Pergamon

Tetrahedron Vol. 51, No. 5, pp. 1483-1494, 1995

0040-4020/95 $9.50+0.00

0040-4020(94)01042-0

Enyne Cyclisation By Photoinduced Electron Transfer (PET) Promoted *In Situ* Generated Electrophilic Selenium Species: A New Carbocyclisation Strategy#

Ganesh Pandey* and B.B.V. Soma Sekhar

Division of Organic Chemistry (Synthesis)
National Chemical Laboratory
Pune-411 008, INDIA,
FAX:91-0212-330233

Abstract: *A new strategy for the carbocyclisation of enynes by PET initiated in situ generated electrophilic selenium species from diphenyldiselenide (PhSeSePh) is reported. The structure of the reactive selenium intermediate is also discussed.*

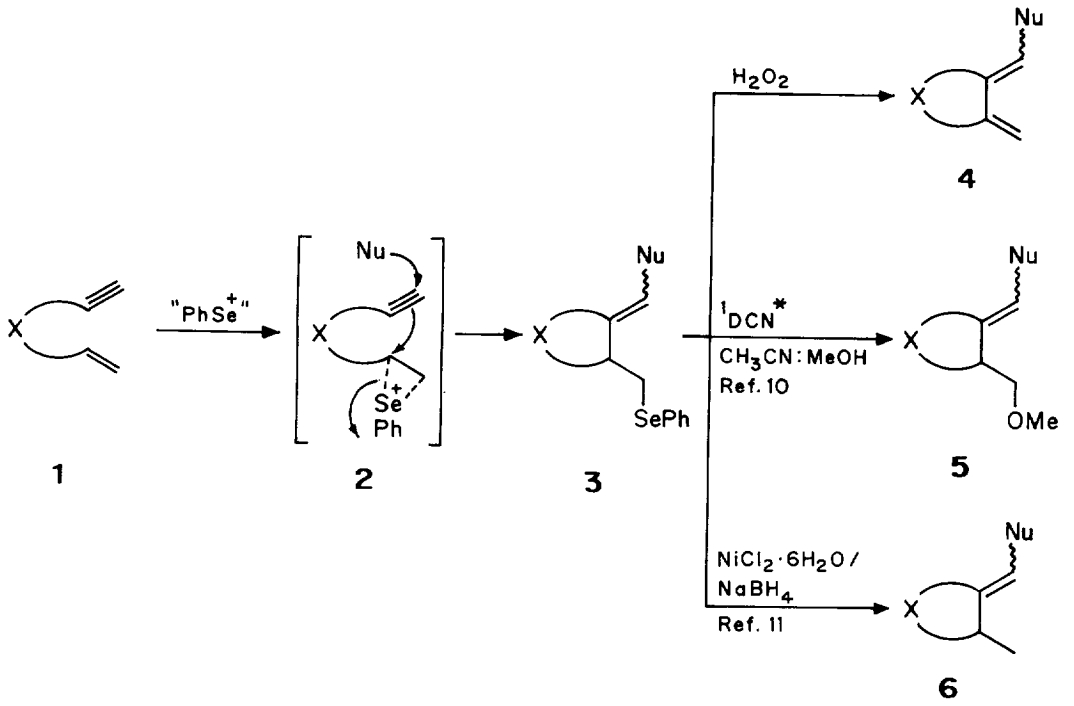
INTRODUCTION

There has been a considerable interest in the development of methods for the construction of carbocyclic ring systems owing to their occurrence in a diverse range of natural product molecules.[1] In recent years, among several other approaches[2,3], transition metal catalyzed cyclisation of enynes[4,5] have occupied a prominent position. However, inventing an alternative strategy for the enyne cyclisations would, in principle, be of great value. We have recently reported[6] an efficient strategy for the *in situ* generation of electrophilic selenium ($PhSe^+$) species that is devoid of any counter anion[7], from the PET dissociation of PhSeSePh. We were also aware that there exists[8] a marked electrophilicity difference between the olefins and acetylenes. Therefore, it occurred to us that the generation of electrophilic selenium species in a strong nucleophilic environment[9] containing enyne **1** could lead to the cyclised product **3** *via* episelenonium cation intermediate **2** (**SCHEME-I**). The additional advantage

NCL Communication No. 6143.

of this approach was viewed by considering the unique structural features of **3**, possessing multifunctional appendages which may be exploited for further synthetic manipulation to compounds such as **4**, **5**[10] and **6**[11]. We are pleased to disclose the full details of our preliminary work[12] in this paper.

SCHEME-I

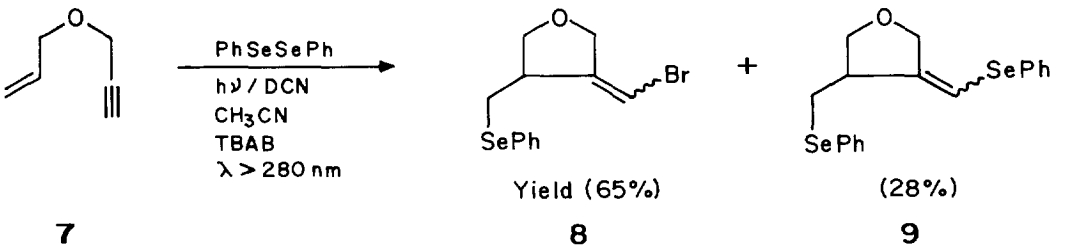


RESULTS AND DISCUSSION

In order to realize the concept as outlined in **SCHEME-I**, a 500 mL acetonitrile solution containing **7** (1.80 mmol), PhSeSePh (0.90 mmol), DCN (1,4-dicyanonaphthalene, 0.90 mmol) and tetrabutylammonium bromide (TBAB, 18.0 mmol)[9] was irradiated by Pyrex filtered light ($\lambda > 280$nm, all light absorbed by DCN only) by 450-W Hanovia medium pressure mercury vapor lamp without removing the dissolved oxygen from the reaction mixture[6]. Irradiation was discontinued, after 70% consumption of PhSeSePh (13 h, monitored by VPC). Removal of the solvent followed by the extraction with ether, usual workup and purification by column chromatography furnished two products **8** and **9** (**SCHEME-II**) in 65% and 28% yields, respectively. DCN was recovered quantitatively (98%)[6]. Products **8** and **9** were characterized by IR, ^{1}H NMR, ^{13}C NMR and mass spectral data. A control experiment by heating the above reaction mixture or irradiation without DCN failed to show any observable product, suggesting the initiation of this cyclisation by PET process.

