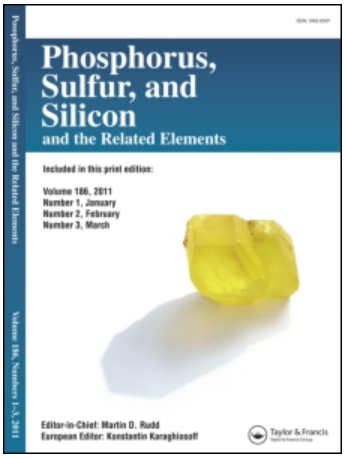

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Thiol Additions To Dissymmetrical 1,4-Diary Sulfonyl-2-Butynes Regioselectivity And Stereoselectivity

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THIOL ADDITIONS TO DISSYMMETRICAL 1,4-DIARYSULFONYL-2-BUTYNES REGIOSELECTIVITY AND STEREOSELECTIVITY.

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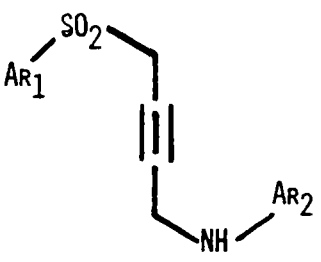
Regioselectivity is restored in the addition of thiols to 1,4-diarylsulfonyl-2-butynes based on differing electron-demands of the substituents on the aromatic rings attached to the butynyl sulfones. Kinetic control of addition leading to preponderant formation of the less stable vinyl sulfide with an E geometry is observed. Thermodynamic stability favors the Z isomer of the vinyl sulfide. The results are consistent with and confirm the rationale proposed earlier, implicating the intermediacy of an allene.

In two recent publications,[1,2] we outlined the impressive regiospecificity and high stereoselectivity observed in the base-catalyzed addition of thiols to the butynes **1**,**2**, and **3**. Of the three, the symmetrical 1,4-diarylsulfonyl-2-butynes (**3**) could only exhibit stereoselectivity but not regiospecificity owing to the symmetry of the system.

In view of this, the present study was undertaken to examine whether regiospecificity (or even regioselectivity) could be induced in such butynes, based solely on the differing electron demands of the two aromatic rings (as in structure **4**).



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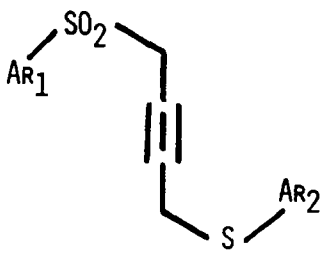

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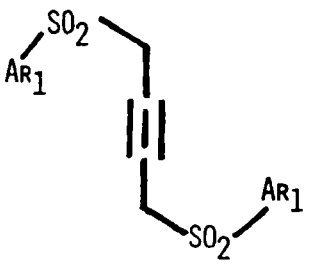

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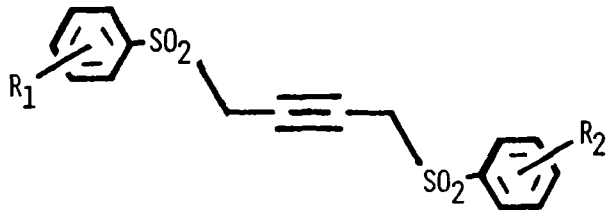

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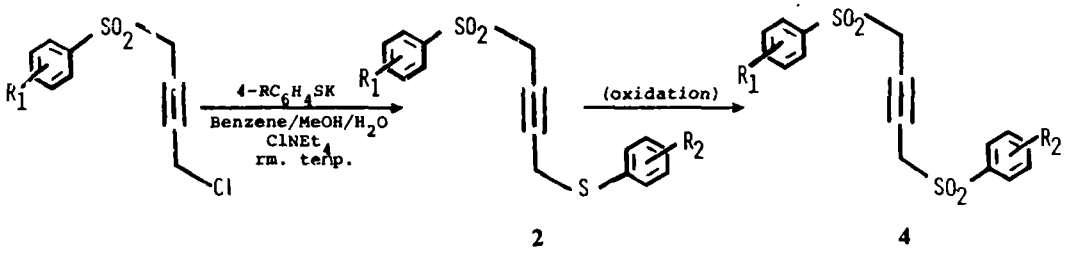
*Author to whom all correspondence should be addressed.

