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DIPOLAR CYCLOADDITION REACTION OF DIAZOALKANES WITH TRIMETHYLSILYL SUBSTITUTED ALKYNES. STERIC CONTROL OF REGIOCHEMISTRY BY THE TRIMETHYLSILYL GROUP

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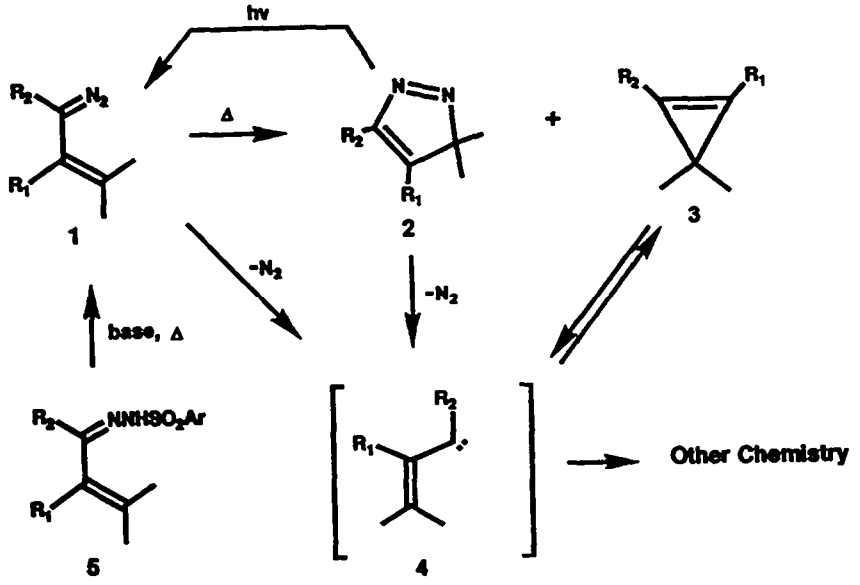
Abstract: A study of the cycloaddition behavior of several trimethylsilyl substituted alkynes with 2-diazopropane and diazomethane has been carried out. Aryl or alkyl ethynyl sulfones react to give 5-sulfonyl substituted 3H-pyrazoles which extrude nitrogen on photolysis to produce cyclopropenes in high yield. The regiochemical results are compatible with FMO considerations in that the favored adduct is the result of the union of the larger diazoalkane HO coefficient with that of the larger dipolarophile LU coefficient. Dipolar cycloaddition of several 2-(trimethylsilyl) substituted alkynes led to the unexpected regioisomer. Regiochemical control can be attributed to steric rather than to stereoelectronic factors when a bulky trimethylsilyl group is attached to the dipolarophile. In certain cases some of the cycloadducts undergo rearrangement to pyrazoles when subjected to Lewis acid catalysis.

Vinylcarbenes 4 have attracted considerable interest as intermediates in a variety of reactions.[1,2] Examples include the pyrolysis[3] or singlet induced photochemistry of cyclopropenes 3,[4,5] the intramolecular addition of α-diazoketones onto acetylenic pi-bonds[6] and the photolysis or pyrolysis of vinyldiazomethanes 1.[7] Cyclization of the vinylcarbene 4 to the cyclopropene ring is considered to be their most common reaction.[8] However, this intramolecular process is not always observed and a number of competing reactions have been reported.[9-14] Vinyldiazomethanes 1 are generally synthesized either by heating the tosylhydrazone salts of ketones 5 or by irradiating the corresponding 3H-pyrazole 2 with filtered light to avoid photochemical decomposition of the diazo compound.[15] Thermolysis of vinyldiazomethanes 1, on the other hand, gives 3H-pyrazoles 2 and cyclopropenes 3 as products.[16] The ratio of these two products is very dependent on the substituent pattern and in many simple alkyl substituted cases only the pyrazoles are observed.[17] The 3H-pyrazoles 2 are most easily obtained by 1,3-dipolar cycloaddition of disubstituted diazoalkanes onto electrophilic acetylenes.[18]

The additions of diazoalkanes to pi-bonds are among the most thoroughly studied 1,3-dipolar cycloadditions.[19] The reaction of simple diazoalkanes are HO(1,3-dipole)-LU (dipolarophile) controlled.[20,21] Both conjugating and electron-attracting groups accelerate reactions of dipolarophiles with diazoalkanes. With these dipolarophiles, 3-substituted Δ^1-pyrazolines are favored, a result of the union of the larger diazoalkane HO coefficient on carbon with that of the larger dipolarophile LU coefficient on the unsubstituted carbon.[20] As a consequence of our interest in silyl substituted cyclopropenes as precursors to vinylcarbenes[22], we became interested in the 1,3-dipolar cycloaddition of 2-diazopropane with silyl substituted

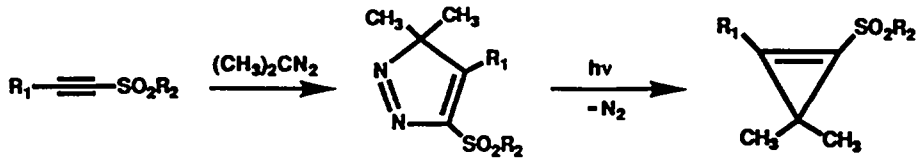


alkynes as a means of preparing 3H-pyrazoles for eventual nitrogen extrusion. During the course of our investigations, we encountered an unusual regiochemical effect in the cycloaddition whereby the product of the reaction appears to be controlled by steric rather than stereoelectronic factors. We report here the results of these studies.

Results and Discussion

Chemical reactivity and regioselectivity in cycloaddition processes can be significantly modified by the appropriate choice of substituent groups.[23] Frontier MO theory predicts that attachment of a sulfonyl group onto a pi-bond will significantly lower the energy of the LUMO and thereby enhance the cycloaddition rate.[24] An interesting application of such an effect has been provided by the Paquette[25] and DeLucchi[26] groups in their use of bis(phenylsulfonyl)ethylene as an acetylene equivalent in Diels-Alder chemistry. During the course of our studies dealing with the chemistry of sulfonyl substituted cyclopropenes[22], we prepared a series of 3H-pyrazoles by the 1,3-dipolar cycloaddition of 2-diazopropane with several sulfonyl substituted alkynes.[19] In all the case examined (R=CH_3 or Ph), the only 3H-pyrazole obtained from the 1,3-dipolar cycloaddition corresponds to the expected regioisomer derived by attachment of the diazo carbon atom onto the β-carbon atom of the alkyne. Photolysis of these sulfonyl substituted 3H-pyrazoles in benzene afforded the corresponding cyclopropenes in excellent yield.

