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PREPARATION AND REACTIVITY OF ARYLSULFONYL SUBSTITUTED CYCLOPROPENES

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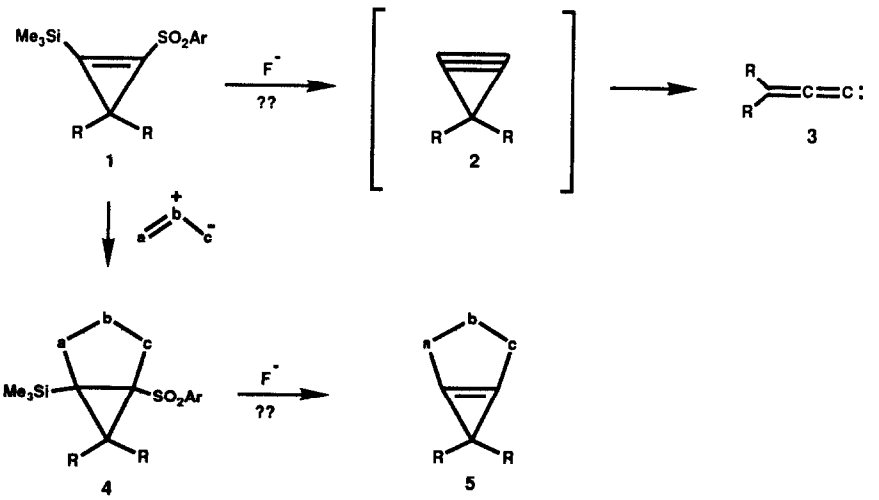
Abstract: A study of the cycloaddition behavior of several arylsulfonyl substituted alkynes with 2-diazopropane has been carried out. These activated acetylenes react to give 3H-pyrazoles which extrude nitrogen on photolysis to produce cyclopropenes in high yield. Soft nucleophiles such as thiophenoxide readily add to the activated pi-bond to give thiophenyl substituted cyclopropanes. Reaction of 1-phenylsulfonyl-2,3,3-trimethylcyclopropene with n-butyllithium followed by alkylation with various electrophiles produces arylsulfonyl substituted methylene cyclopropanes. These compounds undergo thermal rearrangement to the thermodynamically more stable isopropylidine cyclopropane.

The fluoride ion promoted elimination of β-substituted organosilanes is a powerful technique for the generation of highly strained pi-bonds.[1-5] A great advantage of this method is the fact that the reagent, alkali fluoride, as well as the products, alkali halide and trimethylfluorosilane, are generally neutral and inert toward most functionalities.[1] The reaction has been applied to the preparation of benzyne[4], strained alkenes[1] and allenes[5], but not to strained alkynes. In recent years, an enormous effort has been devoted toward exploration of structural limits in organic compounds.[6] In several studies the effect of ring size on the reactivity of cyclic alkynes has been examined.[7-12] Cyclooctyne was found to be the smallest isolable unsubstituted cycloalkyne [13] The most intensively investigated cycloalkyne is benzyne, the chemistry of which has been reviewed.[14] Convincing evidence for the existence of cyclopentyne[15], norbornyne[16], cyclohexyne[9] and cycloheptyne[9] has been presented. The assignment of a C≡C stretch frequency at 1930 cm^{-1} obtained for acenaphthyne indicates a considerable loss of bond strength for the bent triple bond.[17] Attempts to generate cyclobutyne have been unsuccessful.[13,18] Chapman has speculated that both cyclobutyne and cyclopropyne might exist at very low temperatures in the rigid matrix.[19] However, molecular orbital calculations by Pople[20] and Schaefer[21] suggest that isomerization of cyclopropyne **2** to propadienylidene **3** should proceed with no barrier at all. As part of our continuing interest in the chemistry of strained rings[22], we set out to investigate the use of silyl sulfonyl substituted cyclopropenes as cyclopropyne equivalents for cycloaddition chemistry. Scheme I outlines how a silyl sulfonyl substituted cyclopropene could be utilized as an equivalent for cyclopropyne in its reaction with 1,3-dipoles. Cyclopropenes are known to readily undergo dipolar cycloaddition with a variety of 1,3-dipoles.[23-30] Our hope was that the initially

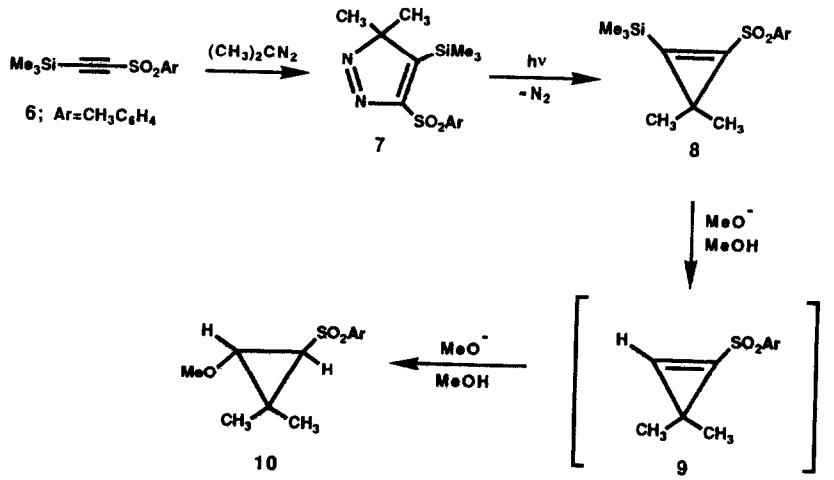
formed cycloadduct **4** might undergo a subsequent fluoride ion induced desilylsulfonyl elimination and generate the highly strained cyclopropene **5** The present paper documents the results of our investigations in this area.

Scheme I



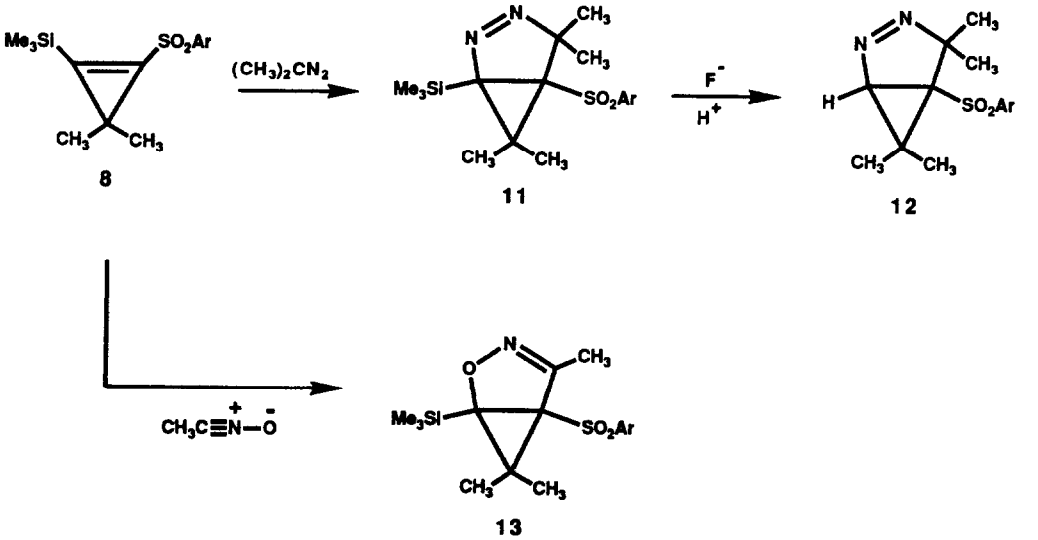
Results and Discussion

Silyl sulfonyl substituted 3H-pyrazole **7** was readily synthesized by the 1,3-dipolar cycloaddition of 2-diazopropane with alkyne **6**.[31] Photolysis of this material in benzene afforded cyclopropene **8** in excellent yield. All of our attempts to generate and trap a cyclopropyne from the reaction of **8** with fluoride ion failed. The only compound that could be isolated corresponded to the *trans* 1-methoxy-2-sulfonyl substituted cyclopropene **10**.[31] The formation of **10** can be

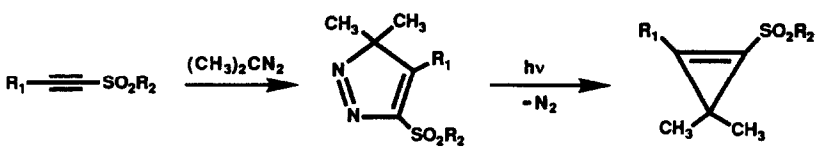


interpreted in terms of a process that involves attack of the alkoxide ion on the silicon atom to give a cyclopropenyl carbanion which is subsequently protonated to produce **9**. This highly activated cyclopropene reacts with more alkoxide ion under the conditions used to give the observed product.

