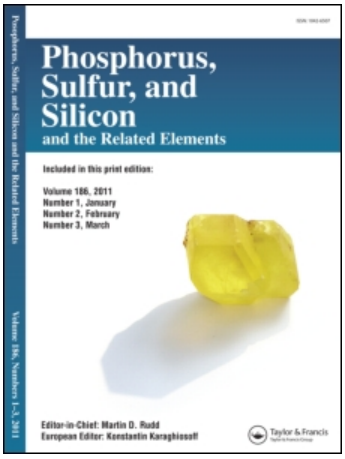

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A NEW APPROACH TO THE SYNTHESIS OF ISOMERIC *E,Z*- AND *E,E*-BIS(STYRYL)SULFONES AND A STUDY OF THEIR CYCLOPROPANATION

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The *E,Z*- and *E,E*-bis(styryl)sulfones (**V** & **X**) have been synthesized from 4-methylphenylacetylene (**I**) and 4-methylstyrene (**VI**), respectively. The cyclopropanation of **V** and **X** with dimethylsulfoxonium methylide by PTC or Corey and Chaykovsky methods gave *E,E*-1,1′-bis(2-arylcyclopropyl)sulfones (**XI**) only. The spectral parameters of these compounds have been discussed.

Key words: *E,Z* and *E,E*-bis(styryl)sulfones; Knoevenagel condensation; cyclopropanation; phase transfer catalysis; dimethylsulfoxonium methylide.

INTRODUCTION

Recent years have witnessed an impressive number of publications devoted to organosulfur chemistry.[1] Sulfones are probably the best known for their biological activity. Chlorothiazide and hydrochlorothiazide series having sulfone group find application as diuretics.[2] Sulfonal, trional and tetronal are known as sedatives and hypnotics.[3] Some bis(alkylthio)haloethylenes, aryl vinyl sulfones and alkylsulfonyl aryl acetylenes are used as effective fungicides.[4,5] Moreover, the bis(styryl)sulfones are recognized as good Michael acceptors and as versatile synthons for the synthesis of many carbocyclic and heterocyclic systems,[6,7] which possess sulfone moiety as a potential pharmacophore. Apart from these, the chemistry of unsaturated sulfones has also received much attention as they are useful as dienes,[8] dienophiles[9] and precursors of vinyl anions[10] for the synthesis of relatively complex molecules.

Earlier, we have reported the synthesis of some *E,Z*-[11,12] and *E,E*[6]-bis(styryl)sulfones and used them for the synthesis of a variety of organic compounds. Encouraged by their increasing importance in organic synthesis, some new isomeric bis(styryl)sulfones have been synthesized by different strategies and studied their cyclopropanation reaction.

RESULTS AND DISCUSSION

The *E,Z*-bis(styryl)sulfones (**V**) have been prepared by the Knoevenagel condensation of *Z*-4-methylstyrylsulfonylacetic acid (**IV**) with araldehydes in the presence

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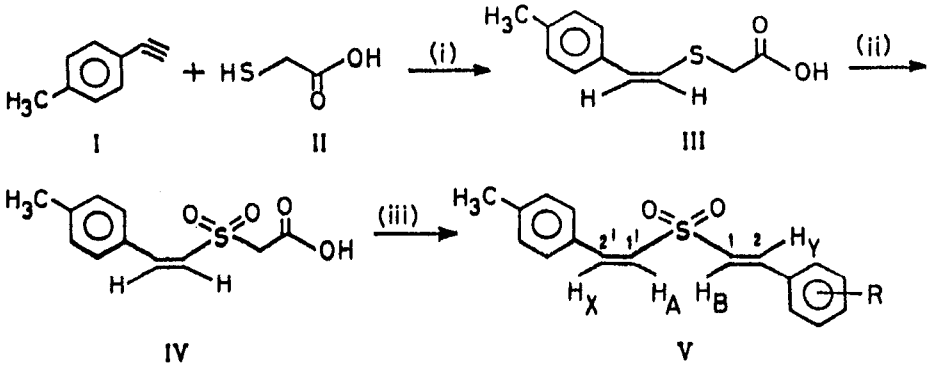
of a catalytic amount of benzylamine. The **IV** has been obtained by the nucleophilic addition of mercaptoacetic acid (**II**) with 4-methylphenylacetylene (**I**) in methanolic sodium hydroxide and subsequent oxidation of the resultant 4-methylstyrylthioacetic acid (**III**) with hydrogen peroxide (Scheme 1 and Table I).

