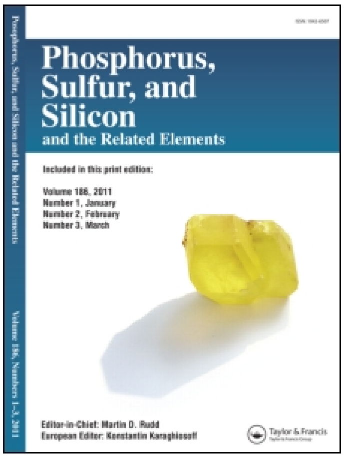

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DICHOTOMY IN THE ISOMERIZATIONS OF 1-ARYLSULFONYL-3-ARYLTHIO-2-BUTENES AND DERIVATIVES THEREOF

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DICHOTOMY IN THE ISOMERIZATIONS OF 1-ARYLSULFONYL-3-ARYLTHIO-2-BUTENES AND DERIVATIVES THEREOF

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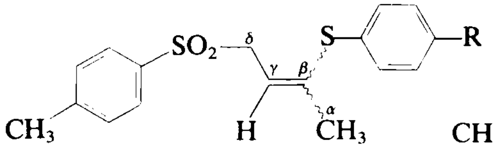
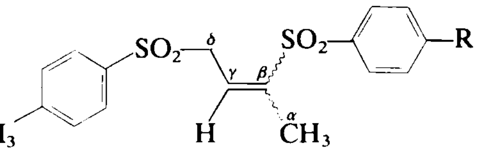
A dichotomy in the mechanism for the isomerizations of the title compounds is described. An elimination-readdition pathway promotes isomerization of 1,4-diarylsulfonyl-2-arylthio-2-butenes and 1,2,4-triarylthio-2-butenes. However, 1-arylsulfonyl-3-arylthio-2-butenes and 1,3-diarylsulfonyl-2-butenes require stronger bases and more polar solvents for isomerization and occur without any eliminations.

In a recent publication[1] we described the stereo-selective addition of arene thiols to 1,4-diarylsulfonyl-2-butynes (**1**) and the unusual equilibration of the vinyl sulfides (**2**(*E*) and **2**(*Z*)) by an elimination-readdition mechanism. (*Vide infra.*) In order to elucidate the importance of this pathway for geometric isomerization of the vinyl sulfides, we have extended our studies to include the 1-arylsulfonyl-3-arylthio-2-butenes (**4**) and the 1,3-diarylsulfonyl-2-butenes (**5**).



