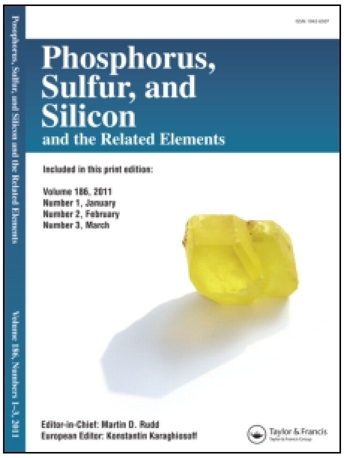

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STEREOSELECTIVE ADDITION OF ARENE THIOLS TO 1,4-DISUBSTITUTED-2-BUTYNES

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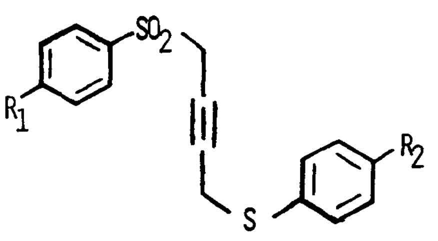
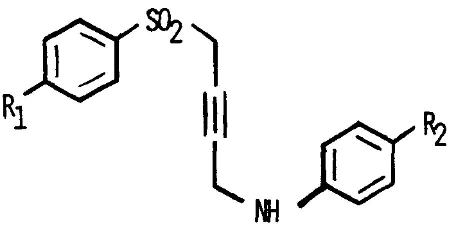
Base-catalyzed addition of arene thiols to 1,4-disubstituted-2-butynes (**1** and **2**) afford the β,γ-unsaturated sulfones (**8E** and **8Z**). In addition to the regiospecificity observed, the vinyl sulfides are formed with a high degree of stereoselectivity. Product formation through a less-hindered approach by the nucleophile appears to favor the E over the Z isomer, consistently in all the 11 cases investigated.

Nucleophilic additions to alkynes occur in two distinctly different modes.[1] Where no activating groups, like a carbonyl or sulfonyl, are present at the alpha carbon, addition takes place strictly across the triple bond, often in accordance with the Truce-Miller Rule of "trans nucleophilic addition".[2] But when the acidifying functions are present at the alpha carbon, base-catalyzed nucleophilic addition then proceeds via an initial isomerization to the allene. The latter then governs the site of addition.[3] Unfailingly, such additions occur at the middle carbon of the allene and exhibit a high order of regiospecificity. The involvement of such alkyne–allene isomerism preceding nucleophilic additions has been fruitfully invoked in the case of several enzyme-inhibitor reactions.[4]

The present study was undertaken to broaden the basis of regioselectivity observed initially by Stirling and coworkers.[3,5] Additionally, it is our objective to ascertain the degree of stereoselectivity or stereospecificity obtainable under these conditions. We have also attempted to determine whether the approaching nucleophile in the addition to the allene[6] is influenced by other functions like —S— or —NH— in determining the overall geometry of the alkene formed. The two different systems we chose to study in the present work are shown below:



(1)



(2)

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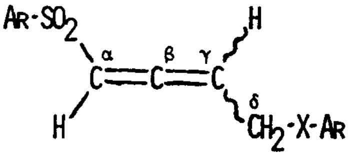
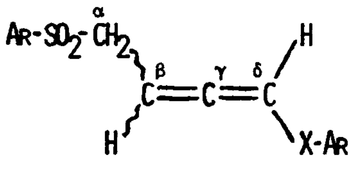
*Author to whom all correspondence should be addressed.

Owing to the greater acidity of the protons alpha to the sulfone function than those adjacent to the amino or the sulfide moiety, we anticipated that any allene formation should occur between the α,β- and the β,γ-carbons rather than the β,γ- and γ,δ-carbons (*vide infra*).



