Organic Disulfides and Related Substances. 40. Reactions of Disulfides with Sulfur Ylides[1]

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Reactions of typical disulfides were studied with five sulfur ylides and two related species. The oxo ylide $\mathrm{Me_2S^+(O)CH_2^-}$ (**1**) reacted with diphenyl disulfide (**2**) to give the bissulfide insertion product $\mathrm{(PhS)_2CH_2}$ (**8**) but in low yield and in a molar percentage of product from 5 to 22%. Major products were the monosulfide PhSMe (**5**, 55%) and trissulfide $\mathrm{(PhS)_3CH}$ (**10**, 69%), which varied in molar percentage from 25–81 and 13–60%, respectively. The trissulfide **10** did not appear to form via the bissulfide **8**. The ylide $\mathrm{Me_2S^+CH_2^-}$ (**11**) gave monosulfide **5** and trissulfide **10**, in respective yields of 66 and 38%, but no bissulfide **8**. The resonance-stabilized ylide $\mathrm{Ph_2S^+C^-(CO_2Me)_2}$ (**12**) gave the insertion product, $\mathrm{(PhS)_2C(CO_2Me)_2}$, in 20–26% yield (perhaps 70% by NMR), but only with catalysis by $\mathrm{BF_3 \cdot Et_2O}$. The ylide $\mathrm{Me_2S^+CH^-CO_2Et}$ (**14**) with several diaryl disulfides gave 31–61% yields of α-(arylthio) ylides, $\mathrm{Me_2S^+C^-(SAr)CO_2Et}$ (which gave a sulfonium picrate), and the ylide $\mathrm{Me_2S^+CH^-COPh}$ (**18**) reacted similarly to give the known ylide, $\mathrm{Me_2S^+C^-(SPh)COPh}$. Aliphatic disulfides, such as diethyl disulfide and 1,2-dithiane, apparently gave insertion products in low yield with **1** and **12** ($\mathrm{BF_3 \cdot Et_2O}$) but no reaction with **14**. Other ylidelike species (a sulfilimine and isocyanide) did not react with **2** under mild conditions where products might survive.

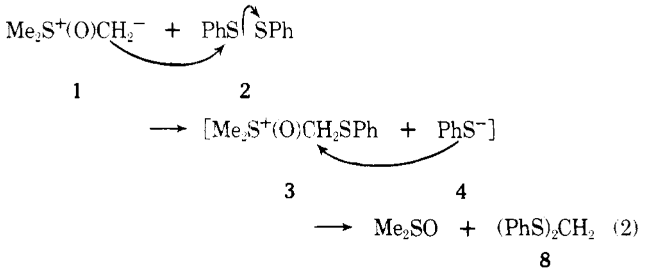
In a continuing investigation of organic disulfides,[1a] we reported studies of reactions of disulfides with carbenoids, carbenes, a phosphonium ylide, and nitrenes; earlier work was summarized.[1a] Insertion reactions, illustrated by eq 1

$$\mathrm{RSSR + Z \rightarrow RSZSR} \qquad (1)$$

and of special interest to us, were seen with carbenoids but only to trace extent with a phosphonium ylide.[1a] In addition to insertions summarized before,[1a] that of the phenylphosphinothioylidene moiety, $\mathrm{Ph\ddot{P}(S)}$, has been reported.[2,3]

Insertion reactions with sulfur ylides and disulfides appear to be unreported. The only apparent reports of reactions of such ylides with disulfides have dealt with transylidations catalyzed by electron-deficient disulfides.[4] The general subject of sulfur ylides has been reviewed.[5] The present paper describes patterns of reactions of disulfides with sulfur ylides that illustrate a range of ylide types including sulfoxonium, sulfonium, biscarbomethoxy, carbethoxy, and phenacyl methylides, with passing attention to some ylidelike species.

Dimethylsulfoxonium methylide (**1**) is a sulfur ylide of intermediate reactivity and stability. Table I shows the results of reactions with diphenyl disulfide (**2**). The mass of the reaction products, assuming combination of **2** with $\mathrm{CH_2}$, ranged from 79 to 91% of theory and averaged 86%. Bis(phenylthio)methane, the insertion product **8** of eq 2, was formed. However, the major products always were methyl phenyl sulfide (**5**) and tris(phenylthio)methane (**10**). All three products first were detected by mass and NMR spectra. Identities then were confirmed in the mixture by NMR peak augmentation using authentic **5**, **8**, and **10**.

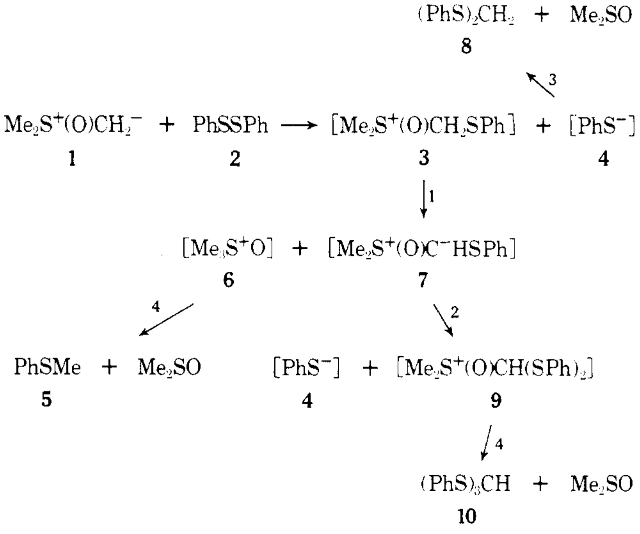


$$\underset{\mathbf{1}}{\mathrm{Me_2S^+(O)CH_2^-}} + \underset{\mathbf{2}}{\mathrm{PhSSPh}} \longrightarrow [\underset{\mathbf{3}}{\mathrm{Me_2S^+(O)CH_2SPh}} + \underset{\mathbf{4}}{\mathrm{PhS^-}}] \longrightarrow \mathrm{Me_2SO} + \underset{\mathbf{8}}{\mathrm{(PhS)_2CH_2}} \qquad (2)$$

Experiment 1 of Table I was done at ~25 °C to assess the reactivity and stability of the ylide **1**. These conditions led to the highest proportion of the trissulfide **10**. Experiment 2 was done three times at 50 °C for 1 h, conditions used for reactions of **1** with carbonyl compounds. In expt 3, the increased proportion of bissulfide **8** (the highest found) indicated that longer reaction favors **8**. In expt 4, inverse addition of the ylide **1** to the disulfide **2**, to eliminate the possibility that excess **1** attacked an intermediate instead of **2**, led to a minimal ratio of **8**, as did the similar expt 5–7. Changes of the relative amounts of **1** and **2** from a 1:1 ratio proved undesirable for insertion (expt 6–8), and an effort to ensure that enough ylide **1** would survive to react with 1 equiv of disulfide in a long reaction period led only to the maximum proportion formed of monosulfide **5** (expt 8). Results described below suggested that catalysis with $\mathrm{BF_3 \cdot Et_2O}$ deserved trial, but repetition of expt 3 except with two molar proportions of $\mathrm{BF_3 \cdot Et_2O}$ led only to a mixture shown by NMR to contain molar percentages of **2**, **5**, and **8** of 88, 8, and 4%, respectively; failure to find trissulfide **10** (and the high recovery of the disulfide **2**) indicates that most of ylide **1** simply decomposed. The results of Table I thus point to dim prospects for increasing the proportion of **8** much above 22%.

