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Total Stereochemical Control in the Addition of Thiols to *p*-Toluenesulfonylacetylene. Synthesis of *Z*- and *E*-2-Sulfanylvinylsulfonyl Derivatives

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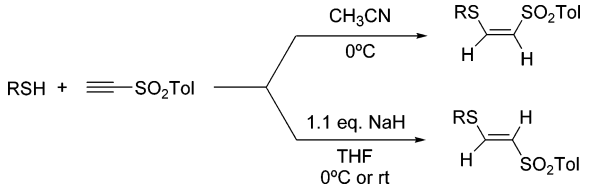
Received September 9, 2004



Alkyl and aryl sulfides react with equimolecular amounts of *p*-toluenesulfonylacetylene in CH_3CN at 0 °C or rt without the use of any catalytic reagent to give good yields of *Z*-2-sulfanylvinylsulfonyl derivatives with total diastereoselectivity. On the other hand, in the presence of 1.1 equiv of NaH in THF, the same reaction affords the corresponding *E*-diastereomer also with total diastereoselectivity.

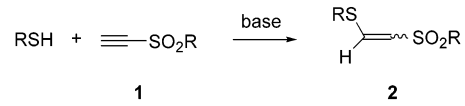
The base-catalyzed addition of thiols to acetylenic sulfones **1** to give the corresponding sulfanyl-substituted vinyl sulfones **2** has been known for many years (Scheme 1).[1]

The application of this reaction as a new method for the protection of the thiol group has recently been reported.[2] In all cases, this reaction follows the "*trans*-rule"; i.e., *trans* addition of the RS and H moieties gives the *Z* derivatives ***Z*-2**.

In a previous paper,[3] we have described the uncatalyzed addition of aromatic and aliphatic thiols to *p*-toluenesulfonylacetylene to give variable yields of the expected addition products mainly as *Z*-isomers. The best conditions for this transformation were the use of an excess of thiol which was always recovered in 90−100% yield and, in general, long reaction times. In some cases, reactions under reflux of CH_2Cl_2 were necessary in order to obtain moderate to good isolated yields of the final product.

With the exception of this previous account, the uncatalyzed addition of thiols to arylsulfonylacetylenes has

SCHEME 1



no precedent in the literature.[4] Thus, considering the interesting functionality present in vinyl sulfones such as **2** we decided to optimize this uncatalyzed addition with respect to stereoselectivity, economical ratio of reagents, as well as reaction conditions.

In addition, for both catalyzed and uncatalyzed addition, the "*trans*-rule" appears to be followed without exception. Then, our second objective was a search of experimental conditions in order to obtain the corresponding *E*-isomer with a convenient stereoselectivity. The description of how these two goals were achieved is the subject of the present report.

Results

Uncatalyzed Addition: Synthesis of *Z*-2-Sulfanylvinyl Sulfone Derivatives *Z*-2. Assuming that the most likely intermediate for this uncatalyzed addition should be a zwitterionic species (Figure 1) stabilized by the participation of the remote *p*-toluenesulfonyl group,[5] the increase of the solvent polarity of the reaction medium should also increase the reaction rate avoiding the use of an excess of the reagent and shortening the reaction time.[6]

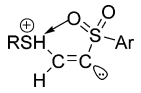


FIGURE 1. Assistance of the *p*-toluenesulfonyl group to a remote positive center.

On the other hand, the participation of the arylsulfonyl group should also secure the *Z*-stereochemistry of the final product. Thus, we decided to carry out the reaction in CH_3CN as solvent. The results, compared with the use of THF, are gathered in Table 1.

By comparison of the results in both solvents, we can make the following conclusions. (i) For aliphatic thiols (entries 1−7) the use of CH_3CN allows for the synthesis of the corresponding *Z*-diastereomers with high diastereoselectivity, in short reaction times, and in excellent

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(1) See, for instance: (a) Stirling, C. J. M. *J. Chem. Soc*. **1964**, 5856−5862. (b) Truce, W. E.; Tichenor, G. J. W. *J. Org. Chem*. **1972**, *37*, 2391−2394. (c) Selling, H. A. *Tetrahedron* **1975**, *31*, 2387−2390.

