(4.3 mmol) of 0.54 *M* *m*-trifluoromethylphenylmagnesium bromide. Distillation of the crude product at 96–97° (0.5 mm) yielded 1.05 g (84%) of 1-*m*-trifluoromethylphenylcyclohexanol: ir (CCl_4) ν 3625 (OH), 3050 (ArH), 2950 and 2875 (aliphatic CH), 1325 (sym CF_3Ar), 1170 (asym CF_3Ar), 1130 (asym CF_3Ar), 702 (aromatic); uv λ_{max}^{EtOH} 271 nm (ϵ 7300), 263 (8700), 257 (7500), 252 sh (6400); nmr (CCl_4) δ 1.4–2.0 (11 H, m, $-(CH_2)_4-$ and OH), 7.3–7.9 (4 H, m, ArH); mass spectrum *m/e* (70 eV) (rel intensity) 244.16381 (calcd for $C_{13}H_{15}OF_3$, 244.16381) (19), 201 (100), 189 (28), 173 (27), 145 (17), 91 (8), 81 (9), 69 (10), 57 (14), 55 (25).

1-*m*-Trifluoromethylphenylcyclohexanol (**43**) (335 mg, 1.32 mmol) was dehydrated as above into 105 mg (66%) of 1-*m*-trifluoromethylcyclohexene: bp 185° (0.5 mm); ir (CCl_4) ν 3049 (–HC=), 2950 (aliph CH), 2874 (aliph CH), 1330 (sym CF_3Ar), 1170 (asym CF_3Ar), 1130 (asym CF_3Ar), 897 (meta-subst aromatic), 698 (aromatic); uv λ_{max}^{EtOH} 251 nm (ϵ 9100), 223 (8200); nmr (CCl_4) δ 1.4–1.95 (4 H, m, $-(CH_2)_2-$), 1.95–2.55 (4 H, m, $-CH_2C=$), 6.12 (1 H, m, –HC=), 7.2–7.65 (4 H, m, ArH); mass spectrum *m/e* (70 eV) (rel intensity) 226.09721 (calcd for $C_{13}H_{13}F_3$, 226.09693) (100), 157 (16).

By the standard method, 1-*m*-trifluoromethylphenylcyclohexene (**44**) (26 mg, 0.12 mmol) was dehydrogenated to 18 mg (31%) of 1-*m*-trifluoromethylbiphenyl: bp 120° (0.5 mm); ir (CCl_4) ν 2941 (ArH), 1335 (sym CF_3Ar), 1170 (asym CF_3Ar), 1134 (asym CF_3Ar), 702 (aromatic); uv λ_{max}^{EtOH} 248 nm (ϵ 14,700); nmr (CCl_4) δ 7.15–7.9 (m, ArH); mass spectrum *m/e* (70 eV) (rel intensity) 222.0661 (calcd for $C_{13}H_9F_3$, 222.0656) (100), 158 (8).

Preparation of *p*-Trifluoromethylbiphenyl. Utilizing the standard method, 423 mg (4.3 mmol) of cyclohexanone reacted with 13.9 ml (4.3 mmol) of 0.31 *M* *p*-trifluoromethylphenylmagnesium bromide to yield 630 mg (58%) of 1-*p*-trifluoromethylphenylcyclohexanol: bp 95–97° (0.5 mm); ir (CCl_4) ν 3636 (OH), 3571–3333 (OH), 2941 (ArH), 2865 (aliph CH), 1325 (asym CF_3Ar), 1168 (sym CF_3Ar), 1130 (sym CF_3Ar), 971 (aromatic), 828 (para-disubst aromatic); uv λ_{max}^{EtOH} 256 nm (ϵ 1000), 217 (6200); nmr (CCl_4) δ 1.2–2.4 (11 H, m, $-(CH_2)_5-$ and O*H*), 7.57 (4 H, s, ArH); mass spectrum *m/e* (70 eV) (rel intensity) 244.10656 (calcd for $C_{13}H_{15}F_3O$, 244.10749) (12), 226 (23), 119 (94), 117 (100), 69 (8).

Dehydration of 1-*p*-trifluoromethylphenylcyclohexanol (630 mg, 2.6 mmol) was achieved by the standard method to yield, after purification by tlc using Skelly B as an eluent, 370 mg (63%) of 1-*p*-trifluoromethylphenylcyclohexene: ir (CCl_4) ν 2959 (ArH), 1328 (asym CF_3Ar), 1168 (sym CF_3AR), 1129 (sym CF_3Ar); uv λ_{max}^{EtOH} 257 nm (ϵ 12,800), 223 (9500), 216 (11,700); nmr (CCl_4) δ 1.3–1.95 (4 H, m, $-CH_2CH_2-$), 1.95–2.50 (4 H, m, $-CH_2C=$), 6.08 (1 H, m, HC=), 7.1–7.7 (4 H, m, ArH); mass spectrum *m/e* (70 eV) (rel intensity) 226.09827 (calcd for $C_{13}H_{13}F_3$, 226.09693) (28), 219 (100), 157 (5).

Dehydrogenation of 1-*p*-trifluoromethylphenylcyclohexene (190 mg, 0.84 mmol) with 800 mg of sulfur as previously described, followed by tlc purification using Skelly B–hexane as the eluent, yielded 119 mg (64%) of *p*-trifluoromethylbiphenyl: ir (CCl_4) ν 1328 (asym CF_3Ar), 1170 (sym CF_3Ar), 1133 (sym CF_3Ar), 696 (aromatic); uv λ_{max}^{EtOH} 253 nm (ϵ 15,300); nmr (CCl_4) δ 7.05–7.75 (m, ArH); mass spectrum *m/e* (70 eV) (rel intensity) 222.06790 (calcd for $C_{13}H_9F_3$, 222.06563) (100), 203 (6), 152 (12), 77 (5), 69 (9).

Acknowledgment. We wish to thank the National Institutes of Health and National Science Foundation for their generous support of our programs.

Preparation of Cyclopropyldiphenylsulfonium and 2-Methylcyclopropyldiphenylsulfonium Fluoroborate and Their Ylides. Stereochemistry of Sulfur Ylides

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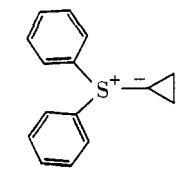
Contribution from the Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706. *Received February 23, 1973*

Abstract: Preparation of 3-halopropyldiphenylsulfonium fluoroborate (halo, chloro, bromo, and iodo) followed by cyclization with either sodium hydride in tetrahydrofuran or potassium *tert*-butoxide in dimethyl sulfoxide–tetrahydrofuran makes cyclopropyldiphenylsulfonium fluoroborate readily available. In a similar fashion from 3-bromo- or 3-chlorobutyldiphenylsulfonium fluoroborate, 2-methylcyclopropyldiphenylsulfonium fluoroborate as either an 80:20 or 70:30 mixture of trans and cis isomers is abundantly available. Generation of the cyclopropylide under irreversible conditions revealed a half-life of approximately 2.5 min indicating no unusual stabilization compared to an acyclic sulfonium alkylide. The 2-methylcyclopropylide shows no loss of stereochemistry at carbon at 50° in methanol–water in the presence of sodium hydroxide under conditions in which complete H–D exchange readily occurs nor in condensation with ketones. Thus, cyclopentanone led to *trans*-2-methyl-1-(1′-cyclopentenyl)cyclopropanol (methyl and hydroxyl cis) upon condensation with the methylated ylide followed by ring opening of the oxaspiropentane with lithium diethylamide. Alternatively, condensation with acetone followed by ring opening with *n*-butyllithium led to a mixture of *trans*- and *cis*-2-methyl-1-(2′-methyl-2′-hexyl)cyclopropanol in a ratio reflecting the stereochemistry of the starting sulfonium salt mixture. On the other hand, the stereochemistry of the ylide appears to be lost in dimethyl sulfoxide in the presence of potassium hydroxide.

The utility of sulfur ylides in synthesis demands that substituted reactive ylides outside of the parent system be investigated.[1] The synthesis of the novel and potentially synthetically useful ylide **1** was achieved by the ligand exchange method *via* the slow addition of cyclopropyllithium to a −78° tetrahydrofuran slurry of triphenylsulfonium fluoroborate.[2] Addition



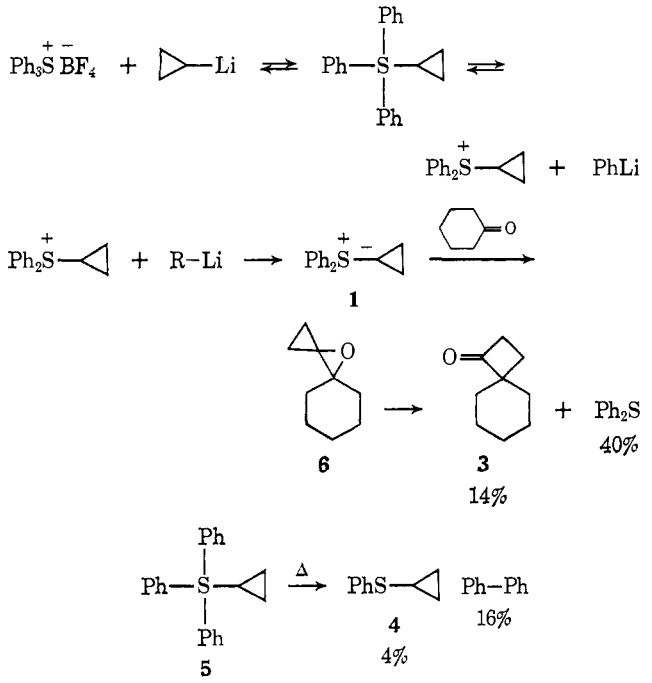
1

of cyclohexanone to the solution quenched the yellow

(1) For existing reviews, see (a) C. Agami, *Bull. Soc. Chim. Fr.*, 1021 (1965); (b) A. W. Johnson, "Ylid Chemistry," Academic Press, New York, N. Y., 1966; (c) J. C. Block, *Ann. Chim. (Paris)*, **10**, 419 (1965); (d) P. A. Lowe, *Chem. Ind. (London)*, 1070 (1970).

