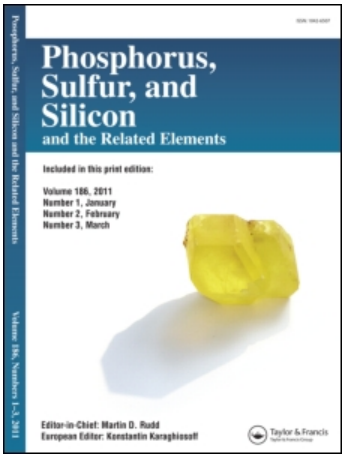

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THIOL ADDITIONS TO 1,4-DIARYLSULFONYL-2-BUTYNES. STEREOCHEMISTRY OF ADDITION AND REGIOSPECIFIC ELIMINATIONS FROM THE ADDUCTS

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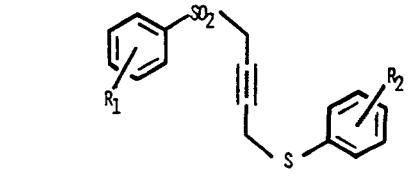
Thiol additions to 1,4-diarylsulfonyl-2-butynes result in stereoselective formation of 1,4-diarylsulfonyl-2-arylthio-2-butenes with a preponderance of the E isomer over the Z. Contrary to the behaviour of similar adducts from 1-arylsulfonyl-4-(*N'*-anilino)-2-butynes and 1-arylsulfonyl-4-arylthio-2-butynes, the vinyl sulfides obtained from the diarylsulfonylbutynes undergo facile isomerization under mild base catalysis. A regiospecific elimination followed by readdition is shown to be the mechanism for such isomerizations.

In a recent publication[1] we outlined the complete regiospecificity and high degree of stereoselectivity observed in the addition of thiols to the alkynes **1** and **2**. The vinyl sulfides **3** and **4** so obtained were also shown to be completely resistent to geometric interconversion between the E and Z isomers.



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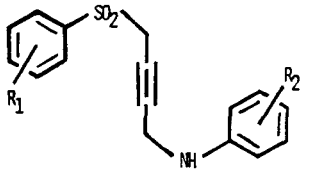

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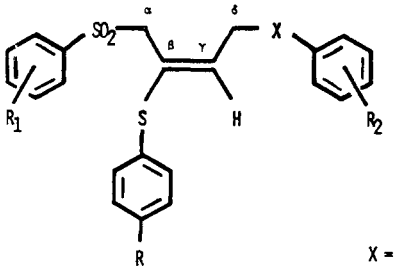

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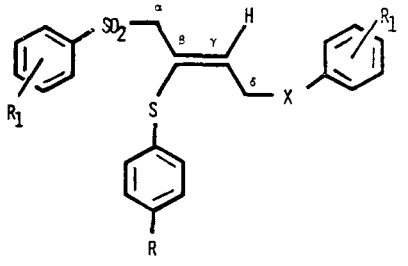
X = S OR NH



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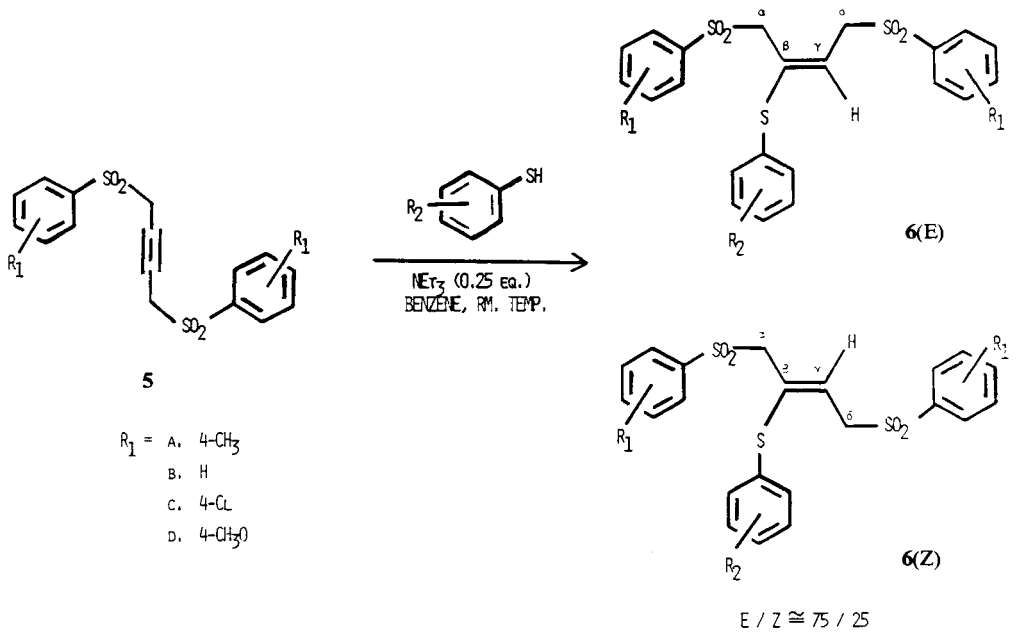
*Author to whom all correspondence should be addressed.