When cyclopropene **8** was treated with 2-diazopropane in ether, a clean 1,3-dipolar cycloaddition occurred producing 2,3-diazobicyclo[3.1.0]hex-2-ene **11** in 90% yield. A related cycloadduct (i.e. **13**) was formed when cyclopropene **8** was allowed to react with methyl nitrile oxide Numerous attempts to introduce a pi-bond into **11** or **13** by desilylsulfonylation using fluoride ion failed. This comes as no real surprise considering the highly strained nature of the bicyclic ring system. The only product that was isolated corresponded to the sulfonyl substituted diazabicyclohexene **12**.



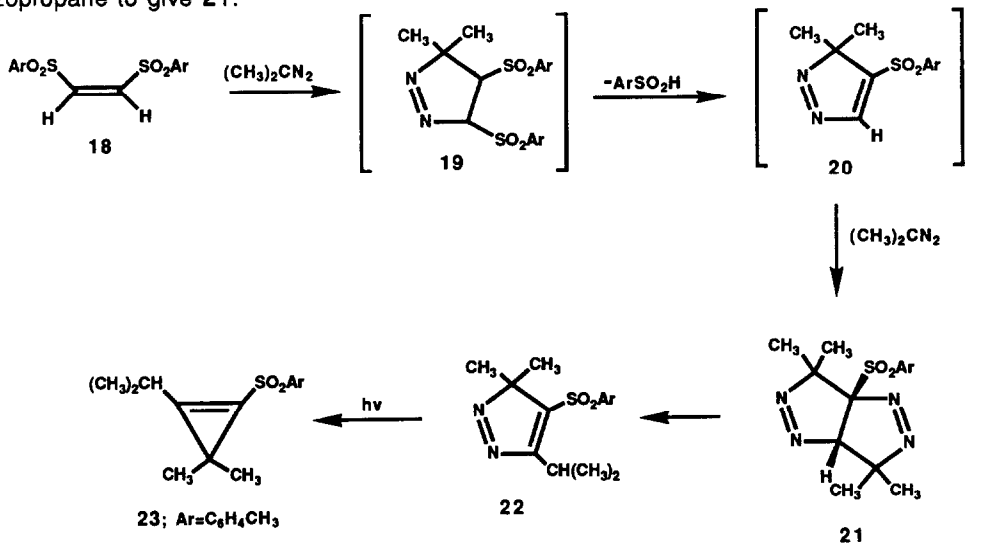
Arylsulfonyl substituted cyclopropenes have the potential to function as valuable synthons in organic chemistry. As a direct consequence of our own involvement with the chemistry of unsaturated sulfones[32], we decided to further explore the chemistry of these cyclopropenyl substituted sulfones. The photolysis of 3H-pyrazoles is well known to give cyclopropenes as



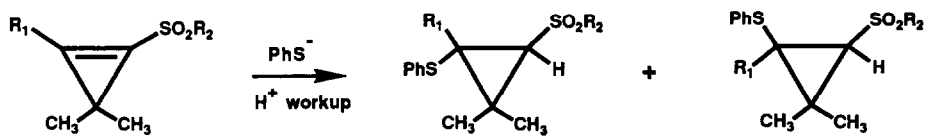
14; R_1=Ph; R_2=CH_3
16; R_1=CH_3; R_2=Ph

15; R_1=Ph; R_2=CH_3
17; R_1=CH_3; R_2=Ph

products.[33-35] We have used this method to prepare arylsulfonyl substituted cyclopropenes **15** and **17**. Cyclopropene **23** was also prepared by photolysis of 3H-pyrazole **22**, which in turn was obtained from the thermolysis of pyrazolo[4,3-c]pyrazole **21**. Preferential loss of nitrogen to give the most stable diradical followed by a 1,2-hydrogen shift nicely rationalizes the selective formation of **22** from **21**. Pyrazolopyrazole **21** is formed by an initial dipolar-cycloaddition of 2-diazopropane with *bis*-sulfone **18** to produce the expected cycloadduct **19**. This compound readily loses *p*-toluenesulfenic acid and the resulting 3H-pyrazole **20** reacts further with excess diazopropane to give **21**.



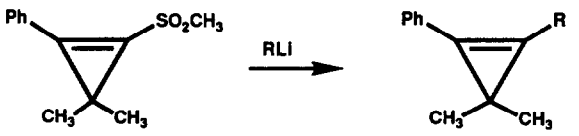
Small ring hydrocarbons possessing a strained π-bond are of considerable interest owing to their reactivity as well as their spectroscopic and structural properties.[6,36] Cyclopropenes represent an intriguing class of molecules where a strained σ-bond is incorporated into a substrate that already possesses a reactive π-system. Addition across the double bond in cyclopropene would proceed quite readily since it reduces ring strain by 26 kcal/mol.[37,38] The high reactivity of the cyclopropene π-bond is demonstrated by the ease with which Diels-Alder additions take place. For example, at 0°C cyclopropene and cyclopentadiene react rapidly and quantitatively to form a cycloadduct in high yield.[39] Earlier work in our laboratory[40] as well as studies by others[41-44]



17; R_1=CH_3; R_2=Ph
23; R_1=iPr; R_2=$C_6H_4CH_3$

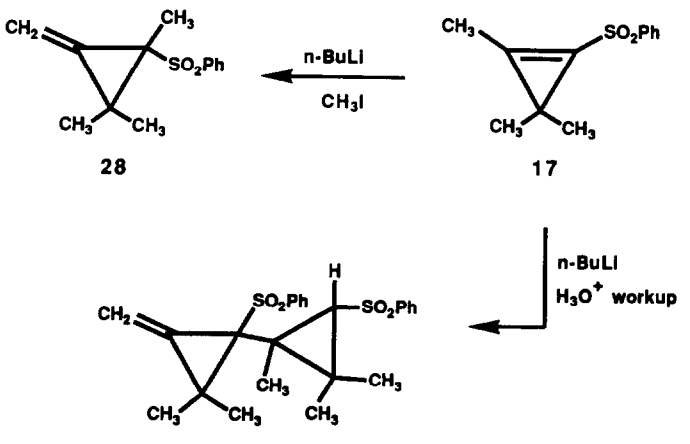
24; R_1=CH_3; R_2=Ph
25; R_1=iPr; R_2=$C_6H_4CH_3$

have established that nucleophiles readily add to cyclopropenes. We have found that a soft nucleophile such a thiophenoxide reacts with cyclopropene **17** (or **23**) to give a 4 3:1 *trans:cis* mixture of cyclopropane **24** (or a 3.6:1 mixture of **25**). We also investigated the reaction of cyclopropene **15** with a hard nucleophile such as an alkyllithium and found that a most unusual reaction occurred.[45] Thus, treatment of **15** with typical alkyllithium reagents under standard conditions afforded cyclopropene **26** in high yield.[45] Vinyl sulfones generally undergo conjugate addition with various reagents, and the resulting α-sulfonyl anions may be protonated or trapped with an assortment of electrophiles.[46] The above reaction is unique in that it formally involves addition of the lithium reagent across the *"wrong"* end of the vinyl sulfone.



