205.0559, found 205.0562, error = 1.4 ppm; IR ($CDCl_3$, cm^{-1}) 3400 (NH), 1700 (C=O); 200-MHz NMR ($CDCl_3$, ppm) 7.95-7.10 (2 H, m), 6.72 (1 H, dd, J = 7.3, 1.0 Hz), 6.57 (1 H, dd, J = 8.2, 1.1 Hz), 5.19-5.11 (1 H, m), 4.66 (1 H, br s), 4.54 (1 H, dd, J = 6.9, 3.5 Hz), 3.00-2.86 (4 H, m).

Enaminal 29. Bicyclic ketone **27** (12.4 mg, 0.06 mmol) was dissolved in acetone (0.1 mL), Raney nickel (30 mg in ethanol) was added, and the suspension was refluxed overnight. After filtration through Celite with ethanol, the solvent was removed under reduced pressure, and the residue was purified by PTLC to give **29**, 5.2 mg (50%): oil; silica gel F254, 50% ethyl acetate/hexane, R_f 0.50; m/e, base = 172 amu, exact mass calcd for $C_{11}H_{11}ON$ 173.0838, found 173.0842, error = 2.3 ppm; IR ($CDCl_3$, cm^{-1}) 1570 (NH-=CHO); 200-MHz NMR ($CDCl_3$, ppm) 11.3 (1 H, br s), 9.12 (1 H, dd, J = 2.4, 0.3 Hz), 7.24-6.82 (4 H, m), 5.12 (1 H, d, J = 2.4 Hz), 2.85-2.56 (4 H, m).

***N*-Acetyl Bicyclic Ketone 30.** A solution of **27** (16.3 mg, 0.08 mmol) in methylene chloride (0.3 mL) and pyridine (0.4 mL) was treated with acetyl chloride (distilled; 0.1 mL) for 1 h. The solvent was removed under reduced pressure (15-0.01 Torr), and the residue was purified by PTLC to give **30**, 14.1 mg (71%): oil; silica gel 60, 50% ethyl acetate/hexane, R_f 0.26; m/e, exact mass calcd for $C_{13}H_{13}O_2NS$ 247.0664, found 247.0659, error = 1.9 ppm; IR ($CDCl_3$, cm^{-1}) 1715 (C=O), 1670 (NC=O); 200-MHz NMR ($CDCl_3$, ppm) 7.26-7.10 (4 H, m), 6.60 (1 H, ddd, J = 7.1, 2.2, 2.2 Hz), 4.45-4.42 (1 H, m), 3.13-2.76 (4 H, m), 2.24 (3 H, s).

Ra-Ni Desulfurization of 30 to 31. W-2 Raney nickel was deactivated by refluxing in acetone for 3 h. Amide **30** (10.7 mg, 0.043 mmol) was added and the solution refluxed for an additional 3 h. After cooling to room temperature, the suspension was filtered through Celite and the Celite washed with ethanol. The solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel (300 mg, ethyl acetate) to give **31**, 4.0 mg (43%): oil; silica gel 60, ethyl acetate, R_f 0.29; m/e, base = 132 amu, exact mass calcd for $C_{13}H_{15}O_2N$ 217.1099, found 217.1105, error = 2.7 ppm; IR ($CDCl_3$, cm^{-1}) 1652 (NC=O), 1703 (C=O); 270-MHz NMR ($CDCl_3$, ppm) 7.40-7.20 (4 H, m), 4.95-4.86 (1 H, m), 3.33-3.09 (2 H, m), 2.93-2.80 (3 H, m), 2.67-2.51 (1 H, m), 2.35-2.28 (1 H, m), 1.81 (1.5 H, s), 1.61 (1.5 H, s).

Acknowledgment. This work was supported by the National Institutes of Health (CA17918).

Site Selectivity in the Reactions of Various 1,3-Dipoles with (Phenylsulfonyl)-1,2-propadiene

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The cycloaddition reactions of (phenylsulfonyl)-1,2-propadiene (1) with various 1,3-dipoles have been investigated. MNDO calculations suggest that the reaction of the activated allene will proceed in a highly regioselective fashion and undergo cycloaddition across the more activated π-bond. This proved to be the case in the reactions of diazomethane and diazopropane with 1. The formation of 4-[(phenylsulfonyl)methyl]pyrazole (8) was rationalized in terms of a 1,3-allylic sulfonyl shift from the expected 1,3-dipolar cycloadduct. Related allylic sulfonyl shifts were also proposed to occur in the cycloaddition of 1 with benzonitrile oxide and the silyl nitronate of *aci*-nitrophenylmethane. The isolation of 1,3-diphenyl-5-[(phenylsulfonyl)methyl]pyrazole (16) as the major product from the reaction of 1 with 1-(α-chlorobenzylidene)-2-phenylhydrazine is suggested to proceed via a stepwise Michael addition of the initially formed aza anion onto the central allene carbon. The strongly activated allene promotes conjugate addition as a consequence of its markedly lowered LUMO level.

Allenes are an interesting group of substrates since they contain two positions for attack.[1] (Phenylsulfonyl)-1,2-propadiene (1) represents one of the more reactive allenes known. This material has been shown to undergo the Diels-Alder reaction exclusively across the activated C_1-C_2 double bond.[2] Recently, we reported that (phenylsulfonyl)-1,2-propadiene (1) is also a useful dipolarophile in nitrone cycloaddition chemistry due to its enhanced reactivity.[3] As part of our ongoing interest in the synthetic applications of 1,3-dipolar cycloaddition chemistry,[4] we have further investigated the reactivity of (phenylsulfonyl)allene with other 1,3-dipoles.[5] The phenylsulfonyl group can be readily removed by various methods[6] after the cycloaddition, and thus the dipolar cycloadducts formed should be of some use in organic synthesis.

MNDO calculations of (methylsulfonyl)-1,2-propadiene indicate that the introduction of a sulfonyl group causes a significant lowering of the LUMO energy level compared with allene (ΔE = 1.3 eV) and the largest LUMO coefficient resides on the central carbon and the next on the position bearing the sulfonyl group. This suggests that the reaction of 1 with various type I dipoles[7] will proceed in a highly regioselective fashion and undergo cycloaddition across the activated C_1-C_2 π-bond.

