To study the rate of reaction of 4, we divided 6.01 g of the reaction product (78% by I_2 titration) dissolved in 60 mL of MeOH (previously purged with Ar) into parts A–D. Part A (6 mL) was stored at −26 °C under Ar as a control. Part B (18 mL) was allowed to stir at 23–24 °C under Ar. Concentrated H_2SO_4 (25 μL, 0.9 mequiv) was added to part C (18 mL); this MeOH solution of 4 contained ~9 mmol of 4 (on a weight basis) and had a pH of 2. To part D (18 mL) was added 329 μL of 4.1 N $NaOCH_3$ (1.35 mequiv) to give a pH of 10. The solutions containing H_2SO_4 and $NaOCH_3$, as well as the solution containing only 4, were stored at 23–24 °C under Ar, and 2-mL aliquots were titrated with 0.0922 N KI_3 at various time intervals. The pH of the solutions was checked periodically, with no change being observed. Rate constants were obtained by taking the slope of the least-square lines in Figure 1; Figure 1 shows the I_2 titer after subtraction of the infinity titer determined at 72 h. The rate constants (with check values from a different preparation of 4 in parentheses) were 0.12 h^{-1} (0.14 h^{-1}) for 4 alone, 0.13 h^{-1} (0.13 h^{-1}) for 4 in the presence of H_2SO_4, and 0.10 h^{-1} (0.08 h^{-1}) for 4 in the presence of $NaOCH_3$. The half-lives (calculated as $t_{1/2} = 0.693/k$) were 5.8 (5.0), 5.3 (5.3), and 6.9 h (8.7 h), respectively.

Inspection of the materials, isolated from the infinity titer samples, by TLC (50% EtOAc in hexane), indicated 6 (R_f 0.49) to be the principal component, along with significant amounts of 7 (R_f 0.10) and 8 (R_f 0.74); minor unidentified components were observed at R_f 0.67 and R_f 0.24. The ratios by NMR of the moieties PhS/PhS(O) were 1.0 for 4 alone, 1.0 for 4 in the presence of H_2SO_4, and 0.5 for 4 in the presence of $NaOCH_3$.

Initial attempts were made to study the redox reaction of 4 by NMR. These experiments, done in $CDCl_3$ instead of MeOH, led to significantly slower rates [thus a solution of 4 in $CHCl_3$ (119.7 mg in 1 mL) showed no change by NMR and titration during 8 days (79% SH by I_2 titration vs. 78% initially)]. For example, in early experiments an average of the percent SH based on integrals of SH/all aromatic protons and of SH/CH_2 β to S showed a decrease from an initial ~27% to ~17% in 240 h and to ~11% in 596 h; the ratio for PhS/PhSO increased meanwhile from 0.46 to 0.66 to 0.68, respectively. NMR spectra thus proved useful for qualitatively assessing trends in the loss of SH and the increase of PhS. For several reasons, however, they were unpromising for quantitative work.

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Registry No. 1, 4911-65-3; 2, 13033-58-4; 3, 534-18-9; 4, 77400-50-1; 6, 77400-51-2; 7, 77400-52-3; 8, 77400-53-4; 9, 77400-54-5; 12, 77400-55-6; 3-chloropropyl phenyl sulfone, 19432-96-3; 3-[(2′,4′-dinitrophenyl)thio]propyl phenyl sulfoxide, 77400-56-7; 2,4-dinitrochlorobenzene, 97-00-7.

Vinyl Selenides and Selenoxides: Preparation, Conversion to Lithium Reagents, Diels–Alder Reactivity, and Some Comparisons with Sulfur Analogues[1]

Hans J. Reich,* William W. Willis, Jr., and Peter D. Clark

S. M. McElvain Laboratories of Organic Chemistry, Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706

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A variety of aryl vinyl selenides are prepared by reaction of vinyl Grignard reagents with aryl selenenyl bromides or by reductive elimination of the adducts of [bis(arylseleno)methyl]lithiums with carbonyl compounds. Deprotonation of phenyl vinyl selenide is achieved with LDA at −78 °C in THF. Vinyl selenides with β-alkyl groups require LiTMP and warmer temperatures (−50 °C) for complete deprotonation. Allylic lithium reagents were obtained from 1-propenyl and 2-methyl-1-propenyl selenides whereas 1-butenyl or 3-methyl-1-butenyl selenides gave vinyl lithium reagents. Reaction with electrophiles proceeds in good to excellent yield. Primary halides require HMPA to react well. Unhindered carbonyl compounds react without enolization. Deprotonation with LDA is shown to be reversible, and during competitive deprotonation studies with LDA, aryl vinyl sulfides are found to be thermodynamically less acidic than aryl vinyl selenides ($K_{S/Se}$ = 0.21 for phenyl vinyl and 0.3 for *m*-(trifluoromethyl)phenyl vinyl). Deprotonation with LiTMP is shown to be irreversible, and competitive deprotonation studies showed vinyl selenide to be kinetically more acidic as well [$k_{S/Se}$ = 0.37 (phenyl vinyl), 0.42 (*m*-(trifluoromethyl)phenyl vinyl)]. Most studies have shown sulfur compounds to be more acidic. *m*-(Trifluoromethyl)phenyl allyl sulfide, as expected, is more acidic than the selenium compound ($k_{S/Se}$ = 3.8). Vinyl selenoxides can be prepared with *m*-chloroperbenzoic acid. They are not thermally stable enough to serve as acetylene equivalents in Diels–Alder reactions. Phenyl vinyl selenide gives a Diels–Alder addition product with 1,4-diphenylisobenzofuran but failed to give cycloaddition products with less reactive dienes. Phenyl vinyl selenoxide does not give a useful yield of lithium reagent upon reaction with amide bases.

A number of useful functional group transformations can be achieved by the introduction and removal of selenium functions.[2] Vinyl selenides and selenoxides have the potential of combining such processes with carbon–carbon bond-forming reactions involving the vinyl group. We report here our results on the preparation and deprotonation of vinyl selenides and selenoxides, on the further transformations of the lithium reagents so formed, and on the relative kinetic and thermodynamic acidities of several vinyl and allyl selenides and sulfides. We also report on

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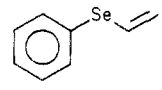
the Diels–Alder reactivity of aryl vinyl selenides, selenoxides, and sulfides.

Vinyl selenides have been prepared by several routes, including the addition of selenols to terminal acetylenes,[3] the dehydrohalogenation of β-halo[1a,b,4] and α-halo selenides[5] and related elimination reactions, the reduction of 1-(phenylseleno)alkynes,[6a] the reaction of alkynyl trialkylborates,[7] alkenylboranes, mercurials,[6a] lithium[6b] and magnesium reagents[6c] with selenenyl halides, the reaction of phenylseleno-substituted Wittig reagents with aldehydes,[3b] the Peterson olefin synthesis (elimination of trimethylsiloxide),[8] the addition of selenenic acid derivatives to acetylenes,[1c,d,9a] the syn elimination of selenoacetal and selenoketal monoselenoxides,[1e,f] and the base-catalyzed isomerization of allyl selenides.[9b]

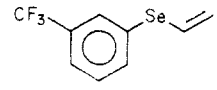
Four groups have independently reported the preparation of vinyl selenide carbanions recently.[1g,10] The procedures used have been the cleavage of ketene selenoacetals with *n*-butyllithium[10c] and the deprotonation of vinyl selenides with lithium diisopropylamide (LDA) in THF[1g] or THF/HMPA[10a] or with potassium diisopropylamide (KDA) in THF.[10b]

Results and Discussion

Synthesis of Vinyl Selenides. We have used two routes for the synthesis of a series of vinyl selenides. The first method involves the reaction of vinyl Grignard reagents with diselenides or areneselenenyl halides. It is the most convenient procedure when the required vinyl bromide is readily available. Phenyl vinyl selenide (**1a**, 67% yield), *m*-(trifluoromethyl)phenyl vinyl selenide (**1b**, 60%), and phenyl 1-propenyl selenide (**7a**, 92%) have been



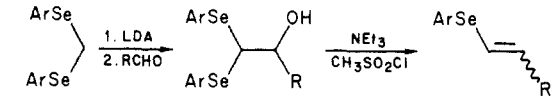
1a



1b

synthesized by using this procedure. Throughout this paper, the "**a**" compounds will refer to phenylseleno and the "**b**" compounds to [*m*-(trifluoromethyl)phenyl]seleno. Many types of selenides have been previously prepared by the reaction of organometallic reagents with electrophilic selenium species.

Table I. Preparation of Vinyl Selenides by "Reductive Elimination" of β-Hydroxy Selenoacetals

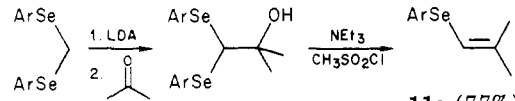


2-5 **6-9**

R	compd no.	% yield of seleno-acetal	compd no.	% yield of selenide	cis/trans
Ar = C_6H_5					
Ph	**2a**	95	**6a**	74	0/100
CH_3	**3a**	92	**7a**	84	50/50
CH_2CH_3	**4a**	98	**8a**	74	50/50
$CH(CH_3)_2$	**5a**	77[a]	**9a**	81[a]	25/75
Ar = *m*-CF_3-C_6H_4					
Ph	**2b**	*b*	**6b**	85	0/100
CH_3	**3b**	91	**7b**	63	50/50
CH_2CH_3	**4b**	98	**8b**	72	50/50
$CH(CH_3)_2$	**5b**	98	**9b**	79	30/70

[a] Reference 1a. [b] Yield not determined.

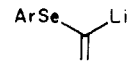
For more complicated vinyl selenides (**6–9, 11**) we have used the addition of [bis(arylseleno)methyl]lithium reagents[11] to aldehydes or ketones, followed by "reductive elimination" of the β-hydroxy selenides (**2–5, 10**) so formed.[1a,h] It was necessary to modify the previously reported conditions for this reaction somewhat to achieve good yields with the *m*-(trifluoromethyl)phenyl vinyl selenides. Apparently the internal displacement of mesylate by selenium to give an episelenonium salt, which is quite rapid in the case of phenylseleno, is sufficiently slow in the case of the less nucleophilic *m*-trifluoromethyl-substituted compounds that several hours at room temperature are needed for completion of the "reductive elimination". Table I presents the preparation of selenides using aldehydes as starting materials. The analogous route with ketones provided the β-disubstituted vinyl selenide 11.



10a (95%)
10b (98%)

11a (77%)
11b (73%)

Deprotonation of Vinyl Selenides. During the search for suitable bases to effect deprotonation of vinyl selenides we observed that alkyllithium reagents gave some deprotonation, accompanied by substantial amounts of cleavage and Michael addition products. Similar observations have been made by several other groups.[10a,d,12] We then turned our attention to lithium dialkylamides, bases which have been successfully used for the deprotonation of a number of other selenium compounds.[2b] Phenyl vinyl selenide is deprotonated by lithium diisopropylamide (LDA) in tetrahydrofuran at −78 °C. With 1.2 equiv of LDA 85% of the vinyllithium **12a** is formed after 2 h, the remaining



12

15% being made up of starting material (7%) and de-

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(8) (a). W. Dumont, D. Van Ende, and A. Krief, *Tetrahedron Lett.*, 485 (1979); (b) B.-T. Gröbel and D. Seebach, *Chem. Ber.*, **110**, 852 (1977).

