1,3-DIPOLAR CYCLOADDITION CHEMISTRY OF 2,3-*BIS*(PHENYLSULFONYL)-1,3-DIENE WITH DIAZOALKANES‡

Albert Padwa,*† Michael Meske, and Augusto Rodriguez§

†*Department of Chemistry, Emory University, Atlanta, Georgia 30322 USA and Clark Atlanta University,§ Atlanta, Georgia 30314 USA*

Abstract- 2,3-*Bis*(phenylsulfonyl)-1,3-butadiene was found to react smoothly with diazomethane and diazopropane to give a mixture of 1:1- and 2:1-cycloadducts. Heating the 1:1-cycloadduct at 110°C resulted in loss of nitrogen and formation of mainly phenylsulfonyl-substituted 1,3-dienes. Cycloaddition of 2-phenylsulfinyl-3-phenylsulfonyl-1,3-butadiene with the same diazoalkanes gave only 1:1-cycloadducts which readily extruded nitrogen producing related 1,3-dienes. The regiochemistry of the dipolar cycloaddition is compatible with FMO considerations.

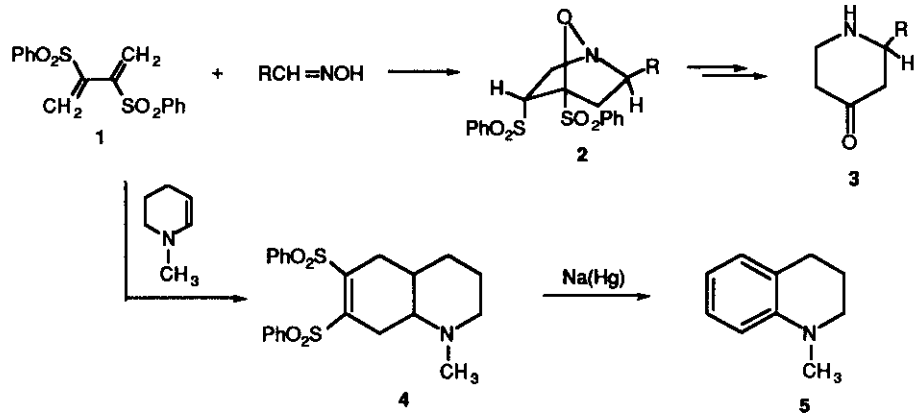
Phenylsulfonyl substituted 1,3-dienes have become established as useful synthetic intermediates in organic synthesis.[1-16] The phenylsulfonyl group not only increases the reactivity of the diene but also adds control to the regioselectivity of the cycloaddition. Indeed, the phenylsulfonyl moiety is enjoying increasing popularity as an activating group undoubtedly as a consequence of its ability to act as a temporary control element in organic synthesis. The sulfonyl group can be removed both reductively and oxidatively with subsequent formation of ketones.[17] It stabilizes adjacent carbanions[18] which are extremely useful in carbon-carbon bond forming reactions. The bulky phenylsulfonyl group has also been shown to be useful for acyclic stereocontrol.[19] In earlier reports, we demonstrated the use of 2,3-*bis*(phenylsulfonyl)-1,3-butadiene (1) as a versatile building block in organic synthesis, particularly for 4+2-cycloaddition chemistry.[5] *Bis*(phenylsulfonyl)diene (1) is a crystalline compound, easily prepared and with indefinite shelf life, adding to its attractiveness as a synthetic reagent.[20]

In our first report, we described the cycloaddition of diene (1) with various oximes as a method of piperidine formation.[21] In an investigation which followed, we demonstrated that diene (1) undergoes cycloaddition to a variety of imines, enamines and ynamines to give 4+2-cycloadducts.[22] In this paper we describe some additional examples of 3+2-cycloaddition chemistry of *bis*(phenylsulfonyl)-1,3-butadiene (1) with several diazoalkanes in an attempt to prepare the corresponding cyclopropyl phenylsulfonyl system.

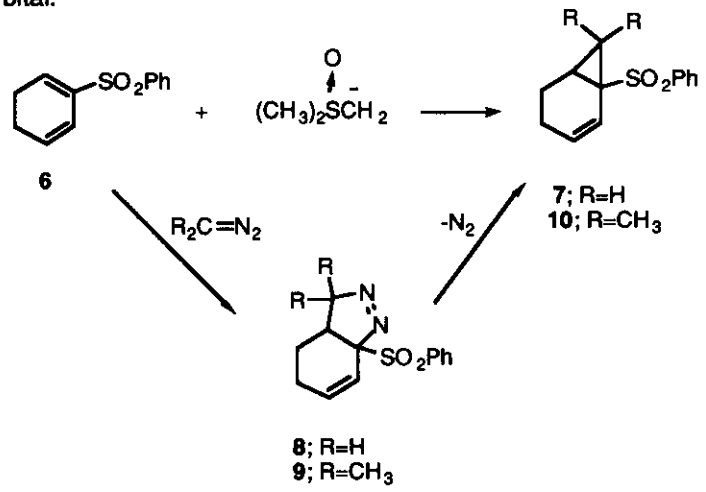
RESULTS AND DISCUSSION

Vinyl sulfones have been converted to cyclopropyl sulfones when treated with the usual reagents for cyclopropanation of electron-deficient double bonds such as enones.[23] Sulfoxonium ylides carry out this conversion efficiently.[24] For example, Bäckvall and coworkers reported that the reaction of 2-(phenyl-

‡ Dedicated to Rolf Hüisgen on the occasion of his 75th birthday.

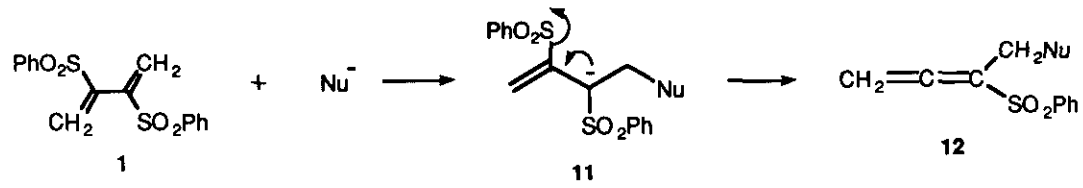


sulfonyl)-1,3-cyclohexadiene (**6**) with dimethyloxosulfonium methylide resulted in a very efficient reaction to give vinylcyclopropane (**7**) in essentially quantitative yield.[25] We have found that the same vinylcyclopropane (**7**) could also be produced by treating diene (**6**) with diazomethane and either heating (110°C) or irradiating the resulting tetrahydro-3*H*-indazole (**8**). A related cycloaddition occurred using 2-diazopropane which afforded the expected cycloadduct (**9**) (92%) which, upon extrusion of nitrogen, gave cyclopropane (**10**) in quantitative yield. The regioselectivity of the cycloaddition is predictable from frontier orbital considerations for addition of a diazo compound to an electron-deficient dipolarophile with a low-lying LUMO orbital.[26]