(3)

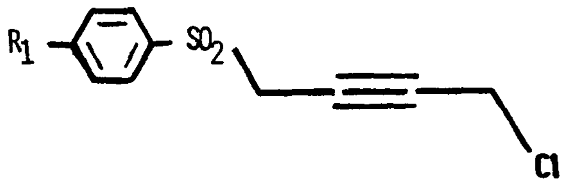
X = S, NH



(4)

If the nucleophilic addition occurred through the intermediacy of the allene, one should observe regiospecificity in the product alkenes. If, however, addition occurred without isomerization to the allene, one can expect addition to occur at either carbon of the alkyne triple bond.

The starting compounds **1** and **2** required for the study were synthesized from 1-arylsulfonyl-4-chloro-2-butyne[7] (**5**).

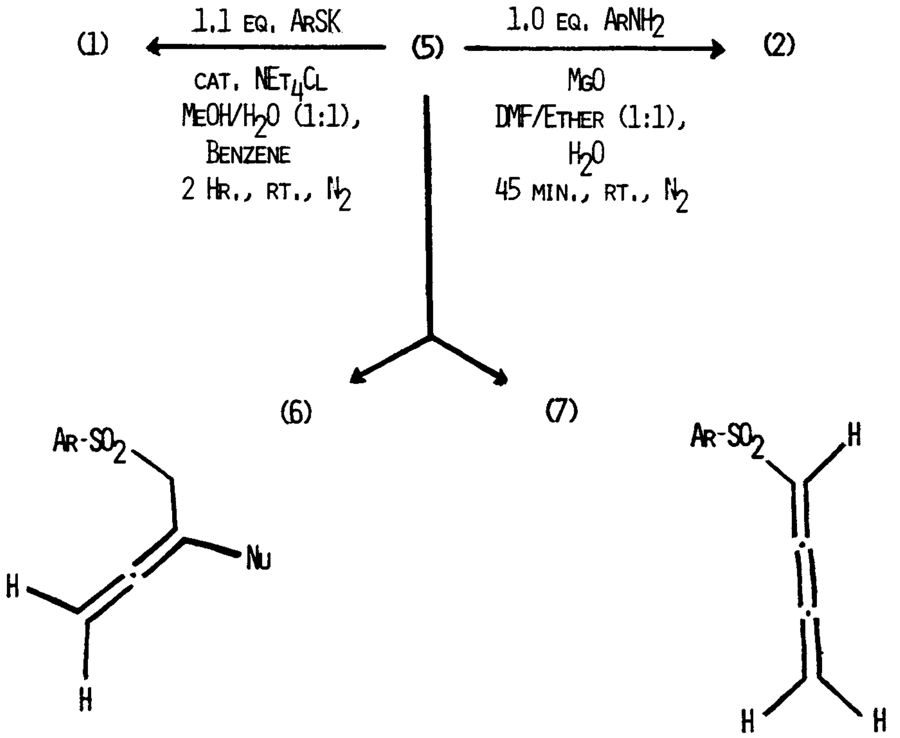


(5)

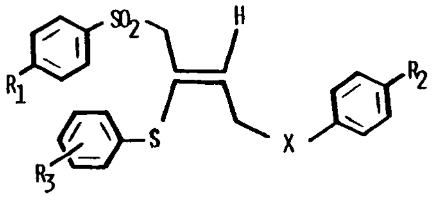
$R_1 = H, CH_3, Cl$

Base-catalyzed nucleophilic substitution of the chloride in **5** was somewhat complicated by the additional possibilities of S_N2' attack at the triple bond (**6**) or even a 1,4-elimination leading to the cumulene **7** which resulted in polymeric materials. These were circumvented by running the reaction under phase transfer conditions or by utilizing MgO as a scavenger for the HCl formed in the reaction (see Experimental).

