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Cobalt-Catalyzed Cyclocarbonylation of Acetylenes under Water Gas Shift Conditions. Selective Synthesis of Indan-1-ones

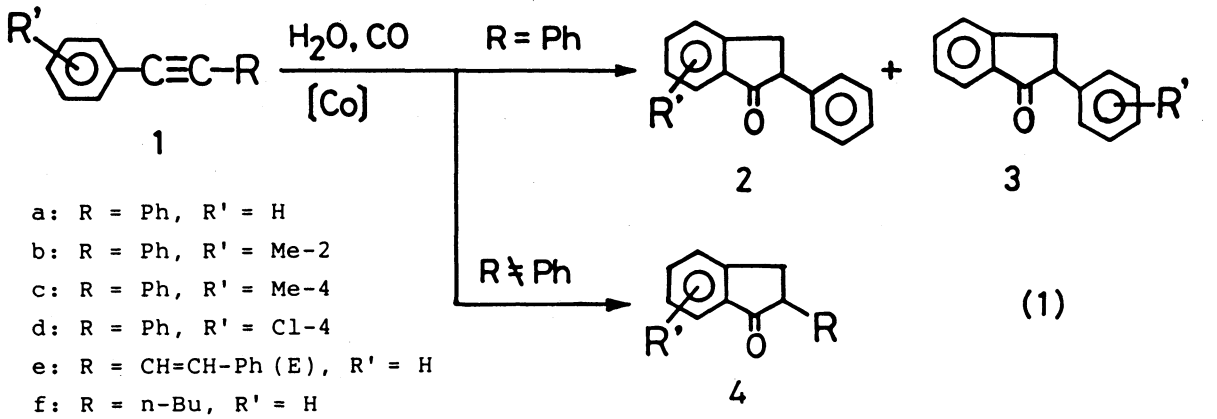
Kazuo DOYAMA, Keisuke FUJIWARA, Takashi JOH,
Kazuo MAESHIMA,† and Shigetoshi TAKAHASHI*
The Institute of Scientific and Industrial Research,
Osaka University, Suita, Osaka 567
†Central Research Laboratory, Sekisui Chemical Co., Ltd.,
Mishima-gun, Osaka 618

Carbonylation of phenylacetylene derivatives by a cobalt catalyst under water gas shift conditions affords indan-1-ones in satisfactory yields.

The C-H bond activation of aromatic compounds by transition metals is one of the current interests in organometallic chemistry and has been successfully applied to unique carbonylation reactions in organic syntheses.1) Recently the stoichiometric reaction of diphenylacetylene with $(\eta^5\text{-}C_5H_5)Fe(CO)_2Ar$ has been reported to give the cyclocarbonylated products, indenones, in good yields.2)

We have previously reported a new method for synthesis of furan-2(5H)-ones by carbonylation of acetylenes under water gas shift conditions.3) This reaction was effectively catalyzed by rhodium carbonyl clusters such as $Rh_4(CO)_{12}$ and $Rh_6(CO)_{16}$, but $Co_2(CO)_8$ was almost inactive for the formation of furan-2(5H)-ones. Now we have found that in the presence of phosphines at temperatures above 200 °C cobalt carbonyl catalyzes the cyclocarbonylation of phenylacetylene derivatives (**1**) to afford indanones **2** and **3**, or **4** in satisfactory yields. This may be the first successful example of the catalytic synthesis of indanones from acetylenes by the carbonylation reaction.

In a typical procedure, diphenylacetylene (**1a**) (5.0 mmol) was reacted with water (56 mmol) and carbon monoxide (100 atm) in the presence of catalytic amounts of $Co_2(CO)_8$ (0.125 mmol) and triphenylphosphine (0.5 mmol) in tetrahydrofuran (40 ml) at 220 °C for 4 hours. The products were isolated by column chromatography on silica and purified by recrystallization. 2-Phenyl-indan-1-one (2a) was obtained as colorless needles in 74% yield together with two by-products, tetraphenylcyclopentenone (9%) and bibenzyl (3%).



a: R = Ph, R' = H
b: R = Ph, R' = Me-2
c: R = Ph, R' = Me-4
d: R = Ph, R' = Cl-4
e: R = CH=CH-Ph (E), R' = H
f: R = n-Bu, R' = H

(1)

Representative results under various conditions using diphenylacetylene (1a) as a reactant were summerized in Table 1. The Table shows that addition of phosphines such as triphenylphosphine and tri-n-butylphosphine resulted in considerable increasing the yield of indanone (2a). Especially, use of tri-n-butylphosphine gave good results. The formation of indanones was largely affected by the solvents employed, that is, tetrahydrofuran and acetonitrile gave good results. It should be noted that the selectivity of indanones also depends upon the concentration of the reactants. At a low concentration of the reactants, the side reactions were depressed, and 2a was obtained almost selectively (run 8). For the catalysts, cobalt-phosphine complexes such as $[Co(CO)_3(PPh_3)]_2$ and $[Co(CO)_3(PBu_3)]_2$ are of choice as well as the two-component system, $Co_2(CO)_8/PR_3$.

