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Ruthenium-Catalyzed Cyclocarbonylation of Allenyl Alcohols and Amines: Selective Synthesis of Lactones and Lactams

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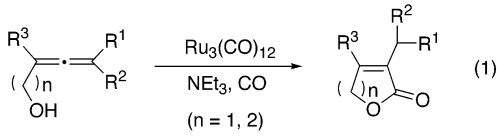
Allenyl alcohols such as 4-hydroxybuta-1,2-dienes and 5-hydroxypenta-1,2-dienes having a variety of substituents undergo cyclocarbonylation in the presence of a ruthenium catalyst under mild conditions selectively to give five- and six-membered lactones in a high yield with 100% atom economy. 5-Aminopenta-1,2-dines are also cyclocarbonylated to give γ-lactams. A possible carbonylation mechanism involving a ruthenium cluster intermediate is proposed on the basis of experimental results.

Introduction

Carbonylation reactions have a long history and still attract much attention in both academic and industrial fields.[1] The innovation of new types of carbonylations has always provided us new methods for efficient syntheses of a variety of useful compounds. Carbonylations of alkenes and alkynes in the presence of nucleophiles such as alcohols and amines often afford carboxylic acid derivatives. Carbonylations of such unsaturated substrates bearing hydroxyl and amino groups at a position neighboring the unsaturated carbon−carbon bond result in intramolecular cyclization, so-called cyclocarbonylation, to give lactones and lactams. The cyclocarbonylations continue to be a challenging area in synthetic organic chemistry since heterocyclic compounds are produced directly from such unsaturated compounds.[2] Previously, we have shown that alkynes bearing adjacent functional groups such as *ortho*-alkynylphenols[3] and *ortho*-anilines[4] undergo cyclocarbonylation by the catalysis of rhodium carbonyls under water−gas shift reaction conditions to produce various heterocyclic compounds such as benzofuranones and dihydroindolones. Recently, we have extended the Rh-catalyzed carbonylation of alkynes to dienes giving polyketones[5] and have now found a new catalytic system that is effective for the cyclocarbonylation of allenes. Although Rh-catalyzed reactions of allenes with carbon monoxide caused polymerization to give 1:1 alternating polymers,[6] we have now found that allenyl alcohols undergo cyclocarbonylation by the catalysis of a ruthenium complex to give lactones in excellent yields. Interestingly, five- and six-membered lactones can be prepared directly from 4-hydroxybuta-1,2-diene and 5-hydroxypenta-1,2-diene, respectively. The present carbonylation may be characterized by high selectivity and yield with atom economy of 100%. The preliminary result has already been communicated,[7] and herein full details on the scope and mechanism of the cyclocarbonylation are described. Application of the carbonylation to allenylamines giving lactams is also reported.



(1)

Results and Discussion

Carbonylation of Allenyl Alcohols. Cyclocarbonylations of alkenes and alkynes giving lactones have been extensively studied,[8] whereas the carbonylation of allenes has been directed to the preparation of methacrylates[9] and there have been no reports so far on the synthesis of lactones from allenes in the literature. In the course

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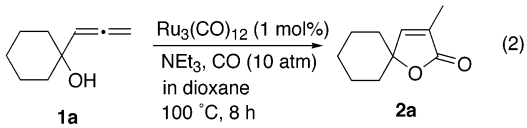
of our studies on rhodium-catalyzed cyclocarbonylation of functionalized alkynes, we have found that ruthenium carbonyls were not effective for the carbonylation of alkynes but catalyze a new cyclocarbonylation of allenyl alcohols exclusively to give lactones. Thus, a simple reaction of 1-propa-1,2-dienylcyclohexan-1-ol **1a** (1 mmol) with 10 atm of carbon monoxide in the presence of $Ru_3(CO)_{12}$ (0.01 mmol) and NEt_3 (0.2 mL) in 1,4-dioxane (15 mL) at 100 °C for 8 h gave a single product (**2a**), which showed an *M*/*z* of 166 (M^+) corresponding to the sum of the mass number of 138 (**1a**) and 28 (CO) and was identified to be 3-methyl-1-oxaspiro[4.5]dec-3-en-2-one[10] by IR and ^1H and ^{13}C NMR spectra. Product **2a** was isolated in 95% yield after simple purification by column chromatography on silica gel.

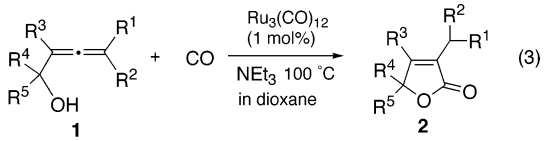


1a 2a (2)

Carbonylation reactions at lower temperatures of 50 and 80 °C gave **2a** in 17 and 75% yields, and 80 and 20% of starting substrate **1a** were recovered, respectively. At 100 °C even under atmospheric pressure of carbon monoxide, the carbonylation took place to give **2a**, though the yield decreased to 62%.