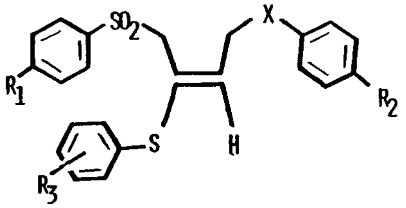
All of the nucleophiles chosen for addition to **1** and **2** are substituted thiophenols. They were added to the alkynes in a nonpolar aprotic medium (benzene), at ambient temperatures. Triethylamine, in less than stoichiometric amounts, was employed as base catalyst. Such mild conditions were selected to ensure that isomerization of the alkyne involved only the most acidic protons available in the system. The addition reactions were clean and afforded high yields of the corresponding vinyl sulfides **8**. In every single case investigated, addition of the thiol occurred solely at the carbon beta to the sulfone. No vinyl sulfides corresponding to addition to the gamma carbon were detected (structure **9**). Nor were any vinyl sulfones observed in the product mixture.[8]



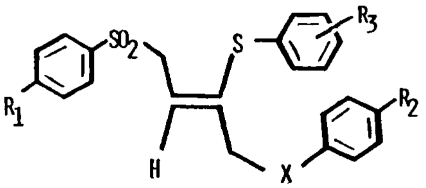
SCHEME 1



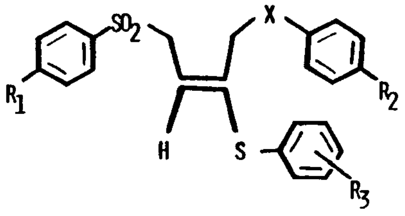
(8 Z)



(8 E)

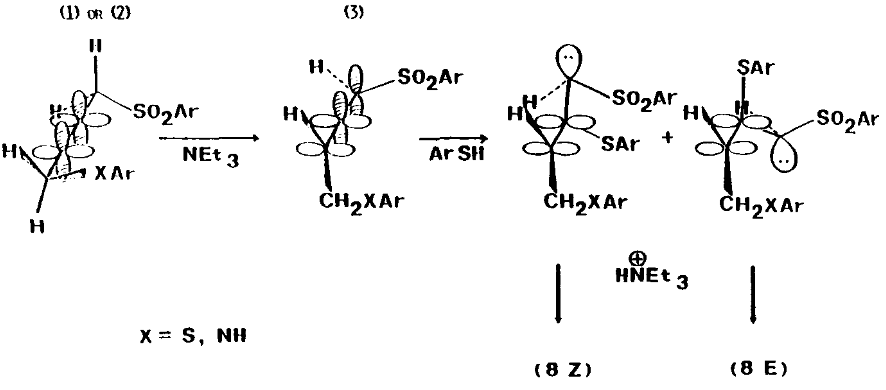


(9 Z)



(9 E)

X = S, NH



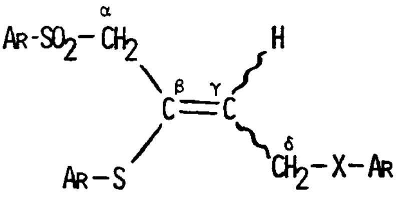
SCHEME 2

Such regiospecificity amply corroborates the observations of Stirling and coworkers,[3,5,6] wherein facile isomerization of propynyl sulfones to the corresponding allenes (under similar conditions) was decisively demonstrated. In addition to the regiospecificity, we observed consistent stereoselectivity in the formation of the vinyl sulfides. The E isomer was the predominant product (greater than 70% isolated yields) in all the additions.[9]

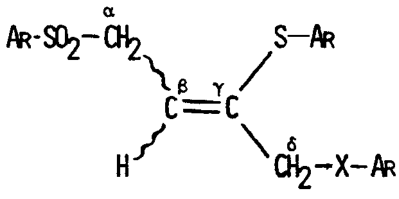
The vinyl sulfides, once formed, did not undergo isomerization in the reaction medium, under the reaction conditions. This was reaffirmed by isolating the pure E and Z isomers and attempting their isomerization in benzene solution with NEt_3 as catalyst, at ambient temperatures. *No isomerization occurred from E to Z or vice versa.* It is indeed interesting that in every single case studied, the major product of addition was the E isomer. Had the addition been governed by the rule of trans nucleophilic addition directly to the alkyne, the major products should have been the Z isomer. Scheme 2 illustrates the two approaches that a nucleophile could take towards the allene. The less hindered approach[9] leads to the E isomer.