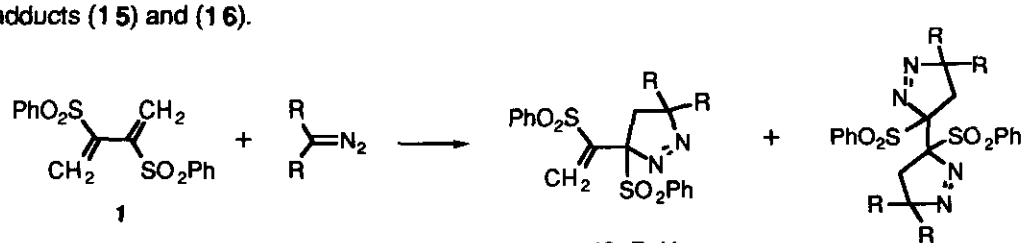
Even though *bis*(phenylsulfonyl)-1,3-butadiene (**1**) is highly activated toward nucleophilic addition,[6] the reaction of **1** with either dimethyloxosulfonium or dimethylsulfonium methylide failed to give any of the desired cyclopropanated product. Instead, a complex mixture of products was obtained which resisted

all attempts at characterization or separation. More than likely, the initial step involves conjugate addition of the ylide onto the terminal position of the diene to produce anion (**11**) which undergoes rapid elimination of phenylsulfinate anion prior to ring closure. Indeed, such a process has been effectively utilized for the synthesis of a variety of 1-phenylsulfonyl substituted allenes of type (**12**).[27]



1 **11** **12**

Since our attempts to obtain a cyclopropanation product from diene (**1**) using Simmons-Smith reagents also failed, we decided to investigate the reaction of *bis*(phenylsulfonyl)diene (**1**) with diazomethane. The additions of diazoalkanes to π-bonds are among the most thoroughly studied 1,3-dipolar cycloadditions.[28] The reaction of simple diazoalkanes are generally HO(1,3-dipole)-LU(dipolarophile) controlled.[29] 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.[29] Stirring a solution of diazomethane and diene (**1**) in ether at 25°C afforded a 1:1-mixture of the expected 3*H*-pyrazole (**13**) as well as the 2:1-*bis*-adduct (**14**). In a subsequent experiment, we found that the reaction of (**13**) with excess diazomethane afforded *bis*-adduct (**14**) in quantitative yield. A related reaction also occurred when diene (**1**) was allowed to react with 2-diazopropane affording cycloadducts (**15**) and (**16**).



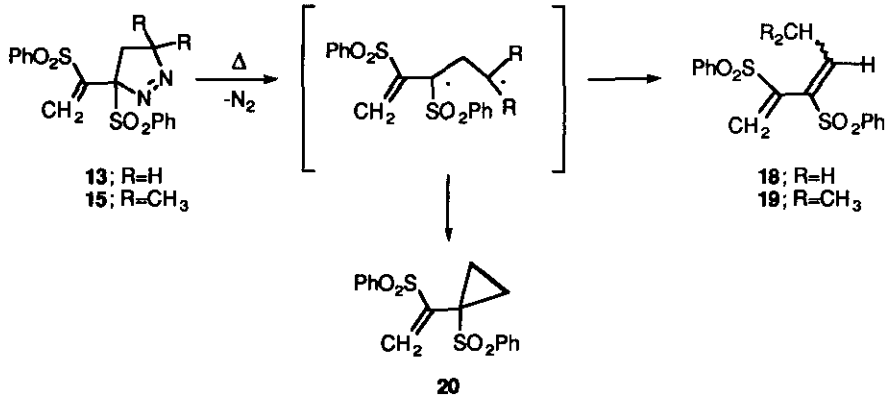
1 **13**; R=H **15**; R=CH_3 **14**; R=H **16**; R=CH_3

The ratio of the two cycloadducts was markedly dependent on the rate of addition of the diazoalkane to the diene. Rapid addition produced mainly the *bis*-adduct (**16**) whereas slower addition afforded much more of the mono-adduct (**15**). In both of the above two cases, the dipolar-cycloaddition occurred with the expected regiochemistry corresponding to attachment of the diazo carbon onto the terminal atom of

the starting diene.

The thermal decomposition of Δ^1-pyrazolines gives both olefins and cyclopropanes and has been of interest from both a synthetic and mechanistic point of view.[30,31] Formation of the olefinic products has been shown to be related to conformational factors.[32] Work carried out by McGreer and coworkers on Δ^1-pyrazolines bearing an electron-withdrawing group at C_3 indicates that the migration of the C_4-hydrogen proceeds in concert with nitrogen extrusion.[32] These Δ^1-pyrazolines undergo loss of nitrogen from the conformer which places the C_4-hydrogen in the pseudoequatorial position, thus orienting it in an *anti* relationship to the breaking C-N bond. The mechanism of cyclopropane formation is a more complex problem since some Δ^1-pyrazoline thermolyses give cyclopropanes in a highly stereospecific manner, others partly so, and still others not at all. The distribution of products is also dependent on the polarity of the solvent used.[33] Quite a number of different mechanistic schemes have been proposed for cyclopropane formation[34-38] ranging from an intermediary planar "*π-cyclopropane*" diradical[34] to a "*snapshot*" mechanism where nitrogen was extruded in a nonlinear fashion.[38]

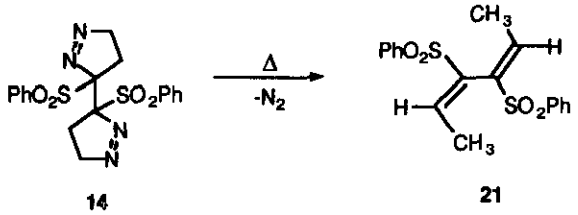
In the case of 3*H*-pyrazole (**13**), thermolysis afforded mainly (71%) diene (**18**) as a 3:1-mixture of *E*- and *Z*-isomers. Cyclopropane (**20**) was formed in low yield (19%) but it was not possible to separate it from the diene mixture. In an analogous fashion, the extrusion of nitrogen from (**15**) took place very rapidly producing diene (**19**) as the exclusive product. Thermal extrusion of nitrogen also occurred from the *bis*-adduct (**14**) producing mainly the *E,E*-diene (**21**) with no signs of any cyclopropanated product.