We examined catalytic activities of other metal carbonyl complexes such as $Co_2(CO)_8$, $Fe_3(CO)_{12}$, $Os_3(CO)_{12}$, and $Rh_6(CO)_{16}$, which are effective for the carbonylation of alkenes and alkynes, but all of the complexes were inactive for the cyclocarbonylation of **1a**. Only ruthenium complexes showed a catalytic activity toward the present reaction. Ruthenium complexes such as $RuCl_3$ and $[RuCl_2(CO)_3]_2$ showed a definite activity to give **2a** in 82 and 92% yield, respectively; however, $RuCl_2(PPh_3)_2$ and $RuClH(CO)(PPh_3)_3$ are almost inactive. In the absence of NEt_3, **1a** was completely consumed; however, the yield of **2a** was reduced to 68%, and an isomer of **2a** was formed as a byproduct (vide infra). As a base, tertiary amines such as Et_3N and $^tBu_3N$ gave a good effect, whereas use of secondary and primary amines such as $HNEt_2$ and H_2NBu decreased the selectivity for **2a** ($HNEt_2$, 56; H_2NBu, 56% yield) and afforded amido derivatives as a byproduct. Addition of one equiamount of water did not affect the carbonylation, although Rh-catalyzed cyclocarbonylation of alkynes proceeded only in the presence of water.[3,4,8d,11]

TABLE 1. Cyclocarbonylation of Allenes[a]



1 2 (3)

allenyl alcohols **1**	R^1	R^2	R^3	R^4	R^5	product **2**	yield (%)[b]	
1a	H	H	H	$(CH_2)_5$		**2a**		99
1b	H	H	H	Me	Me	**2b**	95	
1c	H	H	H	H	Et	**2c**	96	
1d	H	H	H	H	Ph	**2d**	98	
1e	H	H	H	H	H	**2e**	98	
1f	H	H	Me	H	H	**2f**	98	
1g	H	H	*i*Pr	H	H	**2g**	95	
1h	H	H	MeO	$(CH_2)_5$		**2h**	98	
1i	H	H	MeO	Me	Me	**2i**	95	
1j	H	H	MeO	H	Et	**2j**	91	
1k	H	H	MeO	H	Ph	**2k**	93	
1l	Me	H	H	H	H	**2l**	98	
1m	Me	Me	H	$(CH_2)_5$		**2m**	98	

[a] Reaction conditions: substrate, 1 mmol; $Ru_3(CO)_{12}$ 0.01 mmol; 1,4-dioxane, 15 mL; NEt_3, 1.5 mmol; CO pressure, 10 atm; reaction temperature, 100 °C; reaction time, 8 h. [b] Isolated yield.

Carbonylation of Substituted Allenyl Alcohols. On the basis of the above results, we chose the following standard reaction conditions to explore the scope of the present Ru-catalyzed cyclocarbonylation: substrate (1 mmol); catalyst, $Ru_3(CO)_{12}$ (1 mol %); additive, NEt_3 (1.5 mmol); solvent, dioxane (15 mL), CO pressure, 10 atm; reaction temperature, 100 °C. The cyclocarbonylation of various substituted allenyl alcohols were carried out under the standard reaction conditions. We consequently found that the present system is effective for the cyclocarbonylation of mono-, di-, and trisubstituted allenyl alcohols (4-hydroxy-buta-1,2-diene derivatives) **1a**−**m** to give γ-lactones (furanones) **2a**−**m** in almost quantitative yields (Table 1), indicating that primary to tertiary alcohols on the allenic skeleton can take part in the cyclocarbonylation and that substituents on the allenic skeleton do not apparently affect the cyclocarbonylation.

To investigate the reactivity of allenyl alcohols, carbonylations of 4-hydroxy-4-phenylbuta-1,2-dienes **1n**−**s** were carried out (Table 2). Benzylallenyl alcohols bearing chloro, bromo, methoxy, methylthio, and dimethylamino groups on the phenyl substituent exhibited almost the same reactivity toward the present cyclocarbonylation and produced 3-methyl-5-phenylfuranone derivatives **2n**−**r** in good yields (entries 1−5), while allenyl alcohol **1s** bearing a nitro group did not give lactone but gave a complex mixture of products that could not be identified, although the IR spectrum showed disappearance of the nitro group (entry 6). 4-Hydroxybuta-1,2-dienes having a functional group at the 4-position also underwent smooth cyclocarbonylation (entries 7−9). Ferrocenyl (**1t**), vinyl (**1u**), and cyclopropyl groups (**1v**) did not affect the cyclocarbonylation and remained intact after the cyclocarbonylation. The scope suggests that the present cyclocarbonylation affords an excellent method for the