SCHEME 1 Stereoselective addition of thiols to 1,4-diarylsulfonyl-2-butynes 5

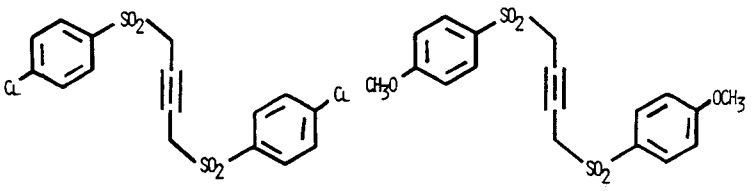
In this study, we present results of similar additions of thiols to 1,4-diarylsulfonyl-2-butynes (**5**). Owing to the inherent symmetry of the system chosen, the question of regiospecificity is obliterated; but the high degree of stereoselectivity observed earlier is found equally prominently in the vinyl sulfides **6**(E) and **6**(Z).

Despite the apparent similarity among the three systems, we have uncovered a number of disparities between the alkynes **1** and **2** on the one hand and the butyne **5** on the other. These are set out in the sequel.

Under comparable conditions, with identical substituents on the two aromatic rings (R_1=R_2=CH_3) in all the three systems **1**, **2**, and **5**, the diarylsulfonyl compounds **5** displayed far greater reactivity in the nucleophilic additions. Whereas, alkyne **1** took 6 hours to undergo completion of addition, and the butyne **2** took 10 hours, the butyne **5** required only 40 minutes for completion of reaction. This striking difference obviously arises from the increased number of acidic sites available in **5** for deprotonation and tautomerization to allene and subsequent addition of the thiol.

In support of the above suggestion, we also observed that the nature of the substituent on the arylsulfonyl moiety affected the relative rates of thiol addition. For instance, under identical conditions, the butyne **5c** required only 10 minutes for completion of addition, while compound **5d** took 2 hours and 40 minutes for complete addition of the same thiol![2] It is clear that the acidity of the proton "alpha" to the sulfone plays a crucial role in the addition of the thiol. If the addition occurred directly on the triple bond, there should be no observable differences among the variously substituted diarylsulfonyl-2-butynes. However, the marked

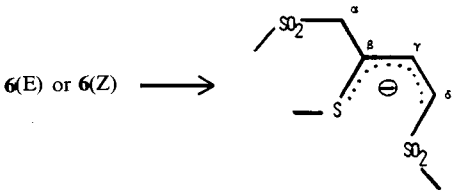
differences noted above offer support to the postulate that the addition of the thiol is to the allene and not to the alkyne.[3]



