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Synthesis and Structural Studies of 2-Phenylimino-3-aroyl/acyl-5-aroyl/acyl hydrazino-1,3,4-thiadiazolidines and Their Acetyl Derivatives

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Synthesis of several 2-phenylimino-3-aroyl/acyl-5-aroyl/acyl hydrazino-1,3,4-thiadiazolidines (**V**) have been carried out by the interaction of *bis*-1,5-aroyl/acyl-3-thiocarbohydrazides (**II**) with N-phenylisocyanodichloride (**III**). The product obtained (**IV**) on basification with dilute ammonium hydroxide afforded the free bases (**V**). The title compounds in 1:1 ratio gave monoacetyl derivatives (**VI**). The structures of all these compounds were established on the basis of elemental analysis and spectral studies.

Key Words: Synthesis, 1,3,4-Thiadiazolidines, Acetyl derivatives.

INTRODUCTION

On the basis of literature survey, the synthesis of 1,3,4-thiadiazolidines have been carried out by cyclization and other routes[1-11]. The synthetic application of arylisocyanodichloride have been investigated earlier[12-18]. The reagent which was prepared by Nef[19], has been shown to have enough potentiality in the synthesis of nitrogen and sulphur containing 5 and 6 membered heterocyclic compounds. Therefore, it appeared sufficiently interesting to prepare arylisocyanodichloride and use this reagent as an intermediate in the synthesis of nitrogen and sulphur containing heterocyclic compounds. With this aim, the reaction of N-phenyl-isocyanodichloride[20] with different *bis*-1,5-aroyl/acyl-3-thiocarbohydrazides was carried out and related 1,3,4-thiadiazolidines have been isolated.

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 *bis*-1,5-cinnamoyl-3-thiocarbohydrazide (IIa): The compound *bis*-1,5-cinnamoyl-3-thiocarbohydrazide (**IIa**) was prepared by refluxing the mixture of thiocarbohydrazide (0.01 mol) and cinnamoyl chloride (**Ia**) (0.02 mol) in refluxing chloroform medium for 2.0 h. On completion of reaction and distilling off the solvent, the solid product was isolated. It was crystallized from ethanol to yield *bis*-1,5-cinnamoyl-3-thiocarbohydrazide (**IIa**), yield 90 %, m.p. 138°C.

This reaction was extended to synthesize other compounds (**IIb-f**) by using different aroyl/acyl chlorides and the related *bis* compounds were isolated in good yield.

Synthesis of 2-phenylimino-3-cinnamoyl-5-cinnamoyl hydrazino-1,3,4-thiadiazolidine (Va): The compound *bis*-1,5-cinnamoyl-3-thiocarbohydrazide (**IIa**) (0.01 mol) was suspended in chloroform (10.0 mL). To this was added a chloroformic solution of N-phenylisocyanodichloride (**III**) (0.01 mol in 10 mL). The reaction mixture was refluxed over a water bath for 3.0 h. The evolution of hydrogen chloride gas was observed. After completion of reaction, the chloroform was distilled off, when a solid mass was obtained. It was crystallized from ethanol and identified as monohydrochloride of 2-phenylimino-3-cinnamoyl-5-cinnamoyl hydrazino-1,3,4-thiadiazolidine (**IVa**), yield 85 %, m.p. 183°C. The compound (**IVa**) on basification with dilute ammonium hydroxide solution afforded a free base (**Va**). It was crystallized from ethanol, m.p. 170°C, m.f. $C_{26}H_{21}N_5O_2S$. Elemental analysis: Found %: C 66.78, H 4.39, N 14.78, S = 6.82. Required %: C 66.80, H 4.49, N 14.98, S 6.85. IR[21,22] : Compound (**Va**) showed absorption bands (cm^{-1}) due to ν_{max} 3273, 3203 (N-H); 1642 (amide C=O); 1529 (C=N); 1489 (Ar C=C); 1284 (C-N) and 755 (S-S). ^{1}H NMR (DMSO-d_6): δ 7.74 (s, 2H, NH); 7.38-7.55 (m, 15H, Ar-H); 6.38-7.64 (dd, 4H, CH=CH).

