salt (1.43 g) was obtained by metathesis with NH_4PF_6 and CH_2Cl_2 extraction as a viscous material which crystallized on standing in vacuo; mp 73–75 °C. This product was recrystallized from ethanol and dried in vacuo: mp 78–79 °C; ^1H NMR (acetone-d_6) δ 5.96 (m, 2 H, olefinic protons), 4.12 (m, 2 H, α-CH_2), 3.50 (m, 2 H, α-CH_2), 2.98 (s, 3 H, SCH_3), 2.84 (m, 2 H, probably C_3 H and C_6 H), 2.42 (m, 4 H, C_7 H_2, C_3 H, C_6 H); ^{13}C NMR (acetone-d_6) 137.3 (C_5), 135.1 (C_4), 58.0 (C_2), 49.2 (C_8), 32.4, 31.9, and 31.3 (C_3, C_6, and C_7 interchangeable), 26.6 (SCH_3).

Anal. Calcd for $C_8H_{15}SPF_6$: C, 33.34; H, 5.24. Found: C, 33.41; H, 5.17.

An attempt was made to see whether the sulfonium salt **9** (0.584 g, 0.002 mol) could be reduced back to the trans sulfide **2**. The reaction was performed as described for **4** and monitored by GLC. No trace of **2** appeared in the chromatogram which consisted of a single peak with a retention time identical with that of the acyclic sulfide formed along with **2** in the cycloelimination of incompletely purified **6**. Workup gave a colorless oil (0.24 g) whose ^{13}C NMR confirmed the presence of *trans*-4-hepten-1-yl methyl sulfide, together with a minor (~10%) unidentified isomer.

***trans*-Thiacyclooct-4-ene 1-oxide** was obtained as an oily material by aqueous periodate oxidation[18] of **2** at 0 °C for 5 h; ν_{SO} 1020 cm^{-1}. The ^1H NMR spectrum has two absorption regions: δ 5.69 (m, 2 H, olefinic protons) and an extremely complex band between δ 3.8 and 1.9 (10 H). Irradiation at δ 3.1 resolved the low-field part of an AB quartet (δ 5.78; J = 15.4 Hz), the high-field part of which (at δ 5.64) was resolved by irradiation at δ 2.5. The ^{13}C NMR spectrum was as follows: 135.3 and 131.1 (C_5 and C_4, interchangeable), 62.1 and 61.7 (C_2 and C_8, interchangeable), 32.1 (C_6), 29.8 (C_3), 27.4 (C_7). The ^{13}C spectrum indicated that the material contained ~15% of *cis*-thiacyclooct-4-ene 1-oxide. Clearly some $E \rightarrow Z$ isomerization takes place during oxidation.

***trans*-Thiacyclooct-4-ene 1,1-Dioxide.** Aqueous periodate oxidation[18] of **2** at 25 °C for 5 h gave after workup a low-melting solid, twice crystallized from *n*-hexane; mp 70–78 °C. The ^{13}C NMR spectrum indicated this material contains the title compound together with *cis*-thiacyclooct-4-ene 1-oxide (~25%) and *trans*-thiacyclooct-4-ene 1-oxide (~15%): ^{13}C NMR 135.6 and 129.5 (C_5 and C_4, interchangeable), 65.0 and 60.2 (C_2 and C_8, interchangeable), 31.8 (C_6), 29.4 (C_3), 25.8 (C_7).

Registry No. 1, 64945-38-6; 1 sulfoxide, 72050-53-4; 1 1,1-dioxide, 72075-87-7; 2, 64945-41-1; 2 sulfoxide, 72074-95-4; 2 1,1-dioxide, 72050-54-5; 3 hexafluorophosphate, 72050-56-7; 3 triflate, 72050-57-8; 4, isomer 1, 72050-59-0; 4, isomer 2, 72074-97-6; 5, 72050-61-4; 6, isomer 1, 72050-62-5; 6, isomer 2, 72074-98-7; 7, 72050-63-6; 8, 72050-64-7; 9 hexafluorophosphate, 72075-00-4; 9 triflate, 72120-46-8.

(18) Leonard, N. J.; Johnson, C. R. *J. Org. Chem.* **1962**, *27*, 282.

S-Ethenylsulfoximine Derivatives. Reagents for Ethylenation of Protic Nucleophiles

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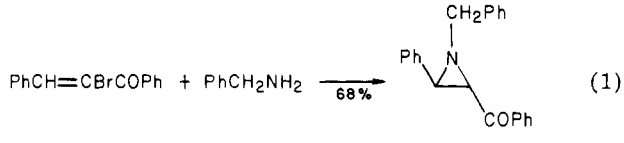
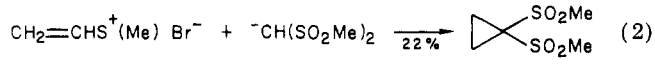
The preparation of *S*-vinyl and *S*-(2-substituted)ethenyl derivatives of sulfoximines is described. Vinyl-, (2-phenylethenyl)-, (2,2-diphenylethenyl)-, (2-methyl-1-propenyl)-, [2-(*p*-tolyl)ethenyl]-, and [2-(2-furanyl)-ethenyl](dimethylamino)phenyloxosulfonium fluoborates were found to undergo an addition–elimination reaction sequence with protic nitrogen and carbon nucleophiles, resulting in ethylenation of the nucleophile and *N,N*-dimethylbenzenesulfinamide. Primary amines gave aziridines, enamines gave cyclopropyl derivatives of iminium salts or pyrrolidinium salts, anions of active methylene compounds gave dihydrofurans and/or cyclopropanes, and anions of nitroalkanes gave cyclic nitronic esters and/or nitrocyclopropanes. In several cases vinyl salts were generated in situ from β-methoxyoxosulfonium salts. Treatment of (-)-(*S*)-(dimethylamino)phenyl-(*trans*-2-phenylethenyl)oxosulfonium fluoborate with methyl cyanoacetate in methanol containing sodium methoxide gave, in 81% yield, (+)-(1*S*,2*R*)-methyl 1-cyano-2-phenylcyclopropanecarboxylate of 25.5% optical purity. The same salt upon treatment with methyl nitroacetate gave, in 95% yield, methyl 4-phenyl-3-isoxazolinecarboxylate 2-oxide with 33% enantiomeric excess. Cyclopropanes were formed upon treatment of *S*-methyl-*S*-(*trans*-2-phenylethenyl)-*N*-(*p*-tolylsulfonyl)sulfoximine with anions of active methylene compounds.

An addition–displacement reaction of nucleophiles of the type ^-NuH or $:NuH_2$ with Michael acceptors such as α-halovinyl ketones has proven to be an interesting approach to aziridines, cyclopropanes, and related compounds[1-3] (e.g., eq 1).[1] In such a reaction the Michael-



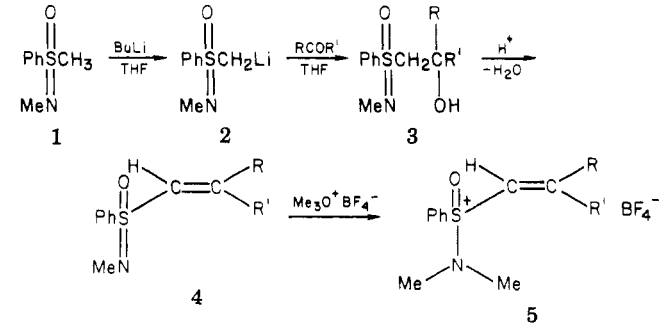
(1)



(2)

activating group and the leaving group are different moieties. Vinylsulfonium salts have been found to undergo similar reactions (e.g., eq 2); in these reactions the sulfonium group plays a dual role—activating group for nucleophilic addition and leaving group.[4]

Scheme I



a, R = R′ = H; b, R′ = H, R = Ph; c, R = R′ = Ph; d, R = R′ = Me; e, R′ = H, R = *p*-tolyl; f, R′ = H, R = 2-furanyl

(1) Cromwell, N. H.; Babson, R. D.; Harris, C. E. *J. Am. Chem. Soc.* **1943**, *65*, 312.

