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Syntheses and characterization of pyrrole containing hydrazones

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ABSTRACT

Pyrrole hydrazones have been extensively studied as a building blocks for the synthesis of various representatives for pyrrole family,especially condenced heterocycles genetically related to pyrrole.Pyrrole hydrazones bearing functional groups on the double bond (or those without them) are highly reactive starting compounds for the targeted synthesis of conjugated and fused heterocycles similar to natural pyrrole assemblies. In the present work we have synthesized Pyrrole hydrazones by condensation reactions between formyl pyrroles (Pyrrole-2-carboxaldehyde, pyrrole 2, 5-dicarboxaldehyde and 2,4-dimethyl-3-formy-l-5-carbethoxy pyrrole) and different hydrazide.The structure of synthesized compounds was confirmed by spectral (IR,^{1}H NMR) data.

KEYWORDS

Isoniazide;
Cyanoacetohydrazide;
Alcohols;
Chemotherapeutic.

INTRODUCTION

Pyrrole derivatives have emerged as chemotherapeutic agents potentially useful for inhibiting the activity of M. tuberculosis and other typical mycobacteria, including M. avium complex, an opportunistic pathogen that greatly contributes to the death of AIDS patients. Thiosemicarbazones[1,2] including those from heterocyclic aldehydes[4-7] show tuberculostatic, bacterial[8] and carcinostatic activity. Thiosemicarbazones[9,10] dithiosemicarbazones made from aliphatic and aromatic aldehydes and ketones are fungistatic. It is reported that some thiosemicarbazones and substituted thiosemicarbazones made from heterocyclic aldehydes are also effective against cellulolyts fungi.

EXPERIMENTAL

Reagents and solvents

The solvents were procured from E. Meck, Ranbaxy, S.D.Fine, Himedia and Qualigens. They were used after purification and drying by conventional methods[11]. The commercially available chemicals of analar grade of B.D.H., guaranteed reagent of Merck and analytical reagents or equivalent grade of others were used as such. Isonicotinic acid hydrazide (isoniazide) was purchased commercially and used as such.

p-nitrophenylhydrazine[12]

p-Nitroaniline 5.0 g (0.0356 mole) was dissolved in concentrated hydrochloric acid, 10.5 g (17.9 ml,

0.2868 mole) in 1ml of water and cooled quickly to a 0ºC in a freezing mixture so as to obtained the hydrochloride of the base in a fine state of division. The diazotization is affected in usual way by the gradual addition of the sodium nitrite 3.0 g (0.0434 mole) in 5 ml of water, cooled to 0ºC. The mixture was being vigorously stirred. The stirring is continued for few minutes after the addition of nitrite solution. The solution filtered quickly and then added from a dropping funnel to the ice cold solution of sodium sulfite 20.5 g (0.1621 mole) in 5 ml of water containing sodium hydroxide 2.0 g (0.050 mole).

The addition required 5 minutes then acidified to 35ml of concentrated hydrochloric acid and warmed on water bath at 55ºC for 3 minutes. It is left overnight, when a mass of yellow needles separated.

They are filtered, drained and the crystals heated on water bath for 7 minutes with 10 c.c. of concentrated hydrochloric acid. While the colour changes to orange, crystals remaining undissolved. After cooling for a time, the sodium salt and the nitro phenyl hydrazine hydrochloride are dissolved in water and 3.5 g (0.025 mole) of a cold saturated solution of sodium acetate added when the base separated. Recrystalised from alcohol. Yield: 2.10 g (38.4%), M.p.: 155-156ºC observed (157 ºC reported).

Cyanoacetohydrazide[13]

Ethyl cyanoacetate 2.26 g (2.12 ml, 0.0199 mole) and 1.0 g (0.97 ml, 0.0199 mole) of 100% hydrazine hydrate were dissolved in 10 ml ethanol each. There was drop wise addition of the solution of ethyl cyanoacetate to hydrazine solution with stirring at 0ºC. After 5 minutes white coloured precipitate obtained. Filter the precipitate and wash with 10 ml of diethylether and dried in air. Yield: 1.60 g (81%), M.p.: 107ºC.

Salicylhydrazide[14]

A mixture of 15.215 g (8.45 ml, 0.1 mole) of methyl salicylate and 7.509 g (7.29 ml, 0.15 mole) of 100% hydrazine hydrate in 100 ml of ethanol was refluxed for 10 hours. Refrigerate the solution for 16 hours. White coloured precipitate obtained. Precipitate was filtered and recyrstallised from 95% of ethanol. Yield: 6.12 g (40%), M.p.: 143-146ºC.

