# Rhodium carbonyl-catalyzed carbonylation of unsaturated compounds

## V *. Cross-hydrocarbonylation of 1-alkyne and ethylene by rhodium carbonyl catalyst modified with phosphines

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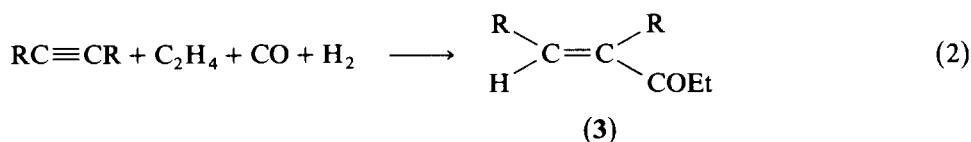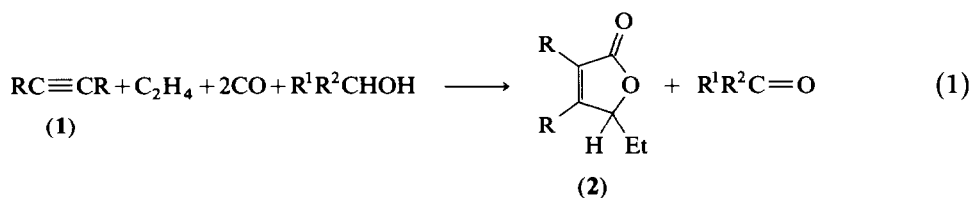
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**Abstract**

In the presence of $Rh_4(CO)_{12}$ catalyst modified with triphenylphosphine the cross-hydrocarbonylation of 1-alkyne ($RC_2H$; R = Me, Et, $^nPr$, $^nBu$, and $^iBu$) and ethylene using 2-propanol as the hydrogen donor gives 3-alkyl-5-ethyl-2(5$H$)-furanone (**4**, 44–69%), along with a small amount of 4-alkyl-5-ethyl-2(5$H$)-furanone (**5**, 1–8%). When acetylene itself is used, γ-caprolactone (**6a**), which is the hydrogenation product of the expected 5-ethyl-2(5$H$)-furanone (**4a**), is obtained. The yield of **6a** depends on the nature of the phosphine employed and decreases in the following order: $PR_3 = P(C_6H_4F-p)_3 > PPh_3 > P(C_6H_4Me-p)_3 > P(C_6H_4OMe-p)_3 > PPh_2Et > PPhEt_2 > PEt_3$.

## Introduction

Carbonylations of alkenes and alkynes with carbon monoxide in the presence of a soluble transition metal catalyst are important synthetic routes to a variety of oxygenates such as aldehydes, ketones, carboxylates, and lactones [2]. We have shown that 3,4-disubstituted 5-ethyl-2(5$H$)-furanone (**2**) is prepared by the $Rh_4(CO)_{12}$-catalyzed cross-hydrocarbonylation of an internal alkyne and ethylene with carbon monoxide when an alcohol is employed as the hydrogen source [3] and that 1,2-disubstituted 1-penten-3-one (**3**) is formed when dihydrogen is used [4,5]. For the synthesis of the pentenone but not for the furanone 1-alkynes can be used. We have now found that rhodium carbonyl catalyzed the cross-hydrocarbonylation

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* For Part IV see ref. 1.

of 1-alkyne and ethylene to give the furanone when it was combined with phosphines.

$$RC\equiv CR + C_2H_4 + 2CO + R^1R^2CHOH \longrightarrow \quad \text{(2)} \quad + \quad R^1R^2C=O \qquad (1)$$
$$\text{(1)}$$

$$RC\equiv CR + C_2H_4 + CO + H_2 \longrightarrow \quad \text{(3)} \qquad (2)$$

## Results and discussion

When a mixture of diphenylacetylene and a catalytic amount of $Rh_4(CO)_{12}$ in 2-propanol is heated at a temperature higher than 150°C under pressures of ethylene (20 kg cm$^{-2}$) and of carbon monoxide (30 kg cm$^{-2}$), 5-ethyl-3,4-diphenyl-2(5H)-furanone (2a) is obtained in good yield [3]. The solvent, 2-propanol, provides the necessary hydrogen for 2a. The furanone 2a consists of one molecule each of acetylene, ethylene, and hydrogen, and two molecules of carbon monoxide. It is noteworthy that these molecules built up the furanone in a well controlled sequence. A variety of internal alkynes was successfully employed in place of diphenylacetylene, but attempts to use 1-alkynes were unsuccessful. For example, the reaction of phenylacetylene (1g) failed to give the furanone expected, and provided a small amount of 1,4-diphenyl-1,3-butadiyne, the formation of which can be ascribed to the oxidative coupling of 1g. A possible explanation of the failure is the deactivation of the catalyst by the acidic hydrogen of 1-alkyne *.

