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Synthesis of Dienoic Acids and Esters by Cationic Palladium Complex Catalyzed Carbonylation of Alkynols and Alkynediols

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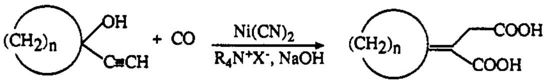
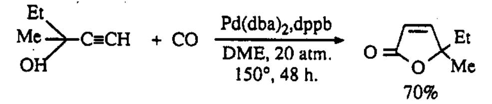
Summary: The cationic palladium(II) aquo hydride, *trans*-$(Cy_3P)_2Pd(H)(H_2O)^+BF_4^-$, is an excellent catalyst for the carbonylation of alkynols to dienoic acids and esters and of alkynediols to cross-conjugated diesters.

Propargylic alcohols, in which the hydroxyl and alkyne units are attached to the same carbon atom, have been used as reactants in a number of metal-catalyzed reactions. One example is the isomerization of alkynemonools to enones catalyzed by bis(dibenzylideneacetone)palladium(0) in the presence of triisopropylphosphine and ethylene glycol.[1] Of particular note are carbonylation reactions of alkynols. For instance, phase transfer catalyzed reaction of an alkynol with carbon monoxide, in the presence of nickel cyanide, affords unsaturated diacids in high yields (eq 1).[2] Several studies have been reported using palladium chloride as the catalyst, under quite drastic conditions, to give mixtures of products including anhydrides.[3-5] Unsaturated lactones are formed when alkynols are carbonylated with the palladium(0) catalyst, bis(dibenzylideneacetone)palladium, and 1,4-bis(diphenylphosphino)butane (dppb) in 1,2-dimethoxyethane [DME] (eq 2).[6]



(eq. 1)

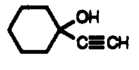
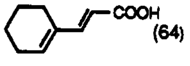
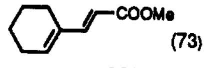
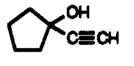
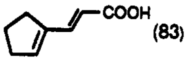
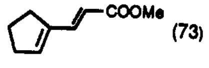
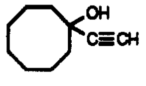
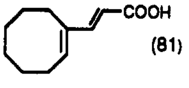
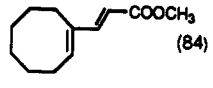


(eq. 2)

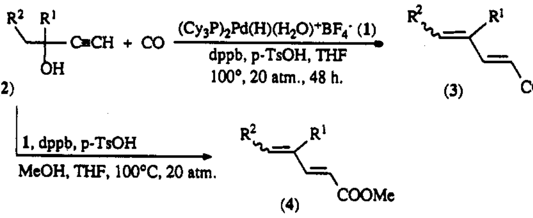
We recently have begun an investigation of the utility of metal complexes containing bulky ligands as catalysts for a variety of transformations.[7,8] We now wish to report that the cationic palladium(II) aquo hydride, *trans*-$[(Cy_3P)_2Pd(H)(H_2O)]BF_4$ (**1**), is an excellent catalyst for the synthesis of dienoic acids and esters in good yields from 2-alkyn-1-ols.

The palladium(II) aquo hydride complex **1** is readily obtained from bis(tricyclohexylphosphine)palladium and tetrafluoroboric acid.[9,10] When 3-ethyl-4-pentyn-3-ol (**2**, R^1 = Et, R^2 = Me) was treated with carbon monoxide (20 atm) in tetrahydrofuran (THF) and a catalytic system consisting of **1** (83/1 ratio of alkynol/**1**), dppb, and *p*-toluenesulfonic acid (p-TsOH) for 48 h at 100 °C, pure 4-ethyl-2,4-hexadienoic acid (**3**, R^1 = Et, R^2 = Me) was isolated in 92% yield (eq 3). The ratio of (*E,E*)/(*Z,E*) isomers for **3** (R^1 = Et, R^2 = Me) was 59/41. Note that reaction does not occur in the absence of *p*-TsOH. The carbonylation of alkynols proceeds in 59–92% yield for both acyclic and cyclic tertiary alkynols, using an 83/1 ratio of **2**/**1**, and the results are listed in Table I. It is also possible to effect the carbonylation reaction in the presence of methanol in order to produce the corresponding methyl ester **4** in comparable yields to those of the acid. While alkyne monoalcohols afford conjugated dienoic acids and esters, alkynediols **5** give cross-conjugated diesters **6** (eq 4).

