Rhodium carbonyl-catalyzed carbonylation of unsaturated compounds

III *. Synthesis of α,β-unsaturated ethyl ketones by cross-hydrocarbonylation of acetylenes and ethylene with carbon monoxide and hydrogen

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Abstract

Rhodium carbonyl-catalyzed cross-hydrocarbonylation of acetylenes and ethylene with carbon monoxide and hydrogen gives α,β-unsaturated ethyl ketones. Under CO (10 kg cm^{-2}) and H$_2$ (50 kg cm^{-2}) at 90°C the reaction of diphenylacetylene with ethylene in the presence of Rh$_4$(CO)$_{12}$ catalyst gave (E)-1,2-diphenyl-1-penten-3-one (3a) in 91% yield. Under similar conditions phenylacetylene (1d), 1-hexyne (1e), 3,3-dimethyl-1-butyne (1f), and trimethylsilylacetylene (1g) gave (E)-1-phenyl-1-penten-3-one (3d), (E)-4-nonen-3-one (3e), (E)-6,6-dimethyl-4-hepten-3-one (3f), and (E)-1-trimethylsilyl-1-pentene-3-one (3g) in 76, 68, 93, and 62% yields, respectively. Thus, the reaction of terminal acetylenes proceeds with high stereo- and regioselectivity: the propionyl group is introduced to the less-sterically hindered acetylenic carbon atom. By comparison of the regioselectivity with that in the formation of 5-ethyl-2(5H)-furanone (2), which is obtained in the presence of a hydrogen donor such as alcohol, these reactions are assumed to include a β-acylvinylrhodium complex as the common key intermediate.

Introduction

Rhodium carbonyl catalysts have received much attention in academic and industrial fields because of the excellent high activities for the addition of carbon monoxide to organic substrates to form oxygenated compounds such as carboxylic

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* For part II see ref. 1.

acids, acid halides, aldehydes, ketones, and isocyanates [2]. In fact they have been employed in the commercial production of linear aldehydes by the hydroformylation of olefins, and of acetic acid by the carbonylation of methanol. We have previously reported that the $Rh_4(CO)_{12}$ catalyst promotes the cross-hydrocarbonylation of acetylenes and ethylene [3], the hydrocarbonylation of acrylates [4], and the alkoxycarbonylation of acetylenes [1] to yield selectively 5-ethyl-2(5H)furanones, 4-oxoheptanedioate, and 5-alkoxy-2(5H)-furanones, respectively. In the reaction of acetylenes and ethylene which yields 5-ethyl-2(5H)-furanones (2a), the solvent alcohol behaves as the hydrogen donor (see eq. 1). During our investigation of the role of the hydrogen donor we found that the introduction of molecular hydrogen into the reaction system resulted in the formation of α,β-unsaturated ethyl ketones (3, in eq. 2) [5]. α,β-Unsaturated ketones are important key intermediates in the synthesis of a wide variety of organic compounds. A number of synthetic methods of the ketones are available. They are classified into three types [6]: (i) the introduction of a double bond into existing ketones such as α-halogenoketones, and α-thio or α-seleno ketones, (ii) the building up of a ketone skeleton from smaller molecules with a double bond or a precursor being formed in the process, and (iii) the conversion of another functional group of an olefinic molecule into a carbonyl group. The cross-hydrocarbonylation described in the present paper will provide a new convenient method for the preparation of the ketones.
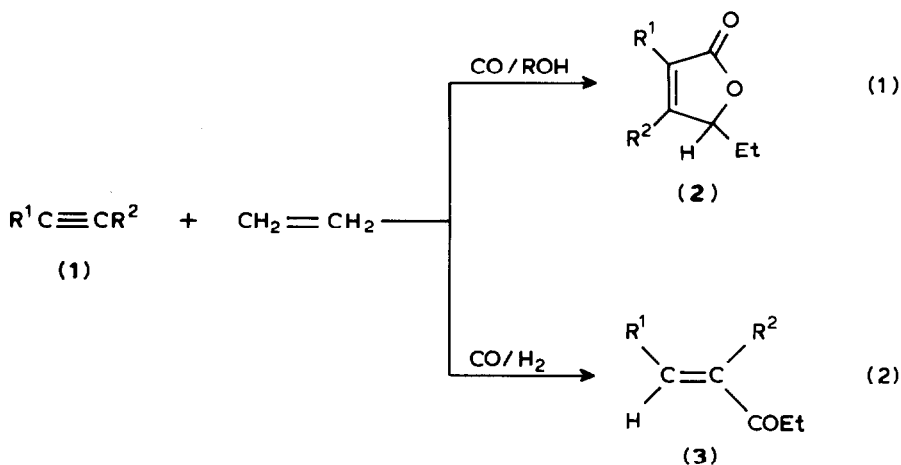
Results and discussion