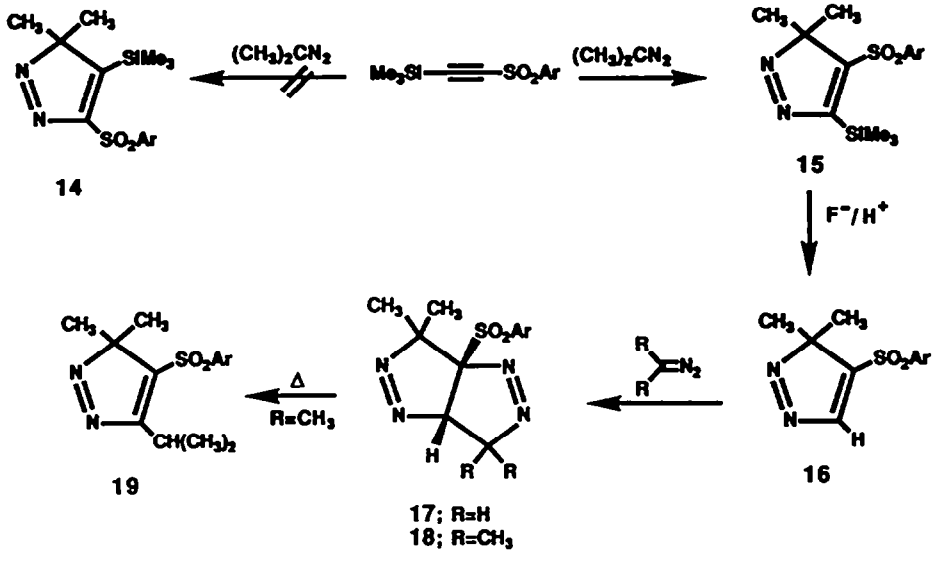
We have also studied the 1,3-dipolar cycloaddition reaction of p-tolyl 2-(trimethylsilyl)-ethynyl sulfone[27] with 2-diazopropane. We originally anticipated that addition would occur in the "normal" regiochemical sense and produce the expected cycloadduct 14. Although the cycloaddition did proceed readily and in high yield, the product actually isolated corresponded to the unexpected regioisomer 15.[28] In order to rigorously establish the regiochemistry of the product,



6; R_1=CH_3; R_2=Ph
7; R_1=Ph; R_2=CH_3
8; R_1=R_2=CH_3
9; R_1=R_2=Ph

10; R_1=CH_3; R_2=Ph
11 R_1=Ph; R_2=CH_3
12 R_1=R_2=CH_3
13; R_1=R_2=Ph

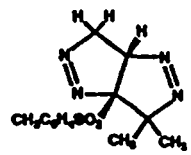
we carried out the fluoride induced desilylation of cycloadduct 15. The desilylated 3H-pyrazole obtained (i.e. 16) was then allowed to react with either diazomethane or 2-diazopropane. The resulting cycloadducts 17 and 18 were assigned on the basis of their spectral data and more importantly, by a single crystal x-ray analysis of both compounds. Heating a sample of pyrazolo-[4,3-c]pyrazole 18 at 80°C lead to the formation of 3H-pyrazole 19 in 85% yield. Preferential loss of nitrogen to give the most stable diradical followed by a 1,2-hydrogen shift nicely accounts for the selective formation of 19.



17; R=H
18; R=CH_3

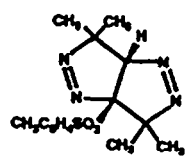
Vinyltrimethylsilanes are known to undergo Friedel-Crafts acylation and alkylation reactions in which the acyl or alkyl group replaces the trimethylsilyl functionality.[29, 30] With this in mind, we treated 3H-pyrazole 15 with methyl iodide in the presence of aluminum chloride with the expectation of obtaining a 5-methyl substituted 3H-pyrazole which would be isomeric with the previously isolated 3H-pyrazole (i.e 6). The only product isolated from this reaction (98%), however, corresponded to the rearranged N-methylpyrazole 20. Desilylation of 20 with tetrabutylammonium fluoride afforded pyrazole 21 in high yield. Treatment of the closely related

Figure 1

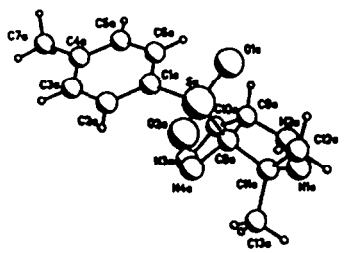


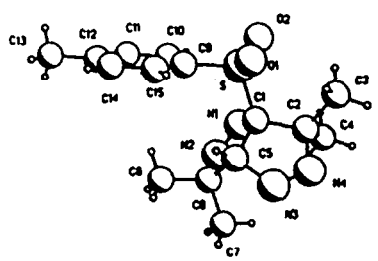
Cycloadduct 17

Figure2

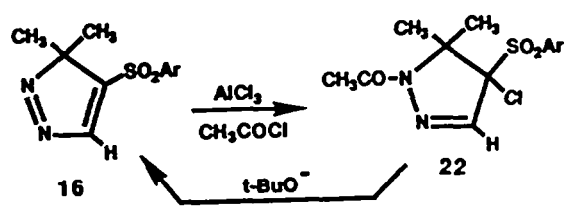


Cycloadduct 18





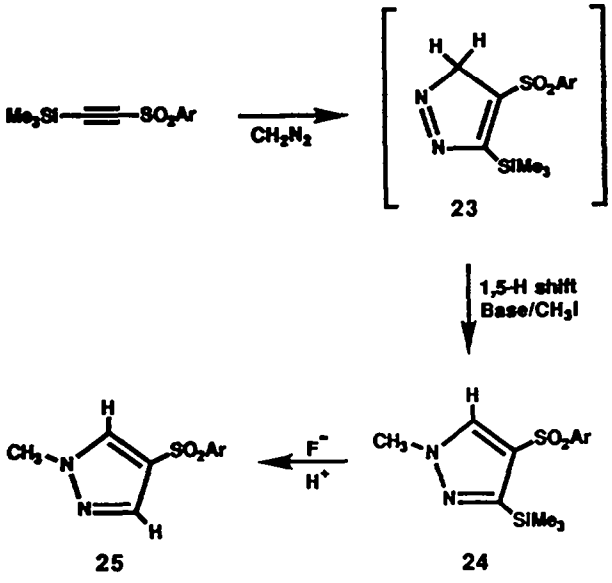
3H-pyrazole 16 with aluminum chloride led to intractable tar. However, reaction of 16 with acetyl chloride in the presence of $AlCl_3$ gave rise to chloropyrazoline 22. This material was reconverted to pyrazole 21 upon treatment with potassium t-butoxide. All of the above transformations are perfectly consistent with the structure assigned to 3H-pyrazole 15.