The basis for such an expectation rested on two features emanating from our earlier studies: 1. Thiol addition occurred exclusively at the carbon adjoining the more acidic methylenes in **1** and **2**, and 2. the relative acidities of the methylenes adjacent to the sulfones–as expressed in the relative ease of addition of thiols to **3**–were affected significantly by the substituents on the aromatic rings. In the sequel, we describe: (A) a method for the synthesis of the dissymmetrical 1,4-diarylsulfonyl-2-butynes **4**; (B) the base-catalyzed addition of thiols to such butynes; (C) the characterization of the appropriate butenes so obtained; and (D) an independent synthetic proof that would clearly and unambiguously establish the site of attachment of the vinyl sulfide.



SCHEME 1 Preparation of unsymmetrical 1,4-diarylsulfonyl-2-butynes (**4**).

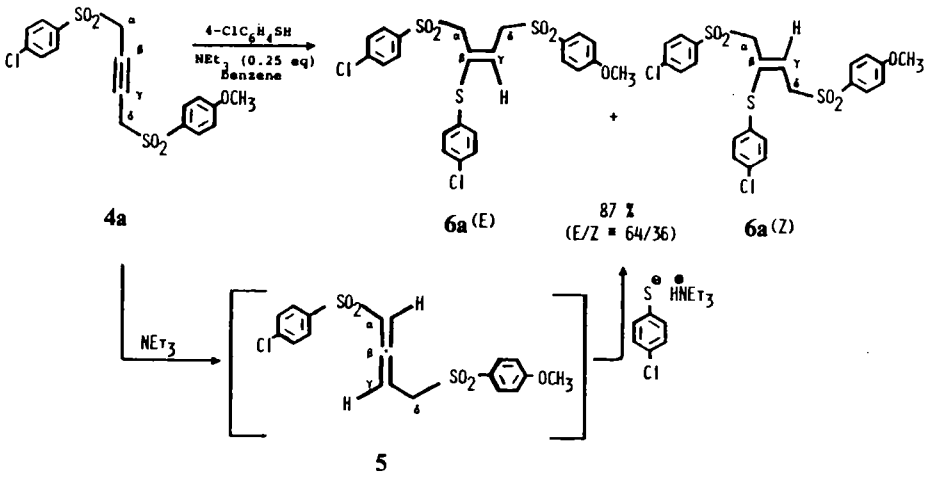
Scheme 1 describes the reaction pathway for the preparation of the starting sulfones, **4**. The numerous sulfones so obtained are listed under Table I.

In order to amplify the effect of the substituents on the aromatic rings, the specific example of **4a** is selected for discussion below. The *para* methoxy and the *para* chloro substituents on the aromatic rings could accentuate the differences in the relative acidities of the methylenes, enhancing the possibility of regiospecific forma-

TABLE I

1,4-Disubstituted-2-butynes **2** and **4**

Compd. No.	R_1	R_2	% Yld.	MP (°C.)	Analysis Fd. (Calc.) %C	%H	^{1}H NMR (δ in $CDCL_3$, ppm)
2a	4-Cl	4-OCH_3	68	65–66	55.55 (55.75)	4.15 (4.10)	7.90-6.7 (m, 8 H), 3.93 (t, 2 H), 3.8 (s, 3 H), 3.4 (t, 2 H)
2b	4-Cl	2-OCH_3	85	74–75	55.87 (55.74)	4.13 (4.10)	7.82-6.7 (m, 8 H), 3.92 (s, 5 H), 3.57 (t, 2 H)
2c	4-CH_3	2,5-Cl_2	73	97–98	52.96 (53.13)	3.57 (3.65)	7.80-6.9 (m, 7 H), 3.90 (t, 2 H), 3.58 (t, 2 H), 2.37 (s, 3 H)
2d	4-CH_3	3,4-Cl_2	85	95–96	53.13 (53.13)	3.65 (3.65)	7.90-7.0 (m, 7 H), 3.93 (t, 2 H), 3.57 (t, 2 H), 2.43 (s, 3 H)
4a	4-Cl	4-OCH_3	92	136–137	51.23 (51.26)	3.61 (3.77)	8.0-6.9 (m, 8 H), 3.93 (s, 3 H), 3.92 (s, 4 H)
4b	4-Cl	2-OCH_3	89	132–133	51.09 (51.26)	3.76 (3.77)	7.9-6.9 (m, 8 H), 4.2 (t, 2 H), 3.97 (s, 3 H), 3.83 (t, 2 H)
4c	4-CH_3	2,5-Cl_2	89	114–115	48.96 (49.03)	3.30 (3.37)	8.0-7.2 (m, 7 H), 4.28 (t, 2 H), 3.83 (t, 2 H), 2.47 (s, 3 H)
4d	4-CH_3	3,4-Cl_2	92	141–142	48.92 (49.03)	3.28 (3.37)	8.0-7.2 (m, 7 H), 3.97 (br. s., 4 H), 2.45 (s, 3 H)