When a mixture of diphenylacetylene (1a) and a catalytic amount of $Rh_4(CO)_{12}$ in ethanol was heated at temperatures higher than 150°C under C_2H_4 (20 kg cm^{-2}) and CO (30 kg cm^{-2}), 5-ethyl-3,4-diphenyl-2(5H)-furanone (2a) was obtained as a main product [3]. The furanone 2a consists of one molecule each of 1a, ethylene, and hydrogen, and two molecules of carbon monoxide. It is noteworthy that these constituents built up the furanone in good sequence. The necessary hydrogen for 2a was donated from the solvent ethanol. Various alcohols such as 2-propanol and 2-butanol and organic solvents containing a small amount of water were also used as the hydrogen donors. We have been interested in comparing these

hydrogen donors with molecular hydrogen. So the reaction of 1a, ethylene, and CO in the presence of molecular hydrogen was performed and it was found that, unexpectedly, 1,2-diphenyl-1-penten-3-one (3a) was obtained instead of furanone 2a. Thus, when a mixture of 1a (10 mmol) and $Rh_4(CO)_{12}$ (0.05 mmol) in acetone (70 ml) was heated for 6 h under C_2H_4 (25 kg cm^{-2}), CO (30 kg cm^{-2}), and H_2 (5 kg cm^{-2}) at 150°C, 3a was obtained in 62% yield, accompanied by 2a (2%), 1,2-diphenyl-3-pentanone (4a, 1%), (E)- and (Z)-stilbene (1%), and 2,3,4,5-tetraphenyl-2-cyclopentenone (12%). The hydroformylation product of ethylene – propionaldehyde (7.9 mmol), and the hydrocarbonylation product – diethyl ketone (1.0 mmol) were also formed. When the pressure of H_2 was increased to 30 kg cm^{-2} under otherwise similar conditions, the yield of 3a reached 84%. The structure of 3a was determined on the basis of its analytical and spectroscopic data. The IR spectrum showed bands at 1685 (νC=O) and 1615 cm^{-1} (νC=C), indicating the presence of a conjugated carbonyl group and the ^{1}H NMR spectrum indicated the presence of an ethyl group (δ 1.10 (t), 2.58 (q)) and an olefinic proton (δ 7.66 (s)). The absence of the geometrical isomer of 3a indicates that the reaction proceeds in a stereospecific manner.

In order to gain the optimum conditions for the formation of 3a, the cross-hydrocarbonylation of 1a and ethylene was carried out under various conditions. First of all the influence of reaction temperature with pressures of 25 kg cm^{-2} for C_2H_4, 30 kg cm^{-2} for CO, and 5 or 30 kg cm^{-2} for H_2 was examined. The results are summarized in Table 1. Under 5 kg cm^{-2} pressure of H_2, there was no significant change in the conversion of 1a and yield of 3a, at temperatures between 120°C and 180°C (runs 1–3), and the yield was lowered slightly at 90°C (run 4). At higher temperatures (150°C and 180°C) the amount of propionaldehyde obtained was nearly equal to that of 3a, but at lower temperatures (90°C and 120°C) the amount increased considerably. When the partial pressure of hydrogen was increased to 30 kg cm^{-2}, the yield of 3a improved, and that of propionaldehyde increased remarkably. Even at 90°C, 99% conversion and 77% yield were attained. Under these conditions the ratio of propionaldehyde to 3a increased greatly at lower temperature.

Table 1

Influence of reaction temperature in the cross-hydrocarbonylation of diphenylacetylene and ethylene [a]

Run	Temp. (°C)	H_2 (kg cm^{-2})	Conv. (%)	Product		
				3a [c] (%)	EtCHO (mmol)	EtCHO/3a
1	180	5	87	65	6.7	1.03
2	150	5	82	62	7.9	1.27
3	120	5	83	66	13.2	2.02
4	90	5	73	48	17.2	3.55
5	150	30	98	84	64.0	7.63
6	120	30	99	83	79.0	9.51
7 [b]	90	30	99	77	77.2	9.99
8	60	30	23	10	27.4	28.2

[a] Diphenylacetylene (10 mmol), ethylene (25 kg cm^{-2}), CO (30 kg cm^{-2}), $Rh_4(CO)_{12}$ (0.05 mmol), acetone (70 ml), 6 h. [b] 3 h. [c] Yield based on diphenylacetylene used.

Table 2

Influence of partial pressures of hydrogen, carbon monoxide, and ethylene in the cross-hydrocarbonylation of diphenylacetylene and ethylene [a]

Run	C_2H_4	CO	H_2	$Rh_4(CO)_{12}$	Conv.	Product		
		(kg cm^{-2})		(mmol)	(%)	3a [c] (%)	EtCHO (mmol)	EtCHO/3a
4 [b]	25	30	5	0.05	73	48	17.2	3.55
9 [b]	25	30	10	0.05	80	56	26.9	4.80
10 [b]	25	30	20	0.05	96	79	53.4	6.72
7	25	30	30	0.05	99	77	77.2	9.99
11	15	30	30	0.05	100	81	78.4	9.63
12	10	30	30	0.05	95	73	79.5	8.21
13	5	30	30	0.05	71	43	37.8	8.79
14	10	50	10	0.05	74	36	24.7	6.96
15	10	10	50	0.05	100	91	36.9	4.08
16	10	10	50	0.025	88	82	43.1	5.27
17	10	10	50	0.013	79	71	45.9	6.51

[a] Diphenylacetylene (10 mmol), acetone (70 ml), 3 h. [b] 6 h. [c] Yield based on diphenylacetylene used.