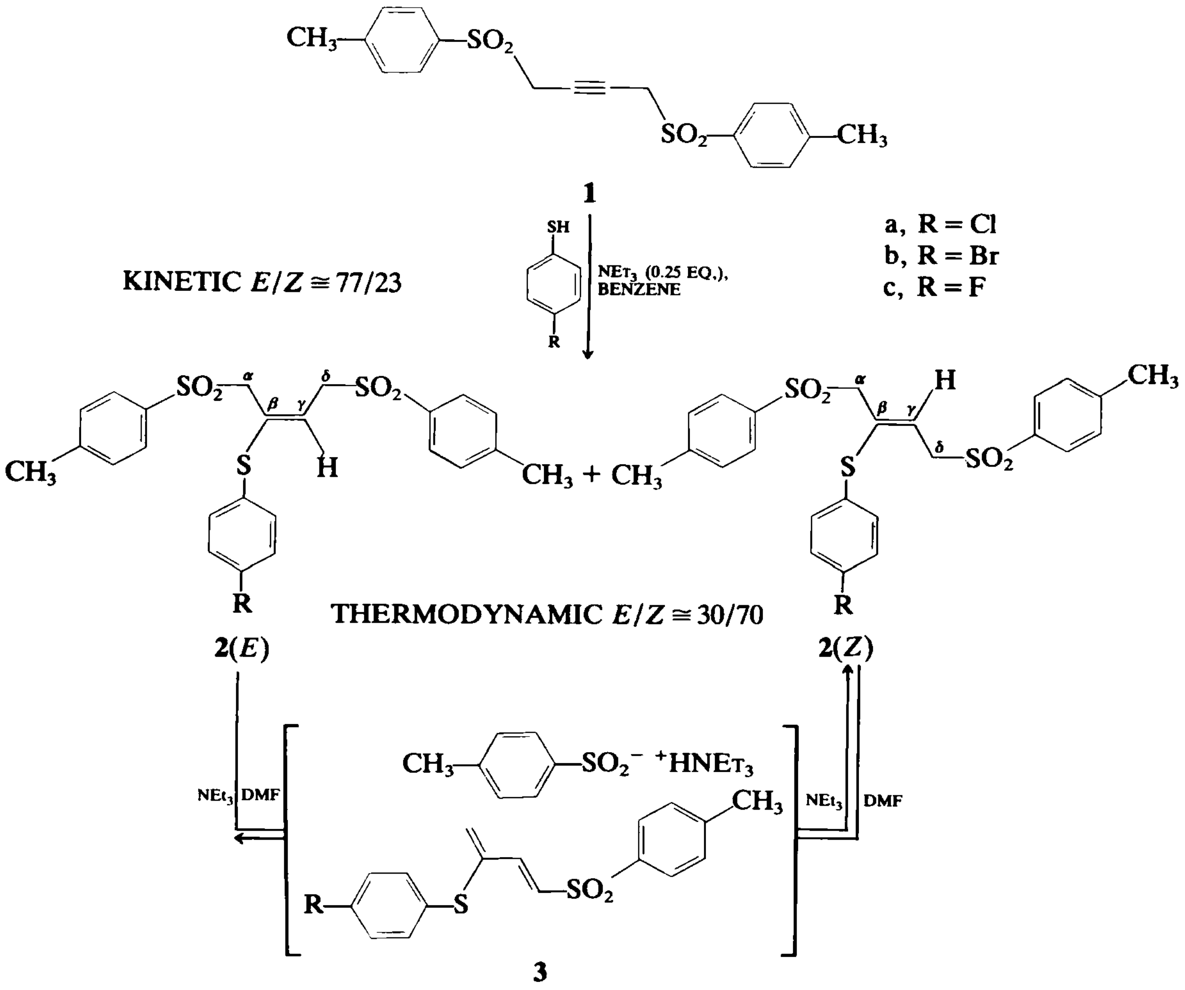
4
a, R = Cl
b, R = Br
c, R = F



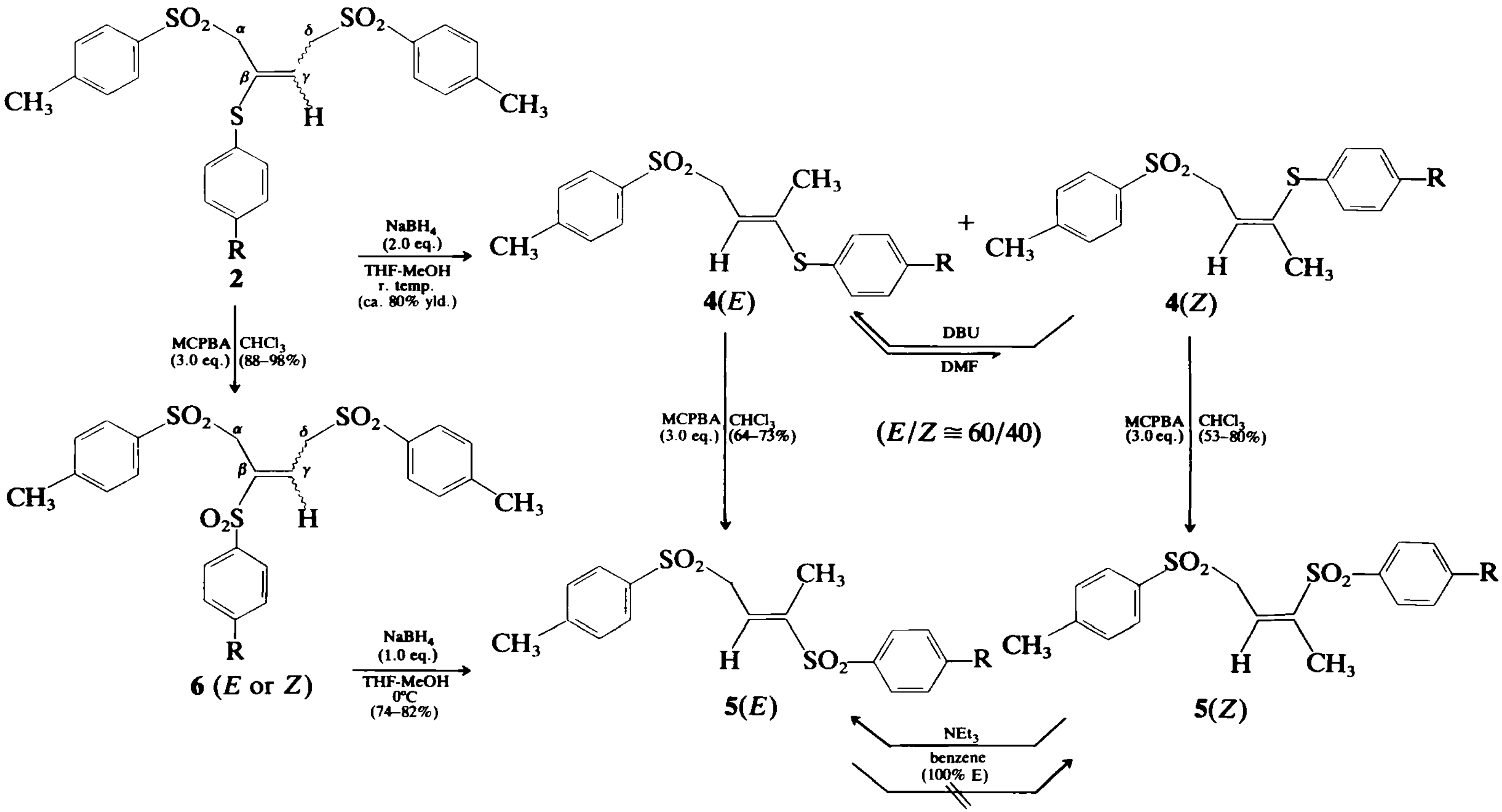
5
a, R = Cl
b, R = Br
c, R = F

These butenes, unlike **2**(*E*) and **2**(*Z*), lack the eliminatable group at the α-carbon. We present below a number of interesting features in the synthesis as well as the thermodynamic stabilities of the configurational isomers of **4** and **5**. The reaction sequence for obtaining all the four isomers of the two butenes is shown under Scheme 2.

While the geometric integrity of **2**(*E*) and **2**(*Z*) was preserved in their respective oxidations to **6**(*E*) and **6**(*Z*), such was not the case at the borohydride reduction stages.[2] Both **2**(*E*) and **2**(*Z*) (or even a mixture of the two) gave predominantly the *Z* isomer of butene **4**. The trisulfones **6**, on the other hand, gave **5**(*E*) (as well as trace quantities of an overreduction product—See Experimental).



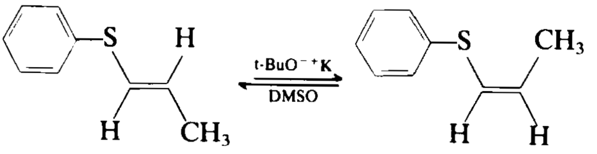
SCHEME 1: Synthesis of and Equilibrations Between Butenes 2(*E*) and 2(*Z*).



SCHEME 2: Equilibrations in Butenes 4 and 5.

