cis-**28a**, 116809-03-1; *cis*-**28b**, 116808-94-7; **29**, 114105-45-2; **30**, 114083-16-8; **31**, 114083-15-7; **32**, 114083-17-9; **33**, 114083-18-0; $PhMe_2SiLi$, 3839-31-4; MeCHO, 75-07-0; EtCHO, 123-38-6; PrCHO, 123-72-8; *t*-BuCHO, 630-19-3; PhCHO, 100-52-7; $PhCH_2CHO$, 122-78-1; KSeCN, 3425-46-5; Me_3SiCH_2Cl, 2344-80-1; $ClCH_2CN$, 107-14-2; $ClCH_2COCH_3$, 78-95-5; $BrCH_2CO_2Et$, 105-36-2; $ClCH_2COPh$, 532-27-4; $ClCH_2C_6H_4$-4-NO_2, 100-14-1; $BrCH_2C_6H_3$-2,4-$(NO_2)_2$, 3013-38-5; CH_2=C(OEt)CH=CH_2, 4747-05-1; (*E*)-CH_2=C(CH_3)CH=$CHCH_3$, 926-54-5; (*E*)-CH_2=CHCH=$CHCH_3$, 2004-70-8; CH_2=C(CH_3)C-H=CH_2, 78-79-5; cyclopentadiene, 542-92-7; 2-[(*tert*-butyldimethylsilyl)oxy]-1,3-cyclohexadiene, 71106-34-8; 2,4,6-trimethylbenzonitrile *N*-oxide, 2904-57-6.

Supplementary Material Available: General experimental procedures and ^1H and ^{13}C NMR, IR, and MS data (26 pages). Ordering information is given on any current masthead page.

Preparation and Cycloaddition Reactions of Selenoketones

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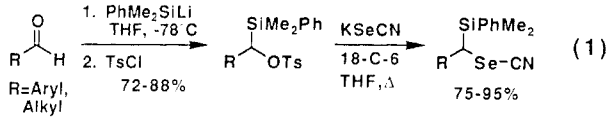
Abstract: Dienophilic selenoketones have been prepared by base-induced elimination of cyanide from selenocyanates containing electron-withdrawing or conjugating substituents. Cycloaddition reactions of selenoketones with dienes or dipolar reagents proceed efficiently to generate highly functionalized selenopyran and oxaselenazole derivatives. The cycloaddition regiochemistry is discussed in the context of frontier molecular orbital theory and the reactivity modeling approach of Kahn and Hehre.

During the past decade, significant interest in the chemistry of highly reactive carbon–heteroatom double bonds has developed. Notable accomplishments include the synthesis of carbon–silicon double bonds by West et al.[1] and by T. Barton[2] and the synthesis of reactive carbon–sulfur bonds in thioaldehydes by Vedejs,[3] Baldwin,[4] and others.[5] The synthesis of selenium–carbon double bonds also has attracted attention, with the first synthesis of sterically hindered selenoketones by D. H. R. Barton and co-workers[6a,b] and by Guziec et al.,[6b–n] and more recently, with the first synthesis of unstabilized aryl and alkyl selenoaldehydes in our laboratories.[7] Since our description of selenoaldehyde cycloaddition reactions, Kirby has reported the synthesis of ethyl selenoxoacetate,[8] and Fischer has reported elegant chemistry involving selenoaldehydes and selenoketones stabilized by tungsten and chromium complexes.[9]

Recently, we communicated the simple and efficient generation of selenofluorenone and its cycloaddition reactions with dienes and dipoles.[10] In this paper we present further details of that study and describe methodology that expands the scope and generality of selenoketone synthesis. We also describe a variety of selenoketone cyloaddition reactions with electronically biased diene and dipole components.

The present study was motivated by our initial work involving selenoaldehyde generation via fluoride-mediated desilylative elimination of cyanide from α-silyl selenocyanates and their cycloaddition reactions with various diene and dipole reactants.[7,11] The α-silyl selenocyanates were readily accessible from aldehydes via silyl anion addition, tosylation, and displacement by KSeCN, as illustrated in eq 1. Extension of this methodology to the



(1)

synthesis of selenoketones was anticipated to be difficult, since formation and selenocyanate displacement of tertiary tosylates would be required. Further difficulty was expected from competing deprotonation of enolizable ketones in the silyl anion addition reaction, diminishing the overall efficiency of this strategy. A reasonable alternative for selenoketone generation was the base-induced elimination of cyanide from simple selenocyanates, since the analogous sulfur-based reactions involving conversion of thiocyanates to thioketones had been demonstrated by Miotti

Table I[a]

Selenocyanate			Method	Diene		Product(s)			Yield (%)[†]
1	R_1	R_2 =		R_3 =	R_4 =	3	:	4	
a	CO_2Et	$P(OEt)_2$ (O)	A	Me	H	2.0	:	1	63
b	CO_2Et	Ph	A	Me	H	2.0	:	1	54
c	CO_2Et	Me	A	Me	H	2.0	:	1	62
d	PhC(O)	Me	A	Me	H	2.1	:	1	45
e	Ph	CN	B	Me	H	3.3	:	1	95
f	$PhSO_2$	Me	B	Me	H	2.8	:	1	85
g	CO_2Et	CO_2Et	A	H	Me	>25	:	1[††]	65
h	Ph	Ph	C	Me	Me	>25	:	1[††]	70
d	PhC(O)	Me	D	Me	Me	>25 (endo exo 4.2 1)	:	1[††]	68

[a] Method: (A) Et_3N, EtOH, heat, 1–2 h; (B) Et_3N, THF, heat, 1–2 h; (C) *t*-BuOK, THF, heat, 1–2 h; (D) KH, THF, heat, 1–2 h. [†] Yields correspond to isolated purified material. Regioisomers were not separable by HPLC or GC. [††] A single regioisomer was detected by ^1H NMR. >25:1 is a conservative estimate of detection limit.

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(1) Drahnak, T. J.; Michl, J.; West, R. *J. Am. Chem. Soc.* **1981**, *103*, 1845–1846.
(2) Barton, T. J.; Burns, G. T. *Tetrahedron Lett.* **1983**, *24*, 159–163.
(3) (a) Vedejs, E.; Eberlein, T. H.; Varie, D. L. *J. Am. Chem. Soc.* **1982**, *104*, 1445–1447. (b) Vedejs, E.; Perry, D. A. *J. Am. Chem. Soc.* **1983**, *105*, 1683–1684. (c) Vedejs, E.; Perry, D. A.; Houk, K. N.; Rondan, N. G. *J. Am. Chem. Soc.* **1983**, *105*, 6999–7001. (d) Vedejs, E.; Perry, D. A.; Wilde, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 2985–2989. (e) Vedejs, E.; Wilde, R. G. *J. Org. Chem.* **1986**, *51*, 117–118. (f) Vedejs, E.; Eberlein, T. H.; Mazur, D. J.; McClure, C. K.; Perry, D. A.; Ruggeri, R.; Schwartz, E.; Stults, J. S.; Varie, D. L.; Wilde, R. G.; Wittenberger, S. *J. Org. Chem.* **1986**, *51*, 1556–1562.
(4) (a) Baldwin, J. E.; Lopez, R. C. G. *J. Chem. Soc., Chem. Commun.* **1982**, 1029–1030. (b) Baldwin, J. E.; Lopez, R. C. G. *Tetrahedron* **1983**, *39*, 1487–1498.
(5) (a) Krafft, G. A.; Meinke, P. T. *Tetrahedron Lett.* **1985**, *26*, 1947–1950. (b) Okazaki, R.; Ishii, A.; Fukuda, N.; Oyama, H.; Inamoto, N. *J. Chem. Soc., Chem. Commun.* **1982**, 1187–1188. (c) Kirby, G. W.; Lochead, A. W. *J. Chem. Soc., Chem. Commun.* **1983**, 1325–1327. (d) Bladon, C. M.; Ferguson, I. E. G.; Kirby, G. W.; Lochead, A. W.; McDougall, D. C. *J. Chem. Soc., Chem. Commun.* **1983**, 423–425. (e) Kirby, G. W.; Lochead, A. W.; Sheldrake, G. N. *J. Chem. Soc., Chem. Commun.* **1984**, 922–923. (f) Kirby, G. W.; Lochead, A. W.; Sheldrake, G. N. *J. Chem. Soc., Chem. Commun.* **1984**, 1469–1470.

