washed with aqueous $NaHSO_3$ solution and analyzed by glc. Liquid and solid reaction products were also dissolved in ether and analyzed, after washing with $NaHSO_3$, by ir, nmr, and glc (after adding an internal standard to the solutions for quantitative analysis). The volatile products, such as methyl chloride, were also analyzed by mass spectroscopy.

$AgSbF_6$ Catalyzed Chlorination. A sample (0.03 mol) of the individual alkane was dissolved in 10 ml of CH_2Cl_2 and added to a solution of 0.015 mol of chlorine in 10 ml of CH_2Cl_2 in the dark at $-78°$. This mixture was then added at once into a well stirred solution of 0.003 mol of $AgSbF_5$ in 10 ml of CH_2Cl_2, which was kept at -15 or 25°, respectively. After the reaction was completed (for reaction conditions and times, see Table II), the reaction mixture was poured into an ice-cold aqueous solution of $NaHSO_3$ (to remove unreacted chlorine). After separation and drying the organic layer, a known amount of an internal standard was added and the products analyzed by ir, nmr, and glc. Attempts to chlorinate unbranched alkanes were carried out at 25 or 70° in a Monel reaction bomb.

Analysis of Reaction Mixtures. Product analyses were carried out using the following. Nmr analyses were carried out using a Varian Associates Model A56/60A spectrometer, with gas chromatographic analysis performed on a Perkin-Elmer Model 226 chromatograph, equipped with an electronic integrator and automatic readout system. Ir spectra were obtained on a Beckmann Model IR 10 spectrometer.

Gas chromatographic conditions and retention time (rt) were as follows.

Ethane: column A stainless steel open tubular column, 150 ft × 0.01 in.; stationary phase, squalane; column temperature, 60°; 12 psi He, pressure; retention times (sec) ethyl chloride (309), 1,1-dichloroethane (369), 1,2-dichloroethane (442), 1,1,1-trichloroethane (461), *n*-propyl chloride (506, standard).

Propane: column A (60°/12 psi); rt (sec), isopropyl chloride (464), *n*-propyl chloride (506), *n*-butyl chloride (610, standard).

***n*-Butane**: column A (80°/12 psi); rt (sec) 2-chlorobutane (365), 1-chlorobutane (395), *tert*-butyl chloride (331, standard).

Isobutane: column B stainless steel open tubular column, 150 ft × 0.01 in.; stationary phase; *m*-bis(*m*-phenoxyphenoxy)benzene + Apiezon L; column temperature, 40°; 20 psi He; rt (sec) *tert*-butyl chloride (220), *n*-butyl bromide (380, standard).

Isopentane: column B (40°/10 psi); rt (sec) 2-chloro-2-methylbutane (522), *n*-butyl bromide (780, standard).

Neopentane: column A (80°/20 psi); rt (sec) neopentyl chloride (265), 1,1-dichloro-2,2-dimethylpropane (650), norbornane (380, standard).

Cyclopropane: column B (40°/10 psi); rt (sec) isopropyl chloride (398), *n*-propyl chloride (429), *n*-butyl bromide (780, standard), 1,3-dichloropropane (339, 80°/30 psi).

Cyclopentane: column B (80°/30 psi); rt (sec) cyclopentyl chloride (324), 1,2-dichlorocyclopentane (490), cyclohexyl bromide (610, standard).

Cyclohexane: column B (80°/30 psi); rt (sec) cyclohexyl chloride (357), cyclohexyl bromide (610, standard).

Norbornane: column C stainless steel open tubular column, 150 ft × 0.01 in.; stationary phase; Carbowax 1540; column temperature, 60°; 30 psi He; rt (sec) norbornane (167), 7-chloronorbornane (552), 2-*exo*-chloronorbornane (571), 2-*endo*-chloronorbornane (593).

Adamantane: column D stainless steel open tubular column, 100 ft × 0.02 in.; stationary phase, butanediole succinate; column temperature, 80°; 20 psi He; rt (sec) 1-chloroadamantane (175), 2-chloroadamantane (190), 1-hydroxyadamantane (503), adamantane (30).

Acknowledgment. Support of our work by the National Science Foundation and the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

Nucleophilic Alkylidene Transfer Reagents. Ethylides, Isopropylides, and Cyclopropylides Derived from Salts of Sulfoximines[1]

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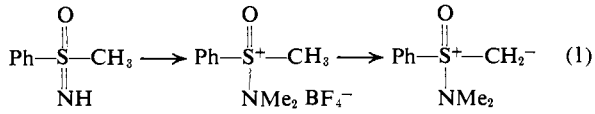
Contribution from the Department of Chemistry, Wayne State University, Detroit, Michigan 48202. *Received May 18, 1973*

Abstract: *S*-Ethyl-*S*-(*p*-tolyl)sulfoximine was converted to (dimethylamino)ethyl-*p*-tolyloxosulfonium fluoroborate (**4**), which provided ethylide **5** upon treatment with base. Ethylide **5** reacted to insert an ethylidene group across the double bond of the carbonyl of aldehydes and ketones, an imine, and electrophilic olefins to yield oxiranes, aziridine, and cyclopropanes (Table I). *S*-Isopropyl-*S*-(*p*-tolyl)sulfoximine was converted to (dimethylamino)isopropyl-*p*-tolyloxosulfonium fluoroborate, which was the precursor to ylide **9**. Ylide **9** was also generated by reaction of ylide **5** with methyl iodide followed by treatment with 1 equiv of base. Isopropylide **9** was shown to react with benzalacetophenone to yield *trans*-1-benzoyl-2-phenyl-3,3-dimethylcyclopropane and with *trans*-dibenzoylethylene to give *trans*-1,2-dibenzoyl-3,3-dimethylcyclopropane. *S*-Phenyl-*S*-cyclopropylsulfoximine was prepared and converted to (dimethylamino)cyclopropylphenyloxosulfonium fluoroborate which upon treatment with sodium hydride provided the cyclopropylide **13**. Ylide **13** reacted with benzalacetophenone to give *trans*-1-benzoyl-2-phenylspiropentane, with β-dimethylaminopropiophenone to give benzoylspiropentane, with α-methyl-β-dimethylaminopropiophenone to give 1-benzoyl-1-methylspiropentane, with mesityl oxide to give 1-acetyl-2,2-dimethylspiropentane, and with cyclohexanone to give 10-oxadispiro[2.0.5.1]decane which rearranged to spiro[3.5]nonan-1-one. (+)-(*R*)-(Dimethylamino)cyclopropyl-*p*-tolyloxosulfonium fluoroborate was prepared and used to generate a chiral cyclopropylide, from which several optically active spiropentanes were prepared. *S*-3-Chloropropyl-*S*-(*p*-tolyl)sulfoximine spontaneously cyclized to *S*-(*p*-tolyl)-*N*,*S*-trimethylenesulfoximine which was reacted with trimethyloxonium fluoroborate to yield 2-methyl-1-oxo-1-*p*-tolyl-2,1-azathiolanium fluoroborate.

Sulfonium ylides are extensively used in organic chemistry to achieve the stepwise insertion of a methylene or substituted methylene across the double bond of a carbonyl, an imine, or an electrophilic olefin to yield an oxirane, an aziridine, or a cyclopropane,

(1) Part XLIV in the series Chemistry of Sulfoxides and Related Compounds. We gratefully acknowledge support by the National Science Foundation (GP 19623).

respectively.[2] In a series of previous communications[3] and papers[4,5] we have revealed the production and utility of a new series of oxosulfonium ylides derived from sulfoximines (*e.g.*, eq 1); this chemistry provides



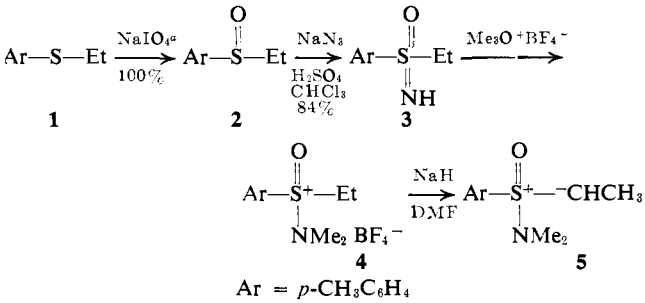
(1)

the only practical method of structural variation of oxosulfonium ylides.

In this paper we detail the preparation of salts and derived ylides useful in nucleophilic ethylidene, isopropylidene, and cyclopropylidene transfer reactions.

Ethyl *p*-tolyl sulfide (**1**) was synthesized as outlined in Scheme I. Conversion of **2** to the sulfoximine **3** using

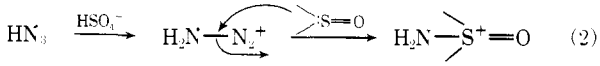
Scheme I



Ar = *p*-$CH_3C_6H_4$

[a] C. R. Johnson and J. E. Keiser, *Org. Syn.*, **46**, 78 (1967).

1 equiv of sodium azide and 2 equiv of sulfuric acid proved facile (84% yield).[6] We suggest that this reaction proceeds by the generation of a protonated hydrazoic acid intermediate which is susceptible to nucleophilic displacement of nitrogen by sulfoxide (eq 2).



(2)

When 1 equiv of concentrated sulfuric acid was used, no reaction took place.