(9) (a) L. Cherici and F. Montanari, *Gazz. Chim. Ital*, **86**, 1269 (1956); (b) E. G. Kataev, T. G. Mannafov, and Yu. Yu. Samitov, *Zh. Org. Khim.*, **11**, 2324 (1975); W. Ried and G. Sell, *Synthesis*, 447 (1976); G. H. Schmid and D. G. Garratt, *Tetrahedron Lett.*, 3991 (1975); D. G. Garratt and G. H. Schmid, *Chem. Scr.*, **11**, 170 (1977); E. G. Kataev, L. M. Kataeva, and L. M. Chmutova, *Zh. Org. Khim.*, **2**, 2244 (1966).

(10) (a) M. Sevrin, J. N. Denis, and A. Krief, *Angew. Chem.*, **90**, 550 (1978); (b) S. Raucher and G. A. Koolpe, *J. Org. Chem.*, **43**, 3794, 4252 (1978); (c) B.-T. Grobel and D. Seebach, *Chem. Ber.*, **110**, 867 (1977).

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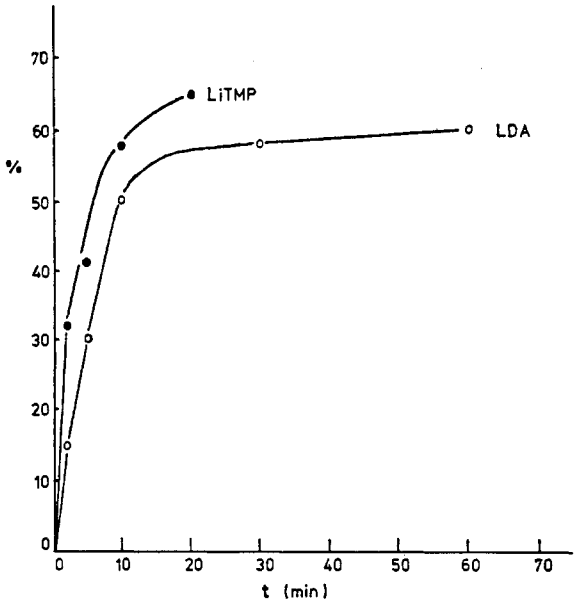


Figure 1. Deprotonation of phenyl vinyl sulfide with LDA (0.8 equiv) and LiTMP (0.8 equiv) at −78 °C. The percentages refer to fraction of base consumed, determined by methylation of the vinyllithium reagent.

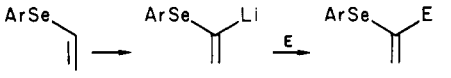
composition (8%) to benzeneselenolate anion and, presumably, acetylene. The decomposition could be occurring by competitive β-elimination of vinyl selenide (α-deprotonation is reversible, see below) or by α-elimination of the lithium reagent **12a** to give the carbene. The rate of deprotonation of **1a** was strongly depressed by the presence of excess amine. With 1.2 equiv of LDA, phenyl vinyl selenide is 50% deprotonated in 5 min at −78 °C, yet it takes 2 h to reach 85% completion. As Figure 1 shows, the effect is even more dramatic for phenyl vinyl sulfide, where the deprotonation with LDA almost stops when half of the amide is consumed. It is reasonable to postulate that a 1:1 complex between LDA and diisopropylamine is a considerably weaker base than LDA itself. These observations can be put to synthetic use: when a mixture of **1a** (or the corresponding sulfide) and a *catalytic* amount of diisopropylamine is treated with 1 equiv of *n*-butyllithium, the deprotonation is rapid and complete in a few minutes. The yields of **12a** are not much improved over the LDA procedure, however, since some competing Michael reaction and attack at selenium by *n*-butyllithium occurred.

We have also studied the deprotonation of **1a** with LDA in the presence of hexamethylphosphoramide (HMPA).[10a] Deprotonation with 1.2 equiv of LDA and 1.2 equiv of HMPA in THF is complete within 5 min at −78 °C. Alkylation of the lithium reagent **12a** with primary halides is complete within 15 min. Overlong reaction times should be avoided since double bond isomerization is promoted by HMPA. Secondary halides do not react and enolizable ketones give substantial amounts of deprotonation, so HMPA was not used in reactions with enolizable ketones.

The [*m*-(trifluoromethyl)phenyl]seleno group enhances the acidity of α-hydrogens relative to the phenylseleno group.[1a,i] To take advantage of this effect we have treated the CF_3-substituted vinyl selenide **1b** with LDA in THF and found deprotonation to be complete in less than 5 min without decomposition. Both **12a** and **12b** had about the same stability (half-life ~15 min in THF at 0 °C) so the cleaner formation of **12b** appears to be due to a shorter reaction time and not any increase in stability.

Table II presents the reactions of the [α-(arylseleno)vinyl]lithium reagents **12** with a variety of electrophiles.

Table II. Reactions of [1-(Arylseleno)vinyl]lithium Reagents (12) with Electrophiles



1 12 13

electrophile	E	% yield 13a[a]	13b[b]
D_2O	D	82[c]	
MeSSMe	SCH_3	66	83
PhSeSePh	SePh		89
Me_3SiCl	Me_3Si	77	99
CO_2	CO_2H	77	80
$Me_2C{=}O$	$C(OH)Me_2$	80	
$Et_2C{=}O$	$C(OH)Et_2$	75	
CH_3I	CH_3	75,[c,d] 77,[e] 75[f]	91
$CH_3(CH_2)_3I$	*n*-Bu	71[e]	85[e]
$Ph(CH_2)_3Br$	$Ph(CH_2)_3$	76[e]	

[a] Ar = C_6H_5. [b] Ar = *m*-CF_3-C_6H_4. [c] NMR estimate. [d] Preparation also described in ref 10b. [e] HMPA (1.2 equiv) added during formation of **12**. [f] Using 1.0 equiv of *n*-BuLi and a catalytic amount of diisopropylamine.

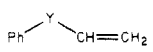
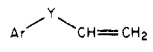
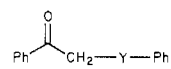
Most occur rapidly at −78 °C, but it was necessary to carry out the reaction with *n*-butyl iodide in the presence of HMPA. The selenenylation of **12b** was attempted with benzeneselenenyl chloride or bromide, but results were poor. Diphenyl diselenide reacted much more cleanly to give the ketene selenoacetal **13b** (E = SePh).

Acidity Comparisons for Vinyl and Allyl Selenides and Sulfides. The surprisingly large acidifying effect of the *m*-trifluoromethyl substituent as well as the qualitative observation that, contrary to other S/Se acidity comparisons, vinyl selenides were deprotonated more rapidly than analogous sulfides led us to carry out some quantitative studies of deprotonation rates of several vinyl and allyl selenides and sulfides. These were carried out as in a previous study[1a] by treating a mixture of two compounds at low temperature with a deficiency of base (either LDA or lithium tetramethylpiperidide, LiTMP[13]) followed by derivatization with methyl iodide. The rate of methylation was shown to be rapid compared to the proton-transfer steps. Product composition was determined by 270-MHz ^1H NMR spectroscopy.

In the course of competitive deprotonations of vinyl selenides and sulfides with LDA in THF at −78 °C, control experiments showed that anion equilibration was occurring and was complete in less than 1 h. The equilibria could be approached from either side. With LiTMP as base, equilibration was very slow, so relative kinetic acidities were determined. The results obtained are summarized in Table III. Both vinyl selenides **1a** and **1b** are more acidic under kinetic and thermodynamic conditions than sulfur analogues by factors of 2.4 to 4.8. For comparison purposes, we have measured the acidity of phenyl allyl sulfides and selenide[1j] using the same technique as for the vinyl compound. Anion equilibration did not occur, so here also relative kinetic acidities were determined. The sulfur compound is deprotonated more rapidly than the selenium compound. Previous measurements of the thermodynamic or kinetic acidity of analogous sulfur and selenium compounds (Table III) have also shown the sulfur compound to be more acidic by approximately an order of magnitude except for one case: selenophene is more acidic than thiophene.[14a]

(13) M. W. Rathke and R. Kow, *J. Am. Chem. Soc.*, **94**, 6854 (1972); R. A. Olofson and C. M. Dougherty, *ibid.*, **95**, 581, 582 (1973).

Table III. Comparison of Kinetic and Thermodynamic Acidities of Selenides and Sulfides

compd	base/solvent/temp, °C	quantity measured	sulfur/selenium	ref
	LDA/THF/−78	K_{eq}	0.21	*a*
	LiTMP/THF/−78	k_{deprot}	0.37	*a*
	LDA/THF/−78	K_{eq}	0.3	*a*
	LiTMP/THF/−78	k_{deprot}	0.42	*a*
Ph−Y−$CH_2CH=CH_2$	LDA/THF/−78	k_{deprot}	7.5	*a*
	KO-*t*-Bu/Me_2SO/25	k_{isotop}	0.67	14a
Ar−Y−CH_3	LiTMP/THF/−78	k_{deprot}	3.8	1a
Ph−Y−CH_3	KNH_2/NH_3/−33	k_{isotop}	10	14b
Ph−Y−$CH_2C\equiv CH$	NaOEt/HOEt/44	k_{isom} [b]	6.14	14c
Ph−Y−$CH=C=CH_2$	NaOEt/HOEt/44	k_{isom} [c]	4.8	14c
	$NaCH_2S(O)CH_3/Me_2SO$	K_{eq}	32	14d

[a] This work. [b] Isomerization of propargyl to allenyl sulfide/selenide. [c] Isomerization of allenyl to 1-propynyl.

Table IV. *m*-Trifluoromethyl Substituent Effects on Thermodynamic and Kinetic Acidities

compd	base/solvent/temp, °C	quantity measured	k_{CF_3}/k_H	ρ	ref
Ar−S−CH_3	LiTMP/THF/−56	k_{deprot}	22.4	3.14	1a
Ar−Se−CH_2−$CH=CH_2$	LDA/THF/−78	k_{deprot}	11.7	2.48	*a*
Ar−S−$CH=CH_2$	LDA/THF/−78	k_{deprot}	16.7	2.83	*a*
	LiTMP/THF/−78	K_{eq}	92	4.75	*a*
Ar−Se−$CH=CH_2$	LDA/THF/−78	k_{deprot}	14.9	2.73	*a*
	LiTMP/THF/−78	K_{eq}	64	4.20	*a*
Ar−CH_3	Cs^+c-HexNH/c-$HexNH_2$/50	k_{isotop}	60	4.0	16a
	$NaCH_2SOCH_3/Me_2SO$/25	K_{eq}	*b*	7.4	15
Ph_2ArCH	PhLi/THF/22	k_{deprot}	14.1	2.2	16b
Ar−C≡C−CH_3	*n*-BuLi/Et_2O/0	k_{deprot}	*b*	13	16c

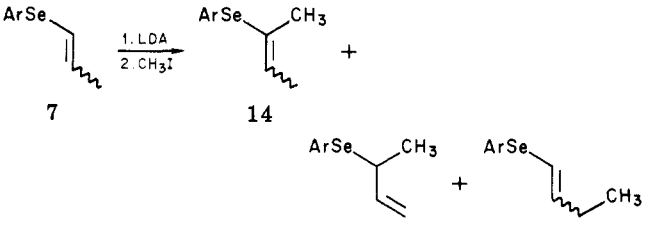
[a] This work. [b] Not measured.

