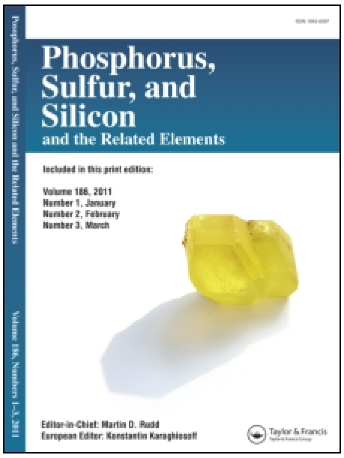

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PHENACYL *E*-STYRYL SULFONES: A POTENTIAL SOURCE FOR BIFUNCTIONAL HETEROCYCLIC SULFONES

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PHENACYL *E*-STYRYL SULFONES: A POTENTIAL SOURCE FOR BIFUNCTIONAL HETEROCYCLIC SULFONES

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The bifunctional heterocyclic sulfones containing selenadiazoles / thiadiazoles and pyrazolines/ isoxazolines have been prepared from phenacyl *E*-styryl sulfones.

Keywords: Phenacyl *E*-styryl sulfones; 1,2,3-selenadiazoles; 1,2,3-thiadiazoles; 2-pyrazolines; isoxazolines; bifunctional heterocyclic sulfones

INTRODUCTION

Amongst different heterocyclic systems, the chemistry of five membered heterocycles which have more than one heteroatoms has gained importance in recent times as many of them exhibit pronounced bioactive nature. One such class of compounds are pyrazolines[1,2], isoxazolines[3,4] 1,2,3-selenadiazoles and 1,2,3-thiadiazoles[5,6]. The present study aims at the development of hitherto unknown bifunctional heterocyclic systems consisting of pyrazolines/isoxazolines in combination with selena/thiadiazole units, which might enhance biological activity. In our earlier communications, the bifunctional nature of phenacyl *E*-styryl sulfones (**1**) was reported to be responsible for the development of bifunctional systems viz., selenadiazoles/thiadiazoles, pyrazolines/cyclopropanes and thiomorpholines[7,8]. This has been accomplished first by exploiting

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α-ketomethylene functionality via its semicarbazone to obtain 4-aryl-5-styrylsulfonyl-1,2,3-selena/ thiadiazoles (**III**). Subsequent addition of diazomethane or dimethylsulfoxonium methylide to **III** led to the formation of 4-aryl-5-(4′-aryl-3′-sulfonyl-2′-pyrazolyl)-1,2,3-selena/thiadiazoles and 4-aryl-5-(2′-arylcyclopropyl-sulfonyl)-1,2,3-selena/thia-diazoles. However, the cycloaddition of dipolar reagents to the ethylenic bond led to new type of bis heterocyclic sulfones. The present communication essentially deals with such results.