On the other hand, the *E,E*-bis(styryl)sulfones (**X**) have been obtained by a different method. Addition of sulfuryl chloride to dimethylformamide at 0°C gave *E*-4-methylstyrylsulfonyl chloride (**VII**) which has been converted to 4-methylstyrylsulfinate (**VIII**) by the reaction of $NaHCO_3$ and Na_2SO_3. The **VIII** on condensation with chloroacetic acid afforded *E*-4-methylstyrylsulfonylacetic acid (**IX**). Knoevenagel condensation of **IX** with araldehydes resulted **X** (Scheme 2 and Table I).

The UV absorption spectra of *E,Z*- and *E,E*-bis(styryl)sulfones (**V** & **X**) exhibited bands in the regions 280–385, 230–241 and 203–220 nm. The high intensity band is due to the conjugation of sulfur atom with the styryl moiety while the second band is ascribed to the 'partial' diconjugative effect of the chromophores.[13] The *E*-band of benzene appeared at 203–226 nm. The *E,E*-isomers showed higher λ_{max} and ε_{max} than *E,Z*-isomers.[14]

The IR spectra of **V** and **X** exhibited absorption bands at 1625–1600 cm^{-1} for the presence of C=C bond. The =CH out-of-plane deformation mode observed in the region 990–975 & 850–810 and 985–960 cm^{-1} confirms the *E,Z*- and *E,E*-geometry of **V** and **X**, respectively.[6,11] Both **V** and **X** displayed strong bands at 1335–1300 & 1130–1110 cm^{-1} for the asymmetric and symmetric stretching vibrations of the SO_2 group.[12]

The ethylenic protons, H_X and H_Y of **V** and **X** experiences more deshielding effect than H_A and H_B and consequently appeared at relatively downfield region (Table II). The J_{AX} (~12) and J_{BY} (~15) values indicates the *Z*- and *E*-geometry of the ethylenic protons of **V**.[11] Similarly, the *J* values obtained in the region 15 Hz shows the *E,E*-geometry of **X**.[15] In case of **Xn** only two doublets have been observed as the substituents at both the phenyl moieties are the same. Both **V** and **X** displayed multiplets in the region 6.92–7.82 ppm for the aromatic ring protons.



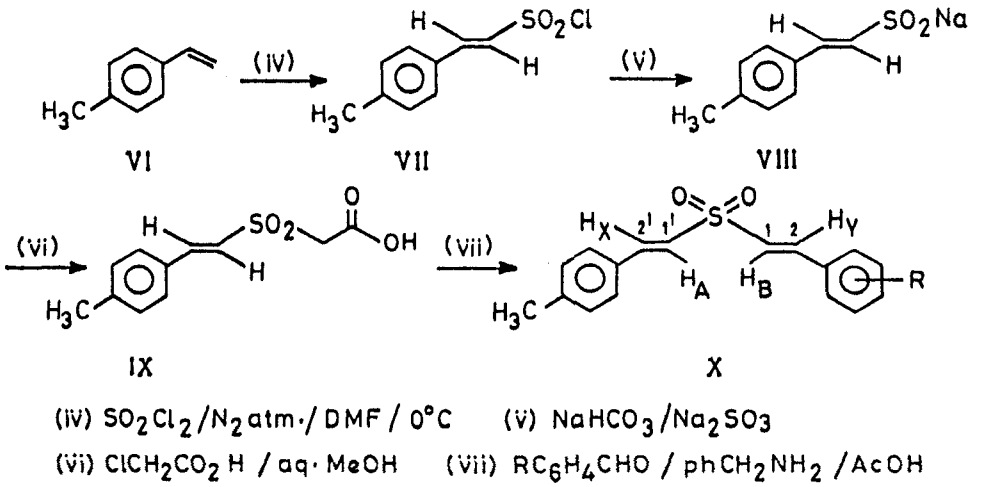
(i) NaOH/MeOH/HCl (ii) H_2O_2/AcOH (iii) RC_6H_4CHO/phCH_2NH_2/AcOH