Results and Discussion

The cycloadditions of simple diazoalkanes are generally HO(1,3-dipole)-LU(dipolarophile) controlled.[7,8] This proved to be the case in the reaction of diazopropane (or diazomethane) with (phenylsulfonyl)-1,2-propadiene (1). Stirring a solution of diazopropane and 1 in ether at 25

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(5) For some related examples, see: Bruche, L.; Zecchi, G. *J. Heterocycl. Chem.* **1983**, *20*, 1705. Bruche, L.; Gelmi, M. L.; Zecchi, G. *J. Org. Chem.* **1985**, *50*, 3206.
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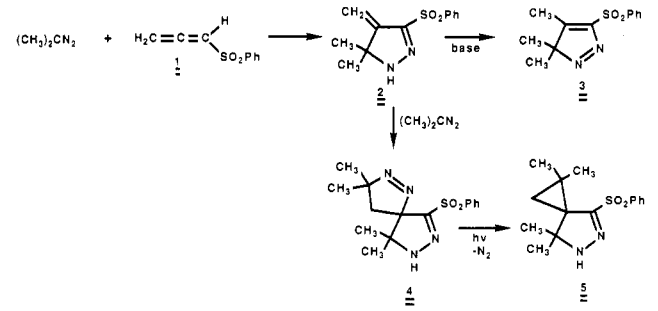
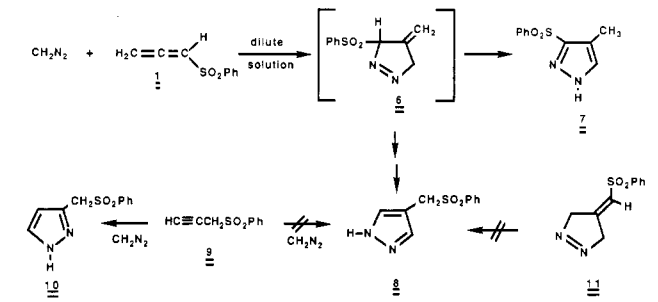


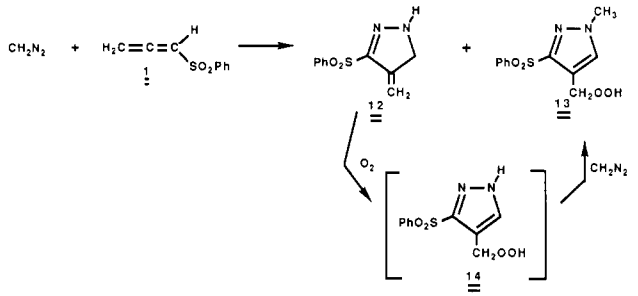
°C produced a mixture of three compounds. The minor product was identified as 5,5-dimethyl-4-methylene-3-(phenylsulfonyl)-2-pyrazoline (**2**) on the basis of a set of methylene protons in the NMR spectrum as well as by its base-catalyzed isomerization to the major cycloadduct **3**. The third component isolated from the cycloaddition was assigned as the diadduct **4** derived from the reaction of **2** with excess diazopropane. The structure of this material was further supported by the photoextrusion of nitrogen to give spiro pyrazoline **5**. The observed regiochemistry of the cycloaddition is perfectly compatible with FMO theory.

Similar regioselectivity was exhibited in the reaction of **1** with diazomethane. When a dilute ether solution of **1** and diazomethane was used, a mixture of two products was formed and identified as pyrazoles **7** (49%) and **8** (16%).



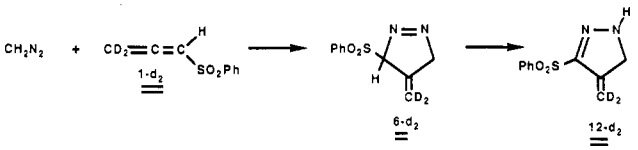
The major cycloadduct **7** can easily be explained in terms of a series of 1,3-hydrogen shifts from the expected cycloadduct **6**. The formation of **8** is not so easy to rationalize. One possibility is that **8** is derived by a partial isomerization of **1** to 3-(phenylsulfonyl)-1-propyne (**9**) followed by a subsequent 1,3-dipolar cycloaddition across the triple bond. We reject this path since (a) the reaction of diazomethane with **1** proceeds much more rapidly than with **9** (i.e., control experiments) and (b) the cycloaddition of **9** with diazomethane actually produces the isomeric pyrazole **10**.[9] An alternate rationale to account for the formation of **8** is that the dipolar cycloaddition of **1** with diazomethane produces a small amount of the isomeric cycloadduct **11**, which is subsequently converted to **8** by a series of proton shifts. Although we cannot eliminate this possibility, we doubt whether **8** is formed via this pathway since the cycloaddition of **1** with other HOMO-controlled dipoles occurs exclusively across the more activated π-bond.

In an attempt to obtain additional information regarding the mechanism for the formation of pyrazole **8**, we studied the cycloaddition reaction under slightly different experimental conditions. When the reaction of diazomethane and **1** was carried out by using a concentrated ether solution, a crystalline compound (mp 161–162 °C) precipitated from the reaction mixture in 52% yield. This material was assigned as 3-(phenylsulfonyl)-4-methylene-2-pyrazoline (**12**) on the basis of its spectral properties [NMR ($CDCl_3$, 300 MHz) δ 4.50 (t, 2 H, J = 4.0 Hz), 5.20 (t, 1 H, J = 4.0 Hz), 5.71 (t, 1 H, J = 4.0 Hz), 6.56 (s, 1 H, exchanged with D_2O), and 7.5–8.0 (m, 5 H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 56.08 and 106.35]. Chromatography of the crude reaction mixture afforded a second crystalline solid (mp 79–80 °C) whose molecular formula ($C_{11}H_{12}N_2SO_4$) and NMR spectrum [($CDCl_3$, 300 MHz) δ 4.05 (s, 3 H), 5.24 (s, 2 H), 7.5–8.1 (m, 6 H), and 8.6 (s, 1 H)] were consistent with the hydroperoxy *N*-methylpyrazole **13**.



The formation of **13** can be rationalized in terms of an "ene" type reaction of **12** with oxygen to give **14** followed by methylation with diazomethane. In fact, treating a sample of **12** with diazomethane in the presence of oxygen produced **13** in good yield.

