

Synthesis of some new *bis(styryl)*sulphones

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Abstract. A series of new *bis(styryl)*sulphones were synthesised by the condensation of various aryl aldehydes with sulphonyldiacetic acid. An attempt has been made to correlate the infrared and proton magnetic resonance spectral data to the configurations of *bis(styryl)*sulphones.

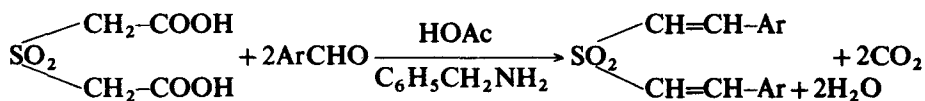
Keywords. *Bis(styryl)*sulphones; configuration; sulphonyldiacetic acid.

1. Introduction

For our studies relating to the synthesis of aryl mono- and dicyclopropyl sulphones, we were interested in preparing a series of new *bis(styryl)*sulphones as intermediates. Only a few methods are found in the literature for the preparation of *bis(styryl)*sulphones. Backer (1953) reported a *bis(styryl)*sulphone by the condensation of sulphonyldiacetic acid with benzaldehyde in the presence of piperidine acetate. Stacey and Harris (1963) synthesised divinyl sulphide by radiation-induced addition of hydrogen sulphide to substituted acetylenes. Aleksiev and Mladenov (1977) reported the synthesis of some divinyl sulphones by the condensation of vinylhalides with styrylsodiumsulphinates. Baliah and Ananthapadmanabhan (1971) reported a few *bis(styryl)*sulphones by extending the procedure of Baliah and Seshapathi Rao (1959) which was originally used for the preparation of α,β -unsaturated sulphones. Otto and Yamamura (1975) reported a few compounds by Backer's method.

2. Results and discussion

A series of new *bis(styryl)*sulphones have been prepared by the condensation of sulphonyldiacetic acid with various aryl aldehydes with fairly high yields (see table 1). In this procedure catalytic amounts of benzylamine and glacial acetic acid were used, instead of piperidine acetate and benzene, as condensing agent and solvent respectively which reduced the reaction time enormously.



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where Ar =

1	C ₆ H ₅	10	3,4-(CH ₃ O) ₂ C ₆ H ₃	19	4-CH ₃ OC ₆ H ₄
2	2-ClC ₆ H ₄	11	3,4,5-(CH ₃ O) ₃ C ₆ H ₂	20	3,4-(—O—CH ₂ —O—)C ₆ H ₃
3	3-ClC ₆ H ₄	12	2-C ₂ H ₅ OC ₆ H ₄	21	4-C ₂ H ₅ O, 3-CH ₃ OC ₆ H ₃
4	4-ClC ₆ H ₄	13	4-C ₂ H ₅ OC ₆ H ₄	22	2-NO ₂ C ₆ H ₄
5	4-BrC ₆ H ₄	14	2-FC ₆ H ₄	23	3-NO ₂ C ₆ H ₄
6	2,4-Cl ₂ C ₆ H ₃	15	3-FC ₆ H ₄	24	4-NO ₂ C ₆ H ₄
7	3,4-Cl ₂ C ₆ H ₃	16	4-FC ₆ H ₄	25	α-naphthyl
8	2,3-(CH ₃ O) ₂ C ₆ H ₃	17	2-CH ₃ C ₆ H ₄	26	cyclohexyl
9	2,5-(CH ₃ O) ₂ C ₆ H ₃	18	4-CH ₃ C ₆ H ₄	27	cyclohexene
				28	3-pyridyl

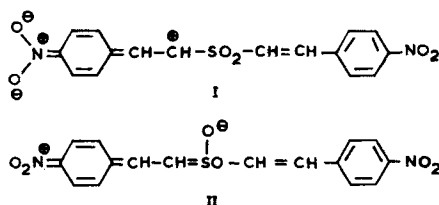
Table 1. ArCH=CH—SO₂—CH=CH—Ar.

