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# Rhodium-Catalyzed Carbonylation of Acetylenes under Water-Gas Shift Reaction Conditions. Selective Synthesis of Furan-2(5*H*)-ones

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Rhodium-catalyzed carbonylation of acetylenes was studied. Under water-gas shift reaction conditions, internal acetylenes are selectively carbonylated to 3,4-disubstituted furan-2(5*H*)-ones (**2**). Use of $D_2O$ gave 5,5-dideuteriofuran-2(5*H*)-one (**3**), which indicates that the hydrogen comes from water. Use of molecular hydrogen in place of water gave hydroxymethylated product **4** and stilbene **5**, and no furanone was obtained, indicating that water-gas shift reaction conditions are indespensable for the formation of furanones. As catalysts, rhodium carbonyl clusters such as $Rh_4(CO)_{12}$ and $Rh_6(CO)_{16}$ are the best among the transition-metal complexes tested. The presence of amines is essential for the selective synthesis of furanones. Effects of additives, solvents, and the pressure of carbon monoxide were examined.

## Introduction

Reactions of acetylenes with carbon monoxide by the catalysis of transition-metal complexes have been extensively studied so far and established as excellent methods for direct synthesis of carbonyl compounds such as ketones, aldehydes, acrylic acid, esters, and lactones.[1] The reactivity of acetylenes and the type of products are mainly affected by the reaction conditions including metals and additives as well as hydrogen sources.

Previously, we have reported a new route to cyclic enones by the carbonylation of conjugated enynes under rhodium-catalyzed hydroformylation conditions.[2] In the cource of our study, we have found that the use of water instead of molecular hydrogen affords, unexpectedly, cyclocarbonylated products, furan-2(5*H*)-ones, from enynes in excellent yields. The reaction has been successfully extended as a new general method for the selective synthesis of furan-2(5*H*)-ones from acetylenes, and we have reported the preliminary results.[3]

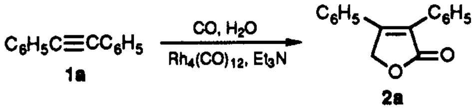
Furan-2(5*H*)-ones are an important class of naturally occurring compounds, some derivatives of which possess significant biological activities.[4] Numerous methods for the synthesis of furanones have been reported so far,[5] and a lot has been published about the formation of furanones via the carbonylation of acetylenes,[6] but little is known about the catalytic preparation of furanones from acetylenes.[6e–i,9,10]

Here we wish to report the details of the synthesis of 3,4-disubstituted furan-2(5*H*)-ones from internal acetylenes by rhodium-catalyzed carbonylation under water-gas shift reaction conditions.

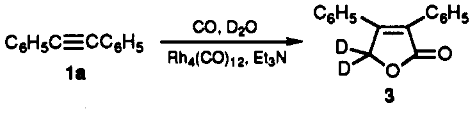
## Results and Discussion

**Reaction of Diphenylacetylene.** Diphenylacetylene (**1a**) was reacted with carbon monoxide (100 atm) and water in the presence of triethylamine and a catalytic amount of $Rh_4(CO)_{12}$ in tetrahydrofuran at 100 °C. The reaction proceeded smoothly and gave 3,4-diphenylfuran-2(5*H*)-ones (**2a**) in 87% yield, which were identified by instrumental analyses such as $^1H$ NMR, IR, and mass spectra as well as elemental analysis.

### Scheme I



### Scheme II



### Scheme III

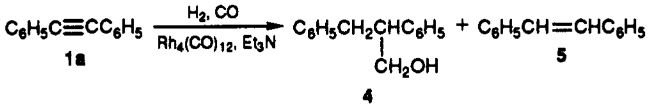


Table I. Catalytic Activities of Metal Complexes for the Carbonylation of 1a[a]

| entry | catalyst (amt, mmol) | reaction temp, °C | reaction time, h | conv, % | selectivity,[b] % |
|---|---|---|---|---|---|
| 1 | $Rh_4(CO)_{12}$ (0.027) | 100 | 5 | 81 | 83 |
| 2 | $Rh_4(CO)_{12}$ (0.027) | 100 | 24 | 100 | 87 |
| 3 | $Rh_6(CO)_{16}$ (0.018) | 100 | 5 | 74 | 80 |
| 4 | $RhCl_3{\cdot}xH_2O$ (0.108) | 100 | 5 | 71 | 90 |
| 5 | $Fe(CO)_5$ (0.27) | 100 | 5 | 0 | 0 |
| 6 | $Fe(CO)_5$ (1.0) | 150 | 15 | 60 | trace[c] |
| 7 | $Ru_3(CO)_{12}$ (0.027) | 120 | 20 | 36 | 89 |
| 8 | $Co_2(CO)_8$ (0.054) | 100 | 5 | 0 | 0 |

[a] Reaction conditions: **1a**, 4.85 mmol; $Et_3N$, 15 mmol; $H_2O$, 56 mmol; THF, 10 mL; CO, 100 atm. [b] Based on **1a** consumed. [c] Hydrogenated products such as *cis*- and *trans*-stilbene were produced.

Judging from the structure, furanone **2a** is constructed by the combination of **1a** with one molecule of hydrogen and two molecules of carbon monoxide. Using $D_2O$ instead of $H_2O$, a deuterated furanone, **3**, was obtained in good

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(1) Pino, P.; Braca, G. In *Organic Synthesis via Metal Carbonyls*; Wender, I., Pino, P., Eds.; Wiley: New York, 1977; Vol. 2, p 419.

(2) (a) Doyama, K.; Joh, T.; Takahashi, S.; Shiohara, T. *Tetrahedron Lett.* **1986**, 4497. (b) Doyama, K.; Joh, T.; Shiohara, T.; Takahashi, S. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 4353.

(3) Doyama, K.; Joh, T.; Onitsuka, K.; Shiohara, T.; Takahashi, S. *J. Chem. Soc., Chem. Commun.* **1987**, 649.

(4) Martin S. F.; Moore, D. R. *Tetrahedron Lett.* **1976**, 4459 and references cited therein.

(5) Lao, Y. S. *Chem. Rev.* **1976**, *76*, 625 and references cited therein.

