Chemical Reactivity and Configurational Properties of Cyclopropyl Carbanions Derived from a Silyl Sulfonyl Substituted Cyclopropene

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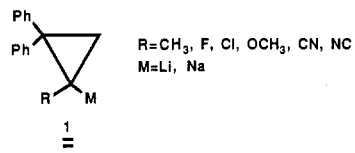
3,3-Dimethyl-1-(*p*-tolylsulfonyl)-2-(trimethylsilyl)cyclopropene was prepared by the 1,3-dipolar cycloaddition of 2-diazopropane with *p*-tolyl 2-(trimethylsilyl)ethynyl sulfone followed by photoextrusion of nitrogen from the resulting 3*H*-pyrazole. Treatment of this material with sodium methoxide produced *trans*-1-methoxy-2-(*p*-tolylsulfonyl)-3,3-dimethylcyclopropane. No detectable quantities of the cis isomer were present in the crude reaction mixture. The cyclopropyl carbanion derived from deprotonation of the (methoxysulfonyl)-substituted cyclopropane reacts smoothly with a variety of electrophiles to give a single stereoisomer. The observed stereoselectivity can be rationalized in terms of intramolecular chelation of the cyclopropyl lithiate with the neighboring methoxy group. The presence of an electronegative β-sulfonyl group also facilitates cyclopropyl carbanion interconversion. In this case the observed stereoselectivity is probably related to an anomeric effect. The favored cyclopropyl carbanion corresponds to the stereoisomer that permits interaction of the carbanion lone pair with the vacant σ* orbital on the adjacent carbon containing the electronegative atom.

The cyclopropyl ring provides a useful framework for the study of carbanions and their barriers to inversion.[1-3] The effect of substituents on the inversion process has been extensively investigated in solution.[4] Ab initio calculations on the cyclopropyl carbanion system indicate that the anion is pyramidal and possesses a high barrier to inversion.[5-10] It is well-known that cyclopropyl carbanions derived from optically active precursors are capable of retaining their configuration to a significant degree.[4] The calculated energy barrier for inversion of the cyclopropyl carbanion is 36.3 kcal/mol.[11] The initial hybridization of the carbon and the constraint in a three-membered ring (*I*-strain) are factors that undoubtedly affect the energy barrier for racemization of the derived cyclopropyl carbanion.[3] Walborsky and co-workers have elegantly demonstrated that the configurational stability of the α-substituted cyclopropyl carbanion depends on the solvating property of the reaction medium and on the type of substituent present—whether it is a delocalizing or nondelocalizing one.[12] The 1-lithium and 1-sodium derivatives of cyclopropane 1, where R = CH_3, are configurationally stable in aprotic solvents.[13] Derivatives of 1 where R is fluoro, chloro, or methoxy are also stable.[12] However, when the 1-substituent is a cyano group, even under aprotic conditions, the carbanion readily loses its configuration.[12] The α-isocyano derivative of 1 shows intermediate behavior, being able to retain its configuration at temperatures as high as −50 °C but undergoing rapid racemization at −5 °C.[1] Carbanions stabilized by sulfonyl groups show high diastereoselectivity and have been characterized as pyramidalized species.[14] There have been a number of cases reported which show that there is no difficulty in preparing cyclopropyl α-sulfonyl carbanions.[15-19]



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Aside from these physical organic aspects, electron-withdrawing-group substituted cyclopropyl nucleophiles are valuable synthons in organic chemistry and have been extensively studied in recent years.[20-35] As a direct con-

(1) Periasamy, M. P.; Walborsky, H. M. *J. Am. Chem. Soc.* **1977**, *99*, 2631.
(2) Peoples, P. R.; Trainor, T. M.; Grutzner, J. B. In *Stereodynamics in Molecular Systems*; Sarma, R. H., Ed.; Pergamon: New York, 1979; p 131.
(3) Cram, D. J. *Fundamentals of Carbanion Chemistry*; Academic Press: New York, 1965.
(4) Walborsky, H. M.; Young, A. E. *J. Am. Chem. Soc.* **1961**, *83*, 2595; **1964**, *86*, 3288. Walborsky, H. M.; Impastato, F. J. *Ibid.* **1959**, *81*, 5835.
(5) Dill, J. D.; Greenberg, A.; Liebman, J. F. *J. Am. Chem. Soc.* **1979**, *101*, 6814.
(6) Gordon, M. S. *J. Am. Chem. Soc.* **1980**, *102*, 7419.
(7) Clark, D. T.; Armstrong, D. R. *J. Chem. Soc. D* **1969**, 850.
(8) Tyrrell, J.; Kolb, V. M.; Meyer, C. Y. *J. Am. Chem. Soc.* **1979**, *101*, 3497.
(9) Hopkinson, A. C.; McKinney, M. A.; Lien, M. H. *J. Comp. Chem.* **1983**, *4*, 513.
(10) Chandrasekhar, J.; Andrade, J. G.; Schleyer, P. v. R. *J. Am. Chem. Soc* **1981**, *103*, 5609.
(11) Dewar, M. J. S.; Shanshal, M. *J. Am. Chem. Soc.* **1969**, *91*, 3654. See ref 10 where the value for inversion of the cyclopropyl carbanion is calculated to be 15 kcal/mol.
(12) Walborsky, H. M.; Allen, L. E.; Traencker, H. J.; Powers, E. J. *J. Org. Chem.* **1971**, *36*, 2937. Walborsky, H. M.; Hornyak, F. *J. Am. Chem. Soc.* **1955**, *77*, 6026. Walborsky, H. M.; Youssef, A. A.; Motes, J. M. *J. Am. Chem. Soc.* **1962**, *84*, 2465; **1970**, *92*, 2445.
(13) Walborsky, H. M.; Impastato, F. J.; Young, A. E. *J. Am. Chem. Soc.* **1964**, *86*, 3283.
(14) Trost, B. M.; Schmuff, N. R. *J. Am. Chem. Soc.* **1985**, *107*, 396.
(15) Zimmerman, H. E.; Thyagarajan, B. S. *J. Am. Chem. Soc.* **1960**, *82*, 2505.
(16) Ratajcak, A.; Anet, F. A. L.; Cram, D. J. *J. Am. Chem. Soc.* **1967**, *89*, 2072.
(17) Bordwell, F. G.; Branca, J. C.; Johnson, C. R.; Vanier, N. R. *J. Org. Chem.* **1980**, *45*, 3884.
(18) Boche, G.; Marsch, M.; Harms, K.; Sheldrick, G. M. *Angew. Chem.* **1985**, *97*, 577.
(19) Boche, G.; Marsch, M.; Harms, K. *Angew. Chem.* **1986**, *98*, 373.
(20) Ainsworth, C.; Chen, F.; Kuo, Y. N. *J. Organomet. Chem.* **1972**, *46*, 59; **1972**, *46*, 73.
(21) Wemple, J. *Tetrahedron Lett.* **1975**, 3255.
(22) Knochel, P.; Seebach, D. *Nouv. J. Chim.* **1981**, *5*, 75; *Helv. Chim. Acta* **1984**, *67*, 261. Häner, R.; Maetzke, T.; Seebach, D. *Helv. Chim. Acta* **1986**, *69*, 1655.
(23) Warner, P. M.; Le, D. *J. Org. Chem.* **1982**, *47*, 893.
(24) Paquette, L. A.; Blankenship, C.; Wells, G. J. *J. Am. Chem. Soc.* **1984**, *106*, 6442.
(25) Hirao, T.; Nagata, S.; Yamana, Y.; Agawa, T. *Tetrahedron Lett.* **1985**, *26*, 5061.
(26) Häner, R.; Laube, T.; Seebach, D. *J. Am. Chem. Soc.* **1985**, *107*, 5396. Häner, R.; Seebach, D. *Chimia* **1985**, *30*, 365.
(27) Ford, W. T.; Newcomb, M. *J. Am. Chem. Soc.* **1973**, *95*, 6277.
(28) Reichelt, I.; Reissig, H. U. *Liebigs Ann. Chem.* **1985**, 650; **1984**, 531; *Chem. Ber.* **1983**, *116*, 3895.
(29) Feit, B. A.; Elser, R.; Melamed, U.; Goldberg, I. *Tetrahedron* **1984**, *40*, 5177.
(30) VanCantfort, C. K.; Coates, R. M. *J. Org. Chem.* **1981**, *46*, 4331.
(31) Chang, Y. H.; Pinnick, H. W. *J. Org. Chem.* **1978**, *43*, 373.
(32) Pohmakotr, M.; Pisutjaroenpong, S. *Tetrahedron Lett.* **1985**, *26*, 3613.
(33) Hirao, T.; Nakamura, T.; Hagihara, M.; Agawa, T. *J. Org. Chem.* **1985**, *50*, 5860.

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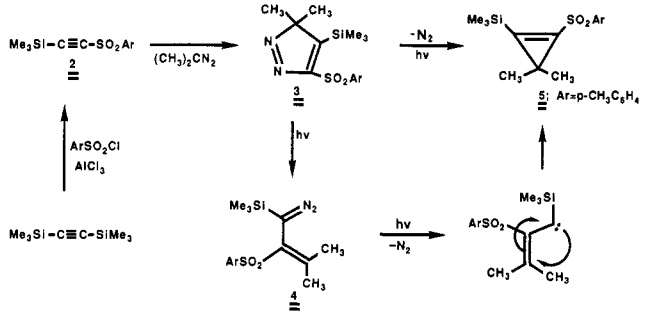
sequence of our own involvement with the chemistry of vinyl and allenyl sulfones,[36] we became interested in the configurational stability and chemical reactivity of cyclopropyl α-sulfonyl carbanions. The present paper describes a situation where substituents adjacent to the cyclopropyl carbanionic center affect the formation and the geometry of its reaction product with electrophiles.

