Cycloaddition of (Phenylsulfonyl)-1,2-propadienes with Diazomethane. Novel Rearrangement Reactions of the Resulting Cycloadducts

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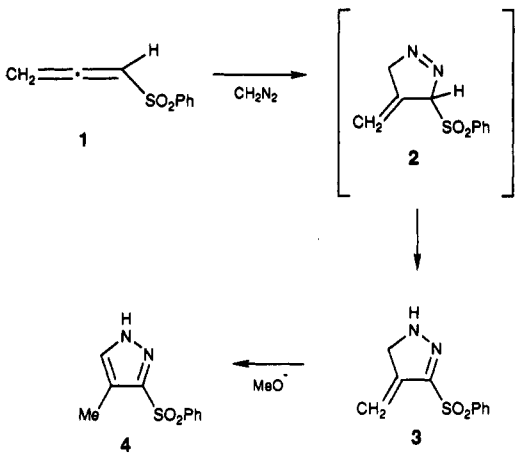
The cycloaddition reactions of several phenylsulfonyl-substituted allenes with diazomethane have been investigated. The major products formed were identified as 3-(phenylsulfonyl)-4-methylene-2-pyrazolines. These pyrazolines engage in a variety of mechanistically interesting transformations, ranging from base-catalyzed rearrangements to addition of Grignard reagents. The dipolar cycloadduct derived from the reaction of diazomethane with 3-(phenylsulfonyl)-1,2-butadiene undergoes a 1,3-phenylsulfonyl shift upon irradiation to give 3-methyl-4-[(phenylsulfonyl)methyl]pyrazole. The cycloadduct derived from the reaction of 2,3-bis(phenylsulfonyl)-1-propene with diazomethane readily loses nitrogen upon photolysis to give 1-[(phenylsulfonyl)methyl]-1-(phenylsulfonyl)cyclopropane. This cyclopropane affords a variety of novel rearranged structures when treated with several different bases. The products obtained can be rationalized in terms of a base-catalyzed rearrangement of the above cyclopropane to α-methyl(phenylsulfonyl)allene which reacts further with the particular base used to produce the observed products.

Allenes play an important role in many aspects of organic chemistry.[1-3] They are considerably more reactive in cycloaddition reactions compared to other alkenes with isolated nonactivated double bonds. Heats of hydrogenation indicate an effective strain of ca. 10 kcal/mol associated with the cumulated double bond;[2] this strain is relieved when the allene undergoes any kind of addition reaction.[4] Apart from this ready reactivity, allenes are also particularly versatile in cycloaddition chemistry, since the contiguous double bonds react independently of one another.[5-18] Manipulation of one double bond may afford a product with the remaining double bond intact, providing a "handle" for further chemical transformation. Such chemical pliability has enticed us to study the cycloaddition behavior of (phenylsulfonyl)allene (1)[19] a compound which has interested us for some time. This highly functional substrate contains a three-carbon array with an electron-rich π-bond, an electron-deficient alkene, and a pendant sulfone moiety useful for subsequent synthetic manipulations.[20-23]

Previous studies in our laboratory have focused upon the 1,3-dipolar cycloaddition of allene 1 toward various dipoles.[24] For example, treatment of 1 with diazomethane produced cycloadduct 3, the product of addition onto the more reactive electron-deficient π-bond.[25] The regioselectivity of the cycloaddition is predictable from frontier



(1) *The Chemistry of Allenes*; Landor, S. R., Ed.; Academic Press: London, 1982; Vols. I-III.
(2) Schuster, H. F.; Coppola, G. M. *Allenes in Organic Synthesis*; Wiley-Interscience: New York, 1984.
(3) Blake, P. In *The Chemistry of Ketenes, Allenes and Related Compounds*; Wiley-Interscience: New York, 1980; p 344.
(4) Greenberg, A.; Liebman, J. F. *Strained Organic Molecules*; Academic Press: New York, 1978.
(5) Pasto, D. J.; Warren, S. E. *J. Am. Chem. Soc.* **1982**, *104*, 3670.
(6) Domelsmith, L. N.; Houk, K. N.; Piedrahita, C. A.; Dolbier, W. R. *J. Am. Chem. Soc.* **1978**, *100*, 6908.
(7) Dolbier, W. R.; Weaver, S. L. *J. Org. Chem.* **1990**, *55*, 711.
(8) Hayakawa, K.; Nishiyama, H.; Kanematsu, K. *J. Org. Chem.* **1985**, *50*, 512.
(9) Barbarella, G.; Cinquini, M.; Colonna, S. *J. Chem. Soc., Perkin Trans. 1* **1980**, 1646.
(10) Guildford, A. J.; Turner, R. W. *J. Chem. Soc., Chem. Commun.* **1983**, 466.
(11) Veniard, L.; Benaim, J.; Pourcelot, G. C. R. *Acad. Sci. Paris, Ser. C* **1968**, *266*, 1092.
(12) Kanematsu, K.; Sugimoto, N.; Kawaoka, M.; Yeo, S.; Shiro, M. *Tetrahedron Lett.* **1991**, 1351.
(13) Himbert, G.; Fink, D. *Tetrahedron Lett.* **1985**, 4363.
(14) Hayakawa, K.; Aso, K.; Shiro, M.; Kanematsu, K. *J. Am. Chem. Soc.* **1989**, *111*, 5312.
(15) Tuffariello, J. J.; Ali, S. A.; Klingele, H. O. *J. Org. Chem.* **1979**, *44*, 4213.
(16) Blechert, S. *Justus Liebigs Ann. Chem.* **1985**, 673. Wilkens, J.; Khuling, A.; Blechert, S. *Tetrahedron* **1987**, *44*, 3237.
(17) Parpani, P.; Zecchi, G. *J. Org. Chem.* **1987**, *52*, 1417.
(18) Padwa, A.; Matzinger, M.; Tomioka, Y.; Venkatramanan, M. K. *J. Org. Chem.* **1988**, *53*, 955.
(19) Padwa, A.; Kline, D. N.; Norman, B. H. *Tetrahedron Lett.* **1988**, *29*, 265. Padwa, A.; Carter, S. P.; Chiacchio, U.; Kline, D. N.; Perumattam, J. *J. Chem. Soc., Perkin Trans. 1* **1988**, 2639. Padwa, A.; Yeske, P. E. *J. Am. Chem. Soc.* **1988**, *110*, 1617. Padwa, A.; Kline, D. N.; Koehler, K. F.; Matzinger, M.; Venkatramanan, M. K. *J. Org. Chem.* **1987**, *52*, 3909.
(20) Stirling, C. J. M. *J. Chem. Soc.* **1964**, 5863. Appleyard, G. D.; Stirling, C. J. M. *J. Chem. Soc.* **1967**, 2686.
(21) Smadja, W. *Chem. Rev.* **1983**, *83*, 263.
(22) Taylor, D. R. *Chem. Rev.* **1967**, *67*, 317.
(23) Pasto, D. J. *Tetrahedron* **1984**, *40*, 2805.
(24) Padwa, A.; Carter, S. P., Chiacchio, U.; Kline, D. N. *Tetrahedron Lett* **1986**, 2683. Padwa, A.; Tomioka, Y.; Venkatramanan, M. K. *Tetrahedron Lett* **1987**, 755. Padwa, A.; Kline, D. N.; Perumattam, J. *Tetrahedron Lett.* **1987**, 913.
(25) Padwa, A.; Craig, S. P., Chiacchio, U.; Kline, D. N. *J. Org. Chem.* **1988**, *53*, 2232.

