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### Ring transformations in the reactions of 1,4-dinitropyrazole with N-nucleophiles

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### Abstract

The reactions of 1,4-dinitropyrazole with primary amines, hydrazines, hydroxylamine and amidines were studied. 1,4-Dinitropyrazole in these reactions served as the synthetic equiv. of nitromalonaldehyde. The reaction of dinitropyrazole with primary arylhydrazines proved to be a convenient approach to the synthesis of 1-aryl-4-nitropyrazoles.

### Keywords

nucleophiles, n, ring, 4, 1, reactions, dinitropyrazole, transformations

### Disciplines

Engineering | Physical Sciences and Mathematics

### Publication Details

Jedrysiak, R., Sawicki, M., Wagner, P. & Suwinski, J. (2007). Ring transformations in the reactions of 1,4-dinitropyrazole with N-nucleophiles. *ARKIVOC*, 2007 (vi), 103-111.

## Ring transformations in the reactions of 1,4-dinitropyrazole with *N*-nucleophiles

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**This paper is dedicated to Professor Jan Epsztajn – a very good colleague on the occasion of his 75<sup>th</sup> birthday**

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### Abstract

The reactions of 1,4-dinitropyrazole with primary amines, hydrazines, hydroxylamine and amidines were studied. 1,4-Dinitropyrazole in these reactions served as the synthetic equivalent of nitromalonaldehyde. The reaction of dinitropyrazole with primary arylhydrazines proved to be a convenient approach to the synthesis of 1-aryl-4-nitropyrazoles.

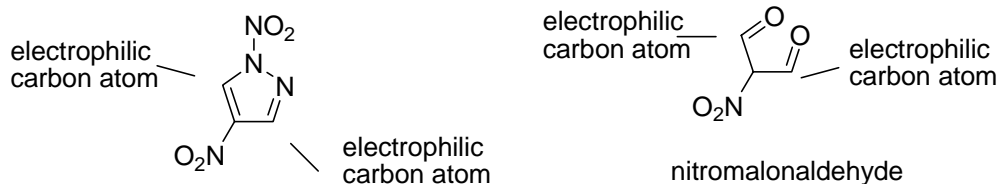
**Keywords:** Dinitropyrazole, nucleophile, amine, hydrazine, arylnitropyrazole, ring transformation

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### Introduction

Recently Nishiwaki *et al.* have shown<sup>1</sup> that  $\beta$ -formyl- $\beta$ -nitroenamines behave as the synthetic equivalents of unstable nitromalonaldehyde. We communicated<sup>2</sup> that 1,4-dinitropyrazole, even more readily available than  $\beta$ -formyl- $\beta$ -nitroenamines, can be used in some syntheses instead of nitromalonaldehyde or its stable but poorly soluble sodium salt. This can be easily understood by looking at structures disclosed below.

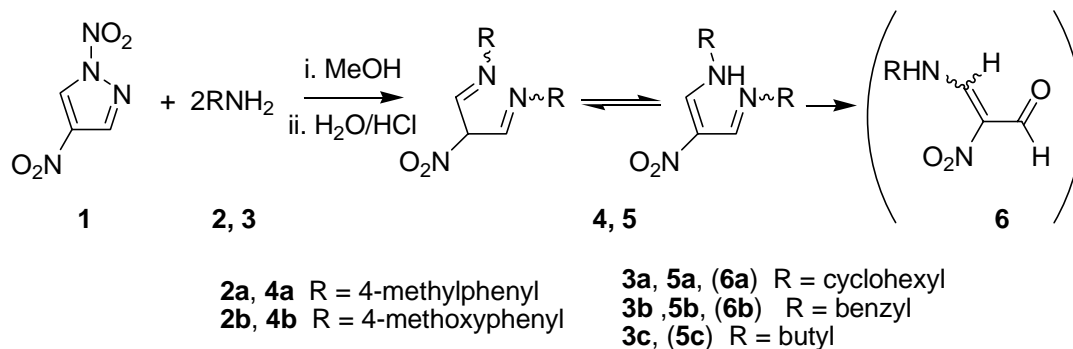
1,4-Dinitropyrazoles reacting with nucleophiles often afford 5-substituted-4-nitropyrazoles in *cine* nucleophilic substitution reactions. These reactions have been widely studied.<sup>3</sup> In contrast; the ring transformation reactions of 1,4-dinitropyrazoles have not been reported<sup>4</sup>, besides our recent preliminary communication.<sup>2</sup>