5c **5d**

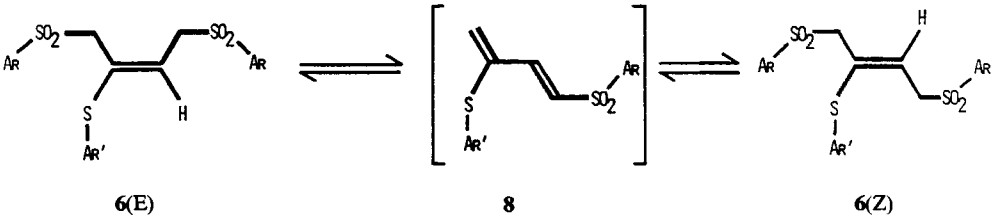
The stereoselectivity observed in the case of the diarylsulfonyl-2-butynes **5** paralleled the results obtained earlier with **1** and **2**. The ratio of **6**(E) to **6**(Z) was close to 75 : 25. (See experimental for details of assignment of geometry based on ^{13}C and ^{1}H NMR spectra.) Under the experimental conditions viz. in benzene solution, in the presence of catalytic amounts of triethylamine as base, there was no interconversion between the E and Z isomers. However, when the solvent was changed to dimethylformamide, even at room temperature and with only one-fourth equivalent of NEt_3, a very rapid equilibration occurred resulting in a ratio of E to Z = 30 : 70! Equilibrium was reached within a matter of 3 hours. Thus for the first time, among the three systems studied so far viz. **1**, **2**, and **5**, it was possible to show that the product distribution of vinyl sulfides, resulting from addition to the diarylsulfonyl butynes, was indeed kinetically controlled. It also raises the additional questions: Why do the vinyl sulfides **6**(E) and **6**(Z) isomerize so readily while their counterparts **3** and **4** fail to do so? What is a possible mechanism for such isomerization? Answers to these questions are considered in the sequel.

Examination of the common elements of the structures **3**, **4**, and **6** offers a clue that only one of the two allylic methylenes may possibly be involved in the isomerization process. The δ-methylene is uniquely different in the three cases. An anion formed at the δ-carbon in **6** has a greater measure of stabilization than an anion formed at the α-carbon (see formula **7** below).



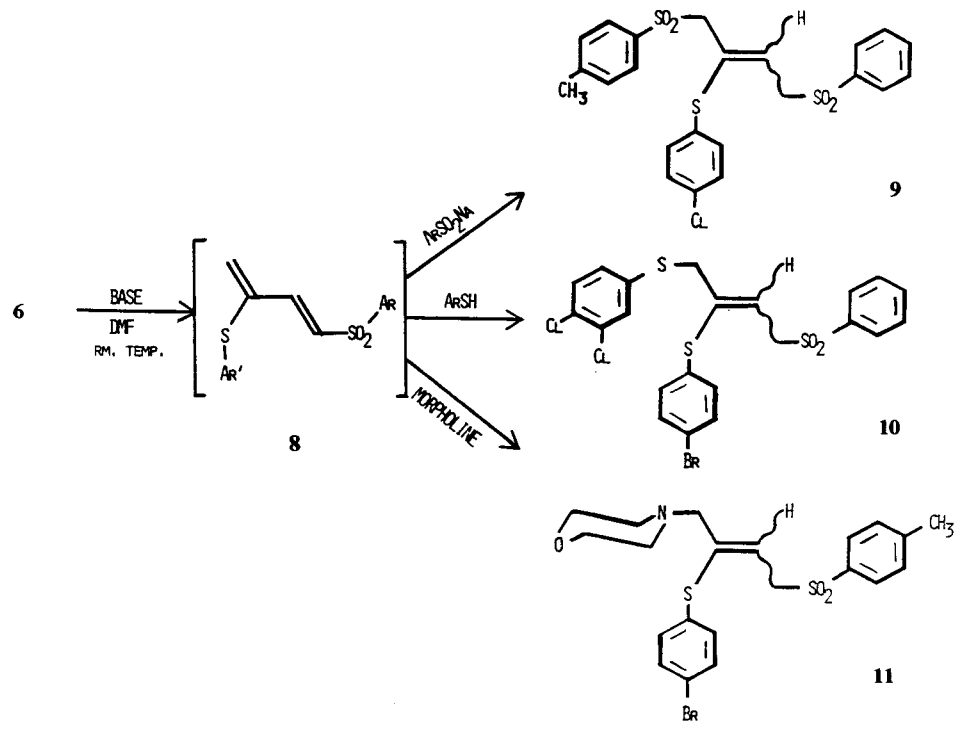
7

The added stabilization of the anion **7** by the arylthio function (in the case of **6**(E) and **6**(Z)) could induce a greater degree of delocalization, thereby lowering the bond order between the β- and γ-carbons, permitting rotation and configurational isomerization.



SCHEME 2 Isomerization via elimination-readdition

An alternative possibility is the elimination of an arylsulfinate function to yield a transient 1-arylsulfonyl-3-arylthio-1,3-butadiene (**8**) which can revert back to **6**(E) and **6**(Z) by 1,4-addition of the nucleophile. This pathway is illustrated in Scheme 2. Such a diene should then be amenable to capture by other nucleophiles just as well. Indeed, we have proven this to be so. In the presence of external arylsulfinates, arylthiolates, or even morpholine, it was possible to intercept the diene and obtain the modified butene derivatives **9**, **10**, and **11** as illustrated in the accompanying Scheme 3.



