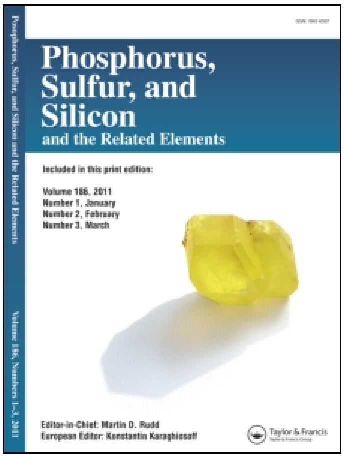

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1,4-DIARYLSULFONYL-1,3-BUTADIENES FROM 1,4-DIARYLSULFONYL-2-BUTYNES

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1,4-DIARYLSULFONYL-1,3-BUTADIENES FROM 1,4-DIARYLSULFONYL-2-BUTYNES

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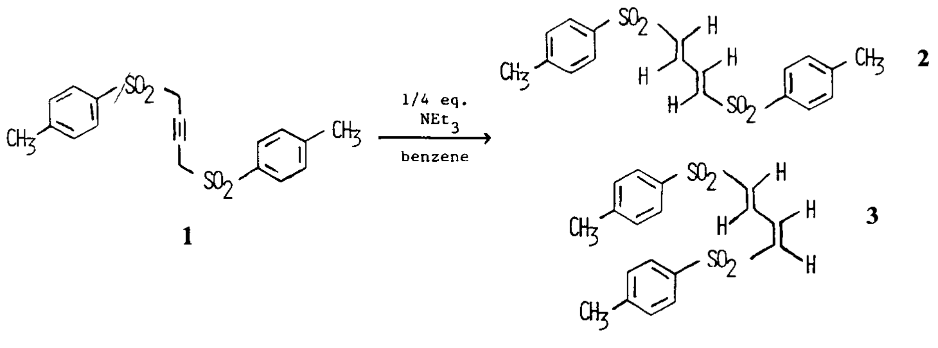
Isomerization of 1,4-diarylsulfonyl-2-butynes under aprotic conditions and ambient temperatures with mild base catalysis leads to the title compounds.

The recent announcement by S. Ramakanth *et al.*[1] of "An unexpected isomerisation of 1,4-diaryloxy-2-butynes to *Z,Z*-1,4-diaryloxy-1,3-butadienes" prompts us to disclose our contemporaneous results in related investigations.[2]

Our study, described below, utilizes the bis sulfone **1**,[3] with the anticipation that the acidifying influence of the sulfone function would make any such isomerization more facile.[4] As expected, the sulfone **1**, under ambient temperatures, in benzene solution (or in a 90/10 v/v mixture of benzene/DMF), with triethylamine (0.25 equivalent) as base catalyst, readily affords a mixture of TWO DIENES in high yields.[5] The dienes are readily separable by fractional crystallization (from benzene and benzene–ether mixtures) and their yields ranging from 60 to 90% reflect the isolated pure products. In all these aspects, the isomerization of the sulfone **1** differs significantly from the reported behavior of 1,4-diaryloxy-2-butynes (loc. cit.) (Scheme 1).



SCHEME 1 Isomerization of 1,4-diarylsulfonyl-2-butyne.

