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Synthesis and characterization of novel benzohydrazide derivatives

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ABSTRACT

The present study provides rapid dissemination of important, original research papers as well as critical, in-depth reviews of reactions, techniques and synthetic methods in organic, inorganic and bioorganic chemistry. Dealing with compounds of organic chemistry, this study covers the synthesis of a series of benzohydrazide derivatives derived from different arylaldehydes, improved synthetic procedures, detailed descriptions of experimental work and characterization. So that results can be reproduced and applied in reader's laboratory research. The synthesized compounds structures were characterized by FT-IR, ^{1}H-NMR, ^{13}C-NMR and Mass Spectral Studies.

Keywords: Schiff base, Benzohydrazide, azomethine, anti-tubercular, FT-IR.

INTRODUCTION

Hydrazones have been demonstrated to possess antimicrobial, anticonvulsant, analgesic, antiinflammatory, antiplatelet, anti-tubercular, anticancer and antitumor activities [1,2]. Hydrazones possessing an azomethine –NHN=CH– proton constitute an important class of compounds for new drug development. Many researchers have therefore synthesized these compounds as target structures and evaluated their biological activities [3]. These observations have served as guides for the development of new hydrazones that possess various biological activities[4,5]. Benzohydrazide and their derivatives are poly functional molecules bearing -CO, –NH– and $–NH_2$ functionalities in their structures [6-8]. Therefore, we can expect these compounds to behave as ambident nucleophiles in several reactions but in our case $–NH_2$ act as a nucleophile [9].

The chemistry of hydrazone derivatives have been investigated intensively in the last decade owing to their coordinative and pharmacological activity as well as their use in analytical chemistry as metal-extracting agents [10,11]. The acid hydrazone derivatives and its metal complexes are known to exhibit a broad spectrum of biological, bactericidal and fungicidal activities and have great interest due to their analytical, industrial and pharmacological importance The condensation of primary amines with aldehydes and ketones give imines. Imines that contain an aryl group bound to the nitrogen or to the carbon atom are called Schiff bases, since their synthesis was first reported by Schiff [12-14].

They have received much attention in the fields of chemistry and biology due to their broad spectrum of activities. They have been utilized as herbicides, insecticides, nematicides, rodenticides, plant growth regulators and sterilants for houseflies. During the past few decades, the field of metal-organic coordination compound application has

developed rapidly due to their structural diversity and application potential in optical, electronic and magnetic materials, as well as applications in molecular sensing, catalysis, and selective gas adsorption [15-19].

The above remarkable considerations and pharmaceutical and industrial applications prompted us to synthesize a new series of benzohydrazide derivatives via Schiff base route.

MATERIALS AND METHODS

All anhydrous solvents and reagents were obtained from commercial suppliers and used without any further purification unless otherwise noted. All the reactions were carried out in the room temperature. The melting points of the synthesized compounds were measured on apparatus. FT-IR spectral measurements were made for the synthesized compounds using Perkin Elmer Spectrum-1 FT IR spectrometer in 4000-400 cm^{-1}. The NMR spectra were recorded on a Bruker 300 MHz spectrometer with DMSO-d_6 as the solvent and TMS as the internal reference. Mass spectra were recorded on a JEOL GCMATE II GC-MS spectrometer using a direct injection method.

General synthesis of benzohydrazide derivatives

To the mixture of benzohydrazide (0.001 mol) and aryl aldehyde (0.001 mol) in 20 mL Water was added three drops of Con. Hydrochloric acid with stirring for 10 min. at room temperature. Insoluble solid was gradually generated, then filter and wash with water. After drying pure target compound was afforded as crude solid. The crude solid was recrystallised from absolute ethanol.

RESULTS AND DISCUSSION

Benzohydrazide derivatives were synthesized via condensation reaction by Schiff base route. The nucleophilic displacement of acid hydrazide with different aromatic aldehydes resulted in the products. The reaction was performed employing various acid catalysts (HCl, H_2SO_4, HNO_3, formic acid and acetic acid (Table 1)) different types of solvents (water, methanol, ethanol, toluene and 1,4-dioxane,) (Table 2)) and at room temperatures. HCl catalyst yields 98% of benzohydrazide derivatives. However the other catalyst of the products was difficult because solubility and separation of products from the reaction mixture. The use of organic solvents such as methanol, ethanol, toluene and 1,4-dioxane and DMF were also not found to be desired product and also toxic in nature. It was noted that none of the solvent other than water was fruitful for considerable yield (Table 3). Finally the use of Con. HCl as catalyst and water as solvent gave fascinating results. Finally the synthesized compounds structures were confirmed by FT-IR, ^{1}H NMR, ^{13}C NMR and Mass spectral studies (Fig 1-3).