Scheme 1

TABLE I

Compd. No.		R	Yield (%)	m.p. (°C)	Mol.formula (mol.wt.)	Found(Calcd.)(%) C	H
V	a	H	75	100-101	$C_{17}H_{16}O_2S$ (284.36)	71.51 (71.80)	5.56 (5.67)
	b	4-CH_3	67	122-123	$C_{18}H_{18}O_2S$ (298.38)	72.67 (72.45)	6.20 (6.08)
	c	4-OCH_3	78	115-116	$C_{18}H_{18}O_3S$ (314.38)	69.00 (68.76)	5.68 (5.77)
	d	4-OC_2H_5	74	93-94	$C_{19}H_{20}O_3S$ (328.41)	69.64 (69.48)	6.29 (6.14)
	e	4-F	70	124-125	$C_{17}H_{15}FO_2S$ (302.35)	67.35 (67.53)	4.84 (5.00)
	f	2-Cl	58	95-96	$C_{17}H_{15}ClO_2S$ (318.81)	63.79 (64.04)	4.62 (4.74)
	g	4-Cl	89	140-141	$C_{17}H_{15}ClO_2S$ (318.81)	64.24 (64.04)	4.64 (4.74)
	h	4-Br	91	142-143	$C_{17}H_{15}BrO_2S$ (363.26)	56.04 (56.20)	4.08 (4.16)
	i	4-CH-$(CH_3)_2$	70	104-105	$C_{20}H_{22}O_2S$ (326.44)	73.80 (73.58)	6.92 (6.79)
	j	3-OCH_3-4-OC_2H_5	76	95-96	$C_{20}H_{22}O_4S$ (358.44)	67.17 (67.01)	6.10 (6.19)
	k	2,4-Cl_2	65	114-115	$C_{17}H_{14}Cl_2O_2S$ (353.25)	57.58 (57.80)	4.05 (3.99)
	l	2,6-Cl_2	82	118-119	$C_{17}H_{14}Cl_2O_2S$ (353.25)	57.55 (57.80)	3.88 (3.99)
	m	R^2-C_6H_5 = 2-$C_{10}H_7$	60	153-154	$C_{21}H_{18}O_2S$ (334.41)	75.60 (75.42)	5.51 (5.42)
X	a	H	79	119-120	$C_{17}H_{16}O_2S$ (284.38)	72.02 (71.80)	5.79 (5.67)
	b	4-CH_3	80	172-173	$C_{18}H_{18}O_2S$ (298.40)	72.63 (72.45)	5.99 (6.08)
	c	4-OC_2H_5	77	141-142	$C_{19}H_{20}O_3S$ (328.43)	69.20 (69.48)	6.06 (6.13)
	d	2-Cl	66	128-129	$C_{17}H_{15}ClO_2S$ (318.82)	63.86 (64.04)	4.86 (4.74)
	e	4-Cl	85	151-152	$C_{17}H_{15}ClO_2S$ (318.82)	64.29 (64.04)	4.87 (4.74)
	f	4-$CH(CH_3)_2$	70	135-136	$C_{20}H_{22}O_2S$ (326.46)	73.42 (73.58)	6.68 (6.79)
	g	3-OCH_3-4-OC_2H_5	78	130-131	$C_{20}H_{22}O_4S$ (358.46)	67.27 (67.01)	6.29 (6.19)
	h	2,4-Cl_2	74	127-128	$C_{17}H_{14}Cl_2O_2S$ (353.27)	57.59 (57.80)	3.89 (3.99)