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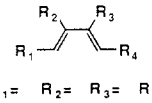
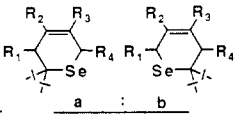
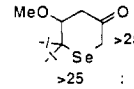
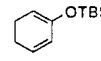
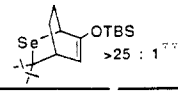
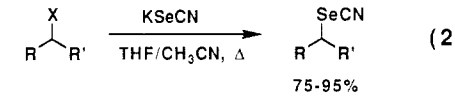
Table II. Selenofluorenone Cycloaddition Reactions

Entry	Diene	Adduct(s)	Yield(%)†
			
	R_1= R_2= R_3= R_4=	a : b	
5	H H H H	—	98
6	H H Me H	7 : 3	93
7	Me H H H	>25 : 1††	82
8	Me H Me H	>25 : 1††	96
9	H Me Me H	—	97
10	$CH=CH_2$ H H H	>25 : 1††	93
11	H H OEt H	4 : 1	94
12	H H OTBS H	5 : 1	91
13	MeO H OTMS H	 >25 : 1††	93
14	CO_2Et H H Me	>25 : 1††	88
15	Cyclopentadiene	—	97
16	Cyclohexadiene	—	97
17		 >25 : 1††	91

† Yields correspond to isolated, purified material. Regioisomers were inseparable by GC or HPLC. †† A single regioisomer was detected by ^{1}H NMR. >25:1 is a conservative estimate of detection limit.

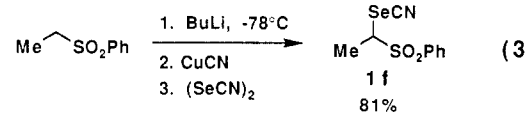
and co-workers.[12] Dittmer et al. also had postulated the likely intermediacy of monoselenobenzil in the NaH/THF-induced formation of oxaselenoles from desyl selenocyanate.[13] The elimination reaction was expected to proceed under relatively mild conditions with bases such as Et_3N, for selenocyanates containing adjacent electron-withdrawing substituents.

The synthesis of selenocyanate precursors to electron-deficient selenoketones was trivial in most cases, proceeding by simple nucleophilic displacement of readily available halides with KSeCN (eq 2). Selenocyanate **1f**, the precursor to phenylsulfonyl methyl selenoketone (**2f**), could not be prepared by this route, since the chloride was unreactive to KSeCN displacement, even at 150 °C



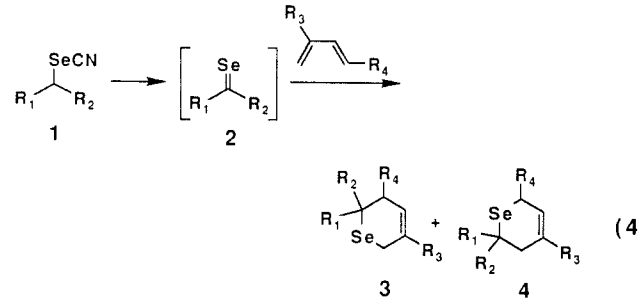
(2)

in HMPA with catalytic $Et_4N^+I^-$.[14] In this instance, the selenocyanate was prepared by cyanoselenation of the lower order cyanocuprate with selenocyanogen $[(SeCN)_2]$,[15] as illustrated in eq 3.



(3)

The generation of selenoketones by base-induced elimination was accomplished with several different sets of conditions. In a typical case, a solution of Et_3N in THF was added via syringe pump over a period of 1–2 h to a THF or anhydrous EtOH solution of selenocyanate in the presence of diene or dipole cycloaddition reactant (eq 4). Most of the selenocyanates required

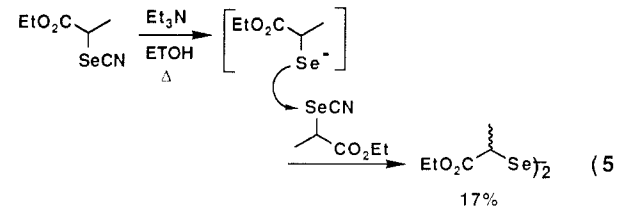


(4)

heating to reflux to induce the elimination reaction, and the selenoketones thus formed reacted rapidly at these elevated temperatures to give cycloadducts in good to excellent yields (Table I). Several of the dienes utilized as reactants in this study (isoprene, *trans*-piperylene, and 2-methyl-1,3-pentadiene) were quite volatile, requiring the use of a significant excess to insure efficient trapping.

The benzoyl methyl substituted selenoketone **2d** could be generated as described above or with KH in refluxing THF. The latter conditions resulted in a higher yield and improved stereoselectivity (4.2:1 vs 1.7:1). Selenobenzophenone (**2h**) generation required inverse addition of its selenocyanate precursor **1h** via syring pump to refluxing solution of potassium *tert*-butoxide in THF, since this selenocyanate was inert to Et_3N in THF or EtOH.

One drawback to the use of EtOH as a solvent for selenoketone generation and cycloaddition was the competing formation of symmetrical diselenide, which occurred via ethoxide attack at the nitrile to generate selenolate anion, and coupling of this anion with a second molecule of selenocyanate by cyanide displacement. Dimeric diselenide byproducts were observed in all of the EtOH reactions (ca. 10–25%), but only in the reaction of ethyl 2-(selenocyanato)propionate was the mixture of *meso* and *d,l* isomers (**18**) fully characterized (eq 5). To avoid this competing reaction,



(5)

THF or THF/CH_2Cl_2 were employed as solvents in all instances except for reactants containing a carbonyl adjacent to the selenocyanate. In these cases, $CaCl_2$ dissolved in the protic solvent was used to suppress intramolecular attack by the enolate oxygen

(6) (a) Back, T. G.; Barton, D. H. R.; Britten-Kelly, M. R.; Guziec, F. S., Jr. *J. Chem. Soc., Chem. Commun.* **1975**, 539. (b) Back, T. G.; Barton, D. H. R.; Britten-Kelly, M. R.; Guziec, F. S., Jr. *J. Chem. Soc., Perkin Trans. 1* **1976**, 2079–2089. (c) Cullen, E. R.; Guziec, F. S., Jr.; Murphy, C. J.; Wong, T. C.; Andersen, K. K. *J. Chem. Soc., Perkin Trans. 2* **1982**, 473–476. (d) Andersen, K. K.; Gash, D. M.; Robertson, J. D.; Guziec, F. S., Jr. *Tetrahedron Lett.* **1982**, 911–912. (e) Wong, T. C.; Guziec, F. S., Jr.; Moustakis, C. A. *J. Chem. Soc., Perkin Trans. 2* **1983**, 1471–1475. (f) Wong, T. C.; Ang, T. T.; Guziec, F. S., Jr.; Moustakis, C. A. *J. Magn. Reson.* **1984**, *57*, 463–470. (g) Guziec, F. S., Jr.; Russo, J. M. *Synthesis* **1984**, 479–481. (h) Guziec, F. S., Jr.; Moustakis, C. A. *J. Chem. Soc., Chem. Commun.* **1984**, 63–64. (i) Guziec, F. S., Jr.; SanFilippo, L. J.; Murphy, C. J.; Moustakis, C. A.; Cullen, E. R. *Tetrahedron* **1985**, *41*, 4843–4852. (j) Guziec, F. S., Jr.; Murphy, C. J.; Cullen, E. R. *J. Chem. Soc., Perkin Trans. 1* **1985**, 107–113. (k) Guziec, F. S., Jr.; Murphy, C. J.; Cullen, E. R. *J. Chem. Soc., Perkin Trans. 1* **1985**, 107–113. (l) Cullen, E. R.; Guziec, F. S., Jr.; Murphy, C. J.; Wong, T. C.; Andersen, K. K. *J. Am. Chem. Soc.* **1981**, *103*, 7055–7057. (m) Cullen, E. R.; Guziec, F. S., Jr.; Hollander, M. I.; Murphy, C. J. *Tetrahedron Lett.* **1981**, *22*, 4563–4566. (n) Cullen, E. R.; Guziec, F. S., Jr.; Murphy, C. J. *J. Org. Chem.* **1982**, *47*, 3563–3566.