For several years, we have been studying the reactions of 1,4-dinitroimidazoles with *N*-nucleophiles. The reactions with compounds containing primary amino groups, when performed in polar protic solvents, have afforded high yields of the respectively 1-substituted 4-nitroimidazoles *via* a degenerated ring transformation reaction. An *anrorc*<sup>4</sup> mechanism of the reaction involves: i) the addition of the amine with the formation of a respective  $\sigma^H$  complex, ii) proton transfer, iii) the ring opening, and iv) the ring closure reaction followed by v) the elimination of nitroamide and rearomatization of the ring. The mechanism has been proved by us using spectroscopy, kinetic measurements, labeled and chiral nucleophiles.<sup>5</sup> We assumed that the reactions of 1,4-dinitropyrazole with some amino compounds would occur according to a similar mechanism. It was rather obvious that 1,4-dinitropyrazole would not undergo ring transformation reactions with mononucleophilic primary amines. In this case the reaction should afford only ring opening products since ring closure reactions would lead to unstable four member azacyclobutene derivatives. For 1,4-dinitropyrazole ring transformation reactions, dinucleophilic reagents would be necessary.

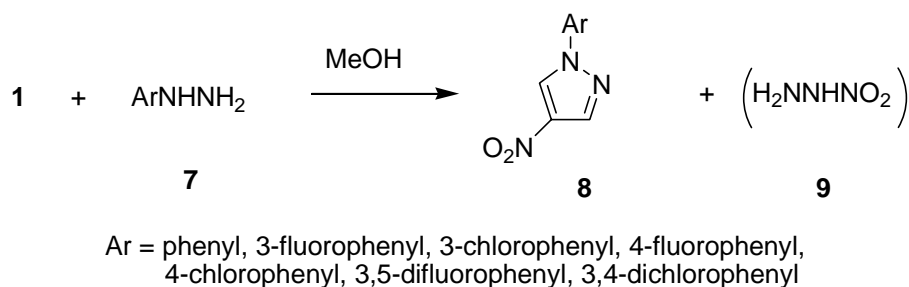
## Results and Discussion

One- or two-step nitration of commercially available pyrazole affords good yields of 1,4-dinitropyrazole (**1**).<sup>6</sup> Compound **1** is a reasonably stable and well soluble in many common organic solvents. The reactions of dinitropyrazole **1** (Scheme 1) with two equivalents of primary aromatic amines **2**, performed in aqueous methanol at ambient temperature, led to the pyrazole ring opening with the formation of known stereoisomeric 1,5-bis(aryl)-3-nitro-1,5-diaza-1,4-pentadienes (**4**).<sup>7</sup> The structures of products **4** were confirmed by a comparison of data obtained by us with those described in the chemical literature.<sup>7</sup> When similar reactions were carried out with aliphatic amines **3** only small amounts of linear compounds **5**<sup>8</sup> were present in the reaction solution together with mixtures of stereoisomeric 3-alkylamino-2-nitropropenals **6** ( $\beta$ -formyl- $\beta$ -nitroenamines)<sup>1,8</sup>. The structures of the later compounds were deduced from <sup>1</sup>H NMR and MS spectra of the mixtures.



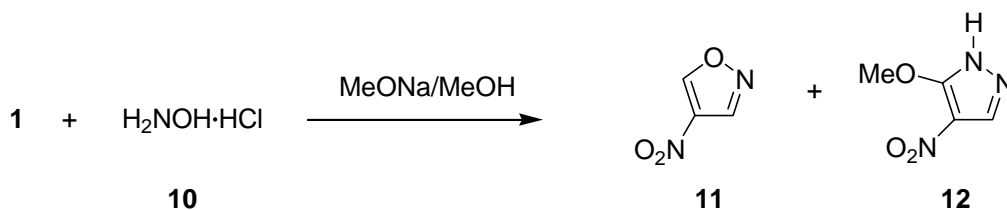
### Scheme 1

The reactions of dinitropyrazole **1** with equimolar amounts of arylhydrazines (**7**) afforded respective 1-aryl-4-nitropyrazoles (**8**)<sup>9</sup> in a new degenerated ring transformation reaction (Scheme 2). The formation of nitrohydrazide (**9**) was assumed considering the elimination of nitroamide in the reactions of 1,4-dinitroimidazoles with primary amines<sup>5</sup> since the reactions of amino-compounds with 1,4-dinitropyrazoles and 1,4-dinitroimidazoles probably follow similar mechanisms.<sup>2</sup>



