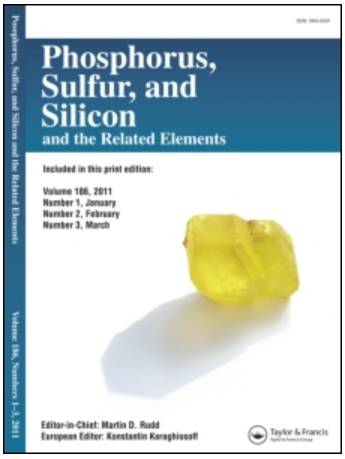

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2-Arylethenyl-2''-Arylethynyl Sulfones: A Potential Source for New Heterocycles

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2-ARYLETHENYL-2′-ARYLETHYNYL SULFONES: A POTENTIAL SOURCE FOR NEW HETEROCYCLES

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Different heteroatoms viz., N, S & Se have been incorporated into 2-arylethenyl-2′-arylethynyl sulfones by nucleophilic reaction with benzylamine, hydrogen sulfide and sodium hydrogen selenide.

Keywords: dihydrothiazine; dihydrodithiin; dihydrothiaselenin; nucleophilic reaction

INTRODUCTION

Over a decade we have been actively involved in the synthesis of different bis unsaturated sulfones[1–4] and incorporated various heteroatoms viz., N, S, Se leading to new types of heterocycles[5,6]. Encouraged by our earlier results on the insertion of heteroatoms as part of six membered cyclic systems[7,8], attempts have been made to introduce N, S, Se into 2-arylethenyl-2′-arylethynyl sulfones[7,10] to obtain hitherto unknown heterocycles. The present communication deals with the results accomplished in this perspective.

RESULTS AND DISCUSSION

The synthetic method involves the incorporation of different heteroatoms into 2-arylethenyl-2′-arylethynyl sulfones (I). The latter were obtained by the reaction of sodium acetylide with styrylsulfonyl chloride at room tem-

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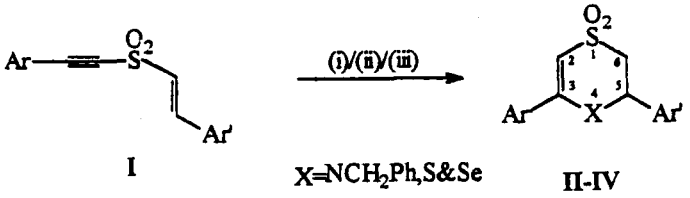
perature. The nucleophilic reaction of **I** with benzylamine in alcohol in the presence of barium carbonate resulted 3,5-diaryl-5,6-dihydro-4-benzyl-1,4-thiazine-1,1-dioxides (**II**). Similarly, when H_2S gas was passed into the refluxing solution of **I** and sodium acetate in equimolar quantities in alcohol, 3,5-diaryl-5,6-dihydro-1,4-dithiin-1,1-dioxides (**III**) were obtained. (Scheme and Table I). On the other hand, by the treatment of **I** with sodium hydrogen selenide[11] (prepared from selenium and sodium borohydride in 1:2 ratio under nitrogen atmosphere) and sodium acetate in alcohol furnished 3,5-diaryl-5,6-dihydro-1-thia-4-selenin-1,1-dioxides (**IV**). The IR spectra (ν, cm^{-1}) of **II-IV** displayed bands around 1635–1640 (C=C), 1325–1342 and 1125–1140 (SO_2) indicating their formation. The absence of an absorption band corresponding to acetylenic moiety supports that cyclization has taken place.



(i)$PhCH_2NH_2$,$BaCO_3$,EtOH.Δ (ii)H_2S,NaAc,EtOH, Δ(iii)NaHSe,EtOH, Δ

SCHEME

The PMR spectra (δ, ppm) of **IIa, IIIa** and **IVa** are taken as representative examples to relate spectral data to structures (Table II). The possible conformations of **II-IV** are represented below[12,13] (Fig A & Fig B).