(2) Arjona, O.; Medel, R.; Rojas, J. K.; Costa, A. M.; Vilarrasa, J. *Tetrahedron Lett*. **2003**, *44*, 6369−6373.

(3) Arjona, O.; Iradier, F.; Medel, R.; Plumet, J. *J. Org. Chem*. **1999**, *64*, 6090−6093.

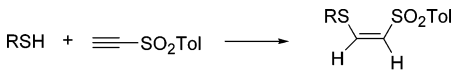
(4) The UV-irradiation-induced addition of thiols to monosubstituted propargilyc alcohols has been also reported. See: (a) Mantione, R.; Normant, H. *Bull. Soc. Chem. Fr.* **1973**, 2261−2265. For other additions of thiols to alkynes under radical conditions, usually giving stereoisomeric mixtures, see: (b) Kuniyasu, H.; Ogawa, A.; Sato, K.; Ryu, I.; Kambe, N.; Sonoda, N. *J. Am. Chem. Soc.* **1992**, *114*, 5902−5903. (c) Kuniyasu, H.; Ogawa, A.; Sato, K.; Ryu, I.; Sonoda, N. *Tetrahedron Lett*. **1992**, *33*, 5525−5528. (d) Ogawa, A.; Kudo, A.; Hirao, T. *Tetrahedron Lett*. **1998**, *3*, 5213−5216 and references therein. For the uncatalyzed addition to methylpropiolate, see: (e) Kodomari, M.; Saitoh, G.; Yoshitomi, S. *Bull. Soc. Chem. Jpn.* **1991**, *64*, 3485−3487.

(5) See, for instance: Lambert, J. B.; Beadle, B. M.; Kuang, K. *J. Org. Chem*. **1999**, *64*, 9241−9246.

(6) For instance, the rate constant for the reaction between piperidine and methylpropiolate increases by a factor of 865 from cyclohexane to acetonitrile. See: Giese, B.; Huisgen, R. *Tetrahedron Lett*. **1967**, 1889−1892.

10.1021/jo0402576 CCC: $30.25
Published on Web 12/22/2004

TABLE 1. Uncatalyzed Addition of Thiols to *p*-Toluenesulfonylacetylene[a]

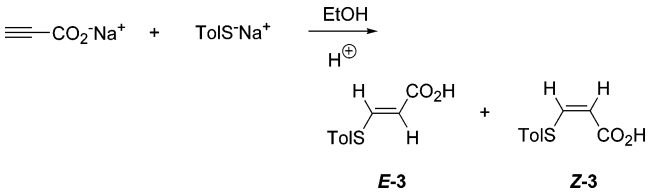


1 **Z-2**

entry	R	solvent	reaction time (h)	*T* (°C)	compd (isolated yield, %)[b]	*Z*/*E* ratio[c]
1	Bn	CH_3CN	0.5	0	***Z*-2a** (98)	100:0
2	*p*-$ClC_6H_4CH_2$	THF	5	rt[d]	***Z*-2b** (70)	100:0
3	*p*-$ClC_6H_4CH_2$	CH_3CN	2	0	***Z*-2b** (92)	90:10
4	*p*-$MeOC_6H_4CH_2$	THF	5	rt	***Z*-2c** (85)	100:0
5	*p*-$MeOC_6H_4CH_2$	CH_3CN	1	0	***Z*-2c** (100)	90:10
6	$CH_3(CH_2)_6CH_2$	THF	5	rt	***Z*-2d** (31)	100:0
7	$CH_3(CH_2)_6CH_2$	CH_3CN	1.5	0	***Z*-2d** (100)	98:2
8	C_6H_5	THF	5	rt	***Z*-2e** (49)	100:0
9	C_6H_5	CH_3CN	0.5	0	***Z*-2e** (99)	100:0
10	*p*-$NO_2C_6H_4$	THF	5	rt	***Z*-2f** (49)	100:0
11	*p*-$NO_2C_6H_4$	CH_3CN	19	0	***Z*-2f** (63)	100:0[e]
12[f]	*p*-$NO_2C_6H_4$	CH_2Cl_2	2	rt	***Z*-2f** (89)	100:0
13	*p*-$MeOC_6H_4$	CH_3CN	1	0	***Z*-2g** (67)	100:0

