imidazole. Hexamethyldisilazane (10 mL, 43 mmol) was then added and the mixture was heated at reflux for 2 h. The mixture was concentrated and the residue distilled under reduced pressure, affording 2.29 g (84%) of a colorless oil, bp 124 °C (0.05 Torr), which solidified on scratching. Recrystallization from cyclohexane afforded **22** as a white solid: mp 57–58 °C; NMR ($CDCl_3$) δ 0.32 (s, 9), 1.52 (s, 3), 1.7–2.9 (m, 6), 5.50 (s, 1); IR (neat) 2210 (nitrile) cm^{-1}. Satisfactory microanalytical values could not be obtained for this compound, since it hydrolyzed back to **23** with extreme ease (Found: C, 47.63; H, 5.30; N, 6.96; S, 32.32; *m/e* 201).

Method B. In a dry 50-mL three-necked round-bottomed flask, swept with dry nitrogen and equipped with a magnetic stirrer and condenser, was placed 2.76 g (10.0 mmol) of keto ester **2** and 0.04 g (0.06 mmol) of recrystallized imidazole. Hexamethyldisilazane (10 mL, 43 mmol) was then added and the mixture was heated at reflux for 2 h. The mixture was concentrated and the residue was distilled at reduced pressure, affording 2.70 g of a colorless oil, bp 127 °C (0.08 Torr), which solidified on scratching. Recrystallization from cyclohexane afforded a white solid, mp 57–58 °C, identical in all respects with the material prepared by method A.

Registry No.—**1**, 64714-77-8; **2**, 64714-78-9; **3**, 64714-79-0; **7**, 18554-39-7; **8**, 7424-91-1; **9**, 64714-80-3; **10**, 64714-81-4; **11**, 64714-82-5; **12**, 65714-83-6; **14**, 64714-84-7; **15**, 64714-85-8; **16**, 5849-13-8; **17**, 64714-86-9; **20**, 64714,87-0; **22**, 64714-88-1; **23**, 64714-89-2; propane-1,3-dithiol, 109-80-8; imidazole, 288-32-4; *tert*-butyl ethyl malonate, 32864-38-3; ethyl chloroformate, 541-41-3; 2-methyl-1,3-dithiane-2-carboxylic acid, 4901-19-3; *tert*-butyl acetate, 540-88-5; ethyl acetoacetate, 141-97-9; bis(ethylthio)methane, 4396-19-4; bromoacetaldehyde diethyl acetal, 2032-35-1; benzyl chloromethyl ether, 3587-60-8; acetonitrile, 75-05-8; hexamethyldisilazane, 999-97-3.

References and Notes

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(2) NIH Postdoctoral Fellow (CA 05017-2), 1975–1977.

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A Convenient One-Flask Synthesis of Dialkyl Selenides and Diselenides via Lithium Triethylborohydride Reduction of Se_x

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Commercially available $Li(C_2H_5)_3BH$ rapidly and quantitatively cleaves gray elemental Se_x in THF to Li_2Se or Li_2Se_2, depending upon stoichiometry. Only volatile byproducts (H_2 and $(C_2H_5)_3B$) are formed. The heterogeneous Li_2Se and Li_2Se_2 preparations may be alkylated in 50–95% yield, optimally in the presence of *tert*-butyl alcohol cosolvent. This one-flask procedure constitutes a substantial improvement over conventional dialkyl selenide and dialkyl diselenide syntheses. $Li(C_2H_5)_3BH$ (2 equiv) also effects reduction of diselenides to selenolates, which may be alkylated to give unsymmetrical selenides.

During the last few years, organoselenium compounds[1] have emerged as important reagents and intermediates in organic synthesis.[2] Starting materials for their preparation are often symmetrical selenides (R_2Se) and diselenides (R_2Se_2). Hence, convenient high-yield syntheses of these key parent molecules are desirable. Current methodology,[3-14] however, suffers from various combinations of (a) low yields, (b) lack of demonstrated generality, (c) cumbersome manipulations, and (d) the use of toxic and malodorous H_2Se.

During the course of another research project underway in this laboratory, it was discovered that commercially available trialkylborohydrides such as $Li(C_2H_5)_3BH$ effect rapid reductive cleavage of several types of metal–metal bonds in THF at room temperature.[15] As a result, we were able to develop a preparation for metal carbonyl monoanions from the corresponding metal–metal dimers (eq 1)[15] which is substantially more convenient than existing procedures.[16]

$$L_n(CO)_xM\text{–}M(CO)_xL_n + 2Li(C_2H_5)_3BH \rightarrow 2Li[L_n(CO)_xM] + 2(C_2H_5)_3B + H_2 \quad (1)$$

Consequently, one objective of this study was to determine if trialkylborohydrides could be used in *metalloid* anion synthesis. Due to the independent need for several organoselenium compounds in our laboratory, we decided to investigate the feasibility of Li_2Se and Li_2Se_2 syntheses from gray elemental selenium. Dialkyl selenides and dialkyl diselenides would be available via the transformations depicted in eq 2–5.

