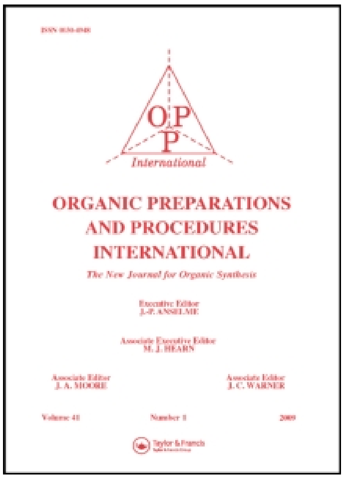

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SYNTHESIS OF (E,E)-BIS(ARYLCYCLOPROPYL) SULFONES FROM NOVEL (E,E)-BIS(STYRYL) SULFONES

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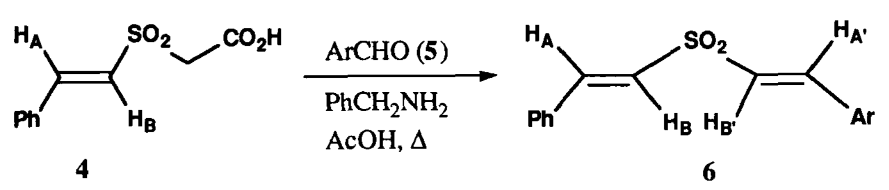
Although some symmetrical bis(styryl) sulfones with (E,E)-configurations have been known for some time,[1] the synthesis of mixed (E,E)-bis(styryl) sulfones are of recent vintage.[2] Kobayashi *et al.*[3] synthesized (E,E)-mixed bis(styryl) sulfones by ruthenium(II) complex-catalyzed addition of arylethenesulfonyl chlorides to styrenes. This communication reports a simple procedure for the synthesis of (E,E)-mixed bis(styryl) sulfones, which are valuable precursors for the synthesis of



a) Ar = C_6H_5	b) Ar = 4-$CH_3C_6H_4$	c) Ar = 4-$Me_2CHC_6H_4$
d) Ar = 4-$EtOC_6H_4$	e) Ar = 3-MeO,4-$EtOC_6H_3$	f) Ar = 4-FC_6H_4
g) Ar = 4-ClC_6H_4	h) Ar = 2,4-$Cl_2C_6H_3$	i) Ar = 2,6-$Cl_2C_6H_3$
j) Ar = 3,4-$Cl_2C_6H_3$	k) Ar = 4-$NO_2C_6H_4$	l) Ar = 2-$C_{10}H_7$

cyclopropanes,[2] pyrazolines,[4] thiomorpholines and dithiane oxides.[5] Compared to the Kobayashi procedure, this method offers simpler reaction conditions, comparable yields and the use of inexpensive chemicals. These bis(styryl) sulfones have also been converted to cyclopropanes by the Corey and Chaykovsky method[6] to form (E,E)-bis(arylcyclopropyl) sulfones.

The mixed bis(styryl) sulfones (**6**) were prepared by the Knovenagel condensation of (E)-styrylsulfonylacetic acid (**4**) with araldehydes (**5**) in the presence of a catalytic amount of benzylamine and glacial acetic acid (in 91% yield). The (E)-styrylsulfonylacetic acid (**4**) was obtained in 63% yield by the condensation of chloroacetic acid (**3**) with (E)-sodium styrylsulfinate (**2**), itself prepared by treatment of (E)-styrylsulfonyl chloride (**1**) with sodium bicarbonate and sodium sulfite. The purity of **6** (Table 1) was checked by TLC on silica gel-H using hexane/ether (3:2) eluent.