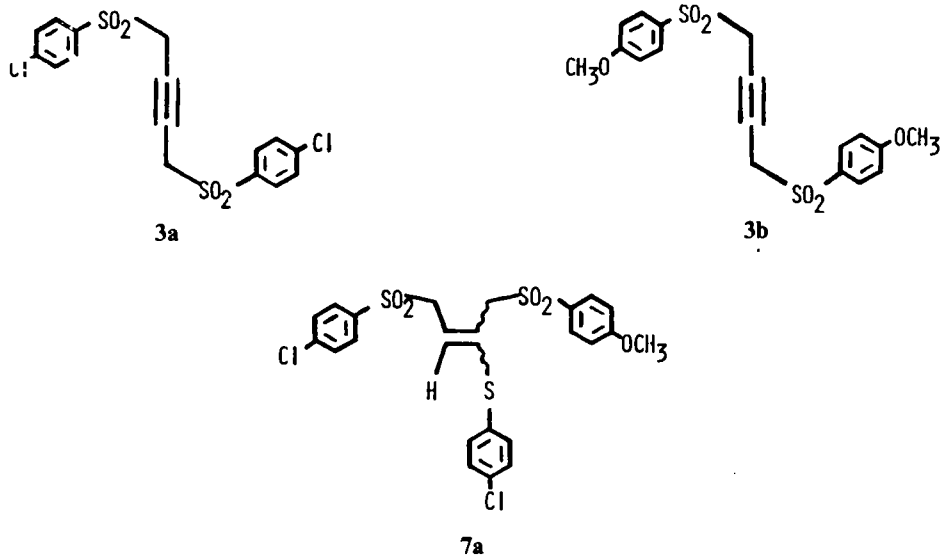


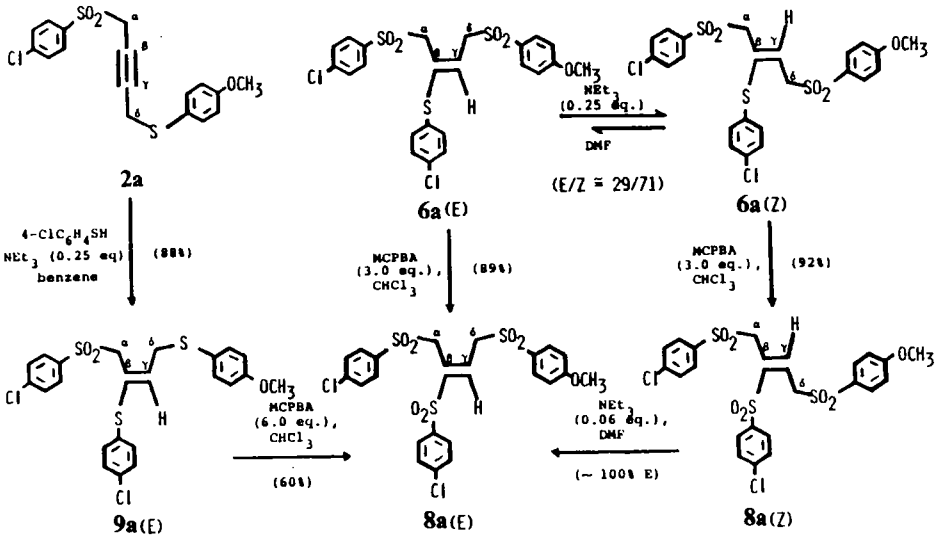
SCHEME 2 Addition of 4-chlorobenzenethiol to butyne **4a**.

tion of the allene, **5**, and consequently, promoting regiospecific addition of the thiol to **4a** at the β-carbon (see Scheme 2).