These results indicate the importance of the partial pressure of hydrogen in determining the product distribution. The influence of the partial pressure of hydrogen at 90°C was examined in more detail (Table 2, runs 4, 9, 10, and 7). The yields of 3a and propionaldehyde increased with an increase in pressure. Under CO (30 kg cm^{-2}) and H_2 (30 kg cm^{-2}) the effect of the partial pressure of ethylene was also examined (Table 2, runs 7, 11, 12, and 13). Pressures of ethylene in the range of 10 kg cm^{-2} to 25 kg cm^{-2} had no significant influence on the formation of 3a. The total pressure and the partial pressure of C_2H_4 were kept at 70 kg cm^{-1} and 10 kg cm^{-2}, respectively, and the ratio of CO and H_2 were varied (Table 2, runs 12, 14 and 15) so that the optimal conditions of the reaction could be found; thus the reaction at a partial pressures of 10 kg cm^{-2} for C_2H_4, of 10 kg cm^{-2} for CO, and of 50 kg cm^{-2} for H_2, at 90°C gave the best yield of 3a (91%), with a comparatively low ratio of propionaldehyde to 3a.

Table 3

Activities of several catalysts in the cross-hydrocarbonylation of diphenylacetylene and ethylene [a]

Catalyst	Conv. (%)	Product			
		3a [b] (%)	4a [b] (%)	Stilbene [b] (%) ((Z)/(E))	EtCHO (mmol)
$Rh_4(CO)_{12}$	100	91	2	8 (57/43)	36.9
$Rh_6(CO)_{16}$	60	51	1	6 (100/0)	40.7
$CpRh(CO)(PPh_3)$	22	2	11	6 (100/0)	55.3
Rh_2O_3	37	10	0.2	24 (100/0)	22.3
$RhCl_3 \cdot 3H_2O$	4	–	–	–	0.9
$RhH(CO)(PPh_3)_3$	100	0.4	0.3	58 (65/35)	43.8
$PtCl_2(PPh_3)_2$-$SnCl_2$	78	–	–	77 (83/17)	36.0

[a] Diphenylacetylene (10 mmol), ethylene (10 kg cm^{-2}), catalyst (0.2 mg atom), acetone (70 ml), CO (10 kg cm^{-2}), H_2 (50 kg cm^{-2}), 90°C, 3 h. [b] Yield based on acetylene used.

The effect of catalyst concentration was also examined (Table 2, runs 15, 16, and 17). The yields, based on rhodium atom, were 4550–14200%. At lower concentrations the amount of propionaldehyde produced increased slightly.

Besides $Rh_4(CO)_{12}$, there are several other rhodium carbonyl complexes and their precursors which were used as catalyst. The results are listed in Table 3. $Rh_6(CO)_{16}$ showed slightly lower activity, but the selectivity to **3a** was comparable to that of $Rh_4(CO)_{12}$. On the other hand, $(\eta^5\text{-}C_5H_5)Rh$ $(CO)(PPh_3)$), Rh_2O_3, and $RhCl_3 \cdot 3H_2O$ showed low activities. In the case of $HRh(CO)(PPh_3)_3$, which is a well-known catalyst of the hydroformylation of olefins, stilbene (58%, $(E)/(Z) = 35/65$) was mainly obtained. Similarly, the catalyst $PtCl_2(PPh_3)_2\text{-}SnCl_2$ resulted in the selective formation of stilbene (77%, $(E)/(Z) = 17/83$).

Under conditions similar to run 15, the reaction of 2-butyne (**1b**) and 2-butyne-1,4-diol dimethyl ether (**1c**) gave 4-methyl-4-hexen-3-one (**3b**) and 4-methoxymethyl-6-methoxy-4-hexen-3-one (**3c**) in 73% and 75% yields, respectively. Since the ^1H NMR spectrum of **3b** was consistent with that of the (E)-isomer [7], **3a** and **3c** also seem to be (E)-isomers.

$$RC \equiv CR \quad + \quad C_2H_4 \quad \xrightarrow{CO/H_2} \quad \underset{H}{\overset{R}{>}}C = C\underset{COEt}{\overset{R}{<}} \quad (3)$$

(**1a–1c**)　　　　　　　　　　　　　　　(**3a–3c**)

R = Ph , Me , CH2OMe

It was found that the cross-hydrocarbonylation of terminal acetylenes and ethylene occurs in an anti-Markonikov addition and that the resulting vinyl group has the (E)-configuration, as shown in eq. 4. For example, the reaction of phenylacetylene (**1d**) gave (E)-1-phenyl-1-penten-3-one (**3d**) in 76% yield. Similarly, reaction with 1-hexyne (**1e**), 3,3-dimethyl-1-butyne (**1f**), and trimethylsilylacetylene (**1g**) gave (E)-4-nonen-3-one (**3e**), (E)-6,6-dimethyl-4-hepten-3-one (**3f**) and (E)-1-trimethylsilyl-1-penten-3-one (**3g**) in 68, 93, and 62% yields, respectively. The (E)-configuration of these products was revealed by the $^3J_{HH}$ coupling constant (ca. 16 Hz) across the C=C double bond. It is noteworthy that neither the (Z)-isomer nor the other regioisomer, 2-substituted 1-penten-3-one, was detected in the reaction of these terminal acetylenes, which indicates that the reaction is highly regio- and stereoselective.

$$RC \equiv CH \quad + \quad C_2H_4 \quad \xrightarrow{CO/H_2} \quad \underset{H}{\overset{R}{>}}C = C\underset{COEt}{\overset{H}{<}} \quad (4)$$

(**1d–1g**)　　　　　　　　　　　　　　　(**3d–3g**)