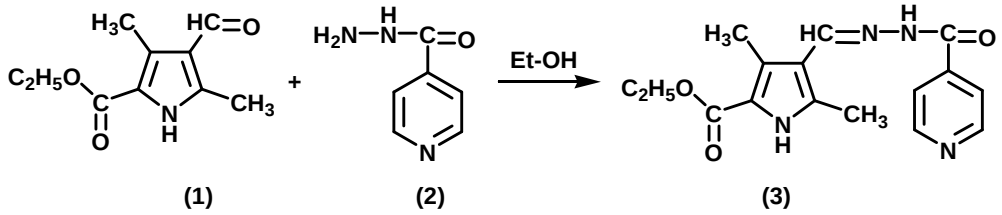
Oxalyldihydrazide[15]

14.614 g (13.5 ml, 0.1 mole) of diethyl oxalate was added drop wise to solution of 10.012 g (9.7 ml, 0.2 mole) of 100% hydrazine hydrate in a 100 ml beaker. The entire addition was carried out in an ice cooled bath with vigorous stirring. A white precipitate obtained was allowed to stand overnight, filtered, washed with ethanol and dried in air. Yield: 7.08 g (60%), M.p.: 240º C decomposed (243-244º C reported).

Pyrrole-2-carboxaldehyde[16]

In a 250 ml three necked round bottomed flask, fitted with a stirrer, a dropping funnel and a reflux condenser is placed 7.31 g (7.7 ml, 0.1 mole) of DMF. The flask is immersed in an ice-bath and the internal temperature is maintained at 10-20ºC. while 15.333 g (9.32 ml 0.1 mole) of $POCl_3$ is added through the dropping funnel over a period of 15 minutes. An exothermic reaction occurs with a formation of phosphorus oxy chloride dimethyl formamide complex. The ice-bath is removed and the mixture is stirred for 15 minutes. The ice-bath is replaced and 25ml of ethylene dichloride is added to the mixture when the internal temperature has been lowered to 5ºC, a solution of 6.7 g (6.9 ml, 0.1 mole) of freshly distilled pyrrole in 25ml of ethylene dichloride is added through a clean dropping funnel to the stirred cooled mixture over a period of 1hour.

After addition is completed, the ice-bath is replaced with a heating mantle and the mixture is stirred at the reflux temperature for 15 minutes during which time there is copious evolution of hydrogen chloride. The mixture is cooled to 25-35ºC and it is added through the dropping funnel a solution of 74 g (0.5 mole) of sodium acetate trihydrate in about 100 ml of water cautiously at first then as rapidly as possible. The reaction mixture is again refluxed for 15 minutes. Vigorous stirring maintained all the while. Cooled mixture is transferred to a 250 ml separatory funnel and the ethylene dichloride layer is removed. The aqueous phase is extracted three times with a total of 100 ml of ether. The ether and ethylene dichloride solutions are combined and washed with three 10ml portion of saturated aqueous sodium carbonate solution which is added cautiously at first to avoid too rapid evolution of CO_2. The non aqueous solution is then dried over anhydrous sodium carbonate. The solvent are distilled and remaining liquid is trans-



Scheme 1

ferred to a distilling flask with splash head condenser and distilled from an oil-bath under reduced pressure. Yield: 6.2 g (65%), M.p.: 41-42ºC.

Pyrrole-2,5-dicarboxaldehyde

In spite of the growing demand in recent years in pyrrole 2,5-dicarbaldehydes and its analogues, few procedures for their synthesis have been reported with the Clzy[17] and Vilsmeier-Haack[18], remaining the method of choice. pyrrole 2,5-dicarbaldehydes was prepared as per following procedure[19].

Aqueous 3M sodium hydroxide (30 ml) was refluxed for two hours with ethyl α-cyano-5-formyl 2-pyrrole acrylate[20] 1.650 g, 0.0075 mole) which dissolved within few minutes. The solution was acidified below 20ºC with 2M H_2SO_4 to pH 4.5 and then extracted with ethyl acetate (3x100ml). Solvent was distilled and residue obtained was purified by sublimation in vacuum to give a shiny white crystalline compound. Yield: 1.020 g (62%), M.p.: 121-122ºC observed (122-123ºC reported).