The results obtained earlier[2] with the symmetrical disulfones, **3a** and **3b**, suggested that thiol addition to **4a** would occur more readily at the β-carbon rather than at the γ-carbon.

When the butyne **4a** was treated with one equivalent of *p*-chlorobenzenethiol and one-fourth equivalent of triethylamine in benzene solution at room temperature, the corresponding butenes, **6a**(E) and **6a**(Z), were obtained in a combined yield of 87%. That these products did indeed conform to structure **6a** and not to structure **7a** was established by the sequence of reactions shown in Scheme 3.

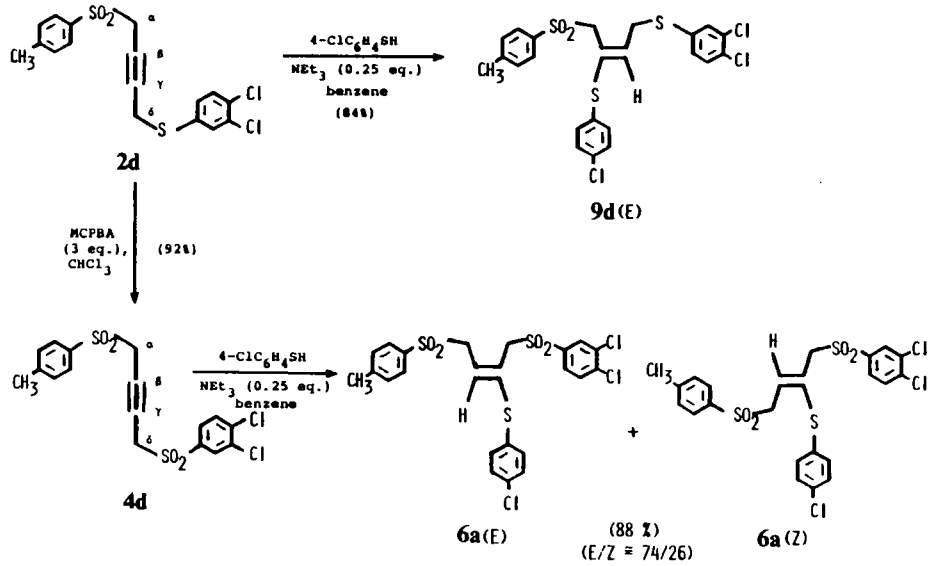




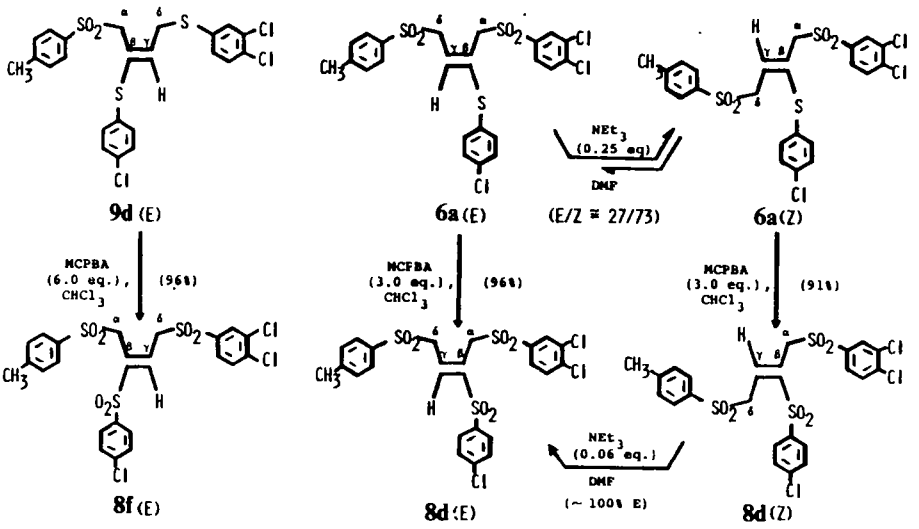
SCHEME3 Identity relationship among the trisulfones secured from vinyl sulfides of different origin.

