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# RHODIUM CARBONYL-CATALYZED CARBONYLATION OF ACETYLENES IN THE PRESENCE OF OLEFINS AND PROTON DONORS. SYNTHESIS OF 5-ALKYL-2(5H)-FURANONES

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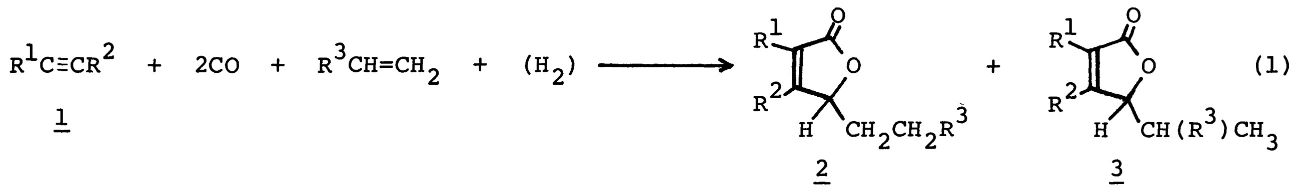
Rhodium carbonyl-catalyzed reactions of internal acetylenes with ethylene and CO in protic solvents, e.g., ethanol, gave 3,4-disubstituted-5-ethyl-2(5H)-furanones in good yields. By using propylene or methyl acrylate instead of ethylene, small amounts of 5-*n*-/*iso*-propyl-2(5H)-furanones or 5-[2-(methoxycarbonyl)ethyl]-2(5H)-furanone were obtained.

Carbonylation of acetylenes in the presence of homogeneous metal catalysts is of much scientific and industrial importance, because it is possible to obtain derivatives of mono- and dicarboxylic acids, cyclic ketones, hydroquinones, and butenolides in one step from acetylenes and CO.[1)] As examples of catalytic synthesis of butenolides (2(5H)-furanones), which are an important class of naturally occurring compounds,[2)] bifurandiones by $Co_2(CO)_8$ catalyst[3)4)] and 3,4-diphenyl-2(5H)-furanone by $PdCl_2$ catalyst[5)] have been known. We now wish to report a new synthetic method of 5-alkyl-2(5H)-furanones by rhodium carbonyl-catalyzed carbonylation of acetylenes in the presence of olefins and proton donor such as alcohol and water. The general synthesis is represented by the equation 1.



(1)

In a typical experiment, ethylene (20Kg/cm$^2$) and CO (30Kg/cm$^2$) were introduced into a 200ml stainless steel autoclave containing diphenylacetylene (1a, 10mmol), $Rh_4(CO)_{12}$ (4a, 0.025mmol), and ethanol (50ml). The reaction was carried out at

180°C for 6hrs. 5-Ethyl-3,4-diphenyl-2(5H)-furanone (2a, 73%)$^{6)}$ was isolated by column chromatography on silica gel. It was confirmed by GLC that acetaldehyde diethylacetal and diethylketone constituted the major by-products. The former is a condensation product of ethanol with its dehydrogenation product, acetaldehyde, and the latter is a hydrocarbonylation product of ethylene.$^{7)}$ The formation of 2a and the by-products shows that ethanol acts as both the hydrogen donor and the solvent medium in this reaction. Ethanol could be replaced by other alcohols such as *n*-/*iso*-propanol and methanol, and acetone cotaining water. These results are summarized in Table 1.

Several rhodium carbonyl complexes and their precursors, e.g., $Rh_6(CO)_{16}$ (4b), $RhCl(CO)(PPh_3)_2$ (4c), $RhCl(PPh_3)_3$ (4d), $RhCl_3 \cdot 3H_2O$ (4e), $Rh_2O_3$ (4f), and 5% Rh/C (4g) could be used as the catalyst (Table 2). At 220°C the activities of these catalysts except 4d did not vary greatly from that of 4a. However, catalytic activities of 4f and 4c at 150°C were low as compared with those of rhodium carbonyl clusters 4a and 4b.

5-Ethyl-3,4-dimethyl-2(5H)-furanone (2b, 47%) was similarly obtained from 2-butyne (1b). From 1-phenylpropyne (1c) the regio-isomers 2c ($R^1$=$CH_3$, $R^2$=Ph, $R^3$=H) and 2d ($R^1$=Ph, $R^2$=$CH_3$, $R^3$=H) were formed in 48% and 4% yields, respectively, indicating this reaction to be regioselective.$^{8)}$ But the use of terminal acetylenes such as phenylacetylene and 1-hexyne gave no furanones.