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**Scheme IV**

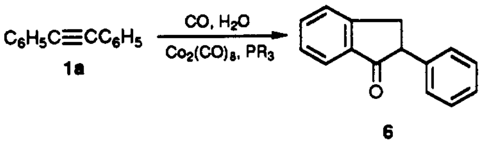


**Table II. Effect of Additives**[a]

| entry | additives | conv, % | selectivity,[b] % 2a | selectivity,[b] % 7 |
|---|---|---|---|---|
| 1 | | 77 | 28 | 0 |
| 2 | $Et_3N$ | 81 | 83 | 0 |
| 3 | $(CH_3)_2N(CH_2)_3N(CH_3)_2$ | 84 | 71 | 0 |
| 4 | $Et_2NH$ | 97 | 80 | 0 |
| 5 | piperidine | 80 | 28 | 50 |
| 6 | $BuNH_2$ | 59 | 26 | 54 |
| 7 | NaOH | 0 | 0 | 0 |
| 8 | NaOAc | 58 | 72 | 0 |

[a] Reaction conditions: **1a**, 4.85 mmol; $Rh_4(CO)_{12}$, 0.027 mmol; additives, 15 mmol; $H_2O$, 56 mmol; THF, 10 mL; CO, 100 atm; reaction temperature, 100 °C; reaction time, 5 h. [b] Based on **1a** consumed.

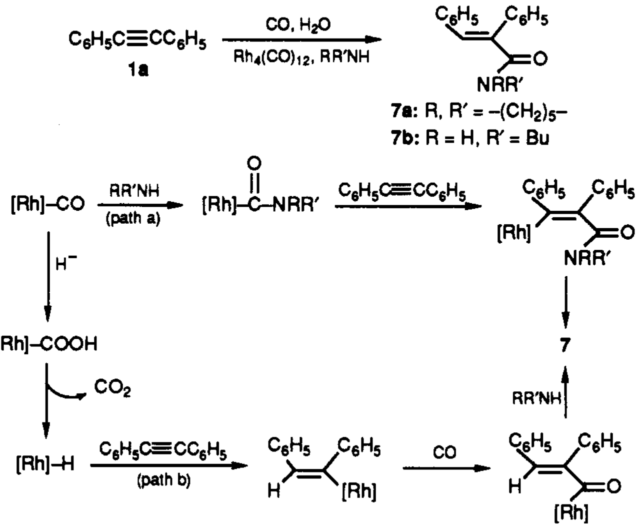
yield. This fact indicated that the hydrogen atoms are derived from water. The use of hydrogen gas as a hydrogen source in place of water gave hydroxymethylated product **4** and stilbene **5**, and no furanone was obtained. Therefore, water-gas shift reaction conditions are indespensable for the selective formation of furan-2(5*H*)-ones from acetylenes.

The selectivity of the formation of **2a** was largely affected by the reaction conditions such as catalysts, additives, hydrogen sources, and the pressure of carbon monooxide.

For the catalyst, metal clusters gave good results, as shown in Table I. Thus, rhodium carbonyl clusters such as $Rh_4(CO)_{12}$ and $Rh_6(CO)_{16}$ were the best among the metal complexes tested. $RhCl_3$, which is considered to form the same metal carbonyl species as $Rh_4(CO)_{12}$ or $Rh_6(CO)_{16}$ under the reaction conditions, was also a suitable catalyst. $Ru_3(CO)_{12}$ also catalyzed the present reaction, though the reactivity was lower than that for the rhodium catalysts.

Metal complexes active for water-gas shift reaction do not necessarily catalyze the present reaction, because furanone **2a** was not formed by a catalysis of $Co_2(CO)_8$ or $Fe(CO)_5$ even under severer conditions. In the case of using a $Co_2(CO)_8$–phosphine catalyst system, indan-1-one **6** was obtained in place of furanone **2a**,[7] of which the details will be soon published.[8] These results indicate that not only activity for the water-gas shift reaction but also cluster structure play an important role for catalysts in the present reaction.

**Scheme V**



**Scheme VI**

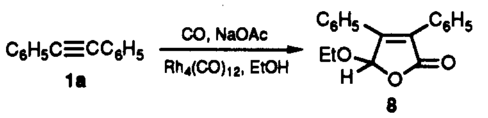


**Table III. Effect of Solvent**[a]

| entry | solvent | conv, % | selectivity,[b] % |
|---|---|---|---|
| 1 | THF | 81 | 83 |
| 2 | acetone | 100 | 72 |
| 3 | acetonitrile | 93 | 78 |
| 4 | benzene | 82 | 83 |
| 5 | ethanol | 100 | 80 |

[a] Reaction conditions: **1a**, 4.85 mmol; $Rh_4(CO)_{12}$, 0.027 mmol; $Et_3N$, 15 mmol; $H_2O$, 56 mmol; THF, 10 mL; CO, 100 atm; reaction temperature, 100 °C; 5 h. [b] Based on **1a** consumed.

**Table IV. Effect of the Amount of $H_2O$ in Ethanol**[a]

| entry | amt of $H_2O$, mmol | yield,[b] % 2a | yield,[b] % 8 |
|---|---|---|---|
| 1 | 56 | 80 | 0 |
| 2 | 28 | 81 | 0 |
| 3 | 5.6 | 27 | 60 |
| 4 | 0 | 0 | 86 |

[a] Reaction conditions: **1a**, 4.85 mmol; $Rh_4(CO)_{12}$, 0.027 mmol; $Et_3N$, 15 mmol; EtOH, 10 mL; CO, 100 atm; reaction temperature, 100 °C; reaction time, 5 h. [b] Isolated yield.

The presence of amines are necessary for the selective syntheses of furanone (Table II). Tertiary amines such as triethylamine and 1,3-bis(dimethylamino)propane and some of secondary amines such as diethylamine were suitable for this reaction. With piperidine or butylamine, aminocarbonylated products **7** were obtained. It is uncertain at this time why an aminocarbonylated product was not formed when diethylamine was used as an additive. The formation of **7** is supposed to be attained via path a or b in Scheme V. Weak bases such as NaOAc also gave good results, but the presence of strong bases like NaOH lowered the reactivity.

A wide variety of solvents can be used for the present reaction, regardless of their polarity, acidity or basicity, and miscibility with water, as shown in Table III.

Yamazaki and his co-workers reported the new method for the selective synthesis of 5-alkoxyfuran-2(5*H*)-ones **8** by the carbonylation of acetylenes in the presence of a catalytic amount of $Rh_4(CO)_{12}$ and bases in alcohols.[6e,f]

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(6) (a) Tsuji, J.; Nogi, T. *J. Am. Chem. Soc.* **1966**, *88*, 1289. (b) Heck, R. F. *J. Am. Chem. Soc.* **1964**, *86*, 2819. (c) Alper, H.; Currie, J. K.; Abbayes, H. D. *J. Chem. Soc., Chem. Commun.* **1978**, 311. (d) Carmona, E.; Gutierrez-Puebla, E.; Monge, A.; Marin, J. M.; Paneque, M.; Poveda, M. L. *Organometallics* **1989**, *8*, 967. (e) Hong, P.; Mise, T.; Yamazaki, H. *Chem. Lett.* **1981**, 989. (f) Mise, T.; Hong, P.; Yamazaki, H. *Chem. Lett.* **1981**, 993. (g) Yamazaki H.; Hong, P. *J. Mol. Catal.* **1983**, *21*, 133. (h) Inoue, Y.; Taniguchi, M.; Hashimoto, H.; Ohuchi, K.; Imaizumi, S. *Chem. Lett.* **1988**, 81. (i) Arzoumanian H.; Petrignani, J.-F. *Tetrahedron Lett.* **1986**, *27*, 5979. (j) Buchwald, S. L.; Fang, Q.; King, S. M. *Tetrahedron Lett.* **1988**, *29*, 3445. (k) DeShong, P.; Sidler, D. R.; Rybczynski, P. J.; Slough, G. A.; Rheingold, A. L. *J. Am. Chem. Soc.* **1988**, *110*, 2575. (l) Cowell A.; Stille, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 4193.