$$Se + 2Li(C_2H_5)_3BH \rightarrow Li_2Se + 2(C_2H_5)_3B + H_2 \quad (2)$$

$$Li_2Se + 2RX \rightarrow R_2Se \quad (3)$$

$$2Se + 2Li(C_2H_5)_3BH \rightarrow Li_2Se_2 + 2(C_2H_5)_3B + H_2 \quad (4)$$

$$Li_2Se_2 + 2RX \rightarrow R_2Se_2 \quad (5)$$

We report in this paper that symmetrical dialkyl selenides and diselenides can be conveniently prepared in a one-flask operation in good to high yields via the simple sequences depicted above. Unsymmetrical dialkyl selenides are also easily

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Table I. Dialkyl Selenides and Dialkyl Diselenides Prepared

R	Yield,[a] %	Previous ref
	Selenides, R_2Se	
n-Pentyl	61	17
Benzyl	88 (66)	5
p-Chlorobenzyl	78 (53)	18
2-Phenylethyl	95 (88)	*b*
	Diselenides, R_2Se_2	
Methyl	73[c]	4
Ethyl	69	4
n-Propyl	50 (40)	19
n-Pentyl	64	14
Cyclohexyl	60 (46)	14
Benzyl	77 (75)	5
p-Chlorobenzyl	66 (58)	14

[a] Isolated yields are in brackets; other yields are by ^1H NMR with reference to toluene or *p*-xylene internal standard, unless noted. [b] New compound; spectral characterization is in Experimental Section. [c] Determined by GC with reference to an internal standard and corrected for detector response factor

synthesized when a slight procedural modification is employed.

Results

The addition of 1.0 equiv of gray powdered selenium to 2.1 equiv of $Li(C_2H_5)_3BH$ in THF (sold as a 1.0 M THF solution under the trade name Super Hydride) under dry N_2 with stirring resulted in gas evolution, lasting ca. 2 min (eq 2). Stirring was continued for at least 20 min, during which time the reaction mixture became a heterogeneous milky white. The subsequent efficaciousness of this Li_2Se preparation was not diminished by overnight stirring.

Addition of THF solutions of alkyl halides (2.1 equiv) to the Li_2Se preparation did afford dialkyl selenides (eq 3). Slightly superior yields, however, resulted when some *tert*-butyl alcohol (1.7–5.3 equiv) was added with the alkyl halide as cosolvent or directly to the Li_2Se just prior to the addition of alkyl halide. Reaction time depended upon alkyl halide reactivity, and workup consisted of ether extraction, washing, and drying. Subsequent solvent evaporation removed the triethylborane byproduct. Yields were obtained by reference to a ^1H NMR internal standard, or by isolating the product by recrystallization or distillation. Product deterioration was noted upon column chromatography. Yields are given in Table I.

The addition of 1.0 equiv of gray powdered selenium to 1.05 equiv of stirred $Li(C_2H_5)_3BH$ in THF resulted in gas evolution and the formation of a dark brown–red suspension (eq 4). After a minimum of 20 min stirring, a THF solution containing alkyl halide (usually 1.05 equiv) and 1.7–5.3 equiv of *tert*-butyl alcohol was added to the Li_2Se_2 preparation (eq 5). Alternately, the *tert*-butyl alcohol could be added to the Li_2Se_2 just prior to the alkyl halide. Workup was analogous to that used with the selenides, and the diselenides that were prepared are listed in Table I.

When two side-by-side preparations of dibenzyl diselenide were attempted, one with *tert*-butyl alcohol and the other without, product yields (^1H NMR) were 77 and 42%, respectively. When pyridine was used instead of *tert*-butyl alcohol, a 41% yield of dibenzyl diselenide was obtained.

Unsymmetrical selenides and diselenides could not be synthesized via sequential addition of RX and R′X to the Li_2Se and the Li_2Se_2 preparations. Only symmetrical products were detected. The addition of 2.1 equiv of $Li(C_2H_5)_3BH$ to symmetrical diselenide reaction mixtures as prepared in eq 5 followed by the addition of 2.1 equiv of a second alkyl halide did not afford clean yields of unsymmetrical dialkyl selenides (eq 6 and 7). Presumably the *tert*-butyl alcohol present now plays a deliterious role by reacting with the $Li(C_2H_5)_3BH$ faster than the diselenide. However, rapid formation of lithium alkylselenolates or arylselenolates (eq 6) was observed when *isolated* diselenides were treated with 2.1 equiv of $Li(C_2H_5)_3BH$ in THF alone. Addition of 2.1 equiv of benzyl chloride to 2.0 equiv of lithium phenylselenolate prepared from diphenyl diselenide afforded a 92% yield (^1H NMR) of benzyl phenyl selenide. By an identical procedure, benzyl methyl selenide was prepared from dibenzyl diselenide and methyl iodide in 92% yield (^1H NMR).

