Carbonylation of Enynes under Hydroformylation Conditions Catalyzed by Rhodium Carbonyl. A New Method for Synthesis of Cyclic Enones

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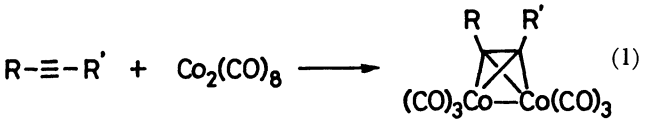
The reactivities of 1-buten-3-yne derivatives toward hydroformylation were studied using a rhodium catalyst. Unexpectedly, cyclopentenone derivatives were obtained in moderate yields together with formyl-substituted dienes and unsaturated lactones. This reaction offers a new method for the catalytic synthesis of cyclopentenones. A mechanism for the cyclic carbonylation of enynes is also discussed.

The transition-metal-catalyzed carbonylation of unsaturated compounds with carbon monoxide is one of the most important reactions in synthetic organic chemistry, and a number of reports have appeared so far.[1]

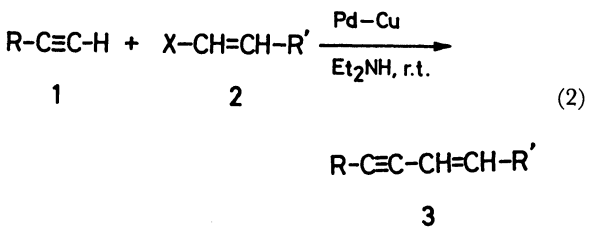
Using synthetic gas (H_2/CO), olefins are effectively carbonylated by the catalysis of such transition metal complexes as Co and Rh to yield the hydroformylated products (oxo process).[2] Although this method is applicable to a variety of olefins such as alkenes, acrylates, and dienes, the reports dealing with the hydroformylation of acetylenes are few. It is known that acetylenes show lower reactivities than olefins toward cobalt-catalyzed hydroformylation. This may be attributed to the formation of a stable cobalt-acetylene complex[3] (Eq. 1) resisting hydroformylation



(1)

under usual reaction conditions.[4] Under drastic conditions, i.e., higher reaction temperature and higher CO pressure, acetylenes are converted mainly to saturated aldehydes in analogy with the case of hydroformylation of olefins.[5]

Thus, we attempted to compare the reactivity of carbon-carbon triple bonds with that of double bonds toward hydroformylation. Enynes, R-C≡C-CH=CH-R′, are a suitable candidate for this purpose because they have carbon-carbon triple molecular bonds and double bonds. Moreover, a variety of their derivatives can be conveniently prepared from the palladium-catalyzed reaction (Eq. 2) which we reported previously.[6] Then, we have examined the

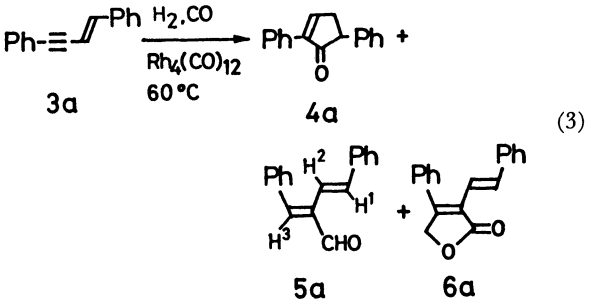


(2)

reactivity of the enynes toward rhodium-catalyzed hydroformylation, and found that the triple bonds are much more reactive than the double bonds and, unexpectedly, the cyclic enones are obtained in moderate yields which might be derived from the hydrocarbonylation of the acetylene group along with the participation of the olefinic part.[7] Here, we wish to report on the results in detail as well as the reaction mechanism.

Results and Discussion

Reactions of 1,4-Diphenyl-1-buten-3-yne (3a) under Hydroformylation Conditions. Enyne **3a** was reacted with carbon monoxide and hydrogen in the presence of a catalytic amount of $Rh_4(CO)_{12}$ at 60 °C. The reaction mixture was concentrated in vacuo and chromatographed on silica. Gradient elution by hexane-benzene gave three carbonylated products, **4a**, **5a**, and

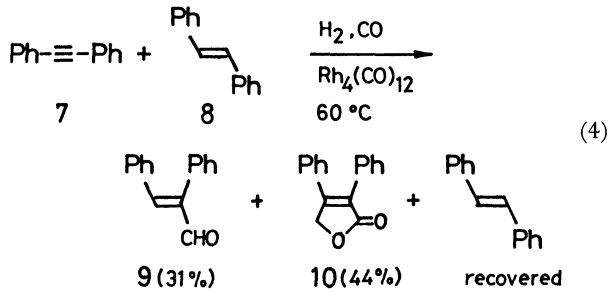


(3)

6a, together with a small amount of the recovered starting material (Eq. 3). One of them was identified as an unexpected cyclocarbonylation product, cyclopentenone **4a**, and others were a normal monoformylated compound **5a** and lactone **6a**. The structure of **4a** was determined by ^1H NMR, which showed a characteristic AMX pattern in the aliphatic region and a double-doublet at δ 7.96 (olefinic proton). The parent ion peak at m/z 234 in the mass spectrum and the CO stretching band at 1700 cm^{-1} in the IR spectrum are also consistent with the assigned structure of **4a**. The major product **5a** showed a CO stretch at 1695 cm^{-1} in the IR spectrum and a ^1H NMR signal at δ 9.65 (s),

indicating that this compound is α,β-unsaturated aldehyde. To confirm the structure, **5a** was led to 2,4-dinitrophenylhydrazone, which showed ^{1}H NMR signals at δ 7.07 (s) and 7.15 (d, J=16.5 Hz) attributable to H^3 and H^1, respectively. Product **6a** showed a parent ion peak at m/z 262 in the mass spectrum, indicating that two molecules of carbon monoxide and one molecule of hydrogen were introduced to the starting material. The IR spectrum exhibited ν_{CO} at 1760 cm^{-1} and the ^{1}H NMR spectrum signals appeared at δ 5.05 (s, 2H), 7.02 (d, 1H, J=16.3 Hz), and 8.98 (d, 1H, J=16.3 Hz). These spectral data indicate that **6a** has an unsaturated lactone ring and a trans-olefinic part; the structure was then defined as that shown in Eq. 3.