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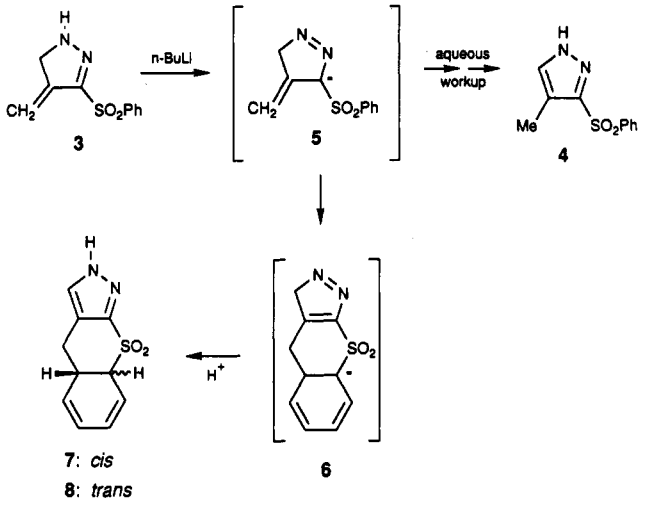
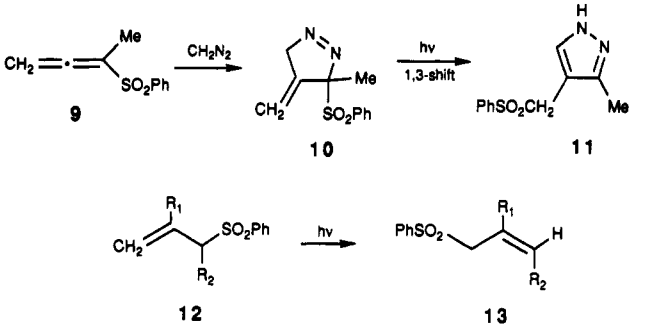
orbital considerations for addition of a diazo compound to an electron-deficient dipolarophile with a low lying LUMO orbital.[26] We were struck by the fact that pyrazoline 3 was isolable with the exomethylene functionality still intact, in light of the seemingly large driving force for aromatization. In an attempt to induce such aromatization, we discovered some interesting behavior. Whereas treatment of 3 with sodium methoxide easily catalyzed the aromatization, the use of stronger bases proved less straightforward. Thus, exposure of 3 to *n*-butyllithium resulted in the formation of pyrazole 4 only as a minor product (14%), the balance consisting of two isomeric compounds, which bore little resemblence to the starting material. Spectroscopic evidence (see Experimental Section) indicated the structural assignments 7 and 8, products of internal cyclization onto the sulfone phenyl ring.

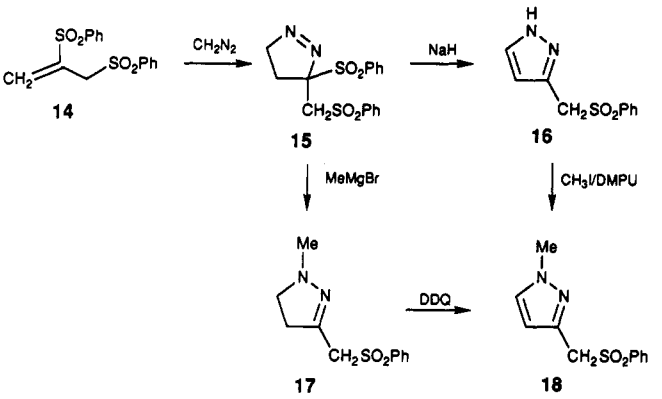


The conversion of 3 into 7 and 8 appears to be an example of a Truce–Smiles rearrangement,[27] even though it is rare for the phenylsulfonyl moiety to participate in such anionic cyclizations.[28] In fact, one of the favorable properties of this functionality is chemical "inertness". This is due in part to the insulating effect of the sulfone, as well as the unfavorable thermodynamics of disrupting the aromaticity of the benzene ring. In this case, however, a particularly favorable electronic and geometric configuration of the initially formed anion 5 apparently compensates for these other factors. The novelty here is that tautomerization of the initially formed pyrazole anion is preferred, presumably thermodynamically, to protomeric rearomatization of the benzo ring.

As part of our studies in this area, we were curious as to what alternate chemical behavior might be induced in these potentially reactive compounds. Toward this end, the methyl analogue was prepared by the reaction of diazomethane with the (phenylsulfonyl)allene 9.[29] In this case the resulting pyrazoline 10 is blocked from deprotonation or facile hydrogen shifts. With these thermal routes to isomerization precluded, this compound avails itself to a photochemical pathway previously observed with other β-alkylidene sulfones (e.g., 12 → 13).[30-35] In this instance, the 1,3-phenylsulfonyl shift is driven by quite favorable dynamics to provide the disubstituted pyrazole 11 in 86% yield upon irradiation with a 300-nm sunlamp for 2 h.



Earlier work from our laboratory[36] demonstrated that 2,3-bis(phenylsulfonyl)-1-propene (14) can be considered a complementary "equivalent" to allene 1 for cycloadditions. As an example of this idea, propene 14 undergoes reaction with diazomethane upon the locus which corresponds to the less reactive terminal double bond of the allene.[25] A facile 1,3-dipolar cycloaddition cleanly provides pyrazoline 15 (96%), with the two phenylsulfonyl groups intact. Treatment of 15 with sodium hydride in THF

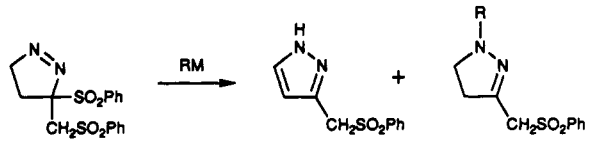


induces the elimination of benzenesulfinate, ultimately producing pyrazole 16 (92%), the regioisomeric counterpart to pyrazole 4. The clean and exclusive formation of 16 is deceptive though, an entirely different mode of reaction is concealed within this ambivalent pyrazoline, the key to which is the choice of base. Thus, in contrast to the example above, treatment of 15 with methylmagnesium bromide resulted in the exclusive formation of the *N*-methylpyrazoline 17 (90%). The structure of this unexpected product was confirmed by DDQ oxidation to the corresponding *N*-methylpyrazole 18, which is the same compound as that obtained from the methylation of pyrazole 16.

The mechanism of this reactivity crossover is not totally clear. An S_N2'-type of reaction, or even an addition–elimination sequence, could certainly be invoked to explain the results.

(26) Houk, K. N.; Yamaguchi, K. Theory of 1,3-Dipolar Cycloadditions in *1,3-Dipolar Cycloaddition Chemistry*, Vol. 2; Padwa, A., Ed.; Wiley-Interscience, 1984; p 407. Geittner, J.; Huisgen, R.; Sustmann, R. *Tetrahedron Lett.* **1977**, 881.
(27) Truce, W. R.; Modaj, E. J., Jr. *Sulfur Rep.* **1983**, *3*, 259.
(28) *The Chemistry of Sulfones and Sulfoxides*; Patai, S., Ed.; The Chemistry of Functional Groups; Wiley-Interscience: New York, 1988.
(29) Braverman, S.; Mechoulam, H. *Tetrahedron* **1974**, *30*, 3883.
(30) Padwa, A.; Bullock, W. H.; Dyszlewski, A. D. *J. Org. Chem.* **1990**, *55*, 955.
(31) Myong, S. O.; Linder, L. W.; Seike, S. C.; Little, R. D. *J. Org. Chem.* **1985**, *50*, 2244.
(32) Lin, P.; Whitham, G. H. *J. Chem. Soc., Chem. Commun.* **1983**, 1102. Knight, D. J.; Lin, P.; Whitham, G. H. *J. Chem. Soc., Perkin Trans 1* **1987**, 2707.
(33) Bordwell, F. G.; Pagani, G. A. *J. Chem. Soc.* **1975**, *97*, 118.
(34) Kocienski, P. *J. Chem. Soc., Perkin Trans. I* **1983**, 945.
(35) Barre, V.; Uguen, D. *Tetrahedron Lett.* **1987**, 6045.
(36) Padwa, A.; Kline, D. N.; Norman, B. H. *J. Org. Chem.* **1989**, *54*, 810.