[a] 1.1 equiv of **1** was used. [b] Isolated yields after purification of reaction crude by column chromatography (hexanes−EtOAc, 10:1). [c] Determined in the ^1H NMR spectra of the crude residue product. For the *Z*-isomer δ_H = 6.16−6.43 and 6.92−7.26, J = 10.2−10.3 Hz. For the *E*-isomer data, see below. [d] rt means between 20 and 23 °C. [e] A ratio of *Z*/*E* = 95:5 was observed after column chromatography. [f] 1.5 equiv of thiol was used.

SCHEME 2



***E*-3** ***Z*-3**

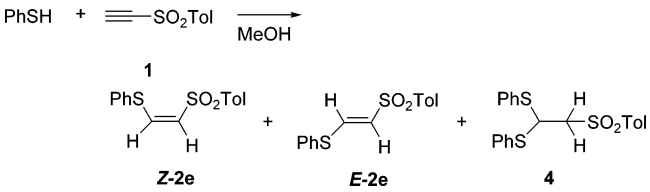
yields. Particularly notorious is the effect of the change of the solvent in the case of *n*-octanethiol (compare entries 6 and 7, Table 1). Almost equimolecular amounts of reagents were used in all cases (thiol/sulfone ratio = 1:1.1). (ii) For aromatic thiols with different electronic demand we have observed in all cases an excellent diastereoselectivity. In the case of the *p*-nitro derivative (entries 10−12, Table 1), the best results were obtained in CH_2Cl_2 using a slight excess of thiol (1.5:1) whereas for the *p*-methoxybenzenethiol the adduct was obtained only with acceptable yield (entry 13). It should be pointed out that, for this compound, the best results using CH_2Cl_2 as solvent require the use of a 3:1 thiol/sulfone ratio. In this case and after 7 days, a quantitative yield of the vinyl sulfone was obtained but in diastereomeric ratio *Z*/*E* = 1.5:1.[3]

NaH-Promoted Addition: Synthesis of *E*-2-Sulfanylvinyl Sulfone Derivatives (*E*-2). To obtain the corresponding *E*-isomers we turned our attention to an old report of Truce and Heine[7] in which the addition of *p*-toluenethiol to propiolic acid in the presence of catalytic amounts of EtONa in EtOH afforded the mixture of *Z*- and *E*-alkenes **3**. Thus, and at least partially, the "*trans*-rule" has been violated (Scheme 2).

Then we decided to use these strongly basic conditions for the preparation of the corresponding ***E*-2** derivatives.

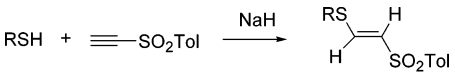
(7) Truce, W. E.; Heine, R. F. *J. Am. Chem. Soc.* **1957**, *79*, 5311−5313.

SCHEME 3



***Z*-2e** ***E*-2e** **4**

TABLE 2. NaH-Promoted Addition of Thiols to *p*-Toluenesulfonylacetylene[a]



1 ***E*-2**

entry	R	reaction time (min)	*T* (°C)	compd (isol yield, %)[b]	*Z*/*E* ratio[c]
1	Bn	20	0	***E*-2a** (100)	0:100
2	*p*$ClC_6H_4CH_2$	20	0	***E*-2b** (100)	0:100
3	*p*$MeOC_6H_4CH_2$	20	0	***E*-2c** (100)	0:100
4	$CH_3(CH_2)_6CH_2$	20	0	***E*-2d** (100)	0:100
5	C_6H_5	90	0 to rt[d]	***E*-2e** (100)	<2:>98
6	*p*$NO_2C_6H_4$	60	0 to rt	***Z*-2f** (100)	100:0
7	*P*$MeOC_6H_4$	300	0 to rt	***E*-2g** (40)	0:100