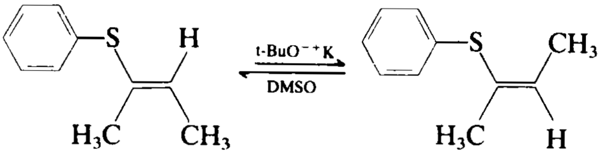
VINYL SULFIDES

Several striking differences are observed in the configurational stabilities of the vinyl sulfides **2**(*E*), **2**(*Z*), **4**(*E*), and **4**(*Z*) on the one hand and the vinyl sulfones **5** and **6** on the other. Of the four vinyl sulfides, none showed any tendency to isomerize when reacted with triethylamine in benzene solution at ambient temperatures. However, when reacted with the same base but in dimethylformamide (DMF) solutions, **2**(*E*) and **2**(*Z*) readily converted to an equilibrium mixture[1] of $E/Z = 30/70$. The sulfides **4**(*E*) and **4**(*Z*), in contrast, were resistant to isomerization even with the change in solvent. But when a slightly stronger base like DBU was employed in DMF solution, they readily isomerized to an equilibrium composition of $E/Z = 60/40$. Thus the subtle differences noticed among **2** and **4** point up the greater ease in equilibrations of **2** through the elimination-readdition pathway. This becomes particularly relevant in the light of the observation by Sataty and Meyers[3] who reported that the following equilibrations required the use of t.BuOK in DMSO.



7(*E*) **7**(*Z*)

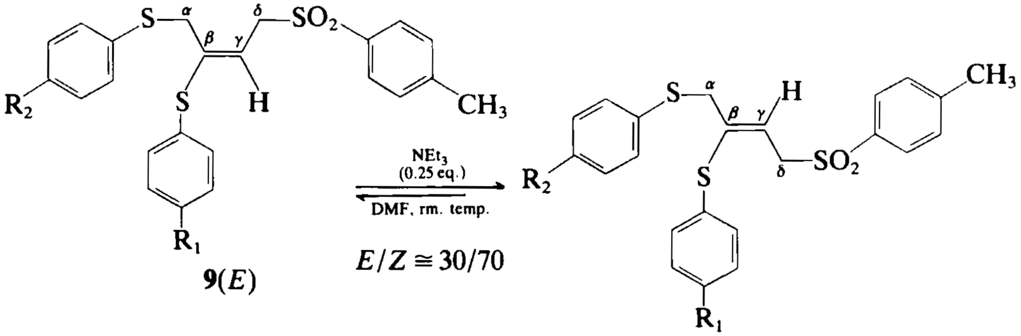
$E/Z = 52/48$



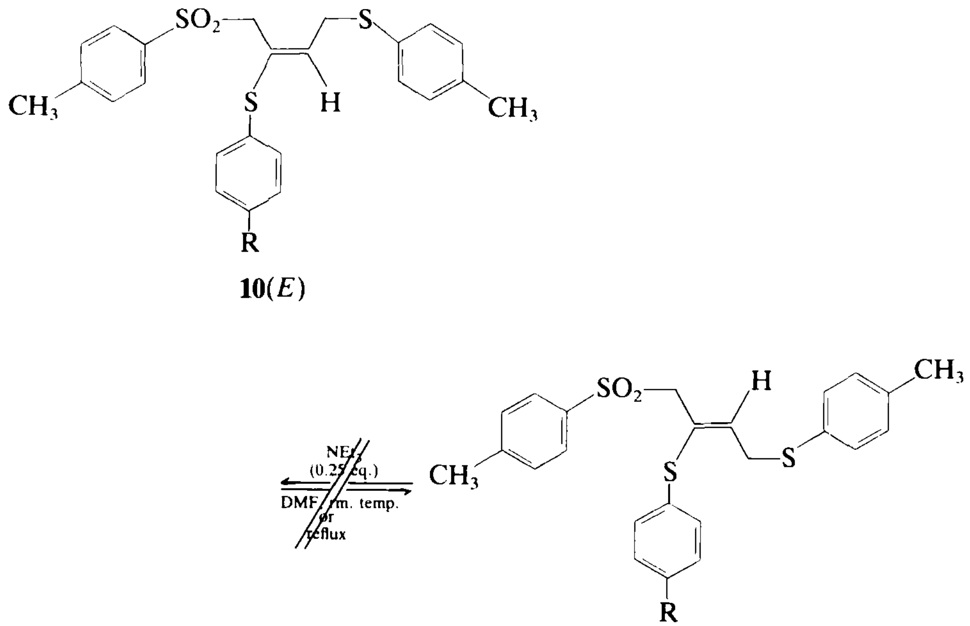
8(*E*) **8**(*Z*)

$E/Z = 54/46$

Thus the increased acidity at the δ-carbon in **2** and **4** by substitution with a sulfone function enhances the ease of equilibration. Substitution with a sulfone function at both the α- and the δ-carbon makes it even more easy through the elimination-readdition sequence. In this picture, the location of the vinyl sulfide with respect to the sulfone is also a factor of critical importance. This is suggested by the two compounds, **9** and **10**, shown below.



9(*E*) **9**(*Z*)



10(*E*)

10(*Z*)

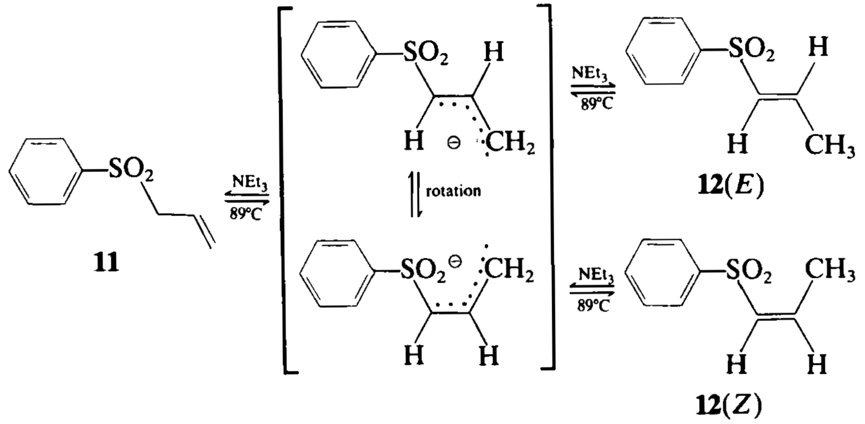
The disulfide **9** undergoes equilibration via the elimination-readdition pathway (See Experimental) when treated with NEt_3 in DMF, giving an equilibrium mixture of $E/Z = 30/70$. In contrast, the disulfide **10** fails to isomerize under the same conditions.[4]

VINYL SULFONES 5 AND 6

While the vinyl sulfides displayed the varying base requirements and solvent requirements for isomerization discussed above, the disulfone **5** and the trisulfone **6** exhibited extreme readiness to isomerize even under the mildest of conditions. Catalytic amounts of triethylamine in benzene solution at ambient temperature were adequate to change the *Z* isomer completely into the *E*. At equilibrium, none of the *Z* isomer was present. Such equilibration occurred within a matter of minutes (10 minutes at the most!) whereas the vinyl sulfides required several hours to attain equilibrium.