SCHEME 3 Capture of the diene **8** by nucleophiles

Irrespective of the nature of the nucleophile employed, addition to the diene **8** always led predominantly to the Z isomer. In the simple isomerization of a vinyl sulfide such as **6**, the arylsulfinate that is eliminated rejoins the parent molecule resulting in the altered isomer ratio of E to Z. We attempted to adduce further support to this possibility by conducting the base catalyzed isomerization in high dilution, in the hope the larger dilution can slow down the 1,4-addition to the diene. In the event, this proved true (see Experimental). However, numerous attempts to isolate the diene resulted only in a polymeric material being formed.[4] The capture of the diene **8** by a wide variety of other nucleophiles has amply been demonstrated in the study. Further work is in progress to devise conditions for the possible isolation of the diene and its exploitation in synthetic applications.

EXPERIMENTAL

General Comments. Nuclear magnetic resonance spectra were recorded on a Varian T-60A spectrometer using tetramethylsilane as the internal standard in $CDCl_3$ solution. Melting points were determined by using a Buchi SMP-20 capillary melting point apparatus and are uncorrected. Elemental analyses were carried out by MicAnal Laboratories, Inc., Tucson, Arizona.

The 1,4-diarylsulfonyl-2-butynes **5** were prepared by known procedures.[5] They were characterized by their spectral properties and melting points, all of which showed excellent agreement with the reported values.

The ratios of the E and Z isomers were determined by measuring the ^1H NMR spectra of aliquots collected from the reaction mixtures. (The numbers reflect the relative absorptions by the vinylic protons in each isomer.) The values are accurate within $\pm 5\%$. This was confirmed by data from the spectra of authentic mixtures containing each isomer.[6]

1,4-Diarylsulfonyl-2-arylthio-2-butenes, **6**. A mixture of triethylamine (0.76 g, 0.0075 mole) and the arene thiol (0.03 mole) in benzene (100 ml) was added, in one lot, to a vigorously stirred solution of the appropriate 1,4-diarylsulfonyl-2-butynes **5** (0.03 mole) in benzene (300 ml). This mixture was stirred at ambient temperature under nitrogen until full consumption of the starting materials was observed (10–160 minutes) by TLC analysis. The reaction mixture was diluted with benzene (500 ml), washed with water (6 × 150 ml) and dried over sodium sulfate. A small aliquot (10 ml) from the reaction mixture was evaporated; and the resulting oil was analyzed by ^1H NMR for determination of the kinetic E/Z product ratio (Table I). This aliquot was recombined with the bulk solution and the excess benzene was removed by rotary evaporation. The E isomer was isolated by diluting the chilled concentrate (30 ml benzene) with 15 ml ether and allowing the slow crystallization of the product. After complete removal of the E isomer

TABLE 1

1,4-Diarylsulfonyl-2-arylthio-2-butenes **6** from **5**

Compd. **6**	R_1	R_2	Rxn. Time (minutes)	Overall %Yield	E/Z Ratio Kinetic	E/Z Ratio Thermo
a	4-CH_3	4-Cl	40	84	78/22	30/70
b	4-CH_3	4-Br	40	85	77/23	30/70
c	4-CH_3	4-CH_3	40	84	68/32	31/69
d	4-CH_3	4-OCH_3	40	86	68/32	36/64
e	4-CH_3	3,4-Cl_2	40	89	70/30	26/74
f	H	4-Cl	40	83	77/23	29/71
g	H	4-Br	40	68	76/24	29/71
h	H	4-CH_3	40	72	70/30	34/66
i	H	4-OCH_3	40	70	70/30	34/66
j	4-Cl	4-Cl	10	80	77/23	26/74
k	4-Cl	4-OCH_3	10	80	66/34	38/62
l	4-OCH_3	4-Cl	160	85	80/20	30/70
m	4-OCH_3	4-OCH_3	180	78	75/25	38/62

