Synthesis and Reactions of a Stable 2-Selenanaphthalene, 1-Cyano-2-methyl-2-selenanaphthalene

Mikio Hori,* Tadashi Kataoka, Hiroshi Shimizu, Kazuhiro Tsutsumi, and Mitsuhiro Yoshimatsu

Gifu Pharmaceutical University, 6-1 Mitahora-higashi 5-chome, Gifu 502, Japan

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A stable 2-selenanaphthalene, 1-cyano-2-methyl-2-selenanaphthalene (**7**), was prepared by deprotonation of 1-cyano-2-methylisoselenochromenium salt (**6**) with triethylamine in ethanol. The selenanaphthalene **7** was air-sensitive and rearranged thermally in aprotic polar solvents to form 1-cyano-1-methylisoselenochromene (**8**) in good yield. Reaction of the selenanaphthalene **7** with dimethyl acetylenedicarboxylate in benzene afforded a benzocycloheptene derivative **15**, whereas the same reaction in sulfolane afforded a naphthalene derivative **16** besides **15**. Furthermore, the reaction in acetonitrile yielded a novel bisbenzocycloheptenyl derivative **17** together with **15**. In contrast, the reaction of **7** with methyl propiolate gave a 2:1 adduct **23** in addition to the rearranged product **8** and isoselenochromene **3**. Reactions with olefins bearing an electron-withdrawing group gave cyclopropane derivatives **27–32**.

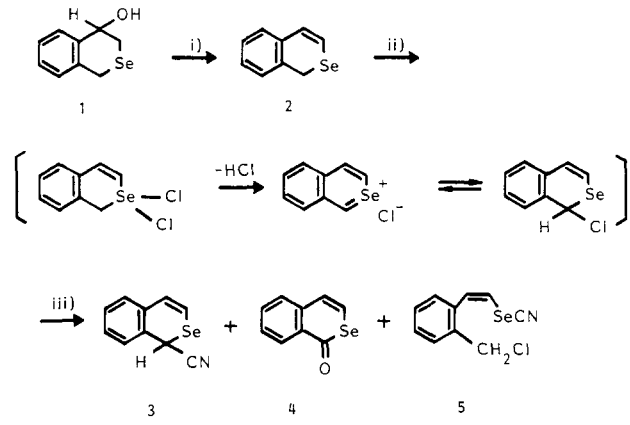
In 1973 we reported that the reaction of selenoxanthylium salts with phenyllithium afforded 10-phenyl-10-selenaanthracenes.[1] However, 10-(*p*-methoxyphenyl)-9-phenyl-10-selenaanthracene generated by deprotonation of 10-(*p*-methoxyphenyl)-9-phenylselenoxanthenium salt rearranged easily to 9-(*p*-methoxyphenyl)-9-phenylselenoxanthene.

Mislow and his workers reinvestigated these reactions in order to clarify these contradictory results and reported that selenabenzenes are ylides and less stable than thiabenzenes.[2] They also claimed that the products resulting from reaction of selenoxanthylium salts with phenyllithium were oligomers of undetermined composition. However, on the basis of our study on thiaanthracenes[3] we believe that these products are mixtures of compounds produced through radical reactions. Cyclic selenium ylides, selenabenzenes without an electron-withdrawing group, have not been isolated because they are labile and easily rearrange as mentioned above. Therefore, we planned to synthesize stable selenabenzene derivatives in which the ylidic C–Se bond would constitute a part of a cyclic conjugated system involving six electrons. For this purpose, 2-cyano-1-methyl-1-selenanaphthalene was prepared, and its thermal and photochemical reactions were examined.[4]

On the other hand, the C–Se bond is weaker than the corresponding C–S bond, and the C–Se–C bond angle is smaller than that of C–S–C.[5] We expected that these physicochemical differences between selenium and sulfur compounds might explain the different reactivities of cyclic selenium ylides and cyclic sulfur ylides which we have much studied.[6]

This report describes the synthesis and reactions of a selenanaphthalene stabilized by a cyano group, 1-cyano-2-methyl-2-selenanaphthalene.

Scheme I



Reagents: i, PPSE, $ClCH_2CH_2Cl$; ii, SO_2Cl_2 or NCS; iii, Me_3SiCN

Table I. Preparation of 1-Cyanoisoselenochromene (3)

reagents (molar ratio to **2**)		products (% yield)			
chlorination	cyanation	**2**	**3**	**4**	**5**
SO_2Cl_2 (1)	Me_3SiCN (2.3)		29	11	
SO_2Cl_2 (1)	Me_3SiCN (3) Et_3N (2)		33	34	
SO_2Cl_2 (1)	Me_3SiCN (2.3) CsF (0.1)		35		
SO_2Cl_2 (1)	Me_3SiCN (2.3) Bu_4NF (0.1)	7	76		
SO_2Cl_2 (1)	Me_3SiCN (2.3) $SnCl_4$ (0.3)			37	
NCS (2)	Me_3SiCN (3) $SnCl_4$ (0.3)		52		

Results and Discussion

Synthesis of 1-Cyano-2-methyl-2-selenanaphthalene (7). The synthesis of 1-cyanoisoselenochrome (**3**) from isoselenochroman-4-ol (**1**) is shown in Scheme I. Dehydration of **1** with polyphosphoric acid trimethylsilyl ester (PPSE)[7] afforded isoselenochromene (**2**), quantitatively. In order to introduce a cyano group into the 1-position of **2**, we planned to prepare 2-selenanaphthylium perchlorate from **2**, and then to carry out a cyanation with sodium cyanide. However, an explosion occurred in the synthesis of selenanaphthylium perchlorate. (*Warning! Isoseleno-*

(1) (a) Hori, M.; Kataoka, T.; Shimizu, H.; Hsue, C. F. *Chem. Lett.* **1973**, 391. (b) Hori, M.; Kataoka, T.; Hsue, C. F. *Chem. Pharm. Bull.* **1974**, *22*, 15. (c) Hori, M.; Kataoka, T.; Shimizu, H.; Hsu, C. F.; Asahi, Y.; Mizuta, E. *Ibid.* **1974**, *22*, 32.

(2) Stackhouse, J.; Senkler, G. H., Jr.; Maryanoff, B. E.; Mislow, K. *J. Am. Chem. Soc.* **1974**, *96*, 7835.

(3) Hori, M.; Kataoka, T.; Shimizu, H.; Itagaki, Y.; Higuchi, T. *Tetrahedron Lett.* **1979**, 1603. Hori, M.; Kataoka, T.; Shimizu, H.; Ban, M.; Matsushita, H. *J. Chem. Soc., Perkin Trans. 1* **1987**, 187.