Sataty and Meyers[3] had proposed that β,γ-unsaturated terminal alkenyl sulfones (**11**) undergo base-catalyzed isomerization to α,β-unsaturated sulfones (**12**) and equilibrate as well between the disubstituted cis and trans alkenes. (See Scheme 3). Our results suggest[5] that a similar mechanism may be equally viable for the trisubstituted alkenes **4** and **5**, but not necessarily for the vinyl sulfides **2** and **9**, nor the vinyl sulfone **6**. These three derivatives adopt the elimination-readdition pathway instead, as exemplified in Scheme 4.

Equilibrium compositions among these butenes also vary depending upon the



RATIO OF 11/12(*E*)/12(*Z*) = 28/69/3.

SCHEME 3: Tautomerism in Phenyl Allyl Sulfone (11) and Phenyl Propenyl Sulfones (12).

nature of substitution at the double bond. While **2** and **9** favor the *Z* isomer to the extent of 70 to 30 over the *E* isomer, the latter is favored 60 to 40 over the former in the case of butenes **4**. The vinyl sulfones **5** and **6**, in contrast, show total conversion to the *E* isomer at equilibrium, without a trace of the *Z* isomer present.

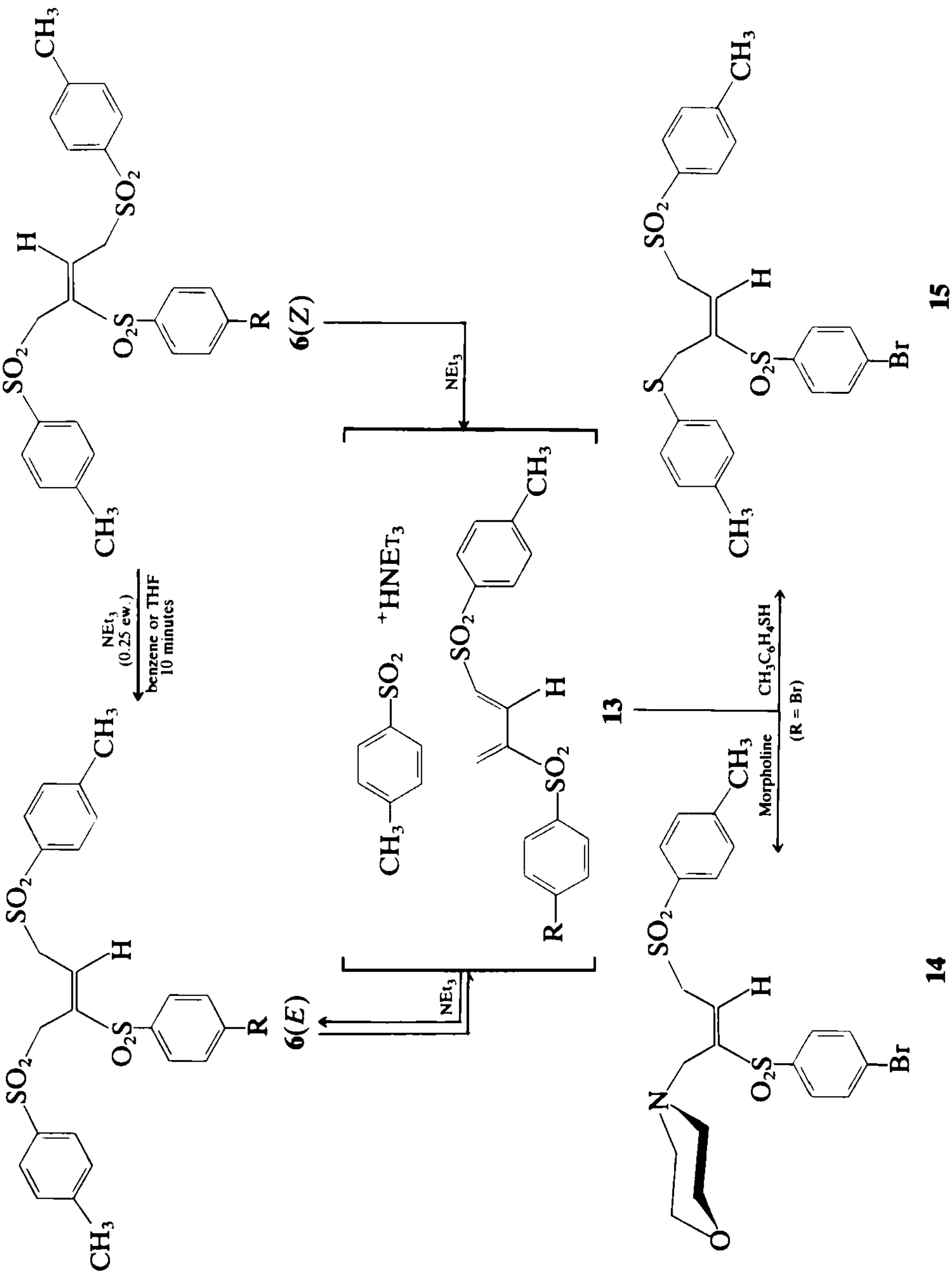
EXPERIMENTAL

General Comments. Melting points, determined on a Buchi SMP-20 Capillary melting point apparatus, are uncorrected. Nuclear magnetic resonance spectra were recorded on a Varian T-60A spectrometer, using tetramethylsilane as the internal standard in $CDCl_3$ solution. Carbon-13 NMR spectra ($CDCl_3$, TMS) were recorded[6] on a JEOL FX-90Q spectrometer (22.5 MHz). Elemental analyses were determined by MicAnal Laboratories, Inc. of Tucson, Arizona or by Midwest Microlabs, of Indianapolis, Indiana.