13; R=H
15; R=CH_3

18; R=H
19; R=CH_3

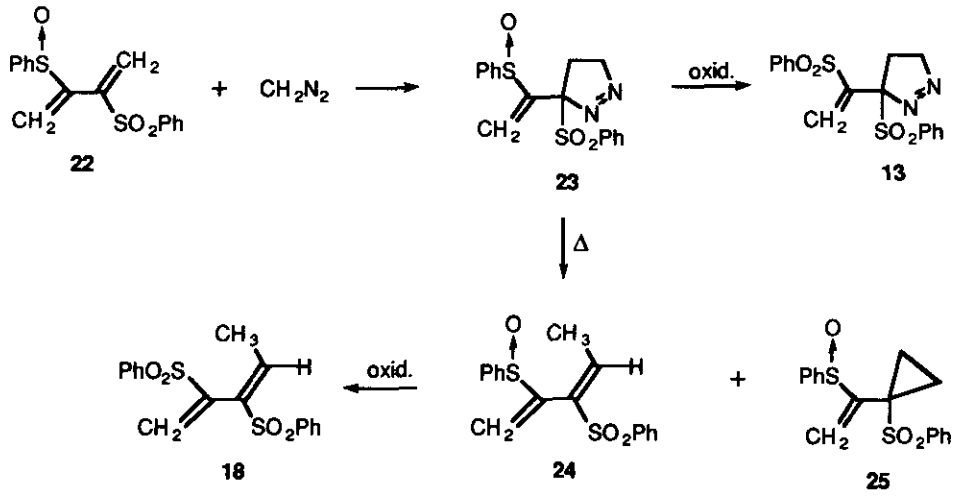
20



14

21

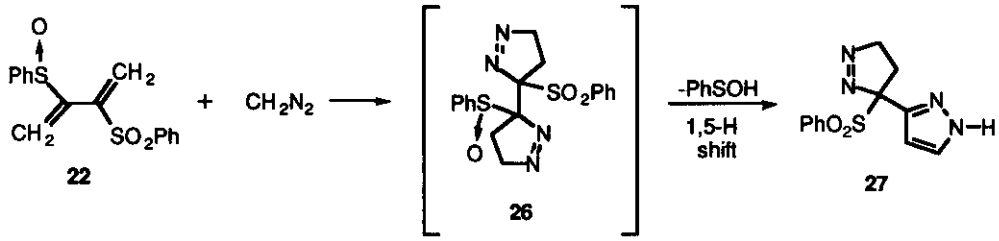
As part of our studies in this area, we also investigated the reaction of 2-phenylsulfinyl-3-phenylsulfonyl-1,3-butadiene (**22**) with diazomethane and diazopropane. Molecular mechanics calculations show that both dienes (**1**) and (**22**) exist in the transoid form and possess a substantial barrier for rotation about the 2,3-π bond. MNDO calculations clearly indicate that phenylsulfonyl substituted alkenes possess a much lower lying LUMO than phenylsulfinyl alkenes and therefore represents the site of higher reactivity with HOMO derived dipoles. Since diene (**22**) is markedly twisted from coplanarity, there should be a significant difference in the reactivity of the two π-systems toward the diazoalkane. This would suggest that reaction of diene (**22**) with the diazoalkane should take place exclusively at the phenylsulfonyl end and thereby avoid the complication of *bis*-cycloaddition which occurred with diene (**1**) (*i.e.*, formation of



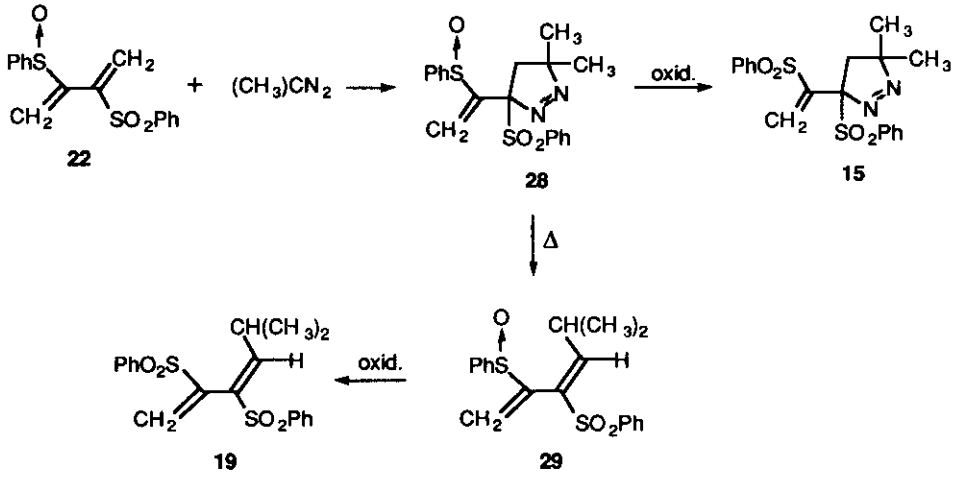
14 and **16**). Indeed, the reaction of **22** with diazomethane occurred only across the more activated phenylsulfonyl substituted π-bond affording 3*H*-pyrazole (**23**) in 84% yield. In addition, there were no detectable signs of any 2:1-adduct in the crude reaction mixture as was the case with diene (**1**). The structure of **23** was unequivocally established by oxidation with *m*-chloroperbenzoic acid producing Δ^1-pyrazoline (**13**) in 86% yield. Thermolysis of **23** afforded mostly diene (**24**) (60%) along with lesser quantities (33%) of cyclopropane (**25**). Diene (**24**) was smoothly oxidized to diene (**18**) which had previously been obtained from the thermolysis of 3*H*-pyrazole (**13**).

When an excess of diazomethane was allowed to react with diene (**22**) and for longer periods of time, the only product that could be isolated (73%) corresponded to dihydro-3*H*,1'*H*-[3,3']bipyrazolyl (**27**). The formation of **27** can best be explained by reaction of diazomethane (excess) with both π-bonds in a sequential manner giving the 2:1-adduct (**26**) as a transient species. This intermediate undergoes a

subsequent *syn* elimination of PhSOH followed by a 1,5-sigmatropic hydrogen shift. In support of this suggestion, we found that the treatment of 3*H*-pyrazole (**23**) with excess diazomethane also afforded **27** in high yield.



Similar chemoselectivity was exhibited in the reaction of diene (**22**) with diazopropane. When a dilute ether solution of **22** and diazopropane was used, the major product formed (62%) corresponded to the expected 3*H*-pyrazole (**28**). Oxidation of **28** with MCPBA afforded **15** in high yield. A sample of **28**



proved to be rather labile in solution and rapidly lost nitrogen producing diene (**29**) in 85% yield. Oxidation of diene (**29**) afforded the *bis*(phenylsulfonyl)diene (**19**) in 85% yield. In this case there were no detectable quantities of any cyclopropanated product.

In conclusion, the reactions of 2,3-*bis*(phenylsulfonyl)-1,3-butadiene (**1**) and 2-phenylsulfinyl-3-phenylsulfonyl-1,3-butadiene (**22**) with diazoalkanes proceeds smoothly and in high yield producing 3*H*-pyrazoles which readily lose nitrogen to give phenylsulfonyl substituted 1,3-butadienes. The generalization of these findings and their implications for the synthesis of various heterocyclic compounds containing phenylsulfonyl groups are the objects of ongoing investigations.

EXPERIMENTAL SECTION

Melting points are uncorrected. Mass spectra were determined at an ionizing voltage of 70 eV. Unless otherwise noted, all reactions were performed in oven dried glassware under an atmosphere of dry nitrogen. Solutions were evaporated under reduced pressure with a rotary evaporator and the residue was chromatographed on a silica gel column using an ethyl acetate-hexane mixture as the eluent unless specified otherwise.