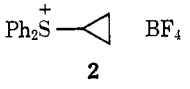
(2) (a) R. W. LaRochelle and B. M. Trost, *J. Amer. Chem. Soc.*, **93**, 6077 (1971); (b) B. W. Trost, R. LaRochelle, and M. J. Bogdanowicz, *Tetrahedron Lett.*, **39**, 3449 (1970).

Scheme I. Ligand Exchange Method for the Generation of **1**



color (see Scheme I). The isolation of **3** is consistent with the initial formation of the cyclopropyl oxirane **6** and subsequent rearrangement to the cyclobutanone during work-up. The ligand exchange procedure for the generation of ylide **1** resulted in two other compounds besides those expected from the reaction of the ylide. These compounds, biphenyl and cyclopropyl phenyl sulfide (**4**), arise from the decomposition of sulfurane **5**.[2] The novel transformation of a ketone to a cyclobutanone and the applications of these compounds as intermediates in organic synthesis induced us to explore an improved synthesis of ylide **1**.[3] Further, the unusual structure of the ylide would allow probing of the factors affecting ylide stability. In this paper of the series on new synthetic reactions, we deal with these questions. In the subsequent papers, we will deal with the synthetic applications of these fascinating and exceedingly useful intermediates.

To circumvent the low yields inherent in the ligand exchange preparation of ylide **1**, we sought to prepare independently the immediate precursor sulfonium salt **2**. Cyclopropyltriphenylphosphonium bromide (**7**),



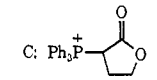
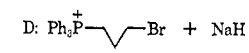
the phosphonium salt analogous to sulfonium salt **2**, has been prepared by a variety of methods (Table I). It should be noted that the ylide formed by the base treatment of **7** reacts as a normal Wittig reagent with carbonyl compounds, resulting in an olefin.[4]

Since application of method A seemed less than promising and method B was analogous to the ligand exchange reaction previously described, attempted utilization of method C was explored. Unfortunately,

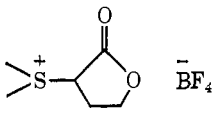
(3) (a) For the related dimethylaminophenyloxosulfonium cyclopropylide, see C. R. Johnson, G. F. Katekar, R. F. Huxol, and E. R. Janiga, *J. Amer. Chem. Soc.*, **93**, 3771 (1971). (b) For a preliminary report of a portion of this work, see B. M. Trost and M. J. Bogdanowicz, *J. Amer. Chem. Soc.*, **93**, 3772 (1971).

(4) E. E. Schweizer, C. J. Berninger, and J. G. Thompson, *J. Org. Chem.*, **33**, 336 (1968).

Table I. Preparation of Cyclopropyltriphenylphosphonium Bromide (7)

	% yield of 7	Ref
A: Ph_3P +  $\xrightarrow[168\,hr]{150^\circ}$	<1	4
B: $Ph_4P^+Br^-$ +  $\longrightarrow$	35	*a*
C:  $\xrightarrow{180^\circ}$	99+	4, *b*
D: 	78	4

[a] D. T. Longone and R. R. Doyle, *Chem. Commun.*, 300 (1967). [b] H. J. Bestmann, H. Hartung, and I. Pils, *Angew. Chem., Int. Ed. Engl.*, **4**, 957 (1965).

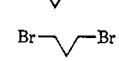
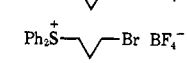
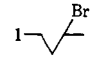
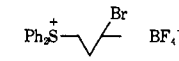


8

sulfonium salt **8**[5] decomposed to nonsulfonium salt products at 170°. Finally, a route analogous to method D was explored to prepare cyclopropyldiphenylsulfonium fluoroborate.

Whereas dialkyl sulfides are sufficiently powerful nucleophiles that alkylation usually takes place under mild conditions in the absence of catalysts to afford sulfonium salts in good yields, diphenyl sulfide, unlike triphenylphosphine, is too weak a nucleophile to undergo alkylation under normal conditions. On the other hand, silver(I)[6] (also mercury(II))[7] is known to complex with electron-rich sites, such as halides, olefins, sulfides, aromatic rings, and strained σ bonds. Thus, silver tetrafluoroborate can be utilized to increase the propensity of nucleophilic attack by diphenyl sulfide on an alkyl halide.[4,6,7] The tetrafluoroborate anion is a relatively nonnucleophilic counterion. Alkylation of diphenyl sulfide with a variety of alkyl halides and silver tetrafluoroborate led to the sulfonium salts listed in Table II. Ring closure of the 3-haloalkyl-

Table II. Alkylation of Diphenyl Sulfide

Halide	Sulfonium salt	% yield	Mp, °C
	 BF_4^- (9)	81	98.5–99
	 BF_4^- (10)	26	114–115
	BF_4^- (11)	87	106–107
	 BF_4^- (12)	31	95–96
	 BF_4^- (13)	81	94–95

diphenylsulfonium fluoroborates was accomplished by two methods: either by sodium hydride in tetrahydro-

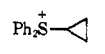
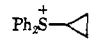
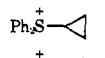
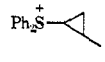
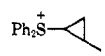
(5) Prepared by H. C. Arndt, these laboratories.

(6) (a) V. Franzen, H. J. Schmidt, and C. Mertz, *Chem. Ber.*, **94**, 2942 (1961); (b) V. Franzen and H. E. Driesen, *ibid.*, **96**, 1881 (1963); (c) T. Hashimoto, K. Ohkubo, H. Kitano, and K. Fukui, *Nippon Kagaku Zasshi*, **87**, 456 (1966).

(7) J. Van der Veen, *Recl. Trav. Chim. Pays-Bas*, **84**, 540 (1965).

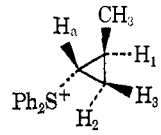
furan or by potassium *tert*-butoxide in dimethyl sulfoxide and tetrahydrofuran (Table III).

Table III. Ring Closure of 3-Haloalkyldiphenylsulfonium Fluoroborates

Open chain sulfonium salt	Method of closure[a]	Product	% yield
9	A	 $\bar{B}F_4$	40
11	A	 $\bar{B}F_4$	79
11	B	 $\bar{B}F_4$	83
13	A	 $\bar{B}F_4$ Trans:cis, 70:30	83
13	B	 $\bar{B}F_4$ Trans:cis, 80:20	87

[a] Method A, sodium hydride in tetrahydrofuran, 24 hr; method B, potassium *tert*-butoxide in dimethyl sulfoxide and tetrahydrofuran, 5 min.

The 100-MHz nmr spectrum of the mixture of **14** and

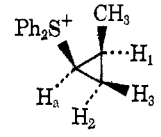


14

$J_{1\text{-}\alpha} = J_{2\text{-}\alpha} = 8.7$ Hz

$J_{3\text{-}\alpha} = 7.5$ Hz

$H_\alpha = \delta$ 3.62



15

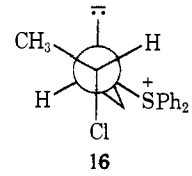
$J_{1\text{-}\alpha} = J_{2\text{-}\alpha} = 7.5$ Hz

$J_{3\text{-}\alpha} = 4.5$ Hz

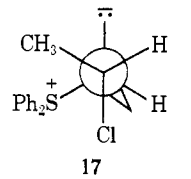
$H_\alpha = \delta$ 3.88

15 distinctly differentiates between the isomers and allows unambiguous assignment of stereochemistry. The only proton which is distinctly separable in the nmr of **14** and **15** is H_α. Sulfonium salt **14** exhibits a slight shielding of H_α by the methyl group relative to **15**. Cyclopropane ring protons exhibit larger cis coupling than trans coupling;[8,9] thus H_α in **14** appears as a doublet of triplets, the cis-doublet coupling being the largest. On the other hand, H_α in **15** appears as a triplet of doublets due to the large cis-triplet coupling being the greatest.

The predominance of *trans*-2-methylcyclopropyldiphenylsulfonium fluoroborate (**14**) over *cis*-2-methylcyclopropyldiphenylsulfonium fluoroborate (**15**) can be explained by the preferred conformation of the transition state during ring closure. Ring closure of **13** proceeds through one or both of the conformers **16** and



16



17

17. Clearly, the eclipsing interaction of the methyl and bulky diphenylsulfonium moieties disfavors **17** relative to **16**. This would account for the predominance of **14** in the ring closure.

Cyclopropyldiphenylsulfonium fluoroborate (**2**), formed by the aforementioned cyclization, can be used to generate diphenylsulfonium cyclopropylide (**1**) either irreversibly or reversibly. Irreversible generation of cyclopropylide **1** from **2** was attempted with many hard bases. Low deuterium incorporation resulted upon inverse addition of **1** (generated by addition of either *n*-butyl, *tert*-butyl or phenyllithium to **2** in tetrahydrofuran at −78°) into deuterioacetic acid. However, generation of the ylide **1** with lithium diisopropylamide in dimethoxyethane resulted in a moderate yield of spiro[3.5]nonan-1-one (**3**) (Table IV). No oxaspiro-

Table IV. Irreversible Generation of Diphenylsulfonium Cyclopropylide (**1**) with Lithium Diisopropylamide

Solvent/temp, °C	Yields,[a,b] 3	4	Ph_2S	Recovered 2, %	Time before quenching with ketone, min
THF/−78	6.5		34.7	38	45
DME/−78	16.3	3.1	31.5	40	40
DME/−45	5.7	4.6	26.5	70.6	15
DME/−22	22.2	10.0	50.5		5
DME/0	23.7	14.8	46.7	34.9	0.5

[a] Yields determined by vpc analysis with an internal standard. [b] Yields based on 1 mmol of **2** and an excess of cyclohexanone.

pentane **6** was observed, presumably due to lithium salt catalysis to cyclobutanone **3**.[10]

At higher temperatures ylide formation proceeds faster, as noted by both the disappearance of some salt in the slurry and by a deep yellow-orange color.[11] Accompanying the rapid ylide generation is its decomposition to cyclopropyl phenyl sulfide[12] and presumably benzyne.[13] The low yields of spirocyclobutanone may be attributed to enolization of cyclohexanone by either lithium diisopropylamide or ylide **1**.

