[Cycloalkyl(phenylseleno)methylene]triphenylphosphoranes: Synthesis and Reactions of (Phenylseleno)alkenes

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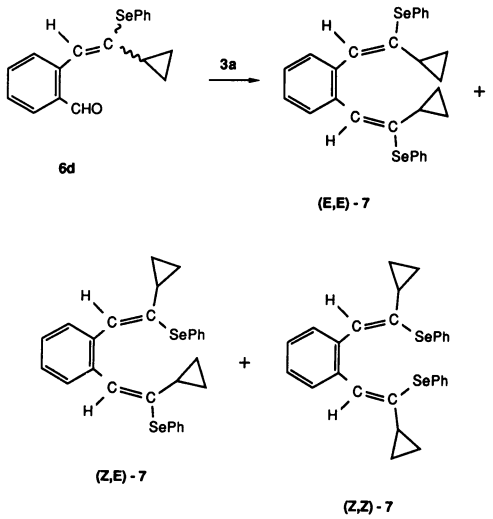
Synopsis. The Wittig reaction of [cyclopropyl(phenylseleno)methylene]- and [cyclobutyl(phenylseleno)methylene]-triphenylphosphoranes with aldehydes produced (*Z*)- and (*E*)-(1-cyclopropyl-1-phenylseleno)- and (1-cyclobutyl-1-phenylseleno)alkenes in moderate to good yields. The oxidation of the (*E*)-selenoalkenes to the corresponding selenoxides and subsequent thermolysis of the selenoxides led to cyclopropyl- and cyclobutylacetylene derivatives in good yields.

We have recently reported the synthesis of [cycloalkyl(phenylseleno)methyl]triphenylphosphonium salts by the reaction of (cycloalkylmethylene)triphenylphosphoranes with benzeneselenenyl bromide.[1] Although selenenylated phosphonium salts are expected to be useful intermediate reagents, their synthetic utilization has, to our knowledge, been little reported.[1-4] In this paper we report the reaction of [cycloalkyl(phenylseleno)methylene]triphenylphosphoranes derived from the corresponding selenophosphonium salts and base with various aldehydes; we also report on a convenient synthesis of cycloalkylacetylene derivatives from the resulting selenoalkenes.

Results and Discussion

Treatment of a [cyclopropyl(phenylseleno)methyl]-triphenylphosphonium salt **2a** with 1.1 molar equiv of *n*-BuLi at room temperature for 0.5 h in THF, followed by a reaction with benzaldehyde (**4a**) at room temperature for 1 h, gave a 1:1 mixture of (*Z*)- and (*E*)-1-cyclopropyl-2-phenylethene (**5a**) (76%) together with butyl phenyl selenide (75%). This result indicates that the phosphonium salt **2a** underwent facile deselenation with *n*-BuLi to give (cyclopropylmethylene)triphenylphosphorane (**1a**). Replacement of *n*-BuLi by NaH in the same reaction led to a mixture of **5a** (30%) and (*Z*)- and (*E*)-1-cyclopropyl-1-phenylseleno-2-phenylethene (**6a**) (2:3 mixture, 48%), while the reaction using lithium bis(trimethylsilyl)amide [LiN(SiMe$_3$)$_2$] as the base produced a 3:4 mixture of (*Z*)- and (*E*)-**6a** in 70% yield. The Wittig condensation of various aldehydes **4a—d** with the phosphorane **3a**, generated from **2a** and LiN(SiMe$_3$)$_2$, gave mixtures of (*Z*)- and (*E*)-(phenylseleno)alkenes **6b—d** in 26—89% yields (see Table 1). Further treatment of isolated **6d** with **3a** led to a 7:6:1 mixture of (*E,E*)-, (*Z,E*)-, and (*Z,Z*)-*o*-bis[2-cyclopropyl-2-(phenylseleno)ethenyl]benzene (**7**) in 62% yield (Eq. 1). Treatment of **3a** with