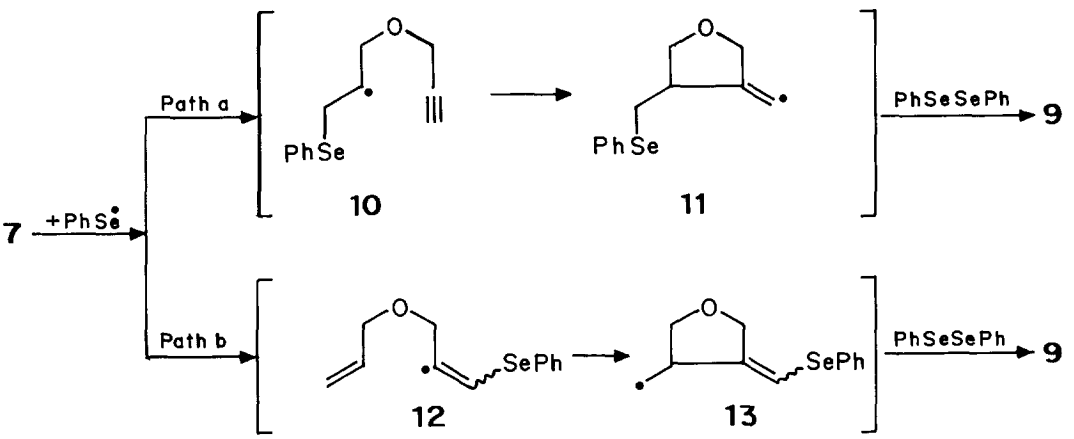
Mechanistically, the formation of **8** can be rationalized by considering the intramolecular nucleophilic addition of polarized acetylenic bond, due to the presence of strong nucleophilic environment created by TBAF to the episelenonium cation (*cf.* **SCHEME-I**) in a concerted manner followed by the termination of the resultan

SCHEME-II



vinyl cation by bromide (Br^-) anion. However, the formation of unexpected product **9** remains unexplained. First to explain the formation of **9**, we consider the possibility of the involvement of vinyl radicals **11** or **12**, produced by the addition of phenylselenyl radical (PhSe·) either on to olefin (***path a***) or acetylene (***path b***), respectively (**SCHEME-III**). However, this hypothesis does not gain enough support due to the following literature precedences. The addition of PhSe· to an olefinic π-bond (***path a***) is reported[13] to be negligible due to its faster rate of recombination and reversible nature of its addition to π-bond[14]. Therefore, invoking ***path a*** to explain the formation of **9** appears illogical. Similarly, the involvement of ***path b*** can also be eliminated based on the work of Back[14] and Sonoda[15] where they have shown that the addition of PhSe· to acetylenic bond occurs only under special experimental conditions.

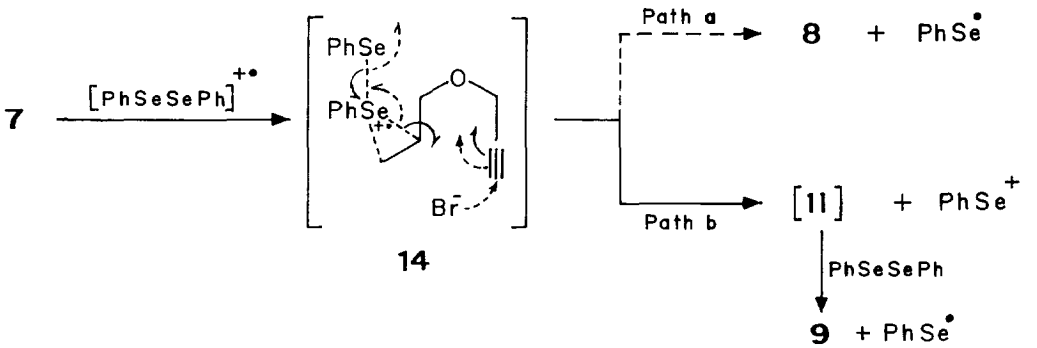
SCHEME-III



To provide the exclusive experimental support for the non-mediation of PhSe· for the formation of **9**, a control experiment, under which PhSe· is reported to be formed[16], was performed. Irradiation of a mixture of **7** and PhSeSePh, but without DCN, using 500-W tungsten lamp[16] for 24 h neither showed any significant loss in the concentration of PhSeSePh (monitored by VPC) nor the formation of the product corresponding to the retention time of **9**. This experiment, therefore, provides the sufficient evidence to rule out the mediation of PhSe· in the formation of **9**. To rationalize a plausible explanation for the formation of **9**, we were compelled to reevaluate