The ^{13}C NMR spectra of both **V** and **X** showed δ_C values for the ethylenic carbons C-1 & C-1′ and C-2 and C-2′ in the regions 140.17–144.98 and 129.87–132.27, respectively. The C-1 & C-1′ being adjacent to sulfur, displayed resonance signals at relatively downfield region than C-2 & C-2′.[16] The mass spectra of **V** and **X** exhibited low intense molecular ion peaks corresponding to their chemical com-



Scheme 2

TABLE II

Compd. No.	^{1}H NMR($CDCl_3$) δ, ppm				Coupling constants, Hz	
	H_A	H_B	H_X	H_Y	J_{AX}	J_{BY}
V a	6.52	6.70	7.13	7.44	12.12	15.36
d	6.58	6.42	7.40	7.24	12.20	15.38
f	6.45	6.76	7.20	7.58	12.15	15.35
g	6.65	6.84	7.45	7.64	12.16	15.32
h	6.36	6.67	7.36	7.46	12.15	15.30
k	6.60	6.85	7.54	7.67	12.20	15.36
m	6.55	6.74	7.25	7.45	12.16	15.42
X a	6.82	6.88	7.61	7.63	15.36	15.38
b	6.79	-	7.62	-	15.38	-
c	6.80	6.69	7.58	7.55	15.39	15.37
e	6.80	6.87	7.63	7.67	15.37	15.39
h	6.86	7.08	7.68	7.73	15.38	15.40

position. Base peak is derived from the molecular ion by the loss of SO_2H radical. The extrusion of SO_2 is a facile process resulting in moderately abundant diphenylbutadiene radical cation.[17] The other important fragmented ions observed in the spectra (Table III) are due to sulfonylsulfinate rearrangement[18] and McLafferty-type rearrangement[19] of the M^+. It is of interest to note that the fragmentation pattern of the isomers (**V** and **X**) have been found to be almost identical irrespective of their geometry.

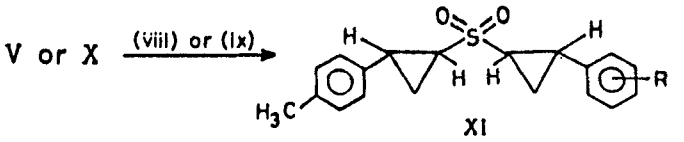
Cyclopropanation of **V** or **X** with non-stabilized sulfur ylide, dimethyl sulfoxonium methylide, generated *in situ* by the reaction of trimethylsulfoxonium iodide under phase transfer catalyzed conditions (PTC) afforded *E,E*-1,1′-bis(2-arylcyclopropyl) sulfones (**XI**) (Scheme 3 and Table IV). The **XI** was also obtained by

TABLE III

Compd.No./ ions	Va	Vb	Vg	Xa	Xc
$M^{+\cdot}$	284(4)	298(6)	318(7)	284(5)	318(4)
$[M\text{-}SO_2]^{+\cdot}$	220(26)	234(52)	254(34)	220(40)	264(36)
$[M\text{-}SO_2H]^{+}$	219(100)	233(100)	253(100)	219(100)	263(100)
$[C_{11}H_9O_2S]^{+}$	205(16)	205(28)	-	205(17)	-
$[C_9H_9OS]^{+}$	-	165(12)	-	151(6)	151(10)
$[RC_8H_6OS]^{+}$	151(9)	165(12)	185(12)	151(6)	-
$[C_{11}H_{10}]^{+\cdot}$	142(12)	142(18)	142(13)	142(12)	142(14)
$[C_9H_{10}O]^{+}$	133(15)	133(10)	133(25)	133(4)	133(8)
$[C_8H_7]^{+\cdot}$	118(18)	118(32)	118(24)	118(29)	118(16)
$[RC_8H_6]^{+}$	103(21)	117(18)	137(15)	103(28)	147(14)
$[RC_8H_5]^{+\cdot}$	102(13)	116(14)	136(8)	102(27)	146(6)
$[C_8H_9]^{+}$	105(52)	105(46)	105(64)	105(38)	105(23)
$[RC_6H_4]^{+}$	77(38)	91(68)	111(47)	77(58)	121(23)

Note: Values in the parenthesis indicate the percentage intensity.