The regiospecificity observed in the products and the stereochemical assignments for the E and Z isomers are amply corroborated by their ^{1}H and ^{13}C NMR spectral data. Table IV lists the ^{13}C NMR signals observed and clearly shows the excellent consistency in the chemical shifts for the δ methylene within each series (X = NH or X = S). The most downfield signals were for the methylenes alpha to the sulfone, followed by the ones next to the —NH— and then the ones adjacent to the —S—.

Of the two possible gross structures for the vinyl sulfides (**8** and **9**), structure **8** should exhibit a three-bond coupling between the carbon next to the sulfone and the vinylic hydrogen, while structure **9** should show a two-bond coupling of the order of only 1 to 2 Hz for the similar interaction.



(8)



(9)

The long range coupling, observed in this study, for the α methylene carbon was 7.9 Hz for the E isomer and 5.5 Hz for the Z isomer. These values are consistent with the reported values for a variety of compounds, including the data for simple propylene (where the $^3J_{CH}$ value is larger for the *trans* proton than for the *cis* proton[10]). The geometric assignments (E vs. Z) made above (based on the long range coupling) were further reaffirmed by the ^{13}C signals observed for the α methylene carbon in relation to the δ methylene. When the two methylene groups are *cis* to each other, the α methylene carbon is shifted to a more shielded position (see Table IV) than when the two methylenes are *trans* to each other.[11]

While the above work was in progress, a communication by Denmark and Harmata[12] reported that "kinetically controlled addition of nucleophiles to sulfonyl allenes affords β,γ-unsaturated sulfones." Their study, utilizing *a strong base* like NaH in Tetrahydrofuran as solvent, led *them* as well to postulate "a least-hindered approach model of attack at the central carbon". Although the homogeneity of products was "assured by sharp melting points... and ^1H and ^{13}C NMR spectroscopy" no further details were given concerning the possible formation of any Z isomers nor was the possibility of interconversion between the two discussed by these authors. Our results independently corroborate the suggestion of a less-hindered approach by the nucleophile to the central carbon of allenes, generated *in situ*, from 1,4-disubstituted-2-butynes (*vide supra*: Scheme 2).

EXPERIMENTAL

General Comments. Melting points, determined on a Buchi SMP-20 Capillary melting point apparatus, are uncorrected. Proton NMR spectra were measured in $CDCl_3$ on a Varian T-60A spectrometer using TMS as the internal standard. ^{13}C NMR spectra ($CDCl_3$, TMS) were determined on a JEOL FX-90Q spectrometer (22.5 MHz). Infrared spectra (KBr) were determined on a Beckman 4220 spectrophotometer. Elemental analyses were determined by Galbraith Laboratories, Inc. of Knoxville, Tennessee, and by MicAnal Laboratories, Inc. of Tucson, Arizona.

1-Arylsulfonyl-4-arylthio-2-butynes (**1a–c**). Compounds **1a–c** were prepared, following the general method described below.[13]

To a solution of KOH (0.023 moles) and tetraethyl ammonium chloride (0.002 moles) in 200 ml of 50% aqueous methanol, stirred vigorously under nitrogen, the required thiophenol (0.023 moles) was added over 30 minutes. This mixture was then added over an hour to a well-stirred solution of **5** (0.022 moles) in 100 ml benzene. After stirring for an additional 2 hours, the aqueous methanolic layer was separated and extracted thoroughly with benzene (3 × 100 ml). The benzene extracts were combined, washed with water, dried over sodium sulfate and concentrated *in vacuo* to approximately 20–25 ml. Upon chilling and adding pet. ether (15–25 ml) to the concentrate, the product **1** separated as a white solid. Further purification was achieved by recrystallization from benzene–pet. ether. Table I lists the compounds obtained in this study.

