Mild Palladium-catalysed Carbonylation of Alkynylphenyliodonium Toluene-*p*-sulphonates under Carbon Monoxide at Atmospheric Pressure

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Alkoxycarbonylation of alkynylphenyliodonium toluene-*p*-sulphonates catalysed by a palladium catalyst proceeded under carbon monoxide at atmospheric pressure at room temperature to give alkyne carboxylates in high yields.

Carbonylation reactions using transition metals are of considerable importance in synthetic organic chemistry.[1] Carbonylation of alkynes has been studied[2] but frequently the triple bond was reduced to give alkenyl-carboxylic acid derivatives.[3] Carbonylation reactions of 1-halogenoalkynes are little known.[4] Recent success in the carbonylation of 1-halogenoalkynes[4] without reduction of the triple bond involved platinum-catalysed CO insertion, but the carbonylation of alkynyl iodides (*e.g.*, 1-iodooct-1-yne) catalysed by a $PtCl_2(PPh_3)_2$–Et_3N system required 20—30 kg cm^{-1} of CO at 60 °C.

Recent developments in hypervalent iodine chemistry have shown that organoiodine(III) compounds are useful for organic synthesis.[5] Our current success in the use of alkynyl-

Table 1. Alkoxycarbonylation of alkynylphenyliodonium tosylates (**1**)

Iodonium tosylate (**1**), $\mathrm{R^1}$	Alcohol	Base	Product	% Yield[d]
Ph	EtOH	$\mathrm{Et_3N}$	$\mathrm{PhC{\equiv}CCO_2Et}$	80
	EtOH[b]	$\mathrm{Et_3N}$		60
	EtOH	$\mathrm{Bu_3N}$		80
	MeOH	$\mathrm{Et_3N}$	$\mathrm{PhC{\equiv}CCO_2Me}$	66
	MeOH	$\mathrm{Bu_3N}$		70
An[c]	EtOH	$\mathrm{Et_3N}$	$\mathrm{AnC{\equiv}CCO_2Et}$	64
	EtOH	$\mathrm{Bu_3N}$		69
	MeOH	$\mathrm{Et_3N}$	$\mathrm{AnC{\equiv}CCO_2Me}$	70
$\mathrm{Bu^n}$	EtOH	$\mathrm{Et_3N}$	$\mathrm{Bu^nC{\equiv}CCO_2Et}$	59
	MeOH	$\mathrm{Et_3N}$	$\mathrm{Bu^nC{\equiv}CCO_2Me}$	64

[a] A solution of the alkynyliodonium tosylate (**1**) (0.5 mmol) in EtOH or MeOH (10—15 ml) was added dropwise to a stirred mixture of $\mathrm{Pd(OAc)_2}$ (0.1 mmol), the base ($\mathrm{Et_3N}$, 5.0 mmol; $\mathrm{Bu_3N}$, 2.5 mmol), and the alcohol (10 ml) under CO (1 atm) at room temperature for 1 h and stirred for 1 h. [b] Reaction was carried out at 0 °C for 1 h. [c] An = p-$\mathrm{MeOC_6H_4}$. [d] Self-coupling products ($\mathrm{R^1\,C{\equiv}CC{\equiv}CR^1}$; $\mathrm{R^1}$ = Ph, An, or $\mathrm{Bu^n}$) were detected in 1—9% yields.

phenyliodonium toluene-p-sulphonates (tosylates) in the stereoselective formation of 1,3-enynes[6] led us to explore their use in alkoxycarbonylation reactions. Here we report a new mild effective alkoxycarbonylation of alkynylphenyliodonium tosylates using a palladium catalyst without reduction of the triple bond.

Alkynylphenyliodonium tosylates (**1**) were easily prepared by treatment of 1-alkynes with PhI(OH)OTs[7] (Ts = p-$\mathrm{MeC_6H_4SO_2}$) or by reaction of 1-trimethylsilyl-1-alkynes with iodosylbenzene activated with boron trifluoride–diethyl ether, followed by treatment with sodium tosylate.[8] Alkynylphenyliodonium tosylates (**1**) were carboxylated in ethanol or methanol in the presence of a base and a catalytic amount of palladium(II) acetate [reaction (1)]. The carbonylation was carried out at room temperature under an atmospheric pressure of carbon monoxide for 1 h. After work-up, the alkyne carboxylates (**2**) were isolated by column chromatography on silica gel and the yields were determined by GC (Table 1). Table 1 shows that this carboxylation gives good to high yields of the esters (**2**). A small amount of the homocoupling product, $\mathrm{R^1{-}C{\equiv}C{-}C{\equiv}C{-}R^1}$, was detected.

$$\underset{\textbf{(1)}}{\mathrm{R^1{-}C{\equiv}C{-}I^+{-}Ph\ {}^-OTs}} \xrightarrow[\mathrm{R^2OH,\,CO}]{\mathrm{Pd(OAc)_2,\,base}} \underset{\textbf{(2)}}{\mathrm{R^1{-}C{\equiv}C{-}COOR^2}} \quad (1)$$

The advantage of the use of alkynyliodonium tosylates is that the carbonylation proceeds under an atmospheric pressure of carbon monoxide at room temperature, or even at 0 °C. This high reactivity of the alkynylphenyliodonium tosylates is attributable to the higher reactivity of the carbon–iodine(III) bond by transition metals,[6,9—11] compared with alkynyl iodides.

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