(4) Hori, M.; Kataoka, T.; Shimizu, H.; Tsutsumi, K.; Imaoka, S. *Heterocycles* **1987**, *26*, 2365.

(5) Hargittai, I.; Rozsondai, B. In *The Chemistry of Organic Selenium and Tellurium Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1986; Vol. 1, Chart 3.

(6) Hori, M.; Kataoka, T. *Yuki Gosei Kagaku Kyokai Shi* **1987**, *45*, 232.

(7) Imamoto, T.; Yokoyama, M. *Tetrahedron Lett.* **1981**, *22*, 1803.

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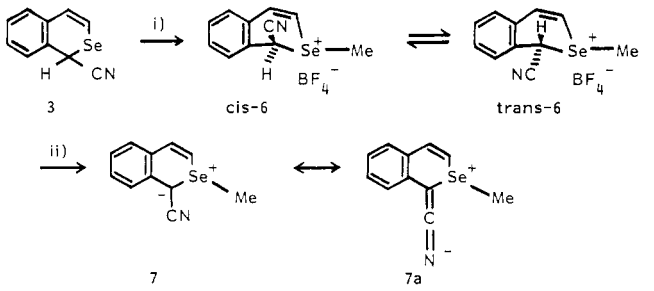
Scheme II



chromene (2) was treated with sulfuryl chloride and then 70% perchloric acid to give the precipitate of selenanaphthylium perchlorate. When the perchlorate was filtered with a glass filter, the explosive decomposition took place.) Moreover, the selenanaphthylium salt was labile to water. Therefore, we explored a one-pot synthesis of 1-cyanoisoselenochromene (**3**) by chlorination and cyanation of **2**. Reagents used for the procedure and the products are shown in Table I.

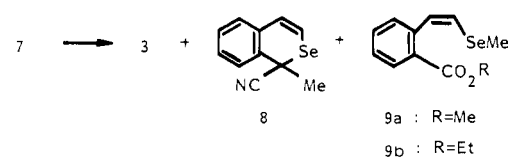
Compound **2** was treated with sulfuryl chloride and then trimethylsilyl cyanide in the presence of tetrabutylammonium fluoride to afford a cyanated product **3** in 76% yield. The use of cesium fluoride, triethylamine, or tin(VI) chloride[8] was not effective for enhancing the reactivity of 2-selenanaphthylium chloride (or 1-chloroisoselenochromene) or trimethylsilyl cyanide. The structures of by-products, isoselenocoumarin (**4**) and 2-[(*o*-chloromethyl)phenyl]vinylselenocyanate (**5**), were determined by mass, NMR, and IR spectroscopy.

Methylation of 1-cyanoisoselenochromene (**3**) with methyl iodide and silver tetrafluoroborate afforded 1-cyano-2-methylisoselenochromenium tetrafluoroborate (**6**) in 86% yield. The ^1H NMR spectrum of the selenonium salt **6** showed two methyl signals at δ 2.68 and 2.75, indicating the presence of trans and cis isomers. On the basis of the anisotropic effect of the cyano group, the methyl signal appearing at lower field by 0.07 ppm was assigned to the cis compound. A long-range coupling (J = 1.5 Hz) was observed between the olefinic proton at C-3 and the methine proton at C-1 in *cis*-**6**. The isomer ratio of the selenonium salt **6** was cis/trans = 3/1 immediately after dissolving the crude product and changed to 1/1.1 after heating a solution of the mixture in $CDCl_3$ at 50 °C for 15 min or after recrystallization from acetonitrile–hexane. This facile inversion indicates that *cis*-**6** is the kinetically favored and *trans*-**6** is the thermodynamically stable isomer.

The mixture of *cis*- and *trans*-**6** was treated with triethylamine in ethanol to give 1-cyano-2-methyl-2-selenanaphthalene (**7**) as orange needles in 75% yield. The IR absorption band of the cyano group of the selenanaphthalene **7** was observed at 2130 cm^{-1} as a broad, very strong absorption, shifted to lower frequency than normal by about 100 cm^{-1}. This observation provides strong evidence that the selenanaphthalene **7** is stabilized by contribution of the ketenimine canonical structure **7a**.

Thermal Stability of the Selenanaphthalene 7. Scheme III shows the thermal reactions of the selenanaphthalene **7**; the results obtained under various conditions are summarized in Table II.

Scheme III



Scheme IV

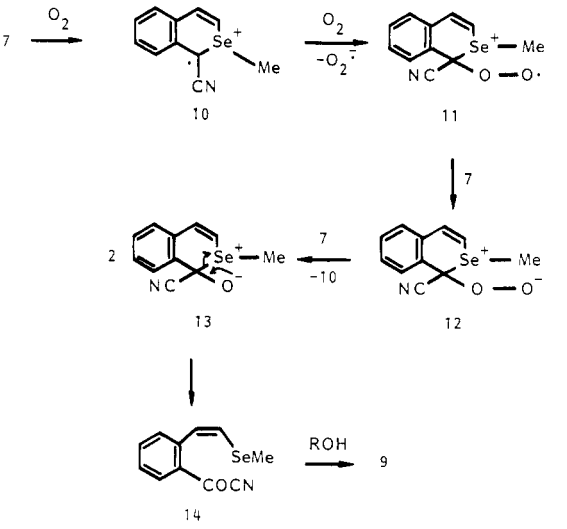


Table II. Thermal Reactions of Selenanaphthalene 7

entry no.	conditions	products (% yield)
1	benzene, reflux, 3 h	**8** (11)
2	dichloromethane, reflux, 3 h	**8** (12)
3	benzene, rt,[a] 24 h	**8** (16)
4	acetonitrile, rt, 24 h	**3** (10), **8** (38)
5	nitromethane, rt, 24 h	**3** (12), **8** (73)
6	sulfolane, rt, 48 h	**3** (20), **8** (53)
7	acetone, rt, 48 h	**3** (10), **8** (15), **9a** (6)
8	methanol, rt, 48 h	**8** (40), **9a** (7)
9	ethanol, rt, 43 h	**3** (5), **8** (24), **9b** (7)
10	dimethyl sulfoxide, rt, 48 h	**3** (11), **8** (48)

[a] rt, room temperature.