TABLE 2

Physical and spectral properties of **6**

Compd. 6		MP (°C.)	Elemental Analysis %C (%H) Calculated	Found	^{1}H NMR Data (δ in $CDCl_3$, ppm) $CH_2(\alpha)$*	$CH_2(\delta)$**	$CH(\gamma)$***	other absorptions
a	E	162–163	56.92 (4.54)	56.96 (4.72)	3.86	3.96	5.60	7.7–6.95 (m, 12 H), 2.43 (s, 6 H)
	Z	123–124		56.71 (4.42)	3.68	4.15	6.05	7.9–6.68 (m, 12 H), 2.45 (s, 6 H)
b	E	164–165	52.27 (4.17)	52.39 (4.20)	3.90	4.00	5.67	7.8–7.20 (m, 12 H), 2.47 (s, 6 H)
	Z	124–125		52.26 (3.96)	3.73	4.20	6.12	7.9–6.67 (m, 12 H), 2.47 (s, 6 H)
c	E	147–148	61.73 (5.35)	61.44 (5.43)	3.80	3.90	5.50	7.8–7.10 (m, 12 H), 2.4 (s, 6 H), 2.3 (s, 3 H)
	Z	127–128		61.76 (5.35)	3.70	4.23	6.00	7.9–6.67 (m, 12 H), 2.47 (s, 6 H), 2.3 (s, 3 H)
d	E	163–164	59.76 (5.18)	59.70 (5.32)	3.80	3.90	5.30	7.8–6.70 (m, 12 H), 3.7 (s, 3 H), 2.4 (s, 6 H)
	Z	140–141		59.84 (5.21)	3.70	4.20	5.90	7.9–6.80 (m, 12 H), 3.8 (s, 3 H), 2.5 (s, 6 H)
e	E	174–175	53.33 (4.07)	53.21 (4.00)	3.88	4.00	5.75	7.8–6.80 (m, 11 H), 2.47 (s, 6 H)
	Z	112–113		53.20 (4.02)	3.77	4.20	6.17	7.9–6.45 (m, 11 H), 2.47 (s, 6 H)
f	E	136–137	55.23 (3.97)	55.33 (4.13)	3.87	4.00	5.62	7.9–6.90 (m, 14 H)
	Z	123–124		55.52 (4.06)	3.77	4.21	6.10	8.0–6.67 (m, 14 H)
g	E	129–130	50.48 (3.63)	50.68 (3.62)	3.90	4.03	5.67	7.9–6.87 (m, 14 H)
	Z	118–119		50.51 (3.64)	3.75	4.20	6.10	8.0–6.60 (m, 14 H)
h	E	136–137	60.26 (4.80)	60.45 (4.80)	3.82	3.98	5.50	7.9–6.77 (m, 14 H), 2.3 (s, 3 H)
	Z	127–128		59.94 (4.77)	3.72	4.25	6.02	8.0–6.63 (m, 14 H), 2.27 (s, 3 H)
i	E	153–154	58.23 (4.64)	58.38 (4.72)	3.83	3.98	5.33	7.9–6.67 (m, 14 H), 3.77 (s, 3 H)
	Z	130–131		58.03 (4.07)	3.75	4.20	5.90	8.0–6.70 (m, 14 H), 3.67 (s, 3 H)
j	E	184–185	48.35 (3.12)	48.09 (3.14)	3.97	4.07	5.62	7.8–6.80 (m, 12 H)
	Z	160–161		48.60 (2.88)	3.80	4.23	6.17	8.0–6.60 (m, 12 H)
k	E	165–166	50.92 (3.69)	50.82 (3.55)	3.92	4.01	5.27	7.8–6.70 (m, 12 H), 3.8 (s, 3 H)
	Z	158–159		50.61 (3.41)	3.67	4.20	5.93	8.0–6.73 (m, 12 H), 3.77 (s, 3 H)
l	E	139–140	53.53 (4.28)	53.34 (4.26)	3.87	3.95	5.63	7.9–6.90 (m, 12 H), 3.87 (s, 3 H)
	Z	131–132		53.37 (4.05)	3.70	4.17	6.08	8.0–6.60 (m, 12 H), 3.88 (s, 3 H)
m	E	174–175	56.18 (4.87)	55.88 (4.82)	3.78	3.92	5.33	7.8–6.70 (m, 12 H), 3.87 (s, 6 H), 3.78 (s, 3 H)
	Z	156–157		56.28 (4.89)	3.67	4.20	5.92	7.9–6.70 (m, 12 H), 3.87 (s, 6 H), 3.73 (s, 3 H)

*Singlet. **Doublet. ***Triplet.

by filtration, the Z isomer was crystallized by dropwise addition of pet. ether. These crude solids of **6** (70–90% overall yield) were recrystallized from benzene-pet. ether. Table II lists the physical properties of all the vinyl sulfides **6**(E) and **6**(Z) produced in this study.

