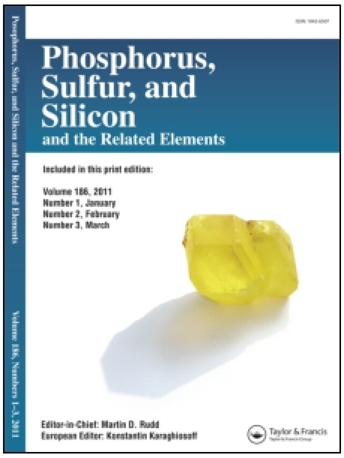

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SYNTHESIS AND CYCLOPROPANATION OF *E,E* AND *Z,Z*-1,3-BIS(STYRYLSULFONYL)BENZENE

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SYNTHESIS AND CYCLOPROPANATION OF *E,E* AND *Z,Z*-1,3-BIS(STYRYLSULFONYL)BENZENE

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The synthesis of 1,3-bis(styrylsulfonyl)benzene in two isomeric forms (*Z, Z* and *E, E*) and their cyclopropanation with dimethylsulfonium methylide has been described. The configurational assignments of these compounds have been made on the basis of IR, ^{1}H NMR and ^{13}C NMR spectral data.

Key words: Bis(styrylsulfonyl)benzene; configuration, cyclopropanation, cyclopropyl disulfones and dimethylsulfonium methylide.

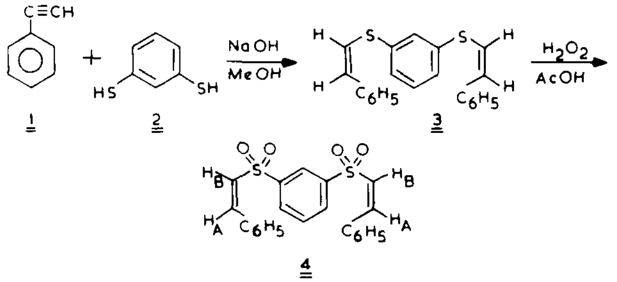
INTRODUCTION

Many of the α,β-unsaturated sulfones such as styryl phenyl sulfones,[1-5] styryl benzyl sulfones,[6] bis(styryl)sulfones[7-9] and bis(styrylsulfonylmethyl) benzenes[10-12] were reported earlier by the condensation of sulfonylacetic acid or sulfonyldiacetic acid with araldehydes. The synthetic methodology adopted in this process leads to the formation of *E* or *E, E* isomers. However, only in few cases *Z*[13], *Z, Z*[14] or *Z, E*[15] isomers of the above type of compounds are known. But there are no instances where isomeric pairs (*Z, Z* and *E, E*) of bis(styryl)sulfones or bis(styrylsulfonylmethyl)benzenes were reported so far. Hence, we report herein the synthesis of 1,3-bis(styrylsulfonyl)benzene in two isomeric forms and their cyclopropanation with dimethylsulfonium methylide.

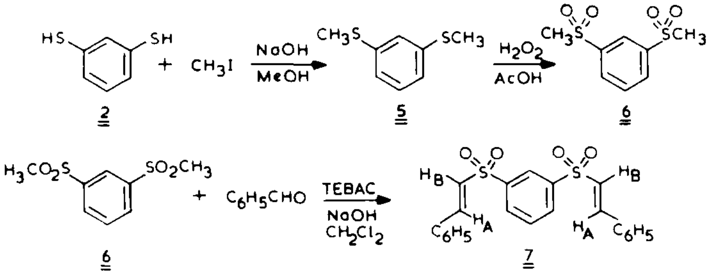
RESULTS AND DISCUSSION

The *Z, Z*-1,3-bis(styrylsulfonyl)benzene is prepared by the reaction of 1,3-benzenedithiol with phenylacetylene (Scheme **I**) whereas its *E, E* isomer by two different methods; a) the phase transfer catalysed condensation of 1,3-bis(methylsulfonyl)benzene with benzaldehyde (Scheme **II**) and b) the Knoevenagel type reaction of 1,3-benzenedisulfonylacetic acid with benzaldehyde (Scheme **III**).