Ylide **1** can also be generated with sodium methylsulfinyl carbanion[14] in dimethoxyethane at various temperatures (Table V). Overall, the irreversible generation of cyclopropylide **1** with dimsylsodium gives better yields of cyclobutanone **3**. However, two

(8) J. A. Landgrebe and D. E. Applequist, *J. Amer. Chem. Soc.*, **86**, 1536 (1964).

(9) D. J. Patel, M. E. H. Howden, and J. D. Roberts, *ibid.*, **85**, 3218 (1963).

(10) B. Rickborn and R. M. Gerkin, *ibid.*, **93**, 1693 (1971).

(11) Deep yellow-orange, red, or red-amber colors usually develop in ylide reactions. These colors are not necessarily the ylide itself, but may be associated with alternative processes occurring simultaneous to ylide generation.

(12) W. E. Truce, K. R. Hollister, L. B. Lindy, and J. E. Parr, *J. Org. Chem.*, **33**, 43 (1968).

(13) This process can be envisioned as a reverse of the preparation of sulfur ylides with benzyne and a sulfide: V. Franzen, H. I. Joschek, and C. Mertz, *Justus Liebigs Ann. Chem.*, **654**, 82 (1962); H. Hellmann and D. Eberle, *ibid.*, **662**, 188 (1963).

(14) E. J. Corey and M. Chaykovsky, *J. Amer. Chem. Soc.*, **87**, 1345 (1965).

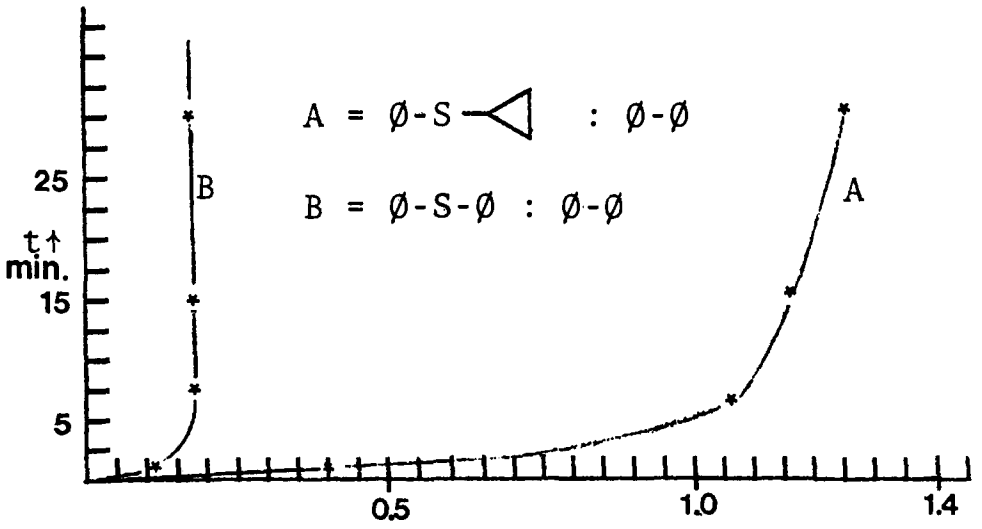
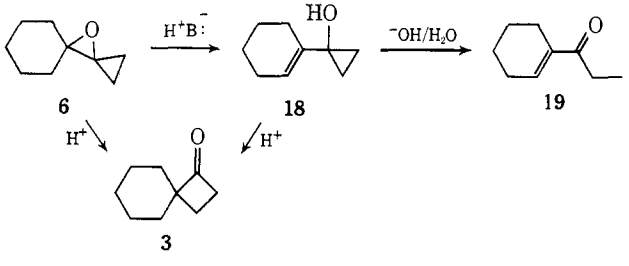


Figure 1. Rate of decomposition of diphenylsulfonium cyclopropylide. Abscissa represents ratio of decomposition product to biphenyl as an internal standard.

Table V. Generation of the Ylide with Dimsylsodium in Dimethoxyethane

Temp, °C	Yields 3	Yields 4	Yields Ph_2S	Mixture of 18 + 19	Recovered 2, %	Time before quench, min
−45	47.6		82.1	13.2	17	5
−45	49.6		101.6	18.6	2	4
−22	22.8		73.9	Trace	17.5	10
0	15.3	19.1	78.2		2.1	4

[a] Yields determined by vpc analysis with an internal standard. [b] Yields based on 1 mmol of ylide and excess cyclohexanone.

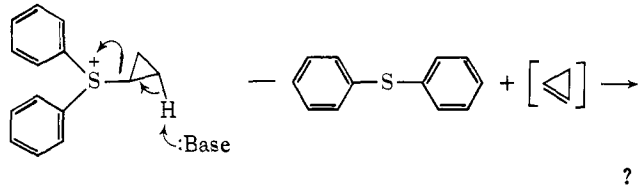


other products **18**[15] and **19**[15] are generated; these are not a result of the ylide or base, but of work-up. The reversible generation of cyclopropylide **1** is accomplished by treating sulfonium salt **2**, dissolved in dimethyl sulfoxide, with powdered potassium hydroxide at 25° in the presence of a carbonyl compound. This procedure results in routinely high (90%) yields of *either* oxaspiropentane or cyclobutanone with little or none of the ylide decomposition previously observed.

Diphenylsulfonium cyclopropylide (**1**) is expected to be on the borderline regarding thermal stabilization. Current literature seems to indicate that stabilizing substituents on sulfur such as phenyl, etc., have less effect on the ylide stability than an electron-withdrawing group on the α carbon.[16] Groups on sulfur which can delocalize positive charge lead to lower lying d orbitals on sulfur. The d orbitals become less diffuse as their energy is lowered; thus this leads to greater 2p–3d overlap in the ylide. The overlap between p and d orbitals is geometrically inefficient; thus when a carbon substituent is placed on the α carbon which has p orbitals available for overlap, such as a carbonyl group, the p–p overlap is much better resulting in greater stability. Cyclopropylide **1** is stabilized not only by the phenyl substituents on sulfur, but also by the carbanion being associated with a cyclopropane ring. As the s-character of the carbon–hydrogen bond increases, the pK_a decreases.[17] Since carbon–hydrogen bonds of cyclopropane are higher in s-character than normal hydrocarbons, the increased acidity of the hydrogens results in increased carbanion stability.

To determine the stability of the ylide **1**, sulfonium salt **2** was treated with sodium dimethylsulfinylcarbanion in dimethoxyethane at 25°. Aliquots were taken and vpc determinations of cyclopropyl phenyl sulfide and diphenyl sulfide were performed using biphenyl as an internal standard.

Figure 1 clearly shows that diphenyl sulfide is produced rapidly, then remains constant, while cyclopropyl phenyl sulfide is produced at a slower rate. These results indicate that β-elimination of diphenyl sulfide to produce presumably cyclopropene occurs as a competing reaction with α-proton removal at 25°. Also, it is clear than when the ylide is generated it

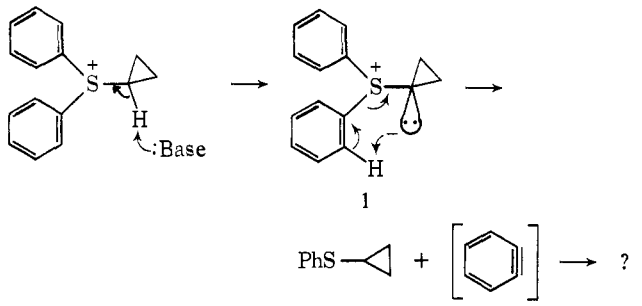


slowly decomposes to cyclopropyl phenyl sulfide and presumably benzyne by either an intra- or intermolecular elimination.[13,16] The final ratio of cyclopropyl phenyl sulfide to diphenyl sulfide (7.2:1.0) reflects the initial competition between α-proton abstraction and E2 elimination. This competition is surprising since the product of elimination is cyclopropene. The half-life

(15) Identified by comparison to authentic samples: B. M. Trost and M. J. Bogdanowicz, *J. Amer. Chem. Soc.*, **95**, 5311 (1973). See, however, B. M. Trost and M. J. Bogdanowicz, *ibid.*, **95**, 289 (1973).

(16) K. W. Ratts, *J. Org. Chem.*, **37**, 848 (1972); A. W. Johnson and R. T. Amel, *Can. J. Chem.*, **46**, 461 (1968).

(17) D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press, New York, N. Y., 1965.



of the ylide measured at 25° is approximately 2.5 min as determined from these data. The half-life of a similar ylide, diphenylsulfonium ethylide, at 20° is approximately 5 min.[18] It is interesting to note that the relative difference in acidities of cyclopropane and ethane are not reflected in the stability of the corresponding ylides.