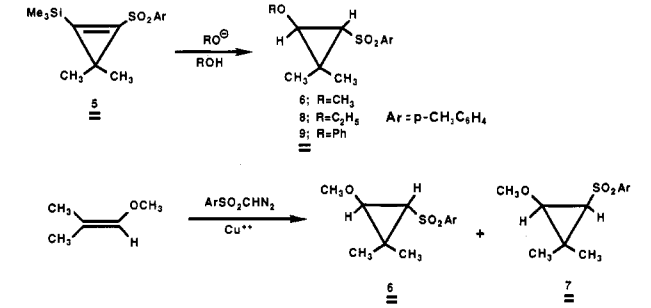
Results and Discussion

The photolysis of 3*H*-pyrazoles is well-known to give vinyldiazomethanes and cyclopropenes as products.[37-39] The ratio of these two products is very dependent on the substitution pattern, and in many simple alkyl-substituted cases, only the cyclopropenes are observed.[40] We have



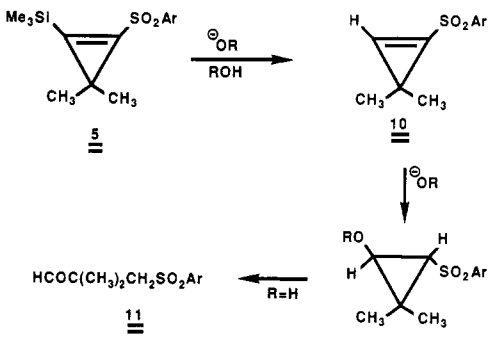
used this method to prepare 3,3-dimethyl-1-(*p*-tolylsulfonyl)-2-(trimethylsilyl)cyclopropene (**5**). Silyl sulfonyl substituted 3*H*-pyrazole **3** was readily synthesized by the 1,3-dipolar cycloaddition of 2-diazopropane with alkyne **2**.[41] Photolysis of this material in benzene for 90 min afforded cyclopropene **5** in excellent yield. Irradiation of **3** in benzene for only 30 min resulted in the formation of vinyldiazomethane **4**. This material was characterized by a strong band in the IR spectrum at 2045 cm^{-1}. Further photolysis of **4** gave cyclopropene **5**. The reaction proceeds via cyclization of a transient vinyl carbene intermediate formed by extrusion of nitrogen.[37]

Treatment of cyclopropene **5** with sodium methoxide in methanol for 30 min at 25 °C produced trans 1-methoxy 2-sulfonyl substituted cyclopropane **6** in 98% yield. A similar reaction occurred when sodium ethoxide or potassium phenoxide was used. No detectable quantities of the cis isomer **7** were present in the crude reaction mixture



as evidenced by NMR spectroscopy. A sample of the cis cyclopropane **7** was independently prepared by treating 1-methoxy-2-methylpropene with (*p*-tolylsulfonyl)diazomethane.[42]

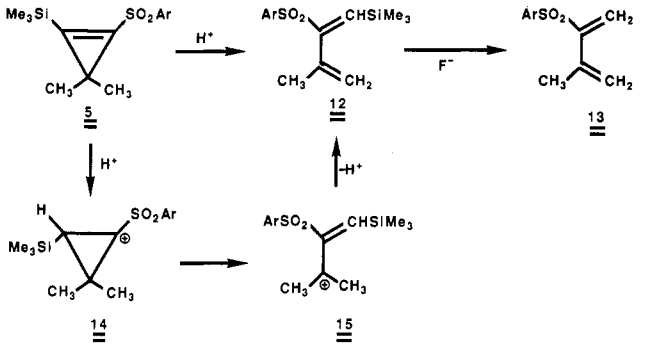
The formation of the alkoxy-substituted cyclopropane ring system can be viewed in terms of a process that involves attack of the alkoxide ion on the silicon atom to give a cyclopropenyl carbanion, which is subsequently protonated to afford cyclopropene **10** as a transient species. All of our attempts to isolate the desilylated cyclopropene, however, failed. Apparently, structure **10** readily reacts with more alkoxide ion under the reaction conditions used. Addition of nucleophiles to cyclopropenes containing electron-withdrawing substituents has previously been reported in the literature,[43] thereby providing good analogy for this step. A related result was encountered when **5** was allowed to stir in the presence of an aqueous potassium carbonate solution. In this case, the major product isolated corresponded to 2,2-dimethyl-3-(*p*-tolylsulfonyl)propionaldehyde (**11**). It would appear that the initially formed cyclopropanol readily undergoes ring opening to give aldehyde **11**.



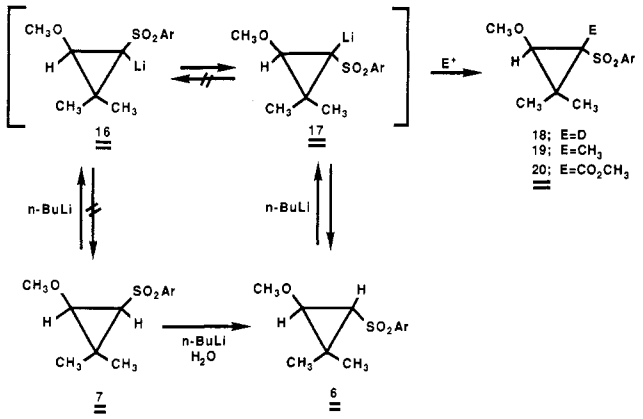
In dramatic contrast with the base-induced chemistry outlined above, exposure of a dilute benzene solution of **5** to *p*-toluenesulfonic acid resulted in the formation of diene **12** in good yield. This material was readily desilylated on treatment with tetrabutylammonium fluoride to give diene **13**. The reaction of electrophilic reagents with the strained σ bonds of cyclopropene derivatives has been previously reported in the literature.[44] Cyclopropenes represent an unusual class of molecules where a strained σ bond is incorporated into a substrate that already possesses a reactive π system. Fragmentation of the σ bond of cyclopropenes thermodynamically releases ca. 55 kcal/mol of strain.[45] In line with earlier work dealing with the metal-promoted rearrangement of cyclopropenes,[46] it is tempting to suggest that protonation occurs on the π bond to give cyclopropyl cation **14** which undergoes a subsequent ring-opening reaction followed by proton loss to produce diene **12**. The preferential formation of **14** is probably the result of stabilization of the β-cationic center by the trimethylsilyl group[47] which more than offsets the inductively destabilizing effect of the sulfonyl group.[48]

The cyclopropyl carbanion derived from the deprotonation of sulfone **6** with LDA at −78 °C reacted smoothly

(34) Haller, A.; Benoist, E. *Liebigs Ann. Chim.* **1921**, *17*, 25.
(35) Piehl, F. J.; Brown, W. G. *J. Am. Chem. Soc.* **1953**, *75*, 5023.
(36) For a preliminary report, see: Padwa, A.; Wannamaker, M. W. *Tetrahedron Lett.* **1985**, *26*, 3613.
(37) Franck-Neumann, M.; Buchecker, C. D. *Tetrahedron* **1978**, *34*, 2797. Franck-Neumann, M.; Miesch, M. *Tetrahedron* **1983**, *39*, 1247; *Tetrahedron Lett.* **1984**, *25*, 2909; **1982**, *23*, 1409.
(38) Palmer, G. E.; Bolton, J. R.; Arnold, D. R. *J. Am. Chem. Soc.* **1974**, *96*, 3708.
(39) Pincock, J. A.; Mathur, N. C. *J. Org. Chem.* **1982**, *47*, 3699.
(40) Zimmerman, H. E.; Hovey, M. C. *J. Org. Chem.* **1979**, *44*, 2331.
(41) Regitz, M.; Heydt, H. In *1,3-Dipolar Cycloaddition Chemistry*; Padwa, A., Ed.; Wiley-Interscience: New York, 1984; Vol. 1.
(42) Van Leusen, A. M.; Strating, J. *Org. Synth.* **1977**, *57*, 95.
(43) Hauck, G.; Durr, H. *J. Chem. Res.* **1981**, 180. Gardner, P. D.; Shields, T. C. *J. Am. Chem. Soc.* **1967**, *89*, 5425. Hashem, A.; Weyerstahl, P. *Tetrahedron* **1984**, *40*, 2003. Gritsenko, E. I.; Plemenkov, V. V.; Butenko, G. G.; Bolesov, I. G. *Zh. Org. Khim.* **1985**, *21*, 459.
(44) Bishop, K. C. *Chem. Res.* **1976**, *76*, 461.
(45) Schleyer, P. v. R.; Williams, J. E.; Blanchard, K. R. *J. Am. Chem. Soc.* **1970**, *92*, 2377.
(46) Padwa, A.; Blacklock, T. J.; Loza, R. *J. Org. Chem.* **1982**, *47*, 3712.
(47) Colvin, E. W. *Chem. Soc. Rev.* **1978**, *7*, 15.
(48) Creary, X.; Mehrsheikh-Mohammadi, M. E.; Eggers, M. D. *J. Am. Chem. Soc.* **1987**, *109*, 2435.

