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FACILE SYNTHESIS OF ACETYLENECARBOXYLATES BY THE OXIDATIVE CARBONYLATION OF TERMINAL ACETYLENES CATALYZED BY $PdCl_2$ UNDER MILD CONDITIONS

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Summary: Terminal acetylenes were converted to acetylenecarboxylates in high yields under atmospheric pressure of carbon monoxide at room temperature using a catalytic amount of $PdCl_2$ and a stoichiometric amount of $CuCl_2$.

Considerable studies have been carried out on the palladium-catalyzed carbonylation of acetylenic compounds to give α,β-unsaturated mono- and diesters, and saturated di- and triesters.$^{1)}$ But none of these carbonylation reactions proceeds without reducing the triple bonds.$^{2)}$ We now wish to report a new type of carbonylation of terminal acetylenes to give acetylenecarboxylates under mild conditions as shown below.

$$\mathrm{R{-}C{\equiv}C{-}H \;+\; CO \;+\; R'OH \xrightarrow[CuCl_2]{PdCl_2} R{-}C{\equiv}C{-}CO_2R'}$$

The reaction proceeds under 1 atm of carbon monoxide at room temperature in alcohol using a catalytic amount of $PdCl_2$ and a stoichiometric amount of $CuCl_2$ in the presence of sodium acetate to afford acetylenecarboxylates in high yields.

In a typical example, $PdCl_2$ (10 mg, 0.056 mmol), $CuCl_2$ (268.8 mg, 2 mmol), and NaOAc (164.1 mg, 2 mmol) were mixed in methanol (10 ml) in a two-necked flask, and phenylacetylene (102.1 mg, 1 mmol) was added. A rubber balloon filled with carbon monoxide was attached to the flask, and the mixture was magnetically stirred. The green solution turned to black after 2 h, at which time the reaction was stopped. After the usual work-up, methyl phenylacetylenecarboxylate (118.2 mg, 74% yield) was isolated by column chromatography. Results of the reactions of different acetylenic compounds and alcohols are shown in the table.

Mechanistically this reaction is an oxidative carbonylation with $PdCl_2$, which is reduced to Pd(0), and the addition of reoxidant of Pd(0) is neccessary in order to make the reaction catalytic. For this purpose, $CuCl_2$ is the best one. Benzoquinone can be used, but the reaction was rather slow.

$$\begin{aligned}
&\mathrm{R{-}C{\equiv}C{-}H + CO + R'OH + PdCl_2 \longrightarrow R{-}C{\equiv}C{-}CO_2R' + Pd + 2HCl}\\
&\mathrm{Pd + 2CuCl_2 \longrightarrow PdCl_2 + 2CuCl}\\
&\mathrm{HCl + AcONa \longrightarrow NaCl + AcOH}
\end{aligned}$$

In this reaction the presence of bases such as sodium acetate is essential as an acid trapper. In the absence of the bases, the reaction was not clean and a mixture of unsaturated diesters was formed, and no acetylenecarboxylate was obtained. A side reaction is the oxidative coupling of terminal acetylenes to diacetylenes which proceeds easily by the catalysis of $Cu(OAc)_2$ or CuCl in the presence of tertiary amines.[3] Actually the coupling reaction took place in a considerable extent when triethylamine was used instead of sodium acetate.

Usually acetylenecarboxylates are produced by the oxidation of corresponding alcohols, or from olefinic acids. In comparison, the direct carbonylation reported here offers the better synthetic method, because of its easy procedure and high yields.

Table Carbonylation of Terminal Acetylenes

Acetylenes	Alcohols	Catalysts[a)]	Base	Time (h)	Products (% Yield)
Ph-C≡CH	MeOH	A	NaOAc	2	$Ph-C\equiv C-CO_2Me$ (74)
Ph-C≡CH	MeOH	B	none	10	$Ph-C\equiv C-CO_2Me$ (70)
Ph-C≡CH	MeOH	C	NaOAc	5	$Ph-C\equiv C-CO_2Me$ (70)
Ph-C≡CH	MeOH	A	KOAc	2	$Ph-C\equiv C-CO_2Me$ (58)
Ph-C≡CH	$^{i}PrOH$	A	NaOAc	2	$Ph-C\equiv C-CO_2{}^{i}Pr$ (67)
$C_5H_{11}-C\equiv CH$	MeOH	A	NaOAc	2	$C_5H_{11}-C\equiv C-CO_2Me$ (74)
$C_5H_{11}-C\equiv CH$	$^{i}PrOH$	A	NaOAc	2	$C_5H_{11}-C\equiv C-CO_2{}^{i}Pr$ (59)
$PhOCH_2-C\equiv CH$	MeOH	A	NaOAc	2	$PhOCH_2-C\equiv C-CO_2Me$ (60)

a) A. acetylene (1 mmol), $PdCl_2$ (0.056 mmol), $CuCl_2$ (2 mmol), and base (2 mmol)
B. acetylene (1 mmol), $Pd(OAc)_2$ (0.056 mmol), and *p*-benzoquinone (1 mmol)
C. acetylene (1 mmol), $PdCl_2$ (0.011 mmol), $CuCl_2$ (2 mmol), and base (2 mmol)

References and Notes

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