Scheme I. Syntheses of Symmetrical Dialkyl Selenides

$$\mathrm{Se} \xrightarrow{\mathrm{Na/NH_3}} \mathrm{Na_2Se} \xrightarrow{\mathrm{2RX}} \mathrm{R_2Se} \qquad (8)^{3}$$

$$\mathrm{Se} \xrightarrow[\mathrm{aq\ NaOH}]{\mathrm{HOCH_2SO_2Na}} \mathrm{Na_2Se} \xrightarrow{\mathrm{2RX}} \mathrm{R_2Se} \qquad (9)^{4}$$

$$\mathrm{Se} \xrightarrow[\mathrm{H_2O\ or\ C_2H_5OH}]{\mathrm{NaBH_4}} \mathrm{NaHSe\ and\ Na_2Se} \xrightarrow{\mathrm{2RX}} \mathrm{R_2Se} \qquad (10)^{5}$$

$$\mathrm{SeO_2 + RMgX\ or\ RLi} \rightarrow \mathrm{R_2Se} \qquad (11)^{6a}$$

$$\mathrm{SeO_2 + R_3B} \xrightarrow{\mathrm{THF}} \mathrm{R_2Se} \qquad (12)^{6b}$$

$$\mathrm{H_2Se + CH_2CH_2} \xrightarrow[350\ ^\circ\mathrm{C}]{12\ \mathrm{atm}\cdot} \mathrm{(CH_3CH_2)_2Se} \qquad (13)^{7}$$

$$\mathrm{SeCl_2 + 2CHCl{=}CHCl} \rightarrow \mathrm{(CHCl_2CHCl)_2Se} \qquad (14)^{8}$$

Scheme II. Syntheses of Symmetrical Dialkyl Diselenides

$$\mathrm{Se} \xrightarrow[\mathrm{NH_3}]{\mathrm{Na\ or\ Li}} \mathrm{Se_2^{2-}} \xrightarrow{\mathrm{2RX}} \mathrm{R_2Se_2} \qquad (15)^{3a,9}$$

$$\mathrm{Se} \xrightarrow[\mathrm{aq\ NaOH}]{\mathrm{HOCH_2SO_2Na}} \mathrm{Na_2Se_2} \xrightarrow{\mathrm{2RX}} \mathrm{R_2Se_2} \qquad (16)^{10}$$

$$\mathrm{Se} \xrightarrow[\mathrm{H_2O\ or\ C_2H_5OH}]{\mathrm{NaBH_4}} \mathrm{Na_2Se_2} \xrightarrow{\mathrm{2RX}} \mathrm{R_2Se_2} \qquad (17)^{5}$$

$$\mathrm{Se} \xrightarrow[\mathrm{CH_3OH}]{\mathrm{Mg}} \mathrm{(CH_3OMg)_2Se} \xrightarrow{\mathrm{2RX}} \mathrm{R_2Se_2} \qquad (18)^{11}$$

$$\mathrm{KSeCN + RX} \rightarrow \mathrm{RSeCN} \xrightarrow{^{-}\mathrm{OH}} \mathrm{R_2Se_2} \qquad (19)^{12}$$

$$\mathrm{H_2Se + 2RCOR} \xrightarrow[\mathrm{pyridine/(C^2H^5)^3N,}]{\mathrm{HCl\ or}} \mathrm{(R_2CH)_2Se_2} \qquad (20)^{13,14}$$

$$\mathrm{RSeSeR + 2Li(C_2H_5)_3BH} \rightarrow \mathrm{2RSeLi + 2(C_2H_5)_3B + H_2} \qquad (6)$$

$$\mathrm{2RSeLi + 2R'X} \rightarrow \mathrm{RSeR'} \qquad (7)$$

Discussion

The dialkyl selenide and diselenide syntheses described herein have the following attributes: (a) only a single reaction flask is required, and most reactions proceed satisfactorily at room temperature; (b) starting materials are conveniently handled and inexpensive on moderate scales ($Li(C_2H_5)_3BH$ costs \$42/mol); (c) no detectable byproducts are formed, and workup procedures are simple.

The yields presented in Table I are by no means optimized. However, in nearly every case the best reported literature yield is matched or exceeded. The pervasive odor of diethyl diselenide, dipropyl diselenide, and dipentyl diselenide deterred us from further experimentation strictly for yield's sake. Benzyl organoselenium compounds were prepared from benzyl chlorides, and alkyl organoselenium compounds were prepared from alkyl bromides or iodides. Only in the case of dicyclohexyl diselenide was the starting alkyl halide (cyclohexyl bromide) unreactive enough to require a reflux period.

Representative synthetic routes to symmetrical dialkyl selenides and diselenides are listed in Schemes I and II, respectively, While Se^{2-} and Se_2^{2-} can be readily prepared by alkali metal–ammonia reduction of Se_x (eq 8 and 15), this procedure is operationally cumbersome. Sodium formaldehyde sulfoxylate or "Rongalite" can effect identical reductions (eq 9 and 16), but aqueous solvent systems are required. Several selenide syntheses employ SeO_2 and carbon nucleophiles (eq 11 and 12), and the addition of Se–H and Se–Cl bonds across olefins has been observed (eq 13 and 14). These methods lack in convenience, generality, and yield. A recently developed route to secondary alkyl diselenides utilizes ketones as starting materials but requires the use of H_2Se (eq 20).