[a] All reactions were conducted in THF using 1.1 equiv of **1** and in the presence of 1.1 equiv of NaH. [b] Isolated yields after purification of reaction crude by column chromatography (hexanes−EtOAc, 10:1). [c] Determined in the ^1H NMR spectra of the crude residue product. For the *E*-isomer δ_H = 5.83−7.24, 7.57−7.80, J = 14.2−14.7 Hz. [d] rt means 21.5−23 °C.

In a first approach the use of MeOH as solvent appears not to be convenient because, in a control experiment, the uncatalyzed addition of benzenethiol to sulfone **1** in MeOH afforded a mixture of ***Z*-2e** and ***E*-2e** in 65% isolated yield (ratio *Z*/*E* = 4:1) together with the product arising for a second addition of thiol **4** in 30% isolated yield (Scheme 3).

However, when 1.1 equiv of NaH was used in THF, excellent yields of the corresponding ***E*-2** isomers were obtained (Table 2) with the exception of compound **2f** (entry 6, Table 2). For this thiol and after 1 h (0 °C to rt) only diastereomer ***Z*-2f** was obtained in quantitative yield. In this case, an increase of temperature and/or reaction time led to extensive decomposition of the reaction crude. On the other hand, for compound ***E*-2g**, excellent stereoselectivity albeit in low yield (40%) was obtained (entry 7, Table 2).

Conclusions

In summary, in this paper, convenient methods for the stereoselective synthesis of *Z*- and *E*-2-sulfanylvinyl sulfone derivatives have been described. Especially significant is the development of an uncatalyzed procedure for the synthesis of *Z*-isomers probably through a stepwise, sulfone-assisted mechanism. The detailed mechanism is currently under study in our laboratory. Moreover, given the importance of vinylsulfonyl and vinylsulfanyl derivatives, the combination of both functionalities in a single molecule offers new synthetic possibilities which are currently under consideration.

Experimental Section

General Procedure for the Synthesis of *Z*-2-Sulfanylvinyl Sulfone Derivatives (*Z*-2a−g). To a solution of *p*-

toluenesulfonylacetylene **1** (0.33 mmol) in 3 mL of CH_3CN or THF (see Table 1) was added the corresponding thiol (0.30 mmol). The mixture was stirred at the temperature and for the time indicated in Table 1. The solvent was removed in vacuo without heating. The ratio of isomers was determined in the ^1H NMR spectra of the crude residue product, and the crude residue was sometimes purified (it was not always required) by column chromatography on silica gel using a mixture of hexanes−EtOAc (10:1) as eluant. Compounds ***Z*-2e−g** have been previously described as thiosulfonylethylene derivatives.[3]

1-[[(*Z*)-2-(Benzylsulfanyl)vinyl]sulfonyl]-4-methylbenzene, *Z*-2a. White solid. Mp: 109−110 °C. IR (KBr): ν 3090, 1590, 1350. ^1H NMR ($CDCl_3$, 200 MHz): δ 2.44 (s, 3 H), 3.96 (s, 2 H), 6.18 (d, 1 H, J = 10.3 Hz), 6.98 (d, 1 H, J = 10.3 Hz), 7.31−7.34 (m, 7 H), 7.84 (d, 2 H, J = 8.30 Hz). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 21.6, 39.3, 123.4, 127.2, 127.8, 128.9, 129.0, 129.7, 136.1, 138.5, 144.3, 144.6. Anal. Calcd for $C_{16}H_{16}O_2S_2$: C, 63.13; H, 5.30. Found: C, 63.08; H, 5.40.