Table 1. Formation of the furanone 2a in several proton donors$^{a)}$

| Solvent | 2a (%)$^{b)}$ |
|---|---|
| $CH_3OH$ | 30 |
| $C_2H_5OH$ | 60 |
| *n*-$C_3H_7OH$ | 53 |
| *iso*-$C_3H_7OH$ | 61 |
| $(CH_3)_2CO/H_2O$ (10/1) | 44 |
| (5/1) | 49 |

a) Operating conditions: 1a, 10mmol; $Rh_4(CO)_{12}$, 0.025mmol; solvent, 50ml; CO, 30Kg/cm$^2$; $C_2H_4$, 20Kg/cm$^2$; 220°C, 6hr.

b) The yields were based on 1a used and were determined by GLC.

Table 2. The activities of several rhodium catalysts in the carbonylation of 1a$^{a)}$

| Catalyst | Temp (°C) | The yield of 2a (%) |
|---|---|---|
| $Rh_4(CO)_{12}$ (4a) | 220 | 60 |
| | 150 | 67 |
| $Rh_6(CO)_{16}$ (4b) | 150 | 59 |
| $RhCl(CO)(PPh_3)_2$ | 220 | 48 |
| (4c) | 150 | 30 |
| $RhCl(PPh_3)_3$ (4d) | 220 | 27 |
| $RhCl_3 \cdot 3H_2O$ (4e) | 220 | 41 |
| $Rh_2O_3$ (4f) | 220 | 58 |
| | 150 | 22 |
| 5% Rh/C (4g) | 220 | 49 |

a) Operating conditions: 1a, 10mmol; catalyst, 0.1mg atom; EtOH, 50ml; CO, 30Kg/cm$^2$; $C_2H_4$, 20Kg/cm$^2$; 6hr.

Table 3. Influence of the reaction temperature in the carbonylation of 1a in the presence of ethylene and ethanol[a)]

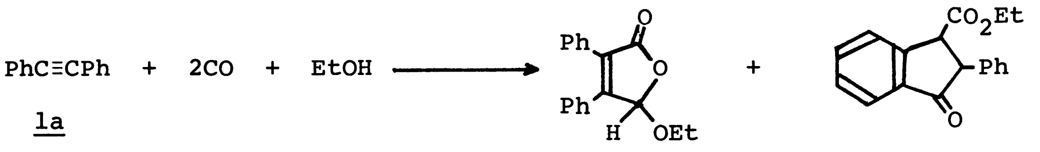
| Temp (°C) | 2a (%)[b)] | 5 (%)[b)] | 6 (%)[b)] | $CH_3CH(OCH_2CH_3)_2$ (mmol) | $(CH_3CH_2)_2CO$ (mmol) |
|---|---|---|---|---|---|
| 220 | 60 | - | - | 49.4 | 56.6 |
| 180 | 73 | - | - | 25.5 | 41.7 |
| 150 | 67 | - | 3 | 4.6 | 14.4 |
| 125 | 31 | 4 | 11 | 0.5 | 0.2 |
| 100 | 10 | 13 | 10 | - | - |

a) Operating conditions: 1a, 10mmol; $Rh_4(CO)_{12}$, 0.025mmol; CO, 30Kg/cm$^2$; $C_2H_4$, 20Kg/cm$^2$; EtOH, 50ml; 6hr.

b) The yields were based on 1a used and were determined by GLC.

Instead of ethylene, monosubstituted olefins such as propylene and methyl acrylate could be used, but the formation of the corresponding furanones resulted in low yields. From propylene and 1a a mixture of 2e ($R^1$=$R^2$=Ph, $R^3$=$CH_3$) and 3 ($R^1$=$R^2$=Ph, $R^3$=$CH_3$) (1:1) was obtained in 5% total yield. From methyl acrylate and 1a only 2f ($R^1$=$R^2$=Ph, $R^3$=$CO_2CH_3$) was obtained in 17% yield.