15 **26** (R=CH_3, Ph, n-C_4H_9)

In order to obtain additional information concerning the mechanism of this process, we decided to investigate the reaction of the closely related methyl phenylsulfonyl substituted cyclopropene **17** with several alkyllithiums. Treatment of this particular cyclopropene with n-butyllithium (or methyllithium) followed by aqueous workup afforded dimer **27** as the only isolable product in 48% yield. No signs of any *ipso* substitution product could be found in the crude mixture. Reaction of **17** with n-butyllithium followed by alkylation with methyl iodide gave methylene cyclopropane **28** as the exclusive product in 95% yield. The above products can be rationalized in terms of removal of the acidic proton by the strong base. In the absence of an electrophile, the initially produced carbanion adds to the activated cyclopropene π-bond eventually giving rise to dimer **27** on aqueous workup. Apparently, this process is much faster

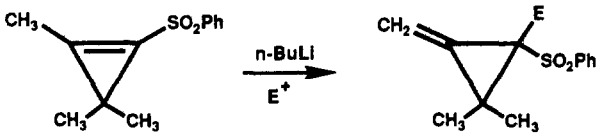


28 **17**

27

than replacement of the phenylsulfonyl group by the alkyllithium reagent. Other workers have also noted the formation of methylene cyclopropanes from alkyl substituted cyclopropenes upon treatment with a strong base.[47,48]

We have found that the allylic carbanion derived from cyclopropene **17** could be alkylated with a variety of electrophiles producing methylene cyclopropanes **29-33** in good yield Having a

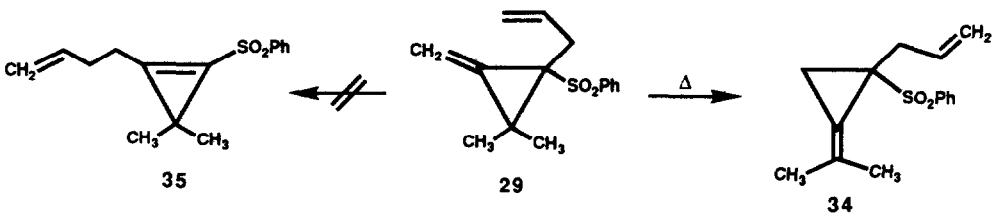


17

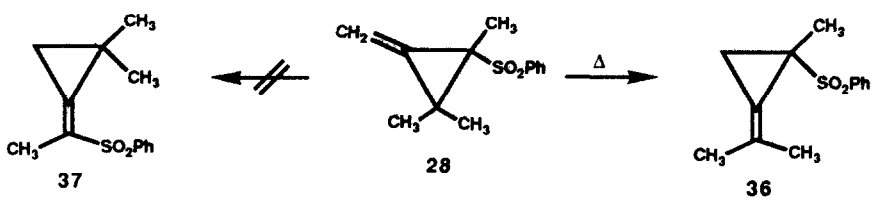
29; E=allyl
30; E=crotyl
31; E=cinnamyl
32; E=SCH_3
33; E=CH_2SiMe_3

supply of these compounds on hand, we became interested in knowing whether the allyl substituted cyclopropene **29** would undergo a Cope rearrangement upon thermolysis. In an earlier report we had established that allyl substituted cyclopropenes readily undergo a 3,3-sigmatropic rearrangement via a 1,4-cyclohexylene biradical intermediate.[49] Since there are very few reports of Cope rearrangements involving methylene cyclopropanes, we decided to investigate the thermal behavior of cyclopropane **29**.

Heating a sample of **29** to 140°C for 4 h afforded a single isomeric product whose structure was established as the rearranged isopropylidine cyclopropane **34**. No signs of the 3,3-sigmatropic shift product **35** could be detected in the crude reaction mixture. A related transformation occurred when cyclopropane **28** was heated at 140°C producing the isomeric cyclopropane **36** as

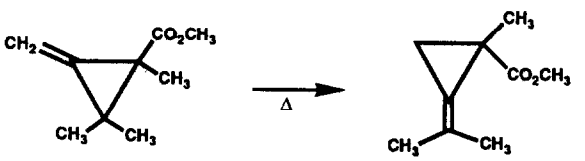


35 **29** **34**



37 **28** **36**

the exclusive product in 99% yield. Apparently, the activation energy associated with the Cope rearrangement is much higher than σ-bond fragmentation to generate the relatively stable trimethylenemethane diradical. Some of the energy difference is undoubtedly related to the problem of having to reintroduce a strained pi-bond in the three-membered ring for the Cope process. The degenerate thermal rearrangement of methylene cyclopropane has been studied by experimental and theoretical chemists for over two decades.[50-55] Theoretical studies have suggested that the most likely intermediate for the rearrangement is a singlet diradical in which one of the methylene groups lies in a plane orthogonal to the plane of all the other atoms.[54,55] Presumably a similar species is involved in the rearrangement of **28** to **36**. It is worth noting that only a single rearranged compound is formed, even though a mixture (i.e., **36** and **37**) could have been produced from the unsymmetrically substituted cyclopropene **28**. A similar observation had



38 **39**

been made earlier with the closely related carbonmethoxy substituted cyclopropane **38**.[56] It seems that the carbon which can best stabilize the radical center is the one which preferentially migrates.

In conclusion, arylsulfonyl substituted cyclopropenes are readily available from the 1,3-dipolar cycloaddition of diazoalkanes with arylsulfonyl alkynes followed by photolysis of the resulting 3H-pyrazole ring. Soft nucleophiles such as thiophenoxide readily add to the activated pi-bond to give thiophenyl substituted cyclopropanes. Reaction of 1-phenylsulfonyl-2,3,3-trimethylcyclopropene with n-butyllithium followed by alkylation with various electrophiles produces arylsulfonyl substituted methylene cyclopropanes. These compounds undergo thermal rearrangement to the thermodynamically more stable isopropylidine cyclopropane. The further generalization of these findings and their implications for the synthesis of novel strained rings are the objects of ongoing investigations.

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 a Varian EM-390, a Nicolet 360 and a GE QE-300 MHz spectrometer. ^{13}C-NMR spectra were recorded on a Varian CFT-20 NMR spectrometer (20 MHz) or on a Brucker WP-200-SY NMR spectrometer (50 MHz). Microanalyses were performed at Atlantic

Microlabs, Atlanta, Ga. Mass spectra were determined with a VG MM-7070S mass spectrometer at an ionizing voltage of 70 eV.

1,3-Dipolar Cycloaddition of 3,3-Dimethyl-1-(p-tolylsulfonyl)-2-(trimethylsilyl)-cyclopropene (8) with 2-Diazopropane. A solution of 2-diazopropane was prepared using 35 g of acetone hydrazone, 140 g of mercury (II) oxide and 12 mL of a 3.0 M potassium hydroxide solution in methanol. To the deep red solution was added 8.72 g (29.6 mmoles) of cyclopropene **8**[31] in anhydrous ether at -78°C. The mixture was slowly warmed to room temperature and was stirred for an additional 12 h under a nitrogen atmosphere. The ether was washed with a 10% hydrochloric acid solution followed by brine, dried over magnesium sulfate and concentrated under reduced pressure to give 9.72 g (90% yield) of a solid. This material was recrystallized from dichloromethane and petroleum ether to give a white solid whose structure was assigned as 4,4,6,6-tetramethyl-5-(p-tolylsulfonyl)-1-(trimethylsilyl)-2,3-diazabicyclo[3.1.0]hex-2-ene (**11**) on the basis of the following spectral properties: mp 150-151°C; IR (KBr) 3080, 1600, 1540, 1500, 1320, 1165, 850, 680 and 610 cm^{-1}; ^{1}H-NMR (90 MHz, $CDCl_3$) δ 0.40 (s, 9H), 0.79 (s, 3H), 0.82 (s, 3H), 1.35 (s, 3H), 1.81 (s, 3H), 2.40 (s, 3H), 7.31 (d, 2H, J= 9.0 Hz), and 7.60 (d, 2H, J= 9.0 Hz); ^{13}C-NMR (20 MHz, $CDCl_3$) δ 0.53, 20.5, 21.3, 21.4, 27.4, 37.4, 62.9, 82.7, 91.6, 127.0, 129.5, 138.5, and 144.0; UV (95% ethanol) 228 nm (ε=14,000), 265 nm (ε=1,000), and 330 nm (ε=150), Anal. Calcd. for $C_{18}H_{28}O_2N_2SSi$: C, 59.30; H, 7.74; N, 7.68; S, 8.79. Found: C, 59.43; H, 7.79; N, 7.66; S, 8.89.