(7) Krafft, G. A.; Meinke, P. T. *J. Am. Chem. Soc.* **1986**, *108*, 1314–1315.

(8) Kirby, G. W.; Trethewey, A. N. *J. Chem. Soc., Chem. Commun.* **1986**, 1152–1154.

(9) (a) Fischer, H.; Zeuner, S.; Riede, J. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 726–727. (b) Fischer, H.; Gerbing, U.; Riede, J.; Benn, R. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 78–79. (c) Fischer, H.; Tiriliomis, A.; Gerbling, B.; Muller, G. *J. Chem. Soc., Chem. Commun.* **1987**, 559–560.

(10) Meinke, P. T.; Krafft, G. A. *Tetrahedron Lett.* **1987**, *28*, 3887–3890.

(11) (a) Meinke, P. T.; Krafft, G. A. *Tetrahedron Lett.* **1987**, *28*, 5121–5124. (b) Meinke, P. T.; Krafft, G. A. *J. Am. Chem. Soc.*, preceeding paper in this issue.

(12) Miotti and co-workers had reported the base-induced elimination of aryl thiocyanates and disulfides to form thiones: (a) Ceccon, A.; Miotti, U.; Tonellato, U.; Padovan, M. *J. Chem. Soc. B* **1969**, 1084–1090. (b) Miotti, U.; Tonellato, U.; Ceccon, A. *J. Chem. Soc. B* **1970**, 325–331.

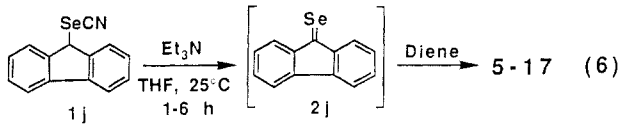
(13) Gramza, J.; Mitchell, R. B.; Dittmer, D. C. *J. Org. Chem.* **1984**, *49*, 2057–2058.

(14) Displacements of α-halo sulfones are known to proceed slowly: Kay, D. G.; Langler, R. F.; Trenholm, J. E. *Can. J. Chem.* **1979**, *57*, 2185–2190.

(15) Meinke, P. T.; Guram, A.; Krafft, G. A. *J. Org. Chem.* **1988**, *53*, 3632–3634.

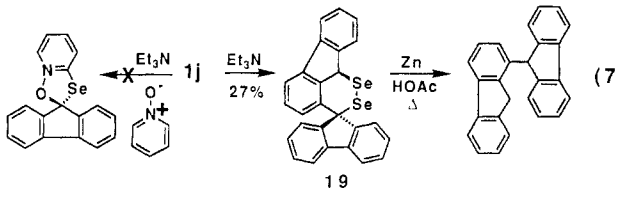
on the selenocyanate nitrile,[16] a process that resulted in complex reaction mixtures and poor cycloadduct yields when THF was used as solvent.

The formation of selenofluorenone **2j** proceeded efficiently at room temperature by syringe pump addition of Et_3N in THF to a solution of 9-fluorenyl selenocyanate (**1j**) and the diene or dipole reactant in THF/CH_2Cl_2 over a period of 1–6 h (eq 6). Cy-



(6)

cloadducts **6–17** were obtained in remarkably high yield, as shown in Table II. In the attempted trapping of selenofluorenone by the dipolar reactant pyridine *N*-oxide, no cycloadduct was formed, and a 27% yield of the dimeric selenofluorenone adduct **19** was isolated. The structure of **19** was determined by NMR, mass spectral data, and reductive deselenation (Zn/HOAc) to the known 9,1′-bifluorenyl (eq 7). Compound **19** also had been

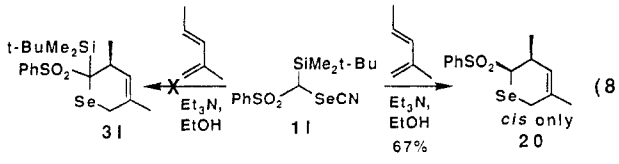


(7)

observed in several successful [4 + 2] cycloaddition reactions involving relatively less reactive dienes, though only in small quantities (2–10%). The analogous disulfide dimer had been obtained upon heating of thiofluorenone at 140 °C[17] and was rationalized by Schoenberg to be a product of head-to-head coupling of sulfur atoms to generate a fluorenyl disulfide diradical that subsequently collapsed to form the six-membered ring. A similar process could account for the formation of **19**, or it is conceivable that a [4 + 2] cycloaddition could occur involving one selenofluorenone molecule reacting as a 4π-electron component, with subsequent rearomatization to generate **19**.

A number of experiments involving base treatment of selenocyanates in the absence of cycloaddition reactant were conducted in an attempt to generate and isolate selenoketones in dilute solution. However, these experiments invariably resulted in complex mixtures of products that included diselenide dimers and other unidentified selenium-containing materials. At no time during these experiments or during experiments involving diene or dipole trapping reagents was the characteristic blue color attributed to sterically hindered selenoketones[6d,l] detected, indicating the high reactivity of these selenocarbonyl species.

In two instances, base treatment of selenocyanates in the presence of a diene reactant failed to provide selenoketone cycloadducts. Addition of Et_3N to (phenylsulfonyl)(*tert*-butyldimethylsilyl)methyl selenocyanate (**1l**)[11b] in the presence of (*E*)-2-methyl-1,3-pentadiene led to the isolation of the cis cycloadduct of the phenylsulfonyl-substituted selenoaldehyde **20**,[18] rather than the silyl selenoketone adduct **31** (eq 8). This product



(8)

(16) KSeCN opens epoxides to give a β-alkoxy selenocyanate in which the alkoxide attacks the selenocyanate nitrile, eventually leading to olefins via an episelenide. A similar process involving the adjacent enolate oxygen of (*Z*)-enolates may be occurring in these EtOH reactions.

(17) (a) Schoenberg, A.; Brosowski, K.-H.; Singer, E. *Chem. Ber.* **1962**, *95*, 1910–1916. (b) Schoenberg, A.; Brosowski, K.-H.; Singer, E. *Chem. Ber.* **1962**, *95*, 2144–2154. (c) Ried, W.; Klug, H. *Chem. Ber.* **1961**, *94*, 368–373.

(18) This adduct (**20**) was prepared independently by fluoride-induced desilylation of the α-silyl selenocyanate (ref 11).

may have formed by desilylation after selenoketone cycloadduct formation, or by ethoxide-mediated desilylative selenoaldehyde formation and subsequent cycloaddition. It is somewhat surprising that only the cis isomer is isolated in this reaction, since these basic conditions would be expected to effect epimerization. However, this cis adduct was the only isomer obtained in the (*E*)-2-methyl-1,3-pentadiene cycloaddition with selenoaldehyde generated via fluoride desilylation of **1l** and was completely resistant to epimerization under a variety of strongly basic conditions.[11b]

Numerous attempts to generate selenoacetophenone by treatment of 1-(selenocyanato)-1-phenylethane (**1j**) with a variety of bases in THF or EtOH were unsuccessful. In most experiments, the selenocyanate did not react when base was added and disappeared only after prolonged heating, giving no evidence of cycloadduct formation. This result was not entirely unexpected in view of the relatively more vigorous conditions required for selenobenzophenone generation (vide supra). It also provided an indication of the approximate limit of this methodology with respect to the required acidity of α protons in the selenocyanate precursors.