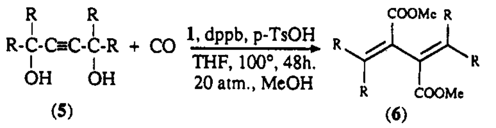
Table I. Conversion of Alkynols and Alkynediols to Dienoic Acids and Esters Catalyzed by 1[a]

substrate	product[a] acid (%)	ester (%)
2, R^1 = Et, R^2 = Me	**3** (92)[b]	**4** (86)[c]
2, R^1 = Me, R^2 = H	**3** (59)	**4** (56)
2, R^1 = Et, R^2 = H	**3** (78)[d]	**4** (86)[e]
	 (64)	 (73)
	 (83)	 (73)
	 (81)	 (84)
5, R = H		**6**(55)
5, R = Me		**6**(55)

[a] Products were identified by comparison of physical data (e.g., spectral data (IR, NMR (^{1}H, ^{13}C), MS)) with literature results. [b] 59:41 (*E,E*)/(*Z,E*). [c] 62:38 (*E,E*)/(*Z,E*). [d] 63:37 (*E,E*)/(*Z,E*). [e] 63.37 (*E,E*)/(*Z,E*).



(eq. 3)



(eq. 4)

Dienoic esters have been synthesized by a variety of methods, including the addition of vinyl cuprates to alkynes,[11] and Wittig-type reactions of α,β-unsaturated aldehydes.[12,13] Such compounds have also been prepared

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by palladium-catalyzed coupling of vinylic halides with unsaturated esters[14] and by allylic alkylation of dimeric π-allyl palladium chloride complexes.[15] Finally, while palladium-catalyzed carbonylation of propargylic carbonates usually affords allenic esters, a dienoic ester was obtained using the methyl propargylic carbonate derived from 1-ethynylcyclohexanol as reactant.[16] No allenic acids or esters were detected in any of the alkynol carbonylation reactions investigated here.

The carbonylation of alkyne diols is an effective method for the synthesis of cross-conjugated dienoic esters. This method is attractive when compared with known reactions, including the ring opening of 2,5-dihydrothiophene derivatives[17] or cyclobutanes[18] and the oxidation of tetramethylbutatriene(hexacarbonyl)diiron.[19]

The following general procedure was used: a mixture of alkynol (1.0 mmol), 1 (10.0 mg, 0.012 mmol), dppb (5.2 mg, 0.0121 mmol), and *p*-TsOH (4.6 mg, 0.0242 mmol) in THF (5.0 mL) was heated in an autoclave, with stirring, for 2 days at 100 °C and 20 atm of carbon monoxide. The reaction mixture was cooled to room temperature and filtered through Celite, and ether (15 mL) was added to the filtrate. The solution was treated with 3 × 10 mL of 0.5 N NaOH, and the aqueous phase was acidified with 1 N HCl. The aqueous phase was extracted with ether (3 × 10 mL), and the combined ether extract was dried and concentrated by rotary evaporation to give the acid.

Esters were prepared by using the same procedure as that for the acid except for the addition of 0.2 mL of methanol to the mixture at the beginning of the reaction.

In conclusion, complex 1, together with dppb and *p*-TsOH, is an excellent catalytic system for the carbonylation of alkynols to dienoic acids or esters and of alkynediols to cross-conjugated diesters.

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