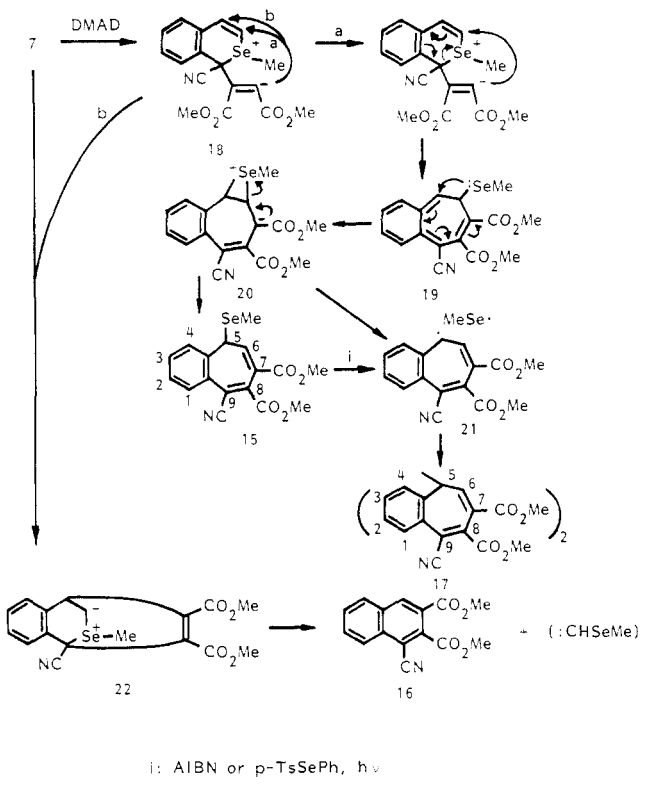
Selenanaphthalene **7** was heated to give 1-cyano-1-methylisoselenochromene (**8**), but, since the yield of the rearranged product **8** was not affected by temperature, the reactions were conducted in an appropriate solvent at room temperature. The rearranged product **8** was obtained in good yields together with the demethylated product **3** in aprotic polar solvents such as nitromethane, sulfolane, and dimethyl sulfoxide. Esters **9a** and **9b** were formed as by-products by methyl and ethyl alcohol, respectively. Methyl ester **9a** was also obtained in 6% yield from the reaction in acetone. This can be explained as intermediate **14** reacts with methanol, a stabilizer for dichloromethane, during preparative TLC.

To explain the elimination of the cyano and introduction of the oxygen-containing functional group, we propose the mechanism shown in Scheme IV in which oxygen in the air reacts with selenanaphthalene **7**. Russell and Bemis[9] have proposed a mechanism for the formation of alkoxide anions by reaction of carbanions with oxygen. This mechanism can be applied to the formation of betaine **13** by reaction of the ylide carbanion with oxygen. Benzoyl cyanide **14** is formed by isomerization with cleavage of the C_1–Se bond of **13** and then reacts with an alcohol to give ester **9**. The mechanism shown in Scheme IV is supported

(8) Reetz, M. T.; Chatziiosifidis, I.; Kuenzer, H.; Mueller-Starke, H. *Tetrahedron* **1983**, *39*, 961.

(9) Russell, G. A.; Bemis, A. G. *J. Am. Chem. Soc.* **1966**, *88*, 5491.

Scheme V



by the yield of ester **9** which increased to 14% when the reaction was carried out in an oxygen atmosphere.

Reactions with Acetylenic Electrophiles. It is well known that ylides react with electrophiles.[6] Since selenanaphthalene **7** is cyclic, we expected some interesting ring transformation reactions.

Reaction of ylide **7** with dimethyl acetylenedicarboxylate (DMAD) in benzene at room temperature gave a benzocycloheptene derivative **15** in 61% yield. The reaction in sulfolane afforded naphthalene derivative **16** (37%) together with benzocycloheptene **15** (17%), while the reaction in acetonitrile produced **15** (17%) and a bisbenzocycloheptenyl derivative **17** (56%).

The structure of the benzocycloheptene **15** was elucidated by comparing its spectral features with those of the corresponding sulfur compound.[10] The ^{1}H NMR spectrum showed a characteristic broad signal due to a methine proton (H-5) of 5*H*-benzocycloheptene at δ 4.75. It has been shown that the H-5 signal of 5*H*-benzocycloheptene is broadened by ring inversion of the cycloheptene ring.[11] The signal of an olefinic proton (H-6) overlapped multiplets of the aromatic protons at δ 7.26–7.51. The methylseleno group appeared as a singlet at δ 1.94 and two methoxycarbonyl groups as two singlets at δ 3.73 and 3.94. The ^{13}C NMR spectrum exhibited the C-5 signal at δ 38.98 as a doublet. The IR spectrum showed two absorption bands due to the ester carbonyl groups at 1740 and 1725 cm^{-1} and a sharp band of the cyano group at 2230 cm^{-1}. Compound **16** was identical with dimethyl 1-cyanonaphthalene-2,3-dicarboxylate[10] in terms of IR and ^{1}H NMR spectra and mixture melting point. The structure of **17** was based on its spectral data and the molecular formula of $C_{32}H_{24}N_2O_8$. The ^{1}H NMR spectrum showed the absence of the methylseleno group. The methine protons (H-5,5′) appeared as a broad singlet at δ 4.19, and two methoxy protons of the ester groups as two singlets at δ 3.69 and 3.91. The signals of the olefinic protons (H-6,6′) overlapped the multiplets of the aromatic protons at δ 6.88–7.96. The ^{13}C NMR spectrum exhibited the C-5 signal at δ 40.85 as a doublet and the C-4 signal at δ 120.74, also as a doublet. The UV spectrum closely resembles that of 5*H*-benzocycloheptene **15**. Therefore, the two compounds have the same conjugated system, and hence structure **17** was assigned as bis(9-cyano-7,8-dimethoxycarbonyl-5*H*-benzocyclohepten-5-yl).

Scheme V shows a plausible mechanism for formation of the benzocycloheptene **15** and the naphthalene **16**. The first intermediate, betaine **18**, is formed by Michael addition of the carbanion of the ylide **7** to DMAD. Fission of the C_1–Se bond of the betaine **18**, followed by shift of the double bonds, generates a carbocation at the α-position of the selenium atom (path a), which is attacked by the vinylic carbanion. The resulting 6*H*-benzocycloheptene **19** has an unstable ortho-quinoid structure, so that a shift of the double bonds takes place and the methylseleno group migrates to the 5-position through an episelenonium betaine **20**. Alternatively, ylide **7** may react with DMAD by a concerted (Diels–Alder reaction) or stepwise mechanism (path b from **18**) in which the vinylic carbanion of the betaine **18** attacks the 4-position to give an ylide intermediate **22**. The ylide **22** decomposes to naphthalene **16** and methylselenocarbene.

In order to elucidate the mechanism for the formation of the bisbenzocycloheptenyl **17**, the experiments were carried out. We assumed that oxidative elimination of the methylseleno group is the first step in the formation of **17**. However, **17** was not formed when air was bubbled into a solution of **15** in acetonitrile or when **15** was exposed to an oxygen atmosphere. Oxidation of **15** with *m*-chloroperbenzoic acid (*m*-CPBA) also did not furnish **17**.