For isolation of products, separation of excess **2** was troublesome, and selective reduction of **2** was attempted. However, $\mathrm{LiAlH_4}$ partially reduced the bissulfide **8**, and zinc–acetic acid partially reduced the trissulfide **10**. Based on the stoichiometries of eq 2 and 3, distillation and chromatography of a typical product ultimately separated the mono (**5**), bis-

Scheme I



$$\underset{\mathbf{1}}{\mathrm{Me_2S^+(O)CH_2^-}} + \underset{\mathbf{2}}{\mathrm{PhSSPh}} \longrightarrow [\underset{\mathbf{3}}{\mathrm{Me_2S^+(O)CH_2SPh}}] + [\underset{\mathbf{4}}{\mathrm{PhS^-}}]$$

$$\mathbf{3} \xrightarrow{3} \underset{\mathbf{8}}{\mathrm{(PhS)_2CH_2}} + \mathrm{Me_2SO}$$

$$\mathbf{3} \xrightarrow{1} [\underset{\mathbf{6}}{\mathrm{Me_2S^+O}}] + [\underset{\mathbf{7}}{\mathrm{Me_2S^+(O)C^-HSPh}}]$$

$$\mathbf{6} \xrightarrow{4} \underset{\mathbf{5}}{\mathrm{PhSMe}} + \mathrm{Me_2SO}$$

$$\mathbf{7} \xrightarrow{2} [\underset{\mathbf{4}}{\mathrm{PhS^-}}] + [\underset{\mathbf{9}}{\mathrm{Me_2S^+(O)CH(SPh)_2}}]$$

$$\mathbf{9} \xrightarrow{4} \underset{\mathbf{10}}{\mathrm{(PhS)_3CH}} + \mathrm{Me_2SO}$$

Table I. Reactions of Dimethylsulfoxonium Methylide (1) with Diphenyl Disulfide (2)

Expt	Reaction time, h (50 °C)	Molar ratio of 1/2	Mode of addition[a]	Molar % of product[b]		
				PhSMe (5)	$(PhS)_2CH_2$ (8)	$(PhS)_3CH$ (10)
1	168 (25 °C)	1	2 → 1	30	10	60
2	1	1	2 → 1	49–55	5–17	28–53
3	5	1	2 → 1	25	22	53
4	5	1	1 → 2	47	6	47
5	24	1	1 → 2	36	7	57
6	24	2	1 → 2	60	7	33
7	24	0.5	1 → 2	39	5	56
8	48	2	2 → 1	81	6	13

[a] The notation 1 → 2 refers to a solution of ylide 1 in Me_2SO added to one of disulfide 2 in Me_2SO, and 2 → 1 refers to the reverse. [b] Molar percentages are calculated from the appropriate relations of integrals in NMR spectra for aliphatic CH peaks of 5, 8, and 10 to the total of such integrals; they total 100%.[1c] Residual 2 was disregarded (see ref 1c).

(**8**), and trissulfide (**10**) in respective overall yields of 55, 3, and 69%.

Scheme I shows the paths that seem most probable for formation of the monosulfide **5** and trissulfide **10** (as well as for the interrelationship of bissulfide **8**).[1c] In this view, nucleophilic attack of the ylide **1** on the disulfide **2** first leads to the intermediate **3**, perhaps as an ion pair with thiolate ion **4**. Although **3** and **4** then may give the insertion product **8**, in the major reaction **3** may lose a proton to ylide **1** to form a new ylide **7**, along with **6**. The new ylide **7** further reacts with disulfide **2**, giving **4** and **9**. Nucleophilic attack of the thiolate **4** on **9** then gives tris(phenylthio)methane (**10**). The ylide **1**, having abstracted a proton, becomes the methylating agent **6**,[6] which then methylates **4** to produce methyl phenyl sulfide (**5**). Equation 3 is a summation of reactions that may account

$$\underset{\mathbf{1}}{2\mathrm{Me_2S^+(O)CH_2^-}} + \underset{\mathbf{2}}{2\mathrm{PhSSPh}} \longrightarrow \underset{\mathbf{5}}{\mathrm{PhSMe}} + \underset{\mathbf{10}}{\mathrm{(PhS)_3CH}} + 2\mathrm{Me_2SO} \quad (3)$$

for monosulfide **5** and trissulfide **10**.

Before Scheme I was developed, we thought that trissulfide **10** might be formed by abstraction of a proton from bissulfide **8** by ylide **1**, followed by attack of the resulting carbanion on disulfide **2**. Three tests appear to argue against this possibility:[1c] (1) A mixture of bissulfide **8**, toluene (internal standard), and ylide **1** was stirred at about 25 °C for 1 h and then was treated with D_2O. If proton abstraction from bissulfide **8** by ylide **1** occurred, replacement of H by D should be reflected in reduced intensity and splitting of the methylene peak of **8**. No splitting for the peak of **8** was seen, however, and the decrease in intensity was less than 10%. Thus ylide **1** evidently is too weakly basic to abstract a proton from **8** significantly. (2) Equation 4 suggests that addition of one molar proportion

$$\underset{\mathbf{1}}{\mathrm{Me_2S^+(O)CH_2^-}} + \underset{\mathbf{2}}{\mathrm{(PhS)_2}} + \underset{\mathbf{8}}{\mathrm{(PhS)_2CH_2}} \longrightarrow \underset{\mathbf{5}}{\mathrm{PhSMe}} + \underset{\mathbf{10}}{\mathrm{(PhS)_3CH}} + \mathrm{Me_2SO} \quad (4)$$

of **8** to the usual 1:1 mixture of **1** and **2** might result in consumption of the **8** and thus increase the yield of **10** (cf. the 1:1 ratio for **2**:**10** in eq 4 vs. 1:0.5 in eq 3). This experiment was done with a 2:1 molar ratio of **1**:**2** to allow for losses of the ylide **1**. NMR showed ~95% survival of **8** (along with considerable monosulfide **5** and negligible trissulfide **10**; 0.5-h reaction period). (3) Reactions of Scheme I suggest that if the carbanion of **8** were evoked by ylide **1**, **6** produced should methylate it. However, after interaction of **8** and **1** at 50 °C for 0.5 h NMR showed 95% survival of **8** and no methylated product.