It is known that the hydroformylation of 1-alkyne with rhodium catalysts such as $Rh_2O_3$ and $RhH(CO)(PPh_3)_3$ is only successful when carried out in the presence of a large excess of triphenylphosphine [6,7]. The phosphine appears to prevent deactivation of the catalyst. Accordingly, the effect of addition of triphenylphosphine to $Rh_4(CO)_{12}$ catalyst in the cross-hydrocarbonylation of 1-hexyne and ethylene was examined and the results are summarized in Table 1.

When a mixture of 1-hexyne (1e), $Rh_4(CO)_{12}$, and $PPh_3$ ($PPh_3/Rh = 3$) in 2-propanol was heated at 180°C for 5 h under the pressure of ethylene (20 kg cm$^{-2}$) and of CO (30 kg cm$^{-2}$), 3-butyl-5-ethyl-2(5H)-furanone (4e, 39%) was formed, together with the regioisomer 4-butyl-5-ethyl-2(5H)-furanone (5e, 7%) (run 1). Further products, namely acetone, 3-petanone, and propanal were detected. Formation of acetone is ascribed to the dehydrogenation of 2-propanol. 3-Pentanone and propanal are respectively, the hydrocarbonylation and hydroformylation products of ethylene. Increasing the amount of triphenylphosphine ($PPh_3/Rh = 6$ (run 2) or 15 (run 3)), scarcely affected the yields of 4e and 5e, but those of acetone

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* The IR spectrum of the reaction mixture revealed carbonyl streching bands at 2055 and 1980 cm$^{-1}$, indicating that the catalyst was converted into complexes containing the $Rh(CO)_2$ moiety.

Table 1

Cross-hydrocarbonylation of 1-hexyne and ethylene in the presence of $Rh_4(CO)_{12}$–$PPh_3$ catalyst [a]

| Run No. | Temp. (°C) | $PPh_3$/Rh | Products (%) | | $Me_2CO$ (mmol) | $Et_2CO$ (mmol) | EtCHO (mmol) |
|---|---|---|---|---|---|---|---|
| | | | 4e | 5e | | | |
| 1 | 180 | 3 | 39 | 7 | 15.5 | 8.1 | 0.9 |
| 2 | 180 | 6 | 38 | 5 | 11.6 | 4.2 | 0.7 |
| 3 | 180 | 15 | 39 | 6 | 8.0 | 2.1 | 0.6 |
| 4 | 200 | 15 | 46 | 7 | 21.9 | 9.9 | 5.7 |
| 5 | 220 | 15 | 65 | 8 | 34.7 | 12.9 | 13.1 |
| 6 | 240 | 15 | 45 | 6 | 23.6 | 6.6 | 6.8 |

[a] 1-Hexyne (10 mmol), $Rh_4(CO)_{12}$ (0.025 mmol), 2-propanol (50 ml), $C_2H_4$ (20 kg $cm^{-2}$), CO (30 kg $cm^{-2}$), 5 h.

and 3-pentanone decreased, indicating suppression of the dehydrogenation of 2-propanol.

The yield of **4e** increased with reaction temperature, and maximum yield (65%) was attained at 220°C (run 5). The ratio of the regioisomers remained almost unaffected by temperature. In the reaction at 200°C or above the formation of 3-pentanone and propanal increased considerably.

Under conditions similar to those of run 5, the reaction of 1-propyne (**1b**) gave 3- and 4-methyl-5-ethyl-2(5*H*)-furanones (**4b** and **5b**) in 66 and 6% yields, respectively. Similarly, the reactions of 1-butyne (**1c**), 1-pentyne (**1d**), and 3,3-dimethyl-1-butyne (**1f**) gave the corresponding furanones **4** and **5**. As shown in Table 2, the ratio of **4** to **5** is high in every case, indicating that the reactions proceed regioselectively.
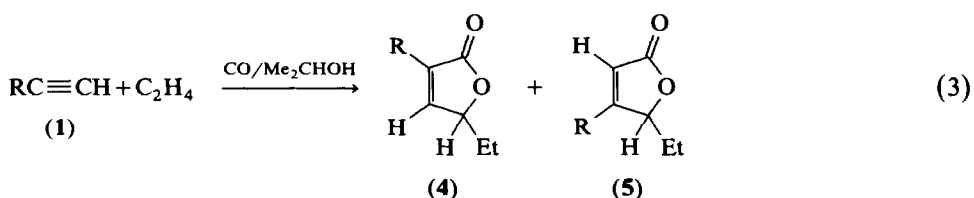
$$RC{\equiv}CH + C_2H_4 \xrightarrow{\text{CO/Me}_2\text{CHOH}} \quad (4) \quad + \quad (5) \qquad (3)$$