The $NaBH_4$ reduction of Se_x recently described by Klayman and Griffin (eq 10 and 17) is related to our procedure and has many attributes in common. However, water or ethanol were required as solvents, and due to their reactivity only one hydride per BH_4^- could be utilized. In water, Na_2Se_2 was not prepared directly as depicted in eq 17 but via addition of further Se_x to NaHSe (eq 10). In ethanol, Na_2Se_2 formation was accompanied by an equivalent amount of H_2Se. While only benzyl selenides and diselenides were prepared by this procedure, it may have generality similar to ours and be superior for large scale preparations.

The exact role of the *tert*-butyl alcohol cosolvent in the Li_2Se and Li_2Se_2 alkylation steps is uncertain. Since the K_a of NaHSe is 10^{-15} (22 °C),[20] Li_2Se is probably not significantly protonated by *tert*-butyl alcohol in THF. Any excess trialkylborohydride would be quenched by *tert*-butyl alcohol and thus prevented from depleting the alkyl halide pool by nucleophilic attack.[21] However, this should result in only a slight increase in yield. The *tert*-butyl alcohol could act in part by increasing the polarity of the reaction medium and the concentration of dissolved Li_2Se and Li_2Se_2. We have also considered the possibility of *tert*-butyl alcohol or *t*-alkoxide catalysis by addition to selenium to form a hypervalent species of enhanced nucleophilicity. In the alkylation of selenolates (RSe^-) prepared from diselenides (eq 6 and 7), *tert*-butyl alcohol is not needed. We emphasize that *tert*-butyl alcohol is not in any way required for the actual production of Li_2Se and Li_2Se_2 suspensions from $Li(C_2H_5)_3BH$ and Se_x.

In aprotic solvents, $NaBH_4$ is incorporated into chalcogens to form products such as $NaBH_2S_3$, $NaBH_2Te_3$, and H_2.[22] Gray elemental selenium consists of polymeric, unbranched helical chains[23] which are apparently broken down completely by $Li(C_2H_5)_3BH$ in THF. The enhanced nucleophilicity of trialkylborohydrides relative to other boron and aluminum hydride reagents has been previously noted.[21]

The $(C_2H_5)_3B$ which is produced as a byproduct in these reactions is removed as a codistillate with THF and workup solvents. These solvent mixtures are not pyrophoric,[21c] and we have handled all product workups detailed herein and elsewhere[15] without special precaution and without incident. Other researchers have suggested[21d] that rotary evaporator vacuums be broken with N_2 when $(C_2H_5)_3B$ is among the volatiles. Since $Li(C_2H_5)_3B$ is readily formed from LiH and $(C_2H_5)_3$,[21e] Li_2Se and Li_2Se_2 might be equally well produced from LiH and a catalytic amount of $(C_2H_5)_3B$.

Unsymmetrical selenides are generally prepared by reduction of symmetrical diselenides to selenolates (RSe^-) and subsequent alkylation.[24] Although this can be accomplished with $NaBH_4$,[2a,24a] we have found $Li(C_2H_5)_3BH$ to be equally effective (eq 6). Unsymmetrical selenides, however, cannot be prepared in one flask from Se_x unless the *tert*-butyl alcohol is omitted from the initial symmetrical diselenide synthesis (eq 5). Since this adversely affects the diselenide yield, we recommend diselenide isolation before further reaction with $Li(C_2H_5)_3BH$.

At this time, we have not yet extended our methodology to the preparation of diaryl selenides or diselenides. However, arylation of carbon nucleophiles through use of transition metal catalysts is becoming increasingly common,[25] and a similar approach may prove effective with Li_2Se and Li_2Se_2. We also envision no difficulty in reacting our Li_2Se and Li_2Se_2 preparations with other classes of electrophiles such as esters or epoxides.

In conclusion, on scales where the moderate expense of $Li(C_2H_5)_3BH$ is inconsequential, we believe the procedure reported herein for dialkyl selenide and diselenide syntheses is the method of choice. Further applications of trialkylborohydrides to transition metal and metalloid anion syntheses are under active investigation.

Experimental Section

General. All experiments were carried out under an atmosphere of dry N_2. Selenium was used in its powdered gray form and stored in a desiccator. Tetrahydrofuran was dried and deoxygenated by distillation from sodium benzophenone ketyl. In initial experiments, *tert*-butyl alcohol was dried by distillation from magnesium turnings and subsequently deoxygenated by either a freeze–thaw cycle or by passage of dry N_2 through the alcohol. The alkyl halides were purified by distillation and subsequent deoxygenation with a stream of dry N_2. $Li(C_2H_5)_3BH$ (Super Hydride) was obtained from Aldrich as a 1.0 M THF solution and used at the stated bottle concentration. Melting points were taken on a Büchi Schmeltzpunktbestimmungsapparat and are uncorrected. ^1H NMR spectra were taken on a Varian T-60 spectrometer; NMR yields are with reference to toluene or *p*-xylene and are based on the starting amount of lithium selenide or diselenide. ^{13}C NMR spectra were taken on a Varian CFT-20 spectrometer. ^1H and ^{13}C NMR chemical shifts are reported with reference to Me_4Si. Mass spectra were taken on an AEI MS-9 instrument. All products were identified either by comparison to authentic samples or by analysis of spectral data.