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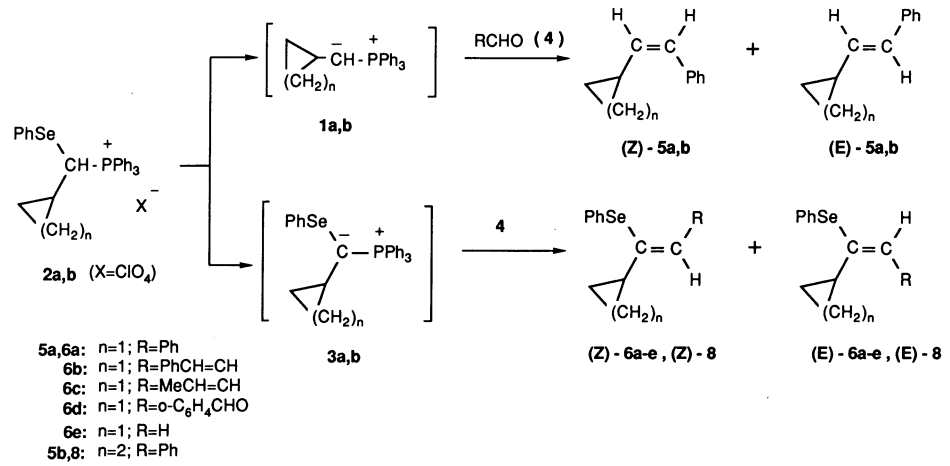
paraformaldehyde smoothly led to the formation of 1-cyclopropyl-1-(phenylseleno)ethene (**6e**) in 74% yield. The [cyclobutyl(phenylseleno)methyl]triphenylphosphonium salt **2b**,[1] on similar treatment with NaH or LiN(SiMe$_3$)$_2$ and **4a** in THF, afforded a 1:1 mixture of (*Z*)- and (*E*)-1-cyclobutyl-1-phenylseleno-2-phenylethene (**8**) (23 or 54%) along with 1-cyclobutyl-2-



Scheme 1.

Table 1.[a] The Reaction of [Cycloalkyl(phenylseleno)methyl]phosphonium Salts **2a, b** with Aldehydes **4** in the Presence of Base

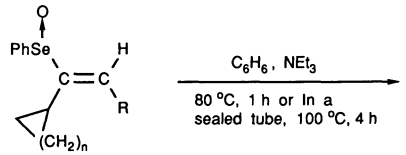
Entry	Salt **2**	Starting materials **4** (R)	Base	Products (% yield,[b] ratio of $Z:E$[c])	
1	**2a**	**4a** (Ph)	BuLi	**5a** (76, 1:1)	
2	**2a**	**4a** (Ph)	NaH	**5a** (30)	**6a** (48, 2:3)
3	**2a**	**4a** (Ph)	$LiN(SiMe_3)_2$		**6a** (70, 3:4)
4	**2a**	**4b** (PhCH=CH)	$LiN(SiMe_3)_2$		**6b** (89, 2:7)
5	**2a**	**4c** (MeCH=CH)	$LiN(SiMe_3)_2$		**6c** (26, 1:3)
6	**2a**	**4d** (*o*-C_6H_4CHO)	$LiN(SiMe_3)_2$		**6d** (62, 1:1)
7	**2a**	**4e** (H)	$LiN(SiMe_3)_2$		**6e** (74)
8	**2b**	**4a** (Ph)	BuLi	**5b** (70, 3:2)	
9	**2b**	**4a** (Ph)	NaH	**5b** (6)	**8** (23, 1:1)
10	**2b**	**4a** (Ph)	$LiN(SiMe_3)_2$	**5b** (8)	**8** (54, 1:1)

a) Unless othewise indicated, all reactions were carried out using **2** (1 mmol), **4** (1.2 mmol), and base (1.1 equiv) in THF (5 cm^3). b) Isolated yields. c) Based on ^1H and/or ^{13}C NMR spectrum.

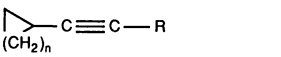
phenylethene (**5b**) (Table 1, Entries 9 and 10). This result exhibits that, even using $LiN(SiMe_3)_2$ as well as NaH, the salt **2b** underwent not only deprotonation but deselenation to generate ylides **1b** and **3b**, leading to the products (Scheme 1).

In an attempt to investigate the reactivities of alkenyl selenides, the oxidation of the selenides (**6a, b, 7**, and **8**) with H_2O_2 at room temperature was carried out to produce the corresponding selenoxides (**9a, b, 10**, and **11**) in good yields.