The vinyl sulfides, **6a**(E) and **6a**(Z), were readily oxidized to the trisulfones, **8a**(E) and **8a**(Z), under mild conditions using *meta*-chloroperoxybenzoic acid (MCPBA). Independently, the same trisulfone, **8a**(E), was obtained: (a) by isomerizing trisulfone **8a**(Z) and (b) by adding the thiol to the butyne **2a**, followed by oxidation of the vinyl sulfide **9a**.

The case of the disulfone **4a** provides identical trisulfones from the two different approaches, because the sequence of reactions were so chosen as to emphasize this



SCHEME 4 Addition of 4-Chlorobenzenethiol to butynes **2d** and **4d**.



SCHEME 5 Nonidentity in trisulfones secured from vinyl sulfides of different origin.

feature. Both at the stage of the butyne **2a** and at the disulfone **4a** stage, addition occurs at the same carbon center – this being adjacent to the more acidic methylene. We have also examined and present below, another case of a dissymmetrical disulfone, **4d**, where the two trisulfones obtainable through the above pathways *do not have to be* and *are not* identical. Such a system is illustrated in Scheme 4.

In this series, at the stage of the monosulfone (**2d**), the more acidic site is the α-carbon. At that stage, addition of thiol occurs at the β-carbon. However, at the stage of the disulfone (**4d**) the more acidic site shifts to the δ-carbon, owing to its attachment to the dihaloarylsulfone. Addition at this stage is shifted to the γ-carbon. Thus the trisulfones from each stage (see Scheme 5) are not identical (as one would expect).

This example illustrates that when the aromatic substitution changes so as to alter the acidity of the methylenes adjacent to the sulfones,[3] regiospecificity also changes correspondingly reflecting addition adjacent to the more acidic methylene. Additional examples of this same phenomenon are described in the Experimental.

EXPERIMENTAL

General Comments. Melting points were determined by using a Buchi SMP-20 Capillary melting point apparatus and are uncorrected. Nuclear magnetic resonance spectra were recorded on a Varian T-60A spectrometer, using tetramethylsilane as the internal standard in $CDCL_3$ solution. Infrared spectra (KBr) were measured on a Beckman 4220 spectrophotometer. Elemental analyses were determined by MicAnal Laboratories, Inc. of Tucson, Arizona.

The E to Z ratios of butenes **6**, determined by measuring the ^1H NMR absorptions of the vinylic protons in each isomer, reflect the distribution of the two products in aliquots collected from the reaction mixtures.[2]

1-Arylsulfonyl-4-arylthio-2-butynes, **2a–2d**. The preparation of butynes **2a** and **2b** from 1-(4′-chlorobenzenesulfonyl)-4-chloro-2-butyne[4] and butynes **2c** and **2d** from 1-chloro-4-(4′-methylbenzenesulfonyl)-2-butyne[4] employed the general procedure outlined in our previous study.[1] Table I lists the compounds obtained in this study.

Oxidation of Butynes **2a** *and* **2b** *to* **4a** *and* **4b**. The butynes **2a** and **2b** (7.0 g., 0.019 mole) were oxidized by 30% H_2O_2 (35ml) in a gently refluxed (5 hours) mixture of acetic acid and ether (110 ml and 85 ml, respectively). The dissymmetrical sulfones **4a** and **4b** were precipitated by pouring the reaction mixture over ice (one liter). The solids were collected by suction filtration, washed with water (two liters), and then dried *in vacuo* for 24 hours. The products (ca. 90% yield) were recrystallized from chloroform/ether/pet. ether solutions (see Table I).

Oxidation of Butynes **2c** *and* **2d** *to* **4c** *and* **4d**. The butynes, **2c** and **2d**, (7.68 g each, 0.02 mole) and 80% MCPBA (12.9 g) in chloroform (150 ml) were stirred for 4 hours at room temperature. The reaction mixtures were then diluted with chloroform (500 ml), washed with saturated aqueous potassium carbonate solution (5 × 300 ml), and then washed with water (5 × 300ml). The excess chloroform was removed by evaporation. Addition of ether (30 ml), followed by dropwise addition of pet. ether, to the chilled concentrate (20 ml $CHCL_3$) caused the crystallization of the product. The dissymmetrical sulfones, **4c** and **4d**, isolated (ca. 90% yield) by filtration, were recrystallized from chloroform/ether/pet. ether. Table I lists all the sulfones **4** produced in this study.