R = Ph , n-Bu , t-Bu , Me3Si

The reaction of 1-phenylpropyne (**1h**) also proceeded regio- and stereoselectively, to give (E)-2-methyl-1-phenyl-1-penten-3-one (**3h-A**) and (E)-4-phenyl-4-hexen-3-

one (**3h-B**) in 62 and 11% yields, respectively. The ^{1}H NMR spectra of the compounds obtained were consistent with those of authentic samples [8,9].

$$PhC \equiv CMe \ + \ C_2H_4 \ \xrightarrow{CO/H_2} \ \underset{\text{H}}{\overset{\text{Ph}}{>}}C = C\underset{\text{COEt}}{\overset{\text{Me}}{<}} \ + \ \underset{\text{H}}{\overset{\text{Me}}{>}}C = C\underset{\text{COEt}}{\overset{\text{Ph}}{<}}$$

(1h)   (3h-A)   (3h-B)

$$(5)$$

In the present cross-hydrocarbonylation functionally-substituted acetylenes such as methyl 3-methylpropiolate (**1i**) and methyl 3-phenylpropiolate (**1j**) could be used to give the corresponding α,β-unsaturaed ethyl ketones. From **1i** (E)-methoxy-carbonyl-2-methyl-1-penten-3-one (**3i-A**) and 3-methoxycarbonyl-2-hexen-4-one (**3i-B**, (E)/(Z) = 1/1) were obtained in 69 and 3% yields, respectively. The structures of **3i-A** and **3i-B** were determined on the basis of the coupling between the methyl proton and the olefinic proton; **3i-A** (1.5 Hz) and **3i-B** (7 Hz). On the other hand, reaction of **1j** gave 2-methoxycarbonyl-1-phenyl-1-penten-3-one (**3j-A**, (E)/(Z) = 33/67) and 1-methoxycarbonyl-2-phenyl-1-penten-3-one (**3j-B**) in 29 and 3% yields, respectively. The structure of **3j-A** was confirmed by the following chemical transformation to 1-phenyl-3-pentanones; (i) the hydrogenation of **3j-A** over Pd/C to give 2-methoxycarbonyl-1-phenylpentan-3-one, (ii) the hydrolysis of the hydrogenation product to give 2-hydroxycarbonyl-1-phenylpentan-3-one, and (iii) the decarboxylation of the carboxylic acid.

$$MeC \equiv CCO_2Me \ + \ C_2H_4 \ \xrightarrow{CO/H_2} \ \underset{\text{H}}{\overset{\text{MeO}_2C}{>}}C = C\underset{\text{COEt}}{\overset{\text{Me}}{<}} \ + \ \underset{\text{H}}{\overset{\text{Me}}{>}}C = C\underset{\text{COEt}}{\overset{\text{CO}_2Me}{<}} \qquad (6)$$

(1i)   (3i-A)   (3i-B)

$$PhC \equiv CCO_2Me \ + \ C_2H_4 \ \xrightarrow{CO/H_2} \ \underset{\text{H}}{\overset{\text{Ph}}{>}}C = C\underset{\text{COEt}}{\overset{\text{CO}_2Me}{<}} \ + \ \underset{\text{H}}{\overset{\text{MeO}_2C}{>}}C = C\underset{\text{COEt}}{\overset{\text{Ph}}{<}} \qquad (7)$$

(1j)   (3j-A)   (3j-B)
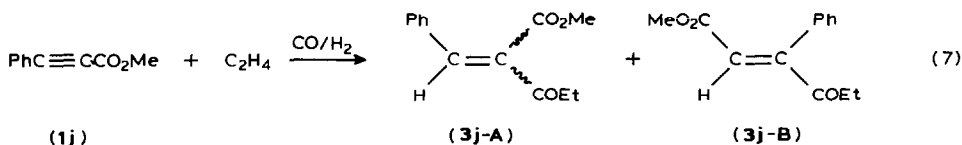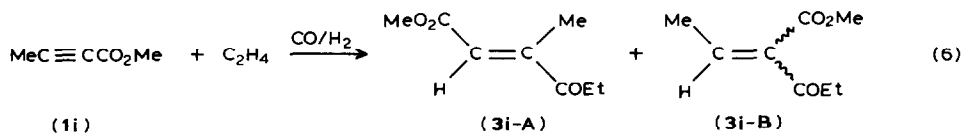
The cross-hydrocarbonylation of acetylenes and ethylene with CO and H_2 can introduce hydrogen and propionyl group onto acetylene compounds directly to yield α,β-unsatured ethyl ketones. In the reaction of unsymmetrical acetylenes high regioselectivity was observed (Table 4). It is important to clarify the origin of the regioselectivity from a synthetic viewpoint. The reactions of **1i** and **1j** gave the regioisomers **3i-A** and **3j-A** as the main products, in which the propionyl group was introduced into the position adjacent to the methyl group in **1i**, and to the methoxycarbonyl group in **1j**, respectively. These results show that the electronic effect is less important and that steric effect is more important. If the electronic effect is operative, the propionyl group should be introduced either onto the acetylenic carbon adjacent to the COOMe group or to that adjacent to the Me or Ph group in **1i** and **1j**, respectively, since the electron-withdrawing order of these substituents is COOMe > Ph > Me. If the steric effect is operative, the introduction
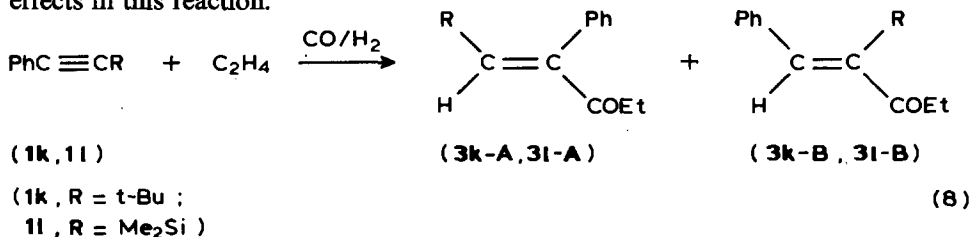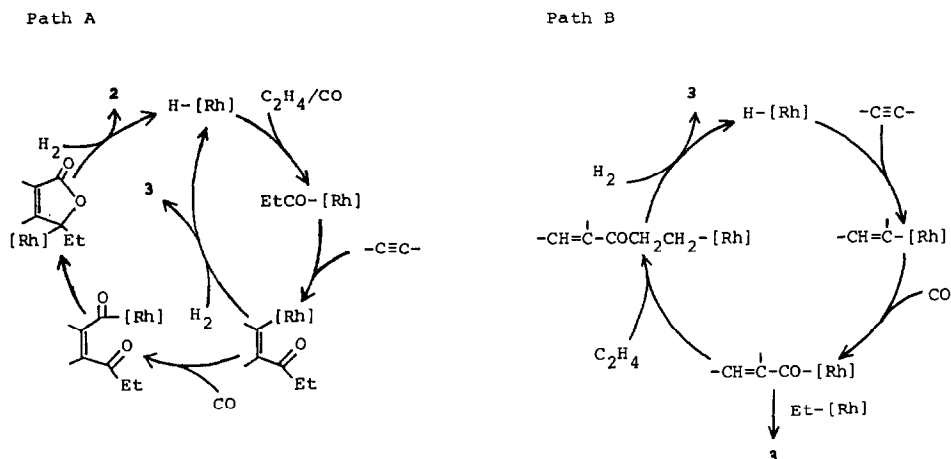
Table 4