Studies in the field of phosphorus ylide chemistry found that the bond order of the carbon–phosphorus bond is significantly greater than one.[19] In particular, a cyclopropylphosphonium ylide has been calculated to have a bond order of 1.53.[20] Thus, extrapolation of these results to sulfur chemistry would result in a planar cyclopropylidene sulfurane (ylide) rather than a carbanion with retained stereochemistry (**1b**). It

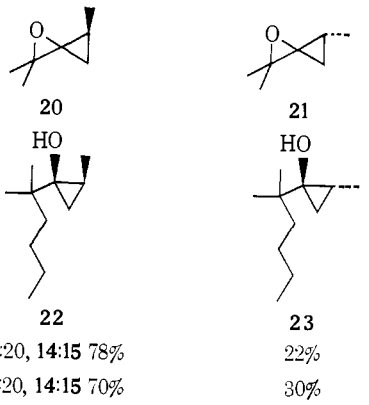
1a **1b**

should be noted that structure **1a** is indistinguishable from a rapidly inverting carbanion **1b** if the inversion barrier is very low. To elucidate this problem, sulfonium salts **14** and **15** were utilized. Since it was known that sulfonium salt **2** incorporated deuterium α to sulfur with sodium deuteroxide in deuterium oxide at 75° for 2 hr without decomposition, a similar treatment of the mixture of sulfonium salts **14** and **15** was performed. However, due to the decreased solubility of **14** and **15** in water, an alternative solvent system, methanol–water, was chosen. Table VI summarizes

Table VI. Hydroxide Catalyzed Equilibration of **14** and **15**

Initial ratio of **14**:**15**	Solvent	Temp, °C	Time, hr	Final ratio of **14**:**15**
80:20	CH_3OD/D_2O	50	2	Complete deuterium incorporation
80:20	CH_3OH/H_2O	50	2	80:20
70:30	CH_3OH/H_2O	50	2	70:30
70:30	CH_3OH/H_2O	50	12	70:30
70:30	CH_3OH/H_2O	50	36	70:30
70:30	DMSO	25	36	80:20
80:20	DMSO	25	2	80:20

the results of base treatment of sulfonium salts **14** and **15**. Thus, under conditions of deuterium incorporation in methanol–water with potassium hydroxide, the composition of the salts remains constant even at 50° for 36 hr. However, in dimethyl sulfoxide (DMSO) at 25° the 70:30 (**14**:**15**) salt appears to have equilibrated to an 80:20 mixture. Since under certain circumstances inversion of the α-carbon atom appears to occur, exploration of the relative rate of inversion to carbonyl addition was explored. Transference of stereochemistry of the mixture of salts **14** and **15** to an oxaspiropentane is observed in the reaction of these salts with a ketone. Reaction of an 80:20 (**14**:**15**) mixture with acetone resulted in the isolation of a mixture of oxaspiropentanes **20** and **21**. Treatment with *n*-butyl-



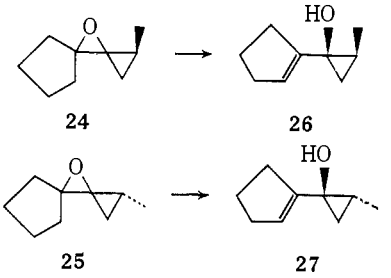
20 **21**

22 **23**

80:20, **14**:**15** 78% 22%

80:20, **14**:**15** 70% 30%

lithium resulted in an alkylative ring opening to **22** and **23**. Utilization of the two salt mixtures to prepare **20** and **21** resulted in different ratios of **22**:**23** separated by vpc. These ratios reflect the stereochemical composition of the starting sulfonium salts. Similarly, reaction of an 80:20 mixture of **14** and **15** with cyclopentanone resulted in **24** and **25**. A europium(III)



24 **26**

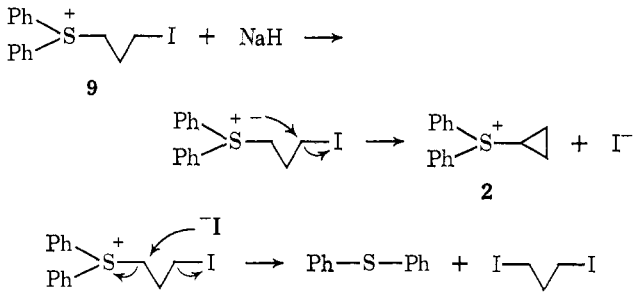
25 **27**

shift study on the lithium diethylamide ring-opened compounds **26** and **27** showed a large downfield shift of the methyl group in the major isomer **26**. The methyl group of **27** was buried beneath other proton absorptions. Therefore, the stereochemistry of the precursor salt is translated into the product which is in accord with the structure **1b** of the ylide. However, since inversion can occur under proper conditions, carbonyl addition leading to oxaspiropentane formation must be fast relative to inversion at the α carbon.

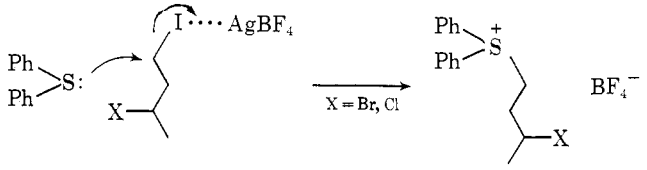
Discussion

Although the method of ylide generation from the sulfonium salt appears straightforward, some problems exist in the previous steps. In the generation of cyclopropyl salt **2** from **9** with sodium hydride in tetrahydrofuran, the maximum yield obtained was 40%. The product was pure **2**; no **9** was detected. Analysis of the reaction mixture provided the answer. Approximately 50% of 1,3-diiodopropane was recovered. Sodium iodide was quite soluble in tetrahydrofuran which, coupled to its high nucleophilicity, favored attack on 1 mol of starting material for each mole of

(18) E. J. Corey and W. Oppolzer, *J. Amer. Chem. Soc.*, **86**, 1899 (1964).
(19) W. Luttke and K. Wilhelm, *Angew. Chem., Int. Ed. Engl.*, 4, 875 (1965).
(20) D. B. Boyd and R. Hoffmann, *J. Amer. Chem. Soc.*, **93**, 1064 (1971).

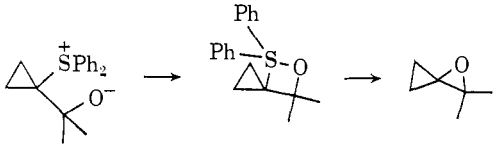


iodide formed, lowering the theoretical yield to 50%! This drawback was eliminated by production of 3-chloropropyldiphenylsulfonium fluoroborate (**11**). The chloride to be displaced will have a lower solubility and a lower relative nucleophilicity by 10^3.[21] As expected, then, cyclization of **11** generated the cyclopropyl salt **2** in 79% yield. The preparation of sulfonium salt **13** is most interesting in terms of the positional selectivity for alkylation. The Lewis basicity of iodide compared to chloride dictates preferential com-

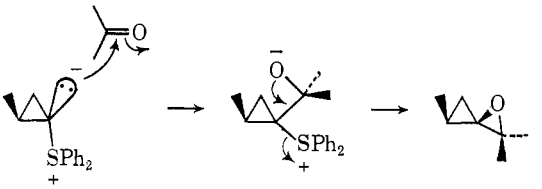


plexation at iodide. To ensure a greater complexation at halide over diphenyl sulfide, a large excess (approximately fivefold) of halide is normally employed. However, if reaction proceeds by a carbonium ion mechanism, the substantially greater stability of a secondary *vs.* primary carbonium ion should lead to substitution at the secondary center.[22] Thus, the substitution reaction most likely proceeds by displacement by diphenyl sulfide on a silver complexed halide.[23]

The facile reaction of the cyclopropylide with carbonyl partners to generate oxaspiropentanes in near quantitative yields even at −40° must be considered extremely surprising. The transition state of an S_N2 displacement necessitates that the carbon undergoing inversion become planar. Thus, for a cyclopropyl ring, which obviously has difficulty adopting such a geometry, the process is negligible in an intermolecular reaction. For this reason, several alternative mechanisms were considered, the most prominent involving a ring expansion to a σ-sulfurane followed by collapse to products.[24,25] The present results, however, are in excellent accord with the straightforward rationale.[26]



The initial attack involves retention of configuration at the carbanion followed by inversion of configuration in the displacement. It is interesting to note that such studies may be used to determine the preferred stereo-



chemical course of carbanions in the absence of the interfering counterion.

The instability of the ylide is somewhat surprising. Although an approximate half-life of the isopropylide is not known, the fact that the cyclopropylide has a half-life somewhat shorter than the ethylide even though cyclopropane hydrogens are more acidic than the hydrogens of ethane by 3 pK_A units suggests that because of geometric constraints the cyclopropylide does not receive as much stabilization from the positive sulfur center as a typical alkylide. While it is tempting to speculate that the tetrahedral-like geometry at carbon of the cyclopropylide precludes efficient orbital overlap with sulfur as the cause of this phenomenon, other explanations are clearly applicable. The fact that inversion of the cyclopropyl anion appears rapid (compared to typical cyclopropylorganometallics) in dimethyl sulfoxide may be viewed as supportive of the above speculation.

Experimental Section

General. Melting points were taken on a Thomas-Hoover melting point apparatus and are uncorrected. Unless otherwise stated, infrared spectra were determined in carbon tetrachloride solution on a Beckman IR-8 spectrophotometer; ultraviolet spectra were determined in 95% ethanol on a Cary Model 15 spectrometer. Nmr spectra were determined in carbon tetrachloride solution on Varian A60 or A60A spectrometers; chemical shifts are given in δ with TMS as the internal standard. Splitting patterns are designated as s, singlet; d, doublet; t, triplet; q, quartet; bs, broad singlet; mult, multiplet. Coupling constants are given in hertz. Mass spectra were taken on the AEI MS 902 high resolution mass spectrometer or a Consolidated Electronic Corporation 103C mass spectrometer at an ionizing voltage of 70 eV and an ionizing current of 98 mA. All exact mass determinations were obtained on the MS-902 instrument. Analyses were performed by Spang Microanalytical Laboratories, Ann Arbor, Mich. Vpc analyses were performed on an Aerograph Model 90P instrument with a helium flow rate of 60 ml/min.

All experiments were carried out under an atmosphere of dry nitrogen unless noted otherwise. In experiments requiring dry solvents, ether, tetrahydrofuran, and dimethoxyethane were distilled from sodium–benzophenone. Methylene chloride and dimethyl sulfoxide were distilled from calcium hydride. Apparatus for experiments requiring dry conditions were dried either by flaming under reduced pressure or in a nitrogen stream, or drying in an oven at 120° for 12 hr. During work-up of the reactions, general drying of the solvent was performed over anhydrous magnesium sulfate unless otherwise stated. Thin layer or preparative thick layer plates were made of E. Merck AG Darmstadt silica gel PF-254 activated by drying for 2 hr at 140°. The general eluent was 10% ether in hexane unless described in the text. Removal of material from the silica gel was accomplished by successive washings with ether.