Desilylation of 4,4,6,6-Tetramethyl-5-(p-tolylsulfonyl)-1-(trimethylsilyl)-2,3-diazabicyclo[3.1.0]hex-2-ene (11). A 200 mg (0.55 mmoles) sample of the above bicyclohexene was dissolved in 10 mL of anhydrous tetrahydrofuran at 25°C. To this mixture was added 0.55 mL (0.55 mmoles) of a 1.0 M solution of tetrabutylammonium fluoride in tetrahydrofuran. The progress of the reaction was followed by TLC and was found to be instantaneous. The solution was diluted with 100 mL of ether, washed several times with water, once with brine, and dried over magnesium sulfate. Removal of the solvent under reduced pressure gave 215 mg of an oil which was chromatographed on a silica gel column using a 10% acetone:hexane mixture as the eluent. Removal of the solvent left 148 mg (93% yield) of an oil which was identified as 4,4,6,6-tetramethyl-5-(p-tolylsulfonyl)-2,3-diazabicyclo[3.1.0]hex-2-ene (**12**) on the basis of the following spectral properties: mp 100-101°C; ^{1}H-NMR (90 MHz, CCl_4) δ 0.72 (s, 3H), 1.30 (s, 3H), 1.42 (s, 3H), 1 65 (s, 3H), 2.42 (s, 3H), 5.00 (s, 1H), 7.29 (d, 2H, J= 9.0 Hz), and 7.65 (d, 2H, J= 9.0 Hz); ^{13}C-NMR (20 MHz, $CDCl_3$) δ 19.1, 20.5, 21.2, 21.9, 27.2, 33.2, 58.0, 77.9, 91.7, 126.8, 129.5, 138.6, and 144.1; UV (95% ethanol) 231 nm (ε=14,000), 265 nm (ε=1,200) and 325 nm (ε=330); Anal. Calcd. for $C_{15}H_{20}O_2N_2S$: C, 61.62; H, 6.89; N, 9.58. Found: C, 61.51; H, 6.94; N, 9.57.

1,3-Dipolar Cycloaddition of 3,3-Dimethyl-1-(p-tolylsulfonyl)-2-(trimethylsilyl)-cyclopropene (8) with Methyl Nitrile Oxide. An oven dried 25 mL three-neck, round-bottomed flask equipped with spin bar and nitrogen line was charged with 500 mg (1.7 mmoles) of cyclopropene **8**, 0.14 mL (1.9 mmoles) of nitroethane, 0.21 mL of phenyl isocyanate (1.9 mmoles)

and 15 mL of dry benzene. To the stirred solution was added 3 drops of triethylamine. Reaction was evidenced by the evolution of carbon dioxide and the precipitation of sym-dimethyl urea The mixture was stirred for 2 h at 25°C, dried over magnesium sulfate and filtered to give 470 mg of an oil which was chromatographed on silica gel using a 5% acetone:hexane mixture as the eluent. The major fraction contained 310 mg (67% yield) of an oil which crystallized to give a white solid which was identified as 4,6,6-trimethyl-5-(p-tolylsulfonyl)-1-(trimethylsilyl)-2-oxa-3-azabicyclo-[3.1.0]hex-3-ene (**13**) on the basis of the following spectral data: mp 85-86°C; IR (KBr) 3060, 2980, 1600, 1500, 1320, 1150, 850 and 670 cm^{-1}; ^{1}H-NMR (90 MHz, CCl_4) δ 0.31 (s, 9H), 0.82 (s, 3H), 1.55 (s, 3H), 1.80 (s, 3H), 2.41 (s, 3H), 7.30 (d, 2H, J= 9.0 Hz), and 7.71 (d, 2H, J= 9.0 Hz); UV (95% ethanol) 229 nm (ε= 17,000); Anal. Calcd. for $C_{17}H_{25}O_3NSSi$: C, 58.08; H, 7.17; N, 3.98. Found: C, 58.12; H, 7.22; N, 3.93.

Preparation of 3,3-Dimethyl-1-methylsulfonyl-2-phenylcyclopropene (15). Phenylacetylene (25.5 g, 0.25 moles) was cautiously added to a suspension of sodamide in liquid ammonia (prepared from 5.46 g (0.24 moles) of sodium metal) at -78°C. After stirring for 15 min, 8 0 g (0.25 moles) of powdered sulfur was added in 1.0 g portions followed by 46.2 g (0.32 moles) of iodomethane. Stirring was continued until most of the ammonia had evaporated and then water was added and the mixture was extracted with ether. The organic layer was dried over magnesium sulfate and evaporated to give a brown oil which was distilled under reduced pressure to give 21.5 g (58% yield) of a yellow oil [bp 95°C (1.5 mm)] which was identified as methyl phenylethynylsulfide on the basis of its characteristic NMR: ^{1}H-NMR (CCl_4, 90 MHz) δ 2.35 (s, 3H), and 7.10-7.40 (m, 5H).

To a mechanically stirred solution containing 20.7 g (0.14 moles) of the above sulfide in 100 mL of chloroform at 0°C was added 63.4 g (0.37 moles) of m-chloroperoxybenzoic acid in small portions so as to keep the temperature of the reaction below 10°C. After the addition was complete, stirring was continued for an additional 12 h at which time the suspension was filtered, washed twice with 100 mL portions of saturated sodium bisulfite, twice with saturated sodium bicarbonate, and dried over magnesium sulfate. The solvent was evaporated under reduced pressure to give 24 g (95% yield) of a white solid which was identified as methyl phenylethynylsulfone on the basis of the following data: mp 61-62°C; ^{1}H-NMR ($CDCl_3$, 90 MHz) δ 3.10 (s, 3H) and 7.21-7.58 (m, 5H); IR (KBr) 3050, 2950, 2240, 1590, 1330, and 1150 cm^{-1}; Anal. Calcd. for $C_9H_8O_2S$: C, 59.98; H, 4.47; S, 17.79. Found: C, 59.72; H, 4.56; S, 17.67.

To a solution of 2-diazopropane in ether at -78°C was added 11.3 g (63 mmoles) of methyl phenylethynylsulfone in 60 mL of tetrahydrofuran. The red solution was stirred for 30 min at -78°C under nitrogen then warmed to 25°C and stirred for 12 h. The organic layer was washed twice with dilute aqueous hydrochloric acid, once with brine, dried over magnesium sulfate and concentrated to dryness to give a yellow solid which was recrystallized from benzene:hexane to give 14 1 g (94% yield) of a yellow solid which was identified as 3,3-dimethyl-5-methylsulfonyl-4-phenyl-3H-pyrazole (**14**) on the basis of its spectral properties: mp 90-91°C; ^{1}H-NMR ($CDCl_3$, 360 MHz)

δ 1.79 (s, 6H), 2.86 (s, 3H), 7 56-7.58 (m, 3H) and 8 17-8.20 (m, 2H); IR (KBr) 3020, 2940, 1620, 1600, 1320, 1150, 990, 770, 705, and 560 cm^{-1}; UV (95% ethanol) 228 nm (ε=9,600) and 288 nm (ε=7,600); ^{13}C-NMR ($CDCl_3$, 20 MHz) δ 20.3, 43.0, 99.7, 126.9, 128.5, 129.8, 130.8, 147.8, and 153 0; Anal Calcd. for $C_{12}H_{14}O_2N_2S$: C, 57.58; H, 5.64; N, 11 19; S, 12.81. Found: C, 57.42, H, 5 65, N, 11.01; S, 12.70

