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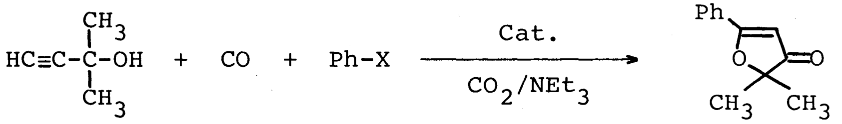
Synthesis of a 3(2*H*)-Furanone Derivative from Propargylic Alcohol, CO, and Phenyl Halide Catalyzed by Transition Metal Complexes

Yoshio INOUE,* Masaaki TANIGUCHI,+ Harukichi HASHIMOTO,+
Kunihiro OHUCHI, and Shin IMAIZUMI
Department of Engineering Science, Faculty of Engineering,
Tohoku University, Aoba, Sendai 980
+Department of Applied Chemistry, Faculty of Engineering,
Tohoku University, Aoba, Sendai 980

2-Methyl-3-butyn-2-ol reacted with CO and phenyl halides in the presence of a catalytic amount of transition metal complexes to afford 2,2-dimethyl-5-phenyl-3(2*H*)-furanone (bullatenone) under the influence of CO_2.

The carbonylation of acetylenic compounds catalyzed by transition metal complexes is usually performed in alcoholic media to afford various types of unsaturated esters depending on the catalysts and conditions employed.1) Carbonylation of propargyl alcohol in methanol-hydrochloric acid over Pd/C gives a mixture of itaconate and aconitate.2) Itaconic anhydrides were formed by the carbonylation of substituted propargyl alcohols in benzene.2,3) Synthesis of unsymmetrical ketones *via* carbonylation of terminal acetylenes in the presence of organic halides has also been reported.4,5)

Now we report the synthesis of a 3(2*H*)-furanone derivative from 2-methyl-3-butyn-2-ol, CO, and phenyl halides in the presence of a catalytic amount of transition metal complexes under the influence of CO_2. The 3(2*H*)-furanone ring is contained in many naturally occurring compounds characterized by important biological activity as antitumor agents (jatrophone, geiparvarin, *etc.*) or aroma constituents.6) The product, 2,2-dimethyl-5-phenyl-3(2*H*)-furanone (1), is called bullatenone, which occurs in the essential oil of *Myrtus bullata*, a shrub endemic to New Zealand.7)



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Typically, 2-methyl-3-butyn-2-ol (10 mmol), iodobenzene (10 mmol), and $Pd(PPh_3)_3$8) (0.2 mmol) were agitated in triethylamine at 100 °C for 8 h under the pressure of CO and CO_2 in an autoclave. This procedure gave 1 in 79% GLC yield. Kugelrohr distillation of the mixture gave 1 in 76% yield.9) Various Group VIII metal-triphenylphosphine complexes were active as catalyst as shown in Table 1. The reaction took place in the absence of CO_2, however the yields dropped considerably. Bromobenzene can be employed instead of iodobenzene at the sacrifice of the yield, *e.g.*, 48% to 35% with $PdCl_2(PPh_3)_2$ as catalyst. In the present

Table 1. Effects of catalyst on the synthesis of $\underline{1}^{a)}$

Catalyst	Solvent	Base	Yield of $\underline{1}^{b)}$/%
$FeCl_2(PPh_3)_2$	NEt_3	-	62 (21)
$CoCl_2(PPh_3)_2$	NEt_3	-	61 (29)
$NiCl_2(PPh_3)_2$	NEt_3	-	57 (36)
$RuCl_2(PPh_3)_3$	NEt_3	-	52 (19)
$RhCl(PPh_3)_3$	NEt_3	-	18 (3)
$PdCl_2(PPh_3)_2$	NEt_3	-	48 (38)
$PdCl_2(PPh_3)_2$	DMF	Na_2CO_3	18
$PdCl_2(PPh_3)_2$	CH_3CN	K_2CO_3	20
$Pd(PPh_3)_3$	NEt_3	-	79 (26)
$Pd(PPh_3)_4$	NEt_3	-	45 (40)
$PtCl_2(PPh_3)_2$	NEt_3	-	45 (23)
$Pt(PPh_3)_4$	NEt_3	-	64 (35)

a) 2-Methyl-3-butyn-2-ol 10 mmol, iodobenzene 10 mmol, CO 10 atm (initial), CO_2 10 atm (initial), catalyst 0.2 mmol, solvent 10 cm^3, base 15 mmol, 100 °C, 8 h.

b) GLC yield. The figures in the parentheses represent the yields of the reactions performed without CO_2.

reaction, triethylamine functions as base as well as solvent. Alkali metal carbonate can be employed as base using *N*,*N*-dimethylformamide (DMF) or acetonitrile as solvent. Propargyl alcohol and 3-butyn-2-ol did not give the corresponding furanone under similar conditions. Further investigation including the understanding of the role of CO_2 is in progress.

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