(2) Schmidt, U.; Schroer, R.; Hochrainer, A. *Justus Liebigs Ann. Chem.* **1970**, *733*, 180.

(3) Saegusa, T.; Yonezawa, K.; Murase, I.; Konoike, T.; Tomita, S.; Ito, Y. *J. Org. Chem.* **1973**, *38*, 2319.

0022-3263/80/1945-0264$01.00/0

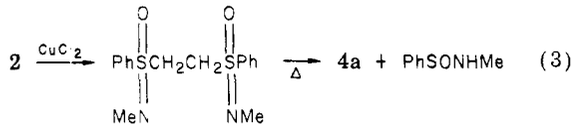
The investigation which we describe here centered on the use of salts derived from vinylsulfoximines as reagents for ethylene transfer to protic nucleophiles.[5] Although these compounds are not as easily prepared as are the simple vinylsulfonium salts, they consistently provide the desired cyclic products in greater yield. A major side reaction with reagents such as dimethylvinylsulfonium bromide appears to be S_N2 methylation of the nucleophile.

Results and Discussion

The preparation of the vinylsulfoximine salts is illustrated in Scheme I. The dehydration step gives erratic results; both retroaddition products and regioisomeric alkenes are observed. Dehydration conditions examined included hot polyphosphoric acid, toluenesulfonic acid in refluxing toluene, warm acetic anhydride, alumina in refluxing benzene, and concentrated sulfuric acid at 0 °C. The last was the method of choice for the production of **4b** (99%), **4c** (96%), and **4d**. Dehydration of **3d** gave, in good yield, a mixture of **4d** and its allyl isomer, *N*-methyl-*S*-(2-methylpropenyl)-*S*-phenylsulfoximine. Methylation of the mixture with trimethyloxonium tetrafluoroborate and brief treatment of the mixed salts with triethylamine in dichloromethane gave exclusively **5d**.

The generation of **4a** by way of the alcohol **3a** is complicated by several factors. Under all conditions tried, the reaction of **2** with formaldehyde or paraformaldehyde gave **3a** contaminated with sizeable quantities of diadduct 2-(*N*-methylphenylsulfonimidoyl)-1,3-propanediol. The mixture was acetylated with acetic anhydride, and the mixed acetates were treated with sodium carbonate suspended in refluxing benzene. Silica gel chromatography gave the desired product **4a** in 21% yield based on *N*,*S*-dimethyl-*S*-phenylsulfoximine.

In an alternate approach to **4a**, **2** was treated with cupric chloride to yield the dimer **6** in 72% yield.[6] The dimer in benzene at reflux quantitatively gave a 1:1 mixture of **4a** and *N*-methylbenzenesulfinamide (eq 3). Unfortu-



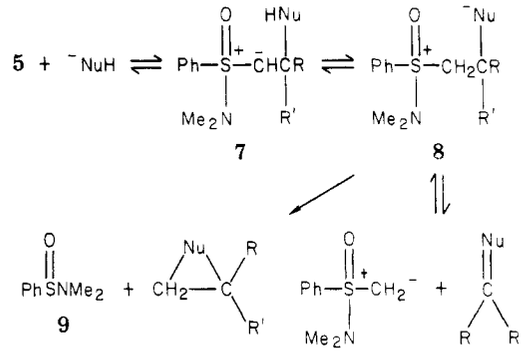
6

nately we were unable to effect separation of **4a** and the sulfinamide by either chromatography or distillation.

Table I summarizes the results of reactions of our vinyl substrates with a variety of protic nucleophiles. The styryl derivative **5b** is of moderate activity and gives products of lower symmetry than the other vinyl derivatives. This latter property, along with the anisotropy generated by the phenyl ring often allowed unambiguous assignment of both ring structure and relative ring stereochemistry from the ^1H NMR spectra. For these reasons and its ease of synthesis, **5b** was studied more extensively than the other vinyl derivatives.

In most cases the ^1H NMR of the reaction mixture after workup showed only the products (as the geometrical isomers indicated) and the byproduct sulfinamide **9**. All reactions were run at or near room temperature. Since yields were generally quite high, little effort was made to maximize them. Reactions were usually complete within a few hours, often within minutes. Somewhat longer reaction times were needed with the more congested substrates **5c** and **5d** and with strongly basic nucleophiles. In the latter case the ylide adducts **7** (Scheme II) are expected to be strongly favored in the equilibrium with betaine **8** which would lead to considerable slowing of the rate of the displacement step.[7]

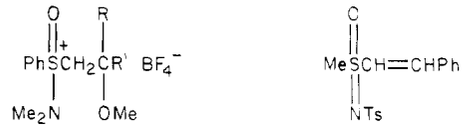
Scheme II



Several reaction pathways (Scheme II) are available to the initial "Michael" adduct **7** of the vinylsulfoximine derivative and the nucleophilic reagent (Table I). A significant product in entry 5 is the result of a "retroaddition" of an ylide to an electrophilic double bond. The addition of an oxosulfonium ylide to a carbonyl of a ketone is known to be a readily reversible process; the observation of the imine product (entry 5) indicates the addition of oxosulfonium ylides to imines is also reversible. It is interesting to note that the more crowded amines tend to give higher yields of aziridines (compare entries 5, 6, and 7). The reaction of aniline with salt **5b** resulted in nucleophilic addition, but the adduct failed to yield aziridine under conditions of heating or extended reaction time. The product shown in entry 3 is probably the result of ring opening of an intermediate aziridine.

In those cases where the nucleophilic moiety ($^-$Nu) of the adduct **8** is ambident, either three- or five-membered rings can result from internal alkylation. In those examples where five-membered ring formation occurs (entries 9, 11, 12, 13, 15, 16, and 17) the products are not readily accessible by other routes. The nitroalkanes present an interesting series; no cyclic nitronic ester is observed with nitromethane (entry 14) whereas cyclic esters are major products when nitroethane and 1-nitropropane are used (entries 15 and 16). The cyclic nitronic ester is the exclusive product with methyl nitroacetate (entry 17).

In an attempt to circumvent the above-noted difficulties in the dehydration step (Scheme I), β-methoxysulfoximine salts were prepared. The β-methoxysulfoximines were prepared by direct methylation of the lithium alkoxides prepared by addition of **2** to the appropriate carbonyl compound. Salts were prepared by N-alkylation with trimethyloxonium fluoborate. It was envisioned that salts **10** would undergo base-promoted elimination of methanol



10a, R = R′ = CH_3
b, R = CH_3; R′ = Ph

11, Ts = *p*-$CH_3C_6H_4SO_2$

in situ upon treatment with nucleophiles under basic conditions, and the resulting vinyl compound would then participate in the normal ethylene transfer sequence.

(4) Becker, G.; Gosselck, J. *Tetrahedron Lett.* **1971**, 4081.
(5) For a preliminary report see: Johnson, C. R.; Lockard, J. P. *Tetrahedron Lett.* **1971**, 4589.
(6) These experiments were performed by Dr. Tsueno Immamoto.
(7) Johnson, C. R.; Schroeck, C. W.; Shanklin, J. R. *J. Am. Chem. Soc.* **1973**, *95*, 7424.