TABLE 1. Yield, mp. and Analysis of **6** and **8**

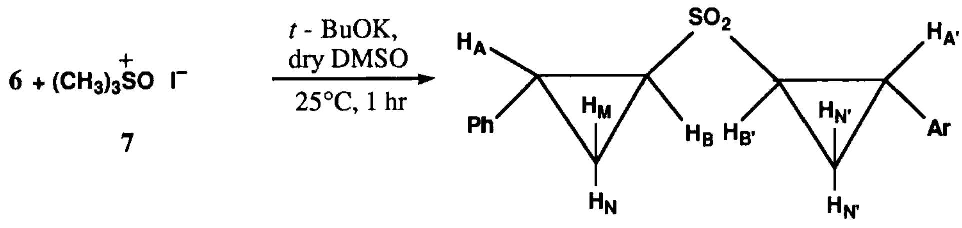
Product	Yield (%)	mp (°C)	Elemental Analysis (Calcd.) C	H
6a	78	97-98	71.31(71.09)	5.16 (5.12)
6b	82	114-115	71.52 (71.78)	5.94 (5.67)
6c	86	107-108	72.90 (73.04)	6.38 (6.45)
6d	74	105-106	69.03 (68.75)	5.64 (5.76)
6e	83	150-151	66.11 (66.25)	5.74 (5.85)
6f	88	126-127	67.93 (67.82)	4.46 (4.62)
6g	84	146-147	63.22 (63.04)	3.49 (3.57)
6h	80	100-101	56.82 (56.63)	3.64 (3.57)
6i	79	133-134	56.60 (56.63)	3.64 (3.57)
6j	81	187-188	61.12 (60.94)	3.98 (4.15)
6k	78	135-136	72.84 (72.93)	5.27 (5.44)
8a	62	132-134	72.17 (72.44)	5.96 (6.07)
8b	73	135-136	73.28 (73.04)	6.34 (6.45)
8c	58	126-127	69.42 (69.48)	6.25 (6.13)
8d	61	116-118	73.98 (74.07)	6.98 (7.10)
8e	54	143-145	67.76 (67.70)	6.41 (6.49)
8f	76	156-157	65.14 (64.95)	5.08 (5.15)
8g	66	149-150	59.12 (58.85)	4.25 (4.39)

The configuration of these compounds was determined on the basis of the chemical shifts and coupling constants of vinylic protons in the ^{1}H NMR spectra (Table 2).

TABLE 2. IR and ^{1}H NMR Data of **6**

Cmpd	IR (KBr) SO_2 (cm^{-1})	^{1}H NMR -CH=CH- (δ ppm)	J_{AB} (Hz)	$J_{A'B'}$ (Hz)	ArH (m)
6a	1320, 1117	6.85, 7.62	15.48	15.48	7.32-7.52
6b	1328, 1112	6.78, 6.85	15.54	15.82	7.15-7.68
6c	1325, 1124	6.82, 6.89	15.43	15.63	7.22-7.69
6d	1318, 1122	6.78, 6.88	15.52	15.47	7.18-7.64
6e	1320, 1110	6.72, 6.89	15.84	15.72	7.00-7.68
6f	1330, 1124	6.77, 6.86	15.72	15.66	7.24-7.71
6g	1330, 1128	6.82, 6.89	15.62	15.52	7.16-7.58
6h	1328, 1116	6.82, 6.91	15.64	15.48	7.22-7.59
6i	1325, 1128	6.84, 6.88	15.44	15.67	7.18-7.69
6j	1334, 1124	6.78, 6.84	15.48	15.42	7.21-7.53
6k	1334, 1128	6.88, 6.93	15.54	15.82	7.21-7.78
6l	1322, 1117	6.78, 6.87	15.39	15.49	7.14-7.63

Since **6** are Michael acceptors, we studied the cyclopropanation of the two olefinic bonds with sulfur ylides. Cyclopropanation of activated double bonds have usually been performed by generating the ylide *in situ* from the sulfonium salts or by preparing the stable ylide first and then adding it to the Michael acceptor.[7] We now report the synthesis of mixed bis(arylcyclopropyl) sulfones (**8**) by the addition of dimethylsulfoxonium methylide generated *in situ* from trimethylsulfoxonium iodide (**7**) in the presence of potassium *t*-butoxide to **6**. The configurational assignment of **8** is supported by ^{1}H NMR and IR spectral data (Table 3).



8

a) Ar = C_6H_5 b) Ar = 4-$CH_3C_6H_5$ c) Ar = 4-$EtOC_6H_4$ d) Ar = 4-$(CH_3)_2CHC_6H_4$
e) Ar = 3-MeO,4-$EtOC_6H_3$ f) Ar = 4-ClC_6H_4 g) Ar = 2,6-$Cl_2C_6H_3$

TABLE 3. ^{1}H NMR data of **8**

Cmpd	CH$_2$ (t)	SO$_2$-(CH)$_2$ (m)	Ar-CH C$_5$H$_5$-CH (m)	J_{AB} (Hz)	$J_{A'B'}$ (Hz)	Ar-H (m)
8a	2.45-2.71	3.15-3.35	3.55-3.90	3.99	3.90	7.05-7.53
8b	2.35-2.62	3.08-3.30	3.41-3.53 3.88-3.53	4.03	3.99	6.90-7.49
8c	2.36-2.62	3.08-3.29	3.42-3.52 3.90-3.98	4.08	4.02	6.85-7.49
8d	2.45-2.69	3.12-3.32	3.43-3.57 3.87-4.00	3.93	3.88	6.98-7.51
8e	2.44-2.68	3.12-3.33	3.42-4.53 3.91-3.97	4.02	3.89	7.18-7.48
8f	2.32-2.64	3.14-3.32	3.42-3.59 3.87-3.93	4.18	4.08	7.10-7.49
8g	2.36-2.691	3.07-3.30	3.46-3.54 3.89-3.92	4.12	4.00	7.05-7.68