1-Chloro-4-[[[(*Z*)-2-[(4-methylphenyl)sulfonyl]vinyl]sulfanyl]methyl]benzene, *Z*-2b. White solid. Mp: 123−124 °C. IR (KBr): ν 3100, 1630, 1150. ^1H NMR ($CDCl_3$, 300 MHz): δ 2.45 (s, 3 H), 3.91 (s, 2 H), 6.18 (d, 1 H, J = 10.3 Hz), 6.92 (d, 1 H, J = 10.3 Hz) 7.19−7.33 (m, 6 H), 7.82 (d, 2 H, J = 8.0 Hz). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 21.5, 38.6, 123.8, 127.1, 128.9, 129.6, 130.2, 133.6, 134.2, 138.2, 144.0, 144.7. Anal. Calcd for $C_{16}H_{15}ClO_2S_2$: C, 56.71; H, 4.46. Found: C, 56.68; H, 4.50.

1-Methoxy-4-[[[(*Z*)-2-[(4-methylphenyl)sulfonyl]vinyl]-sulfanyl]methyl]benzene, *Z*-2c. White solid. Mp: 119−120 °C. IR (KBr): ν 3080, 1615, 1310. ^1H NMR ($CDCl_3$, 200 MHz): δ 2.43 (s, 3 H), 3.79 (s, 3 H), 3.90 (s, 2 H), 6.16 (d, 1 H, J = 10.3 Hz), 6.84 (d, 2 H, J = 8.5 Hz), 6.93 (d, 1 H, J = 10.3 Hz), 7.18−7.32 (m, 4 H), 7.83 (d, 2 H, J = 8.3 Hz). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 21.6, 38.8, 55.3, 114.3, 123.2, 127.2, 128.0, 129.7, 130.3, 138.5, 144.3, 144.8, 159.2. Anal. Calcd for $C_{17}H_{18}O_3S_2$: C, 61.05; H, 5.42. Found: C, 60.97; H, 5.48.

1-Methyl-4-[[(*Z*)-2-(octylsulfanyl)vinyl]sulfonyl]benzene, *Z*-2d. Pale yellow oil. IR ($CHCl_3$): ν 1643, 1425, 1314. ^1H NMR ($CDCl_3$, 200 MHz): δ 0.88 (t, 3 H, J = 6.8 Hz) 1.25−1.39 (m, 10 H), 1.56−1.70 (m, 2 H), 2.43 (s, 3 H), 2.74 (t, 2 H, J = 7.1 Hz), 6.20 (d, 1 H, J = 10.3 Hz), 7.03 (d, 1 H, J = 10.3 Hz), 7.32 (dd, 2 H, J = 8.3, 0.7 Hz), 7.86 (d, 2 H, J = 8.3 Hz). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 13.9, 21.5, 22.5, 28.1, 28.9, 29.9, 31.6, 36.1, 122.6, 127.1, 129.5, 138.6, 144.1, 146.7. Anal. Calcd for $C_{17}H_{26}O_2S_2$: C, 62.57; H, 7.97. Found: C, 62.51; H, 8.05.

1-Methyl-4-[[(*Z*)-2-(phenylsulfanyl)vinyl]sulfonyl]-benzene, *Z*-2e. White solid. Mp 107−108 °C. IR (KBr): ν 3045, 1319, 1290. ^1H NMR ($CDCl_3$, 300 MHz): δ 2.45 (s, 3 H), 6.26 (d, 1 H, J = 10.3 Hz), 7.22 (d, 1 H, J = 10.3 Hz), 7.34−7.40 (m, 5 H), 7.42−7.47 (m, 2 H), 7.92 (d, 2 H, J = 8.3 Hz). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 21.6, 122.9, 127.2, 128.7, 129.5, 129.8, 131.2, 134.6, 138.3, 144.5, 146.1. Anal. Calcd for $C_{15}H_{14}O_2S_2$: C, 62.07; H, 4.83. Found: C, 62.12; H, 4.66.

