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A New Synthetic Route to 1,3-Diamino-5-methylamino-2,4,6-trinitrobenzene

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Abstract: A new synthetic route for preparation of 1, 3-diamino-5-methylamino-2, 4, 6-trinitrobenzene with chlorobenzene as the starting material was reported. Via the sequence nitration-nucleophilic substitution-vicarious nucleophilic substitution of hydrogen reaction, the title product was obtained with yield of 60.3%. The structure of the title product and its intermediate products were identified by IR, ^{1}H NMR, and elemental analysis. DSC curve of the title product shows the peak temperature of thermal decomposition is 303 ℃, which indicates its molecule is stable to heat.

Key words: organic chemistry; vicarious nucleophilic substitution of hydrogen; 1, 3-diamino-5- methylamino-2, 4, 6-trinitrobenzene

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1 Introduction

Fully substituted derivatives of 1,3,5-trinitrobenzene are of interest for structure-property relationship studies, such as 1,3,5-triamino-2,4,6-trinitrobenzene (TATB) and 1,3-diamino-2,4,6-trinitrotoluene (DATNT), both of these compounds are good examples of a general structure-property relationship found among the energetic ingredients, that the addition of amino-groups to a polynitroaromatic increases the density and thermal stability and decreases the sensitivity compared to the corresponding H-atom-substituted material. The structure-property relationship studies will play an important role to design new energetic materials.

1,3-Diamino-5-methylamino-2,4,6-trinitrobenzene is one of the fully substituted derivatives. In order to study the correlation of structure-property, William M Koppes[1] et al have synthesized 1,3-diamino-5-methylamino-2,4,6-trinitrobenzene, taking 1,3,5-trifluoro-2,4,6-trinitrobenzene as the starting materials. The route wasn't satisfactory because unwanted single substitution 1-acetylamino-3, 5-difluro-2, 4, 6-trinitrobenzene existed in the first step, and 1, 3-diacetylamino-5-fluoro-2, 4, 6-trinitrobenzene wasn't the main product, which resulted in the overall yield was lower than 10%. Moreover, 1, 3, 5-trifluoro-2, 4, 6-trinitrobenzene is less readily available[2].

In order to test its performance and lay a foundation for further study on the correlation of structure-property, we have developed a new synthetic route to 1,3-diamino-5-methylamino-2,4,6-trinitrobenzene, which avoids the unwanted displacement and takes the moderate VNS (vicarious nucleophilic substitution of hydrogen) amination.

2 Experimental

2.1 Instrument and agent

4-Amino-1, 2, 4-triazole was purchased from Shenyang Shenpan Fine Chemicals Co. Ltd. and recrystallized from ethanol before using. Chemically pure solid sodium methoxide was procured from Zibo Huixin Chemicals Co. Ltd. The rest reagents were analytically pure and purchased from Beijing chemical reagents company.

^{1}H NMR spectra were measured by ARX-400 FTNM2 instrument. Infrared spectra were recorded on a Spectra one IR spectrophotometer (KBr pellet) with a resolution of 4 cm^{-1}, in the range 4000 – 400 cm^{-1}. Melting points were determinated using XT4A microscope melting point apparatus. Elemental analysis was measured by Vario EL Ⅲ elemental analysis instrument. DSC was measured by Mettler-Toledo DSC-1 with a heating rate of 10 K · min^{-1}. DSC data for 1, 3-diamino-5-methylamino-2, 4, 6-trinitrobenzene samples refer to the onset temperature for endothermic procedure and exothermic decomposition.

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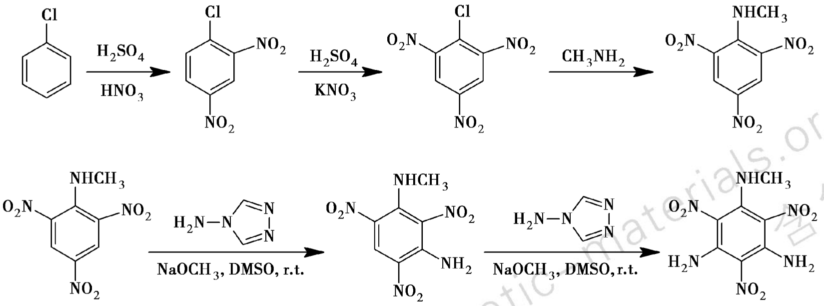
2.2 Synthetic route



2.3 Synthesis

2.3.1 Preparation of 2, 4-dinitrochlorobenzene

Chlorobenzene (20.0 g, 0.18 mol) was added dropwise to fuming nitric acid (75.0 g, 50 mL), whilst maintaining the temperature below 55 ℃. Ninety-eight percent of sulphuric acid(92 g,50 mL) was added to the red solution. An exothermic reaction occurred, producing a yellow oil, then the resultant solution was stirred for 1 h at 80 ℃. The cooled solution was poured onto ice, and the resultant precipitate was filtered off, washed with water, recrystallized from 95% ethanol and dried to yield 2,4-dinitrochlorobenzene (36.4 g, 92%), m. p. 49 - 50 ℃ (Ref. m.p. 53 ℃)[3]. IR (KBr) 3094.20,1598.96, 1537.52,1346.03,1042.54 and 728.20 cm^{-1} (in accordance with standard spectra).