Cyclopentenone derivative **4a** is derived from the hydrocarbonylation of the acetylene group along with a participation of the olefinic part. On the other hand, formyl-substituted diene **5a** and lactone **6a** are formed by the carbonylation of just the acetylene group of **3a**; the olefinic moiety remains intact. This implies that the acetylenic part in the conjugated enynes is more reactive than the olefinic part under the hydroformylation conditions. This idea is also supported by a competitive reaction between diphenylacetylene (**7**) and



(4)

diphenylethylene (**8**), which gave only the carbonylated product derived from diphenylacetylene, whereas diphenylethylene was recovered, as shown in Eq. 4.

In order to investigate the effect of the partial pressure of carbon monoxide and hydrogen on the product distribution, **3a** was reacted at 60 °C under the conditions shown in Table 1. In these experiments, the total pressure was kept constant at 200 atm and the ratio of carbon monoxide to hydrogen was varied as shown in Table 1. The conversion and the product distribution are plotted against the partial pressure (Fig. 1). As can be seen from Fig. 1, the conversion of **3a** increases with the partial pressure of hydrogen. The selectivities for both **4a** and **5a** have a maximum point around a pressure of H_2/CO=1. Thus, the pressure dependence of the selectivity is commonly observed in hydroformylation reactions.[2] On the other hand, the selectivity of **6a** is almost constant to the H_2/CO ratio. This fact implies that the catalytic cycle producing compounds, **4a** and **5a**, would be different from that of **6a**, which will be discussed later.

In order to obtain further information on the reac-

Table 1. Partial Pressure Dependence of the Reactivity of **3a**[a]

H_2	CO	Conversion	Selectivity[b]/%		
atm	atm	%	**4a**	**5a**	**6a**
20	180	29	9	12	11
50	150	57	17	28	13
100	100	91	23	32	9
120	80	97	19	22	23

a) Reaction conditions: **3a**, 4.85 mmol; $Rh_4(CO)_{12}$, 0.027 mmol; benzene, 10 ml; 60 °C; 6 h. b) Isolated yields based on **3a** consumed.

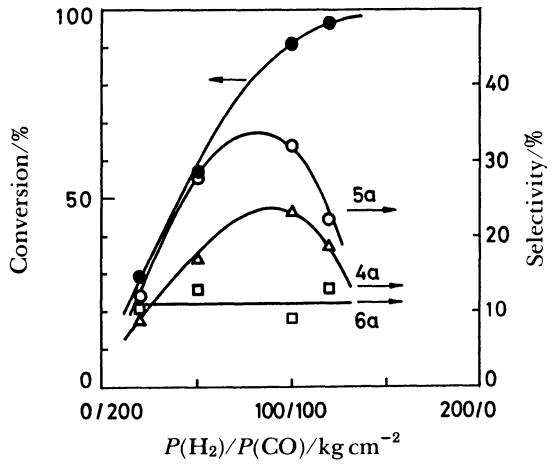
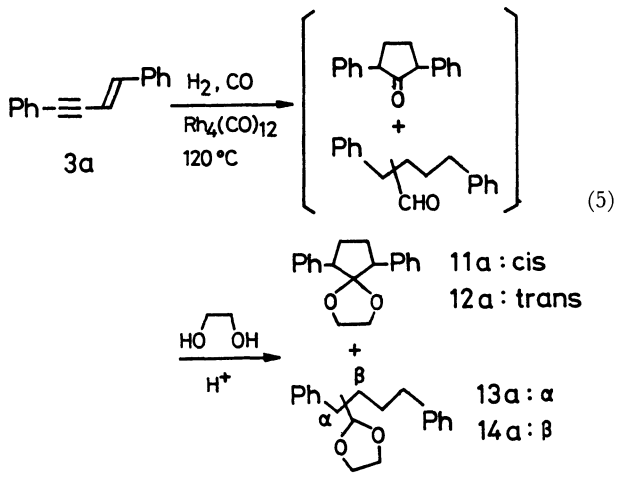


Fig. 1. Partial pressure dependence of conversion (●) and selectivity of **4a** (△), **5a** (○), and **6a** (□).

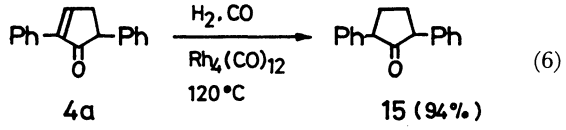
tion, the reaction temperature was increased to 120 °C. A direct isolation of the carbonylated products was so difficult in this case that the reaction mixture was first led to the stable acetals by treating with ethylene glycol in the presence of a catalytic amount of *p*-toluenesulfonic acid. Then, the resultant products were separated by silica column chromatography, giving four acetals **11a**—**14a** (Eq. 5). Thus, in this reaction at



(5)

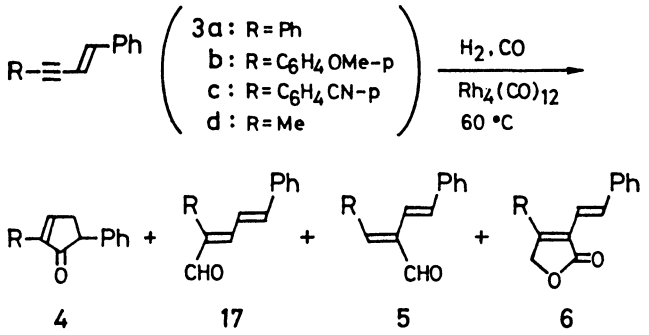
120 °C, saturated cyclic ketone and aldehyde were formed, meaning that **4a** and **5a** once formed would be hydrogenated at a higher temperature under the

hydroformylation conditions to give saturated aldehydes and kotones. In fact, **4a** was hydrogenated at 120 °C and gave 2,5-diphenylcyclopentanone (**15**) in an almost quantitative yield.