If it is assumed that the rather approximate techniques used both in our work and many of the literature examples cited provide reliable estimates of the direction if not the magnitude of the relative ability of sulfur and selenium to stabilize carbanions, then there is an interesting dichotomy: vinyl anions are less stabilized by sulfur than selenium, whereas methyl, allyl, and other conjugated anions are more stabilized by sulfur. We suggest the following working hypothesis: those anions capable of effective conjugative overlap (i.e., negative charge in an orbital high in p character) are better stabilized by sulfur, whereas those not capable of such overlap (i.e., negative charge in an orbital high in s character) are better stabilized by selenium.

The *m*-CF_3 substituent effects we have measured together with several related literature examples, are summarized in Table IV. Both sulfur and selenium are very effective at transmitting negative charge from the carbanionic center to the aromatic ring, comparable to that observed for directly conjugated systems. Only the substituted toluene pK_a measurements by Bordwell in the highly dissociating dimethyl sulfoxide[15] show a markedly higher ρ value.

Transmission coefficients for sulfur and selenium have been estimated at 0.4 in arylthio- and arylseleno-substi-

Table V. Reaction of 1-(Arylseleno)propenes with LDA at −78 °C



vinyl selenide	time, h	% deprot	product composition, % 14	15 + 16	15/16	decomp[a]
7a	2	42	9	86	6	5
	4	72	7	90	8	3
	5.8	74	5	82	8	13
	9	88	4	92	4	4
7b	1	66	30	58	7	12
	3	84	27	63	6	10
	5	84	20	70	6	10
	7	93	12	79	6	9

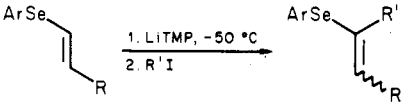
[a] Calculated from the amount of $PhSeCH_3$ formed by methylation of $PhSe^-$.

(14) (a) A. I. Shatenshtein, N. N. Magdesieva, Yu. I. Ranneva, I. O. Shapiro, and A. I. Serebryanskaya, *Teor. Eksp. Khim.*, 3, 343 (1967); *Chem. Abstr.*, 68, 58799 (1968); (b) A. I. Shatenshtein and H. A. Gvozdeva, *Tetrahedron*, 25, 2749 (1969); (c) G. Pourcelot and C. Georgoulis, *Bull. Soc. Chim. Fr.*, 866 (1964); G. Pourcelot and J.-M. Cense, *ibid.*, 1578 (1976); (d) F. G. Bordwell, J. E. Bares, J. E. Bartmess, G. E. Drucker, J. Gerhold, G. J. McCollum, M. Van Der Puy, N. R. Vanier, and W. S. Matthews, *J. Org. Chem.*, 42, 326 (1977).

(15) F. G. Bordwell, D. Algrim, and N. R. Vanier, *J. Org. Chem.*, 42, 1817 (1977); D. Algrim, J. E. Bares, J. C. Branca, and F. G. Bordwell, *ibid.*, 43, 5024 (1978).

(16) (a) A. Streitwieser, Jr., and H. F. Koch, *J. Am. Chem. Soc.*, 86, 404 (1964); (b) P. West, R. Waack, and J. I. Purmort, *J. Organomet. Chem.*, 19, 267 (1969); (c) J. Y. Becker, *ibid.*, 118, 247 (1976).

Table VI. Alkylation of 1-(Arylseleno)alkenes



8b, R = Et
9b, R = *i*-Pr

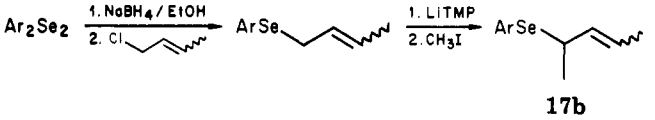
18b, R = Et
19b, R = *i*-Pr

selenide	R'I	% yield 18b	% yield 19b	E/Z
8b	CH_3I	63		1/1
8b	$CH_3(CH_2)_3I$	61		1/1
9b	CH_3I		62	7/3
9b	$CH_3(CH_2)_3I$		63	7/3

tuted acetic acids.[17] Our results would indicate a more efficient transmission. Reynolds and McClelland have studied ^{13}C chemical shifts as a function of ring substitution for aryl vinyl ethers, sulfides, and selenides.[18] Their results parallel ours to the extent that sulfur transmitted substituent effects slightly better than selenium, and both sulfur and selenium showed transmission approaching that observed for direct conjugation (i.e., styrenes).

Deprotonation of β-Alkyl-Substituted Vinyl Selenides. Table V summarizes the results obtained when the 1-(arylseleno)propenes (**7**) are treated with LDA in THF. As before, the deprotonation proceeds quite rapidly until approximately half of the LDA is used up and then slows down. Both the vinyl and allylic protons are removed;[19] the vinyl and allyl anions formed were identified by methylation (CH_3I) and 270-MHz NMR analysis of the products. For both **7a** and **7b** the 1-propenyllithium isomerizes to the allyllithium reagent, probably by a mechanism involving reversible proton transfer between selenide and LDA. The *m*-CF_3-substituted selenide **7b** is deprotonated more rapidly than is **7a**, although by a smaller margin than for the parent vinyl selenides, and gives more of the vinyllithium compound. It is reasonable that an inductively electron-withdrawing substituent should increase the kinetic acidity of the nearby vinyl hydrogen more than that of a distant allylic hydrogen. The ~sp^2 hybridized vinyl anion should also be more effectively stabilized by electron withdrawal than would be the delocalized allyl anion.

The acidity of the 1-butenyl (**8**) and 1-butenyl-3-methyl (**9**) selenides is so much lower than that of the propenyl selenides (**7**) that satisfactory deprotonations in neither the phenyl nor *m*-(trifluoromethyl)phenyl series can be achieved with LDA in THF. Even lithium tetramethylpiperidide (LiTMP) did not deprotonate **8a** and **9a** cleanly. Only when 1.5 equiv of LiTMP and the CF_3-substituted selenides **8b** and **9b** were used at −50 °C in THF could complete deprotonation be achieved, although not without some decomposition. Raucher and Koolpe[10b] have used the more powerful base system BuLi/KO-*t*-Bu/$HNiPr_2$ (KDA) to deprotonate **9a**.[10b] Like the analogous sulfides,[19] both **8b** and **9b** give exclusively vinyllithium reagents. Since even the 270-MHz NMR spectra of the methylation products from **8b** were quite complex, authentic allyl products (**17b**) were prepared as shown.[1j] No **17b** could



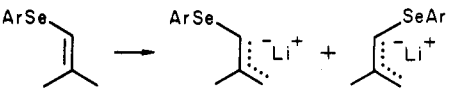
17b

be detected among the products from deprotonation and methylation of **8b**. Table VI presents the yields of several alkylations carried out with **8b** and **9b**. It is interesting to note that pure (*E*)- or (*Z*)-**9b** gave the same 7/3 *E*/*Z* mixture of products upon deprotonation and alkylation. It was not determined how the isomerization occurred. α-(Phenylseleno)vinyl anions prepared by deprotonation with potassium diisopropylamide react with retention of configuration.[10b]

We have also looked briefly at the deprotonation of three additional vinyl selenides—2-phenylethenyl (**6a**) and 2-methyl-1-propenyl (**11a** and **11b**).

Compound **6a** could be deprotonated with LDA at −78 °C, but poor yields of products were obtained (40% with CH_3I), owing to the decomposition which accompanies the deprotonation, as well as the poor nucleophilicity of the lithium reagent. The mode of decomposition is not known. Phenylacetylene was not detected as a product. Grobel and Seebach[10c] have prepared the same lithium reagent by selenium–lithium interchange (cleavage of ketene selenoacetal with *n*-butyllithium).

Deprotonation of **11a** and **11b** can be successfully carried out with LDA (very slow for **11a**) or LiTMP in THF at −78 to −50 °C. Only allyllithium products were detected, a result that parallels observations by Raucher and Koolpe on the deprotonation with KDA.[10b] When the allyllithium reagents formed were derivatized with acetone, both *E* and *Z* isomers of the γ-product were observed, indicating that stereoisomeric lithium reagents **20** and **21** were formed. It could not be established whether this was a consequence of similar rates of deprotonation at the two methyl groups of **11** or of interconversion of the allylic lithium reagents **20** and **21**.



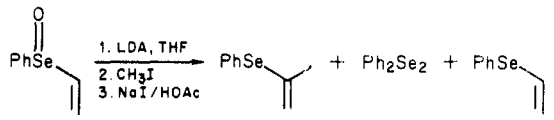
11 **20** **21**

Deprotonation of Phenyl Vinyl Selenoxide. The results on the deprotonation of a series of vinyl selenides detailed above show that these compounds are at the limits of the basicity range of lithium dialkylamides, since only a few of them can be satisfactorily deprotonated to give phenylseleno-substituted vinyllithium reagents. It was therefore considered of interest to examine the deprotonation of vinyl selenoxides to see if these offered any advantages. Selenoxides are considerably more acidic than selenides,[1k] and it was hoped that vinyl selenoxides might be deprotonated more easily and with greater selectivity to the vinyl proton than are the selenides. Vinyl sulfoxides have been deprotonated successfully.[20]

Phenyl vinyl selenide (**1a**) was converted to the selenoxide **21a** in 90% yield by oxidation with *m*-chloroperbenzoic acid at −10 °C. Deprotonation with LDA was attempted at −78 and −90 °C for varying amounts of time (Table VII). A maximum of 50% of the expected methylation product **13a** (E = CH_3) was isolated after reduction of selenoxide with NaI/HOAc.[1k] Deprotonation in the presence of methyl iodide gave even poorer results.

