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Synthesis of 1,2,4-Dithiazolidines with Arylidene Amino and Arylidene Hydrazino Groups

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Several 3-phenylimino-4-arylidene amino-5-arylidene hydrazino-1,2,4-dithiazolidines (V) have been synthesized by one step condensation reaction of phenylimino-chloromethane sulphenyl chloride (N-phenyl-S-chloroisothiocarbamoyl chloride) and bis-1,5-arylidene-3-thiocarbohydrazides followed by basification of resultant compounds (IV). The structures of the compounds were established on the basis of elemental analysis, titrimetric analysis and spectral studies.

Key Words: Synthesis, 1,2,4-dithiazolidines, Arylidene amino, Arylidene hydrazino.

INTRODUCTION

Schiff's bases exhibit anticancer and antibacterial activities[1, 2]. Coumarin Schiff's bases act as antibacterial[3], antifungal[4] agents. With the aim to explore new methods for the synthesis of nitrogen and sulphur containing five-membered heterocyclic compounds containing biologically active substituents, the synthesis of 1,2,4-dithiazolidines with arylidene amino and arylidene hydrazino groups has been reported.

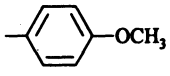
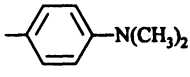
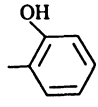
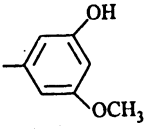
EXPERIMENTAL

The melting points were recorded using hot paraffin bath and are uncorrected. Chemicals used were AR grade. IR spectra were recorded on Perkin-Elmer spectrophotometer in the range 4000–400 cm^{-1} in Nujol mull and as KBr pellets. PMR spectra were recorded with TMS as internal standard using $CDCl_3$ and DMSO-d_6 as solvent.

Synthesis of 3-phenylimino-4-benzylideneamino-5-benzylidenehydrazino-1,2,4-dithiazolidine (Va)

The compound bis-1,5-benzylidene-3-thiocarbohydrazide **(IIa)** was prepared by refluxing the mixture of thiocarbohydrazide (0.01 mol), benzaldehyde (0.02 mol) **(Ia)** in 1 : 2 ratio with chloroform (20 mL) for 2 h. On completion of reaction and distilling off the solvent, the product was isolated (yield 90%). It was crystallised from ethanol, m.p. 196°C. This reaction was extended to synthesize the other compounds **(IIb–IIg)** using different aryl/alkyl aldehydes **(Ib–Ig)**.

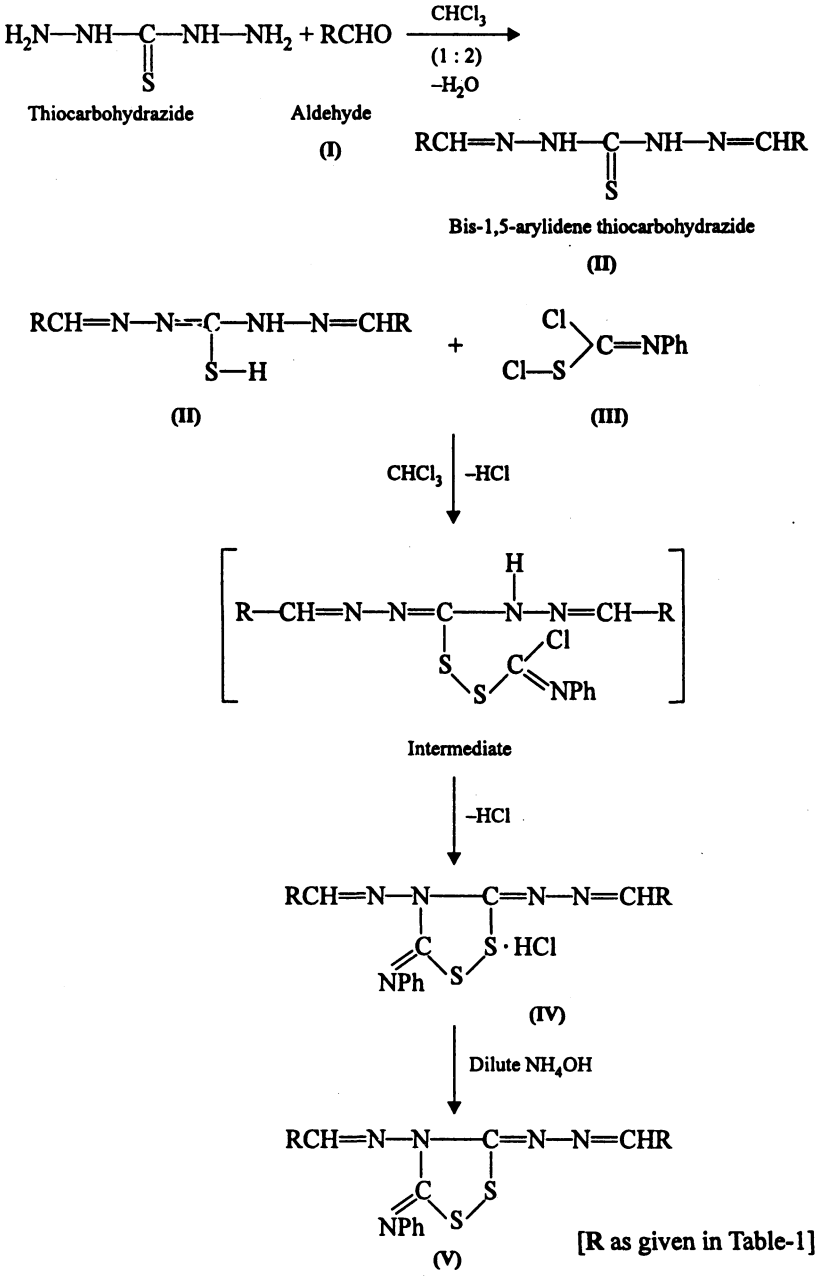
TABLE-1
PHYSICAL DATA AND ELEMENTAL ANALYSIS OF COMPOUND (V)