1-Arylsulfonyl-4-(N′-anilino)-2-butynes (**2a–d**). The procedure described below is an improved version of an earlier method.[14]

A 40 ml solution of **5** (0.044 moles) in DMF/ether (1 : 1) was added, in one lot, to a vigorously stirred mixture of the required aniline (0.044 moles) and magnesium oxide (0.044 moles) in 40 ml DMF/ether (1 : 1) and 15 ml H_2O. After stirring under nitrogen for 45 minutes at room temperature, the reaction mixture was diluted with 300 ml benzene. The benzene layer was washed with water (5 × 200 ml), dried over sodium sulfate and concentrated *in vacuo* to ca. 30 ml. Addition of pet. ether to the chilled concentrate afforded the solid product. Further purification by recrystallization from benzene-pet. ether gave the compounds listed in Table I.

TABLE I

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

Compd. No.	X	R_1	R_2	mp. (°C)	% Yld.	Analysis Fd. %C	(Calc.) % H	^{1}H NMR (δ in $CDCl_3$, ppm)	IR (KBr, cm^{-1}) —C≡C—	NH	SO_2 (sym.)	(asym.)
1a	S	CH_3	CH_3	73–74	81	65.31 (65.45)	5.64 (5.45)	7.9–6.7 (m, 8 H), 3.9 (t, 2 H), 3.48 (t, 2 H), 2.38 (s, 3 H), 2.30 (s, 3 H)	2220	—	1140	1315
1b	S	Cl	Cl	125–126	70	51.84 (51.75)	3.26 (3.23)	7.9–6.7 (m, 8 H), 3.95 (t, 2 H), 3.5 (t, 2 H)	2225	—	1145	1325
1c	S	H	Br	94–95	75	50.18 (50.39)	3.42 (3.41)	7.95–6.7 (m, 9 H), 3.95 (t, 2 H), 3.5 (t, 2 H)	2212	—	1125	1295
2a	NH	CH_3	CH_3	86–87	77	68.93 (69.01)	6.01 (6.07)	7.9–6.25 (m, 8 H), 3.87 (s, 4 H), 3.2 (br., 1 H), 2.4 (s, 3 H), 2.23 (s, 3 H)	*	3430	1133	1314
2b	NH	Cl	Cl	99–100	65	54.08 (54.24)	3.66 (3.71)	7.9–6.4 (m, 8 H), 3.81 (s, 4 H), 3.8 (br., 1 H)	*	3420	1142	1312
2c	NH	H	Br	118–119	80	52.66 (52.76)	3.79 (3.87)	8.0–6.4 (m, 8 H), 4.0 (s, 4 H), 4.1–3.7 (br., 1 H)	*	3440	1139	1321
2d	NH	H	Cl	125–126	75	60.24 (60.09)	4.52 (4.41)	8.0–6.4 (m, 8 H), 4.0 (s, 4 H), 4.1–3.7 (br., 1 H)	*	3420	1144	1313

*This absorption was not observed.

TABLE II

1-Arylsulfonyl-2,4-diarylthio-2-butenes (**8**, X = S)