Exhaustive alkylation of **3** with trimethyloxonium fluoroborate gave pure (dimethylamino)ethyl-*p*-tolyloxonium fluoroborate (**4**) in 79% yield. Dimethylamino-*p*-tolyloxosulfonium ethylide (**5**) was generated from salt **4**. The only advantage of using DMF rather than DMSO (mp 18°) was that **5** could be generated and reacted at 0° without the solvent freezing; this allowed the control of initial exothermicity and the possible resulting ylide decomposition. Ylide **5** was formed at 0° and allowed to stir at that temperature for 5 days, after which time 1 equiv of dimethyl maleate was added, resulting in a 62% yield of the expected cyclopropane (see Table I). When this experiment was repeated at 25°, a yield of only 19% was obtained.

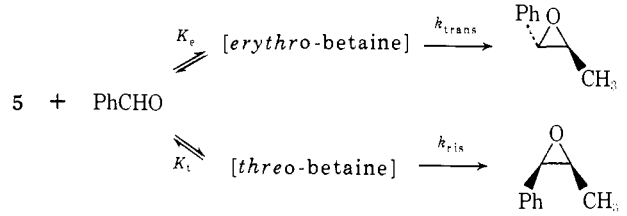
Ylide **5** underwent reaction with a variety of α,β-unsaturated esters, ketones, nitriles, and also with Mannich bases to give cyclopropanes in 66–95% yield (Table I). The formation of *trans*-cyclopropanes from the reaction of electrophilic cis olefins with dimethylaminophenyloxosulfonium methylide has been reported.[4] Similarly, ylide **5** reacted with dimethyl maleate to produce exclusively the *trans*-dicarbomethoxymethylcyclopropane. The trans/cis ratios, where shown in Table I, were judged based on the generality that the *cis*-methyl is that appearing at higher field[7] in the nmr spectrum of a mixture of the isomers.

Lehmann, Miller, and Wiechert have demonstrated that dimethyloxosulfonium methylide formed cyclopropanes by reaction with appropriate Mannich bases.[8] Although our ylide **5** performed well with the Mannich bases of acetophenone and propiophenone as shown in Table I, the ethylide failed to react with either the Mannich base of cyclohexanone or its quaternary salt.

Ethylide **5** reacted with a variety of electrophilic substrates containing doubly bonded oxygen or nitrogen, to give the corresponding three-membered heterocycle (Table I). With 4-*tert*-butylcyclohexanone only the (*Z*)-oxirane was found. The trans/cis stereochemical relationship of aryl *vs.* methyl for the adducts of benzaldehyde, *p*-chlorobenzaldehyde, acetophenone, and benzalaniline was determined by nmr chemical shift and coupling constant data.[7] The trans isomers were found, as expected, to be predominant in the adducts of *p*-chlorobenzaldehyde and benzaldehyde. However, the cis isomer prevailed in the adduct of acetophenone and was the exclusive product in the reaction with benzalaniline.

A detailed rationalization of the stereochemical results presented by the products in Table I does not seem to be justified on the basis of the limited data. To focus on the complexity of the situation consider the reaction of **5** with benzaldehyde (Scheme II). Based on a study

Scheme II



involving methylene transfer, we assume that betaine formation is reversible.[9] The final product ratios will depend on K_e/K_t and k_{trans}/k_{cis}. The stabilities of the diastereomeric betaines may be influenced, not only by steric factors, but also by electronic interactions including the possibility of sulfurane formation.

Isopropylide

Reaction of sulfoxide **6** with sodium azide–sulfuric acid produced the desired sulfoximine **7** in only 17% yield. As an alternate approach the *N*-tosylsulfoximine **8** was hydrolyzed with sulfuric acid; again the yield of the desired sulfoximine was low (eq 3). These problems can be traced to heterolysis of the carbon–sulfur bond of the sulfonium salts formed by protonation of sulfoxides or sulfoximines in the acidic and polar reaction media. This is a serious and very gen-

(2) A. W. Johnson, "Ylid Chemistry," Academic Press, New York, N. Y., 1966.

(3) (a) C. R. Johnson, E. R. Janiga, and M. Haake, *J. Amer. Chem. Soc.*, 90, 3890 (1968); (b) C. R. Johnson and C. W. Schroeck, *ibid.*, 90, 6852 (1968); (c) C. R. Johnson, G. F. Katekar, R. F. Huxol, and E. R. Janiga, *ibid.*, 93, 3771 (1971).

(4) C. R. Johnson, M. Haake, and C. W. Schroeck, *ibid.*, 92, 6594 (1970).

(5) (a) C. R. Johnson and L. J. Pepoy, *J. Org. Chem.*, 37, 671 (1972); (b) C. R. Johnson and P. E. Rogers, *ibid.*, 38, 1793, 1798 (1973).

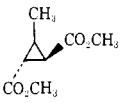
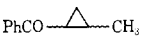
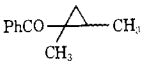
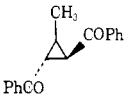
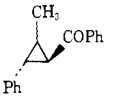
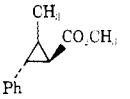
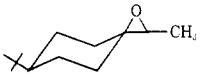
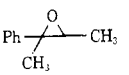
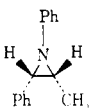
(6) H. R. Bentley and J. K. Whitehead, *J. Chem. Soc.*, 2081 (1950).

(7) L. M. Jackman and S. Sternhill, "Application of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, London, 1969, p 227.

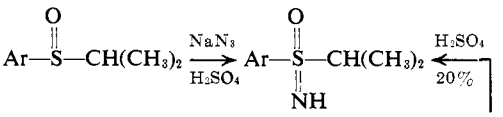
(8) H.-G. Lehmann, H. Miller, and R. Wiechert, *Chem. Ber.*, 98, 1470 (1965).

(9) C. R. Johnson and C. W. Schroeck, *J. Amer. Chem. Soc.*, 93, 5303 (1971).

Table I. Reactions of Ylide 5

Substrate	Product	Stereochemistry[a]	Isolated yield, %
Dimethyl fumarate			73
Dimethyl maleate			66
trans-Cinnamonitrile		9:1[b]	73
β-Dimethylaminopropiophenone		*c*	69
α-Methyl-β-dimethylamino-propiophenone		*c*	74
trans-Dibenzoylethylene			93
trans-Chalcone		1:1[b]	85
trans-Methyl cinnamate		3:2[b]	86
4-*tert*-Butylcyclohexanone		*Z* only	88
p-Chlorobenzaldehyde		55:45[b]	78
Benzaldehyde		3:2[b]	67
Acetophenone		2:3[b]	62
Benzalaniline		Cis only	35

[a] Ascertained by nmr chemical shift and coupling constant data. [b] Approximate ratio of trans/cis phenyl/methyl determined by integration of nmr spectra. [c] Stereochemical ratio not determined.



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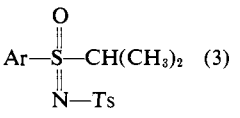
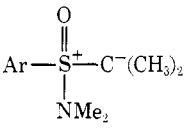


8

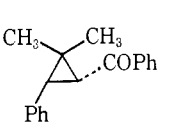
eral problem in sulfur chemistry; tertiary and even secondary alkyl groups tend to be lost from sulfur (as carbonium ions) when positive charge is built up on sulfur in polar media.

The N,N-dimethylated salt of **7** was prepared and treated with sodium hydride in DMF to provide ylide **9**. Isopropylide **9** upon reaction with benzalacetophenone and *trans*-dibenzoylethylene gave **10** (51%) and **11** (85%), respectively.

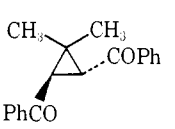
It was hoped that alkylation[10] of the ethylide **5** with a slight excess of methyl iodide would provide the isopropylsulfonium salt free of **4**. When the reaction was run the new salt was not isolated but converted directly to ylide **9** by reaction with 1 equiv of sodium hydride.



9



10



11

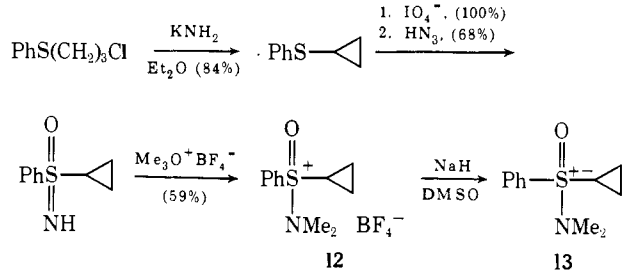
Reactions of solutions of **9** thus prepared with benzalacetophenone and dibenzolyethylene gave the cyclopropanes **10** (67%) and **11** (88%) in yields comparable to those previously obtained. Contaminants from ethylide adducts went unnoticed since **10** and **11** were purified by recrystallization. An analysis by vpc of the product mixture obtained by reaction of **9** (prepared from **5**) and dimethyl fumarate revealed that the *trans*-dimethyl 3,3-dimethylcyclopropane-1,2-dicarboxylate was contaminated with 5% of the ethylide adduct.

(10) For an earlier example of alkylation of an ylide, see E. J. Corey, M. Jautelat, and W. Oppolzer, *Tetrahedron Lett.*, 2325 (1967).