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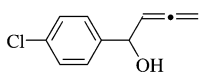
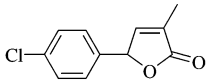
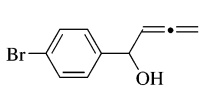
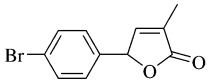
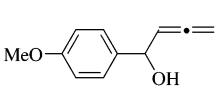
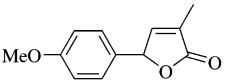
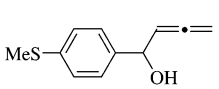
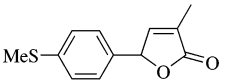
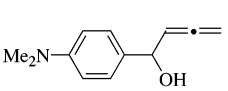
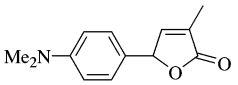
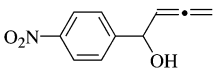
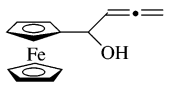
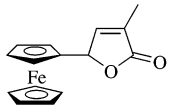
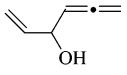
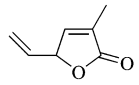
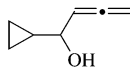
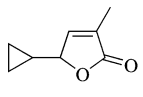
TABLE 2. Cyclocarbonylation of Allenyl Alcohols[a]

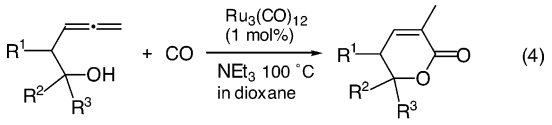
entry	substrate	product	yield(%)[b]
1	 **1n**	 **2n**	94
2	 **1o**	 **2o**	92
3	 **1p**	 **2p**	88
4	 **1q**	 **2q**	85
5	 **1r**	 **2r**	93
6	 **1s**	complex mixture	
7	 **1t**	 **2t**	99
8	 **1u**	 **2u**	92
9	 **1v**	 **2v**	91

[a] Reaction conditions: substrate, 1 mmol; $Ru_3(CO)_{12}$ 0.01 mmol; 1,4-dioxane, 15 mL; NEt_3, 1.5 mmol; CO pressure, 10 atm; reaction temperature, 100 °C; reaction time, 8 h. [b] Isolated yield.

preparation of furanones having a wide variety of substituents on the skeleton.

The present catalytic system is also effective for the cyclocarbonylation of allenyl alcohols that contain a dimethylene spacer between the hydroxyl and allenyl groups. 5-Hydroxypenta-1,2-dienes **3a**−**c** similarly underwent cyclocarbonylation to give *δ*-lactones **4a**−**c**, respectively, in a high yield (eq 4). Substituents on the methylene spacer do not seem to give undesirable effects on the formation of six-membered lactones.

Carbonylation of Allenylamines. Amines are well-known to act as a nucleophile in carbonylation reactions of alkenes and alkynes giving amides. Allenylamines such as 4-aminobuta-1,2-diene and 6-aminohexa-1,2-diene are also carbonylated by the catalysis of palladium



3 **4**

3a: $R^1=R^2=R^3=H$; **4a**: 95% yield
3b: $R^1=H$, $R^2=R^3=Me$; **4b**: 98% yield
3c: $R^1=Me$, $R^2=R^3=H$; **4c**: 98% yield

complexes to give vinylamide and acrylic acid derivatives,[12] respectively, but not cyclocarbonylation products, lactams. We applied the present ruthenium-catalyzed carbonylation to allenylamines and found that 5-aminopenta-1,2-dienes were carbonylated to give *δ*-lactams (eq 5). Thus, 5-aminopenta-1,2-diene (**5a**) was reacted with carbon monoxide in the presence of $Ru_3(CO)_{12}$ (1 mol %) in triethylamine at 80 °C. Analysis by TLC showed the products to be a 1:1 mixture of two components **6a** and **7a**, which were separated by column chromatography on alumina. By spectral analyses, **6a** was identified as 5-methyl-1*H*,2*H*,3*H*-azin-6-one, and **7a** was identified as its isomer, 5-methylenepyperidin-2-one.[38] Similarly, 4-methyl-5-aminopenta-1,2-diene **5b** gave *δ*-lactams as a 1:1 mixture of two isomers **6b** and **7b**. Recently, Kang

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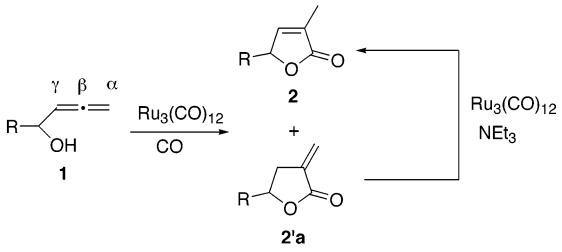
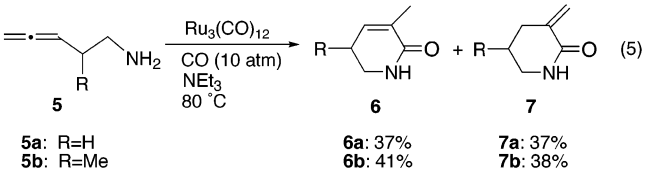
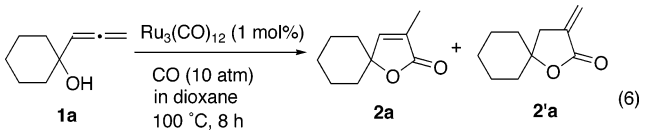
SCHEME 1