Syntheses of α,β-unsaturated ethyl ketones by the crosshydrocarbonylation of acetylenes and ethylene [a]

$R^1C{\equiv}CR^2$ (1)			Conv. (%)	Products (%) [b]	
	R^1	R^2		(3-A)	(3-B)
1a	Ph	Ph	100	91	
1b	Me	Me	100	73	
1c	CH_2OMe	CH_2OMe	91	75	
1d	Ph	H	99	78	−
1e	n-Bu	H	100	68	−
1f	t-Bu	H	100	93	−
1g	Me_3Si	H	80	62	−
1h	Ph	Me	91	62	11
1i	CO_2Me	Me	75	69	3 [c]
1j	Ph	CO_2Me	72	29 [c]	3
1k	t-Bu	Ph	26	20	4
1l	Me_3Si	Ph	51	17	3
1m	s-Bu	Me	94	53	8

[a] Acetylene (10 mmol), $Rh_4(CO)_{12}$ (0.05 mmol), Acetone (70 ml), ethylene (10 kg cm^{-2}), CO (10 kg cm^{-2}), H_2 (50 kg cm^{-2}), 90 °C, 3h. [b] Yield based on acetylene used. [c] Mixture of (E)- and (Z)-isomers.

of the propionyl group should be dependent on the size of the substituent on the acetylene. In order to confirm this, reactions of 1-phenyl-3,3-dimethyl-1-butyne (1k) and trimethylsilylphenylacetylene (1l) were carried out, since the phenyl group is sterically smaller than the t-butyl and trimethylsilyl groups. The conversion of these acetylenes was low, probably because of steric hindrance, but 6,6-dimethyl-4-phenyl-4-hepten-3-one (3k-A) from 1k and 1-trimethylsilyl-2-phenyl-1-penten-3-one (3l-A) from 1l were obtained as the major products, respectively. The structure of 3k-A was determined by comparison of the chemical shift of the vinylic proton (δ 6.82) with that (δ 7.36) of (E)-2-t-butyl-1-phenyl-1-penten-3-one (3k-B), because the signal of the vinylic proton adjacent to the phenyl group appears in lower magnetic field. Also the structure of 3l-A was confirmed by the chemical transformation to 2-phenyl-1-penten-3-one; the trimethylsilyl group was replaced by hydrogen upon treatment with H_2O and I_2 [10]. The propionyl groups in 3k-A and 3l-A bind to the originally acetylenic carbon atom adjacent to the phenyl group and the positions are opposite to that in 3h-A obtained from 1-phenylpropyne (1h). These results clearly show that the propionyl group is introduced at the less-sterically hindered acetylenic carbon atom and that steric effects dominate over electronic effects in this reaction.

$$PhC{\equiv}CR \ + \ C_2H_4 \ \xrightarrow{CO/H_2} \ $$

(1k, 1l) (3k-A, 3l-A) (3k-B, 3l-B)

(1k, R = t-Bu ;
 1l, R = Me$_3$Si)

(8)

