

New Routes to Substituted 1,3-Dienes, Allylic Alcohols, and α,β -Unsaturated Ketones

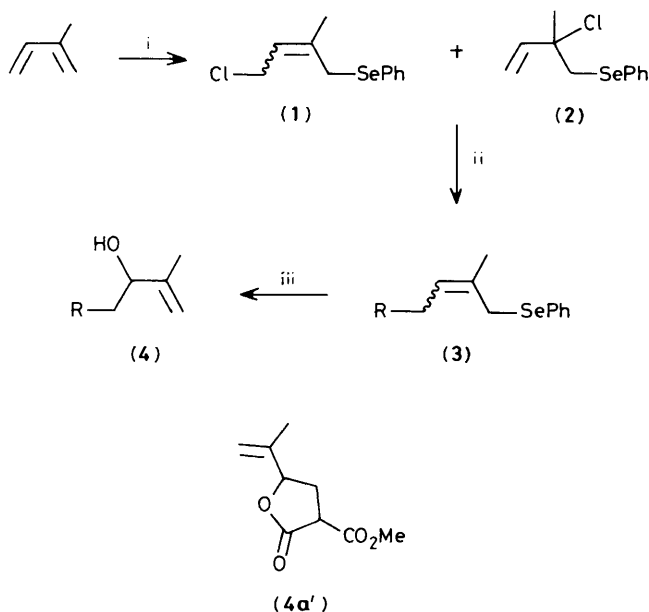
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Phenylselenenyl chloride reacts with isoprene giving chloroselenides (1) and (2) which are converted by alkylation and subsequent oxidation into synthetically useful dienes, allylic alcohols, or α,β -unsaturated ketones.

Substituted 1,3-dienes are useful intermediates in organic synthesis¹ but are often difficult to prepare. In this paper we report a new alkylative method for diene synthesis, which by simple modification provides allylic alcohol or enone syntheses. Although the reaction of olefins with selenenyl halides has been extensively investigated,² the corresponding reaction with 1,3-dienes has not been synthetically exploited.



Scheme 1. Reagents and conditions: i, PhSeCl, CCl₄; ii, NaH-tetrahydrofuran (THF)-hexamethylphosphoric triamide (HMPA)-NaI; iii, aq. H₂O₂ (10 equiv.) (ultrasonication accelerates the reaction), pyridine, 0 °C.

Treatment of isoprene with phenylselenenyl chloride gave a mixture of chloroselenides (1) and (2), the isomeric ratio observed being dependent on reaction temperature, as determined by ¹H n.m.r. spectroscopy. When this mixture was treated with a range of nucleophiles the selenides (3) were obtained as a mixture of *cis* and *trans* isomers. Oxidation of the selenides (3) with aqueous hydrogen peroxide gave the allylic alcohols (4) with the exception of (3a) which gave the lactone (4a') (Scheme 1; Table 1).

The allylic alcohols (4) arise from the oxidation of the selenide to a selenoxide which undergoes a [2,3] sigmatropic shift to yield a selenenic ester as an intermediate which is readily hydrolysed to the allylic alcohol.³

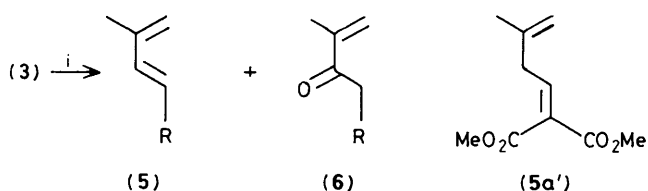
Oxidation of the selenides (3) with *m*-chloroperbenzoic acid (*m*CPBA; 1 equiv.) followed an entirely different reaction course to that observed with aqueous hydrogen peroxide.

Table 1. Dependence of the ratio of (1) to (2) on temperature, and yields of (1)–(4).

Compd.	R	% Yield	
		(3)	(4)
		T/°C	
		(1) + (2)	
		Ratio (1):(2)	
		0	1:1
		60	2:5
		69	
		%	
		Yield	
		(3)	(4)
a	(MeO ₂ C)CH ^b	60	0 ^c
b	PhO	70	60
c	<i>o</i> -allylC ₆ H ₄ O	36	50
d	Ac(Ph)N	14	55
e	PhS	60	20

^a Based on PhSeCl consumed. ^b No HMPA or NaI used in this case.

^c Lactone (4a') isolated in 80% yield.



Scheme 2. Reagent: *i*, *m*-CPBA-THF, -15°C . The mixture was poured into boiling CCl_4 after 30 min.

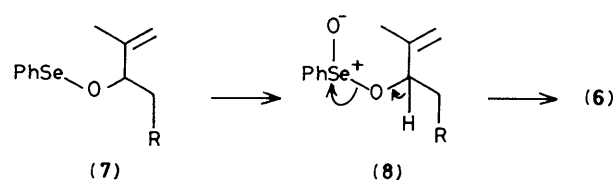
Table 2. Yields of (5) and (6).

Compd.	R	% Yield ^a	
		(5)	(6) ^b
a	(MeO ₂ C) ₂ CH	13 ^c	0(0)
b	PhO	25	25(44)
c	<i>o</i> -allylC ₆ H ₄ O	0	12(25)
d	Ac(Ph)N	40	58

^a Yields were not optimized; all compounds were fully characterized.

^b Yields in parentheses are from use of 2 equiv. *m*CPBA. ^c The isomeric product (5a') was also obtained (62% yield).

Dienes (5) and enones (6) were the only products observed together with diphenyl diselenide. Compound (3a) gave the two dienes (5a) and (5a') as products. By the use of two equivalents of *m*CPBA the enone (6) was obtained as the exclusive product (Scheme 2; Table 2).



The postulated mechanism for the formation of α,β -unsaturated ketones is that oxidation of the selenide to the selenoxide occurs, followed by a [2,3] sigmatropic shift to give the selenenic ester (7). The selenenic ester (7) is oxidised by the second equivalent of *m*CPBA to the seleninic ester (8) which collapses to the enone (6).⁴

In summary, this chemistry offers a new route to synthetically useful allylic alcohols (4), dienes (5), and enones (6).

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