Compd.	R	m.f.	Equivalent Weight Found (Reqd.)	m.p. (°C)	Yield (%)	Elemental Analysis Found (Calcd.) %	
						N	S
Va		$C_{22}H_{17}N_5S_2$	447.0 (451.5)	172	72	16.72 (16.86)	15.38 (15.42)
Vb		$C_{24}H_{21}N_5O_2S_2$	508.0 (511.5)	181	73	14.62 (14.73)	13.35 (13.47)
Vc		$C_{26}H_{27}N_7S_2$	532.0 (537.5)	153	69	19.58 (19.56)	12.78 (12.77)
Vd	—CH_3	$C_{12}H_{13}N_5S_2$	324.0 (327.5)	158	78	23.95 (24.05)	21.93 (21.99)
Ve		$C_{22}H_{17}N_5O_2S_2$	481.0 (483.5)	192	79	15.54 (15.65)	14.27 (14.31)
Vf		$C_{18}H_{13}N_5O_2S_2$	426.8 (431.5)	152	75	17.61 (17.72)	16.12 (16.20)
Vg		$C_{24}H_{21}N_5O_4S_2$	535.0 (543.5)	158	72	13.74 (13.80)	12.53 (12.62)

All the compounds gave satisfactory C and H analyses.

Bis-1,5-benzylidene-3-thiocarbohydrazide (0.01 mol) **(IIa)** was suspended in chloroform (20 mL). To this, a solution of N-phenyl-S-chloro-isothiocarbamoyl chloride (0.01 mol) in chloroform was added. The reaction mixture was refluxed on a water bath for 3 h. The evolution of hydrogen chloride gas was clearly noticed as tested with moist blue litmus paper. After completion of reaction chloroform was distilled off, when a solid mass was obtained (yield 72%). It was crystallised from ethanol, m.p. 181°C. The solid was found to be acidic to litmus. On determination of equivalent weight, it was identified as monohydrochloride of 3-phenylimino-4-benzylidene amino-5-benzylidinehydrazino-1,2,4-dithiazolidine **(IVa)**. (Equivalent weight of $C_{22}H_{17}N_5S_2 \cdot HCl$ was found 447.0, required 451.5).

On basification with dilute ammonia a free base **(Va)** was obtained. It was crystallised from aqueous ethanol, m.p. 172°C.



3-phenylimino-4-arylidene amino-5-arylidenehydrazino-1,2,4-dithiazolidine

Scheme-1

Elemental analysis: Found C = 63.53%, H = 4.02%, N = 16.72%, S = 15.38%; Required C = 63.61%, H = 4.09%, N = 16.86%, S = 15.42%

IR: Compound **(Va)** showed absorption bands due to ν_{max} 1600 (C=N); 1534 (C=C); 1309 (C—N) and 584 (S—S band).

PMR: The methylidene proton were observed at δ 8.4 ppm and aromatic proton at δ 7.32–8.1 ppm.

RESULTS AND DISCUSSION

Initially, thiocarbohydrazide was reacted with benzaldehyde **(Ia)** in 1 : 2 ratio in chloroform medium for 2 h. On cooling the reaction mixture and distilling off chloroform, the solid residue of bis-1,5-benzylidene-3-thiocarbohydrazide **(IIa)** was obtained. It was then crystallized with ethanol. The other bis-1,5-benzylidene/alkylidene-3-thiocarbohydrazides were prepared by extending this reaction to other aryl/alkyl aldehydes.

Bis-1,5-benzylidene-3-thiocarbohydrazide **(IIa)** was then reacted with N-phenyl-S-chloroisothiocarbamoyl chloride[5] **(III)** in chloroform for 3 h. Evolution of hydrogen chloride gas was noticed during the reaction. On cooling the reaction mixture and distilling off chloroform, solid compound separated out. It was recrystallised with ethanol. It was acidic to litmus and on determination of equivalent weight it was found to be a monohydrochloride of 3-phenylimino-4-benzylidene amino-5-benzylidenehydrazino-1,2,4-dithiazolidines **(IVa)**, which on basification with aqueous ammonia afforded a free base 3-phenylimino-4-benzylidene amino-5-benzylidene hydrazino-1,2,4-dithiazolidine **(Va)**. The other compounds **(IVb–IVg)** were prepared by extending the above reaction to other bis-1,5-arylidene/alkylidene-3-thiocarbohydrazides and related 1,2,4-dithiazolidines were isolated in good yield (Table-1).

The structures of all these synthesized compounds were assigned on the basis of elemental analysis, PMR and IR spectral data.

The formation of **II, IV** and **V** can be shown as given in Scheme-1.

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