Preparation of 1,3-Diiodopropane.[26] A solution of sodium iodide (44.7 g, 0.30 mol) in 100 ml of acetone was stirred and 1,3-dibromopropane (20.19 g, 0.10 mol) was added rapidly. A light yellow precipitate formed and the reaction continued without evolution of heat. After 2 hr, the mixture was suction filtered and the precipitated sodium bromide washed with acetone. The acetone was evaporated, and ether (300 ml) was added to precipitate

(21) H. Wells, *Chem. Rev.*, **63**, 171 (1963).
(22) I. Lazdins Reich, A. Diaz, and S. Winstein, *J. Amer. Chem. Soc.*, **91**, 5635, 5637 (1969); P. C. Myhre and K. S. Brown, *ibid.*, **91**, 5639 (1969); P. C. Myhre and E. Evans, *ibid.*, **91**, 5641 (1969).
(23) G. A. Dafforn and A. Streitwieser, Jr., *Tetrahedron Lett.*, 3159 (1970).
(24) M. J. Bogdanowicz and B. M. Trost, *ibid.*, **94**, 887 (1972).
(25) Collapse of a four-membered ring sulfurane to a cyclopropane has been observed: B. M. Trost, W. L. Schinski, F. Chen, and I. B. Mantz, *J. Amer. Chem. Soc.*, **93**, 676 (1971).
(26) J. M. Townsend and K. B. Sharpless, *Tetrahedron Lett.*, 3313 (1972).

inorganic salts. The ether solution was evaporated and the resulting oil dried *in vacuo* to yield 24.6 g (84%). This oil was used without further purification. Nmr (CCl_4): δ 2.28 (quintet, J = 6.5, 6.5 Hz, 2 H), 3.2 (t, J = 6.5 Hz, 4 H).

Preparation of 1-Chloro-3-iodopropane.[27] In a similar fashion, 393 g (2.63 mol) of sodium iodide and 394 g (2.50 mol) of 1-bromo-3-chloropropane in 1 l. of acetone gave 454 g (89%) of 1-chloro-3-iodopropane: nmr (CCl_4) δ 2.23 (quintet, J = 6, 6 Hz, 2 H), 3.30 (t, J = 6 Hz, 2 H), 3.62 (t, J = 6 Hz, 2 H).

Preparation of 3-Bromo-1-iodobutane. In a similar fashion, 167 g (1.12 mol) of sodium iodide and 199.8 g (0.9250 ml) of 1,3-dibromobutane in 1.5 l. of acetone gave 234 g (96%) of oil distilling at 54° (1.0 mm) (lit.[28] bp 66–67° (15 mm)) and identified as 3-bromo-1-iodobutane: ir (CCl_4) 2976, 2933, 1379, 1206, 1175, 1109, 973, 873 cm^{-1}; nmr (CCl_4) δ 1.75 (d, J = 7 Hz, 3 H), 2.2 (mult, 2 H), 3.31 (t, J = 7 Hz, 2 H), 4.18 (sextet, J = 7 Hz, 1 H), ms *m/e* (%) 264 (13), 262 (14), 183 (5), 128 (3), 127 (4), 55 (100).

Preparation of 3-Chloro-1-iodobutane. In similar fashion, 280 g (1.87 mol) of sodium iodide and 200 g (1.57 mol) of 1,3-dichlorobutane in 1.5 l. of acetone gave 268 g (78%) of 3-chloro-1-iodobutane after distillation at 39° (0.8 mm) (lit.[28] bp 52–54° (5 mm)); ir (CCl_4) 2976, 2933, 1377, 1239, 1176, 1111, 979, 873 cm^{-1}; nmr (CCl_4) δ 1.53, (d, J = 7 Hz, 3 H), 2.1 (mult, 2 H), 3.28 (t, J = 7 Hz, 2 H), 4.09 (sextet, J = 7 Hz, 1 H); ms *m/e* (%) 220 (12), 218 (38) 183 (22), 155 (15), 128 (8), 127 (14), 93 (27), 91 (86), 55 (100).

Preparation of Diphenyl-3-iodopropylsulfonium Fluoroborate (9). To a solution of diphenyl sulfide (2.05 g, 0.011 mol) and 1,3-diiodopropane (14.80 g, 0.050 mol) was added 10 ml of nitromethane. The solution was stirred vigorously and solid silver tetrafluoroborate (1.95 g, 0.010 mol) added rapidly. This solution was stirred under nitrogen for 24 hr. (Similar experiments reacted for 2 and 17 hr resulted in yields of 39.6 and 80.5%, respectively.) Methylene chloride (50 ml) was added and the solution filtered through a sintered glass funnel with 0.5 in. of Fluorisil. An oil was obtained after evaporation of the volatile components, which solidified upon triturating with ether to yield 3.86 g (80.5%) after recrystallization from ethanol. The resultant white crystals melted at 98.5–99°: ir (CCl_4) 3100–3000, 2950, 1587, 1484, 1448, 1337, 1290, 1150–950 very intense (BF_4^-), 680, 665 cm^{-1}; nmr ($CDCl_3$) δ 2.30 (b quintet, J = 7.5, 8.0 Hz, 2 H), 3.36 (t, J = 7.5 Hz, 2 H), 3.75 (t slightly broadened, J = 8.0 Hz, 2 H), 50–7.83 (mult (m + p ring protons), 6 H), 7.83–8.16 (mult (o-ring protons), 4 H); uv λ_{max} (ϵ) 234 (2920), 258 (600), 265 (657), 273 (535). *Anal.* Calcd for $C_{15}H_{16}BF_4IS$: C, 40.76; H, 3.65; S, 7.25. Found: C, 40.84; H, 3.80; S, 7.27.

Preparation of 3-Bromopropyldiphenylsulfonium Fluoroborate. Diphenyl sulfide (2.05 g, 0.011 mol), 1,3-dibromopropane (10.1 g, 0.050 mol), and nitromethane (10 ml) were stirred at room temperature. Silver tetrafluoroborate (1.95 g, 0.010 mol) was added rapidly. After 22 hr, methylene chloride (50 ml) was added and the mixture filtered through a sintered glass funnel. Upon evaporation and trituration with ether a light amber solid was collected. After recrystallization from 95% ethanol, 1.01 g (25.6%) of a white crystalline solid, mp 114–115°, was collected: nmr ($CDCl_3$) δ 2.34 (quintet, J = 6.5, 7.5 Hz, 2 H), 3.60 (t, J = 6.5 Hz, 2 H), 4.32 (bt, J = 7.5 Hz, 2 H), 7.5–8.2 (mult (ratio of 3:2), 10 H); uv λ_{max} (ϵ) 235 (3262), 261 (593), 268 (690), 725 (536). *Anal.* Calcd for $C_{15}H_{16}BBrF_4S$: C, 45.60; H, 4.08; S, 8.12. Found: C, 45.64; H, 4.20; S, 8.09.

Preparation of 3-Chloropropyldiphenylsulfonium Fluoroborate. Method A. A solution of diphenyl sulfide (93.0 g, 0.05 mol), 1-chloro-3-iodopropane (347 g, 1.70 mol), and 200 ml of nitromethane was stirred at room temperature under nitrogen. The flask is shielded from light. Silver tetrafluoroborate (78.0 g, 0.40 mol) was added in one portion. Initially the temperature rose to 40°, then gradually fell to room temperature. No external cooling was necessary. After 16 hr, 200 ml of methylene chloride was added and the mixture was filtered through a sintered glass funnel prepared with a pad of 35 g of Fluorisil to facilitate removal of the suspended silver salts. The solid was washed with methylene chloride and the methylene chloride portions were combined. This methylene chloride solution was evaporated until a solid appeared, then 1 l. of ether was utilized to precipitate the sulfonium salt. Initially an oil separated. Vigorous shaking of the mixture to extract out of the oily sulfonium salt layer the excess starting material induces crystallization. The crystals were collected, washed with ether, and dried *in vacuo* at 25°. The yield was 122.1 g (87%): mp 104–105°; nmr ($CDCl_3$) δ 2.22 (bq, J = 8 Hz, J = 6.5 Hz, 2 H), 3.74 (t, J = 6.5 Hz, 2 H), 4.27 (t, J = 8 Hz, 2 H), 7.5–8.1 (mult, 10 H); uv λ_{max} (ϵ) 233 (3125), 248 (547), 265 (625), 273 (500). *Anal.* Calcd for $C_{15}H_{16}BClF_4S$: C, 51.39; H, 4.60; S, 9.15. Found: C, 51.25; H, 4.68; S, 9.20.

Method B. Diphenyl sulfide (118 g, 0.633 mol) and 1-chloro-3-iodopropane (234 g, 1.15 mol) were dissolved in 800 ml of methylene chloride and the mixture was cooled to −78°. Then, rapidly, silver tetrafluoroborate (114 g, 0.575 mol) was added. Upon warming to room temperature, precipitation of silver iodide was observed. Continued stirring at 25° for 60 hr resulted in a light amber solution with precipitated silver iodide. The reaction mixture was filtered through 1 in. of Celite and the solid material washed with 200 ml of methylene chloride. Removal of the methylene chloride *in vacuo* resulted in a slurry of solid sulfonium salt in excess unreacted starting materials. This mixture was triturated with ether to remove any starting materials. The resulting amber solid was dissolved in 600 ml of hot 95% ethanol, Norit was added, and the mixture was filtered rapidly. Upon cooling in the freezer (−20°) white crystals formed and were collected yielding 171 g (85%), mp 106–107°.