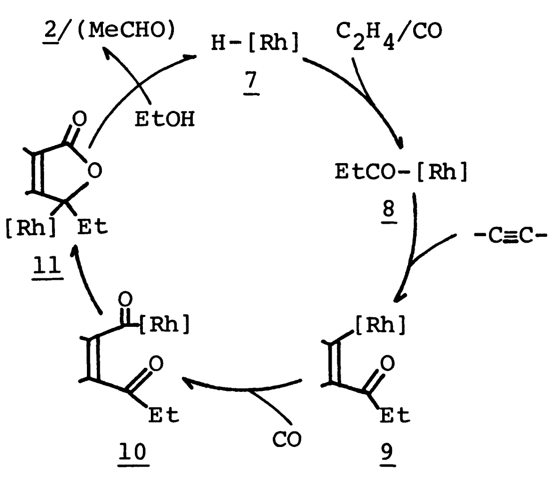
As shown in the equation 1, the formation of the furanone requires formally one hydrogen molecule, which can be derived from proton donors used as solvent. When ethanol was used as the solvent at higher temperature (180-220°C), the dehydrogenation occurred beyond the requirement for the formation of the furanone, and consequently considerable amounts of diethylketone and acetaldehyde diethylacetal were produced. In order to suppress the by-products, the influence of the reaction temperature was studied. The results are summarized in Table 3. This table shows that the temperature at about 150°C is suitable for keeping the sufficient yield of the furanone and for depressing the by-products. Then we found that at lower temperature (100-125°C) ethanol itself took part in the carbonylation, instead of ethylene, to afford 5-ethoxy-3,4-diphenyl-2(5H)-furanone (5) and 2-phenyl-3-(ethoxycarbonyl)-indanone (6) in low yields.[9)]



(2)

1a 5 6

A possible mechanism for the formation of the furanone is outlined in the Scheme. The acyl complex 8[10] seems to be an important intermediate, which would be given by stepwise insertion of ethylene and CO into the Rh-H bond (7) arising from the catalyst and the proton donor. The subsequent addition of 8 to the acetylene and CO would give 10 which would be converted to the $\sigma$-allyl lactonyl complex 11.[11] The furanone 2 would be derived by the reduction of 11.



Scheme

References and Notes

1) P.Pino and G.Braca, "Organic Syntheses via Metal Carbonyls", ed. by I.Wender and P.Pino, Wiley, New York (1977), vol.2, p419.

2) Y.S.Rao, Chem. Rev., 76, 625 (1976).

3) J.S.Sauer, R.D.Cramer, V.A.Engelhardt, T.A.Ford, H.E.Holmquist, and B.W.Houk, J. Am. Chem. Soc., 81. 3677 (1959).

4) G.Albanesi and M.Tovaglieri, Chem. Ind.(Milan), 41, 189 (1959).

5) J.Tsuji and T.Nogi, J. Am. Chem. Soc., 88, 1289 (1966).

6) 2a: Colorless crystals (m.p. 133-4°C); NMR (CDCl$_3$), $\delta$0.90(t,3H,CH$_3$), 1.56(m,1H,CHaHb), 1.89(m,1H,CHaHb), 5.41(dd,1H,CH), and 7.27(m,10H,2Ph); IR (KBr), 1732 ($\nu$C=O) and 1642cm$^{-1}$($\nu$C=C).

7) Y.Iwashita and M.Sakuraba, Tetrahedron Lett., 2409 (1971).

8) 2c: Colorless crystals (m.p. 84-5°C); NMR (CDCl$_3$), $\delta$0.97(t,3H,CH$_3$), 1.37(m,1H,CHaHb), 2.05(m,1H,CHaHb), 2.69(s,3H,CH$_3$), 4.82(dd,1H,CH), and 7.4(m,5H,Ph). 2d (not isolated): NMR (CDCl$_3$), $\delta$0.85(t,3H,CH$_3$), 1.0-2.0(m,2H,CH$_2$), 2.02(d,2Hz,3H,CH$_3$), 5.32(m,1H,CH), and 7.4(m,5H,Ph).

9) We now found that the formation of the furanone 5 was favored by the use of the rhodium catalyst in combination with basic alkali metal salts. The results will be reported in the following paper.

10) It has been reported that Rh$_4$(CO)$_{12}$ reacts with ethylene in aqueous acetone to give [Rh$_6$(CO)$_{15}$(COEt)]$^-$; P.Chini, S.Martinengo, and G.Carlaschelli, J. Chem. Soc., Chem. Commun., 709 (1972).

11) $\pi$-Allyl lactonyl complexes of Co[12] and Mo[13] have been isolated in the reactions of acyl complexes with acetylenes.

12) R.F.Heck, J. Am. Chem. Soc., 86, 2819 (1964).

13) M.Green, J.Z.Nyathi, C.Scott, F.G.A.Stone, A.J.Welch, and P.Woodward, J. Chem. Soc., Dalton, 1067 (1978).

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