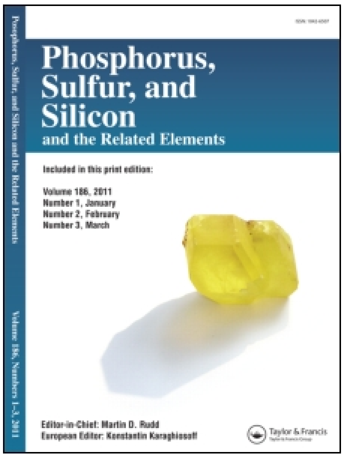

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SYNTHESIS AND SPECTRAL STUDIES OF SOME UNSATURATED SULPHONES

D. Bhaskar Reddy[a]; B. Sankaraiah[a]; T. Balaji[a]
[a] Department of Chemistry, Sri Venkateswara University, Tirupati, India

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SYNTHESIS AND SPECTRAL STUDIES OF SOME UNSATURATED SULPHONES

D. BHASKAR REDDY,* B. SANKARAIAH and T. BALAJI,

Department of Chemistry, Sri Venkateswara University, Tirupati-517502
India

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A new 5-chloro-2-methylbenzenesulphonylacetic acid has been prepared from 4-chlorotoluene. The condensation of this acid and 4-bromo, 4-methoxy, 3,4-dichloro and 4-chloro-3-methylbenzenesulphonylacetic acids with different araldehydes gave some new unsaturated sulphones. The *trans*-structure for these compounds has been arrived at on the basis of infrared and proton magnetic resonance spectral data.

INTRODUCTION

Although benzenesulphonyl and 4-tolylsulphonylacetic acids have been known[1,2] since 1954, until recently only a very few arylsulphonylacetic acids were reported in the literature. Baliah and Rathinasamy[3] obtained 3-bromo, 2,6-dimethyl and 4-methoxybenzenesulphonylacetic acids by the reaction of an appropriate thiophenol with chloroacetic acid in the presence of a base and oxidising the resultant mercaptoacetic acid with hydrogen peroxide. However, the benzenesulphonyl and 4-tolylsulphonylacetic acids were obtained following essentially the procedure of Gabriel.[4] In our earlier communication[5] we reported the preparation of 4-chloro-3-methylbenzenesulphonyl, 3,4-dichlorobenzenesulphonyl and 4-bromonaphthalenesulphonylacetic acids adopting the same method with slight modifications. In an attempt to prepare a series of new unsaturated sulphones, which are intermediates for the synthesis of aryl cyclopropyl sulphones, the preparation of new arylsulphonylacetic acids were of greater interest to us. Since a very few arylsulphonylacetic acids are known in the literature, any addition to this would be of considerable significance and importance. Amongst the various methods that are known for the synthesis of α,β-unsaturated sulphones, the one that involves the condensation of arylsulphonylacetic acids with araldehydes seems to involve simpler experimental conditions affording fairly good yields.

RESULTS AND DISCUSSION

A new arylsulphonylacetic acid has been prepared in fairly high yield following the procedure of Gabriel.[4] 4-Chlorotoluene was converted into 5-chloro-2-methylbenzenesulphonyl chloride by chlorosulphonylation.[6] The corresponding arylsulphinate[7] was condensed with chloroacetic acid at pH 10 to result 5-chloro-2-methylbenzenesulphonylacetic acid.

The infrared spectra of this acid exhibited a strong band in the region 1760 cm^{-1} characteristic of carbonyl stretching frequency of carboxylic acid. The increase in the carbonyl stretching frequency of the carboxylic acid may be due to the inductive effect of the sulphonyl group in the α-position. The characteristic absorptions of the sulphonyl group,[8,9] i.e., 1330–1300 cm^{-1} and 1140–1130 cm^{-1} and of S-aryl[10] 1105–1092 cm^{-1} were also displayed by this acid.

The preparation of a few *trans*-α,β-ethylenic sulphones were reported by Truce and Goralski.[11] By a Horner–Wittig reaction *via* phosphonate carbanions, Popoff *et al.*[12] and Shahak and Almog[13] reported the preparation of a few more sulphones. Posner and Brunelle[14] modified the former procedure, which was limited to the arylidene sulphones, to obtain a few more alkylidene sulphones. The sulphones thus prepared were indeed confirmed to be *trans*-isomers by nuclear magnetic resonance spectral studies.

Baliah and Seshapathi Rao[15] obtained a few unsaturated sulphones by the condensation of alkyl and arylsulphonylacetic acids with araldehydes in glacial acetic acid in the presence of a catalytic amount of benzylamine. Later, adopting this procedure, the preparation of a series of α,β-unsaturated sulphones in good yields was reported.[5,16,17,18] A few more α,β-unsaturated sulphones have been prepared by the condensation of 4-bromo, 4-methoxy, 3,4-dichloro, 4-chloro-3-methyl and 5-chloro-2-methylbenzenesulphonylacetic acids with different araldehydes (see Table I). The α,β-unsaturated sulphones obtained by this method were considered to be *trans*-isomers.

