



SYNTHESES OF IMINE AND ACYL DERIVATIVES FROM N-AMINOPYRAZOLE

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ABSTRACT

N-Pyrazoles are important auxiliary because of its biological and chemical relevance. Carefully examination has shown that little is known about the fundamental chemistry of *N*-aminopyrazole, so we have synthesized imine and acyl derivatives of *N*-aminopyrazole **5a-d** and **7a-b**, respectively.

Keywords: Aminating agent , *N*-Aminopyrazole, Imines, Pyrazole.

I. INTRODUCTION

The search for the promising high-energy materials during the last one-decade has led to the discovery of numerous of energetic oxidizers, fuels and explosives for possible use as an energetic ingredient in explosives formulations.^{1,2,3} Several heterocyclic compounds bearing nitro and N-oxide substituents have been studied as possible replacement for sensitive explosives, viz., 2,6-Bis(picrylamino)-3,5-dinitropyridine and nitrotriazolone. N-Aminoazoles are important building block used for the synthesis of energetic materials and energetic salts, ligands for metal complexes in gas-generating agents, fungicides, nitrification inhibitors in combination with fertilizers.

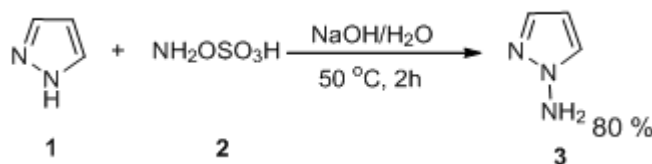
Pyrazole derivatives have high formation enthalpy, good thermal stability and safety characteristics which enable them to be used in energetic formulations as oxidizers, plasticizers and elastomeric binders.⁴ Few examples include explosive ingredients such as 4-amino-3,5-dinitropyrazole and 3,6-dinitropyrazolo[4,3-*c*]pyrazoles (DNPP) with good thermal stability, performance and density 1.90 and 1.84 g/ml, respectively.^{3,5-6}

Surprisingly, very less is known about the fundamental chemistry of 1-aminopyrazole in terms of its reaction with aldehydes, ketones, and acylating agents. We therefore aim to discover the best methods for the synthesis of novel Schiff bases and acylated salts and of 1-aminopyrazole.

II. RESULTS AND DISCUSSION

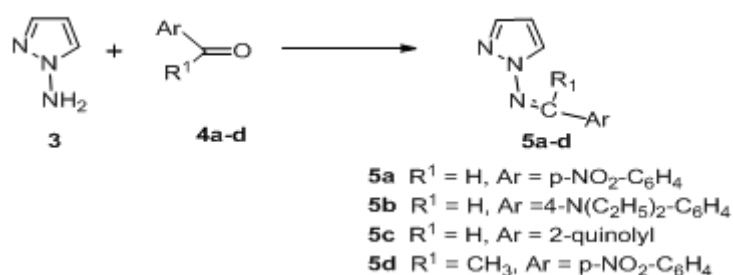
Syntheses

1-Aminopyrazole **3** was synthesized from pyrazole **1** and hydroxylamine O-sulfonic acid by modifying the literature procedure (Scheme 1).⁷ The literature procedure utilizes 3 equivalents of the aminating agent. However, experiments under similar conditions repeatedly yielded a crude product containing 75% of the product with 25% of the starting material. The use of 5 equivalents of the aminating agent undergoes complete conversion and after workup, 1-aminopyrazole was obtained in 70% yield.



Scheme 1. Syntheses of 1-aminopyrazole

1-Aminopyrazole **3** was coupled with aromatic aldehydes **4a-c** and ketone **4d** under different experimental conditions (Scheme 2, Table 1) to yield corresponding imines **5a-c** and **5d** in 60-73% yield.

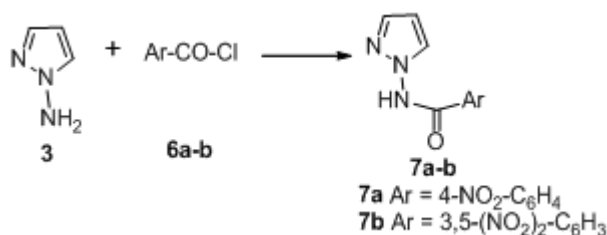


Scheme 2. Syntheses of imine derivatives of 1-aminopyrazole.