Compound number	Yield* %	m.p. °C	Formula	Analysis (%)			
				Calculated		Found	
				C	H	C	H
1	20 (25)	99–100 ^a	C ₁₆ H ₁₄ O ₂ S	—	—	—	—
2	50 (22)	173–174 ^d	C ₁₆ H ₁₂ Cl ₂ O ₂ S	—	—	—	—
3	74	126–127 ^b	C ₁₆ H ₁₂ Cl ₂ O ₂ S	56.62	3.56	56.82	3.72
4	53 (24)	215–216 ^d	C ₁₆ H ₁₂ Cl ₂ O ₂ S	—	—	—	—
5	48 (18)	230–231 ^d	C ₁₆ H ₁₂ Br ₂ O ₂ S	—	—	—	—
6	46	165–166 ^a	C ₁₆ H ₁₀ Cl ₄ O ₂ S	45.94	2.41	45.92	2.48
7	43	160–161 ^a	C ₁₆ H ₁₀ Cl ₄ O ₂ S	45.94	2.41	45.98	2.50
8	25	126–127 ^b	C ₂₀ H ₂₂ O ₆ S	61.53	5.67	62.23	5.79
9	29	185–186 ^a	C ₂₀ H ₂₂ O ₆ S	61.53	5.67	61.83	5.62
10	64	184–185 ^a	C ₂₀ H ₂₂ O ₆ S	61.53	5.67	61.16	5.54
11	33	219–220 ^c	C ₂₂ H ₂₆ O ₈ S	58.66	5.77	58.96	5.74
12	31	102–103 ^a	C ₂₀ H ₂₂ O ₄ S	67.02	6.18	67.08	6.28
13	33	148–150 ^c	C ₂₀ H ₂₂ O ₄ S	67.02	6.18	67.39	6.08
14	45	143–144 ^c	C ₁₆ H ₁₂ F ₂ O ₂ S	62.75	3.92	62.74	4.42
15	56	209–211 ^c	C ₁₆ H ₁₂ F ₂ O ₂ S	62.75	3.92	62.71	3.93
16	52	185–186 ^c	C ₁₆ H ₁₂ F ₂ O ₂ S	62.75	3.92	63.09	3.69
17	49	130–131 ^a	C ₁₈ H ₁₈ O ₂ S	72.46	6.08	72.34	6.14
18	63	180–182 ^b	C ₁₈ H ₁₈ O ₂ S	72.46	6.08	72.08	6.23
19	60	164–165 ^f	C ₁₈ H ₁₈ O ₄ S	65.43	5.49	65.21	5.52
20	42	164–165 ^c	C ₁₈ H ₁₄ O ₆ S	60.32	3.93	60.52	4.27
21	24	198–199 ^c	C ₂₂ H ₂₆ O ₆ S	64.18	6.04	64.15	6.08
22	56	182–183 ^d	C ₁₆ H ₁₂ N ₂ O ₆ S	53.31	3.35	53.43	3.44
23	50	158–160 ^c	C ₁₆ H ₁₂ N ₂ O ₆ S	53.31	3.35	53.8	3.7
24	52	292–293 ^h	C ₁₆ H ₁₂ N ₂ O ₆ S	53.31	3.35	53.23	3.37
25	33	175–177 ^d	C ₂₄ H ₁₈ O ₂ S	77.80	4.89	77.49	4.98
26	56	228–229 ^c	C ₁₆ H ₂₆ O ₂ S	68.11	9.22	68.29	8.73
27	46	213–214 ^c	C ₁₆ H ₂₂ O ₂ S	69.07	7.91	68.98	7.69
28	34 (30)	147–149 ^a	C ₁₄ H ₁₂ N ₂ O ₂ S	—	—	—	—

Products recrystallized from (a) 95% ethanol, (b) methanol, (c) *n*-propanol, (d) glacial acetic acid, (e) *n*-butanol, (f) *n*-butanol–95% ethanol mixture, (g) 95% ethanol–acetone mixture and (h) 95% ethanol–dimethylformamide mixture.

* The percentage yields in parentheses are those reported by others (Baliah and Ananthapadmanabhan 1971) and (Otto and Yamamura 1975).