(1)

Table 2

Formation of 3- and 4-alkyl-5-ethyl-2(5*H*)-furanones (**4** and **5**) by the cross-hydrocarbonylation of 1-alkynes and ethylene [a]

| Run No. | $RC_2H$ (1) R | Products (%) | | Ratio 4/5 |
|---|---|---|---|---|
| | | 4 | 5 | |
| 7 | Me | 66 | 6 | 92/8 |
| 8 | Et | 69 | 8 | 89/11 |
| 9 | $^nPr$ | 58 | 7 | 90/10 |
| 5 | $^nBu$ | 65 | 8 | 89/11 |
| 10 | $^tBu$ | 44 | 1 | 99/1 |
| 11 | Ph | 27 [b] | – | – |

[a] 1-Alkyne (10 mmol), $Rh_4(CO)_{12}$ (0.025 mmol), $PPh_3$ (1.5 mmol), 2-propanol (50 ml), $C_2H_4$ (20 kg $cm^{-2}$), CO (30 kg $cm^{-2}$), 220°C, 5 h. [b] A mixture of diastereomers of 5-ethyl-3-phenyl-3,4-dihydro-2(5*H*)-furanone (**6b**).

Table 3

$^1$H NMR and IR spectra of 3- and 4-alkyl-5-ethyl-2(5$H$)-furanones (4 and 5)

| Compound | R | $^1$H NMR ($\delta$) | | | | | IR (cm$^{-1}$) | |
|---|---|---|---|---|---|---|---|---|
| | | H$^3$ | H$^4$ | H$^5$ | CH$_2$CH$_3$ | R | $\nu$ (C=O) | $\nu$ (C=C) |
| 4a | H | 6.10 (dd) | 7.48 (dd) | 5.02 (m) | 1.6–2.0 (m); 1.02 (t) | 1.95 (t) | 1753 | 1640 |
| 4b | Me | – | 7.12 (m) | 4.88 (m) | 1.6–1.9 (m); 1.02 (t) | | 1760 | 1661 |
| 4c | Et | – | 7.04 (m) | 4.88 (m) | 1.6–1.9 (m); 1.02 (t) | 2.3 (m, 2H); 1.20 (t, 3H) | 1761 | 1660 |
| 4d | $^n$Pr | – | 7.00 (m) | 4.85 (m) | 1.4–1.9 (m); 0.97 (t) | 2.3 (m, 4H); 1.00 (t, 3H) | 1760 | 1660 |
| 4e | $^n$Bu | – | 7.02 (m) | 4.88 (m) | 1.2–2.0 (m); 1.00 (t) | 2.32 (t, 2H); 1.2–2.0 (m, 4H); 1.00 (t, 3H) | 1760 | 1656 |
| 4f | $^t$Bu | – | 6.98 (d) | 4.83 (m) | 1.75 (m); 1.00 (t) | 1.28 (s, 9H) | 1755 | 1640 |
| 5b | Me | 5.82 (m) | – | 4.86 (m) | 1.4–2.2 (m); 0.96 (t) | 2.08 (d) | 1760 | 1646 |
| 5c | Et | 5.79 (m) | – | 4.88 (m) | 1.4–2.2 (m); 0.96 (t) | 2.4 (m, 2H); 1.24 (t, 3H) | 1760 | 1640 |
| 5d | $^n$Pr | 5.78 (m) | – | 4.84 (m) | 1.4–2.2 (m); 0.96 (t) | 2.3 (m, 2H); 1.4–2.2 (m, 2H); 1.04 (t, 3H) | 1760 | 1640 |
| 5e | $^n$Bu | 5.78 (m) | – | 4.86 (m) | 1.2–2.5 (m); 0.96 (t) | 1.2–2.5 (m, 6H); 0.96 (t, 3H) | 1760 | 1640 |
| 5f | $^t$Bu | 5.80 (d) | – | 4.96 (m) | 1.5–2.9 (m); 1.00 (t) | 1.24 (s, 9H) | 1760 | 1623 |

