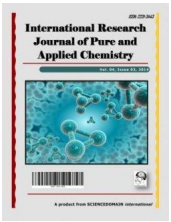

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Synthesis and Characterization of Thiazolo Pyridin-2-Amine and Their Schiff Bases

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Authors' contributions

This work was carried out in collaboration among all authors. Authors MVS, SBC, JPS and SSP was done to design and managed literature survey for these research. Author AVP preformed the laboratory experiments and author MRS helps to analysis of spectral data. All authors read and approved the final manuscript.

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ABSTRACT

The efficient synthesis of thiazolo pyridine 2-amine(3) by reaction of 2-amino pyridine with ammonium thiocyanate(2). The reaction carried out in presence of ceric ammonium nitrate and Dimethyl Sulphoxide as a solvent. The aromatic aldehyde reacts with synthesized compound thiazolo pyridin-2-amine (3) by using catalytic amount of Ni $(NO_3)_2$.$6H_2O$ at room temperature. Advantages of this protocol are its very good yields.

Keywords: Ceric ammonium nitrate; thiazolo pyridin-2-amine; Ni (NO3)2 .6H2O.

1. INTRODUCTION

Nitrogen, sulfur and oxygen containing heterocycles have been under investigation for a long time due to their important medicinal properties [1]. Synthesis of schiff bases from aromatic amines and aromatic aldehydes have a wide variety of applications in many fields,

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because it posses' antimicrobial activity [2], anti-inflammatory activity [3], antikinetoplastid, antimitotic activity [4], antitumor activity [5] and anticonvulsant activity [6].

There are several synthetic methods have been reported for the synthesis of Schiff bases. However, most of time they have some limitations including long reaction times, required a special catalyst, low yields, and difficulty in recrystallization. [7-10] Therefore, design the more convenient and practical synthetic methods for preparation of thiazolo pyridine 2-amine. Several catalysts are used in organic synthesis like inorganic salts [11] and zeolites [12,13].

We studied a simple and efficient synthetic method for the preparation of schiff bases containing thiazolo moiety in the presence of inorganic salts as homogeneous catalysts.

2. MATERIALS AND METHODS

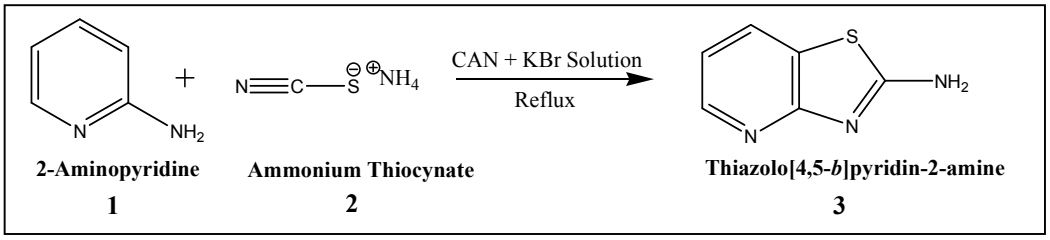
2.1 General

All chemicals were purchased from Sigma-Aldrich and S.D. Fine Chemicals India Pvt. Ltd. Reactions were monitored by thin-layer chromatography (TLC). Melting points of the synthesized compounds were determined by open capillary method and are uncorrected. UV spectra were recorded on Shimadzu 1700 UV–Visible spectrophotometer and IR spectra were recorded on Shimadzu 8400S FTIR spectrometer using KBr pellets. The 1H NMR were recorded on Bruker WM-300 (at 300 MHz) using CDCl3 as solvent. Chemical shifts are reported in δ ppm units with respect to TMS as internal standard. Purity of the compounds was checked on precoated TLC plates using silica gel plates.

2.2 Synthesis of Thiazolo [4, 5-B] Pyridin-2-Amine

Take a mixture of 2-aminopyridine (0.02 mol) and ammonium thiocyanate (0.1 mol) in Dimethyl Sulphoxide (15 ml) in a 250 ml round bottom flask with magnetic bar stirrer and add a (15 ml) solution of KBr &CAN was allowed to run through the dropping funnel drop wise during 30 min. The mixture was reflux 80-90^{0}C for 1 hr. The reaction mixture was diluted with water the precipitated substance was collected and recrystallized from a suitable solvent to obtain compound (3).