The geometric assignments of the E and Z isomers of butenes **6** are secured from ^{13}C NMR spectral evidence based on similar grounds to those reported.[1] Typical ^{13}C NMR absorptions for these stereoisomers are provided by **6h**. For the E isomer, these values are: 140.6, 138.7, 138.3, 134.6, 134.2, 134.0, 130.5, 129.4, 129.0, 128.3, 126.7, 120.5, 57.6 ($^3J_{CH}$ = 8.5 Hz), 56.3 ($^2J_{CH}$ = 2.7 Hz), and 21.4. For the Z isomer, these values are: 138.9, 138.7, 138.4, 134.2, 134.0, 133.3, 132.3, 130.1, 129.5, 129.1, 128.6, 128.3, 127.4, 126.9, 60.9 ($^3J_{CH}$ = 4.9 Hz), 57.4 ($^2J_{CH}$ = 22.4 Hz), and 21.2.

Attempted Equilibration of **6b** *Under Addition Reaction Conditions.* A pure E and a pure Z sample (0.25 g, 0.0454 mmole) of compound **6b** were each stirred at room temperature in the presence of triethylamine (0.01 g, 0.0113 mmole) in benzene (10 ml). No change in the reaction mixtures was observed (by TLC analysis) after 8 hours. Each mixture was diluted with benzene (200 ml), washed with water (4 × 200 ml), dried over sodium sulfate, and evaporated. ^1H NMR analysis of the residue confirmed that the E and Z isomers did not interconvert.

Equilibration of 1,4-Diarylsulfonyl-2-arylthio-2-butenes, **6**. Samples of the pure E, pure Z, and mixtures of the two isomers of **6** were each equilibrated in dimethylformamide (DMF) using the following general procedure.

Triethylamine (0.0005 mole) and the appropriate sample of **6** (0.002 mole) were stirred in DMF (5 ml) under nitrogen at ambient temperature. After 30 minutes, 3 hours, and 17 hours, aliquots (0.5 ml) of the reaction mixture were diluted with benzene (50 ml), washed with water (5 × 30 ml), dried over sodium sulfate, and evaporated. The remaining oil was then analyzed. The E to Z ratio was determined by ^1H NMR analysis for each of these aliquots. The data showed equilibrium was reached within 3 hours in all the cases (see Table I).

The remaining reaction mixture was diluted with benzene (300 ml), washed with water (4 × 200 ml), and dried over sodium sulfate. The products crystallized as mixtures of the two isomers (70% yield) after the solution was concentrated to ca. 10 ml, chilled, and pet. ether was added. The separation of the isomers required fractional recrystallization of the E isomer from chloroform-ether solutions and the Z isomer from benzene-pet. ether. The spectral properties and the melting points of the pure solids were measured and each value agreed exactly with those compounds listed in Table II.

Treatment of **6f** *with Sodium 4-Toluenesulfinate.* A solution containing sodium 4-toluenesulfinate dihydrate (4.28 g, 0.02 mole) and acetic acid (0.90 g, 0.015 mole) in DMF and water (30 ml and 10 ml, respectively) was added, in one lot, to **6f** in DMF (2.39 g or 0.004 mole **6f** per 30 ml DMF). This mixture was stirred under nitrogen for 17 hours at room temperature. Addition of benzene (500 ml) forced the precipitation of sulfinate salts which were removed by suction filtration. The filtrate was washed with water (6 × 300 ml) and dried over sodium sulfate.

An aliquot (20 ml) was removed from the reaction mixture. Evaporation of the benzene left behind an oil, which when analyzed by ^1H NMR, showed two sets of triplets in the vinylic region, viz. at 6.05 and 5.58 ppm. The relative peak heights of these signals indicated that the Z to E ratio was 73 to 27. A peak (singlet) at 2.45 ppm (Ar—CH_3) showed that the 4-$CH_3C_6H_4SO_2$—group was incorporated to the extent of 80% into the reaction products.