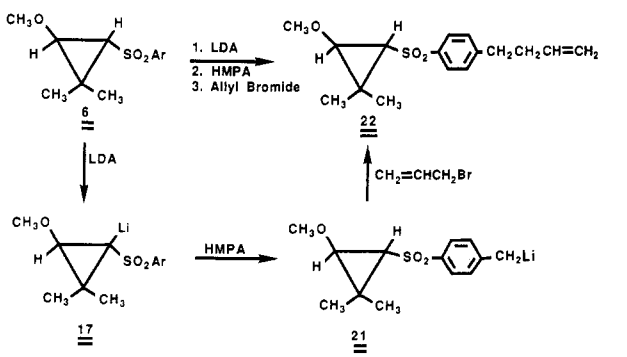


with several electrophiles (D_2O, CH_3I, $ClCO_2CH_3$) to give exclusively a single stereoisomer.[49] The same alkylated set of cyclopropanes was also formed from the cis isomer **7**. We found that *cis*-**7** was efficiently and quantitatively converted to *trans*-**6** by a deprotonation-protonation sequence. Thus, the presence of the β-methoxy functionality seems to have altered a precedented behavioral pattern in that it readily facilitates cyclopropyl carbanion (**16** → **17**) interconversion even at −78 °C. During the course of



our alkylation studies with sulfone **6**, we found that its reaction with LDA in the presence of HMPA followed by quenching with allyl bromide produced cyclopropane **22**. Apparently, the additional solvation provided by HMPA facilitates proton exchange, thereby leading to the thermodynamically more stable benzylic carbanion **21** which further reacts with allyl bromide.

The stereoselectivity observed in the formation of compounds **18**–**20** from *cis*-cyclopropyl sulfone **7** implies that the initially formed lithiated cyclopropane **16** isomerizes to the more stable, intramolecularly solvated carbanion **17**,[50] which is the actual precursor of compounds **18**–**20**.

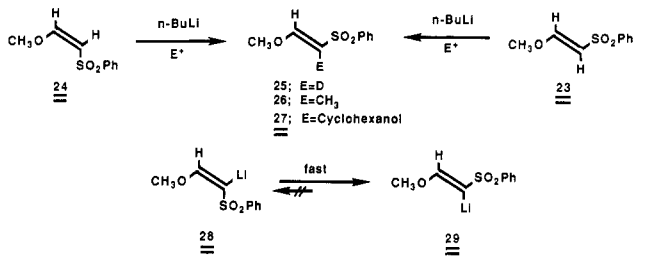


(49) For some related reactions of cyclopropanes carrying sulfonyl groups, see ref 31, 32.

(50) For an interesting discussion concerning intramolecular solvation of lithium by oxygen in lithiated enol ethers, see: Lau, K. S. Y.; Schlosser, M. *J. Org. Chem.* **1978**, *43*, 1595.

Intramolecular coordination of lithium to an adjacent oxygen atom has been invoked to account for the directed lithiation of cyclopropyl carbinols and related species,[51] the stereochemical integrity of ((*E*)-2-alkoxy-1-(arylthio)vinyl)lithium,[52] the stability of ((*Z*)-2-ethoxyvinyl)lithium,[53] and the metalation of 3-methoxynortricyclene by alkylpotassium and alkylsodium reagents.[54] This intramolecular chelation also nicely accommodates the high diastereoselection observed by Reissig and co-workers in the alkylation of siloxy-substituted methyl cyclopropanecarboxylates.[28,55]

A similar phenomenon was encountered with the closely related phenyl 2-methoxyvinyl sulfonyl system. To examine the configurational stability of [(*Z*)-2-methoxy-1-(phenylsulfonyl)vinyl]lithium (**28**), the *Z*-sulfone **24** was prepared and treated with *n*-butyllithium followed by trapping with several electrophiles at −70 °C. In marked contrast to alkyl-substituted [(*Z*)-1-(phenylsulfonyl)-vinyl]lithium species,[56] which isomerize quite slowly at −60 °C, the *Z*-methoxy lithiate **28** isomerized rapidly and



completely to the *E*-methoxy lithiate **29**, even at −90 °C. Thus, reaction of **24** with *n*-butyllithium (1 min, −70 °C) followed by D_2O quenching gave **25**, whereas reaction with methyl iodide and cyclohexanone afforded **26** and **27**, identical with samples prepared from the *E*-olefin **23**. This rapid *Z* → *E* isomerization may be facilitated by reduced double-bond order in a "push–pull" olefin such as **23** (or **24**) and is quite analogous to the situation found for 2-methoxy-1-(*p*-toluenesulfonyl)cyclopropyl carbanion **17** where stabilization of the *E* isomer was attributed to lithium chelation by the β-methoxy substituent.

β-(Alkoxycyclopropyl)carbonyl derivatives undergo a ready ring opening and this reaction has been widely utilized to effect many synthetically useful transformations.[57] The ease of ring fission is provided by the unique combination of the strain energy inherent in a compound of this type and the complementary donor–acceptor electronic effects of the substituent groups. Reissig was among the first to realize the high reactivity of the 2-(siloxy)-cyclopropane esters toward electrophilic species, and a few years ago he reported their ready equilibration by Lewis acid catalysts.[58] As a direct consequence of our own involvement with the chemistry of alkoxysulfonyl substituted cyclopropanes, it was envisioned that a similar equilibration would occur with sulfonyl cyclopropanes **6** and **7**. All of our attempts, however, to equilibrate these substrates

(51) Klumpp, G. W.; Kool, M.; Veefkind, A. H.; Schakel, M.; Schmitz, R. F. *Recl. Trav. Chim. Pays-Bas* **1983**, *102*, 542. Klumpp, G. W.; Kool, M.; Schakel, M.; Schmitz, R. F.; Boutkan, C. *J. Am. Chem. Soc.* **1979**, *101*, 7065.

(52) Vlatas, I.; Vecchia, L.; Lee, A. O. *J. Am. Chem. Soc.* **1976**, *98*, 2008.

(53) Lau, K. S. Y.; Schlosser, M. *J. Org. Chem.* **1978**, *43*, 1595.

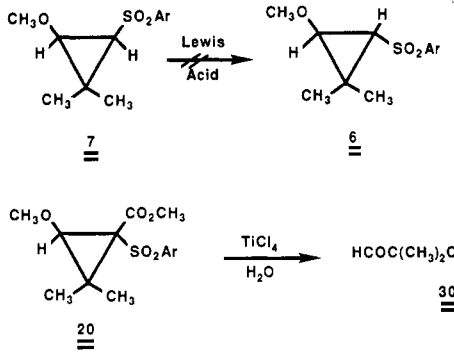
(54) Hartmann, J.; Schlosser, M. *Helv. Chim. Acta* **1976**, *59*, 453.

(55) Reissig, H. U.; Böhm, I. *J. Am. Chem. Soc.* **1982**, *104*, 1735.

(56) Kleijn, H.; Vermeer, P. *J. Organomet. Chem.* **1986**, *302*, 1.

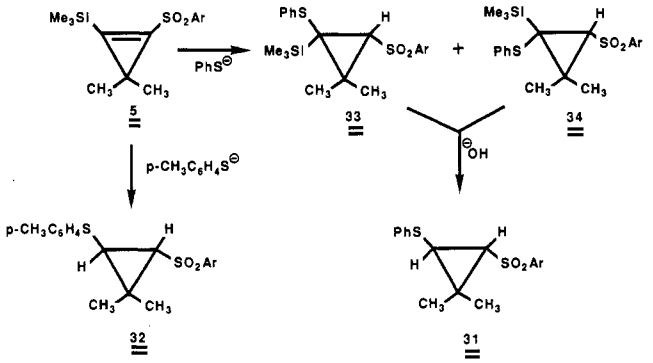
(57) Reviews: Wenkert, E. *Acc. Chem. Res.* **1980**, *13*, 27. Wenkert, E. *Heterocycles* **1980**, *14*, 1703. Conia, J. M. *Pure Appl. Chem.* **1975**, *43*, 317. Schollkopf, U. *Angew, Chem., Int. Ed. Engl.* **1968**, *7*, 588.

(58) Reissig, H. U. *Tetrahedron Lett.* **1981**, *22*, 2981. Reissig, H. U.; Hirsch, E. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 813.

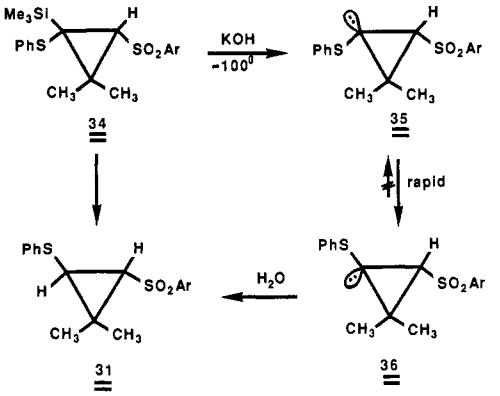


using Reissig's conditions failed. Ring opening could not be affected under even more forcing conditions. This result clearly establishes the importance of the nature of the donor-acceptor groups in facilitating the ring-fission reaction. We did observe that the diactivated carbomethoxy sulfonyl substituted cyclopropane **20** does undergo ring opening upon treatment with titanium tetrachloride.

The reaction of trimethylsilyl sulfonyl cyclopropene **5** with thiophenol and potassium hydroxide in methanol was also examined. In the presence of excess base, trans cyclopropane **31** proved to be the exclusive product (95%) isolated. A similar result was encountered with *p*-thiocresol. When the reaction was carried out with thiophenol for shorter periods of time and using an equivalent amount of base, the silyl-substituted cyclopropanes **33** and **34** (1:2) were formed in excellent yield. Both of these compounds were readily desilylated to give only **31**. Thus, the polarizable and softer thiophenoxide anion prefers to attack the highly strained cyclopropene π bond. The harder and less polarizable methoxide ion, on the other hand, preferentially reacts on silicon.