2,4-dimethyl-3-formyl-5-carbethoxy pyrrole[21]

To a cold mixture of 2.68 g (0.0160 mole) of 2-carbethoxy-3,5-dimethyl pyrrole[22] and 1.46 g (1.54 ml, 0.0199 mole) of DMF, there was gradually added 3.08 g (1.86 ml, 0.0200 mole) $POCl_3$ through a condenser which was then connected to a calcium chloride tube. After the vigorous reaction was over, the reaction mixture was refluxed on a steam-bath for two hours. The brown mass was then stirred with ice-water and neutralized to congo red with a saturated solution of sodium acetate. The crude 2,4-dimethyl-3-formyl-5-carbethoxy pyrrole was filtered, washed with a small amount of cold water and recrystallized with 50% alcohol. Yield: 2.65 g (89.5%), M.p.: 140-142ºC observed (145-145.5º C reported).

Physico-chemical techniques

TLC was routinely used to check the formation and status of products on silica Gel-G or alumina. Ambassador® melting point apparatus based on electrically controlled heating device was used for melting point determination using capillary tubes open on one side and are uncorrected. Ambassador® melting point apparatus provided a temperature range from room temperature to 360°C. The infrared spectra of products were recorded (4000-500 cm^{-1}) in KBr disc, using a Schimadzu 8201 PCFT IR spectrometer in Regional Sophisticated Instrumentation Centre, at Central Drug Research Institute, Lucknow. Proton nuclear magnetic Resonance (^1H NMR spectrum) was recorded on Bruker DRX-300 spectrometer (300 MHz FT NMR) instrument using tetramethylsilane as an internal reference. The ^1H NMR spectra were taken in $CDCl_3$, MeOD, unless otherwise stated. The chemical shift values are expressed in δ-scale.

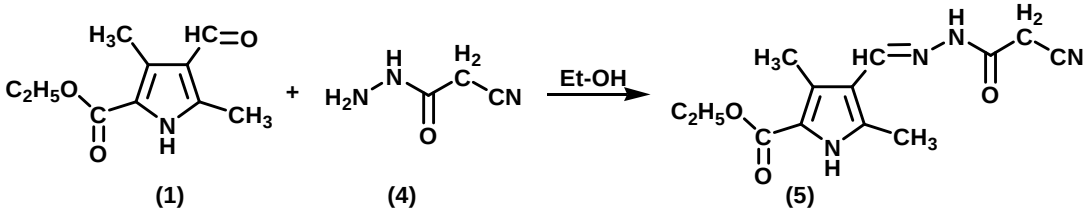
Synthesis of pyrrole hydrazones

Synthesis of 2,4-dimethyl 5-carbethoxy 3-formyl pyrrole isonicotinic acid hydrazone (3) (Scheme 1)

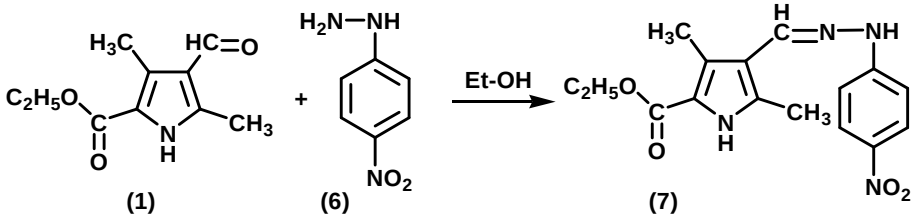
2.380 g (0.01219 mole) 2,4-dimethyl-3-formyl-5-carbethoxy pyrrole was dissolved in 50 ml absolute ethyl alcohol and 1.671 g (0.01218 mole) of Isoniazide was dissolved in 50 ml of absolute ethyl alcohol. At room temperature (28°C) isonicotinic acid hydrazide solution was added drop-wise to solution of pyrrole with stirring. Colour of the solution was changed to light yellow on reflux the solution for 28 hours. Yellow precipitate occurred on refluxing for 52 hours. Solution was concentrate and the precipitate was filtered. The product was recrystallised from 95 % alcohol. Yield: 3.06 g (79.89 %), M.p.: Compound melts at 210°C with decomposition up to 240°C.

Infrared spectra

IR (KBr) cm^{-1}: 3273.1 (NH, pyrrole), 3482.01 (br, NH, amide), 1672.8 (C=O, ester), 1605.91 (C=N), 1642.9 (C=O, amide) 2982.7 (CH_3), 2922.1 (CH_2)



Scheme 2



Scheme 3

and 1448.41 (C-H bending), 1234.61 (C-O st.), 1569.9 (C=C).