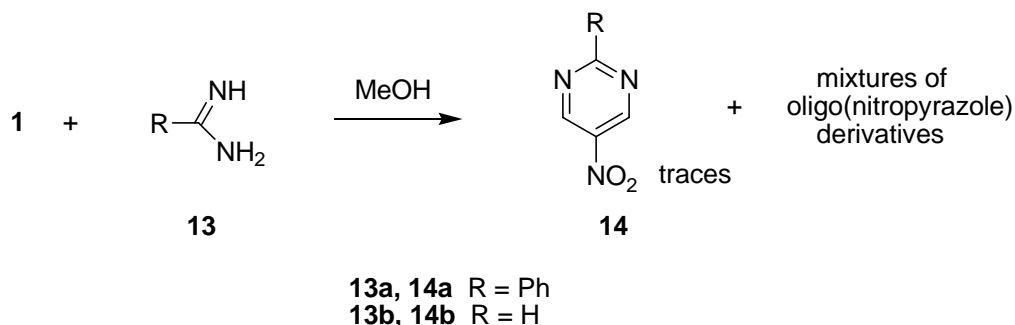
### Scheme 2

Azole derivative **1** reacted also with hydroxylamine, liberated from salt **10** in the presence of sodium methoxide, to afford 77% of 4-nitroisoxazole<sup>10</sup> (**11**) and a small amount of 5-methoxy-4-nitro-(1*H*)-pyrazole (**12**) (Scheme 3). For a comparison, compound **12** was also prepared by the reaction of dinitropyrazole **1** with potassium methoxide in methanol.



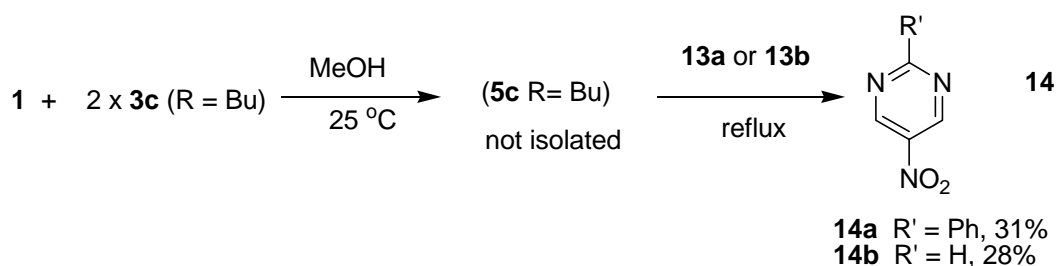
### Scheme 3

We also performed the reactions of dinitropyrazole **1** with amidines **13**, supposing that in this case they would lead to the pyrazole ring expansion with the formation of respective 5-nitropyrimidines (**14**, Scheme 4).  $^1\text{H}$  NMR and MS spectra of the crude products revealed only very small amounts of compounds **14**<sup>11</sup> accompanied by mixtures of oligo(nitropyrazole) derivatives. We think that oligo(nitropyrazoles) are formed in the cascades of *cine* nucleophilic substitution reactions from compound **1**, methanol and methoxynitropyrazole **12**, the latter two compounds being partly deprotonated in the presence of amidines **13**, which are strong bases.



#### Scheme 4

An exchange of methanol by DMSO or sulfolane in the reactions of azole **1** with amidines **13** led again to the formation of oligo(nitropyrazoles) following 1-denitration of the starting azole. Performing a two-step one-pot reaction (Scheme 5) allowed us to avoid unwanted *cine* nucleophilic substitution reactions. Initially, compound **1** was dissolved in methanol and then treated with two equivalents of butylamine (**3**, R = Bu) until the complete decay of the starting material. Later (without the isolation of intermediate **5**, R = Bu), amidine **13a** or **13b** was added and the resulting mixture was refluxed for a few hours. This one-pot procedure led to the formation of pyrimidines **14a** or **14b** in more acceptable yields.



#### Scheme 5

## Conclusions

The studied reactions of 1,4-dinitropyrazole with *N*-nucleophiles performed under very mild conditions probably involve the initial formation of the respective  $\sigma^H$  complexes derived from attacks of the nucleophiles on 5-th carbon atom of the pyrazole ring. Possible ways of further conversions of the  $\sigma^H$  complexes mainly depend on the type of the nucleophile. In general, the reactions of 1,4-dinitropyrazole with mononucleophilic primary amines give ring opening products, and the reactions with 1,2-dinucleophilic hydrazines and hydroxylamine or 1,3-dinucleophilic amidines lead to the formation of ring transformation products. 1,4-Dinitropyrazole reacting with easily deprotonated mononucleophiles affords *cine* nucleophilic substitution products.

