H. Itatani, *Bull. Chem. Soc. Jpn.*, **46**, 2490 (1973).
18) T. Ukai, H. Kawazura, and Y. Ishii, *J. Organomet. Chem.*, **65**, 253 (1974).
19) Y. Tamaru, M. Hojo, S. Kawamura, S. Sawada, and Z. Yoshida, *J. Org. Chem.*, **52**, 4062 (1987).
20) Y. Tamaru, S. Kawamura, T. Bando, K. Tanaka, M. Hojo, and Z. Yoshida, *J. Org. Chem.*, **53**, 5491 (1988).