Preparation of Lithium Selenide Suspension in THF. A representative procedure is as follows. Gray selenium (0.220 g, 2.780 mmol) was added portionwise to 5.80 mL of $Li(C_2H_5)_3BH$ solution (5.80 mmol) with magnetic stirring. Gas evolution occurred and ceased within 2 min; the solution gradually turned a heterogeneous milky white. THF (3 mL) was added, and the suspension was allowed to stir for at least 20 min.

General Method of Product Workup. After the specified reaction between alkyl halide and Li_2Se (or Li_2Se_2), the reaction mixture was taken up in ethyl ether/water. After separation, the aqueous layer was extracted twice more with ether. The organic phases were combined and dried with $MgSO_4$ or Na_2SO_4. After filtration, the solvent was removed under vacuum. If a ^1H NMR yield was desired, the internal standard was added at this point. This procedure was followed in all cases unless noted. *Caution*! Flammable byproducts [H_2, $(C_2H_5)_3B$] are produced during these reactions. Larger scale reactions may require cautionary measures in addition to those discussed.

Dipentyl Selenide. A solution of 1-bromopentane (0.725 mL, 5.85 mmol) and *tert*-butyl alcohol (0.5 mL, 5.3 mmol) in 5 mL of THF was added overnight to Li_2Se (2.78 mmol) suspended in 9 mL of THF. When the addition was completed, the reaction mixture was worked up as previously described. The yield of product, as determined by ^1H NMR, was 61%: ^1H NMR ($CDCl_3$) δ 0.92 (t, 3 H), 1.43 (m, 6 H), 2.50 (t, 2 H); ^{13}C NMR ($CDCl_3$) 14.0, 22.3, 24.0, 30.5, 32.3 ppm; mass spectrum, *m/e* 222 (M^+, ^{80}Se).

Dibenzyl Selenide. Benzyl chloride (0.69 mL, 6.00 mmol) in 5 mL of THF was added dropwise to Li_2Se (2.94 mmol) suspended in 0.5 mL (4.3 mmol) of *tert*-butyl alcohol and 11 mL of THF. After the addition was completed, the reaction mixture was stirred overnight and worked up as previously described. The product yield was 88% by ^1H NMR. Recrystallization from hexane yielded 0.501 g (66%) of white crystals, mp 44–45 °C (lit.[5,26] mp 45.5 °C): ^1H NMR ($CDCl_3$) δ 3.67 (s, 2 H), 7.25 (s, 5 H); ^{13}C NMR ($CDCl_3$) 27.5, 126.7, 128.4, 129.0 ppm (no pulse delay; one arene carbon absent).

Di(*p*-chlorobenzyl) Selenide. α-*p*-Dichlorotoluene (0.966 g, 6.00 mmol) in 7 mL of THF was added dropwise to Li_2Se (2.79 mmol) suspended in 0.5 mL (5.3 mmol) of *tert*-butyl alcohol and 11 mL of THF. After addition was completed, the reaction mixture was stirred overnight and worked up as previously described. The product yield was 78% by ^1H NMR. Recrystallization from hexane afforded 0.486 g (53%) of fluffy white crystals, mp 49.5–51 °C (lit.[18] mp 57.5 °C), which were recrystallized a second time, mp 51.5–52 °C: ^1H NMR ($CDCl_3$) δ 3.63 (s, 4 H), 7.23 (s, 8 H); ^{13}C NMR ($CDCl_3$) 26.7, 128.7, 130.3, 132.6 (weak), 137.4 (weak) ppm; mass spectrum, *m/e* 330 (M^+, $^{35}Cl_2$, ^{80}Se).

Di(2-phenylethyl) Selenide. (2-Iodoethyl)benzene (1.458 g, 6.28 mmol) in 4 mL of THF was added overnight to Li_2Se (2.79 mmol) in 0.5 mL (5.3 mmol) of *tert*-butyl alcohol and 7 mL of THF. Following workup as previously described, the product yield by ^{1}H NMR was 95%. In a separate experiment, (2-iodoethyl)benzene (1.439 g, 6.2 mmol) in 5 mL of THF was added over a 0.5-h period to Li_2Se (2.96 mmol) suspended in 0.5 mL (5.3 mmol) of *tert*-butyl alcohol and 11 mL of THF. After stirring overnight, the reaction mixture was worked up as previously described, and the resulting light yellow oil was washed with 50 mL of hot hexane. Solvent removal under high vacuum afforded 0.761 g (89%) of a light yellow liquid that was pure by ^{1}H NMR analysis. The compound could not be induced to crystallize. ^{1}H NMR (CCl_4) δ 2.77 (m, 4 H), 7.13 (s, 5 H); ^{13}C NMR ($CDCl_3$) 25.0, 37.2, 126.3, 128.39, 128.42, 141.2 ppm; mass spectrum, *m/e* 290 (M^+, ^{80}Se); exact mass (calcd) 290.0574; exact mass (found) 290.0569 ± 0.001; IR ($CHCl_3$) 3085 w, 3063 w, 3009 w, 2967 w, 2936 w, 1495 s, 1453 s, 1259 br, 696 vs cm^{-1}.