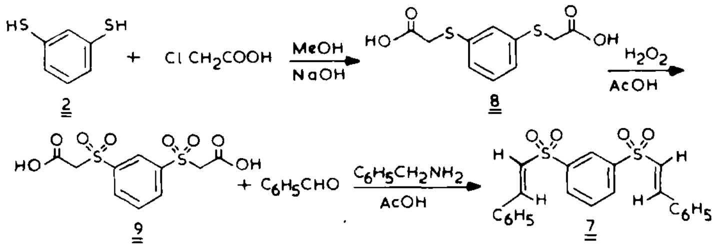
The configurational assignments of **4** and **7** are based on the analysis of ^{1}H NMR spectral data. It has been observed that the *E, E* isomer has larger coupling constants ($J_{AB} = 14.8$ Hz) than *Z, Z* isomer ($J_{AB} = 11.3$ Hz)[15]. The CMR spectra of **4** and **7** also showed variation in their chemical shifts of the ethylenic



SCHEME I



SCHEME II

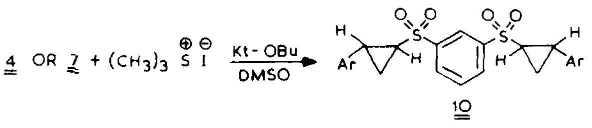


SCHEME III

carbons. The chemical shifts of *Z, Z* isomers (C-H_A = 141.82; C-H_B = 130.48) always occur at higher fields than *E, E* isomers (C-H_A = 143.78; C-H_B = 132.87) because of shielding effect due to their steric interaction.[16]

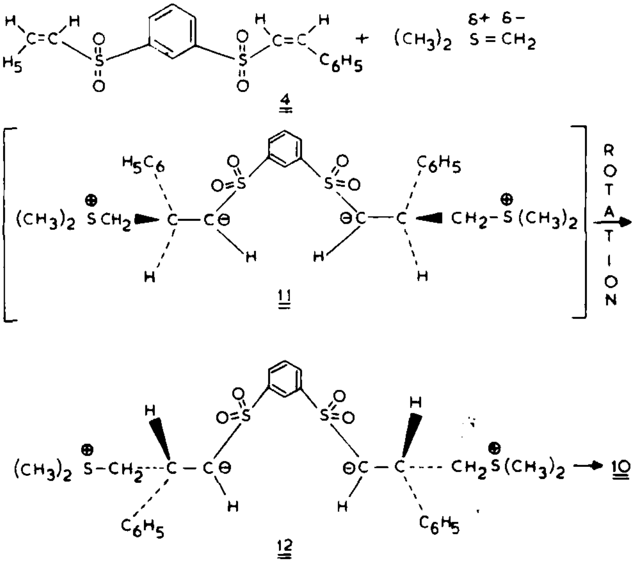
Treatment of **4** and **7** with dimethylsulfonium methylide in presence of potassium t-butoxide in dimethylsulfoxide gave *E, E*-1,3-bis(phenylcyclopropylsulfonyl)benzene(**10**) (Scheme **IV**).

Cyclopropanation of *E*-unsaturated esters, amides and conjugated nitroolefins with dimethylsulfonium methylide were reported to yield stereoselectively the corresponding *E*-cyclopropane derivatives.[17,18] Indeed, a number of *trans* α,β-



SCHEME IV

unsaturated sulfones have been cyclopropanated with dimethylsulfonium methylide to obtain stereoselectively *E*-cyclopropyl sulfones.[17,19–24] Thus, it is clear the **7** with dimethylsulfonium methylide would give **10**. However the **4** by the addition of dimethylsulfonium methylide may form an intermediate **11** which on rotation would give a more stable isomer **12** in which the phenyl and bulky phenylsulfonyl groups are *trans* oriented. (Scheme **V**). The product **10** may be formed from the latter, with the formation of a bond between the carbanion and methylene carbon of dimethyl sulfonium methylide moiety with the simultaneous elimination of dimethylsulfide.



SCHEME V

The ^1H NMR spectra of **10** shows chemical shifts in the region 1.28–2.12 and 2.56–3.03 as multiplets for methylene and methine protons respectively which are characteristic of *E*, *E* configuration.[18] The methylene carbons in cyclopropane are more shielded than methine carbons in both the isomers.[25,26] Thus there is no appreciable difference in ^{13}C chemical shifts of methine carbons[27] where as the methylene carbons exhibit a larger effect owing to the steric interaction and appear at 14.2 Hz which is characteristic of *E*, *E* configuration.[28]

EXPERIMENTAL

All melting points are uncorrected and are measured on Tempo apparatus. The infrared spectra are run on a Perkin–Elmer model 983 spectrometer. The ^1H NMR spectra are obtained on Perkin–Elmer R-32 (90 MHz) and ^{13}C NMR on Varian CFT-20, with tetramethylsilane as an internal standard. Micro analyses are performed by Central Drug Research Institute, Lucknow, India.