Table 1. Pyrazole Imines

S.No.	Aromatic aldehydes/ketone(Ar) (R^1) (4a-d)	Reaction conditions	Imines (5a-d)	Yield (%)	Mp °C
1.	($p\text{-O}_2\text{N-C}_6\text{H}_4$ -), (H)	EtOH/ H_2SO_4	5a	73	143-158
2.	4-N(C_2H_5) ₂ - C_6H_4), (H)	EtOH/ H_2SO_4 , 12 h	5b	88	104-106
3.	(2-Quinolyl-), (H)	EtOH, 80 °C, 12 h	5c	60	104-105
4.	($p\text{-O}_2\text{N-C}_6\text{H}_4$ -), (CH_3)	THF/ $\text{CH}_3\text{SO}_3\text{H}$ / rt	5d	68	80-81

1-aminopyrazole **3** was acylated with 4-nitrobenzoylchloride **6a** and 3,5-dinitrobenzoyl chloride **6b** in refluxing with toluene (Scheme 3, Table 2) in the presence of triethyl amine to yield corresponding (1H-pyrazol-1-yl)benzamides **7a-b** in 65 and 68%, respectively. These compounds were characterized by ^1H and ^{13}C NMR spectroscopy.



Scheme 3. Syntheses of acyl derivatives of 1-aminopyrazole

Table 2. Pyrazolylacylamides

S.No.	Aromatic acyl chlorides (Ar) (6a-b)	Reaction conditions	Acylatedpyrazoles (7a-b)	Yield (%)	Mp °C
1.	<i>p</i> -NO ₂ -C ₆ H ₄ -	Toluene, reflux, Et ₃ N, 12 h	7a	65	204-210
2.	3,5-(NO ₂) ₂ -C ₆ H ₃	Toluene, reflux, Et ₃ N, 7 h	7b	68	165-168

III. CONCLUSION

1-Aminopyrazole **3** was synthesized in good yield from pyrazole **1** by modifying the literature procedure. We also discover the best methods for the synthesis of novel imine salts **5a-c** and acylated **7a-b** of 1-aminopyrazole and further these compounds can be used as explosive potential candidates.

IV. EXPERIMENTAL SECTION

1H-Pyrazol-1-amine (3)

To a solution of pyrazole **1** (2 g, 0.029 mol) in 30 ml water was added crushed sodium hydroxide (7.0 g, 0.17 mol). The solution was left to stir for 10 min at 60 °C. Hydroxylamine-O-sulfonic acid **2** (16.6 g, 0.14 mol) was added cautiously in small portions. The resulting mixture was heated at 70 °C for 2 h and stirred at room temperature for 1 h. The aqueous layer was extracted with 3X 30 mL of chloroform and dried over sodium sulfate, filtered and concentrated to give compound **3**. Colourless oil; Yield: 63 %; ¹H NMR (CDCl₃) δ: 5.54 (br s, 2H), 5.77 (s, 1H), 7.01 (d, *J* = 9.3 Hz, 2H); ¹³C NMR (CDCl₃) δ: 103.7, 128.8, 136.4.

N-(4-Nitrobenzylidene)-1H-pyrazol-1-amine (5a)

To a solution of 1-Aminopyrazole **3** (200 mg, 2.4 mmol) in ethanol (7 mL) was added *p*-Nitrobenzaldehyde **4a** (360 mg, 2.4 mmol) and conc. H₂SO₄ (2-3 drops) and the reaction mixture was stirred at room temperature for 6 h. The solid separated was filtered and dried under vacuum to yield compound **5a**. Yellow solid. Yield: 73 %; ¹H NMR (CDCl₃) δ: 6.44 (br s, 1H), 7.60 (br s, 1H), 7.74 (m, 1H), 7.96-8.02 (m, 2H), 8.27-8.36 (m, 2H), 9.21 (br s, 1H); ¹³C NMR (CDCl₃) δ: 107.2, 124.3, 128.9, 130.1, 138.9, 139.3, 147.0.