(17) O. Exner in "Advances in Linear Free Energy Relationships", N. B. Chapman and J. Shorter, Eds., Plenum Press, New York, p 25.
(18) W. F. Reynolds and R. A. McClelland, *Can. J. Chem.*, **55**, 536 (1977).
(19) Competitive vinyl and allyl metalations have been reported for 1-propenyl sulfide (R. Muthukrishnan and M. Schlosser, *Helv. Chim. Acta*, **59**, 13 (1976)) and ethers (J. Hartmann, M. Stähle, and M. Schlosser, *Synthesis*, 888 (1974)). 1-Propenyl selenide gives only allyl anion with KDA.[10b]
(20) K. Okamura, Y. Mitsuhira, M. Miura, and H. Takei, *Chem. Lett.*, 517 (1978); G. H. Posner, P.-W. Tang, and J. P. Mallamo, *Tetrahedron Lett.*, 3995 (1978).

Table VII. Reactions of Phenyl Vinyl Selenoxide with LDA



22a 13a 1a

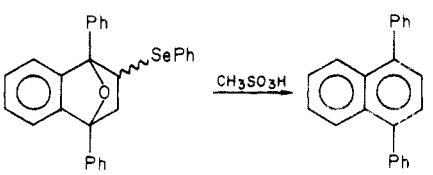
		product composition, %		
time[a]	temp, °C	13a	Ph_2Se_2	1a
10 s	−78	40	47	13
10 min	−78	35	44	22
30 min	−78	19	67	14
5 s	−90	43	38	20
15 s	−90	49	43	8
b	−78	12	23	65
c	−78	22	67	11

[a] Time between addition of LDA and addition of CH_3I. [b] LDA (1.2 equiv) was added to a solution of selenoxide and CH_3I (2 equiv) in THF. [c] As for *b*, except that 2.0 equiv of LDA was used.

We conclude from the results in Table VII that a significant fraction of the vinyl selenoxide is decomposed during the deprotonation (probably by β-elimination) and that the α-lithiovinyl selenoxide has a half-life of under 30 min at −78 °C in THF.

Diels–Alder Reactions of Vinyl Selenides and Selenoxides. Vinyl selenides and selenoxides have the potential of serving as ethylene or acetylene equivalents in Diels–Alder reactions. We have been unable to obtain good yields of adducts between phenyl vinyl selenoxide (**22a**) and several dienes including 9,10-dimethylanthracene. The previously reported syn elimination of vinyl selenoxide[11] to give acetylene is faster than Diels–Alder reaction with all but the most reactive dienes. 1,3-Diphenylisobenzofuran reacts exothermically with **22a** to give a complex mixture of products, including much phenyl vinyl selenide. If the reaction is carried out with triethylamine present, less redox reduction occurs, but the reaction is still not very clean. Phenyl vinyl sulfoxide has been successfully employed as a dienophile.[21] Syn elimination to acetylene is much slower than for the selenoxide.

Phenyl vinyl selenide reacts cleanly with 1,3-diphenylisobenzofuran to give the adduct **23**, which was converted to 1,4-diphenylnaphthalene on treatment with acid. The aromatization presumably involves "reductive elimination"[1a,h] of PhSeOR and dehydration.



23

Phenyl vinyl sulfide and *m*-(trifluoromethyl)phenyl vinyl selenide also reacted to form, after acid treatment, 1,4-diphenylnaphthalene. Relative rates of cycloaddition were determined by treating a mixture of two vinyl compounds with 1 equiv of 1,3-diphenylisobenzofuran and measuring the relative amounts of starting material and product by 270-MHz NMR. Selenium reacted faster than sulfur (k_{Se}/k_S = 1.3) and the trifluoromethyl group accelerated the reaction by a factor of 2.3 (ρ = 0.84).

(21) L. A. Paquette, R. E. Moerck, B. Harirchian, and P. D. Magnus, *J. Am. Chem. Soc.*, **100**, 1597 (1978).

Reactions of Vinyl Selenoxides. A number of useful transformations can be envisaged for vinyl selenoxides. Thermolysis under carefully controlled condtions gives acetylenes and allenes.[11] Our efforts to employ phenyl vinyl selenoxide as an ethylene cation equivalent by a β-dicarbonyl enolate Michael addition, protonation, and syn elimination sequence analogous to the sulfoxide reaction described by Koppel[22] were not successful. Shimizu and Kuwajima[23] have recently reported that vinyl selenoxides can be used for the cyclopropanation of enolates by a Michael addition, proton transfer, and substitution sequence.

Vinyl selenoxides are acid-sensitive compounds. Treatment of **22a** with dilute hydrochloric acid results in conversion to a mixture of 1,2- and 2,2-dichloro-1-(phenylseleno)ethanes, a process probably analogous to the formation of 1,2-bis(benzoyloxy)-1-(phenylseleno)ethane on treatment of **10a** with dibenzoyl peroxide.[6c]

Summary

A variety of vinyl selenides can be easily prepared by selenation of alkenyl Grignard reagents or by reductive elimination of the reaction products of [bis(phenylseleno)methyl]lithium and aldehydes or ketones. The vinyl selenides can be deprotonated to give either vinyllithium reagents (α-deprotonation), allyllithium reagents (γ-deprotonation), or mixtures of both, depending on structural factors. The vinyllithium reagents react with a variety of electrophiles. Vinyl phenyl selenide is kinetically more acidic than vinyl phenyl sulfide in contrast to most other S/Se comparisons where the sulfur analogue is more acidic. Vinyl selenoxides can be prepared by oxidation of vinyl selenides. They are not thermally stable enough to serve as acetylene equivalents in Diels–Alder cycloadditions.

Experimental Section

General Methods. Nuclear magnetic resonance (NMR) spectra were obtained on a JEOL JNM-MH-100, FX-60, or Brucker WH-270 spectrometer. Proton Fourier transform NMR spectra to be integrated were measured with a pulse delay of 30 s. Infrared (IR) spectra were obtained on a Perkin-Elmer IR-267 or Beckman Acculab 7 spectrophotometer, and mass spectra were obtained on an AEI MS-902 spectrometer. Unless otherwise specified, NMR spectra were measured at 100 MHz in CCl_4 solution and IR spectra were taken of the neat liquid between salt plates. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN. Melting points and boiling points are uncorrected.

Short-path distillations were carried out with a Kugelrohr apparatus, and bath temperatures are reported. Preparative gas–liquid chromatography (GLC) was performed with a Varian 90-P3 gas chromatograph, using a 12 × $^3/_8$ in. column packed with 20% SE-30 on Chromosorb W, acid washed and dimethyldichlorosilane treated. Preparative thin-layer chromatography (TLC) was carried out by using EM or MN PF-254 silica gel. All reactions involving organolithium reagents, selenols, or selenolate anions were run in an atmosphere of dry nitrogen. Apparatus for anhydrous reactions was dried in a 140 °C oven for at least 1 h. Reaction temperatures were measured externally.

Tetrahydrofuran (THF) and ether solvents were freshly distilled from sodium benzophenone ketyl. Diisopropylamine and 2,2,6,6-tetramethylpiperidine were distilled from solid KOH and stored over 4-Å molecular sieves. (HMPA was distilled and stored over 4-Å molecular sieves.)

Lithium diisopropylamide (LDA) solution was prepared by the addition of a 1.56 M solution of *n*-butyllithium in hexane to a stoichiometric amount of diisopropylamine at −78 °C under

(22) G. A. Koppel and M. D. Kinnick, *J. Chem. Soc., Chem. Commun.*, 473 (1975).
(23) M. Shimizu and I. Kuwajima, *J. Org. Chem.*, **45**, 2921 (1980).

nitrogen, with enough THF to adjust the titer to 1.0 M.

Lithium 2,2,6,6-tetramethylpiperidide (LiTMP) solution was prepared fresh for each experiment by the addition of a stoichiometric amount of 1.56 M *n*-butyllithium in hexane to a solution of tetramethylpiperidine in THF (ca. 0.1 M) at 0 °C under nitrogen. The solution was stirred for 10 min at 0 °C before cooling to the temperature of interest and using.

Normal workup procedure involved addition of the reaction mixture to 10% aqueous HCl and extraction with an equal volume of 1:1 ether–pentane. The organic layer was washed with 10% HCl, twice with water, and once with saturated NaCl solution and dried over anhydrous $MgSO_4$. The solvent was removed at reduced pressure on a rotary evaporator.

Diphenyl diselenide,[24] *m,m'*-bis(trifluoromethyl)diphenyl diselenide,[24] and bis(phenylseleno)methane[11b] were prepared by literature procedures.

Caution: Organoselenium compounds are toxic and should be handled with care.

Phenyl Vinyl Selenide (1a). To a dry three-neck flask, equipped with an addition funnel and dry ice/EtOH condenser, was added 0.49 g (20 mmol) of magnesium turnings. The system was purged with dry N_2, and just enough THF was added to cover the turnings. Then a solution of 2.0 mL (28 mmol) of vinyl bromide in 40 mL of THF was added at a rate fast enough to maintain reflux. If necessary, the reaction may be heated to get it started. After the addition was completed, the mixture was heated under reflux until all of the magnesium had reacted (ca. 20 min) and a solution of PhSeBr in 25 mL of THF, made by the addition of 0.51 mL (10 mmol) of Br_2 to a solution of 3.12 g (10 mmol) of Ph_2Se_2 in 25 mL of THF, was added dropwise over 15 min. After being stirred for an additional 30 min, the reaction was worked up. Short-path vacuum distillation (50–55 °C, 0.2 mm) gave 7.34 g (67% yield) of **1a**;[6c] NMR (270 MHz, C_6D_6) δ 5.39 (d, J = 16.4, J_{SeH} = 10.4 Hz, 1 H), 5.50 (d, J = 9.4, J_{SeH} = 23.3 Hz, 1 H), 6.63 (dd, J = 16.4, 9.4, J_{SeH} = 21.3 Hz, 1 H), 6.97–7.01 (m, 3 H), 7.36–7.42 (m, 2 H); IR 3070, 3050, 1575, 1475, 730, 685 cm^{-1}.

***m*-(Trifluoromethyl)phenyl Vinyl Selenide (1b).** The procedure for this was exactly the same as that for phenyl vinyl selenide, except for the substitution of 4.48 g (10 mmol) of *m,m'*-bis(trifluoromethyl)diphenyl diselenide for Ph_2Se_2. Short-path distillation (50 °C, 0.2 mm) gave 3.01 g (60% yield) of **1b**: NMR (270 MHz, C_6D_6) δ 5.38 (d, J = 16.9 J_{SeH} = 10.8 Hz, 1 H), 5.48 (d, J = 9.4, J_{SeH} = 22.3 Hz, 1 H), 6.47 (dd, J = 16.9, 9.4, J_{SeH} = 19.1 Hz, 1 H), 6.81 (t, J = 7.7 Hz, 1 H), 7.16 (d, J = 7.7 Hz, 1 H), 7.27 (d, J = 7.7 Hz, 1 H), 7.66 (s, 1 H); IR 3060, 3030, 3000, 1600, 1585 cm^{-1}. Anal. Calcd for $C_9H_7F_3Se$: C, 43.05; H, 2.81. Found: C, 43.09; H, 2.96.