Substitution of diethyl for diphenyl disulfide in expt 3 led to bis(ethylthio)methane and tris(ethylthio)methane in respective yields of ~18 and ~7%; addition of authentic bis- and trissulfides enhanced the NMR peaks assigned. In this instance, actual yields were estimated by quantitating the peak augmentations with amounts of the authentic compounds added, in the hope that this method could be used to determine actual yields of products in other mixtures. However, results were so variable that the method was not used elsewhere. Substitution of 1,2-dithiane in expt 3 apparently led to insertion to give 1,3-dithiepane, but the yield did not exceed 10%.

Dimethylsulfonium methylide (**11**) was of interest since the negative charge presumably is less well delocalized than in **1** so that ylide **11** is more nucleophilic. Ylides **1** and **11** differ significantly.[5b,6b] Three experiments at 0–25 °C gave a mass of product that corresponded to 90% of theory for combination of **2** and CH_2. NMR spectra showed that the trissulfide **10** and monosulfide **5** were produced but *no* bissulfide **8**. The molar percentages of **10** and **5** were 33–38 and 62–67%, respectively. Actual separation of products gave yields of 38% for **10** and 66% for **5**, based on eq 5. The overall result of eq 5 can be ra-

$$\underset{\mathbf{11}}{2\mathrm{Me_2S^+CH_2^-}} + \underset{\mathbf{2}}{2\mathrm{(PhS)_2}} \longrightarrow \underset{\mathbf{5}}{\mathrm{PhSMe}} + \underset{\mathbf{10}}{\mathrm{(PhS)_3CH}} + 2\mathrm{Me_2S} \quad (5)$$

tionalized by paths like those of Scheme I for the oxy ylide **1**. The result with the sulfonium ylide **11** resembles that with triphenylphosphonium methylide, which gave trissulfide **10** and monosulfide **5** in 64 and 6% yields (with ratios of **10**:**5** from 9:1 to 0.7:1).[1a] However, the phosphonium ylide did produce at least a trace of bissulfide **8** (~0.3%).[1a]

Since the sulfonium ylide **11** gave no bissulfide, the phosphonium ylide a trace, and the sulfoxonium ylide **1** ~ 3%, less nucleophilic ylides became of interest. Diphenylsulfonium bis(carbomethoxy)methylide (**12**) was attractive for this reason.[7] Moreover, **12** cannot form a trissulfide and is so stable that it can be recrystallized from ethanol. Initial attempts to achieve reaction of **12** with disulfide **2** led to no insertion product. However, catalysis with $BF_3 \cdot Et_2O$ led to the formation of dimethyl bis(phenylthio)malonate (**13**) in yields that appeared by NMR to reach 70%, although difficulties in isolation reduced yields of solid **13** to 20–26% (eq 6). The **13** had

$$\underset{\mathbf{12}}{\mathrm{Ph_2S^+C^-(CO_2Me)_2}} + \underset{\mathbf{2}}{\mathrm{(PhS)_2}} \xrightarrow{2\mathrm{BF_3 \cdot Et_2O}} \mathrm{Ph_2S} + \underset{\mathbf{13}}{\mathrm{(PhS)_2C(CO_2Me)_2}} \quad (6)$$

Table II. Reactions of Diphenylsulfonium Bis(carbomethoxy)methylide (12) with Diphenyl Disulfide (2)[a]

Expt	Reaction: Temp, °C	Reaction: Time, h	Reaction: Solv[b]	Molar proportion: Of $BF_3 \cdot Et_2O$ to 12 used	Molar proportion: Of 13 in product, %[c]	Yield of 13 isol, % (mp, °C)
1	83	24	Glyme	2	50	26 (91.5–92)
2	83	24	Glyme	3[d]	*e*	*f*
3	60	18	Glyme	2[g]	0	0
4	25	168	Glyme[h]	2	0	0
5	80	24	None	2	50	21 (90–91.5)
6	80	6	None	2	50	20 (86–88)
7	60	24	None	2	70	*f*
8	40[i]	144	None	2	70	20 (87–89)
9	80	24	None	1	*e*	*f*
10	80	24	None	4	*e*	*f*

[a] Unless otherwise specified, the molar ratio of 12:2 was 1. [b] Glyme = 1,2-dimethoxyethane. [c] Calculated from the NMR integrals using the ratio of the OCH_3 peak at $\delta \sim 3.60$ (13) to all OCH_3 peaks (3.60, 3.70 for 12, etc.) times 100. Presumably this percentage approximates the yield of 13 before isolation. [d] The ratio of ylide 12 to disulfide 2 was increased from 1 to 1.5. [e] Complex NMR spectrum at δ 3.80–3.50. The proportion of 13 seemed not to exceed 30%. [f] Isolation not attempted. [g] $AlCl_3$ was used instead of $BF_3 \cdot Et_2O$. TLC showed no indication of reaction in 6 h at 25 °C. After the heating period, although NMR suggested presence of 13, none could be isolated by TLC. [h] TLC showed no reaction. Use of Et_2O during 30 days led to the same result (and to 96% recovery of 2). [i] The 12, 2, and $BF_3 \cdot Et_2O$ were mixed at 60 °C to give oil, which did not solidify when cooled to 40 °C.

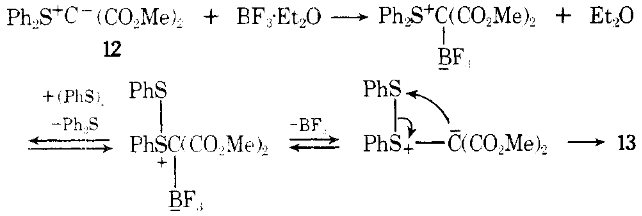
appropriate spectra and analyses and could be converted to bis(phenylthio)acetic acid.

Table II shows the effects of conditions. Heating of the ylide 12 and disulfide 2 in refluxing glyme gave the best result (expt 1). An increase in ylide 12 (and $BF_3 \cdot Et_2O$), to compensate for destruction of 12, gave a more complex mixture (expt 2). Substitution of aluminum chloride as catalyst led to no 13 (expt 3), nor did longer reaction at about 25 °C in glyme or ether (expt 4). Omission of solvent (expt 5) gave about the same result as expt 1, even with shortening of the reaction period (expt 6) or lowering of the temperature (expt 7, 8). An increase or decrease in the amount of $BF_3 \cdot Et_2O$ from the molar ratio of 2 proved undesirable (expt 9, 10; in most experiments of Table II, slightly more than 2 molar proportions of $BF_3 \cdot Et_2O$ were used owing to uncertainties of volume).