The conversion of 15 to 20 (Van Alphen-Huttel rearrangement), for which ample precedence exists[31,32], involves a 1,5-sigmatropic migration of the substituent group in the 3-position. This can occur to either the adjacent carbon or nitrogen atoms.[33] Usually, migration of the alkyl group to the carbon atom predominates, although there have been reports of competitive rearrangements.[33,34] The exclusive formation of N-methylpyrazole 20 from the aluminum catalyzed reaction is probably due to the presence of the bulky arylsulfonyl group which prevents migration to the adjacent carbon atom. N-Methylpyrazoles are also much more thermodynamically

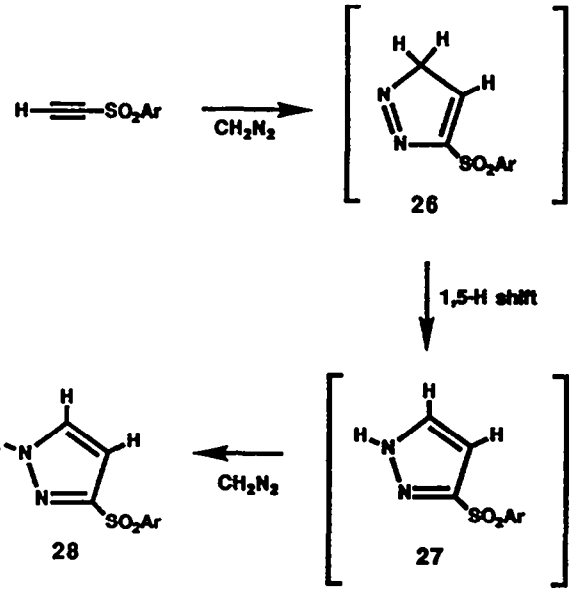
stable than the 4,4-disubstituted isomers. The resonance energy of pyrazole itself has been calculated to be *ca* 10 kcal mol^{-1}.[35] The acid catalyzed rearrangement of the 3H-pyrazole system is well known and provides good analogy for the $AlCl_3$ catalyzed reaction.[36-38]

At this point of our studies, we were uncertain as to whether the regioselectivity of the cycloaddition of 2-diazopropane with *p*-tolyl 2-(trimethylsilyl)ethynyl sulfone was due to stereoelectronic factors or to a general steric effect associated with the trimethylsilyl functionality. In an attempt to elucidate the factors controlling the process, we investigated the cycloaddition of the silyl substituted alkyne with diazomethane. The reaction afforded a single cycloadduct which was then alkylated with methyl iodide. Desilyation of the resulting N-methylpyrazole 24 with fluoride ion afforded N-methyl-4-(*p*-tolylsulfonyl)pyrazole 25. The ring protons of 25 appeared as singlets at 7.07 and 7.84 ppm in benzene-d_6.

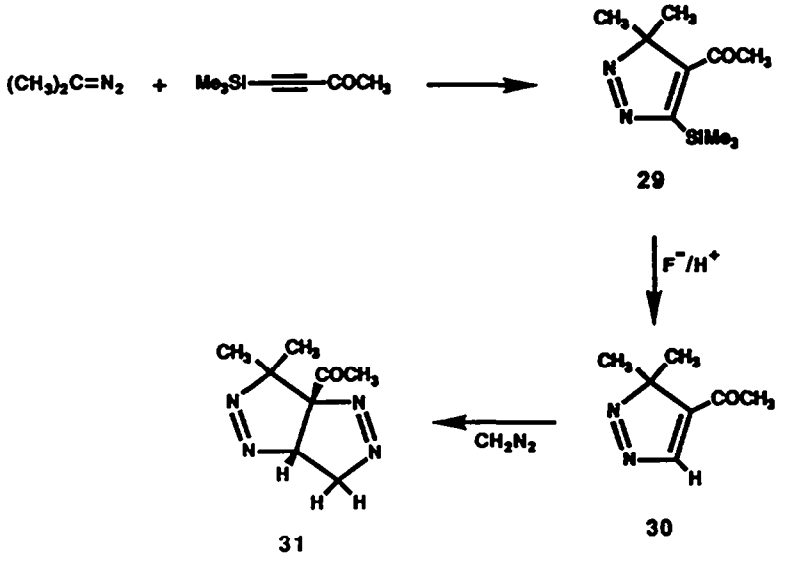


We were able to prepare the regioisomer of 25 (i.e. 28) by treating ethynyl p-tolyl sulfone with excess diazomethane. This reaction proceeds via an initial dipolar cycloaddition, followed by a 1,5-hydrogen shift and then methylation of the resulting pyrazole with excess diazomethane. The NMR spectrum of 28 shows the pyrazole protons as doublets at 6.84 and 7.45 ppm with a coupling constant of 2.2 Hz.[39]

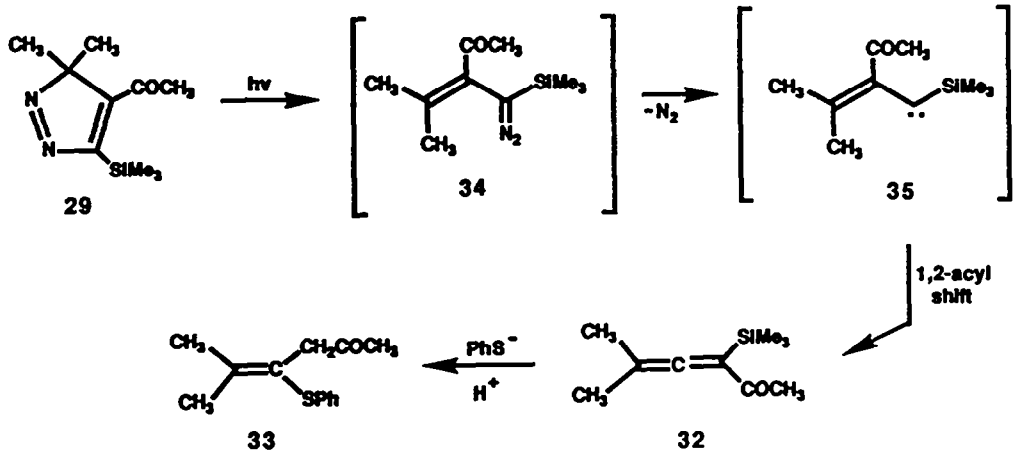
We reasoned that the difference in regioselectivity encountered with the silyl substituted alkyne was most likely a consequence of steric hindrance by the trimethylsilyl group and was not dependent on the presence of the sulfonyl group. In order to test this hypothesis, we examined the reaction of 2-diazopropane with 4-(trimethylsilyl)-3-butyn-2-one. The exclusive product obtained here corresponded to 3H-pyrazole 29. Desilylation of this material afforded 30 which, in turn, gave 31 upon treatment with diazomethane (see Experimental Section). As was the case with the sulfonyl substituted system, regiochemical control in the [3+2]-cycloaddition of 2-diazo-



propane with the silyl substituted 3-butyn-2-one appears to be steric rather than electronic in nature. It should be pointed out that DeShong and coworkers have demonstrated that the regioselectivity of nitrone cycloadditions with vinylsilanes is dependent on the particular silane employed as the dipolarophile.[40] The alteration in regioselectivity may be the consequence of subtle changes in HOMO/LUMO coefficients or a manifestation of steric factors in the cycloaddition step.



