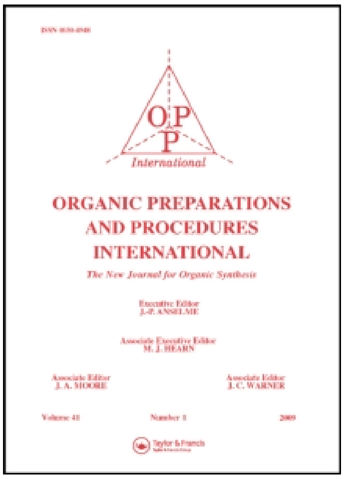

**Organic Preparations and Procedures International**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t902189982

# PREPARATION OF STYRYL BENZYLSULFONES AND 1, 2-BIS (STYRYLSULFONYLMETHYL)-4, 5-DIMETHYLBENZENES

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**To cite this Article** Reddy, D. Bhaskar , Reddy, N. S. , Reddy, S. , Reddy, H. V. R. and Balasubramanyan, S.(1988) 'PREPARATION OF STYRYL BENZYLSULFONES AND 1, 2-BIS (STYRYLSULFONYLMETHYL)-4, 5-DIMETHYLBENZENES', Organic Preparations and Procedures International, 20: 3, 205 — 211

**To link to this Article: DOI:** 10.1080/00304948809355812

**URL:** http://dx.doi.org/10.1080/00304948809355812

ORGANIC PREPARATIONS AND PROCEDURES INT. 20(3), 205-212 (1988)

# PREPARATION OF STYRYL BENZYLSULFONES AND 1,2-BIS(STYRYLSULFONYLMETHYL)-4,5-DIMETHYLBENZENES

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The synthesis of unsaturated mono[1-3] and bis-sulfones[4-7] has been reported by different routes. This communication describes the preparation of several new styryl benzylsulfones (**5**, Scheme 1) and bis(styrylsulfonylmethyl)benzenes (**9**, Scheme 2)

## SCHEME 1

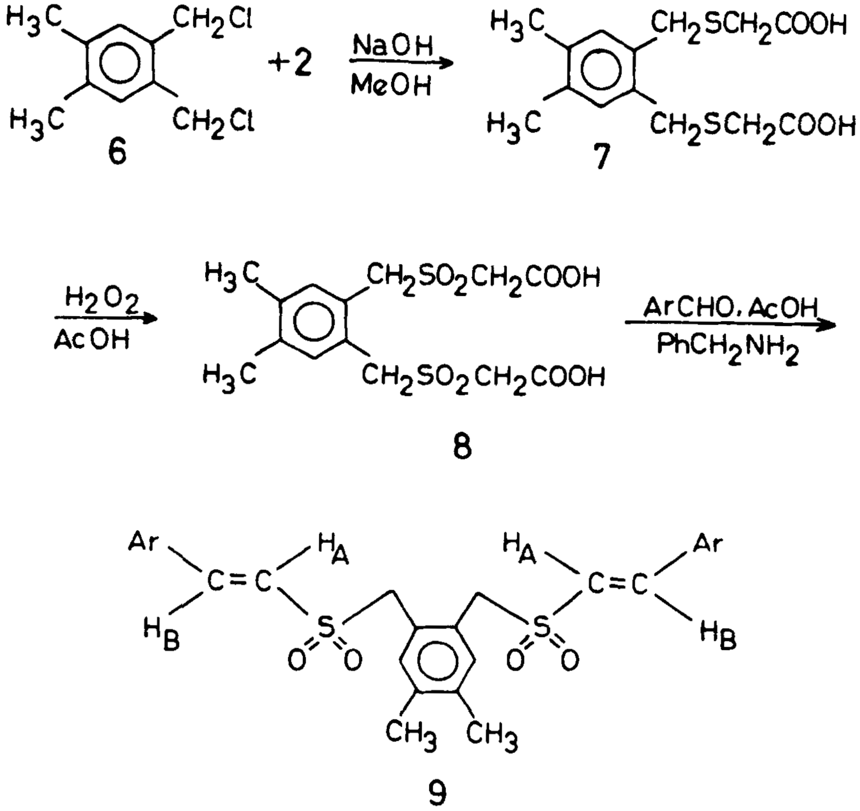
$$\underset{\mathbf{1}}{ArCH_2Cl} + \underset{\mathbf{2}}{HSCH_2COOH} \xrightarrow[MeOH]{NaOH} \underset{\mathbf{3}}{ArCH_2SCH_2COOH} \xrightarrow[AcOH]{H_2O_2}$$

$$\underset{\mathbf{4}}{ArCH_2SO_2CH_2COOH} \xrightarrow[PhCH_2NH_2]{Ar'CHO,\ AcOH} \underset{\mathbf{5}}{ArCH_2SO_2CH=CHAr'}$$