With diethyl disulfide and 1,2-dithiane, 12 and $BF_3 \cdot Et_2O$ gave products that could not be purified but appeared to contain dimethyl bis(ethylthio)malonate and 1,3-dithiepane-2,2-dicarboxylate (NMR peaks for OCH_3 different from those of 12). The yields at best were 15–17%.

Scheme II suggests a sequence for conversion of ylide 12 to the insertion product 13. This reaction probably has much in common with copper-catalyzed and BF_3-catalyzed insertion reactions of diazo esters which we reported earlier.[1a] The final step shown, rearrangement to give 13, may well involve homolysis (cf. ref 8).

Scheme II



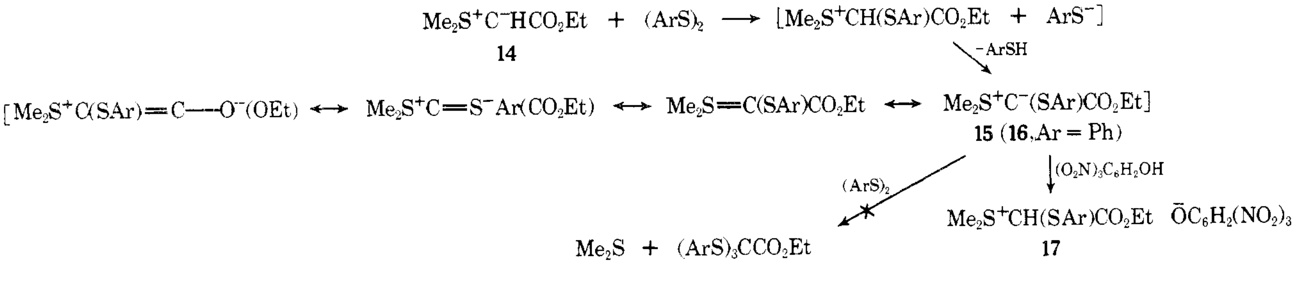
Dimethylsulfonium carbethoxymethylide (14)[9] should be intermediate in nucleophilicity between the sulfoxonium ylide 1 and the bis(carbomethoxy) ylide 12. Reaction of 14 with disulfide 2 neat gave a solid which was shown by NMR, IR, mass spectrum, and elemental analysis to be the ylide 16 (60% yield, Scheme III). Marked delocalization of charge presumably stabilizes 16 and accounts for its facile formation (Scheme III). Thiophenol was a conspicuous by-product. Further evidence for the structure of 16 was afforded by formation of the picrate 17 in 91% yield.

Analogy with the behavior proposed for carbanion 7 of Scheme I suggested that 16 might form a trissulfide (Scheme III). It proved too unreactive to do so. Thus when 2 and 16 were heated in CCl_4 under reflux for 24 h, 2 was recovered in 82% yield and TLC showed only a trace of a third product. Under the same conditions, one molar proportion of 2 and 16 with two of $BF_3 \cdot Et_2O$ led to recovery of 90% of the 2.

Other diaryl disulfides with ylide 14 also gave sulfur-stabilized ylides of structure 15. With Ar = *p*-MePh, *p*-MeOPh, and *p*-O_2NPh (Scheme III), respective yields were 36, 31, and 55% [bis(*p*-nitrophenyl) disulfide gave the impression of reacting most readily, but all diaryl disulfides reacted exothermically; of the products, 15 with Ar = *p*-MeOPh was significantly less stable]. Two dialkyl disulfides, diethyl and di-*n*-pentyl, failed to react; TLC of mixtures indicated no loss of either disulfide at 25 °C, and heating at 85 °C led to darkening but no new TLC spot.

Dimethylsulfonium phenacylide (18) followed the same pattern of reaction as 14 and gave 19 in 49% yield (eq 7), a known compound.[10a] Actually, the yield of 19 probably is greater than 49% because part of the limiting reagent 18 is likely to be lost in competition with thiolate ion for deproto-

Scheme III



$$\underset{\mathbf{18}}{\mathrm{Me_2S^+C^-HCOPh}} + \mathrm{(PhS)_2} \longrightarrow \underset{\mathbf{19}}{\mathrm{Me_2S^+C^-(SPh)COPh}} + \mathrm{PhSH} \quad (7)$$

nating an intermediate in eq 7; a similar reaction has been reported with a phosphorus ylide.[10b] Yields of **15** and **16**, as well, probably are higher than reported.

Two other compounds with ylidelike character, the sulfilimine **20** and isocyanide **21**, did not react under conditions

$$\underset{\mathbf{20}}{p\text{-}\mathrm{CH_3C_6H_4SO_2N^-S^+Me_2}}$$

$$p\text{-}\mathrm{CH_3C_6H_4SO_2CH_2\ddot{N}{=}C{:}} \longleftrightarrow p\text{-}\mathrm{CH_3C_6H_4SO_2CH_2N^+{\equiv}C^-{:}}$$

21

where (insertion) products seemed likely to be stable. Thus when **20** was heated with disulfide **2** in Me_2SO in steps of 10 °C every 15 min to 165 °C, TLC showed no indications of clean reaction to give the product p-$CH_3C_6H_4SO_2N(SPh)_2$. After disulfide **2** had been heated with **21** under reflux in glyme for 7 days, 95% of the **2** was recovered, and no indication was seen of the product p-$CH_3C_6H_4SO_2CH_2N{=}C(SPh)_2$ at any time by TLC.

Overall, it appears that reactions of the ylides studied tend more to stop at intermediary products as one proceeds along the reactivity sequence $Me_2S^+CH_2^-$ (**11**) ~ $Ph_3P^+CH_2^-$ ~ $Me_2S^+(O)CH_2^-$ (**1**) > $Me_2S^+CH^-CO_2Et$ (**14**) ~ $Me_2S^+CH^-COPh$ (**18**) > $Ph_2S^+C^-(CO_2Me)_2$ (**12**). Thus **11** gave no insertion, $Ph_3P^+CH_2^-$ 0.3%, and **1** about 3%. With **14** and **18**, the intermediate en route to insertion formed very readily but was stable. Late in the series, with **12**, strong acidic catalysis led to insertion, but otherwise there was no reaction.