Addition of 4-Chlorobenzenethiol to the Dissymmetrical Sulfones, **4a–d**, *to form Butenes* **6a–d**. Triethylamine (0.25 g, 0.0025 mole) and 4-chlorobenzenethiol (1.45 g, 0.01 mole) in benzene (60 ml) were added, in one lot, to a mixture of the appropriate dissymmetrical sulfone, **4**, in benzene (100 ml). This mixture was stirred at ambient temperature under nitrogen until full consumption of the starting materials was observed (3–30 minutes) by TLC analysis (eluting solvent: benzene/ether (8:2)). The reaction mixture was diluted with benzene (400 ml), washed with water (6 × 150ml), and dried over sodium sulfate. An aliquot (10 ml) from the reaction mixture was evaporated; and the residue was analyzed by ^1H NMR for determination of the E to Z product ratio (Table II). This aliquot was recombined with the bulk solution and the excess benzene was removed by rotary evaporation. Ether (15 ml) was added to the chilled concentrate (30 ml benzene), causing the products, **6**, to crystallize as mixtures of the two isomers (80-90% overall yield). The E isomer was separated from the Z isomer by fractional recrystallization from chloroform/ether/pet. ether solutions. After complete removal of the E isomer by filtration, the Z isomer was isolated from the filtrate by dropwise addition of more pet. ether. These crude solids of **6** were further purified by recrystallization from benzene/pet. ether, giving the pure E and Z isomer samples whose physical properties are listed in Table III.

The stereochemical assignments of the E and Z isomers of butenes **6** were made on the same basis as used in the case of the vinyl sulfides derived from *symmetrical* 1,4-diarylsulfonyl-2-butynes.[2]. The ^1H NMR data are listed in Table III. The vinylic proton absorption for the E isomer occurs upfield relative to that of the Z isomer in every case – consistent with our earlier deductions, as well as related examples from the literature.[5]

Equilibration of the 1,4-Diarylsulfonyl-2(4'-chlorobenzenethio)-2-butenes, **6**. Samples of the pure E and pure Z isomers of **6** were each equilibrated in dimethylformamide (DMF) using the following general procedure. The equilibrium ratios (listed in Table II) were confirmed by approaching it from both directions.

The appropriate sample of butene **6** (0.002 Mole) and triethylamine (0.056 g., 0.0005 mole) were stirred for 3 hours in DMF (25 ml) under nitrogen at ambient temperature. The reaction mixture was diluted with benzene (150 ml), washed with water (6 × 100 ml), and dried over Na_2SO_4. The E to Z ratio of butene **6** was determined by measuring the ^1H NMR spectra of an aliquot (10 ml) collected from the reaction mixture. The isomers were isolated as solid mixtures (ca. 70% overall yield) from the remaining reaction mixture after concentration to 10 ml benzene and addition of pet. ether to the chilled concentrate. The Z isomer was separated from the E isomer by fractional recrystallization from chloroform/benzene/pet. ether solutions. The melting points and spectral properties of the pure solids agreed exactly with those of the compounds listed in Table III.

TABLE II

Preparation of **6** from **4**

Compd. No. **6**	R_1	R_2	Rxn. Time (minutes)	% Yld.	E/ZRatio kinetic	thermo.
a	4-Cl	4-OCH_3	20	87	64/36	29/71
b	4-Cl	2-OCH_3	30	83	82/18	27/73
c	2,5-Cl_2	4-CH_3	3	80	78/22	24/76
d	3,4-Cl_2	4-CH_3	5	88	74/26	27/73