Unsymmetrically substituted acetylenes (1b-f) also afforded corresponding indanones as shown in Table 2. Diphenylacetylene derivatives (1b,c,d), bearing a substituent R' on the o- or p-position of one of the phenyl groups, gave two structural isomers 2 and 3. It seems that the ratio is mainly affected by the electronic nature of the substituents rather than the steric one, because o-substituted diphenylacetylene derivative (1b) which has steric hindrance around the acetylenic bond gave almost the same isomer ratio (about 1:1) as p-substituted one (1c). A conjugated enyne like 1,4-diphenylbut-1-en-3-yne (1e)

Table 1. Synthesis of 2-phenylindan-1-one (**2a**) from diphenylacetylene (**1a**)[a]

Run	Catalyst[b]	Solvent (ml)	Conversion %	Yield[c] %
1	$Co_2(CO)_8$	THF, 40	66	56
2	$Co_2(CO)_8/PPh_3$	THF, 40	100	73
3	$Co_2(CO)_8/PPhMe_2$	THF, 40	100	85
4	$Co_2(CO)_8/PBu_3$	THF, 40	100	88
5	$Co_2(CO)_8/PPh_3$	MeCN, 40	100	79
6	$Co_2(CO)_8/PPh_3$	DMF, 40	50	33
7	$Co_2(CO)_8/PPh_3$	THF, 10	96	54
8[d]	$Co_2(CO)_8/PPh_3$	THF, 120	100	89
9	$[Co(CO)_3(PPh_3)]_2$	THF, 40	100	68
10	$[Co(CO)_3(PBu_3)]_2$	THF, 40	100	89

[a] Reaction conditions: diphenylacetylene, 5.0 mmol; catalyst, 0.125 mmol; H_2O, 56 mmol; CO, 100 atm; 220 °C; 4 h.

[b] Phosphine, 0.5 mmol (runs 2-8).

[c] Based on **1a** consumed (determined by GLC).

[d] Diphenylacetylene, 2.5 mmol; H_2O, 167 mmol.

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

Acetylenes	Products	Yield / %[b]	Isomer ratio **2**/**3**
1a: R = Ph, R' = H	**2a**	77	——
1b: R = Ph, R' = Me-2	**2b** + **3b**	65	50/50[c]
1c: R = Ph, R' = Me-4	**2c** + **3c**	74	52/48[c]
1d: R = Ph, R' = Cl-4	**2d** + **3d**	63	41/59
1e: R = CH=CH-Ph(E), R' = H	**4e**	41	——
1f: R = n-Bu, R' = H	**4f**	18	——

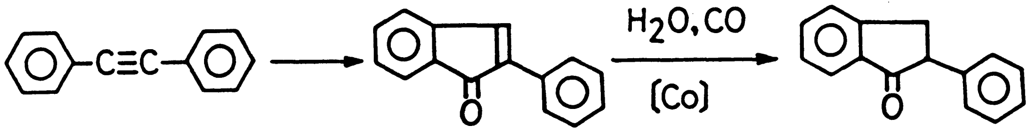
[a] Reaction conditions: acetylene, 5.0 mmol; $[Co(CO)_3(PBu_3)]_2$, 0.125 mmol; H_2O, 56 mmol; CO, 100 atm; 220 °C; 4 h.

[b] Isolated yield.

[c] Determined by ^1H-NMR spectroscopy.

gave indanone (**4e**) in a moderate yield. Present reaction may be applicable to alkyl substituted acetylenes such as 1-phenylhexyne (**1f**) and 1-phenylpropyne, though the yields are not so high. The hydrogenated products were major in these cases.

Indanones **2**, **3**, and **4** thus obtained are derived formally from the cyclocarbonylation of **1** with each one molecule of carbon monoxide and hydrogen via aromatic C-H bond activation. Using D_2O instead of H_2O, diphenylacetylene gave the deuterated indanone, which indicates the hydrogen comes from water. Use of molecular hydrogen as the hydrogen source gave only bibenzyl in 85% yield. Therefore water gas shift conditions may be indispensable for the formation of indanones from acetylenes. For the reaction path, it is supposed that indenone derivatives are formed at the first step through the cyclocarbonylation of **1**, followed by hydrogenation to afford indanones. In fact, a separate experiment showed that 2-phenylinden-1-one (**5a**) was hydrogenated under the same conditions to give 2-phenylindan-1-one (**2a**) in 88% yield.4)



1a **5a** **2a** (2)

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References

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