Table 4

Cross-hydrocarbonylation of acetylene (1a) and ethylene [a]

| Run No. | Pressure (kg cm$^{-2}$) | | | Temp. (°C) | Time (h) | Products (mmol) | |
|---|---|---|---|---|---|---|---|
| | C$_2$H$_2$ | C$_2$H$_4$ | CO | | | 4a | 6a |
| 12 | 5 | 20 | 30 | 220 | 5 | 0.1 | 10.9 |
| 13 | 5 | 20 | 30 | 220 | 1 | 0.1 | 10.7 |
| 14 | 5 | 20 | 30 | 220 | 0.3 | 3.1 | 7.9 |
| 15 | 5 | 20 | 30 | 200 | 1 | 0.6 | 5.7 |
| 16 | 5 | 20 | 30 | 180 | 1 | 2.8 | 0.04 |
| 17 | 2.5 | 20 | 30 | 220 | 1 | 0.1 | 7.1 |
| 18 | 10 | 20 | 30 | 220 | 1 | 0.3 | – |
| 19 | 10 | 40 | 50 | 220 | 1 | 2.1 | 7.8 |
| 20 | 5 | 20 | 60 | 220 | 1 | 0.2 | 9.3 |
| 21 | 5 | 55 | 35 | 220 | 1 | 1.0 | 7.5 |

[a] Rh$_4$(CO)$_{12}$ (0.025 mmol), PPh$_3$ (1.5 mmol), 2-propanol (50 ml).

The structures of 4 and 5 were deduced form the IR and $^1$H NMR spectra (Table 3). Their IR spectra reveal characteristic C=O and C=C stretching bands of unsaturated 5-membered lactones at 1750–1760 and 1640–1660 cm$^{-1}$. In the $^1$H NMR spectra of a series of major products 4 the signals due to an olefinic proton appear at $\delta$ 7.0–7.1, while in those of a series of minor products 5 the signals appear at $\delta$ 5.8. The olefinic proton signals of 2(5$H$)-furanone itself are observed at $\delta$ 7.63 and 6.15 ppm, which are assignable to those of H$^4$ and H$^3$ protons, respectively [8]. The products 4 and 5 were therefore deduced to be 3-alkyl- and 4-alkyl-2(5$H$)-furanones, respectively. This conclusion is also supported by the fact that the spectrum of 4b (R = Me) is consistent with that in the literature [9]. Further, the olefinic proton signals of 5 appear in a similar part of the spectrum to that where analogous signals are found in the spectra of 4-methyl-5-propyl-2(5$H$)-furanone and 4-methyl-5,5-dimethyl-2(5$H$)-furanone ($\delta$ 5.60 and 5.55) [10].

Under similar conditions the reaction of phenylacetylene (1g) gave a 1 : 1 mixture of diastereomers of 5-ethyl-3-phenyl-3,4-dihydro-2(5$H$)-furanone (6b, 27%), which is the hydrogenation product of the expected furanone 4g (R = Ph) (run 11). Similarly the reaction of acetylene (1a) gave γ-caprolactone (6a) in preference to

Table 5

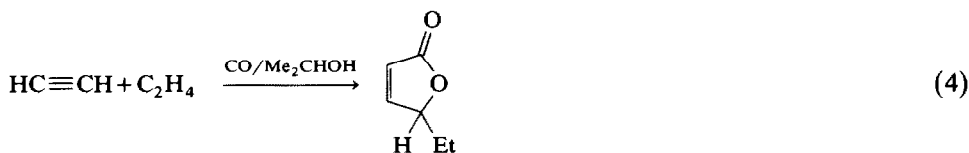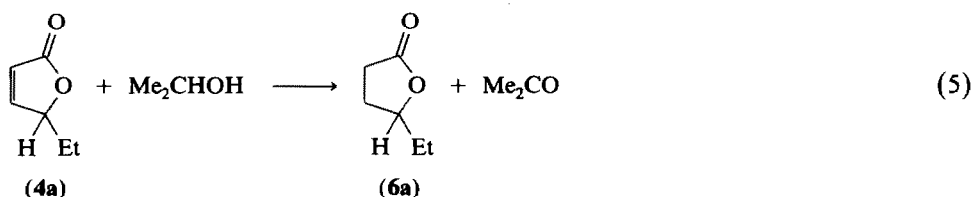Influence of phosphine as additive in the cross-hydrocarbonylation of acetylene (1a) and ethylene [a]

