BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 48 (3), 1091—1092 (1975)

Synthesis of α,β-Ethylenic Sulfones

M. SESHAPATHI RAO NAIDU and D. BHASKAR REDDY
Department of Chemistry, Post-Graduate Centre, Sri Venkateswara University, Anantapur 515003, India

(Received June 24, 1974)

Synopsis. A series of new α,β-ethylenic sulfones were prepared by the condensation of *p*-chlorophenylsulfonylacetic acid with various aryl aldehydes. The UV and IR spectra of all these compounds were recorded. Their IR spectra exhibited medium to strong bands in the region 1000—975 cm^{-1}, characteristic of *trans* ethylenic compounds.

The preparation of α,β-ethylenic sulfones by several routes has been reported.[1-5] For our current investigation on aryl cyclopropyl sulfones we were interested in preparing a series of unsaturated sulfones as intermediates. A number of new α,β-ethylenic sulfones prepared (see Table 1) by a slightly improved procedure of Baliah and Seshapathirao[1] are reported in this paper. Aromatic aldehydes were condensed with *p*-chlorophenylsulfonylacetic acid in glacial acetic acid solution in the presence of catalytic amounts of benzylamine. The synthetic utility of this procedure appears to be more elegant and convenient under simpler experimental conditions, affording fairly high yields of the unsaturated sulfones.

The UV spectra of all these unsaturated sulfones exhibited a long wavelength band around 245—320 nm, a second band around 220—236 nm and a third band with high intensity at 200 nm region.

The IR spectra of most of these sulfones showed a band in the region 1680—1620 cm^{-1} (ν C=C) and a strong band in the region 1000—975 cm^{-1} (δ CH out-of-plane) characteristic of *trans* ethylenic compounds.[4] In case of compounds containing polynuclear and heterocyclic substituents this band has

TABLE 1. *p*-$ClC_6H_4SO_2CH{=}CHR$

					Analysis (%)					
Sl. No.	R	Yield %	Mp °C	Formula	Calcd			Found		
					C	H	Cl	C	H	Cl
1	4-$CH_3CONHC_6H_4$	69.0[a]	206—208	$C_{16}H_{14}ClNO_3S$	57.24	4.21		56.99	4.33	