The *E* to *Z* ratios of butenes **2**, **4**, and **9** were determined in the usual manner;[1] namely, by measuring the relative ^1H NMR absorptions of the vinylic protons in each reaction mixture. The geometric assignments of *E* versus *Z* were secured from ^{13}C NMR spectral data and are based upon the same arguements presented in our earlier study.[4] Table V lists the typical absorptions collected for a representative number of the butenes prepared in this study.

Preparation of and Isomerizations in the 1,4-Di(4'-methylbenzene-sulfonyl)-2-arylthio-2-butenes, **2**. The results obtained in the preparation of and isomerizations in the butenes **2a** and **2b** were outlined in our earlier study.[1] In the case of the previously unreported butenes, **2c**, the *E* and *Z* isomers were isolated in 85% overall yield from a kinetic mixture equal to 78% *E* and 22% *Z*, by using the general procedure already described.[1] Equilibration of **2c** by treatment with triethylamine (one-fourth equivalent) in dimethylformamide (DMF), formed the thermodynamic distribution of the two isomers (i.e. 30% *E* to 70% *Z*). The following data confirmed the structural and geometric assignments of the butenes **2c**. For **2c**(*E*) (mp. 151.5–152°C.): ^1H NMR δ 7.8–6.8 (m, 12H), 5.47 (t, 1H), 3.92 (d, 2H), 3.83 (s, 2H), and 2.43 (s, 6H). Analysis calculated for $C_{24}H_{23}S_3O_4F$: %C, 58.78; %H, 4.69. Found: %C, 58.64; %H, 4.50. For **2c**(*Z*) (mp. 120–120.5°C.): ^1H NMR δ 7.9–6.8 (m, 12H), 6.00 (t, 1H), 4.20 (d, 2H), 3.68 (s, 2H), and 2.45 (s, 6H). Analysis calculated for $C_{24}H_{23}S_3O_4F$: %C, 58.78; %H, 4.69. Found: %C, 58.60; %H, 4.77.

Preparation of 1-(4'-Methylbenzenesulfonyl)-3-arylthio-2-butenes, **4**. The following generalized



SCHEME 4: Intermediacy of the 1,3-Diarylsulfonyl-1,3-butadiene (13).

procedure describes the preparation of the butenes **4** from **2** (pure *E*, pure *Z*, or mixtures of the two isomers).

Sodium borohydride (0.95 g, 0.025 mole) was added in one lot to a well-stirred mixture of butene **2** (0.01 mole) in THF (100 ml) and methanol (10 ml). After being stirred at room temperature for 10 minutes (when the hydrogen evolution ceased), the reaction mixture was diluted with benzene (500 ml). This was then filtered through a bed of sea sand, washed with water (6 × 400 ml), and dried over sodium sulfate. An aliquot (15 ml) of this solution was analyzed by ^{1}H NMR, showing a ratio of the *E* to *Z* isomers of **4** equal to 20 to 80. The products were isolated as mixtures of the two isomers (in an overall yield of 75–80%) when the bulk reaction mixture was evaporated and the solid was crystallized from ether/pet. ether solutions (or from ethanol/water solutions). The crude solids were further purified by recrystallization from benzene/ether/pet. ether mixtures to afford the pure *Z* isomer always in greater than 70% yield. The *E* isomer was isolated in trace amounts (less than 5% yield) from remaining filtrates. Table I lists the ^{1}H NMR spectral data and the physical properties for all the butenes **4** prepared in this study.

Determination of the Equilibrium Ratios of **4**(*E*) *to* **4**(*Z*). The *E* to *Z* equilibrium ratios of the butenes **4** were determined by treating each isomer (200 mg) with DBU (23 mg) in DMF (4 ml). After being stirred for 3 hours (shorter time periods gave incomplete equilibrations) at room temperature under nitrogen, the reaction mixtures were diluted with benzene (50 ml), washed with water (6 × 30 ml), and dried over sodium sulfate. The solvent was completely stripped away and the residues were examined by ^{1}H NMR, showing absorptions consistent with a mixture of the two isomers. The equilibrium values listed in Table I (based on the relative vinylic, methylene, and methyl absorptions in each mixture) were the same, regardless of the direction that they were approached.

Large-scale Equilibrations of **4**(*Z*). A mixture of the butene **4**(*Z*) (0.01 mole) and DBU (0.0025 mole) in DMF (20 ml) was stirred for 3 hours at room temperature under nitrogen. After the reaction mixture was worked-up in the usual fashion, the excess solvent was evaporated. Pet. ether was added dropwise to the chilled concentrate (20 ml benzene), causing the crystallization of trace quantities (ca. 10% yield) of the unchanged *Z* isomer. The filtrate, upon being chilled further, gave the pure *E* isomer (ca. 25% yield) of **4**. These solids were identified by their physical and spectral properties, all of which were identical to those listed in Table 1. Subsequent fractions of **4** (ca. 40% yield) were isolated from the remaining reaction mixture as unseparable mixtures of the two isomers.

Attempted Isomerization of **4** *with Triethylamine.* A mixture of **4** (60 mg) and triethylamine (15 mg, 1 equivalent) in 5 ml benzene (or in 5 ml DMF) was stirred at room temperature for 42 hours. The reaction mixture was worked-up by using the methods described above and then analyzed by ^{1}H NMR, revealing that the sample was unchanged by treatment with triethylamine. This was true for both the *E* and the *Z* isomers of **4**.