One last point worth noting deals with the photochemistry of 3H-pyrazole 29. As was mentioned earlier, the photolysis of 3H-pyrazoles is known to give vinyldiazomethanes and cyclopropenes as products.[7,15,18] The ratio of the two products depends on the nature of the substituent groups present. We found that irradiation of the nonsilylated 3H-pyrazoles 6-9 produced the corresponding cyclopropenes in high yield. In contrast, direct photolysis of 29 in benzene afforded allene 32 in almost quantitative yield. The structure of 32 was based on its spectral properties (see Experimental Section) and by its reaction with lithium thiophenolate to give 5-methyl-4-(phenylthio)-4-hexen-2-one (33).[41] A reasonable mechanism to account for the



formation of allene 32 involves the initial formation of vinyldiazomethane 34 as a transient species. Loss of nitrogen from 34 generates vinylcarbene 35 which then undergoes a subsequent 1,2-migration of the acyl group. In this case, migration of the acyl functionality is preferred over ring closure to the cyclopropene.

In conclusion, the regioselectivity of the dipolar cycloaddition of diazoalkanes with activated alkynes can be altered by the presence of a bulky trimethylsilyl group. In certain cases some of the dipolar cycloadducts undergo rearrangement to pyrazoles when subjected to Lewis acid catalysis. The further generalization of these findings and their implications for the synthesis of various heterocyclic compounds 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.

Preparation and Photochemistry of 5-Phenylsulfonyl-3,3,4-trimethyl-3H-pyrazole (6). To a solution of 2-diazopropane[43] in ether at -78°C was added 11.3 g of phenyl 1-propynyl-sulfone[44] 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 14.25 g (95% yield) of a light yellow oil which was identified as 5-phenylsulfonyl-3,3,4-trimethyl-3H-pyrazole (6) 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 6 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-phenyl-sulfonyl-2,3,3-trimethylcyclopropene (10) 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 and Photochemistry of 3,3-Dimethyl-5-methylsulfonyl-4-phenyl-3H-pyrazole (7). To a solution of 2-diazopropane in ether at -78°C was added 11.3 g of methyl phenylethynylsulfone[45] in 60 mL of tetrahydrofuran. The resulting red solution was stirred for 30 min at -78°C under a nitrogen atmoshere and then warmed to 25°C and stirred for 12 h. The organic layer was washed twice with a dilute aqueous hydrochloric acid solution, 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-methyl-sulfonyl-4-phenyl-3H-pyrazole (7) 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, 129.9, 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 of pyrazole 7 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 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 (11) 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, 32.9, 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 and Photochemistry of 5-Methylsulfonyl-3,3,4-trimethyl-3H-pyrazole (8). To a solution of 2-diazopropane in ether at -78°C was added 7.5 g of methyl 1-propynyl-sulfone[44] in 30 mL of tetrahydrofuran. The resulting red solution was stirred for 30 min at -78oC under a nitrogen atmoshere and 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. The solid that formed was recrystallized from benzene-hexane to give11.6 g (96% yield) of a yellow solid which was identified as 5-methylsulfonyl-3,3,4-trimethyl-3H-pyrazole (8) on the basis of its spectral properties: mp 73-74°C; ^{1}H-NMR ($CDCl_3$, 90 MHz) δ 1.50 (s, 6H), 2.60 (s, 3H) and 2.89 (s, 3H); IR (KBr) 3020, 2940, 1630, 1575, 1320, 1140, 970 and 780 cm-1; UV (95% ethanol) 368 nm (ε 230); ^{13}C-NMR ($CDCl_3$, 20 MHz) δ 12.8, 20.2, 44.5, 96.9, 147.5 and 156.7; Anal. Calcd. for $C_7H_{12}O_2N_2S$: C, 44.66; H, 6.43; N, 14.88; S, 17.03. Found: C, 44.73; H, 6.44; N, 14.80; S, 16.97.

A solution containing 5.0 g of pyrazole 8 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 20% ethyl acetate-hexane mixture as the eluent. The major fraction contained 4.0 g (94% yield) of a yellow oil whose structure was assigned as 1-methylsulfonyl-2,3,3-trimethyl-cyclopropene (12) on the basis of the following spectral properties: ^{1}H-NMR (CCl_4, 90 MHz) δ 1.28 (s, 6H), 2.20 (s, 3H) and 2.91 (s, 3H); IR (neat) 2920, 1810, 1310, 1140, 970 and 770 cm-1; ^{13}C-NMR ($CDCl_3$, 20 MHz) δ 9.4, 24.2, 32.5, 43.5, 68.9 and 141.4; Anal. Calcd. for $C_7H_{12}O_2S$: C, 52.47; H, 7.55; S, 20.01. Found: C, 52.45; H, 7.55; S, 20.02.

Preparation and Photochemistry of 3,3-Dimethyl-2-phenyl-1-phenylsulfonylcyclo-propene (9). To a stirred solution containing 23.4 g of phenyl acetylene in 350 mL of anhydrous tetrahydrofuran at 0°C under a nitrogen atmosphere was added 154 mL of a 1.3 M solution of n-butyllithium in hexane. The resulting anion was stirred at 0°C for an additional 30 min at which time a solution containining 43.6 g of phenyl disulfide in 150 mL of anhydrous tetrahydrofuran was added dropwise via addition funnel. The resulting mixture was warmed to room temperature, stirred for an additional hour and then 100 mL of water was added and the solvent was removed under reduced pressure. The residue was dissolved in 500 mL of ether and washed twice with a 10% of sodium hydroxide solution. The ether layer was dried over magnesium sulfate and the solvent was removed under reduced pressure to give 41.5 g of phenyl phenylethynyl sulfide which was immediately subjected to oxidation. To a mechanically stirred solution containing 41.5 g of

the above sulfide in 500 mL of chloroform at 25°C was added 90.0 g of 85% 3-chloroperoxybenzoic acid in small portions so as to keep the temperature of the reaction between 30-35°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 solution and then dried over magnesium sulfate. The solvent was removed under reduced pressure and the residue was crystallized from ether-hexane to give 40 g (83% yield) of a white solid which was identified as phenyl phenylethynyl sulfone on the basis of the following data: mp 67-68°C; ^{1}H-NMR ($CDCl_3$, 90 MHz) δ 7.08-7.48 (m, 8H) and 7.71-7.90 ppm (m, 2H); IR (KBr) 3080, 2200, 1590, 1345, 1180, 855, 770, and 740 cm^{-1}.