Table I. Reactions of Vinylsulfoximine Derivatives with Protic Nucleophiles

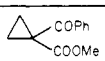
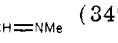
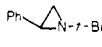
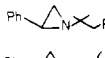
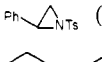
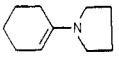
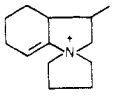
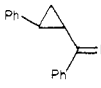
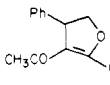
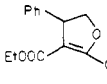
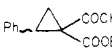
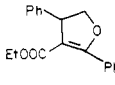
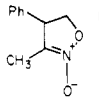
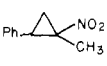
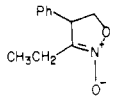
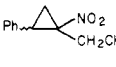
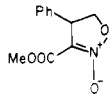
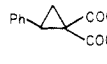
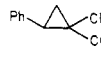
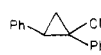
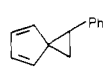
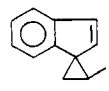
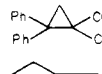
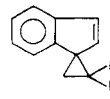
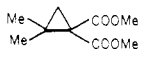
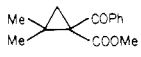
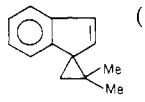
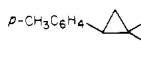
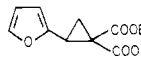
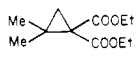
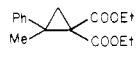
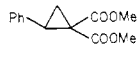
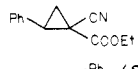
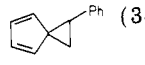
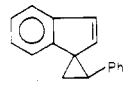
entry no.	sulfoximine derivative	solvent	base	nucleophilic component	product (yield, %)[a]
1	5a	MeOH	NaOMe	$PhCOCH_2COOMe$	 (71%)
2	5a	CH_2Cl_2	Et_3N	$PhCH_2C(CH_3)_2NH_2$	 (32%)
3	5a	CH_2Cl_2		$PhCH_2C(CH_3)_2NH_2$ (excess)	$[PhCH_2C(CH_3)_2NHCH_2]_2$ (78%)
4	5a	THF	BuLi	indene	 (11%)
5	5b	THF		CH_3NH_2	 (34%)  (34%)
6	5b	THF		t-$BuNH_2$	 (86%)
7	5b	THF	Et_3N	$PhCH_2C(CH_3)_2NH_2$	 (82%)
8	5b	THF	BuLi	$TsNH_2$	 (21%)
9	5b	THF			 (91%)
10	5b	THF		$CH_2=C(Ph)NMe_2$	 (79%)
11	5b	MeOH	NaOMe	$CH_3COCH_2COCH_3$	 (86%)
12	5b	MeOH	NaOMe	CH_3COCH_2COOEt	 (65%)  (32%)
13	5b	MeOH	NaOMe	$PhCOCH_2COOEt$	 (76%)  (19%)
14	5b	Me_2SO	$MeSOCH_2Na$	CH_3NO_2	 (77%)
15	5b	Me_2SO	$MeSOCH_2Na$	$CH_3CH_2NO_2$	 (77%)  (16%)
16	5b	Me_2SO	$MeSOCH_2Na$	$CH_3CH_2CH_2NO_2$	 (64%)  (16%)
17	5b[b]	EtOH	Et_3N	$MeOOCCH_2NO_2$	 (95%; 33% ee)
18	5b	MeOH	NaOMe	$CH_2(COOMe)_2$	 (90%)
19	5b[b]	MeOH	NaOMe	$MeOOCCH_2CN$	 (82%; 25% optically pure)
20	5b	EtOH	NaOEt	$EtOOCCH_2CN$	 (95%)
21	5b	THF	BuLi	$PhCH_2CN$	 (59%)
22	5b	THF	BuLi	cyclopentadiene	 (86%)
23	5b	THF	BuLi	indene	 (59%)
24	5c	MeOH	NaOMe	$CH_2(COOMe)_2$	 (82%)
25	5c	THF	BuLi	indene	 (41%)

Table I. (Continued)

entry no.	sulfoximine derivative	solvent	base	nucleophilic component	product (yield, %)[a]
26	5d	MeOH	NaOMe	$CH_2(COOMe)_2$	 (84%)
27	5d	MeOH	NaOMe	$PhCOCH_2COOMe$	 (52%)
28	5d	DME	BuLi	indene	 (63%)
29	5e	EtOH	NaOEt	$CH_2COOEt)_2$	 (79%)
30	5f	EtOH	NaOEt	$CH_2(COOEt)_2$	 (59%)
31	10a	EtOH	NaOEt	$CH_2(COOEt)_2$	 (57%)
32	10b	EtOH	NaOEt	$CH_2(COOEt)_2$	 (44%)
33	11	THF	NaH	$CH_2(COOMe)_2$	 (77%)
34	11	THF	NaH	$EtOOCCH_2CN$	 (31%)
35	11	THF	BuLi	cyclopentadiene	 (34%)
36	4b	THF	BuLi	indene	 (60%)

[a] The products were characterized by IR, ^1H NMR, and mass spectra and/or microanalysis. Characterization data and references to earlier citations of known compounds or model systems are provided as supplementary material. The yields cited are for isolated products. [b] Optically active **5b**.

Entries 32 and 33 (Table I) indicate reasonable success with this approach.

Earlier work from our laboratory had shown that optically active oxosulfonium ylides were capable of generating optically active oxiranes and cyclopropanes with modest to good optical purity.[8] Similarly, asymmetric inductions were observed in the reactions of optically active vinyloxosulfonium salts. Treatment of optically pure **5b** with methyl cyanoacetate (entry 19) gave the known cyanocyclopropane with 26% optical purity, and with methyl nitroacetate (entry 17) an oxazoline oxide was obtained in 33% enantiomeric excess as ascertained by using a chiral shift reagent.

We have noted earlier that α-carbanions of *N*-tosylsulfoximines are useful methylene transfer reagents.[9] It follows that vinyl-*N*-tosylsulfoximines should act as ethylene transfer reagents to dibasic nucleophiles. Compound **11** was prepared from the readily available *S,S*-dimethyl-*N*-(*p*-tolylsulfonyl)sulfoximine by condensation with benzonitrile, reduction of the keto sulfoximine, and dehydration. Compound **11** is less reactive than corresponding salt **5b**. Reactions of **11** are shown in Table I, entries 34, 35, and 36.

In one instance (entry 36) we found that a simple *N*-methyl-*S*-vinylsulfoximine was effective in a cyclopropanation reaction. This is the only case that we have observed in which an unactivated sulfinamide anion ($PhSONMe^-$) has acted as a leaving group.

Experimental Section

General Methods. (*N*-Methyl-*S*-phenylsulfonimidoyl)methyllithium (**2**) was generated from *N,S*-dimethyl-*S*-phenylsulfoximine (**1**)[8] in tetrahydrofuran (THF) at 0 °C by titrating to the triphenylmethane red end point with butyllithium in hexane.

Unless otherwise specified, the workup procedure consisted of pouring the reaction mixture into aqueous sodium hydrogen carbonate, transferring this mixture to a separatory funnel followed by a water and an organic solvent wash of both previous vessels, and extracting it one to four times with an organic solvent. The combined organic phases were dried over sodium sulfate and stripped of solvent near room temperature on a rotary evaporator.

***N*-Methyl-*S*-phenyl-*S*-vinylsulfoximine (4a).** A solution of **2** (0.1 mol) in 250 mL of THF was cooled to −78 °C, and dry paraformaldehyde (4.5 g, 0.16 mol) was added all at once; the suspension was allowed to warm slowly to 0 °C. After 2 h at 0 °C and 0.5 h at room temperature the suspension was poured into 500 mL of ice-water containing concentrated hydrochloric acid (13 mL). The mixture, made slightly basic with solid sodium carbonate, was extracted with dichloromethane. After the usual workup the crude product was treated with excess acetic anhydride in chloroform to give the acetate of **3a**. Refluxing the crude acetate for 3 h in benzene with excess anhydrous sodium carbonate followed by silica gel chromatography with pentane/ether gave **4a** (3.8 g, 21% based on **1**) as an oil.

(Dimethylamino)phenylvinyloxosulfonium Fluoborate (5a). To **4a** in dichloromethane at 0 °C was added all at once 1.05 equiv of trimethyloxonium fluoborate. After 0.5 h at 0 °C and 1 h at room temperature a small amount of water was added; the organic layer was dried and stripped of solvent to give **5a** as a light yellow oil. Stirring the oil under dry ether produced an amorphous solid which resisted crystallization. The crude salt, which had IR and ^1H NMR spectra consistent with the assigned structure, performed satisfactorily as an ethylene transfer reagent in subsequent experiments.