(7) Doyama, K.; Fujiwara, K.; Joh, T.; Maeshima, K.; Takahashi, S. *Chem. Lett.* **1988**, 901.

(8) Joh, T.; Doyama, K.; Fujiwara, K.; Maeshima, K.; Takahashi, S. *Organometallics*, in press.

(9) Albanesi G.; Tovaglieri, M. *Chem. Ind.* (*Milan*) **1959**, *41*, 189.

(10) Sauer, J. C.; Cramer, R. D.; Engelhardt, V. A.; Ford, T. A.; Holmquist, H. E.; Howk, B. W. *J. Am. Chem. Soc.* **1959**, *81*, 3677.

Table V. Effect of CO Pressure[a]

| entry | initial pressure of CO, atm | conv, % | selectivity,[b] % | yield,[c] % |
|---|---|---|---|---|
| 1 | 20 | 70 | 67 | 47 |
| 2 | 50 | 71 | 77 | 55 |
| 3 | 100 | 81 | 83 | 67 |
| 4 | 150 | 87 | 83 | 72 |
| 5 | 195 | 87 | 87 | 76 |
| 6 | 250 | 67 | 85 | 57 |
| 7 | 275 | 69 | 84 | 58 |

[a] Reaction conditions: **1a**, 4.85 mmol; $Rh_4(CO)_{12}$, 0.027 mmol; additives, 15 mmol; $H_2O$, 56 mmol; THF, 10 mL; CO, 100 atm; reaction temperature, 100 °C; reaction time, 5 h. [b] Based on **1a** consumed. [c] Based on **1a** used.

When alcohols were used as solvents, this reaction would be competitive to ours. With ethanol as a solvent, furanones **2a** and/or 8 were obtained, depending on the amount of $H_2O$ added, as shown in Table IV. When the water content increased to 5%, the formation of 8 was completely suppressed. This indicates that the reaction with water was much faster than that with alcohol in water-containing ethanol.

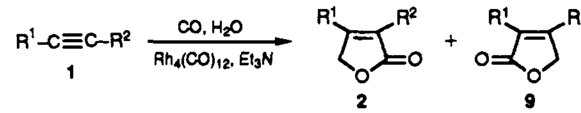
In order to obtain the information of the pressure dependence of the present reaction, a series of reactions were carried out under carbon monoxide pressures in the range 20–275 atm. The results are shown in Table V. Thus, a maximum in the conversion (87%) was attained around a carbon monoxide pressure in the range 150–200 atm, while the selectivity of the furanone formation was almost constant (about 85%) under pressures above 100 atm of carbon monoxide.

**Application to Other Acetylenes.** In order to examine the scope of the present reaction and to obtain further information on the reaction mechanism, carbonylation of various acetylenes 1 was carried out. The results are summarized in Table VI, which shows that furan-2-(5*H*)-ones 2 and/or 9 were obtained in satisfactory yields for internal acetylenes bearing alkyl, alkenyl, and aryl substituents.

Attempts to obtain furanones from monosubstituted acetylenes such as phenylacetylene were not successful under the adopted reaction conditions. In these cases, no definite products could be isolated and the catalyst was found to decompose to the metal, perhaps due to oxidative addition and polymerization of the terminal acetylene having an active C–H bond.

The reactivity of acetylenes was influenced by the substituents; it tends to decrease in the order alkenyl > aryl > alkyl, suggesting that electronically deficient acetylenes are more favorable for the present reaction.

Scheme VII



Unsymmetrically substituted acetylenes afforded two structural isomers 2 and 9, the ratio of which varied depending on the substituents. As the isomers could not be separated by column chromatography on silica in most cases, the isomer ratio was determined by the integration of $^1H$ NMR analysis of the isomeric mixtures. The isomers 2 and 9 are easily discriminated in the $^1H$ NMR spectrum of the isomeric mixtures obtained from the alkyl-substituted acetylenes (**1j** and **1k**) on the basis of the presence of homoallylic coupling between the methylene protons and the α-protons of $R^2$ in 2. In order to distinguish the isomers obtained from the monosubstituted diphenylacetylenes (**1b–f**) by the $^1H$ NMR spectra, a NOE technique was applied. Irradiating the methylene protons at their resonance frequency resulted in the increase of the signal intensity of the ortho protons of $R^1$ in 2 or $R^2$ in 9, which is spacially close to that of the methylene protons. Similarly, the signal intensity of the methylene protons increased when the *o*-hydrogens of the aromatic ring ($R^1$ in 2 and $R^2$ in 9) were irradiated. By this technique the isomer 2 or 9 could be discriminated from the other in the $^1H$ NMR spectra of the isomeric mixtures. The results show that the isomer ratio and the reactivity are affected by both the steric and electronic nature of the substituents of the acetylenes.

The isomers 2, which bear the substituent $R^2$ at the 3-position of the furanone ring, are generally the major products in the reaction of unsymmetrical acetylenes. This suggests that the formation of furanones is controlled by the bulkiness of the substituents $R^1$ and $R^2$, since $R^2$ is always greater than $R^1$ in steric bulkiness.

Much reduced reactivity of the *o*-methyl-substituted derivative **1f** in comparison with the *p*-methyl-substituted **1c** might also be due to steric factors. However, in the reaction of *o*-methoxy-substituted derivative **1e**, the reactivity was not so reduced in comparison with para-substituted **1b**. In the latter case, it may be considered that the conformation which is free from the steric interaction by the rotation of the $C_6H_4$–$OCH_3$ bond could be possible.