Selenoxides (*E*)-**9a** and (*E*)-**11** were smoothly converted in benzene containing triethylamine at 80°C for 1 h into cyclopropylethynyl- and cyclobutylethynylbenzenes (**12** and **13**) in 74 and 79% yields. The thermolysis of



(E)-9a, (E)-11, (1E,3E)-9b



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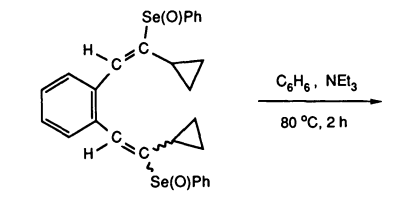
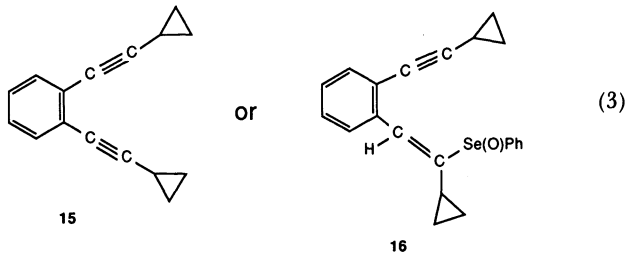
12, 13, 14

(E)-9a, 12 ; n = 1, R = Ph
(E)-11, 13 ; n = 2, R = Ph
(1E,3E)-9b, 14 ; n = 1, R = CH=CHPh

the selenoxide (1*E*,3*E*)-**9b** under rather vigorous conditions (100°C, 4 h) gave a mixture of 4-cyclopropyl-1-phenyl-1-buten-4-yne (**14**) (37%) and the reduced product **6b** (40%)[5] (Eq. 2). A similar thermolysis of diselenoxides (*E,E*)-**10** and (*Z,E*)-**10** formed *o*-bis(cyclopropylethynyl)benzene (**15**) and (*Z*)-1-cyclopropylethynyl-2-[2-cyclopropyl-2-(phenylseleninyl)ethenyl]benzene (**16**) in 96% and quantitative yields (Eq. 3).



(E,E)-10, (Z,E)-10



15 16

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Thus, we have found that phosphonium salts **2a, b** can be used as useful intermediate reagents for the synthesis of alkenes and alkynes bearing small-membered cycloalkyl substituents.

Experimental

General. ^1H NMR spectra were obtained on a JEOL JNM-FX-60 spectrometer in $CDCl_3$ operating at 60 MHz with Me_4Si as an internal standard. IR spectra were recorded with a Shimadzu IR-408 instrument. Mass spectra were taken with a JEOL DX-300 spectrometer.

Reaction of 2a, b[1] with *n*-BuLi (or NaH) or $LiN(SiMe_3)_2$ and 4a—e. General Procedure. To solutions of phosphonium ylides, generated in situ from **2a, b** (1 mmol) and *n*-BuLi or $LiN(SiMe_3)_2$ (1.1 mmol) in dry THF (5 cm^3) at 0°C for 0.5 h or −75°C for 1 h, was added **4a—e** (1.2 mmol). The mixture was stirred at room temperature for 10 or 12 h. After an aqueous NH_4Cl solution was added to the reaction mixture the mixture was concentrated in vacuo, extracted with CH_2Cl_2, washed with water, and dried over Na_2SO_4. After evaporation of CH_2Cl_2, the residue was chromatographed on preparative TLC (silica gel, Wakogel B-5F, hexane) to give pure samples **5a, b** (or **5a, b** and **6a** or **8**) and butyl phenyl selenide or **6a—e** and **8**. The yields of the products are summarized in Table 1.

1-Cyclopropyl-2-phenylethene (**5a**): yield 0.11 g; IR (neat) 1650, 1600 cm^{-1}; ^1H NMR δ=0.39—0.97 (m, 4H, CH_2), 1.20—2.20 (m, 1H, CH), 5.00 (dd, J=9.67 Hz, 11.43 Hz, 0.5H, cis ***H***C=CPhH), 5.65 (dd, J=8.43 Hz, 15.70 Hz, 0.5H, trans ***H***C=CPhH), 6.31 (d, J=11.43 Hz, 0.5H, cis HC=CPh***H***), 6.43 (d, J=15.70 Hz, 0.5H, trans HC=CPh***H***); Found: *m/z* 144.0987. Calcd for $C_{11}H_{12}$: M, 144.0939.