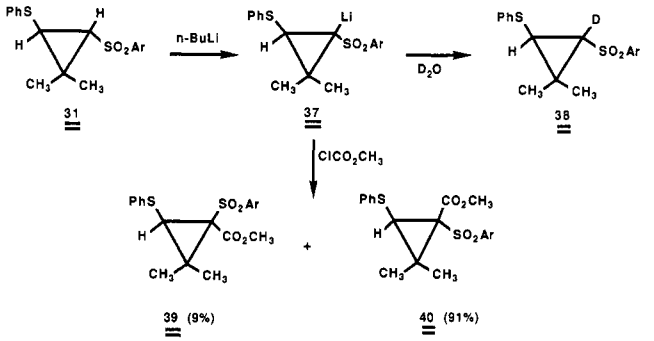


Removal of the α-trimethylsilyl group from the three-membered ring undoubtedly involves initial cyclopropyl carbanion generation.[59] Most importantly, both desilylation reactions generate only the trans isomer **31**. Thus, the presence of the electronegative β-sulfonyl group also facilitates carbanion interconversion even at −100 °C as was previously encountered with the methoxy system.[60] In this case, however, it is highly unlikely that the inversion of carbanion **35** to **36** is a consequence of intramolecular chelation. Rather, we believe that this reaction is a manifestation of the anomeric effect.[61] This effect is associated with the preference of electronegative substituents to assume axial rather than the expected equatorial position at the anomeric carbon in pyranose rings.[62] This conformational situation, unusual in hydrocarbon rings, has been attributed to the presence of two electronegative groups on a carbon atom. Theoretically, the anomeric effect was first interpreted in terms of electrostatic interactions and then by an n → σ^* overlapping between a free electron pair of oxygen and the antibonding σ^* orbital of the neighboring C–X bond (X = electronegative atom).[63] This kind of stereoelectronic control nicely accounts for the exclusive formation of trans cyclopropane **31**. The favored cyclopropyl carbanion (i.e., **36**) will be the one that



permits interaction of the carbanion lone pair with the vacant σ^* orbital on the adjacent carbon that contains the electronegative atom (or group). Such hyperconjugative interactions have been substantiated by theoretical investigations and are now well-established for a variety of systems.[64] Both energetic and structural consequences are often dramatically large.

Additional support for the above rationale was obtained by treating the carbanion derived from phenylthiosulfonyl cyclopropane **31** with both deuterium oxide and methyl chloroformate. We found that the deuterium atom was incorporated cis to the thiophenyl group even though the sulfur atom is not a particularly effective chelating group. When methyl chloroformate was used as the electrophile, a 1:10 mixture of cyclopropanes **39** and **40** was formed. Again, the major product corresponds to trapping the cyclopropyl carbanion (i.e., **37**) which is hyperconjugatively stabilized by the adjacent thiophenyl moiety.[65]



In conclusion, cyclopropyl carbanions that possess a β-methoxy group undergo stereoselective alkylation with a variety of electrophiles to give a single alkylated product.

(59) Paquette, L. A.; Uchida, T.; Gallucci, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 335.

(60) Control experiments show that cyclopropyl carbanion **35** does not undergo a 1,2-hydrogen shift to give cyclopropyl carbanion **37** under the reaction conditions used since no deuterium was incorporated adjacent to the sulfonyl group when the reaction was quenched with CH_3OD.

(61) Kirby, A. J. *The Anomeric Effect and Related Stereoelectronic Effects in Organic Chemistry*; Pergamon Press: London, 1983; Chapter 2.

(62) Deslongchamps, P. *Stereoelectronic Effects in Organic Chemistry*; Wiley Interscience: New York, 1983.

(63) Romers, C.; Altona, C.; Buys, H. R.; Havinga, E. *Topics in Stereochemistry*; Eliel, E. L., Allinger, N. L., Eds.; Wiley Interscience: New York, 1969; Vol. 4, p 39.

(64) Wolfe, S.; Whangbo, M. H.; Mitchell, D. J. *Carbohydr. Res.* **1979**, *69*, 1.

(65) Cyclopropene **31** was also converted to **38** on treatment with KOD in CH_3OD.

The observed stereochemistry can be rationalized in terms of intramolecular chelation of the cyclopropyl lithiate with the neighboring methoxy group. The presence of an electronegative β-sulfonyl group also facilitates cyclopropyl carbanion interconversion as was encountered with the methoxy system. In this case, however, the observed stereoselectivity is probably related to an anomeric effect. The favored cyclopropyl carbanion corresponds to the stereoisomer that permits interaction of the carbanion lone pair with the vacant σ* orbital on the adjacent carbon containing the electronegative atom.

Experimental Section

Melting points were determined on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Infrared spectra were run on a Perkin-Elmer Model 283 infrared spectrometer. Proton NMR spectra were obtained on Varian EM-390 and Nicolet NMC-360 MHz spectrometers. ^{13}C NMR spectra were recorded on an IBM NB 200 SY FT spectrometer. Microanalyses were performed at Atlantic Microlabs, Atlanta, GA. Mass spectra were determined with a Finnegan 4510 mass spectrometer at an ionizing voltage of 70 eV.

Preparation and Photolysis of 3,3-Dimethyl-4-(*p*-tolylsulfonyl)-5-(trimethylsilyl)-3*H*-pyrazole (3). To a solution of 2-diazopropane[66] in ether at −78 °C was added 10.89 g of *p*-tolyl 2-(trimethylsilyl)ethynyl sulfone.[67] The resulting red solution was stirred for 30 min at −78 °C under a nitrogen atmosphere, was then allowed to warm to 25 °C, and was stirred for 12 h. The organic layer was washed with dilute aqueous hydrochloric acid and once with brine, dried over magnesium sulfate, and concentrated to dryness to give a yellow-brown solid which was chromatographed on a silica gel column using a 5% acetone–hexane mixture as the eluent. Removal of the solvent under reduced pressure left 13.65 g (98% yield) of a bright yellow solid which was identified as 3,3-dimethyl-4-(*p*-tolylsulfonyl)-5-(trimethylsilyl)-3*H*-pyrazole (3) on the basis of its spectral properties: mp 91–92 °C; IR (KBr) 3080, 2980, 2960, 1600, 1500, 1325, 1250, 1150, 1100, 850, and 700 cm^{-1}; ^1H NMR (CCl_4, 90 MHz) δ 0.52 (s, 9 H), 1.13 (s, 6 H), 2.42 (s, 3 H), 7.30 (d, 2 H, J = 9.0 Hz), and 7.72 (d, 2 H, J = 9.0 Hz); ^{13}C NMR (20 MHz, $CDCl_3$) δ −0.6, 21.1, 21.4, 96.4, 127.8, 129.8, 136.8, 145.2, and 164.9; UV (95% ethanol) 225 nm (ε 11 400) and 263 (7300); MS, m/e 307, 185, 149, 139 (base), 124, 123, and 99. Anal. Calcd for $C_{15}H_{22}O_2N_2SSi$: C, 55.86; H, 6.88; N, 8.69; S, 9.94. Found: C, 55.77; H, 6.88; N, 8.67; S, 9.99.

A solution containing 5.0 g of 3 in 1.5 L of benzene was irradiated for 90 min by using a 450-W Hanovia medium pressure mercury arc lamp equipped with a Pyrex filter sleeve under an argon atmosphere. Analysis of the crude photolysate after 30 min showed the presence of an intense diazo band at 2045 cm^{-1}. Irradiation was continued for an additional 90 min. The solvent was removed under reduced pressure and the crude residue was chromatographed on a silica gel column using a 5% acetone–hexane mixture as the eluent. The major fraction contained 4.5 g (99% yield) of a light yellow oil whose structure was assigned as 3,3-dimethyl-1-(*p*-tolylsulfonyl)-2-(trimethylsilyl)cyclopropene (5): mp 44–45 °C; IR (neat) 3080, 2970, 1730, 1600, 1500, 1320, 1150, 1090, 850, and 680 cm^{-1}; ^1H NMR (90 MHz, CCl_4) δ 0.11 (s, 9 H), 1.21 (s, 6 H), 2.42 (s, 3 H), 7.32 (d, 2 H, J = 9.0 Hz), and 7.75 (d, 2 H, J = 9.0 Hz); ^{13}C NMR (20 MHz, $CDCl_3$) δ −1.68, 21.4, 26.2, 33.4, 127.6, 129.6, 137.9, and 144.5; UV (95% ethanol) 238 nm (ε 13 000); MS, m/e 149, 141, 140, 139, 123, 109, 98, and 97 (base). Anal. Calcd for $C_{15}H_{22}O_2SSi$: C, 61.18; H, 7.53; S, 10.89. Found: C, 61.05; H, 7.54; S, 10.81.

Preparation of *trans*-2,2-Dimethyl-3-(*p*-tolylsulfonyl)-cyclopropyl Methyl Ether (6). An oven-dried, 100-mL round-bottomed flask equipped with a magnetic stirring bar and nitrogen inlet was charged with 500 mg of sodium metal and 50 mL of absolute methanol at 25 °C. After the sodium had completely dissolved, 2.0 g of cyclopropene 5 was added. The resulting mixture was stirred for 30 min and then 10 mL of a saturated ammonium chloride solution was added. The solvent was removed under reduced pressure and the residue was dissolved in 100 mL of ether. The organic layer was washed with water and brine and then dried over magnesium sulfate. Evaporation of the solvent left 1.71 g (98% yield) of an oil which was crystallized from dichloromethane and petroleum ether to give *trans*-2,2-dimethyl-3-(*p*-tolylsulfonyl)cyclopropyl methyl ether (6) as a white solid: mp 64–65 °C; IR (KBr) 3070, 2970, 2830, 1600, 1500, 1460, 1305, 1150, 1090, 870, and 670 cm^{-1}; ^1H NMR (90 MHz, CCl_4) δ 1.19 (s, 3 H), 1.39 (s, 3 H), 1.95 (d, 1 H, J = 3.0 Hz), 2.41 (s, 3 H), 3.25 (s, 3 H), 3.62 (d, 1 H, J = 3.0 Hz), 7.25 (d, 2 H, J = 9.0 Hz), and 7.69 (d, 2 H, J = 9.0 Hz); deuterium exchange under normal conditions gave 6-*d* δ 1.18 (s, 3 H), 1.39 (s, 3 H), 2.41 (s, 3 H), 3.25 (s, 3 H), 3.63 (s, 1 H), 7.21 (d, 2 H, J = 9.0 Hz), and 7.69 (d, 2 H, J = 9.0 Hz); ^{13}C NMR (20 MHz, $CDCl_3$) δ 18.4, 19.8, 21.6, 30.8, 50.2, 58.8, 69.4, 127.2, 129.8, 139.2, and 144.1; UV (95% ethanol) 228 nm (ε 9200) and 262 (620). Anal. Calcd for $C_{13}H_{18}O_3S$: C, 61.39; H, 7.13; S, 12.61. Found: 61.47; H, 7.17; S, 12.66.