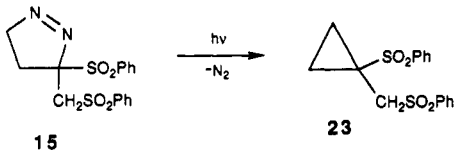
Scheme I



NaH	100	:	0	
MeMgBr	0	:	100	17; R=Me
n-BuMgBr	0	:	100	19; R=n-Bu
sec-BuMgBr	0	:	100	20; R=sec-Bu
PhMgBr	0	:	100	22; R=Ph
t-BuMgBr	12	:	88	21; R=t-Bu
MeLi	50	:	50	17; R=Me
n-BuLi	17	:	83	19; R=n-Bu
sec-BuLi	67	:	33	20; R=sec-Bu
t-BuLi	33	:	67	22; R=t-Bu

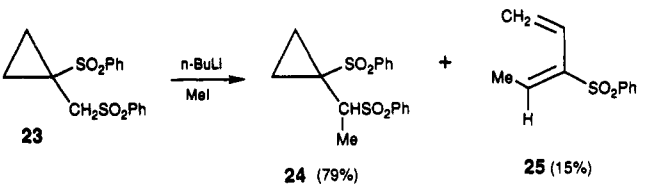
On the other hand, single electron transfer (SET) processes cannot be ruled out.[37-39] Attempting to shed light on this mystery, we examined a variety of bases for their reactivity toward the pyrazoline **15** (Scheme I). Interestingly, reaction with Grignard reagents afforded the *N*-alkyl addition products **17** and **19–22**. Only *tert*-butylmagnesium bromide gave an isolable quantity of the elimination product **16**. The story is somewhat different with alkyllithium reagents. From *n*-butyllithium (which favors addition by 5:1) to *sec*-butyllithium (which favors elimination by 2:1), all experiments yielded mixtures of the two products. The product ratios could be attributed to the hard–soft characteristics of the reagents or to their relative propensity to engage in electron-transfer processes. To further probe this question, pyrazoline **15** was treated with *sec*-butylmagnesium chloride in the presence of 1 equiv of 1,4-dinitrobenzene. Under these conditions, no reaction occurred. This result, along with the apparent lack of sensitivity toward steric factors (i.e., *t*-Bu vs Me), seems to point toward a radical anion mechanism in the formation of pyrazolines **17–22**.

In addition to these interesting base-catalyzed reactions, pyrazoline **15** was found to undergo facile photochemical extrusion of nitrogen.[40] Thus, by irradiating a chloroform solution of **15** with a 300-nm sunlamp for 2 h, the crystalline bis(phenylsulfonyl) cyclopropane **23** was isolated in 86% yield. This conversion is also catalyzed by dilute hydro-

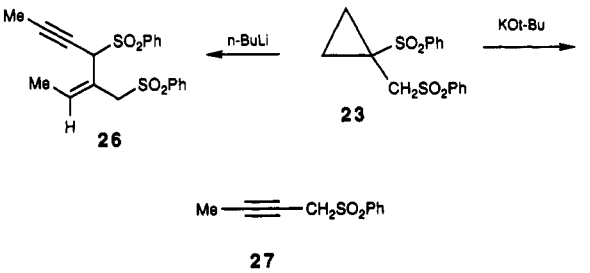


chloric acid in acetone solution in dark storage (90%). So facile is the loss of nitrogen that cyclopropane **23** can be prepared in 98% yield simply by passing pyrazoline **15** through a silica gel column at room temperature.

Since cyclopropane **23** contains relatively acidic α-sulfonyl methylene protons,[41] we decided to investigate the behavior of this substrate toward alkylation. Toward this end, a solution of **23** in THF was treated with a slight excess of *n*-butyllithium at −78 °C, followed by quenching with methyl iodide. The isolation of the expected α-methylation product **24** in 79% yield confirmed our assumption that the initially formed phenylsulfonyl carbanion would be well-behaved at low temperature. Upon closer scrutiny, however, the reaction mixture was found to contain a small amount (15%) of a byproduct characterized as having structure **25**, based upon the spectroscopic evidence (see Experimental Section). We were initially confounded by the presence of this compound, apparently the outcome of an extensive rearrangement.



To help elucidate the mechanism of this puzzling rearrangement, an experiment was carried out omitting the potentially complicating effect of the electrophile (i.e. methyl iodide). Thus, a THF solution of cyclopropane **23** was treated with 1.5 equiv of *n*-butyllithium and allowed to warm to room temperature. The reaction mixture contained a compound (**26**, 39%) which was unmistakably the product of a bimolecular process, although the exact pathway which the reactant must have traveled remained an enigma.

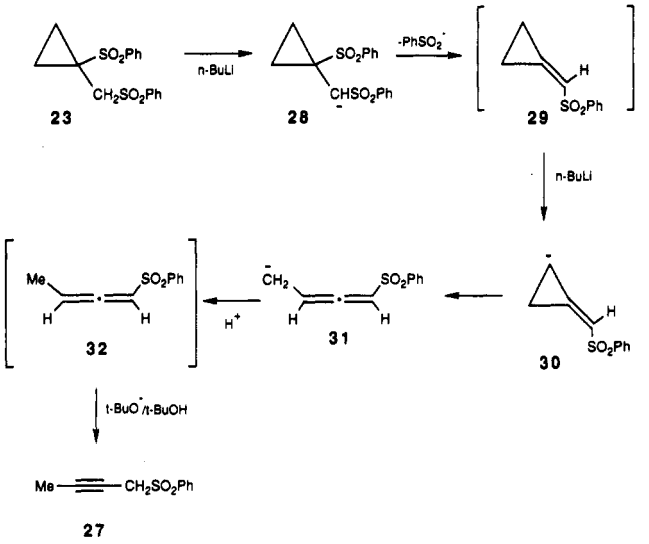


We also explored the reaction of **23** with other base/solvent systems. One such trial involved the treatment of a THF solution of cyclopropane **23** with an excess of potassium *tert*-butoxide at room temperature. This procedure quickly and cleanly afforded a single product (88%) which was identified as 1-(phenylsulfonyl)-2-butyne (**27**). A different result still, but this data provided a basis for some mechanistic propositions.

From the isolation of the methylated cyclopropane **24** we had established the fact that (a) the α-phenylsulfonyl carbanion **28** is the first species formed in basic media and (b) this species was stable for some finite period of time. It seems reasonable to assume that, failing capture by an electrophile, the anion would eject benzenesulfinate ion through β-elimination[42] to give a methylene cyclopropane (i.e., **29**) as the next step. In the presence of excess base, this substrate could be deprotonated to give the highly strained cyclopropyl anion **30**. Driven by the relief of sizable ring strain, rearrangement involving cyclopropane scission ensues. The allylic anion **31** so formed is then protonated to give α-methyl(phenylsulfonyl)allene (**32**). Stirling has shown that such electron-deficient allenes are part of an equilibrium mixture in basic media, so that the alkynyl sulfone, the sulfonylallene, and the propargylsulfone all interconvert through a facile base-catalyzed

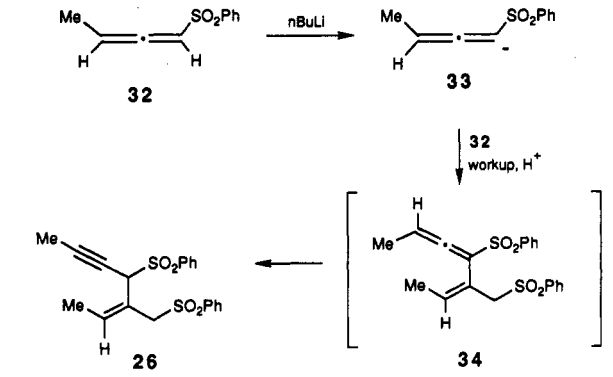
(37) Beckwith, A. L. J.; Wang, S.; Warkentin, J. *J. Am. Chem. Soc.* **1987**, *109*, 5289.
(38) Benati, L.; Placucci, G.; Spagnolo, P.; Tundo, A.; Zanardi, G. *J. Chem. Soc., Perkin Trans. I* **1977**, 1684.
(39) Lui, H.; Warkentin, J. *Can. J. Chem.* **1973**, *51*, 1148.
(40) Franck-Neumann, M.; Buchecker, C. D. *Tetrahedron* **1978**, *34*, 2797.
(41) Magnus, P. D. *Tetrahedron* **1977**, *33*, 2019.
(42) Julia, M.; Badet, B. *Bull. Soc. Chim. Fr.* **1975**, 1363.

isomerization.[43] Therefore, having attained the intermediate allene **32**, the formation of substituted propargylsulfone **27** under the equilibrium conditions of potassium *tert*-butoxide easily follows.