(6)

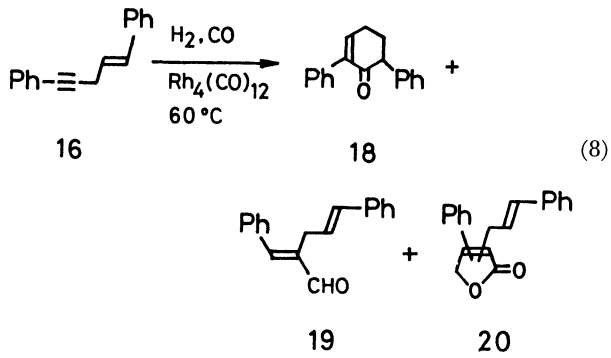
Reaction of Enynes other than 3a under the Hydroformylation Conditions. In order to examine the scope of the present reaction and to obtain information about the reaction mechanism, the hydroformylation of conjugated enynes **3b**, **3c**, and **3d**, and a nonconjugated enyne **16** was also carried out. The results are summerized in Table 2.



(7)

Of the enynes having aryl substituents at the acetylenic part (**3a**, **3b**, and **3c**), the reactivity increases with increasing the electron density of the acetylenic part: **3c**<**3a**<**3b**. But this electronic effect is not clearly reflected by the product distribution.[8] The methyl-substituted enyne **3d** showed a lower reactivity than the aryl substituted enynes and gave a different result: that not cyclopentenone derivative **4d** but (*E*,*E*)-α-formyldiene **17d** was formed with 19% selectivity. It is noteworthy that the latter **17** was not found among the products from the hydroformylation-yielding cyclopentenones. This phenomenon is discussed later.

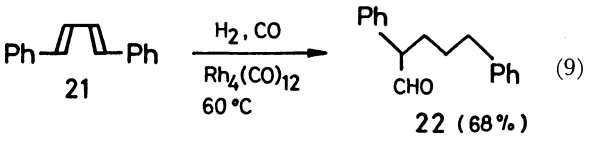
On the other hand, a nonconjugated enyne, 1,5-diphenyl-1-penten-3-yne (**16**), showed a similar reactivity to that of the conjugated ones toward hydroformylation, giving cyclohexenone **18**, 2-formyl-1,4-alkadiene **19**, and lactone **20** in 40, 11, and 18% selectivity, respectively (Eq. 8). This result indicates that the formation of cyclic enones does not require the conjugation of unsaturated bonds.



(8)

There are some examples[9-11] of carbonylations of enynes to afford cyclopentenones using cobalt carbonyl. The carbonylation of titana- or zirconacyclopentene complexes, obtained from the reaction of enynes with an equimolar amount of dichlorotitanium or zirconium complexes, also affords cyclopentenones in good yields.[12] With respect to these reactions, all of which being the stoichiometric syntheses from enynes, our method may be characterized in terms of the "catalytic" synthesis of cyclopentenones from the conjugated enynes, though the selectivity is not so high at the present stage.

Reaction Mechanism. First of all, in order to determine whether the formation of cyclic products is characteristic to the enynes, 1,4-diphenyl-1,3-butadiene (**21**), having the same carbon skeleton as enyne **3a**, was reacted under the same conditions as adopted for **3a**. At 60 °C, **21** gave only an α-monoformylated product **22** with 68% selectivity; no cyclization product was formed (Eq. 9). This suggests that the cyclization of



(9)

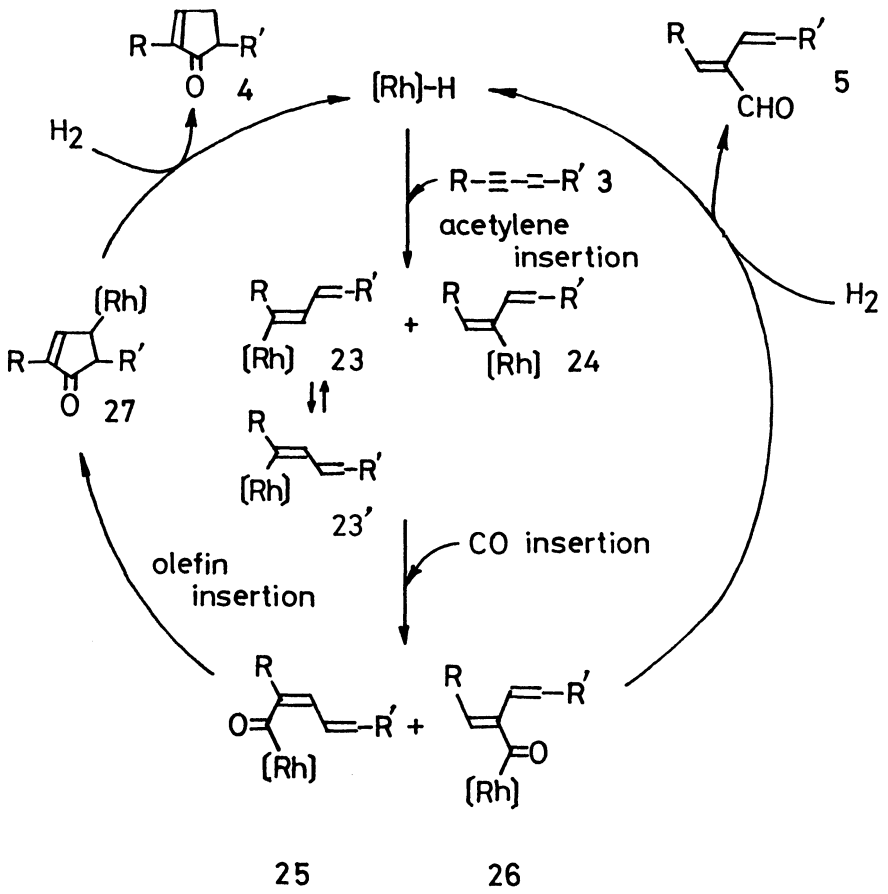
enynes does not pass through butadiene derivatives which might be formed under the conditions if the addition of hydrogen to the acetylenic part of enynes occurs during the first step. Thus, it should be emphasized that the cyclopentenone derivatives are formed directly from the conjugated enynes by the catalysis of the rhodium complex under the hydroformylation conditions.