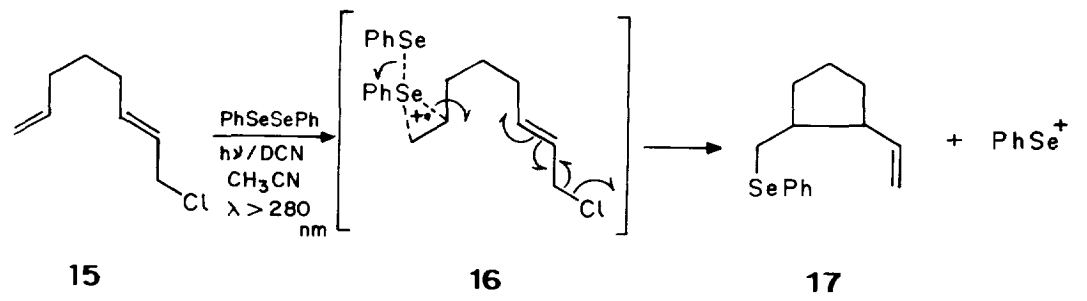
the structure of electrophilic selenium species produced during the PET cleavage of PhSeSePh. We had originally believed that the PET generated $PhSeSePh^{+\cdot}$ cleaves to give free $PhSe^{+}$ as an electrophilic selenium species and that participates in the selenylation reactions. The reason we were led to this conclusion was the types of substrates selected for the study of selenylation reaction. Those substrates did not distinguish between the $PhSe^{+}$ or $PhSeSePh^{+\cdot}$, as both of these reactive electrophilic selenium species would give the same product. However, the present result led us to suspect the involvement of $PhSeSePh^{+\cdot}$ itself as a reactive electrophilic selenium species and considering the episelenonium radical cation **14** as an intermediate (**SCHEME-IV**) from which the formation of both **8** and **9** can be explained. Although, nucleophilic addition to a radical cation is reported[17] to be energetically unfavorable, a recent report from Parker's group[18], suggests that the radical cations possessing stabilizing functionalities tend to participate into direct nucleophilic additions. Therefore, as it was proposed, the electrophilic addition of $PhSeSePh^{+\cdot}$ to the olefinic component of **7** to give intermediate **14** seems to be quite reasonable.

SCHEME-IV



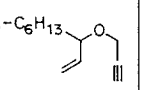
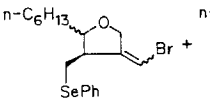
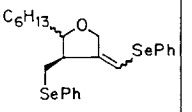
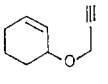
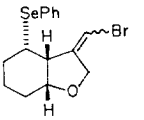
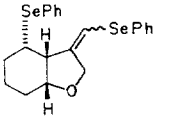
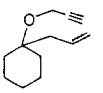
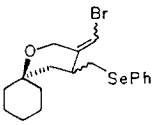
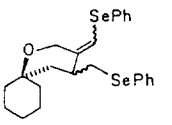
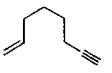
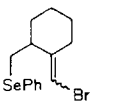
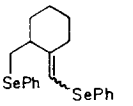
To substantiate experimentally, the implication of $PhSeSePh^{+\cdot}$ as a reactive electrophilic selenium species, we elected to study the cyclisation of 1-chloro-2,7-octadiene (**15**). It was envisaged, if $PhSeSePh^{+\cdot}$ is the reactive species, it should initiate a radical chain process from **15** to produce cyclised product **17** as shown in **SCHEME-V**. Identical irradiation, as described for **7**, of a mixture of **15** (1.80 mmol), PhSeSePh (0.90 mmol) and DCN (0.90

SCHEME-V



mmol) gave **17** (70% yield) exclusively. The formation of **17** can be explained by considering **16** as an intermediate since the involvement of PhSe· has been shown to be ineffective for initiating radical cyclisation as mentioned earlier in this text. This observation lends support conclusively that the $PhSeSePh^{+\cdot}$ is the reactive selenium species responsible for the initiation of PET cyclisation of **7** to **8** and **9**.

Table-1: Enyne Cyclisation by PET generated Electrophilic Selenium Species

Entry	Substrate	Irr time[a] (h)	Products[b,c,d]
1	 **18**	18	 (64%) trans/cis (2·8:1) **22a** +  (28%) (1:1) **22b**
2	 **19**	18	 (65%) **23a** +  (20%) **23b**
3	 **20**	16	 (60%) **24a**[e] +  (20%) **24b**[e]
4	 **21**	14	 (50%) **25a** +  (28%) **25b**

a) Irradiated till ~ 70% consumption of the substrate. b) Isolated yields (not optimised); yields calculated on the basis of consumption of the substrate. c) characterized by IR, ^1H NMR, ^{13}C NMR and mass spectral data. d) inseparable E/Z mixture e) Stereochemistry not confirmed.

Although heterocyclisation, *via* episelenonium cation intermediate from the unsaturated compounds bearing proximate nucleophile, has emerged as an synthetic methodology in recent years[19], the carbocyclisation

intermediacy of episelenonium cation has remained limited to only two reports[20,21] that too indirectly. However, to the best of our knowledge, the enyne cyclisation mediated by electrophilic selenium species is unprecedented.

To add to the generality of such cyclisations a number of enynes (**18-21**) were studied and the results are shown in **Table-1**.

ACKNOWLEDGEMENTS: We are indebted to DST, New Delhi for the partial support of this work.

EXPERIMENTAL

General: The chemicals and reagents used in this study were commercial grade pure and some of them were used after further purification. PhSeSePh[22], DCN[23], 1-allylcyclohexanol[24] were prepared by standard procedures. The chromatography was performed using silica gel (Acme, India, finer than 200 mesh). The solvents used during experiments were purified unless or otherwise stated by standard literature procedure.

All the compounds were characterized by IR, ^{1}H NMR, ^{13}C NMR and Mass spectroscopy. Nuclear magnetic resonance spectra obtained for ^{1}H and ^{13}C were recorded on Bruker-200 MHz and Varian Gemini 200 MHz, in $CDCl_3$ using tetramethyl silane as an internal standard. Chemical shifts are given in (ppm) scale and the coupling constants are reported in Hertz (Hz). Infrared spectra were recorded on Perkin-Elmer model 283B and the values are reported in cm^{-1}. Mass spectra were recorded on VG-micro mass 7070 model. GC analysis was performed by using phenylmethylsilicone (10 m X 0.5 mm X 0.2 μm) capillary column.

Equipment used for the photolysis were 450-W Hanovia medium pressure mercury lamp, Pyrex filtered immersion well and reaction vessels (Ace glass, USA).