| Run No. | PR$_3$ | Products (mmol) | | Catalytic activity [b] |
|---|---|---|---|---|
| | | 4a | 6a | |
| 22 | PEt$_3$ | 1.6 | 0.2 | 18 |
| 23 | PPhEt$_2$ | 0.4 | 3.6 | 40 |
| 24 | PPh$_2$Et | 0.3 | 5.9 | 62 |
| 25 | P(C$_6$H$_4$OMe-$p$)$_3$ | 0.2 | 7.6 | 78 |
| 26 | P(C$_6$H$_4$Me-$p$)$_3$ | 0.3 | 8.3 | 86 |
| 13 | PPh$_3$ | 0.1 | 10.7 | 108 |
| 27 | P(C$_6$H$_4$F-$p$)$_3$ | 0.1 | 11.7 | 118 |

[a] Acetylene (5 kg cm$^{-1}$), C$_2$H$_4$ (20 kg cm$^{-2}$), CO (30 kg cm$^{-2}$), Rh$_4$(CO)$_{12}$ (0.025 mmol), PR$_3$ (1.5 mmol), 2-propanol (50 ml). 220°C, 1 h. [b] 4a + 6a (mol)/Rh (atom).

5-ethyl-2-ethyl-2($5H$)-furanone (**4a**). The results are summarized in Table 4. When the reaction of **1a** (5 kg cm$^{-2}$, 33 mmol) was carried out at 220°C for 5 h under the pressure of ethylene (20 kg cm$^{-2}$) and of CO (30 kg cm$^{-2}$), **6a** (10.9 mmol) and **4a** (0.1 mmol) were obtained (run 12). The relative yield of **4a** to **6a** increased when the reaction time was shortened (run 14) and when the reaction temperature was lowered (run 15 and 16). These results show that **4a**, formed first, was converted to **6a** under the reaction conditions. In fact, when **4a** was heated together with a mixture of Rh$_4$(CO)$_{14}$ and PPh$_3$ in 2-propanol catalytic hydrogenation occurred to give **6a**.

$$HC\equiv CH + C_2H_4 \quad \xrightarrow{\text{CO/Me}_2\text{CHOH}} \qquad\qquad\qquad (4)$$

(**4a**)

$$\qquad\qquad + \ Me_2CHOH \quad \longrightarrow \qquad\qquad + \ Me_2CO \qquad (5)$$

(**4a**)                    (**6a**)

Under fixed pressures of ethylene (20 kg cm$^{-2}$) and of CO (30 kg cm$^{-2}$) **6a** was formed in good yield when 5 kg cm$^{-2}$ was applied for **1a** as the initial pressure (run 12 and 13), but not at all when the initial acetylene pressure was increased to 10 kg cm$^{-2}$ (run 18). When the pressures of ethylene and CO were increased to 40 kg cm$^{-2}$ and 50 kg cm$^{-2}$, respectively, the good yield of **6a** was restored (run 19). These results show that the partial pressure of acetylene is important in determining the yield of **6a** and that the catalyst is deactivated in the presence of excess acetylene.

In order to examine the effect of additives, a series of phosphines was added to the catalytic system in place of triphenylphosphine. The results presented in Table 5 show that catalytic activity of the rhodium carbonyl significantly decreased when more basic phosphines such as PEt$_3$, PPhEt$_2$, and PPh$_2$Et were employed. When

Table 6

The cross-hydrocarbonylation of acetylene (**1a**) and ethylene catalyzed by rhodium complexes [a]

| Run No. | Catalyst [b] | Additive [b] | Products (mmol) | |
|---|---|---|---|---|
| | | | 4a | 6a |
| 28 | RhH(CO)(PPh$_3$)$_3$ | none | 0.6 | 7.3 |
| 29 | Rh$_4$(PPh$_2$)$_4$(CO)$_6$ | none | trace | trace |
| 30 | Rh$_4$(CO)$_{12}$ | none | trace | trace |
| 31 | RhH(CO)(PPh$_3$)$_3$ | PPh$_3$ | 0.6 | 10.4 |
| 32 | Rh$_4$(PPh$_2$)$_4$(CO)$_6$ | PPh$_3$ | 0.3 | 10.8 |
| 13 | Rh$_4$(CO)$_{12}$ | PPh$_3$ | 0.1 | 10.7 |

