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, Imine, Pyrazole.

I. INTRODUCTION

The search for the promising high-energy materials during the last one-decade has led to the discovery of numerous 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(picrylaminio)-3,5-dinitropyridine and nitrotiazolone. N-Aminopyrazoles 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.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 pyrazole¹ 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

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Aromatic aldehydes/ketone(Ar)</th>
<th>Reaction conditions</th>
<th>Imines (5a-d)</th>
<th>Yield (%)</th>
<th>Mp °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>(p-O2N-C6H4)-, (H)</td>
<td>EtOH/H2SO4</td>
<td>5a</td>
<td>73</td>
<td>143-158</td>
</tr>
<tr>
<td>2.</td>
<td>4-N(C2H5)2-C6H4), (H)</td>
<td>EtOH/H2SO4, 12 h</td>
<td>5b</td>
<td>88</td>
<td>104-106</td>
</tr>
<tr>
<td>3.</td>
<td>(2-Quinoyl-), (H)</td>
<td>EtOH, 80 °C, 12 h</td>
<td>5c</td>
<td>60</td>
<td>104-105</td>
</tr>
<tr>
<td>4.</td>
<td>(p-O2N-C6H4)-, (CH3)</td>
<td>THF/CH3SO3H/ rt</td>
<td>5d</td>
<td>68</td>
<td>80-81</td>
</tr>
</tbody>
</table>

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 13C NMR spectroscopy.
Scheme 3. Syntheses of acyl derivatives of 1-aminopyrazole

Table 2. Pyrazolylacylamides

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Aromatic acyl chlorides (Ar) (6a-b)</th>
<th>Reaction conditions</th>
<th>Acylatedpyrazoles (7a-b)</th>
<th>Yield (%)</th>
<th>Mp °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>p-NO$_2$C$_6$H$_4$</td>
<td>Toluene, reflux, Et$_3$N, 12 h</td>
<td>7a</td>
<td>65</td>
<td>204-210</td>
</tr>
<tr>
<td>2.</td>
<td>3,5-(NO$_2$)$_2$C$_6$H$_3$</td>
<td>Toluene, reflux, Et$_3$N, 7 h</td>
<td>7b</td>
<td>68</td>
<td>165-168</td>
</tr>
</tbody>
</table>

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 %; $^1$H NMR (CDCl$_3$) $\delta$: 5.54 (br s, 2H), 5.77 (s, 1H), 7.01 (d, $J = 9.3$ Hz, 2H); $^{13}$C NMR (CDCl$_3$) $\delta$: 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. H$_2$SO$_4$ (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 %; $^1$H NMR (CDCl$_3$) $\delta$: 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); $^{13}$C NMR (CDCl$_3$) $\delta$: 107.2, 124.3, 128.9, 130.1, 138.9, 139.3, 147.0.
N-(Pyridine-4-ylmethylene)-1H-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 (CDCl₃) 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); 13C NMR (CDCl₃) 107.1, 121.9, 130.0, 138.8, 140.5, 147.2, 150.6.

N-(Quinolin-2-ylmethylene)-1H-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 (CDCl₃) 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); 13C NMR (CDCl₃) 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)-1H-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 (CDCl₃) 2.84 (s, 3H), 6.40 (br s, 1H), 7.62 (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); 13C NMR (CDCl₃) 18.9, 105.9, 123.8, 128.2, 129.4, 130.6, 137.9, 144.8, 158.9.

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

To a solution of 1-aminopyrazole 3 (200 mg, 2.4 mmol) in dry THF (15 mL), 4-nitrobenzoyl chloride 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 (DMSO-d₆) 6.52 (br s, 1H), 7.40 (br s, 1H), 8.11-8.18 (m, 2H), 8.44-8.47 (m, 2H); 13C NMR (DMSO-d₆) 103, 124, 129, 131, 138.1, 151.3.

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

To a solution of 1-aminopyrazole 3 (200 mg, 2.4 mmol) in dry THF (10 mL), 3,5-dinitrobenzoyl chloride 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 (DMSO-d₆) 6.56 (br s, 1H), 7.36 ((br s, 1H), 8.0 (s, 1H), 8.12 (s, 2H), 9.0-9.12 (m, 3H); 13C NMR (DMSO-d₆) 103.2, 121.5, 129, 131.1, 136, 138.1, 148.9.

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REFERENCES