TABLE I

1-(4′-Methylbenzenesulfonyl)-3-arylthio-2-butenes, **4**

Compd.		%	*E*/*Z* Ratio			MP	Elem. An. %C(%H)		^{1}H NMR (δ in $CDCl_3$, ppm)			
No. **4**	R	Yld.	Kinetic	Thermo.		(°C)	Calc.	Found	CH_3 (α)†	CH (γ)‡	CH_2 (δ)§	other
a	Cl	78	19/81	58/42	*E*	83–84	57.95 (4.83)	57.68 (4.84)	1.67	5.22	3.80	7.8–7.2 (m, 8H), 2.47 (s, 3H)
					Z	107–108		57.95 (4.84)	1.87	5.80	4.17	7.9–6.8 (m, 8H), 2.48 (s, 3H)
b	Br	80	18/82	61/39	*E*	75–76	51.39 (4.28)	51.57 (4.24)	1.67	5.23	3.80	7.8–7.0 (m, 8H) 2.45 (s, 3H)
					Z	111–112		51.45 (4.22)	1.87	5.77	4.17	7.8–6.5 (m, 8H) 2.45 (s, 3H)
c	F	80	20/80	60/40	*E*	65–66	60.71 (5.06)	60.56 (5.12)	1.65	5.10	3.80	7.8–6.8 (m, 8H), 2.47 (s, 3H)
					Z	63–64		60.58 (5.09)	1.80	5.73	4.17	7.9–6.8 (m, 8H), 2.47 (s, 3H)

† singlet ‡ triplet § doublet

TABLE II

1,4-Di(4′-methylbenzenesulfonyl)-2-arylsulfonyl-2-butenes, **6**

Compd. No. **6**	R	% Yld.	MP (°C)	Elem. An. %C(%H)		^{1}H NMR (δ in $CDCl_3$, ppm)			
				Calc.	Found	CH_2 (α)†	CH (γ)‡	CH_2 (δ)§	other
a	Cl	96	*E* 201–201.5	53.53 (4.28)	53.46 (4.28)	4.07	7.18	4.37	7.85–7.25 (m, 8H), 2.45 (s, 6H)
		88	*Z* 184–185		53.39 (4.16)	4.03	6.93	4.60	7.90–7.50 (m, 8H) 2.45 (s, 6H)
b	Br	90	*E* 213–213.5	49.40 (3.95)	49.23 (4.06)	4.02	7.08	4.30	7.75–7.50 (m, 8H), 2.43 (s, 6H)
		98	*Z* 203–204		49.33 (3.98)	4.05	6.90	4.57	7.85–7.15 (m, 8H), 2.45 (s, 6H)
c	F	94	*E* 185–185.5	55.17 (4.41)	54.93 (4.55)	4.05	7.08	4.35	7.90–7.15 (m, 8H), 2.42 (s, 6H)
		97	*Z* 186.5–188		54.94 (4.26)	4.03	6.83	4.60	7.90–6.90 (m, 8H), 2.43 (s, 6H)

† singlet ‡ triplet § doublet

Oxidation of **2**(*E*) *to* **6**(*E*). A mixture of vinyl sulfide **2**(*E*) (0.01 mole) and 80% MCPBA (6.45 g, 0.03 mole) in chloroform (70 ml) was stirred for 3 hours at room temperature. The reaction mixture was diluted with ether (500 ml), chilled, and pet. ether was added dropwise, causing the crystallization of the trisulfone, **6**(*E*). The solid was collected by filtration and then washed with additional ether (100 ml) to afford **6**(*E*) in 94–96% yield. Recrystallization from methylene chloride/pet. ether solutions gave the analytical samples of **6**(*E*) whose spectral data and physical properties are listed in Table II.

Oxidation of **2**(*Z*) *to* **6**(*Z*). The pure *Z* isomer of **2** (0.01 mole) was oxidized to the trisulfone **6**(*Z*) (in 88–98% yield) by using the same procedure described above for **2**(*E*) (See Table II).

Oxidation of Butenes **4**(*Z*) *to Disulfones* **5**(*Z*). A mixture of the butene **4**(*Z*) (0.01 mole) and 80% MCPBA (6.45 g, 0.03 mole) in chloroform (30 ml) was stirred for 3 hours at room temperature. The disulfone **5**(*Z*) was isolated in 53–80% yield by diluting the reaction mixture with chilled ether (100 ml), followed by filtration of the precipitate by suction. The pure samples of **5**(*Z*) (reported in Table III) were obtained after the solids were recrystallized from benzene/pet. ether solutions.

TABLE III

1-(4′-Methylbenzenesulfonyl)-3-arylsulfonyl-2-butenes, **5**

Compd. No. **5**	R	% Yld.†	MP (°C)	Elem. An. %C(%H)		^{1}H NMR (δ in $CDCl_3$, ppm)			
				Calc.	Found	CH_3 (α)‡	CH (γ)§	CH_2 (δ)¶	other
a	Cl	64(75)	*E* 140–140.5	53.13 (4.43)	53.00 (4.64)	1.60	6.71	3.92	7.8–7.1 (m, 8H), 2.42 (s, 3H)
		70	*Z* 121.5–122		53.17 (4.62)	1.92	6.17	4.68	7.8–7.2 (m, 8H), 2.48 (s, 3H)
b	Br	(82)	*E* 152.5–153	47.55 (3.96)	47.54 (4.14)	1.60	6.73	3.93	7.8–7.0 (m, 8H), 2.4 (s, 3H)
		80	*Z* 145–145.5		47.56 (4.03)	1.93	6.20	4.68	7.9–7.2 (m, 8H), 2.48 (s, 3H)
c	F	73(74)	*E* 117–117.5	55.43 (4.62)	55.22 (4.65)	1.63	6.71	3.93	8.0–7.0 (m, 8H), 2.43 (s, 3H)
		53	*Z* 99.5–100		55.21 (4.86)	1.92	6.17	4.70	8.0–7.0 (m, 8H), 2.48 (s, 3H)

† The values without parenthesis indicate the isolated yield of **5** obtained by the oxidation of the respective isomer of butene **4**. The values within parenthesis indicate the yield of **5** obtained by the reduction of the trisulfone **6**.

‡ singlet § triplet ¶ doublet

Oxidation of Butenes **4**(*E*) *to Disulfones* **5**(*E*). Since the butenes **4**(*E*) were formed as minor products in their conversions from **2**, only trace quantities of this isomer were oxidized to the disulfone **5**(*E*). A scaled-down version of the procedure described above produced the disulfone **5**(*E*) (in 64–73% yield) from **4**(*E*) (200 mg). See Table III. The following reduction reaction was the method of choice for the preparation of larger quantities of the disulfone **5**(*E*) from the trisulfones **6**.