Preparation of Lithium Diselenide Suspension in THF. Gray selenium (0.319 g, 4.04 mmol) was added portionwise to a solution of 4.15 mmol of $Li(C_2H_5)_3BH$ in THF with magnetic stirring. Gas evolution occurred, and the suspension turned a dark brown–red. The Li_2Se_2 reaction mixture was allowed to stir for at least 20 min before proceeding.

Dimethyl Diselenide. Iodomethane (0.265 mL, 4.25 mmol) in 5 mL of THF was added over a period of 5 h to a suspension of Li_2Se_2 (2.02 mmol) in 0.5 mL (5.3 mmol) of *tert*-butyl alcohol and 6 mL of THF prepared in the manner described above. After workup as previously indicated, gas chromatography with reference to an internal standard and a commercial (Alfa-Ventron) authentic product indicated a yield of 73%;

Diethyl Diselenide. Iodoethane (0.726 mL, 9.01 mmol) in 5 mL of THF was added dropwise to a suspension of Li_2Se_2 (2.145 mmol) in 0.5 mL (5.3 mmol) of *tert*-butyl alcohol and 9.9 mL of THF, and the reaction mixture was stirred overnight. Workup as previously described afforded the product as a foul-smelling yellow oil (yield 69% by ^{1}H NMR). Subsequent experiments showed the excess iodoethane employed in this preparation to have only a slight influence on the yield. ^{1}H NMR (CCl_4) δ 1.45 (t, 3 H), 2.88 (q, 2 H); mass spectrum, *m/e* 218 (M^+, $^{80}Se_2$).

Dipropyl Diselenide. 1-Iodopropane (0.22 mL, 2.30 mmol) in 5 mL of THF was added dropwise to Li_2Se_2 (2.12 mmol) suspended in 0.5 mL (5.3 mmol) of *tert*-butyl alcohol and 9.7 mL of THF. After stirring overnight, workup as previously described afforded a yellow oil in 50% yield by ^{1}H NMR (92% yield if based upon 1-iodopropane). In a separate experiment, 1-iodopropane (0.41 mL, 4.2 mmol) in 3 mL of THF was added slowly to a suspension of Li_2Se_2 (1.01 mmol) in 0.5 mL (5.3 mmol) of *tert*-butyl alcohol and 2 mL of THF. Workup as previously described and vacuum distillation afforded 0.10 g (40%) of product as a red–brown foul-smelling liquid. ^{1}H NMR ($CDCl_3$) δ 0.98 (t, 3, H), 1.70 (m, 2 H), 2.90 (t, 2 H); mass spectrum, *m/e* 246 (M^+, $^{80}Se_2$).

Dipentyl Diselenide. 1-Bromopentane (0.350 mL, 2.83 mmol) in 0.5 mL (5.3 mmol) of *tert*-butyl alcohol and 5 mL of THF was added over a period of 2 h to a solution of Li_2Se_2 (1.35 mmol) in 5 mL of THF. After workup, ^{1}H NMR revealed a 64% yield of product as well as 15% unreacted halide (to account for 94% of the mass balance). Chromatography on silica gel with 25% v/v ethyl acetate in hexane as the eluent yielded pure product for spectral analysis. ^{1}H NMR ($CDCl_3$) δ 0.88 (t, 3 H), 1.35 (m, 4 H), 1.72 (m, 2 H), 2.92 (t, 2 H); ^{13}C NMR ($CDCl_3$) 13.9, 22.2, 30.4, 30.8, 31.8 ppm; mass spectrum, *m/e* 302 (M^+, $^{80}Se_2$).

Dicyclohexyl Diselenide. Bromocyclohexane (0.345 mL, 2.83 mmol) in 5 mL of THF was added over a 1-h period to a solution of Li_2Se_2 (1.33 mmol) in 0.5 mL (5.3 mmol) of *tert*-butyl alcohol and 5 mL of THF. The absence of a color change upon completion of the addition suggested that no reaction had taken place. After 13 h of stirring at room temperature, the reaction flask was heated to 45 °C for 11 h and then to 70 °C for 8 days. After workup in the usual way, ^{1}H NMR indicated a 60% yield. Distillation under reduced pressure yielded 0.20 g (46%) of product: ^{1}H NMR (CCl_4) δ 1.62 (broad multiplet, 10 H), 2.97 (m, 1 H); ^{13}C NMR ($CDCl_3$) 25.7, 27.0, 34.6, 43.4 ppm (area ratios ca. 1:2:2:1); mass spectrum, *m/e* 326 (M^+, $^{80}Se_2$).