'-' indicates absence of a peak.



(VIII) $(CH_3)_3S(O)I$ / 50% aq. NaOH / BTEAC / CH_2Cl_2

(ix) $(CH_3)_3S(O)I$ / dry DMSO / t-BuO^-K^+

Scheme 3

TABLE IV

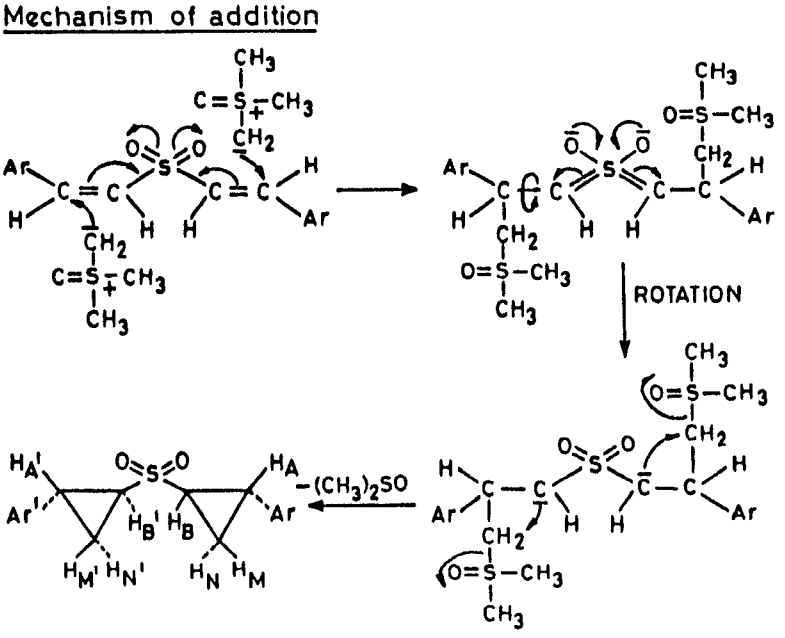
Compd. No.		R	Yield (%) Method 'A'	Yield (%) Method 'B'	m.p. (°C)	Mol.formula (mol.wt.)	Found (Calcd.) (%) C	H
XI	a	H	70	55	138-139	$C_{19}H_{20}O_2S$ (312.43)	72.88 (73.04)	6.56 (6.45)
	b	4-CH_3	74	50	116-118	$C_{20}H_{22}O_2S$ (326.46)	73.83 (73.58)	6.87 (6.79)
	c	4-OC_2H_5	72	56	124-125	$C_{21}H_{24}O_3S$ (356.46)	70.55 (70.75)	6.67 (6.79)
	d	2-Cl	65	45	156-157	($C_{19}H_{19}ClO_2S$ (346.87)	65.61 (65.79)	5.44 (5.52)
	e	4-Cl	77	60	126-127	$C_{19}H_{19}ClO_2S$ (346.49)	66.07 (65.79)	5.66 (5.52)
	f	3-OCH_3-4-OC_2H_5	70	50	125-126	$C_{22}H_{26}O_4S$ (386.49)	68.12 (68.36)	6.65 (6.78)
	g	2,4-Cl_2	68	60	168-170	$C_{19}H_{18}Cl_2O_2S$ (381.32)	59.70 (59.85)	4.89 (4.76)

Corey & Chaykovsky method[20] with trimethylsulfoxonium iodide in dry DMSO in the presence of a strong base, potassium *t*-butoxide. In PTC method, higher yields (65–77%) have been obtained in comparison to Corey & Chaykovsky method (55–69%). This shows the elegancy and facile nature of PTC method.

