Enyne Cyclization *via* Photoinduced Electron Transfer (PET) Generated Electrophilic Selenium Species: a New Carbon–Carbon Bond Formation Strategy

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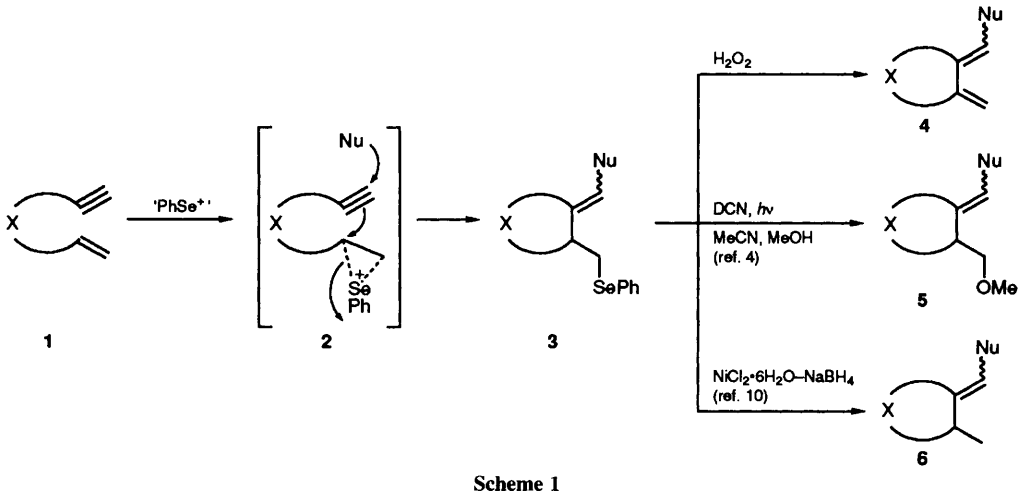
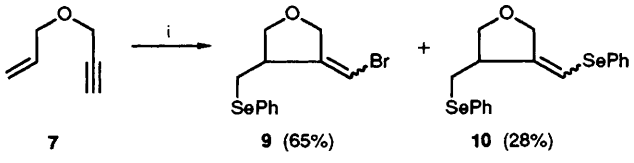
An efficient and mild methodology of enyne cyclization using PET-generated diphenyl diselenide radical cation as electrophilic species is reported.

The development of a simple methodology for the direct conversion of enynes into the corresponding monocyclic organic compounds would, in principle, be of great value. Although enyne cyclization occurs by carbometallation,[1] an alternative strategy would be of considerable use. In our ongoing study on the synthetic applications of PET reaction of organoselenium compounds,[2,3] it was envisaged that PET-

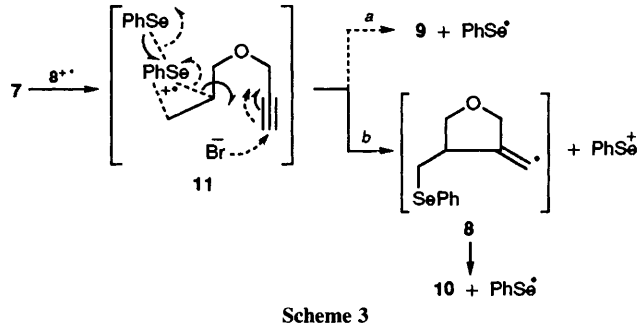
† NCL Communication No. 5700.



Scheme 1



Scheme 2 *Reagents and conditions*: i, **8**, DCN, MeCN, TBAB, *hv*, λ > 280 nm, 13 h



Scheme 3

generated electrophilic selenium species ($PhSe^+$),[2] which is devoid of counter anion,[4] would react selectively with the olefinic component of enyne **1** owing to marked differences in the rate of typical electrophile addition to acetylene *vs.* olefin.[5] Subsequent cyclization of the acetylenic moiety to episelenium cation would lead to the cyclized product **3** as shown in Scheme 1. Our initial results are reported in this communication.

Heterocyclization *via* the episelenonium cation intermediate from unsaturated compounds bearing a neighbouring nucleophile has emerged as a useful synthetic methodology in recent years.[6] A few examples of carbocyclizations involving episelenonium cation, generated either by direct addition of $PhSe^+$ to olefin[7] or by an alternative route of trifluoroacetic acid reaction on β-hydroxy selenides,[8] have been reported. However, to the best of our knowledge, this is the first report of enyne cyclization mediated by an electrophilic selenium species. The additional advantage of this method is the unique structure of **3** which may be exploited for further synthetic manipulation (*e.g.*, **4**, **5** and **6**).[3,9]

In order to illustrate the reaction, a mixture containing **7** (1.8 mmol), diphenyl diselenide (**8**, 0.9 mmol), 1,4-dicyanonapthalene (DCN, 0.9 mmol) and tetrabutylammonium bromide (TBAB, 18 mmol)[10] in 500 ml of MeCN was irradiated (450 W Hanovia mercury vapour lamp, Pyrex filter, >280 nm, all light absorbed by DCN only) without removing dissolved oxygen from the solution till 70% consumption of **7** (*ca.* 13 h, monitered by vapour phase chromatography, phenyl methyl silicone column, 10 m × 0.50 mm × 0.2 μm). Removal of the solvent followed by extraction with diethyl ether, usual workup and purification by column chromatography gave cyclized products **9** (65%) and **10** (28%), (Scheme 2), which were characterized by ^1H NMR, ^{13}C NMR and mass spectral data. DCN was recovered quantitatively (97%) at the end of the reaction. Heating of the above reaction mixture or irradiation without DCN failed to give any reaction product, which further support the PET-initiation for this reaction.