Dibenzyl Diselenide. Benzyl chloride (0.310 mL, 2.69 mmol) in 3 mL of THF was added over a period of 1.5 h to a suspension of Li_2Se_2 (1.29 mmol) in 0.6 mL (6.4 mmol) of *tert*-butyl alcohol and 3 mL of THF. After stirring overnight, the reaction mixture was worked up by the addition of 4 mL of $CHCl_3$ and 1 mL of water to the flask, separation of the aqueous phase, and drying of the organic phase with $MgSO_4$. After filtration, the solution was evaporated to dryness. The crude dibenzyl diselenide was recrystallized from hexane. Several crops were obtained, giving a combined yield of 0.330 g (75%) of product, mp 91.0–92.0 °C (lit.[27] mp 92–93 °C).

The use of pyridine as a cosolvent was attempted. Benzyl chloride (0.310 mL, 2.69 mmol) in 5 mL of THF was added over a 2-h period to a solution of Li_2Se_2 (1.28 mmol) in 0.6 mL (7.4 mmol) of dry pyridine and 3 mL of THF. The workup was identical to that in the previous paragraph. Recrystallization from hexane yielded 0.179 g (41%) of product, obtained in several crops, mp 90.0–91.0 °C.

Two side-by-side experiments were conducted, one with and one without *tert*-butyl alcohol. In one reaction, benzyl chloride (0.168 mL, 1.46 mmol) in 5 mL of THF was added dropwise to a suspension of Li_2Se_2 (1.33 mmol) in 8 mL of THF and 0.5 mL (5.3 mmol) of *tert*-butyl alcohol. In another experiment, benzyl chloride (0.168 mL, 1.46 mmol) in 5 mL of THF was added dropwise to a suspension of Li_2Se_2 (1.4 mmol) in 8 mL of THF. After stirring overnight and employing the general method of product workup previously described, ^{1}H NMR analysis indicated the yield of the reaction done with *tert*-butyl alcohol to be 77% and the yield of the reaction done without it to be 42%; ^{1}H NMR ($CDCl_3$) δ 3.83 (s, 2 H), 7.27 (s, 5 H).

Di(*p*-chlorobenzyl) Diselenide. α-*p*-dichlorotoluene (0.5766 g, 3.58 mmol) in 5 mL of THF was added over a 2.5-h period to a suspension of Li_2Se_2 (1.78 mmol) in 0.5 mL (5.3 mmol) of *tert*-butyl alcohol and 6 mL of THF. The reaction mixture was then heated to 67 °C for 20 h. After workup, ^{1}H NMR analysis indicated a 66% yield of product. In a separate experiment, α-*p*-dichlorotoluene (0.699 g, 4.34 mmol) in 5 mL of THF was added slowly to Li_2Se_2 (2.12 mmol) suspended in 0.5 mL (5.3 mmol) of *tert*-butyl alcohol and 9.6 ml of THF. After stirring overnight, workup as previously described and recrystallization from hexane afforded 0.501 g (58%) of fluffy yellow crystals, mp 73.5–75 °C (lit. mp 76.5–77 °C,[18] 82 °C[28]), and subsequent recrystallizations increased the melting point to 77–78 °C: ^{1}H NMR ($CDCl_3$) δ 3.82 (s, 4 H), 7.25 (m, 8 H); ^{13}C NMR ($CDCl_3$) 31.7, 128.6, 130.3, 133.0 (weak), 137.5 (weak) ppm; mass spectrum, *m/e* 410 (M^+, $^{35}Cl_2$, $^{80}Se_2$). Anal. Calcd for $C_{14}H_{12}Cl_2Se_2$: C, 41.11; H, 2.96; Cl, 17.33; Se, 38.60. Found: C, 41.22; H, 2.90; Cl, 17.14; Se, 38.72.

Phenyl Benzyl Selenide. Diphenyl diselenide (2.11 mmol, 0.6585 g) in 5 mL of THF was treated with 4.4 mL of $Li(C_2H_5)_3BH$ solution (4.4 mmol), and the mixture was stirred for 0.5 h. THF (5 mL) and 0.5 mL of *tert*-butyl alcohol were added followed by 4.22 mmol (0.486 mL) of benzyl chloride in 2 mL of THF. The reaction was stirred for 4 h and worked up as previously described. ^{1}H NMR analysis indicated a product yield of 92%. The crude oil was recrystallized from hexane to afford white crystals, mp 33–34 °C (lit.[29] mp 32.5 °C): ^{1}H NMR ($CDCl_3$) δ 4.08 (s, 2 H), 7.3 (m, 10 H); ^{13}C NMR ($CDCl_3$) 32.3, 126.8, 127.3, 128.4, 128.8, 128.9, 133.6 ppm; mass spectrum, *m/e* 248 (M^+, ^{80}Se).