[a] Acetylene (5 kg cm$^{-2}$), C$_2$H$_4$ (20 kg cm$^{-2}$), CO (30 kg cm$^{-2}$), 2-propanol (50 ml), 220°C, 1 h. [b] Rh (0.1 mg-atom), PPh$_3$ (1.5 mmol).
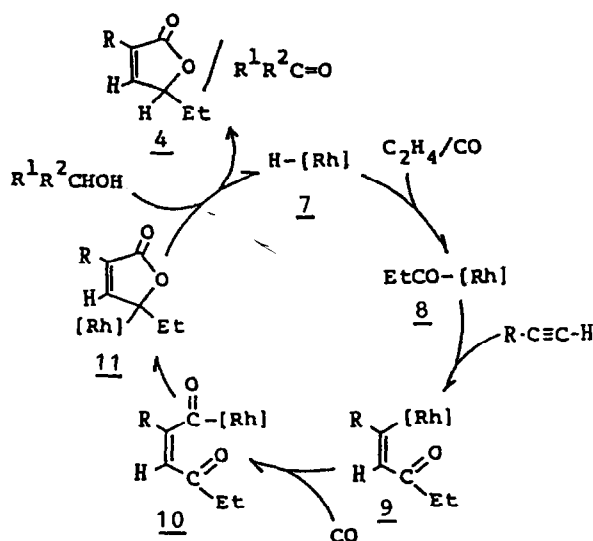
Scheme 1.

tris( *para*-substituted phenyl)phosphines were used, the yield of **6a** increased in the following order: $P(C_6H_4OMe-p)_3 < P(C_6H_4Me-p)_3 < P(C_6H_5)_3 < P(C_6H_4F-p)_3$, i.e. in step with a declining tendency to electron donation. Tris( *o*-tolyl)phosphine and diphosphines such as $Ph_2P(CH_2)_nPPh_2$ ($n = 1$ and 2) were found to be ineffective as the additive.

As mentioned above, the ability of the $Rh_4(CO)_{12}$ catalyst to produce 3-alkyl-5-ethyl-2(5*H*)-furanone (**4**) or the dihydrofuranone (**6**) from 1-alkyne, ethylene, carbon monoxide, and 2-propanol was improved by coupling with triphenylphosphine. Apparently the phosphine plays an important role in preventing the deactivation of the catalyst and in smoothing the reaction. It was found that the phosphine, however, decomposed during the reaction to give ethyldiphenylphosphine, benzene, and propiophenone, indicating cleavage of the phosphorus–phenyl bond *. A similar degradation of the phosphine has been observed in rhodium-catalyzed hydroformylation of propene [11,12].

The yield of **6a** varied with the rhodium catalyst used, as shown in Table 6. The mononuclear complex $RhH(CO)(PPh_3)_3$ showed moderate catalytic activity. The phosphido-bridged cluster $Rh_4(PPh_2)_4(CO)_6$ had no activity of its own, but, when triphenylphosphine was added, catalytic activity of a similarly elevated extent as that of $Rh_4(CO)_{12}/PPh_3$ was observed. The activity of $RhH(CO)(PPh_3)_3$ was also increased by the addition of phosphine. In such cases the phosphine decomposed considerably and was converted to ethyldiphenylphosphine. From these results we believe that the catalytically active species is a mononuclear rhodium carbonyl complex coordinated with phosphines such as $PPh_3$ and $PPh_2Et$.

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* In the reaction mixture (run 13) the presences of ethyldiphenylphosphine (0.47 mmol), benzene (1.05 mmol), and propiophenone (0.16 mmol), along with triphenylphosphine (0.15 mmol) and triphenyl-phosphine oxide (0.18 mmol), were confirmed by GC analysis.

In Scheme 1 we suggest a reaction pathway for the formation of 3-alkyl-5-ethyl-2(5$H$)-furanones (4) from 1-alkyne, ethylene, CO, and 2-propanol. Successive insertions of ethylene and CO into Rh–H species will form an acyl rhodium intermediate 8. That formation of the 3-substituted furanone 4 is preferred to that of the 4-substituted 5 suggests that the intermediate 8 adds to 1-alkyne regioselectively; the rhodium atom and the acyl group bind preferentially to the internal and the terminal acetylenic carbons, respectively. A similar regioselectivity has been observed in the formation of 1-penten-3-one, in which we also assumed the presence of a similar acyl rhodium intermediate [5]. We again suggest the importance of steric effects in the determination of the regioselectivity of the product.

## Experimental

$^1$H NMR spectra were recorded with a JEOL JNM-PS-100 spectrometer using tetramethylsilane as an internal standard in $CDCl_3$. IR spectra were recorded with a JASCO A-202 spectrometer. GC-MS spectra were recorded with a Hitachi RMU-6MG spectrometer equipped with a 3.0 mm × 1.0 m glass column packed with 1% OV-1. GC analyses were carried out with a Shimadzu GC-4CMPF gas chromatograph using internal standards, in which peak areas were calculated using a Shimadzu Chromatopac E1A integrator.