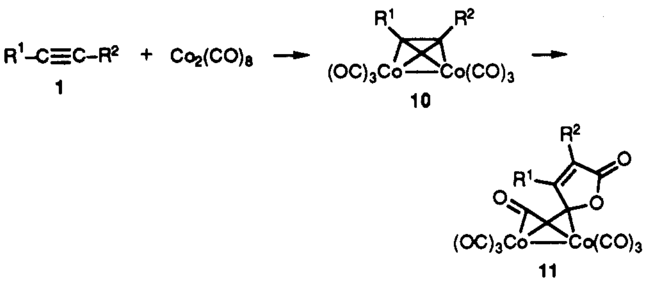
By introducing a cyano group to the para position of one phenyl group of **1a**, the reactivity was increased and the isomer **9d** became the major product. On the other hand,

Table VI. Reaction of Various Acetylenes[a]

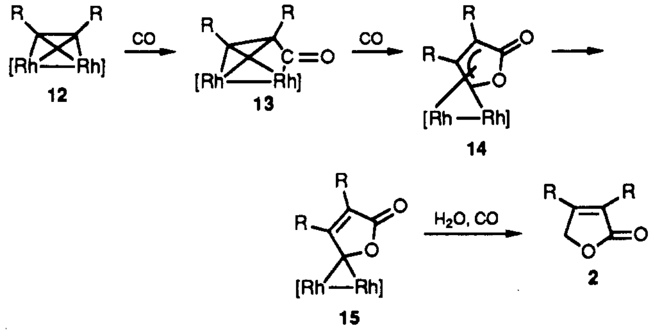
| acetylenes | $R_1$ | $R_2$ | conv, % | selectivity,[b] % | isomer ratio[c] 2/9 |
|---|---|---|---|---|---|
| **1a** | Ph | Ph | 81 | 83 | |
| **1b** | Ph | $C_6H_4OMe$-*p* | 74 | 68 | 55/45 |
| **1c** | Ph | $C_6H_4$-Me-*p* | 62 | 92 | 49/51 |
| **1d** | Ph | $C_6H_4CN$-*p* | 100 | 69 | 24/76 |
| **1e** | Ph | $C_6H_4OMe$-*o* | 64 | 87 | 56/44 |
| **1f** | Ph | $C_8H_4Me$-*o* | 17 | 51 | 68/32 |
| **1g** | Ph | CH=CHPh(E) | 100 | 87 | 64/36 |
| **1h** | $C_6H_4OMe$-*p* | CH=CHPh(E) | 100 | 91 | 63/37 |
| **1i** | CH=CHPh(E) | CH=CHPh(E) | 100 | 50 | |
| **1j**[d] | Me | Ph | 95 | 77 | 73/27[e] |
| **1k**[d] | Me | $C_6H_4OMe$-*p* | 96 | 78 | 77/23[e] |
| **1l** | Me | CH=CHPh(E) | 94 | 96 | 78/22[e] |
| **1m**[f] | Et | Et | 100 | 69 | |

[a] Reaction conditions: 1, 4.85 mmol; $Rh_4(CO)_{12}$, 0.027 mmol; $Et_3N$, 15 mmol; $H_2O$, 56 mmol; THF, 10 mL; CO, 100 atom; reaction temperature, 100 °C; reaction time, 5 h. [b] Based on 1 consumed. [c] Determined by $^1H$ NMR spectroscopy. [d] Conditions: 1, 8.70 mmol; $Rh_4(CO)_{12}$, 0.107 mmol; $Et_3N$, 23.6 mmol; $H_2O$, 112 mmol; THF, 15 mL; reaction time, 8 h. [e] Calculated from isolated yields. [f] Conditions: **1m**, 9.7 mmol; $Rh_4(CO)_{12}$, 0.107 mmol; $Et_3N$, 23.6 mmol; $H_2O$, 112 mmol; THF, 15 mL; CO, 150 atm; reaction time, 17 h.

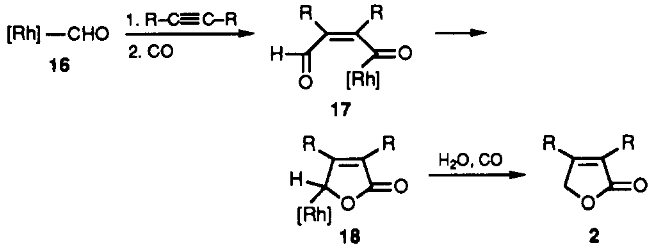
**Scheme VIII**



**Scheme IX**



**Scheme X**



introduction of electron-donating groups, such as a methyl or methoxy group, increased the **2**/**9** isomer ratio. These tendencies can be explained by the electron density on the acetylene carbons. That is, the carbonyl group of furanones prefers to be introduced to the carbon atom having less electron density.

On the contrary, the carbonyl group of furanones prefers to be introduced to the carbon atom having higher electron density in the reaction of **1j–l**. In these cases, a steric effect seems to be predominant over an electronic effect for determining the product distribution.

**Mechanistic Consideration.** The synthetic procedure described in this paper provides a simple route to 3,4-disubstituted furan-2(5*H*)-ones, which are difficult to prepare otherwise. Although there is only a little evidence for the mechanistic aspects of our reaction at the present time, some considerations have been made.

Acetylenes can be carbonylated in the presence of catalytic amounts of $Co_2(CO)_8$ in polar solvents to give bifuranones[9,10] and with stoichiometric amounts of $Co_2(CO)_8$ to give $\mu,\eta^1$-furanone complexes $Co_2(CO)_7(C_4O_2R^1R^2)$ (**11**), which are thought to be the intermediate in catalytic carbonylation.[11-13] It was reported that the formation of these complexes is controlled by the bulkiness of the substituents $R^1$ and $R^2$ and only one isomer, in which the bulkier substituent is always in the 3-position of the furanone ring, is formed.[12,13] It was also found that, in $\mu,\eta^1$-furanone dicobalt complexes from an asymmetric internal acetylene, the sp carbon atom which has the higher value of the $^{13}C$ NMR chemical shift ($\delta$) occupied the 3-position, while that with the lower value occupied the 4-position of the furanone ring.[14]

A similar tendency for steric and electronic effects was observed in our reactions, although the regioselectivity was not as high as that of the $\mu,\eta^1$-furanone dicobalt complex formation. From these observations, one possible reaction pathway for the formation of furanones in our reaction can be written as shown in Scheme IX. Acetylene could interact with the rhodium cluster to give $\mu,\eta^2$-acetylene complex **12**, which could react with carbon monoxide to afford $\mu,\eta^1$-furanone complex **15** via the intermediates **13** and **14**. Complex **15** could be reduced by $H_2O$ and CO under water-gas shift reaction conditions to form the final product **2** and/or **9**. It is believed that the addition of a base promotes the reaction in this reducing step, although the roll of the base is not clear at the present time.

Another possible reaction pathway, as shown in Scheme X, which involves a formyl complex **16** as the intermediate, can also be considered. The formation of the formyl complex is thought to be possible under the water-gas shift reaction conditions. Acetylene and carbon monoxide could successively insert into the formyl complex **16** to give acyl complex **17**, which could cyclize to form $\sigma$-furanoyl complex **18**. This could be hydrogenated by $H_2O$ and CO to afford the furanone **2** and/or **9**.