a) Ar=$C_6H_5$ Ar'=$C_6H_5$
b) Ar=$C_6H_5$ Ar'=2-$NO_2C_6H_4$
c) Ar=$C_6H_5$ Ar'=9-anthryl
d) Ar=4-$CH_3C_6H_4$ Ar'=4-$FC_6H_4$
e) Ar=4-$CH_3C_6H_4$ Ar'=4-$ClC_6H_4$
f) Ar=4-$CH_3C_6H_4$ Ar'=4-$BrC_6H_4$
g) Ar=4-$ClC_6H_4$ Ar'=4-$CH_3C_6H_4$
h) Ar=$ClC_6H_4$ Ar'=4-$FC_6H_4$
i) Ar=4-$ClC_6H_4$ Ar'=4-$ClC_6H_4$
j) Ar=4-$ClC_6H_4$ Ar'=4-$NO_2C_6H_4$
k) Ar=4-$NO_2C_6H_4$ Ar'=4-$CH_3C_6H_4$
l) Ar=4-$NO_2C_6H_4$ Ar'=4-$CH_3OC_6H_4$
m) Ar=4-$NO_2C_6H_4$ Ar'=4-$FC_6H_4$
n) Ar=4-$NO_2C_6H_4$ Ar'=4-$ClC_6H_4$
o) Ar=4-$NO_2C_6H_4$ Ar'=4-$NO_2C_6H_4$

by the Knoevenagel condensation of respective benzylsulfonylacetic acids (**4**) and 4,5-dimethyl-1,2-xylylenedisulfonylacetic acids (**8**) with araldehydes in the presence of benzylamine in glacial acetic acid. The relevant data of these compounds are presented in Table 1. Since α,β-ethylenic sulfones obtained by the Knoevenagel condensation of alkyl and arylsulfonylacetic acids with araldehydes were considered to possess <u>trans</u> configuration,[1,7,8] the compounds reported in the present investigation may also be regarded as <u>trans</u>-

**SCHEME 2**



a) Ar=$C_6H_5$ b) Ar=4-$CH_3C_6H_4$ c) Ar=4-$CH_3OC_6H_4$
b) Ar=4-$FC_6H_4$ e) Ar=2-$ClC_6H_4$ f) Ar=4-$ClC_6H_4$
g) Ar=2-$NO_2C_6H_4$ h) Ar=4-$NO_2C_6H_4$ i) Ar=3,4-$(CH_3O)_2C_6H_3$
j) Ar=2,4-$Cl_2C_6H_3$ k) Ar=3-$CH_3O$-4-$C_2H_5O$-$C_6H_3$

Table 1. Yield, mp. and Analysis of **5** and **9**

| Compound | Yield (%) | mp. (°C) | Elemental Analysis (Calcd) C | H |
|---|---|---|---|---|
| **5a** | 67 | 145-146 | 69.47(69.74) | 5.62(5.46) |
| **5b** | 69 | 127-128 | 59.68(59.39) | 4.37(4.32) |
| **5c** | 58 | 246-247 | 77.38(77.60) | 5.02(5.15) |
| **5d** | 64 | 170-171 | 59.87(59.60) | 4.92(4.69) |
| **5e** | 72 | 183-184 | 56.64(56.71) | 4.30(4.46) |
| **5f** | 68 | 217-218 | 50.27(50.13) | 4.04(3.94) |
| **5g** | 70 | 192-193 | 62.90(62.63) | 4.87(4.92) |
| **5h** | 74 | 161-162 | 58.13(57.97) | 4.02(3.89) |
| **5i** | 76 | 170-171 | 55.17(55.07) | 3.86(3.70) |
| **5j** | 78 | 194-195 | 53.65(53.40) | 3.72(3.58) |
| **5k** | 76 | 166-167 | 60.28(60.55) | 4.92(4.76) |
| **5l** | 78 | 170-171 | 57.82(57.64) | 4.60(4.53) |
| **5m** | 78 | 199-200 | 56.24(56.06) | 3.96(3.76) |
| **5n** | 82 | 165-166 | 53.18(53.33) | 3.74(3.58) |
| **5o** | 84 | 225-226 | 51.95(51.72) | 3.64(3.47) |
| **9a** | 70 | 159-160 | 66.84(66.93) | 5.59(5.62) |
| **9b** | 76 | 172-173 | 68.04(67.99) | 6.18(6.11) |
| **9c** | 68 | 179-180 | 63.74(63.86) | 5.82(5.74) |
| **9d** | 80 | 194-196 | 62.26(62.13) | 4.78(4.81) |
| **9e** | 75 | 232-233 | 58.38(58.32) | 4.59(4.52) |
| **9f** | 83 | 209-210 | 58.34(58.32) | 4.56(4.52) |
| **9g** | 64 | 252-253 | 56.26(56.10) | 4.26(4.35) |
| **9h** | 87 | 274-275 | 56.22(56.10) | 4.26(4.35) |
| **9i** | 32 | 164-165 | 61.84(61.41) | 5.78(5.84) |
| **9j** | 82 | 195-196 | 51.84(51.67) | 3.72(3.66) |
| **9k** | 43 | 191-192 | 62.38(62.51) | 6.30(6.29) |