2	2-BrC_6H_4	60.4[b]	149—150	$C_{14}H_{10}BrClO_2S$	47.01	2.82		46.62	2.57	
3	4-BrC_6H_4	75.0[c]	184—185	$C_{14}H_{10}BrClO_2S$	47.01	2.82		47.02	2.83	
4	3-Br-4-$OCH_3C_6H_3$	62.0[d]	149—150	$C_{15}H_{12}BrClO_3S$	46.48	3.12		46.40	3.07	
5	2-ClC_6H_4	87.9[b]	139.5—140.5	$C_{14}H_{10}Cl_2O_2S$	53.70	3.22	22.64	53.43	3.17	22.90
6	3-ClC_6H_4	84.7[d]	130—131	$C_{14}H_{10}Cl_2O_2S$	53.70	3.22	22.64	53.77	3.21	22.80
7	4-ClC_6H_4	57.5	167—167.5[f]							
8	2,4-$Cl_2C_6H_3$	79.3[d]	153—154	$C_{14}H_9Cl_3O_2S$	48.38	2.61		48.43	2.65	
9	3,4-$Cl_2C_6H_3$	57.6[d]	164—165	$C_{14}H_9Cl_3O_2S$	48.38	2.61		48.27	2.59	
10	4-$(CH_3)_2NC_6H_4$	81.0	158—159[g]							
11	2,3-$(CH_3O)_2C_6H_3$	80.6[d]	125—126	$C_{16}H_{15}ClO_4S$	56.72	4.46		56.73	4.41	
12	2,5-$(CH_3O)_2C_6H_3$	44.3[e]	114—115	$C_{16}H_{15}ClO_4S$	56.72	4.46		57.09	4.40	
13	3,4-$(CH_3O)_2C_6H_3$	45.9	147—147.5[h]							
14	2-$C_2H_5OC_6H_4$	42.1[e]	110—111	$C_{16}H_{15}ClO_3S$	59.53	4.68		59.18	4.58	
15	2-FC_6H_4	92.3[d]	103—104	$C_{14}H_{10}FClO_2S$	56.66	3.39	11.95	56.90	3.45	12.10
16	4-FC_6H_4	51.8[b]	118—118.5	$C_{14}H_{10}FClO_2S$	56.66	3.39		56.78	3.55	
17	4-$(CH_3)_2CHC_6H_4$	42.4[d]	97—97.5	$C_{17}H_{17}ClO_2S$	63.66	5.34		63.54	5.32	
18	2-$CH_3C_6H_4$	78.8[b]	135.5—136	$C_{15}H_{13}ClO_2S$	61.55	4.47		61.47	4.49	
19	4-$CH_3C_6H_4$	66.9[d]	124—125	$C_{15}H_{13}ClO_2S$	61.55	4.47		61.61	4.59	
20	4-$CH_3OC_6H_4$	62.2	144—145[i]							
21	2-$NO_2C_6H_4$	77.4[c]	174—175	$C_{14}H_{10}ClNO_4S$	51.94	3.11	10.95	52.11	3.11	10.90
22	3-$NO_2C_6H_4$	80.5[d]	141—142	$C_{14}H_{10}ClNO_4S$	51.94	3.11	10.95	52.14	3.07	10.80
23	4-$NO_2C_6H_4$	76.7[c]	197—198	$C_{14}H_{10}ClNO_4S$	51.94	3.11	10.95	51.69	3.17	11.20
24	1-Naphthyl	63.4[d]	136.5—137	$C_{16}H_{13}ClO_2S$	65.75	3.98	10.78	65.85	3.95	10.80
25	2-Naphthyl	61.0[c]	182—183	$C_{18}H_{13}ClO_2S$	65.75	3.98		65.81	4.02	
26	9-Anthryl	82.0[e]	184—185	$C_{22}H_{15}ClO_2S$	69.72	3.99		69.45	3.91	
27	1-Pyrene	84.4[c]	204—205	$C_{24}H_{15}ClO_2S$	71.37	3.75		70.98	3.57	
28	2-Thienyl	90.1	134.5—135.5[j]							