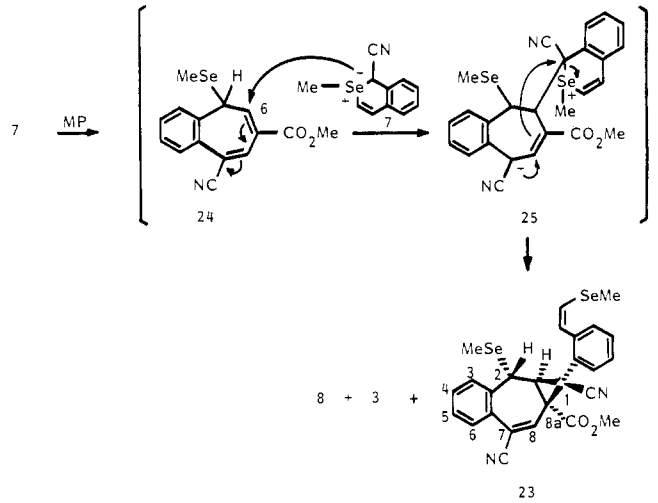
Next, we examined the reaction of **15** with certain radical sources. Treatment of **15** with 0.1 equiv of azobisisobutyronitrile (AIBN) afforded **17** in 30% yield. Compound **17** was also formed by the reaction of **15** with phenylseleno radical generated from a photochemical decomposition with *Se*-phenyl *p*-tolueneselenosulfonate in 80% yield. Reactions of **15** with ylide **7** or with catalytic amounts of **7** and DMAD were conducted, but the yield of dimer **17** did not increase significantly. These results indicate that radical **21** may be formed in the step involving the 5*H*-benzocycloheptene **19** to the episelenonium betaine **20** or by radical decomposition of betaine **20**.

In contrast to the reaction with DMAD, reaction of the ylide **7** with methyl propiolate (MP) gave a 2:1 adduct **23** of **7** and MP in 10–28% yield, accompanied by rearranged product **8** and demethylated product **3**. Elemental analysis and mass spectral data showing the molecular ion peak at *m/z* 554 indicate a molecular formula of $C_{26}H_{22}N_2O_2Se_2$, corresponding to **23**. The IR spectrum showed the characteristic absorption bands of the cyano and ester groups at 2240 and 1740 cm^{-1}, respectively. The ^{1}H NMR spectrum exhibited two singlets due to the methylseleno groups at δ 2.23 and 2.24, a doublet (J = 11.5 Hz) due to the methine proton at δ 3.27, a doublet (J = 11.5 Hz) due to the cyclopropane methine proton at δ 4.37, and two doublets (J = 10.3 Hz) due to the cis olefinic protons at δ 6.89 and 7.09. The H-8 proton appeared in the aromatic region. The coupling constant (J = 11.5 Hz) between the methine protons at the 1a- and 2-positions indicates that their configuration is trans. In the ^{13}C NMR spectrum, two methylseleno groups appeared as two quartets at δ 6.13

(10) Hori, M.; Kataoka, T.; Shimizu, H.; Narita, K.; Ohno, S.; Ogura, H.; Takayanagi, H.; Iitaka, Y.; Koyama, H. *J. Chem. Soc., Perkin Trans. 1* **1988**, 1885.

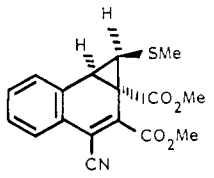
(11) (a) Tochtermann, W.; Schnabel, G.; Mannschreck, A. *Ann. Chem.* **1968**, *711*, 88. (b) Foehlisch, B.; Fischer, C.; Rogler, W. *Chem. Ber.* **1978**, *111*, 213.

Scheme VI



and 8.28, the cyclopropane ring at δ 28.88, 40.23, and 40.43, the C-2 at δ 44.43, two cyano groups at δ 115.72 and 117.87, the carbonyl group at δ 165.26, and aromatic and olefinic carbons in the region of δ 120.46–138.83. Comparison of these spectral data with those of the corresponding sulfur compound whose structure has been determined by X-ray analysis[10] provides firm evidence for the proposed structure. Scheme VI shows a plausible mechanism for formation of **23**. The benzocycloheptene intermediate **24** is formed by reaction of the ylide **7** with MP in a way similar to the reaction with DMAD. Michael addition of the carbanion of another molecule of **7** to the 6-position and attack of the resulting anion on the carbon adjacent to the selenonio group followed by cyclopropanation and ring-opening of the isoselenochromene, leads to product **23**.

The reactions of selenanaphthalene **7** with electron-deficient acetylenes differ in some respects from those of the corresponding thianaphthalene. Thus bisbenzocycloheptenyl **17** was not formed from the thianaphthalene. The thianaphthalene gave dihydrocyclopropa[*a*]-naphthalene **26**, but the selenanaphthalene did not pro-



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duce the corresponding selenium analogues. Although the thianaphthalene did not react with the electron-deficient olefins, the differences in the reactivities of the selenanaphthalene and the thianaphthalene toward the acetylenes mentioned above led us to examine the reaction of selenanaphthalene **7** with the olefins.

Reactions with Olefins. The selenanaphthalene did not react with styrene, dimethyl fumarate, and vinyl sulfones as shown in Table III. However, yields of the 1,2-rearranged product **8** increased considerably in the presence of vinyl sulfones such as *trans*-styryl tolyl sulfone and 3-(*p*-tosyl)sulfolene, although, in the presence of only 0.1 equiv of *trans*-styryl tolyl sulfone, the yield was as low as that without the vinyl sulfone (see Table III). The function of the vinyl sulfones in increasing the yields is not clear. Scheme VII shows the reaction of the ylide **7** with monosubstituted olefins. Reaction with acrylonitrile afforded *r*-1,*t*-2-dicyano-1-[2-(*cis*-2-methylselenovinyl)-phenyl]cyclopropane (**27**) and the *r*-1,*c*-2-dicyano isomer

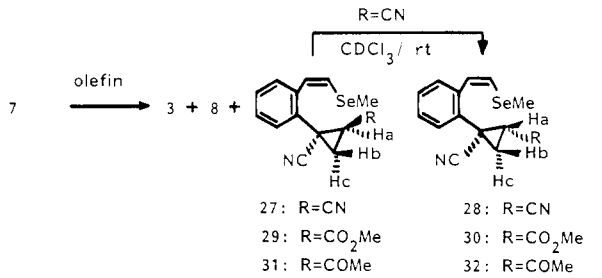
Table III. Reactions of Ylide 7 with Electron-Deficient Olefins

entry no.	olefins (molar ratio)	solvent	products (% yield)
1	(*E*)-styryl *p*-tolyl sulfone (1.7)	MeCN	**8** (61)
2	(*E*)-styryl *p*-tolyl sulfone (1.7)	C_6H_6	**8** (59)
3	(*E*)-styryl *p*-tolyl sulfone (0.1)	C_6H_6	**3** (14), **8** (18)
4	3-(*p*-tosyl)sulfolene (1.7)	MeCN	**3** (6), **8** (66)
5	styrene (1.7)	C_6H_6	**3** (9), **8** (17)
6	acrylonitrile (1.1)	MeCN	**3** (trace), **27** (29), **28** (53)
7	methyl acrylate (1.1)	MeCN	**8** (13), **29** (18), **30** (33)
8	methyl vinyl ketone (1.1)	MeCN	**8** (3), **31** (37), **32** (55)