Z,Z-1,3-Bis(styrylsulfonyl)benzene (**4**). To a refluxing methanolic solution of sodiumbenzenedithiolate prepared from 920 mg (0.04 g atom) of sodium 2.84 g (0.02 mol) of 1,3-benzenedithiol and 60 ml of absolute methanol, was added 4.04 g (0.04 mol) of freshly distilled phenylacetylene. The mixture was refluxed for 20 hrs cooled and then poured on crushed ice. The crude product was filtered, dried and recrystallized from methanol to give 5.60 g (82%) of **3** mp 94–95°C; IR (KBr) 1630, 1080 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 6.32 (d, 2H, $J = 11.0$ Hz), 6.74 (d, 2H, $J = 11.0$ Hz), 7.10–7.45 (m, 14 H). Anal. Calcd for $C_{22}H_{18}S_2$: C, 76.26; H, 5.24. Found: C, 76.38; H, 5.16. An ice cold solution of 3.46 g (0.01 mol) of **3** in 30 ml of glacial acetic acid was treated with 12 ml of 30% hydrogen peroxide, refluxed for 1 hr and then poured on crushed ice. The solid separated was filtered, dried and recrystallized from 95% ethanol to yield 3.0 g (74%) of **4**: mp 184–185°C; IR (KBr) 1620, 1325, 1130, 680 cm^{-1}; ^{1}H NMR (CD_3SOCD_3) δ 6.7 (d, 2H, $J = 11.3$ Hz); 7.0–7.4 (m. 14 H), 7.48 (d, 2H, $J =$ 11.3 Hz); ^{13}C NMR (CD_3SOCD_3) δ 130.48, 141.82.

1,3-Bis(methylsulfonyl)benzene (**6**). Methyl iodide (5.68 g, 0.04 mol) was added dropwise to an ice cold solution of sodiumbenzenedithiolate which was prepared in similar way as in **3**. After the addition the reaction mixture was refluxed for 3 hr and then poured in ice water. The dense liquid separated was extracted with ether dried and distilled at reduced pressure to give 3.14.g (92%) of **5** bp 197–199°C (6 mm). IR(KBr) 1080 cm^{-1}; ^{1}H NMR ($CDCl_3$) 2.40 (s, 6H), 7.50–7.98 (m, 4H). Anal. Calcd for $C_8H_{10}S_2$: C, 56.42; H, 5.92. Found: C, 56.54; H 6.01. The above sulfide **5** (2.55 g, 0.015 mol) was dissolved in 30 ml of glacial acetic acid and cooled. To this 12 ml of 30% hydrogen peroxide was added, refluxed for 1 hr and then poured on crushed ice. The product obtained was filtered, dried and recrystallized from glacial acetic acid to give 2.80 g (80%) of **6**: mp 202–203°C; IR(KBr) 1310, 1130 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.62 (s, 6H), 7.42–7.88 (m, 4H). Anal. Calcd for $C_8H_{10}S_2O_4$: C, 41.01; H, 4.30. Found: 41.19; H, 4.21.

1,3-Benzenedisulfonylacetic acid (**9**). Chloroacetic acid (3.78 g, 0.04 mol) in 20 ml of methanol was added to a refluxing solution of sodium benzenedithiolate prepared in a similar way as in **3**. The contents were refluxed for 5 hrs cooled, poured onto crushed ice and neutralized with dilute hydrochloric acid (100 ml). The product formed was filtered, dried and recrystallized from hot water to give 4.0 g (77%) of **8**: mp 128–130°C; IR(KBr) 1734, 1720 cm^{-1}, ^{1}H NMR ($CDCl_3$) δ 3.74 (s, 2H), 3.80 (s, 2H), 7.15–7.48 (m, 4H). Anal. Calcd for $C_{10}H_{10}S_2O_4$: C, 46.50; H, 3.90. Found: C, 46.41; H, 3.97. An ice cold solution of 2.58 g (0.01 mol) of **8** in 35 ml of glacial acetic acid was treated with 12 ml of 30% hydrozen peroxide, refluxed for 1 hr and poured onto crushed ice. The solid obtained was filtered and recrystallized from hot water to give 1.93 g (60%) of **9**: mp 136–137°C; IR(KBr) 1744, 1725, 1325, 1128 cm^{-1}; ^{1}H NMR (CD_3SOCD_3) δ 4.60 (s, 2H), 4.67 (s, 2H), 7.25–7.55 (m, 4H). Anal. Calcd for $C_{10}H_{10}S_2O_8$: C, 37.26; H, 3.13: Found: C, 37.19; H, 3.21.