^{1}H NMR spectrum

^{1}H NMR (Me-OH) δ in ppm: 8.12 (s,1H), 6.88 (s, 1H, Schiff), 2.766-2.695 (q, 2H), 0.971-0.913 (t, 3H), 6.31 (d, 2H, pyridine C_3-H and C_5-H), 7.17 (d, 2H, pyridine C_2-H and C_6-H), 2.25(α-CH_3), 1.748 (β-CH_3), 4.93(NH, amide).

Synthesis of 2,4-dimethyl 5-carbethoxy 3-formyl-pyrrole cyanoacetic acid hydrazone (5) (Scheme 2)

0.195 g (0.001 mole) of 2, 4-dimethyl-3-formyl-5-carbethoxy pyrrole was dissolved in 15 ml of absolute ethyl alcohol and 0.099 g (0.001 mole) of cyanoacetohydrazide was dissolved in 15 ml of absolute alcohol. At room temperature (35ºC) there was drop-wise addition of solution of hydrazide to solution of pyrrole with stirring. Resulting solution was refluxed for 2 days. White color precipitate was obtained. Precipitate was filter and washed with 15 ml of alcohol and dried in air. Yield: 150 mg (54.2 %), M.p.: 233ºC decomposed without melting.

Infrared spectra

IR (KBr) cm^{-1}: 3282.0 (NH, pyrr), 2261.6 (C=N), 1661.61 (C=O), 1600 (C=N), 2987.0 (CH_3), 2927.1 (CH_2), 1569.8 (C=C).

^{1}H NMR spectrum

^{1}H NMR (Me-OH) δ in ppm: 8.205 (s, 1H, pyrrole), 8.053 (s, 1H, Schiff), 4.277-4.348 (q, 2H), 1.310-1.401 (t, 3H), 2.450 (α-CH_3), 2.423 (β-CH_3), 2.482-2.474 (CH_2).

Synthesis of 2,4-dimethyl 5-carbethoxy 3-formyl pyrrole p-nitrophenyl hydrazone (7) (Scheme 3)

0.19521 g (0.001 mole) of 2, 4-dimethyl-3-formyl-5-carbethoxy pyrrole was dissolved in 15 ml of absolute ethyl alcohol and 0.15314 g (0.001 mole) of p-nitro phenyl hydrazine was dissolved in 15 ml of absolute ethyl alcohol. At room temperature (30°C) there was drop wise addition of the solution of p-nitro phenylhydrazine to solution of pyrrole with stirring. Color changed to dark yellow. Color changes to orange red and slight amount of red colored precipitate occurred when solution was refluxed two hours. Further solution was refluxed for 19 hrs, amount of precipitate increased. Precipitate was filtered, washed with 10 ml of alcohol and recrystallised from alcohol. Yield: 210 mg (63.63%), M.p.: while melting point determination compound turns black at 210ºC with rising in capillary up to 240ºC.

Infrared spectra

IR (KBr) cm^{-1}: 3297.3 (NH, pyrrole), 1673.11 (C=O), 1602.61 (C=N), 1351.41 (NO_2), 1230.1 (C-O-C, bending), 2972.7 (CH_3), 2882.7 (CH_2), 1500.6 (C=C).

^{1}H NMR spectrum

^{1}H NMR ($CDCl_3$) δ in ppm: 8.829 (br, 1H, pyrr), 7.871 (1H, Schiff), 1.407-1.359 (t, 3H), 4.349-4.327 (q, 2H), 2.5104 (α-CH_3), 1.256 (β-CH_3), 4.67(NH), 8.158 (d, 2H, benzene C_2-H and C_6-H), 7.0128 (d,

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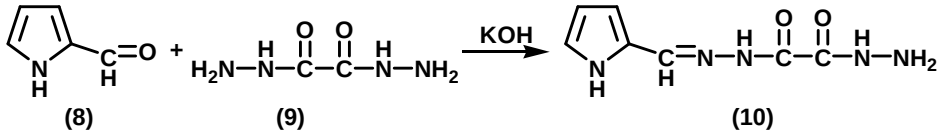
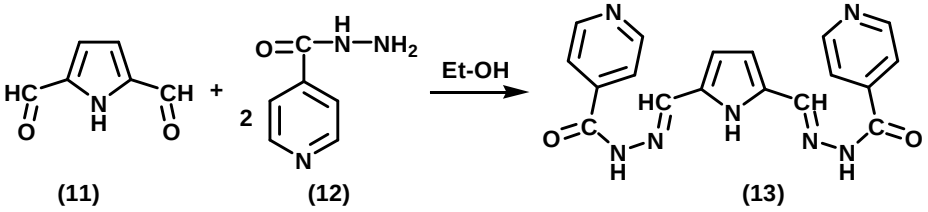


Scheme 4



Scheme 5

2H, benzene C_3-H and C_5-H).