Table IV. Chemical Shifts and Coupling Constants of Cyclopropane Ring Protons of Products 27–32

	chemical shifts (δ)			coupling constants (Hz)		
compd no.	H_a	H_b	H_c	J_{ab}	J_{bc}	J_{ca}
27	2.52	2.10	1.96	6	6	9
28	2.08–2.14	1.84–1.92	2.08–2.14			
29	2.71	2.11	1.99	7	6	9
30	2.31	1.71	2.15–2.21	9	5	7
31	2.95	2.12–2.20	1.90	7	5	9
32	2.49	1.69	2.12–2.20	8	5	6

Scheme VII



(**28**) in 29% and 53% yields, respectively. The high resolution mass spectrum of **27** indicated molecular formula $C_{14}H_{12}N_2Se$ corresponding to a 1:1 adduct of the ylide and acrylonitrile. In the ^1H NMR spectrum, the cyclopropane ring protons (H_a, H_b, and H_c) were each observed as a doublet of doublets at δ 2.52 (J = 6, 9 Hz), 2.10 (J = 6, 6 Hz), and 1.96 (J = 9, 6 Hz), respectively (Table IV). Assignment of the signals was made on the basis of relative chemical shifts and coupling constants. This cis coupling of cyclopropane ring protons is larger than the trans coupling.[12] The cis geometrical configuration of the vinyl group of **27** was determined by the vicinal coupling constant (J = 10 Hz). The ^{13}C NMR spectrum showed the cyclopropane carbons at δ 13.78 (doublet), 19.44 (singlet), and 20.32 (triplet).

The ^1H NMR spectrum of **28** was so complex that chemical shifts and coupling constants of the cyclopropane ring protons could not be determined exactly. The ^{13}C NMR spectrum exhibited the cyclopropane carbons at δ 13.53, 20.87, and 20.99.

In $CDCl_3$ the *r*-1,*t*-2-dicyano compound **27** gradually isomerized to the stable *r*-1,*c*-2 isomer **28** at room temperature. Viehe and his co-workers have reported cis–trans isomerizations of cyano-substituted cyclopropanes.[13]

(12) Graham, J. D.; Rogers, M. T. *J. Am. Chem. Soc.* **1962**, *84*, 2249. Trost, B. M.; Arndt, H. C. *J. Org. Chem.* **1973**, *38*, 3140.

Methyl acrylate and methyl vinyl ketone reacted similarly with **7** to afford cis–trans mixtures of the cyclopropane derivatives **29**, **30** and **31**, **32**, respectively. Their structures were determined spectroscopically in a way similar to that of **27**. The cis–trans isomerization in $CDCl_3$ was not observed between **29** and **30** or between **31** and **32** at room temperature.

Experimental Section

Melting points were determined by using a Yanagimoto micromelting point apparatus and are uncorrected. Elemental analyses were performed at the Microanalytical Laboratory of Gifu Pharmaceutical University. ^1H nuclear magnetic resonance (^1H NMR) spectra were run on Hitachi R-20B (60 MHz) and JEOL GX-270 (270 MHz) spectrometers. ^{13}C nuclear magnetic resonance (^{13}C NMR) spectra were determined with a JEOL GX-270 spectrometer. Chemical shifts are expressed in parts per million (ppm) with respect to tetramethylsilane as an internal standard. Splitting patterns are designated as follows: s, singlet; d, doublet; t, triplet; q, quartet. Infrared (IR) spectra were determined on a JASCO IR A-100 infrared spectrometer and are expressed in reciprocal centimeters. Mass spectra (MS) were obtained using a JEOL JMS-D300 spectrometer with a direct-insertion probe, at an ionization voltage of 70 eV. High resolution mass determination was conducted on the JMA 2000 on-line system. Analytical and preparative thin-layer chromatography (preparative TLC) were performed using E.M. Merck silica gel 60PF-254.

Isoselenochromene (2). A solution of polyphosphoric acid trimethylsilyl ester (PPSE) in 1,2-dichloroethane was prepared by refluxing a mixture of phosphorus pentoxide (13 g) and hexamethyldisiloxane (27.5 mL) in dry 1,2-dichloroethane (53 mL) for 1 h under nitrogen.[7] Isoselenochroman-4-ol[14] (**1**) (6.0 g, 28 mmol) was added to the PPSE solution. The mixture was refluxed for 1 h under nitrogen and then cooled. Water (100 mL) was added to it and the organic layer was separated. The aqueous layer was extracted with dichloromethane. The organic layer and the extracts were combined, washed with water, and dried ($MgSO_4$). The solvent was evaporated to dryness and the residue was purified by column chromatography on silica gel, eluting with hexane–dichloromethane (10:1). A pale yellow oil (4.72 g, 86%) was obtained: ^1H NMR (60 MHz) ($CDCl_3$) δ 3.83 (2 H, s, 1-H), 6.60–7.76 (6 H, m, ArH, 3-H and 4-H). High resolution mass calcd for C_9H_8Se: m/z 195.9790. Found: m/z 195.9774.

1-Cyanoisoselenochromene (3). (a) Sulfuryl chloride (3.46 g, 26 mmol) was added to a cooled solution of isoselenochromene (**2**) (5.00 g, 26 mmol) in dry 1,2-dichloroethane (130 mL) at −30 °C under nitrogen. After the mixture was stirred for 1 h at that temperature, trimethylsilyl cyanide (7.62 g, 76.8 mmol) was added to it. The temperature was gradually raised to 0 °C and tetrabutylammonium fluoride (0.53 g, 2.6 mmol) was added at once. After stirring for 10 h at 0 °C, the reaction mixture was poured into water. The organic layer was separated and the mixture was extracted with dichloromethane. The organic layer and the extracts were combined and dried ($MgSO_4$). The solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel, eluting with hexane–dichloromethane (5:1). Recrystallization from hexane–dichloromethane afforded colorless needles (5.2 g, 76%), mp 97.5–98 °C: IR (KBr, cm^{-1}) 2240 (CN); ^1H NMR (270 MHz) ($CDCl_3$) δ 4.76 (1 H, br s, 1-H), 6.88 (1 H, d, J = 9.8 Hz, 3-H), 7.10 (1 H, d, J = 9.8 Hz, 4-H), 7.22–7.66 (4 H, m, ArH). Anal. Calcd for $C_{10}H_7NSe$: C, 54.56; H, 3.21; N, 6.36. Found: C, 54.31; H, 3.16; N, 6.27.