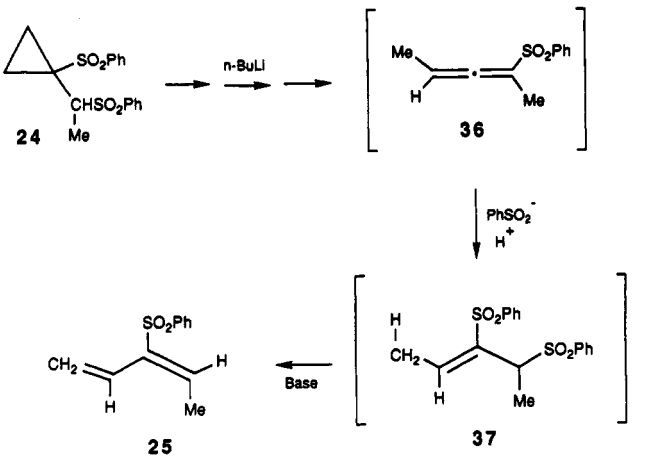
When *n*-butyllithium is used as the base, the nonequilibrating environment allows for a longer lifetime of the allene. In the presence of excess base, the α-phenylsulfonyl allenyl anion **33** can be formed,[44] which simply adds to another allene molecule giving triene **34**. The allene moiety most likely isomerizes during workup to the triple bond as seen in the isolated product **26**.

In order to account for the unusual methylation product **25**, we found it necessary to invoke a similar intermediate along the reaction pathway. Since benzenesulfinate anion was present in the reaction medium, we felt that it was very likely that this potential nucleophile could engage in conjugate addition across the activated double bond of **36**, which would result in the formation of 3,4-bis-

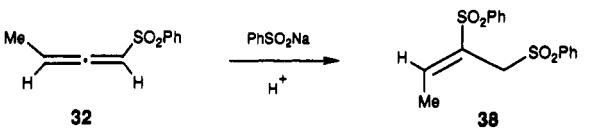


(phenylsulfonyl)-2-pentene (**37**).[45] Once formed, this species could then be induced by excess base to eliminate the alternative phenylsulfonyl group, which would lead directly to the observed byproduct **25**. Indeed, treatment of **24** with *n*-BuLi cleanly afforded **25** after aqueous workup.

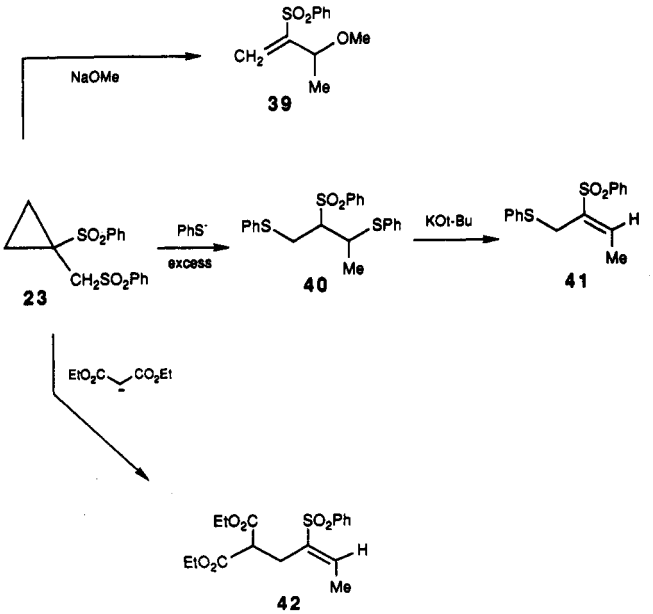
We sought to verify the tenability of these assertions by experimentation. Thus, we found that allene **32**, which had been independently synthesized, did indeed undergo addition with benzenesulfinate anion to give the resultant 3,4-bis(phenylsulfonyl)-2-butene (**38**), providing support



for the connectivity of the proposed intermediates **36** and **37**. Compound **38** corresponds to the methyl analogue of



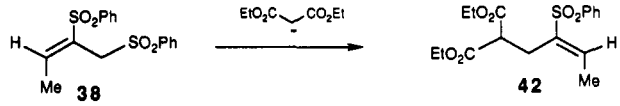
the allene equivalent **14**, which we had previously shown to exhibit predictable behavior in the presence of nucleophiles.[46] In this vein, we were interested in observing the reaction of various nucleophilic bases with bis(phenylsulfonyl) cyclopropane **23**. The results are telling. When sodium methoxide is used as the base, the only isolable product (29%) corresponds to the unsaturated methoxy-substituted sulfone **39**. On the other hand, treatment of **23** with an excess of sodium thiophenolate produced compound **40** in 39% yield. The reaction of **40** with potassium *tert*-butoxide in THF resulted in the elimination of 1 equiv of thiophenolate to give the unsaturated sulfone **41**. The choice of reagents was not limited to heteronucleophiles, even the sodium salt of diethylmalonate induced the reaction with cyclopropane **23**, providing sulfone diester **42** in 58% isolated yield.



These transformations can be accounted for by assuming that cyclopropane **23** is first converted to 3,4-bis(phenyl-

(43) Stirling, C. J. M. *J. Chem. Soc.* **1964**, 5856. Campbell, D. S.; Stirling, C. J. M. *J. Chem. Soc.* **1964**, 5869.
(44) Eisch, J. J.; Galle, J. E. *J. Org. Chem.* **1979**, *44*, 3279.
(45) Padwa, A.; Yeske, P. E. *J. Org. Chem.* **1991**, *56*, 6386.
(46) Padwa, A.; Kline, D. N.; Murphree, S. S.; Yeske, P. E. *J. Org. Chem.* **1992**, *57*, 298.

sulfonyl)-2-butene (38) through the pathway described above. Indeed, we found that the reaction of 38 with sodium methoxide, sodium thiophenolate, or sodium diethyl malonate afforded compounds 39, 40, and 42 in good yield. In the case of diethyl malonate anion, the reaction afforded the product of an S_N2 displacement as opposed to an S_N2' reaction, which is operative in the other examples. The moderate yields of these products (i.e., 39, 40, 42) starting from bis(phenylsulfonyl) cyclopropane 23 are not surprising, considering the complexity of the overall pathway. More than likely, some of the intermediates



along the way succumb to nucleophile-promoted decomposition. That the observed products are isolated at all speaks strongly for the facility with which 38 is formed, further promoting our assumptions about its significance in the reaction sequence. Moreover, the parallels between these products and those observed in previous work using the allene equivalent 14 strongly suggests that the same type of chemistry is operative.

In conclusion, the variety of chemical conversions that occur with pyrazolines 3 and 15 are illustrative of the synthetic potential contained in these highly functionalized compounds. Of course, many different kinds of interesting heterocycles are available through 1,3-dipolar cycloadditions onto allene 1 and the allene equivalent 14. Work continues in our laboratories directed toward the examination of this chemistry and its application to the area of synthetic methodology.

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 extra dry nitrogen. Solutions were evaporated under reduced pressure with a rotary evaporator and the residues were chromatographed on a silica gel column using an ethyl acetate–hexane mixture as the eluent unless specified otherwise.