1-Methyl-4-[[(*Z*)-2-[(4-nitrophenyl)sulfanyl]vinyl]sulfonyl]-benzene, *Z*-2f. White solid. Mp: 152−153 °C. IR (KBr): ν 3651, 1545, 1342. ^1H NMR ($CDCl_3$, 200 MHz): δ 2.46 (s, 3 H), 6.43 (d, 1 H, J = 10.2 Hz), 7.26 (d, 1 H, J = 10.2 Hz), 7.37 (d, 2 H, J = 8.1 Hz), 7.58 (d, 2 H, J = 8.8 Hz), 7.88 (d, 2 H, J = 8.6 Hz), 8.22 (d, 2 H, J = 9.0 Hz). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 21.6, 124.4, 125.7, 127.3, 130.0, 130.2, 137.7, 141.2, 143.2, 145.0. Anal. Calcd for $C_{15}H_{13}NO_4S_2$: C, 53.73; H, 3.88. Found: C, 53.81; H, 3.65.

1-Methoxy-4-[[(*Z*)-2-[(4-methylphenyl)sulfonyl]vinyl]sulfanyl]benzene, *Z*-2g. White solid. Mp: 138−139 °C. IR (KBr): ν 3385, 1493, 1249. ^1H NMR ($CDCl_3$, 200 MHz): δ 2.45 (s, 3 H), 3.80 (s, 3 H), 6.18 (d, 1 H, J = 10.2 Hz), 6.88 (d, 2 H, J = 9.0 Hz), 7.11 (d, 1 H, J = 10.2 Hz), 7.35 (d, 2 H, J = 8.1 Hz), 7.37 (d, 2 H, J = 9.0 Hz), 7.91 (d, 2 H, J = 8.3 Hz). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 21.6, 55.4, 115.0, 122.0, 125.1, 127.1, 129.7, 133.7, 138.4, 144.4, 148.0, 160.3. Anal. Calcd for $C_{16}H_{16}O_3S_2$: C, 60.00; H, 5.00. Found: C, 60.14; H, 4.92.

General Procedure for the Synthesis of *E*-2-Sulfanylvinyl Sulfone Derivatives (*E*-2a−g). Thiol (0.30 mmol) was added to a stirred suspension of NaH (0.33 mmol, 60% in mineral oil) in THF at 0 °C. After 10 min, the solution was added dropwise to a solution of *p*-toluenesulfonylacetylene **1** (0.33 mmol) in THF (1.5 mL) at 0 °C, under Ar. The mixture was stirred at the temperature and for the time indicated in Table 2. The reaction was quenched with phosphate buffer and extracted with CH_2Cl_2. The organic extracts were collected and dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The ratio of isomers was determined in the ^1H NMR spectra of the crude residue product, and the crude reaction product was sometimes purified (it was not always required) by column chromatography on silica gel using a mixture of hexanes−EtOAc (10:1) as eluant. Compounds ***E*-2e−g** have been previously described as thiosulfonylethylene derivatives.[3]

1-[[(*E*)-2-(Benzylsulfanyl)vinyl]sulfonyl]-4-methylbenzene, *E*-2a. White solid. Mp: 115−116 °C. IR (KBr): ν 3090, 1583, 1297. ^1H NMR ($CDCl_3$, 200 MHz): δ 2.44 (s, 3 H), 3.99 (s, 2 H), 6.19 (d, 1 H, J = 14.4 Hz), 7.23−7.33 (m, 7 H), 7.66−7.73 (m, 3 H). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 21.5, 37.0, 122.9, 127.3, 128.0, 128.7, 128.9, 129.8, 134.6, 138.2, 144.0, 144.2. Anal. Calcd for $C_{16}H_{16}O_2S_2$: C, 63.13; H, 5.30. Found: C, 63.19; H, 5.38.