Cycloaddition Reactivity

Acceptor-Substituted Selenoketones. Two types of selenoketones were investigated in this study: selenoketones XRC=Se containing at least one electron-withdrawing substituent X and selenoketones Ar_2C=Se containing two conjugated aromatic substituents Ar. The electron-deficient selenoketones exhibited characteristics quite similar to their all-carbon dienophile counterparts, reacting with electronically biased dienes to give typical Diels–Alder regiochemistry in which the electron-withdrawing substituents X prefer the ortho or para positions relative to diene donor substituents in product cycloadduct. The levels of regioselectivity ranged from >25:1 (only one isomer detected) in reactions with (*E*)-1,3-pentadiene or (*E*)-2′-methyl-1,3-pentadiene to 2.0:1–3.3:1 in reactions with isoprene, as determined by integration of suitable NMR resonances (Table I). None of the regioisomer mixtures was separable by flash chromatography, HPLC, or capillary GC. Similar regioselectivities have been observed for acceptor-substituted selenoaldehydes,[11] thioaldehydes,[3] and dithioester dienophiles,[19] and comparable loss of selectivity has been noted for 2-substituted dienes relative to 1-substituted dienes.[20]

The acceptor-substituted selenoketone dienophiles were considerably more reactive than the all-carbon analogues, and probably more reactive than acceptor-substituted thioesters and thioketones, though a direct reactivity comparison to these sulfur analogues is not possible from our experiments or information in the literature.

Stereoselectivity in the selenoketone cycloaddition reactions was not an issue in most instances, due to appropriate selection of diene and selenoketone substituents in the reactions examined. However, in the reaction of the benzoyl-substituted selenoketone **1d**, generated by KH in refluxing THF in the presence of (*E*)-2-methyl-1,3-pentadiene, an inseparable mixture of stereoisomers in the ratio 4.2:1 was obtained. This same selenoketone gave a 1.7:1 ratio of stereoisomers with (*E*)-1,3-pentadiene when generated by Et_3N in refluxing EtOH. NOE experiments involving irradiation of the C-1 methyl protons, the C-2 proton, and the C-2 methyl protons implicated the endo cycloadduct as the predominant product. Endo selectivity would be consistent with the stereoselectivity manifest in the cycloaddition reactions of acceptor-substituted selenoaldehydes[11] and thioaldehydes.[3]

Conjugated Selenoketones. Selenofluorenone was studied more thoroughly than any other selenoketone. Its formation and cycloaddition reactions proceeded with remarkable efficiency and could be carried out easily (Table II). The regiochemistry exhibited by selenofluorenone with donor-substituted dienes was identical with that observed for the acceptor-substituted seleno-

(19) Vedejs, E.; Arnost, M. J.; Dolphin, J. M.; Eustache, J. *J. Org. Chem.* **1980**, *45*, 2601–2604.

(20) Burnier, J. S.; Jorgensen, W. L. *J. Org. Chem.* **1983**, *48*, 3923–3941.

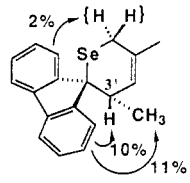
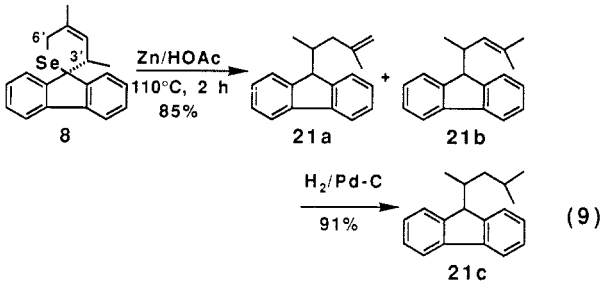


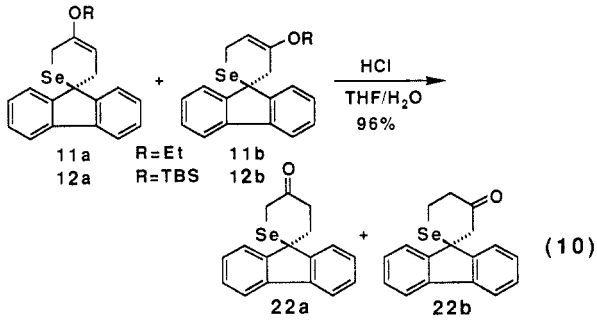
Figure 1. Nuclear Overhauser enhancements for selenofluorenone adduct **8**.

ketones and opposite that exhibited by selenobenzaldehyde[11] and thiobenzaldehyde.[3] No reaction of thiofluorenone with electronically biased, donor-substituted dienes has been reported; however, the regiochemistry displayed in reactions of thiofluorenone with dipoles[21a] and with azoalkenes[21b] is consistent with the selenofluorenone results obtained in this study, on the basis of frontier molecular orbital considerations.[22] The regioselectivities for cycloadditions with 1-substituted dienes were excellent, with only one adduct detectable by ^1H and ^{13}C NMR, while cycloadditions with 2-substituted dienes gave somewhat diminished regioselectivities ranging from 2.3:1 to >25:1. Apparently, the fluorenyl ring system exerts a strong electron-accepting influence on the selenocarbonyl, due to the significant stability of the aromatic fluorenyl anion, placing the large coefficient of selenofluorenone LUMO on selenium.

The regiochemistry of selenofluorenone cycloadducts was determined by extensive NOE studies in which qualitatively consistent enhancements were observed in the proton resonances at C-3′ when the aromatic resonances were irradiated, as illustrated in Figure 1. Verification of NOE interpretations and definitive structural proof were obtained by reductive deselenation and hydrogenation of the (*E*)-2-methyl-1,3-pentadiene adduct **8** to generate 9-(1,3-dimethylbutyl)fluorene (**21c**),[23] as shown in eq 9. The inseparable isomeric enol ether adducts **11a** and **11b**, and



12a and **12b**, were hydrolyzed with aqueous acid/THF, generating isomeric ketones **22a** and **22b** which were readily separable by flash chromatography (eq 10). ^1H NMR spectra of these isomeric ketones provided corroboration of regioisomeric assignments for adducts **12** and **13**.



(21) (a) Mazzanti, G.; Maccagnani, G.; Bonini, B. F.; Pedrini, P.; Zwanengurg, B. *Gazz. Chim. Ital.* **1980**, *110*, 163–166. (b) Bonini, B. F.; Maccagnani, G.; Mazzanti, G.; Rosini, G.; Foresti, E. *J. Chem. Soc., Perkin Trans. 1* **1981**, 2322–2326.

(22) (a) Fukui, K. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 801–809, and references therein. (b) Houk, K. N. *Acc. Chem. Res.* **1975**, *8*, 361–369, and references therein.

(23) Heller, H. G.; Jenkins, G. A. *J. Chem. Soc., Perkin Trans. 1* **1984**, 2871–2875.

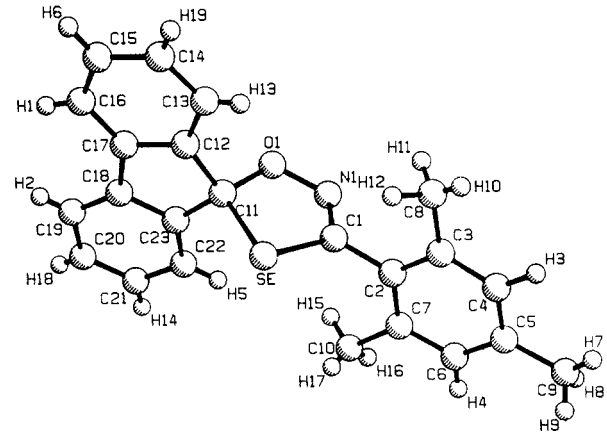
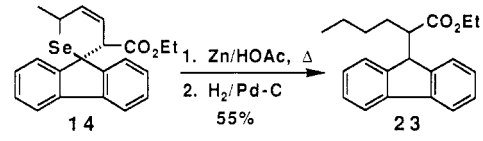


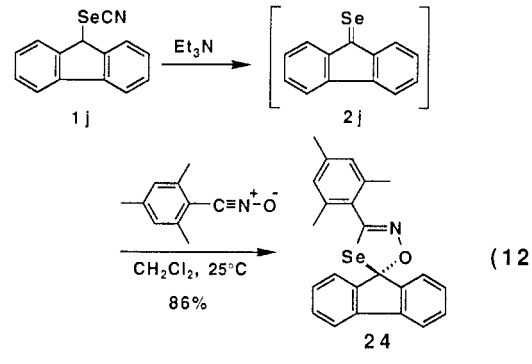
Figure 2. Structure of **24**, determined by X-ray diffraction studies.