Path A   Path B

Scheme 1

The characteristics of regio- and stereoselectivities in this reaction were applied to the synthesis of an alarm pheromone, mannicone [11], in a one pot reaction from 4-methyl-2-hexyne (**1m**), C_2H_4, CO, and H_2. Thus the reaction of **1m** gave (E)-4,6-dimethyl-4-octen-3-one (**3m-A**, manicone) and (E)-4-(2-butyl)-4-hexene-3-one in 53% and 8% yields, respectively. The ^1H NMR spectrum of manicone was consistent with that of an authentic sample [11].
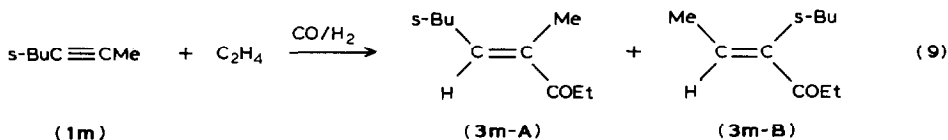
The insertions of unsaturated hydrocarbons into metal-hydrogen and metal-carbon bonds are very important steps in homogeneous catalytic cycles. In the formation of α,β-unsaturated ethyl ketones (**3**) two possible paths are assumed to occur during acetylene insertion; (a) insertion of acetylene into the Rh–COEt bond, consisting of stepwise insertion of ethylene and carbon monoxide into the Rh–H bond, and (b) insertion of acetylene into the Rh–H bond (Scheme 1).

Considering the regioselectivity, insertion of acetylene in path (a) should occur in such a way that the rhodium metal and the EtCO group are attached to the more- and less-hindered acetylenic carbon atoms, respectively, giving a β-acylvinylrhodium intermediate. Similar stoichiometric insertion reactions, in which the metal atom adds to the more sterically-hindered acetylenic carbon atom, have been reported. The reaction of $RMn(CO)_5$ (R = Me, MeCO, and Ph) [12], $RCONiCl(PMe_3)_2$ [13], and $MeNi(acac)(PPh_3)$ [14] with unsymmetrical acetylenes are good examples. In the reactions of the manganese complexes and the acylnickel complexes, β-acylvinyl complexes are obtained. In path (b) insertion of acetylene should occur so as to connect the rhodium metal with a sterically less-hindered acetylene carbon atom, giving a vinylrhodium intermediate. Some examples of complexes derived from a metal hydride complex and acetylene are described in ref. 15. However, it is not enough to compare the regioselectivity of the reaction because the number of

acetylenes employed is limited. Although it is difficult to reach a definite conclusion, we assume that path (a) is operative in the present system, because the same regioselectivity in the formation of the furanones (2) from terminal acetylenes [16] and from 1-phenylpropyne [1,3] can be explained by the common intermediacy of an acylrhodium complex. Thus, the hydrogenolysis of the β-acylvinylrhodium complex gives α,β-unsaturated ketones, and the subsequent insertion of CO leads to 5-ethyl-2(5H)-furanones. In the presence of molecular hydrogen the hydrogenolysis is dominant over the CO insertion.

Experimental

^{1}H NMR spectra were recorded with a JEOL JNM-PS-100 or a JNM-FX-400 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 1.0 m × 3.0 mm 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. All boiling points are uncorrected.

Materials

Diphenylacetylene (1a), 2-butyne (1b), Rh$_4$(CO)$_{12}$, and Rh$_6$(CO)$_{16}$ were prepared by procedures described previously [1]. 2-Butyn-1,4-diol dimethyl ether (1c) [17], 1-hexyne (1e) [17], 3,3-dimethyl-1-butyne (1f) [17], methyl 3-methylpropiolate (1i) [18], methyl 3-phenylpropiolate (1j) [17], 1-phenyl-3,3-dimethyl-1-butyne (1k) [19], trimethylsilylphenylacetylene (1l) [17], and 4-methyl-2-hexyne (1m) [20] were prepared according to the published procedures. All other chemicals were commercially available reagents of the best purity and were used without further purification. Carbon monoxide and ethylene were also obtained commercially and were used as received.

General procedures for the cross-hydrocarbonylation of acetylenes (1) and ethylene

A 150 ml glass tube was charged with acetylenes (1, 10 mmol), Rh$_4$(CO)$_{12}$ (0.05 mmol), and acetone (70 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, carbon monoxide, and hydrogen to the desired pressures, heated and agitated at the desired temperature. The reaction mixture was analyzed by gas chromatography (3% Silicone OV-17 on Chromosorb W for the analysis of the cross-hydrocarbonylation products, and 15% PEG 20M on Chromosorb W for those of propionaldehyde and diethyl ketone). The products were isolated by vacuum fractional distillation and/or column chromatography on silica gel. The identity of the products was established by ^{1}H NMR, IR, and GC/MS spectroscopy.

Cross-hydrocarbonylation of diphenylacetylene (1a) and ethylene

A mixture of 1a (1.78 g, 10 mmol) and Rh$_4$(CO)$_{12}$ (38 mg, 0.05 mmol) in acetone (70 ml), under ethylene (10 kg cm^{-2}), CO (10 kg cm^{-2}), and H$_2$ (50 kg cm^{-2}) was heated at 90°C for 3 h. GC analysis of the resulting yellow solution indicated the presence of 2.14 g (91%) of 1,2-diphenyl-1-pentene-3-one (3a), 0.042 g (2%) of

1,2-diphenylpentan-3-one, 0.138 g (8%) of stilbene ($(E)/(Z) = 43/57$) and 2.14 g (36.9 mmol) of propionaldehyde. The solvent was removed from the reaction mixture in vacuo and the residue was distilled at reduced pressure to yield 1.72 g (73%) of **3a**; colorless oil: Bp 145–146°C/1 Torr. MS: M^+ 236. IR (neat): νC=O 1685, νC=C 1615 cm^{-1}. ^{1}H NMR: δ 1.10 (t, COCH$_2$*CH$_3$*), 2.58 (q, CO*CH$_2$*CH$_3$), 6.9–7.5 (m, *C$_6$H$_5$*), 7.66 (s, =*CH*). 2,4-Dinitrophenylhydrazone of **3a**: red crystals; mp 159–160°C. Anal. Found: C, 66.12; H, 4.88; N, 13.45. C$_{23}$H$_{20}$N$_4$O$_4$ calcd.: C, 66.34; H, 4.84; N, 13.45%.