Examples of 1,4-dinitropyrazole reactions performed by us with dinucleophilic aminocompounds represent three types of ring transformation reactions: i) transformation without a change of the ring size but with a change of the ring heteroatoms, ii) degenerated transformation without a change of the ring size and heteroatoms, iii) transformation with the ring expansion.

## Experimental Section

**General Procedures.** Melting points were determined either in open capillary tubes or using a Boetius apparatus and were uncorrected.  $^1\text{H}$  NMR spectra (300 MHz) and  $^{13}\text{C}$ -NMR spectra (75.5 MHz) were recorded on a Varian XL-300 spectrometer. Chemical shifts ( $\delta$ ) were given from TMS (0 ppm) as internal standard for  $^1\text{H}$  and  $^{13}\text{C}$  NMR. Some mixtures of products were analyzed using Waters HPLC Integrity Systems with a Termabeam Mass Detector (EI, 70 eV), using a direct inlet. Plastic plates (Kieselgel HF<sub>254</sub> type 60(Merck)) were used in TLC analysis with UV/VIS ( $\lambda=254, 366$  nm) CAMAG lamp for spots visualization. Starting materials, besides 1,4-dinitropyrazole (**1**), were commercially purchased. Known compounds were identified by  $^1\text{H}$  NMR and a comparison of their properties with the literature data. The structures of new 1-aryl-4-nitropyrazoles (**8**) were proposed by analyzing EA,  $^1\text{H}$  and  $^{13}\text{C}$  NMR data obtained by us. The MS spectra of compounds **8** and their fragmentation pattern will be published elsewhere.

**1,4-Dinitropyrazole (1).** Yield 59%, m. p. 53-54 °C (lit.<sup>3</sup> 54 °C) was obtained according to the procedure given by Hüttel et al.<sup>6</sup> and then improved by Habraken et al.<sup>3</sup>

**The general procedure for the reaction 1,4-dinitropyrazole (1) and aromatic primary amines (2). The formation of 1,5-bis(aryl)-3-nitro-1,5-diaza-1,3-pentadiens (4).**

Aniline derivative **2** (4 mmole) was added to a stirred, ice-cooled solution of **1** (2 mmole) in methanol (10 mL). The forming solutions turned orange. The stirring was continued for 30 minutes and then yellow needles precipitated. The precipitations were collected by filtration and

grinded with acetone (50 mL). Insolubilities were discarded and the solutions evaporated to dryness leaving crude products. Crystallization of the products from methanol gave **4**<sup>7</sup>.

**(E+Z) 1,5-Bis(4-methylphenyl)-3-nitro-1,5-diaza-1,4-pentadiene (4a).** Yield 54%, m. p. 156-158 °C (lit.<sup>7</sup> 154 °C), <sup>1</sup>H NMR δ (ppm, DMSO-d<sub>6</sub>): 2.32 (s, 6H, 2<sup>x</sup>CH<sub>3</sub>) 7.28 (d, 4H, *J*=8 Hz, Ar) 7.45 (d, 4H, *J*=8 Hz, Ar) 9.08 (s, 2H, 2<sup>x</sup>CH). MS m/z (%): 295 (19.7, M<sup>+</sup>), 247 (98.4), 278 (15), 181 (13.2), 145 (12.5), 130 (21.6), 118 (37.5), 91 (100).

**(E+Z) 1,5-Bis(4-methoxyphenyl)-3-nitro-1,5-diaza-1,4-pentadiene (4b).** Yield 42% m. p. 133-134 °C (lit.<sup>7</sup> 130 °C), <sup>1</sup>H NMR δ (ppm, DMSO-d<sub>6</sub>): 3.79 (s, 6H, 2<sup>x</sup>OCH<sub>3</sub>), 6.99 (d, 4H, *J*=8 Hz, Ar) 7.45 (d, 4H, *J*=8 Hz, Ar) 9.07 (s, 2H, 2<sup>x</sup>CH). MS m/z (%): 327 (<0.1, M<sup>+</sup>), 280 (55), 160 (30.1), 145 (60.1), 134 (32.2), 108 (100).

### General procedure for the reactions of 1,4-dinitropyrazole (**1**) with aliphatic primary amines (**3**). The formation of nitrodiazadienes (**5**)

Amine **3** (4 mmole) was added to a stirred solution of **1** (2 mmole) in methanol (10 mL). Stirring was continued for two hours at 25 °C and then the reaction mixture was acidified by diluted hydrochloric acid to pH 3. The forming precipitations were collected by filtration and chromatographed on silica gel with methanol chloroform (1:99) to afford respective products.