TABLE III

Physical and spectral properties of butenes **6**

Compd. No. **6**	R_1	R_2		MP (°C.)	Analysis %C(%H) Calc.	FD.	^{1} NMR Data (δ in $CDCl_3$, ppm) $CH_2(\alpha)$*	$CH_2(\gamma)$**	$CH_2(\delta)$***	other
a	4-Cl	4-OCH_3	E	181–182	50.92 (3.69)	50.48 (3.57)	3.92	5.67	4.00	7.83-6.80 (m, 12 H), 3.87 (s, 3 H)
			Z	126–127		50.96 (3.73)	3.75	6.13	4.18	7.95-6.68 (m, 12 H), 3.88 (s, 3 H)
b	4-Cl	2-OCH_3	E	111–112	50.92 (3.69)	51.15 (3.61)	4.07	5.85	4.33	7.97-6.77 (m, 12 H), 4.00 (s, 3 H)
			Z	179–180		50.82 (3.61)	3.73	6.10	4.47	7.97-6.70 (m, 12H), 3.90 (s, 3 H)
d	2,5-Cl_2	4-CH_3	E	130–131	49.29 (3.39)	49.27 (3.35)	4.23	5.73	4.10	7.90-6.97 (m, 11 H), 2.45 (s, 3 H)
			Z	141–142		49.62 (3.38)	4.12	6.20	4.17	8.00-6.73 (m, 11 H), 2.45 (s, 3 H)
e	3,4-Cl_2	4-CH_3	E	160–161	49.29 (3.39)	49.11 (3.30)	3.98	5.67	4.07	7.80-6.87 (m, 11 H), 2.47 (s, 3 H)
			Z	155–156		49.15 (3.42)	3.76	6.13	4.17	7.90-6.67 (m, 11H), 2.47 (s, 3 H)

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

TABLE IV

Trisulfones **8**

Compd. No. **8**	R_1	R_2		% Yld.	MP (°C.)	Analysis %C(%H) Calc.	Fd.	^{1}H NMR Data (δ in $CDCl_3$, ppm) $CH_2(\alpha)$*	$CH_2(\delta)$**	other
a	4-Cl	4-OCH_3	E	89	174–175	48.08 (3.48)	47.72 (3.36)	4.05	4.33	7.8-6.8 (m, 13 H), 3.83 (s, 3 H))
			Z	92	171–172		48.05 (3.33)	4.07	4.60	8.0-6.8 (m, 13 H), 3.87 (s, 3 H))
b	4-Cl	2-OCH_3	E	76	154–155	48.08 (3.48)	48.05 (3.39)	4.17	4.63	7.9-6.8 (m, 13 H), 4.00 (s, 3 H)
			Z	85	98–99		48.07 (3.45)	4.02	4.90	8.0-6.8 (m,13 H), 4.00 (s, 3 H)
c	2,5-Cl_2	4-CH_3	E	98	198–199	46.62 (3.21)	46.45 (3.05)	4.33	4.37	7.8-7.1 (m, 12 H), 2.45 (s, 3 H)
			Z	96	149–150		46.52 (3.14)	4.35	4.61	7.8-7.2 (m, 11 H), 6.88 (t, 1 H), 2.47 (s, 3 H)
d	3.4-Cl_2	4-CH_3	E	96	210–211	46.62 (3.21)	46.48 (3.10)	4.10	4.36	7.8-7.2 (m, 11 H), 7.13 (t, 1 H), 2.45 (s, 3 H)
			Z	91	161–162		46.39 (3.09)	4.10	4.60	7.8-7.2 (m, 11 H), 6.95 (t, 1 H), 2.47 (s, 3 H)
e	4-CH_3	2,5-Cl_2	E	73	142–143	46.62 (3.21)	46.61 (3.21)	4.18	4.67	8.0-7.2 (m, 11 H), 7.13 (t, 1 H), 2.43 (s, 3 H)
f	4-CH_3	3,4-Cl_2	E	96	189–190	46.62 (3.21)	46.31 (3.10)	4.13	4.40	7.9-7.2 (m, 11 H), 7.13 (t, 1 H), 2.47 (s, 3 H)

*Singlet. **Doublet.

TABLE V

Physical and Spectral Properties of Butenes **9**

Compd. No. **9**	R_1	R_2	% Yld.	MP (°C.)	Analysis %C(%H) Calc.	Fd.	^{1}H NMR Data (δ in $CDCL_3$, ppm) $CH_2(\alpha)$*	$CH(\gamma)$**	$CH_2(\delta)$***	other
a	4-Cl	4-OCH_3	88	122–123	54.12 (3.92)	54.22 (3.78)	3.57	6.07	3.43	7.8-6.68(m, 12 H), 3.77 (s, 3 H)
b	4-Cl	2-OCH_3	79	99–100	54.12 (3.92)	53.93 (3.97)	3.70	6.10	3.53	7.8-6.50 (m, 12 H), 3.87 (s, 3 H)
c	4-CH_3	2,5-Cl_2	86	103–104	52.27 (3.60)	52.16 (3.55)	3.83	5.91	3.50	7.8-6.83 (m, 11 H), 2.43 (s, 3 H)
d	4-CH_3	3,4-Cl_2	84	119–120	52.27 (3.60)	52.28 (3.49)	3.83	5.97	3.57	7.8-6.83 (m, 11 H), 2.46 (s, 3 H)