Reaction of 4,5-Dihydro-4-methylene-3-(phenylsulfonyl)-1*H*-pyrazole (3) with *n*-Butyllithium. To a solution containing 400 mg (1.8 mmol) of 4,5-dihydro-4-methylene-3-(phenylsulfonyl)-1*H*-pyrazole[25] (3) in 25 mL of anhydrous THF at −78 °C under N_2 was added 1.65 mL of a 1.6 M solution of *n*-butyllithium in hexane. The reaction mixture was slowly allowed to warm to rt, and the reaction was quenched with a saturated NH_4Cl solution. The solution was extracted with $CHCl_3$, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure to give an orange oil which was subjected to silica gel chromatography. The major fractions contained a 1:1 mixture of pyrazoles 7 and 8 (61%) as well as 4-methyl-3-(phenylsulfonyl)pyrazole (4)[25] (14%). Pyrazole 7 was assigned on the basis of the following spectral properties: mp 146–147 °C; IR (KBr) 1635, 1555, 1400, 1305, 1095, 705, and 695 cm^{-1}; NMR ($CDCl_3$, 360 MHz) δ 2.68 (dd, 1 H, J = 16.4 and 10.4 Hz), 2.76 (dd, 1 H, J = 16.4 and 5.6 Hz), 3.35 (m, 1 H), 4.12 (m, 1 H), 6.04 (dd, 1 H, J = 9.5 and 2.5 Hz), 6.11 (dd, 1 H, J = 9.5 and 4.5 Hz), 6.15 (dd, 1 H, J = 9.5 and 5.4 Hz), 6.24 (m, 1 H), and 7.60 (s, 1 H); UV (95% ethanol) 232 (ε 4660) and 260 nm (3200). Anal. Calcd for $C_{10}H_{10}N_2O_2S$: C, 54.04; H, 4.54; N, 12.60. Found: C, 53.94; H, 4.56; N, 12.61.

Pyrazole 8 exhibited the following spectral properties: mp 184–185 °C; IR (KBr) 1645, 1565, 1365, 1105, 765, 700, and 695 cm^{-1}; NMR ($CDCl_3$ 360 MHz) δ 2.71 (dd, 1 H, J = 16.1 and 12.4 Hz), 3.09 (dd, 1 H, J = 16.1 and 4.4 Hz), 3.61 (m, 1 H), 4.15 (d, 1 H, J = 17.7 Hz), 5.65 (d, 1 H, J = 9.5 Hz), 6.05 (m, 1 H), 6.10 (d, 1 H, J = 9.5 Hz), 6.30 (m, 1 H), and 7.62 (s, 1 H); UV (95% ethanol) 230 (ε 4800) and 262 nm (3370); MS, m/e 222 (M^+), 205 (base), 157, 130, and 115. Anal. Calcd for $C_{10}H_{10}N_2O_2S$: C, 54.04; H, 4.54; N, 12.61. Found: C, 53.89; H, 4.51; N, 12.47.

Reaction of Diazomethane with 3-(Phenylsulfonyl)-1,2-butadiene (9). A 120-mL ethereal solution of diazomethane prepared from 5.8 g of Diazald was added at rt to 860 mg (4.43 mmol) of 3-(phenylsulfonyl)-1,2-butadiene[29] (9) in 30 mL of ether. After the solution was stirred at 25 °C for 18 h, 840 mg (80%) of a white solid crystallized out of the solution. The structure of this material was assigned as 3-methyl-4-methylene-3-(phenylsulfonyl)-1-pyrazoline (10) on the basis of the following spectral data: mp 83–84 °C; IR (KBr) 1590, 1480, 1445, 1385, 1300, 1150, 900, and 690 cm^{-1}; NMR ($CDCl_3$, 360 MHz) δ 1.90 (s, 3 H), 4.95 (dt, 1 H, J = 22.7 and 2.7 Hz), 5.33 (dt, 1 H, J = 22.7 and 2.7 Hz), 5.63 (t, 1 H, J = 2.7 Hz), 5.72 (t, 1 H, J = 2.7 Hz), 7.61 (t, 2 H, J = 7.8 Hz), 7.75 (t, 1 H, J = 7.8 Hz), and 7.92 (d, 2 H, J = 7.8 Hz). Anal. Calcd for $C_{11}H_{12}N_2O_2S$: C, 55.90; H, 5.13; N, 11.86. Found: C, 55.83; H, 5.15; N, 11.81.

Irradiation of 3-Methyl-4-methylene-3-(phenylsulfonyl)-1-pyrazoline (10). A solution containing 525 mg (2.22 mmol) of 10 in 50 mL of $CHCl_3$ was irradiated with a 300-nm sunlamp for 2 h. The reaction mixture was concentrated under reduced pressure to leave behind an oily white solid. Recrystallization of this material using a $CHCl_3$–hexane mixture gave 3-methyl-4-[(phenylsulfonyl)methyl]pyrazole (11) in 86% yield: mp 169–170 °C; IR (KBr) 2910, 1290, 1135, 740, and 680 cm^{-1}; NMR ($CDCl_3$, 360 MHz) δ 2.00 (s, 3 H), 4.20 (s, 2 H), 7.29 (s, 1 H), 7.48 (t, 2 H, J = 7.6 Hz), 7.63 (t, 1 H, J = 7.6 Hz), and 7.69 (d, 2 H, J = 7.6 Hz); MS m/e 236 (M^+) and 95 (base). Anal. Calcd for $C_{11}H_{12}N_2O_2S$: C, 55.92; H, 5.12; N, 11.86. Found: C, 55.75; H, 5.03; N, 11.74.

Reaction of Diazomethane with 2,3-Bis(phenylsulfonyl)-1-propene (14). An ethereal solution (190 mL) of diazomethane was prepared from 11.1 g of Diazald and was added at 25 °C to 3.0 g (9.31 mmol) of 2,3-bis(phenylsulfonyl)-1-propene[25] (14) in 40 mL of CH_2Cl_2. After the solution was stirred at 25 °C for 18 h, 2.5 g of a white solid crystallized out of the reaction mixture. An additional 0.75 g of this same material was obtained upon concentration of the solution under reduced pressure. The structure of this solid was assigned as 3-[(phenylsulfonyl)methyl]-3-(phenylsulfonyl)-1-pyrazoline (15): mp 149–150 °C; IR (KBr) 1590, 1455, 1170, 790, 770, and 700 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 2.42 (ddd, 1 H, J = 14.7, 9.9, and 4.8 Hz), 2.65 (ddd, 1 H, J = 14.7, 9.9, and 6.3 Hz), 4.02 (d, 1 H, J = 14.5 Hz), 4.20 (d, 1 H, J = 14.5 Hz), 4.53 (ddd, 1 H, J = 18.6, 9.9, and 6.3 Hz), 4.97 (ddd, 1 H, J = 18.6, 9.9, and 4.8 Hz), 7.48–7.58 (m, 4 H), 7.65 (t, 1 H, J = 8.0 Hz), 7.73 (t, 3 H, J = 8.0 Hz), and 7.81 (d, 2 H, J = 8.0 Hz). Anal. Calcd for $C_{16}H_{16}N_2O_4S_2$: C, 52.72; H, 4.43; N, 7.69. Found: C, 52.82; H, 4.47; N, 7.66.

Treatment of 3-[(Phenylsulfonyl)methyl]-3-(phenylsulfonyl)-1-pyrazoline (15) with Sodium Hydride. To a solution containing 110 mg (0.3 mmol) of 15 in 5 mL of THF at 25 °C under N_2 was added 20 mg (2.8 equiv) of NaH. The reaction mixture was stirred at 25 °C for 1 h and was then quenched with a 10% HCl solution and extracted with $CHCl_3$. The $CHCl_3$ layer was dried over anhydrous $MgSO_4$ and concentrated under reduced pressure to give a colorless oil which crystallized on standing. Recrystallization using a $CHCl_3$–hexane mixture afforded 3-[(phenylsulfonyl)methyl]pyrazole (16) in 92% yield: mp 142–143 °C; IR (KBr) 1300, 1155, 780, 755, and 695 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 4.50 (s, 2 H), 6.30 (s, 1 H), 7.47 (t, 2 H, J = 7.5 Hz), 7.52 (d, 1 H, J = 2.0 Hz), 7.60 (t, 1 H, J = 7.5 Hz), 7.74 (d, 2 H, J = 7.5 Hz), and 10.60 (s, 1 H). Anal. Calcd for $C_{10}H_{10}N_2O_2S$: C, 54.04; H, 4.54; N, 12.60. Found: C, 53.93; H, 4.55; N, 12.52.