The product **9**(Z) was isolated by evaporating the reaction mixture to approximately 10 ml benzene. Addition of ether (15 ml) to this chilled solution afforded relatively pure **9**(Z) (1.36 g, 55% yield). Recrystallization from benzene-pet. ether afforded an analytical sample (mp = 143–144°C.): calculated for $C_{23}H_{21}S_3O_4Cl$ gave: C, 56.10; H, 4.27. Found: C, 56.30; H, 4.12. The ^1H NMR signals for this product are δ 8.0–6.67 (m, 13 H), 6.05 (t, 1 H), 4.23 (d, 2 H), 3.72 (s, 2 H), and 2.45 (s, 3 H). Subsequent crops (0.50 g) obtained from the filtrate were composed of the E and Z isomers of **9** and **6f**. The E isomer of **9** was not isolated because of the complexity of this mixture.

Reaction of **6g** *with 3,4-Dichlorobenzenethiol.* Triethylamine (3.86 g, 0.038 mole), 3,4-dichlorobenzenethiol (4.09 g, 0.023 mole), and compound **6g** (4.0 g, 0.00765 mole) in DMF were stirred (1 hr.) under nitrogen at room temperature. This was diluted with benzene (400 ml), washed with 0.2 N KOH (4 × 250 ml), and washed with water (5 × 250 ml). After drying over sodium sulfate, a small aliquot of the reaction mixture was evaporated and analyzed by ^1H NMR (E to Z ratio was 21/79). This aliquot was recombined with the bulk solution for complete evaporation of the solvent. The oil which resulted was dissolved in ether (25 ml), chilled, and pet. ether added for crystallization of the product **10** (3.46 g, 81%) as a mixture of the E and Z isomers. Fractional recrystallization (chloroform-pet. ether) of this material by slow crystal growth at room temperature allowed for the removal of pure **10**(Z) (mp. 97.5–98°C.). The pure **10**(E) (mp. 104–105°C.) was isolated from the filtrate after removal of the Z isomer.

Support for the geometric assignments of the isomers of **10** is provided below. For **10**(E): ^{1}H NMR: δ 7.93–6.90 (m, 12 H), 5.33 (t, 1 H), 3.73 (d, 2 H), 3.47 (s, 2 H). ^{13}C NMR: ($CDCl_3$) 141.6, 138.4, 134.9, 134.7, 133.8, 132.7, 132.5, 132.4, 131.5, 130.5, 130.2, 129.2, 128.1, 123.0, 117.6, 55.9 ($^2J_{CH}$ = 2.4 Hz), and 35.3 ($^3J_{CH}$ = 8.5 Hz). Analysis calculated for $C_{22}H_{17}S_3O_2BrCl_2$: C, 47.23; H, 3.04. Found: C, 47.24; H, 3.01. For **10**(Z): ^{1}H NMR: δ 7.93–6.70 (m, 12 H), 6.07 (t, 1 H), 4.2 (d, 2 H), 3.47 (s, 2 H). ^{13}C NMR ($CDCl_3$): 139.1, 138.3, 135.1, 133.5, 132.7, 132.4, 132.0, 130.9, 130.5, 130.3, 129.1, 129.0, 127.9, 122.8, 121.8, 56.9 ($^2J_{CH}$ = 2.4 Hz), and 39.9 ($^3J_{CH}$ = 5.5 Hz). Analysis calculated for $C_{22}H_{17}S_3O_2BrCl_2$: C, 47.23; H, 3.04. Found: C, 47.34; H, 3.00.

Reaction of **6b** *with Morpholine.* Morpholine (1.27 g, 0.0146 mole) and the vinyl sulfide **6b** (4.0 g, 0.0073 mole) in DMF (30 ml) were stirred (1 hr.) under nitrogen. After the usual workup procedure in benzene solution, the solvent was stripped away by rotary evaporation. A ^{1}H NMR spectra of the resulting oil showed an absorption at 6.1 ppm (triplet) corresponding to the Z isomer of **11**. Another triplet observed at 5.67 ppm corresponded to trace amounts of unreacted **6b**. These assignments were confirmed by the selective crystallization of **6b** (0.28 g) and **11**(Z) (1.40 g, 49%) from ether-pet. ether solutions. The morpholino product was recrystallized from ether-pet. ether. The pure sample of **11**(Z) showed the following properties: mp. 70–71°C.; ^{1}H NMR; δ 7.92–6.93 (m, 8 H), 6.1 (t, 1 H), 4.23 (d, 2 H), 3.67–3.5 (m, 4 H), 2.83 (s, 2 H), 2.17 (s, 3 H), and 2.27–2.1 (m, 4 H). Analysis calculated for $C_{21}H_{24}S_2O_3NBr$: C, 52.28; H, 4.98. Found: C, 52.64; H, 4.79.