Preparation of 1-(Phenylsulfonyl)bicyclo[4.1.0]hept-2-ene (7). To a solution of 528 mg (2.4 mmol) of 2-phenylsulfonyl-1,3-cyclohexadiene (**6**) in 20 ml of ether at room temperature under N_2 was added 15 ml (3.7 mmol) of freshly prepared diazomethane in ether. The mixture was stirred for 10 h at room temperature and the solvent was removed under reduced pressure to leave behind a yellow solid which was subjected to silica gel column chromatography (9:1 ethyl acetate-hexane) to give 622 mg (99 %) of 7a-phenylsulfonyl-3a,4,5,7a-tetrahydro-3*H*-indazole (**8**); mp 84-85°C; ir (KBr) 1636, 1578, 1537, 1438, 1298, 1143, 1080, 863, 757, 683, and 600 cm^{-1}; ^{1}H-nmr ($CDCl_3$, 300 MHz) δ 1.05 (m, 1H), 1.91 (m, 1H), 1.98 (m, 2H), 2.93 (m, 1H), 4.47 (dd, 1H, J=18.0 and 3.9 Hz), 4.76 (dd, 1H, J=18.0 and 8.4 Hz), 5.98 (d, 1H, J=10.2 Hz), 6.36 (m, 1H), 7.58 (m, 2H), 7.70 (m, 1H), and 7.91 (m, 2H); ^{13}C-nmr ($CDCl_3$, 75 MHz) δ 21.8, 25.1, 30.3, 83.9, 109.8, 118.2, 129.0, 130.4, 134.4, 135.6, and 138.7; Anal. Calcd for $C_{13}H_{14}N_2O_2S$: C, 59.52; H, 5.38; N, 10.69. Found: C, 59.27; H, 5.29 ; N, 10.53.

A sample of 40 mg (0.15 mmol) of **8** in 12 ml of toluene was heated at reflux for 1 h under N_2. The solvent was removed under reduced pressure and the residue was subjected to flash silica gel chromatography (9:1 ethyl acetate-hexane) to give 36 mg (100%) of 1-phenylsulfonylbicyclo[4.1.0]hept-2-ene (**7**)[25]; mp 49-50°C; ir (KBr) 1438, 1296, 1133, 1062, 848, and 720 cm^{-1}; ^{1}H-nmr ($CDCl_3$, 300 MHz) δ 1.14 (dd, 1H, J=6.6 and 5.1 Hz), 1.39 (m, 1H), 1.62 (m, 1H), 1.87 (m, 3H), 2.20 (m, 1H), 5.57 (m, 1H), 6.04 (dd, 1H, J=10.2 and 2.1 Hz), 7.43-7.57 (m, 3H), and 7.79 (m, 2H); ^{13}C-nmr ($CDCl_3$, 75 MHz) δ 17.0, 18.4, 19.6, 21.7, 39.9, 121.4, 127.2, 127.8, 128.8, 133.0, and 139.1; HRms Calcd for $C_{13}H_{14}SO_2$: 234.0714. Found: 234.0714.

A 50 mg (0.19 mmol) sample of **8** was irradiated in 130 ml of benzene using a 450-W Hanovia medium pressure mercury arc lamp equipped with a Pyrex filter sleeve under a N_2 atmosphere for 3 h. The solvent was removed under reduced pressure and the crude residue was subjected to flash silica gel chromatography (10:1 ethyl acetate-hexane) to give 44 mg (98%) of **7** which was identical in all aspects with the sample isolated above.

Preparation of 1-Phenylsulfonyl-7,7-dimethylbicyclo[4.1.0]hept-2-ene (10). To a solution of 264 mg (1.2 mmol) of 2-phenylsulfonyl-1,3-cyclohexadiene (**6**) in 10 ml of ether at 0°C under N_2 was

added 4 ml (2.0 mmol) of freshly prepared diazopropane. The mixture was stirred for 7 h and the solution was then allowed to warm to room temperature and was quenched with a 10% HCl solution. The layers were separated and the aqueous layer was extracted with CH_2Cl_2. The combined organic layer was washed with water, brine and dried over Na_2SO_4. The solvent was removed under reduced pressure leaving behind a yellow solid which was subjected to silica gel column chromatography (9:1 ethyl acetate-hexane) to give 319 mg (92%) of 7a-phenylsulfonyl-3,3-dimethyl-3a,4,5,7a-tetrahydro-3*H*-indazole (**9**) as a white solid; mp 125-126°C; ir (KBr) 1640, 1579, 1440, 1300, 1145, and 726 cm^{-1}; ^{1}H-nmr ($CDCl_3$, 300 MHz) δ 1.19 (s, 3H), 1.48 (s, 3H), 1.56-1.65 (m, 1H), 1.95-2.05 (m, 2H), 2.12-2.18 (m, 1H), 2.46 (m, 1H), 5.74 (d, 1H, J=9.9 Hz), 6.18-6.24 (m, 1H), 7.54-7.68 (m, 3H), and 7.95 (m, 2H); ^{13}C-nmr ($CDCl_3$, 75 MHz) δ 18.3, 21.4, 21.8, 26.8, 37.1, 93.3, 109.1, 117.3, 128.6, 130.3, 134.1, 135.3, and 136.8; Anal. Calcd for $C_{15}H_{18}N_2O_2S$: C, 55.68; H, 5.53; N, 11.81. Found: C, 55.54; H, 5.38; N, 11.73.

A 50 mg (0.17 mmol) sample of **9** in 12 ml of toluene was heated at reflux for 1 h under N_2. The solvent was removed under reduced pressure and the residue was subjected to flash silica gel chromatography (9:1 ethyl acetate-hexane) to give 42 mg (92%) of 1-phenylsulfonyl-7,7-dimethylbicyclo[4.1.0]hept-2-ene (**10**); mp 108-109°C; ir (KBr) 1444, 1291, 1138, 765, 705, and 612 cm^{-1}; ^{1}H-nmr ($CDCl_3$, 300 MHz) δ 1.03 (s, 3H), 1.46-1.64 (m, 3H), 1.67 (s, 3H), 1.86-1.95 (m, 1H), 2.13 (m, 1H), 5.72-5.82 (m, 2H), 7.45 (t, 2H, J=7.4 Hz), 7.54 (m, 1H), and 7.81 (d, 2H, J=7.4 Hz); ^{13}C-nmr ($CDCl_3$, 75 MHz) δ 18.1, 21.6, 22.2, 28.7, 35.6, 49.1, 121.8, 128.1, 128.4, 132.8, 133.6, and 141.0; HRms Calcd for $C_{15}H_{18}SO_2$: 262.1027. Found: 262.1027.

A 50 mg (0.17 mmol) sample of **9** was irradiated in 130 ml of benzene using a 450-W Hanovia medium pressure mercury arc lamp equipped with a Pyrex filter sleeve under a N_2 atmosphere for 1.5 h. The solvent was removed under reduced pressure and the crude mixture was subjected to flash silica gel chromatography to give 38 mg (85%) of **10**, which was identical in all aspects with the sample isolated above.