In order to provide additional support for structure **12**, we carried out the reaction of diazomethane with (phenylsulfonyl)-1,2-propadiene-3-d_2. Earlier work by Stirling[10] has shown that, among the three possible acetylenic and allenic tautomers of **1**, the allene is the thermodynamically most stable species. Treatment of any tautomer with a basic reagent rapidly leads to isomerization to the allene. We prepared the 3,3-dideuteriated allene (**1**-d_2) by treating alkyne **9** with triethylamine in the presence of ethanol-d_1. The fully deuteriated species was chromatographed on a silica gel column, which resulted in the rapid exchange of the deuterium atom adjacent to the sulfonyl group. Cycloaddition of **1**-d_2 with diazomethane afforded **12**-d_2 in 50% isolated yield. The NMR spectrum of **12**-d_2 showed



a two-proton singlet at δ 4.50 as well as an exchangeable singlet for the NH proton at 6.56 ppm. The formation of **12**-d_2 can be easily rationalized in terms of a facile 1,3-hydrogen shift of the expected cycloadduct **6**-d_2. Treatment of **12** with a trace of acid or base afforded pyrazole **7** in quantitative yield. Most interestingly, when a chloroform solution of **12** was allowed to stand at room temperature, it slowly isomerized to pyrazole **8** in 98% yield. At first we thought that this was a thermal reaction, but we found that it did not occur in solution in the dark. The 1,3-shift does occur in solution on exposure to light, even daylight diffused through the window and a Pyrex flask. It can be prevented simply by wrapping the flask in aluminum foil. The formation of pyrazole **8** from **12** can be viewed in terms of a process involving an initial 1,3-hydrogen shift so as to regenerate cycloadduct **6** followed by a subsequent 1,3-sulfonyl shift. Lately, there have been several reports in the literature that indicate that substituted allylic sulfones can undergo 1,3-rearrangement, thereby providing good support for the above sugges-

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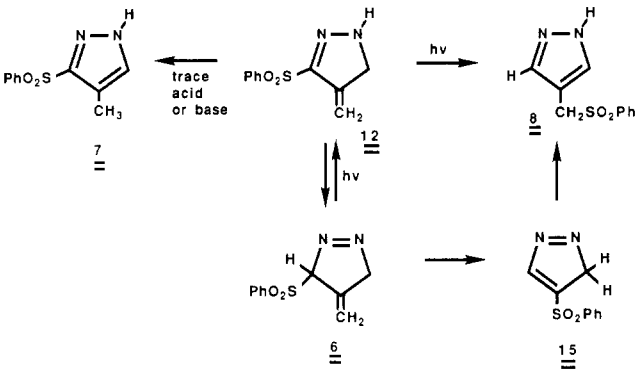
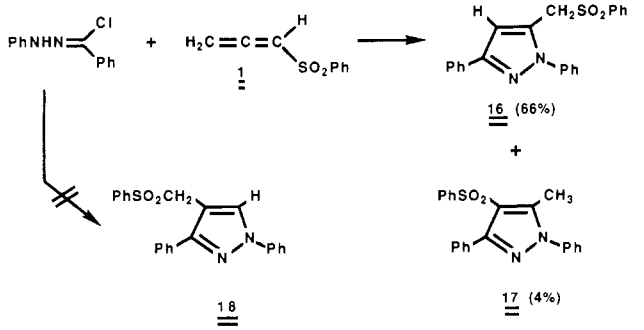
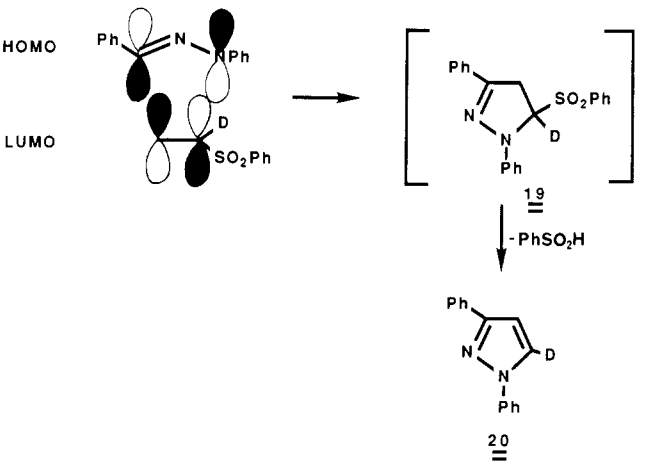


tion.[11-21] The fact that 2-pyrazoline **12** gives both pyrazoles **7** and **8** (depending on the experimental conditions) accounts for their formation when a dilute ether solution was used. Presumably a small amount of base was present in solution and isomerization to **7** occurred prior to precipitation of the pyrazoline.

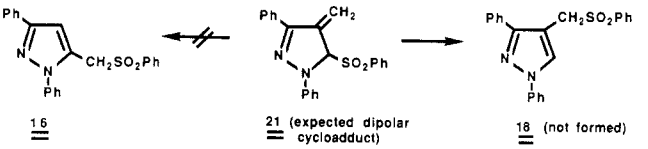
The above results prompted us to examine the cycloaddition between 1,3-diphenylnitrilimine and (phenylsulfonyl)allene. We found that the reaction proceeded in a related fashion to that encountered with diazomethane and gave a mixture of pyrazoles **16** (66%) and **17** (4%). The identity of **16** was determined by its straightforward spectral properties [NMR ($CDCl_3$, 300 MHz) δ 4.45 (s, 2 H), 6.72 (s, 1 H), and 7.06–7.88 (15 H)]. The isomeric 4-[(phenylsulfonyl)methyl]-substituted pyrazole **18** would have shown a NMR signal for the vinyl proton at ca. 7.9–8.7 ppm.[22]



Nitrilimines have been long known to react with various types of monosubstituted olefins to give predominantly 5-substituted 2-pyrazolines.[23,24] The cycloadditions of simple nitrilimines with electron-rich dipolarophiles are LU(1,3-dipole)–HO(dipolarophile) controlled.[25,26] For conjugated dipolarophiles, both HO and LU interactions are important, but the greater difference in LU coefficients leads to a preference for the 5-substituted pyrazolines.[8] With electron-deficient dipolarophiles the regioselectivity becomes controlled by the HO(1,3-dipole)–LU(dipolarophile) interaction. The regioselectivity has been rationalized by taking into account the HOMO of the dipole where the coefficient on the carbon atom is slightly larger than that on the nitrogen atom.[24,27] Recently, the details of the reaction of diphenylnitrilimine with vinyl phenyl sulfone were reported[22,28] and the formation of the 4,5-unsubstituted pyrazole via elimination of benzene sulfinic acid from the initial cycloadduct was described. The results with 1-deuteriovinyl phenyl sulfone clearly established the intermediacy of the 5-(phenylsulfonyl)-2-pyrazoline regioisomer **19** prior to the elimination step.[22]



The formation of **16** cannot be easily accounted for in terms of the 1,3-dipolar cycloaddition path. Dipolar cycloaddition of the nitrilimine dipole with (phenylsulfonyl)propadiene should have proceeded analogously to the above vinyl sulfone system and given the related 5-sulfonyl-substituted pyrazoline **21**. There seems to be no sensible route by which **21** can produce pyrazole **16**. A



1,3-allylic sulfonyl shift would have produced **18**. Thus, if 1,3-dipolar cycloaddition had occurred in the normal fashion, then one should have isolated the 4-[(phenylsulfonyl)methyl]-substituted isomer **18**. This was not the case. Structure **16** could in principle be derived by a prior isomerization of allene **1** to propyne **9** followed by dipolar cycloaddition across the triple bond. Although the isomerization does take place when triethylamine is used (ratio 1:9 = 4:1), allene **1** is still the predominant isomer present in solution and it also reacts much more readily with the dipole. Thus, this alternate route cannot account for the formation of cycloadduct **16**.