Experimental Section

General Procedures and Starting Materials. Melting points, taken in capillary tubes using a Hoover stirred-liquid apparatus, are corrected. Elemental analyses were by Galbraith Microanalytical Laboratories, Knoxville, Tenn. IR spectra were obtained using a Perkin-Elmer Model 727 spectrophotometer and NMR spectra with a JEOL Model JNM-MH-100 or a Varian EM-360 spectrometer using Me_4Si as the internal standard. NMR assessments of compositions and yields were based on the assumption that only the disulfide used and products considered were present; the amounts of other products usually seemed small enough to warrant this assumption. TLC of reaction products was performed on Brinkmann PF-254 preparative TLC plates of silica gel (0.25 mm) or using 3 × 8 cm glass slides coated with Brinkmann silica gel G, with solvents specified and with development by I_2 vapor. Column chromatography was performed using Woelm silica gel with hexane or benzene. Moist extracts ordinarily were dried over anhydrous $MgSO_4$ or Na_2SO_4, and solvent then was evaporated using a rotating-flask evaporator under reduced pressure.

Starting materials of unspecified source were commercial products used as received. Bis(p-nitrophenyl) disulfide was purified by repeated recrystallization from EtOAc and xylene. Bis(p-methoxyphenyl) disulfide was kindly provided by C. H. Banks.[1a] Methyl phenyl sulfide (**5**), bis(phenylthio)methane (**8**), and bis(ethylthio)methane were prepared through reactions of CH_3I or CH_2I_2 with NaOEt and the thiols by reported procedures;[1c,11a] **8** (recrystallized from EtOH) had mp 36–37 °C (lit.[11b] 36 °C). Tris(ethylthio)methane and tris(phenylthio)methane (**10**) were similarly prepared from $CHCl_3$;[1c,11c] **10** (recrystallized from EtOH) had mp 39–40 °C (lit.[11c] 40 °C). 1,2-Dithiane was prepared from tosyl chloride and 1,4-butanedithiol.[1c,12] N-p-Toluenesulfonyl-S,S-dimethylsulfilimine was prepared according to King's procedure A,[13] mp 157–158 °C (lit.[13] 157–158 °C). p-Toluenesulfonyl chloride and $BF_3{\cdot}Et_2O$ were purified by reported procedures.[14]

Reactions of Dimethylsulfoxonium Methylide (1). Ylide **1** was prepared by the procedure of Corey and Chaykovsky,[15] typically from 50 mmol of NaH and of $Me_3S(O)I$ in Me_2SO (150 mL), and was used within 5 min. Illustratively, a solution of disulfide **2** (10.90 g, 50 mmol) in 30 mL of Me_2SO was dropped into the solution of 50 mmol (assumed) of the ylide **1** during 5 min with stirring. The mixture then was heated at 50 °C for 1–48 h (Table I). The mixture was cooled to ~25 °C, 500 mL of H_2O was added (3–6 times the volume of the reaction mixture), and the mixture was extracted with several 50-mL portions of Et_2O until evaporation left no residue. The combined extracts then were washed twice with 50-mL portions of H_2O to remove Me_2SO completely, dried, and evaporated; mass of a typical reaction product, 9.43 g (81% of theory for 50 mmol of **2** + CH_2). NMR showed the product to be sulfide **5** (δ 2.40; typically, **5** ranged ~2.2–2.4), bissulfide **8** (δ 4.25; typically, **8** ranged ~4.2–4.3), and trissulfide **10** (δ 5.30; typically, **10** ranged ~5.3–5.4); each appropriate peak was augmented upon addition of authentic **5**, **8**, or **10**. Molar ratios were calculated as stated in footnote b of Table I. Table I shows the results of variations.

For isolation of products, a mixture (5.0 g) from several trials of expt 2 (Table I) was distilled using a simple distilling head until the bath temperature reached 60 °C (6 mm), at which distillation ceased; yield of methyl phenyl sulfide (**5**; identity confirmed by NMR), 0.9 g. The remaining mixture was separated on 100 g of silica gel in a 1.6 × 60 cm column with hexane as eluent. Disulfide **2** was eluted first, followed by bissulfide **8** and trissulfide **10**. All three components were recrystallized from EtOH. Melting point, mixture melting point, and NMR confirmed identities. Calculated on the basis of eq 2 and 3, yields were PhSSPh (**2**), 0.1 g, 2% recovery; PhSMe (**5**), 0.9 g, 55% yield; $(PhS)_2CH_2$ (**8**), 0.2 g, mp 36–37 °C, 3% yield; and $(PhS)_3CH$ (**10**), 3.1 g, mp 39–40 °C, 69% yield.

Reactions with $(EtS)_2$ and 1,2-dithiane were done in the same way, with a reaction period of 5 h. The product from $(EtS)_2$ was shown to contain $(EtS)_2CH_2$ and $(EtS)_3CH$ by enhancement of peaks at δ 3.48 and 4.64, respectively, by authentic material. The effort (see Discussion) to relate integrals for each to known amounts added, so that actual yields of bis- and trissulfide present could be determined, gave variable results. Thus the percent yield calculated in four determinations for $(EtS)_2CH_2$ ranged from 15 to 21% (average, 18 ± 4−) and that for $(EtS)_3CH$ from 5 to 11% (7 ± 3%). The product from 1,2-dithiane showed a new NMR peak at δ 3.50 (s, $CDCl_3$), which was assigned to the moiety SCH_2S of 1,3-dithiepane by analogy to the peak at δ 3.48 for $(EtS)_2CH_2$ and to that at δ 3.69 (CCl_4) of 1,3-dithiane which has been assigned to SCH_2S;[16] based on this assumption, about one-sixth of the product appeared to be 1,3-dithiepane; the yield was estimated to be perhaps 10%.

Reactions of Dimethylsulfonium Methylide (11) with Diphenyl Disulfide (2). The ylide **11** was prepared according to Corey and Chaykovsky,[15] typically using 50 mmol of NaH and of Me_3SI in 70 mL of Me_2SO and 30 mL of THF. The **11** was used immediately to obviate decomposition. In a typical reaction, a solution of disulfide **2** (10.90 g, 50 mmol) in 30 mL of Me_2SO was added to the solution of 50 mmol (assumed) of **11** during 2 min. The mixture was stirred at ca. −18 °C for 5 min in an ice-salt bath and for 1 h with the bath removed and then was poured into 800 mL of H_2O and extracted with several 100-mL portions of Et_2O until evaporation left no perceptible residue. The extracts were combined, washed twice with 50-mL portions of H_2O, and dried. Evaporation of the Et_2O left 10.47 g (90% of the mass calculated for 50 mmol of **2** + CH_2). The NMR spectrum showed that the product contained sulfide **5** (δ 2.24) and trissulfide **10** (δ 5.36; peak enhancement with authentic **10**), along with unreacted **2**; bissulfide **8** was not found. Molar ratios of **5** and **10** were calculated from the relative integrals in NMR spectra of the aliphatic CH peaks for **5** and **10** and total 100%; residual **2** was disregarded.