Synthesis of 2-phenylimino-3-cinnamoyl-4-acetyl-5-cinnamoyl hydrazino-1,3,4-thiadiazolidine (VIa): A mixture of 2-phenylimino-3-cinnamoyl-5-cinnamoyl hydrazino-1,3,4-thiadiazolidine (**Va**) (0.01 mol) and acetic anhydride (0.01 mol) in glacial acetic acid (10 mL) was refluxed for 2 h. The reaction mixture was cooled and poured on a little crushed ice, when a white coloured solid was precipited. It was crystallized from ethanol to yield 2-phenylimino-3-cinnamoyl-4-acetyl-5-cinnamoyl hydrazino-1,3,4-thiadiazolidine (**VIa**), yield 75 %, m.p. 120°C, m.f. $C_{28}H_{23}N_5O_3S$. IR: Compound (**VIa**) showed absorption bands (cm^{-1}) due to ν_{max} 1683 (Acetyl C=O); 1626 (Amide C=O); 1493 (C=N); 1480 (Ar C=C); 1282 (C-N) and 766 (C-S).

RESULTS AND DISCUSSION

The compounds *bis*-1,5-aroyl/acyl-3-thiocarbohydrazide (**IIa-f**) were prepared by refluxing thiocarbohydrazide (0.01 mol) and different aroyl/acyl chlorides (0.02 mol) (**Ia-f**) in 1:2 ratio in chloroform medium for 2 h. On completion of reaction and distilling off chloroform, the solid products were separated out. They were recrystallized from ethanol and identified as *bis*-1,5-aroyl/acyl-3-thiocarbohydrazides (**IIa-f**) and were obtained in good yield.

The interaction of *bis*-1,5-cinnamoyl-3-thiocarbohydrazide (**IIa**) (0.01 mol) and N-phenylisocyanodichloride (**III**) (0.01 mol) was carried in chloroform medium by refluxing the mixture for 3 h. The elimination of hydrogen chloride gas was clearly noticed. After completion of reaction and distilling off chloroform, a solid crystalline mass was obtained. It was crystallized from ethanol. It was found acidic to litmus and on determination of equivalent weight, was found to be a monohydrochloride of 2-phenylimino-3-cinnamoyl-5-cinnamoyl hydrazino-1,3,4-thiadiazolidine (**IVa**), yield 85 %, m.p. 183°C, which on basification with aqueous NH_3 afforded a free base, 2-phenylimino-3-cinnamoyl-5-cinnamoyl hydrazino-1,3,4-thiadiazolidine (**Va**). It was crystallized from ethanol, m.p. 170°C. The structure of compound (**Va**) was established on the basis of chemical properties, elemental analysis and spectral data.

The other compounds (**Vb-f**) were prepared by extending the above reaction to other *bis*-1,5-aroyl/acyl-3-thiocarbohydrazides (**IIb-f**) and the corresponding thiadiazolidines (**Vb-f**) were isolated in good yield (Table-1).