***N*-Methyl-*S*-phenyl-*S*-(*trans*-2-phenylethenyl)sulfoximine (4b).** Compound **3b** (13 g) as a mixture of diastereomers was added slowly with vigorous stirring to 130 mL of concentrated sulfuric acid at 0 °C. After 1 h, the solution was poured into 800 mL of ice–water and, with cooling, was neutralized with concentrated ammonium hydroxide. The solution was filtered

(8) Johnson, C. R.; Schroeck, C. W. *J. Am. Chem. Soc.* **1973**, *95*, 7418.
(9) Johnson, C. R.; Kirchhoff, R. A.; Reischer, R. J.; Katekar, G. F. *J. Am. Chem. Soc.* **1973**, *95*, 4287.

through glass wool to remove the tars which had oiled out. Additional treatment with ammonium hydroxide yielded a tan oil which was extracted into dichloromethane. The extract was dried (Na_2SO_4) and stripped of solvent to give 12 g (99%) of **4b** as an oil. When allowed to stand, the oil solidified and upon recrystallization from hexane gave **4b**, mp 69–71 °C.

(Dimethylamino)phenyl(*trans*-2-phenylethenyl)oxosulfonium Fluoborate (5b). In the same manner as for **5a** above, **4b** was alkylated with trimethyloxonium fluoborate to give **5b** (86% recrystallized from dichloromethane/ether), mp 130–131.5 °C. A sample of this material made from optically active (*S*)-**1** had the following: mp 113–115 °C; $[\alpha]^{25}_D$ −5.7° (*c* 1.05, acetone).

2-(*N*-Methyl-*S*-phenylsulfonimidoyl)-1,1-diphenylethanol (3c). To a THF solution of the anion **2** (14.8 mmol) at 0 °C was added benzophenone (2.8 g, 15.5 mmol). After 5 min at 0 °C and 0.5 h at room temperature, workup gave a tan solid. Recrystallization from hexane–acetone gave **3c** (4.39 g, 85%), mp 141–143 °C.

***S*-(2,2-Diphenylethenyl)-*N*-methyl-*S*-phenylsulfoximine (4c).** In a manner similar to that for **4b** above, **3c** was treated with cold sulfuric acid for 5 min to give **4c** as a white crystalline solid (96% yield), mp 113.5–114.4 °C (from chloroform/pentane).

(Dimethylamino)(2,2-diphenylethenyl)phenyloxosulfonium Fluoborate (5c). Alkylation of **4c** with trimethyloxonium fluoborate gave **5c**, mp 140–141 °C (from ethanol).

(Dimethylamino)(2-methyl-1-propenyl)phenyloxosulfonium Fluoborate (5d). To a solution of **2** (17.8 mmol) generated in THF at −78 °C was added acetone (1.1 g, 18.9 mmol) all at once. The reaction mixture was allowed to come to room temperature over 4 h and, after standard workup, gave **3d** as a colorless oil in almost quantitative yield. Dehydration of **3d** as described above for **3b** took 2 h at 0 °C and gave, in good yield, a mixture of **4d** and the allyl isomer. The mixture (4.1 g, 1.96 mmol) was alkylated with trimethyloxonium fluoborate. Recrystallization of a sample of the crude product from methanol/ether gave the salt of the allyl isomer, (dimethylamino)(2-methyl-2-propenyl)phenyloxosulfonium fluoborate, mp 104–107 °C. Brief treatment of the salt mixture with triethylamine in dichloromethane was found to convert the mixture entirely to **5d**, mp 112–114 °C.

(Dimethylamino)phenyl(2-*p*-tolylethenyl)oxosulfonium Fluoborate (5e). To the anion **2** (10 mmol) in THF at 0 °C was added *p*-tolualdehyde (1.2 g, 10 mmol). After 1 h the mixture was worked up, and the resulting oil, after being cooled to 0 °C, was treated with 10 mL of concentrated sulfuric acid. The solution was poured onto ice, neutralized with concentrated ammonium hydroxide, and extracted with dichloromethane. The solution was dried and concentrated. The crude product was recrystallized from ether to give **4e** (1.4 g) as white solid, mp 119–120 °C. An additional 0.4 g of **4e** (total yield 63%) was obtained by chromatography of the mother liquor residue on silica gel. Alkylation of **4e** with trimethyloxonium fluoborate gave **5e**, mp 174–175 °C (methanol/ether).

(Dimethylamino)[2-(2-furanyl)ethenyl]phenyloxosulfonium Fluoborate (5f) (Cis/Trans Mixture). Salt **5f**, mp 98–108 °C, was prepared in the same manner as **5e** described above.

***S*-(2-Methoxy-2-methylpropyl)-*N*-methyl-*S*-phenylsulfoximine.** Acetone (0.58 g, 10 mmol) was added to anion **2** (10 mmol) in THF at −23 °C. After 10 min, hexamethylphosphoric triamide (20 mL) and methyl iodide (1 mL) were added. The mixture was stirred for 1 h at −23 °C, allowed to warm to 0 °C, and stirred for an additional 1 h. The reaction mixture was poured into 40 mL of aqueous saturated ammonium chloride solution and extracted with ether. The ether extract was washed with several small portions of water, dried, and evaporated. The residue was chromatographed on silica gel with ether as eluent to yield the desired product as a white solid (1.05 g, 49%), mp 55–56 °C.

(Dimethylamino)(2-methoxy-2-methylpropyl)phenyloxosulfonium fluoborate (10a) was prepared by alkylation of the above sulfoximine with trimethyloxonium fluoborate. The crude product was recrystallized from methanol/ether to yield a white solid, mp 140–141.5 °C.

(Dimethylamino)(2-methoxy-2-phenylpropyl)phenyloxosulfonium Fluoborate (10b). Acetophenone (1.2 g, 10 mmol) was added to anion **2** (10 mmol) in THF at 0 °C under a nitrogen atmosphere. After 10 min hexamethylphosphoric triamide (20 mL) was added. Ten minutes later methyl iodide (1 mL) was added. The mixture was stirred for several hours and then poured into 40 mL of aqueous saturated ammonium chloride. The mixture was extracted with ether, and the ether layer was washed with 5 mL of 1 M aqueous sodium sulfite and several small portions of water. Drying ($MgSO_4$) and removal of the ether left a solid residue which ^1H NMR revealed to be a 3:1 mixture of diastereomers. Recrystallizaton of the crude product from ether/pentane yielded the major diastereomer (0.77 g), mp 111–112.5 °C. (An additional 0.7 g of a mixture of diastereomers was obtained by chromatography of the mother liquor on silica gel with ether as the eluent.) Alkylation of the major diastereomer with trimethyloxonium fluoborate gave **10b**, mp 114–115 °C (from methanol/ether).

1-Phenyl-2-[*N*-(*p*-tolylsulfonyl)methylsulfonimidoyl]-1-ethanone. *S,S*-Dimethyl-*N*-(*p*-tolylsulfonyl)sulfoximine (15 g, 61 mmol) in 150 mL of dimethyl sulfoxide was treated at room temperature with butyllithium (73 mmol) followed by addition of benzonitrile (7.5 g, 73 mmol). After being stirred overnight, the mixture was poured into 500 mL of ice–water, and the gummy precipitate was filtered onto Celite. The residue was washed with chloroform, and the organic phase was washed twice with water, dried (Na_2SO_4), and stripped of solvent. The resulting brown solid was dissolved in 125 mL of 4 M HCl, heated on the steam bath for 0.5 h, and poured into a large amount of water. Extraction with chloroform, drying (Na_2SO_4), stripping of solvent, and recrystallization from methanol gave the keto sulfoximine (13 g, 61%) as white crystals, mp 83–84 °C.

***S*-Methyl-*S*-(*trans*-2-phenylethenyl)-*N*-(*p*-tolylsulfonyl)sulfoximine (11).** The keto sulfoximine from above (2 g, 5.7 mmol) was reacted with excess sodium borohydride in ethanol at room temperature for 0.5 h. Dilute HCl was added until vigorous bubbling stopped, and the solution was stripped of most of the solvents. The residue, dissolved in chloroform, was washed with water, dried (Na_2SO_4), and stripped of solvent to give the adduct alcohol which was dehydrated by refluxing overnight in benzene with toluenesulfonic acid using a Dean–Stark trap. The benzene solution was washed twice with saturated aqueous sodium hydrogen carbonate and the aqueous layer back-washed with chloroform. The combined organic phases were dried (Na_2SO_4) and stripped of solvent, giving a tan solid which on recrystallization from benzene/hexane gave **11** (1.5 g, 78%) as white crystals, mp 150–152.5 °C.

