Generation, Trapping, and Adduct Rearrangement of 3-Phenylselenoalk-1-enylidene Carbenes: a Novel Direct Route to 1-Hetero-substituted 1-Vinylcyclopropanes

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3-Phenylselenoalk-1-enylidene carbenes, generated *in situ* by base-induced Horner–Wadsworth–Emmons condensation of α-phenylseleno carbonyl compounds and diethyl diazomethylphosphonate, may be efficiently trapped to give alkylidene-cyclopropane adducts which undergo either [1,3]allyl selenide rearrangement or oxidative selenoxide[2,3]sigmatropic rearrangement to produce 1-heterosubstituted 1-vinylcyclopropanes.

The direct addition of a heterosubstituted allylic carbene (**1**) to an olefin (Scheme 1) would constitute, in principle, a most direct and attractive route to 1-substituted 1-vinylcyclopropanes (**2**), precursors which have served as a cornerstone in the elaboration of cyclopentanoids.[1] However, the influence of the neighbouring heteroatom is generally recognised[2] to increase the nucleophilic character of such carbenes, and hence to render them much less reactive towards simple olefinic partners or electron-rich alkenes. Moreover, in the case of the carbenes (**1**), this effect would certainly be exacerbated by the adjacent π-system.

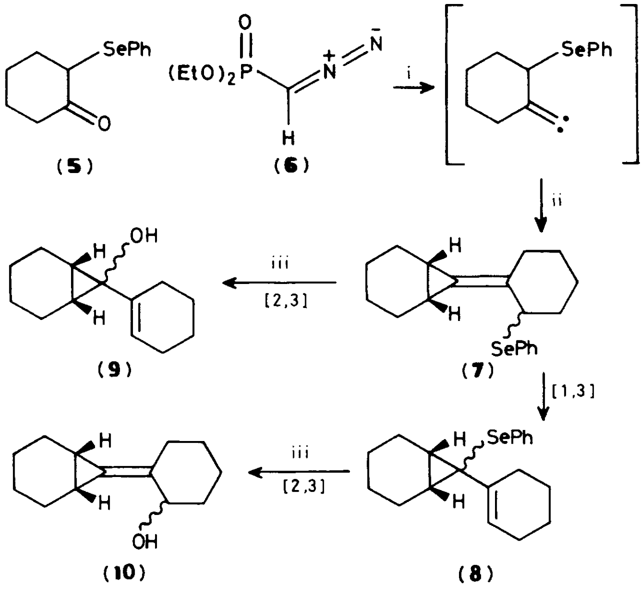
We conceived, however, that a much more reactive and flexible synthetic equivalent of (**1**) could be developed through the generation of hitherto unknown 3-phenylselenoalk-1-enylidene carbenes of type (**3**) (Scheme 1). The propensity of the selenide moiety itself to act as a carbene trap would require that external trapping of the carbene by olefins should compete effectively in the system against other possible inter- and intra-molecular insertion and rearrangement reactions. The resultant adducts (**3**) could then undergo the [1,3]allyl selenide rearrangement[3] to give synthetically useful 1-phenylseleno-1-vinylcyclopropanes (**2**; X = SePh), the versatile chemistry of which has been explored by Krief and his co-workers.[4] Alternatively, oxidation and selenoxide-mediated [2,3]sigmatropic rearrangement[5] would furnish valuable 1-vinylcyclopropanols (**2**; X = OH) (Scheme 1).

The highly convergent and efficient three-component, one-pot condensation of a carbonyl compound, a diazoalkyl phosphonate, and an olefin, developed by Gilbert[6] as a route to alkylidenecyclopropanes and involving generation of the alkylidene carbene *via* Horner–Wadsworth–Emmons reaction, was selected for initial study.

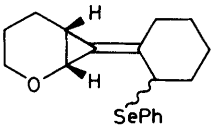
Accordingly, reaction of 2-phenylselenocyclohexanone (**5**) with diethyl diazomethylphosphonate (DAMP) (**6**) in the presence of freshly sublimed potassium t-butoxide and cyclohexene afforded the allylic selenide (**7**) (Scheme 2) (% yields based on selenoketone: 55% in tetrahydrofuran, 82% in 1,2-dimethoxyethane; see later). As expected in view of the 11 kcal mol^{-1} of strain energy released on rehybridisation at C-7 of the norcarane, the selenide (**7**) underwent [1,3]allyl selenide rearrangement particularly readily to give (**8**) [$t_{\frac{1}{2}}$ for (**7**) to (**8**) at 4 °C *ca.* 4 days]. The essentially irreversible nature of this process now confirms the speculation by Krief[4] that the reverse reaction is precluded in the parent system.

Controlled [2,3]sigmatropic rearrangement of the derived selenoxides also proved possible. Thus, low-temperature oxidative work up of the initial adduct (**7**) gave the 1-cyclohexenylcyclopropanol (**9**) (58% yield), thereby confirming the basic tenets of Scheme 1. A more striking testimony to the irreversible nature of the selenoxide rearrangement was observed in the transformation of the selenoxide derived from (**8**), which gave (**10**) (53% yield) with reinstatement of the strained cyclopropylidene double bond.