Preparation of allyl propargyl ether (**7**):[25]

Aqueous 4N KOH solution (3.54 g in 16 mL of water) was added dropwise to a stirring solution of allyl bromide (6.10 g, 50.0 mmol) and propargyl alcohol (3.50 g, 62.5 mmol) at 0 °C for 10 min. After the addition was completed, external cooling was removed and the contents were allowed to reflux at 70 °C for 6 h. Reaction mixture was cooled, extracted into ether (50 mL) and washed with water (2 X 20 mL) to remove the unreacted propargyl alcohol. Ether layer was dried over anydrous Na_2SO_4, concentrated and fractionally distilled (bp 105 °C, 760mmHg) at atmospheric pressure to give **7** (5.2 g, 86%). ^{1}H NMR (200 MHz): 6.00-5.80 (m, 1H), 5.40-5.15 (m, 2H), 4.16-4.14 (d, 2H, J = 2.4 Hz), 4.09-4.05 (m, 2H), 2.44-2.42 (t, 1H, J = 2.4 Hz); ^{13}C NMR (50.4 MHz): 133.91, 117.74, 79.67, 74.25, 70.53, 57.04; IR (Neat): 3300 (sharp), 2140, 1650; Mass: 96 (M^+).

Photolysis of allyl propargyl ether (**7**):

A mixture containing **7** (0.173 g, 1.80 mmol), PhSeSePh (0.281 g, 0.90 mmol), DCN (0.160g, 0.90 mmol) and TBAB (5.86 g, 18.0 mmol) in acetonitrile (500 mL) was irradiated by using 450-W Hanovia medium pressure mercury vapor lamp at ambient temperature without removing the dissolved oxygen from the photolysis mixture. The lamp was housed in a Pyrex jacketed immersion well which allows only $\lambda > 280$nm light to pass through. The reaction progress was monitored by VPC analysis (column: phenylmethylsilicone, 10 m X 0.5 mm X 0.2

μm). Irradiation was performed till 70% consumption of PhSeSePh (~13 h), solvent was removed under reduced pressure, extracted into ether, washed with water and brine successively. The ether layer was dried over anhydrous Na_2SO_4, concentrated and the residue was purified by silica gel column chromatography to furnish two yellow oily products **8** (0.271 g, 65%) and **9** (0.145 g, 28%) in pure form. Yields were calculated based on the consumption of PhSeSePh.

8: ^{1}H NMR (200 MHz): 7.66-7.55 (m, 2H), 7.40-7.25 (m, 3H), 6.05 (sd, 1H, J = 0.8 Hz), 4.60 (d, 1H, J = 13.0 Hz), 4.10-4.05 (m, 1H), 3.90 (d, 1H, J = 13.0 Hz), 3.55 (t, 1H, J = 9.0 Hz), 3.45-3.30 (m, 1H), 2.95-2.85 (dd, 1H, J = 4.3 and 14.6 Hz), 2.45-2.30 (t, 1H, J = 14.5 Hz); ^{13}C NMR (50.4 MHz): 138.02, 135.08, 131.44, 129.06, 128.02, 101.46, 72.20, 68.04, 39.42, 38.78; IR (Neat): 1660, 1580, 1480, 1060; Mass: 332 (M^+).

9: ^{1}H NMR (200 MHz): 7.60-7.55 (m, 2H), 7.55-7.45 (m, 6H), 6.45 (s, 1H), 4.25-2.00 (m, 3H), 3.65 (t, 1H, J = 9.0 Hz), 3.45-3.30 (m, 3H), 3.15-3.05 (dd, 1H, J = 4.3 and 14.6 Hz), 2.40-2.35 (t, 1H, J = 14.5 Hz); ^{13}C NMR (50.4 MHz): 138.94, 135.35, 132.12, 130.81, 129.45, 116.91, 72.93, 72.74, 40.16, 36.34; IR (Neat): 1630, 1580, 1480, 1460, 1060; Mass: 408 (M^+).

Preparation of 1-chloro-2,7-octadiene **(15)**:

a) *Preparation of 3-hydroxy-1,7-octadiene* (**26**): A solution of 1-pentenylmagnesium bromide was prepared by reacting the magnesium turnings (0.33 g, 0.014 g.atm) with 5-bromo-1-pentene (2.0 g, 13.5 mmol) in anhydrous ether (75 mL) under the positive pressure of dry nitrogen at 0 °C. To this stirring solution of Grignard reagent at 0 °C, pure acrolein (0.75 g, 13.5 mmol) was added slowly for 20 min. After the addition was completed, cooling was removed and the reaction mixture was allowed to reflux for 30 min on water bath. The contents were poured into a ice-water mixture (75 mL) and quenched with conc. H_2SO_4 (8N, 65 mL). Organic layer was separated and aqueous layer was extracted with ether (200 mL). Combined organic layers were washed with water, dried over anhydrous Na_2SO_4 and filtered. The filtrate was concentrated and fractionally distilled under reduced pressure (bp 70 °C, 9 mmHg) to afford 1.40 g (83%) of **26**. ^{1}H NMR (200 MHz): 5.95-5.70 (m, 2H), 5.25-4.90 (m, 4H), 4.10 (m, 1H, D_2O exchangeable), 2.05 (m, 2H), 1.60-1.25 (m, 4H); IR (Neat): 3400 (br), 3100, 1650, 1440; Mass: 126 (M^+).

b) Freshly distilled $SOCl_2$ (1.40 g, 11.8 mmol) was added to a stirring solution of **26** (1.0 g, 7.90 mmol) and propylene oxide (0.59 g, 10.3 mmol) in dry CH_2Cl_2 (25 mL) at 0 °C. After 3 h of stirring at 0 °C, the reaction mixture was quenched with water and extracted into CH_2Cl_2 (30 mL). The organic layer was dried over anhydrous $CaCl_2$, filtered and concentrated. Purification by silica gel column chromatography using hexane as an eluent gave 0.89 g of **15** (72%). ^{1}H NMR (200 MHz): 5.98-5.38 (m, 3H), 5.14-4.78 (m, 2H), 3.99 (d, 2H, J = 5.9 Hz), 2.21-1.88 (m, 4H), 1.64-1.30 (m, 2H); ^{13}C NMR (50.4 MHz): 138.62, 135.93, 126.52, 45.59, 33.34, 31.64, 28.27; IR (Neat): 1670, 1640, 970, 730; Mass: 145 (M^+).