The E isomer of **11** was barely detectable by ^{1}H NMR and could not be isolated in pure form from the mixture.

Treatment of **6j** *with Triethylamine in a Dilute Solution of DMF.* Pure E and pure Z **6j** (0.54 g, 0.001 mole) were each stirred with triethylamine (0.10 g, 0.001 mole) in DMF (2000 ml) at room temperature. Aliquots (300 ml) of the reaction mixture were removed after 3, 19, and 48 hours. Each aliquot was worked up as follows: The aliquot was poured into water (one liter) and the products were extracted into ether (6 × 200 ml). The combined ether solution was washed with more water (5 × 300 ml). After concentrating the solution to about 50 ml ether, the mixture was washed again with water (3 × 50 ml) for complete removal of the DMF. The remaining ether was dried over sodium sulfate and completely evaporated. The residual oil was dissolved in $CDCl_3$ and analyzed by ^{1}H NMR.

The spectra of aliquots taken after 3 and 19 hours revealed the presence of unchanged E and Z isomers of **6j**. In addition they also showed four new signals at 6.67, 6.41, 5.90, and 5.57 ppm suggestive of the diene **8**. The 48 hour aliquot showed complete elimination of the starting material. However all attempts to isolate the diene afforded only tarry, dark oils—an experience parallelled by the reports of earlier work.[4]

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2. To our knowledge there is no available data of acidities of methylenes adjacent to an arylsulfonyl function nor of their sensitivity to the nature of the substituent on the aromatic ring. We plan to explore this aspect of our study in a more quantitative fashion in future publications.
3. This point was brought out in our earlier publication based upon the observed regiospecificity of the addition of thiols to **1** and **2** (ref. 1). Further support that **5** rearranges to the allene was demonstrated by the fact that **5** affords 1,4-diarylsulfonyl-1,3-butadienes under similar conditions (however, in the absence of ArSH). See B. S. Thyagarajan, B. F. Wood, Jr. and N. F. Swynnerton, *Phosphorus and Sulfur*, **21** 5 (1984).
4. This has been observed for sulfide- and sulfone-substituted dienes: a. A. J. Bridges and J. W. Fischer, *J. Org. Chem.*, **49**, 2954 (1984); b. B. Akermark, J. Nystrom, T. Rein, J. Backvall, P. Helquist and R. Aslanian, *Tetrahedron Lett.*, **25**, 5719 (1984); c. Although 1,3-butadien-1-yl phenyl sulfone has been described in 2 + 2 addition reactions by J. J. Eisch, J. E. Galle and L. E. Hallenback, *J. Org. Chem.*, **47**, 1610 (1982), the diene itself was not characterized as a pure entity. Instead, 1-amino-4-(phenylsulfonyl)-2-butene was employed as "a convenient, storable source of" the diene.

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6. The relative peak heights of the signals from the vinylic protons were determined at two different spectrum amplitudes (12.5 and 40). All the E/Z ratios determined from these spectra were within ±5% the "true" composition of the mixtures at sp. amp. 12.5 and within ±1% at sp. amp. 40. See below:

Authentic E/Z Ratio of Comp. **6c**	E/Z Ratios Determined from the Relative Peak Heights of Vinyl Protons			
	sp. amp. 12.5	(±error)	sp. amp. 40	(±error)
80/20	78.0/22.0	(2.0)	79.6/20.4	(0.4)
70/30	66.1/33.9	(3.9)	69.3/30.7	(0.7)
60/40	62.5/37.5	(2.5)	57.6/42.4	(2.4)
40/60	45.1/54.9	(5.1)	39.6/60.4	(0.4)
30/70	28.9/71.1	(1.1)	29.5/70.5	(0.5)
20/80	20.8/79.2	(0.8)	19.2/80.8	(0.8)