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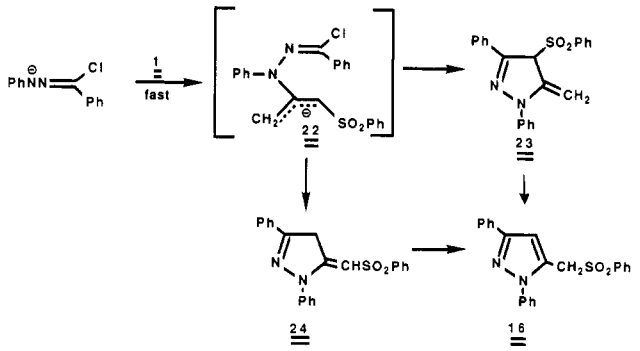
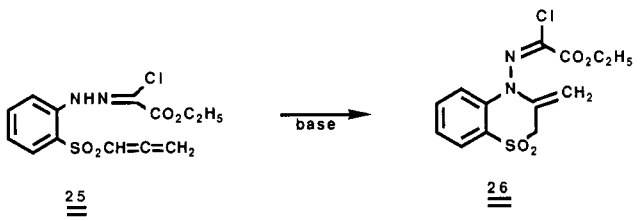
Scheme I

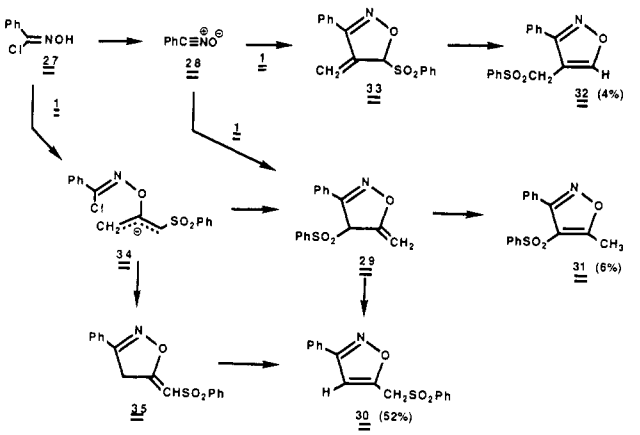


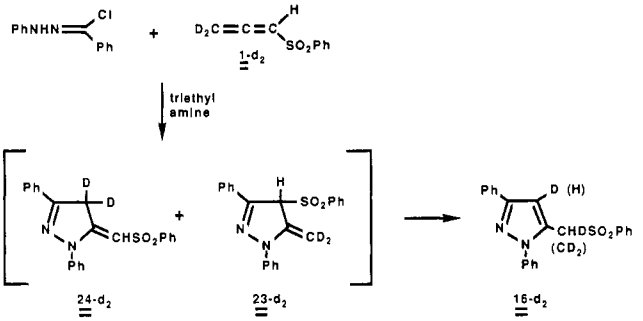
We propose that the formation of pyrazole **16** results from the operation of an alternate mechanism which does not involve a nitrilimine intermediate (Scheme I). Structure **16** can be thought of as being derived from a deprotonation of the NH bond of the hydrazonyl chloride followed by subsequent attack of the aza anion on the central carbon of the allene prior to chloride ion loss. The resulting carbanion **22** can undergo cyclization in either of two directions to give **23** or **24**. Both of these structures will ultimately be converted to **16** by either a 1,3-hydrogen or 1,3-sulfonyl shift. This stepwise sequence constitutes a different reaction mode from that usually encountered with hydrazonyl chlorides. The base-induced reactions of hydrazonyl chlorides almost always result in cycloaddition products derived from nitrilimine intermediate.[18] Apparently, the strong electron-withdrawing character of the sulfonyl group significantly enhances the electrophilicity of the allene and promotes the stepwise conjugate addition of the aza anion. In fact, (phenylsulfonyl)propadiene is known to be extremely susceptible toward nucleophilic addition as a consequence of its markedly lowered LUMO energy, and its reactions with heteronucleophiles have been well investigated.[29-33] Recent work by Bruche and Zecchi provides good support for the above mechanism.[34] These workers found that only one σ-bond is formed between the central allene carbon and the nitrogen atom of the hydrazone moiety when hydrazonyl chloride **25** was treated with base. The formation of 1,4-benzothiazine *S,S*-dioxide **26** was rationalized in terms of a stepwise Michael-type addition of the aza anion onto the central allene carbon.



Further support for the stepwise mechanism outlined in Scheme I was obtained from the reaction of the 3,3-dideuteriated allene (**1**-d_2) with 1-(α-chlorobenzylidene)-2-phenylhydrazine in the presence of triethylamine. Pyrazole **16** was found to contain 50% of deuterium on the 4-position of the pyrazole ring and 75% deuterium on the methylene carbon atom. This is perfectly consistent with anion **22** undergoing cyclization to give a 1:1 mixture of **23** and **24** which are subsequently converted to pyrazole **16**-d_2.

Scheme II





Similar considerations can also explain the behavior encountered in the reaction of benzonitrile oxide with (phenylsulfonyl)propadiene. Treatment of benzohydroximinoyl chloride (**27**) with triethylamine in the presence of allene **1** gave three compounds, which were identified as isoxazoles **30** (52%), **31** (4%), and **32** (6%) on the basis of their straightforward spectral properties. Control experiments established that (phenylsulfonyl)propadiene (**1**) is at least 10 times more reactive than 3-(phenylsulfonyl)-1-propyne (**9**) toward nitrile oxide **28**, thereby ruling out reaction across the acetylenic π-bond. The dipolar cycloaddition of nitrile oxides to monosubstituted alkenes generally yields 5-substituted isoxazolines.[35] In a few cases, 4-substituted regioisomers have been isolated, especially when strong electron-withdrawing groups are attached to the π-bond. FMO theory predicts that the 4-substituted regioisomer will be formed in larger quantities by increasing the HOMO(dipole)–LUMO(dipolarophile) interaction.[8] Traditional 1,3-dipolar cycloaddition across the more activated π-bond of the allene would give rise to cycloadducts **29** and **33**. This route would require that these substances rearrange to the observed products by 1,3-allylic sulfonyl and hydrogen shifts (see Scheme II). An alternate possibility is that the reaction proceeds in a stepwise manner to give carbanion **34**, which cyclizes to produce cycloadducts **29** and **35**.