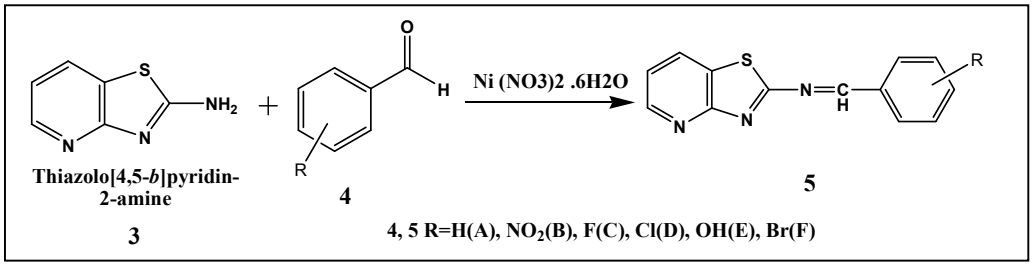
REACTION



2.3 General Preparation of Schiff Bases

The aromatic aldehyde (1 mmole) is added to a solution of thiazolo pyridin-2-amine (1 mmole) in Dimethyl Sulphoxide (10 ml).Then Ni $(NO_3)_2$ .6H_2O5 mol % was added and the reaction mixture stirred at room temperature for the desired time. After completion of the reaction, cold water (15-25 ml) was added to give the product. The solid product was filtered and washed with cold water and air dried.

REACTION



2.4 Spectral Data

SYNTHESIS OF THIAZOLO [4, 5-B] PYRIDIN-2-AMINE (3)

^{1}H-NMR (300 MHz, $CDCl_3$) δ: 8.59 (S, 1H, Ar-H), 7.38 (S, 1H, Ar-H), 7.75 (S, 1H, Ar-H), 7.22 (S, 2H, NH_2) ppm. **^{13}C-NMR ($CDCl_3$) *δ*:** 167.3, 119.5, 158.9, 148.0, 120.5, 130.1ppm. **FT-IR (KBr):**3212-3350 (NH_2), 840 (C-S-C), 1555 (C=N).

SYNTHESIS OF N-BENZYLIDENETHIAZOLO [4, 5-B] PYRIDIN-2-AMINE (5A)

^{1}H-NMR (300 MHz, $CDCl_3$) δ: 7.6 (S, 1H, CH), 7.5 (S, 1H, CH), 7.53(S, 1H, CH), 7.55(S, 1H, CH), 7.61(S, 1H, CH), 8.10(S, 1H, N=CH), 8.59(S, 1H, CH), 8.59(S, 1H, CH), 7.9(S, 1H, CH) ppm.**^{13}C-NMR ($CDCl_3$) *δ*:** 130, 129.3, 128.4, 132.6, 159.9, 172.5, 128.9, 162.7, 148.1, 121.2, 129.9 ppm. **FT-IR (KBr):**847 (C-S-C), 1627 (Imine C=N), 1514 (C=N Pyridine).

SYNTHESIS OF N-4-NITROBENZYLIDENETHIAZOLO [4, 5-B] PYRIDIN-2-AMINE (5B)

^{1}H-NMR (300 MHz, $CDCl_3$) δ: 7.7 (S, 1H, CH), 7.4 (S, 1H, CH), 7.48(S, 1H, CH), 7.65(S, 1H, CH), 7.61(S, 1H, CH), 8.15(S, 1H, N=CH), 8.49(S, 1H, CH), 8.59(S, 1H, CH), 7.50(S, 1H, CH) ppm.**^{13}C-NMR ($CDCl_3$) *δ*:** 129.5, 128.3, 127.4, 133.6, 159.9, 173.5, 128.9 163.7, 145.1, 122.2, 130.9 ppm. **FT-IR (KBr):** 850 (C-S-C), 1633 (Imine C=N), 1525 (C=N Pyridine).

SYNTHESIS OF N-4-FLUOROBENZYLIDENETHIAZOLO [4, 5-B] PYRIDIN-2-AMINE (5C)

^{1}H-NMR (300 MHz, $CDCl_3$) δ: 7.55 (S, 1H, CH), 7.33 (S, 1H, CH), 7.58(S, 1H, CH), 7.65(S, 1H, CH), 7.62(S, 1H, CH), 8.12(S, 1H, N=CH), 8.59(S, 1H, CH), 8.55(S, 1H, CH) ppm.**^{13}C-NMR ($CDCl_3$) *δ*:** 130.5, 129.3, 125.4, 133.6, 169.9, 173.5, 129.9 163.7, 145.1, 122.2, 132.9 ppm. **FT-IR (KBr):** 842 (C-S-C), 1640 (Imine C=N), 1545 (C=N Pyridine).

SYNTHESIS OF N-4-CHLOROBENZYLIDENETHIAZOLO [4, 5-B] PYRIDIN-2-AMINE (5D)

^{1}H-NMR (300 MHz, $CDCl_3$) δ: 7.66 (S, 1H, CH), 7.54 (S, 1H, CH), 7.52(S, 1H, CH), 7.15(S, 1H, CH), 7.56(S, 1H, CH), 8.22(S, 1H, N=CH), 8.60(S, 1H, CH), 8.45(S, 1H, CH) ppm.**^{13}C-NMR ($CDCl_3$) *δ*:** 128.5, 130.3, 127.4, 135.6, 169.9, 174.5, 139.9 161.7, 145.1, 122.2, 132.9 ppm. **FT-IR (KBr):** 815 (C-S-C), 1611 (Imine C=N), 1558 (C=N Pyridine).