The reaction of selenofluorenone with ethyl sorbate provide a single adduct **14** with regiochemistry opposite that observed in its reactions with all other dienes. Structure determination was accomplished by NMR analysis, NOE experiments, and reductive deselenation to 9-(1-carbethoxypentyl)fluorene **23** (eq 11). This



apparently anomalous regiochemistry may be the result of an inverse electron demand reaction[24] involving the selenofluorenone HOMO and the ethyl sorbate LUMO, though other attempts in our laboratory to obtain cycloadducts from inverse electron demand reactions involving electron-rich selenoaldehydes and electron-deficient dienes (e.g., ethyl sorbate, methyl coumalate, tetraphenylcyclopentadienone) failed.[11]

A number of dipolar cycloaddition reactions of selenofluorenone were attempted, but only in the reaction with 2,4,6-trimethylbenzonitrile *N*-oxide was a dipolar cycloadduct obtained (eq 12).



^{13}C NMR data suggested that the crystalline adduct was the 1′,4′,2′-oxaselenole **24**, and single-crystal X-ray diffraction analysis provided unambiguous conformation of this structural assignment, as illustrated in Figure 2.[25] This is the same regiochemistry obtained for the nitrile oxide dipolar cycloaddition involving selenobenzaldehyde.[7,11] However, this regiochemistry is opposite the regiochemistry that would be expected on the basis of the selenofluorenone–diene cycloadducts and opposite the regiochemistry exhibited by thiofluorenone with nitrones.[20] A similar difference of regiochemistry has been observed for nitrone and nitrile oxide dipolar cycloadditions of thiofluorenone *S*-oxide.[21] It is likely that the uncharacteristic selenofluorenone regiochemistry (and thiofluorenone *S*-oxide regiochemistry) results from

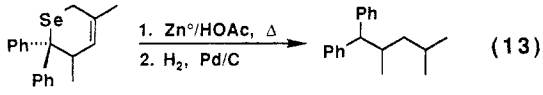
(24) For examples and discussion of inverse electron demand cycloadditions, see: Boger, D. L. *Chem. Rev.* **1986**, *86*, 781–793, and references therein.

(25) Krafft, G. A.; Meinke, P. T.; Pfluger, C. E.; Spencer, J. T. *Acta Crystallogr., Sect. B: Struct. Sci.*, in press.

sensitivity of the benzonitrile *N*-oxide dipole to steric interactions, rather than from inherent electronic characteristics of the selenofluorenone. Similar steric effects have been noted in the reactions of all-carbon dipolarophiles with aryl nitrile oxides. For instance, regioselectivities for benzonitrile oxide reverse completely when the dipolarophile changes from ethyl acrylate to ethyl crotonate.[26-28]

Several other dipoles failed to provide identifiable dipolar cycloadducts. Pyridine *N*-oxide and pyridinium carbethoxymethylide did not react with selenofluorenone, and these reactions resulted in formation of the selenofluorenone dimer **19** as the major identifiable product. Ethyl diazoacetate and a *tert*-butyldimethylsilyl-substituted nitronate ester did react with selenofluorenone, but resulted in complex reaction mixtures from which no cycloadduct could be isolated. It is likely that these latter two reactions did involve initial formation of dipolar cycloadducts with the regiochemistry expected for selenofluorenone on the basis of its [4 + 2] reactions with dienes. The expected nitronate adduct would be unstable due to a highly reactive Se–O bond, while the diazoacetate adduct would be a selenadiazole, capable of facile loss of molecular nitrogen. The failure to obtain stable adducts from these reactions lends support to the supposition that the anomolous nitrile oxide regiochemistry resulted from characteristics inherent to the 2,4,6-trimethylbenzonitrile oxide rather than selenofluorenone.

The reaction of selenobenzophenone **2b** with (*E*,*E*)-2-methyl-1,3-pentadiene (Table I) provided a single adduct **3h**, with regiochemistry identical with that obtained for selenofluorenone, but opposite that exhibited in reactions of selenobenzaldehyde[7,11] and thiobenzaldehyde[3] with a variety of donor-substituted dienes and in the reaction of thiobenzophenone with isoprene.[29] The structure of this adduct was determined by ^1H and ^{13}C NMR and by reductive deselenation to 1,3-dimethyl-1,1-diphenylbutane (**25**) (eq 13).



3h 25 (13)

This regiochemical result can be rationalized by using the reactivity modeling approach of Kahn and Hehre,[30] in which leading bond formation would involve the nucleophilic C-1 diene terminus reacting with the selenocarbonyl selenium atom, with some buildup of electron density at the doubly benzylic carbon. The selenobenzophenone cycloaddition reaction occurs at a sufficiently high temperature (65 °C) that in the transition state the two phenyl rings could assume a geometry more nearly coplanar, minimizing steric interactions and maximizing the electron-acceptor character of the two phenyl rings. The difference in polarizability of a selenocarbonyl π bond vs a thiocarbonyl π bond may account for the difference in regiochemistry, considering that the selenobenzophenone cycloaddition was carried out in the polar solvent THF, compared with nonpolar conditions (neat, excess isoprene) used in the thiobenzophenone cycloaddition.[29] Regiochemistry similar to selenobenzophenone was observed in the reaction of 2,4-dinitroselenobenzaldehyde with 2-[(*tert*-butyldimethylsilyl)oxy]cyclohexadiene, a regiochemical result opposite that obtained in the reaction of selenobenzaldehyde or 4-nitroselenobenzaldehyde.[7,11] In the 2,4-dinitroselenobenzaldehyde case, the ability to stabilize a buildup of electron density at the benzylic carbon is enhanced by the two nitro groups, favoring bond formation between electrophilic selenium and the nucleophilic terminus of the donor-substituted diene.

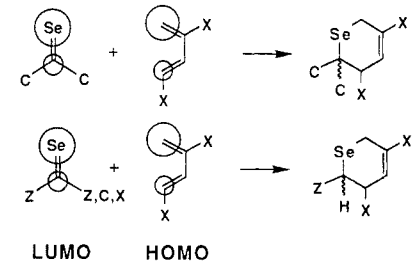


Figure 3. Qualitative frontier molecular orbital summary of selenoketone regiochemistry, based on the normal mode of [4 + 2] cycloaddition ($HOMO_{diene} - LUMO_{dienophile}$). Two conjugating substituents give acceptor-like regiochemistry with electron-rich dienes. X, electron releasing; C, conjugating; Z, electron accepting.

A similar reactivity argument can be invoked to explain the selenofluorenone regiochemistry, though in this instance FMO calculations might well predict that the large LUMO coefficient of selenofluorenone resides on selenium, due to the aromatic character of the 14π-electron fluorenyl anion that would develop in a polarized reaction involving diene nucleophilic attack at selenium.

Figure 3 provides a qualitative summary of the probable FMO situation for selenoketones, based on the majority of our results. In presenting this picture, we assume that these reactions proceed in a concerted rather than stepwise fashion, but this does not rule out the involvement of polar or nonsynchronous bond-making and bond-breaking processes. Acceptor-substituted selenoketones react in a manner indicative of predominant FMO interaction between the selenoketone LUMO and diene HOMO, with the large LUMO coefficient residing on selenium. This characterization is qualitatively identical with the theoretical and experimental picture of acceptor-substituted thiocarbonyls.[3] Selenofluorenone and selenobenzophenone regiochemistry parallels that obtained for acceptor-substituted selenoketones, indicating that these aromatic substituents are capable electron-acceptor groups. The reaction of selenofluorenone with ethyl sorbate is an exception to the normal mode cycloaddition reactions involving predominant $LUMO_{selenoketone} - HOMO_{diene}$ interaction in the transition states and may occur with predominant interaction of the selenofluorenone HOMO and the ethyl sorbate LUMO, in which the carboethoxy group establishes the large coefficient at C-5.