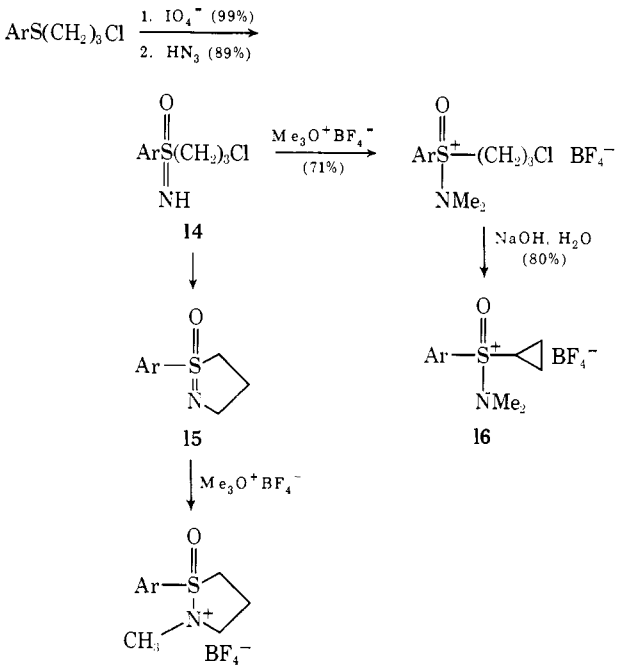
Cyclopropylides

Schemes III and IV outline alternate routes for the

Scheme III

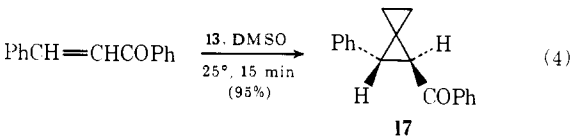


Scheme IV



generation of cyclopropylide precursors. For preparation scale Scheme III is preferable. The slow, spontaneous cyclization of **14** to **15** provided an interesting sidelight to the second route. At the time no previous examples of sulfoximines with the sulfur and nitrogen contained within a ring had been reported.[11]

At room temperature the half-life of the cyclopropylide **13**, estimated by nmr observations in DMSO-d_6 of the production of *N,N*-dimethylbenzenesulfinamide, is approximately 4 days. Reaction of ylide **13** with unsaturated carbonyl compounds (or Mannich bases) gave substituted spiropentanes (eq 4–7). The 1-acetyl-2,2-

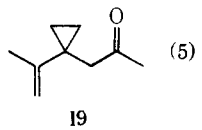


(4)

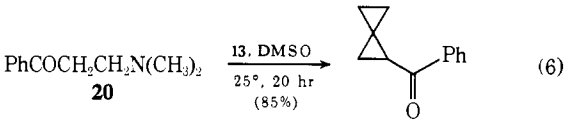
dimethylspiropentane from the mesityl oxide reaction underwent a quantitative rearrangement at 70° to 1-acetonyl-1-isopropenylcyclopropane. A similar thermolysis of 1-acetyl-2,2-dimethylcyclopropane has been reported.[12]

(11) For other examples, see T. R. Williams and D. J. Cram, *J. Amer. Chem. Soc.*, **93**, 7333 (1971); P. Stoss and G. Satzinger, *Angew. Chem., Int. Ed. Engl.*, **10**, 79 (1971).

(12) R. M. Roberts and R. G. Landolt, *J. Amer. Chem. Soc.*, **87**, 2281 (1965).



(5)

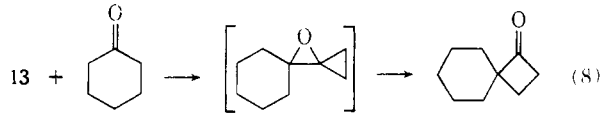


(6)

(7)

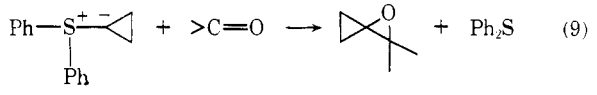
The reactions of several ketones and aldehydes with **13** were examined in an attempt to synthesize the corresponding oxaspiropentanes. The reaction of **13** with benzaldehyde and *p*-chlorobenzaldehyde produced polymeric material, whereas with acetophenone, much starting ketone (40%) was recovered along with polymer. The cyclopropylide reacted as a base with aliphatic ketones, such as 2-pentanone and cyclopentanone, and *n*-heptanal in producing self-condensation products. Cycloheptanone was recovered unchanged after 48 hr of reaction.

In contrast to other ketonic substrates, **13** did react with cyclohexanone to produce the desired adduct. An infrared of the product mixture showed no carbonyl band. However, the oxaspiropentane rearranged to the known cyclobutanone **22** on isolation by preparative vpc (eq 8).[13]



(8)

Trost and coworkers have been more successful in nucleophilic cyclopropylidene transfer to carbonyl groups utilizing ylide **23** (eq 9).[14] Apparently the high

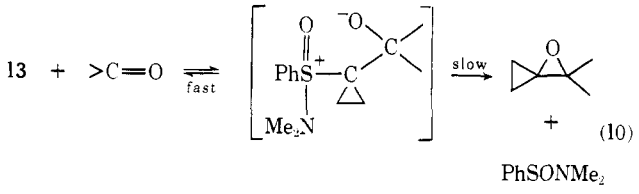


(9)

order of stability of ylide **13** and the relatively unfavorable, even though intramolecular, nucleophilic displacement at a cyclopropyl carbon required for collapse of the betaine to product combine to make the transfer from **13** unfavorable (eq 10). Trost has made the suggestion that such transfers do not occur at all by displacement at carbon, but involve collapse of sulfurane intermediates.[14c,d]

(13) J. R. Wiseman and H.-F. Chan, *ibid.*, **92**, 4749 (1970).

(14) (a) B. M. Trost, R. LaRochelle, and M. J. Bogdanowicz, *Tetrahedron Lett.*, 3449 (1970); (b) B. M. Trost and M. J. Bogdanowicz, *J. Amer. Chem. Soc.*, **93**, 3773 (1971); (c) *Tetrahedron Lett.*, 887 (1972). (d) Recent observations by the Trost group indicate that these reactions in actual fact involve internal nucleophilic displacements at carbon (personal communication from Professor Trost).

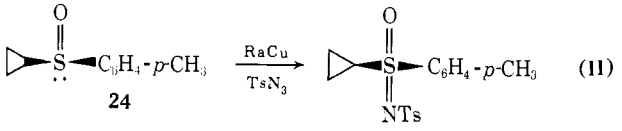


(10)

PhSONMe$_2$

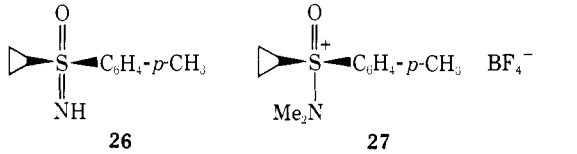
Chiral Cyclopropylide

Cyclopropyl Grignard, formed by an entrainment procedure,[15] was reacted with (−)-menthyl *p*-toluenesulfinate to yield (+)-(*R*)-cyclopropyl *p*-tolyl sulfoxide (**24**).[16] It was found that a range of rotations, $[\alpha]_D$ +218–268° (*c* 1, acetone), was obtained when this reaction was repeated several times. It was suspected that the hydroscopic nature of this sulfoxide was responsible for the inconsistent results, since the infrared and nmr of all the samples prepared were superimposable. However, to allay any doubt that racemization had occurred, the *N*-tosylsulfoximine derivative of the sulfoxides with the highest and the lowest rotation was separately prepared (eq 11).[17] Since there was



(11)

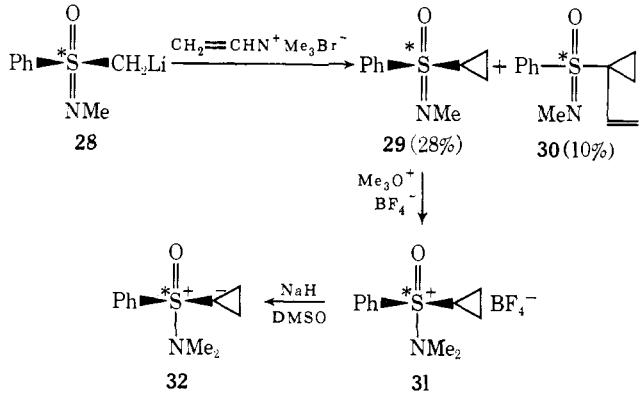
only 2% difference in rotation and the melting points of the two were identical, it seemed reasonable to assume the differences in the rotations of **25** were due to water present. The free sulfoximine **26** was prepared in 95% yield from sulfuric acid hydrolysis of **25**. An alternate method to **26** using hydrazoic acid was not attempted since it was known that sulfoxides racemize under these conditions.[3b] Pure **26** was successively methylated to give the cyclopropyl salt **27**. Although



25 and **26** had sharp melting points, all recrystallization efforts to obtain a narrow melting point (<5°) failed for **27**. All intermediates in the sequence and **25** itself were carefully examined by all applicable techniques of analyses, and the results were found to be consistent with the expected structure. For unexplained reasons, the ylide from **27** gave extremely low yields after reaction with substrates which had previously been successful with cyclopropylide **16**. Therefore, a new method of entry into the cyclopropyl system was devised.

Previously, it has been shown that the lithium anion of (+)-(*S*)-*N*,*S*-dimethyl-*S*-phenylsulfoximine (**28**) would undergo 1,2 addition to carbonyls and 1,4 addition to unsaturated systems.[9] Also, von Doering and Schreiber had reported the failure of weak bases, such as hydroxide, ethoxide, or thioethoxide, to add to vinyltrimethylammonium bromide.[18] However, it was found that the anion of **28** was sufficiently nucleophilic to undergo addition, and, after intermolecular proton exchange, expulsion of trimethylamine by intramolecular cyclization to give the irreversible product **29**. Chiral **29**, which is more acidic than **28**, also reacted to some extent with another mole of the vinyl compound to yield the α-substituted cyclopropane **30** by an addition–β-elimination mechanism. After treatment with trimethyloxonium fluoroborate the dimethylated salt **31** was isolated with little difficulty and in excellent yield (Scheme V).