Photolysis of 1-chloro-2,7-octadiene **(15)** :

A mixture containing **15** (0.13 g, 0.9 mmol), PhSeSePh (0.14 g, 0.45 mmol) and DCN (0.08 g, 0.45 mmol) in 250 mL of acetonitrile was irradiated in the identical conditions as described earlier. Solvent was evaporated under reduced pressure and purified by column chromatography [EtOAc:Hexane (1:19)] to give 0.083 g (70%)

of **17**. ^{1}H NMR (200 MHz): 7.60-7.50 (m, 2H), 7.25 (m, 3H), 6.00-5.80 (m, 1H), 5.25-5.00 (m, 2H), 3.25-3.15 (dd, 1H, J = 5.7 and 12.4 Hz), 3.10-2.90 (dd, 1H, J = 7.2 and 12.4 Hz), 2.10 (m, 1H), 1.80-1.20 (m, 6H); IR (Neat): 1640, 1580, 1460, 1440; Mass: 266 (M^+).

***Preparation of 1-n-hexyl-2-propen-1-yl propargyl ether* (18)**:

a) *Preparation of 1-n-hexyl-2-propen-1-ol* (**27**) : Acrolein (1.25 g, 22.4 mmol) was added to a solution of 1-hexylmagnesium bromide, prepared from Mg (0.54 g, 0.022 g. atm) and 1-bromo hexane (3.68 g, 22.4 mmol), in 100 mL of dry ether at 0 °C. Usual workup as described earlier, followed by the distillation (bp 70 °C, 6 mmHg) of the concentrate under reduced pressure gave 2.80 g of **27** (88%). ^{1}H NMR (200 MHz): 5.75-5.05 (m, 1H), 5.25-5.00 (m, 2H), 4.07-4.02 (m, 1H), 1.66-0.93 (m, 10H), 0.90 (t, 3H, J = 6.5 Hz), D_2O exchangeable proton; IR (Neat): 3400 (br), 1660, 1390, 1060; Mass: 142 (M^+).

b) Sodium hydride (0.75 g, 18.0 mmol, 60% dispersion in mineral oil) was washed twice with dry hexane under dry nitrogen to remove the mineral oil. The residue was dried under reduced pressure and suspended in dry THF (50 mL) under the positive pressure of dry nitrogen. **27** was added (2.27 g, 16.0 mmol) dropwise while stirring the contents for 20 min and allowed to reflux for 1 h at 70 °C after the completion of addition. Propargyl bromide (1.90 g, 16.0 mmol) was added dropwise for 10 min to the cooled reaction mixture and contents were allowed to reflux after the addition was complete. After 11 h of reflux at 70 °C, reaction mixture was quenched with water (20 mL) and extracted into ether (100 mL). The ether layer was washed with brine (60 mL), dried over anhydrous Na_2SO_4 and concentrated. Purification of the crude concentrate by column chromatography with EtOAc:hexane (1:24) as eluent furnished 2.15 g of **18** (75%). ^{1}H NMR (200 MHz): 5.75-5.60 (m, 1H), 5.25 (m, 2H), 4.25-4.00 (m, 2H), 3.90-3.80 (qt, 1H, J = 6.5 Hz), 2.40 (t, 1H, J = 2.3 Hz), 1.75-1.25 (bm, 10H), 0.90 (t, 3H, J = 6.5 Hz); ^{13}C NMR (50.4 MHz): 138.34, 118.03, 80.54, 80.45, 73.86, 55.37, 35.45, 31.99, 25.40, 22.80, 14.23; IR (Neat): 3300 (sharp), 2150, 1660; Mass: 180 (M^+).

***Preparation of 2-cylcohexen-1-yl propargyl ether* (19)**:

a) To a stirring solution of cyclohexenone (5.0 g, 52.0 mmol) and catalytic amount of $CeCl_3.7H_2O$ (0.05 g) in methanol (200 mL) at 0 °C, $NaBH_4$ (1.97 g, 52.0 mmol) was added portion wise by means of a solid addition funnel for 25 min. Reaction mixture was further stirred for an additional 6 h at room temperature. After removal of the solvent, ether (250 mL) and water (100 mL) were added to the crude residue and quenched with 10M HCl (60 mL) to dissolve the solid residue completely. Organic layer was separated, washed with water and brine solution successively, dried over anhydrous Na_2SO_4 and concentrated. Concentrate was distilled (bp 70 °C, 18 mmHg) under reduced pressure to give 2-cyclohexen-1-ol (**28**, 4.6 g, 90%). ^{1}H NMR (200 MHz): 5.67-5.58 (m, 2H), 4.17-3.97 (m, 1H), 2.53 (bm, 1H, D_2O exchangeable), 2.03-1.80 (m, 2H), 1.76-1.43 (m, 4H); IR (Neat): 3400 (br), 1660, 1140; Mass: 98 (M^+).

b) Substrate **19** was prepared by the O-alkylation of **28** (4.0 g, 41.0 mmol) with propargyl bromide (4.90 g, 41.0 mmol) by using sodium hydride (1.8 g, 45.0 mmol, 60 % mineral oil) in the similar manner as described previously for **18**. Usual workup followed by the distillation (bp 72 °C, 4 mmHg) of the crude residue under reduced pressure gave 4.60 g (83%) of **19**. ^{1}H NMR (200 MHz): 5.90-5.72 (m, 2H); 4.28-4.20 (d, 2H, J = 2.4 Hz), 4.18-4.05 (m, 1H), 2.42 (t, 1H, J = 2.4 Hz), 2.10-1.90 (m, 2H), 1.90-1.40 (m, 4H); ^{13}C NMR (50.4 MHz): 131.20, 126.95, 73.58, 71.34, 54.82, 24.71, 18.55; IR (Neat): 3250 (sharp), 2160, 1640, 1100; Mass: 136 (M^+).

