

## SYNTHESIS OF N-2, 4, 6-TRINITROPHENYL-N'-2, 4-DINITROBENZOFUROXAN-3, 5-DINITRO-2, 6-DIAMINOPYRIDINE

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N-2, 4, 6-trinitrophenyl-N'-2, 4-dinitrobenzofuroxan-3, 5-dinitro-2, 6-diaminopyridine has been synthesized from 2, 6-diaminopyridine, dinitrodichlorobenzene and 2, 4, 6-trinitrochlorobenzene. For this compound, the structure has been determined by elemental analysis, IR, <sup>1</sup>HNMR, and MS spectroscopies.

## 1. INTRODUCTION

It has been believed that the replacement of nitro groups by furoxan groups can result in increase of density and detonation velocity of explosives<sup>1)</sup>. And the introduction of amino groups to the explosive molecules can result in an increase of density and heat resistance and a decrease of impact sensitivity. In order to utilize the advantages of furoxan and amino groups, the compound N-2, 4, 6-trinitrophenyl-N'-2, 4-dinitro-benzofuroxan-3, 5-dinitro-2, 6-diaminopyridine (7) was designed and has been synthesized.

## 2. RESULTS

N-2, 4, 6-trinitrophenyl-N'-2, 4-dinitrobenzofuroxan-3, 5-dinitro-2, 6-diaminopyridine (7) has been synthesized by thermal decomposition of N-2, 4, 6-trinitrophenyl-N'-3-azido-2, 4, 6-trinitrophenyl-3, 5-dinitro-2, 6-diaminopyridine (6), which was obtained by treatment of N-2, 4, 6-trinitrophenyl-N'-3-chloro-2, 4, 6-trinitrophenyl-3, 5-dinitro-2, 6-diaminopyridine (5). Compound (5) was prepared by nitrating N-2, 4, 6-trinitrophenyl-N'-5-chloro-2, 4-dinitrophenyl-2, 6-diaminopyridine (4), which was synthesized by reacting of picryl chloride and N-5-chloro-2, 4-dinitrophenyl-2, 6-diaminopyridine

N-5-chloro-2, 4-dinitrophenyl-2, 6-diaminopyridine (3). Compound (3) was synthesized by 2, 6-diaminopyridine and 1, 3-dichloro-4, 6-dinitrobenzene (2), which was obtained by nitrating 1, 3-dichlorobenzene.

Compound (7) is an orange yellow solid, soluble in DMF and DMSO and almost insoluble in other organic solvents, molecular formula C<sub>17</sub>H<sub>6</sub>N<sub>12</sub>O<sub>16</sub>, molecular weight 634, density 1.84 g/cm<sup>3</sup>, melting point 310°C (dec), detonation velocity 8180 m·s<sup>-1</sup>, no weightloss at 100°C for 48h. Comparing with heat resisting explosive PYX<sup>2)</sup>, compound (7) has a higher density and detonation velocity.