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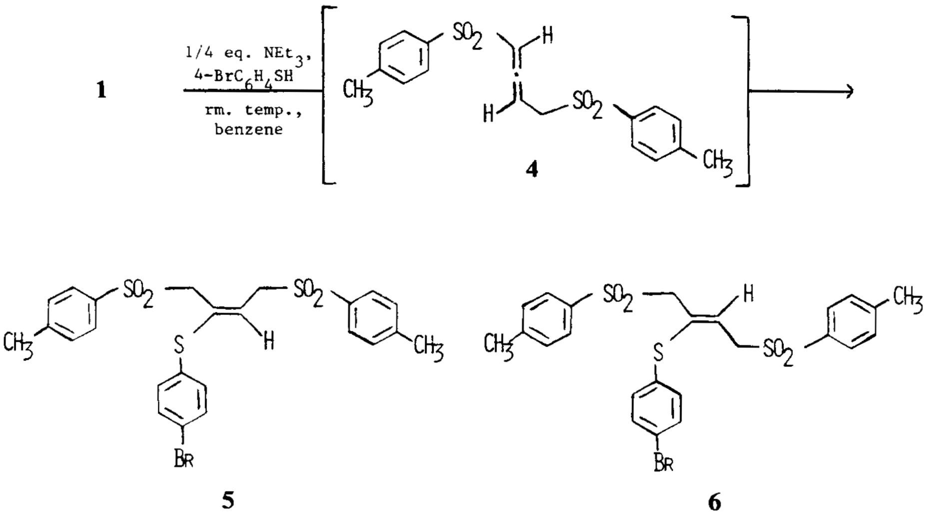
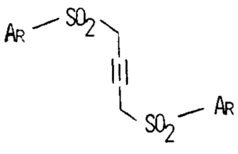


SCHEME 2 Allene trapping by thiophenol.



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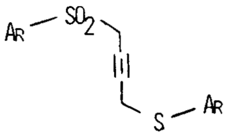

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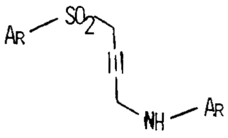

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X = ArSO$_2$, ArS

Y = ArS, ArO, COAr, CO$_2$R, CN, etc.

TABLE I

Stereoisomeric 1,4-diarylsulfonyl-1,3-butadienes

Ar	E,E diene		E,Z diene	
	yield	mp, (°C)	yield	mp, (°C)
4-$CH_3C_6H_4$	57%	202–203	28%	149–150
4-$CH_2OC_6H_4$	40%	213–214	14%	127–128
2-$CH_3C_6H_4$	63%	201–202	8%	136–137
4-BrC_6H_4	52%	250–251	10%	148–149

TABLE II

Spectral properties of 1,4-diarylsulfonyl-1,3-butadienes

Ar	Isomer	IR (KBr, cm^{-1})	^{1}H NMR[a] (δ in CDCl$_3$)	UV (CHCl$_3$) (nm (log ε)]	m/z (rel. intensity)	Analysis Found (Calc.) %C	%H
4-CH$_3$C$_6$H$_4$	EE	1590, 1572, 1310, 1140, 988	7.8–7.2 (m, 8 H), 7.15–6.7 (m, 4 H), 2.4 (s, 6 H)	276 (4.46) 242 (3.92)	362 (M + , 11.5), 207 (3), 139 (100), 91 (43.9), 65 (24.5)	59.84 (59.67)	5.09 (4.97)
	EZ	1590, 1562, 1312, 1140 988	8.6–8.0 (m, 1 H), 7.8–7.2 (m, 8 H), 6.9–6.4 (m, 3 H), 2.4 (s, 6 H)	269 (4.42)	362 (M + , 2.6), 207 (36.6), 139 (100), 91 (35.7), 65 (16.9)	60.06 (59.67)	4.91 (4.97)
4-CH$_3$OC$_6$H$_4$	EE	1588, 1575, 1318, 1140, 970	7.9–6.8 (m, 8 H), 7.15–6.7 (m, 4 H), 3.9 (s, 6 H)	294 (4.44) 246 (4.23)	394 (M + , 44.3), 330 (22), 158 (37), 155 (100), 115 (22), 92 (28), 77 (29.8)	54.80 (54.82)	4.64 (4.57)
	EZ	1588, 1570, 1315, 1140, 1010	8.6–8.0 (m, 1 H), 7.9–6.9 (m, 8 H), 6.8–6.4 (m, 3 H), 3.9 (s, 6 H)	294 (4.22) 247 (4.30)		54.97 (54.82)	4.71 (4.57)
2-CH$_3$C$_6$H$_4$	EE	1590, 1570, 1310, 1144, 993	8.1–7.25 (m, 8 H), 7.2–6.8 (m, 4 H), 2.6 (s, 6 H)	269 (4.53)	(M + not seen), 207 (M—ArSO$_2$, 8), 189 (63.2), 143 (53.4), 142 (100), 141 (73.8), 139 (51), 101 (53), 91 (43), 77 (43.5)	58.97 (59.67)	5.73 (4.97)
	EZ	1590, 1560, 1303, 1142, 993	8.6–8.1 (m, 1 H), 8.05–7.15 (m, 8 H), 7.0–6.5 (m, 3 H),	267 (4.45)	(M + not seen), 207 (M—ArSO$_2$, 41), 189 (64), 143 (51), 142 (97.9), 141 (78.8), 139 (100), 101 (57), 91 (71.9), 77 (61)	59.66 (59.67)	5.14 (4.97)
4-BrC$_6$H$_4$	EE	1575, 1323, 1140, 1010, 981	7.7 (s, 8 H), 7.2–6.7 (m, 4 H)	278 (4.55) 248 (4.22)		38.95 (39.02)	2.28 (2.44)
	EZ	1565, 1318, 1140, 1005, 965	8.6–8.0 (m, 1 H), 7.7 (s, 8 H), 6.9–6.45 (m, 3 H)	277 (4.51) 247 (4.20)	492 (M + , 0.90), 273 (34.6), 271 (34.6), 205 (100), 203 (92), 152 (18), 150 (18)	38.91 (39.02)	2.43 (2.44)