SYNTHESIS OF N-4-HYDROXY BENZYLIDENETHIAZOLO [4, 5-B] PYRIDIN-2-AMINE (5E)

^{1}H-NMR (300 MHz, $CDCl_3$) δ: 7.77 (S, 1H, CH), 7.65 (S, 1H, CH), 7.42(S, 1H, CH), 7.52(S, 1H, CH), 7.46(S, 1H, CH), 8.70(S, 1H, N=CH), 8.51(S, 1H, CH), 8.55(S, 1H, CH)5.55 (s, 1H, OH) ppm.**^{13}C-NMR ($CDCl_3$) *δ*:** 130.5, 128.3, 124.4, 134.6, 168.9, 174.5, 139.9 161.7, 144.1, 132.2, 132.9 ppm. **FT-IR (KBr):** 856 (C-S-C), 1665 (Imine C=N), 1548 (C=N Pyridine) 3167 (OH).

SYNTHESIS OF N-4-BROMO BENZYLIDENETHIAZOLO [4, 5-B] PYRIDIN-2-AMINE (5F)

^{1}H-NMR (300 MHz, $CDCl_3$) δ: 7.57 (S, 1H, CH), 7.45 (S, 1H, CH), 7.32(S, 1H, CH), 7.38(S, 1H, CH), 7.28(S, 1H, CH), 8.61(S, 1H, N=CH), 8.54(S, 1H, CH), 8.15(S, 1H, CH) ppm.**^{13}C-NMR ($CDCl_3$) *δ*:** 135, 129.3, 125.4, 134.6, 168.9, 173.5, 139.9 161.7, 141.1, 130.2, 142.9 ppm. **FT-IR (KBr):** 1569 (C=N Pyridine) 796 (C-S-C), 1609 (Imine C=N).

3. RESULTS AND DISCUSSION

Initially we sought a mild and convenient method for the synthesis of Schiff bases at ambient temperature. Firstly optimize of the amount of catalyst by carried out the model reactions using different amount of catalyst. We carried out the reaction of thiazolo pyridine 2-amine with 4-nitrobenzaldehyde at room temperature by using 5 mol% catalyst to get good results. The use of 5 mol% of Ni $(NO_3)_2$.$6H_2O$ in DMSO for 60 min afforded the corresponding Schiff base in 77% yield.

Thiazolo 2-amino pyridine (3) was prepared by the reaction of 2-aminopyridine with ammonium thiocyanate. On the basis of FT-IR results we confirmed the synthesized compound. IR values give good explanation about compound (3). The compound Thiazolo 2-aminopyridine gives two absorption bands at 3212 cm^{-1} and 3350 cm^{-1} of the asymmetric and symmetric stretching vibrations of (-NH2) group. The absorption band at 1555 cm-1 of the stretching vibration of (C=N)

Table 1. Physical data of synthesized compounds

Compound	Compound	R	Time (Min)	M.P (^oC)	Yield %
$C_{13}H_9N_3S$	5A	H	60	252-256	68
$C_{13}H_8N_4SO_2$	5B	NO_2	45	165	75
$C_{13}H_8N_3SF$	5C	F	65	208-211	64
$C_{13}H_8N_3SCl$	5D	Cl	55	196-197	55
$C_{13}H_9N_3SO$	5E	OH	60	203-204	59
$C_{13}H_8N_3SBr$	5F	Br	60	228-231	67

group of hetero aromatic ring of pyrimidines as well as the stretching vibration of (C-S) at 840 cm-1. All these absorption bands are good evidences for the formation of compound (3).

The Compound (5) N-benzylidene thiazolo [4, 5-b] pyridin-2-amine was prepared from the reaction of (3) with aromatic aldehydes in nickel nitrate. The conversion of compound (3) into N-benzylidene thiazolo [4, 5-b] pyridin-2-amine are confirm by disappearance of two absorption bands of the asymmetric and symmetric stretching vibrations of (-NH2) group of compound (3) and appearance of the band at 1628 cm^{-1} of stretching vibration of (C=N) imine group. The results are summarized in Table 1 above.

4. CONCLUSION

We design the efficient synthesis of Schiff bases from thiazolo pyridine 2- Amine and aromatic aldehydes by using Ni $(NO_3)_2$ $.6H_2O$.The attractive features of this procedure are its good conversions, easy workup, and short reaction times, making it a useful practical method for the synthesis of Schiff bases.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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