1-(Phenylseleno)propene (7a). The Grignard reagent prepared from 3.4 g (28 mmol) of 1-bromopropene, 0.67 g (28 mmol) of Mg, and 25 mL of THF was cooled to 0 °C and a solution of 6.0 g (19.2 mmol) of Ph_2Se_2 in 20 mL of THF was added dropwise. The reaction mixture was warmed to 20 °C and poured into 10% HCl solution. The organic layer was washed with 5% NaOH solution (Ph_2Se_2 can be recovered from the aqueous layer after air oxidation) and saturated $NaHCO_3$ and NaCl solution, dried over Na_2SO_4, and distilled to give 3.45 g (92% yield) of 1-(phenylseleno)propene:[9b] bp 120–124 °C (14 mm); NMR of 58:42 E/Z mixture (C_6D_6, 270 MHz) δ 1.48, 1.64 (dd, J = 6.6, 1.5 Hz; dd, J = 6.6, 1.5 Hz, 3 H), 5.89, 5.78 (dq, J = 15.1, 6.6 Hz; dq, J = 8.8, 6.6 Hz, 1 H), 6.25, 6.38 (dq, J = 15.1, 1.5 Hz; dq, J = 8.8, 1.5 Hz, 1 H), 6.9–7.0 (m, 3 H), 7.34–7.47 (m, 2 H); IR 3010, 2970, 2900, 2870, 2800, 1900, 1830, 1760, 1660, 1580, 1550, 730, 660 cm^{-1}; exact mass (M^+) 197.9947 (calcd 197.9948).

Bis[[*m*-(trifluoromethyl)phenyl]seleno]methane. Sodium borohydride was added in small portions to a solution of *m,m'*-bis(trifluoromethyl)diphenyl diselenide (4.48 g, 10 mmol) in 50 mL of absolute EtOH under N_2 until the yellow color of the diselenide had disappeared. Dibromomethane (0.7 mL, 10 mmol) was added, and the solution was stirred for 2 h at 25 °C. Chloroacetic acid (0.5 g) was added to remove any remaining $ArSe^-$, and the reaction mixture was diluted with water and extracted with 50% ether–pentane. The organic layer was washed with 10% NaOH, water, and brine. Solvent removal gave 4.53 g (98% yield) of product: NMR δ 4.18 (s, J_{SeH} = 13.3 Hz, 2 H), 7.18–7.68 (m, 8 H); IR 3040, 2940, 1590, 1565, 1310, 790, 690 cm^{-1}; exact mass (M^+) 463.9015 (calcd 463.9017).

1-(Phenylseleno)propene (7a). A solution of 0.652 g (2 mmol) of bis(phenylseleno)methane in 5 mL of THF was cooled to −78 °C under N_2 with stirring, and 2.5 mL of 1.0 M LDA was added, followed 5 min later with 0.147 mL (2.5 mmol) of freshly distilled acetaldehyde. After 10 min, the mixture was worked up to give 0.678 g (92% yield) of 1,1-bis(phenylseleno)-2-propanol (**3a**), which was taken on without further purification; NMR δ 1.28 (d, J = 7.2 Hz, 3 H), 2.71 (br s, 1 H), 3.82 (m, 1 H), 4.32 (d, J = 3 Hz, 1 H), 7.05–7.20 (m, 6 H), 7.35–7.52 (m, 4 H).

The product from above was dissolved in 10 mL of CH_2Cl_2 and cooled to 0 °C under N_2. Then 1.41 mL (10 mmol) of NEt_3 was added, followed by the dropwise addition of 0.474 mL (6 mmol) of CH_3SO_2Cl. Upon completion of the addition, the solution was stirred an additional 15 min at room temperature, then extracted into ether, and washed with 10% HCl, 10% NaOH, and brine. Solvent removal and short-path distillation (55 °C, 0.2 mm) gave 0.309 g (84% yield) of **7a** (1:1 E/Z mixture).

1-(Phenylseleno)-2-methylpropene (11a). This procedure was the same as that for **7a**, except that 0.184 mL (2.5 mmol) of freshly distilled acetone was used. Preparative TLC with pentane gave 0.068 g of bis(phenylseleno)methane and 0.622 g (95% yield based on recovered starting material) of 1,1-bis(phenylseleno)-2-methyl-2-propanol (**10**); NMR δ 1.46 (s, 6 H), 2.80 (br s, 1 H), 4.45 (s, 1 H), 7.05–7.19 (m, 6 H), 7.35–7.48 (m, 4 H).

The product from above (0.622 g, 1.62 mmol) was converted to the vinyl selenide as for **7a**. Short-path distillation (55 °C, 0.2 mm) gave 0.272 g (77% yield) of **11a**: NMR (270 MHz, C_6D_6) δ 1.63 (d, J = 1.1 Hz, 3 H), 1.71 (d, J = 1.1 Hz, 3 H), 6.11 (septet, J = 1.1 Hz, 1 H), 7.09–7.22 (m, 3 H), 7.33–7.41 (m, 2 H); IR 3050, 3000, 2950, 2920, 2900, 1585, 1480, 1450, 1070, 1015, 730, 680 cm^{-1}; exact mass (M^+) 212.0105 (calcd 212.0104).

1-[[*m*-(Trifluoromethyl)phenyl]seleno]propene (7b). A solution of 1.85 g (4 mmol) of bis[[*m*-(trifluoromethyl)phenyl]-seleno]methane in 15 mL of THF was cooled to −78 °C under N_2 with stirring, and 4.4 mL of 1.0 M LDA solution was added. After 5 min, 0.245 mL (4.4 mmol) of freshly distilled acetaldehyde was added. The reaction was stirred an additional 10 min and worked up to give 1.935 g (96% yield) of 1,1-bis[[*m*-(trifluoromethyl)-phenyl]seleno]-2-propanol (**3b**); NMR δ 1.38 (d, J = 6.2 Hz, 3 H), 3.17 (br s, 1 H), 4.07 (qd, J = 6.2, 3.3 Hz, 1 H), 4.54 (d, J = 3.3 Hz, 1 H), 7.24–7.72 (m, 8 H).

The product from above (1.935 g, 3.84 mmol) was dissolved in 15 mL of CH_2Cl_2 under N_2, and placed in a 20 °C water bath. Then 2.67 mL (19 mmol) of NEt_3 was added, followed by the dropwise addition of 0.88 mL (11.4 mmol) of CH_3SO_2Cl with stirring. After 3 h, the mixture was poured into ether and washed with 10% HCl, 10% NaOH, and brine. Solvent removal and short-path distillation (60 °C, 0.2 mm), gave 0.613 g (63% yield) of **7b**: NMR (270 MHz, C_6D_6) of 1:1 E/Z mixture δ 1.39, 1.55 (dd, J = 6.6, 1.5 Hz; dd, J = 6.6, 1.5 Hz, 3 H), 5.89, 5.80 (dq, J = 15.0, 6.6 Hz; dq, J = 8.8, 6.6 Hz, 1 H), 6.07, 6.16 (dq, J = 15.0, 1.5 Hz; dq, J = 8.8, 1.5 Hz, 1 H), 6.74 (m, 1 H), 7.12–7.27 (m, 2 H), 7.69 (s, 1 H); IR 3020, 2910, 2850, 1600, 1580, 1125, 795, 690 cm^{-1}.

An analytical sample was purified by GLC. Anal. Calcd for $C_{10}H_9F_3Se$: C, 45.30; H, 3.42. Found: C, 45.54; H, 3.24.

***trans*-1-Phenyl-2-[[*m*-(trifluoromethyl)phenyl]seleno]-ethane (6b).** A solution of 1.0 g (2.2 mmol) of bis[[*m*-(trifluoromethyl)phenyl]seleno]methane in 5 mL of THF was cooled to −78 °C under nitrogen and 3.0 mL of 1.0 M LDA solution was added. After 30 min, benzaldehyde (0.3 mL, 2.5 mmol) was added and the reaction mixture was worked up. The crude 1-phenyl-2,2-bis[[*m*-(trifluoromethyl)phenyl]seleno]ethanol (**2b**) was used directly; NMR δ 3.81 (br s, 1 H), 4.60 (d, J = 4 Hz, 1 H), 5.04 (d, J = 4 Hz, 1 H), 7.02–7.90 (m, 13 H).

The product from above was converted to vinyl selenide as for compound **7b**. Purification by preparative TLC gave 0.61 g (85% overall yield) of **6b**. The product could be further purified by recrystallization from pentane: mp 40–42 °C; NMR δ 6.80 (d, J = 16 Hz, 1 H), 7.01 (d, J = 16 Hz, 1 H), 7.08–7.86 (m, 9 H).

Anal. Calcd for $C_{15}H_{11}F_3Se$: C, 55.06; H, 3.39. Found: C, 54.87; H, 3.22.

(24) H. J. Reich, J. M. Renga, and I. L. Reich, *J. Am. Chem. Soc.*, **97**, 5434 (1975).

1-[[*m*-(Trifluoromethyl)phenyl]seleno]-3-methyl-1-butene (9b). This procedure was the same as that for **7b**, except that 2.31 g (5 mmol) of bis[[*m*-(trifluoromethyl)phenyl]seleno]methane in 20 mL of THF, 5.5 mL of LDA, and 0.433 mL (5.0 mmol) of freshly distilled isobutyraldehyde were used. Workup and solvent removal gave 2.62 g (98% yield) of 1,1-bis[[*m*-(trifluoromethyl)phenyl]seleno]-3-methyl-2-butanol (**5b**); NMR δ 0.86 (d, J = 7.5 Hz, 3 H), 1.04 (d, J = 7.5 Hz, 3 H), 2.19 (octet, J = 7.5 Hz, 1 H), 2.77 (br s, 1 H), 3.46 (dd, J = 7.5, 3.9 Hz, 1 H), 4.76 (d, J = 3.9 Hz, 1 H), 7.20–7.95 (m, 8 H).

The product from above (2.62 g, 4.9 mmol) was converted to vinyl selenide as for **7a**. Short-path distillation (65–70 °C, 0.2 mm) gave 1.11 g (78.5% yield) of **9b** (70:30 E/Z mixture); IR 3038, 2948, 2900, 2840, 1590, 1565, 1300, 785, 680 cm^{-1}.

An analytical sample was purified by preparative GLC. Anal. Calcd for $C_{12}H_{13}F_3Se$: C, 49.16; H, 4.47. Found: C, 49.28; H, 4.49.