As described above, the acetylenic part of enynes is thought to be more reactive than the olefinic one toward the rhodium-catalyzed hydroformylation based on judging the structure of the products. Therefore, the first attack of the rhodium carbonyl hydride species H-[Rh], presumably $HRh(CO)_3$, to the enynes may

Table 2. Conversion and Product Distribution for the Reaction of **3**[a]

Enyne	Conversion	Selectivity[b]/%			
	%	**4**	**17**	**5**	**6**
3a	91	23	0	31	9
3b	100	15	0	20	12
3c	70	17	0	23	6
3d	49	0	19	17	20

a) Reaction conditions: **3**, 4.85 mmol; $Rh_4(CO)_{12}$, 0.027 mmol; benzene, 10 ml; H_2, 100 atm; CO, 100 atm; 60 °C; 6 h. b) Isolated yields based on **3** consumed.



Scheme 1. Proposed reaction mechanism.

occur at the acetylenic part. On the basis of this assumption, a reaction mechanism giving **4** and **5** is proposed in Scheme 1.

The first step may be an insertion of the acetylenic part of the enyne to the Rh-H bond, which gives two η^1-diene intermediates, **23** and **24**, depending on the direction of Rh-H addition to the triple bond. They undergo a CO insertion during the next step, forming an isomeric pair of η^1-acyl intermediates, **25** and **26**. α-Acyl intermediate **25** would cyclize to give **27** by an intramolecular insertion of the olefinic part into the Rh-C bond, followed by a cleavage of the Rh-C bond by hydrogen or H-[Rh] to give cyclopentenone derivative **4**. On the other hand, since β-acyl intermediate **26** wouldn't be able to cyclize, due to the steric factor, it gives β-formyl diene **5** via the direct cleavage of **26** by the action of either H-[Rh] or hydrogen. Under the severer reaction conditions, these unsaturated products would suffer hydrogenation to give saturated products.

The formation of other products may be understood by the following reaction path. Thus, α-formyldiene **17**, which was obtained from the reaction of methyl substituted enyne **3d**, may be formed through intermediate **23** having (*E,E*)-diene structure. Whereas, cyclocarbonylation passing through **27** may require (*Z,E*)-diene structure **23'**. This suggests the isomerization of (*E,E*)-dienyl rhodium intermediate **23** to (*Z,E*)-isomer **23'**. Interchanges between (*Z*)- and (*E*)-alkenyl isomers have been reported concerning transition metal-alkenyls such as iron[13] and nickel[14] complexes. On the other hand, a reaction at 120 °C gave both cyclopentanone and saturated aldehyde **13a** (isolated as acetal), which was formed by hydrogenation of α-formyldiene, implying that the olefin insertion step of **25** may compete with the cleavage of the Rh-C bond by either H-[Rh] or hydrogen.

The mechanism yielding unsaturated lactone **6** is not clear at present. But it may be sure that the first step of the lactone formation would not involve an insertion of the acetylenic part to H-[Rh]. The unsaturated lactone ring is constructed by a carbon-carbon triple bond with two molecules of carbon monoxide and one molecule of hydrogen, and the carbon monoxide formally adds to the triple bond in cis-fashion. There are some reports on the formation of lactones from the transition metal-catalyzed carbonylation of acetylenes in alcoholic media.[15]

In the course of our study on the carbonylation of the enynes, we also found that the acetylenes give, selectively, unsaturated lactones under water gas shift conditions.[16] This suggests that the formation of **6** under hydroformylation conditions may be closely related to the presence of a small amount of water in the reaction mixture.

Experimental

General Methods. High-pressure work was carried out by using a stainless-steel autoclave.

Rhodium carbonyl, $Rh_4(CO)_{12}$, was prepared by methods described in the literature.[17] Solvents were distilled before use. The reagents were purified by either distillation or recrystallization.

Melting points were determined by Yanagimoto micro melting point apparatus and are uncorrected. Infrared spectra were recorded on a Hitachi 295 infrared spectrophotometer. Nuclear magnetic resonance spectra were run on a JEOL JNR-PMX 60SI or a Bruker AM-360. Chemical shifts are expressed in parts per million downfield from internal standard, tetramethylsilane. Mass spectra were obtained with JEOL JMS 06. Elemental analyses were performed by the Material Analysis Center, I. S. I. R., Osaka University.

Preparation of Enynes. Conjugated enynes were prepared by a reported method[6] and the preparation of new enynes, **3b** and **3c**, are described below. Non-conjugated enyne **16** was prepared by the reaction of (*E*)-1-phenyl-3-bromopropane with copper(I)-phenylacetylide in the presence of LiBr.[18]

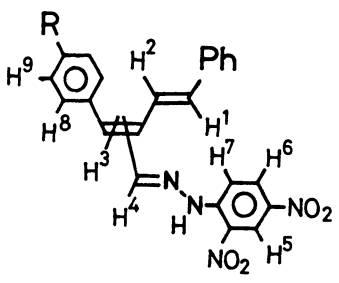
4-(4-Methoxyphenyl)-1-phenyl-1-buten-3-yne (3b). A solution of (4-methoxyphenyl)acetylene (2.0 g, 15.1 mmol), (*E*)-β-bromostyrene (2.8 g, 15.1 mmol), in diethylamine (30 ml) was placed in a 100 ml two-necked round-bottom flask. To the solution were added $PdCl_2(PPh_3)_2$ (35 mg) and CuI (10 mg). Then, the reaction mixture was stirred at room temperature under N_2 for 24 h. The precipitated $Et_2NH \cdot HBr$ was filtered off and washed several times with Et_2NH. The filtrate and the washing were combined and evaporated to dryness. The pale-yellow solid, thus obtained, was dissolved in a small amount of benzene and passed through a short alumina column to remove the catalyst. Elution with benzene gave a crude product, which was recrystallized from EtOH to yield 2.76 g (78%) of **3b**.

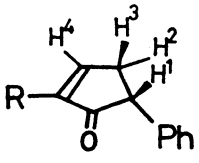
3b: Colorless fine needles from EtOH, mp 94—95 °C; ^{1}H NMR (360 MHz, $CDCl_3$) δ=3.81 (s, 3H, CH_3), 6.38 (d, 1H, PhCH=C<u>H</u>, *J*=16.2 Hz), 6.86 (bd, 2H, *o*-H to OCH_3, *J*=8.7 Hz), 6.99 (d, 1H, PhC<u>H</u>=CH, *J*=6.2 Hz), 7.2—7.5 (m, 9H, arom); IR (Nujol) 2190 cm^{-1}; Found: C, 86.89; H, 5.78%. Calcd for $C_{17}H_{14}O$: C, 87.15; H, 6.02%.