Butyl phenyl selenide:[6] yield 0.16 g.

1-Cyclobutyl-2-phenylethene (**5b**):[7] yield 0.11 g.

(*Z*)-1-Cyclopropyl-1-phenylseleno-2-phenylethene [(*Z*)-(**6a**)]:[8] yield 58 mg; IR (neat) 1595, 1580 cm^{-1}; ^1H NMR

δ=0.30—1.00 (m, 4H, CH_2), 1.00—1.90 (m, 1H, CH), 6.83 (s, 1H, CH=C); Found: *m/z* 300.0417. Calcd for $C_{17}H_{16}Se$: M, 300.0416.

(*E*)-1-Cyclopropyl-1-phenylseleno-2-phenylethene [(*E*)-(**6a**)]:[8] yield 85 mg; IR (neat) 1595, 1580 cm^{-1}; ^1H NMR δ=0.25—0.69 (m, 4H, CH_2), 1.70—2.30 (m, 1H, CH), 6.89 (s, 1H, CH=C); Found: *m/z* 300.0443. Calcd for $C_{17}H_{16}Se$: M, 300.0416.

(*Z*)-1-Cyclobutyl-1-phenylseleno-2-phenylethene [(*Z*)-(**8**)]:[7,8] yield 35 mg.

(*E*)-1-Cyclobutyl-1-phenylseleno-2-phenylethene [(*E*)-(**8**)]:[7,8] yield 35 mg.

(1*E*,3*Z*)-1-Cyclopropyl-4-phenyl-1-phenylseleno-1,3-butadiene [(1*E*,3*Z*)-(**6b**)]:[7,8] yield 65 mg.

(1*E*,3*E*)-1-Cyclopropyl-4-phenyl-1-phenylseleno-1,3-butadiene [(1*E*,3*E*)-(**6b**)]:[7,8] yield 225 mg.

1-Cyclopropyl-1-phenylseleno-1,3-pentadiene (**6c**):[7] yield 70 mg.

o-[2-Cyclopropyl-2-(phenylseleno)ethenyl]benzaldehyde (**6d**):[7] yield 205 mg.

1-Cyclopropyl-1-phenylselenoethene (**6e**)]:[7] yield 165 mg.

o-Bis[2-cyclopropyl-2-(phenylseleno)ethenyl]benzene (**7**).

The reaction was carried out as described above by using **2a** (0.57 g, 1 mmol) and **6d** (0.38 g, 1.2 mmol) to produce 0.33 g (62%) of a 7:6:1 mixture of (*E,E*)-, (*E,Z*)-, and (*Z,Z*)-**7**.[8] Pure samples of individual (*E,E*)-, (*E,Z*)-, and (*Z,Z*)-**7**, were isolated by preparative TLC (hexane).

(*E,E*)-**7**: IR (neat) 1575 cm^{-1}; ^1H NMR δ=0.54—0.71 (m, 8H, CH_2), 1.59—2.05 (m, 2H, CH), 6.82 (s, 2H, CH=C); MS, *m/z* 522 (M^+).

(*E,Z*)-**7**: IR (neat) 1575 cm^{-1}; ^1H NMR δ=0.53—0.75 (m, 8H, CH_2), 1.25—1.98 (m, 2H, CH), 6.69 (s, 1H, CH=C); 6.75 (s, 1H, CH=C); MS, *m/z* 522 (M^+).

(*Z,Z*)-**7**: IR (neat) 1575 cm^{-1}; ^1H NMR δ=0.54—0.81 (m, 8H, CH_2), 1.36—1.69 (m, 2H, CH), 6.68 (s, 2H, CH=C); MS, *m/z* 522 (M^+).