**(E+Z)-1,5-Bis(cyclohexyl)-3-nitro-1,5-diaza-1,4-pentadiene (5a).** Yield 7%, m. p. 86-87 °C, (lit.<sup>8</sup> 86-87 °C), <sup>1</sup>H NMR δ (ppm, CDCl<sub>3</sub>): 1.06-2.26 (m, 20H, 10<sup>x</sup>CH<sub>2</sub>), 4.68 (m, 2H, 2<sup>x</sup>CH), 7.80 (s, 2H, 2<sup>x</sup>CH). MS m/z (%): 279 (1, M<sup>+</sup>), 262 (1), 208 (4) M, 137 (3), 110 (1), 43 (100).

**(E+Z)-1,7-Bis(phenyl)-5-nitro-2,6-diaza-2,4-heptadiene (5b).** Yield 3%, m. p. 80-81 °C, (lit.<sup>7</sup> 82 °C), <sup>1</sup>H NMR δ (ppm, acetone-d<sub>6</sub>): 4.77 (s, 4H, 2<sup>x</sup>CH<sub>2</sub>), 7.24-7.40 (m, 10H, 2<sup>x</sup>Ph), 8.87 (s, 2H, 2<sup>x</sup>CH); [lit.<sup>7</sup> <sup>1</sup>H NMR δ (ppm, DMSO-d<sub>6</sub>): 4.70, 7.10-7.40, 8.88]. MS: m/z (%) 295 (1, M<sup>+</sup>), 278 (1), 145 (18), 118 (35), 91 (100).

### General procedure for the reactions of 1,4-dinitropyrazole (**1**) with arylhydrazines (**7**). Synthesis of 1-aryl-4-nitropyrazoles (**8**)

A solution of arylhydrazine (**7**, 2 mmole) in aqueous methanol (1:2, 5 mL) was added while stirring to **1** (2 mmole) in methanol (10 mL) at 25 °C. The forming precipitations of crude **8** were collected after 24 hours by filtration; the filtrate was evaporated to dryness to give an additional amount of crude **8**. Both portions of **8** were combined, flash chromatographed on silica gel with methanol (1-10%) and chloroform (99-90%) mixture followed by crystallization from methanol.

**1-Phenyl-4-nitropyrazole (8a).** Yield 70%, m. p. 126-128 °C, lit.<sup>9b</sup> 125-126 °C), <sup>1</sup>H NMR δ (ppm, DMSO-d<sub>6</sub>): 7.42-7.52 (m, 1H, H-Ar), 7.54-7.64 (m, 2H, H-Ar), 7.92-8.00 (m, 2H, H-Ar), 8.36 (s, 1H, H-3Py.), 9.26 (s, 1H, H-5Py.).

**1-(3-Fluorophenyl)-4-nitropyrazole (8b).** Yield: 58%, yellowish needles, m. p. 99-99.5 °C, <sup>1</sup>H-NMR δ (ppm, DMSO-d<sub>6</sub>): 7.26-7.33 (m, 1H, H-Ar), 7.57-7.65 (m, 1H, H-Ar), 7.82-7.89 (m, 2H, H-Ar), 8.55 (s, 1H, H-3Py.), 9.71 (s, 1H, H-5Py.). <sup>13</sup>C-NMR, δ (ppm, DMSO-d<sub>6</sub>): 106.85 (d, 1C, *J*=27.2 Hz; C-4'), 114.90 (d, 1C, *J*=21.1 Hz, C-2'), 115.24 (d, 1C, *J*=3.0 Hz, C-6'), 128.42 (s, 1C, C-3Py.), 131.57 (d, 1C, *J*=9.1 Hz, C-5'), 136.99 (s, 1C, C-4Py.), 137.08 (s, 1C, C-5Py.),



139.61 (d, 1C,  $J=10.6$  Hz, C-1'), 162.42 (d, 1C,  $J=244.7$  Hz; C-3'). EA (C, H, N): for  $C_9H_6FN_3O_2$  calc. 52.18%, 2.92%, 20.28%; found: 52.17%, 2.92%, 20.28%.