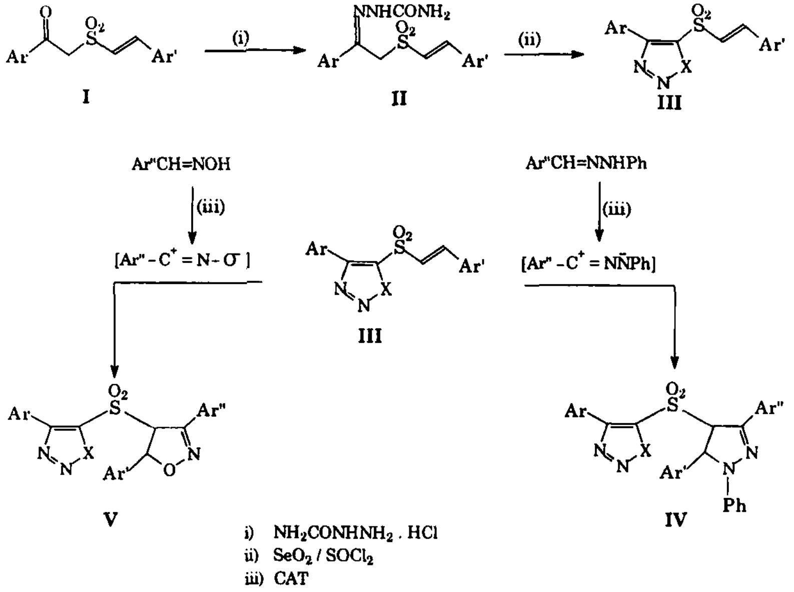
RESULTS AND DISCUSSION

The scheme involves the reaction of 4-aryl-5-styrylsulfonyl-1,2,3-selena/ thiadiazoles (**III**)[7] with araldehyde phenylhydrazones and araldoximes in the presence of chloramine-T (CAT). The dipolar reagents, nitrile imines and nitrile oxides generated *in situ* would cycloadd across the double bond by the principle of 3 + 2 addition[9,10] and results tetrasubstituted pyrazolines and trisubstituted isoxazolines in combination with selena / thiadiazole unit. Thus, a series of 4-aryl-1,2,3-selena / thiadiazolyl-1′,3′,5′-triaryl-2′-pyrazolinyl [5,4′] sulfones (**IV**) and 4-aryl-1,2,3-selena/thiadiazolyl-3′,5′-diaryl-2′-isoxazolinyl [5,4′] sulfones (**V**) have been prepared.

The IR spectra (ν, cm^{-1}) of **IV** and **V** exhibited absorption bands in the region 1340–1320 and 1145–1115 for asymmetric and symmetric stretching vibrations of -SO_2 group. They also exhibited absorption bands around 1480–1500, 1420–1440, 670–720 for C=N, N=N and C-Se/S respectively. The ^1H NMR spectra of these compounds exhibited two doublets at 5.25–5.36 and at 5.71–5.80 for $C_{5'}$-H and $C_{4'}$-H protons of pyrazoline and isoxazoline systems (Table). The *J* values (5.8 – 6.4 Hz) indicated that these two protons are in *trans* – geometry[11]. Thus, the spectral information is in consistent with their structures.

EXPERIMENTAL

Melting points were determined in open capillaries on a Mel-Temp apparatus and are uncorrected. The purity of the compounds was checked by thin layer chromatography (silica gel H, BDH, hexane/ethyl acetate,, 3:1).



i) $NH_2CONHNH_2 . HCl$
ii) $SeO_2 / SOCl_2$
iii) CAT

SCHEME

The IR spectra were recorded on a Perkin-Elmer Grating Infrared Spectrophotometer (γ_{max} in cm^{-1}) model 337 in KBr pellets. The ^1H NMR spectra were recorded in $CDCl_3$/ DMSO-d_6 on a varian EM-360 spectrometers with TMS as an internal standard (chemical shifts in ppm). The microanalytical data were obtained from University of Pune, Pune, India. The 4-aryl-5-styrylsulfonyl-1,2,3-selenadiazoles/ thiadiazoles were prepared as per the literature procedure.[7]

General Procedure for the Preparation of 4-aryl-1,2,3-selena/ thiadiazolyl-1′,3′,5′-triaryl-2′-pyrazolinyl [5,4′] sulfones (IV)

A mixture of araldehyde phenylhydrazone (5 mmol), chloramine-T (5 mmol) and **III** (5 mmol) was dissolved in ethanol (20 ml) and refluxed for 4 h. Then the reaction mixture was concentrated under reduced pressure. The residue was extracted with ether, washed with 1N NaOH, brine solution and dried (an. Na_2SO_4). The solvent was removed under vacuo. The crude product obtained was purified by filtration through a column of silica gel.