Preparation of 1-allylcyclohexan-1-yl propargyl ether (**20**):

Substrate **20** was prepared by the O-alkylation of 1-allylcyclohexanol (2.0 g, 14.3 mmol) with propargyl bromide (2.0 g, 16.8 mmol) by using potassium hydride (1.63 g, 45.0 mmol, 35% dispersion in mineral oil) in the similar manner as described previously for **18**. Usual workup followed by the chromatographic purification of the concentrate using EtOAc:hexane (1:99) as eluent gave 1.80 g (71%) of **20**. ^{1}H NMR (200 MHz): 6.00-5.80 (m, 1H), 5.15-5.00 (m, 2H), 4.15-4.05 (d, 2H, J = 2.3 Hz), 2.45-2.40 (t, 1H, J = 2.3 Hz), 2.35-2.25 (d, 2H, J = 6.6 Hz), 1.85-1.25 (m, 10H); ^{13}C NMR (50.4MHz): 133.93, 117.63, 81.61, 76.90, 73.11, 49.33, 41.78, 34.39, 25.92, 22.03; IR (Neat): 3245 (sharp), 2165, 1640; Mass: 178 (M^+).

Preparation of 1-octene-7-yne (**21**):

To a solution of lithium acetylide at -78 °C (generated by passing the dry acetylene gas into liquid ammonia (250 mL) containing finely cut lithium metal (0.55 g, 0.78 mmol) and catalytic amount of $Fe(NO_3)_3$ (0.02g) at -78 °C) 6-bromo-1-hexene (6.0 g, 39.0 mmol) was added dropwise for a period of 30 min. The reaction mixture was further stirred for 6 h, after the completion of addition. 100 mL of dry CH_2Cl_2 was added to the above reaction mixture, quenched with saturated aq. NH_4Cl solution, cooling was removed and liquid ammonia was allowed to evaporate. Finally, an additional 100 mL of dry CH_2Cl_2 was added, organic layer was separated, dried over anhydrous $CaCl_2$ and concentrated. The concentrate was fractionally distilled (bp 120 °C, 760 mmHg) at atmospheric pressure to give **21** (2.40 g, 56%). ^{1}H NMR (200 MHz): 5.90-5.70 (m, 1H), 5.10-4.85 (m, 2H), 2.30-2.00 (m, 4H), 1.90 (t, 1H, J = 2.3 Hz), 1.70-1.40 (m, 4H); IR (Neat): 3080 (sharp), 2240, 1660; Mass: 108 (M^+).

Substrates **18-21** were also irradiated in the analougous manner as described for **7**. Isolated products are characterized as follows.

22a: ^{1}H NMR (200 MHz): 7.75-7.50 (m, 2H), 7.40-7.25 (m, 3H), 6.30 (m, 0.3H), 6.20 (m, 0.7H), 4.55-4.30 (m, 2H), 4.10-3.90 (m, 1H), 3.15-3.00 (m, 2H), 2.60 (m, 1H), 1.55-1.15 (bm, 10H), 0.90 (t, 3H, J = 6.3 Hz); ^{13}C NMR (50.4 MHz): 148.77, 135.54, 133.25, 131.94, 130.10, 129.51, 129.27, 127.84, 127.57, 98.35, 85.82, 81.04, 72.42, 71.23, 50.10, 48.91, 34.01, 32.00, 30.55, 29.93, 29.43, 25.93, 25.81, 22.81, 14.29; IR (Neat): 1610, 1580, 1460, 1440, 1060, 1030; Mass: 416 (M^+); Yield: 64%.

22b: ^{1}H NMR (200 MHz): 7.75-7.50 (m, 4H), 7.40-7.25 (m, 6H), 6.60 (s, 0.7H), 6.50 (m, 0.3H), 4.50-4.40 (m, 1H), 4.30-4.10 (m, 1H), 4.00-3.95 (m, 0.3H), 3.70-3.60 (m, 0.7H), 3.25-3.10 (m, 2H), 2.80-2.65 (m, 1H), 1.50-1.25 (m, 10H), 0.9 (dt, 3H, J = 6.3 Hz); ^{13}C NMR (50.4 MHz): 149.30, 137.76, 135.42, 133.08, 132.18, 131.70, 130.03, 129.51, 129.42, 129.23, 127.72, 127.36, 127.17, 118.11, 109.83, 84.94, 80.94, 73.75, 70.48, 50.61, 49.85, 37.19, 34.95, 34.34, 32.00, 30.94, 29.47, 26.10, 25.97, 22.81, 14.32; IR (Neat): 1640, 1590, 1480, 1440, 1060, 1030; Mass: 492 (M^+); Yield: 28%.

23a: ^{1}H NMR (200 MHz): 7.70 (m, 2H), 7.40-7.20 (m, 3H), 6.40 (sm, 0.7H), 6.20 (s, 0.3H), 4.60 (sm, 0.5H), 4.50 (sm, 0.5H), 4.30 (d, 0.5H, J = 2.6 Hz), 4.25 (d, 0.5H, J = 2.6 Hz), 4.10-4.00 (m, 1H), 3.10-2.95 (dt, 1H, J =

3.9 and 7.8 Hz), 2.65-2.50 (dd, 1H, J = 4.3 and 10.6 Hz), 2.20-1.80 (m, 2H), 1.50-1.40 (m, 4H); ^{13}C NMR (50.4 MHz): 147.21,136.81, 135.40, 130.29, 128.93, 98.76, 79.62, 70.97, 50.21, 43.83, 33.15, 29.58, 27.35; IR (Neat): 1620, 1580, 1460, 1440, 1060, 1040; Mass: 372 (M^+); Yield: 65%.