2.3.2 Preparation of picryl chloride

15.0 g 2, 4-Dinitrochlorobenzene was added in portions to 80 mL oleum (20% of SO_3) below 55 ℃ under continuous stirring. After 2, 4-dinitrochlorobenzene resolved, the mixture was heated to 80 ℃ and stirred for 0.5 h. Then 35.5 g potassium nitrate was added in portions to the solution, whilst maintaining the temperature at 120 ℃. The mixture was gradually raised to 140 ℃ and stirred for 4 h at this temperature. The cooled solution was poured onto ice under continuous stirring, and the resultant precipitate was filtered off, washed with water to neutral, recrystallized from 95% ethanol and dried to yield picryl chloride (18.3 g, 85%), m. p. 80 - 81 ℃ (Ref. m.p. 83 ℃)[4]. IR(KBr) 3087.70, 1607.71, 1538.45, 1347.30, 1064.33 and 921.62 cm^{-1} (in accordance with standard spectra).

2.3.3 Preparation of 1-methylamino-2, 4, 6-trinitrobenzene

An aqueous solution of methylamine (25% - 30%, 25.5 mL, 3 equiv) was added dropwise to a stirred solution of picryl chloride (12 g, 48 mmol) in 50 mL DMSO at room temperature. The mixture was then stirred for an additional 4 h, was poured into 500 mL ice-water, neutralized with HCl, and filtered. Recrystallization of the solid from 95% ethanol gave 1-methylamino-2, 4, 6-trinitrobenzene (10.34 g, 89.1%), m. p. 112 - 113 ℃ (Ref. m. p. 113 - 114 ℃)[5]. IR (KBr): 3318.90, 3112.83, 3072.46, 2934.78, 1624.46, 1524.21, 1431.80, 1589.72 and 923.51 cm^{-1} (in accordance with standard spectra).

2.3.4 Preparation of 1-amino-3-methylamino-2, 4, 6-trinitrobenzene

Sodium methoxide (10.8 g, 0.20 mol) was added to a solution of 1-methylamino-2, 4, 6-trinitrobenzene (4.84 g, 0.02 mol) and 4-amino-1, 2, 4-triazole (8.40 g, 0.10 mol) in 100 mL DMSO. The brown suspension was stirred at ambient temperature for 5 h. The reaction mixture was poured into 1000 mL ice-water, neutralized with HCl. The resulting precipitate was collected, washed with water and dried to yield 1,3-diamino-5-methylamino-2,4,6-trinitrobenzene (5.37 g, 93%). m. p. 190 - 191 ℃ (Ref. m. p. 190 - 192 ℃)[6]. IR(KBr): 3425.16, 3321.02, 3312.14, 3120.83, 1290.01, 1540.05 cm^{-1}. ^1H NMR(DMSO-d_6): 9.418(s,1H, $NHCH_3$); 9.044(s, 1H,CH); 8.498(s,2H,NH_2); 2.805(d,3H, $NHCH_3$).

2.3.5 Preparation of 1, 3-diamino-5-methylamino-2, 4, 6-trinitrobenzene

Sodium methoxide (10.8 g, 0.20 mol) was added to a solution of 1, 3-diamino-5-methylamino-2, 4, 6-trinitrobenzene (5.14 g, 0.02 mol) and 4-amino-1, 2, 4-triazole (8.40 g, 0.10 mol) in 100 ml DMSO. The reddish brown suspension was stirred for 16 h at ambient temperature. The reaction mixture was poured into 1000 mL ice-water, neutralized with HCl. The resulting precipitate is collected, washed with water and dried to yield 1, 3-diamino-5-methylamino-2, 4, 6-trinitrobenzene (5.33 g, 98%). Recrystallized from nitrobenzene (120 mL) to give 5.06 g (93%) yellowish green solid. m. p. 290.75 ℃ (Ref. m. p. 292 – 293 ℃, decomp.)[1]. ^{1}H NMR (DMSO-d_6): 10.64 (s, 1H, $NHCH_3$); 9.944 (s, 4H, NH_2); 2.840 (d, 3H, $NHCH_3$). IR (KBr): 3430.70, 3326.08, 3265.41, 1591.11, 1544.75 and 912.47 cm^{-1}. DSC analysis exhibited an exotherm at 293.03 ℃. Analysis ($C_7H_8N_6O_6$) calculated: C 30.89, H 2.96, N 30.88. Found: C 30.53, H 2.98, N 30.29.