Methyl 1-Benzoylcyclopropanecarboxylate (Table I, Entry 1). To methyl benzoylacetate (222 mg, 1.25 mmol) in 7 mL of methanol with 1 equiv of sodium methoxide was added, at 0 °C, **5a** (354 mg, 1.25 mmol). After the mixture was stirred overnight at room temperature, aqueous sodium hydrogen carbonate/dichloromethane workup and chromatography on silica gel with dichloromethane/ether gave 185 mg (71%) of the cyclopropane. Recrystallization of the product from hexanes gave white crystals, mp 53.5–55 °C.

1-(1,1-Dimethyl-2-phenylethyl)aziridine (Table I, Entry 2). To a solution of 2-methyl-1-phenyl-2-propanamine (186 mg, 1.25 mmol) and 5 equiv of triethylamine in 7 mL of dichloromethane at 0 °C was added **5a** (354 mg, 1.25 mmol). After 2 h at 0 °C and 2 h at room temperature, the salts were precipitated with ether and the soluble products chromatographed on a preparative silica gel plate (20 cm × 20 cm × 2 mm, EM Reagents) with ether/methanol to give 70 mg (32%) of the aziridine. Refluxing a sample of the aziridine in methanol in the presence of acid gave the ring-opened amino ether *N*-(2-methoxyethyl)-2-methyl-1-phenyl-2-propanamine, which was analyzed as the hydrochloride.

***N,N'*-Bis(1,1-dimethyl-2-phenylethyl)-1,2-ethanediamine (Table I, Entry 3).** To **5a** (354 mg, 1.25 mmol) in 2.5 mL of dichloromethane and 1 mL of ether at room temperature was added 2-methyl-2-phenyl-2-propanamine (558 mg, 3.75 mmol) in 1 mL of dichloromethane and 0.5 mL of ether. After the mixture was stirred overnight, workup and chromatography on a preparative TLC plate (20 cm × 20 cm × 2 mm, EM Reagents) with ether/methanol gave 316 mg (78%) of the diamine.

Spiro[cyclopropane-1,1'-indene] (Table I, Entry 4). To the anion generated from indene (145 mg, 1.25 mmol) in 7 mL of THF with 1 equiv of butyllithium was added, at 0 °C, **5a** (354

mg, 1.25 mmol). After the mixture was stirred at 0 °C for 1 h and at room temperature for 24 h, saturated sodium hydrogen carbonate/pentane workup and chromatography on a preparative silica gel plate (20 cm × 20 cm × 2 mm, EM Reagents) with 3% benzene in pentane gave 52 mg (36%) of indene and 20 mg (11%) of the spiro compound.

1-Methyl-2-phenylaziridine and *N*-Benzylidenemethanamine (Table I, Entry 5). To a suspension of **5b** (500 mg, 1.39 mmol) in THF at −78 °C was added excess methanamine. After being warmed and stirred for 2 h at room temperature, the solution was added to 100 mL of ether and 25 mL of 5% sodium hydroxide. The organic layer was washed with water which was back-extracted with 25 mL of ether. The combined ether phases were dried (Na_2CO_3), stripped of solvent, and chromatographed on Florisil with pentane/ether to give 62 mg (34%) of the aziridine. The IR and ^1H NMR of the reaction mixtures contained resonances assignable to *N*-benzylidenemethanamine with the same integrated area as the aziridine.

1-*tert*-Butyl-2-phenylaziridine (Table I, Entry 6). To a suspension of **5b** (500 mg, 1.39 mmol) in 10 mL of THF at 0 °C was added *tert*-butylamine (303 mg, 4.15 mmol). The resulting solution was stirred overnight at room temperature. Workup followed by chromatography on Florisil with pentane/ether gave 208 mg (86%) of the aziridine.

1-(1,1-Dimethyl-2-phenylethyl)-2-phenylaziridine (Table I, Entry 7). To **5b** (500 mg, 1.39 mmol) in 5 mL of dichloromethane at 0 °C was added 2-methyl-2-phenyl-2-propanamine (207 mg, 1.39 mmol) in 2 mL of dichloromethane followed by an excess of triethylamine. The solution was brought to room temperature for 4 h. Workup followed by chromatography on Florisil with pentane/ether gave 285 mg (82%) of the aziridine.

1-(*p*-Tolylsulfonyl)-2-phenylaziridine (Table I, Entry 8). To the anion generated from *p*-toluenesulfonamide (238 mg, 1.39 mmol) in 10 mL of THF with butyllithium was added, at 0 °C, **5b** (500 mg, 1.39 mmol). After the mixture was stirred 3 h at 0 °C and overnight at room temperature, workup and quick chromatography on Florisil with pentane/ether gave 80 mg (21%) of aziridine as an unstable solid, identified only by IR and ^1H NMR.

2,3,3a,4,5,6-Hexahydro-3-phenylspiro[1*H*-indole-1,1′-pyrrolidinium] Fluoborate (Table I, Entry 9). Compound **5b** (500 mg, 1.39 mmol) was added all at once to a solution of the pyrrolidine enamine of cyclohexanone (220 mg, 1.46 mmol) in 25 mL of THF at room temperature. Solution was achieved in 10 min, and a precipitate began to form after 20 min. After the mixture was stirred overnight, the phases were separated by decantation, and the liquid phase gave 225 mg (98%) of *N,N*-dimethylbenzenesulfinamide (**9**). The solid phase (474 mg, 91%), which was inert to extensive heating with aqueous methanolic HCl, was characterized as the spiro bicyclic ammonium salt, 157.5–159 °C.

1-Phenyl-1-(2-phenylcyclopropyl)-*N,N*-dimethylmethaniminium Fluoborate (Table I, Entry 10). Compound **5b** (500 mg, 1.39 mmol) was added all at once to *N,N*-dimethyl-1-phenylethenamine in 10 mL of THF at 0 °C. After 0.5 h at 0 °C and 0.75 h at room temperature the solution became clear. After being stirred at room temperature overnight, the solution was stripped of solvent, giving, after recrystallization from ether, a very hygroscopic solid. Two further precipitations from the same solvent gave 370 mg (79%) of the iminium salt. A sample of this compound gave an exothermic reaction with aqueous methanolic HCl to yield the known phenyl 2-phenylcyclopropyl ketone.[10]

1-(4,5-Dihydro-4-phenyl-3-furanyl)-1-ethanone (Table I, Entry 11). To the anion generated from 2,4-butanedione (138 mg, 1.38 mmol) with 1 equiv of sodium methoxide in 6 mL of methanol was added, at 0 °C, **5b** (500 mg, 1.39 mmol). After the mixture was stirred at room temperature for 5 h, chromatography on silica gel with pentane/ether gave 240 mg (86%) of the known dihydrofuran.

Ethyl 4,5-Dihydro-2-methyl-4-phenyl-3-furancarboxylate and Ethyl 1-Acetyl-2-phenylcyclopropanecarboxylate (Table I, Entry 12). Reaction of **5b** with ethyl acetoacetate overnight in the same manner as that for acetylacetone above gave, after chromatography, a 97% yield of a mixture of the dihydrofuran and cyclopropane in approximately a 2:1 ratio.

Ethyl 4,5-Dihydro-2,4-diphenyl-3-furancarboxylate and Ethyl 1-Benzoyl-2-phenylcyclopropanecarboxylate (Table I, Entry 13). Reaction of **5b** with the anion of ethyl benzoylacetate overnight in the same manner as that for acetylacetone above gave, after chromatography, a 95% yield of a mixture of the dihydrofuran and the cyclopropane in approximately a 4:1 ratio.

***trans*-1-Nitro-2-phenylcyclopropane (Table I, Entry 14).** To nitromethane (85 mg, 1.39 mmol) and 1 equiv of [(methylsulfinyl)methyl]sodium in 5 mL of dimethyl sulfoxide at 25 °C was added **5b** (500 mg, 1.39 mmol). After the mixture was stirred overnight, aqueous bicarbonate/dichloromethane workup and chromatography on silica gel with pentane/ether gave 175 mg (77%) of the cyclopropane.