A solution containing 5.0 g (20 mmoles) of 3H-pyrazole **14** in 1.5 L of benzene was irradiated for 90 min using a 450-W Hanovia medium pressure mercury arc lamp equipped with a Pyrex filter sleeve under an argon atmosphere. The solvent was removed under reduced pressure and the crude residue was chromatographed on a silica gel column using a 20% ethyl acetate-hexane mixture as the eluent The major fraction contained 4.22 g (95% yield) of a yellow oil whose structure was assigned as 3,3-dimethyl-1-methylsulfonyl-2-phenylcyclopropene (**15**) on the basis of the following spectral properties: ^{1}H-NMR ($CDCl_3$, 360 MHz) δ 1.57 (s, 6H), 3.15 (s, 3H), 7.46-7.50 (m, 3H), and 7.68-7.72 (m, 2H); IR (neat) 3080, 3040, 2930, 1790, 1610, 1585, 1500, 1455, 1315, 1140, 970, 780, and 700 cm^{-1}; UV (95% ethanol) 282 nm (ε=7,900); ^{13}C-NMR ($CDCl_3$, 20 MHz) δ 24.4, 32.96, 43.8, 123 3, 125.1, 128.7, 131.3, and 140.4; Anal. Calcd. for $C_{12}H_{14}O_2S$: C, 64.84; H, 6.35; S, 14.42. Found: C, 64.84; H, 6.33; S, 14.43

Preparation of 1-Phenylsulfonyl-2,3,3-trimethylcyclopropene (17). To a solution of 2-diazopropane in ether at -78°C was added 11.3 g of phenyl 1-propynylsulfone[57] in 60 mL of tetrahydrofuran. The red solution was stirred for 30 min at -78°C under nitrogen then warmed to 25°C and stirred for 12 h. The organic layer was washed twice with dilute aqueous hydrochloric acid, once with brine, dried over magnesium sulfate and concentrated to dryness to give a yellow oil which was chromatographed on a silica gel column using a 10% acetone-hexane mixture as the eluent. Removal of the solvent under reduced pressure left 14.2 g (95% yield) of a light yellow oil which was identified as 5-phenylsulfonyl-3,3,4-trimethyl-3H-pyrazole (**16**) on the basis of its spectral properties: mp 61-62°C; ^{1}H-NMR ($CDCl_3$, 90 MHz) δ 1 45 (s, 6H), 2.69 (s, 3H), and 7.40-8.00 (m, 5H); IR (KBr) 3060, 2980, 2940, 1620, 1590, 1450 and 845 cm^{-1}; UV (95% ethanol) 266 nm (ε 6,700), ^{13}C-NMR ($CDCl_3$, 20 MHz) δ 12.7, 20.4, 96.4, 126.8, 128.9, 133.7, 140.2, 147.9, and 155.9; Anal. Calcd. for $C_{12}H_{14}O_2N_2S$: C, 57.58; H, 5.64; N, 11.19; S, 12 81 Found: C, 57 51, H, 5 66; N, 11.17; S, 12.74.

A solution containing 5.0 g of **16** in 1500 mL of benzene was irradiated for 90 min using a 450-W Hanovia medium pressure mercury arc lamp equipped with a Pyrex filter sleeve under an argon atmosphere. The solvent was removed under reduced pressure and the crude residue was chromatographed on a silica gel column using a 10% acetone-hexane mixture as the eluent. The major fraction contained 4.3 g (97%) of a light yellow oil whose structure was assigned as 1-phenylsulfonyl-2,3,3-trimethylcyclopropene (**17**) on the basis of the following spectral properties ^{1}H-NMR ($CDCl_3$, 90 MHz) δ 1.18 (s, 6H), 2.10 (s, 3H), 7.40-7 65 (m, 3H), and 7.75-8.00 (m, 2H); IR (neat) 3060, 2980, 2940, 1805, 1590, 1450 and 920 cm^{-1}; ^{13}C-NMR ($CDCl_3$, 20 MHz) δ 9.2, 24.1,

33.1, 126.7, 128.4, 128.8, 133.1, 141.2 and 141.4 ; Anal. Calcd. for $C_{12}H_{14}O_2S$: C, 64.84, H, 6 35, S, 14.42. Found: C, 64.87; H, 6.40; S, 14.36.

Preparation of 3,3-Dimethyl-2-(isopropyl)-1-(p-tolylsulfonyl)cyclopropene (23). To a magnetically stirred solution of 15.0 g (55.1 mmoles) of *cis*-1,2-*bis*-(p-tolylthio)ethylene in 70 mL of refluxing acetic acid was slowly added 24.9 g (0.22 moles) of 30-35% hydrogen peroxide dropwise by addition funnel. After the addition was complete, the solution was heated at reflux for 2 h At the end of this time, the solution was cooled to room temperature and the slurry was filtered to give a solid which was dissolved in ether, washed with a saturated solution of sodium bicarbonate, dried over magnesium sulfate, and evaporated to give 17.6 g (95% yield) of a white solid mp 147-153°C; ^{1}H-NMR ($CDCl_3$, 90 MHz): δ 2.40 (s, 6H), 6.78 (s, 2H), 7.30 (d, 4H, J=8 3 Hz), and 7 89 (d, 4H, J=8.3 Hz); IR (KBr) 3040, 1600, 1410, 1325, 1150, 1090, 1025, 950, 825, 730, 715, 695, and 610 cm^{-1}.

A solution containing 2-diazopropane was prepared using 35 g (0.30 moles) of acetone hydrazone, 140 g (0.63 moles) of mercury (II) oxide and 12 mL of a 3.0 M solution of potassium hydroxide in methanol. To the deep red solution of diazopropane at -78°C was added 5 0 g (15 mmoles) of the above *bis*-sulfone. The mixture was slowly warmed to room temperature and was stirred for an additional 12 h under a nitrogen atmosphere. The ether layer was washed with a 10% hydrochloric acid solution, brine, and dried over magnesium sulfate. The solution was concentrated under reduced pressure to give 6.41 g of a crude oil. This material crystallized from petroleum ether to give 2.33 g (50% yield) of 3,3a,6,6a-tetrahydro-3,3,6,6-tetramethyl-3a-(p-tolylsulfonyl)pyrazolo[4,3-c]pyrazole (**21**), mp 142-143°C; IR (KBr) 3080, 3000, 2980, 1600, 1570, 1555, 1500 and 670 cm^{-1}; ^{1}H-NMR (90 MHz, $CDCl_3$) δ 1.20 (s, 3H), 1.39 (s, 3H), 1.40 (s, 3H), 1.65 (s, 3H), 2.41 (s, 3H), 5.20 (s, 1H), 7.30 (d, 2H, J=9.0 Hz) and 7.87 (d, 2H, J=9.0 Hz), ^{13}C-NMR (50 MHz, $CDCl_3$) δ 21.5, 21.6, 22.2, 22.3, 24.8, 93.2, 94.4, 94.9, 117.9, 129.6, 129.8, 134.6 and 145.9 ; UV (95% ethanol) 232 (ε 12,000), 255 (ε 2,100) and 335 nm (ε 220); Anal. Calcd. for $C_{15}H_{20}N_4O_2S$: C, 56.23; H, 6.29, N, 17.49; S, 10.01. Found: C, 56.15, H, 6.34; N, 17.43, S, 9.93.

The supernatant contained 2.4 g of a oil whose structure was assigned as 2-(p-tolylsulfonyl)propane on the basis of its spectral properties: IR (neat) 3020, 2980, 2260, 1600, 1500 and 1380 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 360 MHz) δ 1.24 (d, 3H, J=6.1 Hz), 1.38 (d, 3H, J=6.1 Hz), 2.42 (s, 3H), 4.60 (m, 1H, J=6.1 Hz), 7.32 (d, 2H, J=9 Hz) and 7.60 (d, 2H, J=9 Hz); Anal. Calcd. for $C_{10}H_{14}O_2S$· C, 60.57; H, 7.12. Found: C, 60.11; H, 7.10.