Table 1: Effect of solvents on reaction of 1a with 2a

Entry	Solvents	% Yield of 4a
1	Water	98
2	Methanol	70
3	Ethanol	80
4	Toluene and 1,4-dioxane	NR

*Reaction conditions: 2**a** (1 equiv.), **1a** (1 equiv.), catalyst (0.2 equiv.), room temperature, (30 min), solvents (20 vol.). NR = No Result*

Table 2: Effect of catalyst on reaction of 1a with 2a

Entry	Catalyst	% Yield of 2a
1	HCl	98
2	H_2SO_4	70
3	HNO_3	68
4	HCOOH	40
5	CH_3COOH	46

*Reaction conditions: **2a** (1 equiv.), **1a** (1 equiv.), catalyst (0.2 equiv.), (30 min), solvents (20 vol.).*

(E)-N'-(2,4,5-trifluorobenzylidene)benzohydrazide (B1) was derived from benzohydrazide and 2,4,5-trifluorobenzaldehyde. Yield: 98%. M.P. 167-169°C,

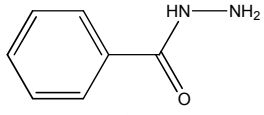
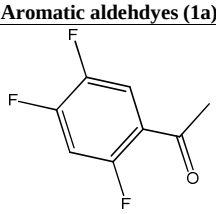
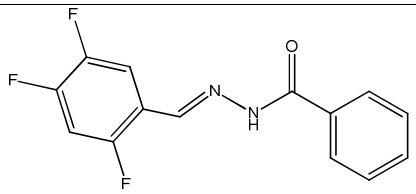
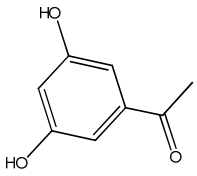
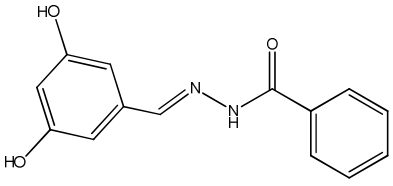
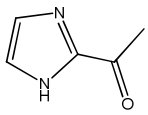
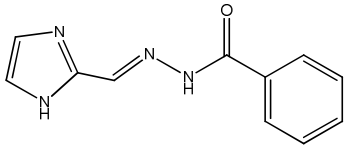
FT-IR: (ν in cm^{-1}) 3409, 3218, 3069, 2848, 1645, 1579, 1142, 699.

^{1}H NMR δ in ppm (300 MHz, DMSO-d_6): 12.1(s, 1H, enolizable NH proton), 8.70 (s, 1H, CH=N), 7.5-7.9 (m, 7H, aromatic rings).

^{13}C NMR δ in ppm (100 MHz, DMSO-d_6) 163 (CO), 138 (CH=N), 133, 132, 128, 127, 119, 113, 106 (aromatic ring).

M/z = 278 (M+1).

Table 3: List of products and their corresponding reactants

Sl. No.	benzohydrazide (2a)	Aromatic aldehdyes (1a)	Product	Yield (%)[b]
1	 **2a**	 **1a**	 **B1**	90%
2	**2a**	 **1b**	 **B2**	95%
3	**2a**	 **1c**	 **B3**	97%

Reaction conditions: ***2a*** *(1 equiv.),* ***1a*** *(1 equiv.), catalyst (0.2 equiv.), room temperature, (10 min), solvents (20 vol.).*

(E)-N'-(3,5-dihydroxybenzylidene)benzohydrazide (B2) was derived from benzohydrazide and 3,5-dihydroxy benzaldehyde. Yield: 92%. M.P. 144-146°C,

FT-IR: (ν in cm^{-1}) 3366, 3161, 2862, 1668, 1613, 1162, 701.

