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Synthesis of *N*-Containing Energy Material Compounds

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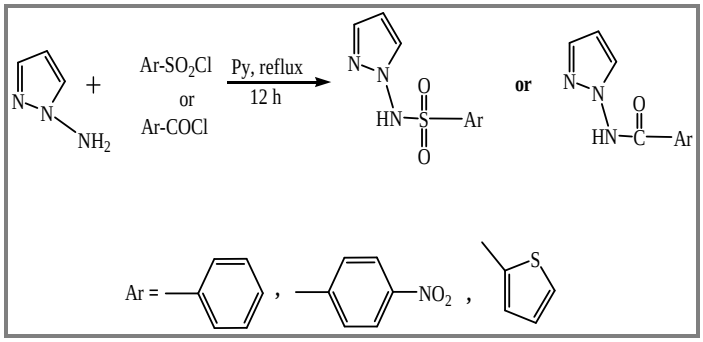
ABSTRACT

Pyrazole analogues are found in organic synthesis for designing of pharmaceutical, agrochemicals and high energy performance materials. In this paper, we designed synthesized and characterized thesulfonyl and acyl derivatives of N-aminopyrazole.

Graphical Abstract



Synthesis of sulfonated/acylated amides of 1-aminopyrazole.

Keywords: Pyrazole, Amino pyrazole, Energetic materials, Sulfonated amide.

INTRODUCTION

In last two decades, pyrazole derivatives have had tremendous impact in agrochemicals [**1**], dyes [**2**], pharmaceuticals with numerousranges of biological activities such as antimicrobial [**3**], antibacterial [**4**], antitumor [**5**], antinociceptive [**6**] and anti-inflammatory [**7**].

Due to increased demand of energetic materials in the past era, functionalization of pyrazole with energetic substituted groups has made progress [**8**]. Consequently; this has become a strong research area for the preparation of such materials in terms of excellent explosion properties, remarkably high

density, high positive heat of formation, positive oxygen balances, good thermal stability and impact insensitivity [9].

Li *et al*., computationally studied the thermal stabilities and heat of formations of amino-, nitro- and azido substituted pyrazole derivatives. The calculations predicted that heat of formations increases with the increasing number of amino and azido groups, while the heat of formations primarily decrease then increase as the number of nitro groups increasing [10]. In this regard, several polynitro-functionalized pyrazoles were designed as high-performance energetic materials and oxidizer [11]. Previously, we have reported the imine and some acyl derivatives of pyrazole [12]. In lieu of all this importance of pyrazole derivatives and efforts to the basic chemistry of *N*-amino pyrazole, herein, a synthetic approach for the preparation of novel sulfonyl and acyl derivatives of *N*-aminopyrazole is described.

MATERIALS AND METHODS

1H-Pyrazol-1-amine (3): Compound **3** was prepared using experimental procedure given in ref [12].

***N*-(1*H*-pyrazol-1-yl)benzenesulfonamide 5a:** A mixture of 1-aminopyrazole (**3**) 500 mg and benzenesulfonyl chloride (**4a**) 1.06 gand pyridine 3 mL in toluene (20mL)was refluxed for 10 h. Then, the solvent was removed under reduced pressure, and the residue was taken in chloroform. The residue was washed with water to give the crude product. Recrystallization of the crude product with DCM and hexane afforded pure product as a crystalline brown solid **5a**. Yield: 66 %; Mp: 160-170^{0}C; ^{1}H NMR (DMSO) δ(ppm):6.28 (t, *J* = 2.4 Hz, 1H), 7.13-7.26 (m, 4H), 7.34 (d, *J* = 1.5 Hz, 1H), 7.46-7.51(m, 1H), 7.54(d, *J* = 1.5, 1H), 9.98 (br s, 1H).^{13}C NMR (DMSO) δ (ppm): 103, 127, 129, 131, 138, 139.

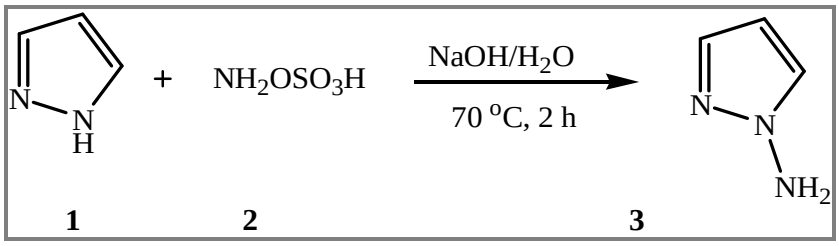
4-Nitro-*N*-(1*H*-pyrazol-1-yl)benzenesulfonamide 5b: A solution of 1-aminopyrazole (**3**) 500 mg in toluene (25 mL), were added 4-nitrobenzenesulfonyl chloride (**4b**) 1.41 g and pyridine (5 mL).The reaction mixture was refluxed for 12 h. The solvent was removed under reduced pressure, and the residue was taken in chloroform. The residue was washed with water to give the crude product. Recrystallization of the crude product with chloroform and hexane afforded pure product as a crystalline brown solid **5b**.Mp: 200-205^{o}C; Yield: 62 %; ^{1}H NMR (DMSO) δ (ppm):2.1 (bs, NH), 6.56 (t, 1H), 7.34 (d, 1H), 8.11-8.14 (m, 3H), 8.39(d, 2H).^{13}C NMR (DMSO) δ (ppm):103 , 124, 128, 129, 138, 151.