Scheme V



The salt **31** was converted to the ylide **32** with sodium hydride in DMSO. Data on reactions of the chiral ylide **32** are summarized in Table II. At this time we cannot comment upon the optical purity of these products. By using optically active methylides in this series we have prepared optically active cyclopropanes in optical purities ranging from 15 to 35%.

Table II. Reactions of Chiral Ylide **32**

Substrate	Product	Rotation, $[\alpha]_D$ 25° (*c* 1, acetone)	Yield, %
Benzalacetophenone	**17**	−10.5	89
3-Dimethylamino-1-phenyl-1-propanone	**20**	−4.1	81
3-Dimethylamino-2-methyl-1-phenyl-1-propanone	**21**	−1.1	41

Experimental Section

General. Melting points were determined with a Thomas-Hoover melting point apparatus and are uncorrected. Optical rotations were measured on a Perkin-Elmer 141 polarimeter using a 1-dm cell. Infrared spectra were obtained on a Perkin-Elmer 137 infracord. Nuclear magnetic resonance (nmr) spectra were obtained on a T-60 spectrometer. Microanalyses were performed by Midwest Microlab, Inc., Indianapolis, Ind. 46226. All sulfoxides were prepared by an adaptation of the periodate procedure for the preparation of methyl phenyl sulfoxide.[19]

Ethyl-*p*-tolylsulfoximine (3). In a 500-ml, three-necked flask equipped with a condenser, mechanical stirrer, and an additional funnel, a mixture of 40.0 g (0.238 mol) of *p*-tolyl ethyl sulfoxide (bp 99–100° (0.12 mm)), 30.9 g (0.476 mol) of sodium azide, and 240 ml of chloroform was cooled in an ice bath. To this slurry, 59.5 ml of concentrated sulfuric acid was added over 15 min. The

(15) H. M. Walborsky and A. E. Young, *J. Amer. Chem. Soc.*, **86**, 3288 (1964).

(16) (a) K. Mislow, M. M. Green, P. Laur, J. T. Melillo, T. Simmons, and A. L. Ternay, Jr., *ibid.*, **87**, 1958 (1965); (b) K. K. Anderson, *Tetrahedron Lett.*, 93 (1962).

(17) H. Kwart and A. A. Kahn, *J. Amer. Chem. Soc.*, **89**, 1950 (1967).

(18) W. von E. Doering and D. C. Schreiber, *ibid.*, 77, 514 (1955).

(19) C. R. Johnson and J. E. Keiser, *Organic Synthesis*, **46**, 78 (1967).

mixture was then warmed to 45° using an oil bath and maintained at this temperature for 13 hr. After cooling, 300 ml of ice–water was added. After all of the salts had dissolved, the chloroform was separated, and the aqueous layer was reextracted with 100 ml of chloroform. The organic portions were dried (Na_2CO_3) and the solvent was removed leaving 6.5 g (16%) of unchanged sulfoxide. The aqueous layer was made slightly alkaline with 20% sodium hydroxide solution and then thoroughly extracted with chloroform. After drying over magnesium sulfate, evaporation of the solvent yielded 36.6 g (84%) of the sulfoximine as a pale yellow oil: ir (neat) 3250, 1600, 1220, 1100, 975, 820, and 720 cm^{-1}; nmr (CCl_4) δ 7.8–8.1 (q, 4), (q, 4), 3.15 (s, 1, NH), 3.0 (q, 2, CH_2), 2.36 (s, 3, CH_3), 1.1 (t, 3).

(Dimethylamino)ethyl-*p*-tolyloxosulfonium Fluoroborate (4). To a magnetically stirred solution of 36.0 g (0.197 mol) of *p*-tolylethylsulfoximine in 250 ml of methylene chloride at 0° was added 37 g (0.25 mol) of trimethyloxonium fluoroborate in a 500-ml erlenmeyer flask. The flask, fitted with a $CaCl_2$ drying tube, was allowed to warm and was maintained at room temperature for 2 hr. Sodium carbonate (30 g, 0.25 mol) was added and the mixture was stirred for 8 hr at room temperature. Another portion (38.5 g, 0.256 mol) of trimethyloxonium fluoroborate was added and stirring continued. After 2 hr at room temperature, an additional 15 g (0.5 equiv) was added to ensure exhaustive alkylation. After 1 hr, the reaction solution was filtered to remove inorganic salts. The solution was concentrated to one-third volume and enough ether (500 ml) was added to precipitate all of the organic salt, yielding 49.2 g (83.5%) of a tan powder (mp 124.5–127.6°). Recrystallization of the sulfoximine salt from isopropyl alcohol yielded 46.2 g (78.5%) of white needles: mp 128–129°; ir (Nujol) 1600, 1220, 1050, 840, 750, 700 cm^{-1}; nmr ($CDCl_3$) δ 8.2–7.5 (q, 4, *p*-tolyl), 4.6–3.8 (m, 2, CH_2CH_3), 3.2 (s, 6, NMe_2), 2.6 (s, 3, *p*-CH_3), 1.35 (s, 3, CH_2CH_3).

(Dimethylamino)-*p*-tolyloxosulfonium Ethylide (5). To a flame-dried 10-ml gas-inlet flask fitted with a serum stopper and exhaust tube was added 76 mg (3.16 mmol) of sodium hydride (as a 59.4% dispersion in mineral oil), while maintaining a continuous stream of anhydrous nitrogen within the reaction vessel. The sodium hydride was washed free of mineral oil by repeated hexane washings and decantings and then blown dry by the nitrogen stream. To the light gray powder was syringed 5 ml of dry dimethylformamide (distilled from calcium hydride and stored over molecular sieves 4A under a cover of nitrogen) and the dispersion was cooled with an ice bath. To this, 1.00 g (3.34 mmol) of (dimethylamino)ethyl-*p*-tolyloxosulfonium fluoroborate was added at once as a solid, whereupon a vigorous evolution of hydrogen took place. After 5 min, the ice bath was removed and the reaction was allowed to warm to 25°. After 30 min of rapid stirring, a homogeneous yellow solution was observed.

Work-up Procedure for Alkylidene Transfer Reactions. At the end of the reaction period the mixture was poured into 25–50 ml of water, followed by extraction three times with equal volumes of ether or pentane. The combined extracts were washed with water, dried (Na_2CO_3 or $MgSO_4$), and concentrated. The residue was chromatographed on silica gel using ether–pentane (5:95) or benzene as eluent.

***trans*-Dimethyl 3-Methylcyclopropane-1,2-dicarboxylate.** The ethylide **5** was prepared from 1.0 g (3.34 mmol) of **4** and 80 mg (3.34 mmol) of sodium hydride in 5 ml of DMF. To the stirring solution was added 400 mg (2.67 mmol) of dimethyl fumarate as a solid. After 5 hr at 25°, the reaction was worked up to yield 0.334 g (72%) of a slightly yellow oil: ir (neat) 1730, 1200 cm^{-1}; nmr ($CDCl_3$) δ 3.75 (s, 3, OCH_3), 3.70 (s, 3, OCH_3), 2.5–1.6 (m, 3, CH's), 1.27 (d, 3, CCH_3). The same product was also obtained by substituting dimethyl maleate for the dimethyl fumarate.

1-Phenyl-2-cyano-3-methylcyclopropane. The ethylide **5** was prepared from 1.50 g (5.02 mmol) of **4** and 0.120 g (5.02 mmol) of sodium hydride in 6 ml of DMF. To the stirring solution was added 0.500 g (3.87 mmol) of *trans*-cinnamonitrile in 2 ml of DMF. After 2 days at 0–5° and 1 day at 25°, the reaction was worked up to yield 0.451 g (73%) of an oil: ir (neat) 2220, 1600, 740, 695 cm^{-1}; nmr ($CDCl_3$) δ 7.4–6.8 (m, 5, Ph), 2.2–1.9 (m, 1), 1.7–1.3 (m, 6, cyclopropylmethyl). See Table I.

1-Benzoyl-2-methylcyclopropane. The ethylide **5** was prepared from 2.00 g (6.68 mmol) of **4** and 4.18 ml (6.68 mmol) of *n*-butyllithium (1.6 *M* in hexane) in 15 ml of DMSO. To the reaction was added a solution of 0.904 g (5.10 mmol) of 3-dimethylaminopropriophenone in 2 ml of DMSO. After stirring for 22 hr at 25°, the reaction was worked up to yield 0.564 g (69%) of a slightly yellow oil: ir (neat) 1670, 1200, 700 cm^{-1}; nmr (CCl_4) δ 8.2–7.1 (m, 5, Ph), 2.8–2.1 (m, 1, CHCO), 1.9–0.6 (m, 6, CH_2CHCH_3).

1-Benzoyl-1,2-dimethylcyclopropane. The ethylide **5** was prepared from 1.80 g (6.0 mmol) of **4** and 3.61 ml (6.0 mmol) of *n*-butyllithium (1.6 *M* in hexane) in 10 ml of DMSO. To the reaction was added a solution of 0.957 g (5.0 mmol) of α-methyl-β-dimethylaminopropiophenone in 2 ml of DMSO. After stirring for 21 hr at 25°, the reaction was worked up to yield 644 mg (74%) of a yellow oil: ir (neat) 1670, 1280, 1200, 990, 710 cm^{-1}; nmr (CCl_4) δ 7.8–7.2 (m, 5, Ph), 1.6–0.8 (m, 8), 0.3–1 (m, 1).