Preparation of 3-Chlorobutyldiphenylsulfonium Fluoroborate. Method A. A solution of diphenyl sulfide (55 g, 0.295 mol), 3-chloro-1-iodobutane (127 g, 0.585 mol), and nitromethane (200 ml) was stirred under nitrogen at 25°. Silver tetrafluoroborate (57 g, 0.292 mol) was added to this solution over 5 min. The reaction vessel was shielded from light and stirred for 48 hr. Methylene chloride (200 ml) was added and the mixture filtered through a sintered glass funnel with a 0.5-in. layer of Fluorisil. The solid silver iodide was washed with methylene chloride, and the methylene chloride solution (now a deep brown) was evaporated *in vacuo* until all the methylene chloride was removed. To the resulting solution was added 3 l. of ether to induce separation of the sulfonium salt from the other organic products. The sulfonium salt oiled out of the ether. Upon decantation of the ether, this oil was dissolved in 50 ml of methylene chloride and then reprecipitated with 1 l. of ether. This was done three times. The oil did not crystallize by shaking with ether so it was dissolved in 250 ml of hot tetrahydrofuran, and cooled to −20°. The crystals which formed, 46.0 g (48%), were collected: mp 94–95°; nmr (DMSO-d_6) δ 1.40 (d, J = 6 Hz, 3 H), 2.0 (mult, 2 H), 4.3 (mult, 3 H), 7.4–8.2 (mult, 10 H); uv λ_{max} (ϵ) 234 (2840), 257 (547), 264 (659), 272 (511). *Anal.* Calcd for $C_{16}H_{18}BClF_4S$: C, 52.70; H, 4.98; S, 8.79. Found: C, 52.78; H, 5.02; S, 8.76.

Method B. A solution of diphenyl sulfide (100 g, 0.536 mol) and 3-chloro-1-iodobutane (234 g, 1.072 mol) in 800 ml of dichloromethane was stirred under nitrogen and cooled to −30° in a Dry Ice–aqueous calcium chloride slush. Silver tetrafluoroborate (98 g, 0.50 mol) was added over a 5-min period. The mixture was stirred and subsequently warmed to room temperature over 3 hr. After an additional 12 hr at 25° the mixture was suction filtered through 1 in. of Celite and the solid rinsed with 200 ml of methylene chloride. The filtrate was evaporated *in vacuo* resulting in an oil. The oil was triturated with 3 × 1 l. of ether. The final ether wash resulted in a solid. This solid was dissolved in 600 ml of hot 95% ethanol. This was filtered and cooled to −20°. The white crystals which formed were collected and dried *in vacuo*, 109 g (60%). The filtrate was concentrated *in vacuo* to 100 ml and 1 l. of ether added slowly resulting in a second crop, 38 g (21%) of light amber crystals.

Preparation of 3-Bromobutyldiphenylsulfonium Fluoroborate. To a solution of diphenyl sulfide (3.72 g, 2.0 mmol) and 1-iodo-3-bromobutane (15.78 g, 60 mmol) in 50 ml of nitromethane was added silver tetrafluoroborate (3.88 g, 20 mmol). After the mixture was stirred at 25° for 24 hr, 100 ml of dichloromethane was added and the solution filtered through a sintered glass funnel with 1 cm of Fluorisil. The solvent was evaporated to yield a black tarry oil which was triturated with 6 × 200 ml of ether. The residue remained an oil. The oil was dissolved in dichloromethane and put on a silica gel column (1 in. diam, 100 g of silica gel) and eluted with dichloromethane until no more colored material came through. The column was unpacked and washed with 250 ml of hot methanol. The methanol was evaporated to an oil which was dissolved in hot ethanol (5 ml), then put in the freezer. After 1 day some crystals appeared in the oil portion and after 1 week the oil completely crystallized. Recrystallization of this solid from ether–ethanol resulted in 2.53 g, 31% yield: mp 95–96°; nmr (CD_3CO-CD_3) δ 1.09 (d, J = 6.5 Hz, 3 H), 1.7–2.1 (mult, 2 H), 3.8–4.2 (mult,

(27) H. Finkelstein, *Ber.*, 43, 1531 (1910).

(28) S. S. Rossander and C. S. Marvel [*J. Amer. Chem. Soc.*, **50**, 1494 (1928)] report the preparation of 1-chloro-3-iodopropane and the boiling point of 47–59° (6 mm). However, the authors mention that it is not pure; some decomposition occurred during distillation.

3 H), 7.0–8.0 (mult, 10 H); uv λ_{max} (ϵ) 235 (2637), 260 (483), 267 (571), 274 (475). *Anal.* Calcd for $C_{16}H_{18}BBrF_4S$: C, 46.98; H, 4.43; S, 7.84. Found: C, 47.01; H, 4.50; S, 8.08.

Cyclization of 3-Halopropyldiphenylsulfonium Fluoroborate to Cyclopropyldiphenylsulfonium Fluoroborate. Method A. Sodium Hydride in Tetrahydrofuran. Use of Diphenyl-3-iodopropylsulfonium Fluoroborate. To 125 ml of freshly distilled tetrahydrofuran was added diphenyl-3-iodopropylsulfonium fluoroborate (58.8 g, 0.133 mol). To this stirred slurry, sodium hydride (3.20 g, 0.133 mol, 5.82 g of 55% mineral oil dispersion) was added over a 15-min period. After 20 hr at room temperature, 50 ml of a 10% aqueous tetrafluoroboric acid solution was added. The mixture was extracted with 3 × 100 ml portions of methylene chloride which were combined, dried, and evaporated to an oil. Ether (1 l.) was added to this oil and upon vigorous shaking crystals formed. The crystals were collected and dried. The yield was 16.6 g (39.7%), mp 139°. The same reaction for 18 hr resulted in a 38.7% yield and 46 hr resulted in a 37.5% yield. The use of dimethylformamide as a solvent gave a 28% yield.

Use of 3-Chloropropyldiphenylsulfonium Fluoroborate. A suspension of 3-chloropropyldiphenylsulfonium fluoroborate (118.7 g, 0.339 mol) in dry tetrahydrofuran (500 ml) was placed in a 2-l. flask under nitrogen. Then 5-g portions of a 55% sodium hydride–mineral oil dispersion (15.2 g, 0.350 mol) were added in 0.5-hr intervals. The resulting mixture was stirred at room temperature for 24 hr. A solution of 25 ml of 48% tetrafluoroboric acid, 15 g of sodium tetrafluoroborate, and 400 ml of water was added to destroy residual hydride and swamp out chloride ion. After 5 min, methylene chloride (300 ml) was added, and the top methylene chloride layer was removed from the lower aqueous layer. The densities of the methylene chloride and water layers are nearly equal. Thus, sometimes upon initial mixing the methylene chloride starts out on the bottom, but the layers reverse on shaking. However, we have found on occasion that the desired methylene chloride layer was in fact the bottom one. It is therefore advisable to check the layers by addition of either water or methylene chloride.

The methylene chloride solution was extracted with 100 ml of water. This aqueous layer was combined with the first aqueous layer and the combined water layers were extracted with an additional 100 ml of methylene chloride. The methylene chloride portions were combined, dried over anhydrous sodium sulfate, and evaporated *in vacuo* until precipitation occurred. The salt was completely precipitated upon addition of ether (1 l.). The crystals were collected, washed with ether, and recrystallized from absolute ethanol (approximately 400 ml). After drying *in vacuo* the yield was 83.5 g (79%); mp 139°.

Method B. Potassium *tert*-Butoxide in Dimethyl Sulfoxide–Tetrahydrofuran. Use of 3-Chloropropyldiphenylsulfonium Fluoroborate. A slurry of 3-chloropropyldiphenylsulfonium fluoroborate (35.0 g, 0.10 mol) in 200 ml of tetrahydrofuran was stirred at 25°. A 1.28 *M* solution of potassium *tert*-butoxide in dimethyl sulfoxide (78 ml, 0.10 mol) was added dropwise. A deep amber color formed which disappeared rapidly. Near the endpoint of the addition of base, the color remained longer. When the base addition was completed, methylene chloride (350 ml) was added and the mixture poured into a (1:1) v/v methylene chloride–water mixture (400 ml). The lower methylene chloride layer was removed and evaporated *in vacuo* to yield an oil. Addition of 1 l. of ether and shaking induced crystallization. The crystals were collected and dried *in vacuo* to yield a light amber solid. These crystals were recrystallized from ether–ethanol to yield 29.2 g (93%) of a white crystalline solid, cyclopropyldiphenylsulfonium fluoroborate (**2**): ir ($CHCl_3$) 3040, 1582, 1477, 1445, 1333, 1284, 912, 868, 829 cm^{-1}, also an extremely intense band from 1175 to 960 cm^{-1} due to the BF_4^- anion; nmr ($CDCl_3$) δ 1.3–1.7 (mult, 4 H), 3.44–3.95 (mult, 1 H), 7.4–8.2 (mult, 10 H); uv (EtOH) λ_{max} 231 nm (ϵ 3840), 261 (515), 267 (654), 274. *Anal.* Calcd for $C_{15}H_{15}BF_4S$: C, 57.35; H, 4.81; S, 10.21. Found: C, 57.47; H, 4.93; S, 10.30.

Preparation of *cis*- (15) and *trans*- (14) 2-Methylcyclopropyldiphenylsulfonium Fluoroborate as a 30:70 Mixture. Method A. A suspension of 3-chlorobutyldiphenylsulfonium fluoroborate (28 g, 0.077 mol) in 150 ml of dry tetrahydrofuran was placed in a 500-ml flask under nitrogen. Sodium hydride (as a 57% oil dispersion) (3.36 g, 0.077 mol) was added and the resulting mixture stirred at 25° for 12 hr. Then 200 ml of methylene chloride followed by a dropwise water (10 m) addition destroyed any sodium hydride left. A solution of 20 g of sodium tetrafluoroborate, 10 ml of 50% aqueous tetrafluoroboric acid, and 100 ml of water was poured into the mixture. Another 100 ml of methylene chloride was added and the methylene chloride layer separated and evaporated *in vacuo*. The resulting oil was triturated with ether to induce crystallization. The white crystals were collected and dried *in vacuo* to yield 20.8 g (83%) of 2-methylcyclopropyldiphenylsulfonium fluoroborate, mp 101–105°.