It should be pointed out that Zecchi and co-workers[5] have studied the related 1,3-dipolar cycloaddition reaction of 3,5-dichloro-2,4-6-trimethylbenzonitrile oxide to (phenylsulfonyl)propadiene and found that isoxazoles similar to **30** and **32** were the major products formed. These

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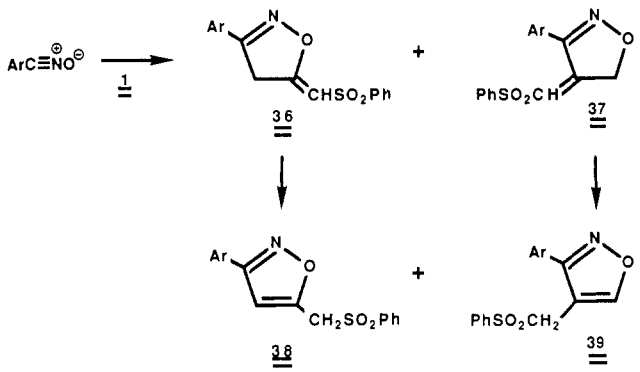
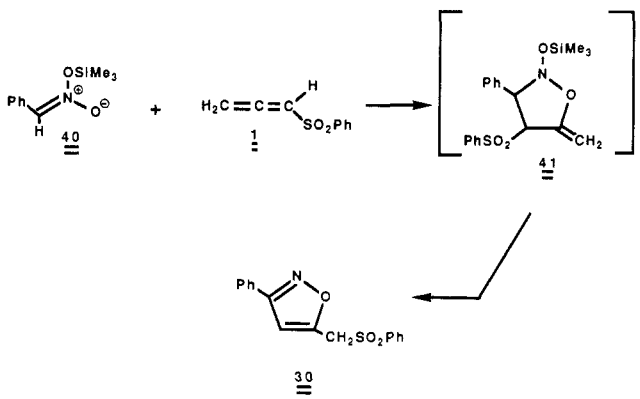
workers suggested that the primary cycloadducts **36** and **37** are the precursors of the final products and are formed



by dipolar cycloaddition across the less activated π-bond. This site selectivity is contrary to our expectation since a HOMO(dipole)–LUMO(dipolarophile) interaction should result in reaction across the α,β-position of the allene. Kanematsu and co-workers had previously established the site selectivity of (phenylsulfonyl)propadiene in related (4 + 2)-cycloadditions.[2] The regioselectivities observed were rationalized by considering the preferential interaction between the LUMO of **1** and the HOMO of the 4-π system. Thus, the formation of **38** and **39** is not easy to explain. More than likely, some combination of dipolar cycloaddition and stepwise conjugate addition is involved in both of these systems.

We have also examined the reaction of (phenylsulfonyl)propadiene with the trimethylsilyl ester of *aci*-nitrophenylmethane (**40**). In this case the only product isolated corresponded to isoxazole **30**. No signs of isoxazoles **31** or **32** were found in the crude reaction mixture. Earlier studies conducted in these laboratories[1] have shown that nitrones undergo dipolar cycloaddition across the activated π-bond of **1** giving rise to 5-*exo*-methylene-substituted isoxazolidines in quantitative yield. The formation of **30** can be rationalized in terms of a related cycloaddition which is then followed by elimination of trimethylsilanol and a subsequent 1,3-allylic sulfonyl shift.



In summary, the reactions of (phenylsulfonyl)-1,2-propadiene with various dipoles and dipole precursors give rise to formal 1,3-dipolar cycloadducts in good yield. In certain cases the reaction does not occur from a 1,3-dipole intermediate but rather involves a stepwise Michael-type addition to the central allene carbon. The strongly activated allene promotes conjugate addition as a consequence of its markedly lowered LUMO level. Some of the dipolar cycloadducts also rearrange via a novel 1,3-allylic sulfonyl shift. The 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 either a Thomas-Hoover capillary melting point or Kofler apparatus and are uncorrected. Infrared spectra were run on either a Perkin-Elmer Model 283 or 684 infrared spectrometer. Proton NMR spectra were obtained on a Brucker FT 80-MHz or a GE 300-MHz spectrometer. ^{13}C NMR spectra were recorded on an IBM NB 200 SY FT spectrometer. Microanalyses were performed at Atlantic Microlabs, Atlanta, GA. Mass spectra were determined with a Finnegan 4510 mass spectrometer at an ionizing voltage of 70 eV.

Reaction of (Phenylsulfonyl)-1,2-propadiene with Diazopropane. To a 1.0-g sample of (phenylsulfonyl)propadiene[36] (**1**) dissolved in 10 mL of ether in a 50-mL round-bottom flask equipped with a magnetic stirrer was added 40 mL of a 2.5 M solution of diazopropane in ether. The reaction mixture was stirred for 18 h under a nitrogen atmosphere at room temperature. The solution was washed with 30 mL of a 10% hydrochloric acid solution followed by 50 mL of a saturated sodium bicarbonate solution and 50 mL of water. The organic layer was dried over sodium sulfate and concentrated under reduced pressure to give a yellow oil. The residue was subjected to silica gel chromatography using a 25% ethyl acetate–hexane mixture. The major band contained 0.44 g of a yellow oil, whose NMR spectrum showed it to contain a 4.5:1 mixture of 5-(phenylsulfonyl)-3,3,4-trimethyl-3*H*-pyrazole (**3**) and 5,5-dimethyl-4-methylene-3-(phenylsulfonyl)-2-pyrazoline (**2**) [NMR (300 MHz, $CDCl_3$) δ 1.19 (s, 6 H), 4.88 (s, 1 H), 5.59 (s, 1 H), 7.12 (s, 1 H), 7.42–7.90 (m, 5 H)]. Treatment of the mixture with triethylamine gave a pure sample of 5-(phenylsulfonyl)-3,3,4-trimethyl-3*H*-pyrazole (**3**): mp 86–87 °C; IR (KBr) 3080, 2990, 2940, 1615, 1450, 1430, 1320, 1210, 1165, 1150, 1095, 1080, 950, 860, 770, 740, 690, 650, 610, and 600 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.29 (s, 6 H), 2.32 (s, 3 H), 7.49–8.05 (m, 5 H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 10.14, 19.80, 96.72, 128.14, 129.07, 129.36, 134.08, 139.81, and 165.72; UV (95% ethanol) 226 (ϵ 10460), 330 nm (1040); MS, *m/e* 235, 145, 141, 125, 86, 81, 79, and 77; HRMS calcd for $C_{12}H_{14}N_2O_2S$ 250.0776, found 250.0759.