***trans*-1,3-Dibenzoyl-2-methylcyclopropane.** The ethylide **5** was prepared from 1.00 g (3.34 mmol) of **4** and 0.076 g (3.16 mmol) of sodium hydride in 5 ml of DMF. To the stirring solution was added 0.711 g (3.01 mmol) of dibenzoylethylene at once as a solid. The resulting tan colored solution was stirred for 30 min at 25° and worked up to yield a viscous oil which crystallized on standing. The crude solid was recrystallized from absolute ethanol, to give 740 mg (93%) of a white solid: mp 76–77°; ir (Nujol) 1670, 1200, 700, 685 cm^{-1}; nmr ($CDCl_3$) δ 8.2–7.3 (m, 10, Bz's), 3.5 (d, 2, CHBz's), 2.7–2.1 (m, 1, $CHCH_3$), 1.25 (d, 3, CH_3).

***trans*-(1-Benzoyl-2-phenyl)-3-methylcyclopropane.** The ethylide **5** was prepared from 1.00 g (3.34 mmol) of **4** and 76.0 mg (3.67 mmol) of sodium hydride in 5 ml of DMF. To the stirring solution was added 0.594 g (2.84 mmol) of *trans*-chalcone at once as a solid. The resulting slightly yellow solution was stirred for 16 hr at 0–5° and 1 hr at 25° and then worked up to yield a crude solid which, after recrystallization from cold pentane, gave 0.574 g (85%) of a white solid: mp 79–80°; ir (melt) 1670, 1220, 740, 700 cm^{-1}; nmr ($CDCl_3$) δ 8.2–7.0 (m, 10, Ph's), 3.2–2.7 (m, 2, PhCHCHCO-Ph), 2.4–1.7 (m, 1, $CHCH_3$), 1.25 and 1.05 (d, 3, isomeric CH_3 [1:1]).

***trans*-(1-Phenyl-2-carbomethoxy)-3-methylcyclopropane.** The ethylide was prepared from 1.00 g (3.34 mmol) of **4** and 80 mg (3.34 mmol) of sodium hydride in 6 ml of DMF. To the stirring solution was added a solution of 0.271 g (1.67 mmol) of methyl cinnamate in 2 ml of DMF. After 100 hr, the mixture was worked up to yield 0.273 g (86%) of an oil: ir (neat) 1730, 1180, 745, 695 cm^{-1}; nmr ($CDCl_3$) δ 7.3–6.9 (m, 5, Ph), 3.74 (s, 3, OCH_3), 3.0–0.8 (m, 6). The methyl in the isomer with the phenyl and carbomethoxy trans appeared as a doublet at δ 1.35 and in the cis isomer at δ 0.9.

2-Methyl-3-*p*-chlorophenyloxirane. The ethylide **5** was prepared from 1.50 g (5.02 mmol) of **4** and 0.120 g (5.02 mmol) of sodium hydride in 5 ml of DMF. To the stirring solution was added 0.500 g (3.56 mmol) of *p*-chlorobenzaldehyde as a solid at once. After 86 hr at 0–5° and 1 hr at 25°, the reaction was worked up to yield 0.465 g (78%) of a slightly yellow oil: ir (neat) 1090, 1010, 955, 865, 835, 810 cm^{-1}; nmr ($CDCl_3$) δ 7.4–6.9 (m, 4, *p*-ClPh), 4.1–3.8 (m, 2, CH's), 1.45 and 1.05 (d, 3, CH_3)—isomeric ratio is approximately 55 trans:45 cis.

Reaction of the Ethylide 5 with 4-*tert*-Butylcyclohexanone. The ethylide **5** was prepared from 1.50 g (5.02 mmol) of **4** and 0.120 g (5.02 mmol) of sodium hydride in 5 ml of DMF. To the stirring solution was added 0.500 g (3.24 mmol) of 4-*tert*-butylcyclohexanone at once as a solid. After 4 days at 0–5° and 1 day at 25°, the reaction was worked up to yield 0.518 g (88%) of an oil whose spectral properties were identical with those of the known[20] *Z*-oxirane: ir (neat) 1030, 890 cm^{-1}; nmr (CCl_4) δ 2.7 (q, 1, CH), 1.2 (d, 3, CH_3), 0.9 (s, 9, *t*-Bu).

2-Phenyl-2,3-dimethyloxirane.[21] The ethylide **5** was prepared from 1.50 g (5.02 mmol) of **4** and 0.120 g (5.02 mmol) of sodium hydride in 5 ml of DMF. To the stirring solution was added a solution of 0.450 g (3.74 mmol) of acetophenone in 2 ml of DMF. After 4 days at 0–5° and 1 day at 25°, the reaction was worked up to yield 0.343 g (62%) of an oil: ir (neat) 1060, 910, 840, 765, 700 cm^{-1}; nmr (CCl_4) δ 7.5–7.1 (m, 5, Ph), 3.2–2.7 (m, 1, CH), 2.9 (s, 3, CH_3), 1.33 and 0.90 (d, 3, isomeric CCH_3).

***cis*-2-Methyl-1,3-diphenylaziridine.** The ethylide **5** was prepared from 1.00 g (3.34 mmol) of **4** and 0.0804 g (3.34 mmol) of sodium hydride in 5 ml of DMSO. To the stirring solution was added 0.543 g (3.00 mmol) of benzalaniline as a solid at once. After 25 hr at 25°, the reaction was worked up in the usual manner except that chromatography was performed on Woelm basic alumina to yield 220 mg (35%) of a yellow oil: ir (neat) 1600, 900, 770, 750,

(20) C. W. Schroeck, Ph.D. Dissertation, Wayne State University, 1971.

(21) E. J. Corey and W. Oppolzer, *J. Amer. Chem. Soc.*, **86**, 1899 (1964).

695 cm^{-1}; nmr ($CDCl_3$) δ 7.6–6.8 (m, 10, Ph's), 3.27 (d, 1, C*H*Ph), 2.5 (p, 1, C*H*CH_3), 1.15 (d, 3, CH_3).

Isopropyl-*p*-tolylsulfoximine (7) was prepared from *p*-tolyl isopropyl sulfoxide and sodium azide–concentrated sulfuric acid in a manner similar to that described previously for *p*-tolylethylsulfoximine. The sulfoximine was purified by sublimation (*ca.* 50° (0.1 mm)) and isolated as a white solid (17%): mp 62–63°; ir (melt) 1600, 1300, 1220, 1150, 1070, 830 cm^{-1}; nmr ($CDCl_3$) δ 7.9–7.3 (q, 4, *p*-tolyl), 3.2 (sept., 1, CH), 2.45 (s, 3, *p*-CH_3), 1.43 and 1.23 (d's, 6, CH(CH_3)$_2$).

(Dimethylamino)isopropyl-*p*-tolyloxosulfonium Fluoroborate. To an erlenmeyer flask containing 3.6 g (0.02 mol) of *p*-tolylisopropylsulfoximine in 20 ml of methylene chloride at 0° was added 5.9 g (0.04 mol) of trimethyloxonium fluoroborate. The reaction was warmed to room temperature and was magnetically stirred for 2 hr. The excess reagent was filtered and washed with methylene chloride. The solvent was removed under reduced pressure, and the resulting oil was dissolved in 10 ml of water. The acidic solution was neutralized to pH 10 and extracted three times with 50 ml of methylene chloride. The combined organic portions were dried (Na_2CO_3) and the volume was reduced to 20 ml. This process was repeated. Trimethyloxonium fluoroborate, 1.5 g (0.5 equiv), was added a third time and the reaction stirred for 1 hr at 25°. After filtration of excess alkylating agent, the methylene chloride was evaporated leaving a light brown precipitate. The precipitate was recrystallized in isopropyl alcohol to yield, after filtration, 2.0 g (35%)[22] of sulfoximine salt: mp 94–95°; ir (Nujol) 1600, 1250, 1175, 1050 (broad), 820 cm^{-1}; nmr ($CDCl_3$) δ 8.1–7.6 (q, 4, *p*-tolyl), 4.9 (septet, 1, CH), 3.15 (s, 6, NMe_2), 2.6 (s, 3, *p*-CH_3), 1.5 (d, 6, CH(CH_3)$_2$).

(Dimethylamino)-*p*-tolyloxosulfonium Isopropylide (9). The isopropylide was prepared from (dimethylamino)isopropyl-*p*-tolyloxosulfonium fluoroborate and sodium hydride in DMF in a manner similar to that previously described for the synthesis of (dimethylamino)-*p*-tolyloxosulfonium ethylide.

***trans*-(1-Phenyl-2-benzoyl)-3,3-dimethylcyclopropane (10). Method A.** The isopropylide **9** was prepared (2.01 mmol) in 5 ml of DMSO. To the stirring solution was added 0.379 g (1.80 mmol) of *trans*-chalcone as a solid at once. After 1 hr at 25° and 1 hr at 50°, the reaction was worked up to yield an oil which solidified on standing. The solid was recrystallized from pentane to give 0.230 g (51%) of white needles: mp 65–66°; ir ($CHCl_3$) 1700, 1600 (d) cm^{-1}; nmr ($CDCl_3$) δ 8.2–7.3 (m, 5, Bz), 7.25 (s, 5, Ph), 3.15 (d, 1, C*H*Ph), 2.90 (d, 1, C*H*Bz), 1.25 (s, 3, CH_3 cis to Bz), 1.15 (s, 3, CH_3 trans to Bz). The tentative assignments were based on comparison with the nmr of *trans*-dibenzoyl-2,2-dimethylcyclopropane.