^{1}H NMR δ in ppm (300 MHz, DMSO-d_6): 11.7(s, 1H, enolizable NH proton), 9.8 (s, 1H, CH=N), 7.6-8.0 (m, 5H, phenyl), 7.4-7.52 (m, 2H, dihydroxyphenyl rings),

^{13}C NMR δ in ppm (100 MHz, DMSO-d_6) 167 (CO), 165 (2C, hydroxyphenyl), 158 (CH=N), 132, 130, 128, 127 (6C, phenyl ring carbon) 107, 106 (hydroxyl phenyl ring).

M/z = 256 (M+1).

(E)-N'-(1H-imidazol-2-yl)methylene)benzohydrazide (B3) was derived from benzohydrazide and imidazole-2-carboxaldehyde. Yield: 96%. M.P. 179-181°C,

FT-IR: (ν in cm^{-1}) 3435, 3236, 3068, 2898, 1655, 1600, 1068, 683.

^{1}H NMR δ in ppm (300 MHz, DMSO-d_6): 12.9(s, 1H, imidazole ring NH proton), 11.9 (s, 1H, enolizable NH proton), 8.4 (s, 1H, CH=N), 7.4-7.9 (m, 5H, phenyl ring), 7.2 & 7.1 (s, 1H, imidazole ring),

^{13}C NMR δ in ppm (100 MHz, DMSO-d_6) 163 (CO), 142 (CH=N), 133, 131, 129, 127 (phenyl ring), 133, 119, 118 (imidazole ring).

M/z = 214 (M+1).