The second band contained 0.58 g of a light-yellow solid, which was identified as the diadduct 5,5-dimethyl-3-(phenylsulfonyl)-2-pyrazoline-4-spiro-3′-(5′,5′-dimethyl-1′-pyrazoline) (**4**): mp 120–121 °C; IR (KBr) 3315, 3000, 2960, 1535, 1455, 1420, 1405, 1380, 1320, 1250, 1220, 1190, 1150, 1130, 1110, 1080, 920, 860, 780, 730, 695, 660, and 600 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.14 (s, 3 H), 1.17 (s, 3 H), 1.37 (s, 3 H), 1.52 (d, 1 H, J = 14 Hz), 1.68 (s, 3 H), 2.32 (d, 1 H, J = 14 Hz), 6.29 (br s, 1 H), and 7.48–7.93 (m, 5 H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 20.17, 24.50, 26.07, 28.03, 31.69, 73.12, 92.56, 106.65, 128.13, 129.01, 129.23, 133.73, and 148.87; UV (95% ethanol) 222 (ϵ 9870), 292 (7810), 348 nm (1890); MS, *m/e* 277 (base), 235, 136, 123, 107, 95, 91, and 77; HRMS calcd for $C_{14}H_{17}N_2O_2S$ (loss of N_2 and CH_3) 277.1011, found 277.0998.

Support for this structure was obtained by the photoextrusion of nitrogen to give spiro pyrazoline **5**. A 52-mg sample of **4** was dissolved in 40 mL of dichloromethane and was placed in a Pyrex test tube. The solution was degassed with argon for 15 min. The tube was stoppered and irradiated at 350 nm for 45 min at room temperature. The solution was then concentrated under reduced pressure to give 47 mg (100%) of a tan solid, which was identified as 5,5-dimethyl-3-(phenylsulfonyl)-2-pyrazoline-4-spiro-1′-(2′,2′-dimethylcyclopropane) (**5**) on the basis of its spectral properties: IR (KBr) 3440, 2980, 2940, 1470, 1450, 1390, 1370, 1310, 1200, 1150, 1080, 920, 790, 760, 730, and 695 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.88 (d, 1 H, J = 5 Hz), 1.05 (s, 3 H), 1.13 (s, 6 H),1.44 (s, 1 H, J = 5 Hz), 1.55 (s, 3 H), 5.38 (br s, 1 H), and 7.38–7.81 (m, 5 H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 23.06, 23.58, 24.29, 24.49, 25.19, 25.29, 25.50, 45.67, 67.92, 128.38, 128.70, 128.90, 129.48, 140.47, and 155.06; UV (95% ethanol) 222 (ϵ 8830), 276 nm (4700); MS, *m/e* 292, 277 (base), 235, 123, 107, 91, and 77; HRMS calcd for $C_{15}H_{20}N_2O_2S$ 292.1245, found 292.1239.

Reaction of Diazomethane with (Phenylsulfonyl)-1,2-propadiene. An ethereal solution of diazomethane (250 mL) was added to an ether solution (100 mL) containing 1.8 g of (phenylsulfonyl)propadiene at 0 °C. After the mixture was stirred

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at 25 °C for 18 h, the solvent was removed under reduced pressure and the residue was subjected to silica gel chromatography using a 30% ethyl acetate–hexane mixture as the eluent. The first fraction contained 932 mg (49%) of a light yellow solid mp 175–176 °C, whose structure was assigned as 3-(phenylsulfonyl)-4-methylpyrazole (**7**) on the basis of the following data: IR (KBr) 3300, 2960, 2940, 2860, 1950, 1560, 1480, 1450, 1325, 1200, 1150, 1075, 940, 730, 690, and 620 cm^{-1}; NMR ($CDCl_3$, 80 MHz) δ 2.23 (s, 3 H) and 7.5–8.01 (m, 7 H); MS, *m/e* 222, 194, 143, 141, 125, 97, 81, and 77. Anal. Calcd for $C_{10}H_{10}N_2O_2S$: C, 54.05; H, 4.50; N, 12.61; S, 14.41. Found: C, 54.03; H, 4.71; N, 12.59; S, 14.38.

The second fraction contained 399 mg of a white solid (16%), mp 125–126 °C, whose structure was assigned as 4-[(phenylsulfonyl)methyl]pyrazole (**8**) on the basis of its spectral properties: IR (KBr) 3320, 2960, 2930, 2860, 1450, 1330, 1200, 1150, 1080, 770, and 690 cm^{-1}; NMR (CD_3CN, 360 MHz) δ 5.14 (s, 2 H), 7.55–7.71 (m, 3 H), 7.78 (s, 1 H), 7.98–8.02 (3 H), and 9.62 (s, 1 H); MS, *m/e* 222, 221 (base), 207, 185, 171, 149, 141, 125, and 77. Anal. Calcd for $C_{10}H_{10}N_2O_2S$: C, 54.05; H, 4.50; N, 12.61; S, 14.41. Found: C, 54.20; H, 4.61; N, 12.58; S, 14.20.

The above reaction was carried out under a slightly different set of conditions. A 170-mL ethereal solution of diazomethane, prepared from 8.4 g of Diazald, was added at 0 °C to 1.8 g of allene **1** in 50 mL of ether. After the mixture was slowly warmed to room temperature over a 24-h period, 1.0 g of a white solid (mp 161–162 °C) crystallized out of the reaction mixture. The structure of this material was assigned as 3-(phenylsulfonyl)-4-methylene-2-pyrazoline (**12**) on the basis of the following data: IR (KBr) 3340, 2960, 2880, 1630, 1590, 1490, 1450, 1410, 1310, 1145, 885, 850, 765, 740, 720, and 690 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 4.50 (t, 2 H, J = 4.0 Hz), 5.20 (t, 1 H, J = 4.0 Hz), 5.71 (t, 1 H, J = 4.0 Hz), 6.56 (s, 1 H, exchanged with D_2O), and 7.5–8.0 (m, 5 H). Irradiation of the signal at δ 4.50 collapsed both the triplets to singlets. External irradiation of the signal at δ 5.20 (or 5.71) had no effect on the other vinyl proton at δ 5.71 (or 5.20) but collapsed the triplet at δ 4.50 to a doublet (J = 4.0 Hz). The dideuteriated pyrazole **12**-d_2 showed a two-proton singlet at δ 4.50 and the NH proton at δ 6.56: ^{13}C NMR ($CDCl_3$, 50 MHz) δ 56.08, 106.35, 127.43, 127.86, 129.13, 133.67, 137.69, and 139.93; MS, *m/e* 222, 157, 125, 97, 81, and 77; HRMS calcd for $C_{10}H_{10}N_2SO_2$ 222.0463, found 222.0461. Anal. Calcd for $C_{10}H_{10}N_2SO_2$: C, 54.04; H, 4.54; N, 12.60; S, 14.42. Found: C, 54.12; H, 4.57; N, 12.54; S, 14.51.

