



0040-4039(94)02357-3

Palladium(0)-Catalyzed Reaction of Propargylic Phosphates with SmI_2 : A Highly Regioselective Route to the Synthesis of Allenes and Acetylenes

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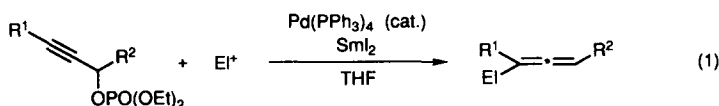
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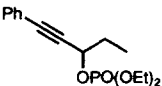
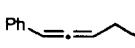


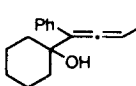
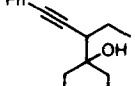
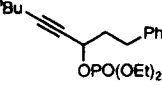


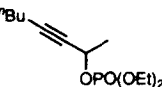

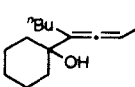
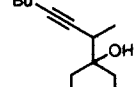
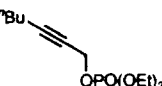

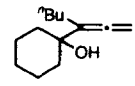
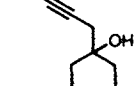

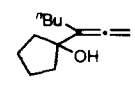
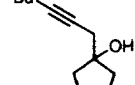
Abstract: A highly regioselective reaction of propargylic phosphates has been established by using SmI_2 and a $\text{Pd}(0)$ catalyst to give allenenes and acetylenes in high isolated yields depending on the substrate used.

A regioselective reduction of propargylic and allylic acetates has been reported by one of the authors using SmI_2 and a catalytic amount of $\text{Pd}(0)$ complex.¹ On the other hand, allylic phosphates have now become excellent allylating agents for the palladium-catalyzed reactions because allylic phosphates are highly reactive toward palladium(0) species and because phosphonyloxy groups have extremely low nucleophilicity.² In the combination, we now wish to report herein the highly efficient reaction of propargylic phosphates rather than the acetates or benzoate (eq. 1) to give the allenenes of biological and synthetic interests,³ in higher regioselectivity.



Typical experimental procedure is as follows: To a solution of propargylic phosphates (0.5 mmol), a catalytic amount (5 mol%) of $\text{Pd}(\text{PPh}_3)_4$, and electrophiles such as *tert*-butyl alcohol (0.55 mmol) as a proton source in THF (2.5 mL) was added a 0.1 M THF solution of SmI_2 (12.5 mL, 1.25 mmol) at room temperature under an argon atmosphere. After stirring 3 h, the reaction mixture was poured into sat. NH_4Cl and filtered through pads of Celite-Florisil. The filtrate was extracted with ether, washed with brine, and dried over Na_2SO_4 . Removal of organic solvent *in vacuo* followed by silica-gel column chromatography provided the allenic products with remarkably high regioselectivity in good yields. The representative results are exemplified in Table 1. Thus, a highly regioselective reaction of propargylic phosphates has been established to give allenenes in high isolated yields using SmI_2 and a $\text{Pd}(0)$ catalyst (entries 1-6). On the other hand, a primary phosphate gave the acetylenic products in high regioselectivity (entries 7-8).⁴

Table 1. Pd(0)-Catalyzed Reaction of Propargylic Esters with SmI_2 .

entry	substrate	electrophile	products (ratio) ^a	% yield ^b
1		H^+ (<i>i</i> -PrOH)	 +  (98 : 2)	66
2		H^+ (<i>t</i> -BuOH)	(>99 : <1)	80
3			 +  (94 : 6)	71
4 ^c		H^+ (<i>i</i> -PrOH)	 +  (>99 : <1)	84
5 ^c		H^+ (<i>t</i> -BuOH)	(>99 : <1)	89
6			 +  (94 : 6)	49
7			 +  (2 : 98)	84
8			 +  (4 : 96)	45

^a Determined by 300- or 400-MHz ^1H NMR and/or GC-MS analysis. ^b Combined yield. ^c The reaction was carried out at 40°C.

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(Received in Japan 22 October 1994; accepted 25 November 1994)