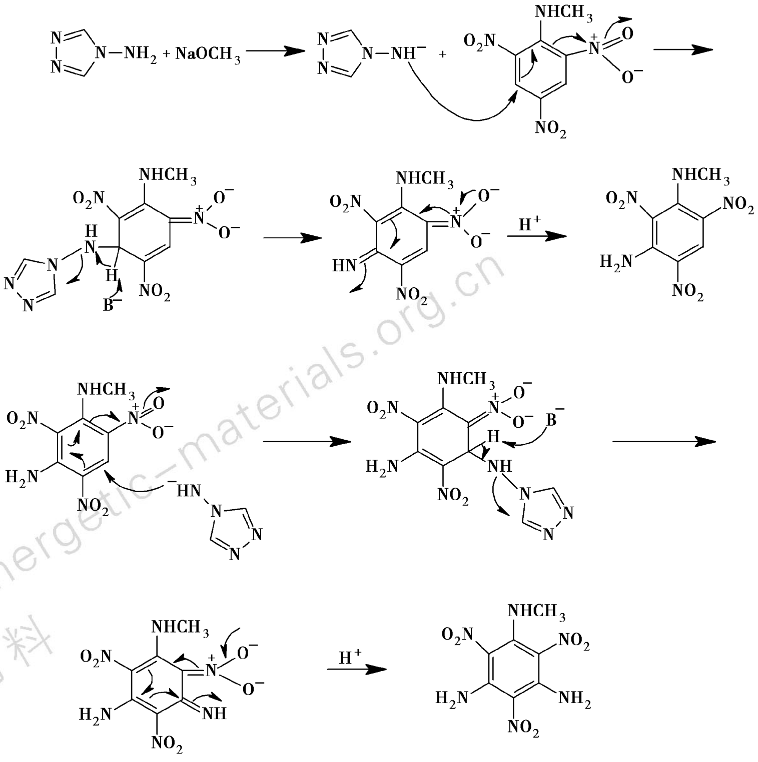
3 Results and discussion

3.1 The mechanism of VNS amination

Hydrogens located at activated positions in electrophilic arenes, e. g. ortho and para hydrogens in nitrobenzenes, can be replaced with a nucleophile moiety provided there is at least one nucleofuge X connected to the nucleophilic center. As the group really leaving in this H substitution process is not the hydride anion but X, which is named vicarious nucleophilic substitution of hydrogen (VNS)[7]. According to Mieczyslaw Makosza[8], the most feasible mechanism for the transformation of 1-methylamino-2, 4, 6-trinitrobenzene into 1, 3-diamino-5-methylamino-2, 4, 6-trinitrobenzene is introduced as follows:

3.2 Selection of aminating reagent

The VNS reaction is moderate and results in good yields, so it has been introduced to the synthesis of polynitroaromatic compounds. 4-Amino-1,2,4-triazole (ATA), 1,1,1-trimethyl-hydrazinium iodine (TMHI) and hydroxylamine are the commonly useful reagents and the reagents in order of increasing reactivity, as well as increasing cost, are hydroxylamine, ATA and TMHI. We take ATA as aminating reagent because TMHI can not compete economically with ATA and hydroxylamine can not compete competently with ATA. The results are satisfactory.



3.3 DSC curve of 1, 3-diamino-5-methylamino-2, 4, 6-trinitrobenzene

Fig. 1 is the DSC curve of 1, 3-diamino-5-methylamino-2, 4, 6-trinitrobenzene. DSC analysis show that it consists of an endothermic melting procedure and an exothermic decomposition procedure. The initial melting temperature of 1, 3-diamino-5-methylamino-2, 4, 6-trinitrobenzene is 290 ℃, and the onset temperature of thermal decomposition is 293 ℃, and the peak temperature of thermal decomposition is 303 ℃. It indicates the molecule is stable to heat.

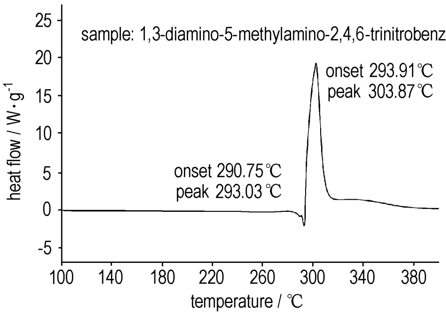


Fig. 1 The DSC curve of 1, 3-diamino-5-methylamino-2, 4, 6-trinitrobenzene

4 Conclusions

A new synthetic route to 1, 3-diamino-5-methylamino-2, 4, 6-trinitrobenzene is developed. The route utilizes the VNS amination successfully, and avoids unwanted displacement and alteration of a nitro-group, which is brought from the traditional reaction of 1, 3, 5-trihalogenotrinitrobenzene with suitable nucleophiles. The overall yield reaches 60.3%.

Although the route is more satisfactory than reported, it still be mended by avoiding the use of halogenated precursors and reducing the steps of the synthesis of 1-methylamino-2, 4, 6-trinitrobenzene.

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新法合成1,3-二氨基-5-甲氨基-2,4,6-三硝基苯

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摘要：以氯苯为原料，经过硝化-亲核氨化-氢的替代亲核取代反应合成了1,3-二氨基-5-甲氨基-2,4,6-三硝基苯，总产率达到了60.3%，产物和中间体的结构通过红外、核磁共振氢谱和元素分析进行了表征。DSC曲线显示1,3-二氨基-5-甲氨基-2,4,6-三硝基苯的热分解峰温是303 ℃，表明它有很好的热稳定性。

关键词：有机化学；氢的替代亲核取代；1,3-二氨基-5-甲氨基-2,4,6-三硝基苯

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