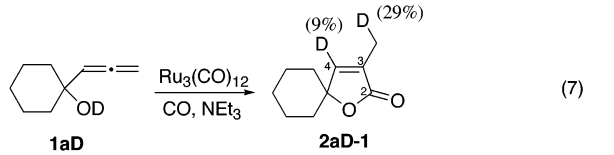
et al. reported that our ruthenium system is also effective for the cyclocarbonylation of allenyl sulfonamides to give lactams.[13]

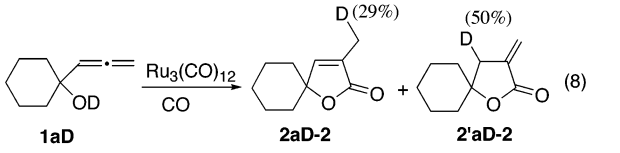


Carbonylation of Allenyl Alcohols in the Absence of Amines. In the course of investigation on the effect of additives in the present carbonylation, we found that the carbonylation of allenyl alcohol **1a** in the absence of amine led to the formation of **2a** in 68% yield along with **2′a** in 27% yield (eq 6).

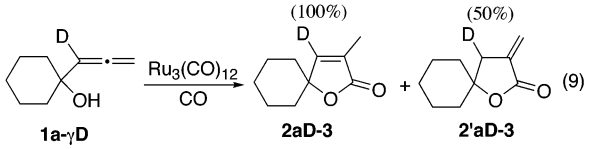


Although product **2′a** could not be isolated as a pure form, the structure was determined by the GC-MASS and ^{1}H and ^{13}C NMR spectra. Interestingly, when a mixture of **2a** and **2′a** was heated in the presence of Et_3N and the ruthenium catalyst, complete isomerization of **2′a** to **2a** was observed, although the isomerization did not occur in the absence of the amine or the catalyst (Scheme 1). To obtain information on hydrogen migration in the reaction, we performed the carbonylation of deuterated allenyl alcohol **1aD** in the presence and in the absence of amine (eqs 7 and 8).





The carbonylation in the presence of Et_3N gave deuterated product **2aD-1** with deuterium contents of 9 and 29% at 4-C and Me, respectively, and in the absence of the amine afforded deuterated products **2aD-2** and **2′aD-2** with deuterium contents indicated in eq 8. The former product contains no deuterium at 4-C, while the latter carries 50% deuterium content at 4-C, suggesting migration of one of the two hydrogen atoms at 4-C to the *exo*-methylene group in **2′a** to form **2a**. This deuterium experiment suggests that amines affect the isomerization of **2′a** to **2a**, but not the construction of the furanone skeleton. Under consideration with the product ratio of **2a**/**2′a** (7/3), deuterium contents of products **2aD-1**, **2aD-2**, and **2′aD-2** are consistent with the calculated values and suggest a transformation of **1a** to **2a** in the presence of amines shown in Scheme 1, where the hydrogen of the OH group in **1** mainly moved to the α-C of allenic group to give **2**, whereas in the minor course the hydrogen added to the γ-C giving **2′a** and then migrated to α-C finally to yield **2**. This transformation route of **1a** to **2a** has been confirmed by the carbonylation of γ-deutero **1a** (**1a-γD**) in the absence of NEt_3. The deuterium contents in the products are shown in eq 9. The lack of deuterium in the methyl and methylene groups at 3-C in products **2aD-3** and **2′aD-3** undoubtedly indicates simultaneous formation of **2** and **2′** from **1**. These dueterium experiments reveal that the carbonylation of **1** simultaneously yields **2** and **2′** despite the absence and presence of amines, followed by transformation of **2′** to **2** in the presence of amines and the Ru catalyst.



Possible Reaction Mechanism. It is known that propargyl alcohol, which is an isomer of allenyl alcohol, is carbonylated to produce furanones by the catalysis of palladium complexes.[8k] However, when propargyl alcohol instead of allenyl alcohol was reacted with carbon monoxide using the ruthenium catalyst, the starting material was recovered quantitatively, indicating that in the present carbonylation, allenyl alcohol does not undergo cyclocarbonylation via isomerization to propargyl alcohol but is directly carbonylated to furanone.

