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SYNTHESIS OF 3-SUBSTITUTED BENZOTHIAZOLYL -1-PHENYL AMINO METHENAMIDES

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ABSTRACT

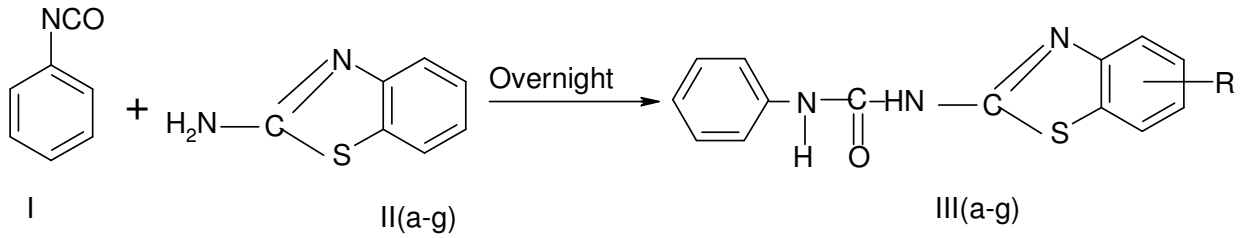
Several 3-substituted benzothiazolyl -1-phenyl amino methenamides have been synthesized by the interaction of phenyl isocyanate with substituted benzothiazoles. The identities of these new compounds have been established on the basis of usual chemical transformations and IR, NMR and Mass spectral studies.

Key words: phenyl isocyanate, Benzothiazoles.

INTRODUCTION

Benzothiazoles have been known from long ago to be biologically active their varied biological features are still of great scientific interest[1-4]. They are bicyclic ring system with multiple applications. Some derivatives of benzothiazoles possess antituberculosis, anticancer, antitumor, antipyretic activities[5,6].

In view of applications of benzothiazoles and its derivatives in medicinal chemistry and in many other ways, we herein report the synthesis of several 3-substituted benzothiazolyl 1-phenyl amino methenamides **(3a-g)** were prepared by the condensation of phenyl isocyanate **1** with 2-aminobenzothiazole/ substituted benzothiazloles **(2a-g).** Required 2-amino benzothiazoles / substituted benzothiazoles were prepared by the already known method of oxidative cyclization of 1-aryl thiocarbamides with the help of molecular bromine and 1-aryl thiocarbamides was prepared by reaction of aryl amine hydrochlorides with ammonium thiocyanate[7,8, 9].



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 ^{0} C in $CHCl_3$. IR spectra were recorded on Perkin-Elmer spectrum RXI FTIR spectrophotometer (4000-450 cm $^{-1}$). ^{1}H 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

Aryl thiocarbamide was obtained by interaction of aromatic amine and concentrated HCl. Mixture was heated in 500ml round bottle flask. When hydrochloric salt was obtained. It was dissolved in water

(500ml) and ammonium thiocyante was added to it (40g in 150 ml and water). It became turbid upon boiling. It was pouned in to 200ml of ice-cold water, thiocarbamides were separated.

Synthesis of Substituted Benzothiazoles

To a chloroformic paste of thiocarbamide (10g in 40ml) 20% bromine solution was added with constant stirring. Mix was allowed to stand for six hours. Resultant hydrobromide was treated with 30ml of cold cold ethyl alchol, when it dissolved. It gave substituted benzthiazole upon basification with cold ammonium hydroxide solution (30 ml). To 2-amino/ substituted benzothiazoles **(2a-g)**.

Synthesis of 3**-substituted benzothiazolyl -1-phenyl amino methenamides (3a-g)(Scheme-1)**

A mixture of phenyl isocyanate **1 (.0**2M,2.3g) and (2M, 2g) 2-aminobenzothiazole/substituted benzothiazoles**(2a-g)** in 30ml of benzene was added to it in a conical flask. The mixture was allowed to stand overnight. The solvent was triturated with petroleum ether (60-80^{0}C) to afford a white solid(**4a-f).** The products were purified from acetone- petroleum ether.

(3a) m.p. 285^{0}C; yield 90%, [α] $^{28}_D$ +90^0 (c,1.11in $CHCl_3$); IR(KBr): 3450 cm^{-1} (N-H)1730 cm^{-1} (C=O), 1600cm^{-1} (C=N), 771cm^{-1} (C-S); ^{1}H NMR (ppm) : δ7.12-7.07(9H, m, aromatic protons), δ 8.05-7.89(s, 2H, NH protons); MASS(m/z): 269(M^+), 270(M^++1), 120($C_6H_5NHCO^+$), 149(C_6H_5NH); Anal.calcd for $C_{14}H_{11}ON_3S$: C,62.45; H,4.08; N,15.61; S,11.80% ; Found: C,67.71; H,4.62; N,15.60; S,11.79%.

(3b) m.p. 325^{0}C; yield 89%, [α] $^{28}_D$ +120^0 (c,1.11in $CHCl_3$); IR(KBr): 3455cm^{-1} (N-H)1729 cm^{-1} (C=O), 1601cm^{-1} (C=N), 769cm^{-1} (C-S); ^{1}H NMR (ppm) : δ7.12-7.07(8H, m, aromatic protons), δ 8.05-7.89(s, 2H, NH protons), δ 2.39(s, 3H, -CH_3 protons); MASS(m/z): 283(M^+), 284(M^++1), 120($C_6H_5NHCO^+$),149(C_6H_5NH); Anal.calcd for $C_{15}H_{13}ON_3S$: C,63.60; H,4.59; N,14.80; S,11.30% ; Found: C,63.71; H,4.62; N,14.81; S,11.29%.

(3e) m.p. 310^{0}C; yield 86%, [α] $^{28}_D$ +132^0 (c,1.11in $CHCl_3$); IR(KBr): 3451 cm^{-1} (N-H)1729 cm^{-1} (C=O), 1599cm^{-1} (C=N), 770cm^{-1} (C-S); ^{1}H NMR (ppm) : δ7.12-7.07(8H, m, aromatic protons), δ 8.05-7.89(s, 2H, NH protons); MASS(m/z): 319(M^+), 320(M^++1), 120($C_6H_5NHCO^+$), 149(C_6H_5NH); Anal.calcd for $C_{14}H_{10}ON_3SCl$: C,52.56; H,3.13; N,13.16; S,10.03% ; Found: C,67.71; H,4.62; N,13.14; S,10.09%.

RESULTS AND DISCUSSION

3-Substituted benzothiazolyl 1-phenyl amino methenamides **(3a-g)** were prepared by the condensation of phenyl isocyanate **1** with 2-aminobenzothiazole/ substituted benzothiazloles **(2a-g)**was added to benzeneand kept overnight . The sticky residue obtained was triturated with petroleum ether (60-80 ^{0}C) to afford a white solid (**3a-g)**. The structure of the products were confirmed on the basis of IR, NMR and Mass spectral analysis. The specific rotation of the products were also recorded[11, 12, 13].

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