Isolation of products followed the procedure for the reaction of **1** and **2**. A mixture (5.00 g aliquot from 10.47 g of total product) of typical reaction products gave 0.97 g of monosulfide **5** (66%), 1.60 g (31% recovery) of disulfide **2**, and 1.56 g of the trissulfide **10** (38%). The percent yields of **5** and **10** are based on eq 5. Identities of **2**, **5**, and **10** were established by melting point and/or NMR.

Reactions of Diphenylsulfonium Bis(carbomethoxy)methylide (12). Ylide **12** was prepared by modifying a reported procedure,[8] thereby facilitating purification. Thus 12.0 g (76 mmol) of dimethyl diazomalonate[8] was dissolved in 12.0 mL of Ph_2S (13.4 g, 72 mmol), and 0.24 g (1.5 mmol) of anhydrous $CuSO_4$ was added. The mixture was heated at 90 °C for 5 h until evolution of N_2 ceased. $CHCl_3$ (50 mL) was added, and undissolved $CuSO_4$ was separated. Removal of solvent left thick oil that solidified when rubbed with petroleum ether. Recrystallization from EtOH gave 20.4 g of **12** (89%): mp 127–128 °C (lit.[8] 127–128 °C); NMR ($CDCl_3$) δ 7.80–7.42 (m, 10 H, aromatic) and 3.70 (s, 6 H, OCH_3).

Initial experiments with 1 molar proportion of **2**, but without catalyst, gave no indication of a promising formation of the insertion product **13**. Thus attempted reaction in $CHCl_3$ (35 °C, 24 h) led to full recovery of **2** and **12** (melting point and mixture melting point). In Me_2SO at 90 or 135 °C (24 h), NMR showed complex absorptions at δ 3.8–3.6 with none predominant. Heating of a neat mixture of **2** and

12 at 160 °C (24 h) led to decomposition of **12** to give presumed tetramethyl ethylenetetracarboxylate [separation by column chromatography gave an impure oil which gave δ 3.86 absorption as the only absorption in NMR (CCl_4)].

In a typical catalyzed reaction (Table II, expt 1), ylide **12** (2.11 g, 6.7 mmol) and disulfide **2** (1.46 g, 6.7 mmol) were dissolved in 50 mL of glyme, $BF_3 \cdot Et_2O$ (2.07 g, 14.6 mmol) was dropped in during 5 min, and the mixture was stirred at ~25 °C. The progress of the reaction was monitored by TLC. The mixture remained unchanged for 15 h. After another 15 h at 40 °C, TLC still showed no reaction. Finally, the mixture was heated under reflux for 24 h until TLC showed that no ylide remained and gave a new spot, R_f 0.7 ($CHCl_3$). The mixture was cooled, and 50 mL of H_2O was added. Two 50-mL Et_2O extracts were washed with H_2O, dried, and evaporated; yield, 3.02 g of oily product (A). Preparative TLC ($CHCl_3$) using 1.00 g of the oil A separated 0.43 g (56%) of still impure **13**, R_f 0.2–0.7, which upon rechromatography and recrystallization from 2-propanol gave 0.19 g (25%) of dimethyl bis(phenylthio)malonate (**13**), mp 81–83 °C. NMR ($CDCl_3$) showed absorptions at δ 7.90–7.30 (m, 10 H, aromatic) and 3.60 (s, 6 H, OCH_3), and addition of ylide **12** produced the expected second methyl peak at δ 3.70. Further recrystallization from 2-propanol gave **13** with a constant melting point of 91.5–92°; IR (KBr) 1730, 1465, 1430, 1240, 1070, 1045, 990, 745, and 690 cm^{-1}.

Anal. Calcd for $C_{17}H_{16}O_4S_2$: C, 58.60; H, 4.63; S, 18.40. Found: C, 58.65; H, 4.60; S, 18.36.

Seeding of 1.00 g of the original oil A with **13**, then recrystallization, gave 0.20 g (26%) of **13**, mp 91.5–92 °C.

Illustratively for reaction neat (Table II, expt 5), a mixture of ylide **12** (2.11 g, 6.7 mmol), disulfide **2** (1.46 g, 6.7 mmol), and $BF_3 \cdot Et_2O$ (2.25 g, ~16 mmol) was stirred at 80 °C for 24 h and then was cooled to ~25 °C and dissolved in 50 mL of $CHCl_3$. The solution was washed with two 50-mL portions of H_2O to remove $BF_3 \cdot Et_2O$, dried, and evaporated; yield of oily **13**, 3.29 g; seeding of 1.61 g of this oil gave solid **13**, which was washed with a little 2-propanol and dried under vacuum; yield of **13**, 0.24 g (21%), mp 90–91.5 °C.

The identity of **13** was confirmed by heating 100 mg (0.29 mmol) in 1 mL of H_2O containing 56 mg of KOH (85.7% purity, 0.86 mmol) and 5 drops of EtOH (to afford solution) under reflux. After reflux for 6 h, 10% HCl was added to pH 1, and reflux was continued for 4 h. An extract with Et_2O was extracted with aqueous KOH. Acidification of the alkaline extract, storage at 5 °C, and decantation gave crude bis(phenylthio)acetic acid, $(PhS)_2CHCO_2H$ [which appeared to contain a small amount of impurity, perhaps α-carbomethoxybis(phenylthio)acetic acid], mp 85–89 °C, undepressed by authentic bis(phenylthio)acetic acid (lit.[1a] mp 102–103 °C, mmp 91–94 °C). The NMR and IR spectra contained all the absorptions of authentic bis(phenylthio)acetic acid.

With **diethyl disulfide** and ylide **12** under conditions of expt 5 (Table II), NMR showed the product to have δ 3.60 (OCH_3) consistent with presence of dimethyl bis(ethylthio)malonate (cf. **13**, having δ 3.60; addition of **12** to the product from **12** gave a new peak at δ 3.70 that ruled out presence of **12**); the NMR also was consistent with presence of the moiety SCH_2CH_3 (integration ratio to the peak for OCH_3 at δ 3.60 of 2.6:1, theory 1.7:1). The maximum yield was estimated to be ~15% of **dimethyl bis(ethylthio)malonate** by comparing the ratio of the new peak at δ 3.60 (OCH_3) to all aromatic protons (presumably of Ph_2S produced). Attempted distillation of the product up to 200 °C (0.5 mm) led to decomposition. With **1,2-dithiane** and ylide **12**, under conditions of expt 7 (Table II) except for 6 h instead of 24 h, product showed a multiple signal (δ 3.20–1.50) and a singlet (δ 3.56; addition of **12** produced a new singlet at 3.70) in the ratio of 1.5:1 (theory 1.3:1) for $S(CH_2)_4S/OCH_3$, consistent with presence of dimethyl 1,3-dithiepane-2,2-dicarboxylate. Dry-column chromatography of the product separated an oil that had an NMR spectrum consistent with dimethyl 1,3-dithiepane-2,2-dicarboxylate containing some Ph_2S (maximum yield, 17%); attempted distillation up to 200 °C (0.5 mm) again caused decomposition.

