

Palladium-catalysed Intermolecular Arylation and Alkenylation of Bicyclic Alkenes

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Bicyclic alkenes undergo facile intermolecular arylation or alkenylation by the corresponding organic iodides, KO_2CH , $n\text{-Bu}_4\text{NCl}$ and 2.5% $\text{Pd}(\text{OAc})_2$.

No simple methods for the intermolecular arylation and alkenylation of bicyclic substrates presently exist (equation 1). Chiusoli and co-workers have observed a wide variety of unusual polycyclic products from the palladium-catalysed cross-coupling of aryl or vinylic halides and bicyclic alkenes.¹⁻⁶ We and others have published methods for the palladium-catalysed dialkylation of norbornene.⁷⁻¹⁰ We wish to report now that we have found reaction conditions which will indeed effect the desired intermolecular arylation and alkenylation of bicyclic alkenes.¹¹

The reaction of iodobenzene and norbornene was chosen as a model system. The use of 2.5% $\text{Pd}(\text{OAc})_2$, $n\text{-Bu}_4\text{NCl}$ (1 equiv.), and NaO_2CH (3 equiv.) in dimethylformamide (DMF) as the solvent at room temperature for 24 h was found to afford the desired product, *exo*-2-phenylnorbornane (**1**) in low yield, accompanied by small amounts of the double

insertion product (**2**) (17:1 ratio, 30% yield) (equation 2). The analogous reaction of bicyclo[2.2.2]octene afforded the single and double insertion products in equal amounts. By changing the cation of the formate salt, the ratio of single to

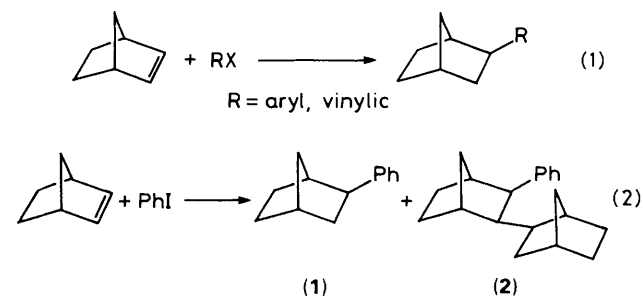
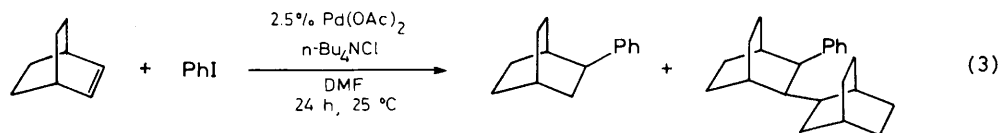


Table 1. Arylation and alkenylation of bicyclic alkenes.^a

			% Yield
	RI		
		R = Ph	71 (25:1) ^b
		R = <i>E</i> -CH=CHMe ₃	72
		R = CH=CMe ₂	71
		R = H ₂ C=C(CH ₂) ₃ Me	78
		R = CH=	66
	PhI		20 (20:1) ^b
	PhI		52
		(5:1)	
	<i>E</i> -Me ₃ CCH=CHI		52
		+	
		(2:1)	
	PhI		45, 56 ^c
	PhI		58
	RI		
		R = Ph	60 (20:1) ^b
		R =	39
		R = <i>E</i> -CH=CHMe ₃	96

^a All reactions were carried out using bicyclic alkene (0.5 mmol), organic iodide (0.5 mmol), n-Bu₄NCl (0.5 mmol), 2.5% Pd(OAc)₂, KO₂CH (1.5 mmol), and DMF (1 ml) at 25°C for 24 h. ^b Ratio of single to double alkene insertion product. ^c CsO₂CH used instead of KO₂CH.



			% yield
NaO ₂ CH	1	:	1 58
(Et ₃ NH)O ₂ CH	9–11	:	1 61–74
KO ₂ CH	20	:	1 60
CsO ₂ CH	40–44	:	1 43–47

double insertion product was improved dramatically (equation 3). The same reaction with lithium formate gave back substantial amounts of iodobenzene and an additional side-product was observed. Potassium formate appears to be the reducing agent of choice for these reactions. While sodium and ammonium or alkylammonium formate salts have previously been used by us¹¹ and others^{7,12–21} to reduce organopalladium intermediates, this is apparently the first observation that a significant difference in the reducing properties of the various formate salts actually exists.

Using KO₂CH and the above-described procedure, we have examined both the arylation and alkenylation of a variety of bicyclic alkenes. The results are summarized in Table 1. A wide variety of bicyclic alkenes and organic iodides have been observed to undergo this palladium-catalysed process in good yield. Only the reactions of iodobenzene and either norbornene, norbornadiene or bicyclo[2.2.2]octene were observed to produce double insertion products. All other reactions were quite clean. We believe this chemistry affords a valuable, efficient and convenient new route to bicyclic substrates bearing aryl and vinylic groups.

We gratefully acknowledge the National Institutes of Health (GM 40036) for their generous financial support and Johnson Matthey, Inc. and Kawaken Fine Chemicals Co., Ltd. for providing the palladium acetate.

Received, 8th May 1989; Com. 9/01912J

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