The stereochemistry of addition of the ylide to unsaturated system is an important aspect of this study. Addition of dimethylsulfoxonium methylide to *E,Z* or *E,E*-bis(styryl)sulfones (**V** or **X**) gave *E,E*-1,1′-bis(2-aryl cyclopropyl)sulfones (**XI**) only. It is presumed that the addition of the ylide to **V** or **X** results an intermediate which may rotate in such a way that the aryl and sulfonyl groups assume *trans*-orientation (Scheme 4). Analysis of the ^{1}H NMR spectra of **XI** showed that J_{AB} is inbetween 5–6 Hz indicating the *trans*-geometry.[21] Indeed, earlier we have shown that the addition of dimethylsulfoxonium methylide to *Z,Z*- or *E,E*-bis(styrylsulfonyl)benzenes resulted in *E,E*-bis(2-arylcyclopropylsulfonyl)benzene only.[22]

The IR spectra of **XI** showed characteristic bands for methylene group, cyclopropane ring system and sulfonyl group in the regions 3090–3080, 1040–1010, 1340–1300 and 1155–1115 cm^{-1}, respectively.[6] Further, bands with varying intensities observed in the regions 1110–1075 and 945–920 cm^{-1} are ascribed to the *E*-geometry of **XI**.[6]

The ^{1}H NMR spectra of **XI** displayed ABMN pattern. The methine and methylene protons of each cyclopropyl unit involved in vicinal and geminal couplings and consequently each one of them appeared as a doublet of a double doublet (ddd). The H_A is absorbed at relatively downfield region than H_B due to the deshielding effect exerted by phenyl moiety[23] (Table V). Besides this, the H_M which



Scheme 4

TABLE V

Compd. No.	^{1}H NMR($CDCl_3$) δ, ppm			
	H_A	H_B	H_M	H_N
XI a	2.92	2.76	2.10	1.68
b	2.89	2.73	2.06	1.65
d	2.90	2.73	2.12	1.65
e	2.94	2.77	2.16	1.68
g	3.00	2.85	2.17	1.80

TABLE VI

Compd.No./ions	XIa	XIb	XIe
$M^{+\cdot}$	312(8)	326(8)	346(6)
$[M-H_2]^{+\cdot}$	310(7)	324(10)	344(5)
$[M-2H_2]^{+\cdot}$	308(29)	322(35)	342(22)
$[M-SO_2]^{+\cdot}$	248(39)	262(56)	282(37)
$[M-RC_6H_4]^+$	235(18)	221(33)	235(15)
$[M-C_{10}H_{11}]^+$	131(100)	131(100)	131(52)
$[M-RC_9H_8]^+$	117(65)	131(100)	151(100)
$[M-RC_9H_7]^{+\cdot}$	116(16)	130(39)	150(20)
$[RC_7H_7]^{+\cdot}$	91(26)	105(37)	125(28)
$[RC_9H_6]^+$	115(48)	129(62)	149(27)
$[C_8H_9]^+$	105(26)	105(37)	105(33)

Note: Values in the parenthesis indicate the percentage intensity.

is *trans*- to phenyl moiety experiences more deshielding effect and consequently appeared at higher δ_H value than H_N.[23]

In cyclopropyl systems $J_{cis} > J_{trans}$(J_{cis} = 8.3, J_{trans} = 5.6 Hz).[24] The J values for the methine and methylene protons of **XI** were found to be J_{AB} = 5.70–5.76, J_{AM} = 8.52–8.60, J_{AN} = 6.60–6.68, J_{BM} = 5.50–5.60, J_{BN} = 10.10–10.15 and J_{MN} = 4.60–4.68 Hz. Thus, the geometry of different protons are H_AH_M = H_BH_M = H_AH_N = *trans*; H_AH_M = H_AH_N = *cis*; H_MH_N = *geminal*. The aromatic protons displayed signals in the region 6.82–7.68 ppm as multiplets.