Method B. The ethylide **5** was prepared from 1.00 g (3.34 mmol) of **4** and 0.0800 g (3.34 mmol) of sodium hydride in 2 ml of DMF. Upon addition of 0.21 ml (3.34 mmol) of methyl iodide, the reaction became white with a thick precipitate. After 5 ml of DMF was added to dissolve the solid, the reaction was treated with 0.076 g (3.16 mmol) of sodium hydride. To the stirring solution was added dropwise a solution of 0.629 g (3.01 mmol) of *trans*-chalcone in 2 ml of DMF. After 5 ml of DMF was added to dissolve the solid, the reaction was treated with 0.076 g (3.16 mmol) of sodium hydride. To the stirring solution was added dropwise a solution of 0.629 g (3.01 mmol) of *trans*-chalcone in 2 ml of DMF. After 10 min of continued stirring, the reaction was poured into 50 ml of water and extracted three times with 25 ml of ether. The combined ether extracts were washed successively with 50 ml of water, twice with 25 ml of 3 *N* aqueous hydrochloric acid (removal of sulfinamide), and with 50 ml of 2.5% aqueous sodium hydroxide. The solution was dried ($MgSO_4$) and concentrated, and the residue was passed over a short column of silica gel eluting with benzene. A crude solid was recrystallized from pentane, to yield 500 mg (67%) of a white solid (mp 63–64°) whose spectral data were identical with that of the above known compound (mp 65–66°).

***trans*-Dibenzoyl-2,2-dimethylcyclopropane (11). Method A.** The isopropylide **9** (2.87 mmol) was prepared in 6 ml of DMF. To the stirring solution was added dropwise a solution of 0.610 g (2.58 mmol) of *trans*-dibenzoylethylene in 4 ml of DMF. The brown solution was poured into a saturated sodium chloride solution (50 ml) immediately after completion of addition (*ca.* 10 min). The mixture was extracted with a total of 100 ml of ether and the organic phase was washed twice with 25-ml portions of water. The organic solution was dried ($MgSO_4$) and concentrated. The residue was chromatographed over a column of silica gel eluting with pentane, benzene, and ether yielding 0.515 g (85%) of an analytically pure white powder: mp 70–71°; ir (melt) 1660 (C=O), 1600, 725, 680 cm^{-1}; nmr ($CDCl_3$) δ 8.2–7.3 (m, 10, Bz), 3.6 (s, 2, CH's), 1.4 (s, 6, CH_3's).

Method B. In a manner similar to that described for the reaction of the isopropylide (prepared from the ethylide) with *trans*-chalcone, the isopropylide (3.34 mmol) was prepared and to it was added 0.711 g (3.01 mmol) of *trans*-dibenzoylethylene. After stirring for 10 min at 25°, the red-brown reaction was worked up in a manner identical with that of the above mentioned synthesis, yielding 0.737 g (88%) of a solid (mp 65–68°). The ir and nmr spectra were identical with that of the above known sample (mp 70–71°).

***trans*-Dimethyl 3,3-Dimethylcyclopropane-1,2-dicarboxylate.** In a manner similar to that previously described for the reaction of the isopropylide (*via* ethylide) with benzalacetophenone, the isopropylide (3.34 mmol) was prepared and to it was added 0.385 g (2.67 mmol) of dimethyl fumarate as a solid at once. After stirring for 3 hr, the reaction was worked up to yield 0.373 mg (75%) of an oil which, by vpc (8 ft–20% DEGS on CS 60–80), was shown to be 93% isopropylide adduct, 5% ethylide adduct, and 2% dimethyl fumarate by comparison with the retention times of known compounds.

***p*-Tolyl 3-chloropropyl sulfide** was prepared from the sodium salt of *p*-thiocresol and 1-bromo-3-chloropropane in a manner similar to that previously described for the synthesis of phenyl 3-chloropropyl sulfide.[23] After removal of solvent, the residue was distilled, bp 87–89° (0.08 mm), yielding 86 g (86%) of a colorless liquid: ir (neat) 1600, 1090, 950, 810 cm^{-1}; nmr ($CDCl_3$) δ 7.4–7.0 (q, 4, *p*-tolyl), 3.65 (t, 2, CH_2Cl), 3.0 (t, 2, CH_2S), 2.35 (s, 3, *p*-CH_3), 2.3–1.7 (m, 2, $CH_2CH_2CH_2$).

3-Chloropropyl *p*-tolyl sulfoxide was prepared from the corresponding sulfide and sodium metaperiodate. The solvent was removed under reduced pressure, and the resulting oil, 43 g (99%), showed one spot on tlc in various solvents: ir (neat) 1600, 1080, 1040, 1010, 950, 810 cm^{-1}; nmr ($CDCl_3$) δ 7.6–7.3 (q, 4, *p*-tolyl), 3.6 (t, 2, CH_2Cl), 3.2–2.7 (m, 2, CH_2S), 2.35 (s, 3, *p*-CH_3), 2.5–1.7 (m, 2, $CH_2CH_2CH_2$).

***S*-3-Chloropropyl-*S*-(*p*-tolyl)sulfoximine (14) and *S*-(*p*-Tolyl)-*N*,*S*-trimethylenesulfoximine (15).** *p*-Tolyl 3-chloropropyl sulfoxide was prepared from the corresponding sulfoxide and concentrated sulfuric acid–sodium azide in a manner similar to that previously described for the synthesis of ethyl-*p*-tolylsulfoximine. The solvent was removed under reduced pressure leaving a yellow oil, 40.2 g (89%). Upon standing, a precipitate formed (mp 151.5–152.0°) which was insoluble in methylene chloride and showed a broad absorption at 2500 cm^{-1} (N^+HCl^-). The compound was dissolved in water and neutralized with aqueous sodium hydroxide solution. After extraction with methylene chloride, drying ($MgSO_4$), and evaporation of solvent, a white solid remained. The solid was recrystallized from ether and determined to be *S*-(*p*-tolyl)-*N*,*S*-trimethylenesulfoximine: mp 74.5–75.5°; ir (melt) 1600, 1200, 1100, 900, 810 cm^{-1}; nmr ($CDCl_3$) δ 7.9–7.3 (q, 4, *p*-tolyl), 4.3–3.5 (m, 2, CH_2S), 3.3 (m, 2, CH_2N), 2.45 (s, 3, *p*-CH_3), 2.8–1.9 (m, 2, $CH_2CH_2CH_2$).

The remaining oil **14** was quickly subjected to alkylation with trimethyloxonium fluoroborate to avoid further loss of the desired free sulfoximine.

2-Methyl-1-oxo-1-*p*-tolyl-2,1-azathiolanium Fluoroborate. The sulfoximine salt was prepared from *S*-(*p*-tolyl)-*N*,*S*-trimethylenesulfoximine and 1 equiv of trimethyloxonium fluoroborate in methylene chloride at room temperature. The salt was precipitated by the addition of ether and recrystallized from tetrahydrofuran, yielding (92%) white crystals: mp 112–113°; ir (Nujol) 1600, 1230 (wk), 1100–1000 cm^{-1}; nmr ($CDCl_3$) δ 8.1–7.5 (q, 4, *p*-tolyl), 4.5–3.8 (m, 4, CH_2S and CH_2N), 3.1–2.6 (m, 2, $CH_2CH_2CH_2$), 2.9 (s, 3, CH_3N), 2.5 (s, 3, *p*-CH_3).

Dimethylamino-3-chloropropyl-*p*-tolyloxosulfonium Fluoroborate. The sulfoximine salt was prepared from 3-chloropropyl-*p*-tolylsulfoximine and trimethyloxonium fluoroborate in a manner similar to that previously described for the synthesis of dimethylaminoethyl-*p*-tolyloxosulfonium fluoroborate. The desired salt proved difficult to separate from the cyclized salt (above) by crystallization. An

(22) Future preparations should employ extraction of the product from a saturated sodium chloride solution to avoid loss of product through water solubility.

(23) H. E. Zimmerman and B. S. Thyagarajan, *J. Amer. Chem. Soc.*, **82**, 2505 (1960).

analytically pure compound was obtained (mp 88–89°) by repeated recrystallizations from methanol at 0°: ir (Nujol) 1600, 1050 (broad), 935 cm^{-1}; nmr ($CDCl_3$) δ 8.2–7.6 (q, 4, *p*-tolyl), 4.9–4.0 (m, 2, CH_2S), 3.7 (t, 2, CH_2Cl), 2.3 (s, 6, NMe_2), 2.55 (s, 3, *p*-CH_3), 2.4–1.8 (m, 2, $CH_2CH_2CH_2$).

Dimethylaminocyclopropyl-*p*-tolyloxosulfonium Fluoroborate (16). Method A. To a sodium hydride dispersion (57% in mineral oil) suspension in 5 ml of DMF at 0° under a nitrogen atmosphere was added at once as a solid 1 g (0.0029 mol) of dimethylamino-3-chloropropyl-*p*-tolyloxosulfonium fluoroborate. The reaction was allowed to warm to room temperature and magnetically stirred for 2 hr. The solvent was stripped under reduced pressure, and 10 ml of saturated sodium chloride solution was added. The aqueous solution was thoroughly extracted with methylene chloride. The combined organic portions were dried ($MgSO_4$), and the volume was reduced to 5 ml. Addition of ether precipitated the product (68%): mp 169.5–171.5°; ir (Nujol) 1600, 1050 (broad), 955 cm^{-1}; nmr ($CDCl_3$) δ 8.2–7.5 (q, 4, *p*-tolyl), 4.0–3.5 (m, 1, CH), 3.2 (s, 6, NMe_2), 2.55 (s, 3, *p*-CH_3), 2.2–0.8 (m, 4, CH_2CH_2).