**1-(3-Chlorophenyl)-4-nitropyrazole (8c).** Yield 79%, colorless micro-crystals, m. p. 110-111 °C,  $^1H$ -NMR  $\delta$  (ppm, DMSO- $d_6$ ): 7.51 (ddd, 1H,  $J=8.1$  Hz,  $J=1.8$  Hz,  $J=0.9$  Hz, H-4'), 7.59 (t, 1H,  $J=8.1$  Hz, H-5'), 7.95 (ddd, 1H,  $J=8.1$  Hz,  $J=2.1$  Hz,  $J=0.9$  Hz, H-6'), 8.08 (t, 1H,  $J=2.1$  Hz, H-2'), 8.56 (sbr., 1H, H-3Py.) 9.73 (d, 1H,  $J=0.6$  Hz, H-5Py.).  $^{13}C$ -NMR  $\delta$  (ppm, DMSO- $d_6$ ): 117.95, 119.23, 128.00, 128.51, 131.35, 134.15, 137.00, 137.14, 139.40. EA (C,H,N): for  $C_9H_6ClN_3O_2$  calc. 48.34%, 2.70%, 18.79%; found: 48.42%, 2.69%, 18.66%.

**1-(4-Fluorophenyl)-4-nitropyrazole (8d).** Yield 76%, yellowish needles, m. p. 138-139 °C,  $^1H$ -NMR  $\delta$  (ppm, DMSO- $d_6$ ): 7.43 (t, 2H,  $J=2.2$  Hz, H-3', H-5'), 7.96-8.03 (m, 2H, H-2', H-6'), 8.55 (sbr., 1H, H-3Py.), 9.63 (s, 1H, H-5Py.).  $^{13}C$ -NMR  $\delta$  (ppm, DMSO- $d_6$ ): 116.49 (d, 2C,  $J=23.6$  Hz; C-3', C-5'), 121.72 (d, 2C,  $J=8.5$  Hz, C-2', C-6'), 128.23 (s, 1C, C-3Py.), 134.88 (d, 1C,  $J=3.1$  Hz, C-1'), 136.81 (s, 1C, C-4Py.), 136.90 (s, 1C, C-5Py.), 161.41 (d, 1C,  $J=245.2$  Hz, C-4'). EA (C, H, N): for  $C_9H_6FN_3O_2$  calc. 52.18%, 2.92%, 20.28%; found: 52.22%, 2.96%, 20.28%.

**1-(4-Chlorophenyl)-4-nitropyrazole (8e).** Yield 66%, yellowish needles, m. p. 162-166 °C with a change of the crystalline form, (lit.<sup>9</sup> 171 °C)  $^1H$ -NMR  $\delta$  (ppm, DMSO- $d_6$ ): 7.60-7.65 (m, 2H, H-2', H-6'), 7.96-8.01 (m, 2H, H-3', H-5'), 8.55 (s, 1H, H-3Py.), 9.67 (d, 1H,  $J=0.6$  Hz, H-5Py.).  $^{13}C$ -NMR  $\delta$  (ppm, DMSO- $d_6$ ): 121.06 (s, 2C), 128.23 (s, 1C), 129.59 (s, 2C), 132.58 (s, 1C), 136.94 (s, 1C), 137.04 (s, 1C), 137.14 (s, 1C). EA (C, H, N): for  $C_9H_6ClN_3O_2$  calc. 48.34%, 2.70%, 18.79%; found: 48.63%, 2.68%, 18.51%.

**1-(3,5-Difluorophenyl)-4-nitropyrazole (8f).** Yield 64%, colorless micro-crystals, m. p. 132-132.5 °C,  $^1H$ -NMR  $\delta$  (ppm, DMSO- $d_6$ ): 7.35 (tt, 1H,  $J=9.2$  Hz,  $J=2.4$  Hz, H-4'), 7.73-7.82 (m, 2H, H-2', H-6'), 8.58 (sbr., 1H, H-3Py.), 9.74 (d, 1H,  $J=0.6$  Hz, H-5Py.).  $^{13}C$ -NMR  $\delta$  (ppm, DMSO- $d_6$ ): 102.98-103.38 (m, 2C, C-2', C-6'), 103.44 (t, 1C,  $J=26.2$  Hz, C-4'), 128.81 (s, 1C, C-3Py.), 137.20 (s, 1C, C-4Py.), 137.34 (s, 1C, C-5Py.), 140.25 (t, 1C,  $J=13.3$  Hz, C-1'), 162.78 (dd, 2C,  $J=246.8$  Hz,  $J=14.6$  Hz, C-3', C-5'). EA (C,H,N): for  $C_9H_5F_2N_3O_2$  calc. 48.01%, 2.24%, 18.66%; found: 48.10%, 2.25%, 18.50%.