Independent Synthesis of *cis*- and *trans*-2,2-Dimethyl-3-(*p*-tolylsulfonyl)cyclopropyl Methyl Ether (6 and 7). To a stirred solution containing 4.0 g of 1-methoxy-2-methylpropene[68] and 100 mg of copper acetoacetonate in 50 mL of anhydrous benzene at exactly 36 °C was added 3.0 g of (*p*-tolylsulfonyl)-diazomethane[42] in 250 mL of dry benzene dropwise by addition funnel over a 6-h period. The reaction was performed in the dark so as to avoid decomposition of the tosyldiazomethane. The solvent was removed under reduced pressure and the residue was diluted with dichloromethane. The resulting solution was passed through a pad of neutral Alumina (activity III) and the solvent was removed to give an oil which was chromatographed on a silica gel column with a 10% acetone–hexane mixture as the eluent. The major fraction contained 920 mg of an oil which was rechromatographed on a 4-mm chromatatron plate by using a 5% acetone-hexane mixture as the eluent. The first fraction contained 296 mg of *trans*-2,2-dimethyl-3-(*p*-tolylsulfonyl)cyclopropyl methyl ether (6) whose structure was established by comparison with the previously synthesized material.

The second fraction contained 107 mg of an oil which was identified as *cis*-2,2-dimethyl-3-(*p*-tolylsulfonyl)cyclopropyl methyl ether (7) on the basis of its spectral properties: IR (neat) 3060, 2940, 1600, 1450, 1400, 1300, 1235, 920, and 815 cm^{-1}; ^1H NMR ($CDCl_3$, 360 MHz) δ 1.05 (s 3 H), 1.55 (s, 3 H), 2.04 (d, 1 H, J = 6.14 Hz), 2.45 (s, 3 H), 3.32 (d, 1 H, J = 6.14 Hz), 3.57 (s, 3 H), 7.35 (d, 2 H, J = 9.0 Hz), and 7.81 (d, 2 H, J = 9.0 Hz); UV (95% ethanol) 228 mm (ε 15 000) and 262 (800); MS, m/e 254 (M^+), 99 (base), and 91. Anal. Calcd for $C_{13}H_{18}O_3S$: C, 61.39; H, 7.13; S, 12.61. Found: C, 61.33; H, 7.12; S, 12.57.

Preparation of *trans*-2,2-Dimethyl-3-(*p*-tolylsulfonyl)-cyclopropyl Ethyl Ether (8). A dry 50-mL round-bottomed flask equipped with a nitrogen inlet and magnetic stirring bar was charged with 25 mL of absolute ethanol and then 200 mg of sodium metal was added. When the sodium had completely dissolved, 500 mg of cyclopropene 5 was added to the solution at room temperature. After stirring for 30 min, 10 mL of a saturated solution of ammonium chloride was added and the ethanol was removed under reduced pressure. The residue was diluted with 100 mL of ether, washed with water and brine, and dried over magnesium sulfate. Evaporation of the solvent left 452 mg (99% yield) of a clear oil which solidified on standing. This material was identified as *trans*-2,2-dimethyl-3-(*p*-tolylsulfonyl)cyclopropyl ethyl ether (8) on the basis of its characteristic spectral properties: mp 86–57 °C; IR (KBr) 3070, 3040, 2940, 1600, 1500, and 670 cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$) δ 1.15 (t, 3 H, J = 6.9 Hz), 1.18 (s, 3 H), 1.39 (s, 3 H), 2.17 (d, 1 H, J = 3.0 Hz), 2.44 (s, 3 H), 3.43 (dq, 1 H, J = 9.0 and 6.9 Hz), 3.52 (dq, 1 H, J = 9.0 and 6.9 Hz), 3.83 (d, 1 H, J = 3.0 Hz), 7.33 (d, 2 H, J = 9.0 Hz), and 7.88 (d, 2 H, J = 9.0 Hz); ^{13}C NMR (20 MHz, $CDCl_3$ δ 14.7, 18.3, 19.9 21.5, 30.4, 50.3, 66.8, 67.5, 127.1, 129.8, 139.4, and 144.0; UV (95% ethanol) 227 nm (ε 15 000) and 262 (160). Anal. Calcd for $C_{14}H_{20}O_3S$: C, 62.66; H, 7.51; S, 11.95. Found: C, 62.54; H, 7.53; S, 11.90.

(66) Day, A. C.; Whiting, M. C. *Org. Synth.* **1970**, *50*, 3.
(67) Bhattacharya, S. N.; Josiah, B. M.; Walton, D. R. M. *Organomet. Chem. Synth.* **1970**, *1*, 145.
(68) Bohme, H.; Bentler, H. *Chem. Ber.* **1956**, *89*, 1468.

Preparation of *trans*-2,2-Dimethyl-3-(*p*-tolylsulfonyl)-cyclopropyl Phenyl Ether (9). A sample containing 340 mg of phenol and 230 mg of potassium hydroxide was stirred together in 50 mL of 95% ethanol. To this mixture was added 300 mg of cyclopropene **5** in 10 mL of 95% ethanol. The mixture was stirred for 3 h at 25 °C and the solvent was removed under reduced pressure. The residue was diluted with ether and washed with a 10% sodium hydroxide solution, water, and brine. The organic layer was dried over magnesium sulfate and concentrated under reduced pressure to give 290 mg (90% yield) of an oil which could be crystallized from a dichloromethane–petroleum ether mixture to give a white solid, mp 117–118 °C, which was assigned as *trans*-2,2-dimethyl-3-(*p*-tolylsulfonyl)cyclopropyl phenyl ether (**9**) on the basis of its spectral data: ^{1}H NMR ($CDCl_3$, 360 MHz) δ 1.22 (s, 3 H), 1.57 (s, 3 H, 2.46 (s, 3 H), 2.48 (d, 1 H, J = 2.88 Hz), 4.32 (d, 1 H, J = 2.88 Hz, 6.93–7.03 (m, 3 H), 7.24–7.30 (m, 2 H), 7.36 (d, 2 H, J = 9.0 Hz), and 7.81 (d, 2 H, J = 9.0 Hz); IR (KBr) 3020, 3060, 2980, 1590, 1490, 1305, 930, and 760 cm^{-1}; UV (95% ethanol) 223 nm (ϵ 17 000) and 268 (1700). Anal. Calcd for $C_{18}H_{20}O_3S$: C, 68.33; H, 6.37. Found: C, 69.18; H, 6.42.

Acid and Base Treatment of 3,3-Dimethyl-1-(*p*-tolylsulfonyl)-2-(trimethylsilyl)cyclopropene (5). A 200-mg sample of **5** was dissolved in 5 mL of *N*,*N*-dimethylformamide at 25 °C. Water was added followed by the addition of 10 drops of an aqueous 10% solution of potassium carbonate. The mixture was stirred for 10 min, diluted with ether, washed with water and brine, dried over magnesium sulfate, and concentrated to give 106 mg (65% yield) of a clear oil whose structure was assigned as 2,2-dimethyl-3-(*p*-tolylsulfonyl)propionaldehyde (**11**) on the basis of the following spectral properties: ^{1}H NMR (90 MHz, CCl_4) δ 1.29 (s, 6 H), 2.41 (s, 3 H), 3.22 (s, 2 H), 7.29 (d, 2 H, J = 9.0 Hz), 7.71 (d, 2 H, J = 9.0 Hz), and 9.49 (s, 1 H); IR (neat) 3060, 2980, 2730, 1730, 1600, 1500, 1320, 1145, 1090, 820 and 670 cm^{-1}; UV (95% ethanol) 226 nm (ϵ 13 000) and 262 (760); ^{13}C NMR (20 MHz, $CDCl_3$) δ 21.4, 21.9, 45.0, 62.4, 127.6, 128.8, 129.8, 137.9, and 201.9. Anal. Calcd for $C_{12}H_{16}O_3S$: C, 59.97; H, 6.71. Found: C, 59.70; H, 6.71.

A mixture containing 500 mg of cyclopropene **5** and 292 mg of *p*-toluenesulfonic acid in 25 mL of anhydrous benzene was heated at reflux for 36 h. The solution was cooled, diluted with ether, washed several times with water and once with brine, and then dried over magnesium sulfate. Removal of the solvent left an oil which was chromatographed on a silica gel column with a 5% acetone–hexane mixture as the eluent. The major fraction contained 320 mg of a white solid whose structure was assigned as trimethyl[3-methyl-2-(*p*-tolylsulfonyl)-1,3-butadienyl]silane (**12**) on the basis of its spectral properties: mp 62–63 °C; IR (KBr) 3080, 2960, 1640, 1600, 1500, 1310, 1140, 870, and 695 cm^{-1}; ^{1}H NMR (90 MHz, CCl_4) δ 0.33 (s, 9 H), 1.72 (s, 3 H), 2.38 (s, 3 H), 4.90 (bd, 2 H, J = 3.0 Hz), 6.21 (s 1 H), 7.15 (d, 2 H, J = 9.0 Hz), and 7.55 (d, 2 H, J = 9.0 Hz); UV (95% ethanol) 238 nm (ϵ 17 000); MS, m/e 294 (M_+), 280, 279, 278, 231, 230, 229, 228, 215, 214, 213, 180, 150, 149 (base), 139, 91, and 73. Anal. Calcd for $C_{15}H_{22}O_2SSi$: C, 61.18; H, 7.53; S, 10.89. Found: C, 60.98; H, 7.60; S, 10.84.