(b) A similar operation without catalysis in dichloromethane at −70 °C gave 1-cyanoisoselenochromene (**3**) (29%) and isoselenocoumarin (**4**) (11%). Compound **4** was recrystallized from hexane–dichloromethane as colorless needles, mp 75–76 °C: IR (KBr, cm^{-1}) 1640 (CO); ^1H NMR (60 MHz) ($CDCl_3$) δ 7.25–8.33 (6 H, m, ArH). High resolution mass calcd for C_9H_6OSe: m/z 209.9584. Found: m/z 209.9598.

(c) A similar operation using $SnCl_4$ in 1,2-dichloromethane at −30 °C gave 2(*Z*)-[2′-(chloromethyl)phenyl]vinylselenocyanate (**5**) as a yellow oil: IR (film, cm^{-1}) 2180 (CN); ^1H NMR (60 MHz) ($CDCl_3$) δ 4.55 (2 H, s, CH_2Cl), 6.93 (1 H, d, J = 9 Hz, 1-H), 7.08–7.33 (5 H, m, ArH and 2-H). High resolution mass calcd for $C_{10}H_8ClNSe$: m/z 256.9510. Found: m/z 256.9486.

1-Cyano-2-methylisoselenochromenium Tetrafluoroborate (6). A mixture of 1-cyanoisoselenochromene (**3**) (2.00 g, 9.1 mmol), methyl iodide (6.45 g, 45.4 mmol), and silver tetrafluoroborate (1.95 g, 10.0 mmol) was stirred for 10 h at room temperature. The precipitate was filtered and washed with dry acetonitrile. The filtrate and washing were combined and concentrated to dryness. Ether was added to the residue. Crystals were filtered and recrystallized from acetonitrile–hexane to give a mixture of cis and trans stereoisomers as colorless needles (2.5 g, 86%), mp 84 °C dec: IR (KBr, cm^{-1}) 2250 (CN), 1000–1150 (BF_4); ^1H NMR (60 MHz) (CD_3CN) δ 2.68 (3 H, s, SeMe trans), 2.75 (3 H, s, SeMe cis), 5.74 (1 H, s, 1-H trans), 5.95 (1 H, d, $J_{1H\text{-}3H}$ = 1.5 Hz, 1-H cis), 6.70 (1 H, d, J = 9 Hz, 3-H trans), 6.75 (1 H, dd, $J_{3H\text{-}4H}$ = 9 Hz, $J_{1H\text{-}3H}$ = 1.5 Hz, 3-H cis), 7.62–7.73 (5 H, m, ArH and 4-H). Anal. Calcd for $C_{11}H_{10}BF_4NSe$: C, 41.04; H, 3.13; N, 4.35. Found: C, 40.79; H, 3.11; N, 4.27. The isomer ratio was determined by the ^1H NMR intensities of the SeMe group.

1-Cyano-2-methyl-2-selenanaphthalene (7). Triethylamine (1.26 g, 12.4 mmol) was added to a solution of 1-cyano-2-methylisoselenochromenium tetrafluoroborate (**6**) (2.00 g, 6.2 mmol) in dry ethanol (50 mL) at 0 °C under nitrogen. The reaction mixture turned orange. After the mixture was stirred for 1 h at that temperature, water (100 mL) was added to it. The resulting mixture was extracted with dichloromethane and the extracts were dried ($MgSO_4$). The solvent was removed under reduced pressure and a little amount of ether was added to the residue. The resulting crystals were filtered and recrystallized from dichloromethane–hexane to afford orange needles (1.10 g, 75%), mp 92 °C: IR (KBr, cm^{-1}) 2130 (CN); ^1H NMR (60 MHz) ($CDCl_3$) δ 2.08 (3 H, s, SeMe), 5.96 (1 H, d, J = 9 Hz, 3-H), 6.78–6.95 (1 H, m, 4-H), 7.15–7.43 (4 H, m, ArH). Anal. Calcd for $C_{11}H_9NSe$: C, 56.42; H, 3.87; N, 5.98. Found: C, 56.36; H, 3.86; N, 6.06.

Thermal Reactions of Selenanaphthalene 7. A solution of selenanaphthalene **7** (0.4 g, 1.71 mmol) in an appropriate solvent (20 mL) was stirred for 48 h at room temperature under nitrogen. The solvent was removed under reduced pressure, and the dark red residue was separated by preparative TLC on silica gel eluting with hexane–dichloromethane (2:1). The results are shown in Table II. 1-Cyano-1-methylisoselenochromene (**8**) was obtained as a yellow oil: IR (film, cm^{-1}) 2250 (CN); ^1H NMR (60 MHz) ($CDCl_3$) δ 2.03 (3 H, s, Me), 7.02 (1 H, d, J = 6 Hz, 3-H), 7.23–7.73 (5 H, m, ArH and 4-H). High resolution mass calcd for $C_{11}H_9NSe$: m/z 234.9899. Found: m/z 234.9891.

Methyl *o*-(2-methylselenovinyl)benzoate (**9a**) was obtained as a yellow oil: IR (film, cm^{-1}) 1720 (CO); ^1H NMR (60 MHz) ($CDCl_3$) δ 2.15 (3 H, s, SeMe), 3.88 (3 H, s, OMe), 6.70 (1 H, d, J = 10 Hz, MeSeCH=), 7.26–7.63 (3 H, m, ArH and ArCH=), 7.93–8.10 (1 H, m, ArH); ^{13}C NMR (67.5 MHz) ($CDCl_3$) δ 7.88 (q), 51.89 (q), 125.22 (d), 126.97 (d), 128.45 (s), 128.85 (d), 129.10 (d), 130.62 (d), 131.75 (d), 138.73 (s), 167.32 (s). The EI mass spectrum of **9a** showed a small molecular ion peak (M^+) at m/z 256. The M^+ was too small to determine the molecular formula by means of high resolution mass spectroscopy.

Ethyl *o*-(2-methylselenovinyl)benzoate (**9b**) was obtained as a colorless oil: IR (film, cm^{-1}) 1720 (CO); ^1H NMR (270 MHz) ($CDCl_3$) δ 1.38 (3 H, t, J = 7 Hz, Me), 2.18 (3 H, s, SeMe), 4.35 (2 H, q, J = 7 Hz, CH_2), 6.63 (1 H, d, J = 10 Hz, MeSeCH=), 7.28–7.55 (4 H, m, ArH and ArCH=), 7.93–7.96 (1 H, m, ArH). The EI mass spectrum of **9b** did not show the M^+ (m/z 270) but showed $(M - SeMe)^+$ at m/z 175.