1-Chloro-4-[[[(*E*)-2-[(4-methylphenyl)sulfonyl]vinyl]sulfanyl]methyl]benzene, *E*-2b. White solid. Mp: 131−132 °C. IR (KBr): ν 2998, 1610, 1220. ^1H NMR ($CDCl_3$, 300 MHz): δ 2.45 (s, 3 H), 3.97 (s, 2 H), 6.17 (d, 1 H, J = 14.7 Hz), 7.22−7.31 (m, 6 H), 7.63−7.70 (m, 3 H). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 21.5, 36.2, 123.4, 127.3, 129.0, 129.8, 130.0, 133.1, 133.9, 138.0, 143.5, 144.0. Anal. Calcd for $C_{16}H_{15}ClO_2S_2$: C, 56.71; H, 4.46. Found: C, 56.67; H, 4.40.

1-Methoxy-4-[[[(*E*)-2-[(4-methylphenyl)sulfonyl]vinyl]-sulfanyl]methyl]benzene, *E*-2c. White solid. Mp: 125−126 °C. IR (KBr): ν 3090, 1590, 1310. ^1H NMR ($CDCl_3$, 200 MHz): δ 2.42 (s, 3 H), 3.80 (s, 3 H), 3.95 (s, 2 H), 6.18 (d, 1 H, J = 14.7 Hz), 6.85 (d, 2 H, J = 8.5 Hz), 7.18−7.32 (m, 4 H), 7.64−7.72 (m, 3 H). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 21.6, 36.5, 55.3, 114.3, 122.8, 126.4, 127.3, 129.8, 130.0, 138.3, 143.9, 144.4, 159.4. Anal. Calcd for $C_{17}H_{18}O_3S_2$: C, 61.05; H, 5.42. Found: C, 61.12; H, 5.37.

1-Methyl-4-[[(*E*)-2-(octylsulfanyl)vinyl]sulfonyl]benzene, *E*-2d. Pale yellow oil. IR ($CHCl_3$): ν 1643,1410,1260. ^1H NMR ($CDCl_3$, 200 MHz): δ 0.89 (t, 3 H, J = 6.8 Hz) 1.26−1.42 (m, 10 H), 1.58−1.73 (m, 2 H), 2.44 (s, 3 H), 2.76 (t, 2 H, J = 7.1 Hz), 6.12 (d, 1 H, J = 14.6 Hz), 7.33 (d, 2 H, J = 8.5 Hz), 7.71 (d, 1 H, J = 14.6 Hz), 7.76 (d, 2 H, J = 8.3 Hz). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 14.0, 21.5, 22.6, 28.3, 28.7, 29.0, 31.7, 32.4, 121.9, 127.3, 129.8, 138.4, 143.9, 145.4. Anal. Calcd for $C_{17}H_{26}O_2S_2$: C, 62.57; H, 7.97. Found: C, 62.50; H, 7.91.

1-Methyl-4-[[(*E*)-2-(phenylsulfanyl)vinyl]sulfonyl]-benzene, *E*-2e. White solid. Mp: 91−92 °C. IR (KBr): ν 3069, 1493, 1277. ^1H NMR ($CDCl_3$, 200 MHz): δ 2.43 (s, 3 H), 5.99 (d, 1 H, J = 14.4 Hz), 7.31 (d, 2 H, J = 8.5 Hz), 7.41−7.46 (m, 5 H), 7.71 (d, 2 H, J = 8.3 Hz), 7.80 (d, 1 H, J = 14.4 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 21.6, 123.5, 127.4, 127.5, 129.8, 129.9, 133.3, 133.4, 135.4, 144.1, 145.6. Anal. Calcd for $C_{15}H_{14}O_2S_2$: C, 62.07; H, 4.83. Found: C, 62.15; H, 4.70.