**1-(3,4-Dichlorophenyl)-4-nitropyrazole (8g).** Yield 61%, yellowish micro-crystals, m. p. 148.5-149 °C,  $^1H$ -NMR  $\delta$  (ppm, DMSO- $d_6$ ): 7.80 (d, 1H,  $J=8.7$  Hz, H-5'), 7.96 (dd, 1H,  $J=8.7$  Hz,  $J=2.7$  Hz, H-6'), 8.26 (d, 1H,  $J=2.7$  Hz, H-2') 8.55 (s, 1H, H-3Py.), 9.73 (s, 1H, H-5Py.).  $^{13}C$ -NMR  $\delta$  (ppm, DMSO- $d_6$ ): 119.30, 121.00, 128.61, 130.58, 131.50, 132.26, 137.09, 137.24, 137.80. EA (C,H,N): for  $C_9H_5Cl_2N_3O_2$  calc. 41.89%, 1.95%, 16.28%; found: 42.06%, 1.96%, 16.09%.

**4-Nitroisoxazole (11).**<sup>10</sup> Hydroxylamine hydrochloride (**10**, 4 mmole) was added to a solution, obtained by the reaction of sodium (3 mmole) with methanol (10 mL). The resulting solution was stirred at 25 °C for 5 min followed by addition of **1** (2 mmole). The mixture turned yellow and gas evolution was observed. After 30 min the solvent was removed under diminished pressure and water (10 mL) was added. The obtained solution was extracted with ethyl acetate (5x10 mL), the combined extracts were dried over anhydrous magnesium sulfate and condensed then under

diminished pressure to afford an oil (0.18 g) solidifying on cooling. Yield 77%, m. p. 43-44 °C (lit.<sup>10</sup> 45-46 °C).

**5(3)-Methoxy-4-nitropyrzole (12).** A solution of **1** (2 mmole) in methanol (2 mL) was added to a stirred solution of potassium hydroxide (1 pellet) in methanol (10mL). Stirring was continued for 5 minutes and the solvent was evaporated under diminished pressure. Water (20 mL) was added to the residue and the resulting mixture was acidified to pH~4,5 followed by extraction with 1,2-dichloroethane (4x10mL). The combined extracts were dried over anhydrous magnesium sulfate and then concentrated to afford **12**. Yield 61%, m. p. 198-201 °C (from methanol) (lit.<sup>8</sup> 200-201 °C), <sup>1</sup>H NMR  $\delta$  (ppm, acetone-d<sub>6</sub>): 3.99 (s, 3H, CH<sub>3</sub>), 8.46 and 8.51 (2<sup>x</sup>s 1:4, 1H, H-3(5)Py.).

### Reactions of 1,4-dinitropyrzole (1) with benzamidine (13) in methanol; formation of 2-phenyl-5-nitropyrimidine (14a)

Amidine **13a** (2 mmole) was added while stirring to **1** (2 mmole) in methanol (10mL). The precipitations forming within two hours were collected, dried and analyzed. The TLC analysis, MS and <sup>1</sup>H NMR spectra of the precipitations revealed the presence of pyrimidine **14a** and mixtures of oligonitropyrzoles.

### Reactions of 1,4-dinitropyrzole (1) with butylamine (5c) in ethanol followed by addition of (13a or 13b); formation of 5-nitropyrimidines 14a or 14b

**2-Phenyl-5-nitropyrimidine (14a).** Butylamine (**5c**, 5 mmole) was added to a stirred solution of **1** (2 mmole) in ethanol (10 mL) and the stirring was continued for 0,5h followed by an addition of benzamidine (**13a**, 2 mmole). The resulting solution was refluxed for 3h and then cooled down. The formed precipitate was collected, rinsed with ethanol and recrystallized from ethanol to give **14a**. Yield 31%, m. p. 218-220 °C (lit.<sup>11b</sup> 222-223 °C), <sup>1</sup>H NMR  $\delta$  (ppm, acetone-d<sub>6</sub>): 7.56-7.72 (m, 3H, C<sub>6</sub>H<sub>5</sub>), 8.54-8.64 (m, 2H, C<sub>6</sub>H<sub>5</sub>), 9.61 (s, 2H, Pyrim.).

**5-Nitropyrimidine (14b).** In a similar manner **1** was treated with formamidine (**13a**). The post-reaction mixture was evaporated under diminished pressure to dryness and then water (20mL) was added to the residue. The obtained solution was extracted with 1,2-dichloroethane (5-10mL). Organic extracts were combined, dried and evaporated to leave an oil, which was chromatographed on silica gel with methanol-chloroform (2:98) to give **14b**. Yield 18%, m. p. 56-57 °C (lit.<sup>10</sup>, m. p. 57-58 °C).

## Acknowledgements

This research was partially financed by a grant N204 065 31/1722 provided by the Foundation for the Polish Science.

