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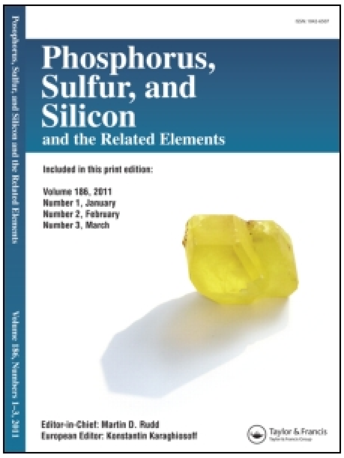

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SYNTHESIS OF SOME NOVEL α,β-ETHYLENIC SULFONES

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SYNTHESIS OF SOME NOVEL α,β-ETHYLENIC SULFONES

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Novel unsaturated sulfones E-alkoxy/carbamoyl benzyl styryl sulfones (**VI**) and E-4(N-benzylcarbamoyl)benzyl styryl sulfones (**IX**) have been prepared by the Knoevenagel condensation of alkoxy/carbamoyl benzylsulfonylacetic acid (**V**) and 4-carboxybenzylsulfonylacetic acid (**VIII**) with araldehydes. The E-geometry of these compounds has been assigned based on IR and ^{1}H NMR spectral data.

Key words: Configuration, Knoevenagel condensation, sulfonylacetic acids, unsaturated sulfones.

INTRODUCTION

Knoevenagel condensation of sulfonylacetic acids with araldehydes in presence of a basic catalyst is one of the most facile and elegant method[1] amongst the methods[1–4] known to be synthetically viable resulting in stable α,β-ethylenic sulfones. Many mono[5–7]- and bis(styryl)sulfones[8–11] have been reported in our earlier communications adopting this method. In our present communication we report some more novel α,β-unsaturated sulfones following the above method as these compounds are potential synthons for the synthesis of cyclopropanes[12,13] and pyrazolines.[14]

RESULTS AND DISCUSSION

The E-alkoxy/carbamoyl benzyl styryl sulfones (**VI**) and E-4(N-benzylcarbamoyl)benzyl styryl sulfones (**IX**) have been obtained by the condensation of araldehydes with alkoxy/carbamoyl benzylsulfonylacetic acid (**V**) and 4-carboxybenzylsulfonylacetic acid (**VIII**) in refluxing glacial acetic acid in presence of benzylamine (see Scheme 1 & 2). Obviously, amination of the carboxylic group might have taken place resulting in 4(N-benzylcarbamoyl) functionality. The α,β-ethylenic sulfones obtained by the Knoevenagel condensation of sulfonylacetic acids with araldehydes were considered to possess E-configuration[5,8,15,16] and hence the compounds reported in the present investigation may also be regarded to possess E-