Compd. No. **8**	R_1	R_2	R_3	Isol. Yld.	E/Z Ratio	Analysis % Calc.	(C/H) % Fd.	mp (°C)	^{1}H NMR (δ in $CDCl_3$, ppm)	IR (cm^{-1}) —SO_2— (sym.)	(asym.)
					E		56.61 4.43	113–14	7.8–6.6 (m, 11 H), 6.2 (t, 1 H), 3.64 (s, 2 H), 3.49 (d, 2 H), 2.46 (s, 3 H), 2.32 (s, 3 H)	1131	1300
a	4-CH_3	4-CH_3	3,4-Cl_2	85	22/1	56.69 4.33					
					Z		56.40 4.44	65–66	7.8–6.6 (m, 11 H), 6.21 (t, 1 H), 3.77 (d, 2 H), 3.75 (s, 2 H), 2.47 (s, 3 H), 2.31 (s, 3 H)	1130	1298
					E		55.64 4.45	124–25	7.8–6.6 (m, 12 H), 6.11 (t, 1 H), 3.66 (s, 2 H), 3.47 (d, 2 H), 2.43 (s, 3 H), 2.35 (s, 3 H)	1131	1300
b	4-CH_3	4-CH_3	4-Br	85	19/1	55.49 4.43					
					Z		55.09 4.52	111–12	7.8–6.6 (m, 12 H), 6.15 (t, 1 H), 3.75 (d, 2 H), 3.71 (s, 2 H), 2.43 (s, 3 H), 2.31 (s, 3 H)	1140	1312
					E		60.70 4.85	125–26	7.8–6.6 (m, 12 H), 6.08 (t, 1 H), 3.63 (s, 2 H), 3.45 (d, 2 H), 2.45 (s, 3 H), 2.33 (s, 3 H)	1133	1300
c	4-CH_3	4-CH_3	4-Cl	80	77/1	60.76 4.85					
					Z		60.68 4.89	98–99	7.8–6.6 (m, 12 H), 6.10 (t, 1 H), 3.73 (d, 2 H), 3.68 (s, 2 H), 2.40 (s, 3 H), 2.30 (s, 3 H)	1135	1310
					E		47.21 2.97	126–27	7.9–6.5 (m, 12 H), 6.07 (t, 1 H), 3.75 (s, 2 H), 3.58 (s, 2 H)	1135	1315
d	4-Cl	4-Cl	4-Br	81	23/1	47.23 3.04					
					Z		46.95 3.05	108–09	7.9–6.5 (m, 12 H), 6.18 (t, 1 H), 3.77 (d, 2 H), 3.75 (s, 1 H)	1138	1308
e	H	4-Br	4-Br	70	*E	46.32 3.11	46.32 3.11	111–12	7.9–6.5 (m, 13 H), 6.02 (t, 1 H), 3.73 (s, 2 H), 3.53 (d, 2 H)	1138	1313

*The residual material balance was too close a mixture of the two isomers to permit clean separation of the Z component.

TABLE III

1-Arylsulfonyl-4-(N′-anilino)-2-arylthio-2-butenes (**8**, X = NH)

