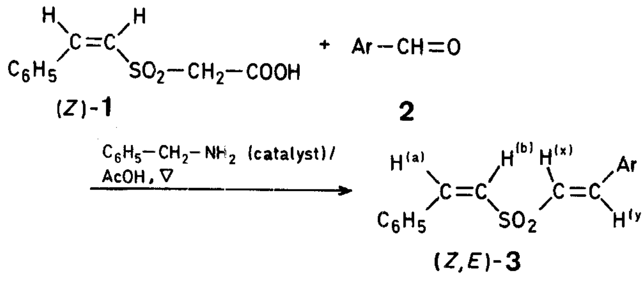
A Novel Synthesis of (*E*)-Substituted Styryl (*Z*)-Styryl Sulfones

M. V. R. Reddy*, S. Reddy

Chemical Laboratories, KSRM College of Engineering, Cuddapah-516001, Andhra Pradesh, India

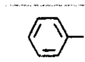
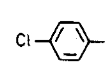
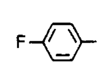
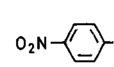
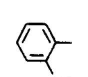
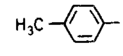
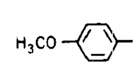
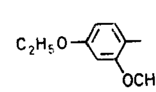
The synthesis and structural studies of divinyl sulfides[1], bis[phenylthiovinyl] sulfones[2], and bis[styryl] sulfones[3] are of recent origin. One of the common procedures adopted for the preparation of bis[styryl] sulfones is the condensation of sulfonyldiacetic acid with various aromatic aldehydes in the presence of an amine as catalyst. The reaction proceeds stereoselectively affording pure (*E*, *E*)-isomers. Very few mixed bis[styryl] sulfones are known so far and they exist either as (*E*, *E*)-isomers[3] or as (*Z*, *Z*)-isomers[1]. The synthesis of mixed bis[styryl] sulfones with (*E*, *Z*)-configurations are quite recent and our present study deals with a series of such new compounds.

We now report the synthesis of some mixed bis[styryl] sulfones **3** by means of Knoevenagel condensation type reaction of (*Z*)-styrylsulfonylacetic acid (**1**) and aromatic aldehydes **2** in the presence of benzylamine and glacial acetic acid (Table).



(*Z*)-Styrylsulfonylacetic acid (**1**) is prepared by the nucleophilic addition of the sodium salt of mercaptoacetic acid (**5**) to phenylacetylene (**4**) in absolute methanol. The addition follows the *trans*-addition rule[4] resulting in the (*Z*)-styrylthioacetic acid (**6**) which, on oxidation with hydrogen peroxide in glacial acetic acid, yields **1**. The stereochemical assignment for **1**, on the basis of the I.R. and ^{1}H-N.M.R. spectra, is established as the (*Z*)-isomer.

Table. (*E*)-Substituted Styryl (*Z*)-Styryl Sulfones **3a–h** prepared[a]

Product	Ar	Yield[b] [%]	m.p. [°C] (solvent)	Molecular formula[c]	I.R. (KBr) ν_{SO_2} [cm^{-1}]	^{1}H-N.M.R. (CDCl$_3$/TMS)[d] δ [ppm]
3a		68	86–87°[e] (2-propanol)	$C_{16}H_{14}O_2S$ (270.3)	1310, 1115	6.68 (d, 1H, H(b), $J_{H(a),H(b)}$ = 11.4 Hz); 6.87 (d, 1H, H(x), $J_{H(x),H(y)}$ = 15.4 Hz); 7.2–7.78 (m, 7H, H(a) + H(y) + H$_{arom}$)
3b		64	108–109° (2-propanol)	$C_{16}H_{13}ClO_2S$ (304.8)	1330, 1100	6.65 (d, 1H, H(b), $J_{H(a),H(b)}$ = 11.2 Hz); 6.81 (d, 1H, H(x), $J_{H(x),H(x),H(y)}$ = 15.4 Hz); 7.0–7.85 (m, 6H, H(a) + H(y) + H$_{arom}$)
3c		68	90–91° (2-propanol)	$C_{16}H_{13}FO_2S$ (283.3)	1340, 1300, 1120	6.55 (d, 1H, H(b), $J_{H(a),H(b)}$ = 10.8 Hz); 6.7 (d, 1H, H(x), $J_{H(x),H(y)}$ = 14.8 Hz); 7.2–7.92 (m, 6H, H(a) + H(y) + H$_{arom}$)
3d		76	148–149° (acetic acid)	$C_{16}H_{13}NO_4S$ (315.3)	1335, 1300, 1125	6.66 (d, 1H, H(b), $J_{H(a),H(b)}$ = 11.8 Hz); 6.91 (d, 1H, H(x), $J_{H(x),H(y)}$ = 15.8 Hz); 7.4–8.5 (m, 6H, H(a) + H(y) + H$_{arom}$)
3e		53	86–87° (acetic acid)	$C_{16}H_{13}NO_4S$ (315.3)	1330, 1140	6.65 (d, 1H, H(b), $J_{H(a),H(b)}$ = 11.0 Hz); 6.82 (d, 1H, H(x), $J_{H(x),H(y)}$ = 15.5 Hz); 7.3–8.3 (m, 6H, H(a) + H(y) + H$_{arom}$)
3f		69	119–120° (2-propanol)	$C_{17}H_{16}O_2S$ (284.4)	1315, 1110	2.48 (s, 3H, CH$_3$); 6.63 (d, 1H, H(b), $J_{H(a),H(b)}$ = 11.0 Hz); 6.75 (d, 1H, H(x), $J_{H(x),H(y)}$ = 15.6 Hz); 7.2–7.9 (m, 6H, H(a) + H(y) + H$_{arom}$)
3g		72	93–94° (2-propanol)	$C_{17}H_{16}O_3S$ (300.4)	1340, 1110	3.88 (s, 3H, OCH$_3$); 6.93 (d, 1H, H(b), $J_{H(a),H(b)}$ = 10.8 Hz); 7.05 (d, 1H, H(x), $J_{H(x),H(y)}$ = 16.0 Hz); 7.3–7.95 (m, 6H, H(a) + H(y) + H$_{arom}$)
3h		74	117–118° (2-propanol)	$C_{19}H_{20}O_4S$ (344.4)	1320, 1115	1.5 (t, 3H, OCH$_2$CH$_3$); 3.95 (s, 3H, OCH$_3$); 4.26 (q 2H, OCH$_2$CH$_3$); 6.65 (d, 1H, H(b), $J_{H(a),H(b)}$ = 11.0 Hz); 6.81 (d, 1H, H(x), $J_{H(x),H(y)}$ = 15.8 Hz); 7.1–7.85 (m, 5H, H(a) + H(y) + H$_{arom}$)