Products recrystallized from (a) aqueous acetone, (b) methanol, (c) glacial acetic acid, (d) 95% ethanol and (e) 2-propranol. W.L. Nobles and B.B. Thomson [*J. Pharm. Sic.*, **54**, 709, 576 (1965)] report (f) mp 163—164 °C, yield 30.2%; (h) mp 144—146 °C, yield 10.2%; (i) mp 142.5—143.5 °C, yield 19%; (g) mp 162—164 °C, yield 1.8%. W.P. Thompson and H.O. Huisman [*Rec. Trav. Chim.*, **85**, 175 (1966)] report (j) mp 135—136.5 °C, yield 19%.

Table 2. UV and IR spectra of α,β-ethylenic sulfones

Compd. No.	IR (cm^{-1}) Nujol					UV, nm, 95% ethanol λ_{max} (ε_{max})
	ν C=C	δ CH in-plane	δ CH out-of-plane	ν SO$_2$		
1	1672	1290	978	1310	1140	317(26470), 235(15410), 203(20850)
2		1282	980	1319	1150	276(17820), 232(13410), 203(17070)
3		1280	983	1316	1145	286(25540), 220(13300), 202(17860)
4	1680	1296	992	1320	1150	311(24680), 295(23910), 239(26110), 202(27490)
5		1278	962	1320	1144	276(19390), 226(14280), 203(21280)
6	1624	1297	1000	1315	1160	275(23700), 205(21040)
7		1272	975	1300	1135	285(29830), 219(18660), 203(23600)
8		1284	979	1323	1150	282(27800), 228(20870), 204(26020)
9	1660	1272	972	1310	1130	283(26260), 230(19050), 204(18990)
10	1665	1278	980	1316	1142	240(15490), 203(25230)
11	1660	1285	998	1312	1140	285(23810), 219(24340), 203(25520)
12	1664	1287	992	1308	1148	279(12480), 236(13070), 203(17440)
13	1686	1286	978	1302	1133	325(20040), 296(13520), 238(18330), 203(20690)
14	1680	1285	988	1305	1138	325(8349), 277(18050), 232(17330), 203(22980)
15	1674	1275	960	1303	1132	272(26570), 235(12040), 203(24290)
16	1640	1285	1005	1307	1132	279(23860), 236(11270), 224(12800), 203(20790)
17		1280	987	1315	1148	289(27130), 226(15360), 203(21280)
18		1266	980	1294	1127	282(21380), 226(14370), 204(25720)
19		1267	974	1305	1138	288(24960), 227(15970), 203(20760)
20		1290	974	1308	1158	310(28980), 233(22710), 203(26360)
21	1623	1282	980	1320	1144	247(19950), 203(22410)
22	1647	1276	982	1319	1146	265(35560), 233(19430), 202(23940)
23		1275	978	1316	1140	294(16780), 225(14970), 203(27490)
24		1295	986	1322	1159	320(7474), 222(47760), 204(37670)
25	1660	1283	990	1320	1160	308(27110), 271(35300), 232(30740), 203(25360)
26	1660	1280	972	1309	1125	256(111000), 221(27040), 203(37070)
27		1275	959	1302	1136	280(22580), 235(50240), 203(38900)
28	1650	1274	962	1310	1140	311(20790), 241(10660), 202(15990)

shifted to around 960 cm^{-1}.[5] These compounds also exhibited bands in the region 1295—1275 cm^{-1} [6] (δ CH in-plane). From the spectral data it may be concluded that all these compounds are *trans* isomers. They have also showed very strong peaks in the regions 1320—1300 and 1160—1120 cm^{-1} which are characteristic of sulfone groups.[7,8]

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. UV absorption measurements were determined in 95% ethanol with a Beckmann model DU-2 Ultraviolet Spectrophotometer and IR spectra were recorded on a Perkin-Elmer model 700 in nujol mulls. *p*-Chlorophenylsulfonylacetic acid[9] and 9-anthraldehyde[10] were prepared by published procedures and other aldehydes were obtained from commercial sources.

General Procedure. A solution of *p*-chlorophenylsulfonylacetic acid (0.01 mol) in acetic acid (6 ml) was mixed with an aryl aldehyde (0.01 mol) and benzylamine (0.2 ml), and refluxed for 90 min. The reaction mixture was cooled, treated with dry ether (50 ml) and any product separated was collected by filtration. The filtrate was diluted with more ether and washed successively with a saturated solution of NaHCO$_3$ (15 ml), NaHSO$_3$ (15 ml), dilute HCl (20 ml) and a finally with water. Evaporation of the dried etherial layer yielded in many cases a solid product. However, in some instances a syrupy substance separated was solidified on treatment with a small amount of methanol or 2-propanol. The relevant data on the compounds synthesized are given in Tables 1 and 2.

References

1) V. Baliah and M. Seshapathirao, *J. Org. Chem.*, **24**, 867 (1959).

2) W. E. Truce and C. T. Goralski, *ibid.*, **36**, 2536 (1971).

3) G. H. Posner and D. J. Brunelle, *ibid.*, **37**, 3547 (1972) and references cited therein.

4) V. Baliah and T. K. Rathinasamy, *Indian J. Chem.*, **9**, 220 (1971).

5) W. P. Trompen, C. Kruk, P. J. van Der Haak, and H. O. Huisman, *Rec. Trav. Chim.*, **85**, 185 (1966).

6) N. Sheppard and G. B. B. M. Sutherland, *Proc. Roy. Soc., Ser. A*, **196**, 195 (1949).

7) D. Bernard, J. M. Fabian, and H. P. Koch, *J. Chem. Soc.*, **1949**, 2442.

8) P. M. G. Bavin, G. W. Gray, and A. Stephenson, *Spectrochim. Acta*, **16**, 1312 (1960).

9) Gabriel, *Ber.*, **14**, 834 (1881).

10) L. Fieser and J. L. Hartwell, *J. Amer. Chem. Soc.*, **60**, 2555 (1938).