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RHODIUM CARBONYL-CATALYZED CARBONYLATION OF ACETYLENES IN ALCOHOL. SYNTHESIS OF 5-ALKOXY-2(5H)-FURANONES

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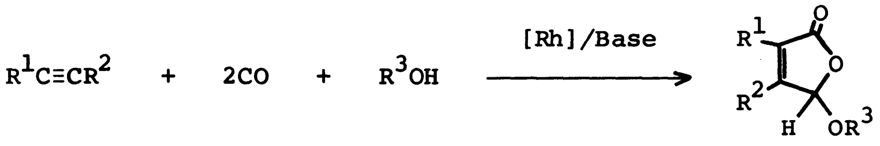
Reactions of internal acetylenes with CO in alcohols gave 5-alkoxy-3,4-disubstituted-2(5H)-furanones in good yields in the presence of rhodium catalysts containing basic alkali metal salts, e.g., $Rh_4(CO)_{12}$ or $RhCl_3 \cdot 3H_2O$ in combination with sodium carbonate or sodium acetate.

Catalytic ring closure reactions with CO present a convenient route for the one-step synthesis of heterocyclic and other cyclic compounds from acetylenes.[1)2)] In the preceding paper we have reported one-step synthesis of 5-alkyl-2(5H)-furanones from acetylenes, olefins, CO, and proton donors in the presence of some rhodium catalysts such as $Rh_4(CO)_{12}$ and $Rh_6(CO)_{16}$.[3)] For example, the reactions of diphenylacetylene (1a) with ethylene and CO in ethanol at 150-220°C gave 5-ethyl-3,4-diphenyl-2(5H)-furanone (2) in 60-73% yields. However, the reaction at lower temperature (100-125°C) gave 5-ethoxy-3,4-diphenyl-2(5H)-furanone (3b) and 2-phenyl-3-(ethoxycarbonyl)-indanone (4) in poor yields, together with 2. The formation of 3b and 4 shows that the ethanol itself used as a solvent takes part in the carbonylation of 1a. In connection to an acylrhodium intermediate in the formation of 2,[3)] we assumed that 3b and 4 were formed via an alkoxycarbonylrhodium intermediate. The addition of a base to the rhodium catalyst seemed to favor the formation of 3. Now we wish to report a new and facile synthetic method of 5-alkoxy-2(5H)-furanones in one step from acetylenes, CO, and alcohols.

When a mixture of 1a (10mmol), ethanol (50ml), $Rh_4(CO)_{12}$ (0.025mmol), and NaOAc (1.0mmol) was heated at 125°C for 6 hrs under the pressure of CO(50Kg/cm^2 at room temperature) in a 200ml stainless steel autoclave, 5-ethoxy-3,4-diphenyl-2(5H)-furanone (3b)4) was obtained in a 87% yield, together with the indanone 4 5) (5%) and diethyl 2,3-diphenylsuccinate (5b, 7%).



1

3

Various basic alkali metal salts such as carbonate, bicarbonate, and acetate could be used in place of NaOAc, but the use of strong bases such as NaOH and NaOEt resulted in low yields of 3b. In the absence of these bases the yield of 3b was very low (2%). These facts indicate that the presence of the basic salts is necessary for the sufficient formation of 3b. Alkali carbonate M_2CO_3 was more effective in the order of Li and Na > K, Rb, and Cs. Sodium acetate was more efficient than sodium carbonate and sodium bicarbonate. As the rhodium carbonyl precursor, $RhCl_3 \cdot 3H_2O$ could be used.

The carbonylation of 1a in various alcohols such as methanol, *n*-/*iso*-propanol and *n*-octanol gave the corresponding furanones 3 in good yields. These results are summarized in Table 1. As the size of alcohol became larger, the yield of 3 decreased.

The carbonylation of 2-butyne (1b) in ethanol using $RhCl_3 \cdot 3H_2O$-Na_2CO_3 catalyst gave 5-ethoxy-3,4-dimethyl-2(5H)-furanone (3f) in a 30% yield. From 1-phenylpropyne (1c) the regio-isomers 3g (R^1=Me, R^2=Ph, R^3=Et) and 3h (R^1=Ph, R^2=Me, R^3=Et) were formed in 69% and 17% yields, respectively, indicating this reaction to be regioselective. Similar regioselectivity has been observed in the carbonylation of 1c in the presence of ethylene and proton donor.3)

A possible mechanism for the formation of the furanone 3 is outlined in Scheme 1. An alkoxycarbonylrhodium complex 7 seems to be an important catalytic intermediate, which would be formed by nucleophilic attack of alkoxide ion on rhodium carbonyl 6.6) Stepwise insertion of the acetylene and CO into the

Table 1 Synthesis of 5-alkoxy-3,4-disubstituted-2(5H)-furanones (3)$^{a)}$

	Furanone R^1	 R^2	 R^3	Catalyst$^{b)}$	Yield (%)$^{c)}$
3a	Ph	Ph	Me	D	86$^{d)}$
3b	Ph	Ph	Et	A	68
				B	72
				C	75
				D	87
3c	Ph	Ph	*n*-Pr	A	57
3d	Ph	Ph	*i*-Pr	A	48
3e	Ph	Ph	*n*-C_8H_{17}	B	21
3f	Me	Me	Et	A	30
3g	Me	Ph	Et	A	69
3h	Ph	Me	Et	A	17

a) Each reaction of the acetylene 1a (10mmol) or other acetylenes 1b, 1c (20mmol) with alcohol (50ml) and CO (50Kg/cm^2 at room temperature) was carried out at 125°C for 6hrs.

b) A : $RhCl_3 \cdot 3H_2O$(0.1mmol)-Na_2CO_3(10mmol), B : $Rh_4(CO)_{12}$(0.025mmol) -Na_2CO_3(1.0mmol), C : $RhCl_3 \cdot 3H_2O$(0.1mmol)-NaOAc(10mmol), D : $Rh_4(CO)_{12}$ (0.025mmol)-NaOAc(1.0mmol).

