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SYNTHESIS OF 1-(4-ARYL-3-ARYLIMINO-5-IMMINO 1, 2, 4-THIADIALIDINE) PHENYL AMINO METHENAMIDES

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ABSTRACT

A series of synthesis of 1-(4-aryl-3arylimino-5-immino 1, 2, 4-thiadialidine) phenyl amino methenamides have been newly synthesized by the interaction of phenyl isocyanate with Hectors base (4-aryl, 3-arylimino-5-immino 1, 2, 4-thidiazolidine). The identities of these new compounds have been established on the basis of usual chemical transformations and IR, NMR and Mass spectral studies.

Key words: Phenyl isocyanate, Hectors base.

INTRODUCTION

Nitrogen and sulphur containing five and six membered heterocyclic compounds has been exhaustively investigated by number of chemists[1-3]. Very few compounds containing thioamido group with phenyl isocyanate have been reported and tested for their biological activity[4-6]. We have synthesized a series of such 1, 2, 4-thiadiazolidine compounds.

In view of applications of 1, 2, 4-thiadiazilidines and its derivatives in medicinal chemistry and in many other ways[7], we herein report the synthesis of several 1-(4-aryl-3-arylimino-5-immino 1,2,4-thiadialidine) phenyl amino methenamides **(IIIa-g)** have been newly synthesized by the condensation of phenyl isocyanate **(I)** with Hectors base (4-aryl, 3-arylimino-5-immino 1,2,4 thidiazolidine) **(IIa-g)**. Required Hectors bases were prepared by the already known method of oxidative cyclization of 1-aryl thiocarbamides with the help of hydrogen peroxide and 1-aryl thiocarbamides was prepared by reaction of aryl amine hydrochlorides with ammonium thiocyanate[8].

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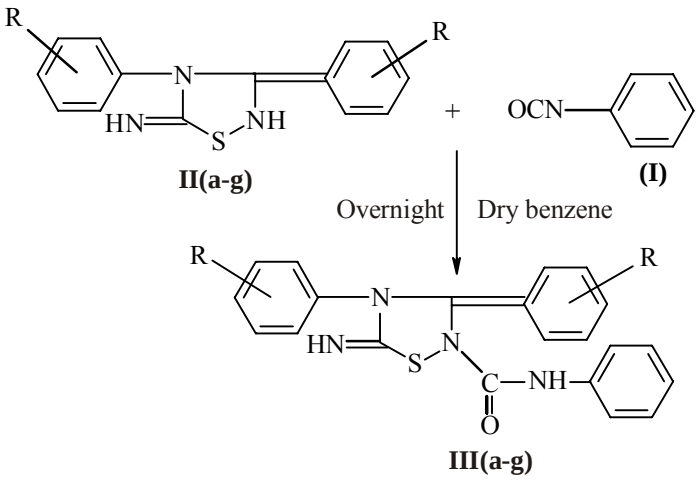

Scheme 1

where, R = (a) phenyl, (b) 4-methyl, (c) 5-methyl, (d) 6-methyl, (e) 4-Cl, (f) 5-Cl, (g) 6-Cl.

EXPERIMENTAL

Specific rotations were measured on Equip-Tronics Digital Polarimeter at 28°C in $CHCl_3$. IR spectra were recorded on Perkin-Elmer spectrum RXI FTIR spectrophotometer (4000-450 cm^{-1}). ^1H NMR was recorded in $CDCl_3$ on Bruker DRX-300 spectrometer operating at 300 MHz. The mass spectra were recorded on Jeol-SX-102 (FAB) instrument.

Preparation of aryl thiocarbamides

Arylthiocarbamide was obtained by interaction of aromatic amine and concentrated HCl. Mixture was heated in 500 mL round bottle flask. When hydrochloric salt was obtained. It was dissolved in water (500 mL) and ammonium thiocyante was added to it (40 g in 150 mL and water). It became turbid upon boiling. It was pouned in to 200 mL of ice-cold water, thiocarbamides were separated.