### Materials

1-Hexyne (1e), 3,3-dimethyl-1-butyne (1f), and $Rh_4(CO)_{12}$ were prepared by procedures described previously [5]. $Rh_4(PPh_2)_4(CO)_6$ [13] and 5-ethyl-2(5$H$)-furanone (4a) [14] were prepared according to published procedures. All other chemicals were commercially available reagents of the highest purity and were used without further purification. Carbon monoxide, acetylene, and ethylene were also obtained commercially and were used as received.

### General procedure for the cross-hydrocarbonylation of 1-alkyne and ethylene

A 150 ml glass tube was charged with 1-alkyne (1, 10 mmol), $Rh_4(CO)_{12}$ (0.025 mmol), $PR_3$, and 2-propanol (50 ml), and the tube was placed in a 200 ml stainless-steel autoclave. The autoclave was flushed three times with ethylene (5 kg cm$^{-2}$), then pressurized with ethylene and carbon monoxide, heated and agitated. The reaction mixture was analyzed by gas chromatography. For the analysis of the cross-hydrocarbonylation products and for those of propionaldehyde and 3-pentanone, 3% Silicone OV-17 on Chromosorb W and 15% PEG 20M on Chromosorb W were used, respectively. The products 4 and 5 were isolated by vacuum fractional distillation and/or column chromatography on silica gel. The identification of the products was accomplished by $^1$H NMR, IR, and GC-MS spectroscopy.

### Cross-hydrocarbonylation of 1-hexyne (1e) and ethylene

A mixture of 1e (0.816 g, 10 mmol), $Rh_4(CO)_{12}$ (0.019 g, 0.025 mmol), and PPh$_3$ (0.393 g, 1.5 mmol) in 2-propanol (50 ml) under ethylene (20 kg cm$^{-2}$) and CO (30 kg cm$^{-2}$) was heated at 220° C for 5 h. GC analysis of the resulting dark brown solution indicated the presence of 1.092 g (65%) of 3-butyl-5-ethyl-2(5$H$)-furanone (4e), 0.141 g (8%) of 4-butyl-5-ethyl-2(5$H$)-furanone (5e), 2.010 g (34.7 mmol) of acetone, 1.110 g (12.9 mmol) of 3-pentanone, and 0.759 g (13.1 mmol) of propanal.

The solvent was removed from the reaction mixture *in vacuo* and the residue was chromatographed on silica gel column. Elution with benzene–dichloromethane (4:1) gave 0.57 g of **4e** as colourless oil. B.p. 76–79 °C (3 mmHg). MS, $m/e$ 168 ($M^+$). Further elution with dichloromethane afforded 0.09 g of **5e** as colourless oil; MS, $m/e$ 168 ($M^+$).

Under similar conditions the cross-hydrocarbonylation of 1-alkyne (**1**) and ethylene was carried out to give the corresponding 3- and 4-alkyl-5-ethyl-2(5*H*)-furanones **4** and **5**. Yields and $^1$H NMR and IR spectra of **4** and **5** are summarized in Table 2 and 3, respectively.

### *Cross-hydrocarbonylation of phenylacetylene (1g) and ethylene*

A mixture of **1g** (1.020 g, 10 mmol), $Rh_4(CO)_{12}$ (0.019 g, 0.025 mmol), and $PPh_3$ (0.314 g, 1.2 mmol) in 2-propanol (25 ml) under ethylene (20 kg cm$^{-2}$) and CO (30 kg cm$^{-2}$) was heated at 220 °C for 6 h. GC analysis of the dark red solution indicated the presence of 0.506 g (27%) of 5-ethyl-3-phenyl-3,4-dihydro-2(5*H*)-furanone (**6b**), which is a 1:1 mixture of diastereomers. After removal of the solvent *in vacuo* the residue was chromatographed. Elution with benzene–dichloromethane (1:1) gave 0.237 g of the diastereomer **A** of **6b** as colourless oil. MS: $m/e$ 190 ($M^+$). $^1$H NMR: $\delta$ 1.04 (t, 3H, CH$_3$); 1.8 (m, 2H, CH$_2$); 2.5 (m, 2H, CH); 3.90 (dd, 1H, CH); 4.6 (m, 1H, CH); 7.28 (bs, 5H, Ph). Further elution with benzene–dichloromethane (1:3) afforded 0.125 g of the diastereometer **B** of **6b** as colourless oil. MS: $m/e$ 190 ($M^+$). $^1$H NMR: $\delta$ 1.04 (t, 3H, CH$_3$); 1.8 (m, 2H, CH$_2$); 2.1 (dd, 1H, CH); 2.75 (m, 1H, CH); 3.90 (dd, 1H, CH); 4.5 (m, 1H, CH); 7.30 (bs, 5H, Ph).