## References

1. (a) Nishiwaki, N.; Okajima, Y.; Tamura, M.; Asaka, N.; Hori, K.; Tohda, Y.; Ariga, M. *Heterocycles* **2003**, *60*, 303. (b) Nishiwaki, N.; Ogihara, T.; Takami, T.; Tamura, M.; Ariga, M. *J. Org. Chem.* **2004**, *69*, 8382.
2. Jędrysiak, R.; Sawicki, M.; Suwinski, J. *Chemik* **2005**, *58*, 327 (in Polish).
3. (a) Habraken, C. L.; Poels, E. K. *J. Org. Chem.* **1977**, *42*, 2893. (b) Buchanan, J. G.; Edgar, A. R.; Hutchinson, R. J.; Stobie, A.; Wightman, R. H. *J. Chem. Soc., Chem. Commun.* **1980**, 237. (c) Zhou, J.; Yang, M.; Schneller, S. W. *Tetrahedron Lett.* **2004**, *45*, 8233. (d) Suwiński, J.; Świerczek, K. *Tetrahedron Reports*, **2001**, *57*, 1639, a review. (e) Makosza, M.; Wojciechowski, K. *Chem. Rev.* **2004**, *104*, 2631, a review.
4. (a) van der Plas, H. C. *Adv. Heterocyclic Chem.* **1999**, *74*, 123. (b) Chauzov, V. A.; Parchinsky, V. Z.; Sinelshchikova, E. V.; Petrosyan, V. A. *Russ. Chem. Bull. Int. Ed.* **2001**, *50*, 1274.
5. (a) Suwiński, J.; Szczepankiewicz, W. *Tetrahedron: Asymmetry* **1991**, *2*, 941. (b) Llempen, H.; Salwińska, E.; Suwiński, J.; Szczepankiewicz W. *Polish J. Chem.* **1992**, *66*, 943. (c) Suwiński, J.; Pawlus, W.; Salwińska, E.; Świerczek, K. *Heterocycles* **1994**, *37*, 1511. (d) Suwiński, J.; Szczepankiewicz, W. *J. Labelled Compds. Radiopharm.* **1996**, *38*, 395.
6. (a) Hüttel, R.; Büchele, F.; Jochum, P. *Chem. Ber.* **1955**, *88*, 1577. (b) Janssen, J. W. A. M., Habraken; C. L. *J. Org. Chem.* **1971**, *36*, 3081. (c) Janssen, J. W. A. M.; Koeners H. J.; Kruse, C. G.; Habraken, C. L. *J. Org. Chem.* **1973**, *38*, 1777.
7. (a) Czupakhin, O. N.; Rusinow, V. L. *Khim. Geterotsikl. Soedin.* **1989**, 179. (b) Rusinov, V. L.; Tumashov, A. A.; Pilicheva, T. L.; Chupakhin, O. N.; *J. Org. Chem. USSR.* **1991**, *27*, 952. (c) Rusinow, V. L.; Tumashov, A. A.; Pilicheva, T. L.; Chupakhin, O. N. *Zh. Org. Khim.* **1991**, *27*, 1100. (d) Kvitko, S. M.; Perekalin, V. V. *J. Gen. Chem. USSR (Engl. Transl.)* **1962**, *32*, 141. (e) Kurbatov *et al.* *J. Gen. Chem. USSR (Engl. Transl.)* **1970**, *40*, 2348.
8. Yasuo, T.; Masahiro, A.; Toshihide, K.; Eizo, M. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 201.
9. (a) Lynch, B. M.; Hung Y-Y. *Can. J. Chem.* **1964**, *42*, 1605. (b) Holzer, W. *Tetrahedron* **1991**, *47*, 1393.
10. (a) Kotschetkov, N. K.; Chomutova, E. D. *Zh. Obsch. Khim.* **1959**, *29*, 525. (b) Reiter, L. A. *J. Org. Chem.* **1987**, *52*, 2714. (c) Dewarte, S. *Bull. Soc. Chim. Fr.* **1969**, *945*, 545 (in French).
11. (a) Reiter, L. A. *J. Org. Chem.* **1987**, *52*, 2714. (b) Barczyński, P.; van der Plas, H. C. *J. Org. Chem.* **1982**, *47*, 1077. (c) Marcelis, A. T. M.; van der Plas, H. C. *Tetrahedron* **1989**, *45*, 2693. (d) Charushin, V. N.; van der Plas, H. C. *Tetrahedron Lett.* **1982**, *23*, 3965. (e) Fanta, P. E.; Hedman, E. A. *J. Am. Chem. Soc.* **1956**, *78*, 1434.