4-(4-Cyanophenyl)-1-phenyl-1-buten-3-yne (3c) was prepared similarly from the reaction of (4-cyanophenyl)acetylene with (*E*)-β-bromostyrene in 78% yield.

3c: Colorless needles from EtOH, mp 127—129 °C; ^{1}H NMR (360 MHz, $CDCl_3$) δ=6.37 (d, 1H, PhCH=C<u>H</u>, *J*=16.2 Hz), 7.10 (d, 1H, PhC<u>H</u>=CH, *J*=16.2 Hz), 7.3—7.45 (m, 5H, Ph), 7.5—7.62 (m, 4H, C_6H_4-CN, AA'BB'); IR (Nujol) 3230, 2210, 2095 cm^{-1}; Found: C, 89.28; H, 5.07; N, 6.10%. Calcd for $C_{17}H_{11}N$: C, 89.06; H, 4.84; N, 6.11%.

Reaction of Enynes. For an assignment of the spectra, the protons of cyclopentenones and 2,4-dinitrophenylhydrazone are numbered as shown below.





Reaction of 1,4-Diphenyl-1-buten-3-yne (3a) at 60 °C. A solution of **3a** (1.0 g, 4.9 mmol) and $Rh_4(CO)_{12}$ (20 mg, 0.027 mmol) in benzene (10 ml) was put into a 20 ml glass ampule, which was placed in a 100 ml stainless-steel autoclave. The autoclave was charged with 100 atm of carbon monoxide and 100 atm of hydrogen, and then shaken for 6 h at 60 °C. After cooling to room temperature, the reaction mixture was poured onto silica gel (2 g) and evaporated to dryness. It was then placed at the top of a column containing 30 g of silica gel. Gradient elution with hexane-benzene gave three carbonylated products, **4a** (23%), **5a** (32%), and **6a** (9%) together with a small amount of the starting material (90 mg; 91% conversion).

4a: Colorless columns from hexane, mp 75—76 °C; ^{1}H NMR (360 MHz, $CDCl_3$) δ=2.83 (ddd, 1H, H^2, J_{12}=2.8 Hz, J_{24}=2.8 Hz, J_{23}=19.8 Hz), 3.26 (ddd, 1H, H^3, J_{23}=19.8 Hz, J_{13}=7.1 Hz, J_{34}=3.0 Hz), 3.77 (dd, 1H, H^1, J_{12}=2.8 Hz, J_{13}=7.1 Hz), 7.1—7.6 (m, 10H, arom), 7.96 (dd, 1H, H^4, J_{24}=2.8 Hz, J_{34}=3.0 Hz); IR (Nujol) 1700 cm^{-1}; MS, *m/z* 234 (M^+); Found: C, 87.29; H, 5.74%. Calcd for $C_{17}H_{14}O$: C, 87.15; H, 6.02%.

5a: Pale-yellow viscous oil; IR (neat) 1695 cm^{-1}. This was led to 2,4-dinitrophenylhydrazone, **5a-(2,4-D)**, and purified by recrystallization.

5a-(2,4-D): Dark-brown crystals from benzene, mp 221—223 °C; ^{1}H NMR (360 MHz, $CDCl_3$) δ=7.07 (s, 1H, H^3), 7.15 (d, 1H, H^1, J_{12}=16.5 Hz), 7.3—7.5 (m, 11H, H^2 and Ph), 7.98 (d, 1H, H^5, J_{56}=9.6 Hz), 8.06 (s, 1H, H^4), 8.35 (dd, 1H, H^6, J_{67}=2.5 Hz, J_{56}=9.6 Hz), 9.17 (d, 1H, H^7, J_{67}=2.5 Hz), 11.32 (s, 1H, NH); IR (Nujol) 3280 1625, 1590, 1515, 1340, 1305, 745, 690 cm^{-1}; MS, *m/z* 414 (M^+); Found: C, 66.86; H, 4.10; N, 13.47%. Calcd for $C_{23}H_{18}N_4O_4$: C, 66.66; H, 4.38; N, 13.52%.

6a: Pale-yellow crystals from hexane-benzene, mp 114—115 °C; ^{1}H NMR (360 MHz, $CDCl_3$) δ=5.05 (s, 2H, CH_2), 7.02 (d, 1H, PhCH=C<u>H</u>, *J*=16.3 Hz), 7.25—7.5 (m, 10H, arom), 7.99 (d, 1H, PhC<u>H</u>=CH); IR (Nujol) 1760 cm^{-1}; MS, *m/z* 262 (M^+); Found: C, 82.13; H, 5.42%. Calcd for $C_{18}H_{14}O_2$: C, 82 42; H, 5.38%.

Reaction of 1,4-Diphenyl-1-buten-3-yne (3a) at 120 °C. In a similar manner to the procedure adopted for the reaction at 60 °C, **3a** was reacted with carbon monoxide and hydrogen in the presence of a catalytic amount of $Rh_4(CO)_{12}$ at 120 °C for 4 h. The reaction mixture was then placed into a 100 ml flask fitted with a Soxhlet extraction apparatus which was filled with Molecular Sieves 3A. To the solution were added ethylene glycol (0.30 g) and a catalytic amount of *p*-toluenesulfonic acid with an additional 20 ml of benzene. Then, azeotropic dehydration was continued under nitrogen for 4 h. The solution was cooled to room temperature, poured onto silica gel (3 g) and evaporated to dryness. It was then placed at the top of a column containing 30 g of silica gel. Gradient elution with hexane-benzene gave four acetals, in the order of increasing polarity, **11a** (8%), **12a** (7%), **14a** (26%), and **13a** (12%). **11a** and **12a** were further purified by recrystallization and **13a** and **14a** by microdistillation.

11a: Colorless columns from hexane, mp 106—107 °C; ^{1}H NMR (360 MHz, $CDCl_3$) δ=2.0—2.3 (m, 4H, C-CH_2-CH_2-C, A_2B_2), 2.96 (t, 2H, O-C<u>H</u>$_2$$CH_2$-O, *J*=6.3 Hz), 3.19 (t, 2H, O-CH_2C<u>H</u>$_2$-O, *J*=6.3 Hz), 3.42 (bt, 2H, PhC<u>H</u>, *J*=7.0 Hz), 7.2—7.4 (m, 10H, arom); IR (Nujol) 1600, 1200, 1055, 750, 700 cm^{-1}; MS, *m/z* 280 (M^+); Found: C, 81.63; H, 6.90%.