3-Methyl-4-phenylisoxazoline 2-Oxide and 1-Methyl-1-nitro-2-phenylcyclopropane (Table I, Entry 15). To nitroethane (220 mg, 2.93 mmol) and 1 equiv of [(methylsulfinyl)methyl]sodium in 10 mL of dimethyl sulfoxide at room temperature was added **5b** (1.0 g, 2.78 mol). Stirring overnight, aqueous sodium hydrogen carbonate/dichloromethane workup, and chromatography on silica gel with pentane/ether gave 80 mg (16%) of the cyclopropane with at least a 9:1 ratio of trans to cis methyl to phenyl stereochemistry, followed by 380 mg (77%) of the isoxazoline oxide as an unstable white solid. A sample of the isoxazoline oxide rearranged very cleanly with 1% aqueous sodium hydroxide in 1 h at 50 °C to give the expected 3-methyl-4-phenylisoxazole.[11]

3-Ethyl-4-phenylisoxazoline 2-Oxide and 1-Ethyl-1-nitro-2-phenylcyclopropane (Table I, Entry 16). Reaction of **5b** and 1-nitropropane as in entry 15 above gave the cyclopropane (16%), mp 51–52 °C, and the isoxazoline oxide (64%). A sample of the isoxazoline oxide rearranged cleanly to 3-ethyl-4-phenylisoxazole upon being heated 1 h at 50 °C with 1% aqueous sodium hydroxide.

3-(Methoxycarbonyl)-4-phenylisoxazoline 2-Oxide (Table I, Entry 17). To a solution of methyl nitroacetate (165 mg, 1.39 mmol) and 1 equiv of triethylamine in 5 mL of ethanol at room temperature was added **5b** (500 mg, 1.30 mmol). After 3.5 h at room temperature, the mixture was stripped of most of the solvent, and the salts were precipitated and washed twice with ether. The ether solution was washed with dilute aqueous sodium hydroxide. The water layer was extracted once with dichloromethane, and the combined organic phases were dried (Na_2SO_4) and stripped of solvent, giving a colorless oil. ^1H NMR of this oil showed only the isoxazoline oxide and sulfinamide **9**. Chromatography on silica gel with pentane/dichloromethane gave the isoxazoline oxide (265 mg, 86%) as a white solid, mp 82.5–84.5 °C (from ether/pentane).

Reaction with optically pure **5b** by a similar procedure for 2 h at −20 °C and then for 2 h at 0 °C, followed by slow warming over 2 h to room temperature, gave 95% of the isoxazoline oxide $[\alpha]^{25}_D$ +21.26° (*c* 1.04, EtOAc). The methyl singlet in the ^1H NMR was split into two almost completely separated singlets by the optically active shift reagent $Eu(TFC)_3$ in $CDCl_3$. Integration in both directions gave an average of a 2:1 ratio of enantiomers or 33% ee.

Dimethyl 2-Phenyl-1,1-cyclopropanedicarboxylate (Table I, Entry 18). To dimethyl malonate (182 mg, 1.38 mmol) and 1 equiv of sodium methoxide in 25 mL of methanol was added, at 0 °C, **5b** (500 mg, 1.39 mmol). After 5 h at room temperature, the solution was concentrated and partitioned between water and dichloromethane, and the organic phase was dried (Na_2SO_4) and stripped of solvent. Chromatography on silica gel with pentane/ether gave 293 mg (90%) of the cyclopropane, mp 40.5–45 °C (from hexane), and 283 mg (100%) of byproduct *N,N*-dimethylphenylsulfinamide (**9**). A sample of the cyclopropane was saponified to give 2-phenyl-1,1-cyclopropanedicarboxylic acid: softens at 93 °C, melts at 99–102 °C.[12]

(1*S*,2*R*)-Methyl 1-Cyano-2-phenylcyclopropanecarboxylate (Table I, Entry 19). To methyl cyanoacetate (59

(10) Johnson, C. R.; Haake, M.; Schroeck, C. W. *J. Am. Chem. Soc.* **1970**, *92*, 6594.

(11) Shechter, H.; Conrad, F. *J. Am. Chem. Soc.* **1954**, *76*, 2716.

(12) Swoboda, G.; Eitel, A.; Swoboda, J.; Wessely, F. *Monatsh. Chem.* **1964**, *95*, 1355.

mg, 0.60 mmol) and 1 equiv of sodium methoxide in methanol was added, at 0 °C, (−)-(*S*)-**5b** (213 mg, 0.59 mmol): $[\alpha]^{25}_{D}$ −5.7° (*c* 1.05, acetone); mp 113–115 °C. After 4 h at 0 °C and 4 h at room temperature, 5 mL of aqueous sodium hydrogen carbonate was added, and the mixture was extracted with dichloromethane and stripped of most of the solvents. The crude product was chromatographed on silica gel with pentane/ether to give 97 mg (82%) of the cyclopropane, $[\alpha]^{25}_{546}$ 63.9° (*c* 0.6, ethyl acetate) (lit.[13] $[\alpha]^{25}_{546}$ 251°). The IR and ^{1}H NMR spectra are the same as those published.[13]

(1*S*,2*R*)-Ethyl 1-Cyano-2-phenylcyclopropanecarboxylate (Table I, Entry 20). Reaction of **5b** with the anion of ethyl cyanoacetate in the same manner as that described below (entry 21) with optically active **5b** and methyl cyanoacetate gave, after chromatography, 95% of the cyclopropane.

(1*R*,2*R*)-1,2-Diphenyl-1-cyclopropanecarbonitrile (Table I, Entry 21). To phenylacetonitrile (165 mg, 1.41 mmol) and butyllithium (triphenylmethane indicator) in 10 mL of THF was added, at room temperature, **5b** (500 mg, 1.39 mmol). After the mixture was stirred at room temperature for 5 h, aqueous sodium hydrogen carbonate/dichloromethane chloride workup and chromatography on silica gel with pentane/ether gave 180 mg (59%) of the cyclopropane.

1-Phenylspiro[2.4]hepta-4,6-diene (Table I, Entry 22). To the anion generated from cyclopentadiene (91 mg, 1.38 mmol) in 10 mL of THF with butyllithium (triphenylmethane indicator) was added, at 0 °C, **5b** (500 mg, 1.39 mmol). After 5 h at room temperature, aqueous sodium hydrogen carbonate/dichloromethane workup and chromatography on silica gel with pentane gave 200 mg (86%) of the spiroheptadiene.

***trans*-2-Phenylspiro[cyclopropane-1,1′-indene] (Table I, Entries 23 and 36).** Reaction of **5b** with the anion of indene in a manner similar to that of cyclopentadiene above gave 59% of the spiro compound, mp 80.5–82.5 °C (from hexane).

By a similar procedure, reaction of the anion with sulfoximine **4b** gave a 60% yield of the same cyclopropane.

Dimethyl 2,2-Diphenyl-1,1-cyclopropanedicarboxylate (Table I, Entry 24). To dimethyl malonate (140 mg, 1.06 mmol) in 7 mL of methanol and 1 equiv of sodium methoxide was added, at room temperature, **5c** (435 mg, 1 mmol). After the mixture was stirred at 33 °C for 1 day and at 40 °C for 3 days, 1 mL of aqueous sodium hydrogen carbonate was added, and most of the solvent was stripped off. The resulting mixture was partitioned between water and dichloromethane. The organic phase, dried (Na_2SO_4) and stripped of solvent, gave, after chromatography on silica gel with pentane/ether, 247 mg (82%) of the cyclopropane as a white solid: softens at 64 °C, melts at 67–69 °C (from hexane).

2,2-Diphenylspiro[cyclopropane-1,1′-[1*H*]indene] (Table I, Entry 25). To indene (81 mg, 0.7 mmol) in 10 mL of THF and 1 equiv of butyllithium was added, at 0 °C, **5c** (305 mg, 0.7 mmol). After the mixture was stirred 5 days at room temperature, aqueous sodium hydrogen carbonate/dichloromethane workup and chromatography on a preparative silica gel plate (20 cm × 20 cm × 2 mm, EM Reagents) with 3% ether/pentane gave 84 mg (41%) of the spiro compound, mp 96–98.5 °C (from ethanol).

