

Preparation of unsaturated sulphones through new aryl sulphonylacetic acids

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Abstract. Three new aryl sulphonylacetic acids have been prepared from 2-chlorotoluene, 1,2-dichlorobenzene and 1-bromonaphthalene. The infrared spectra of these acids exhibited strong bands characteristic of carbonyl stretching frequencies of carboxylic acids. Utilising these sulphonylacetic acids some new unsaturated sulphones were synthesised. An attempt has been made to correlate the infrared and proton magnetic resonance spectral data to the configurations of unsaturated sulphones.

Keywords. Aryl sulphonylacetic acids ; unsaturated sulphones ; configuration.

1. Introduction

Only a few methods are known in the literature for the preparation of aryl sulphonylacetic acids. Baliah and Rathinasamy (1971) obtained 3-bromobenzenesulphonyl, 2,6-dimethylbenzenesulphonyl and 4-methoxybenzenesulphonyl acetic acids by the reaction of chloroacetic acid with the appropriate thiophenol in the presence of a base and oxidising the resultant mercaptoacetic acid with hydrogen peroxide. However Balasubramanian and co-workers (Balasubramanian and Baliah 1954; Balasubramanian *et al* 1955) reported the preparation of benzenesulphonyl and 4-tolylsulphonylacetic acids following essentially the procedure of Gabriel (1881). For our studies relating to the synthesis of aryl cyclopropyl sulphones, we were interested in preparing a series of new unsaturated sulphones as intermediates. Very few sulphonylacetic acids are known in the literature and hence the preparation of more number of them by a simple and unambiguous method would be of considerable interest. Although number of methods are known for the synthesis of α,β -unsaturated sulphones the one which involves the condensation of aryl sulphonylacetic acids with aryl aldehydes seem to be more elegant and convenient,

2. Results and discussion

The new aryl sulphonylacetic acids have been prepared following essentially the procedure of Gabriel (1881) with slight modification affording fairly high yields. 2-chlorotoluene, 1,2-dichlorobenzene and 1-bromonaphthalene were converted into 4-chloro-3-benzenesulphonyl, 3,4-dichlorobenzenesulphonyl and 4-bromonaphthalene-sulphonyl chlorides by chlorosulphonylation (Huntress and Carten 1940). The corresponding aryl sulphinates (Field and Clark 1963) when condensed with chloroacetic acid in an alkaline medium (pH 10) gave respective sulphonylacetic acids.

The infrared spectra of these acids exhibited strong bands in the region 1740–1700 cm^{-1} characteristic of the carbonyl stretching frequency of carboxylic acids. The increase of 20 cm^{-1} in the carbonyl stretching frequency of carboxylic acid may be due to its interaction with the alkali halide (Bellamy 1958). The characteristic absorptions of the sulphonyl group, i.e., 1330–1322 cm^{-1} and 1140–1130 cm^{-1} (Bavian *et al* 1960 ; Robinson 1961) and of S-aryl 1105–1092 cm^{-1} (Ham *et al* 1960) were also displayed by these acids.

Truce and Goralski (1971) reported the preparation of a few new *trans*-1-aryl-2-(arenesulphonyl) ethenes. Popoff *et al* (1969) and later Shahak and Almog (1970) reported the preparation of arylidene sulphones by Horner–Wittig reaction *via* phosphonate carbanions. Since this method was limited to the arylidene-sulphones, Posner and Brunelle (1972) modified the procedure to obtain alkylidene sulphones also. The reaction products are confirmed by them to be *trans*-isomers by nuclear magnetic resonance spectral studies.

Baliah and Seshapathi Rao (1959) achieved fairly good yields of unsaturated sulphones by the condensation of alkyl and aryl sulphonylacetic acids with aryl aldehydes in glacial acetic acid in presence of benzylamine. This procedure has been adopted by Gerstenfeld *et al* (1963) and Nobles and Thompson (1965) for the preparation of a series of unsaturated sulphones. Recently (Seshapathi Rao Naidu and Bhaskar Reddy 1975) a series of α,β -unsaturated sulphones in excellent yields were reported adopting the same procedure. A few new α,β -unsaturated sulphones have been prepared by the condensation of new aryl sulphonylacetic acids mentioned above with different aryl aldehydes (see table 1). The α,β -unsaturated sulphones obtained by this method were usually *trans*-isomers (Truce and Goldhamer 1959; Seshapathi Rao Naidu and Bhaskar Reddy 1975).

The ultraviolet spectra of all these unsaturated sulphones exhibited a long wavelength band around 273–312 nm and a second band around 220–228 nm. Another strong band with high intensity occurs in the spectra of all these compounds at 202–203 nm region except in the case of 1-aryl-2-(4-bromonaphthalene sulphonyl) ethenes.