[a] Reference 7.

To demonstrate the possible intermediacy of an allene **4** in the above isomerization, we have carried out the reaction in the presence of a thiophenol (1.0 equivalent) admixed with the triethylamine. The products under these conditions, are *not the dienes* but the vinyl sulfides **5** and **6**, as depicted in Scheme 2.

The regioselective addition of thiophenols to such allenes generated from analogous propynyl sulfones has been elegantly demonstrated by Stirling.[4] The high degree of stereoselectivity observed in a series of similar sulfones **7**, **8** and **9** was reported on by us recently.[6]

Table I summarizes the different dienes[7] obtained during the course of this study with 1,4-diarylsulfonyl-2-butynes.

Further work is in progress wherein we are extending similar isomerizations to 2-butynes bearing other acidifying functions, as illustrated in structure **10**.

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2. B. S. Thyagarajan, B. F. Wood Jr. and P. J. Franklin, Paper no. 325, 39th Southwest Regional Meeting of the ACS, Dec. 7–9, 1983.
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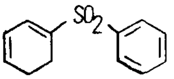
4. C. J. M. Stirling, *J. Chem. Soc.* (1964), 5856.
5. All new compounds are supported by excellent elemental analysis, ultraviolet, infrared, NMR, and mass spectral data (See Table II).
6. B. S. Thyagarajan and B. F. Wood Jr., Paper no. 324, 39th Southwest Regional Meeting of the ACS, Dec. 7–9, 1983.
7. The geometries of the diene systems of **2** and **3** were determined by ^{13}C and ^{1}H NMR spectroscopy. The symmetrical compound **2** gave ^{13}C spectrum of 7 lines, while the unsymmetrical compound **3** produced 12 lines with coincidental chemical shifts of the methyl carbons and two olefinic carbons. Differentiation between the two possible symmetrical structures (E,E or Z,Z) was accomplished by spin simulation of the *observed* centrosymmetric AA′BB′ pattern of the diene systems. The $\nu_A - \nu_B = 32$ Hz, $J_{AB} = +13$ Hz, $J_{BB'} = -10$ Hz, and $J_{AB'} = +1.5$ Hz parameters *reproduced the actual spectrum*, with the J_{AB} value being consistent only with the proposed E,E geometry. Additional confirmation for the E,Z isomer was obtained by comparison[8] of its proton NMR data with those of compound **11**. We thank Professor P. L. Fuchs, Department of Chemistry, Purdue University, for generously providing us with NMR data as well as a sample of **11**.



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