E,E-1,3-Bis(styrylsulfonyl)benzene (**7**). (*Scheme* **II**). A mixture of 1.70 g (0.01 mol) of **6** in 20 ml of dichloromethane and 455 mg (0.002 mol) of triethylbenzylammonium chloride in 20 ml of 50% aqueous sodium hydroxide were placed in a flask equipped with a mechanical stirrer. The contents were stirred for a while and to this 6.12 g (0.06 mol) of benzaldhyde in 10 ml of dichloromethane was added dropwise. The whole mixture was stirred for 4 hrs at room temperature, diluted with 50 ml of water. The organic layer was separated, washed with saturated solium bisulfite, water and dried over anhydrous sodium sulphate. Evaporation of the solvent gave solid which on recrystallization from 2-propanol yielded 76% of **7**: mp 148–149°C; IR(KBr) 1635, 1320, 1125, 965 cm^{-1}; ^{1}H NMR (CD_3SOCD_3) δ 6.90 (d, 2H, $J = 14.8$ Hz), 7.15–7.50 (m, 14 H), 7.58 (d, 2H, $J = 14.8$ Hz); ^{13}C NMR (CD_3SOCD_3) δ 132.87, 143.78. Anal. Calcd for $C_{22}H_{18}S_2O_4$: C, 64.37; H, 4.22. Found: C, 64.29; H, 4.51.

E,F-1,3-Bis(styrylsulfonyl)benzene (**7**)(*Scheme*-**III**). A solution of 1.61 g (0.005 mol) of **9** in 6 ml of glacial acetic acid was mixed with 1.06 g (0.01 mol) of benzaldehyde and 0.2 ml of benzylamine and refluxed for 3 hrs. The reaction mixture was cooled, treated with 50 ml of dry ether and refrigerated overnight. The product separated (0.8 g) was collected by filtration. The filtrate was diluted with more ether and washed successively with saturated solution of sodium bicarbonate, sodium bisulfite, dilute hydrochloric acid and finally with water. Evaporation of the dried ethereal layer gave 1.50 g of **7**. The crude product **7** when recrystallized from glacial acetic acid gave 2.25 g (55%) of pure **7**: mp 148–149°C. The mixture melting point of this with the compound obtained from phase transfer catalysis reaction was not depressed.

E,E-1,3-Bis(phenylcyclopropylsulfonyl)benzene (**10**). In a 100 ml three-necked flask equipped with magnetic stirrer, dropping funnel and calcium chloride tube, were placed (2.05 g, 0.005 mol) **4** or **7**, trimethylsulfonium iodide (2.04 g, 0.01 mol) and absolute dry dimethylsulfoxide (20 ml). The mixture was stirred until a clear solution was obtained. To this solution potassium t-butoxide (1.12 g, 0.01 mol) in dry dimethylsulfoxide (6 ml) was added dropwise at room temperature. The reaction mixture was stirred further for an additional 1 hr diluted with water (200 ml) and stirred overnight. The product separated was filtered, dried and recrystallized from 2-propanol to give (920 mg, 42% with **4**; and 1.05 g, 48.7% with **7**) **10**: mp 157–158°C; IR(KBr) 1310, 1145, 1030, 932 cm^{-1}; ^{1}H NMR (CD_3SOCD_3) 1.28–2.12 (m, 4H), 2.56–3.03 (m, 4H), 6.90–7.98 (m, 14H); ^{13}C NMR (CD_3SOCD_3) 13.9, 24.8, 40.6, 137.5, 137.9, 140.8, 141.2 Anal. Calcd for $C_{24}H_{22}S_2O_4$: C, 65.73; H, 5.06. Found: C, 65.69, H, 5.12.

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