Synthesis of hectors base (4-aryl, 3-arylimino-5-immino 1, 2, 4-thiadiazolidine)

Aryl thiocarbamide (3 g, 0.05 m, 25 mL) was acidified with conc. HCl (5 mL) and 60 mL of H_2O_2 Vol. (20%) solution was gradually added to it when a clear solution was obtained. It wa precipitated by standing for one hour and it was separated by filtration. Solution upon basification with ammonium hydroxides gave 1, 2, 4-thiadiazolidines (Hectors base).

Synthesis of 1-(4-aryl-3arylimino-5-immino 1, 2, 4-thiadialidine) phenyl amino methenamides (IIIa-g) (Scheme 1)

A mixture of phenyl isocyanate **1 (0.0**2M, 2.3 g) was mixed with suspension of substituted 1, 2, 4-thiadiazolidine (0.02 M, 3.5 g) **(IIa-g)**. The mixture was allowed to stand overnight. The solvent was triturated with petroleum ether (60-80^{o}C) to afford a white solid (**IIIa-f)**. The products were purified from acetone-petroleum ether.

3a. m.p. 202^{o}C; yield 81%, $[\alpha]^{28}_{D}$ + 80^{o} (c,1.11 in $CHCl_3$); IR (KBr): 3451 cm^{-1} (N-H) 1730 cm^{-1} (C=O), 1600 cm^{-1} (C=N), 771 cm^{-1} (C-S); ^{1}H NMR (ppm) : δ7.12-7.07 (15H, m, aromatic protons), δ 8.05-7.89 (s, 2H, NH protons); Mass (m/z): 387 (M^{+}), 388 (M^{+} + 1), 120 ($C_6H_5NHCO^{+}$), 149 (C_6H_5NH); Anal.calcd for $C_{21}H_{17}ON_5S$: C,65.11; H,4.39; N,18.08; S,8.26%; Found: C, 65.71; H, 4.42; N, 18.00; S, 8.19%.

3b. m.p. 310^{o}C; yield 89%, $[\alpha]^{28}_{D}$ +180^{o} (c, 1.11 in $CHCl_3$); IR (KBr): 3454 cm^{-1} (N-H) 1729 cm^{-1} (C=O), 1601 cm^{-1} (C=N), 769 cm^{-1} (C-S); ^{1}H NMR (ppm) : δ 7.12-7.07 (13H, m, aromatic protons), δ 8.05-7.89 (s, 2H, NH protons), δ 2.39 (s, 6H, 2-CH_3 protons); Mass (m/z): 401 (M^{+}), 402 (M^{+} + 1), 120 ($C_6H_5NHCO^{+}$), 149 (C_6H_5NH); Anal. calcd for $C_{23}H_{21}ON_5S$: C, 68.82; H, 5.23; N, 17.45; S, 7.98% ; Found: C, 68.71; H, 5.22; N, 17.41; S, 7.89%.

3e. m.p. 152^{o}C; yield 86%, $[\alpha]^{28}_{D}$ +142^{o} (c, 1.11 in $CHCl_3$); IR (KBr): 3452 cm^{-1} (N-H) 1728 cm^{-1} (C=O), 1599 cm^{-1} (C=N), 770 cm^{-1} (C-S); ^{1}H NMR (ppm) : δ 7.12-7.07 (13 H, m, aromatic protons), δ 8.05-7.89 (s, 2H, NH protons); Mass (m/z): 458 (M^{+}), 459 (M^{+} + 1), 120 ($C_6H_5NHCO^{+}$), 149 (C_6H_5NH); Anal.calcd for $C_{21}H_{15}ON_5SCl_2$: C, 55.02; H, 3.27; N, 15.28; S, 6.98% ; Found: C, 55.01; H, 3.22; N, 15.24; S, 6.97%.

RESULT AND DISCUSSION

1-(4-aryl-3arylimino-5-immino 1, 2, 4-thiadialidine) phenyl amino methenamides **(IIIa-g)** have been synthesized by the condensation of phenyl isocyanate **(I)** with Hectors base (4-aryl, 3-arylimino-5-immino 1,2,4-thidiazolidine) **(IIa-g)** in benzene and kept overnight. The sticky residue obtained was triturated with petroleum ether (60-80^{o}C) to afford a white solid (**IIIa-g)**. The structure of the products were confirmed on the basis of IR[9], NMR[10] and Mass[11] spectral analysis. The specific rotation of the products were also recorded[12].

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