The δ_C values at 37.87–39.75, 22.05–24.66 and 13.73–14.98 are assigned to C-1 & C-1′, C-2 & C-2′ and C-3 & C-3′ of **XI**. The C-1 and C-1′, adjacent to sulfone moiety experiences more deshielding effect than C-2 and C-2′, adjacent to phenyl moiety. The upfield signals observed are however, attributed to the unsubstituted carbons C-3 & C-3′ of the cyclopropane rings. The mass spectra (70 eV) of **XI** showed low abundant molecular ion peaks. α-Cleavage process, elimination of SO_2 and ejection of one- and two molecules of hydrogen are some of the common features predominantly observed in the fragmentation of the M^+. The phenylcyclopropyl cation (m/z 117) appeared as the base peak of the spectrum. The different fragmented ions formed in the disintegration of **XI** are given in Table VI.

EXPERIMENTAL

All the melting points are uncorrected and are measured on a Mel-temp apparatus. The IR spectra are recorded on a Perkin-Elmer model 337 Grating Infrared spectrophotometer as KBr pellets and on Hitachi Model 270-80 as nujol mulls. The ^1H NMR spectra are recorded in $CDCl_3$ solution on Bruker spectrometer operating at 270 or 200 or 90 MHz and ^{13}C NMR spectra at 50.78 or 22.5 MHz with TMS as an internal standard. Microanalyses were obtained from the Regional Sophisticated Instrumentation Center, Punjab University, Chandigarh, India.

Z-4-Methylstyrylsulfonylacetic acid (**IV**): To a solution of sodium hydroxide (20.0 g, 0.5 mol) in methanol (125 ml), thioglycollic acid (23.0 g, 0.25 mol) was added slowly through the dropping funnel. On completion of the addition, freshly distilled 4-methylphenylacetylene (29.00 g, 0.25 mol) was added portionwise and refluxed for 24 hrs. The cooled reaction mixture was poured onto crushed ice containing conc. hydrochloric acid. The compound formed was collected, washed with ice-cold water, dried and recrystallized from water to obtain pure *Z*-4-methylstyrylthioacetic acid (**III**, 88%), m.p. 97–98°C.

To an ice-cold solution of **III** (41.6 g, 0.20 mol) in glacial acetic acid (500 ml), 30% hydrogen peroxide (150 ml) was added and kept at 20°C for 3 hrs and at room temperature for an additional 48 hrs. It was poured onto crushed ice and the solid separated was filtered, washed with water, dried and recrystallized from water to get pure **IV** (55%), m.p. 144–45°C. Anal. Calcd. for $C_{11}H_{12}O_4S$: C 54.98, H 5.03; Found: C 54.72, H 4.92; IR (KBr): 1735 (C=O), 1620 (C=C), 1315 & 1120 (SO_2), 820 (CH out-of-plane) cm^{-1}; ^1H NMR ($CDCl_3$): δ 2.28 (s, 3H, CH_3), 3.89 (s, 2H, SO_2CH_2), 6.53 (d, 1H, H_A), 7.49 (d, 1H, H_B, J_{AB} = 12.13 Hz), 6.96–7.24 (m, 4H, Ar-H), 10.60 (s, 1H, COOH).

Bis(styryl)sulfones (**V**): *General procedure*: A mixture of **IV** (2.5 g, 0.01 mol), aromatic aldehyde (0.01 mol) and benzylamine (1 ml) in acetic acid (15 ml) was refluxed for 2–3 hrs. The contents were cooled and treated with dry ether (50 ml). Any product separated was collected by filtration and the filtrate was diluted with more ether and washed successively with a saturated solution of sodium bicarbonate, sodium bisulfite, dilute hydrochloric acid and finally with water. Evaporation of the dried ethereal layer yielded in many cases a solid product. However, in some instances a syrupy substance obtained was solidified on treatment with 2-propanol. The crude product on recrystallization with 2-propanol afforded pure **V**.