Reaction of 3-[(Phenylsulfonyl)methyl]-3-(phenylsulfonyl)-1-pyrazoline (15) with Methylmagnesium Bromide. To a solution containing 107 mg (0.3 mmol) of 15 in 10 mL of anhydrous THF at −78 °C under N_2 was added 0.12 mL of a 3.0 M solution of methylmagnesium bromide in ether. The reaction mixture was slowly warmed to rt and then quenched with a saturated NH_4Cl solution and extracted with $CHCl_3$. The $CHCl_3$ layer was dried over anhydrous $MgSO_4$ and concentrated under reduced pressure to leave behind a red oil which crystallized on standing. Recrystallization using an ether–hexane mixture gave 4,5-dihydro-1-methyl-3-[(phenylsulfonyl)methyl]pyrazole (17) in 90% yield: mp 115–116 °C; IR (CCl_4) 1730, 1550, 1335, 1160, and 920 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 2.63 (s, 3 H), 2.84 (t, 2 H, J = 9.2 Hz), 3.05 (t, 2 H, J = 9.2 Hz), 4.10 (s, 2 H), 7.56 (t, 2 H,

J = 7.5 Hz), 7.65 (t, 1 H, J = 7.5 Hz), and 7.83 (d, 2 H, J = 7.5 Hz); MS, m/e 238 (M^+), 125, 110, 97 (base), and 77. Anal. Calcd for $C_{11}H_{14}N_2O_2S$: C, 55.44; H, 5.93; N, 11.76. Found: C, 55.21; H, 5.75; N, 11.62.

The structure of **17** was further supported by its oxidation to 1-methyl-3[(phenylsulfonyl)methyl]pyrazole (**18**). A solution containing 40 mg (0.17 mmol) of **17** and 48 mg (1.3 equiv) of DDQ in 20 mL of methanol was stirred at 25 °C for 11 h. The reaction mixture was poured into a saturated $NaHCO_3$ solution, extracted with $CHCl_3$, and dried over anhydrous $MgSO_4$. Removal of the solvent under reduced pressure followed by silica gel chromatography left a yellow oil which crystallized on standing. Recrystallization using an ethyl acetate–hexane mixture gave 1-methyl-3-[(phenylsulfonyl)methyl]pyrazole (**18**) in 50% yield: mp 121–122 °C; IR ($CDCl_3$) 1390, 1330, 1170, and 700 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 3.80 (s, 3 H), 4.40 (s, 2 H), 6.22 (d, 1 H, J = 2.0 Hz), 7.27 (d, 1 H, J = 2.0 Hz), 7.47 (t, 2 H, J = 7.6 Hz), 7.60 (t, 1 H, J = 7.6 Hz), and 7.76 (d, 2 H, J = 7.6 Hz); MS, m/e 236 (M^+), 172, 110, and 95 (base). Anal. Calcd for $C_{11}H_{12}O_2N_2S$: C, 55.92; H, 5.12; N, 11.86. Found: C, 55.78; H, 5.04; N, 11.79.

The structure of this material was unequivocally established by comparison with an independently synthesized sample which was prepared in the following fashion. A solution containing 61 mg (0.27 mmol) of 3-[(phenylsulfonyl)methyl]pyrazole (**16**) and 19 mg (1.3 equiv) of sodium methoxide in 5 mL of THF was stirred at 25 °C for 30 min and then 0.09 mL (5.3 equiv) of iodomethane was added. The reaction mixture was stirred at 25 °C for 1 h, quenched with a 10% sulfuric acid solution, extracted with CH_2Cl_2, and dried over anhydrous $MgSO_4$. Removal of the solvent under reduced pressure followed by silica gel chromatography afforded 1-methyl-3-[(phenylsulfonyl)methyl]pyrazole (**18**) in 62% yield as a white solid which was identical in every detail with the sample of **18** obtained from the oxidation reaction.

Reaction of 3-[(Phenylsulfonyl)methyl]-3-(phenylsulfonyl)-1-pyrazoline (15) with Grignard Reagents. A solution containing 104 mg (0.29 mmol) of **15** in 10 mL of THF at −78 °C under N_2 was treated with 0.17 mL of a 2.0 M solution of *n*-butylmagnesium chloride in ether. Standard workup followed by recrystallization from a CH_2Cl_2–hexane mixture gave 4,5-dihydro-1-butyl-3-[(phenylsulfonyl)methyl]pyrazole (**19**) in 91% yield: mp 165–166 °C; IR (neat) 1700, 1330, 1150, 750, and 695 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 0.90 (t, 3 H, J = 7.3 Hz), 1.30 (t, 2 H, J = 7.3 Hz), 1.45 (t, 2 H, J = 7.3 Hz), 2.75–2.90 (m, 4 H), 3.05 (t, 2 H, J = 9.8 Hz), 4.10 (s, 2 H), and 7.50–7.95 (m, 5 H); MS, m/e 280 (M^+), 139 (base), 97, and 83. Anal. Calcd for $C_{14}N_{20}N_2O_2S$: C, 59.97; H, 7.20; N, 10.00. Found: C, 59.84; H, 7.08; N, 9.87.

A solution containing 102 mg (0.28 mmol) of **15** in 10 mL of anhydrous THF at −78 °C under N_2 was treated with 0.17 mL of a 2.0 M solution of *sec*-butylmagnesium chloride in water. Standard workup followed by recrystallization from a CH_2Cl_2–hexane mixture gave 4,5-dihydro-1-*sec*-butyl-3-[(phenylsulfonyl)-methyl]pyrazole (**20**) in 86% yield: mp 64–65 °C; IR (neat) 1755, 1600, 1395, 1335, 1165, 765, 710 cm^{-1}; NMR ($CDCl_3$, 360 MHz) δ 0.80–0.89 (m, 6 H), 1.20–1.31 (m, 1 H), 1.40–1.50 (m, 1 H), 2.80 (t, 2 H, J = 10.0 Hz), 2.89 (q, 1 H, J = 6.7 Hz), 3.07 (dt, 2 H, J = 10.0 and 4.02 Hz), 4.10 (s, 2 H), 7.53 (t, 2H, J = 7.5 Hz), 7.64 (t, 1 H, J = 7.5 Hz), and 7.85 (d, 2 H, J = 7.5 Hz); MS, m/e 280 (M^+), 139, 109, 95 and 83 (base). Anal. Calcd for $C_{14}H_{20}N_2O_2S$: C, 59.97; H, 7.20; N, 10.00. Found: C, 59.73; H, 7.12; N, 9.79.

A solution containing 105 mg (0.29 mmol) of **15** in 10 mL of anhydrous THF at −78 °C under N_2 was treated with 0.12 mL of a 3.0 M solution of phenylmagnesium bromide in ether. Standard workup followed by recrystallization from a CH_2Cl_2–hexane mixture gave 4,5-dihydro-3-[(phenylsulfonyl)methyl]-1-phenylpyrazole (**21**) in 90% yield: mp 125–126 °C; IR (CCl_4) 1615, 1510, 1345, and 1170 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 3.10 (t, 2 H, J = 10.6 Hz), 3.78 (t, 2 H, J = 10.6 Hz), 4.20 (s, 2 H), 6.80 (t, 3 H, J = 7.5 Hz), 7.20 (t, 2 H, J = 7.5 Hz), 7.52 (t, 2 H, J = 7.8 Hz), 7.64 (t, 1 H, J = 7.8 Hz), and 7.87 (d, 2 H, J = 7.8 Hz); MS, m/e 300 (M^+), 159 (base), 110, and 77. Anal. Calcd for $C_{16}H_{16}N_2O_2S$: C, 63.98; H, 5.37; N, 9.33. Found: C, 63.72; H, 5.27; N, 9.16.