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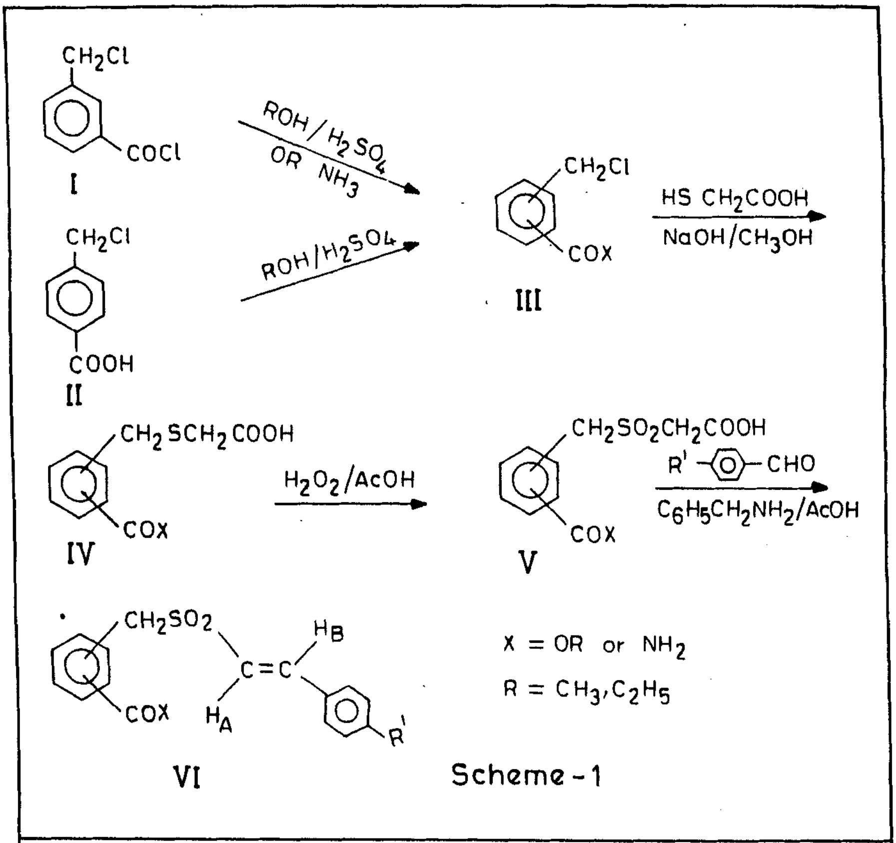
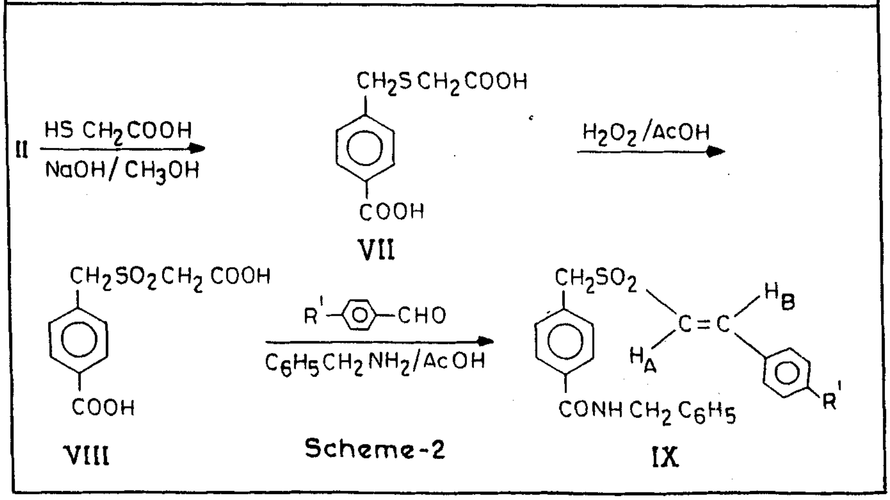


Scheme - 1



Scheme-2

geometry.[5,7,17,18] The IR spectra (ν max in cm^{-1}) of **VI** and **IX** exhibited medium to strong bands in the regions 3310–3290 (NH),[19] 1720–1690 (C=O),[7] 1620–1610 (C=C)[13] and 1310–1290 and 1140–1120 (SO_2).[7,13] These compounds also displayed bands in the region 990–980 (δ CH out-of-plane) characteristic of E-configuration.[5,7]

TABLE I

Alkoxy/carbamoyl benzyl styryl sulfones (**VI**) and 4(N-benzylcarbamoyl)benzyl styryl sulfones (**IX**)