E-4-Methylstyrylsulfonyl chloride (**VII**): Sulfuryl chloride (135 g, 1 mol) was added dropwise, with stirring to distilled N,N-dimethylformamide (70 ml) cooled at 0°C under nitrogen atmosphere. After the addition, stirring was continued for a further period of 1 hr at room temperature and 4-methylstyrene (56.64 g, 0.48 mol) was added all at once and the contents were heated to 85–90°C on a water bath for 4 hrs. The cooled contents were poured onto crushed ice and the pale yellow solid separated was collected, dried and recrystallized from chloroform-petroleum ether (60–80°C) to get **VII** (56%), m.p. 114–115° (lit.[25] 113–114.5°).

Sodium E-4-methylstyrylsulfinate (**VIII**). A solution of sodium bicarbonate (43.68 g, 0.52 mol) and sodium sulfite (63 g, 0.5 mol) in 300 ml of water was taken and stirred at 80–90°C. To this, **VII** (108 g, 0.5 mol) was added portionwise over a period of 30–45 min. After the addition, the reaction mixture was stirred for an additional 1 hr and kept aside overnight. The white crystalline solid **VIII** separated was collected and dried.

E-4-Methylstyrylsulfonylacetic acid (**IX**): A mixture of **VIII** (20.4 g, 0.1 mol) and chloroacetic acid (9.92 g, 0.12 mol) were dissolved in 70 ml of 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 dil. hydrochloric acid and the separated **IX** was collected, dried and recrystallized from hot water to get colourless shining crystals (78%), m.p. 135–136°C. Anal. Calcd. for $C_{11}H_{12}O_4S$: C 54.98, H 5.03; Found: C 54.81, H 4.94; IR (KBr): 1730 (C=O), 1320 & 1115 (SO_2), 960 (CH out-of-plane) cm^{-1}; ^1H NMR ($CDCl_3$): δ 2.27 (s, 3H, CH_3), 4.15 (s, 2H, SO_2CH_2), 6.72 (d, 1H, H_A), 7.42 (d, H, H_B, J_{AB} = 15.70 Hz), 6.74–7.38 (m, 4H, Ar-H).

E,E-Bis(styryl)sulfones (**X**): *General procedure*: A solution of **IX** (2.5 g, 0.01 mol) in glacial acetic acid (10 ml) was mixed with an araldehyde (0.01 mol) and benzylamine (1 ml) and refluxed for 3 hrs. The reaction mixture was cooled, treated with dry ether (50 ml) and refrigerated overnight. Any product separated was collected by filtration and the filtrate was diluted with more ether and washed successively with a saturated solution of sodium bicarbonate, sodium bisulfite, dil. hydrochloric acid and finally with water. Evaporation of the dried ethereal layer afforded a solid which on recrystallization from 2-propanol gave pure **X**.

E-E-1,1'-Bis(2-arylcyclopropyl)sulfones (**XI**): *General procedure.*

Method A: A mixture of **V** or **X** (0.01 mol), trimethylsulfoxonium iodide (4.84 g, 0.022 mol), 50% aq. sodium hydroxide solution (25 ml), methylene chloride (25 ml) were stirred till a clear two-phase system was obtained. Benzyltriethylammonium chloride (100 mg) was then added and continued stirring for a period of 2–3 hrs. Progress of the reaction was monitored by TLC. After completion of the reaction, the reaction mixture was diluted with water (100 ml) and the organic layer was separated, washed with water, brine and dried. Evaporation of the solvent resulted a syrupy substance in most of the cases which was solidified on treatment with 2-propanol. The crude product on recrystallization from 2-propanol resulted pure **XI**.

Method B: A mixture of **V** or **X** (0.01 mol) and trimethylsulfoxonium iodide (4.84 g, 0.022 mol) in dry dimethyl sulfoxide (15 ml) was stirred until a clear solution was obtained. To this solution, potassium *t*-butoxide (2.24 g, 0.02 mol) in dry dimethylsulfoxide (10 ml) was added dropwise at room temperature. After complete addition, the reaction mixture was stirred for an additional 1 hr, diluted with more water and stirred overnight, or until crude **XI** separated as a solid. This on recrystallization from 2-propanol yielded a pure compound.

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