Reaction of 2,3-*Bis*(phenylsulfonyl)-1,3-butadiene (1) with Diazomethane. To solution of 1.0 g (3.0 mmol) of diene **1** in 50 ml of CH_2Cl_2 at 0°C under N_2 was added 16 ml (3.2 mmol) of freshly prepared diazomethane in ether. The mixture was stirred for 30 min at 0°C and then allowed to warm to room temperature. The solvent was removed under reduced pressure and the residue was fractionally crystallized from CH_2Cl_2 and hexane to give a 1:1 mixture (98%) of 3*H*-pyrazole (**13**) and 3*H*,3*H*-[3,3']bipyrazolyl (**14**). A pure sample of 3-phenylsulfonylvinyl-3-phenylsulfonyl-4,5-dihydro-3*H*-pyrazole (**13**) showed the following spectral properties; ir (neat) 1695, 1567, 1439, 1147, 905, 741, and 677 cm^{-1}; ^{1}H-nmr ($CDCl_3$, 300 MHz) δ 2.13-2.23 (m, 1H), 2.77-2.86 (m, 1H), 4.56-4.70 (m, 1H), 4.78-4.88 (m,

1H), 6.81 (d, 2H, J=3.3 Hz), 7.33-7.41 (m, 4H), and 7.50-7.59 (m, 6H); ^{13}C-nmr ($CDCl_3$, 75 MHz) δ 26.0, 79.7, 111.5, 128.5, 128.7, 128.9, 130.7, 133.2, 133.4, 133.9, 134.6, 139.2, and 145.6; HRms Calcd for $C_{17}H_{16}N_2O_4S_2$: 376.0551. Found: 376.0550.

A pure sample of 3,3'-*bis*(phenylsulfonyl)-4,5,4',5'-tetrahydro-3*H*,3*H*'-[3,3']bipyrazolyl (**14**) showed the following spectral properties; mp 146-147°C; ir (KBr) 1579, 1441, 1416, 1303, 1132, 1067, 872, and 717 cm^{-1}; ^{1}H-nmr ($CDCl_3$, 300 MHz) δ 2.50 (m, 4H), 4.53 (m, 2H), 4.84 (m, 2H), 7.49 (m, 4H), 7.64 (m, 2H), and 7.85 (d, 4H, J=8.1 Hz); ^{13}C-nmr ($CDCl_3$, 75 MHz) δ 22.6, 81.3, 115.7, 128.8, 131.1, 134.8, and 136.2; Anal. Calcd for $C_{18}H_{18}N_4O_4S_2$: C, 51.67; H, 4.31; N, 13.40. Found: C, 51.64; H, 4.30; N, 13.43.

A sample of 40 mg (0.1 mmol) of **13** in 6 ml of toluene was heated at reflux for 1 h under N_2. The solvent was removed under reduced pressure. The crude nmr spectrum indicated the presence of a mixture containing 54% of the *E*-isomer (**18**-*E*) of 2,3-*bis*-(phenylsulfonyl)-1,3-pentadiene; ir (KBr) 1766, 1650, 1581, 1439, 1304, 1147, 1076, 969, 748, and 620 cm^{-1}; ^{1}H-nmr ($CDCl_3$, 300 MHz) δ 1.78 (d, 3H, J=7.2 Hz), 5.62 (s, 1H), 6.52 (s, 1H), 7.34 (q, 1H, J=7.2 Hz), and 7.43-7.50 (m, 4H) and7.56-7.71 (6H, 2H); ^{13}C-nmr ($CDCl_3$, 75 MHz) δ 16.4, 128.8, 128.9, 129.0, 129.1, 133.2, 133.6, 133.9, 136.1, 138.4, 138.5, 143.4,and 146.5; HRMs Calcd for $C_{17}H_{16}O_4S_2$: 348.0490. Found: 348.0490. In addition, 17% of the *Z*-isomer of **18** as well as 19% of 1-(1-phenylsulfonylvinyl)-1-phenylsulfonylcyclopropane (**20**) was also *present*; ^{1}*H-nmr* ($CDCl_3$, 300 MHz) δ 1.44 (dd, 2H, J=7.8 and 5.7 Hz), 1.89 (dd, 2H, J=7.8 and 5.7 Hz), 6.11 (s, 1H), 6.53 (s, 1H), and 7.40-7.72 (m, 10H). It was not possible to separate the mixture of the latter two products by column chromatography or fractional crystallization.

A 125 mg (0.3 mmol) sample of **14** in 25 ml of toluene was heated at reflux for 1.25 h. The solvent was removed under reduced pressure and the residue was taken up in 35 ml of CH_2Cl_2 and 3.0 ml of triethylamine. This mixture was heated at reflux for 4 h under N_2. The reaction mixture was quenched with water and the aqueous layer was extracted with CH_2Cl_2. The organic layers were combined and washed with water, brine and dried over Na_2SO_4. The solvent was removed under reduced pressure and the residue was crystallized from a cyclohexane-ethyl acetate mixture to give 78 mg (72%) of 3,4-*bis*(phenylsulfonyl)-2,4-hexadiene (**21**); mp 164-165°C; ir (KBr) 1572, 1444, 1295, 1146, 1075, 747, and 599 cm^{-1}; ^{1}H-nmr ($CDCl_3$, 300 MHz) δ 1.49 (d, 6H, J=6.6 Hz), 7.30 (q, 2H, J=6.6 Hz), 7.45 (t, 4H, J=7.5 Hz), 7.58 (t, 2H, J=7.5 Hz), and 7.69 (d, 4H, J=7.5 Hz); ^{13}C-nmr ($CDCl_3$, 75 MHz) δ 15.5, 128.9, 129.7, 135.6, 139.2, 146.5, and 148.0; Anal. Calcd for $C_{18}H_{18}S_2O_4$: C, 59.66; H, 5.01. Found: C, 59.48; H, 4.97. The two other isomers of hexadiene **21** were detected in the crude reaction mixture by GC-ms as well as by ^{1}H-nmr but could not be separated or purified.

Reaction of 2,3-*Bis*(phenylsulfonyl)-1,3-butadiene (1) with Diazopropane. To suspension

of 200 mg (0.6 mmol) of 2,3-*bis*(phenylsulfonyl)-1,3-butadiene (**1**) in 10 ml of ether at -78°C under N_2 was added 3.0 ml (1.5 mmol) of freshly prepared diazopropane.[39] The mixture was stirred for 3 h at -78°C and then allowed to warm to room temperature. The mixture was quenched with a 10% HCl solution and the aqueous layer was extracted with CH_2Cl_2. The combined organic layer was washed with water and brine and dried over Na_2SO_4. The solvent was removed under reduced pressure and the residue was subjected to silica gel column chromatography (9:1 ethyl acetate-hexane) to give 130 mg (55%) of 3,3'-*bis*(phenylsulfonyl)-5,5,5',5'-tetramethyl-4,5,4',5'-tetrahydro-3*H*,3*H*'-[3,3']bipyrazolyl (**16**); mp 113-114°C; ir (KBr) 1730, 1581, 1446, 1332, 1140, 1076, and 684 cm^{-1}; ^{1}H-nmr ($CDCl_3$, 300 MHz) δ 1.13 (s, 6H), 1.20 (s, 6H), 1.86 (d, 2H, J=15 Hz), 2.12 (d, 2H, J=15 Hz), 7.55 (m, 4H), 7.70 (m, 2H), and 8.08 (d, 4H, J=7.8 Hz); ^{13}C-nmr ($CDCl_3$, 75 MHz) δ 25.4, 25.6, 33.2, 96.8, 116.8, 128.9, 131.6, 135.0, and 136.2; Anal. Calcd for $C_{22}H_{26}N_4O_4S_2$: C, 55.68; H, 5.53; N, 11.81. Found: C, 55.54; H, 5.38; N, 11.73.