23b: ^{1}H NMR (200 MHz): 7.70-7.50 (m, 4H), 7.50-7.20 (m, 6H), 6.70 (sm, 1H), 4.45-4.25 (dqt, 2H, J = 2.6 and 13.7 Hz), 4.00 (m, 1H), 3.15-3.00 (dt, 1H, J = 3.9 and 7.8 Hz), 2.65-2.25 (dd, 1H, J = 4.3 and 10.6 Hz), 2.20-1.80 (m, 2H), 1.60-1.40 (m, 4H); ^{13}C NMR (50.4 Mz): 148.34, 146.20, 135.41, 134.17, 133.75, 133.52, 131.26, 129.36, 129.12, 127.81, 126.86, 122.20, 110.39, 78.90, 77.25, 70.21, 68.34, 52.27, 50.51, 44.12, 43.86, 36.62, 32.85, 27.30, 27.10, 21.09; IR (Neat): 1600, 1580, 1460, 1440, 1060, 1040; Mass: 448 (M^+); Yield: 20%.

24a: ^{1}H NMR (200 MHz): 7.60-7.50 (m, 2H), 7.35-7.25 (m, 3H), 6.05 (s, 0.7H), 6.00 (s, 0.3H), 4.25 (d, 2H, J = 13.0 Hz), 3.15-3.00 (m, 2H), 2.75-2.65 (m, 1H), 2.00-1.25 (m, 12H); ^{13}C NMR (50.4 M Hz): 148.34, 137.45, 135.52, 133.05, 132.02, 130.48, 129.75, 129.52, 127.62, 127.31, 102.91, 73.34, 72.85, 48.40, 42.20, 34.53, 26.10, 22.35; IR (Neat): 1620, 1580, 1460, 1440, 1060, 1040; Mass: 414 (M^+); Yield: 60%.

24b: ^{1}H NMR (200 MHz): 7.70-7.55 (m, 4H), 7.45-7.25 (m, 6H), 6.60 (s, 0.7H) 6.50 (s, 0.3H), 4.30 (d, 2H, J = 1.3 Hz), 3.20-3.05 (m, 2H), 2.80-2.70 (m, 1H), 2.00-1.25 (m, 12H); ^{13}C NMR (50.4 MHz): 149.41, 138.02, 135.57, 133.15, 132.36, 131.81, 130.24, 129.75, 129.37, 129.18, 127.84, 127.52, 127.34, 118.24, 110.20, 73.85, 72.64, 71.38, 48.84, 45.42, 42.74, 41.69, 35.34, 34.48, 28.34, 26.42, 23.22, 22.15; IR (Neat): 1640, 1590, 1480, 1440, 1060, 1030; Mass: 490 (M^+); Yield: 20%.

25a: ^{1}H NMR (200 MHz): 7.65-7.50 (m, 2H), 7.45-7.25 (m, 3H), 6.40 (s, 1H), 3.15 (dd, 1H, J = 5.3 and 13.3 Hz), 2.90-2.80 (dd, 1H, J = 7.9 and 13.2 Hz), 2.45 (m, 1H), 2.20 (m, 2H), 1.70-1.45 (bm, 6H); ^{13}C NMR (50.4 MHz): 136.21, 133.53, 132.96, 129.30, 129.11, 106.18, 37.12, 36.26, 34.77, 32.90, 27.41, 24.96; IR (Neat): 1620, 1580, 1460, 1440; Mass: 344 (M^+); Yield: 50%.

25b: ^{1}H NMR (200 MHz): 7.70-7.50 (m, 4H), 7.45-7.25 (m, 6H), 6.75 (s, 1H), 3.10 (dd, 1H, J = 5.2 and 13.2 Hz), 2.95-2.82 (dd, 1H, J = 7.9 and 13.2 Hz), 2.45 (m, 1H), 2.25 (m, 2H), 1.60-1.45 (bm, 6H); ^{13}C NMR (50.4 MHz): 136.94, 133.62, 132.96, 131.70, 129.30, 129.11, 127.88, 127.15, 118.32, 38.42, 36.80, 35.60, 33.40, 27.41, 24.96; IR (Neat): 1600, 1580, 1460, 1440; Mass: 420 (M^+); Yield: 28%.

REFERENCES

1. Ho, T-L. *Carbocyclic construction in Terpene Synthesis*; VCH: New York, 1988.

2. (a) Beckwith, A.L.J.; O'Shea, D.M. *Tetrahedron Lett.* **1986,** *27,* 4525-4528. (b) Stork, G.; Mook, R. Jr. *Tetrahedron Lett.* **1986,** *27,* 4529-4532.(c) Broka, C. A.; Reichert, D.E.C. *Tetrahedron Lett.* **1987,** *28,* 1503-1506. (d) Ichinose, Y.; Wakamatsu, K.; Nozaki, K.; Birbaum, J-L.; Oshima, K.; Utimoto, K. *Chemistry Lett.* **1987,** 1647-1650. (e) Kataoka, T.; Yoshimatsu, M.; Shimizu, H.; Hori, M. *Tetrahedron Lett.* **1990,** *31,* 5927-5930. (f) Nozaki, K.; Oshima, K.; Utimoto, K. *J. Am. Chem. Soc.* **1987,** *109,* 2547-2549. (g) Brumwell, J. E.; Simpkins, N. S.; Terrett, N. K. *Tetrahedron Lett.* **1993,** *34,* 1215-1218. (h) Brumwell, J. E.; Simpkins, N. S.; Terrett, N. K. *Tetrahedron Lett.* **1993,** *34,* 1219-1222.