The ultraviolet spectra of all these bis(styryl)sulphones exhibited a long wavelength band around the 266–360 nm region and some of these compounds show a second band in the region 242–290 nm. Another strong band with high intensity occurs in the spectra of all these compounds around 200–220 nm region. The long wavelength band around 266–360 nm seems to be due to the conjugation of the sulphone group with the styryl groups. The band near 240 nm may be ascribed to the 'partial' disconjugated styryl (PHC=C-) chromophore (Klyne 1954). The band appearing in the region 200–220 nm is presumably the *E*-band which occurs for benzene at 180 nm. The high intensity of this band may be due to the greater number of phenyl groups present in the molecule. The absorption maxima for *p*-nitro substituted compounds is found at a longer wavelength (383 nm). The spectral behaviour of the compound can be understood if we assume that electron withdrawal by $-\text{NO}_2$ and $-\text{SO}_2$ groups occurs in opposite directions. The $-\text{NO}_2$ group, being a more powerful conjugating group, seems to have a dominating influence. The result is that the *p*-nitro substituted compound will have a greater contribution towards its excited state from the following structure I, rather than from the structure II.



The infrared spectra of most of these bis(styryl)-sulphones exhibited a band with medium intensity in the region $1620\text{--}1615\text{ cm}^{-1}$ ($\nu\text{C}=\text{C}$) (Truce and Boudakian 1956; Colthup *et al* 1964) and another strong band in the region $980\text{--}960\text{ cm}^{-1}$ (δCH out-of-plane) (Baliah and Rathinasamy 1971; Seshapathi Rao Naidu and Bhaskar Reddy 1975; Truce *et al* 1960) characteristic of *trans* disubstituted ethylenes. They also displayed bands in the region $1300\text{--}1330\text{ cm}^{-1}$ and $1120\text{--}1130\text{ cm}^{-1}$ which are characteristic of the sulphonyl group (Bavin *et al* 1960; Robinson 1961).

The PMR spectra of all these compounds show the signals for the ethylenic protons as doublets in the region 7.4–8.4 and 6.6–7.2 ppm. The coupling constants determined for all these compounds gave values from 12–14 Hz. These values indicate that all the compounds are *trans* isomers. Mikolajczyk *et al* (1979) has proposed an improved equation of Matter *et al* (1969) to calculate the chemical shifts of vinylic protons. The equation is given below.

$$\delta_{\text{ppm}} = 5.25 + \sum_i Z_i + \sum \Delta S_j^i$$

where Z_i are the respective shielding increments for the substituents (R) in the *gem*, *cis* and *trans* relationship to proton and ΔS_j^i is the increment due to substituent S in the aromatic ring, i is the *gem*, *cis* or *trans* position of the substituted aromatic ring with respect to the olefinic proton, j is the *para* or *meta* position of the substituent in the aromatic ring. The chemical shifts (δ) for the olefinic protons observed experimentally as well as the values calculated (with the assumption that the protons are in *trans* position) were found to be in full agreement.

Thus the mode of formation, the infrared and proton magnetic resonance spectral studies (coupling constants) confirm that all the *bis*(styryl)sulphones synthesised under the present investigation are *trans* isomers.

3. Experimental

All melting points are uncorrected and were determined on a Mel-Temp, melting point apparatus. The elemental analyses were performed by Dr R D MacDonald, CSIRO, Australia. The ultraviolet absorption spectra were recorded with a Perkin Elmer model-551 spectrophotometer. The infrared spectra were recorded on a Beckmann IR-18A spectrophotometer in potassium bromide discs and in nujol mulls. The proton magnetic resonance spectra were recorded in deuteriochloroform solution using a Varian XL-100 spectrometer with tetramethylsilane as an internal standard.

3.1 Reagents

The aryl aldehydes were commercially obtained and sulphonyldiacetic acid was prepared following the procedure of Backer (1953).

3.2 General procedure for the condensation of sulphonyldiacetic acid with different aryl aldehydes

A solution of sulphonyldiacetic acid (0.01 mole) in glacial acetic acid (10 ml) was mixed with an aryl aldehyde (0.02 mole) and a catalytic amount (1 ml) of benzylamine and the whole mixture was refluxed for 90 minutes. The reaction mixture was cooled and treated with dry ether (50 ml). Any product separated was collected by filtration and the filtrate was diluted with more ether. The ethereal layer was washed successively with a saturated solution of sodium bicarbonate (15 ml), dilute hydrochloric acid (20 ml) and finally with water. Evaporation of the dried ethereal layer yielded in many cases a solid product of *bis*(styryl)sulphone. However, in some instances a syrupy substance which separated was solidified on treatment with a small amount of methanol or 2-propanol. The relevant data on the compounds synthesised are given in table 1.

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