It was also possible to isolate a sample of 3-(1-phenylsulfonylvinyl)-3-(phenylsulfonyl)-5,5-dimethyl-4,5-dihydro-3*H*-pyrazole (**15**) which readily loses nitrogen; ^{1}H-nmr ($CDCl_3$, 300 MHz) δ 1.21 (s, 3H), 1.48 (s, 3H), 2.11 (d, 1H, J=14.7 Hz), 2.51 (d, 1H, J=14.7 Hz), 6.66 (s, 1H), 6.82 (s, 1H), and 7.34-7.65 (m, 10H); ^{13}C-nmr ($CDCl_3$, 75 MHz) δ 25.8, 26.4, 38.2, 94.1, 115.0, 128.3, 128.7, 129.8, 130.2, 131.0, 131.1, 133.5, 133.8, 134.7, and 156.6. Thus, after standing for several hours, 3*H*-pyrazole **15** decomposed giving 2,3-*bis*(phenylsulfonyl)-5-methyl-1,3-hexadiene (**19**); mp 117-118°C; ir (KBr) 1583, 1442, 1302, 1140, 970, and 682 cm^{-1}; ^{1}H-nmr ($CDCl_3$, 300 MHz) δ 0.95 (s, 3H), 0.97 (s, 3H), 2.55 (m, 1H), 5.49 (s, 1H), 6.43 (s, 1H), 7.03 (d, 1H, J=11.1 Hz), and 7.40-7.71 (m, 10H); ^{13}C-nmr ($CDCl_3$, 75 MHz) δ 21.3, 30.3, 128.6, 129.0, 132.5, 133.0, 133.5, 133.8, 138.39, 138.43, 143.6, and 156.5; HRms Calcd for $C_{19}H_{20}S_2O_4$: $[M+H]^+$ 376.0803. Found: 377.0790.

Reaction of 2-Phenylsulfinyl-3-phenylsulfonyl-1,3-butadiene (22) with Diazomethane. To solution of 159 mg (0.5 mmol) of 2-phenylsulfinyl-3-phenylsulfonyl-1,3-butadiene (**22**)[20] in 10 ml of dry CH_2Cl_2 at 0°C under N_2 was added dropwise 3.5 ml (0.5 mmol) of freshly prepared diazomethane in ether. The mixture was stirred for 30 min at 0°C and then the solution was allowed to warm to room temperature. The solvent was removed under reduced pressure and the residue was subjected to silica gel column chromatography (9:1 ethyl acetate-hexane) to give 150 mg (84%) of 3-(1-phenylsulfinylvinyl)-3-phenylsulfonyl-4,5-dihydro-3*H*-pyrazole (**23**) as an oil; ir (neat) 1439, 1304, 1140, 1047, 905, and 727 cm^{-1}; ^{1}H-nmr ($CDCl_3$, 300 MHz) δ 1.06-1.17 (m, 1H), 2.37 (quin, 1H, J=6.6 Hz), 4.56 (q, 2H, J=6.6 Hz), 6.15 (s, 1H), 6.46 (s, 1H), 7.34-7.49 (m, 5H), 7.59-7.65(m, 3H), and 7.81 (d, 2H, J=7.8 Hz); ^{13}C-nmr ($CDCl_3$, 75 MHz) δ 24.3, 79.8, 111.6, 122.9, 126.6, 128.9, 129.4, 130.6, 132.1, 133.9, 134.8, 142.6, and 148.8; HRms Calcd for $C_{17}H_{16}N_2O_3S_2$: 360.0602. Found: 360.0602.

To an ice cold solution of 261 mg (0.72 mmol) of **23** in 20 ml of CH_2Cl_2 was added 250 mg (0.72 mmol) of 50% *m*-chloroperbenzoic acid. The solution was stirred for 36 h at 0°C and the reaction mixture was diluted with CH_2Cl_2 and extracted with $NaHCO_3$. The organic layer was washed with water and dried over Na_2SO_4. The solvent was removed under reduced pressure at 15°C to give 230 mg (84%) of 3-(1-phenylsulfonylvinyl)-3-phenylsulfonyl-4,5-dihydro-3*H*-pyrazole (**13**) which was identical in all respects with a sample prepared from the reaction of diene **1** with diazomethane.

A sample of 47 mg (0.13 mmol) of **23** in 6 ml of toluene was heated at reflux for 1 h under N_2. The solvent was removed under reduced pressure and the residue was subjected to flash silica gel chromatography (9:1 ethyl acetate-hexane) to give 25 mg (60%) of 2-phenylsulfinyl-3-phenylsulfonyl-1,3-pentadiene (**24**), ir (neat) 1723, 1439, 1303, 1076, 1047, 748, and 684 cm^{-1}; ^{1}H-nmr ($CDCl_3$, 300 MHz) δ 0.97 (d, 3H, J=7.2 Hz), 5.22 (s, 1H), 6.32 (s, 1H), 7.04 (q, 1H, J=7.2 Hz), 7.40-7.53 (m, 5H), 7.59 (m, 3H), and 7.82 (d, 2H, J=7.8 Hz); ^{13}C-nmr ($CDCl_3$, 75 MHz) δ 13.8, 123.2, 125.3, 128.7, 129.0, 129.1, 131.4, 133.7, 137.9, 138.0, 141.2, 143.3, and 146.7; HRms Calcd for $C_{17}H_{16}O_3S_2$: 332.0541. Found: 332.0540.

To an ice cold solution of 40 mg (0.12 mmol) of **24** in 15 ml of CH_2Cl_2 was added 59 mg (0.12 mmol) of 35% *m*-chloroperbenzoic acid. The solution was stirred for 24 h at 0°C and the reaction mixture was diluted with CH_2Cl_2 and extracted with Na_2CO_3. The organic layer was washed with water and dried over Na_2SO_4. The solvent was removed under reduced pressure to leave behind 39 mg (93%) of 2,3-(phenylsulfonyl)-1,3-pentadiene (**18**) which was identical in all respects with a sample prepared from the thermolysis of 3*H*-pyrazole **13**.

In addition to the above compound, 14 mg (33%) of 1-(1-phenylsulfinylvinyl)-1-phenylsulfonylcyclopropane (**25**) was isolated, ir (neat) 1723, 1439, 1304, 1140, 941, 827, and 756 cm^{-1}; ^{1}H-nmr ($CDCl_3$, 300 MHz) δ -0.05 (m, 2H), 0.96-1.05 (m, 2H), 5.52 (s, 1H), 6.36 (s, 1H), 7.40-7.56 (m, 5H), 7.66 (t, 1H, J=7.5 Hz), 7.71 (d, 2H, J=6.6 Hz), and 7.81 (d, 2H, J=7.5 Hz); ^{13}C-nmr ($CDCl_3$, 75 MHz) δ 13.1, 13.2, 44.1, 124.6, 126.3, 129.1, 129.3, 131.4, 132.0, 134.0, 137.2, 143.1, and 150.3; HRms Calcd for $C_{17}H_{16}O_3S_2$: 332.0541. Found: 332.0541.