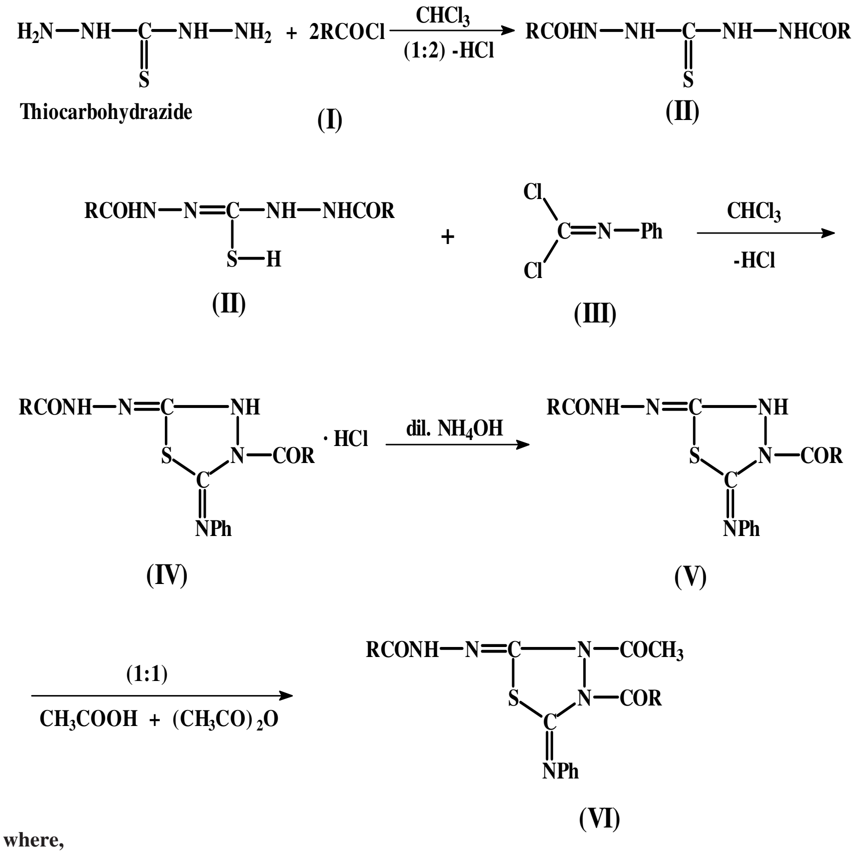
TABLE-1
PHYSICAL DATA AND ELEMENTAL ANALYSIS OF COMPOUNDS (V)

Compound / m.f.	R	m.w. Found (Calcd.)	Yield (%) [m.p. (°C)]	Elemental analysis Found (Calcd.) %	
				N	S
Va	Styryl	491.0	170	14.78	6.82
$C_{26}H_{21}N_5O_2S$		(503.5)	[85]	(14.98)	(6.85)
Vb	*o*-Hydroxyphenyl	472.0	150	15.45	7.05
$C_{22}H_{17}N_5O_4S$		(483.5)	[79]	(15.65)	(7.15)
Vc	Phenyl	436.0	168	16.72	7.61
$C_{22}H_{17}N_5O_2S$		(415.5)	[75]	(16.86)	(7.71)
Vd	Methyl	318.0	162	24.04	10.82
$C_{12}H_{13}N_5O_2S$		(327.5)	[78]	(24.05)	(10.99)
Ve	*n*-Propyl	375.0	148	20.11	9.14
$C_{16}H_{21}N_5O_2S$		(383.5)	[68]	(20.17)	(9.22)
Vf	*p*-Hydroxyphenyl	475.0	190	15.54	7.09
$C_{22}H_{17}N_5O_4S$		(483.5)	[75]	(15.65)	(7.15)

A mixture of 2-phenylimino-3-cinnamoyl-5-cinnamoyl hydrazino-1,3,4-thiadiazolidine (**Va**) (0.01 mol) and acetic anhydride (0.01 mol) in glacial acetic acid (10.0 mL) was refluxed for 2.0 h. The reaction mixture was cooled and poured on a little crushed ice, when a white solid was precipitated out (**VIa**). It was crystallized from ethanol, yield 75 %, m.p. 120°C. The structure of compound (**VIa**) was established on the basis of chemical properties, elemental analysis and spectral data.

The other compounds (**VIb-f**) were prepared by extending the above reaction of acetylation to other 1,3,4-thiadiazolidines (**Vb-f**) and the related acetylated products (**VIb-f**) were isolated in good yield.

The formation of compounds **II, IV, V** and **VI** can be explained by the reaction scheme as shown in **Scheme-I**.



where,
I-VIa : R = styrl; I-VIb : R = *o*-hydroxy phenyl
I-VIc : R = phenyl; I-VId : R = methyl
I-VIe : R = *n*-propyl; I-VIf : R = *p*-hydroxy phenyl

Scheme-I

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