Reduction of **6** *to* **5**(*E*). Both the pure *E* and pure *Z* trisulfone, **6**, formed **5**(*E*) (without simultaneous formation of the *Z* isomer of butene **5**) by reduction of **6** with sodium borohydride. The following generalized procedure describes the preferred method for preparing larger amounts of the *E* isomer of disulfone **5**.

Sodium borohydride (0.76 g, 0.02 mole) was added in one part to a mixture of **6** (0.01 mole), THF (225 ml), and methanol (15 ml) that was being well-stirred at ice bath temperature. Once the hydrogen evolution ceased (10 minutes), benzene (500 ml) was added to the reaction mixture; and this was immediately filtered. The disulfone **5**(*E*) was isolated in ca. 74–82% yield from a 1 : 1 mixture of benzene/ether (50 ml) after the reaction mixture was washed with water (6 × 300 ml) and dried over sodium sulfate. This solid was then further purified by recrystallization from benzene/pet. ether solutions. Table III lists the physical data and spectral properties collected for these solids. A PMR spectrum of the remaining reaction mixture gave absorptions of residual **5**(*E*) along with an additional (overreduction product, viz. the 1,3-di(arylsulfonyl)butane.[7]

Equilibration of **5**. A mixture of the disulfone **5**(*Z*) (1 mmole) and NEt_3 (25 mg, 0.25 mmole) in 10 ml benzene (or in 10 ml DMF) was stirred for 5 minutes at room temperature. The reaction mixture was diluted with benzene (90 ml), washed with water (6 × 50 ml), and dried over sodium sulfate. Evaporation of the solvent left behind a solid (in quantitative yield) which showed the ^1H NMR absorptions for only the *E* isomer of **5**.

Recrystallization of this material from benzene/pet. ether solutions gave a sample of **5**(*E*) (in greater than 90% yield) which had identical physical properties to those listed in Table III. This same result was also obtained when the pure *E* or when isomeric mixtures of **5** were similarly treated with NEt_3.

Equilibration of **6**. The trisulfone **6**(*Z*) (0.2 mmole) was isomerized quantitatively to **6**(*E*) by being stirred (for 5 minutes) with triethylamine (5 mg, 0.05 mmole) as a heterogeneous mixture in 15 ml benzene (or as a homogeneous mixture in 15 ml THF). The solid was isolated by filtration from chilled benzene; and then it was characterized by mixed melting point analyses with the appropriate sample of **6**(*E*). Proton NMR and infrared spectral data collected on the solid confirmed the identity of the trisulfone. Similar treatment of the *E* isomer or isomeric mixtures of **6** gave this same result.

Equilibration of **6b** *in the Presence of Morpholine*. A mixture of **6b** (2.0 g, 0.0034 mole) and morpholine (0.66 g, 0.0076 mole) in THF (150 ml) was stirred for 45 minutes under nitrogen. The reaction mixture was diluted with benzene (800 ml), washed with water (8 × 400 ml), and dried over sodium sulfate. The excess benzene was stripped away by evaporation and the concentrate (20 ml) was chilled. Dropwise addition of pet. ether caused the crystallization of the morpholino product **14** in 94% yield. This solid was recrystallized from benzene/hexanes, giving a sample with the following properties: mp. 123.5–125°C.; ^1H NMR δ 7.8–7.2 (m, 8H), 7.00 (t, 1H), 4.30 (d, 2H), 3.4–3.26 (m, 4H), 3.00 (s, 2H), 2.43 (s, 3H), and 2.13–1.97 (m, 4H) ppm. Analysis calculated for $C_{21}H_{24}S_2O_5NBr$: %C, 49.03; %H, 4.67. Found: %C, 49.34; %H, 5.07.

Equilibration of **6b** *in the Presence of 4-Thiocresol*. A mixture of **6b** (2.0 g), 4-thiocresol (0.51 g, 0.0041 mole), and triethylamine (0.35 g, 0.0034 mole) in THF (140 ml) was stirred for 15 minutes under nitrogen. The reaction mixture was diluted with benzene (600 ml), washed with 0.2N KOH (300 ml), washed with water (6 × 400 ml), and dried over sodium sulfate. This mixture was concentrated to approximately 20 ml benzene. Addition of ether (20 ml), followed by dropwise addition of pet. ether, to the chilled concentrate caused the crystallization of **15** in 87% yield. Recrystallization from benzene/pet. ether afforded an analytical sample with mp. = 108–109°C.: calculated for $C_{24}H_{23}S_3O_4Br$ gave: %C, 52.27; %H, 4.17. Found %C, 52.43; %H, 4.15. The ^1H NMR signals for this product are: δ 7.70–7.00 (m, 12H), 6.78 (t, 1H), 3.57 (d, 2H), 3.45 (s, 2H), 2.43 (s, 3H), and 2.30 (s, 3H) ppm.

Preparation of Butenes **9** *from* **2**. The butenes **9a**–**9c** were produced as isomeric mixtures (*E*/*Z* ratio equal to 25/75) by using the procedure described in our earlier publication.[1] Table IV lists the results obtained in the preparation of **9a** from **2a**, and **9b**–**9c** from **2b**.

TABLE IV

1,2-Di(arylthio)-4-(4′-methylbenzenesulfonyl)-2-butene, **9**

Compd. No. **9**	R_1	R_2	% Yld.	E/Z Ratio†		MP (°C)	Elem. An. %C(%H) Calc.	Elem. An. %C(%H) Found	^{1}H NMR (δ in $CDCl_3$, ppm) CH_2 (α)‡	^{1}H NMR CH (γ)§	^{1}H NMR CH_2 (δ)¶	^{1}H NMR other
a	Cl	Cl	89	24/76	*E*	103–104	55.87 (4.05)	55.75 (4.02)	3.41	5.28	3.60	7.7–7.0 (m, 12H), 2.43 (s, 3H)
					Z	97–98		55.74 (4.00)	3.43	6.03	4.17	7.7–6.8 (m, 12H), 2.43 (s, 3H)
b	Br	Cl	83	23/77	*E*	114–115	51.21 (3.71)	51.13 (3.65)	3.43	5.27	3.60	7.7–7.0 (m, 12H), 2.43 (s, 3H)
					Z	107–108		51.16 (3.66)	3.45	6.05	4.17	7.7–6.7 (m, 12H), 2.43 (s, 3H)
c	Br	CH_3	86	30/70	*E*	99–100	55.49 (4.43)	55.59 (4.44)	3.33	5.30	3.45	7.7–7.0 (m, 12H), 2.43 (s, 3H), 2.30 (s, 3H)
					Z	100–101		55.32 (4.42)	3.40	6.00	4.10	7.6–6.7 (m, 12H), 2.42 (s, 3H), 2.30 (s, 3H)

† These numbers represent the thermodynamic ratio of the two isomers.