To obtain information on a catalytically active species in the present carbonylation, we attempted to isolate an intermediate complex from stoichiometric reactions of the substrate with the catalyst. The reaction of allenyl alcohol **1a** with $Ru_3(CO)_{12}$ in a molar ratio of 1/1 in the presence of Et_3N in benzene at room temperature gave an orange solution, which formed furanone **2a** when heated, but we could not isolate a definite ruthenium complex from the reaction mixture. Since the catalytically active species of the present carbonylation was poorly understood, we tried to investigate the relation between turnover frequency (TOF) and concentration of catalyst, i.e., Laine's kinetic criteria,[14] which may tell us whether the active species is a ruthenium cluster or not. Thus, we chose the carbonylation reaction of **1a** for a mechanistic study and first confirmed the reaction to be of first order between the conversion of **1a** and the reaction time.[15] Then, we established the relation between TOF and the concentration of $Ru_3(CO)_{12}$ in the range of 5×10^{-3} to 3×10^{-2} mol % (substrate **1a**, 6.6 M), which is shown in Figure 1. The proportional increase of TFO with increasing the

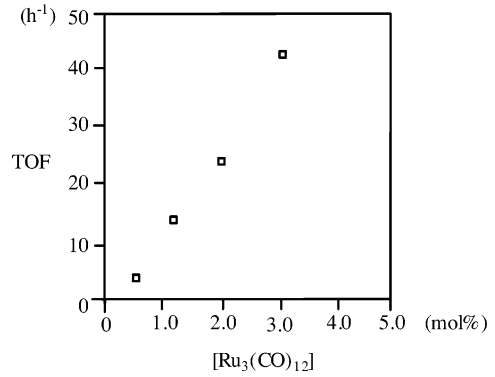
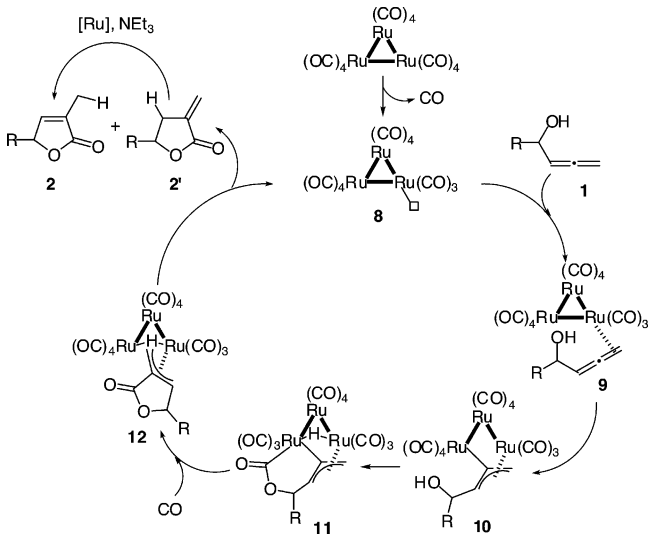


FIGURE 1. Relation between TOF and concentration of the catasyst. Reaction conditions: substrate **1a**, 1 mmol; catalyst, $Ru_3(CO)_{12}$; 1,4-dioxane, 15 mL; NEt_3, 1.4 mmol; CO pressure, 10 atm; reaction temperature, 100 °C.

SCHEME 2. Possible Mechanism of the Cyclocarbonylation



concentration of $Ru_3(CO)_{12}$ catalyst suggests a trinuclear ruthenium cluster species to be responsible for the catalysis.

On the basis of the experimental data described above, a possible reaction mechanism is proposed in Scheme 2. Addition of a large amount of MeOH to the reaction system did not appreciably affect the carbonylation of **1a**, implying the first step of the reaction to be coordination of C═C═C, but not of OH, to the Ru catalyst. The initial step may involve elimination of carbon monoxide from $Ru_3(CO)_{12}$ giving complex **8.** An allenyl alcohol coordinates to a Ru vacant site, followed by transformation to π-allyl intermediate **10** by interaction with ruthenium centers. Although we have no experimental results directly supporting π-allyl species **10**, related dinuclear iron[16] and trinucler osmium[17] complexes have been isolated from the reactions of $Fe_2(CO)_9$ and $Os_3(CO)_{12}$ with allene, respectively. Nucleophilic attack of the neighboring hydroxy group may lead to formation of metallacycle **11**, followed by reductive elimination to give intermediate **12** having a lactone frame. Then, the hydrogen coordinated to Ru selectively transfers to the π-allylic moiety, resulting in the formation of **2** and **2′**. In the presence of NEt_3 and the Ru catalyst, **2′** isomerizes to **2** and finally **2** is obtained as the sole product in this reaction.

Conclusion

We have demonstrated that $Ru_3(CO)_{12}$ catalyzes the cyclocarbonylation of allenyl alcohols to give lactone derivatives with a high selectivity in a high yield, in which the hydroxyl group is incorporated in the cyclization. This carbonylation can be applied to a wide variety of allenyl alcohols having various functional groups and provides useful method for the synthesis of a variety of lactone derivatives directly from allenyl alcohols that may be easily prepared. On the basis of experimental results, we propose a possible carbonylation mechanism involving a ruthenium cluster species as an active intermediate.