Preparation of *cis*- (15) and *trans*- (14) 2-Methylcyclopropyldiphenylsulfonium Fluoroborate as a 20:80 Mixture. Method B. A slurry of 3-chlorobutyldiphenylsulfonium fluoroborate (40.0 g, 0.110 mol) in 250 ml of tetrahydrofuran was stirred at 25°. A 1.28 *M* solution of potassium *tert*-butoxide in dimethyl sulfoxide (86 ml, 0.110 mol) was added dropwise. A deep amber-red color formed when the base hit the tetrahydrofuran solution. At the endpoint, when all the base was added, one drop would result in an intense amber-red color which lasted for over 1 min. When the color disappeared a light tan slurry was present. It should be noted that in the beginning when the first portion of base was added the slurry became homogeneous. The color which resulted during the titration was discharged very fast, only at the endpoint did it remain for any length of time. The reaction again became heterogeneous as more base was added. Methylene chloride (300 ml) was added and the mixture poured into a (1:1) v/v methylene chloride–water mixture (400 ml). The lower methylene chloride layer was removed and evaporated *in vacuo* to yield an oil. Addition of 1 l. of ether and shaking induced crystallization. The light amber crystals were collected and dried *in vacuo* to yield crude 2-methylcyclopropyldiphenylsulfonium fluoroborate. These crystals had no starting sulfonium salt confirmed by the absence of the three proton signal at δ 4.3 in the nmr spectrum. The crystals were recrystallized from 95% ethanol resulting in 31.0 g (87%) of the sulfonium salt: mp 112–116°; nmr (CD_3COCD_3) δ 1.24 (d, J = 5, 3 H), 1.30–2.1 (mult, 3 H), 3.62 (mult, 1 H), 7.5–8.2 (mult in 3:2 ratio, 10 H); uv λ_{max} (ϵ) 234 nm (2124), 258 (579), 264 (669), 273 (534). *Anal.* Calcd for $C_{16}H_{17}BF_4S$: C, 58.56; H, 5.22; S, 9.77. Found: C, 58.59; H, 5.30; S, 9.69.

Reaction of Cyclopropyldiphenylsulfonium Fluoroborate (2) with Sodium Deuteroxide in D_2O. Cyclopropyldiphenylsulfonium fluoroborate (271.8 mg, 0.836 mmol) was added to 12 ml of 15% sodium deuteroxide in deuterium oxide. The sulfonium salt was not readily soluble in deuterium oxide; however, heating to 75° enabled dissolution of the salt. After 2 hr this mixture was poured into 50% aqueous tetrafluoroboric acid (20 ml) and extracted with 3 × 10 ml of methylene chloride. The methylene chloride was evaporated and a solid was obtained, 269.5 mg, 99.6% recovery, mp 134–135°. Analysis by nmr revealed complete loss of the hydrogen α to sulfur from the absence of the 1 H absorption at δ 3.44–3.95. Ir ($CHCl_3$): same as for the all-hydrogen compound except for the C–D stretch at 2288 cm^{-1}; nmr ($CDCl_3$) δ 2.22–2.47 (AA′BB′ pattern, 4 H), 7.4–8.1 (mult, 10 H).

Determination of the Stability of Diphenylsulfonium Cyclopropylide. A solution of cyclopropyldiphenylsulfonium fluoroborate (314 mg, 1.00 mmol) and biphenyl (91 mg) in dimethoxyethane was stirred at 25°. A dimsylsodium solution in dimethyl sulfoxide (2.09 *M* solution, 1.1 mmol, 0.53 ml) was added rapidly. After 1 min an aliquot was taken of the yellow solution (0.3 ml) and quenched with ~0.5 ml of wet ether. Similar aliquots were taken at 7, 15, and 30 min. Table VII below summarizes the results with biphenyl as an internal standard. The aliquots were analyzed by vpc on a 5 ft × 0.25 in. SE-3- on Chromosorb W column at 150°. Cyclopropyl phenyl sulfide isolated: ir (CCl_4) 3096, 3086, 3021, 1587, 1484, 1441, 1282, 1095, 1026, 880, 699, 688 cm^{-1}; nmr (CCl_4) δ 0.50–1.08 (mult, 4 H), 1.87–2.34 (mult, 1 H), 7.15 (bs, 5 H); ms *m/e* (%) 150 (87), 135 (56), 117 (100), 109 (37), 91 (33), 77 (24), 73 (13). *Anal.* Calcd for $C_9H_{10}S$: 150.05032. Found: 150.04807. The spectral properties of cyclopropyl phenyl sulfide were identical with those of an authentic sample.[12]

Table VII. Decomposition of Diphenylsulfonium Cyclopropylide

Time, min	4 (A)	Ph–Ph (B)	Ph–S–Ph (C)	(A/B)	(C/B)
1	32.5	82	9	0.40	0.110
7	74.5	70	12	1.06	0.175
15	66	57	10	1.16	0.175
30	119	95	16.5	1.25	0.174

Generation of Lithium Diisopropylamide. Diisopropylamine (152 mg, 1.50 mmol) was dissolved in 1.0 ml of dry tetrahydrofuran.

This solution was cooled to −78° and *n*-butyllithium in hexane (1.00 ml, 1.5 mmol of 1.50 *M* solution) added. This solution was used after mixing 15 min. The approximate concentration of this solution is 0.375 *M*.

Generation of Diphenylsulfonium Cyclopropylide (1) from Cyclopropyldiphenylsulfonium Fluoroborate (2) with Lithium Diisopropylamide. A typical procedure for the results in Table IV follows, the times and temperatures are as noted in Table IV. The first reaction was carried out in tetrahydrofuran, all subsequent reactions were run in dimethoxyethane. Cyclopropyldiphenylsulfonium fluoroborate (314 mg, 1.00 mmol) and 10 ml of dry solvent (as noted) were mixed. The solution was cooled to the desired reaction temperature, and 3.0 ml of 0.375 *M* lithium diisopropylamide (1.1 mmol) was added by syringe. The solution, which was originally a white suspension of sulfonium salt, turned yellow. The mixture was stirred for the time noted. Then cyclohexanone (150 mg, 1.52 mmol) was added and the yellow color disappeared immediately. After mixing an additional 30 min, the mixture was warmed to room temperature. The mixture was quenched with 30 ml of water, and extracted with 2 × 15 ml of ether. The ether was washed with an aqueous 5% hydrochloric acid solution, dried, and evaporated to yield the solution to which an internal standard (cycloheptanone) was added for vpc analysis. The aqueous layer from the reaction was extracted with 2 × 10 ml of methylene chloride which was evaporated to yield the recovered sulfonium salt as reported in Table I.

Preparation of Sodium Methylsulfinyl Carbanion (Dimsylsodium) in Dimethyl Sulfoxide. A solution of dimsylsodium in dimethyl sulfoxide was prepared by the method of Corey and Chaykovsky.[14] After cooling the solution was transferred to dry bottles for storage. Addition of ~0.5 ml of mineral oil to each bottle provides a protective layer toward air oxidation. Titration with 0.01 *N* hydrochloric acid to a phenolphthalein endpoint for total base indicated 1.105 *M*. With triphenylmethane as an indicator and cyclohexanone as the proton source the methylsulfinyl carbanion concentration was 1.06 ± 0.03 *M*. Refrigeration of the solution at 0° resulted in solidification which enhanced its shelf life.

Generation of Diphenylsulfonium Cyclopropylide with Dimsylsodium in Dimethoxyethane. A suspension of cyclopropyldiphenylsulfonium fluoroborate (314 mg, 1.00 mmol) in 10 ml of dry dimethoxyethane was cooled to the temperature indicated in Table V utilizing Dry Ice–chlorobenzene slush, ice–aqueous calcium chloride solution, or ice–water solution. Dimsylsodium (1.10 ml of 1.06 *M* dimethyl sulfoxide solution, 1.16 mmol) was added rapidly and a deep orange-yellow color developed. The suspended sulfonium salt was no longer present; the mixture appeared homogeneous. The resultant orange-yellow solution was mixed for 4 min at which time 98 mg (1 mmol) of cyclohexanone was added. This solution was stirred for 15 min at the given temperature, then allowed to warm to room temperature over 30 min. Then 5.0 ml of aqueous 1 *M* tetrafluoroboric acid was added. This solution was extracted with 2 × 10-ml portions of ether. The ether was evaporated and a weighed amount of cycloheptanone as internal standard added to yield the mixture for analysis. The aqueous layer was extracted with methylene chloride (10 ml) which resulted in less than 2% of starting sulfonium salt. The results are listed in Table V.

Base Equilibration Reactions of *cis*- and *trans*-2-Methylcyclopropyldiphenylsulfonium Fluoroborate. Method A. Sodium Hydroxide in Aqueous Methanol. Diphenyl-2-methylcyclopropylsulfonium fluoroborate (250 mg) was mixed with 3 ml of methanol and 0.5 ml of water. Four drops of an aqueous 40% sodium hydroxide solution was added. This mixture was stirred at 50° for the time indicated in Table VIII. After the solution cooled to room temperature, 2 ml of water was added and the aqueous mixture extracted with 50 ml of methylene chloride. Upon evaporation of the methylene chloride *in vacuo*, an oil was obtained which crystallizes upon shaking with ether. Analysis of this salt by 100-MHz nmr at 100-Hz sweep width reveals a separation of the *cis*- (**15**) and *trans*- (**14**) sulfonium salts at δ 3.88 and 3.62, respectively. The ratio of the sulfonium salts was determined by integration of the absorptions at δ 3.88 and 3.62 in the nmr spectrum. Under these same conditions, using all deuterated solvents and base, complete incorporation of deuterium α to sulfur in the sulfonium salt was determined by the absence of absorptions at δ 3.88 and 3.62 in the nmr spectrum.