(E)-4-methyl-4-hexene-3-one (3b). Colorless oil. Bp 73°C (43 mmHg). MS: M^+ 112. ^{1}H NMR: δ 1.10 (t, COCH$_2$*CH$_3$*), 1.80 (s, *CH$_3$*), 1.86 (d, *CH$_3$*, *J* 7 Hz), 2.70 (q, CO*CH$_2$*CH$_3$), 6.72 (q, =*CH*, *J* 7 Hz).

(E)-4-methoxymethyl-6-methoxy-4-hexene-3-one (3c). Colorless oil. Bp 103–105°C/10 Torr. ^{1}H NMR: δ 1.12 (t, COCH$_2$*CH$_3$*), 2.78 (q, CO*CH$_2$*CH$_3$), 3.34 (s, O*CH$_3$*), 3.43 (s, O*CH$_3$*), 4.23 (s, *CH$_2$*O), 4.33 (d, *CH$_2$*O, *J* 6 Hz), 6.88 (t, =*CH*, *J* 6 Hz).

(E)-1-phenyl-1-penten-3-one (3d). Colorless crystals. Mp. 41°C. ^{1}H NMR: δ 1.16 (t, COCH$_2$*CH$_3$*), 2.68 (q, CO*CH$_2$*CH$_3$), 6.71 (d, =*CH*, *J* 16 Hz), 7.53 (d, =*CH*, *J* 16 Hz), 7.1–7.6 (m, *C$_6$H$_5$*).

(E)-4-nonen-3-one (3e). Colorless oil: Bp 56–59°C/1 Torr. ^{1}H NMR: δ 0.87 (t, (CH$_2$)$_3$*CH$_3$*), 1.10 (t, COCH$_2$*CH$_3$*), 1.7–2.4 (m, (*CH$_2$*)$_3$), 2.58 (q, CO*CH$_2$*CH$_3$), 6.09 (dd, =*CH*, *J* 16, 2 Hz), 6.82 (dt, =*CH*, *J* 16, 7 Hz).

(E)-6,6-dimethyl-4-hepten-3-one (3f). Colorless oil: Bp 37°C/3 Torr. ^{1}H NMR: δ 1.10 (s, C(*CH$_3$*)$_3$), 1.14 (t, COCH$_2$*CH$_3$*), 2.60 (q, CO*CH$_2$*CH$_3$), 6.01 (d, =*CH*, *J* 16 Hz), 6.81 (d, =*CH*, *J* 16 Hz).

(E)-1-trimethylsilyl-1-penten-3-one (3g). Colorless oil. Bp 83°C/27 Torr. ^{1}H NMR: δ 0.14 (s, Si(*CH$_3$*)$_3$), 1.08 (t, COCH$_2$*CH$_3$*), 2.60 (q, CO*CH$_2$*CH$_3$), 6.43 (d, =*CH*, *J* 19 Hz), 7.02 (d, =*CH*, *J* 19 Hz).

(E)-2-methyl-1-phenyl-1-penten-3-one (3h-A). Colorless oil. ^{1}H NMR: δ 1.16 (t, COCH$_2$*CH$_3$*), 2.08 (d, *CH$_3$*, *J* 1.5 Hz), 2.84 (q, CO*CH$_2$*CH$_3$), 7.38 (m, *C$_6$H$_5$*), 7.50 (q, =*CH*, *J* 1.5 Hz).

(E)-4-phenyl-4-hexen-3-one (3h-B). ^{1}H NMR: δ 1.06 (t, COCH$_2$*CH$_3$*), 1.70 (d, *CH$_3$*, *J* 7 Hz), 2.59 (q, CO*CH$_2$*CH$_3$), 6.97 (q, =*CH*, *J* 7 Hz), 7.0–7.6 (m, *C$_6$H$_5$*).

(E)-1-methoxycarbonyl-2-methyl-1-penten-3-one (3i-A). Colorless oil. Bp 74°C/7 Torr. ^{1}H NMR: δ 1.14 (t, COCH$_2$*CH$_3$*), 2.28 (d, =CH*CH$_3$*, *J* 1.5 Hz), 2.80 (q, CO*CH$_2$*CH$_3$), 3.82 (s, O*CH$_3$*), 6.60 (q, =*CH*, *J* 1.5 Hz).

(E)- and (Z)-3-methoxycarbonyl-2-hexen-4-one (3i-B). ^{1}H NMR: δ 1.88 (d, =CH*CH$_3$*, *J* 7 Hz, (*E*)-isomer), 1.98 (d, =CH*CH$_3$*, *J* 7 Hz, (*Z*)-isomer), 6.98 (q, =*CH*, *J* 7 Hz, (*Z*)-isomer), 7.04 (q, =*CH*, *J* 7 Hz, (*E*)-isomer).