Construction of a furanone ring by sequential insertion of phenylacetylene and carbon monoxide into acyl-metal bonds of mononuclear complexes has been reported.[6b-g]

Although it cannot be concluded at the present time whether the former process or the latter one is reasonable, the former reaction path may be preferred for the present reaction, because metal clusters that possess metal-metal bonds act as excellent catalysts.

## Experimental Section

**General Procedures.** Melting points were recorded on a Yanagimoto micro melting point apparatus and are uncorrected. IR spectra were taken on a Hitachi 295 infrared spectrophotometer. NMR spectra were recorded on a Bruker AM-360 or JEOL JNR-PMX 60SI instrument. NMR spectra are expressed in parts per million from $Me_4Si$ as the internal standard. The mass spectra were obtained on a JEOL JMS 06 apparatus. Elemental analyses were performed by the Material Analysis Center, ISIR, Osaka University. Solvents were purified by standard methods. Other chemicals were distilled or recrystallized before use.

**Reactions of Diphenylacetylene (1a). 1. Reaction of 1a under Standard Reaction Conditions.** Into a 20-mL glass ampule were added 0.86 g (4.85 mmol) of **1a**, 20 mg (0.027 mmol) of $Rh_4(CO)_{12}$, 1.5 g (15 mmol) of $Et_3N$, 10 mL of THF, and 1 mL (56 mmol) of water under nitrogen atmosphere, and the ampule was placed in a 100-mL stainless steel autoclave. The reaction system was flushed three times with CO and then charged at room temperature to an initial CO pressure of 100 atm. The reaction was carried out at 100 °C for 5 h. The reddish purple solution obtained was diluted with 50 mL of benzene and washed subsequently with saturated aqueous sodium chloride, diluted aqueous hydrogen chloride, and saturated aqueous sodium chloride. The benzene solution was then dried over anhydrous sodium sulfate. After removal of solvent, the products were separated by column chromatography on silica gel with dichloromethane as the eluent. Product **2a** (767 mg, 83% selectivity) was isolated and 163 mg (19%) of starting material **1a** was recovered.

When the reaction was carried out under the same conditions for 22.5 h, 100% conversion and 87% yield of **2a** were attained.

**2a**: colorless crystals from hexane–benzene, mp 121.5–123 °C (lit. 115–116 °C[6a]); $^1H$ NMR (60 MHz, $CDCl_3$) $\delta$ 5.10 (s, 2 H, $CH_2$),

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(11) Sternberg, H. W.; Shukys, J. G.; Donne, C. D.; Markby, R. Friedel, R. A.; Wender, I. *J. Am. Chem. Soc.* **1959**, *81*, 2339.

(12) Palyi, Y.; Varadi, G.; Vizi-Orosz, A.; Marko, L. *J. Organomet. Chem.* **1975**, *90*, 85.

(13) Guthrie, D. J. S.; Khand, I. U.; Knox, G. R.; Kollmeier, J.; Pauson, P. L.; Watts, W. E. *J. Organomet. Chem.* **1975**, *90*, 93.

(14) Varadi, G.; Vecsei, I.; Otvos, I.; Palyi, G.; Marko, L. *J. Organomet. Chem.* **1979**, *182*, 415.

7.2–7.5 (m, 10 H, arom). Anal. Calcd for $C_{16}H_{12}O_2$: C, 81.34; H, 5.12. Found: C, 81.06; H, 5.09%.

2. **Reaction of 1a in the Presence of $D_2O$.** By the same procedure described above except use of $D_2O$ (1 mL) instead of $H_2O$, 0.86 g (4.85 mmol) of **1a** was reacted at 100 °C for 22 h to give, after purification by column chromatography on silica gel, 0.73 g (63%) of deuterated furanone **3**.

**3**: colorless crystals from hexane–benzene, mp 111.7–113.2 °C; $^1$H NMR (60 MHz, $CDCl_3$) $\delta$ 7.2–7.5 (m, 10 H, arom); IR (Nujol) 1760 cm$^{-1}$; MS *m/z* 238 ($M^+$).

3. **Reaction of 1a with CO and $H_2$.** Into a 20-mL glass ampule were added 0.71 g (40 mmol) of **1a**, 23 mg (0.031 mmol) of $Rh_4(CO)_{12}$, 0.5 g (5.0 mmol) of $Et_3N$, and 10 mL of THF under nitrogen atmosphere, and the ampule was placed in a 100-mL stainless steel autoclave. Tthe reaction system was flushed three times with hydrogen and charged with a hydrogen pressure of 50 atm and then additionally with carbon monoxide to a pressure of 100 atm. The reaction was carried out at 100 °C for 16 h to afford, after purification by column chromatography on silica gel, 142 mg (20%) of stilbene **5** and 469 mg (56%) of hydroxymethylated product **4**.

**4**: colorless oil; $^1$H NMR (60 MHz, $CDCL_3$) $\delta$ 1.85 (br, 1 H, OH), 2.90 (br, 2 H, Ph–$CH_2$), 3.7 (m, 2 H, $CH_2$–OH), 4.3–4.7 (m, 1 H, CH), 7.0–7.3 (m, 10 H, arom); IR (neat) 3400 cm$^{-1}$ (br).

4. **Reactions of 1a with Various Catalysts.** Activities of various catalysts shown in Table I were examined by the reaction of **1a** under the standard conditions described above. The amount of catalysts used were as follows: $Rh_6(CO)_{16}$, 19.2 mg (0.018 mmol); $RhCl_3$, 28.4 mg (0.108 mmol); $Fe(CO)_5$, 53 mg (0.27 mmol) and 196 mg (1.0 mmol); $Ru_3(CO)_{12}$, 17 mg (0.027 mmol); $Co_2(CO)_8$, 15.3 mg (0.054 mmol) and 30.6 mg (0.108 mmol).

5. **Reaction of 1a in the Presence of Piperidine.** By the procedure of the standard reaction conditions for **1a** and with 1.28 (15 mmol) of piperidine instead of triethylamine, **1a** was reacted to give, after separation by column chromatography on silica gel, 257 mg of **2a** and 562 mg of aminocarbonylated product **7a** with recovery of 173 mg (80% coversion) of unreacted **1a**.

**7a**: pale yellow solid; $^1$H NMR (360 MHz, $CDCl_3$) $\delta$ 1.31 (br s, 2 H, N-$CH_2CH_2CH_2$), 1.58 (br s, 4 H, N-$CH_2CH_2$), 3.47 and 3.61 (br s, br s, 4 H, N-$CH_2$), 6.68 (s, 1 H, Ph-$CH$), 7.1–7.4 (m, 10 H, arom); IR (Nujol) 1630 cm$^{-1}$; MS *m/z* 290 ($M^+$).