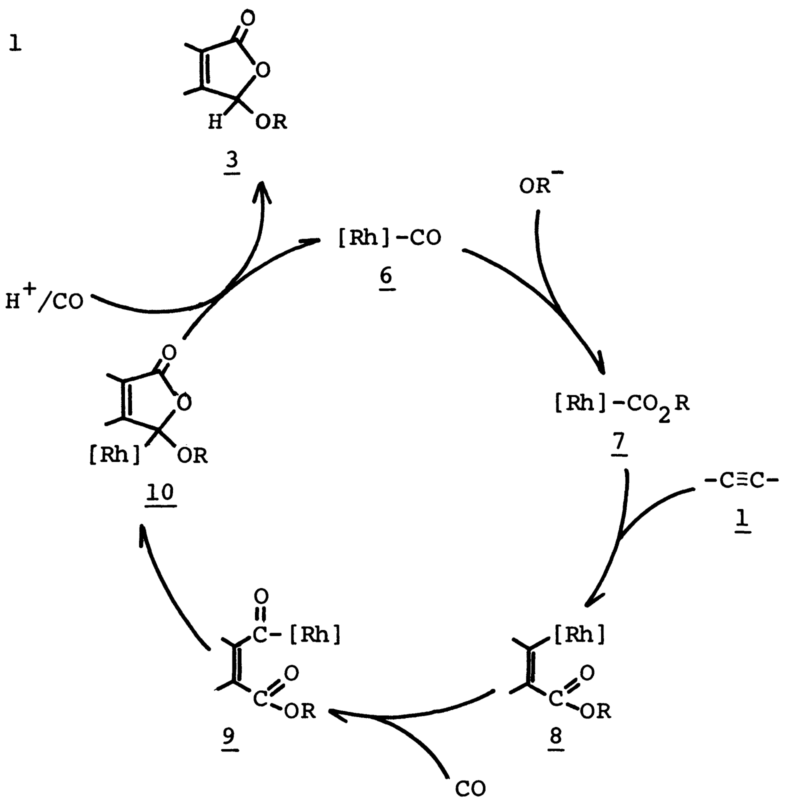
c) Based on the amount of the acetylene 1 used. Determined by GLC.

d) Reaction temperature ; 100°C.

alkoxycarbonyl-metal bond of 7 would give 9, which would be converted to the σ-allyl lactonyl complex 10. Protonation of 10 would give the furanone 3.

Further studies on the extension of this reaction and on the detailed mechanism are in progress.

Scheme 1



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) A.Mullen, "New Syntheses with Carbon Monoxide", ed. by J.Falbe, Springer-Verlag, Berlin (1980), p414.

3) P.Hong, T.Mise, and H.Yamazaki, Chem. Lett., <u>1981</u>,989.

4) <u>3b</u>: Colorless crystals (m.p. 137-8°C) ; ^{1}H-NMR($CDCl_3$), δ 1.28(t,3H,CH_3), 3.89 (m,2H,OCH_2), 6.20(s,1H,CH), and 7.36(m,10H,2Ph); ^{13}C-NMR($CDCl_3$), δ 170.5(CO_2), 153.3(s),130.3(s),129.3(d),129.1(d),128.6(d)(Ph and C=C),101.7(OCHO), 65.5 (OCH_2), and 15.0(CH_3); IR(nujol), 1758(νC=O) and 1654cm^{-1}(νC=C).

5) <u>4</u>: Colorless crystals (m.p. 62-3°C) ; ^{1}H-NMR($CDCl_3$), δ 1.36(t,3H,CH_3), 4.28(q, 2H,OCH_2), 4.38(d,1H,CH), 4.42(d,1H,CH), and 7.10-7.90(m,9H,C_6H_5 and C_6H_4); ^{13}C-NMR($CDCl_3$), δ 203.7(C=O), 171.3(CO_2), 149,9(s),138.2(s),135.6(d),135.3(d), 129.0(d),128.3(d),127.5(d),126.1(d),124.7(s)(C_6H_5 and C_6H_4), 61.8(OCH_2),56.6, 53.4(CHCH), and 14.3(CH_3); IR(nujol), 1728 and 1712cm^{-1}(νC=O).

6) The reaction of $Rh_4(CO)_{12}$ with alcohols in the presence of excess Na_2CO_3 was reported to give alkoxycarbonylrhodium cluster anion $[Rh_6(CO)_{15}(COOR)]^-$; P.Chini, S.Martinengo, and G.Giordano, Gazz. Chimi. Ital., <u>102</u>, 330 (1972).

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