Oxidation of the Selenides 6a, b, 7, and 8. General Procedure. A solution of selenide (1 mmol) in CH_2Cl_2/H_2O (1/1, 10 cm^3) containing H_2O_2 (5 equiv) was stirred at room temperature for 5 h. The reaction mixture was then extracted with CH_2Cl_2, washed with water, and dried over Na_2SO_4. After evaporation of CH_2Cl_2, the residue was chromatographed on preparative TLC (ethyl acetate) to give selenoxides **9a, b, 10**, and **11**.

(*Z*)-1-Cyclopropyl-1-phenylseleninyl-2-phenylethene [(*Z*)-(**9a**)]: yield 258 mg (82%); IR (neat) 1595, 1575 cm^{-1}; ^1H NMR δ=0.00—1.10 (m, 4H, CH_2), 1.60—2.20 (m, 1H, CH), 6.83 (s, 1H, CH=C), 7.00—7.90 (m, 10H, phenyl H).

(*E*)-1-Cyclopropyl-1-phenylseleninyl-2-phenylethene [(*E*)-(**9a**)]: yield 300 mg (95%); IR (neat) 1595, 1575 cm^{-1}; ^1H NMR δ=0.20—1.80 (m, 5H, CH_2 and CH), 7.0—8.0 (m, 11H, CH=C and phenyl H).

(1*E*,3*E*)-1-Phenyl-4-cyclopropyl-4-phenylseleninyl-1,3-butadiene [(1*E*,3*E*)-(**9b**)]:[7] yield 229 mg (70%).

(*E,E*)-*o*-Bis[2-cyclopropyl-2-(phenylseleninyl)ethenyl]benzene [(*E,E*)-(**10**)]:[7] yield 552 mg (quant).

(*E,Z*)-*o*-Bis[2-cyclopropyl-2-(phenylseleninyl)ethenyl]benzene [(*E,Z*)-(**10**)]:[7] yield 550 mg (quant).

(*Z*)-1-Cyclobutyl-1-phenylseleninyl-2-phenylethene [(*Z*)-(**11**)]:[7] yield 330 mg (quant).

(*E*)-1-Cyclobutyl-1-phenylseleninyl-2-phenylethene [(*E*)-(**11**)]:[7] yield 330 mg (quant).

Thermolysis of the Selenoxides (*E*)-9a, (*E*)-11, (*E,E*)-10, (*E,Z*)-10, or (1*E*,3*E*)-9b. General Procedure. A solution of a selenoxide (1 mmol) in dry benzene (5 cm^3) containing small amounts of triethylamine was heated under reflux for 1 h or at 100 °C for 4 h in a sealed tube. After evaporation of benzene, the residue was chromatographed on preparative TLC (hexane or ethyl acetate) to give an acetylene.

(Cyclopropylethynyl)benzene (**12**): yield 105 mg (74%); IR (neat) 2240 cm^{-1}; ^1H NMR δ-0.50—1.00 (m, 4H, CH_2), 1.00—1.70 (m, 1H, CH); Found: *m/z* 142.0754. Calcd for $C_{11}H_{10}$: M, 142.0782.

(Cyclobutylethynyl)benzene (**13**):[7] yield 123 mg (79%).

o-Bis(cyclopropylethynyl)benzene (**15**):[7] yield 198 mg (96%).

(*Z*)-1-Cyclopropylethynyl-2-[2-cyclopropyl-2-(phenylseleninyl)ethenyl]benzene (**16**):[7] yield 375 mg (quant).

1-Phenyl-4-cyclopropyl-1-buten-4-yne (**14**):[7] yield 62 mg (37%).

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5) Thermolysis of the selenoxide (1*E*,3*E*)-**9b** at 80 °C for 2 h gave only the reduced product **6b** in 46% yield.

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7) The new compounds **5b, 6b—e, 8, 9b, 10, 11, 13, 14, 15**, and **16** were fully characterized by the IR, ^1H NMR, and mass spectra, and gave satisfactory high resolution mass spectra.

8) The stereochemistry of each of stereoisomeric vinylselenides **6a—d, 7**, and **8** were tentatively assigned on the basis of their ^1H and/or ^{13}C NMR spectral data of isolated pure isomers or mixture and chemical properties. Furthermore, their stereostructures were unambiguously confirmed by thermolysis of the corresponding selenoxides.