The filtrate was concentrated under reduced pressure and was subjected to silica gel chromatography using a 30% ethyl acetate–hexane mixture. The major fraction contained 1.1 g of a white solid, mp 79–80 °C, whose structure was assigned as *N*-methyl-3-(phenylsulfonyl)-4-(hydroperoxymethyl)pyrazole (**13**) on the basis of its spectral data: IR (KBr) 3200, 1730, 1590, 1540, 1450, 1390, 1350, 1330, 1290, 1170, 1130, 1080, 1000, 980, 870, 820, 740, 690, and 620 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 4.05 (s, 3 H), 5.24 (s, 2 H), 7.4–7.7 (m, 4 H), 8.0 (d, 2 H, J = 7.5 Hz), and 8.6 (s, 1 H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 39.3, 68.93, 121.46, 127.59, 129.56, 134.17, 136.73, 139.79, and 140.29. Anal. Calcd for $C_{11}H_{12}N_2SO_4$: C, 49.25; H, 4.51; N, 10.44. Found: C, 49.33; H, 4.51; N, 10.45.

Treatment of a sample of pyrazoline **12** with sodium methoxide resulted in the formation of pyrazole **7**. To a solution containing 100 mg of **12** in 10 mL of methanol was added 30 mg of sodium methoxide. After the mixture was stirred at 25 °C for 10 min, the solution was quenched with a saturated ammonium chloride solution and extracted with chloroform. The organic layer was dried over anhydrous magnesium sulfate and concentrated to a colorless oil, which crystallized on standing to give 3-(phenylsulfonyl)-4-methylpyrazole (**7**) in 90% yield, mp 174–175 °C. A sample of **12** in 10 mL of chloroform was irradiated with a 300-nm sun lamp for 16 h. The reaction mixture was concentrated, and the residue was subjected to silica gel chromatography using a 35% ethyl acetate–hexane mixture as the eluent to give 4-[(phenylsulfonyl)methyl]pyrazole (**8**) in 75% yield, mp 125–126 °C. Treatment of a sample of **12** with diazomethane in the presence of oxygen afforded a 60% yield of pyrazole **13**, mp 79–80 °C.

Reaction of 1-(α-Chlorobenzylidene)-2-phenylhydrazine with Base in the Presence of (Phenylsulfonyl)-1,2-propadiene. To a solution containing 1.66 g of 1-(α-chlorobenzylidene)-2-phenylhydrazine and 1.0 g of (phenylsulfonyl)-propadiene in 30 mL of benzene was added 287 mg of triethylamine. After the mixture was stirred for 18 h at 25 °C, the solvent was removed under reduced pressure and the residue was subjected to silica gel chromatography using a 10% ethyl acetate–hexane mixture as the eluent. The first fraction contained 82 mg of a white solid, mp 157–158 °C (4%), whose structure was assigned as 1,3-diphenyl-4-(phenylsulfonyl)-5-methylpyrazole (**17**) on the basis of its spectral properties: IR (KBr) 3070, 2930, 1600, 1500, 1310, 1150, 1100, 790, 740, 690, and 610 cm^{-1}; NMR ($CDCl_3$, 80 MHz) δ 2.67 (3, 3 H) and 7.31–7.62 (m, 15 H); MS, *m/e* 374 (base), 357, 310, 309, 294, 268, 233, and 206. Anal. Calcd for $C_{22}H_{18}N_2O_2S$: C, 70.58; H, 4.81; N, 7.48; S, 8.55. Found: C, 70.62; H, 4.85; N, 7.43, S, 8.51.

The second fraction contained 1.3 g of a white solid, mp 140–141 °C (66%), which was identified as 1,3-diphenyl-5-[(phenylsulfonyl)methyl]pyrazole (**16**) on the basis of its characteristic spectral properties: IR (KBr) 3120, 3080, 3050, 1600, 1500, 1320, 1310, 1170, 1150, 1090, 700, 690, and 665 cm^{-1}; NMR ($CDCl_3$, 80 MHz) δ 4.45 (s, 2 H), 6.72 (s, 1 H), and 7.06–7.88 (m, 15 H); MS, *m/e* 374, 233 (base), 217, 206, 155, 130, and 117. Anal. Calcd for $C_{22}H_{18}N_2O_2S$: C, 70.58; H, 4.81; N, 7.48; S, 8.55. Found: C, 70.60; H, 4.85; N, 7.50; S, 8.50.

Reaction of (Phenylsulfonyl)-1,2-propadiene with Benzonitrile Oxide. To a 100-mL round-bottom flask equipped with a magnetic stirrer was placed 1.55 g of benzohydroximinoyl chloride[37] dissolved in 70 mL of carbon tetrachloride. The flask was placed in an ice bath and cooled to 0 °C. To this solution was added 1.80 g of (phenylsulfonyl)propadiene followed by 1.10 g of triethylamine. Stirring was continued under nitrogen for 24 h, and the solution was allowed to warm to room temperature. The mixture was washed with 50 mL of a 10% hydrochloric acid solution followed by 50 mL of a saturated sodium bicarbonate solution followed by 50 mL of water. The organic layer was dried over magnesium sulfate and concentrated under reduced pressure to give a yellow oil. This material was taken up in 20 mL of carbon tetrachloride, and upon addition of ether, 1.4 g (52%) of a white solid was collected and identified as 3-phenyl-5-[(phenylsulfonyl)methyl]isoxazole (**30**) on the basis of its spectral properties: mp 124–125 °C; IR (KBr) 3120, 2990, 2940, 1610, 1585, 1475, 1445, 1410, 1310, 1295, 1250, 1190, 1145, 1130, 1090, 1010, 955, 935, 840, 775, 750, 690, and 640 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 4.59 (s, 2 H), 6.72 (s, 1 H), 7.45–7.90 (m, 10 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 54.12, 104.17, 126.80, 128.30, 128.42, 129.00, 129.44, 130.36, 134.53, 137.71, 160.64, and 162.84; UV (95% ethanol) 246 nm (ϵ 14 140); MS, *m/e* 299, 158 (base) and 77; HRMS calcd for $C_{16}H_{13}NO_3S$ 299.0616, found 299.0615.