A solution containing 104 mg (0.29 mmol) of **15** in 10 mL of anhydrous THF at −78 °C under N_2 was treated with 0.17 mL of a 2.0 M solution of *tert*-butylmagnesium chloride in ether. Standard workup followed by silica gel chromatography of the crude residue gave a 7:1 mixture (85%) of 4,5-dihydro-1-*tert*-butyl-3-[(phenylsulfonyl)methyl]pyrazole (**22**) and 3-[(phenylsulfonyl)methyl]pyrazole (**16**). Dihydropyrazole **22** was assigned on the basis of the following spectral data: IR (CCl_4) 1600, 1370, 1335, 1170, 745, and 700 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 0.99 (s, 9 H), 2.76 (t, 2 H, J = 9.8 Hz), 3.09 (t, 2 H, J = 9.8 Hz), 4.10 (s, 2 H), 7.51 (t, 2 H, J = 7.5 Hz), 7.60 (t, 1 H, J = 7.5 Hz), and 7.75 (d, 2 H, J = 7.5 Hz); MS, m/e 280 (M^+), 139 (base), 124 and 83. Anal. Calcd for $C_{14}H_{20}O_2N_2S$: C, 59.97; H, 7.20; N, 10.00. Found: C, 59.79; H, 7.15; N, 9.83.

Thermolysis of 3-[(Phenylsulfonyl)methyl]-3-(phenylsulfonyl)-1-pyrazoline (15). A solution containing 2.5 g (6.86 mmol) of **15** in 100 mL of toluene was heated at reflux for 15 h under N_2. Removal of the solvent under reduced pressure left a colorless oil which crystallized on standing. Recrystallization of this material from CH_2Cl_2–hexane afforded 1-[(phenylsulfonyl)methyl]-1-(phenylsulfonyl)cyclopropane (**23**) in 89% yield: mp 130–131 °C; IR (KBr) 1640, 1450, 1320, 1310, 1150, 1140, 780, 755, 725, and 690 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 1.95 (s, 2 H), 2.00 (s, 2 H), 4.23 (s, 2 H), and 7.30–7.95 (m, 10); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 16.2, 53.7, 57.2, 127.7, 128.3, 128.4, 128.7, 129.1, 129.3, 132.8, 133.5, 134.2, 139.0, 139.5, and 147.6. Anal. Calcd for $C_{16}H_{16}O_4S_2$: C, 57.12; H, 4.80; S, 19.06. Found: C, 57.05; H, 4.80; S, 18.98.

Alkylation of 1-[(Phenylsulfonyl)methyl]-1-(phenylsulfonyl)cyclopropane (23) with Iodomethane. To a solution containing 73 mg (0.22 mmol) of **23** in 5 mL of THF and 5 mL of DMPU at −78 °C under N_2 was slowly added 0.12 mL of a 1.88 M solution of *n*-butyllithium. After the reaction mixture was stirred for 30 min at −78 °C, 0.14 mL (10.4 equiv) of iodomethane was added. The solution was slowly warmed to rt, quenched with a saturated NH_4Cl solution, poured into a 10% HCl solution, and extracted with ether. The ether layer was dried over anhydrous $MgSO_4$ and concentrated under reduced pressure to give a light yellow oil which was subjected to silica gel chromatography. The major component isolated (60 mg (79%)) was a clear oil which was assigned as 1-[1-(phenylsulfonyl)ethyl]-1-(phenylsulfonyl)cyclopropane (**24**): IR (neat) 1650, 1600, 1460, 1390, 1035, 1025, 735, and 700 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 1.50 (s, 2 H), 1.60 (s, 2 H), 2.30 (d, 3 H, J = 7.0 Hz), 4.25 (q, 1 H, J = 7.0 Hz), and 7.30–7.90 (m, 10 H). Anal. Calcd for $C_{17}H_{18}S_2O_4$: C, 58.27; H, 5.18. Found: C, 58.09; H, 5.24.

The minor component isolated contained 8 mg (15%) of a clear oil which was assigned the structure of (*E*)-3-(phenylsulfonyl)-1,3-pentadiene (**25**): IR (neat) 1460, 1310, 1160, 1145, 765, 745, 710, and 695 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 1.96 (d, 3 H, J = 7.2 Hz), 5.41 (d, 1 H, J = 11.6 Hz), 5.55 (d, 1 H, J = 17.8 Hz), 6.25 (dd, 1 H, J = 17.8 and 11.6 Hz), 7.12 (q, 1 H, J = 7.2 Hz), 7.45–7.60 (m, 3 H), and 7.80–7.85 (m, 2 H); MS, m/e 208 (M^+) and 67 (base). Anal. Calcd for $C_{11}H_{12}SO_2$: C, 63.44; H, 5.81. Found: C, 63.28; H, 5.65.

Treatment of 1-[(Phenylsulfonyl)methyl]-1-(phenylsulfonyl)cyclopropane (23) with *n*-Butyllithium. To a solution containing 158 mg (0.47 mmol) of **23** in 10 mL of THF at −78 °C under N_2 was added 0.38 mL of a 1.88 M solution of *n*-butyllithium in hexane. The reaction mixture was slowly allowed to warm to rt and then was quenched with a saturated NH_4Cl solution, extracted with CH_2Cl_2, and dried over anhydrous $MgSO_4$. Removal of the solvent under reduced pressure followed by silica gel chromatography of the residue afforded a colorless oil which was recrystallized from an ethyl acetate–hexane mixture to give 5-[(phenylsulfonyl)methyl]-4-(phenylsulfonyl)-5-heptene-2-yne (**26**) (39%): mp 156–157 °C; IR (KBr) 1600, 1320, 1150, 775, 750, 705, and 690 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 1.32 (d, 3 H, J = 7.1 Hz), 1.81 (d, 3 H, J = 2.4 Hz), 4.15 (d, 1 H, J = 14.4 Hz), 4.30 (d, 1 H, J = 14.4 Hz), 5.00 (s, 1 H), 6.18 (q, 1 H, J = 7.1 Hz), and 7.49–7.91 (m, 10 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 3.71, 14.0, 56.9, 63.4, 71.0, 86.3, 119.0, 128.4, 128.5, 129.1, 129.7, 133.8, 134.0, 136.0, 138.1. and 139.9. Anal. Calcd for $C_{20}H_{20}O_4S_2$: C, 61.82; H, 5.20; S, 16.50. Found: C, 61.89; H, 5.23; S, 16.42.

Treatment of 1-[(Phenylsulfonyl)methyl]-1-(phenylsulfonyl)cyclopropane (23) with Potassium *tert*-Butoxide. To a solution containing 53 mg (0.16 mmol) of **23** in 5 mL of THF was added 22 mg (1.24 equiv) of potassium *tert*-butoxide. The reaction mixture was stirred for 30 min at rt, quenched with a saturated NH_4Cl solution, extracted with $CHCl_3$, and dried over anhydrous $MgSO_4$. Removal of the solvent under reduced

pressure followed by silica gel chromatography of the residue gave 1-(phenylsulfonyl)-2-butyne (27) (88%): IR (neat) 2255, 1600, 1400, 1320, 1135, 780, and 700 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 1.77 (t, 3 H, J = 2.5 Hz), 3.89 (q, 2 H, J = 2.5 Hz), 7.50–7.72 (m, 3 H), and 7.89–7.98 (m, 2 H). Anal. Calcd for $C_{10}H_{10}O_2S$: C, 61.84; H, 5.19. Found: C, 61.68; H, 5.07.