isomers.[4,9,10] Their IR spectra displayed medium bands in the regions 1640-1620 (C=C), 1340-1320 and 1145-1120 ($SO_2$) cm$^{-1}$.[1] These compounds also exhibited strong bands in the region 990-975 cm$^{-1}$ (CH out-of plane) characteristic of trans-ethylenic compounds.

Table 2. $^1H$ NMR Data of **5** and **9**

| Compound | $^1H$ NMR (δ, ppm) | | | | |
|---|---|---|---|---|---|
| | $CH_3$ (s) | $CH_2$ (s) | -CH=CH- (d) | $J_{AB}$ Hz | ArH (m) |
| **5a** | | 4.30 | 6.78 | 15.7 | 7.26-7.85 |
| **5b** | | 4.34 | 6.82 | 15.9 | 7.24-7.78 |
| **5c** | | 4.32 | 6.91 | 16.2 | 7.30-7.92 |
| **5d** | 2.45 | 4.40 | 6.84 | 16.3 | 7.24-7.88 |
| **5e** | 2.46 | 4.38 | 6.74 | 16.4 | 7.20-7.90 |
| **5f** | 2.45 | 4.38 | 6.72 | 16.2 | 7.32-7.84 |
| **5g** | 2.46 | 4.38 | 6.82 | 16.3 | 7.22-7.76 |
| **5h** | | 4.40 | 6.88 | 16.4 | 7.28-7.92 |
| **5i** | | 4.38 | 6.76 | 16.3 | 7.36-7.84 |
| **5j** | | 4.36 | 6.84 | 16.2 | 7.20-7.88 |
| **5k** | 2.45 | 4.40 | 6.92 | 16.3 | 7.20-7.88 |
| **5l** | | 4.44 | 6.90 | 16.4 | 7.22-7.90 |
| **5m** | | 4.38 | 6.93 | 16.4 | 7.26-7.95 |
| **5n** | | 4.42 | 6.88 | 16.2 | 7.28-7.86 |
| **5o** | | 4.46 | 6.90 | 16.4 | 7.25-7.94 |
| **9a** | 2.24 | 4.62 | 6.81,7.54 | 16.2 | 7.13-7.47 |
| **9b** | 2.28 | 4.58 | 6.82,7.58 | 16.3 | 7.10-7.50 |
| **9c** | 2.24 | 4.60 | 6.93,7.62 | 16.2 | 7.13-7.58 |
| **9d** | 2.28 | 4.60 | 6.88,7.56 | 16.0 | 7.12-7.65 |
| **9e** | 2.24 | 4.68 | 6.86,7.62 | 16.4 | 7.24-7.56 |
| **9f** | 2.26 | 4.62 | 6.90,7.54 | 16.2 | 7.20-7.84 |
| **9g** | 2.28 | 4.60 | 6.82,7.56 | 16.4 | 7.70-8.06 |
| **9h** | 2.26 | 4.64 | 6.82,7.52 | 16.3 | 7.73-8.00 |
| **9i** | 2.26 | 4.65 | 6.80,7.55 | 16.2 | 7.18-7.50 |
| **9j** | 2.28 | 4.62 | 6.85,7.58 | 16.2 | 7.15-7.51 |
| **9k** | 2.24 | 4.62 | 6.84,7.60 | 16.4 | 7.23-7.94 |

The $^1H$ NMR spectra of **5** and **9** show absorptions at δ 4.58-4.64 (s, $C_6H_5CH_2$), 6.80-6.93 (d, $H_A$), 7.52-7.62 (d, $H_B$) and 7.45-7.82 (m, aryl-$\underline{H}$). However, in case of **5**, the vinylic protons ($H_B$) appear at δ 7.20-7.95 as multiplets since they are superimposed by the aromatic ring protons. The coupling constants of 16.0-16.4 Hz for the vinylic protons ($J_{AB}$) are typical for E-geometry. The methyl groups appeared as singlets in the region δ 2.45-2.26. However the methoxy and ethoxy groups of some of these compounds were observed at δ 3.90 (s, $OCH_3$) and 4.30 (q, $O\underline{CH_2}CH_3$), 1.48 (t, $OCH_2\underline{CH_3}$) respectively.

## EXPERIMENTAL SECTION

All melting points are uncorrected. IR spectra were measured on a Beckmann IR 18 spectrophotometer as KBr discs. $^1H$ NMR spectra were recorded on a 90 MHz-Perkin Elmer spectrometer and on Varian HA-100 spectrometer using TMS as an internal standard.