TLC on 7% $AgNO_3$–SiO_2 with 20% ether–pentane gave (*E*)-**9b** (R_f 0.25) and (*Z*)-**9b** (R_f 0.50): NMR (270 MHz, $CDCl_3$) of (*E*)-**9b** δ 1.06 (d, J = 6.8 Hz, 6 H), 2.45 (octet of d, J = 6.8, 0.9 Hz, 1 H), 6.19 (dd, J = 15.3, 6.8, J_{SeH} = 10.3 Hz, 1 H), 6.35 (dd, J = 15.3, 0.9, J_{SeH} = 1.5 Hz, 1 H), 7.34 (t, J = 7.7 Hz, 1 H), 7.39 (d, J = 7.7 Hz, 1 H), 7.57 (d, J = 7.7 Hz, 1 H), 7.67 (s, 1 H); NMR (270 MHz, $CDCl_3$) of (*Z*)-**9b** δ 1.04 (d, J = 6.6 Hz, 6 H), 2.70–2.66 (m, 1 H), 5.98 (t, J = 8.8, J_{SeH} = 15.7 Hz, 1 H), 6.30 (dd, J = 8.8, 0.8, J_{SeH} = 6.4 Hz, 1 H), 7.23–7.77 (m, 4 H).

Deprotonation of Phenyl Vinyl Selenide (1a). Method A. A solution of 0.183 g (1.0 mmol) of **1a** in 5 mL of THF was cooled to −78 °C under N_2, and 1.2 mL (1.2 mmol) of 1.0 M LDA in THF–hexane was added. The solution of **12a** was stirred for 2 h at −78 °C before reaction with an electrophile, as depicted below.

Method B. A solution of 0.183 g (1.0 mmol) of **1a** and 0.014 mL (0.1 mmol) of diisopropylamine in 5 mL of THF was cooled to −78 °C under N_2, and 0.69 mL (1.0 mmol) of a 1.45 M solution of *n*-BuLi in hexane was added dropwise over a 20-min period. The solution was then treated with an electrophile as depicted below.

Method C. A solution of 0.183 g (1.0 mmol) of phenyl vinyl selenide in 10 mL of THF was cooled to −78 °C under N_2 and treated with 1.2 mL (1.2 mmol) of 1.0 M LDA and 0.20 mL (1.2 mmol) of HMPA was added dropwise over a 1-min period. The solution was stirred for 5 min before treatment with an electrophile.

1-(Phenylseleno)-1-(methylthio)ethene. To a solution of α-lithiovinyl phenyl selenide (**12a**) prepared by method A, using 1.87 mmol of phenyl vinyl selenide, was added 0.188 mL (2.0 mmol) of Me_2S_2. After being stirred for 15 min at −78 °C, the mixture was worked up and purified by preparative TLC with pentane to give 0.279 g (66% yield) of 1-(phenylseleno)-1-(methylthio)ethene: NMR δ 2.25 (s, 3 H), 5.56 (s, 1 H), 5.63 (s, 1 H), 7.21–7.29 (m, 2 H), 7.35–7.61 (m, 3 H); IR 3045, 3025, 2895, 1555, 1465, 1425, 725, 675 cm^{-1}.

An analytical sample was purified by preparative GLC. Anal. Calcd for $C_9H_{10}SSe$: C, 47.16; H, 4.39. found: C, 46.93; H, 4.19.

1-(Phenylseleno)-1-(trimethylsilyl)ethene. To a solution of **12a** (2.5 mmol) prepared by method A was added 0.381 mL (3.0 mmol) of trimethylchlorosilane. After the mixture was stirred for 15 min at −78 °C, workup and short-path distillation (55–60 °C, 0.2 mm) gave 0.49 g (77% yield) of 1-(phenylseleno)-1-(trimethylsilyl)ethene: NMR δ 0.18 (s, 9 H), 5.75 (s, 1 H), 6.12 (s, 1 H), 7.32–7.40 (m, 3 H), 7.55–7.67 (m, 2 H); IR 3045, 3025, 2930, 1560, 1465, 1425, 1235 cm^{-1}.

An analytical sample was purified by preparative GLC. Anal. Calcd for $C_{11}H_{16}SiSe$: C, 51.75; H, 6.32. Found: C, 51.92; H, 6.59.

2-(Phenylseleno)propene. Method A. To a solution of **12a** (1.0 mmol), prepared by method A above, was added 0.062 mL (1.0 mmol) of CH_3I. After being stirred for 15 min at −78 °C, the mixture was worked up. Purification by preparative TLC, using pentane, gave 0.19 g of a 3:1 mixture of 1-(phenylseleno)propene and phenyl vinyl selenide (75% yield by NMR estimate).

Method B. To a solution of **12a** (1.0 mmol), prepared by method B above, was added 0.062 mL (1.0 mmol) of CH_3I. After being stirred for 15 min at −78 °C, the mixture was worked up. Short-path distillation (55 °C, 0.2 mm) gave 0.147 g (75% yield) of 2-(phenylseleno)propene: NMR (270 MHz, C_6D_6) δ 1.90 (dd, J = 1.5, 0.9 Hz, 3 H), 5.15 (q, J = 0.8 Hz, 1H), 5.28 (q, J = 1.6 Hz, 1 H), 6.97–7.02 (m, 3 H), 7.49–7.55 (m, 2 H); IR 3050, 3035, 2960, 2900, 1655, 1600, 675 cm^{-1}.

An analytical sample was purified by preparative GLC. Anal. Calcd for $C_9H_{10}Se$: C, 54.83; H, 5.11. Found: C, 54.67; H, 5.12.

Method C. To a solution of 1.0 mmol of **12a** prepared as in method C above, was added 0.062 mL (1.0 mmol) of CH_3I. After being stirred for 5 min at −78 °C, the mixture was worked up. Short-path vacuum distillation (50 °C, 0.2 mm) gave 0.151 g (77%) of 2-(phenylseleno)propene.

2-(Phenylseleno)propenoic Acid. A stream of CO_2 gas was passed first through a drying tower filled with $CaSO_4$ and then through a solution of **12a** (5 mmol) prepared by method A. After 10 min at −78 °C, the solution was allowed to warm slowly to room temperature and was carefully quenched with 10% HCl. The solution was extracted into ether–pentane, and the organic layer was extracted with 10% NaOH. The aqueous layer was then acidified (pH ~3) with concentrated HCl and washed with two portions of ether. The organic layer was dried and removed to give 0.89 g (79% yield) of the acid. This may be further purified by recrystallization from hexane: mp 63 °C; NMR δ 6.45 (s, 1 H), 6.80 (s, 1 H), 7.32–7.43 (m, 3 H), 7.60–7.70 (m, 2 H), 11.63 (s, 1 H); IR 3320–2440, 1680, 1580 cm^{-1}; exact mass (M^+) 227.9684 (calcd 227.9689).

Deprotonation of *m*-(Trifluoromethyl)phenyl Vinyl Selenide (1b). A solution of 0.251 g (1.0 mmol) of **1b** in 5 mL of THF was cooled to −78 °C under N_2, and 1.2 mL (1.2 mmol) of 1.0 M LDA solution was added. The solution of **12b** was stirred for 5 min before reaction with an electrophile, as depicted below.

1-[[*m*-(Trifluoromethyl)phenyl]seleno]-1-(methylthio)-ethene. To a solution of **12b** prepared from 1.23 g (5 mmol) of *m*-(trifluoromethyl)phenyl vinyl selenide at −78 °C was added 0.5 mL (5.7 mmol) of Me_2S_2. The reaction mixture was stirred for 30 min at −78 °C and worked up. Short-path vacuum distillation gave 1.21 g (83% yield) of the sulfide; NMR δ 2.17 (s, 3 H), 5.52 (s, 1 H), 5.63 (s, 1 H), 7.12–7.76 (m, 4 H).

Anal. Calcd for $C_{10}H_9F_3SSe$: C, 40.41; H, 3.05. Found: C, 40.21; H, 2.96.

2-[[*m*-(Trifluoromethyl)phenyl]seleno]propenoic Acid. A stream of CO_2 gas was passed through a drying tower filled with $CaSO_4$ and then through a solution of **12b** (1.0 mmol). Workup as for 2-(phenylseleno)propenoic acid gve 0.269 g (80% yield) of the acid, which could be further purified by recrystallization from hexane: mp 90–92 °C; NMR ($CDCl_3$) δ 5.52 (s, 1 H), 6.79 (s, 1 H), 7.16 (s, 1 H), 7.32–7.90 (m, 4 H).

Anal. Calcd for $C_{10}H_7F_3O_2Se$: C, 40.70; H, 2.39. Found: C, 40.62; H, 2.41.

***m,m'*-Bis(trifluoromethyl)diphenyl Disulfide.** To a dry 250-mL three-neck flask, equipped with a dry ice–EtOH condenser, stopper, and addition funnel under N_2, were added 2.44 g (100 mmol) of Mg turnings and just enough ether to cover them. Then several drops of a solution of 22.5 g (100 mmol) of *m*-bromo-α,α,α-trifluorotoluene in 90 mL of ether were added. The reaction mixture was heated to initiate the reaction and then the rest of the solution was added at a rate fast enough to maintain reflux. The mixture was then refluxed until all of the Mg dissolved (20 min) 3.20 g (100 mmol) of elemental sulfur was carefully added in small portions, and the solution was refluxed another 0.5 h. Then 2.30 mL (45 mmol) of Br_2 was added dropwise over 30 min. The mixture was quenched with aqueous NH_4Cl and extracted into ether–pentane. The organic phase was washed with brine and dried over $MgSO_4$. The solvent was removed in vacuo and short-path distillation (85–100 °C, 0.2 mm) gave 2.0 g (11% yield) of *m*-(trifluoromethyl)thiophenol and 13.87 g (78% yield) of the desired disulfide: NMR (C_6D_6) δ 6.68 (t, J = 7.5 Hz, 1 H), 7.00 (d, J = 7.5 Hz, 1 H), 7.16 (d, J = 7.5 Hz, 1 H), 7.51 (s, 1 H); IR 3050, 1600, 1575, 1150, 795, 695 cm^{-1}; exact mass (M^+) 353.9971 (calcd 353.9972).

***m*-(Trifluoromethyl)phenyl Vinyl Sulfide.** To a dry three-neck flask under N_2, equipped with stopper, dry ice–EtOH condenser, addition funnel, and magnetic stirrer, were added 0.245 g (10 mmol) of Mg turnings and just enough THF to cover them. Then several drops of a solution of 0.987 mL (14 mmol) of vinyl bromide in 25 mL of THF were added, and the mixture was heated until the characteristic Grignard color appeared. The remaining solution was added at a rate fast enough to maintain reflux. After addition was complete, the mixture was heated under reflux until all of the Mg had dissolved (20 min), at which point a solution

of 3.54 g (10 mmol) of *m,m'*-bis(trifluoromethyl)diphenyl disulfide in 10 mL of THF was added at a rate sufficient to maintain reflux. The mixture was then quenched with aqueous NH_4Cl and extracted into ether–pentane. At this point, basic wash of the organic layer yields the side product thiol. The organic layer was then washed with water (3 times) and brine and dried over $MgSO_4$ and the solvent was removed in vacuo. Short-path distillation (50 °C,0.2 mm) gave 3.01 g (60% yield) of the sulfide: NMR (270 MHz, C_6D_6) δ 5.06 (d, J = 9.4 Hz, 1 H), 5.21 (d, J = 16.5 Hz, 1 H), 6.11 (dd, J = 9.4, 16.5 Hz, 1 H), 6.79 (t, J = 7.4 Hz, 1 H), 7.09 (d, J = 7.4 Hz, 1 H), 7.15 (d, J = 7.4 Hz, 1 H), 7.52 (s, 1 H); IR 3020, 1550, 1450, 1100, 790, 690 cm^{-1}.

