Tetrahedron Letters,Vol.27,No.37,pp 4497-4500,1986 0040-4039/86 $3.00 + .00
Printed in Great Britain Pergamon Journals Ltd.

HYDROFORMYLATION AND HYDROCARBONYLATION OF ENYNES BY RHODIUM CARBONYL CLUSTER: A NEW ROUTE TO CYCLIC ENONES

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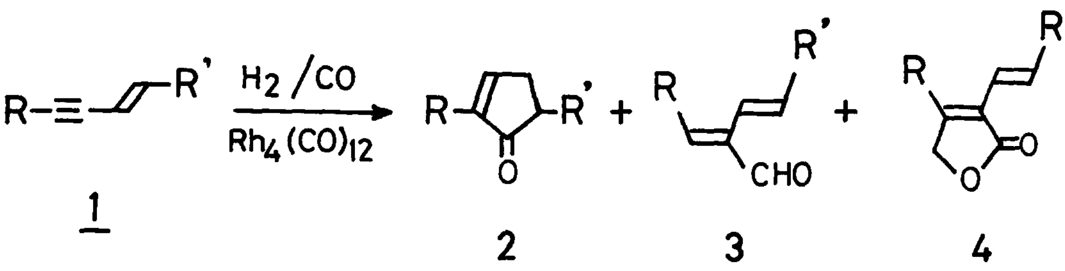
Abstract: The reaction of but-1-en-3-yne derivatives with carbon monoxide and hydrogen in the presence of $Rh_4(CO)_{12}$ catalyst gave formyl-dienes, cyclopentenones and unsaturated lactones, which shows the C≡C is much more reactive than the C=C moiety and may provide a new method for the catalytic synthesis of cyclopentenones.

Although there have been numerous reports on the hydroformylation of olefins (oxo process), few works have been done for acetylenes.[1] Previously we described a new simple method for the synthesis of conjugated enynes from 1-alkynes and alkenyl halides using a palladium-copper catalyst.[2] This method offers us an opportunity to examine the reactivity of carbon-carbon triple bond and double bond co-existig in a molecule towards hydroformylation. Now we have found that triple bond is much more reactive than double bond towards both hydroformylation and hydrocarbonylation, and that hydrocarbonylation of the enynes gives directly cyclopentenones in moderate yields.



a: R = Ph, R' = Ph
b: R = p-$CH_3OC_6H_4$, R' = Ph
c: R = p-NCC_6H_4, R' = Ph

(eq.1)

Thus, 1,4-diphenylbut-1-en-3-yne (1a, 4.85 mmol) was reacted with carbon monoxide (100 atm) and hydrogen (100 atm) in benzene at 60°C in the presence of $Rh_4(CO)_{12}$ (0.027 mmol). After 6 h the reaction mixture was separated by column chromatography on silica to give the products, 2, 3, and 4, which were identified on the basis of elementary analyses including mass spectra, i.r. and n.m.r. spectra. The product 3 was led to the 2,4-dinitrophenylhydrazone and identified as a formyl-diene derivative.

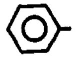
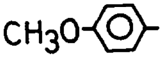
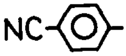
2a: colorless crystals from hexane; m.p. 75 - 76°C (lit.[3] 67 - 68°C).

3a: the 2,4-dinitrophenylhydrazone derivative, dark brown crystals from benzene; m.p., 221 - 223°C; mass spectrum, M/z = 414; n.m.r.(in $CDCl_3$, 360 MHz), δ 7.07(s, 1H), 7.15(d, 1H, J=16 Hz), 7.3 - 7.5(m, 11H), 7.98(d, 1H, J_a=10 Hz), 8.06(s, 1H), 8.35(dd, 1H, J_a=10, J_b=3 Hz), 9.17(d, 1H, J_b=3 Hz), 11.32(s, 1H).

4a: pale yellow crystals from benzene-hexane; m.p., 114 - 115°C; mass spectrum, M/z = 262; i.r., ν_{CO} 1760 cm^{-1}; n.m.r.(in $CDCl_3$, 360 MHz), δ 5.05(s, 2H), 7.02(d, 1H, J=16 Hz), 7.2 - 7.5(m, 10H), 7.99(d, 1H, J=16 Hz).