Calcd for $C_{19}H_{20}O_2$: C, 81.40; H, 7.19%.

12a: Colorless needles from hexane, mp 90.5—91.5 °C; ^{1}H NMR (360 MHz, $CDCl_3$) δ=2.06 (m, 2H, C-C$\underline{H}_2$CH$_2$-C), 2.20 (m, 2H, C-CH$_2$C$\underline{H}_2$-C), 2.96 (m, 2H, O-C$\underline{H}$H'), 3.28 (bt, 2H, PhC$\underline{H}$, J=10 Hz), 3.55 (m, 2H, O-CH$\underline{H}$'), 7.2—7.5 (m, 10H, arom); IR (Nujol) 1600, 1180, 1065, 960, 755, 700 cm^{-1}; MS, m/z 280 (M^+); Found: C, 81.36; H, 6.92%. Calcd for $C_{19}H_{20}O_2$: C, 81.40; H, 7.19%.

13a: Colorless oil; ^{1}H NMR (360 MHz, $CDCl_3$) δ=1.4—2.0 (m, 4H, PhCH$_2$C$\underline{H}_2$C$\underline{H}_2$-), 2.5—2.7 (m, 2H, PhC$\underline{H}_2$-), 2.83 (dt, 1H, C$\underline{H}$Ph, J=10.8, 4.5 Hz), 3.82 (m, 2H, OC$\underline{H}_2$C$\underline{H}_2$O), 4.98 (d, 1H, OCHO, J=4.5 Hz), 7.0—7.3 (m, 10H, arom); IR (neat) 1600, 1130, 1080, 1050, 1030, 740, 700 cm^{-1}; MS, m/z 282 (M^+); Found: C, 80.74; H, 6.88%. Calcd for $C_{19}H_{22}O_2$: C, 80.82; H, 6.78%.

14a: Colorless oil; ^{1}H NMR (360 MHz, $CDCl_3$) δ=1.6—2.1 (m, 3H, PhCH$_2$C$\underline{H}$C$\underline{H}_2$-), 2.6—3.0 (m, 4H, PhC$\underline{H}_2$CH), 3.85, 3.97 (m, 4H, OCH$_2$CH$_2$O), 4.82 (d, 1H, OCHO, J=3.5 Hz), 7.1—7.4 (m, 10H, arom); IR (neat) 1605, 1140, 1080, 1035, 750, 700 cm^{-1}; MS, m/z 282 (M^+); Found C, 80.80; H, 6.88%. Calcd for $C_{19}H_{22}O_2$: C, 80.82; H, 6.78%.

Reaction of 4-(4-Methoxyphenyl)-1-phenyl-1-buten-3-yne (3b). 3b was reacted at 60 °C in a similar manner to the procedure for the reaction of **3a**. The products were separated by column chromatography on silica to give three carbonylated products, **4b** (15%), **5b** (20%), and **6b** (12%).

4b: Colorless needles from hexane-benzene, mp 134—136 °C; ^{1}H NMR (360 MHz, $CDCl_3$) δ=2.80 (ddd, 1H, H^2, J_{12}=2.8 Hz, J_{24}=2.8 Hz, J_{23}=19.8 Hz), 3.24 (ddd, 1H, H^3, J_{13}=7.1 Hz, J_{23}=19.8 Hz, J_{34}=3.2 Hz), 3.74 (dd, 1H, H^1, J_{12}=2.4 Hz, J_{13}=7.1 Hz), 3.81 (s, 3H, -CH$_3$), 6.92 (d, 2H, H^6, J=8.7 Hz), 7.15—7.35 (m, 5H, -Ph), 7.73 (d, 2H, H^5, J=8.7 Hz), 7.87 (dd, 1H, H^4, J_{24}=2.8 Hz, J_{34}=3.0 Hz); IR (Nujol) 1700 cm^{-1}; MS, m/z 264 (M^+); Found: C, 82.04; H, 5.83%. Calcd for $C_{18}H_{16}O_2$: C, 81.79; H, 6.10%.

5b: Pale-yellow viscous oil; IR (neat) 1695 cm^{-1}. **5b** was led to 2,4-dinitrophenylhydrazone, **5b-(2,4-D)**, and purified by recrystallization.

5b-(2,4-D): Red crystals from benzene, mp 201—204 °C; ^{1}H NMR (360 MHz, $CDCl_3$) δ=3.87 (s, 3H, O-CH$_3$), 6.96 (d, 2H, H^9, J_{89}=8.8 Hz), 7.01 (s, 1H, H^3), 7.14 (d, 1H, H^1, J=16.5 Hz), 7.3—7.5 (m, 8H, -Ph, H^2, and H^8), 7.98 (d, 1H, H^7, J_{67}=9.5 Hz), 8.03 (s, 1H, H^4), 8.34 (dd, 1H, H^6, J_{56}=9.2 Hz, J_{67}=2.3 Hz), 9.17 (d, 1H, H^5, J_{56}=2.3 Hz), 11.3 (bs, 1H, NH); IR (Nujol) 3280, 1615, 1590, 1330, 1305, 1260, 1175, 1130, 755, 735 cm^{-1}; MS, m/z 444 (M^+); Found: C, 64.60; H, 4.33; N, 12.42%. Calcd for $C_{24}H_{20}N_4O_5$: C, 64.86; H, 4.54; N, 12.61%.

6b: Pale-yellow crystals from hexane-benzene, mp 123—125 °C; ^{1}H NMR (360 MHz, $CDCl_3$) δ=3.89 (s, 3H, O-CH$_3$), 5.07 (s, 2H, CH$_2$), 7.03 (m, 3H, Ph-CH=C$\underline{H}$ and 2H), 7.2—7.5 (m, 7H, arom), 7.95 (d, 1H, Ph-C$\underline{H}$=CH, J=16.2 Hz); IR (Nujol) 1745 cm^{-1}; MS, m/z 292 (M^+); Found: C, 78.05; H, 5.48%. Calcd for $C_{19}H_{16}O_3$: C, 78.06; H, 5.52%.