Synthesis of pyrrole 2-formaldehyde oxalic acid hydrazone (10) (Scheme 4)

0.095 g (0.001 mole) of pyrrole -2-carboxaldehyde was dissolved in 10 ml of water and 0.132 g (0.001 mole) of oxalyl dihydrazide was dissolved in 30 ml of water. At room temperature, there was drop wise addition of oxalyl dihydrazide solution to solution of pyrrole with stirring. Color changes to very light yellow. 0.114 ml 1N KOH solution was added. After 1 hour stirring precipitation started. Stirring was continued for overnight. Precipitate was filtered and washed with a 10 ml of water and dried in air. Yield: 110 mg (65.80 %), M.p.: At 245ºC colour changes from creamy white to dark brown. At 255ºC sublimation with vapour in the middle of the capillary.

Infrared spectra

IR (KBr) cm^{-1}: 3239.71 (NH, pyrrole), 1654.31 (C=O), 1618.21 (C=N), 1516.2 (C=C), 3285.5 (NH_2).

^{1}H NMR spectrum

^{1}H NMR (Me-OD) δ in ppm: 8.203 (s, 1H, pyrrole), 6.987 (s, 1H, Schiff), 4.594 (s, 1H, NH), 7.893 (s, 1H, C_3, pyrr), 6.228 (d, 1H, C_4, pyrr), 6.560 (dd, 1H, C_5, pyrr), 4.726 (1H, NH).

Synthesis of pyrrole 2,5-diformaldehyde isonicotinic acid hydrazone (13) (Scheme 5)

0.123 g (0.001mole) of pyrrole-2,5-dicarboxaldehyde was dissolved in 50 ml of absolute ethyl alcohol and 0.274 g (0.002 mole) of isonicotinic acid hydrazide was dissolved in 50 ml of absolute ethyl alcohol. At room temperature (32ºC), there was dropwise addition of solution of hydrazide to solution of pyrrole carboxaldehyde with continuous stirring. During addition color changed to light green with slight amount of yellow precipitate. Solution was refluxed for 22 hrs, solvent was evaporated, and residue is washed with a 20 ml of ethanol and dried under vacuum. Yield: 170 mg (47.09 %), M.p.: At 244ºC color changes from fluorescent yellow to black with melting.

Infrared spectra

IR (KBr) cm^{-1}: 3374.21 (NH, pyrrole), 1594.21 (C=N), 1642.1 (C=O), 1481.51 (C=C).

^{1}H NMR spectrum

^{1}H NMR (Me-OD) δ in ppm: 9.412 (NH, pyrr), 8.218 (s, 2H, schiff), 6.663 (1H, pyrr), 4.612 (s, 1H, amide), 7.882-7.903 (dd, 2H, pyridine C_3-H and C_5-H), 8.744-8.765 (dd, 2H, pyridine C_2-H and C_6-H).

RESULT AND DISCUSSION

The structure of the formed compound 3,5,7,10 and 13 are given on the basis of their spectral analysis. The IR spectra of compound 2,4-dimethyl 5-carbethoxy 3-formyl pyrrole isonicotinic acid hydrazone **(3)**, shows Schiff linkage at 1605.9 cm^{-1} and C = C stretching occurs at 1569.9 cm^{-1}. The carbonyl group of ester shows a band at 1672.8 cm^{-1} and of amide is at 1642.9 Cm^{-1}. The band at 3273.1 cm^{-1} shows pyrrolic NH stretching. The presence of carbonyl group of ester and amide and Schiff linkage supports the structure.

^{1}H NMR of the compound shows a quartet of methylene proton at δ 2.742 and triplet of methyl pro-

ton at δ 0.930. A broad singlet peak at δ 8.12 was the pyrrolic NH and one proton of imine linkage appears as a sharp singlet at δ 6.88. The pyridine proton occurs as doublet at δ 7.17 and δ 6.31. Above information support the formation of 2, 4-dimethyl 5-carbethoxy 3-formyl pyrrole isonicotinic acid hydrazone as **(3)**.