TABLE Physical and spectral data of **IV** and **V**

No.	*Ar*	*Ar′*	*Ar″*	*X*	*Yield (%)*	*m.p. (°C)*	*^1H NMR (δ, ppm)*		
							C_4'-H	*C_5'-H*	*Substituen*
	Ph	Ph	Ph	Se	62	178–180	5.72	5.30	–
	4-OMePh	Ph	Ph	Se	64	205–207	5.75	5.35	3.80 (Ar-OM
	4-ClPh	Ph	4-ClPh	Se	66	198–200	5.74	5.31	–
	Ph	4-MePh	4-OMePh	Se	60	220–221	5.78	5.35	2.34 (Ar-M
									3.8 1 (Ar-OM
	4-MePh	4-MePh	4-ClPh	Se	66	224–226	–	–	–
	4-BrPh	4-MePh	Ph	Se	62	197–199	5.73	5.29	2.32 (Ar-M
	4-NO_2Ph	4-MePh	4-ClPh	Se	65	228–230	–	-	–
	Ph	Ph	Ph	S	67	234–236	5.71	5.30	–
	4-OMePh	Ph	Ph	S	71	206–208	5.73	5.31	3.79 (Ar-OM
	4-ClPh	Ph	4-ClPh	S	65	242–244	–	-	–
	Ph	4-MePh	4-OMePh	S	63	202–204	5.76	5.34	2.31 (Ar-M
									3.80 (Ar-OM
	4-MePh	4-MePh	4-ClPh	S	67	197–199	–	–	–
	4-BrPh	4-MePh	Ph	S	65	195–197	5.80	5.35	2.32 (Ar-M
	4-NO_2Ph	4-MePh	4-ClPh	S	67	246–248	–	–	–

No.	Ar	Ar′	Ar″	X	Yield (%)	m.p. (°C)	^1H NMR (δ, ppm)		
							C_4'-H	C_5'-H	Substituen
	Ph	Ph	Ph	Se	67	166–168	5.70	5.25	–
	4-OMePh	Ph	Ph	Se	69	198–200	5.74	5.26	3.81 (Ar-OM
	4-ClPh	Ph	4-ClPh	Se	65	176–178	5.80	5.28	–
	Ph	4-MePh	4-OMePh	Se	62	200–202	5.76	5.29	2.33 (Ar-M 3.80 (Ar-OM
	4-MePh	4-MePh	4-ClPh	Se	64	214–216	–	–	–
	4-BrPh	4-MePh	Ph	Se	66	199–201	5.71	5.24	2.31 (Ar-M
	4-NO_2Ph	4-MePh	4-ClPh	Se	69	202–204	–	–	–
	Ph	Ph	Ph	S	72	206–208	5.74	5.32	–
	4-OMePh	Ph	Ph	S	74	196–198	5.72	5.31	3.79 (Ar-OM
	4-ClPh	Ph	4-ClPh	S	68	213–215	5.78	5.34	–
	Ph	4-MePh	4-OMePh	S	61	189–191	5.75	5.36	2.32 (Ar-M 3.80 (Ar-OM
	4-MePh	4-MePh	4-ClPh	S	64	174–176	–	–	–
	4-BrPh	4-MePh	Ph	S	66	179–181	5.71	5.34	2.32 (Ar-M
	4-NO_2Ph	4-MePh	Ph	S	68	212–214	–	–	–

y elemental analyses were obtained C ± 0.22%, H ± 0.15%, N ± 0.18%

General Procedure for the Preparation of 4-aryl-1,2,3-selena/thiadiazolyl-3′5′-diaryl-2′-isoxazolinyl [5,4′] sulfones (V)

A mixture of **III** (5 mmol), araldoxime (5 mmol) and chloramine-T (5 mmol) was dissolved in ethanol (20 ml) and refluxed for 4 h. Then the reaction mixture was concentrated under vacuo and residue was extracted with dichloromethane. The organic layer was washed with 1N NaOH, brine solution and dried (an. Na_2SO_4). Removal of the solvent under reduced pressure gave crude product, which was purified by filtration through a column of silica gel.

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