***N*-(Pyridine-4-ylmethylene)-1*H*-pyrazol-1-amine (5b)**

To a solution of 1-Aminopyrazole **3** (200 mg, 2.4 mmol) in dry THF (10 mL), 4-Pyridyl aldehyde **4b** (5 mmol) was added and refluxed for 20 h. After the completion of reaction, the mixture was allowed to cool at room temperature. THF was then evaporated completely and the residue was recrystallized by using DCM and hexane to obtain pure product **5b** as crystalline light brown solid. Yield: 62 %; ^1H NMR (CDCl_3) δ : 6.43 (br s, 1H), 7.60 (br s, 1H), 7.70 (br s, 1H), 7.72 (br s, 1H), 8.74 (br s, 1H), 9.11 (s, 1H); ^{13}C NMR (CDCl_3) δ : 107.1, 121.9, 130.0, 138.8, 140.5, 147.2, 150.6.

***N*-(Quinolin-2-ylmethylene)-1*H*-pyrazol-1-amine (5c)**

To a solution of 1-Aminopyrazole **3** (100 mg, 1.2 mmol) in abs ethyl alcohol (10 mL), 2-Quinolinecarbaldehyde **4c** (180 mg, 1.2 mmol) was added and the reaction mixture heated at 80 °C for 12 h. The reaction mixture was cooled at room temperature, and solvent was then evaporated completely to afford the crude product. Recrystallization of the crude product with ethyl alcohol afforded pure product as a brown solid **5c**. Yield: 60 %; ^1H NMR (CDCl_3) δ : 6.43 (br s, 1H), 7.58-7.62 (m, 2H), 7.72-7.88 (m, 3H), 8.15-8.41 (m, 3H), 9.39 (br s, 1H); ^{13}C NMR (CDCl_3) δ : 107.0, 118.7, 127.7, 128.6, 129.8, 129.9, 130.1, 136.7, 138.8, 148.2, 150.3, 152.8.

***N*-(1-(4-Nitrophenyl)ethylidene)-1*H*-pyrazol-1-amine (5d)**

To a solution of 1-aminopyrazole **3** (200 mg, 2.4 mmol) in dry THF (10 mL), *p*-Nitroacetophenone **4d** (397 mg, 2.4 mmol) and 2-3 drops of methane sulfonic acid were added and the reaction mixture stirred at room temperature for 8 h. The reaction mixture was then evaporated completely to afford the crude product. Recrystallization of the crude product with DCM and hexane afforded pure product as a crystalline orange-brown solid **5d**. Yield: 68 %; ^1H NMR (CDCl_3) δ : 2.84 (s, 3H), 6.40 (br s, 1H), 7.60 (br s, 1H), 7.72 (d, J = 1.5 Hz, 1H), 8.05 (s, 1H), 8.08 (s, 1H), 8.27 (s, 1H), 8.30 (s, 1H); ^{13}C NMR (CDCl_3) δ : 18.9, 105.9, 123.8, 128.2, 129.4, 130.6, 137.9, 144.8, 158.9.

4-Nitro-*N*-(1*H*-pyrazol-1-yl)benzamide (7a)

To a solution of 1-aminopyrazole **3** (200 mg, 2.4 mmol) in dry THF (15 mL), 4-nitrobenzoylchloride **6a** (445 mg, 2.4 mmol) was added and the reaction mixture refluxed for 7 h. The reaction mixture was then evaporated completely to afford the crude product. Recrystallization of the crude product with DCM and hexane afforded pure product as a crystalline brown solid **7a**. Yield: 65 %; ^1H NMR ($\text{DMSO}-d_6$) δ : 6.52 (br s, 1H), 7.40 ((br s, 1H), 8.0 (s, 1H), 8.11-8.18 (m, 2H), 8.44-8.47 (m, 2H); ^{13}C NMR ($\text{DMSO}-d_6$) δ : 103, 124, 129, 131, 138.1, 151.3.

3,5-Dinitro-*N*-(1*H*-pyrazol-1-yl)benzamide (7b)

To a solution of 1-aminopyrazole **3** (200 mg, 2.4 mmol) in dry THF (10 mL), 3,5-dinitrobenzoylchloride **6b** (552 mg, 2.4 mmol) was added and the reaction mixture refluxed for 12 h. The reaction mixture was then evaporated completely to afford the crude product. Recrystallization of the crude product with ethanol afforded pure product as a crystalline solid **7b**. Yield: 68 %; ^1H NMR ($\text{DMSO}-d_6$) δ : 6.56 (br s, 1H), 7.36 ((br s, 1H), 8.0 (s, 1H), 8.12 (s, 2H), 9.0-9.12 (m, 3H); ^{13}C NMR ($\text{DMSO}-d_6$) δ : 103.2, 121.5, 129, 131.1, 136, 138.1, 148.9.

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