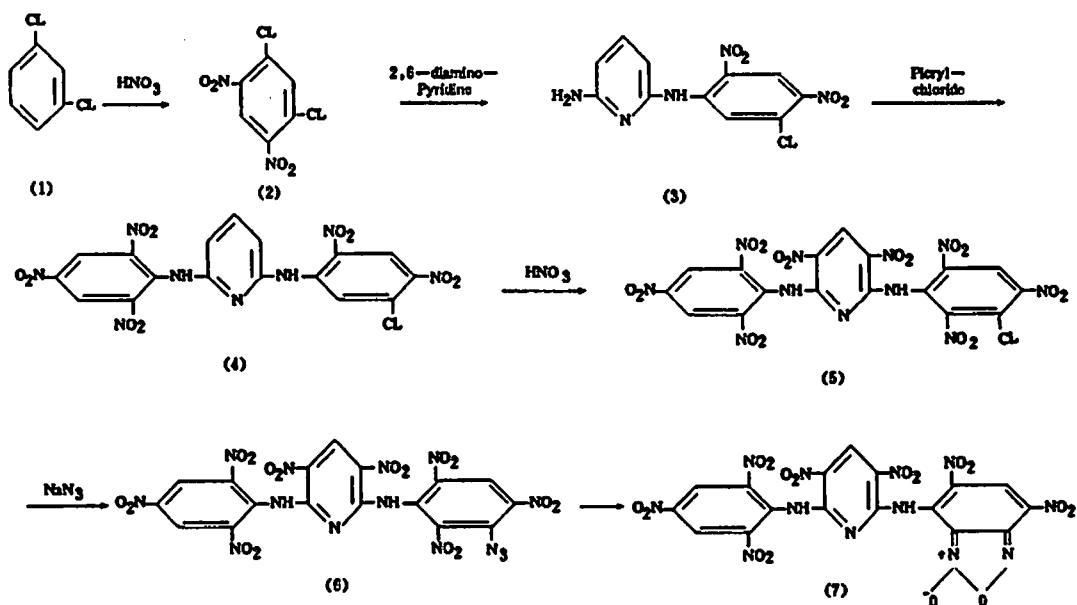
## 3. EXPERIMENTAL

Melting points (uncorrected) were measured on a X<sub>1</sub> hot-stage apparatus and elemental analyses on carlo Erba 1102 instrument. IR spectra were recorded on a shimadzu IR-408 spectrophotometer, MS spectra on a 80 RFA spectrometer and <sup>1</sup>HNMR spectra on a LX-100 spectrometer (TMS as internal standard).

1, 3-dichloro-4, 6-dinitrobenzene (2). To a mixture of 70ml of fuming nitric acid and 110ml of concentrated sulfuric acid was added with stirring, 30 g of 1, 3-dichlorobenzene was added in small portions as 30~40°C, the resulting mixture was stirred at 95~99°C for 2h, cooled to room temperature and poured over 300 g of crushed ice with water. The precipitated yellow solid was collected by filtration,

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washed with 30% sulfuric acid then with water and dried gave 38 g (78.6%) of product which was recrystallized from ethanol. Mp 102°C. IR (KBr) : 3050 (Ar-H). 1575 (C $\equiv$ C). 1540, 1320 (-NO<sub>2</sub>). 920 (Ar-Cl) cm<sup>-1</sup>.

Compound (3). 1, 3-dichloro-4, 6-dinitrobenzene (5.93 g 0.025mol), 2, 6-diaminopyridine (2.73 g 0.025mol) and sodium bicarbonate (2.5 g 0.029mol) were refluxed in 40 ml of propyl alcohol for 3h. The solid was collected by filtration, washed with water until the wash water became neutral, and air dried, recrystallization from acetone, gave 7 g (91%) of product. Mp 183°C. IR (KBr) : 3500, 3400 (-NH<sub>2</sub>). 3300 (-NH-). 3000 (Ar-H). 1600 (C $\equiv$ C). 1540, 1315 (-NO<sub>2</sub>). 965 (Ar-Cl). cm<sup>-1</sup> <sup>1</sup>HNMR (acetone-d<sub>6</sub>) 9.25 (1H Ar-H) 8.85 (1H Ar-H). 7.4 (1H Ar'-H). 6.3 (2H Ar'-H) 3.15 (3H-NH<sub>2</sub>, -NH-) ppm. Anal Calcd for C<sub>11</sub>H<sub>6</sub>N<sub>3</sub>O<sub>4</sub>Cl: C, 42.65; H, 2.58; N, 22.6; Cl, 11.47. Found: C, 42.43; H, 2.36; N, 21.84; Cl, 11.45.

Compound (4). 2, 4, 6-trinitrochlorobenzene (2.1 g 8.22mmol), 2.54 g (8.21mmol) of compound (3), and sodium bicarbonate (0.69 g 8.2mmol) were refluxed in 50ml of ethanol for 3h. After cooling the mixture the solid was collected by filtration, washed well with hot water at 60°C and air dried, gave 4.02 g (93%) of product. IR (KBr) : 3300 (-NH-). 3050 (Ar-H). 1600 C $\equiv$ C. 1545, 1316 (-NO<sub>2</sub>), 1100 (Ar-Cl) Cm<sup>-1</sup> Anal Calcd for C<sub>17</sub>H<sub>9</sub>N<sub>6</sub>O<sub>10</sub>Cl: C, 39.19; H, 1.72;

N, 21.5; Cl, 6.82. Found: C, 39.13; H, 1.68; N, 21.7; Cl, 6.88.

