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SYNTHESIS OF HECTOR'S BASES

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ABSTRACT

3-Imino-5-substituted imino-1, 2, 4-thiadiazolidine **2(a-f)** were synthesized by the oxidative cyclization of 1-substituted-3-formamidinothiocarbamides **1(a-f)** in good yields by using liquid bromine. The isolated products were characterized on the basis of conventional elemental analysis, chemical characteristics and spectral analysis.

Key words: Thiadiazolidine, Thioureas, Diiminobiurates, Isothiocyanates, Oxidative cyclization, 1, 3-Bis (N-Substituted thioamido)guanidines.

INTRODUCTION

Synthesis of 1, 2, 4-thiadiazolidine starting from cyanoamidino substituted thiocarbamides had been explored in sufficient details[1]. Older methods are not general and the reaction conditions are usually harsh and yields are comparatively low. Hector synthesized first Hector's base[2]. After him, many researchers[3-7] synthesized various series of Hector's bases and all synthesized compounds were termed and justified as Hector's bases by them. But, laterally, it was investigated that all the Hector's bases, which are synthesized by them are not Hector's bases[8-11]; some were thiadiazoles and thiadiazolidines and some were actual Hector's bases. The justification of this statement was done on the basis of geometric study, chemical characteristics and spectroscopic evidences[12]. It means that some thiadiazoles as well as thiadiazolidines are Hector's bases but all thiadiazoles and thiadiazolidines are not Hector's bases (For Hector's bases, they must obey some typical properties)[13-15]. The drugs having Hector's base nucleus enhance pharmaceutical, medicinal, agricultural and industrial applications[16-19]. The drugs showed a diverse range of physiological activities[20,21], plant growth promoting activity, antitumour[22], herbicidal[23],

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antibacterial[24,25], amoebicidal[26] and antidibetic[27]. Very few work has been carried out on Hector's bases, as a part of research work being undertaken in the synthesis of nitrogen and sulphur containing heteroacycles and heterocycles having various applications in drug chemistry, pharmaceutical, medicinal, agricultural, industrial and biotechnological sciences. So, it was envisioned that an attractive approach to a general synthesis of the title compounds would involve the interactions of guanidine with various isothiocyanates in 1 : 1 molar proportions followed by making use of different oxidizing agents (liquid bromine, hydrogen peroxide/hydrochloric acid and raney nickel) in various reaction conditions (chloroform and acetone-ethanol medium) to overcome the problem[8-11] of yield, purity and time duration during the synthesis of Hector's bases. We report herein a versatile synthesis of 3-imino-5-substituted imino-1, 2, 4-thiadiazolidine (**2a-f).**

EXPERIMENTAL

All the chemicals used were of Analar grade (India make). Alkyl/arylisothiocyanates were prepared according to literature method[18]. Melting points of all synthesized compounds were determined in open capillary and uncorrected. IR spectra were recorded on Perkin-Elmer spectrophotometer in the range 4000-400 cm^{-1} in KBr pellets. PMR spectra were recorded with TMS as internal standard using $CDCl_3$ and DMSO-d_6. The purity of the compounds was checked on silica gel-G plates by TLC.

In first step, we found that when guanidine was refluxed with various isothiocyanates[28] in 1 : 1 molar proportions in carbon tetrachloride medium for 3 hours on water bath, it gave **1(a-f)**. The products were recrystallized from aqueous ethanol. The details of **1(a-f)** are enlisted in Table 1.

In the second step, the paste of **1(a-f)** was prepared in chloroform and liquid bromine in chloroform (10%) was added to it with constant stirring till the color of bromine persisted in the reaction mixture. It was allowed to stand for 4 hours at room conditions to obtain **2(a-f)**. The products were crystallised from ethanol. The details of **2(a-f)** are enlisted in Table 2.

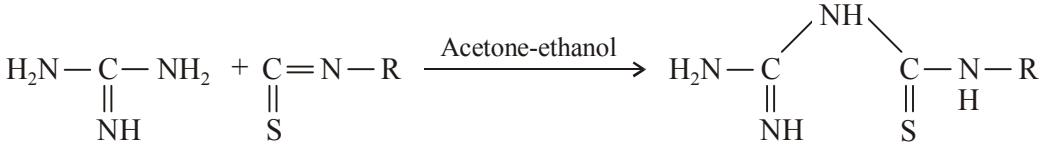
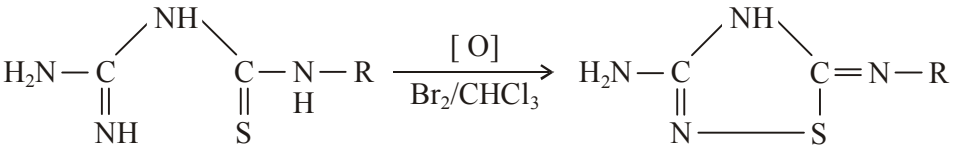


Table 1

Compd. No.	1-Substituted-3-formamidinothiocarbamide	Yield (%)	m.p. (^{o}C)
1a	Phenyl	74	130
1b	p-Chlorophenyl	84	142
1c	p-Tolyl	64	204
1d	Methyl	72	189
1e	Ethyl	59	115
1f	t-Butyl	67	149



1 (a-f) **2 (a-f)**

Table 2

Compd. No.	3-Imino-5-N-substitute dimino 1, 2, 4-thiadiazolidines	Yield (%)	m.p. (^{o}C)
2a	Phenyl	83	112
2b	p-Chlorophenyl	79	127
2c	p-Tolyl	68	120
2d	Methyl	78	157
2e	Ethyl	80	101
2f	t-Butyl	63	110

Experimental data for **1a** (3.4 g, 74%), m. p. 130^{0}C. – It desulphurize, when boiled with alkaline plumbite solution. The benzene solution of this compound on treatment with pure and dry carbon disulphide developed a yellow colour, which clearly indicated presence of basic imino group[29]. It formed picrate (m. p. 101^{0}C). Found (%) : C, 49.16; H, 5.03; N, 28.15; S, 16.17. ($C_8N_4S_1H_{10}$) requires (%) : C, 49.48; H, 5.15; N, 28.86; S, 16.49. IR

υ_{max}/cm^{-1} 3393.6 (N-H), 1661.6 (C=N), 1101.6 (>C=S), 517.3 (>C-S). δ_H (300 MHz, DMSO-d_6) 7.41-8.54 (Ar-H), 6.85 (Ar-NH) and 3.97 (N-H).

Experimental data for **2a** (3.2 g, 83%), m. p.. 112^0C. – It did not desulphurise with sodium plumbite solution, which clearly indicates that sulphur was present in cyclic form. It formed picrate (mp 180^0C). Found (%) : C, 48.48; H, 3.87; N, 29.01; S, 15.17 ($C_8N_4S_1H_8$) requires (%) : C, 50.00; H, 4.16; N, 29.16; S, 16.66, IR υ_{max}/cm^{-1} 3308.6 (N-H), 1660.2 (C=NH), 1332.7 (>C-N), 1154.3 (>C=S). δ_H (300 MHz, DMSO-d_6) 7.26 (Ar-H), 6.16 (Ar-NH), and 4.00 (N-H).

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