6. **Reaction of 1a in the Presence of *n*-Butylamine.** By the procedure of the standard reaction conditions for **1a** and with 1.5 mL (15 mmol) of *n*-butylamine instead of triethylamine, **1a** was reacted to give, after separation by column chromatography on silica gel, 175 mg of furanone **2a** and 431 mg of aminocarbonylated product **7b** with recovery of 350 mg (59% conversion) of unreacted **1a**.

**7b**: pale yellow oil; $^1$H NMR (360 MHz, $CDCl_3$) $\delta$ 0.88 (t, 3 H, $J$ = 7.3 Hz, $CH_3$), 1.26 and 1.43 (m, 4 H, N-$CH_2CH_2CH_2CH_3$), 3.30 (m, 2 H, N-$CH_2$), 5.5 (br s, 1 H, NH), 6.9–7.4 (m, 10 H, arom), 7.85 (s, 2 H, Ph-$CH$); IR (neat) 1670 cm$^{-1}$; MS *m/z* 279 ($M^+$).

7. **Reaction of 1a in Ethanol.** As shown in Table IV, **1a** was reacted in ethanol, varying the content of water. The experiment carried out in anhydrous ethanol (entry 4) is described here. Triethylamine was dried over KOH, and ethanol was distilled from $CaH_2$ and stored over 3A molecular sieves. Carbon monoxide was dried over 3A molecular sieves. By the procedure of the standard reaction conditions for **1a** and with the well-dried reagents and without water, **1a** was reacted to give, after purification by chromatography on silica gel, 1.16 g (86%) of 5-ethoxy-3,4-diphenylfuran-2(5*H*)-one (**8**).

**8**: colorless leaves from hexane–benzene, mp 136–138 °C (lit. 137–138 °C[15]); $^1$H NMR (60 MHz, $CDCl_3$) $\delta$ 1.25 (t, 3 H, $J$ = 7 Hz, $CH_3$), 3.8 (m, 2 H, O-$CH_2$), 6.05 (s, 1 H, CH), 7.05 (s, 10 H, arom); MS *m/z* 280 ($M^+$).

**Reactions of Various Acetylenes. 1. Reaction of (4-Methoxyphenyl)phenylacetylene (1b).** By the procedure of the standard reaction conditions for **1a**, 1.01 g (4.85 mmol) of **1b** was reacted at 100 °C for 5 h to give, after separation by column chromatography on silica gel, 0.66 g (68% selectivity) of the isomeric mixture of **2b** and **9b** with recovery of 0.26 g (74% conversion) of unreacted **1b**. The molar ratio of **2b**/**9b** was found to be about 55/45 from the integration of the $^1$H NMR spectrum. The distinction between **2b** and **9b** was performed by using a NOE technique. The isomers, **2b** and **9b**, could be separated by further column chromatography on silica gel with hexane–ether as the eluent, although only small amounts of the pure products were isolated.

**2b**: colorless crystals, mp 160.8–161.5 °C; $^1$H NMR (360 MHz, $CDCl_3$) $\delta$ 3.82 (s, 3 H, $CH_3$), 5.14 (s, 2 H, $CH_2$), 6.89 (d, 2 H, $J$ = 8.7 Hz, *o*-H to $OCH_3$), 7.3–7.5 (m, 7 H, arom); IR (Nujol) 1740 cm$^{-1}$. Anal. Calcd for $C_{17}H_{14}O_3$: C, 76.68; H, 5.30. Found: C, 76.37; H, 5.24.

**9b**: pale yellow crystals, mp 114.0–115.2 °C; $^1$H NMR (360 MHz, $CDCl_3$) $\delta$ 3.81 (s, 3 H, $CH_3$), 5.16 (s, 2 H, $CH_2$), 6.84 (d, 2 H, $J$ = 8.7 Hz, *o*-H to $OCH_3$), 7.28 (d, 2 H, $J$ = 8.7 Hz, *m*-H to $OCH_3$), 7.3–7.5 (m, 5 H, Ph); IR (Nujol) 1750 cm$^{-1}$. Anal. Calcd for $C_{17}H_{14}O_3$: C, 76.68; H, 5.30. Found: C, 76.42; H, 5.13.

2. **Reaction of (*p*-Tolyl)phenylacetylene (1c).** By the procedure of the standard reaction conditions for **1a**, 0.90 g (4.85 mmol) of **1c** was reacted at 100 °C for 5 h to afford, after separation by column chromatography on silica gel, 0.67 g (92% selectivity) of the isomeric mixture of **2c** and **9c** together with 0.34 g (62% conversion) of unreacted **1c**. The ratio of **2c**/**9c** was found to be about 49/51 from the integration of the $^1$H NMR spectrum.

**2c**/**9c**: colorless solids; $^1$H NMR (360 MHz, $CDCl_3$) $\delta$ 2.29 and 2.31 (s/s, 3 H/3 H, $CH_3$ for **2c**/**9c**), 5.02 and 5.06 (s/s, 2 H/2 H, $CH_2$ for **2c**/**9c**), 7.0–7.5 (m/m, 9 H/9 H, arom for two isomers).

3. **Reaction of (4-Cyanophenyl)phenylacetylene (1d).** By the procedure of the standard reaction conditions for **1a**, 0.99 g (4.85 mmol) of **1d** was reacted at 100 °C for 5 h to afford, after purification by column chromatography on silica gel, 0.87 g (69% selectivity) of the isomeric mixture of **2d** and **9d**. The ratio of **2d**/**9d** was found to be about 24/76 from the integration of the $^1$H NMR spectrum. The isomers, **2d** and **9d**, could be isolated by further column chromatography on silica gel with hexane–ether as the eluent, although only small amounts of the pure products were obtained.

**2d**: colorless crystals, mp 141.0–142.6 °C; $^1$H NMR (360 MHz, $CDCl_3$) $\delta$ 5.21 (s, 2 H, $CH_2$), 7.25–7.5 (m, 5 H, Ph), 7.57 and 7.67 (2 d, 4 H, $J$ = 8.3 Hz, *o*- and *m*-H to CN); IR (Nujol) 2210, 1775 cm$^{-1}$. Anal. Calcd for $C_{17}H_{11}NO_2$: C, 78.15; H, 4.24; N, 5.36. Found: C, 78.40; H, 4.27; N, 5.51.

**9d**: pale yellow crystals, mp 141.2–143.0 °C; $^1$H NMR (360 MHz, $CDCl_3$) $\delta$ 5.19 (s, 2 H, $CH_2$), 7.35–7.5 (m, 7 H, Ph and *m*-H to CN), 7.65 (d, 2 H, $J$ = 8.7 Hz, *o*-H to CN); IR (Nujol) 2215, 1775 cm$^{-1}$. Anal. Calcd for $C_{17}H_{11}NO_2$: C, 78.15; H, 4.24; N, 5.36. Found: C, 78.19; H, 4.06; N, 5.20.