The structure of 27 was further established by an independent synthesis. To a solution containing 100 mg (0.51 equiv) of 1-(phenylsulfonyl)-1,2-butadiene[47] (32) in 7 mL of anhydrous THF were added 90 mg (1.07 mmol) of benzenesulfinic acid sodium salt and several drops of glacial acetic acid. The solution was heated at reflux for 2 days and then a saturated NH_4Cl solution was added. The reaction mixture was extracted with CH_2Cl_2 and then washed with water. The organic solution was dried over anhydrous $MgSO_4$. Removal of the solvent under reduced pressure left a pale yellow oil which was subjected to silica gel chromatography to give 100 mg (30%) of (*E*)-1,2-bis-(phenylsulfonyl)-2-butene (38): IR (neat) 1640, 1600, 1450, 1310, 1160, 1080, 750, and 700 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 2.05 (d, 3 H, J = 7.2 Hz), 4.25 (s, 2 H), 7.40 (q, 1 H, J = 7.2 Hz), 7.55 (m, 3 H), and 7.85 (m, 2 H).

To a stirred solution containing 100 mg (0.3 mmol) of 38 in 2 mL of THF was added 41 mg (1.23 equiv) of potassium *tert*-butoxide. The reaction was stirred for 5 min at 25 °C under N_2 and was then quenched with a saturated solution of NH_4Cl. The two layers were separated and the aqueous layer was extracted with CH_2Cl_2. The combined organic extracts were washed with water and dried over anhydrous $MgSO_4$ and the solvent was removed under reduced pressure. The crude residue was subjected to silica gel chromatography to give 68 mg (88%) of 1-(phenylsulfonyl)-2-butyne (27) which was identical in all respects to a sample of 27 prepared from the reaction of 23 with potassium *tert*-butoxide.

Treatment of 1-[(Phenylsulfonyl)methyl]-1-(phenylsulfonyl)cyclopropane (23) with Sodium Methoxide. To a solution containing 76 mg (0.23 mmol) of 23 in 10 mL of methanol was added 28 mg (2.29 equiv) of sodium methoxide dissolved in 5 mL of methanol. The reaction mixture was stirred at rt for 3.5 h and was then quenched with a saturated NH_4Cl solution. The reaction mixture was concentrated under reduced pressure and then poured into water, extracted with CH_2Cl_2, and dried over anhydrous $MgSO_4$. Concentration of the solution left a yellow oil which was subjected to silica gel chromatography to give 3-methoxy-2-(phenylsulfonyl)butene (39) as a colorless oil in 29% yield: IR (neat) 1590, 1455, 1380, 1310, 1145, 890, 760, and 695 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 1.30 (d, 3 H, J = 6.0 Hz), 2.98 (s, 3 H), 4.05 (q, 1 H, J = 6.0 Hz), 6.08 (s, 1 H), 6.48 (s, 1 H), 7.45–7.65 (m, 3 H), and 7.80–8.00 (m, 2 H); MS, m/e 211 (M − 15), 196, 142, and 125 (base). Anal. Calcd for $C_{17}H_{18}S_2O_4$: C, 58.39; H, 6.24. Found: C, 58.31; H, 6.11.

Preparation of 1,3-Bis(phenylthio)-2-(phenylsulfonyl)-butane (40). To an ice-cold solution containing 14 mg of sodium metal in 5 mL of absolute ethanol was added 0.06 mL (0.98 equiv) of thiophenol dropwise via syringe. The solution was stirred for 30 min under N_2 and then 200 mg (0.59 mmol) of 23 in 7 mL of absolute ethanol was added via syringe. The solution was allowed to warm to rt overnight and then a saturated NH_4Cl solution was added. The reaction mixture was extracted with CH_2Cl_2 and washed successively with a 10% KOH solution and water. The organic layer was collected and dried over anhydrous $MgSO_4$. Evaporation of the solvent under reduced pressure left a white solid which was recrystallized from CH_2Cl_2–hexane to give 100 mg (40%) of 1,3-bis(phenylthio)-2-(phenylsulfonyl)butane (40): mp 109–110 °C; IR (KBr) 1580, 1485, 1435, 1320, 1150, 1090, 760, and 700 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 1.58 (d, 3 H, J = 7.4 Hz), 3.16 (dd, 1 H, J = 14.2 and 9.4 Hz), 3.38 (ddd, 1 H, J = 9.4, 2.2, and 2.2 Hz), 3.46 (dd, 1 H, J = 14.2 and 2.2 Hz), 4.05 (dq, 1 H, J = 7.4 and 2.2 Hz), and 6.93–7.82 (m, 15 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 19.2, 31.4, 42.7, 67.7, 126.9, 127.4, 128.6, 128.9, 129.0, 129.1, 129.9, 132.2, 133.4, 133.8, 134.7, and 138.7. Anal. Calcd for $C_{22}H_{22}O_2S_3$: C, 63.76; H, 5.34; S, 23.17. Found: C, 63.79; H, 5.36; S, 23.14.

Preparation of (*E*)-2-(Phenylsulfonyl)-1-(phenylthio)-2-butene (41). To a solution containing 15 mg (0.9 equiv) of potassium *tert*-butoxide in 5 mL of anhydrous THF under nitrogen was added 60 mg (0.14 mmol) of 40 in 5 mL of dry THF. The mixture was allowed to stir at rt for 4 h and then a saturated solution of NH_4Cl was added. The reaction mixture was extracted with CH_2Cl_2 and washed with water. The organic layer was dried over anhydrous $MgSO_4$. Removal of the solvent under reduced pressure left a pale yellow oil which was subjected to silica gel chromatography to give 30 mg (67%) of (*E*)-2-(phenylsulfonyl)-1-(phenylthio)-2-butene (41): IR (neat) 1640, 1450, 1320, 1160, 1080, 760, and 700 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 1.62 (d, 3 H, J = 7.2 Hz), 3.83 (s, 2 H), 7.19 (q, 1 H, J = 7.2 Hz), 7.24 (br s, 5 H), and 7.50–8.02 (m, 5 H).

Preparation of Ethyl 2(*E*)-(Ethoxycarbonyl)-4-(phenylsulfonyl)-4-hexenoate (42). To an ice-cold solution containing 14 mg of sodium metal in 5 mL of absolute ethanol was added 0.091 mL (1.0 equiv) of diethyl malonate dropwise via syringe. The mixture was stirred for 30 min under N_2 and then 200 mg (0.59 mmol) of 23 in 10 mL of absolute ethanol was added via syringe. The solution was allowed to warm to rt overnight and then a saturated NH_4Cl solution was added. The reaction mixture was extracted with CH_2Cl_2 and washed with water. The organic layer was collected and dried over anhydrous $MgSO_4$. Evaporation of the solvent under reduced pressure left a pale yellow oil which was subjected to silica gel chromatography to give 100 mg (58%) of ethyl 2(*E*)-(ethoxycarbonyl)-4-(phenylsulfonyl)-4-hexenoate (42): IR (neat) 1750, 1600, 1460, 1380, 1320, 1160, 1090, 740, and 700 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 1.10 (t, 6 H, J = 7.2 Hz), 1.95 (d, 3 H, J = 7.4 Hz), 2.90 (d, 2 H J = 7.4 Hz), 3.95 (t, 1 H, J = 7.4 Hz), 4.12 (q, 2 H, J = 7.2 Hz), 4.13 (q, 2 H, 7.2 Hz), 7.05 (q, 1 H, J = 7.4 Hz), 7.60 (m, 3 H), and 7.85 (m, 2 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 13.9, 14.3, 24.8, 50.1, 61.4, 61.5, 127.9, 129.1, 133.2, 138.0, 139.2, 141.0, and 168.6. Anal. Calcd for $C_{17}H_{22}O_6S$: C, 57.61; H, 6.26. Found: C, 57.48; H, 6.15.

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(47) Cadiot, P.; Pourcelot, G. *Bull. Soc. Chim. Fr.* 1966, 3016.