N-(1H-pyrazol-1-yl) thiophene-2-carboxamide 5c: A solution of 1-aminopyrazole (**3**) 500 mg in toluene (30 mL), was added thiophene 2-carbonyl chloride (**4c**) 1.41 g. The reaction mixture was stirred at room temperature for 20 h in the presence of triethyl amine. The expected product was precipitated along with triethylammonium chloride, which upon washing with saturated solution of sodium hydrogen carbonate to yield N-(1H-pyrazol-1-yl)thiophene-2-carboxamide **5c**as a white crystalline solid. Yield:65%.Mp: 135-140^{o}C; ^{1}H NMR (DMSO) δ (ppm): 2.9 (bs, 1H), 6.50-6.57 (t, 3H), 7.34 (d, 1H), 7.42 (d, 1H), 8.0 (bs, NH), 8.11 (d, 1H).^{13}C NMR (DMSO) δ (ppm): 40, 105, 133, 134, 135, 138, 168.

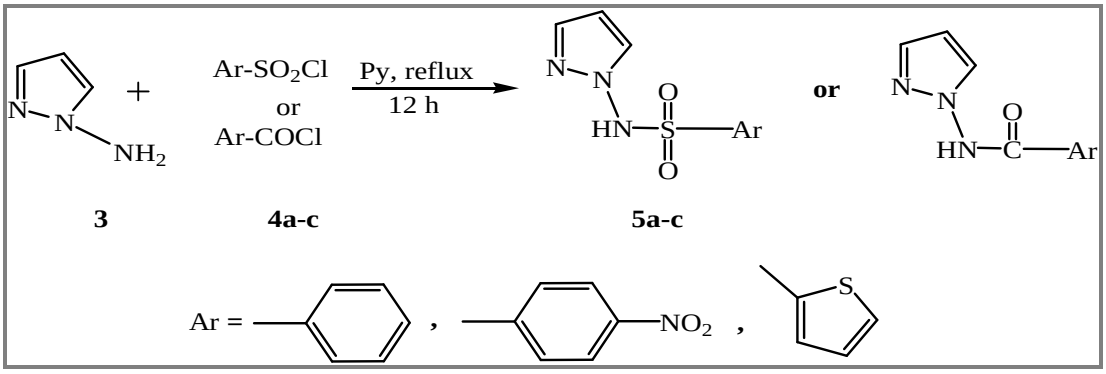
RESULTS AND DISCUSSION

The sulfonated and acylated amides of pyrazole **5a-c** have been synthesized as shown in schemes 1 and 2. First, 1-aminopyrazole **3**was prepared from pyrazole**1**according to a reported procedure (Scheme 1) [12]. Further, 1-Aminopyrazole **3** was refluxed/stirred with aromatic sulfonyl/acyl chlorides **4a-c** to give corresponding sulfonated/acylated amides **5a-c** (Scheme 2, Table 1). All the synthesized compounds **5a-c** were purified by recrystallization and characterized by spectroscopic techniques (IR, ^{1}H-NMR and ^{13}C-NMR) and elemental analysis. The IR spectra of the compound**5a**showed the presence of the characteristic bands for SO_2 in the 1330–1630 cm^{-1} range. In

addition, the ^{1}H-NMR spectra of this compound revealed the presence of a broad singlet amino (NH) peak at 9.98 ppm (br s, 1H) and multiplets due to the aromatic protons 7.13-7.26 ppm (m, 4H).

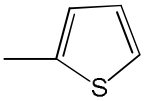


Scheme 1. Synthesis of N-Aminopyrazole.



Scheme 2. Synthesis of Pyrazolyl sulfonated/acyl amide (5a-b) and (5a-c).

Table 1. Pyrazolylsulfonated/acylamide (5a-c)

S.No.	Aromatic sulfonyl /acyl chlorides (Ar) (4a-c)	Reaction conditions	Sulfonated/Acylatedpyrazoles (5a-c)	Yield (%)
1	C_6H_5-	Toluene, Pyridine, reflux, 10 h	**5a**	66
2	*p*-O_2N-C_6H_4-	Toluene,Pyridine, reflux, 12 h	**5b**	62
3		Toluene, rt, triethyl amine 20 h	**5c**	65

APPLICATION

Marra and co-workers have reported some sulphonamide compounds against *Leishmania infantum* and *L. amazonensis* and display their cytotoxicity to mammalian cells [13]. The synthesized pyrazole derivatives can show antiparasitic /antibacterial activities and can be used in the field of energetic materials.

CONCLUSION

Developed a facile and convenient method to synthesize, purify and characterize the newly pyrazolyl sulphonamides/acylated amides **5a-c** from *N*-aminopyrazole.The moderate yield of the pyrazole derivatives were found to be in the range from 62-66% and these molecules were characterized by ^{1}H and ^{13}CNMR spectra.

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Conflict of interest: The author declares no conflict of interest.

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