A 52-mg sample of diene **12** dissolved in 1 mL of anhydrous tetrahydrofuran at 25 °C. To this solution was added 0.18 mL of a 1.0 M solution of tetrabutylammonium fluoride in tetrahydrofuran. After being stirred for 5 min, the mixture was diluted with ether and washed twice with water and once with brine. The ether layer was dried over magnesium sulfate, filtered, and concentrated under reduced pressure to give 39 mg (100% yield) of a clear oil whose structure was assigned as 3-methyl-2-(*p*-tolylsulfonyl)-1,3-butadiene (**13**) on the basis of its characteristic NMR spectrum: ^{1}H NMR (90 MHz, CCl_4) δ 1.83 (s, 3 H), 2.38 (s, 3 H), 5.10 (bs, 1 H), 5.30 (bs, 1 H), 5.74 (s, 1 H), 6.31 (s, 1 H), 7.22 (d, 2 H, J = 9.0 Hz), and 7.65 (d, 2 H, J = 9.0 Hz).

Reaction of *trans*-2,2-Dimethyl-3-(*p*-tolylsulfonyl)cyclopropyl Methyl Ether (6) with Iodomethane. A flame-dried, 100-mL three-neck, round-bottomed flask equipped with spin bar and nitrogen line was charged with 200 mg of **6** and 50 mL of dry ether. The solution was cooled to −78 °C and 0.59 mL of a 1.48 M *n*-butyllithium solution was added via syringe. The resulting yellow carbanion was stirred 10 min followed by the addition of iodomethane. The mixture was warmed to room temperature and stirred for 3 h. The ether was poured into a saturated ammonium chloride solution and the organic layer was separated, washed with water and brine, and dried over magnesium sulfate. Removal of the solvent left a yellow oil which was chromatographed on a silica gel column with a 5% acetone–hexane mixture as the eluent. The major fraction contained 170 mg (80% yield) of *trans*-1-[(3-methoxy-1,2,2-trimethylcyclopropyl)sulfonyl]-4-methylbenzene (**19**): mp 81–82 °C; IR (KBr) 3080, 3000, 2980, 1600, 1500, 1290, 1145, 820, and 665 cm^{-1}; ^{1}H NMR (90 MHz, CCl_4) δ 1.39 (s, 3 H), 1.49 (s, 3 H), 1.82 (s, 3 H), 2.40 (s, 3 H), 3.28 (s, 3 H), 3.70 (s, 1 H), 7.21 (d, 2 H, J = 9.0 Hz), and 7.65 (d, 2 H, J = 9.0 Hz); UV (95% ethanol) 227 nm (ϵ 10 000) and 261 (650). Anal. Calcd for $C_{14}H_{20}O_3S$: C, 62.66; H, 7.51. Found: C, 62.51; H, 7.54.

Reaction of *trans*-2,2-Dimethyl-3-(*p*-tolylsulfonyl)cyclopropyl Methyl Ether (6) with Methyl Chloroformate. An oven-dried, three-neck, 50-mL round-bottomed flask equipped with a magnetic stir bar and nitrogen line was charged with 300 mg of **6** and 25 mL of anhydrous tetrahydrofuran. The solution was cooled to −78 °C and 0.9 mL of a 1.43 M *n*-butyllithium solution was added via syringe. The resulting yellow carbanion was stirred for 10 min and then 0.1 mL of methyl chloroformate was added. The solution was warmed to 25 °C and quenched with a saturated ammonium chloride solution. The mixture was diluted with 200 mL of ether and washed with water and brine. The organic layer was dried over magnesium sulfate and concentrated under reduced pressure to give 401 mg of an oil. This material was chromatographed on a 2-mm plate by using a 10% acetone-hexane mixture as the eluent. The major fraction contained 328 mg (81% yield) of a light yellow oil whose structure was assigned as methyl *trans*-3-methoxy-2,2-dimethyl-1-(*p*-tolylsulfonyl)cyclopropanecarboxylate (**20**) on the basis of its spectral properties: ^{1}H NMR (90 MHz, CCl_4) δ 1.10 (s, 3 H), 1.45 (s, 3 H), 2.41 (s, 3 H), 3.50 (s, 3 H), 3.55 (s, 3 H), 3.91 (s, 1 H), 7.25 (d, 2 H, J = 9.0 Hz), and 7.70 (d, 2 H, J = 9.0 Hz); IR (neat) 2960, 1740, 1600, 1440, 1410, 1385, 1300, 1200, 1150, 1055, 940, 800, 710, 660, and 600 cm^{-1}; UV (95% ethanol) 229 nm (ϵ 13 000) and 256 (1700). Anal. Calcd for $C_{15}H_{20}O_5S$: C, 57.67; H, 6.45. Found: C, 57.77; H, 6.52.

To a stirred solution containing 328 mg of the above cyclopropane in 10 mL of dry dichloromethane at −78 °C was added via syringe 0.12 mL of titanium tetrachloride. The colored solution was allowed to warm to 25 °C and was stirred for an additional hour. The homogeneous brown solution was then quenched with a saturated solution of sodium bicarbonate. The mixture was diluted with dichloromethane, washed several times with water, dried over sodium sulfate, and concentrated to give 300 mg (96% yield) of an oil. This material crystallized on standing and was assigned the structure of methyl 3,3-dimethyl-(*p*-tolylsulfonyl)-succinaldehyde (**30**) on the basis of its spectral data: mp 86–87 °C; IR (KBr) 3000, 2920, 2820, 2720, 1740, 1600, 1320, 890, 685, and 655 cm^{-1}; ^{1}H NMR ($CDCl_3$, 60 MHz) δ 1.25 (s, 3 H), 1.65 (s, 3 H), 2.40 (s, 3 H), 3.52 (s, 3 H), 4.35 (s, 1 H), 7.20 (s, 2 H, J = 9.0 Hz), 7.61 (ns, 2 H, J =9.0 Hz), and 9.55 (s, 1 H); UV (95% ethanol) 229 nm (ϵ 1300) and 263 (850). Anal. Calcd for $C_{14}H_{18}O_5S$: C, 56.36; H, 6.08. Found: C, 56.08; H, 6.12.

Reaction of *trans*-2,2-Dimethyl-3-(*p*-tolylsulfonyl)cyclopropyl Methyl Ether (6) with Allyl Bromide. To an oven-dried, three-neck, 25-mL round-bottomed flask equipped with a spin bar and nitrogen line was added 15 mL of dry tetrahydrofuran, a crystal of 2,2′-dipyridyl indicator, and 0.12 mL of diisopropylamine. The mixture was cooled to 0 °C and 0.59 mL of a 1.48 M solution of *n*-butyllithium in hexane was added. The pink solution was stirred for 5 min at 0 °C and was then cooled to −78 °C. To this solution was added 200 mg of **6** in 2 mL of tetrahydrofuran via syringe. The resulting yellow anion was stirred at −78 °C for an additional 30 min and then 1 mL of HMPA was added. The solution was allowed to warm to −45 °C and was stirred for an additional 30 min. The newly formed red carbanion was cooled to −78 °C followed by the addition of 0.25 mL of allyl bromide. The solution was then warmed to room temperature and was stirred for an additional 3 h. The reaction was quenched with a saturated ammonium chloride solution, diluted with ether, and washed with a 10% hydrochloric acid solution, water and brine. The organic layer was dried over magnesium sulfate and concentrated under reduced pressure to give 226 mg of an oil. This material was chromatographed on a column of silica gel with a 5% acetone-hexane mixture as the eluent. The major fraction contained 215 mg (93% yield) of 3-[(*p*-3-butenylphenyl)-

sulfonyl]-2,2-dimethylcyclopropyl methyl ether (22): IR (neat) 3080, 2990, 1645, 1600, 1500, 1310, 1150, 1090, 920, 860, 800, 715, and 660 cm^{-1}; ^1H NMR (90 MHz, CCl_4) δ 1.19 (s, 3 H), 1.40 (s, 3 H), 2.00 (d, 1 H, J = 3.0 Hz), 2.20–2.90 (m, 4 H), 3.25 (s, 3 H), 3.65 (d, 1 H, J = 3.0 Hz), 4.85–5.10 (m, 2 H), 5.51–5.99 (m, 1 H), 7.25 (d, 2 H, J = 9.0 Hz), and 7.71 (d, 2 H, J = 9.0 Hz); UV (95% ethanol) 228 nm (ϵ 17 000) and 263 (780). Anal. Calcd for $C_{16}H_{22}O_3S$: C, 65.27; H, 7.53; S, 10.89. Found: C, 64.45; H, 7.58; S, 10.72.

