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Carbonylation of Tertiary Propargylic Alcohols Catalyzed by a Cationic Palladium(II) Complex: Synthesis of 2(5H)-Furanones

Koichi Matsushita, Tsunenori Komori, Shuichi Oi and Yoshio Inoue*

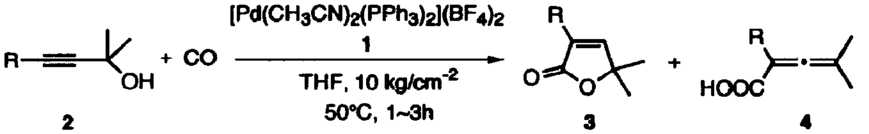
Department of Engineering Science, Faculty of Engineering, Tohoku University,
Aramaki Aoba, Aoba-ku, Sendai 980-77 (Japan)

Abstract; Tertiary propargylic alcohols reacted with carbon monoxide in the presence of catalytic quantities of a cationic palladium(II) complex, $[Pd(CH_3CN)_2(PPh_3)_2](BF_4)_2$, to afford 2(5H)-furanones and/or 2,3-dienoic acids, the precursor of the furanones, in good yields under mild conditions.

The reaction of carbon monoxide with propargyl derivatives catalyzed by palladium compounds has been the subject of many investigations. Halides[1] and carbonates[2] are carbonylated in the presence of nucleophiles such as alcohols,[1,2] amines,[3] active methylene compounds,[4] and water (phase transfer conditions)[5] normally giving rise to allenic esters, amides, ketones, and acids, respectively.

Carbonylation of propargylic alcohols catalyzed by palladium compounds in the absence of a nucleophile has been less studied. For examples, 2-methyl-3-butyn-2-ol and 2,5-dimethyl-3-hexyne-2,5-diol were converted to itaconic and diisopropylidenesuccinic anhydride, respectively, using $PdCl_2$ as the catalyst.[6] A recent example includes the carbonylation of propargylic alcohols to 2(5H)-furanones by a palladium(0)-dppb (dppb = 1,4-bis(diphenylphosphino)butane) catalytic system at higher temperature with prolonged time.[7] The synthesis of 2,4-dienoic acids and esters from propargylic alcohols catalyzed by a cationic palladium(II) aquo hydride complex has also been reported.[8] We previously demonstrated that substituted propargyl alcohols react with carbon monoxide and iodobenzene in the presence of a palladium(0) complex and carbon dioxide to afford 3(2H)-furanones.[9]

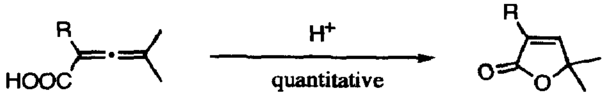
Here we report a different catalytic system involving a cationic palladium(II) complex, $[Pd(CH_3CN)_2(PPh_3)_2](BF_4)_2$ (**1**),[10] for the carbonylation of tretiary propargylic alcohols **2** affording 2(5H)-furanones **3** and/or 2,3-dienoic acids **4** effectively under mild conditions.



		Yield (%)	Product distribution	
R = Ph	(**2a**)	84	100 (**3a**)	0 (**4a**)
R = *n*-Bu	(**2b**)	92	17 (**3b**)	83 (**4b**)
R = *t*-Bu	(**2c**)	99	9 (**3c**)	91 (**4c**)
R = H	(**2d**)	12	17 (**3d**)	83 (**4d**)

Typically a tertiary propargylic alcohol (**2**; 5 mmol) was carbonylated in a stainless steel autoclave at 50°C for 1 to 3 h in THF (4 ml) in the presence of catalytic quantities (2 mol%) of the cationic palladium(II) complex **1** under pressured carbon monoxide (10 kg/cm^{-2}). After the reaction, the mixture was passed through a silica gel short column eluting with ether to remove the catalyst. Then the products were isolated by column chromatography. Chemical yields were determined by ^{1}H NMR or GLC with an internal standard method. Neutral palladium(II) complexes such as $PdCl_2(CH_3CN)_2$ and $PdCl_2(PPh_3)_2$ and a palladium(0) complex, $Pd(PPh_3)_4$, were totally inactive for this carbonylation reaction.

On carbonylation of 2-methyl-4-phenyl-3-butyn-2-ol (**2a**: R = Ph), 5,5-dimethyl-3-phenyl-2(5H)-furanone (**3a**) was obtained as the sole product in an isolated yield of 84% after 3h reaction at 50°C. 4-Alkyl-2-methyl-3-butyn-2-ols (**2**: R = alkyl) behaved in a somewhat different manner. Carbonylation of 2-methyl-3-octyn-2-ol (**2b**: R = *n*-Bu) afforded 3-*n*-butyl-5,5-dimethyl-2(5H)-furanone(**3b**) and 2-*n*-butyl-4-methyl-2,3-pentadienoic acid (**4b**) in a total yield of 92% after 1 h reaction with the acid **4b** being major. 2,5,5-Trimethyl-3-hexyn-2-ol (**2c**: R = *t*-Bu) reacted similarly. The 2,3-dienoic acids **4b** and **4c** gradually isomerized into the furanones **3b** and **3c**, respectively, on standing. Control experiments demonstrated that a rapid conversion of **4** to **3** took place quantitatively on the addition of a trace amount of acid such as *p*-toluenesulfonic acid. On the other hand carbonylation of 2-methyl-3-butyn-2-ol (**2d**: R = H), resulted a complex mixture involving small amount of the furanone **3d** and the 2,3-dienoic acid **4d**. A secondary propargylic alcohol, 3-octyn-2-ol, afforded a corresponding 2(5H)-furanone and a 2,3-dienoic acid in a modest total yield of 36%. The carbonylation took place scarcely with a primary propargylic alcohol, 2-heptyn-1-ol.



4 **3**

The course of the present Pd^{2+}-catalyzed conversion of substituted propargylic alcohols to 2(5H)-furanones via 2,3-dienoic acids is different from that of the Pd(0)-catalyzed conversion[7] of propargylic alcohols to 2(5H)-furanones. The cleavage of carbon-oxygen bond in the propargylic alcohols is not involved in the course of the reaction in the latter case. The high ability of the cationic palladium(II) complex **1** to promote heterolytic cleavage of the carbon-oxygen bond in a tertiary alcohol unit[11] is probably the driving force of this carbonylation reaction.

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