Method B. To 5 ml of a 20% sodium hydroxide solution was added 0.5 g (0.0014 mol) of dimethylamino-3-chloropropyl-*p*-tolyloxosulfonium fluoroborate. The solution was stirred for 1 hr at room temperature and 4 hr at 60°. After the solution was cooled, 20 ml of saturated sodium chloride solution was added, and the aqueous phase was extracted with three 25-ml portions of methylene chloride. The combined organic extracts were dried ($MgSO_4$) and reduced to a volume of 6 ml. Ether was added and 0.357 g (80%) of the desired product was isolated.

***trans*-1-Phenyl-2-benzoylspiropentane (17).** The cyclopropylide (1.6 mmol) was prepared in 5 ml of DMF. To the stirring solution of ylide was added 0.295 g (1.42 mmol) of benzalacetophenone as a solid at once. After 15 min at 25°, the reaction was worked up to yield a yellow oil, which, after recrystallization from pentane, gave 0.332 g (95%) of a white solid: mp 62.5–63.5°; ir (melt) 1670, 1600, 1210, 750, 700 cm^{-1}; nmr ($CDCl_3$) δ 8.1–7.2 (m, 10, Ph and Bz), 3.3–3.1 (m, 2, CH's), 1.4–0.8 (m, 4, CH_2's).

Phenyl cyclopropyl sulfoxide was prepared in 98% yield from the corresponding sulfide[23] and sodium metaperiodate: ir (neat) 1580, 1080, 1040, 880, 750, 690 cm^{-1}; nmr ($CDCl_3$) δ 7.8–7.2 (m, 5, C_6H_5), 2.5–2.0 (m, 1, CH), 1.4–0.6 (m, 4, CH_2CH_2).

Phenylcyclopropylsulfoximine was prepared from the corresponding sulfoxide and concentrated sulfuric acid–sodium azide in a manner similar to that previously described for the synthesis of *p*-tolylethylsulfoximine. The sulfoxide was recovered in 26% yield, and the sulfoximine was produced in 68% yield based on 1 equiv of starting sulfoxide: ir (neat) 3250, 1580, 1220, 1100, 980, 885, 760, 720, 690 cm^{-1}; nmr ($CDCl_3$) δ 8.1–7.2 (m, 5, C_6H_5), 2.9 (s, 1. NH), 2.8–2.3 (m, 1, CH), 1.5–0.6 (m, 4, CH_2CH_2).

(Dimethylamino)cyclopropylphenyloxosulfonium Fluoroborate (12). The sulfoximine salt was prepared from cyclopropylphenyl sulfoximine and trimethyloxonium fluoroborate in a manner similar to that previously described for the synthesis of dimethylaminoisopropyl-*p*-tolyloxosulfonium fluoroborate. The crude fluoroborate was recrystallized from absolute ethanol, yielding 6.4 g (59%) of a white solid: mp 121–122°; ir (Nujol) 1060 (broad, BF_4), 950, 880, 740, 680 cm^{-1}; nmr ($CDCl_3$) δ 8.3–7.7 (m, 5, Ph), 3.9–3.5 (m, 1, CH), 3.2 (s, 6, NMe_2) 2.2–0.8 (m, 4, CH_2CH_2).

(Dimethylamino)phenyloxosulfonium Cyclopropylide (13). The cyclopropylide was prepared from (dimethylamino)cyclopropylphenyloxosulfonium fluoroborate and sodium hydride in DMSO in a manner similar to that previously described for the synthesis of (dimethylamino)-*p*-tolyloxosulfonium ethylide.

Benzoylspiropentane (20). The cyclopropylide (1.9 mmol) was prepared in 7 ml of DMSO. To the stirring solution was added a solution of 0.300 g (1.69 mmol) of β-dimethylaminopropiophenone in 1 ml of DMSO. After stirring for 20 hr at 25°, the reaction mixture was worked up to yield 0.260 g (86%) of a colorless oil: ir (neat) 1675, 1220, 1000, 970, 715, 690 cm^{-1}; nmr (CCl_4) δ 8.0–7.2 (m, 5, Ph), 2.90 (d of d, 1, CHBz), 1.78 (m, 1, CH cis to Bz), 1.7 (d of d, 1, CH trans to Bz), 1.1–0.6 (m, 4, CH_2CH_2).

1-Benzoyl-1-methylspiropentane (21). The cyclopropylide **13** was prepared from 1.00 g (3.37 mmol) of **12** and 0.0789 g (3.20 mmol) of sodium hydride in 5 ml of DMSO. To the stirring solution was added a solution of 0.600 g (3.17 mmol) of α-methyl-β-dimethylaminopropiophenone in 2 ml of DMSO. After 40 hr at 25°, the reaction was worked up to yield 0.334 g (57%) of a slightly yellow oil: ir (neat) 1675, 1600, 1280, 720, 700 cm^{-1}; nmr (CCl_4) δ 7.7–7.3 (m, 5, Ph), 1.85 (d, 1, CH cis to Bz), 1.45 (s, 3, CH_3), 1.2–0.6 (m, 5, CH trans to Bz and CH_2's).

1-Acetyl-2,2-dimethylspiropentane (18) and 1-Acetonyl-1-isopropenylphenylcyclopropane (19). The cyclopropylide **13** (3.2 mmol) was prepared in 5 ml of DMSO. To the stirring solution was added a solution of 0.285 g (2.90 mmol) of mesityl oxide in 2 ml of DMSO. After 24 hr at 25°, the reaction was poured into 50 ml of a saturated aqueous sodium chloride solution and extracted with three 50-ml portions of pentane. The combined pentane extracts were washed with 50 ml of saturated sodium chloride solution, dried (Na_2CO_3), and concentrated by distillation at atmospheric pressure. The residue was passed over a column of silica gel eluting with an ether–pentane mixture (10/90), to yield 0.244 mg (61%) of **18** as a slightly yellow oil: ir (neat) 1695, 1170 cm^{-1}; nmr (CCl_4) δ 2.1 (s, 3, CH_3CO), 1.95 (s, 1, CH), 1.25 (s, 3, CH_3 cis to Ac), 1.10 (s, 3, CH_3 trans to Ac), 1.0–0.5 (m, 4, CH_2CH_2).

Attempted distillation of the spiropentane from the crude reaction mixture resulted in a rearrangement to 1-acetonyl-1-isopropenylcyclopropane (**19**): ir (neat) 1710, 1650 (d), 895 cm^{-1}; nmr (CCl_4) δ 4.8 (m, 2, CH_2=C), 2.4 (s, 2, CH_2Ac), 2.1 (s, 3, CH_3CO), 1.7 (d, 3, CH_3-vinyl), 0.7–0.6 (m, 4, CH_2CH_2).

Reaction of Cyclopropylide with Cyclohexanone. The cyclopropylide **13** was prepared from 2.00 g (6.73 mmol) of **15** and 3.58 ml (6.73 mmol) of *n*-butyllithium (1.9 *M* in hexane) in 15 ml of DMSO. To the stirring solution was added a solution of 0.490 g (5.00 mmol) of cyclohexanone in 3 ml of DMSO. After 72 hr at 25°, the reaction was worked up. The residue, whose infrared showed very little cyclohexanone and no cyclobutanone, gave a streaked tlc plate in various solvent systems. Rearrangement of the dispiroepoxide to the spirocyclobutanone **22** occurred on isolation by preparative vpc (6 ft × 20% Carbowax 20M on C-W 60–80), yielding 0.170 (25%) of an oil whose ir and nmr were identical with that of the known compound: ir (neat) 1775 cm^{-1}; nmr (CCl_4) δ 2.92 (t, 2, CH_2CO), 1.75 (t, 2, CH_2CH_2CO), 1.8–1.2 (m, 10, cyclohexyl).

In a variation of the above synthesis using dimsylsodium as base and a threefold excess of cyclohexanone (later removed by washing with sodium bisulfite), a 40% yield of the spirocyclobutanone **22** was realized under similar reaction conditions and isolation techniques.

(+)-(*R*)-Cyclopropyl *p*-Tolyl Sulfoxide (24). A solution of 28.6 g (0.09 mol) of (−)-menthyl *p*-toluenesulfinate[16] in 300 ml of anhydrous tetrahydrofuran (THF) was added dropwise to a solution of cyclopropylmagnesium bromide at 0°. The Grignard reagent was prepared by an entrainment procedure[15] using 14.6 g (0.078 mol) of ethylene dibromide, a few crystals of iodine, 5.35 g (0.22 g-atom) of magnesium, and 14.5 g (0.12 mol) of cyclopropyl bromide in 50 ml of THF. This reagent was diluted with 100 ml of THF before the addition of the ester. The addition was completed over a 45-min period; the mixture was allowed to stir for an additional 12 hr at 25° and then poured into 500 ml of a saturated aqueous ammonium chloride solution. This mixture was vigorously stirred for 1 hr and thoroughly extracted with methylene chloride. The organic portions were evaporated and 700 ml of 10% sodium hydroxide solution was added to the residue. The menthol was then "steam distilled" by heating on a rotary evaporator under reduced pressure. The water was replenished and the distillation continued until the distillate came over clear. The pot residue was extracted several times with chloroform. The solution was dried over magnesium sulfate and evaporated, to yield 11.3 g of a brown oil. It was necessary to purify the sulfoxide further by elution chromatography using silica gel absorbent on a 3 ft × 1 in. column. Fast moving components were removed with benzene, and the desired sulfoxide was eluted with ether (1.5 l), to yield 8.1 g (50%) of a slightly yellow oil: $[\alpha]D$ +268° (*c* 1, acetone). This sulfoxide is extremely hydroscopic, and an accurate rotation is difficult to obtain.