4. **Reaction of (2-Methoxyphenyl)phenylacetylene (1e).** By the procedure of the standard reaction conditions for **1a**, 1.01 g (4.85 mmol) of **1e** was reacted at 100 °C for 5 h to give, after purification by column chromatography on silica gel, 0.72 g (92% selectivity) of the isomeric mixture of **2e** and **9e** together with 0.36 g (64% conversion) of **1e**. The ratio of **2e**/**9e** was found to be about 56/44 from the integration of the $^1$H NMR spectrum.

**2e**/**9e**: pale yellow oils; $^1$H NMR (360 MHz, $CDCl_3$) $\delta$ 3.59 and 3.72 (s/s, 3 H/3 H, $CH_3$ for **2e**/**9e**), 5.19 and 5.24 (s/s, 2 H/2 H, $CH_2$ for **2e**/**9e**), 6.8–7.3 (m/m, 9 H/9 H, arom for two isomers); IR (Nujol) 1775 cm$^{-1}$.

5. **Reaction of (*o*-Tolyl)phenylacetylene (1f).** By the procedure of the standard reaction conditions for **1a**, 0.90 g (4.85 mmol) of **1f** was reacted at 100 °C for 5 h to give, after purification by column chromatography on silica gel, 0.72 g (86% selectivity) of the isomeric mixture of **2f** and **9f** together with 0.75 g (17% conversion) of **1f**. The ratio of **2f**/**9f** was found to be about 68/32 from the integration of the $^1$H NMR spectrum.

**2f**/**9f**: pale yellow oil; $^1$H NMR (360 MHz, $CDCl_3$) $\delta$ 1.98 and 2.14 (s/s, 3 H/3 H, $CH_3$ for **2f**/**9f**), 5.00 and 5.30 (s/s, 2 H/2 H, $CH_2$ for **2f**/**9f**), 7.2–7.5 (m/m, 9 H/9 H, arom for two isomers); IR (Nujol) 1750 cm$^{-1}$.

6. **Reaction of 1,4-Diphenylbut-1-en-3-yne (1g).** By the procedure of the standard reaction conditions for **1a**, 1.0 g of **1g** was reacted at 100 °C for 5 h to give, after separation by column chromatography on silica gel, **2g** and **9g** in 56% and 31% yields, respectively.

**2g**: pale yellow fine needles from hexane–benzene, mp 114–115 °C; $^1$H NMR (360 MHz, $CDCl_3$) $\delta$ 5.05 (s, 2 H, $CH_2$), 7.01 (d, 1

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[15] Hong, P.; Mise, T.; Yamazaki, H. *Nippon Kagaku Kaishi* 1982, 242.

H, *J* = 16.3 Hz, PhCH=C*H*), 7.25–7.5 (m, 10 H, arom), 7.98 (d, 1 H, *J* = 16.3 Hz, Ph—C*H*=CH); $^{13}$C NMR (CDCl$_3$) δ 70.0 (t, $^1J_{CH}$ = 154.5 Hz, CH$_2$), 172.6 (d, $^3J_{CH}$ = 11 Hz, C=O); IR (Nujol) 1760 cm$^{-1}$; MS *m/z* 262 (M$^+$). Anal. Calcd for $C_{18}H_{14}O_2$: C, 82.42; H, 5.38. Found: C, 82.13; H, 5.42.

**9g**: colorless fine needles from hexane–benzene, mp 152–153.5 °C; $^1$H NMR (360 MHz, CDCl$_3$) δ 5.17 (s, 2 H, CH$_2$), 6.93 (d, 1 H, *J* = 16.6 Hz, Ph—CH=C*H*), 7.25 (d, 1 H, *J* = 16.6 Hz, Ph—C*H*=CH), 7.35–7.6 (m, 10 H, arom): $^{13}$C NMR (CDCl$_3$) δ 69.0 (dt, $^3J_{CH}$ = 6.8 Hz, $^1J_{CH}$ = 154.5 Hz, CH$_2$), 173.4 (s, C=O); IR (Nujol) 1750 cm$^{-1}$; MS *m/z* 262 (M$^+$). Anal. Calcd for $C_{18}H_{14}O_2$: C, 82.42; H, 5.38. Found: C, 82.22; H, 5.24.

**7. Reaction of 4-(4-Methoxyphenyl)-1-phenylbut-1-en-3-yne (1h).** By the standard procedure, 1.15 g (4.85 mmol) of **1h** was reacted to give, after purification by column chromatography on silica gel, **2h** and **9h** in 57% and 34% yields, respectively.

**2h**: pale yellow crystals from hexane–benzene, mp 123–125 °C; $^1$H NMR (360 MHz, CDCl$_3$) δ 3.89 (s, 3 H, CH$_3$), 5.07 (s, 2 H, CH$_2$), 7.03 (m, 3 H, Ph—CH=C*H* and *o*-H to OCH$_3$), 7.95 (d, 1 H, *J* = 16.2 Hz, Ph—C*H*=CH), 7.2–7.5 (m, 7 H, arom); IR (Nujol) 1745 cm$^{-1}$; MS *m/z* 292 (M$^+$). Anal. Calcd for $C_{19}H_{16}O_3$: C, 78.06; H, 5.52. Found: C, 78.05; H, 5.48.

**9h**: pale yellow fine needles from hexane–benzene, mp 128–131 °C; $^1$H NMR (360 MHz, CDCl$_3$) δ 3.87 (s, 3 H, CH$_3$), 5.15 (s, 2 H, CH$_2$), 6.90 (d, 1 H, *J* = 16.5 Hz, Ph—CH=C*H*), 7.25 (d, 1 H, *J* = 16.5 Hz, Ph—C*H*=CH), 7.02 and 7.3–7.6 (m, 9 H, arom); IR (Nujol) 1750 cm$^{-1}$; MS *m/z* 292 (M$^+$). Anal. Calcd for $C_{19}H_{16}O_3$: C, 78.06; H, 5.52. Found: C, 77.80; H, 5.53.

**8. Reaction of 1,6-Diphenyl-1,5-hexadien-3-yne (1i).** By the standard procedure, 1.12 g (4.85 mmol) of **1i** was reacted to give, after purification by column chromatography on silica gel, 706 mg (50%) of **2i**.

**2i**: yellow crystals from hexane–benzene, mp 136–138 °C; $^1$H NMR (360 MHz, CDCl$_3$) δ 5.04 (s, 2 H, CH$_2$), 6.81 (d, 1 H, *J* = 16.4 Hz, =C*H*—C—CH$_2$), 7.04 (d, 1 H, *J* = 16.2 Hz, =C*H*—C—CO), 7.2–7.6 (m, 11 H, PhC*H*=CH—C—CH$_2$ and arom), 7.92 (d, 1 H, *J* = 16.2 Hz, PhC*H*=CH—C—CO); IR (Nujol) 1750 cm$^{-1}$; MS *m/z* 288 (M$^+$). Anal. Calcd for $C_{20}H_{16}O_2$: C, 83.31; H, 5.59. Found: C, 82.54; H, 5.57.