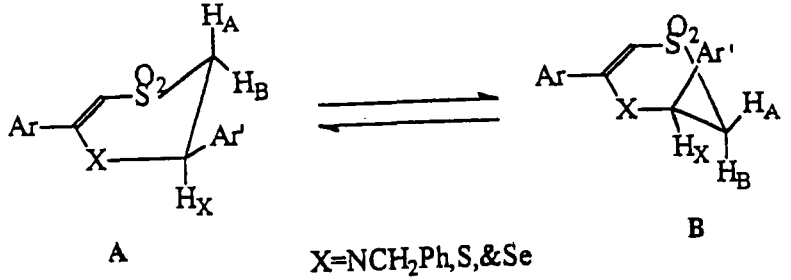


TABLE I Melting points and analytical data of compounds II – IV

Compd. No	*Ar*	*Ar'*	*Yield (%)*	*m.p (°C)*	*Mol. formula (mol. wt)*	*Found (Calcd.) (%)*		
						C	*H*	*N*
IIa	C_6H_5	C_6H_5	62	53–55	$C_{23}H_{21}NO_2S$	73.81	5.41	3.61
					(375.49)	(73.57)	(5.64)	(3.73)
IIb	C_6H_5	4-$CH_3C_6H_4$	60	61–63	$C_{24}H_{23}NO_2S$	73.74	6.40	3.41
					(389.53)	(73.81)	(6.19)	(3.59)
IIc	C_6H_5	4-ClC_6H_4	63	59–60	$C_{23}H_{20}ClNO_2S$	67.60	4.74	3.61
					(409.94)	(67.39)	(4.92)	(3.42)
IIIa	C_6H_5	C_6H_5	70	110- 111	$C_{16}H_{14}O_2S_2$	63.70	4.58	–
					(302.41)	(63.55)	(4.67)	
IIIb	C_6H_5	4-$CH_3C_6H_4$	77	115-117	$C_{17}H_{16}O_2S_2$	64.30	5.01	–
					(316.44)	(64.53)	(5.10)	
IIIc	C_6H_5	4-ClC_6H_4	73	114-115	$C_{16}H_{13}ClO_2S_2$	57.21	3.70	–
					(336.86)	(57.05)	(3.89)	
IVa	C_6H_5	C_6H_5	69	90–92	$C_{16}H_{14}O_2SSe$	55.80	4.01	–
					(345.32)	(55.65)	(4.09)	
IVb	C_6H_5	4-$CH_3C_6H_4$	71	98–99	$C_{17}H_{16}O_2SSe$	56.11	4.64	–
					(363.34)	(56.20)	(4.44)	
IVc	C_6H_5	4-ClC_6H_4	73	87–89	$C_{16}H_{13}ClO_2SSe$	50.23	3.21	–
					(383.76)	(50.68)	(3.41)	

TABLE II PMR spectral data of II-IV

Compd No.	*Chemical Shifts (δ, ppm in $CDCl_3$ / DMSO-d_6)*
IIa	3.00 (d, 2H, C_6-H), 3.82 (t, 1H, C_5-H), 4.02 (s, 2H, CH_2-Ph), 6.40 (s, 1H, C_2-H), 6.96 – 7.37 (m, 10H, Ar-H).
IIb	2.24 (s, 3H, CH_3), 2.95 (d, 2H, C_6-H), 3.79 (t, 1H, C_5-H), 4.03 (s, 2H, CH_2-Ph), 6.42 (s, 1H, C_2-H), 6.95 – 7.38 (m, 9H, Ar-H).
IIc	3.25 (d, 2H, C_6-H), 3.81 (t, 1H, C_5-H), 3.98 (s, 2H, CH_2-Ph), 6.42 (s, 1H, C_2-H), 6.96 – 7.40 (m, 9H, Ar-H).
IIIa	3.10 (d, 2H, C_6-H), 4.50 (t, 1H, C_5-H), 6.58 (s, 1H, C_2-H), 6.98 – 7.40 (m, 10H, Ar-H).
IIIb	2.25 (s, 3H, CH_3), 3.05 (d, 2H, C_6-H), 4.47 (t, H, C_5-H), 6.50 (s, 1H, C_2-H), 6.95 – 7.40 (m, 9H, Ar-H).
IIIc	3.25 (d, 2H, C_6-H), 4.52 (t, 1H, C_5-H), 6.54 (s, 1H, C_2-H), 6.98 – 7.42 (m, 9H, Ar-H).
IVa	2.84 (d, 2H, C_6-H), 3.82 (t, 1H, C_5-H), 6.41 (s, 1H, C_2-H), 6.94- 7.37 (m, 10H, Ar-H).
IVb	2.24 (s, 3H, CH_3), 2.82 (d, 2H, C_6-H), 3.83 (t, 1H, C_5-H), 6.45 (s, 1H, C_2-H), 6.97–7.42 (m, 9H, Ar-H).
IVc	2.87 (d, 2H, C_6-H), 3.84 (t, 1H, C_5-H), 6.43 (s, 1H, C_2-H), 6.97- 7.44 (m, 9H, Ar-H).