A 1.5 g (4.7 mmoles) sample of **21** was dissolved in 15 mL of dry benzene in a Carius tube, degassed with nitrogen then sealed and heated at 125°C for 24 h. Removal of the solvent under reduced pressure left an oil which was chromatographed on a silica gel column using a 10% acetone-hexane mixture as the eluent. The major fraction contained 1.30 g (85% yield) of a solid whose structure was assigned as 3,3-dimethyl-5-isopropyl-4-(p-tolylsulfonyl)-3H-pyrazole (**22**) on the basis of the following spectral data: mp 72-73°C; IR (KBr) 3100, 3080, 3000, 2980, 1600, 1550, 1410, 1190, 1150, 970, 820, 675 and 600 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 360 MHz) δ 1.35 (d, 6H,

J=6 9 Hz), 1.50 (s, 6H), 2.44 (s, 3H), 3.66 (m, 1H, J= 6.9 Hz), 7.36 (d, 2H, J=8.3 Hz) and 7.78 (d, 2H, J=8.3 Hz); UV (95% ethanol) 228 nm (ε=11,000) and 266 nm (ε=5,100); Anal. Calcd. for $C_{15}H_{20}O_2N_2S$: C, 61.61; H, 6.89; N, 9.58. Found: C, 61.52; H, 6.89; N, 9.60.

A solution containing 1.30 g (4.45 mmoles) of pyrazole **22** in 500 mL of anhydrous benzene was irradiated for 90 min using a 450-W Hanovia medium pressure mercury arc lamp equipped with a Pyrex filter sleeve under an argon atmosphere. The solvent was removed under reduced pressure and the crude residue was chromatographed on a silica gel plate using a 5% acetone-hexane mixture as the eluent. The major fraction contained 854 mg (73%) of an oil whose structure was assigned as 3,3-dimethyl-2-(isopropyl)-1-(p-tolylsulfonyl)cyclopropene (**23**) on the basis its spectral properties: mp 60-61°C; IR (neat) 3010, 2960, 1790, 1600, 1320, 1150, 1085, 810 and 670 cm^{-1}; ^{1}H- NMR (CCl_4, 90 MHz) δ 1.50 (s, 6H), 1.50 (d, 6H, J=7.5 Hz), 2.39 (s, 3H), 2.80 (m, 1H, J=7.5 Hz), 7.21 (d, 2H, J=8.5 Hz) and 7.67 (d, 2H, J=8.5 Hz); ^{13}C-NMR ($CDCl_3$, 20 MHz) δ 20.1, 21.3, 24.9, 27.1, 32.9, 123.9, 127.1, 129.5, 138.6, 144.2 and 148.5; UV (95% ethanol) 234 nm (ε=1200); Anal. Calcd. for $C_{15}H_{20}O_2S$: C, 68.14; H, 7.62; S, 12.13. Found: C, 68.04; H, 7.67; S, 12.07.

Reaction of 1-Phenylsulfonyl-2,3,3-trimethylcyclopropene (17) with Lithium Thiophenolate. To a stirred solution containing 594 mg (5.4 mmoles) of thiophenol in 30 mL of anhydrous tetrahydrofuran was added 1.9 mL (2.7 mmoles) of a 1.38 M solution of n-butyllithium in hexane at 0°C. The resulting solution was warmed to 25°C followed by the addition of 600 mg (2.7 mmoles) of cyclopropene **17** in 50 mL of dry tetrahydrofuran. The resulting yellow solution was stirred for 2 h at 25°C and the solvent was removed under reduced pressure. The residue was diluted with ether, washed with a 10% sodium hydroxide solution, water and brine. The ether was dried over magnesium sulfate and concentrated under reduced pressure to give a crude oil which was chromatographed on a silica gel plate using a 5% acetone-hexane mixture as the eluent. The first fraction contained 350 mg (81% yield) of a white solid whose structure was assigned as *trans*-[[1,2,2-trimethyl-3-(phenylsulfonyl)cyclopropyl]thio]benzene (**24a**) on the basis of the following data: mp 99-100°C; ^{1}H-NMR ($CDCl_3$, 360 MHz) δ 1.48 (s, 3H), 1.65 (s, 3H), 1.81 (s, 3H), 2.55 (s, 1H), 7.17 (bs, 5H), 7.50-7.70 (m, 3H), and 7.80-7.88 (m, 2H); ^{13}C-NMR ($CDCl_3$, 20 MHz) δ 16.0, 16.3, 24.8, 31.9, 40.2, 55.1, 126.7, 126.8, 128.8, 129.1, 130.2, 133.1, 133.4, and 142.1; IR (KBr) 3060, 3000, 2980, 1590, 1485, 1450, 1310, 1150, 1090, 910, 770, 750, 700, and 610 cm^{-1}; UV (95% ethanol) 258 nm (ε=8,300); Anal. Calcd. for $C_{18}H_{20}O_2S_2$: C, 65.03; H, 6.06; S, 19.29. Found: C, 65.07; H, 6.09; S, 19.21.

The second fraction contained 80 mg (19% yield) of a yellow gum whose structure was assigned as *cis*-[[1,2,2-trimethyl-3-(phenylsulfonyl)cyclopropyl]thio]benzene (**24b**) on the basis of the following data: ^{1}H-NMR ($CDCl_3$, 360 MHz) δ 1.35 (s, 3H), 1.48 (s, 3H), 1.81 (s, 3H), 2.26 (s, 1H), 7.30 (bs, 5H), 7.55-7.68 (m, 3H), and 7.95-8.00 (m, 2H); IR (neat) 3080, 2940, 1590, 1450, 1300, 1100, 1030, 930, and 850 cm^{-1}; ^{13}C-NMR ($CDCl_3$, 20MHz) δ 16.8, 21.2, 21.9, 31.8, 37.3, 54.4, 124.4, 125.5, 126.8, 127.2, 127.3, 127.5, 127.9, and 131.6; UV (95% ethanol) 256 nm (ε=

10,300); Anal. Calcd. for $C_{18}H_{20}O_2S_2$: C, 65.03; H, 6.06; S, 19.29. Found: C, 64.95; H, 6.13, S, 19.19.

Reaction of 3,3-Dimethyl-2-(isopropyl)-1-(p-tolylsulfonyl)cyclopropene (23) with Lithium Thiophenolate. To a stirred solution containing 209 mg (1.9 mmoles) of thiophenol in 30 mL of anhydrous tetrahydrofuran was added 0.63 mL (0.95 mmoles) of a 1.5 M solution of n-butyllithium in hexane at 0°C. The resulting solution was warmed to 25°C followed by the addition of 250 mg (0.95 mmoles) of cyclopropene **23** in 10 mL of dry tetrahydrofuran. The solution was stirred for 2 h at 25°C and the solvent was removed under reduced pressure. The resulting residue was diluted with ether, washed with a 10% sodium hydroxide solution, water and brine The solution was dried over magnesium sulfate and concentrated under reduced pressure to give a crude oil which was chromatographed on a silica gel plate using a 5% acetone-hexane mixture as the eluent. The first fraction contained 320 mg (76% yield) of a white solid whose structure was assigned as *trans*-1-[[2,2-dimethyl-3-(1-methylethyl)-3-(phenylthio)cyclopropyl]sulfonyl]-4-methylbenzene (**25a**) on the basis of the following data: mp 90-91°C; ^{1}H-NMR ($CDCl_3$, 90 MHz) δ 1.05 (d, 3H, J= 6.8 Hz), 1.29 (s, 3H), 1.31 (d, 3H, J= 6.8 Hz), 1.69 (s, 3H), 2.09 (s, 1H), 2.38 (s, 3H), 2.99 (m, 1H, J= 6.8 Hz), 7.10-7.40 (m, 7H), and 7.55 (d, 2H, J= 8.3 Hz); IR (KBr) 3065, 2958, 1595, 1582, 1493, 1325, 1147, 1086, 750, and 680 cm^{-1}; UV (95% ethanol) 228 nm (ε=18,300), Anal. Calcd. for $C_{21}H_{26}O_2S_2$: C, 67.34; H, 7.00; S, 17.12. Found: C, 67.44; H, 7.01; S, 17.18.