3. For recent papers on the transition metal mediated cyclisations of dienes and diynes see (a) Fu, G.C.; Grubbs, R.H. *J. Am. Chem. Soc.* **1993,** *115,* 3800-3801. (b) Krafft, M. J.; Scott, I.L.; Romero, R.H.; Feibelman, S.; Vanpelt, C.E. *J. Am. Chem. Soc.* **1993,** *115,* 7199-7207. (c) Fu, G. C.; Nguyen, S. T.; Grubbs, R. H. *J. Am. Chem. Soc.* **1993,** *115,* 9856-9857. (d) Chatani, N.; Fukumoto, Y.; Ida, T.; Murai, S. *J. Am. Chem. Soc.* **1993,** *115,* 11614-11615.

4. (a) Trost, B.M.; Lautens, M. *J. Am. Chem. Soc.* **1985,** *107,* 1781-1783. (b) Trost, B.M.; Lautens, M. *Tetrahedron Lett.* **1985,** *26,* 4887-4890. (c) Trost, B. M.; Tour. J.M. *J. Am. Chem. Soc.* **1987,** *109,* 5268-5270. (d) Trost, B.M.; Lautens, M.; Chan, C.; Jebaratnam, D. J.; Muller, T. *J. Am. Chem. Soc.* **1991,** *113,* 636-644.

5. (a) Tamao, K.; Kobayashi, K.;Ito, Y. *J. Am. Chem. Soc.* **1988,** *110,* 1286-1288. (b) Rajan Babu, T. V.; Nugent, W. A.; Taber, D. F.; Fagan, P. J. *J. Am. Chem. Soc.* **1988,** *110,* 7128-7135. (c) Negishi, E-I.; Holmes. S. J.; Tour, J. M.; Miller, J. A. *J. Am. Chem. Soc.* **1985,** *107,* 2568-2569. (d) Chatani, N.; Morimoto, T.; Muto, T.; Murai, S. *J. Am. Chem. Soc.* **1994,** *116,* 6049-6050.

6. (a) Pandey, G.; Rao, V.J.; Bhalerao, U.T. *J. Chem. Soc. Chem. Commun.* **1989,** 416-418. (b) Pandey, G.; Soma Sekhar, B.B.V. *J. Org. Chem.* **1992,** *57,* 4019-4023.

7. Classical electrophilic selenium species are known to add to acetylenes to give vinyl selenylated products, Filer, C.N.; Ahern, D.; Fazio, R.; Shelton, E.J. *J. Org. Chem.* **1980,** *45,* 1313-1315.

8. Yates, K.; Schmid, G.H.; Regulski, T.W.; Garratt, D. G.; Leung, H-W. McDonald, R. *J. Am. Chem. Soc.* **1973,** *95,* 160-165.

9. Acetylenes are poor nucleophiles, however, in the presence of strong nucleophilic environment, the polarisation of acetylenic π-bonds occurs leading to nucleophilic reactions: For leading references see: Overman, L.E.; Sharp, M.J. *J. Am. Chem. Soc.* **1988,** *110,* 612-614.

10. Pandey, G.; Soma Sekhar, B.B.V.; Bhalerao, U.T. *J. Am. Chem. Soc.* **1990,** *112,* 5650-5651.

11. Back. T.G.; Birss, V.I.; Edwards, M.; Krishna, M.V. *J. Org. Chem.* **1988,** *53,* 3815-3822.

12. Pandey, G.; Soma Sekhar, B.B.V. *J. Chem. Soc. Chem. Commun.* **1993,** 780-782.

13. Ito, O. *J. Am. Chem. Soc.* **1983,** *105,* 850-853.

14. Back, T.G.; Krishna, M.V. *J. Org. Chem.* **1988,** *53,* 2533-2536.

15. Ogawa, A.; Yokoyama, H.; Yokoyama, K.; Masawaki, T.; Kambe, N.; Sonoda, N. *J. Org. Chem.* **1991,** *56,* 5721-5723.

16. Franzi, R.; Geoffroy, M. *J. Organometallic Chem.* **1981,** *218,* 321-324.

17. Eberson, L.; Blum, Z.; Helgee, B.; Nyberg, K. *Tetrahedron* **1978,** *34,* 731-739.

18. Reitstoen, B.; Parker, V. D. *J. Am. Chem. Soc.* **1991,** *113,* 6954-6958.

19. (a) For electrophilic organoselenium based ring closure reactions, see: Nicalaou, K. C.; Petasis, N.A.; Claremon, D.A. In *Organoselenium Chemistry*; Liotta, D. Ed.; Wiley-Interscience: New York, **1987**: pp.

127-162. (b) Paulmier, C. *Selenium Reagents and Intermediates in Organic Synthesis*; Pergamon Press: Oxford, **1986**: pp. 228-255.

20. (a) Clive, D. L. J.; Chittattu, G.; Wong, C. K. *J. Chem. Soc. Chem. Commun.* **1978,** 441-442. (b) Toshimitsu, A.; Uemura, S.; Okano, M. *J. Chem. Soc. Chem. Commun.* **1982,** 87-89.
21. (a) Kametani, T.; Suzuki, K.; Kurobe, H.; Nemoto, H. *J. Chem. Soc. Chem. Commun.* **1979,** 1128. (b) Kametani, T.; Kurobe, H.; Nemoto, H. *J. Chem. Soc. Perkin Trans I* **1981,** 756-760.
22. Sharpless, K.B.; Young, M.W. *J. Org. Chem.* **1975**, *40*, 947-949.
23. (a) Bayer, R.W.; O'Reilly, Jr. E.J. *J. Org. Chem.* **1958**, *23*, 311. (b) Newman, M.S. In *Organic Syntheses*; Horning, E.C. Ed.; John Wiley & Sons: London, **1955**: *Collect. Vol. 3*, pp. 631.
24. Katzenellenbogen, J.A.; Lenox, R.S. *J. Org. Chem.* **1973**, *38*, 326-335.
25. Guermont, J-P. *Bull. Soc. Chem. Franc.* **1953**, 386-390.

(*Received in UK* 25 *October* 1994; *accepted* 25 *November* 1994)