Anal. Calcd for $C_9H_7F_3S$: C, 52.93; H, 3.45. Found: C, 52.64; H, 3.40.

Phenyl Vinyl Sulfide. This preparation was the same as for the preparation of *m*-(trifluoromethyl)phenyl vinyl sulfide, except that 2.18 g (10 mmol) of diphenyl disulfide was used. Workup and short-path distillation (40–45 °C, 0.2 mm) gave 0.903 g (67% yield) of the vinyl sulfide: NMR (270 MHz, C_6D_6) δ 5.07 (d, J = 9.6 Hz, 1 H), 5.22 (d, J = 16.5 Hz, 1 H), 6.33 (dd, J = 16.5, 9.6 Hz, 1 H), 6.94–7.04 (m, 3 H), 7.23–7.27 (m, 2 H); IR: 3005, 1550, 1450, 1425, 690 cm^{-1}.

2-(Phenylthio)propene. To a solution of 0.068 g (0.5 mmol) of phenyl vinyl sulfide in 5 mL of THF at −78 °C was added 1.0 mL (1.0 mmol) of LDA. After the mixture was stirred for 30 min, 0.124 mL (2 mmol) of CH_3I was added, and the solution was allowed to slowly warm to room temperature. Workup and NMR analysis gave 80% methylation (80% yield by NMR); NMR (270 MHz, C_6D_6) δ 1.82 (dd, J = 1.3, 0.7 Hz, 3 H), 4.94 (pentet, J = 0.7 Hz, 1 H), 4.96 (dq, J = 1.5, 0.5 Hz, 1 H), 6.91–7.06 (m, 3 H), 7.36–7.42 (m, 2 H).

2-[[*m*-(Trifluoromethyl)phenyl]thio]propene. To a solution of 0.102 g (0.5 mmol) of *m*-(trifluoromethyl)phenyl vinyl sulfide in 5 mL of THF at −78 °C was added 1.0 mL (1.0 mmol) of LDA, followed by 0.062 mL (1 mmol) of methyl iodide. Workup and NMR analysis showed 90% methylation (90% yield by NMR): NMR (270 MHz, C_6D_6) δ 1.71 (dd, J = 1.5, 0.9 Hz, 3 H), 4.94 (q, J = 0.9 Hz, 1 H), 4.95 (q, J = 1.3 Hz, 1 H), 6.82 (t, J = 7.5 Hz, 1 H), 7.17 (d, J = 7.6 Hz, 1 H), 7.26 (d, J = 7.7 Hz, 1 H), 7.67 (s, 1 H); exact mass (M^+) 218.0377 (calcd 218.0377).

Procedure for Competitive Rates—LDA. To a solution of 0.5 mmol of each compound to be examined in 5 mL of THF was added exactly 0.4 mL (0.4 mmol) of LDA. After 5 min, 0.062 mL (1.0 mmol) of CH_3I was added, followed 5 min later with a 10% HCl quench. The mixture was then worked up and analyzed by 270-MHz NMR. Results are summarized in Table 1 and 2 of the supplementary material.

Procedure for Competitive Rates—LiTMP. To a solution of 0.067 mL (0.4 mmol) of 2,2,2,6-tetramethylpiperidine in exactly 4 mL of THF at 0 °C under N_2, was added 0.276 mL (0.4 mmol) of 1.45 M BuLi in hexane. After 10 min, the solution was cooled to −78 °C, and a mixture of 0.5 mmol of each compound to be compared in exactly 1 mL of THF was added via cannula (total addition time no more than 3 s). After 5 min, 0.062 mL of CH_3I (1.0 mmol) was added, followed 5 min later with a 10% HCl quench. The mixture was then worked up, and analyzed by 270-MHz NMR. Results are sumarized in Tables 1 and 2 of the supplementary material.

Procedure for Equilibration of Vinyllithium Reagents. To a solution of 0.5 mmol of the compound to be equilibrated in 5 mL of THF at −78 °C under N_2 was added 0.4 mL (0.4 mmol) of LDA. The solution was then stirred 15 min for the *m*-(trifluoromethyl)phenyl compounds or 2 h for the phenyl compounds, before addition (neat) of 0.5 mmol of the second compound to be equilibrated. After the mixture was stirred for an additional hour, 0.063 mL (1.0 mmol) of CH_3I was added, followed 5 min later with a 10% HCl quench. The mixture was then worked up and analyzed by 270-MHz NMR. Results are summarized in Tables 1 and 2 of the supplementary material.

Methylation of 1-(Phenylseleno)propene (7a). A solution of 0.098 g (0.5 mmol) of **7a** in 5 mL of THF was cooled to −78 °C under N_2, and 0.75 mL (0.75 mmol) of LDA was added. After being stirred for the number of hours specified in Table V, the mixture was quenched with 0.062 mL (1.0 mmol) of CH_3I. Workup and NMR analysis (270 MHz, C_6D_6) gave mixtures of starting material, **8a**, and **15a** (identified by comparison with a spectrum of authentic material), phenyl methyl selenide, and **14a** (1:1 E/Z). When the same reaction was run at −30 °C, with 2 h of stirring before CH_3I quench, **15a** and **8a** (4:1) were obtained, with no detectable **14a**.

Methylation of 1-[[*m*-(Trifluoromethyl)phenyl]seleno]-propene (7b). A solution of 0.132 g (0.5 mmol) of **7b** in 5 mL of THF was cooled to −78 °C under N_2, and 0.75 mL (0.75 mmol) of LDA was added. After the mixture was stirred for the number of hours specified in Table V, 0.062 mL (1.0 mmol) of CH_3I was added. Standard workup and NMR analsis (270 MHz, C_6D_6) showed mixtures of starting material, **8b** and **15b** (identified by comparison with spectra of authentic material), **14b** (1:1 E/Z), and *m*-(trifluoromethyl)phenyl methyl selenide. When the same reaction was run at −30 s°C, only **15b** and **8b** (4:1) were obtained.

Methylation of 1-[[*m*-(Trifluoromethyl)phenyl]-seleno]-1-butene (8b). To a solution of 0.75 mmol of LiTMP in 5 mL of THF was added 0.138 g (0.5 mmol) of **8b**. After being stirred for 3 h at −50 °C, the solution was quenched with 0.062 mL (1.0 mmol) of CH_3I, stirred an additional 15 min, and worked up. Preparative TLC with pentane gave 0.092 g (63% yield) of 2-[[*m*-(trifluoromethyl)phenyl]seleno]-2-pentene (**18a**, R = CH_3): NMR of 1:1 E/Z mixture δ 1.02, 1.09 (t, J = 7.1 Hz; t, J = 7.1 Hz, 3 H), 2.02, 2.00 (d, J = 1.1 Hz; d, J = 1.5 Hz, 3 H), 2.01–2.31 (m, 2 H), 5.86, 5.77 (tq, J = 7.0, 1.1 Hz; tq, J = 7.0, 1.5 Hz, 1 H), 7.13–7.57 (m, 4 H); IR 3060, 2980, 2910, 2870, 1600, 1580, 1125, 795, 685 cm^{-1}.

An analytical sample was purified by preparative GLC. Anal. Calcd for $C_{12}H_{13}F_3Se$: C, 49.16; H, 4.47. Found: C, 48.93; H, 4.52.

Methylation of 1-[[*m*-(Trifluoromethyl)phenyl]-seleno]-3-methyl-1-butene (19b). To a solution of 1.5 mmol of LiTMP in 10 mL of THF at −50 C was added 0.292 g (1.0 mmol) of **19b**. After being stirred for 3 h, the reaction was quenched with 0.124 mL of CH_3I and worked up. Preparative TLC with pentane gave 0.190 g (62% yield) of 2-[[*m*-(trifluoromethyl)-phenyl]seleno]-4-methyl-2-pentene (70:30 E/Z mixture): IR 3040, 2940, 2855, 1590, 1570, 1120, 780, 680 cm^{-1}; exact mass (M^+) 308.0291 (calcd 308.0291).

TLC on 7% $AgNO_3$–SiO_2 with 20% ether–pentane gave the E isomer (R_f 0.25) and Z isomer (R_f 0.4): NMR (270 MHz, C_6D_6) of E isomer δ 0.83 (d, J = 6.6 Hz, 6 H), 1.83 (d, J = 1.4 Hz, 3 H), 2.27–2.40 (m, 1 H), 5.89 (dq, J = 9.6, 1.4, J_{SeH} = 11.3 Hz, 1 H), 6.82 (t, J = 7.5 Hz, 1 H), 7.17 (d, J = 7.5 Hz, 1 H), 7.37 (d, J = 7.5 Hz, 1 H), 7.75 (s, 1 H); NMR (270 MHz, C_6D_6) of Z isomer δ 0.90 (d, J = 6.6 Hz, 6 H), 1.85 (d, J = 1.3 Hz, 3 H), 2.81–2.94 (m, 1 H), 5.47 (dq, J = 9.0, 1.3 Hz, 1 H), 6.74 (t, J = 8.1 Hz, 1 H), 7.21 (d, J = 8.1 Hz, 1 H), 7.30 (d, J = 8.1 Hz, 1 H), 7.75 (s, 1 H).

Phenyl Vinyl Selenoxide (22a). A solution of 0.366 g (2.0 mmol) of phenyl vinyl selenide in 4 mL of CH_2Cl_2 was cooled to 0 °C under N_2, and 0.50 g (2.46 mmol) of 85% *m*-chloroperbenzoic acid was added. After being stirred for 10 min, the mixture was dissolved in more CH_2Cl_2 and washed with 10% NaOH and brine, being careful that the volume of the aqueous phases did not exceed 25% of the volume of the organic phase, due to the high solubility of the selenoxide in water. The solvent was removed in vacuo to give 0.392 g (98.5% yield) of **22a**: NMR δ 5.88 (d, J = 9 Hz, 1 H), 6.22 (d, J = 15.9 Hz, 1 H), 7.11 (dd, J = 15.9, 9 Hz, 1 H), 7.28–7.35 (m, 3 H), 7.62–7.72 (m, 2 H); IR 3010, 2985, 1580, 1560, 850 cm^{-1}.