Conclusions. The experiments presented in this paper demonstrate clearly that unstabilized selenoketones, once synthetically elusive, are easily generated and react with good to excellent efficiency. Acceptor-substituted selenoketones react with donor-substituted dienes, exhibiting regiochemistry analogous to acceptor-substituted selenals and thials, and consistent in most instances with the FMO characterization for thioaldehydes. Selenofluorenone and selenobenzophenone cycloadducts exhibit regiochemistry similar to acceptor-substituted selenoketones and opposite that exhibited for conjugated selenals and thiocarbonyl compounds. These results are consistent with the reactivity modeling approach of Kahn and Hehre, considering the highly polarizable nature of the selenoketone π bond and the anion stabilizing capability of the fluorenyl or diphenylmethane systems. The reactivity modeling approach also explains the regiochemical results for all other cycloaddition reactions of acceptor-substituted selenoketones.

The appropriate selection of selenoketone and diene substituents permits the synthesis of a wide spectrum of functionalized selenopyrans, molecules that will become useful intermediates in synthetic endeavors. Subsequent reports from our laboratory will describe synthetic applications of these selenocarbonyl-derived adducts.

Experimental Section

General Procedure for Selenocyanate Synthesis via Halide Displacement. Diethyl 2-(Selenocyanato)malonate (1g). To a solution containing 1.0 g (4.2 mmol) of biscarbethoxymethyl bromide in anhydrous MeCN (20 mL) at 0 °C was added 600 mg (4.2 mmol) of KSeCN in one portion. After 15 min at 0 °C, precipitation of salt occurred and the

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(27) Christl, M.; Huisgen, R. *Chem. Ber.* **1973**, *106*, 3345–3367.
(28) Huisgen, R.; Sustmann, R.; Wallbillich, G. *Chem. Ber.* **1967**, *100*, 1786–1801.
(29) Ohno, A.; Ohnishi, Y.; Tsuchihashi, G. *Tetrahedron* **1969**, *25*, 871–876.
(30) (a) Kahn, S. D.; Hehre, W. J. *J. Am. Chem. Soc.* **1987**, *109*, 663–666. (b) Kahn, S. D.; Pau, C. F.; Overman, L. E.; Hehre, W. J. *J. Am. Chem. Soc.* **1986**, *108*, 7381–7396, and references therein.
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mixture was allowed to stir at room temperature for an additional 15 min. The reaction was poured into cold H_2O (100 mL), extracted with Et_2O (2 × 20 mL), dried ($MgSO_4$), filtered, and concentrated under reduced pressure. Pure **1g** was obtained in 75% yield (830 mg) after chromatographic purification on silica gel (4:1:1 hexanes/CH_2Cl_2/Et_2O as eluant).

Ethyl 2-(diethoxyphosphinyl)-2-(selenocyanato)acetate (1a): isolated as a pale yellow oil in 55% yield (1.21 g).

Ethyl 2-phenyl-2-(selenocyanato)acetate (1b): isolated as a pale yellow oil in 71% yield (1.78 g).

Ethyl 2-(selenocyanato)propanoate (1c): isolated as a pale yellow oil in 68% yield (2.27 g).

1-Phenyl-2-(selenocyanato)-1-propanone (1d): isolated as white powder (mp 77–79 °C) in 83% yield (1.9 g).

α-(Selenocyanato)phenylacetonitrile (1e): isolated as a pale yellow powder (mp 100–101 °C) in 74% yield (2.21 g).

Diphenylmethyl selenocyanate (1h): isolated as a white solid (mp 48–49 °C) in 86% yield (1.0 g).

1-Phenylethyl-1-selenocyanate (1i): isolated as a viscous, pale yellow oil in 88% yield (1.01 g).

9-(Selenocyanato)fluorene (1j): isolated as a pale yellow powder (mp 109–111 °C) in 78.8% yield (210 mg).

Phenyl 1-(Selenocyanato)ethyl Sulfone (1f). To a solution containing 441 mg (2.59 mmol) of $PhSO_2CH_2CH_3$ in THF (8 mL) at −78 °C was added dropwise 1.2 mL (2.85 mmol) of 2.4 M *n*-BuLi. The solution was stirred for 15 min at −78 °C and 15 min at 0 °C and was recooled to −78 °C. The lithium anion thus formed was transferred via cannula to a THF solution (8 mL) containing 278 mg (3.10 mmol) of Cu^ICN maintained at −78 °C. The mixture immediately turned brown. This solution was stirred for 15 min at −78 °C and 15 min at 0 °C and then recooled to −78 °C. To a solution containing 2.20 g (10.36 mmol) of AgSeCN in THF (8 mL) at 0 °C was added 1.32 g (5.2 mmol) of I_2. This mixture was stirred at 0 °C for 30 min, until a bright yellow solution formed. The selenocyanogen thus generated was cooled to −78 °C and filtered through a glass frit in vacuo. The brown cuprate solution subsequently was added via canula to the $(SeCN)_2$ at −78 °C. After 15 min at −78 °C and 1 h at room temperature, a clear deep red solution resulted. The reaction mixture was diluted with pentane (50 mL), filtered through a 4-in. silica gel plug (2:1:1 hexanes/CH_2Cl_2/Et_2O as eluant), and concentrated at reduced pressure. Pure **1f** was obtained as a white powder (mp 88–90 °C) in 66% yield (275 mg) upon flash chromatography on silica gel (4:1:1 hexanes/CH_2Cl_2/Et_2O as eluant).

General Procedures for Selenoketone Cycloaddition Reactions. Two general procedures were employed frequently to generate selenoketones and trap them with conjugated dienes.

Method A. A solution consisting 0.50 mmol of selenocyanate, 5–10 mmol of freshly distilled diene, and 94 mg (0.50 mmol) of $CaCl_2 \cdot 2H_2O$ in absolute ethanol (10 mL) was prepared. This solution was heated to reflux, and 70 μL (0.50 mmol) of triethylamine was added as a solution in 10 mL of absolute ethanol over 1 h via syringe pump. The reaction mixture was cooled to 0 °C, poured into cold water (50 mL), extracted with CH_2Cl_2 (3 × 15 mL), dried ($MgSO_4$), filtered, and concentrated at reduced pressure. Pure cycloadduct was subsequently obtained upon flash chromatographic separation on silica gel using 4:1:1 hexanes/CH_2Cl_2/Et_2O as eluant.

Method B. A solution containing 0.50 mmol of selenocyanate and 5–10 mmol of freshly distilled diene in THF (10 mL) was heated to reflux. To this solution was added 70 μL (0.50 mmol) of triethylamine as a solution in 10 mL of THF over 1 h via syringe pump. The reaction mixture was cooled to 0 °C, diluted with pentane (30 mL), and filtered through a 4-cm activated neutral alumina plug. The filtrate was concentrated under reduced pressure, and pure cycloadduct was subsequently obtained upon flash chromatographic separation on silica gel using 4:1:1 hexanes/CH_2Cl_2/Et_2O as eluant.

Ethyl 2-(Diethoxyphosphinyl)-3,6-dihydro-5-methyl-2*H*-selenopyran-2-carboxylate (3a) and Ethyl 2-(Diethoxyphosphinyl)-3,6-dihydro-4-methyl-2*H*-selenopyran-2-carboxylate (4a). These cycloadducts, an inseparable mixture of regioisomers prepared via method A, were isolated as a pale yellow oil in 63% yield (115 mg) from the reaction of **2a** with isoprene. The isomer ratio was determined to be 2.0:1 by proton NMR integration, with **3a** predominating.

Ethyl 3,6-Dihydro-5-methyl-2-phenyl-2*H*-selenopyran-2-carboxylate (3b) and Ethyl 3,6-Dihydro-4-methyl-2-phenyl-2*H*-selenopyran-2-carboxylate (4b). These cycloadducts, an inseparable mixture of regioisomers prepared via method A, were isolated as a pale yellow oil in 54% yield (58.7 mg) from the reaction of **2b** with isoprene. The isomer ratio was determined to be 2.0:1 by proton NMR integration, with **3a** predominating.

Ethyl 3,6-Dihydro-2,5-dimethyl-2*H*-selenopyran-2-carboxylate (3c) and Ethyl 3,6-Dihydro-2,4-dimethyl-2*H*-selenopyran-2-carboxylate (4c). These cycloadducts, an inseparable mixture of regioisomers prepared via method A, were isolated as a pale yellow oil in 62% yield (149 mg). The isomer ratio was determined to be 2.0:1 by proton NMR integration, with **3c** predominating.