Reactions of Dimethylsulfonium Carbethoxymethylide (14). Ylide **14** was prepared according to Payne from 22 mmol of (carbethoxymethyl)dimethylsulfonium bromide.[17] Removal of $CHCl_3$ gave 3.0 g (92%) of **14** as an oil, $n^{24.5}_{\mathrm{D}}$ 1.5238 (lit.[17] n^{25}_{D} 1.5253–1.5263); the NMR spectrum agreed with reported data.[17] For reaction with **2** neat, illustratively, freshly prepared ylide **14** (0.30 g, 2.0 mmol) was dropped onto **2** (0.44 g, 2.0 mmol) with shaking. An exothermic reaction ensued. The resulting liquid then changed to an oily solid in 2 min. The solid was rubbed well with 10 mL of Et_2O and removed by filtration; yield of dimethylsulfonium α-(phenylthio)carbethoxymethylide (**16**), 0.31 g (60%); mp 118–121 °C. Recrystallizations from $CHCl_3$–hexane gave **16** with a constant melting point of 126–127 °C; IR (KBr) 1610, 1580, 1510, 1420, 1360, 1260, and 1070 cm^{-1}; NMR ($CDCl_3$) δ 7.25 (m, 5 H, aromatic), 4.20 (q, 2 H, OCH_2), 2.55 [s, 6 H, $S(CH_3)_2$], and 1.20 (t, 3 H, CH_2CH_3).

Anal. Calcd for $C_{12}H_{16}O_2S_2$: C, 56.22; H, 6.29; S, 25.01; mol wt, 256. Found: C, 56.38; H, 6.39; S, 25.05; mol wt, 256 (mass spectrum).

Illustratively for reaction of **14** in solvent, 1.48 g (10.0 mmol) of **14** was added to a solution of 2.18 g (10.0 mmol) of **2** in 20 mL of glyme, and the mixture was stirred at ~25 °C for 3 min. Removal of solvent gave an oil, which solidified on being rubbed with ~20 mL of Et_2O. Recrystallization from $CHCl_3$–hexane gave 1.56 g (61%) of **16**, mp 125–127 °C. The Et_2O washings (strong odor of PhSH), shaken with 150 mL of 0.100 N I_2 solution and back titrated with 116 mL of 0.100 N $Na_2S_2O_3$, contained 0.37 g (34%) of PhSH.

For conversion of **16** to the sulfonium picrate **17** (Scheme III), a nearly saturated solution of the (phenylthio) ylide **16** (0.25 g, 1.0 mmol) at 25 °C in EtOH was added to one of picric acid (0.25 g, 10% H_2O, 1.0 mmol). Removal of the precipitate, which formed immediately, gave 0.43 g (91%) of crude picrate **17** (mp 103–107 °C dec, mixture melting point depressed by either reactant), which was recrystallized once from EtOH to give 0.24 g (51%) of yellow dimethyl [α-(phenylthio)carbethoxymethyl]sulfonium picrate (**17**): mp 106.5–108.5 °C dec, unchanged by further recrystallization; IR (KBr) 1725, 1610, 1560, 1360, 1320, and 1260 cm^{-1}; NMR ($CDCl_3$) δ 8.82 [s, 2 H, $C_6H_2(NO_2)_3$], 7.65–7.30 (m, 5 H, aromatic), 7.04 (m, 1 H, methine H), 4.28 (q, 2 H, $-OCH_2$), 3.34 [d, 6 H, $(CH_3)_2S$], and 1.30 (t, 3 H, $-OCH_2CH_3$).

Anal. Calcd for $C_{18}H_{19}N_3O_9S_2$: C, 44.53; H, 3.94; N, 8.66; S, 13.21. Found: C, 44.60; H, 4.16; N, 9.03; S, 13.06.

Reactions of other diaryl disulfides were done neat, essentially as described for **2**, by adding 0.30 g (2.0 mmol) of **14** to 2.0 mmol of bis(*p*-methyl)-, *p*-methoxy-, or *p*-nitrophenyl disulfide with shaking. After 5 min of swirling, the greasy dimethylsulfonium α(arylthio)carbethoxymethylide (**15**) was rubbed with ~10 mL of Et_2O. Solid that resulted was separated and recrystallized from $CHCl_3$–hexane. Each Et_2O washing had a strong odor of an arenethiol and decolorized considerable amounts of aqueous I_2 in KI solution, as in the preparation of **16**. The yields and melting points obtained (with the melting point after recrystallization to constant melting point in parentheses) were as follows for the three dimethylsulfonium α-(arylthio)carbethoxymethylides, $Me_2S^+C^-(SAr)CO_2Et$ (**15**): Ar = p-$CH_3C_6H_4$, 36%, 125–126 °C (125–126 °C); Ar = p-$H_3COC_6H_4$, 31%, 118–119 °C (122–123 °C); Ar = p-$O_2NC_6H_4$, 55%, 128–129 °C (128–129 °C). NMR ($CDCl_3$) ranges for the three compounds were δ 8.30–6.75 (appropriate aromatic pattern, 4 H), 4.20 (q, 2 H, OCH_2), 2.70–2.55 [s, 6 H, $S(CH_3)_2$], and 1.25–1.20 (t, 3 H, CH_2CH_3); also, for Ar = p-$CH_3C_6H_4$, δ 2.30 (s, $C_6H_4CH_3$) and for Ar = p-$H_3COC_6H_4$, δ 3.80 (s, $C_6H_4OCH_3$). Analyses for C, H, and S were satisfactory for all three compounds (±0.4%), except that with Ar = p-$H_3COC_6H_4$, S found was 21.67 (calcd 22.38; this low value for S is attributed to hydration subsequent to satisfactory C, H analyses and NMR, but the analyst's effort to redry led to decomposition). After 3 months at ambient conditions, the melting points of **15** where Ar = C_6H_5, p-$CH_3C_6H_4$, or p-$O_2NC_6H_4$ changed less than a degree, but the melting point where Ar = p-$H_3COC_6H_4$ decreased to ~108–112 °C.