To a solution of 2-diazopropane in ether at -78°C was added 19.0 g of phenyl phenylethynyl sulfone. The red solution was stirred for 30 min at -78°C under nitrogen and then warmed to 25°C and stirred for 12 h. The organic layer was washed twice with a dilute aqueous hydrochloric acid solution, once with brine, dried over magnesium sulfate and concentrated to dryness to leave behind a yellow solid which was recrystallized from benzene-hexane to give 23.71 g (95% yield) of 3,3-dimethyl-4-phenyl-5-phenyl-sulfonyl-3H-pyrazole (9); mp 76-77°C; ^{1}H-NMR ($CDCl_3$, 90 MHz) δ 1.79 (s, 6H), 7.25-7.59 (m, 8H) and 7.69-7.85 (m, 2H); IR (KBr) 3080, 3000, 2960, 1630, 1600, 1330, 1165, and 740 cm-1; UV (95% ethanol) 286 nm (ε 7,800); ^{13}C-NMR ($CDCl_3$) δ 20.7, 99.3, 125.2, 126.8, 127.8, 128.4, 129.9, 130.3, 133.5, 139.7, 149.5 and 154.6 ; Anal. Calcd. for $C_{17}H_{16}O_2N_2S$: C, 65.36; H, 5.16; N, 8.97; S, 10.26. Found: C, 65.29; H, 5.17; N, 8.96; S, 10.18.

A solution containing 5.0 g of 9 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 20% ethyl acetate-hexane mixture as the eluent. The major fraction contained 4.32 g (95% yield) of a light yellow oil whose structure was assigned as 3,3-dimethyl-2-phenyl-1-phenylsulfonylcyclopropene (13) on the basis of the following spectral properties: ^{1}H-NMR ($CDCl_3$, 90 MHz) δ 1.35 (s, 6H), 7.31-7.62 (m, 8H) and 7.91-8.06 (m, 2H); IR (neat) 3060, 2980, 1780, 1600, 1590, 1450, 1370, 930, and 800 cm-1; UV (95% ethanol) 222 (ε 14,500) and 294 nm (ε 14,000); ^{13}C-NMR ($CDCl_3$, 20 MHz) δ 24.2, 33.1, 124.3, 125.4, 127.0, 128.7, 129.1, 131.1, 131.3, 133.4, 139.5 and 141.4; Anal. Calcd. for $C_{17}H_{16}O_2S$: C, 71.80; H, 5.67; S, 11.28. Found: C, 71.79; H, 5.68; S, 11.26.

Fluoride Ion Desilylation of 3,3-Dimethyl-4-(p-tolylsulfonyl)-5-(trimethylsilyl)-3H-pyrazole (15). A 6.1 g sample of 3,3-dimethyl-4-(*p*-tolylsulfonyl)-5-(trimethylsilyl)-3H-pyrazole (15) was dissolved in 300 mL of ether. To this solution was added 1.0 g of 18-crown-6 followed by 1.1 g of potassium fluoride. The progress of the reaction was monitored by TLC and was found to be complete after 3 h at 25°C. The organic layer was washed with a saturated sodium bicarbonate solution, brine and dried over magnesium sulfate. Removal of the solvent under reduced pressure left 5.32 g of a crude oil which was chromatographed on a silica gel column using a 10% acetone-hexane mixture as the eluent. The major product isolated from the column contained 4.4 g (93% yield) of a solid which was identified as 3,3-dimethyl-4-(p-tolylsulfonyl)-3H-pyrazole (16)

on the basis of the following spectral data: mp 92-93°C; IR (KBr) 3110, 3000, 2940, 1500, 1330, 1155, 1095 and 690 cm^{-1}; ^{1}H-NMR (CCl_4, 90 MHz) δ 1.32 (s, 6H) 2.45 (s, 3H), 7.30 (d, 2H, J=7.5 Hz), 7.60 (s, 1H) and 7.77 (d, 2H, J=7.5 Hz); ^{13}C-NMR (20 MHz, $CDCl_3$) δ 20.3, 21.2, 94.0, 127.8, 129.8, 135.9, 144.6, 145.5 and 158.6; UV (95% ethanol) 226 (ε 9,800) and 260 nm (ε 6,000); m/e 250 (M^+), 165, 156, 140, 139 (base), 92, 93, 84, 67 and 65; Anal. Calcd. for $C_{12}H_{14}O_2N_2S$: C, 57.58; H, 5.64; N, 11.19; S, 12.81. Found: C, 57.64; H, 5.65; N, 11.18; S, 12.89.

Cycloaddition Reaction of 3,3-Dimethyl-4-(p-tolylsulfonyl)-3H-pyrazole (16) with Diazomethane. To a stirred solution containing 500 mg of the above pyrazole in 5 mL of dry tetrahydrofuran at 25°C was added an excess of an etheral solution of diazomethane. The resulting mixture was stirred for 12 h and the solvent was removed under reduced pressure. The resulting oil solidified on standing to give 560 mg of *cis*-6,6a-dihydro-3,3-dimethyl-3a-(p-tolylsulfonyl)pyrazolo[4,3-c]pyrazole (17). The structure was assigned on the basis of its spectral properties and by a single crystal X-ray analysis: mp 119-120°C; IR (KBr) 3060, 2990, 2940, 1600, 1555, 1320, 1300, 1145, 815, 890 and 660 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 90 MHz) δ 1.50 (s, 3H), 1.68 (s, 3H), 2.41 (s, 3H), 4.25 (dd, 1H, J=18.0 and 7.0 Hz), 5.18 (d, 1H, J=18.0 Hz), 5.42 (d, 1H, J=7.0 Hz), 7.25 (d, 2H, J=9.0 Hz) and 7.68 (d, 2H, J=9.0 Hz); UV (95% ethanol) 230 (ε 14,000), 265 (ε 1,100) and 325 nm (ε 470); Anal. Calcd. for $C_{13}H_{16}O_2N_4S$: C, 53.41; H, 5.52; N, 19.16; S, 10.97. Found: C, 53.34; H, 5.55; N, 19.14; S, 10.89.

Colorless crystals of 17 were grown from dichloromethane and petroleum ether. A suitable crystal of approximately 0.2 x 0.2 x 0.4 mm was selected and mounted on a glass fiber with epoxy cement such that the longest crystal dimension was parallel to the fiber axis. Unit cell parameters were determined on a Nicolet R_3 diffractometer using a Molybdenum radiation source. Twenty-five reflections were machine centered and used in the least squares refinement of the lattice parameters and orientation matrix. The unit cell parameters obtained were: a=11.0021(1)A°, b=20.7998(2)A°, c=12.2715(2)A°, b=90.571(2)°, v=2808.09A°3, d_{calcd} = 1.38 g cm^{-3}, F(000)= 1231.73 and Z=8. Crystals of 17 were monoclinic and of the space group $p2_{1/c}$.