Experimental Section

General. ^{1}H NMR and ^{13}C NMR were measured at 400 and 100 MHz, respectively, in $CDCl_3$ with tetramethylsilane as an internal standard. Data are reported as follows: chemical shift in parts per million (δ), multiplicity (s = singlet, d = doublet, t = triplet, or m = multiplet), coupling constant (hertz), integration, and interpretation. Infrared spectral data (IR) were reported in reciprocal centimeters.

Materials. Solvents and reagents were dried and purified prior to use by standard procedures. Allenyl alcohols **1a**,[18a,b] **1b**−**g**,[19] **1h**,[18a,c] **1i**,[20] **1j**,[18a,c] **1k**,[20] **1l**,[19] **1m**,[21] **1p**,[22] **1u**,[19] and **3a**−**c**[19,23] were prepared from propargyl alcohol or methoxyallene with corresponding aldehydes or ketones according to literature methods.[18a,19] New allenyl alcohols **1n**−**t** and **1v** were similarly prepared from 2-prop-2-ynyloxy-tetrahydropyran with aldehydes via 2-butyn-1-ol derivatives. Allenylamines **5** were prepared by the literature method.[24]

The preparation and characterization of new allenyl alcohols **1n**−**t** and **1v** are provided in Supporting Information.

Typical Procedure of the Carbonylation of Allenyl Alcohols. A 100 mL stainless steel autoclave was charged with 1-propa-1,2-dienylcyclohexan-1-ol (**1a**) (1 mmol, 138 mg), 1,4-dioxane (15 mL), triethylamine (1.5 mmol), and $Ru_3(CO)_{12}$ (0.01 mmol, 6 mg). The system was flushed three times with 30 atm of CO. Finally, it was pressurized to 10 atm and stirred at 100 °C. After 8 h, the autoclave was allowed to cool in water, and then the CO was released. The contents were transferred to a round-bottomed flask with ether, and the volatiles were removed in vacuo. The residue was subjected to column chromatography on silica gel using benzene as an eluent to give 3-methyl-5,5-pentamethylene-2(5*H*)-furane (**2a**)[10] (165 mg, 99% yield) as a colorless solid: ^{1}H NMR ($CDCl_3$) δ 1.25−1.89 (10H, m, $CH_2 \times 5$), 1.89 (3H, s, CH_3), 5.56 (1H, s, C═CH); ^{13}C NMR ($CDCl_3$) δ 10.6, 22.5, 24.7, 34.9, 86.0, 128.4, 153.3, 173.7; IR (KBr) ν 1770 cm^{-1} (C═O); MS (EI) m/z 166 (M^+). Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 72.22; H, 8.31.

2(5*H*)-Furanones **2b**,[25] **2c**,[26] **2d**,[27] **2e**,[28] **2f**,[28,29] **2g**,[30] **2h**,[31] **2j**,[32] **2k**,[32] **2l**,[33] **2n**,[34] **2p**,[35] and 2-pyranones **4a**[36] and **4c**[37] are known compounds and were identified by ^{1}H and ^{13}C NMR, IR, and mass spectra. The spectral data are provided in Supporting Information.

4-Methoxy-3,5,5-trimethyl-2(5*H*)-furanone (2i). Pale yellow oil; ^{1}H NMR ($CDCl_3$) δ 1.40 (6H, s, CH_3), 1.99 (3H, s, CH_3), 4.12 (3H, s, OCH_3); ^{13}C NMR ($CDCl_3$) δ 8.4, 24.4, 58.9, 80.8, 94.8, 173.9, 177.0; IR (neat) ν 1751 cm^{-1} (C═O); MS (EI) m/z 156 (M^+). Anal. Calcd for $C_8H_{12}O_3$: C, 61.52; H, 7.75. Found: C, 61.80; H, 7.95.

3-Isopropyl-1-oxaspiro[4,5]-3-en-2-one (2m). Colorless solid; mp 97−98 °C; ^{1}H NMR ($CDCl_3$) δ 1.16 (6H, d, J = 6.8 Hz, $CH_3 \times 2$), 1.25−1.75 (10H, m, $CH_2 \times 5$), 2.61−2.67 (1H,

m, CH), 6.96 (1H, s, C=CH); ^{13}C NMR ($CDCl_3$) δ 21.0, 22.5, 24.7, 25.3, 35.0, 85.7, 139.1, 150.5, 172.7; IR (KBr) ν 1748 cm^{-1} (C=O); MS (EI) *m*/*z* 194 (M^+). Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 74.44; H, 9.28.

3-Methyl-5-(4-bromophenyl)-2(5*H*)-furanone (2o). Colorless solid; mp 94 °C; ^{1}H NMR ($CDCl_3$) δ 1.99 (3H, s, CH_3), 5.87 (1H, s, CH), 7.09 (1H, s, C=CH), 7.14 (2H, d, J = 8.3 Hz, Ar), 7.52 (2H, d, J = 8.1 Hz, Ar); ^{13}C NMR ($CDCl_3$) δ 10.5, 81.2, 123.0, 128.0, 129.8, 132.0, 134.1, 147.7, 173.9; IR (KBr) ν 1750 cm^{-1} (C=O); MS (EI) *m*/*z* 253 (M^+). Anal. Calcd for $C_{11}H_9BrO_2$: C, 52.20; H, 3.58; Br, 31.60. Found: C, 52.18; H, 3.37; Br, 31.60.