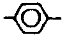
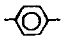
Compd. No.	X	R'	Yield (%)	m.p. (°C)	Mol.formula (Mol. wt.)	Analysis (%)			
						Cacld.		Found	
						C	H	C	H
VI				a) $-CH_2SO_2CH=CH-$$-R'$, COX = 1.3 where					
1	OCH_3	H	74	113-14^a	$C_{17}H_{16}O_4S$ (316)	64.55	5.06	64.55	4.88
2	"	CH_3	78	135-36^a	$C_{18}H_{18}O_4S$ (330)	65.45	5.45	65.42	5.12
3	"	Br	80	165-66^a	$C_{17}H_{15}O_4SBr$ (395)	51.64	3.80	51.20	3.45
4	OC_2H_5	H	72	114-15^a	$C_{18}H_{18}O_4S$ (330)	65.45	5.45	65.15	5.10
5	"	CH_3	75	138-39^a	$C_{19}H_{20}O_4S$ (344)	66.28	5.81	65.85	5.52
6	"	Cl	79	151-52^a	$C_{18}H_{17}O_4SCl$ (364.5)	59.26	4.66	58.80	4.25
7	NH_2	H	68	185-86^a	$C_{16}H_{15}O_3NS$ (301)	63.80	4.98	63.49	4.50
8	"	CH_3	72	215-16^a	$C_{17}H_{17}O_3NS$ (315)	64.76	5.40	64.32	4.98
9	"	Br	79	235-36^b	$C_{16}H_{14}O_3NSBr$ (380)	50.53	3.68	50.15	3.32

TABLE I (*continued*)

b) $-CH_2SO_2CH{=}CH-$  $-R'$, COX = 1,4 where

	1	OCH_3	H	71	167-68[a]	$C_{17}H_{16}O_4S$ (316)	64.55	5.06	64.10	4.75
	2	"	Br	83	217-18[a]	$C_{17}H_{15}O_4SBr$ (395)	51.64	3.80	51.22	3.49
	3	"	Cl	80	203-04[a]	$C_{17}H_{15}O_4SCl$ (350.5)	58.20	4.20	57.84	3.92
IX	1	—	H	69	251-52[c]	$C_{23}H_{21}O_3NS$ (391)	70.58	5.37	70.42	5.10
	2	—	Br	82	284-85[b]	$C_{23}H_{20}O_3NSBr$ (470)	58.72	4.25	58.45	3.95
	3	—	Cl	78	277-78[b]	$C_{23}H_{20}O_3NSCl$ (425.5)	64.86	4.70	64.56	4.42
	4	—	F	75	267-68[c]	$C_{23}H_{20}O_3NSF$ (409)	67.48	4.88	67.10	4.51
	5	—	NO_2	72	251-52[b]	$C_{23}H_{20}O_5N_2S$ (436)	63.30	4.59	63.00	4.32
	6	—	OC_2H_5	76	247-49[b]	$C_{25}H_{25}O_4NS$ (435)	69.00	5.75	69.42	5.20

Solvent for crystallization: a) methanol, b) acetic acid, c) 2-propanol

The PMR spectra of **VI** and **IX** showed δ_H values for vinylic protons at 6.84–7.02 (d, H_A, J_{AB} = 16.0–16.4) and 7.25–8.14 (m, $Ar\underline{H}$ + H_B). The vinylic protons H_B appear as multiplets as they are superimposed by the aromatic ring protons. A singlet around 4.60–4.75,[13] characteristic of benzylic protons was observed in both **VI** and **IX**. In case of **IX** a singlet around 4.26–4.30 in addition to benzylic protons was accounted for the methylene protons of the N-benzylcarbamoyl moiety. A broad singlet around 5.02–5.38[19] exchangeable with D_2O was observed for NH protons.

EXPERIMENTAL

The melting points were determined on a Mel-Temp apparatus and are uncorrected. The IR spectra were recorded on a Perkin-Elmer Infrared spectrophotometer and the ^1H NMR spectra on a Varian EM-360 spectrometer operating at 60 MHz with TMS as internal standard. Elemental analyses were performed by the Regional Sophisticated Instrumentation Centre, Central Drug Research Institute, Lucknow, India.

Esterification of **I** and **II** and amination of **I** gave the following new alkoxy/carbamoyl benzyl chlorides (**III**): 3-methoxycarbonylbenzyl chloride (72%), b.p. 175–76°C/6 mm, 3-ethoxycarbonylbenzyl chloride (69%), b.p. 185–87°C/6 mm, 3-carbamoylbenzyl chloride (74%), m.p. 119–20°C and 4-methoxycarbonylbenzyl chloride (78%), m.p. 37–38°C.