Reaction of 4-(4-Cyanophenyl)-1-phenyl-1-buten-3-yne (3c). 3c was reacted at 60 °C in a similar manner to the procedure for the reaction of **3a**. The products were separated by column chromatography on silica to give three carbonylated compounds **4c** (17%), **5c** (23%), and **6c** (6%) together with a small amount of the starting material (conversion: 70%).

4c: Pale yellow crystals from hexane-benzene, mp 134—136 °C; ^{1}H NMR (360 MHz, $CDCl_3$) δ=2.81 (m, 1H, H^3), 3.27 (m, 1H, H^2), 3.77 (dd, 1H, H^1, J=7.2, 2.5 Hz), 7.2—7.5 (m, 5H, Ph), 7.6—8.0 (m, 5H, H^4, H^5, and H^6); IR (Nujol) 2220, 1705 cm^{-1}; MS, m/z 259 (M^+); Found: C, 82.68; H, 4.73; N, 5.26%. Calcd for $C_{18}H_{13}NO$: C, 83.38; H, 5.05; N, 5.40%.

5c: Pale-yellow viscous oil, IR (neat) 1695 cm^{-1}. **5c** was led to the 2,4-dinitrophenylhydrazone, **5c-(2,4-D)**, and purified by recrystallization.

5c-(2,4-D): Dark-brown powder, mp 233—235 °C; ^{1}H NMR (360 MHz, $CDCl_3$) δ=7.03 (s, 1H, H^3), 7.35—7.5 (m, 6H, -Ph and H^2), 7.58 (d, 2H, H^8, J_{89}=8.4 Hz), 7.70 (d, 2H, H^9, J_{89}=8.4 Hz), 7.98 (d, 1H, H^7, J_{67}=9.6 Hz), 8.05 (s, 1H, H^4), 8.39 (dd, 1H, H^6, J_{67}=9.6 Hz, J_{56}=2.4 Hz), 9.18 (d, 1H, H^5, J_{56}=2.4 Hz), 11.35 (bs, 1H, NH); IR (Nujol) 3280, 2220, 1615, 1330, 1305, 1280, 1140, 1075, 740, 715 cm^{-1}; MS, m/z 439 (M^+); Found: C, 65.61; H, 3.98; N, 15.70%. Calcd for $C_{24}H_{17}N_5O_4$: C, 65.60; H, 3.90; N, 15.94%.

6c: Pale-yellow viscous oil; ^{1}H NMR (360 MHz, $CDCl_3$) δ=5.09 (s, 2H, CH$_2$), 6.93 (d, 1H, Ph-CH=C$\underline{H}$, J=16 Hz), 7.2—7.5 (m, 5H, -Ph), 7.61 (m, 2H, o-H to C=C), 7.82 (m, 2H, o-H to CN), 7.92 (d, 1H, Ph-C$\underline{H}$=CH, J=16 Hz); IR (neat) 1765 cm^{-1}; MS, m/z 287 (M^+).

Reaction of 1-Phenyl-1-penten-3-yne (3d). 3d was reacted at 60 °C in a similar manner to the procedure for the reaction of **3a**. The products were separated by column chromatography on silica gel to give three carbonylated compounds, **5d** (17%), **17** (19%), and **6d** (20%) together with the unreacted starting material (conversion: 49%).

5d: Pale-yellow viscous oil. **5d** was led to the 2,4-dinitrophenylhydrazone, **5d-(2,4-D)**, and purified by recrystallization.

5d-(2,4-D): Orange powder from benzene, mp 191—193 °C; ^{1}H NMR (360 MHz, $CDCl_3$) δ=2.12 (d, 3H, CH$_3$), 6.25 (q, 1H, H^3, J=7.2 Hz), 7.02 (d, 1H, H^1, J_{12}=16.5 Hz), 7.27 (d, 1H, H^2, J_{12}=16.5 Hz), 7.3—7.53 (m, 5H, Ph), 7.86 (s, 1H, H^4), 7.93 (d, 1H, H^7, J_{67}=9.6 Hz), 8.33 (dd 1H, H^6, J_{56}=2.5 Hz, J_{67}=9.8 Hz), 9.16 (d, 1H, H^5), 11.17 (s, 1H, N); IR (Nujol) 3270, 1620, 1590, 1330, 1305, 1260, 1215, 1115, 755, 745 cm^{-1}; MS, m/z 352 (M^+); Found: C, 61.40; H, 4.48; N, 15.65%. Calcd for $C_{18}H_{16}N_4O_4$: C, 61.36; H, 4.58; N, 15.90%.

17: Pale-yellow solid. **17** was led to the 2,4-dinitrophenylhydrazone, **17-(2,4-D)**, and purified by recrystallization.

17-(2,4-D): Dark-red crystals from benzene, mp 232—234 °C; ^{1}H NMR (360 MHz, $CDCl_3$) δ=2.20 (s, 3H, CH$_3$), 6.62 (bd, 1H, H^3, J=10.3, 1 Hz), 6.80 (d, 1H, H^1, J=15.5 Hz), 7.23 (dd, 1H, H^2, J=10.5, 15.4 Hz), 7.3—7.5 (m, 5H, Ph), 7.82 (s, 1H, H^4), 7.99 (d, 1H, H^7, J_{67}=9.6 Hz), 8.33 (dd, 1H, H^6, J_{67}=9.6 Hz), 9.15 (d, 1H, H^5), 11.26 (s, 1H, NH); IR (Nujol) 3280, 1620, 1590, 1330, 1300, 1265, 1205, 1135, 1075, 970, 745 cm^{-1}; MS, m/z 352 (M^+); Found: C, 61.02; H, 4.29; N, 15.91%. Calcd for $C_{18}H_{16}N_4O_4$: C, 61.36; H, 4.58; N, 15.90%.