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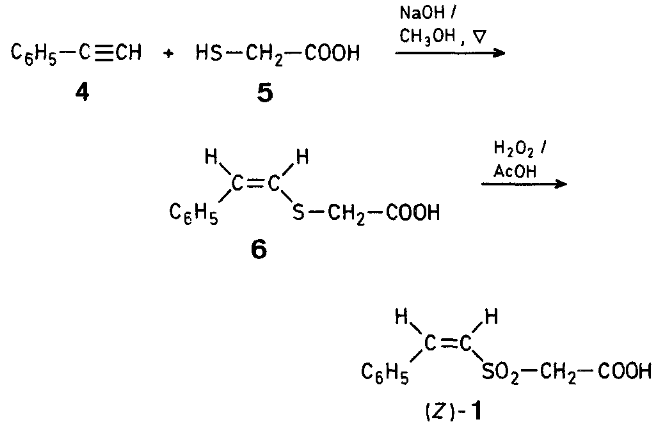
[a] Current *Chemical Abstracts* Index name for mixed sulfones **3**, e.g. **3b** is (*Z*,*E*)-1-chloro-4[2[(2-phenylethenyl)sulfonyl]ethenyl]-benzene (**3b**).

[b] Yield of isolated, analytically pure products.

[c] Satisfactory microanalyses obtained: C ± 0.24, H ± 0.06.

[d] 100-MHz-spectra.

[e] m.p. of the corresponding (*E*,*E*)-bis[styryl] sulfone is 99–100 °C.



The configuration of the (*E*)-substituted styryl (*Z*)-styryl sulfones **3** is determined on the basis of the stereospecific synthesis, the chemical shifts, and coupling constants of the vinylic protons in the ^{1}H-N.M.R. spectra. The I.R. spectra of the products show the characteristic bands for the double bonds and sulfonyl group and are compatible with the structure (Table).

All the sulfones **3** obtained are new products and give satisfactory microanalyses. The purity of the isomers is asby T.L.C. Since these sulfones **3** are Michael acceptors, studies on mono- and di-cyclopropanation of these sulfones with stabilized sulfur ylids are in progress.

(Z)-Styrylsulfonylacetic Acid (1):

Styrylthioacetic Acid (**6**): To freshly distilled phenylacetylene (**4**; 51.07 g, 0.5 mol) is added sodium thioglycolate prepared from thioglycolic acid (**5**; 46 g, 0.5 mol) and sodium hydroxide (40 g, 1 mol) in methanol (250 ml). The mixture is refluxed for 24 h and poured onto crushed ice (500 ml). The styrylthioacetic acid (**6**), formed after neutralization with dilute hydrochloric acid (250 ml), is filtered and dried; yield: 88 g (90%); m.p. 84–86 °C.

$C_{10}H_{10}O_2S$	calc.	C 61.82	H 5.19
(194.3)	found	61.56	5.23

Oxidation of **6** *to* **1**: A mixture of styrylthioacetic acid (**6**; 5 g, 25 mmol) in glacial acetic acid (35 ml) and 30% hydrogen peroxide (15 ml) is heated under reflux for 60 min and the mixture is poured onto crushed ice (200 ml) after cooling. The compound separated is filtered and recrystallized from hot water to give white crystalline flakes of (*Z*)-styrylsulfonylacetic acid (**1**); yield: 2.4 g (41%); m.p. 150–151 °C.

$C_{10}H_{10}O_4S$	calc.	C 53.08	H 4.45
(226.3)	found	52.93	4.52

(E)-Substituted Styryl (Z)-Styryl Sulfones (3); General Procedure: A solution of (*Z*)-styrylsulfonylacetic acid (**1**; 2.263 g, 10 mmol) in glacial acetic acid (6 ml) is mixed with an aromatic aldehyde **2** (10 mmol) and benzylamine (0.2 ml) and refluxed for 3 h. The reaction mixture is cooled, treated with dry ether (50 ml), and any product separated is collected by filtration. The filtrate is diluted with more ether and washed successively with a saturated solution of sodium hydrogen carbonate (15 ml), sodium bisulfite (15 ml), dilute hydrochloric acid (20 ml), and finally with water (30 ml). Evaporation of the dried ether layer yields, in many cases, **3** as a solid product. However, in some instances, a syrupy substance separated is solidified on treatment with a small amount of 2-propanol.

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* Address for correspondence.

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