1-Methyl-4-[[(*E*)-2-[(4-nitrophenyl)sulfanyl]vinyl]sulfonyl]-benzene, *E*-2f. Pale yellow oil. IR ($CHCl_3$): ν 2926, 1599, 1306. ^1H NMR ($CDCl_3$, 200 MHz): δ 2.48 (s, 3 H), 7.24 (d, 1 H, J = 14.2 Hz), 7.39 (d, 2 H, J = 8.1 Hz), 7.57 (d, 1 H, J = 14.2 Hz), 7.76 (d, 2 H, J = 9.0 Hz), 7.81 (d, 2 H, J = 9.0 Hz), 8.43 (d, 2 H, J = 9.0 Hz). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 21.7, 124.6, 125.1, 125.4, 128.2, 130.4, 135.4, 135.4, 145.9, 146.8, 147.7. Anal. Calcd for $C_{15}H_{13}NO_4S_2$: C, 53.73; H, 3.88. Found: C, 53.68; H, 3.70.

1-Methoxy-4-[[(E)-2-[(4-methylphenyl)sulfonyl]vinyl]sulfanyl]benzene, *E*-2g. White solid. Mp: 87−88 °C. IR (KBr): ν 3853, 1496, 1302. ^1H NMR ($CDCl_3$, 200 MHz): δ 2.42 (s, 3 H), 3.82 (s, 3 H), 5.83 (d, 1 H, J = 14.4 Hz), 6.92 (d, 2 H, J = 8.8 Hz), 7.30 (d, 2 H, J = 8.5 Hz), 7.36 (d, 2 H, J = 9.0 Hz), 7.69 (d, 2 H, J = 9.3 Hz), 7.75 (d, 1 H, J = 14.4 Hz). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 21.5, 55.4, 115.5, 118.9, 122.8, 127.3, 129.8, 135.7, 138.1, 143.9, 146.8, 161.0. Anal. Calcd for $C_{16}H_{16}O_3S_2$: C, 60.00; H, 5.00. Found: C, 59.87; H, 4.79.

Procedure for the Reaction between *p*-Toluenesulfonylacetylene 1 and Benzenethiol. To a solution of *p*-toluenesulfonylacetylene **1** (0.33 mmol) in MeOH (3 mL) was added benzenethiol (0.30 mmol). The mixture was stirred at room temperature for 5 h. The solvent was removed in vacuo

without heating. The ratio of products (***Z*-2e**, ***E*-2e**, and **4**) was determined in the ^{1}H NMR spectra of the crude residue product. The crude residue was purified by column chromatography on silica gel using a mixture of hexanes−EtOAc (10:1) as eluant. Compound **4** has been previously described as the bisthiosulfonylethane derivative.[3]

1-[[2,2-Bis(phenylsulfanyl)ethyl]sulfonyl]-4-methylbenzene, 4. Pale yellow oil. IR ($CHCl_3$): ν 3042, 2399, 1323. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 2.38 (s, 3 H), 3.45 (d, 2 H, J = 6.6 Hz), 4.68 (t, 1 H, J = 6.6 Hz), 7.19−7.28 (m, 8 H), 7.31−7.36 (m, 4 H), 7.65 (d, 2 H, J = 8.3 Hz). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 21.7, 50.6, 60.3, 128.4, 128.6, 129.2, 129.8, 132.3, 133.3, 133.4, 145.0. Anal. Calcd for $C_{21}H_{20}O_2S_3$: C, 63.00; H, 5.00. Found: C, 62.89; H, 5.13.

Acknowledgment. Ministerio de Ciencia y Tecnología of Spain (Project BQU2003-04967), Consejería de Educación de la C.A.M (Spain), and COVEX S.A. are gratefully thanked for financial support. Thanks are also due to Professors Dr. Aurelio G. Csákÿ and Dr. Pilar Goya for fruitful discussions.

Supporting Information Available: ^{1}H NMR and ^{13}C NMR spectra copies for compounds ***Z*-2a−d** and ***E*-2−d**. ^{1}H NMR and ^{13}C NMR spectra copies for compounds ***Z*-2e−g, *E*-2e−g**, and **4** have been previously submitted.[3] This material is available free of charge via the Internet at http://pubs.acs.org.

JO0402576