Had it been in either of these two conformations, it should display ABX splitting pattern for methine and methylene protons. However, the spectra indicated a triplet for C_5-H and a doublet for C_6-H at 3.79 – 4.52 and at 2.82 – 3.25, following simple splitting pattern. This might be due to rapid equilibrium between the two conformations, A and B. A sharp singlet was observed at 6.40 – 6.58 for C_2-H. The benzyl protons showed a singlet in the region 3.98 – 4.03 in **II**.

ANTIMICROBIAL ACTIVITY

The compounds **II, III, IV** were tested for their antibacterial activity against the micro organisms, *Staphylococcus aureus, Bacillus subtilis* (Gram positive) and *Escherichia coli* (Gram negative) and fungicidal activity against *Fusarium solani, Curvularia lunata, Aspergillus niger* and *Cunninghemella elegans* at mg/mL concentration by Vincent and Vincent

method.[14] All the test compounds inhibited both Gram positive and Gram negative bacteria. Besides, they have also moderately inhibited the growth of fungi. Compounds **III** showed more inhibitory activity against both bacteria and fungi than others. In general, halogen substituted compounds displayed pronounced activity. Further studies on bioassay of these compounds are in progress.

EXPERIMENTAL

Melting points were determined on a Mel-Temp apparatus and are uncorrected. IR spectra (KBr-disc) were recorded on a Beckmann IR-18 spectrophotometer. NMR spectra were recorded in $CDCl_3$ at 120 MHz on a varian EM-360 spectrophotometer and chemical shifts were reported in ppm with TMS as an internal standard. Elemental analyses were obtained from the University of Pune, Pune, India.

General procedure for the preparation of 3,5-diaryl-5,6-dihydro-4-benzyl-1,4-thiazine-1,1-dioxides (II)

A mixture of **I** (10 mmol), benzylamine (12 mmol) and a catalytic amount of $BaCO_3$ was taken in ethanol (30 ml) and refluxed for a period of 5–6 h. The contents were cooled and kept aside for overnight. The resultant compound was filtered and purified on a column of silica gel (60–120 mesh, BDH) with ethyl acetate / hexane (2:3) as eluents.

General procedure for the preparation of 3,5-diaryl-5,6-dihydro-1,4-dithiin-1,1-dioxides (III)

In a two necked round-bottomed flask equipped with a reflux condenser, calcium chloride guard tube and a gas inlet tube, **I** (10 mmol), NaOAc (12 mmol) and 90% aqueous ethanol (30 ml) were taken. The H_2S gas was passed for 3–4 h, while refluxing. It was then cooled and kept in refrigerator overnight. The solid formed was filtered, washed with water, dried and recrystallized from methanol.

General procedure for the preparation of 3,5-diaryl-5,6-dihydro-1-thia-4-selenin-1,1-dioxides (IV)

In a three necked round – bottomed flask equipped with a reflux condenser, a pressure equalizing funnel and a nitrogen inlet tube, selenium powder (10 mmol) in absolute ethanol (15 ml) was taken. To this $NaBH_4$ (20 mmol) in absolute ethanol (15 ml) was added slowly while stirring at room temperature. Soon a vigorous reaction sets in with the evolution of hydrogen gas. After few minutes a colourless solution of NaHSe was formed to which **I** (5 mmol) and NaOAc (0.5 g) dissolved in absolute ethanol (20 ml) was added. Then the contents were refluxed for 4 h. After completion of the reaction, the solution was cooled. The product separated was filtered and purified by column chromatography using silica gel (60–120 mesh, BDH) with ethyl acetate / hexane (2:3) as eluents.

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