Intensity data were collected by using the omega scan technique with a variable scan rate of 5-29.3° min-1. A scan width of 1.0° was sufficient to collect all of the peak intensity. Control reflections, monitored after each set of 97 scans, showed no significant change during the course of data collection. Lorentz and polarization corrections were made in the usual way. No absorbtion correction was applied. Of the total of 4,158 reflections collected with $3° \leq w \leq 45°$; 3,180 were found to be unique and have $I \geq 3s(I)$. The structure was solved by direct methods with the SHELXTL program. Following anisotropic refinement of the backbone atoms, all hydrogens were located in a weighted electron density difference Fourier synthesis. Refinement of the hydrogens with isotropic thermal parameters reduced the residual to R=0.0451 and R_w= 0.0508 where $R_w = Sw1/2(F_o-F_c)/Sw1/2\ F_o$.

Cycloaddition Reaction of 3,3-Dimethyl-4-(p-tolylsulfonyl)-3H-pyrazole (16) with 2-Diazopropane. To a 500 mg sample of 3H-pyrazole 16 in 30 mL of dry ether at -78°C was added an excess of an ether solution of 2-diazopropane at -78°C. When the orange-red color of diazopropane remained, the addition was discontinued and the solution was allowed to slowly

warm to room temperature and was stirred for 12 h. The yellow solution was washed with a 10% hydrochloric acid solution followed by brine, dried over magnesium sulfate and concentrated under reduced pressure to give 672 mg of a solid. This material was subjected to silica gel chromatography using a 10% acetone-hexane mixture as the eluent. The major fraction contained 572 mg (89% yield) of a crystalline solid whose structure was assigned as 3,3a,6,6a-tetrahydro-3,3,6,6-tetramethyl-3a-(p-tolylsulfonyl)-pyrazolo[4,3-c]pyrazole (**18**) by its spectral properties and an X-ray structure single crystal analysis: 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.

Colorless crystals of **18** were grown from dichloromethane and petroleum ether at -20°C. A suitable crystal of approximately 0.25 x 0.25x 0.30 mm was selected and mounted on a glass fiber with epoxy cement such that the longest crystal dimension was parallel to the fiber axis. Unit cell parameters were determined on a Nicolet R_3 diffractometer using a molybdenum radiation source. Twenty five reflections were machine centered and used in the least squares refinement of the lattice parameters and orientation matrix. The unit cell parameters obtained were: a=8.6884(3)A°, b=8.8363(3)A°, c=21.6415(5)A°, b= 98.771(2), v= 1642.06 A^{o3}, d_{calcd} = 1.30 gcm^{-3}, F(000)= 679.86 and Z= 4. Crystals of **18** were monoclinic and of the space group $P2_{1/n}$.

Intensity data were collected by using the omega scan technique with a variable scan rate of 5-29.3° min-1. A scan width of 1.0° was sufficient to collect all of the peak intensity. Control reflections, monitored after each set of 97 scans, showed no significant change during the course of data collection. Lorentz and polarization corrections were made in the usual way. No absorption correction was applied. Of the total of 2,583 reflections collected with $3^o \leq w \leq 45^o$; 1,939 were found to be unique and have $I \geq 3s(I)$. The structure was solved by direct methods with the SHELXTL program. Following anisotropic refinement of the backbone atoms, all hydrogens were located in a weighted electron density difference Fourier synthesis. Refinement of the hydrogens with isotropic thermal parameters reduced the residuals to R=0.0497 and R_w= 0.0628, where $R_w = Sw^{1/2}(F_o-F_c)/Sw^{1/2}F_o$.

A 1.5 g sample of **18** was dissolved in 15 mL of dry benzene in a Carius tube, degassed with nitrogen, 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 (**19**) 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 (sept, 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 (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.

Lewis Acid Catalyzed Rearrangement of 3,3-Dimethyl-5-(trimethylsilyl)-4-(p-tolyl-sulfonyl)-3H-pyrazole (15). To a stirred solution containing 230 mg of aluminum trichloride in 25 mL of dichloromethane at -10°C was added 25 mL of a dichloromethane solution containing 500 mg of 3,3-dimethyl-5-(trimethylsilyl)-4-(p-tolylsulfonyl)-3H-pyrazole (**15**). The resulting mixture was maintained at -10°C for 2 h and was then warmed to 25°C and stirred for an additional 4 h. The mixture was poured into an ice cold saturated solution of sodium bicarbonate. The organic layer was separated, washed with water, brine and dried over magnesium sulfate. Removal of the solvent left 496 mg (98%) of a white solid whose structure was assigned as 1,5-dimethyl-4-(p-tolyl-sulfonyl)-3-(trimethylsilyl)pyrazole (**20**) on the basis of its spectral data: mp 139-140°C; IR (KBr) 2980, 1600, 1500, 1320, 1250, 1005, 860, 720 and 600 cm^{-1}; ^{1}H-NMR (CCl_4, 90 MHz) δ 0.39 (s, 9H), 2.31 (s, 3H), 2.35 (s, 3H), 3.75 (s, 3H), 7.28 (d, 2H, J=9.0 Hz) and 7.74 (d, 2H, J= 9.0 Hz); UV (95% ethanol) 237 nm (ε 13,000); m/e 322 (M^+), 307 (base) and 167; ^{13}C-NMR ($CDCl_3$, 20 MHz) δ -1.2, 10.0, 21.2, 36.5, 125.1, 126.3, 129.3, 140.7, 141.8 and 142.9; Anal Calcd for $C_{15}H_{22}O_2N_2SSi$: C, 55.86; H, 6.88; N, 8.69; S, 9.94. Found: C, 56.09; H, 6.77; N, 8.53; S, 9.73.

A 150 mg sample of the above pyrazole was dissolved in 5 mL of tetrahydrofuran and 0.5 mL of a 1.0 M solution of tetrabutylammonium fluoride in tetrahydrofuran was added at 25°C. The reaction was poured into an aqueous solution of sodium bicarbonate and diluted with ether. The ether layer was separated, dried over magnesium sulfate and concentrated to give 110 mg (94% yield) of a white solid whose structure was assigned as 1,5-dimethyl-4-(p-tolylsulfonyl)pyrazole (**21**) on the basis of its spectral properties: mp 99-100°C; IR (KBr) 3320, 3110, 3060, 2960, 2200, 1600, 1305, 1295, 1150, 700, 750 and 590 cm-1; 1H-NMR ($CDCl_3$, 90 MHz) δ 2.35 (s, 3H), 2.39 (s, 3H), 3.70 (s, 3H), 7.20 (d, 2H, J=9.0 Hz), 7.69 (s, 1H) and 7.80 (d, 2H, J=9.0 Hz); UV (95% ethanol) 238 (ε 14,000) and 288 nm (ε 3,800); Anal. Calcd. for $C_{12}H_{14}O_2N_2S$: C, 57.58; H, 5.64; N, 11.19. Found: C, 57.66; H, 5.66; N, 11.11.