Dimethyl 2,2-Dimethyl-1,1-cyclopropanedicarboxylate (Table I, Entry 26). To dimethyl malonate (198 mg, 1.5 mmol) in 6.5 mL of methanol and 1 equiv of sodium methoxide was added, at 0 °C, **5d** (467 mg, 1.5 mmol). After being stirred at 0 °C for 10 min and at room temperature for 1 h, the mixture was worked up and chromatographed on silica gel with pentane/ether to give 235 mg (84%) of the cyclopropane as a white solid, mp 49–52 °C.

Methyl 1-Benzoyl-2,2-dimethylcyclopropanecarboxylate (Table I, Entry 27). Reaction of **5d** with methyl benzoylacetate in a manner similar to that for dimethyl malonate above gave, after 3 h at room temperature and 1 h at 30 °C, a 52% yield of the cyclopropane along with 46% of recovered methyl benzoylacetate.

2,2-Dimethylspiro[cyclopropane-1,1′-[1*H*]indene] (Table I, Entry 28). To the anion generated from indene (174 mg, 1.5 mmol) in 10 mL of 1,2-dimethoxyethane with 1 equiv of butyllithium was added, at 0 °C. **5d** (467 mg, 1.5 mmol). After being stirred at room temperature for 4 days, the reaction mixture was worked up and chromatographed on a preparative silica gel plate (20 cm × 20 cm × 2 mm, EM Reagents) with pentane to give 160 mg (63%) of the spiro compound.

Diethyl 2-*p*-Tolyl-1,1-cyclopropanedicarboxylate (Table I, Entry 29). To diethyl malonate (0.102 g, 0.64 mmol) in 5 mL of ethanol containing 1 equiv of sodium at 0 °C was added **5e** (0.239 g, 0.64 mmol). After 24 h the reaction mixture was worked up and chromatographed on silica gel to yield the product (0.104 g, 59%) as an oil.

Diethyl 2-Furanyl-1,1-cyclopropanedicarboxylate (Table I, Entry 30). To diethyl malonate (0.16 g, 1 mmol) in 5 mL of ethanol containing 1 equiv of sodium at 0 °C was added **5f** (0.35 g, 1 mmol) in 10 mL of ethanol. After 3.5 h the reaction mixture was worked up and chromatographed on silica gel with ether to yield the cyclopropane (0.198 g, 79%) as an oil.

Diethyl 2,2-Dimethyl-1,1-cyclopropanedicarboxylate (Table I, Entry 31). To diethyl malonate (0.16 g, 1 mmol) in 5 mL of ethanol containing 2 equiv of sodium at 0 °C was added **10a** (0.34 g, 1 mmol) in 12 mL of ethanol. The mixture was warmed to room temperature and stirred for 6 h. Workup and chromatography on silica gel with ether afforded the cyclopropane (0.12 g, 57%) as an oil.

Diethyl 2-Methyl-2-phenyl-1,1-cyclopropanedicarboxylate (Table I, Entry 32). The procedure was similar to that above (entry 31) but used salt **10b**. The reaction was stirred for 8.5 h. The product was obtained as an oil (44%).

Dimethyl 2-Phenyl-1,1-cyclopropanedicarboxylate (Table I, Entry 33). To dimethyl malonate (132 mg, 1 mmol) in THF with 1 equiv of sodium hydride was added, at room temperature, 11 (335 mg, 1 mmol). The solution was heated to 60 °C for 5 h and cooled. Aqueous sodium hydrogen carbonate was added, and the mixture was stripped of most of the solvent. The resulting mixture was partitioned between water and pentane, and the organic phase was dried (Na_2SO_4) and stripped of solvent, giving cyclopropane contaminated only with a small amount of mineral oil. Chromatography on silica gel with pentane/ether gave 180 mg (77%) of the cyclopropane identical with that described in entry 18.

(1*R,2*R**)-Methyl 1-Cyano-2-phenylcyclopropanecarboxylate (Table I, Entry 34).** Compound **11** was treated with ethyl cyanoacetate in the same manner as that for dimethyl malonate (above). After 3 h at 60 °C, workup, and chromatography, 60 mg (31%) of cyclopropane was obtained, identical with that from **5b**. This sample was saponified and the product recrystallized from pentane to give the cyano acid, mp 137–138 °C (lit.[13] mp 137–138 °C).

1-Phenylspiro[2.4]hepta-4,6-diene (Table I, Entry 35). Compound **11** was reacted with the anion of cyclopentadiene in the same manner as was **5b** (entry 22). After 5 h at room temperature, workup and chromatography gave 80 mg (34%) of the spiro compound identical with that produced from **5b**.

Acknowledgment. This work was supported by a grant from the National Science Foundation.

Registry No. **1**, 30004-67-2; (*S*)-**1**, 33993-53-2; **2**, 42764-56-7; **3a**, 72186-97-1; **3a** acetate, 72186-98-2; **3b**, isomer A, 72174-41-5; **3b**, isomer B, 33903-51-4; **3c**, 72174-42-6; **3d**, 72174-43-7; **4a**, 72174-44-8; **4b**, 72174-45-9; **4c**, 72174-46-0; **4d**, 72174-47-1; **4d**, allyl isomer, 72174-48-2; **4e**, 72174-49-3; *cis*-**4f**, 72174-50-6; *trans*-**4f**, 72174-51-7; **5a**, 72174-53-9; **5b**, 36378-98-0; **5b**, optically active, 36471-09-7; **5c**, 72174-55-1; **5d**, 72174-57-3; **5e**, 72174-59-5; *cis*-**5f**, 72174-61-9; *trans*-**5f**, 72174-63-1; **9**, 5539-54-8; **10a**, 72174-65-3; **10b**, 72174-67-5; **11**, 72174-68-6; formaldehyde, 50-00-0; trimethyloxonium fluoborate, 420-37-1; benzophenone, 119-61-9; acetone, 67-64-1; (dimethylamino)(2-methyl-2-propenyl)phenyloxosulfonium fluoborate, 72174-70-0; *p*-tolualdehyde, 104-87-0; 2-furaldehyde, 98-01-1; *S*-(2-methoxy-2-methylpropyl)-*N*-methyl-*S*-phenylsulfoximine, 72174-71-1; acetophenone, 98-86-2; *S*-(2-methoxy-2-phenylpropyl)-*N*-methyl-*S*-phenylsulfoximine, isomer A, 72174-72-2; *S*-(2-methoxy-2-phenylpropyl)-*N*-methyl-*S*-phenylsulfoximine, isomer B, 72174-73-3; 1-phenyl-2-[*N*-(*p*-tolylsulfonyl)methylsulfonimidoyl]-1-ethanone, 42153-89-9; *S*,*S*-dimethyl-*N*-(*p*-tolylsulfonyl)sulfoximine, 22236-45-9; benzonitrile, 100-47-0; 1-phenyl-2-[*N*-(*p*-tolylsulfonyl)methylsulfonimidoyl]ethanol, 72174-74-4; methyl 1-benzoylcyclopropanecarboxylate, 72174-75-5; methyl benzoylacetate, 614-27-7; 1-(1,1-di-

(13) Yankee, E. W.; Cram, D. J. *J. Am. Chem. Soc.* **1970**, *92*, 6329.

