Synthesis of 2-(dinitromethylene)-1,3-diazacyclopentane (DNDZ) catalyzed by magnesium ion

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Abstract. As an important intermediate for new energetic materials, 2-(dinitromethylene)-1,3-diazacyclopentane (DNDZ) attracts more attentions in recent years. Herein the nucleophilic reaction between 1,1-diamino-2,2-dinitroethylene (FOX-7) and 1,2-diaminoethane catalyzed by magnesium ion had been studied and the DNDZ was synthesized in yield of 83.9% with high purity (99%) under the best conditions. The structure of the product was characterized by IR, NMR, MS and elemental analysis.

1. Introduction
1,1-Diamino-2,2-dinitroethylene (FOX-7) is a new excellent high-energy insensitive energetic material favored by chemists in the field of energetic materials in recent years, which boasts good research value and application prospects. In order to further delve into its superior performance, FOX-7 derivatives were studied to develop new energetic materials with higher research value. A series of FOX-7 derivatives were synthesized at home and abroad, and related theoretical calculations, crystal structure analysis and thermal decomposition studies were conducted[1-4]. 2-(Dinitromethylene)-1,3-diazacyclopentane (DNDZ) is an important one among them. Magnesium ion catalysis has been widely used in organic reactions[5], such as functional group interconversion, carbon-carbon bond formation, and asymmetric carbon-carbon bond formation reactions, but catalytic nucleophilic substitution reactions have rarely been reported. DNDZ is characterized by high thermal explosion temperature (Tb) (261.04 °C, FOX-7: 207.08 °C), and long adiabatic time-to-explosive (263.94 to 289.58 s, FOX-7: 78.94 to 88.93 s); high thermal stability and heat stability endows it the potential to become an insensitive energetic material; at the same time, the natural atomic charge distribution of DNDZ is calculated to infer that DNDZ is also prone to nucleophilic and electrophilic reactions [1]. It can be used as an intermediate for the design and synthesis of new energetic materials.

At present, there are three synthesis methods for DNDZ. Due to the defects of long reaction time and low yield, combined with previous work[6], we tried to catalyze the reaction with magnesium ions and achieved a major breakthrough. Not only are the used catalysts cheap and available, but also the effect is remarkable, so that the yield of DNDZ is improved and the reaction time is greatly shortened (Scheme 1).

![Scheme 1 synthesis route of 2-(dinitromethylene)-1,3-diazacyclopentane(DNDZ)](image-url)
2. Experimental Part

2.1. Reagents and Instruments
1,1-Diamino-2,2-dinitroethylene, with a purity >98%, provided by Xi'an Modern Chemistry Institute; magnesium acetate, homemade [7]; ethylenediamine, analytically pure; N-methyl-2 -pyrrolidone, analytically pure; magnesium acetate tetrahydrate, analytically pure; anhydrous magnesium chloride, analytically pure; magnesium bromide, analytically pure; zinc chloride, analytically pure, the above reagents were purchased from Sinopharm.

US Nexus 870 Fourier Transform Infrared Spectrometer (Thermo Nicolet, USA); HP5989 B Mass Spectrometer (US Hewlett Packard); AV500 Nuclear Magnetic Resonance Instrument (Bruker, Switzerland); elementar Vario ELIII Elemental Analyzer; Varian 5000 High Pressure Fluid Chromatography (Varian, USA).

2.2. Experimental Process
At room temperature, FOX-7 (2.96 g, 0.02 mol) and magnesium acetate (0.85 g, 0.006 mol) were dispersed in NMP (12 mL) into which ethylenediamine (1.44 g, 0.024 mol) was added dropwise. The mixture was stirred and heated to 110 °C in the thermostatic oil bath. After 5.5 hours of reaction, the reaction solution was slowly cooled to room temperature and diluted with water. A lot of pale yellow powder was precipitated immediately. A suction filtration was conducted and it was washed with distilled water several times and after being dried in vacuum a pale yellow solid DNDZ (2.86 g) was obtained, with a yield of 83.9%, and a purity of above 99% (determined by high performance liquid chromatography); m.p: 261-262 °C. IR, 1H NMR, 13C NMR, elemental analysis and structural characterization of MS and so forth were all identified as DNDZ.

3. Results and Discussion
This study focuses on the influence of the type and amount of magnesium ions on the reaction, and proposes the possible mechanism of magnesium ion catalysis.

3.1. Effect of Different Catalysts on Reactions
Under conditions at 110 °C and the reaction time of 5.5 h, both different catalysts and the same catalyst with varied content were selected for nucleophilic substitution. The results are shown in Figure 1 and Figure 2.

![Figure 1. Effect of different content of Mg(OAc)₂ on yield](image)
Among the selected Lewis acids, only the magnesium salt can promote the reaction to proceed smoothly and the yield is high. When the content of homemade Mg(OAc)$_2$ is 30%, the yield of DNDZ is higher than that when other magnesium salts are taken as catalysts. It is possible that the solubility of magnesium acetate as an organic acid salt in NMP may be better. On the other hand, when the magnesium salt absorbs moisture or contains crystal water, it is not conducive to the nucleophilic reaction. This may be due to the presence of water affecting the complexation of Mg$^{2+}$ with FOX-7. If considered comprehensively, choose the new-made Mg(OAc)$_2$ as a catalyst.

3.2. Discussion of Reaction Mechanism
Magnesium ions are hard Lewis acidic ions, tend to coordinate with harder Lewis alkaline ions (or atoms) to form high coordination number complexes (pentacoordinate or hexacoordinate), and the most easily combined ligating atoms are an oxygen atom or a nitrogen atom[5]. Therefore, we speculate that the possible catalytic mechanism is that the magnesium ion complexes with the nitro oxygen atom and the amino nitrogen atom in FOX-7 to form a six-membered ring, making the amino carbon atom more vulnerable to nucleophile attack, so that the reaction proceeds smoothly.

4. Conclusion
In this study, the nucleophilic substitution reaction between FOX-7 and ethylenediamine was rapidly and efficiently performed by magnesium ion catalysis. The yield of product DNDZ was as high as 83.9% and the purity was over 99%. The optimal reaction conditions are: Mg(OAc)$_2$ content is 30%, reaction temperature is 110°C, and reaction lasts for 5.5 h. The possible reaction mechanism after the preliminary investigation is that the strong electron-withdrawing property of magnesium ion makes it easy to complex with the amino nitrogen atom and the nitro oxygen atom on FOX-7 into a six-membered ring, thereby making the double bond amino terminal carbon atoms of FOX-7 molecule positively charged and the ethylenediamine molecules more likely to attack the product DNDZ.

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