The ultraviolet spectra of all these unsaturated sulphones showed a long wavelength band around 275–318 nm, a second band around 222–234 nm and a third band with high intensity in the 200–210 nm region.

The infrared spectra of these sulphones exhibited mostly strong bands in the region 1000–960 cm^{-1} (δ CH out-of-plane) characteristic of *trans*-ethylenic compounds[19] (see Table II). These compounds also displayed characteristic bands around 1665–1620 cm^{-1} (ν C=C)[20,21] and 1288–1268 cm^{-1} (δ CH in-plane).[22] The very strong peaks in the regions 1330–1305 and 1160–1140 cm^{-1} exhibited by these compounds are characteristic of the sulphonyl group.[8,9] Medium to strong bands in the region 1106–1080 cm^{-1} characteristic of the S-aryl group[10] were also displayed by these compounds. The bands in the region 1595–1565 cm^{-1} may be considered as a positive indication of the conjugation of the double bond with an aromatic ring.[23]

The infrared spectral studies for the configurational assignments of α,β-unsaturated sulphones are well augmented. Proton magnetic resonance spectral data are considered to be the most reliable physical evidence for the configurational assignments of *cis*, *trans*-isomers. However, its application to the α,β-unsaturated sulphones seems to be very limited.

The chemical shift values for the *trans*-vinylic protons of α,β-unsaturated sulphones were found to be around 6.82 to 7.00 ppm (H_A) and 7.54 to 7.77 ppm (H_B) and the J_{AB} value at 15 to 17 Hz.[24] The proton magnetic resonance spectra of some of the α,β-unsaturated sulphones prepared in the present investigation have a doublet for the H_A of the vinylic protons between 6.73–6.92 and the J_{AB} is found to be around 15.6 to 16.2 Hz (see Table III). The aromatic ring protons superimposed on the vinylic proton (H_B) appeared in the region 7.10 to 8.45 ppm as a multiplet. The methyl and methoxy groups appeared as singlets at 2.39 ppm and 2.41 ppm;

TABLE I

$ArSO_2CH = CHAr'$

Sl. No.	Ar	Ar′	Yield %	m.p. °C	Formula	Calcd. % C	Calcd. % H	Found % C	Found % H
1	$4\text{-}BrC_6H_4$	$2\text{-}ClC_6H_4$	71.5	153–154	$C_{14}H_{10}BrClO_2S$	47.01	2.82	47.08	3.04
2	$4\text{-}BrC_6H_4$	$3,4\text{-}(CH_3O)_2C_6H_3$	54.7	142–143	$C_{16}H_{15}BrO_4S$	50.13	3.95	50.37	3.95
3	$4\text{-}BrC_6H_4$	$4\text{-}(CH_3)_2NC_6H_4$	48.3	165–166	$C_{16}H_{16}BrNO_2S^{1/2}H_2O$	51.20	4.56	51.57	4.47
4	$4\text{-}BrC_6H_4$	$4\text{-}O_2NC_6H_4$	79.4	208–209	$C_{14}H_{10}BrNO_4S$	45.66	2.74	45.53	2.67
5	$4\text{-}CH_3OC_6H_4$	$2\text{-}ClC_6H_4$	68.4	142–143	$C_{15}H_{13}ClO_3S$	58.33	4.24	58.13	4.30
6	$4\text{-}CH_3OC_6H_4$	$4\text{-}ClC_6H_4$	76.8	177–178	$C_{15}H_{13}ClO_3S$	58.33	4.24	58.66	4.69
7	$4\text{-}CH_3OC_6H_4$	$4\text{-}CH_3OC_6H_4$	65.9	127–128	$C_{16}H_{16}O_4S$	63.13	5.30	62.48	5.30
8	$4\text{-}CH_3OC_6H_4$	$2\text{-}O_2NC_6H_4$	76.4	157–158	$C_{15}H_{13}NO_5S$	56.40	4.10	56.42	4.21
9	$4\text{-}CH_3OC_6H_4$	$4\text{-}O_2NC_6H_4$	81.9	191–192	$C_{15}H_{13}NO_5S$	56.40	4.10	56.21	4.08
10	$3,4\text{-}Cl_2C_6H_3$	C_6H_5	84.7	130–131	$C_{14}H_{10}Cl_2O_2S$	53.70	3.22	53.77	3.21
11	$4\text{-}Cl\text{-}3\text{-}CH_3C_6H_3$	C_6H_5	64.7	116–117	$C_{15}H_{13}ClO_2S$	60.29	4.90	60.02	4.86
12	$5\text{-}Cl\text{-}2\text{-}CH_3C_6H_3$	C_6H_5	61.2	110–111	$C_{15}H_{13}ClO_2S$	60.29	4.90	60.46	4.76

