

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

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Alkoxy carbonylation 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 studied² 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-halogenoalkynes⁴ 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 PtCl₂(PPh₃)₂-Et₃N 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. Alkoxy carbonylation of alkynylphenyliodonium tosylates (1)

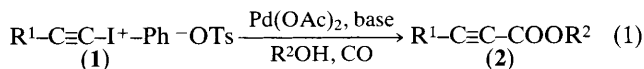
Iodonium tosylate (1), R ¹	Alcohol	Base	Product	% Yield ^d
Ph	EtOH	Et ₃ N	PhC≡CCO ₂ Et	80
	EtOH ^b	Et ₃ N		60
	EtOH	Bu ₃ N		80
	MeOH	Et ₃ N	PhC≡CCO ₂ Me	66
	MeOH	Bu ₃ N		70
An ^c	EtOH	Et ₃ N	AnC≡CCO ₂ Et	64
	EtOH	Bu ₃ N		69
	MeOH	Et ₃ N	AnC≡CCO ₂ Me	70
Bu ⁿ	EtOH	Et ₃ N	Bu ⁿ C≡CCO ₂ Et	59
	MeOH	Et ₃ N	Bu ⁿ C≡CCO ₂ Me	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 Pd(OAc)₂ (0.1 mmol), the base (Et₃N, 5.0 mmol; Bu₃N, 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*-MeOC₆H₄. ^d Self-coupling products (R¹C≡CC≡CR¹; R¹ = Ph, An, or Buⁿ) were detected in 1–9% yields.

phenyliodonium toluene-*p*-sulphonates (tosylates) in the stereoselective formation of 1,3-enynes⁶ led us to explore their use in alkoxy carbonylation reactions. Here we report a new mild effective alkoxy carbonylation 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)OTs⁷ (Ts = *p*-MeC₆H₄SO₂) or by reaction of 1-trimethylsilyl-1-alkynes with iodobenzene 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, R¹C≡C–C≡C–R¹, was detected.



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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