Carbonylation of Acetylenes under Water Gas Shift Conditions: A New Method for Synthesis of Furan-2(5*H*)-ones

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Under water gas shift conditions acetylenes are selectively converted into furan-2(5*H*)-ones with catalysis by rhodium carbonyl clusters.

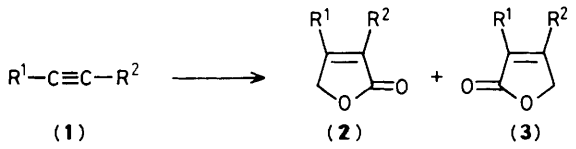
There have been numerous reports on the reaction of acetylenes with carbon monoxide in the presence of transition metal catalysts,[1] but little is known about the formation of lactones *via* the carbonylation of acetylenes.[2—4] Recently the rhodium catalysed carbonylation of acetylenes in alcohols has been reported to give 5-alkoxyfuran-2(5*H*)-ones in satisfactory yields.[5]

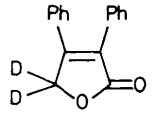
Previously we have shown[6] that under hydroformylation conditions conjugated en-ynes like but-1-en-3-yne derivatives afforded three carbonylated products, cyclopentenones,

Table 1. Synthesis of furan-2(5*H*)-ones from acetylenes.[a]

Acetylene	Reaction time/h	Conversion, %	Furanone	Yield,[b] %	(2) : (3)[c]
(**1a**)	5	81	(**2a**)	83	—
(**1b**)	5	74	(**2b**) + (**3b**)	68	55 : 45
(**1c**)	5	100	(**2c**) + (**3c**)	87	64 : 36
(**1d**)	5	100	(**2d**)	50	—
(**1e**)	8[d]	95	(**2e**) + (**3e**)	77	27 : 73
(**1f**)	16[d]	100	(**2f**)	69	—
(**1g**)	5	94	(**2g**) + (**3g**)	90	78 : 22

[a] Reaction conditions; $Rh_4(CO)_{12}$, 0.027 mmol; substrate, 4.85 mmol; H_2O, 56 mmol; NEt_3, 15 mmol; tetrahydrofuran (THF), 10 ml; CO, 100 atm; 100 °C. [b] Isolated yield based on the substrate (**1**) consumed. [c] Molar ratio of the structural isomers, (**2**) and (**3**), in Scheme 1. [d] $Rh_4(CO)_{12}$, 0.108 mmol; substrate, 8.7 mmol; H_2O, 112 mmol; NEt_3, 30 mmol; THF, 15 ml; CO, 150 atm.





(4)

a; $R^1 = R^2 = Ph$
b; $R^1 = Ph$, $R^2 = C_6H_4OMe$-*p*
c; $R^1 = Ph$, $R^2 = CH{=}CHPh$
d; $R^1 = R^2 = CH{=}CHPh$
e; $R^1 = Ph$, $R^2 = Me$
f; $R^1 = R^2 = Et$
g; $R^1 = Me$, $R^2 = CH{=}CHPh$

Scheme 1. *Reagents* and *conditions:* H_2O–CO, Rh catalyst, amine.

formyl-1,3-dienes, and furan-2(5*H*)-ones, in moderate yields.

We have now found that under water gas shift conditions the en-yne compounds yield furan-2(5*H*)-ones selectively, and the reaction has been successfully extended to a new general method for the selective synthesis of furan-2(5*H*)-ones from acetylenes (Scheme 1).

Thus, diphenylacetylene was treated with water and carbon monoxide (100 atm) in tetrahydrofuran containing triethylamine at 100 °C for 5 h in the presence of $Rh_4(CO)_{12}$ catalyst. The product was isolated by column chromatography on silica. Elution with benzene gave 3,4-diphenylfuran-2(5*H*)-one (**2a**) ($R^1 = R^2 = Ph$) in 83% yield based on diphenylacetylene consumed (81% conversion). The furanone (**2**) is derived from the carbonylation of the triple bond with two molecules of carbon monoxide and one molecule of hydrogen. Use of D_2O gave the furanone (**4**) which indicates that the hydrogen comes from water.

Other internal acetylenes including alkyl-acetylenes similarly gave the corresponding furanones as shown in Table 1.† Asymmetrically substituted acetylenes such as phenyl-4-methoxyphenylacetylene (**1b**) and 1-phenylpent-1-en-3-yne (**1g**) afforded two furanone structural isomers, (**2**) and (**3**), which were separated by column chromatography on silica and identified by spectral analyses. The isomer ratio of the furanones formed seems to be affected by the electronic and steric nature of the substituents.

As catalysts, rhodium carbonyl clusters such as $Rh_4(CO)_{12}$ and $Rh_6(CO)_{16}$ are the best among the transition metal complexes tested. Ruthenium carbonyls showed a very low activity, and cobalt and iron carbonyls were almost inactive for the present reaction, although they are active for the water gas shift reaction.[7] The presence of amines such as diethylamine or triethylamine is essential for the selective synthesis of furanones. The absence of amines resulted in a marked decrease in both catalytic activity and product selectivity, *e.g.*, 77% conversion of (**1a**) and 28% selectivity for formation of (**2a**) in the reaction at 130 °C for 5 h.

We thank Drs. H. Yamazaki and P. Hong of the Institute of Physical and Chemical Research for helpful discussion, and the Material Analysis Center, I.S.I.R., Osaka University for spectral measurement and microanalyses.

Received, 17th November 1986; Com. 1630

References

1 See, for example, P. Pino and G. Braca, in 'Organic Synthesis via Metal Carbonyls,' eds. I. Wender and P. Pino, Wiley, New York, 1977, vol. 2, p. 419.
2 J. Tsuji and T. Nogi, *J. Am. Chem. Soc.*, 1966, **88**, 1289.
3 R. F. Heck, *J. Am. Chem. Soc.*, 1964, **81**, 2819.
4 H. Alper, J. K. Currie, and H. des Abbayes, *J. Chem. Soc., Chem. Commun.*, 1978, 311.
5 P. Hong, T. Mise, and H. Yamazaki, *Chem. Lett.*, 1981, 989; T. Mise, P. Hong, and H. Yamazaki, *ibid.*, 1981, 993.
6 K. Doyama, T. Joh, S. Takahashi, and T. Shiohara, *Tetrahedron Lett.*, 1986, 4497.
7 See, for example, R. B. King, A. D. King, Jr., and D. B. Yang, in 'Catalytic Activation of Carbon Monoxide,' ed. P. C. Ford, American Chemical Society, Washington, D.C., 1981, p. 123.

† All new compounds gave satisfactory elemental, mass, i.r., and n.m.r. data.