The second fraction contained 80 mg (21% yield) of a white solid whose structure was assigned as *cis*-1-[[2,2-dimethyl-3-(1-methylethyl)-3-(phenylthio)cyclopropyl]sulfonyl]-4-methylbenzene (**25b**) on the basis of the following data: mp 161-162°C; ^{1}H-NMR ($CDCl_3$, 360 MHz) δ 0.82 (dd, 6H, J= 8.6 and 6 8 Hz), 1.58 (s, 3H), 1.62 (d, 1H, J= 6.8 Hz), 1.83 (s, 3H), 2.10 (s, 1H), 2.47 (s, 3H), 7.10-7.38 (m, 5H), 7.38 (d, 2H, J=8.3 Hz), and 7.89 (d, 2H, J=8.3 Hz); IR (KBr) 3060, 2985, 1600, 1590, 1485, 1470, 1320, 1310, 1160, 1090, 750, and 670 cm^{-1}; UV (95% ethanol) 230 nm (ε= 18,800) and 254 nm (ε= 12,500); Anal. Calcd. for $C_{21}H_{26}O_2S_2$: C, 67.34; H, 7.00; S, 17.12 Found: C, 67.28; H, 7.02; S, 17.04.

Treatment of 1-Phenylsulfonyl-2,3,3-trimethylcyclopropene (17) with n-Butyllithium. To a stirred solution containing 222 mg (1.0 mmoles) of cyclopropene 17 in 10 mL of anhydrous tetrahydrofuran under a nitrogen atmosphere at -78°C was added 0.65 mL (1.0 mmoles) of a 1.54 M solution of n-butyllithium in hexane. After complete addition, the reaction was warmed to 0°C and was quenched with a saturated ammonium chloride solution. The solvent was removed *in vacuo* and the crude residue was diluted with ether, washed twice with water and dried over magnesium sulfate. The solvent was removed under reduced pressure to give 120 mg of an oil which was recrystallized from dichloromethane and petroleum ether to give 210 mg (48% yield) of a white solid which was identified as (*1R*,3R**)-1,2,2,2',2'-pentamethyl-3'-methylene-1',3-bis(phenylsulfonyl)-1,1'-bicyclopropyl (**27**) on the basis of the following spectral data: mp 199-200°C; ^{1}H-NMR ($CDCl_3$, 360 MHz) δ 1.13 (s, 3H), 1.41 (s, 3H), 1.48 (s, 3H), 1.49 (s, 3H), 1.98 (s, 1H), 2.00 (s, 3H), 5.18 (s, 1H), 5.45 (s, 1H), 7.40-7.70 (m, 6H), and 7.80-7.85 (m, 4H); IR

(KBr) 3025, 2950, 1595, 1455, 1310, 1150, 1090, 955, and 615 cm^{-1}; UV (95% ethanol) 224 nm (ε= 21,000); Anal. Calcd. for $C_{24}H_{28}O_4S_2$: C, 64.84; H, 6.35, S, 14.42. Found: C, 64.70; H, 6.36, S, 14.33

To a stirred solution containing 1.0 g (4.5 mmoles) of cyclopropene **17** in 50 mL of anhydrous tetrahydrofuran under a nitrogen atmosphere at -78°C was added dropwise 3.1 mL (4.7 mmoles) of a 1.54 M solution of n-butyllithium in hexane. After complete addition, stirring was continued for an additional 30 min at which time iodomethane was added to the reaction mixture by syringe. The resulting suspension was slowly allowed to warm to room temperature and was then stirred overnight. The reaction was quenched with a saturated ammonium chloride solution and the solvent was removed *in vacuo*. The crude residue was diluted with ether, washed twice with water, dried over magnesium sulfate and the solvent was removed under reduced pressure to give 1.2 g of an oil which was chromatographed on a silica gel column using a 5% acetone-hexane mixture an the eluent. Evaporation of the solvent gave 1.0 g (95% yield) of a light yellow oil which was identified as 1,2,2-trimethyl-3-methylenecyclopropyl phenyl sulfone (**28**) on the basis of its spectral data: ^{1}H-NMR ($CDCl_3$, 360 MHz) δ 1.26 (s, 3H), 1.41 (s, 3H), 1.74 (s, 3H), 5.54 (s, 1H), 5.56 (s, 1H), 7.50-7.65 (m, 3H), and 7.90-7.95 (m, 2H); ^{13}C-NMR ($CDCl_3$, 20 MHz) δ 16.0, 19.8, 22.7, 28.3, 46.34, 103.7, 128.0, 128.7, 132.9, 139.9, and 141.5; IR (neat) 3050, 2920, 2260, 1590, 1450, 1300, 1160, 910, and 860 cm^{-1}; UV (95% ethanol) 222 nm (ε=11,100); Anal. Calcd. for $C_{13}H_{16}O_2S$: C, 66.07; H, 6.82; S, 13.57. Found: C, 66.05; H, 6.81; S, 13.55.

Preparation of 1-Allyl-2,2-dimethyl-3-methylenecyclopropyl Phenyl Sulfone (29). The procedure used to prepare this material was identical to that used for the preparation of **28** except that the anion was quenched with allyl bromide. After complete reaction and workup, the product was isolated by chromatography on a silica gel column using a 5% acetone-hexane mixture as the eluent. Evaporation of the solvent left 1.0 g (85% yield) of a colorless oil which was identified as 1-allyl-2,2-dimethyl-3-methylenecyclopropyl phenyl sulfone (**29**) on the basis of its spectral data: ^{1}H-NMR ($CDCl_3$, 360 MHz) δ 1.33 (s, 3H), 1.82 (s, 3H), 2.51 (m, 2H), 4.75 (dq, 1H, J= 17.0 and 1.8 Hz), 4.89 (dq, 1H, J= 9.0 and 1.8 Hz), 5.55-5.65 (m, 1H), 5.42 (s, 1H), 5 58 (s, 1H), 7.70-7.50 (m, 3H), and 7.90-7.95 (m, 2H); IR (neat) 3080, 2930, 1640, 1450, 1080, and 920 cm^{-1}; ^{13}C-NMR ($CDCl_3$, 20 MHz) δ 14.9, 20.2, 22.8, 33.7, 65.3, 104.5, 116.5, 127.9, 128.3, 128 8, 130.6, 133.0, and 140.7; UV (95% ethanol) 222 nm (ε=10,900); Anal. Calcd. for $C_{15}H_{18}O_2S$: C, 68.67; H, 6 92; S,12.22. Found: C, 68.81; H, 6.90; S, 12.03.

Preparation of 1-Crotyl-2,2-dimethyl-3-methylenecyclopropyl Phenyl Sulfone (30). The procedure used to prepare this material was identical to that used for the preparation of **28** except that the anion was quenched with crotyl bromide. After complete reaction and workup, the product was isolated by chromatography on a silica gel column using a 5% acetone:hexane mixture as the eluent. Evaporation of the solvent left 995 mg (80% yield) of a clear oil which was identified as 1-crotyl-2,2-dimethyl-3-methylenecyclopropyl phenyl sulfone (**30**) on the basis of its spectral data: ^{1}H-NMR (CCl_4, 90 MHz) δ 1.26 (s, 3H), 1.41 (bd, 3H, J= 9.0 Hz), 1.72 (s, 3H), 2.40

(bs, 2H), 5.00-5.35 (m, 2H), 5.36 (bs, 2H), 7.40-7.58 (m, 3H), and 7.70-7.85 (m, 2H); IR (neat) 3040, 3020, 2920, 1450, 1300, 1080, and 910 cm^{-1}; UV (95% ethanol) 222 nm (ε=10,800); Anal Calcd. for $C_{16}H_{20}O_2S$: C, 69.53; H, 7.29; S, 11.68. Found: C, 69.55; H, 7.30; S, 11.66.