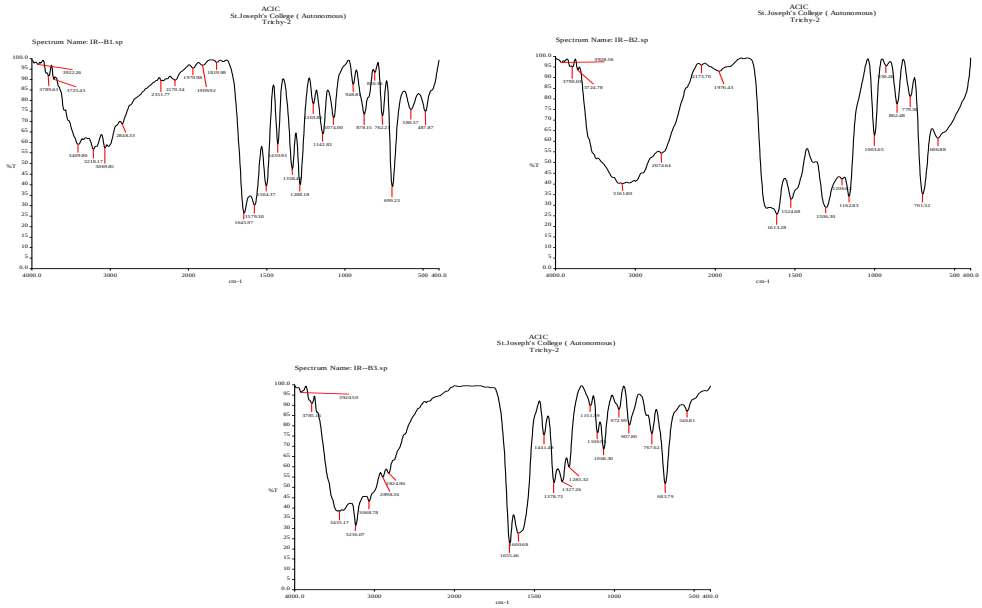


Fig. 1 IR spectra of B1, B2 and B3

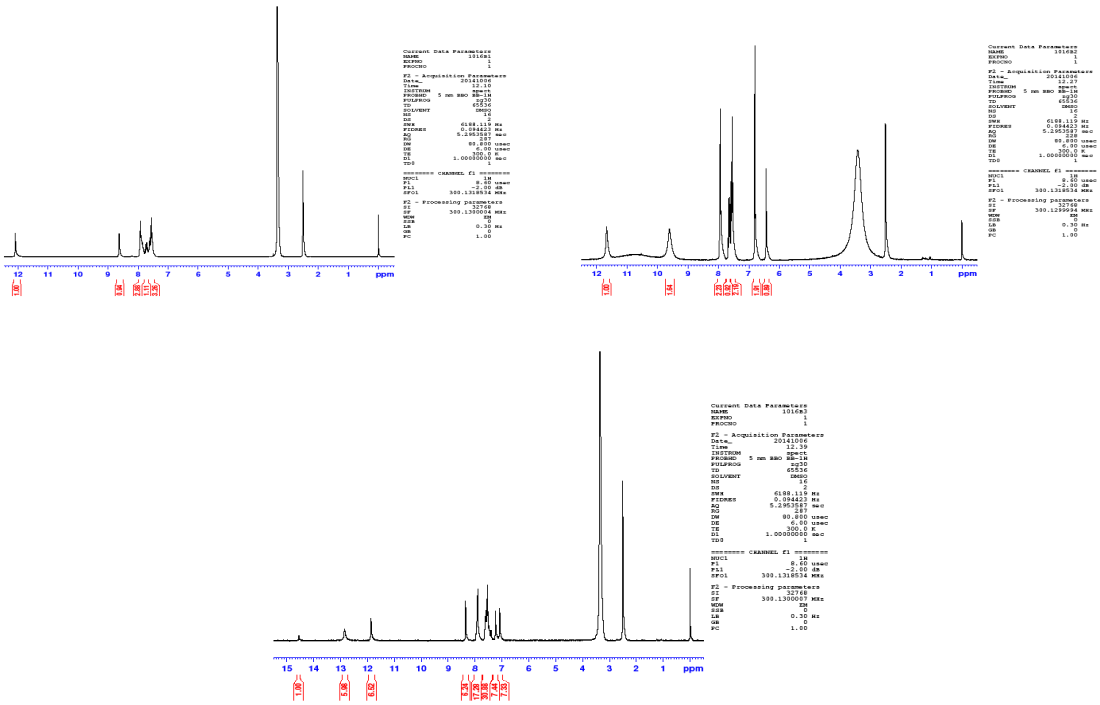


Fig 2. ^{1}H NMR spectrum of B1, B2 and B3

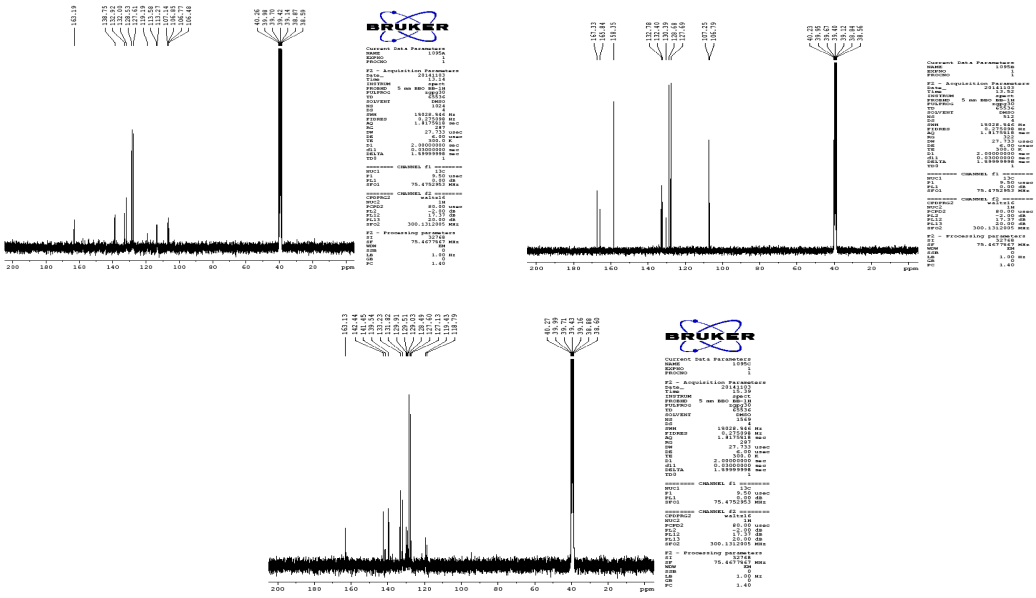


Fig 3. ^{13}C NMR spectrum of B1, B2 and B3

CONCLUSION

In conclusion, we have synthesized of Schiff base using simple and convenient method. This method produces these products in good yields, with a short reaction time and easy workup. Product is isolated by simple vaccum filteration. The isolated products are very pure, do not need any column purification and environmental friendly. This study opens up a new area of cost-effective synthesis of potentially biologically active Schiff base compounds.

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