Reactions of Dimethylsulfonium Phenacylide (18). Ylide **18** was prepared according to Trost from 20.0 mmol of dimethylphenacylsulfonium bromide.[18] Recrystallization ($CHCl_3$–hexane) gave 2.5 g (70%) of anhydrous **18** with (sealed tube) mp 77–78 °C (lit. 78–79,[18] 67–68 °C[19]). The NMR (except no CH singlet was evident δ ~4.3) and IR spectra were in agreement with reported data.[18] The ylide **18** rapidly formed a monohydrate on exposure to air (sticky in ~2 min), mp 56–57 °C (lit.[18] 57–59 °C). Analysis of $\mathbf{18} \cdot H_2O$ has not been reported, and since there has been some confusion over the melting points of **18** and $\mathbf{18} \cdot H_2O$,[18,20] both were analyzed. Anal. Calcd for $C_{10}H_{12}OS$ (anhydrous **18**): C, 66.63; H, 6.71. Found: C, 66.70; H, 6.69. Calcd for $C_{10}H_{14}O_2S$ ($\mathbf{18} \cdot H_2O$): C, 60.57; H, 7.12; H_2O, 9.09. Found: C, 60.41; H, 7.00; H_2O, 9.04.

For reaction with disulfide **2**, a solution of **18** (1.80 g, 10.0 mmol) in 5 mL of $CHCl_3$ was poured into one of **2** (2.18 g, 10.0 mmol) in 10 mL of $CHCl_3$ with stirring, and stirring was continued for 5 min; there was a slightly exothermic reaction. Solvent then was removed to give an oily product (strong odor of thiophenol), which upon being rubbed with 10 mL of Et_2O gave a white solid; yield of crude **19**, 1.50 g (52%). Recrystallization from $CHCl_3$–hexane gave 1.40 g (49%) of dimethylsulfonium α-(phenylthio)phenacylide (**19**): mp 137–138 °C (lit.[10a] 135–136 °C); IR (KBr) 1570, 1530, 1490, 1420, and 1330 cm^{-1}; NMR ($CDCl_3$) δ 7.70–7.00 (m, 10 H, aromatic) and 2.60 [s, 6 H, $(CH_3)_2S$], both of which are consistent with reported data.[10a]

Registry No.—**1**, 5367-24-8; **2**, 882-33-7; **5**, 100-68-5; **8**, 3561-67-9; **10**, 4832-52-4; **11**, 6814-64-8; **12**, 24420-61-9; **13**, 61587-07-3; **14**,

7380-81-6; **15** (Ar = p-$CH_3C_6H_4$), 61587-08-4; **15** (Ar = p-$H_3COC_6H_4$), 61587-09-5; **15** (Ar = p-$C_6H_4NO_2$), 61587-10-8; **16,** 61587-11-9; **17,** 61587-13-1; **18,** 5633-34-1; **19,** 24104-87-8; diethyl disulfide, 110-81-6; 1,2-dithiane, 505-20-4; bis(p-methylphenyl) disulfide, 103-19-5; bis(p-methoxyphenyl) disulfide, 5335-87-5; bis(p-nitrophenyl) disulfide, 100-32-3.

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Selenium Stabilized Anions. Selenoxide Syn Elimination and Sila-Pummerer Rearrangement of α-Silyl Selenoxides

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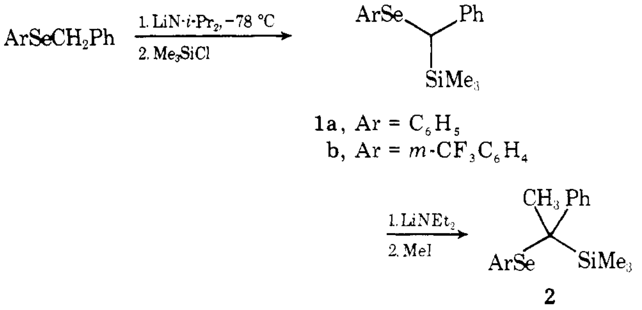
Several α-silyl selenides (**2**, **10**) have been prepared by silylation of α-lithio selenides and alkylation of α-lithio-α-silyl selenides. Oxidation of these selenides to selenoxides results in competitive selenoxide syn elimination to give vinyl silanes (**4**) and sila-Pummerer rearrangement to give vinyl selenides (**8**) and carbonyl compounds. The ratio can be controlled to some extent by control of reaction conditions, but a more pronounced change (favoring syn elimination) can be achieved by making the arylseleno group more electron withdrawing (m-trifluoromethylphenylseleno instead of phenylseleno). These m-trifluoromethylphenyl selenides are also deprotonated substantially more rapidly to give α-lithio selenides than are phenyl selenides. Silaalkene could not be produced by selenoxide syn elimination. The sila-Pummerer rearrangement has been used to prepare α-silyl ketones.

Functionalized organolithium reagents, in which α-heteroatom substituents serve both to facilitate preparation of the anion by acidifying α hydrogens and to mediate subsequent transformations of products derived from the anion, have become important tools for the synthetic organic chemist. As part of our study of selenium stabilized anions,[2] we have developed methods for the generation of several silyl substituted α-lithio selenides, and explored potentially useful synthetic transformations of products derived from them. Of particular interest is the possibility of forming silaalkenes by selenoxide syn elimination, and the competition between selenoxide syn elimination,[3] giving vinyl silanes, and sila-Pummerer rearrangement,[4] giving carbonyl compounds after hydrolysis.

The thermolysis of α-silyl sulfoxides gives only sila-Pummerer products. It was our feeling that the lower activation energy for selenoxide syn elimination[3a] as compared to sulfoxide elimination might enable the elimination pathway to compete favorably with the sila-Pummerer reaction in the selenium system.

We chose selenide **2** for our study. Benzyl phenyl selenide[5] was silylated[2a] to give **1a,** which was in turn deprotonated and methylated to give **2a.** Oxidation of **2a** to the selenoxide **3a** was carried out using m-chloroperbenzoic acid. Decomposition of **3a** occurred with a half-life of ca. 30 min at 0 °C (observed by low-temperature NMR), and gave varying mixtures of products resulting from selenoxide syn elimination (path a) and sila-Plummerer rearrangement (path b), presumably via the ylide **5.**



1a, Ar = C_6H_5
b, Ar = m-$CF_3C_6H_4$

2

The data in Table I show that significant amounts of both path a and path b occur under all conditions tried. The ratio does not respond in a predictable way to changes in reaction conditions such as solvent polarity, temperature, or pH. The partitioning of intermediate **5** to acetophenone (**6** and **7**) and