Compd. No. **8**	R_1	R_2	R_3	Isol. Yld.	E/Z Ratio	Analysis % Calc.	(C/H) % Fd.	mp (°C)	^{1}H NMR (δ in $CDCl_3$, ppm)	Infrared (cm^{-1}) NH	—SO_2— (sym.)	—SO_2— (asym.)
					E		52.03 3.74	141–42	8.0–6.3 (m, 13 H), 6.16 (t, 1 H), 4.05 (br., 1 H), 4.0 (s, 2 H), 3.8 (d, 2 H)	3390	1130	1300
f	H	4-Br	4-Cl	81	16/1	51.97 3.74						
					Z		51.88 3.46	129–30	7.9–6.3 (m, 13 H), 6.07 (t, 1 H), 3.94 (d, 2 H), 3.8 (br., 1 H), 3.79 (s, 2 H)	3400	1130	1290
					E		47.45 3.33	162–63	8.0–6.4 (m, 13 H), 6.18 (t, 1 H), 4.0 (s, 2 H), 3.95 (br., 1 H), 3.80 (d, 2 H)	3400	1140	1300
g	H	4-Br	4-Br	80	50/1	47.73 3.44						
					Z		3.28	47.48 147–48	7.9–6.4 (m, 13 H), 6.11 (t, 1 H), 4.0 (br., 1 H), 3.98 (d, 2 H), 3.82 (s, 2 H)	3410	1135	1295
					E		56.88 4.31	149–50	8.0–6.3 (m, 13 H), 6.15 (t, 1 H), 4.0 (s, 2 H), 3.9 (br., 1 H), 3.47 (d, 2 H)	3404	1149	1306
h	H	4-Cl	4-Cl	78	56/1	56.90 4.12						
					Z		56.82 4.13	127–28	7.9–6.3 (m, 13 H), 6.07 (t, 1 H), 3.92 (d, 2 H), 3.77 (s, 2 H), 3.4 (br., 1 H)	3403	1140	1304
					E		48.44 3.18	167–68	7.9–6.4 (m, 12 H), 6.17 (t, 1 H), 3.97 (s, 2 H), 3.82 (d, 2 H), 3.5 (br., 1 H)	3400	1141	1310
i	4-Cl	4-Cl	4-Br	85	27/1	48.71 3.32						
					Z		48.60 3.17	116–17	7.8–6.3 (m, 12 H), 6.08 (t, 1 H), 3.93 (d, 2 H), 3.8 (br., 1 H), 3.77 (s, 2 H)	3420	1143	1310
j	4-CH_3	4-CH_3	4-Br	75	*E	57.37 4.78	57.12 4.96	130–31	7.9–6.35 (m, 12 H), 6.17 (t, 1 H), 3.97 (s, 2 H), 3.72 (d, 2 H), 3.5 (br., 1 H), 2.43 (s, 3 H), 2.23 (s, 3 H)	3367	1142	1315
k	4-CH_3	4-CH_3	4-Cl	73	*E	63.02 5.25	63.14 5.48	126–27	7.9–6.3 (m, 12 H), 6.17 (t, 1 H), 3.97 (s, 2 H), 3.68 (d, 2 H), 3.4 (br., 1 H), 2.43 (s, 3 H), 2.23 (s, 3 H)	3369	1144	1320

*The residual material balance was too close a mixture of the two isomers to permit a clean separation of the Z component.

TABLE IV

^{13}C NMR chemical shift values (Hz) for 1-arylsulfonyl-2,4-diarylthio-2-butenes and 1-arylsulfonyl-4-(N′-anilino)-2-arylthio-2-butenes

Compd. No.	Isom.	C^α	C^β	C^γ	C^δ	Other Carbons
8a	E	57.6	123.4	139.9	34.5	145.2, 137.9, 135.7, 133.2, 133.1, 132.6, 132.2, 131.9 130.8, 130.3, 130.1, 129.9, 129.7, 128.7, 21.7, 21.1
	Z	62.1	123.2	141.7	34.3	145.0, 137.3, 135.6, 133.1, 133.0, 131.6, 131.5, 130.7, 130.6, 129.8, 129.7, 129.4, 128.7, 128.2, 21.7, 21.1
8b	E	57.7	124.0	138.9	34.3	145.1, 137.7, 135.7, 132.6, 132.5, 132.2, 132.1, 130.5, 129.8, 129.7, 128.6, 121.7, 21.7, 21.1
	Z	61.9	123.9	140.7	34.3	144.8, 137.1, 135.5, 132.1, 131.8, 131.6, 130.9, 129.7, 129.6, 128.7, 121.4, 21.7, 21.1
8f	E	58.0	125.4	138.7	42.9	146.4, 138.9, 134.4, 134.2, 133.2, 132.0, 130.8, 129.6, 129.3, 128.7, 114.8, 109.7
	Z	61.7	124.2	141.6	43.9	146.3, 138.3, 133.9, 132.3, 132.2, 132.0, 131.9, 130.7, 129.5, 129.2, 129.1, 128.6, 114.6, 109.5
8g	E	58.1	125.3	139.0	43.0	146.4, 138.9, 134.2, 133.4, 133.3, 132.5, 132.1, 131.5, 129.3, 129.2, 128.7, 122.4, 114.8, 109.8
	Z	61.8	124.1	141.7	43.1	146.3, 138.4, 133.9, 132.5, 132.3, 130.0, 131.4, 129.1, 128.6, 121.9, 114.6, 109.5

