

NOTE

Synthesis of 3-Phenylimino-4-aryl/acyl-6-aryl/acyl hydrazino-1,2,4,5-dithiadiazine

J.R. CHOUDHARI and B.N. BERAD*

Department of Chemistry, Shri Shivaji Science College, Amravati-444 603, India

Several 3-phenylimino-4-aryl/acyl-6-aryl/acyl hydrazino-1,2, 4,5-dithiadiazines have been synthesized by one step condensation reaction of N-phenyl-S-chloroisothiocarbamoyl chloride and bis-1,5-aryl/acyl-3-thiocarbohydrazides followed by basification of resultant compounds. The structures of the compounds were established on the basis of elemental analysis and spectral studies.

Key Words: Synthesis, Substituted dithiadiazine.

Synthesis of various dithiadiazines are reported in the literature¹⁻⁸. Some of them are shown to possess antifungal activity. Recently, the syntheses of 1,2,4,5-dithiadiazines with γ -picoline oil and aryl substituents have been reported in the literature^{9,10}. In this communication, some new 1,2,4,5-dithiadiazines with aryl/acyl hydrazino substituents have been synthesized and characterized

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

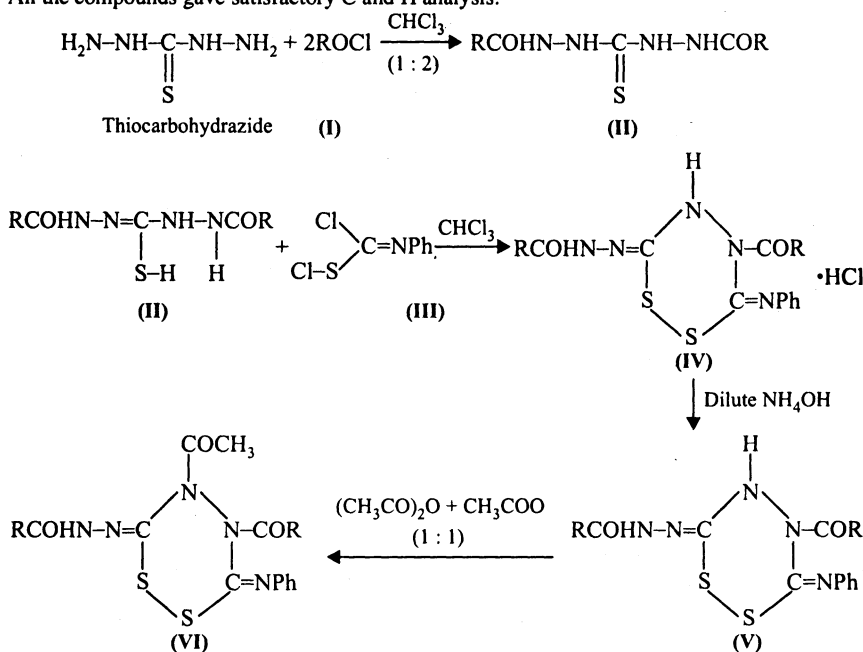
The melting points were recorded using hot paraffin bath and are uncorrected. Chemicals used were of AR grade. IR spectra were recorded on Perkin-Elmer spectrophotometer in the range 4000–400 cm^{-1} in Nujol mull and KBr pellets. PMR spectra were recorded with TMS as internal standard using CDCl_3 and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

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

Compd.	R	m.f.	m.p. (°C)	Yield (%)	Elemental analysis	
					Found	(Calcd.) %
					N	S
Va	<i>o</i> -Hydroxy phenyl	$\text{C}_{22}\text{H}_{17}\text{N}_5\text{O}_4\text{S}_2$	177	75	14.68 (14.61)	13.34 (13.36)
Vb	Phenyl	$\text{C}_{22}\text{H}_{17}\text{N}_5\text{O}_2\text{S}_2$	178	69	15.54 (15.65)	14.11 (14.31)
Vc	Styryl	$\text{C}_{26}\text{H}_{21}\text{N}_5\text{O}_2\text{S}_2$	165	71	13.96 (14.02)	12.79 (12.82)
Vd	<i>p</i> -Hydroxy phenyl	$\text{C}_{22}\text{H}_{17}\text{N}_5\text{O}_4\text{S}_2$	151	74	14.58 (14.61)	13.20 (13.36)
Ve	<i>n</i> -Propyl	$\text{C}_{16}\text{H}_{21}\text{N}_5\text{O}_2\text{S}_2$	168	69	18.26 (18.46)	16.71 (16.88)
Vf	Methyl	$\text{C}_{12}\text{H}_{13}\text{N}_5\text{O}_2\text{S}_2$	164	72	21.23 (21.67)	19.60 (19.81)

Compd.	R	m.f.	m.p. (°C)	Yield (%)	Elemental analysis	
					Found (%)	(Calcd.) %
					N	S
VIa	<i>o</i> -Hydroxy phenyl	C ₂₄ H ₁₉ N ₅ O ₅ S ₂	179	80	13.35 (13.43)	12.20 (12.28)
VIb	Phenyl	C ₂₄ H ₁₉ N ₅ O ₃ S ₂	165	75	14.36 (14.31)	13.10 (13.08)
VIc	Styryl	C ₂₈ H ₂₃ N ₅ O ₃ S ₂	170	76	12.58 (12.93)	11.61 (11.82)
VI d	<i>p</i> -Hydroxy phenyl	C ₂₄ H ₁₉ N ₅ O ₅ S ₂	142	65	13.52 (13.43)	12.11 (12.28)
VIe	<i>n</i> -propyl	C ₁₈ H ₂₃ N ₅ O ₃ S ₂	180	80	16.58 (16.62)	15.18 (15.20)
VI f	Methyl	C ₁₄ H ₁₅ N ₅ O ₃ S ₂	169	75	19.03 (19.17)	17.22 (17.53)

All the compounds gave satisfactory C and H analysis.