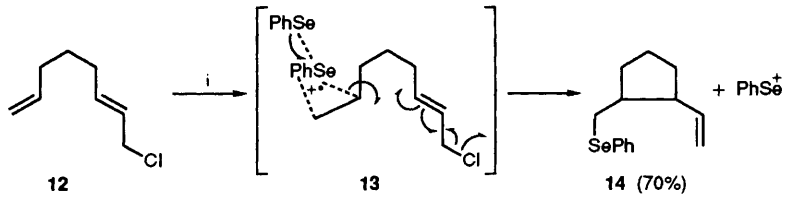
Mechanistically the formation of **10** from this reaction is quite unexpected. The vinyl selenide moiety of **10** can only be envisaged by considering the intermediacy of vinyl radical, formed either by addition of phenyl selenyl radical (PhSe·) to acetylene or cyclization of carbon-centred radical to acetylene followed by trapping of vinyl radical by **8**. However, based on well-established facts such as the low reactivity of PhSe· addition to the π-bond, due to the faster rate of its recombination and reversible nature of addition,[11] this possibility can be easily eliminated. Nevertheless, the addition of PhSe· to acetylenes has been suggested recently by Back and Krishna[12] and Sonoda *et al.*[13] only under special conditions. In order to rule out the mediation of PhSe· in this reaction, a control experiment under which PhSe· is likely to be produced was performed by irradiating[14] (either at 300 or 350 nm) a mixture of **7** (1.8 mmol) and **8** (0.9 mmol) in MeCN solvent; no reaction product was detected. These results made us re-evaluate the nature the electrophilic selenium species generated during the PET-reaction of **8**.

Originally, we believed[2] that the PET-generated $8^{+\cdot}$ cleaves to give $PhSe^+$ as an electrophilic selenium species, however, in the light of the present result, if $8^{+\cdot}$ is considered as the electrophilic selenium species‡ and the episelenonium radical cation **11** as the intermediate, then the formation of both products **9** (path *a*) and **10** (path *b*) can be explained§ (Scheme 3).

Although the nucleophilic addition to a radical cation is reported[15] to be energetically unfavourable, recent work of Reitstoen and Parker,[16] suggests that the radical cation having stabilizing functionalities can undergo direct nucelophilic additions. Therefore, the proposition of electrophilic addition of $8^{+\cdot}$ to olefinic component of **7** to produce intermediate **11** is quite reasonable. To substantiate this argument the PET-cyclization of **12** which is analogous to **7**, was followed by irradiating a mixture of **12** (1.8 mmol), **8** (0.9 mmol) and DCN

‡ From the reaction type studied in our earlier reports (ref. 2), there was no way to distinguish PhSe· or $8^{+\cdot}$ as reactive electrophilic species since both species would give the same product.

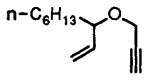
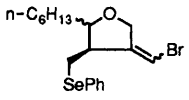
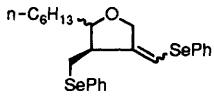
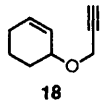
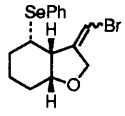
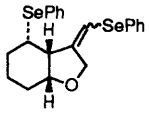
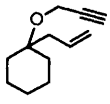
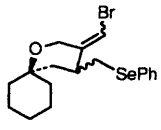
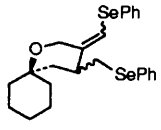
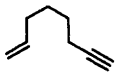
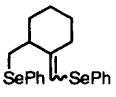
§ Part formation of **9** cannot be ruled out from $PhSe^+$ species.



12 13 14 (70%)

Scheme 4 *Reagents and conditions*: i, 8, DCN, MeCN, *hν*, λ > 280 nm

Table 1 Enyne cyclization by electrophilic selenium species

Entry	Substrate	Irradiation *t* / h[a]	Products[b,c,d]
1	 **15**	18	 **16** (64%) *trans*/*cis* (2.8 : 1) +  **17** (28%) (1 : 1)
2	 **18**	18	 **19** (65%) +  **20** (20%)
3	 **21**	16	 **22**[e] (65%) +  **23**[e] (20%)
4	 **24**	14	 **25** (50%) +  **26** (28%)

[a] Irradiated till *ca.* 75% consumption of the starting material. [b] Isolated yields (not optimised); yields calculated on the basis of consumption of starting material. [c] Characterized by ^{1}H NMR, ^{13}C NMR and mass spectral data. [d] Inseparable *E*/*Z* mixture; ^{1}H NMR confirmed the predominance of *E* isomer. [e] Stereochemistry not confirmed.

(0.9 mmol) in MeCN which gave **14** (70%) exclusively (Scheme 4). The formation of **14** can be explained in this reaction only by considering **13** as intermediate since the involvement of PhSe· has been shown to be ineffective for radical cyclization initiation as mentioned earlier in this text. Examples presented in Table 1 show the generality of the reaction.

In conclusion, we have developed a new, mild and unprecedented approach for enyne cyclization. Further study is in progress.

We are grateful to Dr R. A. Mashelkar, Director, for his keen interest in this work. B. B. V. S. S. thanks CSIR, New Delhi for financial support.

Received, 31st December 1992; Com. 2/06912A

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