Reaction of 3,3-Dimethyl-4-(p-Tolylsulfonyl)-3H-pyrazole (16) and Acetyl Chloride with Aluminum Chloride. To a stirred solution containing 293 mg of aluminum trichloide and 208 mg of acetyl chloride in 50 mL of anhydrous dichloromethane at -10°C under a nitrogen atmosphere was added 25 mL of a dichloromethane solution containing 500 mg of the pyrazole **16**. The resulting mixture was warmed to 25°C and was stirred for an additional 4 h. The solution was poured into an ice cold saturated solution of sodium bicarbonate. The aqueous layer was extracted with dichloromethane. The organic layer was separated, washed with water and brine, dried over magnesium sulfate and concentrated under reduced pressure. The resulting oil was chromatographed on a 2 mm chromatatron plate using a 10% acetone-hexane mixture as the eluent. Removal of the solvent under reduced pressure left 480 mg (73%) of an oil which crystallized upon standing and was identified as 1-acetyl-4-chloro-5,5-dimethyl-4-(p-tolyl-sulfonyl)-2-pyrrazoline (**22**) on the basis of its spectral properties: mp 80-81°C; IR (KBr) 3080,

3200, 2960, 1690, 1600, 1580, 1240, 925 and 710 cm^{-1}; ^{1}H-NMR (CCl_4, 90 MHz) δ 1.68 (s, 3H), 1.99 (s, 3H), 2.20 (s, 3H), 2.45 (s, 3H), 6.45 (s, 1H), 7.31 (d, 2H, J=9.0 Hz) and 7.79 (d, 2H, J=9.0 Hz); UV (95% ethanol) 235 (ε 16,000) and 263 nm (ε 13,000); m/e 328 (M^+), 175, 173, 133, 131 (base) and 91; ^{13}C-NMR ($CDCl_3$, 20 MHz) δ 20.3, 21.6, 23.0, 24.3, 92.3, 129.6, 130.9, 132.8, 137.7, 146.4, 169.8; Anal. Calcd. for $C_{14}H_{17}N_2O_3ClS$: C, 51.14; H, 5.21; N, 8.52; Cl, 10.78; S, 9.75. Found: C, 51.08; H, 5.25; N, 8.49; Cl, 10.87; S, 9.69.

To a stirred solution containing 150 mg of the above pyrrazoline in 15 mL of dry tetrahydrofuran at -10°C, was added 103 mg of potassium t-butoxide. The resulting brown solution was quenched with a saturated solution of ammonium chloride. The mixture was diluted with ether, washed with water, brine and dried over magnesium sulfate. Removal of the solvent left 100 mg of an oil which was identified as 3,3-dimethyl-4-(p-tolylsulfonyl)-3H-pyrazole (16) by comparison with an authentic sample.

Preparation of N-Methyl-4-(p-tolylsulfonyl)pyrazole (25). To a stirred solution containing 550 mg of p-tolyl [2-(trimethylsilyl)ethynyl]sulfone[27] in 10 mL of dry tetrahydrofuran was added an etheral solution of diazomethane. The mixture was stirred at 25°C for 12 h and the solvent was removed under reduced pressure. The resulting residue was stirred together with anhydrous potassium carbonate and iodomethane in 10 mL of N,N-dimethylformamide at 25°C for 6 h. The solution was diluted with ether and filtered. The solution was washed several times with water and dried over magnesium sulfate. Removal of the solvent under reduced pressure afforded 700 mg (100% yield) of a white solid whose structure was identified as N-methyl-4-(p-tolyl-sulfonyl)-5-(trimethylsilyl)pyrazole (24) on the basis of its spectral and chemical properties: mp 128-129°C; IR (KBr) 3120, 2960, 1600, 1510, 1320, 1240, 1150, 840 and 665 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 90 MHz) δ 0.30 (s, 9H), 2.38 (s, 3H), 3.89 (s, 3H), 7.20 (d, 2H, J=9.0 Hz), 7.68 (d, 2H, J=9.0 Hz) and 7.89 (s, 1H); UV (95% ethanol) 238 nm (ε 14,000); Anal. Calcd. for $C_{14}H_{20}O_2N_2SiS$: C, 54.51; H, 6.54; N, 9.08; S, 10.39; Found: C, 54.37; H, 6.55; N, 8.98; S, 10.30.

N-Methyl-4-(p-tolylsulfonyl)-5-(trimethylsilyl)pyrazole (24) was desilylated in the following manner: To a stirred solution containing 200 mg of the above pyrazole in 5 mL of dry tetrahydrofuran was added 0.65 mL of a 1.0 M solution of tetrabutylammonium fluoride in tetrahydrofuran. The mixture was stirred for 10 min at 25°C and then poured into an aqueous solution of sodium bicarbonate and extracted with ether. The organic layer was washed twice with water, brine and dried over magnesium sulfate. Removal of the solvent under reduced pressure afforded 146 mg (95% yield) of a white solid whose structure was identified as N-methyl-4-(p-tolylsulfonyl)pyrazole (25) on the basis of the following spectral data: mp 126-127°C; IR (KBr) 3130, 3120, 3060, 2960, 1600, 1530, 1320, 1310, 1155, 720 and 680 cm^{-1}; ^{1}H-NMR (benzene-d_6, 360 MHz) δ 1.86 (s, 3H), 2.80 (s, 3H), 6.78 (d, 2H, J=8.3 Hz), 7.07 (s, 1H), 7.84 (s, 1H), and 7.91 (d, 2H, J=8.3 Hz); UV (95% ethanol) 238 nm (ε 17,000); Anal. Calcd. for $C_{11}H_{12}O_2N_2S$: C, 55.91; H, 5.12; N, 11.86; S, 13.57. Found: C, 55.96; H, 5.17; N, 11.84; S, 13.62.

Reaction of Ethynyl p-Tolylsulfone with Diazomethane. To a stirred solution containing 1.0 g of ethynyl p-tolylsulfone in a minimum amount of anhydrous tetrahydrofuran at 0°C was added an ethereal solution of diazomethane. The yellow solution was allowed to warm to room

temperature and was stirred for 12 h under a nitrogen atmosphere. Removal of the solvent under reduced pressure left 1.3 g of a crude residue which was chromatographed on silica gel column with a 10% acetone-hexane mixture as the eluent to give 920 mg (66% yield) of a material which was identified as N-methyl-3-(p-tolylsulfonyl)pyrazole (28) on the basis of its spectral properties: mp 61-62°C; IR (KBr) 3110, 3060, 2950, 1600, 1325, 1080, 925, 810, 800 and 670 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 360 MHz) δ 2.43 (s, 3H), 3.99 (s, 3H), 6.84 (d, 2H, J=2.2 Hz), 7.34 (d, 2H, J=8.3 Hz), 7.45 (d, 1H, J=2.2 Hz) and 7.81 ppm (d, 2H, J=8.3 Hz); ^{13}C-NMR ($CDCl_3$, 20 MHz) δ 21.3, 38.2, 111.3, 127.4, 129.3, 137.0, 137.5, 140.3, 144.9; UV (95% ethanol) 240 nm (ε 18,000); Anal. Calcd. for $C_{11}H_{12}O_2N_2S$: C, 55.91; H, 5.12; N, 11.86; S, 13.57. Found: C, 55.99; H, 5.17; N, 11.82; S, 13.48.