Representative results obtained from the similar reactions of some enynes are summarized in Table 1.

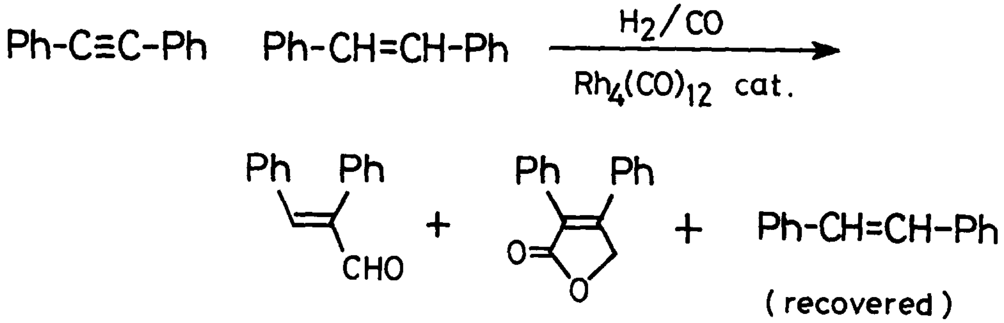
Table 1. Hydroformylation and Hydrocarbonylation of Enynes (RC≡C-CH=CHPh)[a]

Enynes R	Conversion (%)	Products(%)[b] 2	3	4
	91	23	31	9
	70	17	23	6
	100	15	20	12

a) Reaction conditions: catalyst, $Rh_4(CO)_{12}$ 0.027 mmol; substrate, 4.85 mmol; solvent, benzene 10 ml; CO, 100 atm, H_2, 100 atm, 60°C, 6h.

b) Isolated yields based on the enyne compounds consumed, and the conditions are not optimized.

The formyl-dienes 3 are the normal hydroformylation product of the acetylenic group and the olefinic moiety remained intact. The product 4, lactone, is derived from the hydrocarbonylation of the acetylenic part with two molecules of carbon monoxide and one molecule of hydrogen, while the olefinic moiety also remains intact. The similar type of reaction yielding lactones has been observed in the metal-catalyzed reaction of acetylenes with carbon monoxide in alcoholic media.[4,5] The product 2, cyclopentenone derivatives, is derived from hydrocarbonylation of the acetylene group with participation of the olefinic part. These results indicate that acetylenes are more reactive than olefins under hydroformylation conditions. This is also supported by the competitive reaction between diphenylacetylene and diphenylethylene, which gave 5 (31% yield) and 6 (44% yield) derived from diphenylacetylene, whereas unreacted diphenylethylene was recovered (eq. 2).

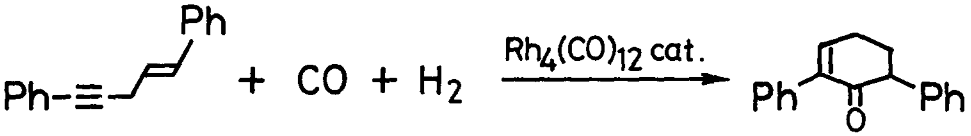


5 6

(eq.2)

It should be noted that cyclopentenones are obtained directly from hydrocarbonylation of the enynes, which may be the first example of catalytic synthesis of the cyclopentenones, though the stoichiometric preparation from cobalt-acetylene complexes with olefins[3,6,7,8] and from titana- or zirconacyclopentene complexes with carbon monoxide[9,10] has been reported.

Similarly, hydrocarbonylation of 1,5-diphenylpent-1-en-4-yne gave 2,6-diphenylcyclohex-2-enone 8 in 40% yield based on 7 comsumed (eq. 3).



(eq. 3)

7 8

Acknowledgement

We thank The Material Analysis Center, I. S. I. R., Osaka University for spectral measurement and microanalysis.

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(Received in Japan 12 June 1986)