**9. Reaction of 1-Phenylpropyne (1j).** Into a 30-mL glass ampule were added 1.0 g (8.7 mmol) of **1j**, 80 mg (0.108 mmol) of Rh$_4$(CO)$_{12}$, 4 g (40.0 mmol) of triethylamine, 15 mL of THF, and 2 mL (112 mmol) of water under nitrogen atmosphere. The ampule was placed in a 100-mL stainless steel autoclave. The reaction system was flushed three times with CO and then charged at room temperature with an initial CO pressure of 150 atm. The reaction was carried out at 100 °C for 8 h. The reaction products were separated by column chromatography on silica gel to afford 1.114 g (77% selectivity) of the isomeric mixture of **2j** and **9j**, together with 50 mg (95% conversion) of the starting compound **1j**.

**2j/9j**: colorless crystalline solids; $^1$H NMR (360 MHz, CDCl$_3$) δ 2.07 (m, 3 H, CH$_3$ for **9j**), 2.18 (s, 3 H, CH$_3$ for **2j**), 4.70 (s, 2 H, CH$_2$ for **2j**), 4.97 (q, 2 H, *J* = 1.9 Hz, CH$_2$ for **9j**), 7.3–7.5 (m/m, 5 H/5 H, Ph for two isomers).

The ratio of **2j**/**9j** was found to be 73/27 from the integration of the $^1$H NMR signals for the hydrogen atoms of the methylene group of the furanone ring.

**10. Reaction of 1-(4-Methoxyphenyl)propyne (1k).** By the procedure described for the reaction of **1j**, 1.27 g (8.7 mmol) of **1k** was reacted to give 1.331 g (78% selectivity) of the isomeric mixture of **2k** and **9k**, together with 55 mg (96% conversion) of **1k**.

**2k/9k**: colorless crystalline solids; $^1$H NMR (360 MHz, CDCl$_3$) δ 2.13 (m, 3 H, C=C—CH$_3$ for **9k**), 2.20 (s, 3 H, C=C—CH$_3$ for **2k**), 3.8–3.9 (m/m, 3 H/3 H, O—CH$_3$ for **2k/9k**), 4.76 (s, 2 H, CH$_2$ for **2k**), 5.03 (q, 2 H, *J* = 2.0 Hz, CH$_2$ for **9k**), 6.9–7.5 (m/m, 4 H/4 H, arom for two isomers).

**11. Reaction of 1-Phenylpent-1-en-3-yne (1l).** By the standard procedure, 0.69 g (4.85 mmol) of **1l** was reacted to give, after purification by column chromatography on silica gel, **2l** and **9l** in 66% and 19% yields, respectively, along with 40 mg (6%) of starting material **1l**.

**2l**: colorless crystals from hexane–benzene, mp 132.5–133.5 °C; $^1$H NMR (360 MHz, CDCl$_3$) δ 2.20 (s, 3 H, CH$_3$), 4.71 (s, 2 H, CH$_2$), 6.79 (d, 1 H, *J* = 16.3 Hz, Ph—CH=C*H*), 7.77 (d, 1 H, *J* = 16.3 Hz, Ph—C*H*=CH), 7.2–7.5 (m, 5 H, Ph); IR (Nujol) 1750 cm$^{-1}$; MS *m/z* 200 (M$^+$). Anal. Calcd for $C_{13}H_{12}O_2$: C, 77.98; H, 6.04. Found; C, 77.54; H, 6.00.

**9l**: colorless leaves from hexane–benzene, mp 136–137.5 °C; $^1$H NMR (360 MHz, CDCl$_3$) δ 2.02 (t, 3 H, *J* = 1.7 Hz, CH$_3$), 5.01 (q, 2 H, *J* = 1.7 Hz, CH$_2$), 6.78 (d, 1 H, *J* = 16.5 Hz, Ph—CH=C*H*), 7.06 (d, 1 H, *J* = 16.5 Hz, Ph—C*H*=CH), 7.2–7.5 (m, 5 H, Ph); IR (Nujol) 1765 cm$^{-1}$; MS *m/z* 200 (M$^+$). Anal. Calcd for $C_{13}H_{12}O_2$: C, 77.98; H, 6.04. Found: C, 77.69; H, 5.94.

**12. Reaction of 3-Hexyne (1m).** By the analogy of the preocedure for **1j**, 0.80 g (9.7 mmol) of **1m** was reacted under 150 atm of initial pressure of CO at 100 °C for 17 h to give, after purification by the distillation under reduced pressure, 0.86 g (63% yield) of **2m**.

**2m**: colorless oil, bp 85–90 °C/6 mmHg; $^1$H NMR (60 MHz, CDCl$_3$) δ 1.10 and 1.15 (2 t, 6 H, two CH$_3$), 2–2.7 (m, 4 H, two CH$_2$), 4.6 (s, 2 H, O–CH$_2$); IR (neat) 1760 cm$^{-1}$; MS *m/z* 140 (M$^+$).

**Registry No.** **1a**, 501-65-5; **1b**, 7380-78-1; **1c**, 3287-02-3; **1d**, 29822-79-5; **1e**, 41398-67-8; **1f**, 14309-60-5; **1g**, 13343-79-8; **1h**, 116156-19-5; **1i**, 116156-20-8; **1j**, 673-32-5; **1k**, 2749-94-2; **1l**, 54157-31-2; **1m**, 928-49-4; **2a**, 5635-16-5; **2b**, 110836-02-7; **2c**, 133984-16-4; **2d**, 116156-23-1; **2e**, 132589-80-1; **2f**, 133984-17-5; **2g**, 116156-12-8; **2h**, 116156-14-0; **2i**, 116156-18-4; **2j**, 33131-14-5; **2k**, 113444-55-6; **2l**, 116156-16-2; **2m**, 54823-84-6; **3**, 110836-08-3; **4**, 3536-29-6; *trans*-**5**, 103-30-0; *cis*-**5**, 645-49-8; **6**, 16619-12-8; **7a**, 78956-18-0; **7b**, 133984-18-6; **8**, 79379-66-1; **9b**, 110836-03-8; **9c**, 133984-19-7; **9d**, 116156-22-0; **9e**, 133984-20-0; **9f**, 133984-21-1; **9g**, 116156-13-9; **9h**, 116156-15-1; **9j**, 1575-48-0; **9k**, 52176-67-7; **9l**, 116156-17-3; Rh$_4$(CO)$_{12}$, 19584-30-6.