Preparation and Photochemistry of 3,3-Dimethyl-5-(trimethylsilyl)-3H-pyrazol-4-yl Methyl Ketone (29). A solution containing 2-diazopropane was prepared in the usual way using 45 g of acetone hydrazone, 180 g of mercury (II) oxide and 15 mL of a 3 M solution of potassium hydroxide in methanol. To the deep red ether solution was added 10 g of 4-(trimethylsilyl)-3-butyn-2-one[46] at -78°C. The resulting mixture was slowly warmed to room temperature and was stirred for an additional 12 h under a nitrogen atmosphere. The ether solution was washed with a 10% hydrochloric acid solution, water, brine and was dried over magnesium sulfate. Removal of the solvent under reduced pressure left a bright yellow oil which was identified as 3,3-dimethyl-5-(trimethylsilyl)-3H-pyrazol-4-yl methyl ketone (29) on the basis of its spectral data: IR (neat) 2980, 1680, 1560, 1460, 1250 and 850 cm^{-1}; ^{1}H-NMR (CCl_4, 90 MHz) δ 0.38 (s, 9H), 1.45 (s, 6H) and 2.32 (s, 3H); UV (95% ethanol) 265 nm (ε 3,800); m/e 210 (M^+), 181, 195 and 167 (base); ^{13}C-NMR ($CDCl_3$, 50 MHz) δ -1.6, 20.2, 31.6, 96.3, 158.9, 164.6, 198.4; Anal. Calcd. for $C_{10}H_{18}ON_2Si$: C, 57.10; H, 8.63; N, 13.32. Found: C, 57.36; H, 8.69; N, 13.28.

A 1.5 g sample of pyrazole 29 in 500 mL of benzene was irradiated for 2.5 h 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 distilled at 65°C (3 mm) to give 1.29 g (100% yield) of a colorless liquid which was identified as 5-methyl-3-(trimethylsilyl)-3,4-hexadiene-2-one (32) on the basis of its spectral properties: IR (neat) 2980, 1940, 1750, 1670, 1350, 1250 and 1220 cm^{-1}; ^{1}H-NMR (CCl_4, 90 MHz) δ 0.11 (s, 9H), 1.72 (s, 6H) and 2.10 (s, 3H); UV (95% ethanol) 229 nm (ε 7,200); m/e 182 (M^+), 167 (base); ^{13}C-NMR ($CDCl_3$, 20 MHz) δ -1.3, 18.6, 27.6, 92.3, 103.0, 201.8 and 214.9; Anal. Calcd. for $C_{10}H_{18}OSi$: C, 65.87; H, 9.95. Found: C, 65.81; H, 9.95.

To a stirred solution containing 453 mg of thiophenol in 20 mL of dry tetrahydrofuran at 0°C under a nitrogen atmosphere was added 1.0 mL of a 1.38 M solution of n-butyllithium in hexane. The mixture was allowed to warm to 25°C at which time 250 mg of the allene 32 in 50 mL of dry tetrahydrofuran was added. The resulting solution was stirred for 12 h and the solvent was removed under reduced pressure. The residue was diluted with ether, washed with a 2% sodium hydroxide solution, water, brine and dried over magnesium sulfate. Evaporation of the solvent afforded 425 mg of an oil which was chromatographed on a 2 mm chromatatron plate using a 5% acetone-hexane mixture as the eluent. The first fraction contained phenyldisulfide. The second fraction contained 270 mg (90% yield) of an oil which was identified as 5-methyl-4-(phenylthio)-4-

hexen-2-one (33) on the basis of its spectral properties: IR (neat) 3060, 3000, 2910, 1715, 1580, 1480, 1440, 1355, 1160, 740 and 690 cm^{-1}; ^{1}H-NMR (CCl_4, 90 MHz) δ 1.78 (s, 3H), 1.95 (s, 3H), 2.01 (s, 3H), 3.21 (s, 2H) and 7.10 (s, 5H); ^{13}C-NMR ($CDCl_3$, 20 MHz) δ 21.5, 23.2, 29.1, 118.7, 125.7, 128.6, 128.8, 135.7, 143.8 and 205.1 ppm.

Preparation and Reaction of 3,3-Dimethyl-3H-pyrazol-4-yl Methyl Ketone (30) with Diazomethane. To a stirred solution containing 1.0 g of 3H-pyrazole 29 in 100 mL of ether was added 500 mg of 18-crown-6 and 560 mg of potassium fluoride at 25°C. The resulting mixture was stirred for 12 h at 25°C and was then quenched with a saturated solution of sodium bicarbonate. The organic layer was washed with water, brine and dried over magnesium sulfate. Removal of the solvent under reduced pressure left 500 mg (76% yield) of a yellow oil which was identified as 3,3-dimethyl-3H-pyrazol-4-yl methyl ketone (30) on the basis of its spectral properties: bp 110°C (1 mm); IR (neat) 3100, 2980, 2940, 1680, 1600, 1380 and 1250 cm^{-1}; ^{1}H-NMR (CCl_4, 90 MHz) δ 1.41 (s, 6H), 2.40 (s, 3H) and 7.85 (s, 1H); UV (95% ethanol) 254 nm (ε 5,500); m/e 138 (M^+), 123 (base) and 95; ^{13}C-NMR ($CDCl_3$, 20 MHz) δ 20.1, 28.5, 93.8, 144.9, 154.4, 191.8; Anal. Calcd. for $C_7H_{10}ON_2$: C, 60.85; H, 7.30; N, 20.27. Found: C, 60.64; H, 7.48; N, 20.53.

To a stirred solution containing 420 mg of pyrazole 30 in 10 mL of ether at 25°C, was added an etheral solution of diazomethane. The resulting mixture was stirred for 12 h and the solvent was removed under reduced pressure. The resulting oil was crystallized from dichloromethane and petroleum ether to give 540 mg of a white solid which was assigned as *cis*-6,6a-dihydro-3,3-dimethylpyrazolo[4,3-c]pyrazol-3a(3H)-yl methyl ketone (31) on the basis of its spectral data: mp 86-87°C; IR (KBr) 2990, 2940, 1710, 1555, 1370, 1205, 905 and 625 cm^{-1}; ^{1}H-NMR (CCl_4, 90 MHz) δ 1.10 (s, 3H), 1.70 (s, 3H), 2.35 (s, 3H), 4.50 (dd, 1H, J=18.0 and 9.0 Hz), 5.10 (d, 1H, J=18.0 Hz) and (d, 1H, J=9.0 Hz); UV (95% ethanol) 240 (ε 2,000) and 326 nm (ε 400); Anal. Calcd. for $C_8H_{12}N_4O$: C, 53.32; H, 6.71; N, 31.09. Found: C, 53.27; H, 6.72; N, 31.08.

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