Treatment of (*E*)- or (*Z*)-2-Methoxy-1-(phenylsulfonyl)ethylene (23 or 24) with Various Electrophiles. A solution containing 114 mg of (*E*)- (23) or (*Z*)-2-methoxy-1-(phenylsulfonyl)ethylene (24)[69] in 5 mL of tetrahydrofuran was cooled to −78 °C under a nitrogen atmosphere. To this solution was added 0.6 mL of a 1.55 M *n*-butyllithium solution in hexane over a 2-min period. The deep orange mixture was stirred for 15 min at −78 °C and was then quenched with 0.28 mL of methanol-*d*. The solvent was removed under reduced pressure and the organic residue was taken up in chloroform and washed with a saturated sodium bicarbonate solution and dried over sodium sulfate. Removal of the solvent under reduced pressure left a pale oil whose NMR spectrum indicated it to consist primarily (>90%) of (*E*)-1-deuterio-2-methoxy-1-(phenylsulfonyl)-ethylene (25): NMR ($CDCl_3$, 300 MHz) δ 3.67 (s, 3 H), 7.40–7.75 (m, 4 H), and 7.8–8.0 (m, 2 H). No signs of the vinyl signal at δ 5.70 could be detected in the crude NMR spectrum.

Quenching of the above carbanion derived from 23 and 24 with methyl iodide gave (*E*)-2-methoxy-1-methyl-1-(phenylsulfonyl)-ethylene (26) in 98% as a clear oil: IR (neat) 3060, 2940, 2840, 1650, 1445, 1300, 1245, 1140, 1080, 960, 780, 760, and 690 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 1.71 (s, 3 H), 3.87 (s, 3 H), 7.35 (s, 1 H), 7.4–7.65 (m, 3 H), and 7.8–7.9 (m, 2 H); MS, *m/e* 212 (M^+), 125, 84 (base), and 77% HRMS calcd for $C_{10}H_{12}O_3S$ 212.0507, found 212.0482.

When the anion derived from either 23 or 24 was treated with cyclohexanone, a clear oil was obtained which corresponded to the 1,2-addition product 27 in 73% yield: IR (neat) 3520, 2920, 2840, 1620, 1450, 1250, 1140, 1080, 980, 960, 880, 850, 760, 720, 690 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 1.1–2.0 (m, 10 H), 2.79 (s, 1 H), 3.96 (s, 3 H), 7.53 (s, 1 H), 7.50–7.75 (m, 3 H), and 7.8–8.0 (m, 2 H).

Reaction of 3,3-Dimethyl-1-(*p*-tolylsulfonyl)-2-(trimethylsilyl)cyclopropene (5) with Thiophenoxide Anion. A 250-mL, three-neck, round-bottomed flask equipped with a spin bar, addition funnel, reflux condensor, and nitrogen line was charged with 1.12 g of thiophenol, 590 mg of potassium hydroxide, and 80 mL of 95% ethanol. The mixture was stirred at 25 °C for 10 min followed by the addition of 1.0 g of cyclopropene 5 in 50 mL of 95% ethanol. The mixture was heated at reflux for 3 h and cooled to 25 °C, and the solvent was removed in vacuo. The resulting residue was dissolved in 175 mL of ether, and washed with a 10% sodium hydroxide solution, water, and brine. The organic layer was dried over magnesium sulfate and concentrated under reduced pressure to give 1.19 g of a crude oil. This material was chromatographed on a silica gel column with a 10% acetone–hexane mixture as the eluent. The major fraction was rechromatographed on a 4-mm plate by using a 5% acetone–hexane mixture to give 890 mg (100% yield) of a yellow oil which was assigned the structure *trans*-2,2-dimethyl-3-(*p*-tolylsulfonyl)cyclopropyl phenyl sulfide (31) on the basis of the following spectral properties: IR (neat) 3070, 2970, 1600, 1590, 1500, 1485, 1445, 1310, 1150, 1090, 820, and 670 cm^{-1}; ^1H NMR (90 MHz, CCl_4) δ 1.22 (s, 3 H), 1.59 (s, 3 H), 2.19 (d, 1 H, J = 6.0 Hz), 2.30 (s, 3 H), 3.00 (d, 1 H, J = 6.0 Hz), 7.23–7.00 (m, 7 H), and 7.69 (d, 2 H, J = 9.0 Hz); ^{13}C NMR (20 MHz, $CDCl_3$) δ 20.0, 21.8, 30.4, 34.1, 52.1, 65.8, 126.1, 127.3, 128.1, 129.9, 135.7, 138.7, and 144.3; UV (95% ethanol) 227 nm (ϵ 17 000) and 250 (8600). Anal. Calcd for $C_{18}H_{20}O_2S_2$: C, 65.03; H, 6.06; S, 19.29. Found: C, 64.89; H, 6.08; S, 19.16.

A sample containing 90 mg of 31 was dissolved in 5 mL of anhydrous ether under a nitrogen atmosphere. The solution was cooled to −78 °C and 0.2 mL of a 1.43 M solution of *n*-butyllithium in hexane was added. The solution was stirred for 30 min, quenched with 1 mL of deuterium oxide, warmed to room temperature, and diluted with ether. The organic layer was washed with water and brine, dried over magnesium sulfate, filtered, and concentrated under reduced pressure to give 87 mg of deuteriated 38: ^1H NMR (90 MHz, CCl_4) δ 1.29 (s, 3 H), 1.59 (s, 3 H), 2.40 (s, 3 H), 3.05 (s, 1 H), 7.29–7.05 (m, 7 H), and 7.69 (d, 2 H, J = 9.0 Hz).

Preparation of *trans*-2,2-Dimethyl-3-(*p*-tolylsulfonyl)-cyclopropyl *p*-Tolyl Sulfide (32). A 250-mL, three-neck, round-bottomed flask equipped with a spin bar, addition funnel, reflux condensor, and nitrogen line was charged with 1.81 g of potassium hydroxide, 3.76 g of *p*-thiocresol, and 100 mL of 95% ethanol. The mixture was stirred at room temperature for 10 min followed by the addition of 2.98 g of cyclopropene 5 in 50 mL of 95% ethanol. The resulting solution was heated at reflux for 3 h and cooled to 25 °C, and the solvent was removed under reduced pressure. The residue was dissolved in 200 mL of ether and washed with a 10% sodium hydroxide solution, water, and brine. The organic layer was dried over magnesium sulfate and the solvent was removed to give 3.76 g of a crude oil. This material was chromatographed on a silica gel column with a 10% acetone–hexane mixture as the eluent to give 3.69 g of a clear oil which was further purified by chromatography on a 4-mm plate by using a 5% acetone–hexane mixture. The major fraction contained 3.00 g (86% yield) of a white solid whose structure was assigned as *trans*-2,2-dimethyl-3-(*p*-tolylsulfonyl)cyclopropyl *p*-tolyl sulfide (32) on the basis of its spectral data: mp 78–79 °C; IR (neat) 3040, 2970, 1600, 1500, 1460, 1310, 1150, 1090, 815, 740, 710, and 670 cm^{-1}; ^1H NMR (90 MHz, CCl_4) δ 1.29 (s, 3 H), 1.60 (s, 3 H), 2.20 (d, 1 H, J = 6.0 Hz), 2.30 (s, 3 H), 2.42 (s, 3 H), 3.00 (d, 1 H, J = 6.0 Hz), 6.93 (d, 2 H, J = 9.0 Hz), 7.10 (d, 2 H, J = 9.0 Hz), 7.19 (d, 2 H, J = 9.0 Hz), and 7.60 (d, 2 H, J = 9.0 Hz); ^{13}C NMR (20 MHz, $CDCl_3$) δ 21.0, 21.6, 21.9, 30.5, 34.9, 52.3, 127.3, 129.1, 129.8, 136.4, 138.8, 144.2; UV (95% ethanol) 226 nm (ϵ 19 000) and 253 (8700). Anal. Calcd for $C_{19}H_{22}O_2S_2$: C, 65.86; H, 6.40; S, 18.51. Found: C, 65.92; H, 6.44; S, 18.49.

Short-Term Reaction of 3,3-Dimethyl-1-(*p*-tolylsulfonyl)-2-(trimethylsilyl)cyclopropane (5) with Lithium Thiophenolate. To a stirred solution containing 750 mg of thiophenol in 100 mL of anhydrous tetrahydrofuran was added 2.4 mL of a 1.43 M solution of *n*-butyllithium in hexane at 0 °C. The resulting solution was warmed to 25 °C followed by the addition of 1.0 g of cyclopropene 5 in 50 mL of dry tetrahydrofuran. The resulting yellow solution was stirred for 2 h at 25 °C followed by the addition of 10 mL of water. The solvent was removed under reduced pressure and the resulting residue diluted with ether and washed with a 10% sodium hydroxide solution, water, and brine. The ether was dried over magnesium sulfate and concentrated under reduced pressure to give 1.21 g of a crude solid. This material was chromatographed on a silica gel column with a 5% acetone–hexane mixture as the eluent. The first fraction contained 400 mg (30% yield) of a white solid whose structure was assigned as *trans*-[2,2-dimethyl-1-(phenylthio)-3-(*p*-tolylsulfonyl)cyclopropyl]trimethylsilane (33) on the basis of the following data: mp 96–97 °C; IR (KBr) 3080, 3000, 2960, 1600, 1590, 1485, 1150, 1090, 850, 745, and 670 cm^{-1}; ^1H NMR (90 MHz, CCl_4) δ 0.38 (s, 9 H), 1.29 (s, 3 H), 1.58 (s, 3 H), 2.29 (s, 1 H), 2.39 (s, 3 H), 7.39–7.10 (m, 7 H), and 7.65 (d, 2 H, J = 9.0 Hz); ^{13}C NMR (20 MHz, $CDCl_3$) δ 1.85, 19.4, 21.4, 24.8, 34.1, 35.4, 59.7, 125.8, 127.0, 128.6, 129.3, 129.7, 136.4, 139.2 and 144.0; UV (95% ethanol) 228 nm (ϵ 20 000) and 265 (7700). Anal. Calcd for $C_{21}H_{28}O_2S_2Si$: C, 62.33; H, 6.97. Found: C, 62.22; H, 7.03.