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

Oxidation of the Butenes **6a–6d** *to the Trisulfones* **8a-8d**. Pure E and pure Z samples of the compounds **6a–6d** were each oxidized to the respective trisulfone, **8**(E) and **8**(Z) by using the following procedure.

A mixture of the butene (**6**, 0.003 mole) and 80% MCPBA (0.006 mole) in chloroform (25 ml) was stirred at room temperature for 3 hours. The reaction mixture was diluted with ether (100 ml), chilled, and pet. ether added dropwise, causing the crystallization of the trisulfone **8**. The solid (76–98% yield) was collected by suction filtration and then recrystallized from chloroform/pet. ether solutions. The physical properties and ^{1}H NMR spectral data of the trisulfones **8** are listed in Table IV.

(E)-1-Arylsulfonyl-2,4-diarylthio-2-butenes **9a–9d**. These compounds were synthesized and characterized by procedures described in our earlier publication.[1] Their spectral data and physical constants are given under Table V.

Oxidation of the Vinyl Sulfides **9a–9d** *to the Trisulfones* **8a**, **8b**, **8e**, *and* **8f**. A mixture of the butene **9**(E) (0.002 mole) and 80% MCPBA (2.58 g, 0.012 mole) in chloroform (25 ml) was stirred for 3 hours at room temperature. Crystallization of the trisulfone was effected by diluting the reaction mixture with ether (100 ml), chilling, and dropwise addition of pet. ether.

The trisulfones **8a** and **8b** were isolated in 60% and 51% yield, respectively. The melting points, mixed melting points, and ^{1}H NMR spectral data for these solids were identical with those for the products obtained from oxidation of **6a**(E) and **6a**(Z) (*vide supra*). The trisulfones obtained from both approaches gave superimposable infrared spectra.

The physical properties and the ^{1}H NMR spectral data (Table IV) for the trisulfones **8e** and **8f**, were completely different from those for the trisulfones **8c** and **8d**. Melting point analyses of mixtures containing **8d** and **8f** (and mixtures of **8c** and **8e**) were depressed and broadened. The ^{1}H NMR spectra of all these butenes *were non-superimposable*. The infrared absorptions listed below characterize differences observed in the trisulfones (**8c**, **8d**, **8e**, and **8f**). For **8c**(E): IR (KBr) 1212, 1038, 990, 842, 630, and 610 cm^{-1}. For **8c**(Z): IR (KBr) 1200, 1130, 1010, 895, 730, and 530 cm^{-1}. For **8d**(E): IR (KBr) 818, 675, 650, 630, 600, and 570 cm^{-1}. For **8d**(Z): IR (KBr) 1195, and 710 cm^{-1}. For **8e**(E): IR (KBr) 1058, 1026, 888, and 543 cm^{-1}. For **8f**(E): 850, 807, 665, 625, and 592 cm^{-1}.

Isomerization of the Z Isomers of Trisulfones **8** *to the E Isomers*. Samples of the pure E and pure Z trisulfones, **8**, were reacted as follows:

The trisulfone (**8**, 0.5 mmole) and triethylamine (0.03 mmole) in DMF (5 ml) were stirred (10 minutes) at room temperature under nitrogen. The reaction mixture was diluted with chloroform (50 ml), washed with water (8 × 30 ml), and dried over sodium sulfate. Proton NMR analysis of an aliquot (15 ml) of the reaction mixture showed only the absorptions consistent with the E isomer of **8**. In all cases, the Z isomer converted completely to the E isomer, while the E isomer remained unaffected. The residual mixture was concentrated to 10 ml chloroform, chilled, and diluted with ether (20 ml), causing the crystallization of the trisulfone. The product was isolated by filtration. Melting point and mixed melting point analyses of the pure samples confirmed the identity of the trisulfones, **8**.

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