1-Arylsulfonyl-2,4-diarylthio-2-butenes (**8a–e**, *X* = *S*). A mixture of the appropriate thiophenol (0.02 moles) and triethylamine (0.005 moles) in 30 ml benzene was added in one lot to a well-stirred solution of **1** (0.02 moles) in 45 ml benzene. This solution was stirred for 6 hours under nitrogen at room temperature. Completion of reaction was monitored by disappearance of starting materials (TLC: Cyclohexane/methyl ethyl ketone/benzene (16 : 5 : 1)). The reaction mixture was then diluted with 500 ml benzene, washed with water (5 × 200 ml) and dried over sodium sulfate. After concentrating to ca. 20 ml, ether (20 ml) was added and the mixture chilled. Dropwise addition of pet. ether to the cold mixture afforded the E isomer which was removed by filtration. After complete removal of the E isomer, the filtrate was evaporated to an oil, redissolved in ether (15 ml), chilled and treated with pet. ether to give the Z isomer. Further recrystallization from benzene–pet. ether gave analytically pure samples of each isomer. Table II lists all the compounds obtained by this procedure.

1-Arylsulfonyl-4-(N′-anilino)-2-arylthio-2-butenes (**8f–k**, *X* = *NH*). A mixture of the appropriate thiophenol (0.04 moles) and triethylamine (0.01 moles) in 100 ml benzene was added, in one lot, to a well-stirred solution of **2** (0.04 moles) in 200 ml benzene. This solution was stirred for 8–10 hours under nitrogen at room temperature. Completion of reaction was monitored by disappearance of starting materials (TLC: Benzene/ether (9 : 1)). The reaction mixture was then filtered for removal of precipitated product (exclusively E isomer). The reaction mixture was diluted with 200 ml benzene, washed with water (4 × 200 ml) and dried over sodium sulfate. After concentrating the solution *in vacuo* to ca. 40 ml, chilling and adding pet. ether afforded a crude solid mixture of E and Z isomers of the vinyl sulfide product. Further fractions of crude solid mixtures containing the E and Z isomers were obtained by reconcentrating, chilling, and adding pet. ether to the filtrate. The yield of vinyl sulfide products (E and E/Z mixtures) obtained was always greater than 80%.

Separation of the E and Z isomers from the crude mixture was accomplished by repeated fractional crystallization from chloroform–pet. ether to afford, after filtration, pure E vinyl sulfide. The Z isomer was obtained from the combined filtrates only after removal of the E isomer. Crystallization of the Z isomer was achieved by removal of the chloroform–pet. ether solvents, redissolving the oil in benzene, chilling and adding pet. ether. Further recrystallization of each isomer from benzene–pet. ether gave analytically pure products. Table III lists all the compounds obtained by this procedure.

Attempted Isomerization of **8E** *and* **8Z** (*X* = *S*, *NH*). The isomerization of **8E** and **8Z** was examined by the following general procedure.

Pure **8** (E and Z isomers) and an E/Z (1 : 1) mixture (0.0002 moles) were each stirred with NEt_3 (0.0001 moles) in 2.5 ml benzene at room temperature under nitrogen. Thin-layer chromatographic analysis revealed no apparent change within the reaction mixture even after 20 hours. The solutions were then refluxed for 7 hours, after which they were diluted with 100 ml benzene, washed with water (3 × 50 ml) and dried over Na_2SO_4. The solvent was removed *in vacuo* and the resultant solid (oil in the case of the E/Z mixture) was examined by ^1H NMR. Comparison of these spectra with authentic spectra showed no apparent changes in absorption patterns or relative peak intensities. The E isomer and the Z isomer did not interconvert.

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