### *Cross-hydrocarbonylation of acetylene (1a) and ethylene*

A mixture of $Rh_4(CO)_{12}$ (0.019 g, 0.025 mmol) and $PPh_3$ (0.393 g, 0.15 mmol) in 2-propanol (50 ml) under **1a** (5 kg cm$^{-2}$), ethylene (20 kg cm$^{-2}$), and CO (30 kg cm$^{-2}$) was heated at 220 °C for 1 h. GC analysis of the resulting dark brown-red solution indicated the presence of 1.225 g (10.7 mmol) of $\gamma$-caprolactone (**6a**), 0.016 g of **4a**, 2.110 g (36.4 mmol) of acetone, 0.401 g (4.7 mmol) of 2-pentanone, 0.370 g (6.4 mmol) of propanol, 0.039 g (0.15 mmol) of $PPh_3$, and 0.100 g (0.47 mmol) of $PPh_2Et$. From the reaction mixture the solvent was removed *in vacuo* and the residual oil was chromatographed. Elution with benzene–dichloromethane (3:1–1:1) gave 0.620 g of **6a** as colourless oil. B.p. 60–61 °C (3 mmHg). The $^1$H NMR and IR spectra were identical to those of a commercially available sample.

### *Hydrogenation of 4a using 2-propanol as the hydrogen source*

A mixture of **4a** (0.496 g, 4.4 mmol), $Rh_4(CO)_{12}$ (0.019 g, 0.025 mmol), and $PPh_3$ (0.393 g, 1.5 mmol) in 2-propanol (25 ml) under ethylene (20 kg cm$^{-2}$) and CO (30 kg cm$^{-2}$) was heated at 220 °C for 1 h. GC analysis of the resulting dark brown solution indicated the presence of 0.453 g (91%) of **6a**, 0.148 g (46%) of $PPh_2Et$, 0.051 g (25%) of $PPhEt_2$, 0.059 g (15%) of $PPh_3$, and 0.023 g (5%) of $OPPh_3$.

### References

1  P. Hong, T. Mise and H. Yamazaki, Bull. Chem. Soc. Jpn., 63 (1990) 247.
2  (a) P. Pino, G. Braca, in I. Wender and P. Pino (Eds.), Organic Syntheses via Metal Carbonyls, Vol. 2, Wiley, New York, 1977, p. 419; (b) A. Mullen, in J. Falbe (Ed.), New Syntheses with Carbon Monoxide, Springer-Verlag, West Berlin, 1980, p. 414.

3 (a) P. Hong, T. Mise and H. Yamazaki, Nippon Kakagu Kaishi, (1982) 242; (b) P. Hong, T. Mise and H. Yamazaki, Chem. Lett., (1981) 989.

4 T. Mise, P. Hong and H. Yamazaki, Chem. Lett., (1982) 401.

5 P. Hong, T. Mise and H. Yamazaki, J. Organomet. Chem., 334 (1987) 129.

6 C.K. Brown, D. Georgion and G. Wilkinson, J. Chem. Soc. (A), (1971) 3120.

7 B. Fell and M. Beutler, Tetrahedron Lett., (1972) 3455.

8 L.M. Jackman and S. Sternhell, Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry, 2nd ed., Pergamon Press, New York, 1969, p. 188.

9 M.K. Wit, D.J. Frost and J.P. Ward, Recl. Trav. Chim. Pays-Bas., 90 (1971) 1207.

10 Y. Inoue, T. Hibi, M. Satake and H. Hashimoto, J. Chem. Soc., Chem. Commun., (1979) 982.

11 G. Gregorio, G. Montrasi, M. Tampieri, P. Cavalieri d'Oro, G. Pagani and A. Andreetta, Chim. Ind. (Milan), 62 (1980) 389.

12 A.G. Abatjoglou, E. Billig and and D.R. Bryant, Organometallics, 3 (1984) 923.

13 R.B. English, R.J. Haines and N.D.C.T. Steen, S. Afr. J. Chem., 34 (1981) 88.

14 A. Nobuhara, Agr. Biol. Chem., 34 (1970) 1745.