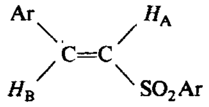
TABLE II

Infrared spectra of $ArSO_2CH = CHAr'$

Compd. No.	Band range cm^{-1} ν C=C	δ CH (in-plane)	δ CH (out-of-plane)	ν SO_2		S-Aryl	Aromatic ring conjugation with C=C
1	1632	1284	990	1324	1158	1080	1572
2	—	1280	1000	1305	1152	1100	1595
3	1660	—	985	1322	1156	1080	1568
4	—	1288	980	1320	1160	1100	1578
5	—	1268	980	1330	1153	1106	1591
6	1662	1261	—	1320	1160	1102	1592
7	1644	1262	998	1312	1145	1100	1568
8	1665	1275	985	1316	1160	—	1580
9	1630	—	980	1345	1150	1100	1592
10	1620	1270	960	1308	1150	1087	1560
11	1625	1288	960	1315	1140	1090	1565
12	1609	1270	975	1305	1150	1102	1570

TABLE III

Proton magnetic resonance spectra of



	Ar	Ar'	H_A doublet δ, ppm	J_{AB} Hz	Aromatic protons superimposed on H_B, multiplet, δ, ppm	Methoxy/methyl group, singlet, δ, ppm
1.	$4\text{-}BrC_6H_4$	$2\text{-}ClC_6H_4$	6.73	15.6	7.10–7.89	—
2.	$4\text{-}BrC_6H_4$	$4\text{-}O_2NC_6H_4$	6.92	16.2	7.50–8.45	—
3.	$4\text{-}CH_3OC_6H_4$	$4\text{-}ClC_6H_4$	6.76	15.8	7.28–7.97	3.82 (OCH_3)
4.	$4\text{-}CH_3OC_6H_4$	$4\text{-}O_2NC_6H_4$	6.89	16.0	7.42–8.38	3.79 (OCH_3)
5.	$3,4\text{-}Cl_2C_6H_3$	C_6H_5	6.75	15.8	7.15–7.94	—
6.	$4\text{-}Cl\text{-}3\text{-}CH_3C_6H_3$	C_6H_5	6.88	16.0	7.36–8.20	2.41 (CH_3)
7.	$5\text{-}Cl\text{-}2\text{-}CH_3C_6H_3$	C_6H_5	6.86	15.8	7.34–8.06	2.39 (CH_3)

3.79 ppm and 3.82 ppm respectively. Hence, the method of preparation and the correlation of infrared and proton magnetic resonance spectral data confirm that all the α,β-unsaturated sulphones under the present investigation are *trans*-isomers.

EXPERIMENTAL

All melting points were determined on a Mel-Temp apparatus and are uncorrected. The elemental analyses were performed by Dr. R. D. MacDonald, Australian Microanalytical Service. Ultraviolet absorption measurements were determined in 95% ethanol with a Carl-Zeiss DMR 21 spectrophotometer and infrared spectra were recorded on a Perkin-Elmer infrared spectrophotometer model 700 in nujol mulls. The proton magnetic resonance spectra were recorded in deutero chloroform solution using a Varian T-60 spectrometer with tetramethylsilane (TMS) as an internal standard.

Reagents. Bromobenzene, anisole, 1,2-dichlorobenzene, 2-chlorotoluene, 4-chlorotoluene and the araldehydes were commercially obtained and purified wherever necessary.

The above hydrocarbons were converted into corresponding sulphonyl chlorides by chlorosulphonylation[6] which were later converted into sodium arylsulphinates.[7]

General Procedure For The Preparation of Arylsulphonylacetic Acids. The pure sodium aryl sulphinate (0.5 mole) and chloroacetic acid (0.6 mole) were dissolved in water (150 ml) and the mixture was treated with sodium hydroxide to maintain a pH of 10. The solution was heated under reflux on a sand bath for 2 hr and cooled and extracted thrice with 50 ml portions of benzene to remove any aryl methyl sulphone formed during this reaction. The aqueous solution was acidified to congo red with dilute hydrochloric acid and was left overnight in the refrigerator. The separated compound was filtered, washed with cold water, dried and recrystallized.

5-Chloro-2-methylbenzenesulphonylacetic acid. Yield 73%, Crystallized from water as colourless needles, *m.p.* 165–166°, $C_9H_9ClO_4S$. Calcd.: C, 43.47; H, 3.65; Found: C, 43.69; H, 3.57; IR (KBr) 1100 (s) (S-aryl), 1140 (s) (SO_2), 1300 (s) (SO_2) and 1760 (s) (COOH) cm^{-1}.

General Procedure For The Condensation of Arylsulphonylacetic Acids With Different Aryl Aldehydes. Arylsulphonylacetic acid (0.01 mole) dissolved in glacial acetic acid (6 ml) was mixed with an araldehyde (0.01 mole) and a catalytic amount (0.2 ml) of benzylamine. The whole mixture was refluxed for 90–120 minutes. After cooling the reaction mixture, dry ether (50 ml) was added and kept in refrigerator overnight. Any product that separated was filtered. The filtrate was diluted with more ether and washed successively with a saturated solution of sodium bicarbonate (15 ml), sodium bisulphite (15 ml) dilute hydrochloric acid (20 ml) and finally with water. Evaporation of the dried ethereal layer yielded in many cases a solid product. In some cases a syrupy substance that separated was treated with a small amount of methanol or 2-propanol to obtain a solid product. The relevant data on the compounds synthesized are given in Table I.

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