Reactions of Selenanaphthalene 7 with Dimethyl Acetylenedicarboxylate (DMAD). DMAD (0.31 g, 2.2 mmol) was added to a solution of selenanaphthalene **7** (0.3 g, 1.3 mmol) in benzene (10 mL) under nitrogen; the reaction mixture was stirred for 24 h at room temperature. The solvent was removed under reduced pressure. The residue was separated by preparative TLC on silica gel, eluting with hexane–ethyl acetate (5:1). Dimethyl 9-cyano-5-selenomethyl-5*H*-benzocycloheptene-7,8-dicarboxylate (**15**) was obtained by recrystallization from dichloromethane–

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hexane as yellow needles (0.30 g, 61%), mp 133–134 °C: IR (KBr, cm^{-1}) 2230 (CN), 1740, 1725 (CO); ^1H NMR (270 MHz) ($CDCl_3$) δ 1.94 (3 H, s, SeMe), 3.73 (3 H, s, 7-OMe), 3.94 (3 H, s, 8-OMe), 4.75 (1 H, br s, 5-H), 7.26–7.51 (4 H, m, olefinic H and ArH), 7.93 (1 H, d, J = 7.3 Hz, ArH); ^{13}C NMR (67.5 MHz) ($CDCl_3$) δ 5.81 (q), 38.98 (d), 52.62 (q), 53.13 (q), 116.77 (s), 128.09 (d), 131.13 (s), 131.32 (d), 131.72 (d), 140.72 (s), 147.93 (d), 164.79 (s), 165.20 (s). Anal. Calcd for $C_{17}H_{15}NO_4Se$: C, 54.27; H, 4.02; N, 3.72. Found: C, 54.17; H, 4.11; N, 3.81. UV (MeCN) λ max: 221 ($\epsilon \approx 14800$), 254 ($\epsilon \approx 4300$), 320 ($\epsilon \approx 2400$).

The reaction in acetonitrile was similarly conducted and afforded the 5*H*-benzocycloheptene **15** (17%) and bis(9-cyano-7,8-dimethoxycarbonyl-5*H*-benzocyclohepten-5-yl) (**17**) (56%). The bisbenzocycloheptenyl **17** was recrystallized from acetonitrile–hexane to give colorless needles, mp 132 °C: IR (KBr, cm^{-1}) 2230 (CN), 1730 (CO); ^1H NMR (270 MHz) (DMSO-d_6) δ 3.69 (6 H, s, 7,7′-OMe), 3.91 (6 H, s, 8,8′-OMe), 4.19 (2 H, br s, 5,5′-H), 6.88–7.96 (10 H, m, ArH and olefinic H); ^{13}C NMR (67.5 MHz) ($CDCl_3$) δ 40.85 (d), 52.59 (s), 53.02 (s), 116.79 (s), 120.74 (d), 125.42 (d), 126.47 (d), 126.91 (d), 127.14 (d), 128.66 (d), 131.62 (s), 138.66 (d), 139.43 (s), 146.99 (d), 164.48 (s), 164.70 (s). High resolution mass calcd for $C_{32}H_{24}N_2O_8$: m/z 564.1532. Found: m/z 564.1506. UV (MeCN) λ max: 222 ($\epsilon \approx 16400$), 257 ($\epsilon \approx 4600$), 297 ($\epsilon \approx 3500$).

The reaction in sulfolane afforded compound **15** (17%) and dimethyl 1-cyanonaphthalene-2,3-dicarboxylate (**16**) (37%). The naphthalene derivative **16** was recrystallized from dichloromethane–hexane to give colorless needles, mp 134 °C (lit.[10] 133–134 °C). This sample was identical with the authentic sample obtained from the reaction of the corresponding thianaphthalene with DMAD[10] in terms of ^1H NMR and IR spectra.

Reaction of 5*H*-Benzocycloheptene (15) with Azobisisobutyronitrile (AIBN). AIBN (4 mg, 0.03 mmol) was added to a solution of compound **15** (0.1 g, 0.27 mmol) in acetonitrile (1 mL) at room temperature. The reaction mixture was stirred for 24 h and the solvent was removed under reduced pressure. The residue was separated by preparative TLC on silica gel, eluting with hexane–ethyl acetate (5:1). Bis(9-cyano-7,8-dimethoxycarbonyl-5*H*-benzocyclohepten-5-yl) (**17**) (22 mg, 30%) was obtained as colorless crystals.

Reaction of 5*H*-Benzocycloheptene 15 with *Se*-Phenyl *p*-Tolueneselenosulfonate. A solution of compound **15** (0.1 g, 0.27 mmol) and *Se*-phenyl *p*-tolueneselenosulfonate (78 mg, 0.27 mmol)[15] in dichloromethane (5 mL) was irradiated with a 400-W high-pressure mercury lamp for 30 min. The solvent was evaporated under reduced pressure. The residue was separated by preparative TLC on silica gel, eluting with hexane–ethyl acetate (5:1) to give 5*H*-benzocycloheptenyl dimer **17** (81 mg, 89%).

Reaction of Selenanaphthalene 7 with Methyl Propiolate (MP). A mixture of selenanaphthalene **7** (0.5 g, 2.1 mmol) and MP (0.30 g, 3.63 mmol) in benzene (30 mL) was stirred for 4 days under nitrogen. The solvent was evaporated under reduced pressure. The reddish black residue was separated by preparative TLC on silica gel, eluting with hexane–dichloromethane (1:1). Methyl 1,7-dicyano-1-[*o*-(2-methylselenovinyl)phenyl]-2-methylseleno-1a,8a-dihydro-2*H*-benzo[*a*]cyclopropa[*d*]cycloheptene-8a-carboxylate (**23**) (0.17 g, 28%) was obtained as colorless needles, mp 158 °C, after recrystallization from dichloromethane–hexane: IR (KBr, cm^{-1}) 2240 (CN), 1740 (CO); ^1H NMR (270 MHz) ($CDCl_3$) δ 2.23 (3 H, s, SeMe), 2.24 (3 H, s, SeMe), 3.27 (1 H, d, J = 11.5 Hz, 2-H), 3.40 (3 H, s, OMe), 4.37 (1 H, d, J = 11.5 Hz, cyclopropane H), 6.89 (1 H, d, J = 10.3 Hz, olefinic H), 7.09 (1 H, d, J = 10.3 Hz, olefinic H), 7.26–7.60 (8 H, m, ArH and 8-H), 7.92–7.95 (1 H, m, ArH); ^{13}C NMR (67.5 MHz) ($CDCl_3$) δ 6.13 (q), 8.28 (q), 28.88 (s), 40.23 (s), 40.43 (d), 44.43 (d), 53.20 (q), 115.72 (s), 117.87 (s), 120.46 (d), 124.79 (s), 127.93 (d), 128.00 (d), 128.93 (s), 128.52 (d), 129.30 (d), 129.44 (d), 129.56 (s), 129.67 (d), 130.31 (d), 130.49 (d), 130.61 (d), 137.48 (d), 137.85 (d), 138.83 (s), 165.26 (s). Anal. Calcd for $C_{26}H_{22}N_2O_2Se_2$: C, 56.53; H, 4.01; N, 5.07. Found: C, 56.24; H, 3.98; N, 5.07.