[R as given in Table-1]

Scheme-1

Synthesis of 3-phenylimino-4-salicyloyl-6-salicyloyl hydrazino-1,2,4,5-dithiadiazine (Va): The compound bis-1,5-salicyloyl-3-thiocarbohydrazide (IIa) was prepared by refluxing the mixture of thiocarbohydrazide (0.01 mol) and salicyloyl chloride (0.02 mol) (1 : 2) ratio with chloroform (20 mL) for 2 h. On completion of reaction and distilling off the solvent, the product was isolated (IIa) (yield 92%). It was crystallized from ethanol (m.p. 141°C). This reaction was extended to synthesize the other compounds (IIb-f) using different aroyl/acyl chlorides (IIb-f).

Bis-1,5 salicyloyl-3-thiocarbohydrazide (0.01 mol) (**IIa**) was suspended in chloroform (20 mL). To this, a solution of N-phenyl-S-chloroisothiocarbonyl chloride (0.01 mol) in chloroform was added. The reaction mixture was refluxed on boiling water bath for 3 h. The evolution of hydrogen chloride gas was clearly noticed as tested with moist blue litmus. After completion of reaction chloroform was distilled off, when a solid mass was obtained (yield 75%). It was crystallized from ethanol, m.p. 183°C. The solid was found to be acidic to litmus. On determination of an equivalent weight, it was identified as monohydrochloride of 3-phenyl imino-4-salicyloyl-6-salicyloyl hydrazino 1,2,4,5-dithiadiazine (**IVa**). (Equivalent weight of $C_{22}H_{17}N_5O_4S_2 \cdot HCl$, found 514, requires 515.5).

On basification with dilute ammonia a free base (**Va**) was obtained. It was crystallized from aqueous ethanol, m.p. 177°C.

Elemental Analysis (%) Found (Calcd.): C, 55.05 (55.11); H, 3.62 (3.54); N, 14.58 (14.61); O, 13.38 (13.36); S, 13.34 (13.36). IR^{11,12} (ν_{max} , cm^{-1}): 3314 $\nu(-OH)$, 3217, 3118 $\nu(N-H)$; 1610 $\nu(C=O)$; 1485 $\nu(C=C)$; 1293 $\nu(C-N)$; 1528 $\nu(C=N)$; 464 $\nu(S-S)$; 758 $\nu(C-S)$. PMR δ (9.61, 2H, S, OH); (7.84, 2H, S, NH), (6.83–7.73, 13H, m, Ar-H). The other compounds (**Vb–g**) were prepared by extending the above reaction to other bis-1,5-aryloyl/acyl-3-thiocarbohydrazides and were isolated in good yield.

Synthesis of 3-phenyl imino-4-salicyloyl-5-acetyl-6-salicyloyl-hydrazino-1,2,4,5-dithiadiazine (VIa): A mixture of 3-phenyl imino-4-salicyloyl-6-salicyloyl hydrazino 1,2,4,5-dithiadiazine (**Va**) (0.01 mol) and acetic anhydride (0.01 mole) in glacial acetic acid (10 mL) was refluxed for 2 h. The reaction mixture was cooled and poured in a little crushed ice with water. A whitish product was precipitated (yield 80%). It was crystallized from aqueous ethanol and identified as 3-phenyl imino-4-salicyloyl-5-acetyl-6-salicyloyl hydrazino-1,2,4,5-dithiadiazine (**VIa**), m.p. 179°C. IR (ν_{max} , cm^{-1}): 3316 $\nu(-OH)$, 3124 $\nu(N-H)$, 1640 $\nu(C=O)$, 1529 $\nu(C=N)$; 1493 $\nu(C=C)$, 1309 $\nu(C-N)$, 743 $\nu(C-S)$, 525 $\nu(S-S)$. The other compounds (**VIb–f**) were prepared by extending the above reaction to other 1,2,4,5-dithiadiazines and were isolated in good yield.

REFERENCES

1. D.H.R. Barton, J.W. Ducker, W.A. Lord and P.D. Mangus, *Am. J. Chem. Soc., Perkin Trans. 1*, 28 (1976).
2. T. Masashi and M. Shuntaro, *Heterocycles*, 4, 1243 (1976).
3. Y. Katusmi and S. Isao, *Bull. Chem. Soc. (Japan)*, 62, 2407 (1989).
4. J.M.M. Smits, P.T. Beurskens, B.G. Lenz and B. Zwanenburg, *Acta Crystallogr., Sect. C. Cryst. Struct. Commun.*, 41, 1086 (1985).
5. M.K. Shrivastava, R.K. Khare and H. Sing, *Bio. Chim. Farm*, 138, 511 (1999).
6. K.T. Poots, J.S. Baum and Jonathans, *Heterocycl. J. Chem.*, 298, 1637 (1991).
7. A. Sing, P. Rajendra and V.K. Verma, *Heterocycles*, 27, 2373 (1988).
8. Yonemoto, Kastami, Shibuya, Isao, Honda and Kazumasa, *Bull. Chem. Soc. (Japan)*, 61, 232 (1988).
9. C.S. Bhaskar, N.N. Vidhale and B.N. Berad, *Asian J. Chem.*, 14, 162 (2002).
10. R.S. Deshmukh and B.N. Berad, *Indian J. Heterocycl. Chem.*, 11, 153 (2002).
11. G. Otman and H. Hook, *J. Org. Chem.*, 31, 838 (1966).
12. N.B. Colthup, L.H. Daly and S. Wiberly, *Introduction to Infrared and Raman Spectroscopy*, Academic Press, New York (1964).