2-Benzoyl-3,6-dihydro-2,5-dimethyl-2*H*-selenopyran (3d) and 2-Benzoyl-3,6-dihydro-2,4-dimethyl-2*H*-selenopyran (4d). These cycloadducts were isolated as a pale yellow viscous oil in 45% yield (78.9 mg) as an inseparable mixture of regioisomers from the reaction of **2d** with isoprene. The isomer ratio was determined to be 2.0:1 by proton NMR integration, with **3d** predominating.

2-Cyano-3,6-dihydro-5-methyl-2-phenyl-2*H*-selenopyran (3e) and 2-Cyano-3,6-dihydro-4-methyl-2-phenyl-2*H*-selenopyran (4e). These cycloadducts, an inseparable mixture of regioisomers prepared via method B, were isolated as a colorless oil in 95% yield (169 mg) from the reaction of **2e** with isoprene. The isomer ratio was determined to be 3.3:1 by proton NMR integration, with **3e** predominating.

3,6-Dihydro-2,5-dimethyl-2-(phenylsulfonyl)-2*H*-selenopyran (3f) and 3,6-Dihydro-2,4-dimethyl-2-(phenylsulfonyl)-2*H*-selenopyran (4f). These cycloadducts, an inseparable mixture of regioisomers prepared via method B, were isolated as a colorless oil in 85% yield (182 mg) from the reaction of **2f** with isoprene. The isomer ratio was determined to be 2.8:1 by proton NMR integration, with **3f** predominating.

Diethyl 3,6-Dihydro-3-methyl-2*H*-selenopyran-2,2-dicarboxylate (3g). This selenopyran was prepared via method A and was obtained as a pale yellow liquid in 65% yield (33.9 mg) from the reaction of **2g** with (*E*)-1,3-pentadiene.

3,6-Dihydro-3,5-dimethyl-2,2-diphenyl-2*H*-selenopyran (3h). Method C. A solution containing 132 mg (1.10 mmol) of *t*-BuOH and 1.14 mL (10.0 mmol) of (*E*)-2-methyl-1,3-pentadiene in THF (20 mL) was prepared and heated to reflux. To this solution was added 150 mg (0.551 mmol) of diphenylmethyl selenocyanate as a solution in THF (10 mL) over 1 h via syringe pump. The solution was cooled to 0 °C, diluted with pentane (30 mL), and filtered through a 4-cm activated neutral alumina plug. The filtrate was concentrated at reduced pressure. Pure **3h** subsequently was obtained in 70% yield (126 mg) upon flash chromatographic separation on silica gel using 25:1:1 hexanes/CH_2Cl_2/Et_2O as eluant.

***endo*-2-Benzoyl-3,6-dihydro-2,3,5-trimethyl-2*H*-selenopyran (3i) and *exo*-2-Benzoyl-3,6-dihydro-2,3,5-trimethyl-2*H*-selenopyran (3j). Method D.** A THF solution containing selenocyanate **1d** was added via syringe pump to a refluxing THF solution containing KH (1.1 equiv) and (*E*)-2-methyl-1,3-pentadiene (5.0 equiv). The solution was cooled to 0 °C, diluted with pentane (30 mL), and filtered through a 4-cm activated neutral alumina plug. The filtrate was concentrated at reduced pressure. **3i** and **3j** were obtained in 68% yield (84.4 mg) as a viscous, pale yellow oil as an inseparable mixture of isomers by flash chromatography (silica gel, 25:1:1 hexanes/CH_2Cl_2/Et_2O). The endo/exo isomer was determined to be 4.2:1, respectively, by ^1H NMR integration. The predominant isomer was identified as the endo isomer by NOE experiments. Irradiation of the C-2 methyl resonance gave no enhancement in the C-3 methyl of the major isomer, but did give an 8% enhancement in the C-3 methyl resonance of the minor isomer. Irradiation of the C-3 methine of the major isomer resulted in a 12% of the C-2 methyl resonance. None of the regioisomeric products were observed.

General Procedure for the Cycloaddition Reactions of Fluoreneselone. 3′6′-Dihydrospiro[9*H*-fluorene-9,2′-[2′*H*]selenopyran] (5). To a solution containing 200 mg (0.74 mmol) of 9-(selenocyanato)fluorene and excess butadiene in anhydrous CH_2Cl_2 (10 mL) at room temperature was added 207 mL (1.48 mmol) of anhydrous Et_3N as a solution in 10 mL of THF via syringe pump over 6.5 h at room temperature. The reaction mixture was diluted to 50 mL with pentane and filtered through a 4-cm neutral alumina plug. The solution was concentrated at reduced pressure and purified by flash chromatography on silica gel using 25:1:1 hexanes/Et_2O/CH_2Cl_2 as eluant yielding 215 mg (98%) of **5** as a pale yellow powder (mp 116–119 °C).

3′,6′-Dihydro-5′-methylspiro[9*H*-fluorene-9,2′-[2′*H*]selenopyran] (6a) and 3′,6′-Dihydro-4′-methylspiro[9*H*-fluorene-9,2′-[2′*H*]selenopyran] (6b). These selenopyrans were obtained in 93% yield (214 mg) as a pale yellow powder (mp 85–87 °C) from the reaction of fluoreneselone with isoprene. The regioisomers were inseparable by HPLC and GC. The isomer ratio was determined to be 2.3:1 by proton NMR integration of the vinyl resonances.

3′,6′-Dihydro-3′-methylspiro[9*H*-fluorene-9,2′-[2′*H*]selenopyran] (7). This selenopyran was obtained in 82% yield (189 mg) as a pale yellow solid from the reaction of fluoreneselone with (*E*)-1,3-pentadiene.

3′,6′-Dihydro-3′,5′-dimethylspiro[9*H*-fluorene-9,2′-[2′*H*]selenopyran] (8). This selenopyran was obtained in 96% yield (231 mg) as a pale, yellow powder from the reaction of fluoreneselone with (*E*)-2-methyl-1,3-pentadiene.

3′,6′-Dihydro-4′,5′-dimethylspiro[9*H*-fluorene-9,2′-[2′*H*]selenopyran] (9). This selenopyran was obtained in 97% yield (233 mg) as a pale

yellow powder from the reaction of fluoreneselone with (*E*)-2,3-dimethyl-1,3-butadiene.

3′,6′-Dihydro-3′-ethenylspiro[9*H*-fluorene-9,2′-[2′*H*]selenopyran] (10). This selenopyran was obtained in 93% yield (223 mg) as a white powder from the reaction of fluoreneselone with 1,3,5-hexatriene.

3′,6′-Dihydro-5′-ethoxyspiro[9*H*-fluorene-9,2′-[2′*H*]selenopyran] (11a) and 3′,6′-Dihydro-4′-ethoxyspiro[9*H*-fluorene-9,2′-[2′*H*]selenopyran] (11b). This selenopyran, a pale yellow powder (mp 96–99 °C), was obtained in 91% yield (39 mg) as an inseparable mixture of regioisomers from the reaction of fluoreneselenone with 2-ethoxybutadiene. The isomer ratio was determined to be 4:1 by proton NMR integration of the vinyl resonances, with **11a** predominating.

5′-[(*tert*-Butyldimethylsilyl)oxy]-3′,6′-dihydrospiro[9*H*-fluorene-9,2′-[2′*H*]selenopyran] (12a) and 4′-[(*tert*-Butyldimethylsilyl)oxy]-3′,6′-dihydrospiro[9*H*-fluorene-9,2′-[2′*H*]selenopyran] (12b). This selenopyran, a viscous, pale yellow oil, was obtained in 93% yield (295 mg) as an inseparable mixture of regioisomers from the reaction of fluoreneselenone with 2-[(*tert*-butyldimethylsilyl)oxy]butadiene. The isomer ratio was determined to be 5:1 by proton NMR integration of the vinyl resonances, with **12a** predominating.

3′,6′-Dihydro-3′-methoxy-5′-oxospiro[9*H*-fluorene-9,2′-[2′*H*]-selenopyran] (13). This selenopyran was obtained in 97% yield (233 mg) as a white powder (mp 159–161 °C) from the reaction of fluoreneselone with Danishefsky's diene.