3-Methyl-5-(4-methylthiophenyl)-2(5*H*)-furanone (2q). Colorless solid; mp 57 °C; ^{1}H NMR ($CDCl_3$) δ 1.99 (3H, s, CH_3), 2.48 (3H, s, SCH_3), 5.82 (1H, s, CH), 7.09 (1H, s, C=CH), 7.16 (2H, d, J = 8.3 Hz, Ar), 7.25 (2H, d, J = 8.1 Hz, Ar); ^{13}C NMR ($CDCl_3$) δ 10.6, 15.5, 81.7, 126.5, 126.9, 129.6, 131.5, 140.0, 148.0, 174.2; IR (KBr) ν 1748 cm^{-1} (C=O); MS (EI) *m*/*z* 220 (M^+). Anal. Calcd for $C_{12}H_{12}O_2S$: C, 65.43; H, 5.49; S, 14.56. Found: C, 65.38; H, 5.32; S, 14.70.

3-Methyl-5-(4-(*N*,*N*-dimethylamino)phenyl)-2(5*H*)-furanone (2r). Colorless solid; 200 mg (93%), mp 91 °C; ^{1}H NMR ($CDCl_3$) δ 1.99 (3H, s, CH_3), 2.96 (6H, s, CH_3 × 2), 5.78 (1H, s, CH), 6.68 (2H, d, J = 8.3 Hz, Ar), 7.07 (1H, s, C=CH), 7.10 (2H, d, J = 8.1 Hz, Ar); ^{13}C NMR ($CDCl_3$) δ 10.5, 40.2, 82.5, 112.1, 121.7, 129.2, 148.4, 150.9, 174.5; IR (KBr) ν 1752 cm^{-1} (C=O); MS (EI) *m*/*z* 217 (M^+). Anal. Cacld for $C_{13}H_{15}NO_2$: C, 71.87; H, 6.96; N, 6.45. Found: C, 71.96; H, 6.68; N, 6.30.

3-Methyl-5-ferrocenyl-2(5*H*)-furanone (2t). Brown solid; mp 119 °C; ^{1}H NMR ($CDCl_3$) δ 1.99 (3H, s, CH_3), 4.19−4.24 (4H, m, Cp), 4.21 (5H, s, Cp), 5.85 (1H, s, CH), 7.18 (1H, s, C=CH); ^{13}C NMR ($CDCl_3$) δ 10.6, 66.6, 67.6, 68.7, 68.9, 79.4, 82.7, 130.0, 147.8, 174.0; IR (KBr) ν 1746 cm^{-1} (C=O); MS (FAB) *m*/*z* 282 (M^+). Anal. Calcd for $C_{15}H_{14}O_2Fe$: C, 63.86; H, 5.00. Found: C, 63.70; H, 4.82.

3-Methyl-5-vinyl-2(5*H*)-furanone (2u). Colorless oil; ^{1}H NMR ($CDCl_3$) δ 1.88 (3H, s, CH_3), 5.23−5.25 (2H, m, C=CH_2), 6.01−6.05 (1H, m, C=CH), 6.21 (1H, br, CH), 7.55 (1H, s, C=CH); ^{13}C NMR ($CDCl_3$) δ 18.0, 83.1, 115.1, 131.6, 135.6, 137.5, 170.3; IR (neat) ν 1745 cm^{-1} (C=O); MS (EI) *m*/*z* 124 (M^+). Anal. Calcd for $C_7H_8O_2$: C, 67.73; H, 6.50. Found: C, 67.56; H, 6.27.

3-Methyl-5-cyclopropyl-2(5*H*)-furanone (2v). Colorless oil; ^{1}H NMR ($CDCl_3$) δ 0.35−0.43 (1H, m, CH_2), 0.45−0.51 (1H, m, CH_2), 0.56−0.69 (2H, m, CH_2), 0.90−1.01 (1H, m, CH), 1.92 (3H, s, CH_3), 4.36−4.38 (1H, m, CH), 7.03 (1H, s, C=CH); ^{13}C NMR ($CDCl_3$) δ 1.1, 2.7, 10.4, 12.9, 84.3, 129.9, 147.7, 174.0; IR (neat) ν 1753 cm^{-1} (C=O); MS (EI) *m*/*z* 138 (M^+). Anal. Calcd for $C_8H_{10}O_2$: C, 69.54; H, 7.30. Found: C, 69.38; H, 7.34.