Reaction of 1,3-Diphenylisobenzofuran with Phenyl Vinyl Selenide (1a). A solution of 0.540 g (2 mmol) of 1,3-diphenylisobenzofuran and 0.366 g (2 mmol) of **1a** in 5 mL of toluene was heated to 100 °C under N_2. After 23 h, the selenide had reacted completely to give an adduct (endo/exo mixture): NMR (270 MHz, C_6D_6) (partial) (major, minor) δ 4.20, 3.88 (dd, J = 9.2, 3.3 Hz; dd, J = 7.9, 4.0 Hz, 1 H), 2.93, 2.76 (dd, J = 11.8, 9.3 Hz; dd, J = 9.9, 4.3 Hz, 1 H), 2.33, 2.54 (dd, J = 11.7, 3.3 Hz; dd, J = 9.9 7.4 Hz, 1 H). The solvent was removed in vacuo, and the adduct treated with 1 drop of CH_3SO_3H in CH_2Cl_2 overnight at 25 °C. The 1,4-diphenylnaphthalene obtained was recrystallized from ethyl acetate [mp 135 C (lit.[25] mp 135–137 °C] to give 0.356 g (64% yield) of white needles: NMR (270 MHz, C_6D_6) δ 7.22–7.29 (m, 6 H), 7.33 (s, 2 H), 7.45 (dm, J = 8.1 Hz, 4 H), 7.20, 8.06 (AA'BB',

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J_{AB} = 8.6, $J_{AA'}$ = 1.1, $J_{BB'}$ = 0.5 Hz, 4 H).

Phenyl Vinyl Sulfide Cycloaddition. This procedure was identical with that above except 0.270 g (1.0 mmol) of the furan and 0.136 g (1 mmol) of phenyl vinyl sulfide in 2 mL of toluene were used. Heating for 27 h gave the adduct, which was converted to 1,4-diphenylnaphthalene as above. Partial NMR (270 MHz, C_6D_6) of adduct: δ 2.15 (dd, J = 11.6, 3.4 Hz, 1 H), 2.86 (dd, J = 11.6, 9.4 Hz, 1 H), 4.22 (dd, J = 9.0, 3.1 Hz, 1 H).

***m*-(Trifluoromethyl)phenyl Vinyl Selenide Cycloaddition.** This procedure was identical with that above, except 0.270 g (1.0 mmol) of furan and 0.251 g (10 mmol) of **2a** in 2 mL of toluene were used. Heating at 100 °C for 18 h gave the adduct, which was converted to 1,4-diphenylnaphthalene as above. Partial NMR (270 MHz, C_6D_6) of adduct (major, minor): δ 2.21, 2.53 (dd, J = 11.8, 3.3 Hz; d, J = 7.1 Hz, 1 H), 2.89, 2.54 (dd, J = 9.6, 11.9 Hz; d, J = 4.6 Hz, 1 H), 4.07, 3.83 (dd, J = 9.4, 3.5 Hz; dd, J = 6.9, 4.9 Hz, 1 H).

Competitive Cycloaddition Rates. Sample Procedure. A solution of 0.027 g (0.1 mmol) of the furan, 0.018 g (0.1 mmol) of **1a**, and 0.014 g (0.1 mmol) of phenyl vinyl sulfide in 0.3 mL of C_6D_6 was sealed under N_2 into an NMR tube. The reaction mixture was heated to 90 °C for 2 h, and the relative amounts of starting materials and products were determined by NMR. The procedure was repeated for 12 h of heating as well. Data are summarized in Table 3 of the supplementary material.

Check of Reversibility. A solution of 0.041 g (0.15 mmol) of the furan and 0.018 g (0.1 mmol) of phenyl vinyl selenide in 0.3 mL of C_6D_6 with 0.5 drop of Et_3N was heated at 90 °C for 23 h, at which time the phenyl vinyl selenide had reacted. Then 0.037 g (0.15 mmol) of *m*-(trifluoromethyl)phenyl vinyl selenide was added. Heating an additional 24 h resulted in no liberation of phenyl vinyl selenide.

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Registry No. 1a, 35167-28-3; **1b**, 75599-83-6; **2a**, 77461-29-1; **2b**, 77461-30-4; **3a**, 77461-31-5; **3b**, 77461-32-6; **4a**, 77461-33-7; **4b**, 77461-34-8; **5a**, 72474-66-9; **5b**, 77461-35-9; (*E*)-**6a**, 60466-40-2; (*E*)-**6b**, 77461-36-0; (*E*)-**7a**, 68001-61-6; (*Z*)-**7a**, 68001-62-7; (*E*)-**7b**, 77461-37-1; (*Z*)-**7b**, 77461-38-2; (*E*)-**8a**, 60466-43-5; (*Z*)-**8a**, 60466-33-3; (*E*)-**8b**, 77461-39-3; (*Z*)-**8b**, 77461-40-6; (*E*)-**9a**, 67649-79-0; (*Z*)-**9a**, 68001-63-8; (*E*)-**9b**, 77461-41-7; (*Z*)-**9b**, 77461-42-8; **10a**, 77461-43-9; **10b**, 77461-44-0; **11a**, 77461-45-1; **11b**, 77461-46-2; **12a**, 56529-37-4; **12b**, 77461-47-3; **13a** (E = SMe), 77461-48-4; **13a** (E = TMS), 77461-49-5; **13a** (E = Me), 63017-57-2; **13a** (E = CO_2H), 77461-50-8; **13a** (E = Bu), 63831-76-5; **13a** (E = $C(OH)Et_2$), 77461-51-9; **13a** (E = $(CH_2)_3Ph$), 74866-73-2; **13a** (E = $C(CH_3)(OH)CH_2CH_2Ph$), 74866-72-1; **13a** (E = $C(OH)Me_2$), 77461-71-3; **13b** (E = PhSe), 77461-72-4; **13b** (E = TMS), 77461-73-5; **13b** (E = SMe), 77461-52-0; **13b** (E = CO_2H), 77461-53-1; **13b** (E = Bu), 74866-71-0; **13b** (E = Me), 77461-54-2; (*E*)-**14a**, 24225-10-3; (*Z*)-**14a**, 24213-07-8; (*E*)-**14b**, 77461-55-3; (*Z*)-**14b**, 77461-56-4; **15a**, 17417-82-2; **15b**, 77461-57-5; **17b**, 77461-58-6; (*E*)-**18b** (R^1 = Me), 77461-59-7; (*Z*)-**18b** (R^1 = Me), 77461-60-0; (*E*)-**18b** (R^1 = Bu), 77461-61-1; (*Z*)-**18b** (R^1 = Bu), 77461-62-2; (*E*)-**19b** (R^1 = Bu), 77461-63-3; (*Z*)-**19b** (R^1 = Bu), 77461-64-4; (*E*)-19b (R^1 = Me), 77481-98-2; (*Z*)-**19b** (R^1 = Me), 77461-65-5; **19b** (R^1 = H), 77461-66-6; **22a**, 38447-66-4; *endo*-**23**, 77461-67-7; *exo*-**23**, 77519-41-6; vinyl bromide, 593-60-2; benzeneselenenyl bromide, 34837-55-3; diphenyl diselenide, 1666-13-3; *m,m'*-bis(trifluoromethyl)diphenyl diselenide, 53973-75-4; 1-bromopropene, 590-14-7; bis[[*m*-(trifluoromethyl)phenyl]seleno]methane, 77481-99-3; dibromomethane, 74-95-3; bis(phenylseleno)methane, 20343-90-2; acetaldehyde, 75-07-0; acetone, 67-64-1; benzaldehyde, 100-52-7; isobutyraldehyde, 78-84-2; dimethyl disulfide, 624-92-0; *m,m'*-bis(trifluoromethyl)diphenyl disulfide, 18715-44-1; *m*-bromo-α,α,α-trifluorotoluene, 401-78-5; *m*-(trifluoromethyl)thiophenol, 937-00-8; *m*-(trifluoromethyl)phenyl vinyl sulfide, 75599-82-5; phenyl vinyl sulfide, 1822-73-7; diphenyl disulfide, 882-33-7; 2-(phenylthio)propene, 7594-43-6; 2-[[(*m*-trifluoromethyl)phenyl]thio]propene, 77461-68-8; phenyl methyl selenide, 4346-64-9; *m*-(trifluoromethyl)-phenyl methyl selenide, 37773-24-3; 1,3-diphenylisobenzofuran, 5471-63-6; 1,4-diphenylnaphthalene, 796-30-5; 1,2,3,4-tetrahydro-1,4-diphenyl-2-(phenylthio)-1,4-epoxynaphthalene, 77482-00-9; *endo*-1,2,3,4-tetrahydro-1,4-diphenyl-2-[[(*m*-trifluoromethyl)-phenyl]seleno]-1,4-epoxynaphthalene, 77461-69-9; *exo*-1,2,3,4-tetrahydro-1,4-diphenyl-2-[[(*m*-trifluoromethyl)phenyl]seleno]-1,4-epoxynaphthalene, 77519-42-7; propionaldehyde, 123-38-6; 3-pentanone, 96-22-0; 1-bromo-3-phenylpropane, 637-59-2; 4-phenyl-2-butanone, 2550-26-7; *m*-(trifluoromethyl)phenyl allyl selenide, 77461-70-2; phenyl allyl selenide, 14370-82-2; 3-(phenylthio)-1-butene, 701-75-7; crotyl chloride, 591-97-9; phenyl allyl sulfide, 5296-64-0.

Supplementary Material Available: Experimental details for the preparation of **2a, 4a, 4b, 5a, 6a, 8a, 8b, 9a, 10b, 11b, 13a** (E = *n*-Bu, $C(OH)Et_2$, $CH_2CH_2CH_2Ph$, $C(CH_3)(OH)CH_2CH_2Ph$), **13b** (E = *n*-Bu, CH_3), **15a, 15b, 17b, 18b** (R' = *n*-Bu), **19b** (R' = *n*-Bu), phenyl allyl selenide, *m*-(trifluoromethyl)phenyl allyl selenide, 3-(phenylthio)-1-butene. Kinetic data are summarized in tabular form for the relative acidities and rates of Diels–Alder addition (11 pages). Ordering information is given on any current masthead page.

Notes

Potential Causes of Erroneous Results of Analysis of Lanthanide-Induced Shifts: Contamination of $Ln(fod)_3$ NMR Shift Reagents with $Ln(fod)_3 \cdot Mfod$ and Self-Association of $Ln(fod)_3$

Joop A. Peters,* P. J. Wijnand Schuyl, Wim M. M. J. Bovée,[1] J. Henk Alberts,[1] and Herman van Bekkum

Laboratory of Organic Chemistry, Delft University of Technology, Julianalaan 136, 2628 BL Delft, The Netherlands

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Introduction

Lanthanide shift reagents have become valuable tools in NMR spectroscopy.[2] First of all these reagents have found widespread use in the simplification of NMR spectra of organic compounds able to act as lanthanide ligands. In addition, information on molecular structure in solution can be obtained by fitting the dipolar contribution to the bound shift of the complex between shift reagent and substrate to the McConnell–Robertson equation.[3] The evaluation of bound shifts requires knowledge of the equilibria involved in the complexation of the substrate (S) with the coordinatively unsaturated lanthanide shift reagent (L). For $Ln(fod)_3$ (fod = 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionate) shift reagents several complexes should be envisaged, viz., LS, LS_2, and L_2.[4]

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