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RHODIUM CARBONYL-CATALYZED CROSS-HYDROCARBONYLATION OF ACETYLENES AND ETHYLENE. SYNTHESIS OF α,β-UNSATURATED KETONES

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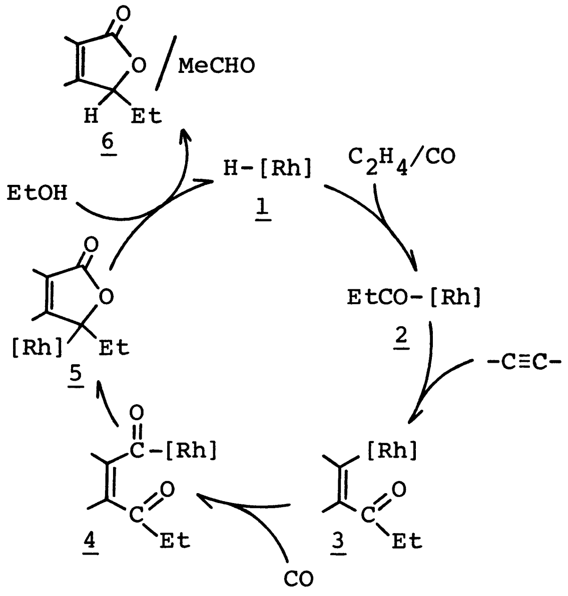
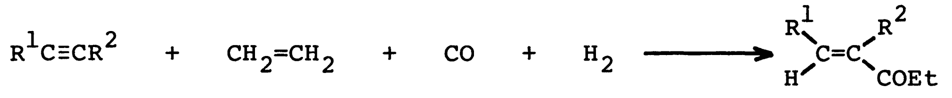
The cross-hydrocarbonylation of acetylenes and ethylene with CO and H_2 in the presence of $Rh_4(CO)_{12}$ gave α,β-unsaturated ethyl ketones regio- and stereoselectively.

The transition metal catalyzed hydroformylation of olefins is still the most important carbonylation reaction industrially and has been extensively investigated.1),2) However, the hydroformylation of acetylenes has not been studied as much as that of olefins because of its low selectivity.2) Previously we have reported that the rhodium carbonyl-catalyzed carbonylation of internal acetylenes and ethylene in hydrogen donating solvent such as ethanol give 5-ethyl-3,4-disubstituted-2(5H)-furanones, which would be formed via course as shown in Scheme; (1) stepwise insertions of ethylene, CO, and acetylene into the Rh-H bond of 1 to form σ-vinyl complex 3, (2) insertion of CO to 3 to give 4 which would be converted to the σ-allyl lactonyl complex 5, and (3) reduction of 5 by hydrogen donor to produce the furanone 6.3) In the course of the study to explore the role of hydrogen donor in the reaction, we found that the use of molecular hydrogen as hydrogen donor gave selectively α,β-unsaturated ethyl ketones, which might be formed by hydrogenolysis of the σ-vinyl



Scheme

intermediate 3. We now wish to report that the reaction of acetylenes and ethylene in the presence of CO and H_2 (under hydroformylation conditions) produces α,β-unsaturated ethyl ketones (8) as expressed by equation 1, which we term the cross-hydrocarbonylation of acetylenes and olefins.



$$\underset{\textstyle 7}{R^1C\equiv CR^2} + CH_2{=}CH_2 + CO + H_2 \longrightarrow \underset{\textstyle 8}{\overset{R^1}{\underset{H}{}}C{=}C\overset{R^2}{\underset{COEt}{}}} \qquad (1)$$

In a typical experiment, ethylene (25 kg/cm^2), CO (30 kg/cm^2) and H_2 (5 kg/cm^2) were introduced into a 200 ml stainless steel autoclave containing diphenylacetylene (7a, 10 mmol), $Rh_4(CO)_{12}$ (0.05 mmol), and acetone (70 ml) and the autoclave was heated at 150 °C for 6 h. 1,2-Diphenylpent-1-en-3-one (8a, 60% yield based on the amount of 7a used) was isolated from the reaction mixture by column chromatography on silicagel together with 2,3,4,5-tetraphenylcyclopent-2-enone (12%) and 7a (21%). In the present reaction, small amounts of (*E*)/(*Z*)-stilbene (1%), 1,2-diphenyl-3-pentanone (1%) and 5-ethyl-3,4-diphenyl-2(5H)-furanone (2%) were formed; it should be noted that the furanone was the main product (up to 73% yield) when ethanol was used as hydrogen donor.3) The formation of propionaldehyde (7.9 mmol) and diethyl ketone (1.0 mmol) was also observed as by-products. Although 8a was the main product (84%) with an increase in the pressure of hydrogen (30 kg/cm^2), propionaldehyde was produced in a large amount (64 mmol).