Alkoxy/carbamoyl benzylsulfonylacetic acids (**V**) *and 4-carboxybenzylsulfonylacetic acid* (**VIII**).

General Procedure: To a solution of (20 g, 0.5 mol) sodium hydroxide in methanol (300 ml), mercaptoacetic acid (23 g, 0.25 mol) was added slowly. Then alkoxy/carbamoyl benzyl chlorides (**III**) or 4-carboxybenzyl chloride (**II**) (0.25 mol) was added in portions and the reaction mixture refluxed for 4–5 h. The cooled contents were poured onto crushed ice and neutralized with dilute hydrochloric acid (200 ml). The resulting thioacetic acids (**IV**) and (**VII**) were collected and purified: 3-methoxycarbonylbenzylthioacetic acid (82%), m.p. 38–39°C, 3-ethoxycarbonylbenzylthioacetic acid (78%), m.p. 40–41°C, 3-carbamoylbenzylthioacetic acid (76%), m.p. 166–68°C, 4-methoxycarbonylbenzylthioacetic acid (81%), mp. 64–65°C and 4-carboxybenzylthioacetic acid (82%), m.p. 75–78°C.

The above thioacetic acids (**IV**) and (**VII**) (0.1 mol) were subjected to oxidation with 30% hydrogen peroxide (0.12 mol) in glacial acetic acid (25 ml) by refluxing for 1–2 h. The contents were cooled and poured onto crushed ice and the solid separated was collected and recrystallized from hot water to give pure sulfonylacetic acids (**V**) and (**VIII**): 3-methoxycarbonylbenzylsulfonylacetic acid (79%), m.p. 85–87°C, 3-ethoxycarbonylbenzylsulfonylacetic acid (76%), m.p. 115–116°C, 3-carbamoyl benzylsulfonylacetic acid (78%), m.p. 232–34°C, 4-methoxycarbonylbenzylsulfonylacetic acid (80%), m.p. 173–74°C and 4-carboxybenzylsulfonylacetic acid (82%), m.p. 238–39°C.

Condensation of sulfonylacetic acid (**V**) *and* (**VIII**) *with araldehydes.*

General Procedure: A mixture of the appropriate sulfonylacetic acid (**V**) or (**VIII**) (0.001 mol), an aromatic aldehyde (0.001 mol) and benzylamine (1 ml) in acetic acid (15 ml) was refluxed for 2–3 h. The contents were cooled and treated with dry ether (50 ml). Any product separated was collected by filteration. The filterate was diluted with more ether and washed successively with a saturated solution of sodium bicarbonate (20 ml), sodium bisulfite (20 ml), dilute hydrochloric acid (20 ml) and finally with water (35 ml). Evaporation of the dried ethereal layer yielded in many cases a solid product. However, in some cases a syrupy substance separated was solidified on treatment with 2-propanol. The purity of the compounds was checked by TLC (Silica gel BDH, hexane/ethyl acetate 3:1). **VI** and **IX**: IR (KBr) 3310–3290 (NH), 1720–1690 (C=O), 1620–1610 (C=C), 1310–1290 and 1140–1120 (SO_2) and 990–980 (δ CH out-of-plane); PMR ($CDCl_3$/DMSO-d_6) 3.60 (s, OCH_3), 4.10 (q, $OC\underline{H}_2CH_3$), 1.10 (t, $OCH_2C\underline{H}_3$), 4.26–4.30 (s, $C\underline{H}_2C_6H_5$), 4.60–4.75 (s, $ArC\underline{H}_2$), 5.02–5.20 (s, NH_2), 5.23–5.40 (s, NH), 6.84–7.02 (d, H_A, J_{AB} = 16.0–16.4) and 7.25–8.14 (m, $Ar\underline{H}$ + H_B).

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