Preparation of 3-Phenylsulfonyl-4,5-dihydro-3*H*,1'*H*-[3,3']bipyrazolyl (27). To solution of 318 mg (1.0 mmol) of 2-phenylsulfinyl-3-phenylsulfonyl-1,3-butadiene (**22**)[20] in 20 ml of dry CH_2Cl_2 at 0°C under N_2 was added 24 ml (4.2 mmol) of freshly prepared diazomethane in ether. The mixture was stirred for 30 min at 0°C and was then allowed to warm to room temperature. The solvent was removed under reduced pressure to give 20 mg (73%) of 3-phenylsulfonyl-4,5-dihydro-3*H*,1'*H*-[3,3']bipyrazole (**27**) as a white solid; mp 140-141°C, ir (KBr) 3161, 1439, 1303, 1140, 720, and 684 cm^{-1}; ^{1}H-nmr ($CDCl_3$, 300 MHz) δ 2.25-2.35 (m, 1H), 2.81-2.90 (m, 1H), 4.74-4.82 (m, 2H), 6.19 (d, 2H, J=1.8 Hz), 7.39 (t, 2H,

J=7.5 Hz), and 7.56-7.64 (m, 4H); ^{13}C-nmr (DMSO-d_6, 75 MHz) δ 23.0, 78.4, 105.0, 111.6, 128.9, 129.6, 130.0, 134.6, 134.9, and 143.1; Anal. Cacld for $C_{12}H_{12}N_4O_2S$: C, 52.17; H, 4.35; N, 20.29. Found: C, 52.28; H, 4.42; N, 20.21.

Reaction of 2-Phenylsulfinyl-3-phenylsulfonyl-1,3-butadiene (22) with Diazopropane. To solution of 159 mg (0.5 mmol) of 2-phenylsulfinyl-3-phenylsulfonyl-1,3-butadiene (**22**)[20] in 5 ml of CH_2Cl_2 at 0°C under N_2 was added dropwise 1.0 ml (0.5 mmol) of freshly prepared diazopropane in ether. The mixture was stirred for 1 h at 0°C and the solution was allowed to warm to room temperature and was quenched with a 10% HCl solution. The layers were separated and the aqueous layer was extracted with CH_2Cl_2. The combined organic layer was washed with water, brine and dried over Na_2SO_4. The solvent was removed under reduced pressure and the crude residue was subjected to silica gel column chromatography (9:1 ethyl acetate-hexane) to give 120 mg (62%) of 3-(1-phenylsulfinylvinyl)-3-phenylsulfonyl-5,5-dimethyl-4,5-dihydro-3*H*-pyrazole (**28**); mp 115-116°C, ir (KBr) 1441, 1309, 1148, 1045, 752, and 671 cm^{-1}; ^{1}H-nmr ($CDCl_3$, 300 MHz) δ 0.49 (s, 3H), 1.42 (s, 3H), 1.53 (d, 1H, J=14.4 Hz), 2.52 (d, 1H, J=14.4 Hz), 6.29 (d, 1H, J=0.9 Hz), 6.66 (d, 1H, J=0.9 Hz), 7.26-7.33 (m, 3H), 7.41 (m, 2H), 7.66 (t, 2H, J=7.8 Hz), 7.76-7.81 (m, 1H), and 7.93 (d, 2H, J=7.8 Hz); ^{13}C-nmr ($CDCl_3$, 75 MHz) δ 25.4, 25.8, 38.9, 92.8, 115.0, 121.2, 126.9, 128.9, 129.3, 131.4, 131.8, 135.1, 143.2, 148.5, and 152.2; Anal. Calcd for $C_{19}H_{20}N_2O_3S_2$: C, 58.75; H, 5.19; N, 7.22. Found: C, 58.62; H, 5.08; N, 7.06. Oxidation of **28** with MCPBA in CH_2Cl_2 afforded 3*H*-pyrazole (**15**) in 92% yield thereby providing good support for the structure assignment of **28**.

A 40 mg (0.1 mmol) sample of **28** in 3 ml of toluene was heated at reflux for 1 h under N_2. The solvent was removed under reduced pressure and the residue was subjected to flash silica gel chromatography (9:1 ethyl acetate-hexane) to give 31 mg (85%) of 2-phenylsulfinyl-3-phenylsulfonyl-5-methyl-1,3-hexadiene (**29**); mp 135-136°C, ir (KBr) 1441, 1302, 1140, 1045, 752, 686, and 612 cm^{-1}; ^{1}H-nmr ($CDCl_3$, 300 MHz) δ 0.21 (d, 3H, J=6.6 Hz), 0.82 (d, 3H, J=6.9 Hz), 1.74 (m, 1H), 5.24 (s, 1H), 6.29 (s, 1H), 6.74 (d, 1H, J=10.8 Hz), 7.44 (m, 3H), 7.51 (t, 2H, J=7.2 Hz), 7.58-7.66 (m, 3H), and 7.81 (d, 2H, J=7.5 Hz); ^{13}C-nmr ($CDCl_3$, 75 MHz) δ 20.6, 22.6, 28.8, 123.4, 125.6, 128.6, 129.10, 129.15, 131.6, 133.7, 138.1, 138.2, 141.5, 145.0, and 153.1; Anal. Calcd for $C_{19}H_{20}S_2O_3$: C, 63.32; H, 5.60. Found: C, 63.19; H, 5.48.

To a solution of 51 mg (0.14 mmol) of **29** in 5 ml of water and 10 ml of methanol was added 158 mg (0.26 mmol) of Oxone®. The mixture was stirred at room temperature for 36 h and the methanol was removed under reduced pressure. The aqueous layer was extracted with CH_2Cl_2 and the organic layer was washed with water, brine and dried over Na_2SO_4. Purification by silica gel chromatography (9:1 ethyl acetate-hexane) gave 45 mg (85%) of 2,3-*bis*-(phenylsulfonyl)-5-methyl-1,3-hexadiene (**19**).

ACKNOWLEDGEMENT

We gratefully acknowledge the U.S. Army CRDEC (no. DAAA15-90-C-1076) and the National Institutes of Health (CA-26750) for support of this work. M. M. thanks the Deutschen Akademischen Austauschdienst for a scholarship.