(−)-(*R*)-*N*-(*p*-Tolysulfonyl)-*S*-cyclopropyl-*S*-(*p*-tolyl)sulfoximine (25). This compound was prepared from (+)-cyclopropyl *p*-tolyl sulfoxide (**24**) and tosyl azide.[17] After removal of solvent, the viscous oil was crystallized from absolute ethanol. The hydroscopic nature of the sulfoxide is evident from the data for three of the azide reactions. For sulfoxides with $[\alpha]D$ +218, +240, +268° (*c* 1, acetone) yields of 43, 51, and 63%, respectively, were obtained of a white solid: mp 117.5–118.5°; $[\alpha]D$ −146, −143, and −149°, respectively (*c* 1, acetone); ir (KBr) 1590, 1300, 1230, 1150, 1050 (broad), 870, 820, 760 cm^{-1}; nmr ($CDCl_3$) δ 8.0–7.1 (m, 8, *p*-tolyl), 3.1–2.5 (m, 1, CH), 2.5 (s, 3, *p*-methylphenylsulfoximine), 2.4 (s, 3, *p*-methylphenylsulfonyl), 1.8–0.6 (m, 4, CH_2CH_2).

(−)-(*R*)-*S*-Cyclopropyl-*S*-(*p*-tolyl)sulfoximine (26). A solution of 7.0 g (0.02 mol) of (−)-(*R*)-**25**, $[\alpha]D$ −149.3° (*c* 1, acetone), in 35 ml of concentrated sulfuric acid was stirred at 25° for 15 min. The slightly yellow solution was added dropwise to 250 ml of 20%

sodium hydroxide solution maintained at 0°. The alkaline solution was extracted several times with methylene chloride, and the combined organic extracts were dried (Na_2CO_3) and evaporated, to yield 3.8 g of a yellow oil which solidified. The crude precipitate was dissolved in ether; pentane was added until no more crystallization took place, to yield 3.7 g (95%) of a white solid: mp 66.0–67.5°; $[\alpha]D$ −24.0° (*c* 1, acetone); ir (KBr) 3250, 1200, 970, 880, 810 cm^{-1}; nmr ($CDCl_3$) δ 8.0–7.2 (q, 4, tolyl), 2.7 (s, 1, NH), 2.5 (s, 3, *p*-CH_3), 2.8–2.3 (m, 1, CH), 1.5–0.6 (m, 4, CH_2CH_2).

(+)-(*R*)-(Dimethylamino)cyclopropyl-*p*-tolylsulfonium Fluoroborate (27). To a solution of 3.0 g (0.0154 mol) of (−)-*S*-cyclopropyl-*S*-(*p*-tolyl)sulfoximine (**16**), $[\alpha]D$ −24.0° (*c* 1, acetone), in 20 ml of methylene chloride was added 2.5 g (0.017 mol) of trimethyloxonium fluoroborate. The reaction, initially at 0°, was allowed to warm to 25° and was stirred for 1 hr. The excess alkylating agent was filtered and 10% sodium hydroxide was added until the mixture was alkaline. The organic portion was drawn off and the aqueous layer extracted several times with methylene chloride. The combined extracts were dried (Na_2CO_3) and the volume was reduced to 20 ml. The above procedure was repeated twice. After removal of solvent, the residue was dissolved in ethanol and ether was added until no further precipitation occurred, to yield 4.6 g (95%) of yellowish solid. All attempts to obtain a constant, narrow range melting point were futile. The solids with various melting points were triturated to yield 3.8 g (80%) of a white solid: mp 101–115°; $[\alpha]^{25}D$ +61.8° (*c* 1, acetone); ir (Nujol) and nmr ($CDCl_3$) are identical with the authentic racemic compound.

(+)-(*S*)-*N*-Methyl-*S*-cyclopropyl-*S*-phenylsulfoximine (29). To a cooled (15°) solution of 0.25 g (1.5 mmol) of (+)-(*S*)-*N*,*S*-dimethyl-*S*-phenylsulfoximine, $[\alpha]D$ +178° (*c* 1, acetone, 97% optically pure), in 3 ml of DMSO was added dropwise 0.98 g (1.5 mmol) of *n*-butyllithium (1.6 *M* in hexane).[9] To the orange solution was added 0.50 g (0.030 mol) of trimethylvinylammonium bromide[18] at once as a solid, whereupon a moderately exothermic reaction took place. (On a larger scale the sulfoximine anion should be cooled to 0° to minimize frothing.) The reaction mixture was allowed to stir for 72 hr at 25°. The deep orange solution was poured into 20 ml of a saturated sodium chloride solution and extracted four times with 20 ml each of ether. The combined ether extracts were washed twice with a small amount of water to remove DMSO. The organic phase was dried (Na_2CO_3) and evaporated, yielding 200 mg of a dark orange oil which was decolorized with Norit. The desired product was separated from other components by elution chromatography on alumina using an ether–chloroform solvent mixture (3:2). The product was further purified by sublimation, 55° (0.25 mm), and finally by recrystallization from pentane, to yield 84 mg (28%) of a white solid: mp 70.0–71.5°; $[\alpha]D$ +118° (*c* 1, acetone); ir (melt) 1240, 1140, 855, 720, 690 cm^{-1}; nmr ($CDCl_3$) δ 8.0–7.4 (m, 5, C_6H_5), 2.75 (s, 3, NCH_3), 2.7–2.3 (m, 1, CH), 1.7–0.5 (m, 4, CH_2CH_2).

A major difficulty in purification of the desired cyclopropylsulfoximine was the presence of a product resulting from the addition of the cyclopropyl anion to another mole of vinyltrimethylammonium bromide. The resultant *N*-methyl-*S*-phenyl-*S*-(1-vinylcyclopropyl)sulfoximine (**30**) was isolated as an oil (~10% yield): ir (neat) 1640, 1240, 1140, 860 cm^{-1}; nmr ($CDCl_3$) δ 8.0–7.4 (m, 5, C_6H_5), 6.7–6.2 (m, 1, CH=C), 5.3–4.8 (m, 2, CCH_2), 2.9 (s, 3, NCH_3), 2.2–0.8 (m, 4, CH_2CH_2).

(−)-(*S*)-(Dimethylamino)cyclopropylphenyloxosulfonium Fluoroborate (31). The optically active salt was prepared from the corresponding *N*-methylsulfoximine, $[\alpha]D$ + 118° (*c* 1, acetone), by the usual alkylation procedure. Recrystallization from methylene chloride–ether gave in 87% yield a white solid: mp 139–141°; $[\alpha]D$ +49.2° (*c* 1, acetone); the spectral properties were identical with those of the racemic salt. Reactions of the chiral ylide **32** derived from the salt are reported in Table II.

Supplementary Material Available. A table of microanalytical data will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 20× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number JACS-73-7692.

Reactivity Studies of Bridgehead Organosilicon Compounds with Nucleophilic Reagents

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Abstract: The reactivity of 1-chloro-1-silabicyclo[2.2.1]heptane (IIa), a highly angle-strained bridgehead organosilicon chloride, 1-chloro-3,5,7-trimethyl-1,3,5,7-tetrasilaadamantane (Ib), a relatively unstrained bridgehead organosilicon chloride, and tris(trimethylsilylmethyl)chlorosilane (IIIa), the acyclic analog of Ib, toward a variety of nucleophilic reagents was investigated. Both IIa and IIIa were found to be much more reactive than Ib. Most of the results for nucleophilic displacement at bridgehead silicon in both Ib and IIa are best accounted for by an SN2-Si mechanism involving substantial d-orbital participation and proceeding with *retention* of configuration.

The relative reactivity of bridgehead carbon compounds has been extensively studied and several excellent reviews are available.[1–3] Knowledge gained from these studies has played an important part in the fundamental understanding of reaction mechanisms at carbon centers. Similar studies for analogous bridgehead organosilicon compounds have been quite limited in comparison.

The initial work in this area was reported by Sommer and Bennett in 1957.[4] They synthesized 1-chloro-1-silabicyclo[2.2.1]heptane, IIa, and found that this silicon chloride, in sharp contrast to relatively inert structurally analogous angle-strained bridgehead carbon compounds, was highly reactive toward both hydrolysis and reduction by $LiAlH_4$. A similar reactivity was also found for 1-chloro-1-silabicyclo[2.2.2]octane.[5] A quantitative comparison reported for these two sys-

(1) R. C. Fort, Jr., and P. v. R. Schleyer, *Advan. Alicyclic Chem.*, **1**, 283 (1966).
(2) R. C. Fort, Jr., and P. v. R. Schleyer, *Chem. Rev.*, **64**, 277 (1964).
(3) R. C. Bingham and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **93**, 3189 (1971).
(4) L. H. Sommer and O. F. Bennett, *J. Amer. Chem. Soc.*, **79**, 1008 (1957).
(5) L. H. Sommer and O. F. Bennett, *J. Amer. Chem. Soc.*, **81**, 251 (1959).