The IR spectra of compound 2, 4-dimethyl 5-carbethoxy 3-formyl pyrrole cyanoacetic acid hydrazone **(5)** show Schiff linkage at 1600.0 cm^{-1} and C=C stretching occurs at 1569.8 cm^{-1}. The carbonyl group shows a band at 1661.6 cm^{-1}. The band at 3282.0 cm^{-1} shows pyrrolic NH stretching. A sharp band at 2261.6 cm^{-1} shows the presence of nitrile.

^1H NMR of the compound shows a quartet of methylene proton at δ 4.324 and a triplet of methyl proton at δ 1.378. A singlet peak at δ 8.205 shows pyrrolic NH and one proton of imine linkage as a sharp singlet at δ 8.053. The above data support the formation of 2, 4-dimethyl 5-carbethoxy 3-formyl pyrrole cyanoacetic acid hydrazone as structure **(5)**.

The IR spectra of compound 2,4-dimethyl 5-carbethoxy 3-formyl pyrrole p-nitrophenyl hydrazone **(7)** shows Schiff linkage at 1602.6 cm^{-1} and C=C stretching occurs at 1500.6 cm^{-1}.The carbonyl group of ester shows a band at 1673.1 cm^{-1}. The band at 3297.3 cm^{-1} shows pyrrolic NH stretching. The band at 1351.4 cm^{-1} shows stretching of NO group.

^1H NMR of the compound shows a quartet of methylene proton at δ 4.327 and triplet of methyl proton at δ 1.3594. A broad singlet peak at δ 8.829 shows pyrrolic NH and one proton of imine linkage as a sharp singlet at δ 7.871. Above information gives the possible structure of compound as **(7)**.

The IR spectrum of the compound pyrrole 2-formaldehyde oxalic acid hydrazone **(10)** shows schiff linkage at 1618.2 cm^{-1}. The band at 3239.7 cm^{-1} shows pyrrolic NH stretching and a band at 3285.5 cm^{-1} shows the NH stretching. The carbonyl group stretching appears at 1654.3 cm^{-1}.

^1H NMR of the compound shows a singlet peak at δ 8.203 of pyrrolic NH and one proton of imine linkage shows a sharp singlet at δ 6.987. A singlet peak of amino group appears at δ 4.594. Above information gives the possible structure of compound as **(10)**.

The IR spectrum of the compound pyrrole 2,5-diformaldehyde isnicotinic acid hydrazone **(13)** shows Schiff linkage at 1594.2 cm^{-1}. A broad absorption at 1642.1 cm^{-1} indicates the presence of carbonyl group too. The C=C stretching occurs at 1481.5 cm^{-1}. The band at 3374.2 cm^{-1} shows pyrrolic NH stretching.

^1H NMR of the compound shows a singlet peak at δ 9.412 of pyrrolic NH and one proton of imine linkage appears as a sharp singlet at δ 8.218. The pyridine proton occurs as quartet at δ 8.759 and δ 7.898. A singlet peak of amino group appears at δ 4.612. Above information gives the possible structure of compound as **(13)**.

CONCLUSIONS

Pyrrole is a heterocyclic aromatic organic compound, a five-membered ring with the formula C_4H_5N. Pyrrole undergoes electrophilic substitution predominantly at the 2 and 5 positions, though the substitution product at positions 3 and 4 is obtained in low yields. Keeping in mind the antibacterial activities of above pyrrole derivatives some new pyrrole acid hydrazides have been synthesized. Therefore, the investigation with objectives of synthesis and characterization hydrazones of pyrrole-2-carboxaldehyde, pyrrole 2, 5-dicarboxaldehyde and 2, 4-dimethyl-3-formyl-5-carbethoxy pyrrole with isonicotinic acid hydrazide, salicylhydrazide, cyanoacetohydrazide, oxalyl dihydrazide and p-nitrophenylhydrazine were carried out.

ABBREVIATIONS

KOH = Potassium hydroxide
$CDCl_3$= Deuterated chloroform
EtOH=Ethanol
$POCl_3$= Phosporous oxychloride
DMF = Dimethylformamide
s = singlet
hrs = hours
d = doublet
t = triplet
q = quartet
pyrr=pyrrole
dd=double doublet

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