The remaining material contained 300 mg (10%) of a yellow oil, which was identified as a 3:2 mixture of 3-phenyl-4-[(phenylsulfonyl)methyl]isoxazole (**32**) and 5-methyl-3-phenyl-4-(phenylsulfonyl)isoxazole (**31**) on the basis of their spectral properties: (**32**) ^1H NMR (300 MHz, $CDCl_3$) δ 4.28 (s, 2 H), 7.2–7.8 (m, 10 H), and 8.50 (s, 1 H). An authentic sample of **31** was prepared in the following fashion. To a stirred ice-cold suspension containing 450 mg of benzohydroximinoyl chloride (**27**) in 3 mL of water was added 2.5 mL of a 10% sodium hydroxide solution at 0 °C. The mixture was extracted with ether, and the organic layer was washed with a dilute sodium phosphate solution followed by water and drying over magnesium sulfate. This cold solution was added to a 180-mg sample of 1-(phenylsulfonyl)propyne at 0 °C. The solution was stirred for 18 h at 25 °C. Normal silica gel workup afforded 153 mg of **31** (51%): mp 126–127 °C; IR (KBr) 3060, 3030, 1650, 1620, 1560, 1490, 1330, 1170, 900, 690 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 2.87 (s, 3 H) and 7.3–7.7 (m, 10 H); MS, *m/e* 299 (base), 284, 256, 235, 158, and 77. Anal. Calcd for $C_{16}H_{13}NO_3S$: C, 64.21; H, 4.34; N, 4.68; S, 10.70. Found: C, 64.19; H, 4.37; N, 4.63; S, 10.67.

Reaction of the Trimethylsilyl Ester of *aci*-Nitrophenylmethane (40) with 1-(Phenylsulfonyl)-1,2-propadiene (1). A solution containing 800 mg of the trimethylsilyl ester of *aci*-nitrophenylmethane (**40**)[38] and 570 mg of 1-(phenylsulfonyl)propadiene (**1**) in 20 mL of benzene was heated at 60 °C for 1.5 h under a nitrogen atmosphere. Removal of the solvent under reduced pressure left a yellow solid, which was recrystallized

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by using methylene chloride–hexane to give 640 mg (68%) of 3-phenyl-5-[(phenylsulfonyl)methyl]isoxazole (**30**) as a white crystalline solid: mp 123–124 °C; IR (KBr) 3130, 2995, 2940, 1610, 1585, 1445, 1310, and 1150 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 4.55 (s, 2 H), 6.65 (s, 1 H), and 7.35–7.85 (m, 10 H). Anal. Calcd for $C_{16}H_{13}NO_3S$: C, 64.20; H, 4.38; N, 4.68. Found: C, 64.10; H, 4.29; N, 4.59.

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Registry No. **1**, 2525-42-0; **1**-d_2, 113648-18-3; **2**, 113648-12-7; **3**, 113648-13-8; **4**, 113648-14-9; **5**, 113648-15-0; **7**, 51105-55-6; **8**, 113648-17-2; **9**, 2525-40-8; **12**, 51445-25-1; **12**-d_2, 113648-16-1; **13**, 113668-34-1; **16**, 106910-59-2; **16**-d_2, 113648-19-4; **17**, 106910-54-7; **30**, 106808-15-5; **31**, 113648-20-7; **32**, 113648-21-8; **40**, 51146-39-5; CH_2N_2, 334-88-3; PhNHN=CClPh, 15424-14-3; diazopropane, 764-02-3; benzohydroximinoyl chloride, 698-16-8.

Peracid Oxidation of 4-Isoxazolines as a Method for the Preparation of α,β-Unsaturated Carbonyl Compounds

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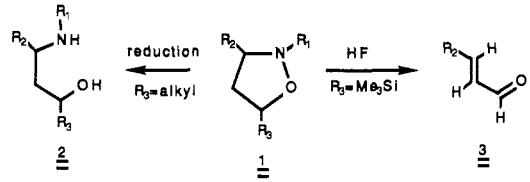
Received October 29, 1987

A study of the MCPBA peracid oxidation of a series of 4-isoxazolines has been carried out. A variety of isoxazolines were synthesized by treating nitrones with electron-deficient alkynes. An alternate approach involves dipolar cycloaddition of nitrones with activated allenes followed by a subsequent base-catalyzed isomerization of the initially formed cycloadduct. Treatment of the 5-*exo*-methyleneisoxazolidine derived from the reaction of *N*-benzylidenemethylamine *N*-oxide and (phenylsulfonyl)propadiene with LDA followed by γ-alkylation also produced substituted 4-isoxazolines. The peracid oxidation of the isoxazoline ring afforded α,β-unsaturated carbonyl compounds in excellent yield. Reductive cleavage of the sulfonyl group of some of the enones was achieved by initial protection of the carbonyl functionality by cyanosilylation using trimethylsilyl cyanide, and this was followed by aluminum-amalgam reduction. The cycloaddition–oxidation procedure provides an attractive route to synthesize α,β-unsaturated ketones since it avoids acidic or basic conditions.

The presence of a nitrogen atom within the isoxazolidine ring has made this heterocycle moiety especially attractive for the synthesis of a wide variety of alkaloids and other nitrogen-containing natural products.[1-11] Through the use of nitrone cycloaddition chemistry,[12] numerous isoxazolidines have been synthesized with excellent stereochemical control.[13] The key feature of this approach generally involves the subsequent reductive cleavage of the isoxazolidine ring to give a γ-amino alcohol, which is further manipulated into other functional groups.[14-18] Recent work by DeShong and Leginus[19] has demonstrated that nitrone cycloadditions with vinyltrimethylsilane give 5-silylisoxazolidines, which can easily be transformed into α,β-unsaturated aldehydes. This methodology is quite useful since it allows for the homologation of aldehydes by two carbons while avoiding strongly basic reaction conditions.



2 1 3

As part of an ongoing program aimed at the development of general methods for the construction of nitrogen-containing heterocycles,[20] we have been investigating the 1,3-dipolar cycloadditions of nitrones with allenes[21]

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