Benzyl Methyl Selenide. Dibenzyl diselenide (1.02 mmol, 0.348 g) in 5 mL of THF was treated with 2.2 mL of $Li(C_2H_5)_3BH$ solution (2.2 mmol). After stirring for 0.5 h, 2.04 mmol (0.128 mL) of iodomethane in 2 mL of THF was added, and the reaction mixture was stirred for 4 h. Workup as previously described afforded a yellow oil.[30] ^{1}H NMR analysis indicated a 92% yield: ^{1}H NMR ($CDCl_3$) δ 2.23 (s, 3 H), 4.07 (s, 2 H), 7.63 (s, 5 H); mass spectrum, *m/e* 186 (M^+, ^{80}Se).

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Registry No.—Li_2Se, 12136-60-6; Li_2Se_2, 65027-50-1; $Li(C_2H_5)_3BH$, 22560-16-3; selenium, 7782-49-2; dipentyl selenide, 14835-67-7; 1-bromopentane, 110-53-2; dibenzyl selenide, 1842-38-2; benzyl chloride, 100-44-7; di(*p*-chlorobenzyl) selenide, 56344-10-6; α-*p*-dichlorotoluene, 104-83-6; di(2-phenylethyl) selenide, 65027-51-2; (2-iodoethyl)benzene, 17376-04-4; diethyl diselenide, 628-39-7; iodoethane, 75-03-6; dipropyl diselenide, 7361-89-9; 1-iodopropane, 107-08-4; dipentyl diselenide, 52056-07-2; dicyclohexyl diselenide, 56592-97-3; bromocyclohexane, 108-85-0; dibenzyl diselenide, 1482-82-2; di(*p*-chlorobenzyl) diselenide, 56344-11-7; phenyl benzyl selenide, 18255-05-5; diphenyl diselenide, 1666-13-3; benzyl methyl selenide, 5925-78-0; dimethyl diselenide, 7101-31-7.

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Chlorosulfenylation–Dehydrochlorination Reactions. New and Improved Methodology for the Synthesis of Unsaturated Aryl Sulfides and Aryl Sulfones

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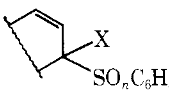
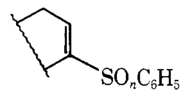
An improved procedure has been developed for the chlorosulfenylation of olefins. The method utilized is based on the quantitative reaction of aryl thiols with *N*-chlorosuccinimide to afford a reagent solution (A) which contains arylsulfenyl chloride as well as the "inert" co-product succinimide. Reaction of this reagent with a representative group of olefins (ethylene, cyclopentene, cyclohexene, cycloheptene, norbornene, butadiene, cyclohexadiene, Δ^2-cholestene, 1,2-dimethylcyclohexene, 1-methylcyclohexene, and 3-sulfolene) generates β-chlorophenyl sulfides in nearly quantitative yield. Aryl-substituted olefins react with reagent A in the presence of sodium carbonate to produce allylic or vinylic sulfides. The β-chloroaryl sulfides produced in the chlorosulfenylation reaction can be dehydrohalogenated with DBU to yield allyl, vinyl, or dienyl sulfides. Alternatively, the β-chloro sulfides can be oxidized to β-chloro sulfones, which may then be dehydrochlorinated with DBU under very mild conditions to afford excellent yields of α,β-unsaturated sulfones.

Unsaturated sulfur systems are valuable weapons in the arsenal of the synthetic organic chemist. Deprotonation reactions, fostered by the propensity of the sulfur moiety to stabilize an adjacent negative charge of allyl sulfides[3,4] (**1a**), allyl sulfoxides[4] (**1b**), and allyl sulfones[5,6] (**1c**), provide thioallylic anions (**2a–c**) of exceptional synthetic utility. A related area of growing interest involves the chemistry of vinyl sulfides[7–9] (**3a**), sulfoxides[8] (**3b**), and sulfones[10] (**3c**). In connection with our synthetic program, we have been investigating methods of producing several of these unsaturated sulfur systems (**1**, **3**) based upon chlorosulfenylation–dehydrochlorination reactions.

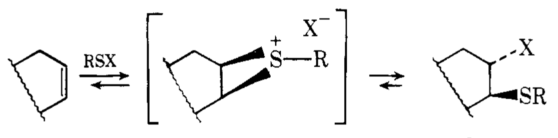


1a, X = H; $n = 0$
b, X = H; $n = 1$
c, X = H; $n = 2$
2a, X = Li; $n = 0$
b, X = Li; $n = 1$
c, X = Li; $n = 2$



3a, $n = 0$
b, $n = 1$
c, $n = 2$

The reaction of aryl- and alkylsulfenyl halides with olefins (**4**) to produce *trans*-β-haloaryl (alkyl) sulfides (**6**) is a very well-known process.[11] The reaction proceeds through an episulfonium salt intermediate (**5**)[12] which yields products usually resulting from predominant or exclusive attack of the halide ion at the more positively polarized carbon atom.[11,13–16] The β-halo sulfides so formed have been shown to undergo retrosulfenylation reactions (at elevated temperatures) as well as secondary rearrangements.[16–18] The facility with which these rearrangements occur is directly related to the electron



4 **5** **6**

R = aryl or alkyl