Preparation of 1-Cinnamyl-2,2-dimethyl-3-methylenecyclopropyl Phenyl Sulfone (31). The procedure used to prepare this material was identical to that used for the preparation of **28** except that the anion was quenched with cinnamyl bromide. After complete reaction and workup, the product was isolated by chromatography on a silica gel column using a 5% acetone-hexane mixture as the eluent. Evaporation of the solvent left 1.22 g (80% yield) of a yellow oil which was identified as 1-cinammyl-2,2-dimethyl-3-methylenecyclopropyl phenyl sulfone (**31**) on the basis of its spectral data: ^{1}H-NMR (CCl_4, 90 MHz) δ 1.28 (s, 3H), 1.78 (s, 3H), 2.55 (bd, 2H, J= 6.0 Hz), 5.45 (bs, 2H), 5.89 (bs, 2H), 7.10 (bs, 5H), 7.28-7.50 (m, 3H), and 7.75-7.85 (m, 2H); IR (neat) 3060, 3040, 2920, 1450, 1300, 1080, and 910 cm^{-1}; UV (95% ethanol) 210nm (ε=27,100) and 254 nm (ε=17,600); ^{13}C-NMR ($CDCl_3$, 20 MHz) δ 120.4, 23.1, 29.6, 33.1, 50.2, 104.8, 125.8, 125.9, 127.2, 128.3, 128.5, 128.9, 131.8, 133.2, 140.5, and 140.8; Anal. Calcd. for $C_{21}H_{22}O_2S$. C, 74.52; H, 6.55; S, 9.47. Found: C, 74.31; H, 6.56; S, 9.40.

Preparation of 2,2-Dimethyl-3-methylene-1-(phenylsulfonyl)cyclopropyl Methyl Sulfide (32). The procedure used to prepare this material was identical to that used for the preparation of **28** with the following modification. A 500 mg (2.25 mmoles) sample of cyclopropene **17** in 25 mL of anhydrous tetrahydrofuran at -78°C was treated with 1.6 mL (2.5 mmoles) of 1 5 M n-butyllithium in hexane followed by 284 mg (2.26 mmoles) of methyl methanethiosulfonate. After complete reaction and workup, the product was isolated by chromatography on a silica gel plate using a 5% acetone-hexane mixture as the eluent. Evaporation of the solvent left 422 mg (70% yield) of a yellow oil which was identified as 2,2-dimethyl-3-methylene-1-(phenylsulfonyl)-cyclopropyl methyl sulfide (**32**) on the basis of its spectral data: ^{1}H-NMR ($CDCl_3$, 90 MHz) δ 1.50 (s, 3H), 1.75 (s, 3H), 2.05 (s, 3H), 5.45 (s, 1H), 5.49 (s, 1H), 7.40-7.55 (m, 3H), 7.80-7.95 (m, 2H); IR (neat) 3070, 2920, 2260, 1590, 1450, 1300, 1240, 910, and 735 cm^{-1}; ^{13}C-NMR ($CDCl_3$, 20 MHz) δ 15.9, 16.4, 20.2, 25 2, 35.7, 105.5, 128.4, 129.0, 129.4, 133.1, and 140.0; Anal. Calcd. for $C_{13}H_{16}O_2S_2$: C, 58.18; H, 6.01; S, 23.89. Found: C, 57.97; H, 6.06; S, 23.75.

Preparation of [[2,2-Dimethyl-3-methylene-1-(phenylsulfonyl)cyclopropyl]methyl] Trimethylsilane (33). The procedure used to prepare this material was identical to that used for the preparation of **28** with the following modification. A 3.09 g (13.92 mmoles) sample of cyclopropene **17** in 125 mL of anhydrous tetrahydrofuran at -78°C was treated with 9.5 mL (14.6 mmoles) of 1.5 M n-butyllithium in hexane followed by 1.70 g (13.92 mmoles) of chloromethyltrimethylsilane. After complete reaction and workup, the product was isolated by chromatography on silica gel using a 5% acetone-hexane mixture as the eluent. Evaporation of the solvent left 1.0 g (23% yield) of a yellow oil which was identified as [[2,2-dimethyl-3-methylene-1-(phenylsulfonyl)cyclopropyl]methyl]trimethylsilane (**33**) on the basis of its spectral data: ^{1}H-NMR (C_6D_6, 90 MHz) δ 0.19 (s, 9H), 1.10 (s, 3H), 1.30 (s, 2H), 1.80 (s, 3H), 5.49 (s, 1H), 5.51 (s, 1H), 7 00-7.15

(m, 3H), 7.91-8.10 (m, 2H); IR (neat) 3060, 2940, 2280, 1590, 1450, 1300, 1150, and 860 cm^{-1}; ^{13}C-NMR ($CDCl_3$, 20 MHz) δ -0.5, 17.4, 20.4, 23.2, 42.6, 48.8, 105.0, 128.5, 128.7, 132.8, 140.5, and 141.9; UV (95% ethanol) 220 nm (ε=10,900).

Thermal Rearrangement of 1-Allyl-2,2-dimethyl-3-methylenecyclopropyl Phenyl Sulfone (29). A 262 mg (1.0 mmoles) sample of methylenecyclopropane **29** was dissolved in 5 mL of anhydrous benzene in a thermolysis tube. The tube was sealed, heated at 140°C for 4 h and cooled to room temperature. The solvent was evaporated and the residue was chromatographed on a silica gel column using a 5% acetetone:hexane mixture as the eluent. Evaporation of the solvent left 260 mg (99% yield) of an oil which was identified as 1-allyl-2-isopropylidinecyclopropyl phenyl sulfone (**34**) on the basis of its spectral data: ^1H-NMR ($CDCl_3$, 360 MHz) δ 1.37 (m, 1H), 1.74 (t, 3H, J= 2.1 Hz), 1.86 (t, 3H, J= 1.6 Hz), 2.04 (m, 1H), 2.53 (dd, 1H, J= 13.9 and 7.9 Hz), 2.75 (dd, 1H, J= 14.3 and 6.5 Hz), 4.92-4.98 (m, 2H), 5.39-5.50 (m, 1H), 7.51-7.66 (m, 3H), and 7.85-7.89 (m, 2H); IR (neat) 3080, 2980, 2920, 2260, 1650, 1595, 1450, 1310, 1145, 920, 740, and 700 cm^{-1}; ^{13}C-NMR ($CDCl_3$, 50 MHz) δ 13.6, 22.3, 22.7, 33.6, 44.9, 113.3, 118.4, 128.8, 128.9, 129.2, 129.5, 132.2, 133.3, and 138.8; Anal. Calcd. for $C_{15}H_{18}O_2S$: C, 68.67; H, 6.92; S,12.22. Found: C, 68.62; H, 6.81; S, 11.97.

Thermal Rearrangement of 1,2,2-Trimethyl-3-methylenecyclopropyl Phenyl Sulfone (28). A 200 mg (0.85 mmoles) sample of methylenecyclopropane **28** was dissolved in 10 mL of anhydrous benzene in a thermolysis tube. The tube was sealed, heated at 140°C for 4 h and was then cooled to room temperature. The solvent was evaporated and the residue was chromatographed on a silica gel column using a 5% acetetone:hexane mixture as the eluent. The major fraction contained 198 mg (99% yield) of an oil which was identified as 2-isopropylidine-1-methylcyclopropyl phenyl sulfone (**36**) on the basis of its spectral data: ^1H-NMR ($CDCl_3$, 360 MHz) δ 1.31 (dq, 1H, J= 8.3 and 1.8 Hz), 1.48 (s, 3H), 1.74 (t, 3H, J= 1.8 Hz), 1.86 (t, 3H, J= 1.8 Hz), 2.16 (dq, 1H, J= 8.3 and 1.8 Hz), 7.53-7.66 (m, 3H), and 7.87-7.91 (m, 2H); IR ($CHCl_3$) 3070, 3020, 2970, 2935, 1590, 1450, 1300, 1140, 820, 760, 690, and 640 cm^{-1}; ^{13}C-NMR ($CDCl_3$, 50 MHz) δ 16.5, 16.6, 16.9, 22.2, 22.5, 41.3, 115.7, 128.4, 128.8, 133.2, and 138.6; Anal. Calcd. for $C_{13}H_{16}O_2S$: C, 66.07; H, 6.82; S, 13.57. Found: C, 65.87; H, 6.74; S, 13.39.

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