Compound (5). To 45ml of fuming nitric acid, compound (4) (3.5 g 6.72mmol) in small portions was added with stirring. The mixture was stirred at 50°C for 0.5h, then refluxed for 3h. After being cooled to room temperature, about 250 g crushed ice was added bit by bit without stirring. The precipitated solid was collected by filtration. The crude product was soaked in hot water at 75°C for 0.5h, yellow solid was filtered again and washed well with water, and dried to give 3.8 g (86.36%) product. Mp 386°C, IR (KBr) : 3200 (-NH-), 3000 (Ar-H), 1600 (C $\equiv$ C), 1320, 1540 (-NO<sub>2</sub>), 950 (Ar-Cl) cm<sup>-1</sup>. Anal Calcd for C<sub>17</sub>H<sub>6</sub>N<sub>11</sub>O<sub>16</sub>: C, 31.12; H, 0.91; N, 23.4; Cl, 5.42. Found: C, 31.96; H, 0.90. N, 22.77; Cl, 5.44.

Compound (6). 0.17 g (2.61mmol) of sodium azide in 6ml of water was added dropwise with stirring, to a solution of 1.2 g (1.93mmol) of compound (5) in 25ml DMF. After being stirred at 35°C for 2h, the mixture was poured into cold water. The resulting yellow precipitate was collected by filtration and washed well with water to give 1.09 g (90.8%) of compound (6). IR (KBr) : 3200 (-NH-), 3000 (Ar-H), 2150 (-N<sub>3</sub>), 1600 (C $\equiv$ C), 1540, 1320 (-NO<sub>2</sub>).

Compound (7) 0.83 g (1.25mmol) of compound (6) was added to 18ml of propionic acid, the mixture was heated to 125°C, and then kept at 125~130°C

for about 1h until the evolution of nitrogen gas was completed<sup>3)</sup>. After being cooled to room temperature, the mixture was poured to water, and a precipitate was formed. It was separated by filtration, washed well with water and dried at 110°C to yield 0.68 g (86%) of compound (7). The product decomposed at 310°C, and has a crystal density of 1.84 g/cm<sup>3</sup>. IR (KBr) : 3250 (-NH-), 1620, 1590 (-ONO-), 1535, 1315 (-NO<sub>2</sub>) cm<sup>-1</sup>. <sup>1</sup>HNMR. (acetone-d<sub>6</sub>) : 9.55 (1H Ar-H) ; 9.15 (3H Ar-H) ; 3.4 (2H-NH-) ppm. MS (FAB) 635 (M+1) · Anal Calcd for C<sub>17</sub>H<sub>6</sub>N<sub>12</sub>O<sub>16</sub> : C, 32.17 ; H, 0.94 ; N, 26.49. Found : C, 32.26 ; H, 0.

87 ; N, 26.41

#### REFERNECES

- 1) A. Gasce, A. J. Boulton : Furoxans and Benzofuroxan. *Adv Hete chem* 29. University of Florida, New York, 1981, PP 284-286.
- 2) Hudson Frederick Mitchecl : Eur Pat 104717 (1984), Tronics Chemical Comp, Chem. Abstr. 101 (1984) 110736.
- 3) Chen Boren and Liao Zhiyuan : Synthesis of 6-Nitro-tetrafuloxano (b, d, b', d') Biphenyl. *J. Propellants, Explos, Pyrotech.* 15(3), 97-98(1990).

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### N-2, 4, 6-トリニトロフェニル-N'-2, 4-ジニトロベンゾフロキササン-3, 5-ジニトロ-2, 6-ジアミノピリジンの合成

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2, 6-ジアミノピリジン, ジニトロジクロロベンゼンおよび2, 4, 6-トリニトロクロロベンゼンを原料として, N-2, 4, 6-トリニトロフェニル-N'-2, 4-ジニトロベンゾフロキササン-3, 5-ジニトロ-2, 6-ジアミノピリジンの合成を行った。化学構造の同定には, 元素分析, 赤外吸収スペクトル, プロトンNMR, 質量分析法を用いた。得られた物質は比較的耐熱性の高い爆薬であり, 密度1.84 g/cm<sup>3</sup>, 爆速8180 m/sを示した。

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