‡ singlet § triplet ¶ doublet

Equilibration of **9**. Samples of pure *E*, pure *Z*, and isomeric mixtures of **9** (0.36 mmole) and triethylamine (0.09 mmole) in DMF (5 ml) were each stirred at room temperature for 4 hours. Each reaction mixture was diluted with benzene (20 ml), washed with water (5 × 15 ml), dried over sodium sulfate, and evaporated. The residues were then analyzed by ^{1}H NMR, showing an *E* to *Z* ratio equal to 25 to 75 in all the cases.

TABLE V

Carbon-13 NMR Spectral Data (ppm)

Compd. No.		C(α) ($^3J_{CH}$)†	C(δ) ($^2J_{CH}$)†	Other Absorptions
4a	*E*	17.7	56.4	144.8, 141.7, 135.6, 134.7, 134.5, 130.4, 129.8, 129.4, 128.3, 113.6, 21.6
	Z	23.8	57.0	144.3, 139.6, 135.6, 133.8, 132.5, 130.7, 129.4, 128.7, 128.0, 119.4, 21.3
5a	*E*	11.6 (7.3)	55.5 (2.4)	145.5, 136.7, 135.1, 134.7, 130.0, 129.7, 129.6, 129.4, 128.2, 126.6, 21.6
	Z	20.2 (6.1)	54.8 (2.4)	145.2, 142.1, 140.5, 137.2, 135.8, 130.0, 129.6, 129.4, 128.2, 127.3, 21.7
6b	*E*	53.3	56.4	145.9, 145.8, 139.0, 137.6, 136.7, 135.5, 132.7, 130.2, 130.1, 130.0, 128.4, 128.2, 21.8
	Z	56.1	56.8	145.7, 145.5, 138.0, 136.2, 135.9, 135.8, 135.4, 132.7, 130.2, 130.1, 129.8, 129.6, 128.6, 128.4, 21.7
9a	*E*	36.0 (8.5)	56.0 (2.4)	145.0, 142.0, 135.7, 134.9, 134.7, 133.9, 133.3, 133.1, 130.2, 129.9, 129.6, 129.3, 129.1, 128.2, 117.5, 21.6
	Z	40.6 (5.5)	57.2 (2.4)	144.7, 139.5, 135.8, 133.8, 133.5, 132.9, 132.7, 131.9, 130.4, 129.7, 129.2, 129.0, 128.2, 123.0, 21.6
9b	*E*	35.9 (8.5)	55.9 (2.4)	144.9, 141.7, 135.6, 134.7, 133.7, 133.1, 132.4, 130.8, 129.8, 129.1, 129.0, 128.1, 122.8, 117.8, 21.5
	Z	40.7 (5.5)	57.2 (2.4)	144.6, 139.3, 135.8, 133.3, 132.9, 132.7, 132.1, 131.9, 131.8, 131.0, 129.7, 129.0, 128.9, 128.2, 123.1, 121.8, 21.5
9c	*E*	36.6 (8.5)	55.9 (2.4)	144.9, 142.0, 138.1, 135.7, 134.7, 132.9, 132.5, 131.3, 130.7, 129.8, 128.2, 122.7, 117.9, 21.6, 21.1
	Z	41.2 (5.5)	57.3 (2.4)	144.6, 139.6, 137.1, 135.8, 132.7, 132.1, 131.3, 129.7, 128.3, 123.1, 121.6, 21.6, 21.0

† Hz

Equilibration of ***9b*** *in the Presence of 4-Thiocresol.* A mixture of **9b** (200 mg, 0.37 mmole), 4-thiocresol (90 mg, 0.742 mmole), and triethylamine (94 mg, 0.093 mmole) in DMF (5 ml) was stirred (under nitrogen) at room temperature for 4 hours. The reaction mixture was worked-up in the standard fashion and then evaporated to the oil. PMR spectral analysis of this residue showed absorptions for an equilibrium mixture of butene **9c** (See Table IV).

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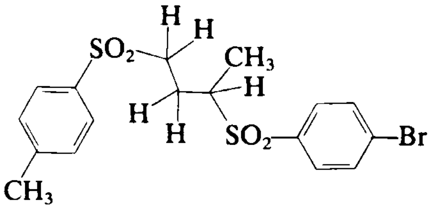
5. There is no shift in the position of the double bond in the isomerization of compounds **4** and **5**. However, in the Sataty and Meyers' example,[3] the double bond does shift in and out of conjugation with the sulfone.
6. We thank Dr. N. F. Swynnerton (of the Southwest Research Institute, San Antonio, Texas) for his generous assistance in providing the ^{13}C NMR spectra.
7. This same compound was produced in 70% yield when the trisulfone **6** (0.0017 mole) was reacted with a large excess of $NaBH_4$ (1.0 g) (or when the disulfone **5** (0.0035 mole) was treated with $NaBH_4$ (0.40 g)). For instance, **6b** and **5b** formed the butane **16**: mp. 89–90°C.; ^{1}H NMR δ 7.8–7.2 (m, 8H), 3.4–3.0 (m, 3H), 2.45 (s, 3H), 2.03 (p, 2H), and 1.23 (d, 3H) ppm. Analysis calculated for $C_{17}H_{19}S_2O_4Br$: %C, 47.33; %H, 4.41. Found: %C, 47.53; %H, 4.55.



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