Table VIII. Stereochemistry of 2-Methylcyclopropyldiphenylsulfonium Fluoroborate

—Initial—		—Recovered—		Wt recovered,	
Trans	Cis	Trans	Cis	mg (%)	Time, hr
80	20	80	18	241 (96.4)	2
80	20	80	20	209 (83.5)	24
80	20	79	21	218 (87.3)	48
70	30	70	30	226 (90.5)	36

Method B. Potassium Hydroxide in Dimethyl Sulfoxide. A solution of diphenyl-2-methylcyclopropylsulfonium fluoroborate (trans:cis, 70:30) (250 mg, 0.76 mmol) in 3 ml of dimethyl sulfoxide was treated with 5 mg of KOH (0.076 mmol) for 36 hr at 25°. At that time, 100 ml of methylene chloride was added and then 100 ml of water. Separation of the methylene chloride layer and evaporation *in vacuo* resulted in an oil which solidified upon stirring with ether (50 ml). The recovered salt, 210 mg (84%), was analyzed by integration of the δ 3.88 and 3.62 regions of the 100-MHz nmr resulting in an 80:20 trans:cis salt mixture.

Preparation of *cis*- (26) and *trans*- (27) 1-(1′-Hydroxy-2′-methylcyclopropyl)cyclopentene from *cis*- and *trans*-1-Methyl-3-oxadispiro[2.1.4.0]nonane *via* Lithium Diethylamide Ring Opening. 1-Methyl-3-oxadispiro[2.1.4.0]nonane[29] (1.12 g, 0.81 mmol) was dissolved in 10 ml of hexane and diethylamine added (1.46 g, 20 mmol). Upon cooling to −78°, *n*-butyllithium in hexane (12 ml of a 1.5 *M* solution, 18 mmol) was added. A white solid formed. The solution was allowed to warm to room temperature. The solution was stirred for 30 min. Then 30 ml of hexane followed by 10 ml of water was utilized to halt the reaction. Separation of the hexane layer, and drying over anhydrous sodium sulfate, resulted in 1.06 g (94%) of an oil, **26** and **27**, upon evaporation of the solvent *in vacuo*. This material was analyzed without further purification: ir (CCl_4) 3610, 3425, 3077, 1639, 1372, 1333, 1253, 1211, 1085, 1038, 1018, 981, 952, 909, 866 cm^{-1}; nmr (CCl_4) δ 0.4 (mult, 1 H), 0.7–1.3 (mult, 5 H), 1.7–2.5 (mult, 6 H), 3.85 (bs, 1 H), 5.62 (bs, 1 H); ms *m/e* (%) 138 (28), 123 (30), 95 (100), 67 (47), 55 (25). *Anal.* Calcd for $C_9H_{14}O$: 138.10446. Found: 138.10372. Nmr analysis utilizing 45 mol % $Eu(fod)_3$ shift reagent resulted in a 180-Hz downfield shift of the major three hydrogen signal for the methyl group on the cyclopropane ring. This result is in accord with a structure where the alcohol and methyl groups are cis to one another.

Preparation of *cis*- (23) and *trans*- (22) 1-(1′,1′-Dimethylpentyl)-2-methylcyclopropan-1-ol from 2,2,3-Trimethyloxaspiropentane and *n*-Butyllithium. A solution of 2,2,3-trimethyloxaspiropentane[30] in 10 ml of hexane was cooled to −78°. A 1.5 *M* *n*-butyllithium in hexane solution was added rapidly. The reaction mixture was allowed to warm to room temperature and then mixed for 1 hr. The reaction was stopped by the addition of 10 ml of water followed by 150 ml of hexane The hexane layer was separated, dried over anhydrous magnesium sulfate, and evaporated to yield an oil (see Table IX). Vpc analysis on a 11 ft × 0.25 in. 5% Carbowax 20M on a Chromosorb W column at 88° resulted in separation of **22** and **23**, 16 and 18 min, respectively. *cis*-1-(1′,1′-Dimethylpentyl)-2-methylcyclopropan-1-ol (**23**): ir (CCl_4) 3636, 3590, 2959, 1379, 1236, 1014 cm^{-1}; nmr (CCl_4) δ 0.8–1.2 (mult, 15 H), 1.2–2.1 (mult, 7 H); ms *m/e* (%) 170 (0.6), 152 (0.4), 178 (27), 101 (24), 100 (10), 86 (40), 70 (90), 58 (100). *Anal.* Calcd for $C_{11}H_{22}O$: 170.16706. Found: 170.16645.

Table IX

2,2,3-Trimethyloxaspiropentane[a]	Wt, g (mmol)	*n*-Butyllithium, ml (mmol)	Product wt, g	% yield	Ratio of 22	Ratio of 23
A	0.350 (3.12)	5 (7.5)	0.487	91	70	30
B	0.250 (2.23)	5 (7.5)	0.314	83	78	22

[a] A: the oxaspiropentane was prepared from a 70:30 mixture of *trans*:*cis*-2-methylcyclopropyldiphenylsulfonium fluoroborate in 100% yield. **B:** the oxaspiropentane was prepared from an 80:20 mixture of *trans*:*cis*-2-methylcyclopropyldiphenylsulfonium fluoroborate in 98% yield.

(29) S. Mamedov and B. K. Zeinalov, *Zh. Obshch. Khim.*, **28**, 1831 (1958).

(30) B. M. Trost and M. J. Bogdanowicz, *J. Amer. Chem. Soc.*, **95**, 5307 (1973). For method of preparation, see ref 3b.

trans-1-(1′,1′-Dimethylpentyl)-2-methylcyclopropan-1-ol (**22**): ir (CCl_4) 3630, 3410, 2967, 1346, 1230 cm^{-1}; nmr (CCl_4) δ 0.5–2.1 (mult, 22 H); ms *m/e* (%) 170 (1), 152 (1), 128 (36), 101 (24), 100 (10), 86 (53), 70 (92), 58 (100). *Anal.* Calcd for $C_{11}H_{22}O$: 170.16706. Found: 170.16791.

A $Eu(fod)_3$ shift study on a 70:30 mixture of **22**:**23** produced a 50-Hz shift of the methyl doublet of the major isomer **22**.

Acknowledgment. We wish to express our sincere appreciation to the National Science Foundation and the National Institutes of Health for their generous support of our programs. We also express our thanks to the National Science Foundation and the Wisconsin Alumni Research Foundation for funds enabling the purchase of nmr and mass spectrometers utilized in this study.

New Synthetic Methods. Spiropentanes

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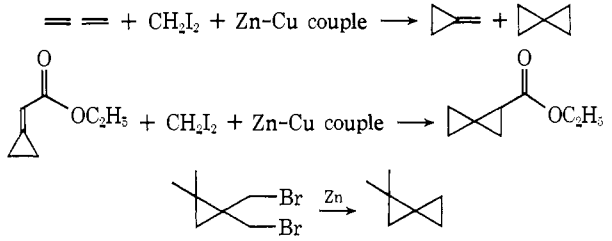
Abstract: The facile conjugate addition of diphenylsulfonium cyclopropylide to chalcone, carvomenthone, and methyl acrylate constitutes a new useful spiropentane synthesis. Even utilizing the potassium hydroxide reversible ylide generation technique, the sensitive ester remained intact although excess base allows isolation of the corresponding acid. Use of the 2-methylcyclopropylide with chalcone leads to the four possible isomers possessing phenyl and benzoyl trans. The isomer ratio reflects the stereochemistry of the starting ylide mixture, demonstrating that in conjugate addition reactions, like carbonyl addition reactions, no loss of configuration at ylidic carbon occurs.

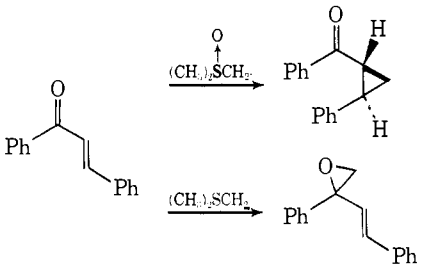
Sulfur ylides have been utilized as a convenient source of cyclopropanes from α,β-unsaturated carbonyl compounds.[2] A novel approach to the synthesis of an unusual class of cyclopropanes, spiropentanes, may be derived from a suitable sulfur ylide. The relative difficulties associated with spiropentane synthesis led us to explore this route which starts with readily available α,β-unsaturated carbonyl compounds and diphenylsulfonium cyclopropylide.[3]

Previously, spiropentanes have been prepared from allenes or alkylidene cyclopropanes *via* a Simmons–Smith or diazoalkane cyclopropanation reaction.[4] Other cyclopropane syntheses such as 1,3 elimination



reactions also have been utilized to form spiropentanes. Usually the yields of spiropentanes are at best moderate.

The ambient nature of α,β-unsaturated ketones toward sulfur ylide attack enables cyclopropanation to occur. One of the earliest examples of this duality of pathways available to sulfur ylides is the cyclopropanation of chalcone with dimethylsulfoxonium methylide as contrasted to the epoxide formation with dimethylsulfonium methylide.[2]



The stability of the ylide carbanion and the rate of 1,3 elimination usually govern how the molecule will react with α,β-unsaturated ketones. With highly reactive anions, they undergo carbonyl addition, whereas with stabilized anions they undergo conjugate addition. Alternatively, if the rate of 1,3 elimination in the betaine derived from carbonyl addition is slowed, as in the case of the isopropylide,[5] again products from conjugate addition prevail. However, the α,β-unsaturated carbonyl compound may also influence the course of reaction: either bulky substituents on the β carbon or higher relative reactivity of the carbonyl (*i.e.*, aldehyde > ketone > ester) leads to carbonyl addition.

Diphenylsulfonium cyclopropylide (**1**) behaves like dimethyloxosulfonium methylide in reactions with α,β-unsaturated carbonyl compounds. Thus, irreversible generation of ylide **1** *via* treatment of cyclopropyldiphenylsulfonium fluoroborate (**2**) with sodium methylsulfinyl carbanion in dimethoxyethane at −40°

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(2) For reviews, see E. J. Corey and M. Chaykovsky, *J. Amer. Chem. Soc.*, **87**, 1353 (1965).

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