The second fraction to elute from the column contained 675 mg (60% yield) of a white powder whose structure was assigned as *cis*-[2,2-dimethyl-1-(phenylthio)-3-(*p*-tolylsulfonyl)cyclopropyl]trimethylsilane (34) on the basis of its spectral properties: mp 187–188 °C, IR (KBr) 3070, 2960, 1600, 1590, 1500, 1480, 1310, 1150, 1090, 845, 750, and 665 cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) δ −0.18 (s, 9 H), 1.41 (s, 3 H), 1.80 (s, 3 H), 2.40 (s, 3 H), 2.47 (s, 1 H), 7.25–7.10 (m, 5 H), 7.34 (d, 2 H, J = 9.0 Hz), and 7.88 (d, 2 H, J = 9.0 Hz); ^{13}C NMR (20 MHz, $CDCl_3$) δ 0.97, 18.6, 21.4, 26.1, 31.0, 34.8, 54.4, 125.1, 127.3, 127.6, 128.3, 129.6, 136.8, 139.3, and 144.1; UV (95% ethanol) 227 nm (ϵ 18 000) and 261 (11 000). Anal. Calcd for $C_{21}H_{28}O_2S_2Si$: C, 62.33; H, 6.97; S, 15.85. Found: C, 62.45; H, 7.00; S, 15.90.

(69) Marchese, G.; Naso, F. *Chim. Ind. (Milan)* **1971**, *53*, 760.

Treatment of either of the above compounds with potassium hydroxide in methanol (or tetrahydrofuran) afforded cyclopropane **31** as the exclusive product.

Preparation of Methyl *cis*- and *trans*-2,2-Dimethyl-1-(*p*-tolylsulfonyl)-3-(phenylthio)cyclopropanecarboxylate (39 and 40). To a stirred solution containing 1.0 g of *trans*-2,2-dimethyl-3-(*p*-tolylsulfonyl)cyclopropyl phenyl sulfide (**31**) in 50 mL of dry tetrahydrofuran at 0 °C was added 2.2 mL of a 1.43 M solution of *n*-butyllithium in hexane. The yellow solution was stirred for an additional 15 min followed by the addition of 0.22 mL of methyl chloroformate. The resulting solution was stirred for an additional 30 min at 0 °C, then warmed to 25 °C, and stirred for 12 h. The reaction was quenched with a saturated ammonium chloride solution, diluted with ether, washed several times with water, dried over magnesium sulfate, and evaporated to give 1.38 g of a yellow oil. This material was chromatographed on a 4-mm chromatatron plate by using a 5% acetone–hexane mixture as the eluent. The first fraction contained 880 mg (91%) of an oil which crystallized on standing and was identified as methyl *trans*-2,2-dimethyl-1-(*p*-tolylsulfonyl)-3-(phenylthio)cyclopropanecarboxylate (**40**) on the basis of its spectral data: mp 104–105 °C; IR (KBr) 3010, 3000, 2970, 1750, 1600, 1590, 1305, 1250, 750, 660, and 600 cm^{-1}; ^1H NMR (CCl_4, 90 MHz) δ 1.20 (s, 3 H), 1.68 (s, 3 H), 2.40 (s, 3 H), 3.50 (s, 4 H), 7.0–7.39 (m, 7 H), and 7.68 (d, 2 H, J = 9.0 Hz); UV (95% ethanol) 230 nm (ϵ 19000) and 248 (11000). Anal. Calcd for $C_{20}H_{22}O_4S_2$: C, 61.51; H, 5.68; S, 16.42. Found: C, 61.59; H, 5.73; S, 16.46.

The second fraction contained 90 mg (9%) of a white solid whose structure was assigned as methyl *cis*-2,2-dimethyl-1-(*p*-tolylsulfonyl)-3-(phenylthio)cyclopropanecarboxylate (**39**) on the basis of its characteristic spectral properties: mp 122–123 °C; IR (KBr) 3020, 2970, 1735, 1600, 1590, 1350, 1250, 820, 670, and 615 cm^{-1}; ^1H NMR (CCl_4, 90 MHz) δ 1.25 (s, 3 H), 1.70 (s, 3 H), 2.35 (s, 3 H), 3.11 (s, 1 H), 3.48 (s, 3 H), 7.10–7.35 (m, 7 H), and 7.70 (d, 2 H, J = 9.0 Hz); UV (95% ethanol) 228 nm (ϵ 18000) and 250 (9600). Anal. Calcd for $C_{20}H_{22}O_4S_2$: C, 61.51; H, 5.68; S, 16.42. Found: C, 61.67; H, 5.72; S, 16.36.

Preparation of Methyl *trans*-2,2-Dimethyl-3-(phenylsulfonyl)-1-(*p*-tolylsulfonyl)cyclopropanecarboxylate (41). To a stirred solution containing 350 mg of cyclopropane **40** in 25 mL of chloroform was added 0.33 g of *m*-chloroperoxybenzoic acid in 25 mL of chloroform at −10 °C under a nitrogen atmosphere. The resulting mixture was slowly warmed to 25 °C and was stirred for an additional 12 h. At the end of this time, the solution was washed with a saturated solution of sodium bicarbonate. The organic layer was dried over magnesium sulfate and concentrated to give a brown oil. This material was crystallized from a dichloromethane–petroleum ether mixture to give 200 mg (52% yield) of a white solid whose structure was assigned as methyl *trans*-2,2-dimethyl-3-(phenylsulfonyl)-1-(*p*-tolylsulfonyl)cyclopropanecarboxylate (**41**) on the basis of its spectral data: mp 121–122 °C; IR (KBr) 3040, 3000, 2980, 1740, 1600, 1590, 1320, 1150, 1080, 660, and 610 cm^{-1}; ^1H NMR ($CDCl_3$, 360 MHz) δ 1.64 (s, 3 H), 1.67 (s, 3 H), 2.44 (s, 3 H), 3.56 (s, 1 H), 3.58 (s, 3 H), 7.20 (d, 2 H, J = 9.0 Hz), 7.45–7.80 (m, 5 H), and 8.01 (d, 2 H, J = 9.0 Hz); UV (95% ethanol) 222 nm (ϵ 21000) and 265 (1800). Anal. Calcd for $C_{20}H_{22}O_6S_2$: C, 56.85; H, 5.25. Found: C, 56.95; H, 5.29.

A 75-mg sample of **41** was treated with 1 equiv of LDA at −78 °C and the mixture was allowed to warm to −20 °C and was then quenched with methanol. Normal workup resulted in a clear oil whose NMR spectrum showed it to consist of a 1:1 mixture of **41** and **42**. NMR ($CDCl_3$, 360 MHz) of **42**: δ 1.65 (s, 3 H), 1.68 (s, 3 H), 2.46 (s, 3 H), 3.43 (s, 1 H), 3.62 (s, 3 H), 7.21 (d, 2 H, J = 9.0 Hz), 7.45–7.80 (m, 5 H), and 8.02 (d, 2 H, J = 9.0 Hz).

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Perturbation of SDS and CTAB Micelles by Complexation with Poly(ethylene oxide) and Poly(propylene oxide)

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Pseudo-first-order rate constants have been determined for the neutral hydrolysis of 1-benzoyl-3-phenyl-1,2,4-triazole in aqueous solutions in the presence of SDS and CTAB micelles and SDS–PEO, SDS–PPO, and CTAB–PPO mixed micelles. The micellar rate inhibition of the hydrolysis is clearly modified as a result of micelle–polymer complexation, the effects being rather specific for the nature of the surfactant and the polymer. The kinetic data were analyzed by a simple pseudophase model. The results revealed stabilization of the micelles by interaction with the polymer and polymer-induced microenvironmental changes at the micellar binding sites of the substrate. Results from conductivity measurements facilitated the interpretation of the kinetic data.

There is considerable recent interest in the complexes formed between micelles and uncharged water-soluble polymers.[1-4] However, neither the morphology of these polymer-complexed micelles ("mixed micelles") nor the interactions governing the complex formation have been clearly established. In the present study we compare micelle–polymer complexes formed from an anionic surfactant (sodium dodecyl sulfate, SDS) and a cationic surfactant (cetyltrimethylammonium bromide, CTAB) and two structurally related water-soluble polymers, poly(ethylene oxide) (PEO) and poly(propylene oxide) (PPO). Emphasis is placed on a comparison of the inhibitory effects of these complexes on a water-catalyzed hydrolysis reaction.[5] The interpretation of the kinetic data is facilitated by results from conductivity studies.

Results and Discussion

Conductivity Measurements. Figures 1 and 2 show specific conductivities (κ) as a function of the SDS concentration in aqueous solution in the presence of fixed concentrations of PEO (weight-averaged MW 10000) or PPO (weight-averaged MW 1000, relatively low in order to ensure water solubility). For both polymers there is an initial linear increase of κ with increasing SDS concentration up to the first break at a well-defined SDS con-

(1) For an authoritative review, see: Goddard, E. D. *Colloids Surf.* **1986**, *19*, 255.
(2) Breuer, M. M.; Robb, I. D. *Chem. Ind. (London)* **1972**, *13*, 530.
(3) Cabane, B. *J. Phys. Chem.* **1977**, *81*, 1639.
(4) Nagarajan, R. *Colloids Surf.* **1985**, *13*, 1.
(5) For previous studies, see: (a) Fadnavis, N. W.; Engberts, J. B. F. N. *J. Am. Chem. Soc.* **1984**, *106*, 2636. (b) Fadnavis, N. W.; Van de Berg, H.; Engberts, J. B. F. N. *J. Org. Chem.* **1985**, *50*, 48.

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