3,6,6-Trimethyl-2*H*-pyran-2-one (4b). Pale yellow oil; ^{1}H NMR ($CDCl_3$) δ 1.43 (6H, s, CH_3 × 2), 1.93 (3H, s, CH_3), 2.39 (2H, d, J = 6.0, CH_2), 6.46 (1H, d, J = 5.8, C=CH); ^{13}C NMR ($CDCl_3$) δ 16.9, 27.6, 35.8, 80.1, 127.6, 137.4, 165.4; IR (neat) ν 1716 cm^{-1} (C=O). Anal. Calcd for $C_8H_{12}O_2$: C, 68.54; H, 8.63. Found: C, 68.76; H, 8.41.

Typical Procedure of the Carbonylation of Allenylamines. A 100 mL stainless steel autoclave was charged with penta-3,4-dienylamine (**5a**)[24] (2 mmol, 166 mg), $Ru_3(CO)_{12}$ (0.02 mmol, 13.8 mg), and 30 mL of triethylamine. The system was flushed three times with 30 atm of CO. Finally it was pressurized to 10 atm and stirred at 100 °C. After 8 h, the autoclave was allowed to cool in water, and then the CO was released. The contents were transferred to a round-bottomed flask with ether, and the volatiles were removed in vacuo. The residue was subjected to column chromatography on deactivated alumina using methyl acetate as an eluent to give 3-methyl-5,6-dihydro-1*H*-pyridin-2-one (**6a**) in 37% yield and 3-methylenepiperidin-2-one (**7a**) in 37% yield. Similar carbonylation of 2-methylpenta-3,4-dienylamine (**5b**)[24] gave 3,5-dimethyl-5,6-dihydro-1*H*-pyridin-2-one (**6b**) and 3-methylene-5-methyl-piperidin-2-one (**7b**) in 41 and 38% yields, respectively. Lactam **7a**[38] is a known compound and was identified by ^{1}H and ^{13}C NMR, IR, and mass spectra.

3-Methyl-5,6-dihydro-1*H*-pyridin-2-one (6a). Pale yellow oil; ^{1}H NMR ($CDCl_3$) δ 1.87 (3H, s, CH_3), 2.28−2.32 (2H, m, CH_2), 3.39 (2H, t, J = 7.8 Hz, NCH_2), 6.37 (1H, br, C=CH), 6.64 (1H, br, NH); ^{13}C NMR ($CDCl_3$) δ 16.7, 24.0, 39.8, 130.9, 135.5, 167.8; IR (neat) ν 3257 (NH), 1680 (C=O), 1631 cm^{-1} (C=C); MS (EI) *m*/*z* 111 (M^+). Anal. Calcd for C_6H_9NO: C, 64.84; H, 8.16; N, 12.60. Found: C, 64.58; H, 8.02; N, 12.80.

3,5-Dimethyl-5,6-dihydro-1*H*-pyridin-2-one (6b). Pale yellow oil; ^{1}H NMR ($CDCl_3$) δ 1.16 (3H, s, CH_3), 1.93 (3H, s, CH_3), 2.55−2.58 (1H, m, CH), 2.75−2.77 (1H, m, CH_2), 2.81−2.84 (1H, m, CH_2), 5.99 (1H, br, C=CH), 6.80 (1H, br, NH); ^{13}C NMR ($CDCl_3$) δ 17.2, 18.8, 32.1, 48.6, 128.2, 140.4, 165.8; IR (neat) ν 3255 (NH), 1675 (C=O), 1631 cm^{-1} (C=C); MS (EI) *m*/*z* 125 (M^+). Anal. Calcd for $C_7H_{11}NO$: C, 67.17; H, 8.86; N, 11.19. Found: C, 67.01; H, 8.75; N, 10.89.

3-Methylene-5-methylpiperidin-2-one (7b). Pale yellow oil; ^{1}H NMR ($CDCl_3$) δ 1.06 (3H, s, CH_3), 1.84−1.90 (2H, m, CH_2), 2.24−2.32 (1H, m, CH), 2.78−2.80 (1H, m, CH_2), 2.85−2.88 (1H, m, CH_2), 5.38 (1H, br, C=CH_2), 6.35 (1H, br, C=CH_2), 6.69 (1H, br, NH); ^{13}C NMR ($CDCl_3$) δ 17.3, 33.1, 42.7, 52.2, 120.3, 145.5, 166.5; IR (neat) ν 3248 (NH), 1688 (C=O), 1629 cm^{-1} (C=C); MS (EI) *m*/*z* 125 (M^+). Anal. Calcd for $C_7H_{11}NO$: C, 67.17; H, 8.86; N, 11.19. Found: C, 67.02; H, 8.75; N, 11.09.

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Supporting Information Available: Preparation and characterization of new allenyl alcohols (**1n**−**t**, **1v**) and data for identification of compounds **2b**−**h**, **2j**−**l**, **2n**, **2p**, **4a**, **4c**, and **7a** are provided in Supporting Information. This material is available free of charge via the Internet at http://pubs.acs.org.

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