6d: Colorless crystals from hexane-benzene, mp 132.5—133.5 °C; ^{1}H NMR (360 MHz, $CDCl_3$) δ=2.20 (s, 3H, CH$_3$), 4.71 (s, 2H, CH$_2$), 6.79 (d, 1H, C$\underline{H}$=CH-Ph, J=16.3 Hz), 7.2—7.5 (m, 5H, Ph), 7.77 (d, 1H, CH=C$\underline{H}$-Ph, J=16.3 Hz); IR (Nujol) 1750 cm^{-1}; MS, m/z 200 (M^+); Found: C, 77.54; H, 6.00%. Calcd for $C_{13}H_{12}O_2$: C, 77.98; H, 6.04%.

Reaction of 1,5-Diphenyl-1-penten-4-yne (16). 16 was reacted at 60 °C in a similar manner to the procedure for the reaction of **3a**. The products were isolated by column chromatography on silica gel to give carbonylated compounds, **18** (40%), **19** (11%), and **20** (18%) together with the unreacted starting material (conversion: 45%).

18: Colorless crystals from hexane, mp 72—74 °C; ^{1}H NMR (360 MHz, $CDCl_3$) δ=2.0—2.2 (m, 1H, Ph-CH-CHH′), 2.5—2.7 (m, 1H, Ph-CH-CHH′), 2.9—3.1 (m, 1H, =CH-CHH′), 3.1—3.2 (m, 1H, =CH-CHH′), 3.61 (dd, 1H, Ph-CH, J=9.7, 10 Hz), 7.2—7.6 (m, 11H, Ph and C=CH); IR (Nujol) 1725 cm^{-1}; MS, m/z 248 (M^+); Found: C, 87.21; H, 6.80%. Calcd for $C_{18}H_{16}O$: C, 87.06; H, 6.49%.

19: Pale-yellow viscous oil; IR (neat) 1685 cm^{-1}. **19** was led to 2,4-dinitrophenylhydrazone, **19-(2,4-D)**, and purified by recrystallization.

19-(2,4-D): Orange-red powder from benzene, mp 218—220 °C; ^{1}H NMR (360 MHz, $CDCl_3$) δ=3.65 (bd, 2H, CH_2, J=5.5 Hz), 6.46 (dt, 1H, H^2, J=5.2, 16 Hz), 6.54 (d, 1H, H^1, J=16 Hz), 7.03 (s, 1H, H^3), 7.2—7.5 (m, 10H, Ph), 7.95 (s, 1H, H^4), 7.95 (d, 1H, H^7, J_{67}=9.5 Hz) 8.29 (dd, 1H, H^6, J_{67}=9.5 Hz, J_{56}=2.3 Hz), 9.14 (d, 1H, H^5), 11.27 (s, 1H, NH); IR (Nujol) 3280, 1610, 1325, 1120, 1085, 750 cm^{-1}; MS, m/z 428 (M^+); Found: C, 67.27; H, 4.64; N, 12.90%. Calcd for $C_{24}H_{22}N_4O_4$: C, 67.28; H, 4.71; N, 13.08%.

20 was a mixture of two isomeric lactones and unable to separate each of the isomers by column chromatography.

20: Pale-yellow viscous oil; ^{1}H NMR (360 MHz, $CDCl_3$) δ=3.43 and 3.49 (d/d, 2H/2H, =C-CH_2-C= for two isomers, J=6.1 Hz/6.7 Hz), 4.85 and 5.09 (s/s, 2H/2H, O-CH_2 for two isomers), 6.18 and 6.32 (dt/dt, 1H/1H, Ph-CH=CH for two isomers, J=15.8, 6.7 Hz/J=15.9, 6.1 Hz), 6.47 and 6.50 (d/d, 1H/1H, Ph-CH for two isomers, J=15.8 Hz/J=15.8 Hz), 7.2—7.6 (m/m, 10H/10H, Ph for two isomers); IR (Nujol) 1770 cm^{-1}; MS, m/z 276 (M^+).

Reaction of 1,4-Diphenyl-1,3-butadiene (21) at 60 °C. 21 (1.0 g, 4.85 mmol) was reacted at 60 °C in a similar manner to the procedure for the reaction of **3a**. After a reaction for 6 h, the reaction mixture was poured to silica gel (1.5 g) and concentrated to dryness. Then, the silica gel was put onto the top of a column containing 20 g of silica gel. Elution by hexane-benzene gave 0.54 g of unreacted **21** (conversion: 46%) and 0.36 g (68% based on **21** consumed) of monoformylated product, **22**.

22: Colorless oil; ^{1}H NMR (60 MHz, $CDCl_3$) δ=1.1—2.1 (m, 4H, Ph-CH_2-(CH_2)$_2$), 2.55 (t, 2H, Ph-CH_2, J=7 Hz), 3.45 (dt, 1H, Ph-CH, J=7, 1 Hz), 7.1—7.5 (m, 10H, Ph), 9.55 (d, 1H, CHO, J=1 Hz); IR (neat) 1735 cm^{-1}. The structure of **22** was also supported by a comparison with the hydrated product of acetal **13a**.

Competitive Reaction between Diphenylacetylene (7) and *trans*-Stilbene (8). An equimolar mixture of **7** (0.86 g, 4.85 mmol) and **8** (0.87 g, 4.85 mmol) was reacted at 60 °C in a similar manner to the procedure for the reaction of **3a**. After a reaction for 6 h, the reaction mixture was evaporated to dryness and chromatographed on silica gel, giving two carbonylated products **9** and **10** in 31 and 44% yields, respectively, which were derived from **7**, while **8** was recovered almost quantatively.

Reaction of Cyclopentenone (4a) at 120 °C. 4a (210 mg) was treated at 120 °C in a similar manner to the procedure for the reaction of **3a**. After a reaction for 4 h, the reaction mixture was passed through a short column of alumina and the eluent was evaporated to dryness, affording 200 mg (94%) of cyclopentanone **15a**.

15a:[19] Colorless crystals from hexane, mp 75—80 °C; *^{1}H NMR (60 MHz, $CDCl_3$) δ=1.9—2.7 (m, 4H, -CH_2-CH_2-),* 3.5 (m, 2H, CH), 7.2—7.5 (m, 10H, Ph); IR (Nujol) 1775 cm^{-1}; MS, m/z 236 (M^+).

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8) Erratum: Ref. 7, page 4498, in Table 1: The data of **1b** (R=*p*-CH_3O-C_6H_4) should be replaced by those of **1c** (R=*p*-NC-C_6H_4).

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