Sulfonylacetic acids (**4** and **8**). General Procedure.- To a solution of 40 g (1 mol) of sodium hydroxide in 600 ml of methanol, was added 46 g (0.5 mol) of **2** slowly over 30 minutes. A vigorous reaction set in at the beginning which slowly subsided after the complete addition of **2**. Then 0.50 mol of **1** (or 0.25 mol **6**) was added in portions and the mixture was refluxed for 6 hrs. Then it was poured on to 800 g of ice and neutralized with 400 ml of 2N hydrochloric acid. The products thus formed were collected and dried. Recrystallization from hot water gave the following compounds (**3** and **7**): 3a) benzylthioacetic acid (82.4%), mp. 61-62°; 3b) 4-methylbenzylthioacetic acid (78.0%) mp. 65-66°; 3c) 4-chlorobenzylthioacetic acid (80.5%) mp. 51-52°; 3d) 4-nitrobenzylthioacetic acid (83.6%) mp. 104-105°; 7) 4,5-dimethyl-1,2-xylylenedithioacetic acid (85.5%) mp. 111-112°.

The thioacetic acids (0.8 mol of **3** and **7**) were oxidized with 0.96 mol (or 1.92 mol) of 30% hydrogen peroxide in 225 ml of glacial acetic acid and refluxing for 1-2 hrs. The contents were cooled and acetic acid was removed under vacuum. The dense liquid which separated was then poured on crushed ice.

The crude sulfonylacetic acids (**4** and **8**) when recrystallized from hot water: 4a) benzylsulfonylacetic acid (76.2%) mp. 139-140°; 4b) 4-methylbenzylsulfonylacetic acid (70.5%) mp. 134-135°; 4c) 4-chlorobenzylsulfonylacetic acid (71.3%) mp. 144-145°; 4d) 4-nitrobenzylsulfonylacetic acid (72.5%) mp. 166-167°; 8) 4,5-Dimethyl-1,2-xylylenedisulfonylacetic acid (70.8%) mp. 220-221° were obtained.

Condensation of Sulfonylacetic Acids with Araldehydes. General Procedure.- A solution of 10 mmol of **4** (or **8**) dissolved in 15 ml of glacial acetic acid was treated with 10 mmol (or 20 mmol) of araldehyde in presence of catalytic amounts of benzylamine. The reaction mixture was refluxed for 1.5-2 hrs. After cooling it was treated with 50 ml of dry ether and refrigerated overnight. Any product which separated was collected and the filtrate was diluted with more ether. In some instances, a solid product separated immediately upon cooling or upon addition of ether. The ethereal layer was washed successively with a saturated solution of sodium carbonate (15 ml), sodium bisulphite (15 ml), dilute hydrochloric acid (20 ml) and finally with water. Evaporation of the dried ethereal layer yielded a solid product. The combined solid thus obtained was recrystallized either from ethanol or acetic acid to give pure **5** or **9**. The purities of these compounds were checked by thin layer chromatography.

**ACKNOWLEDGEMENT.-** The authors wish to express their thanks to Dr. S. Rame Gowda, Principal, Pondicherry Engineering College, Pondicherry.

## REFERENCES

1. D. B. Reddy, B. Sankariah and T. Balaji, Phosphorus and Sulfur, 16, 293 (1983) and references cited therein.

2. M. Mikolajczyk, S. Grejszczk, W. Midura and A. Zatorski, Synthesis, 278 (1975).

3. M. V. R. Reddy and S. Reddy, Acta Chim. Acad. Sci. Hung., 115, 269 (1984); C. A., 101, 23063r (1984).

4. H. H. Otto and H. Yamamura, Arch. Pharm. Japan, 308, 768 (1975).

5. P. Magee, U. S. Patent, 3,984,481; C. A., 85, 192368 (1976).

6. B. A. Trofimov, S. V. Amosova, N. I. Kazantseva, O.A. Tarasova, V. V. Kryuchkov, V. V. Noyzova and N. N. Skatova, Dokl. Nauchn. Sers. Khim. Teknol. Org. Soedin. Sery serinstykh Neflei, 13, 117 (1974); C. A., 85, 159554 (1976).

7. M. V. R. Reddy and S. Reddy, Synthesis, 322 (1984).

8. D. B. Reddy, R. Krishnamurthy and N. Subba Reddy, Proc. Indian Acad. Sci. (Chem. Sci), 89, 397 (1980) and references cited therein.

9. H. J. Backer, Rec. Trav. Chim. Pays-Bas, 72, 119 (1953).

10. V. Baliah and T. Rangarajan, J. Chem. Soc., 3068 (1958).

(Received March 9, 1987; in revised form September 8, 1987)