(E)- and (Z)-2-methoxycarbonyl-1-phenyl-1-penten-3-one (3j-A). ^{1}H NMR: (*E*)-isomer, δ 1.11 (t, COCH$_2$*CH$_3$*), 2.59 (q, CO*CH$_2$*CH$_3$), 3.83 (s, O*CH$_3$*), 7.35 (m, *C$_6$H$_5$*), 7.72 (s, =*CH*). (*Z*)-isomer, δ 1.16 (t, COCH$_2$*CH$_3$*), 2.78 (q, CO*CH$_2$*CH$_3$), 3.82 (s, O*CH$_3$*), 7.41 (m, *C$_6$H$_5$*), 7.63 (s, =*CH*). $(E)/(Z) = 33/67$. A mixture of (*E*)- and (*Z*)-isomers was hydrogenated over Pd/C to give 2-methoxycarbonyl-1-phenyl-3-pentanone, which indicates that the isomers are geometrical.

Cross-hydrocarbonylation of 1-phenyl-3,3-dimethyl-1-butyne (1k) and ethylene

Reaction of **1k** (1.58 g) and ethylene was carried out under the conditions mentioned above. GC analysis of the reaction mixture showed the presence of

(*E*)-6,6-dimethyl-4-phenyl-4-hepten-3-one (**3k-A**, 0.423 g), (*E*)-2-t-butyl-1-penten-3-one (**3k-B**, 0.082 g), 6,6-dimethyl-4-phenyl-3-heptanone (**4k**, 0.053 g), **1k** (1.17 g) and propionaldehyde (2.13 g). The products **3k-A**, **3k-B** and **4k** were separated by column chromatography and were identified by ^{1}H NMR spectroscopy: **3k-A**. ^{1}H NMR: δ 0.93 (s, C(CH_3)$_3$), 1.00 (t, COCH$_2$$CH_3$), 2.37 (q, CO$CH_2CH_3$), 6.82 (s, =$CH$), 7.0–7.4 (m, C_6H_5); **3k-B**. ^{1}H NMR: δ 1.07 (s, C(CH_3)$_3$), 1.14 (t, COCH$_2$$CH_3$), 2.72 (q, CO$CH_2CH_3$), 7.36 (s, =$CH$), 7.1–7.4 (m, C_6H_5).

1-Trimethylsilyl-2-phenyl-1-penten-3-one (3l-A). Colorless oil. ^{1}H NMR: δ −0.12 (s, (CH_3)$_3$Si), 1.05 (t, COCH$_2$$CH_3$), 2.56 (q, CO$CH_2CH_3$), 6.92 (s, =$CH$), 7.0–7.4 (m, C_6H_5). **3l-A** was treated with H$_2$O and I$_2$ to give 2-phenyl-1-penten-3-one.

Synthesis of (E)-4,6-dimethyl-4-octen-3-one (3m-A, manicone)

A mixture of 2-methyl-2-hexyne (**1m**, 12.4 mmol), Rh$_4$(CO)$_{12}$ (0.05 mmol) and acetone (70 ml), under C$_2$H$_4$ (10 kg cm^{-2}), CO (10 kg cm^{-2}), and H$_2$ (50 kg cm^{-2}) was heated at 90°C for 3 h. GC analysis of the reaction mixture showed the presence of **3m-A** (6.51 mmol, 53%), (*E*)-4-(2-butyl)-4-hexen-3-one (**3m-B**, 0.99 mmol, 8%), **1m** (0.8 mmol) and propionaldehyde (34.8 mmol). The reaction mixture was distilled in vacuo. The fraction collected (bp. 93–97°C/25 Torr, 0.845 g) consisted of **3m-A** and **3m-B** in 85/15 ratio. They were subsequently separated by column chromatography: **3m-A**. ^{1}H NMR (400 MHz): δ 0.87 (t, CH(CH$_3$)CH$_2$$CH_3$), 1.02 (d, CH($CH_3$)CH$_2CH_3$, *J* 6.7 Hz), 1.10 (t, COCH$_2$$CH_3$), 1.36 (m, CH(CH$_3$) CH_AH$_BCH_3$), 1.45 (m, CH(CH$_3$)CH$_A$$H_BCH_3$), 1.79 (d, =C-$CH_3$, *J* 1.5 Hz), 2.50 (m, CH(CH$_3$)CH$_2$CH$_3$), 2.69 (q, COCH_2CH$_3$), 6.37 (dq, =CH, *J* 9.7, 1.5 Hz); **3m-B**. ^{1}H NMR (400 MHz): δ 0.78 (t, CH(CH$_3$)CH$_2$$CH_3$), 1.06 (t, COCH$_2$$CH_3$), 1.13 (d, CH($CH_3$)CH$_2CH_3$, *J* 7.0 Hz), 1.53 (m, CH(CH$_3$)CH_AH$_B$CH$_3$), 1.65 (m, CH(CH$_3$)CH$_A$$H_BCH_3$), 1.85 (d, =CH-$CH_3$, *J* 7.0 Hz), 2.62 (q, COCH_2CH$_3$), 2.64 (m, CH(CH$_3$)CH$_2$CH$_3$), 6.61 (q, =CH, *J* 7.0 Hz).

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