methyl-2-phenylethyl)aziridine, 72174-76-6; 2-methyl-1-phenyl-2-propanamine, 122-09-8; *N*-(2-methoxyethyl)-2-methyl-1-phenyl-2-propanamine·HCl, 72174-77-7; *N,N'*-bis(1,1-dimethyl-2-phenylethyl)-1,2-ethanediamine, 72174-78-8; spiro[cyclopropane-1,1'-indene], 19770-38-8; indene, 95-13-6; 1-methyl-2-phenylaziridine, 4164-25-4; *N*-benzylidenemethanamine, 622-29-7; methanamine, 74-89-5; 1-*tert*-butyl-2-phenylaziridine, 18366-49-9; *tert*-butylamine, 75-64-9; 1-(1,1-dimethyl-2-phenylethyl)-2-phenylaziridine, 72174-79-9; 1-(*p*-tolylsulfonyl)-2-phenylaziridine, 24395-14-0; *p*-toluenesulfonamide, 70-55-3; 2,3,3a,4,5,6-hexahydro-3-phenylspiro[1*H*-indole-1,1'-pyrrolidinium] fluoborate, 72174-81-3; pyrrolidine enamine of cyclohexanone, 1125-99-1; 1-phenyl-1-(2-phenylcyclopropyl)-*N,N*-dimethylmethaniminium fluoborate, 72174-83-5; *N,N*-dimethyl-1-phenylethenamine, 14548-16-4; 1-(4,5-dihydro-4-phenyl-3-furanyl)-1-ethanone, 5831-65-2; 2,3-butanedione, 431-03-8; ethyl 4,5-dihydro-2-methyl-4-phenyl-3-furancarboxylate, 19225-61-7; ethyl 1-acetyl-2-phenylcyclopropanecarboxylate, 72174-84-6; ethyl acetoacetate, 141-97-9; ethyl 4,5-dihydro-2,4-diphenyl-3-furancarboxylate, 34878-89-2; ethyl 1-benzoyl-2-phenylcyclopropanecarboxylate, 39626-45-4; ethyl benzoylacetate, 94-02-0; *trans*-1-nitro-2-phenylcyclopropane, 15267-27-3; nitromethane, 75-52-5; 3-methyl-4-phenylisoxazoline 2-oxide, 60239-09-0; *cis*-1-methyl-1-nitro-2-phenylcyclopropane, 72174-85-7; *trans*-1-methyl-1-nitro-2-phenylcyclopropane, 72174-86-8; nitroethane, 79-24-3; 3-ethyl-4-phenylisoxazoline 2-oxide, 72174-87-9; 1-ethyl-1-nitro-2-phenylcyclopropane, 72174-88-0; 1-nitropropane, 108-03-2; 3-ethyl-4-phenylisoxazole, 72174-89-1; 3-(methoxycarbonyl)-4-phenylisoxazoline 2-oxide, 72174-90-4; methyl nitroacetate, 2483-57-0; (+)-3-(methoxycarbonyl)-4-phenylisoxazoline 2-oxide, 72174-91-5; dimethyl 2-phenyl-1,1-cyclopropanedicarboxylate, 3709-20-4; dimethyl malonate, 108-59-8; (+)-(1*S*,2*R*)-methyl 1-cyano-2-phenylcyclopropanecarboxylate, 31002-43-4; (1*S*,2*R*)-ethyl 1-cyano-2-phenylcyclopropanecarboxylate, 72204-01-4; 2-phenyl-1,1-cyclopropanedicarboxylate, 3709-34-0; methyl cyanoacetate, 105-34-0; ethyl cyanoacetate, 105-56-6; (1*R*,2*R*)-1,2-diphenyl-1-cyclopropanecarbonitrile, 72204-02-5; phenylacetonitrile, 140-29-4; 1-phenylspiro[2.4]hepta-4,6-diene, 13189-30-5; cyclopentadiene, 542-92-7; *trans*-2-phenylspiro[cyclopropane-1,1'-indene], 66374-17-2; dimethyl 2,2-diphenyl-1,1-cyclopropanedicarboxylate, 72174-92-6; 2,2-diphenylspiro[cyclopropane-1,1'-[1*H*]indene], 72174-93-7; dimethyl 2,2-dimethyl-1,1-cyclopropanedicarboxylate, 18795-95-4; methyl 1-benzoyl-2,2-dimethylcyclopropanecarboxylate, 72174-94-8; 2,2-dimethylspiro[cyclopropane-1,1'-[1*H*]indene], 60584-81-8; diethyl 2-*p*-tolyl-1,1-cyclopropanedicarboxylate, 72174-95-9; diethyl malonate, 105-53-3; diethyl 2-furanyl-1,1-cyclopropanedicarboxylate, 72174-96-0; diethyl 2,2-dimethyl-1,1-cyclopropanedicarboxylate, 16783-05-4; diethyl 2-methyl-2-phenyl-1,1-cyclopropanedicarboxylate, 72174-97-1.

Supplementary Material Available: Analytical and spectral data (8 pages). Ordering information is given on any current masthead page.

Triphenylphosphine Decomposition of Sulfenyl Thiocarbonates[1]

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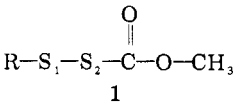
Several sulfenyl thiocarbonates ($RSSCO_2CH_3$) have been decomposed with triphenylphosphine. In the case of R = alkyl, desulfurization takes place to give the *S*-alkyl thiocarbonate while in the case of R = aryl, a phosphonium salt is likely formed which on chromatographic workup on silica gel is converted to a thiol and triphenylphosphine oxide and sulfide. A mechanistic interpretation is offered.

Sulfenyl thiocarbonates (**1**, $RSSCO_2CH_3$) are a stable class of compounds which has experienced relatively little study.[1,2] As part of our program involved with phosphine



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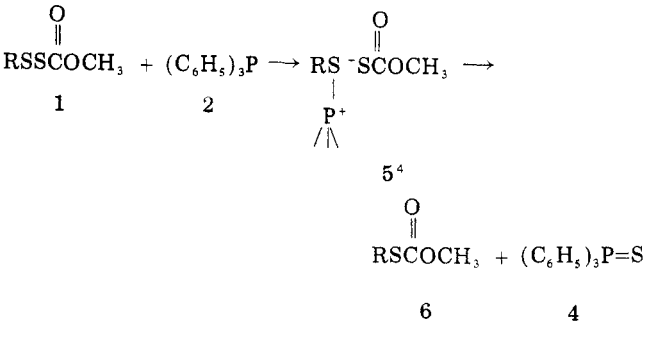
decompositions of various sulfur derivatives,[3] we felt it was of interest to examine the title compounds (Table I). In principle, there are three reasonable decomposition pathways involving triphenylphosphine (**2**) attack on oxygen or *either* sulfur atom. We have found that the main pathway involves attack at S_1 (Scheme I). When sulfenyl thiocarbonate **1a** (R = $C_6H_5CH_2$) was treated with 1 equiv of triphenylphosphine (**2**) in benzene and the products were chromatographed[5] on silica gel, benzyl mercaptan

Scheme I



(21%), methyl *S*-benzyl thiocarbonate **6a** (R = $C_6H_5CH_2$, 78%), triphenylphosphine sulfide (**4**, 76%), and triphenylphosphine oxide (24%) were isolated. Parallel results were obtained for **1b** (R = *p*-$ClC_6H_5CH_2$) (Table II). These products can best be accounted for by the pathway shown in Scheme I. Decomposition of any unreacted phosphonium salt **5** on the silica column would explain the

(1) Organic Sulfur Chemistry. Part 37. For part 36, see D. N. Harpp and A. Granata, *J. Org. Chem.*, **44**, 4144 (1979).

(2) G. Zumach and E. Kühle, *Angew. Chem., Int. Ed. Engl.*, **9**, 54 (1970); S. J. Brois, J. F. Pilot, and M. W. Barnum, *J. Am. Chem. Soc.*, **92**, 7629 (1970); R. G. Hiskey, N. Muthukumaraswamy, and R. Vunnam, *J. Org. Chem.*, **40**, 950 (1975); D. N. Harpp and A. Granata, *Tetrahedron Lett.*, 3001 (1976); K. Nokihara and H. Berndt, *J. Org. Chem.*, **43**, 4893 (1978).

(3) D. N. Harpp, J. Adams, J. G. Gleason, D. Mullins, and K. Steliou, *Tetrahedron Lett.*, 3989 (1978), and references cited therein.

(4) C. N. Murphy and G. Winter, *Aust. J. Chem.*, **26**, 755 (1973).

(5) When the reaction was carried out and the residue distilled directly, a 78% yield of benzyl methyl sulfide was obtained (Table II). That compound **6a** is the precursor of benzyl methyl sulfide was independently demonstrated (Experimental Section). This thermal degradation has been studied; see J. L. Kice, R. A. Bantsch, M. A. Darkleff and S. L. Schwartz, *J. Am. Chem. Soc.*, **87**, 1734 (1965).

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