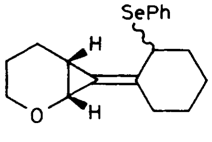
In similar fashion, we have subjected a variety of olefinic substrates and α-phenylseleno ketones to these reaction conditions. The resultant data (Table 1) reveal several features of interest. Thus, use of the more electron-rich olefin, dihydropyran, gives an excellent yield of isomeric adducts (**11**) and (**12**) which smoothly rearrange to (**13**). Whilst initial experiments using α-phenylselenoacetone in tetrahydrofuran gave the isomeric selenides (**14**) and (**15**) in only 7% yield, replacement of this solvent by 1,2-dimethoxyethane led to considerable improvement. We have previously noted this solvent tendency in other work which required condensation of an inductively stabilised phosphonate carbanion with a hindered carbonyl compound,[7] and suggest that it be more generally employed. Although isolation of the initial adduct



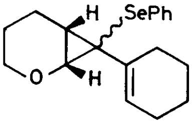
Scheme 2. *Reagents:* i, $K^+Bu^tO^-$; ii, cyclohexene; iii, H_2O_2.



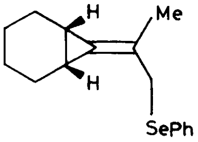
(**11**)



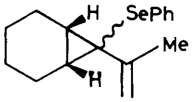
(**12**)



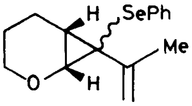
(**13**)



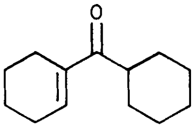
(**14**)



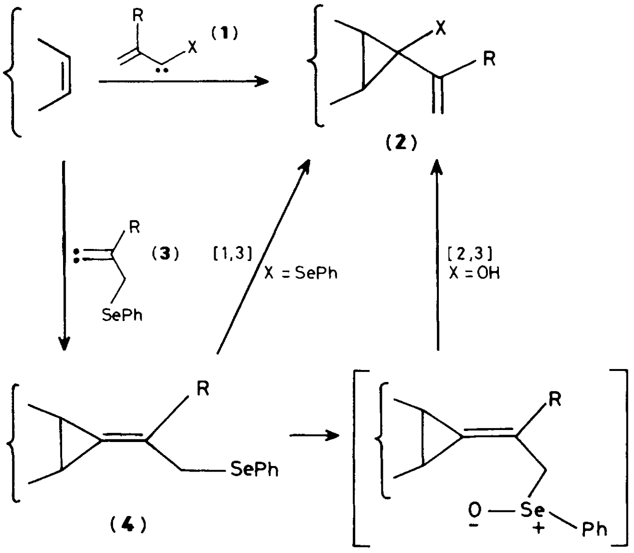
(**15**)



(**16**)



(**17**)



Scheme 1

Table 1. Reactions of 3-phenylselenoalk-1-enylidene carbenes with olefins.

Olefin	α-Phenylseleno ketone	Phenylseleno-alkylidene-cyclopropane	1-Phenylseleno-1-vinyl-cyclopropane[a]	Yield (%)[b]
Cyclohexene	(5)	(7)	(8)	55[c]
				82[d]
Dihydropyran	(5)	(11) + (12)	(13)	99[d]
Cyclohexene	α-Phenylselenoacetone	(14)	(15)	7[c]
				43[d]
Dihydropyran	α-Phenylselenoacetone		(16)	28[d]

[a] The allyl selenide rearrangement is quantitative in all cases. [b] Based on selenocarbonyl compound. [c] Tetrahydrofuran solvent. [d] 1,2- Dimethoxyethane solvent.

(**14**) from phenylselenoacetone is possible, the ensuing rearrangement to give (**15**) takes place even more readily, presumably as a consequence of the fact that the allylic transposition leads to a terminal double bond which is less strained than in the cyclohexene case. The diminished yields with respect to utilisation of α-phenylselenoacetone are most probably a reflection of the increased acidity of the adjacent protons leading to competing enolate formation.[8] Support for this hypothesis may be adduced from the observation that the use of the even more acidic 2-phenylselenocyclopentanone as substrate failed to give the required adducts.

It was also of interest to examine the possibility of conducting the oxyanion-assisted version of the vinylcyclopropane rearrangement which has been so successfully used by Danheiser[9] in the case of 2-vinylcyclopropanols. Unpublished observations by Salaun[10] state that this effect is not operative in the case of 1-vinylcyclopropanols, although no product determination was reported. In the event, we find that thermolysis of the sodium alkoxide derived from (**9**) in toluene gives cleanly the enone (**17**) (72% yield) in a process which is most easily rationalised by invoking a stepwise fragmentation to the homoenolate followed by prototropic rearrangement.

The strategy reported herein, within the cited limitation of α-phenylseleno carbonyl basicity, thus provides a simple direct route to allylically substituted phenylselenoalkylidenecyclopropanes, and thence, by sequential thermal or oxidative sigmatropic rearrangement, to the important class of 1-heterosubstituted 1-vinylcyclopropanes.

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