REFERENCES AND NOTES

1. J. E. Bäckvall and S. K. Juntunen, *J. Am. Chem. Soc.*, **1987**, *109*, 6396. J. E. Bäckvall and S. K. Juntunen, *J. Org. Chem.*, **1988**, *53*, 2398. J. E. Bäckvall and F. Rise, *Tetrahedron Lett.*, **1989**, *30*, 5347. J. E. Bäckvall and N. A. Plobeck, *J. Org. Chem.*, **1990**, *55*, 4528. N. A. Plobeck and J. E. Bäckvall, *J. Org. Chem.*, **1991**, *56*, 4508.
2. Y. Masuyama, H. Yamazaki, Y. Toyoda, and Y. Kurusu, *Synthesis*, **1985**, 964. L. E. Overman, C. B. Petty, T. Ban, and G. T. Huang, *J. Am. Chem. Soc.*, **1983**, *105*, 6335. J. J. Eisch, J. E. Galle, and L. E. Hallenbeck, *J. Org. Chem.*, **1982**, *47*, 1608.
3. S. J. Lee, J. C. Lee, M. L. Peng, T-S. Chou, S. C. Hung, and H. H. Tso, *J. Org. Chem.*, **1987**, *52*, 3394. T. Chou and S. C. Hung, *J. Org. Chem.*, **1988**, *53*, 3020. T-S. Chou, *J. Chem. Soc., Chem. Commun.*, **1989**, 1020.
4. S. A. Hardinger and P. L. Fuchs, *J. Org. Chem.*, **1987**, *52*, 2739.
5 A. Padwa, B. Harrison, and B. H. Norman, *Tetrahedron Lett.*, **1989**, *30*, 3259. A. Padwa, Y. Gareau, and B. H. Harrison, *J. Org. Chem.*, **1991**, *56*, 2713.
6 A. Padwa and B. H. Norman, *Tetrahedron Lett.*, **1988**, *29*, 3041. A. Padwa and B. H. Norman, *J. Org. Chem.*, **1990**, *55*, 4801.
7. *Organic Chemistry of Sulfur*, S. Oae, Ed., Plenum, New York, 1977. F. Bernardi and E. Mangini, *Organic Sulfur Chemistry: Theoretical and Experimental Advances*, Elsevier, Amsterdam, 1985.
8. A. Padwa and S. S. Murphree, *Org. Prep. and Proced. Int.*, **1991**, *23*, 545.
9. B. M. Trost, *Bull. Chem. Soc. Jpn.*, **1988**, *61*, 107.
10. P. D. Magnus, *Tetrahedron*, **1977**, *33*, 2019.
11. K. Schank, *Methoden der Organischen Chemie*, (Houben-Weyl) 4th ed., Thieme, Stuttgart, 1985, Vol. E11, p. 1129.
12. T. Durst, *Comprehensive Organic Chemistry*, D. H. R. Barton and W. D.Ollis, Eds., Pergamon Press, Oxford, 1979; Vol. 3, p. 171, 197.
13. *The Chemistry of Sulfones and Sulfoxides*, S. Patai, Z. Rappaport, C. J. M. Stirling, Eds., Wiley: Chichester, 1988, pp. 1-1210.
14. P. L. Fuchs and T. F. Braish, *Chem. Rev.*, **1986**, *86*, 903.
15. M. Julia and J. M. Paris, *Tetrahedron Lett.*, **1973**, 4833. N. W. Hird, T. V. Lee, A. J. Leigh, J. R. Maxwell, and T. M. Peakman, *Tetrahedron Lett.*, **1989**, *30*, 4867.
16. B. Lythgoe and I. Waterhouse, *J. Chem. Soc., Perkin Trans. I*, **1979**, 2429.
17. R. D. Little and S. O. Myong, *Tetrahedron Lett.*, **1980**, *21*, 3339. J. R. Hwu, *J. Org. Chem.*, **1983**,

48, 4432. K. Tanaka , S. Matsui, and A. Kaji, *Bull. Chem. Soc. Jpn.,* **1980**, *53,* 3619.

18. B. M. Trost, *Angew. Chem., Int. Ed. Engl.,* **1989**, *28,* 1173. J. F. Biellmann and J. B. Ducep, *Org. React.,* **1982**, *27,* 1.
19. C. Najera, B. Mancheno, and M. Yus, *Tetrahedron Lett.,* **1989**, *30,* 6085.
20. W. H. Okamura and S. Jeganathan, *Tetrahedron Lett.,* **1982**, *23,* 4763.
21. A. Padwa and B. H. Norman, *Tetrahedron Lett.,* **1988**, *29,* 2417. B. H. Norman, Y. Gareau, and A. Padwa, *J. Org. Chem.,* **1991**, *56,* 2154.
22. A. Padwa, Y. Gareau, B. Harrison, and A. Rodriguez, *J. Org. Chem.,* **1992**, *57,* 3540.
23. M. S. R. Naidu and R. M. Rani, *Phosphorous and Sulfur,* **1984**, *19,* 259. D. B. Reddy, B. Sankaraiah, and T. Balaji, *Ind. J. Chem.,* **1980**, *19B,* 563.
24. E. J. Corey and M. Chaykovsky, *J. Am. Chem. Soc.,* **1965**, *87,* 1353.
25. J. E. Bäckvall, C. Löfström, S. K. Juntunen, and M. Mattson, *Tetrahedron Lett.,* **1993**, *34,* 2007.
26. K. N. Houk and K. Yamaguchi, *Theory of 1,3-Dipolar Cycloadditions in 1,3-Dipolar Cycloaddition Chemistry,* Vol. 2, A. Padwa, Ed.; Wiley-Interscience, 1984, p. 407. J. Geittner, R. Huisgen, and R. Sustman, *Tetrahedron Lett.,* **1977**, 881.
27. A. Padwa, M. A. Filipkowski, M. Meske, S. S. Murphree, S. H. Watterson, and Z. Ni, *J. Org. Chem.,* **1994**, *59,* 588.
28. M. Regitz and H. Heydt, in *"1,3-Dipolar Cycloaddition Chemistry"* , A. Padwa, Ed.; Wiley-Interscience, New York, Vol. 1, 1984.
29. K. N. Houk, J. Sims, C. R. Watts, and L. J. Luskus, *J. Am. Chem. Soc.,* **1973**, *95,* 7301.
30. D. S. Wulfman, G. Linstrumelle, and C. F. Cooper, "Synthetic Applications of Diazoalkanes" *Chemistry of Diazonium and Diazo Groups*, Part 2, S. Patai, Ed., Wiley, New York, 1978, p. 821.
31. P. S. Engel, *Chem. Rev.,* **1980**, *80,* 99.
32. D. E. McGreer and W. S. Wu, *Can. J. Chem.,* **1967**, *45,* 461. D. E. McGreer and J. W. McKinly, *Can. J. Chem.,* **1971**, *49,* 105. D. E. McGreer, I. M. Masters, and M. T. Liu, *J. Chem. Soc., Perkin Trans. 2,* **1975**, 1791.
33. M. Hamaguchi and T. Nagai, *J. Chem. Soc., Chem. Commun.,* **1987**, 1299. M. T. Begley, F. M. Dean, L. E. Houghton and B. K. Park, *J. Chem. Soc., Chem. Commun.,* **1978**, 461.
34. R. J. Crawford and A. Mishra, *J. Am. Chem. Soc.,* **1966**, *88,* 3963.
35. E. L. Allred and R. L. Smith, *J. Am. Chem. Soc.,* **1967**, *89,* 7133. *ibid.,* **1969**, *91,* 6766.
36. W. R. Roth and M. Martin, *Liebigs Ann. Chem.,* **1967**, *702,* 1. W. R. Roth and M. Martin, *Tetrahedron Lett.,* **1967**, 4695.
37. P. B. Condit and R. G. Bergman, *J. Chem. Soc., Chem. Commun.,* **1971**, 4. D. H. White, P. B. Condit, and R. G. Bergman, *J. Am. Chem. Soc.,* **1972**, *94,* 1348. D. H. White, P. B. Condit, and R. G. Bergman, *ibid.,* **1972**, *94,* 7931.
38. T. C. Clarke, L. A. Wendling, and R. G. Bergman, *J. Am. Chem. Soc.,* **1977**, *99,* 2740.
39. S. D. Andrews, A. C. Day, P. Raymond, and M. C. Whiting, *Org. Synth.,* **1970**, *50* , 27.

Received, 10th March, 1994