

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 recognised² 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 rearrangement³ 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 rearrangement⁵ would furnish valuable 1-vinylcyclopropanols (**2**; X = OH) (Scheme 1).

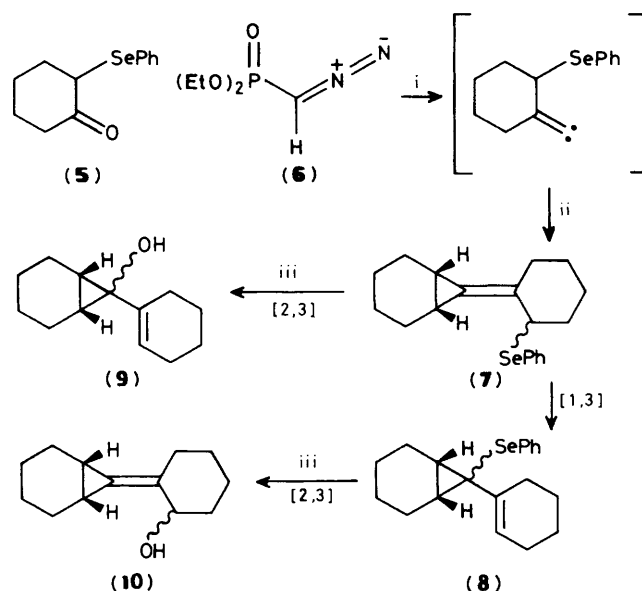
The highly convergent and efficient three-component, one-pot condensation of a carbonyl compound, a diazoalkyl phosphonate, and an olefin, developed by Gilbert⁶ as a route to alkylidenecyclopropanes and involving generation of the alkylidene carbene *via* Horner–Wadsworth–Emmons reaction, was selected 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

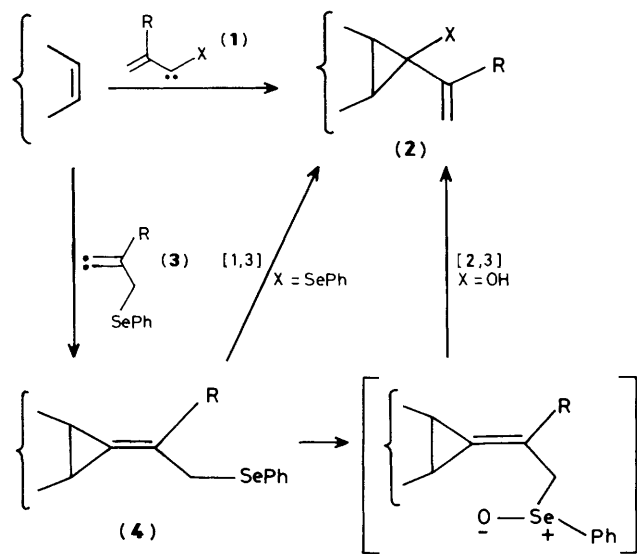
selenide rearrangement particularly readily to give (8) [t_4 for (7) to (8) at 4 °C ca. 4 days]. The essentially irreversible nature of this process now confirms the speculation by Krief⁴ that the reverse reaction is precluded in the parent system.

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, $K^+Bu_4O^-$; ii, cyclohexene; iii, H_2O_2 .



Scheme 1

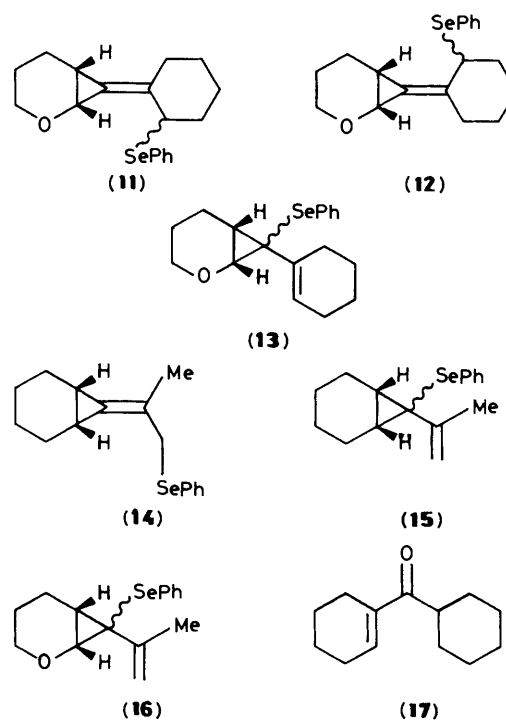


Table 1. Reactions of 3-phenylselenoalk-1-enylidene carbenes with olefins.

| 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 Danheiser⁹ in the case of 2-vinylcyclopropanols. Unpublished observations by Salaun¹⁰ 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.

We thank the S.E.R.C. for a studentship (to R. T. L.)

Received, 17th February 1988; Com. 8/00599K

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