In this reaction various kinds of substituted acetylenes could be used to give the corresponding α,β-unsaturated ethyl ketones. The results obtained from terminal acetylenes such as phenylacetylene (7d), 1-hexyne (7e), and 3,3-dimethyl-1-butyne (7f) and functionally substituted acetylenes such as 2-butyne-1,4-diol dimethyl ether (7g), methyl 3-methylpropiolate (7h), and methyl 3-phenylpropiolate (7i) are tabulated in Table 1.

Terminal acetylenes (7d-7f) gave *trans*-α,β-unsaturated ketones (8d-8f) regio- and stereospecifically.6) From 7b and 7h the regioisomers, (*E*)-8b (R^1=Ph, R^2=Me) and 8h (R^1=COOMe, R^2=Me) were predominantly formed over the other isomers, (*E*)-9b (R^1=Me, R^2=Ph) and (*E*)/(*Z*)-9h (R^1=Me, R^2=COOMe) respectively.5),7) From 7i, only one regioisomer (*E*)/(*Z*)-8i (R^1=Ph, R^2=COOMe) was formed.8) These results indicate that the EtCO-Rh intermediate 2 in Scheme added to the acetylene triple bond mainly in the *cis* fashion and the EtCO group was introduced to the less sterically hindered carbon atom of the acetylene.

Table 1 Synthesis of α,β-unsaturated ethyl ketones[a)]

	Acetylene		Conversion		Product	
		(mmol)	(%)			(Yield, %)[b)]
7a	$\mathrm{PhC{\equiv}CPh}$	(10)	82	8a	$\mathrm{PhCH{=}C(Ph)COEt}$[4)]	(75)
7b	$\mathrm{PhC{\equiv}CMe}$	(20)	99	8b	(E)-$\mathrm{PhCH{=}C(Me)COEt}$[5)]	(49)
				9b	(E)-$\mathrm{MeCH{=}C(Ph)COEt}$[5)]	(6)
7c	$\mathrm{MeC{\equiv}CMe}$	(20)	100	8c	(E)-$\mathrm{MeCH{=}C(Me)COEt}$[5)]	(25)
7d	$\mathrm{PhC{\equiv}CH}$	(20)	93	8d	(E)-$\mathrm{PhCH{=}CHCOEt}$[6)]	(48)
7e	n-$\mathrm{BuC{\equiv}CH}$	(20)	100	8e	(E)-n-$\mathrm{BuCH{=}CHCOEt}$[6)]	(42)
7f	t-$\mathrm{BuC{\equiv}CH}$	(20)	100	8f	(E)-t-$\mathrm{BuCH{=}CHCOEt}$[6)]	(61)
7g	$\mathrm{MeOCH_2C{\equiv}CCH_2OMe}$	(20)	75	8g	$\mathrm{MeOCH_2CH{=}C(CH_2OMe)COEt}$[4)]	(76)
7h	$\mathrm{MeC{\equiv}CCOOMe}$	(10)	80	8h	$\mathrm{MeOOCCH{=}C(Me)COEt}$[4),7)]	(76)
				9h	$\mathrm{MeCH{=}C(COOMe)COEt}$[7)] [($E$)/($Z$)=1/1][9)]	(4)
7i	$\mathrm{PhC{\equiv}CCOOMe}$	(10)	83	8i	$\mathrm{PhCH{=}C(COOMe)COEt}$[8)] [($E$)/($Z$)=33/67][9)]	(40)

a) Operating conditions: $Rh_4(CO)_{12}$, 0.05 mmol; acetone, 70 ml; C_2H_4, 25 kg/cm^2; CO, 30 kg/cm^2; H_2, 5 kg/cm^2; 150 °C; 6 h.

b) Determined by GLC. Based on the amounts of acetylenes converted.

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4) The configurations of 8a, 8g, and 8h are not clear yet. But these products seem to be the isomers having trans disposition with regard to the α-carbonyl group and the β-substituent.

5) The ^{1}H NMR spectra of 8b10), 9b11), and 8c12) were identical to those reported.

6) Trans structures of 8d-8f were confirmed by their ^{1}H NMR spectra; spin-spin coupling constants between two olefinic protons were 16 Hz.

7) The structures of 8h and 9h were confirmed by their ^{1}H NMR spectra; spin-spin coupling constants between a methyl proton and a olefinic proton were 1.5 Hz in 8h and 7 Hz in 9h.

8) The structure of 8i was confirmed by its chemical transformation; hydrogenation of 8i on 5% Pd/C and subsequent hydrolysis and decarboxylation gave PhCH$_2$CH$_2$COEt which was identical with the hydrogenated product of 8d.

9) The configurations of 8i and 9h were postulated by comparison of their chemical shifts of olefinic protons with those calculated by empirical additivity rules13); (*E*)-8i: δ 7.72, (*Z*)-8i: δ 7.63, (*E*)-9h: δ 7.04, and (*Z*)-9h: δ 6.98.

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