The infrared spectra of most of these unsaturated sulphones exhibited a band with medium to weak intensity in the region 1680–1620 cm^{-1} (ν C=C) (Boonstra and Rinzema 1960; Jones *et al* 1960) and another strong band in the region 980–960 cm^{-1} (δ CH out-of-plane) (Truce and Simms 1956; Truce and Goldhamer 1959; Truce *et al* 1960) characteristic of *trans* disubstituted ethylenes (see table 2). They also displayed bands in the region 1297–1280 cm^{-1} ; 1370–1308 cm^{-1} and 1150–1137 cm^{-1} and 1105–1091 cm^{-1} which are characteristic for δ CH in-plane deformation (Sheppard and Simpson 1952), sulphonyl group (Bavian *et al*

Table 1. Ar CH = CH SO₂Ar'

Ar	Ar'	Yield (%)	m.p. °C	Formula	Analysis%			
					Calcd.		Found	
					C	H	C	H
C ₆ H ₅	4-Cl-3-CH ₃ C ₆ H ₄	64.75	116-117	C ₁₃ H ₁₃ ClO ₂ S	60.29	4.90	59.95	5.26
2-ClC ₆ H ₄	4-Cl-3-CH ₃ C ₆ H ₄	75.13	134-135	C ₁₃ H ₁₃ Cl ₂ O ₂ S	55.05	3.70	54.93	3.78
4-ClC ₆ H ₄	4-Cl-3-CH ₃ C ₆ H ₄	78.46	166-167	C ₁₃ H ₁₃ Cl ₃ O ₂ S	55.05	3.70	54.68	3.84
4-CH ₃ OC ₆ H ₄	4-Cl-3-CH ₃ C ₆ H ₄	69.27	155-156	C ₁₃ H ₁₃ ClO ₃ S	59.93	4.68	59.22	4.65
4-NO ₂ C ₆ H ₄	4-Cl-3-CH ₃ C ₆ H ₄	82.14	207-208	C ₁₃ H ₁₃ ClNO ₄ S	53.33	3.58	53.24	3.80
4-ClC ₆ H ₄	3, 4-Cl ₂ C ₆ H ₃	76.15	166.5-168	C ₁₄ H ₉ Cl ₃ O ₂ S	48.37	2.61	48.24	2.92
4-CH ₃ OC ₆ H ₄	3, 4-Cl ₂ C ₆ H ₃	72.89	138-139	C ₁₃ H ₁₂ Cl ₂ OS	52.49	3.52	52.81	3.57
2-ClC ₆ H ₄	4-BrC ₁₀ H ₆	67.45	133-134	C ₁₃ H ₁₂ BrClO ₂ S	53.02	2.97	52.80	2.85
4-ClC ₆ H ₄	4-BrC ₁₀ H ₆	71.23	149-150	C ₁₃ H ₁₂ BrClO ₂ S	53.02	2.97	52.67	3.01

Table 2. Infrared spectra of Ar CH=CH SO₂ Ar.

Ar	Ar'	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	
C ₆ H ₅	4-Cl-3-CH ₃ C ₆ H ₃	..	1297	975	1317	1140	1088	1580
2-Cl C ₆ H ₄	4-Cl-3-CH ₃ C ₆ H ₃	..	1289	970	1313	1147	1089	1585
4-Cl C ₆ H ₄	4-Cl-3-CH ₃ C ₆ H ₃	1610	1286	978	1308	1138	1084	1578
4-CH ₃ O C ₆ H ₄	4-Cl-3-CH ₃ C ₆ H ₃	..	1285	980	1310	1137	1089	1575
4-O ₂ NC ₆ H ₄	4-Cl-3-CH ₃ C ₆ H ₃	1618	1290	960	1309	1139	1085	1592
4-Cl C ₆ H ₄	3,4-Cl ₂ C ₆ H ₃	1613	1290	979	1309	1150	1085	1590
4-CH ₃ O C ₆ H ₄	3,4-Cl ₂ C ₆ H ₃	..	1290	980	1310	1149	1087	1570
2-ClC ₆ H ₄	4-BrC ₁₀ H ₆	1640	1280	978	1310	1150	1105	1586
4-ClC ₆ H ₄	4-BrC ₁₀ H ₆	1610	1292	977	1310	1150	1081	1590

1960; Robinson 1961) and S-aryl group (Ham *et al* 1960) respectively. They showed bands with variable intensity in the region 1590–1570 cm⁻¹ (Rasmussen and Brattain 1947) which may indicate the conjugation of the ethylenic bond with the aromatic ring present in the unsaturated sulphones.

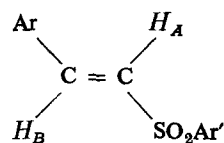
The configurational assignments for α,β -ethylenic sulphones by infrared spectral studies are well-known. Although the proton magnetic resonance spectral data appear to be the most reliable physical evidence for the configurational assignments, its application to the vinylic sulphones seem to be very sparse.