General Procedure for Reactions of Selenanaphthalene 7 with Olefins. A solution of the ylide **7** (1 mmol) and an olefin (1.7 mmol) in an appropriate dry solvent (3 mL) was stirred for 12 h under nitrogen at room temperature. The solvent was evaporated, and the residue was separated by preparative TLC on silica gel, eluting with hexane–dichloromethane (3:1) (entries 1–5 in Table III) or hexane–ethyl acetate (5:1) (entries 6–8 in Table III). Results are shown in Table III.

Reaction with acrylonitrile afforded *r*-1,*t*-2-dicyano-1-[2-(*cis*-2-methylselenovinyl)phenyl]cyclopropane (**27**) (29%) and *r*-1,*c*-2-dicyano isomer **28** (53%). Their ^1H NMR spectral data of cyclopropane ring protons are listed in Table IV. **27**, pale yellow oil: IR (film, cm^{-1}) 2250 (CN); ^1H NMR (270 MHz) ($CDCl_3$) δ 2.20 (3 H, s, SeMe), 6.91 (1 H, d, J = 10 Hz, olefinic H), 7.13 (1 H, d, J = 10 Hz, olefinic H), 7.24–7.61 (4 H, m, ArH); ^{13}C NMR (67.5 MHz) ($CDCl_3$) δ 8.14 (q), 13.78 (d), 19.44 (s), 20.32 (t), 115.46 (s), 118.60 (s), 125.19 (d), 127.40 (d), 127.84 (d), 128.92 (d), 129.59 (d), 129.68 (d), 130.00 (s), 138.64 (s). High resolution mass calcd for $C_{14}H_{12}N_2Se$: m/z 288.0165. Found: m/z 288.0180. **28**, pale yellow oil: IR (film, cm^{-1}) 2250 (CN); ^1H NMR (270 MHz) ($CDCl_3$) δ 2.21 (3 H, s, SeMe), 6.92 (1 H, d, J = 10 Hz, olefinic H), 7.10 (1 H, d, J = 10 Hz, olefinic H), 7.12–7.49 (4 H, m, ArH); ^{13}C NMR (67.5 MHz) ($CDCl_3$) δ 7.86 (q), 13.53 (d), 20.87 (s), 20.99 (t), 116.59 (s), 117.27 (s), 124.90 (d), 127.71 (d), 128.54 (d), 129.14 (d), 129.20 (d), 129.49 (d), 129.58 (s), 138.30 (s).

Reaction with methyl acrylate afforded a mixture of methyl *r*-1,*t*-2-cyano-2-[2-(*cis*-2-methylselenovinyl)phenyl]cyclopropane-1-carboxylate (**29**) and the *r*-1,*c*-2-isomer **30** as a pale yellow oil in 51% yield. The isomer ratio (**29**/**30** = 6/11) was determined by the intensities of methoxy groups in the ^1H NMR spectrum: IR (film, cm^{-1}) 2250 (CN), 1740 (CO_2Me); ^1H NMR (270 MHz) ($CDCl_3$) δ 2.17, 2.21 (3 H, s, SeMe), 3.48, 3.84 (3 H, s, OMe), 6.79 (d, J = 11 Hz, olefinic H), 6.83 (d, J = 10 Hz, olefinic H), 7.14 (d, J = 10 Hz, olefinic H), 7.15 (d, J = 11 Hz, olefinic H), 7.21–7.49 (4 H, m, ArH); ^{13}C NMR (67.5 MHz) ($CDCl_3$) δ 7.86 (q), 7.98 (q), 19.21 (d), 20.46 (s), 20.72 (d), 20.95 (s), 28.48 (t), 28.62 (t), 52.08 (q), 52.50 (q), 117.99 (d), 120.20 (d), 125.06 (d), 125.53 (d), 127.30 (d), 127.57 (d), 127.86 (d), 128.02 (d), 128.10 (d), 128.43 (d), 128.55 (d), 128.76 (d), 128.95 (d), 129.41 (d), 130.28 (s), 131.90 (s), 137.85 (s), 138.18 (s), 167.35 (s), 168.76 (s). High resolution mass calcd for $C_{15}H_{15}NO_2Se$: m/z 321.0268. Found: m/z 321.0284.

Reaction with methyl vinyl ketone afforded a mixture of *r*-1-acetyl-*t*,2-cyano-2-[2-(*cis*-2-methylselenovinyl)phenyl]cyclopropane (**31**) and the *r*-1-acetyl-*t*,2-cyano isomer **32** as a pale yellow oil in 92% yield. The isomer ratio (**31**/**32** = 1/18.4) was determined by the intensities of cyclopropane protons in the ^1H NMR spectrum: IR (film, cm^{-1}) 2250 (CN), 1720 (CO); ^1H NMR (270 MHz) ($CDCl_3$) δ 2.15, 2.16 (3 H, s, SeMe), 2.18, 2.42 (3 H, s, Me), 6.81 (d, J = 11 Hz, olefinic H), 7.11 (d, J = 10 Hz, olefinic H), 7.16 (d, J = 11 Hz, olefinic H), 7.21–7.49 (4 H, m, ArH); ^{13}C NMR (67.5 MHz) ($CDCl_3$) δ 7.59 (q), 7.73 (q), 19.58 (t), 21.02 (t), 22.42 (s), 22.61 (s), 30.90 (q), 30.99 (q), 34.14 (d), 34.83 (d), 117.62 (s), 120.33 (s), 125.09 (d), 125.64 (d), 127.18 (d), 127.51 (d), 127.64 (d), 127.92 (d), 128.13 (s), 128.26 (d), 128.46 (d), 128.72 (d), 129.21 (d), 130.45 (d), 132.15 (s), 137.50 (s), 137.89 (s). High resolution mass calcd for $C_{15}H_{15}NOSe$: m/z 305.0317. Found: m/z 305.0294.

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