Ethyl 3′,6′-Dihydro-6′-methylspiro[9*H*-fluorene-9,2′-[2′*H*]-selenopyran]-3′-carboxylate (14). This selenopyran was obtained in 88% yield (125 mg) as a colorless, viscous oil from the reaction of fluoreneselone with ethyl sorbate.

Spiro[2′-selena[2.2.1]bicyclohept-5′-ene-3′,9-fluorene] (15). This selenopyran was obtained in 97% yield (445 mg) as a pale yellow powder from the reaction of fluoreneselone with cyclopentadiene.

Spiro[2′-selena[2.2.2]bicyclooct-5′-ene-3′,9-fluorene] (16). This selenopyran was obtained in 95% yield (113 mg) as a pale yellow powder from the reaction of fluoreneselone with cyclohexadiene.

6′-[(*tert*-Butyldimethylsilyl)oxy]spiro[2′-selena[2.2.2]bicyclo-5-ene-3′,9-fluorene] (17). This selenopyran was obtained in 91% yield (304 mg) as a viscous, colorless oil form the reaction of fluoreneselone with 2-[(*tert*-butyldimethylsilyl)oxy]butadiene.

***meso*-Diethyl 2,2′-diselenopropanoate (18a) and *d,l*-diethyl 2,2′-diselenopropanoate (18b)**: byproducts isolated as an inseparable mixture of isomers (1:2 meso:*d,l*) in 17% yield (210 mg) from the reaction of **1c** with Et_3N in refluxing EtOH.

9,9′-Epidiseleno-9,1′-bifluorenyl (19). This diselenide was isolated in 27% yield (64 mg) as a pale yellow powder (mp 178–180 °C dec) from the reaction of 9-(selenocyanato)fluorene (**1k**) with pyridine *N*-oxide under standard conditions.

9-(1,3-Dimethyl-3-butenyl)fluorene (21a) and 9-(1,3-Dimethyl-2-butenyl)fluorene (21b). To a solution containing 20 mg (61 μmol) of the cycloadduct **8** in 5 mL of glacial HOAc was added 25 mg (390 μmol) of activated Zn dust. The mixture was heated to reflux for 5 h. After being cooled to room temperature, the solution was filtered through a 1-in. Celite pipet plug with CH_2Cl_2 as eluant. The filtrate was diluted with H_2O (25 mL), extracted with CH_2Cl_2 (3 × 10 mL), dried ($MgSO_4$), filtered, and concentrated under reduced pressure. The colorless oil thus obtained was purified by flash chromatography (silica gel, 25:1:1 hexanes/CH_2Cl_2/Et_2O) to yield 13 mg (85%) of **21a** and **21b**. The ratio of **21a** to **21b** was determined by capillary GLC to be 2:1, respectively.

9-(1,3-Dimethylbutyl)fluorene (21c). To a solution containing 21 mg (85 μmol) of a mixture of olefin isomers **21a** and **21b** in THF (5 mL) at room temperature was added 5 mg (5.6 mol %) of 10% Pd/C. An atmosphere of H_2 was established via use of a balloon attached to the reaction flask. The reaction was stirred for 3 h at room temperature. The appearance of a single product with concomitant disappearance of the two positional olefin isomers was observed via monitoring by GLC. The solids were filtered through Celite, and the solvent was removed at reduced pressure. The residue was purified by gravity chromatography on silica gel (25:1:1 hexanes/CH_2Cl_2/Et_2O) to yield 19 mg (91%) of **21c** as a colorless oil.

3′,6′-Dihydro-5′-oxospiro[9*H*-fluorene-9,2′-[2′*H*]selenopyran] (22a) and 3′,6′-Dihydro-4′-oxospiro[9*H*-fluorene-9,2′-[2′*H*]selenopyran] (22b). To a solution containing 2 drops of H_2O and 39 mg (0.11 mmol) of a 4:1 mixture of regioisomeric cycloadducts **12a** and **12b** in THF (1 mL) at ambient temperature was added 2 drops of 0.1 N HCl. The solution was allowed to stir for 1.5 h. K_2CO_3 (100 mg) was subsequently added (to desiccate and neutralize the solution). The solids were filtered, and the solution was concentrated at reduced pressure. Isomeric ketones **22a** and **22b** were readily separated via chromatographic purification on silica gel using 25:1:1 hexanes/Et_2O/CH_2Cl_2 as eluant [combined yield 96% (34 mg)].

3′-(2,4,6-Trimethylphenyl)spiro[9*H*-fluorene-9,5′-[5′*H*]-1′,4′,2′-oxaselenazole] (24). This oxaselenazole was obtained in 86% yield (276 mg) as a pale yellow powder (mp 163–165 °C) from the reaction of fluoreneselone with 2,4,6-trimethylbenzonitrile *N*-oxide.

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Registry No. 1a, 117183-99-0; **1b**, 117184-00-6; **1c**, 117184-01-7; **1d**, 114908-25-7; **1e**, 117184-02-8; **1f**, 117184-03-9; **1g**, 117184-04-0; **1h**, 27805-30-7; **1i**, 117184-05-1; **1j**, 114263-69-3; **3a**, 117184-06-2; **3b**, 117184-07-3; **3c**, 117184-08-4; **3d**, 117184-09-5; **3e**, 117184-10-8; **3f**, 117184-11-9; **3g**, 117184-12-0; **3h**, 117184-13-1; **3i**, 117184-14-2; **3j**, 117184-15-3; **4a**, 117201-62-4; **4b**, 117184-16-4; **4c**, 117184-17-5; **4d**, 117184-18-6; **4e**, 117184-19-7; **4f**, 117184-20-0; **5**, 114263-70-6; **6a**, 114263-71-7; **6b**, 114263-72-8; **7**, 114263-73-9; **8**, 114263-74-0; **9**, 117184-21-1; **10**, 114263-75-1; **11**, 114083-22-6; **11a**, 114263-78-4; **11b**, 114263-79-5; **12a**, 114263-76-2; **12b**, 114263-77-3; **13**, 114263-80-8; **14**, 114263-81-9; **15**, 114263-82-0; **16**, 117184-22-2; **17**, 114263-83-1; **18a**, 117184-23-3; **18b**, 117184-24-4; **19**, 114263-86-4; **20**, 116809-01-9; **21a**, 117184-25-5; **21b**, 117184-26-6; **21c**, 96107-16-3; **22a**, 117184-27-7; **22b**, 117184-28-8; **23**, 117184-29-9; **24**, 114263-85-3; **25**, 117184-30-2; KSeCN, 3425-46-5; $PhSO_2CH_2CH_3$, 599-70-2; $(SeCN)_2$, 27151-67-3; AgSeCN, 5169-33-5; ethyl 2-(diethoxyphosphinyl)-2-bromoacetate, 23755-73-9; ethyl 2-phenyl-2-bromoacetate, 2882-19-1; ethyl 2-bromopropanoate, 535-11-5; 1-phenyl-2-bromo-1-propanone, 2114-00-3; α-bromophenylacetonitrile, 5798-79-8; bis(carbethoxymethyl) bromide, 685-87-0; diphenylmethyl bromide, 776-74-9; 1-(phenylethyl) 1-bromide, 585-71-7; 9-bromofluorene, 1940-57-4; isoprene, 78-79-5; (*E*)-1,3-pentadiene, 2004-70-8; (*E*)-2-methyl-1,3-pentadiene, 926-54-5; butadiene, 106-99-0; (*E*)-2,3-dimethyl-1,3-butadiene, 1625-49-6; 1,3,5-hexatriene, 2235-12-3; 2-ethoxybutadiene, 4747-05-1; 2-[(*tert*-butyldimethylsilyl)-oxy]butadiene, 80738-05-2; Danishefsky's diene, 59414-23-2; ethyl sorbate, 2396-84-1; cyclopentadiene, 542-92-7; cyclohexadiene, 29797-09-9; 2,4,6-trimethylbenzonitrile *N*-oxide, 2904-57-6.

Supplementary Material Available: General experimental procedures and ^1H and ^{13}C NMR, IR, and MS data (22 pages). Ordering information is given on any current masthead page.