For the *trans* vinylic protons of α,β -unsaturated sulphones the chemical shift values 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 (Ciuliana *et al* 1975). The pmr spectra of the compounds under investigation gave a clear doublet for the H_A of the vinylic protons between 6.63 to 6.95 ppm and the J_{AB} is found to be around 15.6 to 16 Hz (see table 3). The aromatic ring protons superimposed on vinylic proton (H_B) lines appeared in the region 7.10 to 8.43 ppm as multiplet. The methyl and methoxy groups appeared as singlets at 2.43 ppm and 3.83 ppm respectively. Thus the mode of formation, the infrared and proton magnetic resonance spectral studies confirm that all the α,β -unsaturated sulphones 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, Australian Microanalytical Service. The infrared spectra were recorded on Perkin-Elmer Model 397 infrared spectrometer in potassium bromide discs. The ultraviolet absorption spectra were recorded with a Carl Zeiss DMR-21 spectrometer. The proton magnetic resonance spectra were recorded in deuterio-

Table 3. Proton magnetic resonance spectra of



Ar	Ar'	H_A doublet δ , ppm	J_{AB} HZ	Aromatic protons superimposed on H_B multiplet δ , ppm	Methyl group singlet δ , ppm
4-ClC ₆ H ₄	3, 4-Cl ₂ C ₆ H ₃	6.76	15.6	7.34-8.00	..
4-ClC ₆ H ₄	4-Cl-3-CH ₃ C ₆ H ₃	6.72	16.0	7.36-7.83	2.43
4-NO ₂ C ₆ H ₄	4-Cl-3-CH ₃ C ₆ H ₃	6.95	16.0	7.52-8.43	2.43
2-ClC ₆ H ₄	4-Cl-3-CH ₃ C ₆ H ₃	6.86	15.6	7.16-8.20	2.43
4-CH ₃ OC ₆ H ₄	4-Cl-3-CH ₃ C ₆ H ₃	6.63	15.6	7.10-7.92	2.43 3.83*

*Methoxy group

chloroform solution using a Varian T-60 spectrometer with tetramethylsilane (TMS) as an internal standard.

3.1. Reagents

2-Chlorotoluene, 1,2-dichlorobenzene, 1-bromonaphthalene and the aryl aldehydes were commercially obtained and used after purification wherever necessary.

The substituted hydrocarbons were converted into corresponding sulphonyl chlorides by chlorosulphonylation (Huntress and Carten 1940). The sulphonyl chlorides were converted into sodium aryl sulphinates (Field and Clark 1963).

3.2. General procedure for the preparation of arylsulphonylactic acids

Recrystallised sodium arylsulphinate (0.5 mol) and chloroacetic acid (0.6 mol) were dissolved in water (250 ml) and the mixture was made alkaline to a pH of 10. The solution was heated under reflux on a sand bath for 2 hr and cooled. Aryl methyl sulphone if any formed during this reaction was removed by extraction thrice with 50 ml portions of benzene. The aqueous solution was acidified to conged with dilute hydrochloric acid when crystals of aryl sulphonylactic acid began to separate. The solution was left overnight in the refrigerator to complete the separation of the compound. The product was collected on a Buchner, washed with cold water, dried and recrystallised.

3.2a. 4-Chloro-3-methylbenzenesulphonylactic acid

Yield 78%, crystallised from water as colourless shining prisms melting at 127-128°, C₉H₉ClO₄S Calcd. C, 43.47; H, 3.65; Found: C, 43.42; H, 3.44%; IR (KBr) 1092 (m) (S-aryl), 1140 (m) (SO₂), 1330 (s) (SO₂), 1722 (s) and 1743 (s) (COOH) cm⁻¹.

3.2b. 3,4-Dichlorobenzenesulphonylacetic acid

Obtained in 74% yield, recrystallisation from water gave fine long needles, m.p. 149–150°, $C_8H_6Cl_2O_4S$ Calcd. C, 35.70; H, 2.25; Found : C, 35.78; H, 2.38%; IR (KBr) 1094 (s) (S-aryl), 1130 (m) (SO_2), 1322 (s) (SO_2) and 1702 (s) (COOH) cm^{-1} .

3.2c. 4-Bromonaphthalenesulphonylacetic acid

Yield 60%, crystallised from water as colourless needles which melted at 140–141°, $C_{12}H_9BrO_4S \frac{1}{2} H_2O$ Calcd, C, 42.61; H, 2.98; Found : C, 42.43; H, 3.07%; IR (KBr) 1105 (s) (S-aryl), 1140 (m) (SO_2), 1325 (s) (SO_2) and 1743 (s) (COOH) cm^{-1} .

3.3. General procedure for the condensation of aryl sulphonylacetic acids with different aryl aldehydes

A solution of aryl sulphonylacetic acid (0.01 mol) in glacial acetic acid (6 ml) was mixed with an aryl aldehyde (0.01 mol) and a catalytic amount (0.2 ml) of benzylamine and the whole mixture was refluxed for 90 minutes. But in certain condensations the heating was continued for 100–120 minutes. The reaction mixture was cooled, treated with dry ether (50 ml) and refrigerated overnight. 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), sodium bisulphite (15 ml), dilute hydrochloric acid (20 ml) and finally with water. Evaporation of dried ethereal solution yielded in many cases a solid product. However in some instances a syrupy substance that 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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