The ^{1}H NMR peaks at δ 2.35-2.65 may be assigned[2,8] to the methylene protons H_M, H_N, $H_{M'}$, $H_{N'}$. The methine protons attached to aromatic groups are more deshielded than the tow protons which are in adjacent positions to the "sulfonyl" group. Hence H_A and $H_{A'}$ absorb at higher frequency as two quarters at δ 3.40-3.95; whereas H_B and $H_{B'}$ appear as two other quarters in the higher field around δ 3.50-3.30. Analysis of the spectra also show that the coupling constants J_{AB} and $J_{A'B'}$ around 4.0 Hz which confirms their geometry.[7,9] The IR spectra of **8** exhibit medium to strong bands in the region 1025-1010 cm^{-1} (cyclopropane ring deformation) indicating the presence of the cyclopropane ring system. They also show strong bands around 1330 and 1125 cm^{-1} for the sulfonyl group.[2,9]

EXPERIMENTAL SECTION

All melting points are uncorrected. IR spectra were measured on a Perkin-Elmer 781 Infrared Spectrophotometer as KBr discs. ^{1}H NMR spectra were recorded on Bruker 250 and 500 MHz spectrophotometer using TMS as an internal standard.

Styrylsulfonyl Chloride (1).- Sulfuryl chloride (70 g, 81 mmol) was added dropwise with stirring to N-methylpyrrolidine cooled at 0° under nitrogen; then the reaction mixture was brought to room temperature and styrene (50 g, 48 mmol) was added all at once. The contents were gradually heated to 90° and maintained at this temperature for 4 hrs, cooled and then poured onto crushed ice (900 g). The separated pale yellow solid was collected and recrystallized from chloroform-light petroleum (60-80°) to give **1** (76 g, 79%) of white crystals, mp. 87-88°, lit.[10] mp. 86.5°.

Sodium Styrylsulfinate (2)[11].- Styrylsulfonyl chloride (4.67 g, 33 mmol) in portions was added to a stirred solution of sodium bicarbonate (5.2 g, 62 mmol) and sodium sulfite (7.5 g, 60 mmol) over a period of 30-45 min. After the addition the reaction mixture was stirred for 1 hr and kept aside for overnight. The white crystalline solid **2** separated was collected and dried.

Styrylsulfonylacetic Acid (4)[12].- Dried **2** (19.09 g, 100 mmol) and chloroacetic acid **3** (9.4 g, 1.00 mmol) were dissolved in water and the solution was made alkaline to pH 10. The mixture was heated on a sand bath for 3 hrs, cooled and poured onto crushed ice. The contents were neutralized with dilute HCl and the separated **4** was collected and dried to yield 14 g (63%) of white solid. Recrystallization from hot water gave colorless shining crystals, mp. 121-122°.

IR (KBr): 1730 (CO_2H); 1618 (C=C); 1320, 1116 (SO_2) cm^{-1}.

^1H NMR($CDCl_3$): δ 6.95 (d, 1H, H_A, J_{AB} = 15.72 Hz); 7.15-7.42 (m, 5H arom), 7.48 (d, 1H, H_B, J_{BA} = 15.72 Hz).

Anal. Calcd. for $C_{10}H_{10}O_4S$: C, 53.08; H, 4.45. Found: 6, 53.24; H, 4.41

(E,E)-Bis(styryl) sulfones 6. General Procedure[13].- A solution of (E)-styrylsulfonylacetic acid (**4**) (2.263 g, 10 mmol) in glacial acetic acid (6 ml) was mixed with an araldehyde **5** (10 mmol) and benzylamine (0.2 ml) and refluxed for 3 hrs. The reaction mixture was cooled, treated with dry ether (50 ml) and any product which separated was collected by filtration. The filtrate was diluted with more ether and washed successively with a saturated solution of sodium bicarbonate (1.5 ml), sodium bisulfite (1.5 ml), dilute hydrochloric acid (20 ml) and finally with water (30 ml). Evaporation of the dried ethereal layer yielded **6** as a solid product.

(E,E)-Bis(arylcyclopropyl) sulfones 8. General Procedure.- A mixture of **6** (10 mmol) and **7** (20 mmol) in dry dimethyl sulfoxide (25 mL) was stirred until a clear solution was obtained. To this solution, potassium *t*-butoxide (20 mmol) in dry dimethyl sulfoxide (25 ml) was added dropwise at 25°. After complete addition, the reaction mixture was stirred for an additional hr, diluted with more water arid stirred overnight, or until crude **8** separated as a solid, which was collected (Table 1).

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