

# Improved Synthesis and Characterization of 2-(Dinitromethylene)-1-nitro-1,3-diazacyclopentane

Xu Zhibin<sup>a</sup>, Liu Pan<sup>a</sup>, Xu Guangrui<sup>a</sup>, Cui Kejian<sup>a</sup>, Wang Peng<sup>a</sup>, Lin Zhihui<sup>a</sup>, Meng Zihui<sup>a</sup>, Wang Bozhou<sup>b</sup>, Ge Zhongxue<sup>b</sup>, Qin Guangmin<sup>b</sup>, and Yu Tao<sup>b</sup>

<sup>a</sup> School of Chemical & Environmental Engineering, Beijing Institute of Technology, 100081, Beijing, P. R. China

<sup>b</sup> Xi'an Modern Chemistry Research Institute, 710065, Xi'an, P. R. China

Reprint requests to Prof. Meng Zihui. Tel. & Fax: 86-10-68913065. E-mail: [m\\_zihui@yahoo.com](mailto:m_zihui@yahoo.com).

*Z. Naturforsch.* **2014**, *69b*, 77–82 / DOI: 10.5560/ZNB.2014-3160

Received May 26, 2013

A new approach is described to synthesize 2-(dinitromethylene)-1-nitro-1,3-diazacyclopentane (**4**). 2-(Dinitromethylene)-1,3-diazacyclopentane (**1**) was synthesized first by the nucleophilic substitution of ethylenediamine and 1,1-diamino-2,2-dinitroethylene (FOX-7) catalyzed by Mg(OAc)<sub>2</sub>, then **1** was transformed to **4** through nitration, reduction and hydrolysis. The crystal morphology of **4** was investigated by scanning electron microscopy (SEM). Compound **4** was also characterized by IR, NMR, MS and elemental analysis, and by thermogravimetry (TG) and differential scanning calorimetry (DSC), which revealed that **4** decomposes at 126 °C. The explosive performance of **4** was calculated using the VLW equation. The crystal density of **4** was determined as 1.79 g·cm<sup>-3</sup>. The experimental results indicate that **4** is sensitive towards impact and spark stimuli, but insensitive to friction.

*Key words:* 2-(Dinitromethylene)-1,3-diazacyclopentane, Thermal Stability, Energetic Material

## Introduction

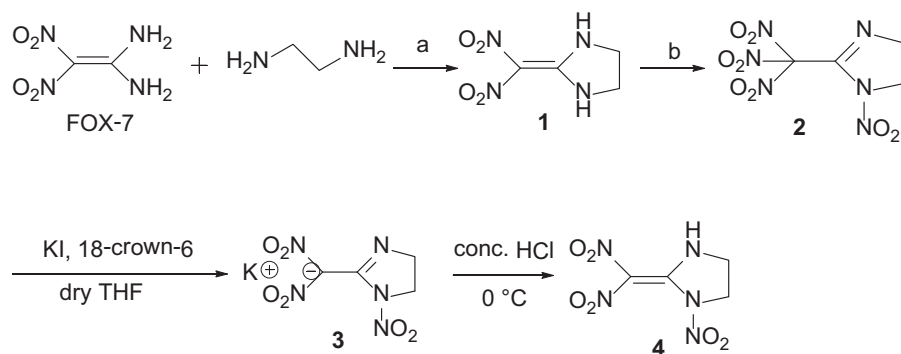
As a well-known high energy insensitive explosive with a simple structure but very unusual properties, 2,2-dinitroethene-1,1-diamine (FOX-7) was synthesized in 1998 [1]. One part of this molecule contains two geminal electron-withdrawing nitro groups as a strong oxidation center and the other part contains two electron-donating amino groups. The combination of these property-opposite parts in FOX-7 creates the so-called electron “push-pull” effect [2–4]. The unbalanced electron distribution enables the typical intramolecular electron transfer reactions of energetic materials. Recently, due to the increasing need for new energetic materials with both higher energy and lower sensitivity [5–9], some insensitive energetic materials have been modified to further reduce the sensitivity and increase the energy. FOX-7 has been considered as an ideal candidate for further transformation because nucleophilic substitution reactions can take place on its two amino-connected carbon

atoms [10–13], and many derivatives of FOX-7 have been reported [14–24]. Among these derivatives, 2-(dinitromethylene)-1-nitro-1,3-diazacyclopentane (**4**), synthesized by Baum *et al.* in 1992 [2], has recently been used as an important precursor to synthesize nitrogen-rich energetic ionic liquids [25], however its properties have not been investigated systematically. Herein we report an improved procedure to synthesize **4** in which a cheap catalyst and nitration agent were used. The thermal stability and sensitivity of **4** were investigated experimentally, and its detonation performance has been predicted.

## Results and Discussion

### *Synthesis of 2-(dinitromethylene)-1-nitro-1,3-diazacyclopentane (4)*

According to the literature [2], compound **1** was nitrated using nitric acid and trifluoroacetic anhydride in



Scheme 1. Improved synthetic route for 2-(dinitromethylene)-1-nitro-1,3-diazacyclopentane (**4**). Literature method: (a) NMP, 110 °C, 48 h; (b) (CF<sub>3</sub>CO)<sub>2</sub>O/90% HNO<sub>3</sub>, 0 °C. Improved method: (a) NMP, 110 °C, Mg(OAc)<sub>2</sub>, 5.5 h; (b) (CH<sub>3</sub>CO)<sub>2</sub>O/98% HNO<sub>3</sub>, 0 °C.

methylene chloride to produce **2**. Then **2** was denitrated by potassium iodide to form the corresponding nitronate salt **3**. After being acidified with concentrated HCl, compound **3** was finally transformed into the target compound **4** (Scheme 1). However, in order to synthesize **1** which is the crucial starting material for **4**, FOX-7 has to be heated in the presence of an excessive amount of diamine for a long time due to its very low reactivity. Therefore, a low-cost and efficient synthetic method of **1** is needed in order to synthesize **4** more efficiently.

In our previous work, we found that magnesium salts could catalyze the nucleophilic substitution reaction between FOX-7 and 1,2-diaminoethane, and that freshly prepared Mg(OAc)<sub>2</sub> is to be preferred [26]. As the alkaline earth metal with the largest ratio of charge to radius after beryllium, magnesium has the highest tendency to form strong bonds with high coordination numbers (up to 6) [27]. The high Lewis acidity, oxyphilicity and coordination ability of Mg<sup>2+</sup> [28] results in its wide applications in organic synthesis as catalyst [29–37]. Herein, **1** was synthesized using this method in a yield of 83.9% with very high purity (99%) under the optimized conditions, which was a significant increase from the literature yield of 61%. Furthermore, the required reaction time was also reduced from 48 h to 5.5 h. The synthesis of **2** was improved as well. A more economic nitration system, using acetic anhydride and 98% HNO<sub>3</sub>, has been shown to give almost the same result as that with trifluoroacetic anhydride and 90% HNO<sub>3</sub> (Scheme 1).

#### Thermal and structure analysis

The thermal stability of **4** was studied by using DSC with a heating rate of 5 °C min<sup>-1</sup> (Fig. 1).

Exothermic decomposition occurred with  $T_{\max}$  at 126.01 °C without melting, and the decomposition heat was 1.135 kJ · g<sup>-1</sup>. The thermogram of **4** (Fig. 2) revealed that most of weight loss (73%) occurred at

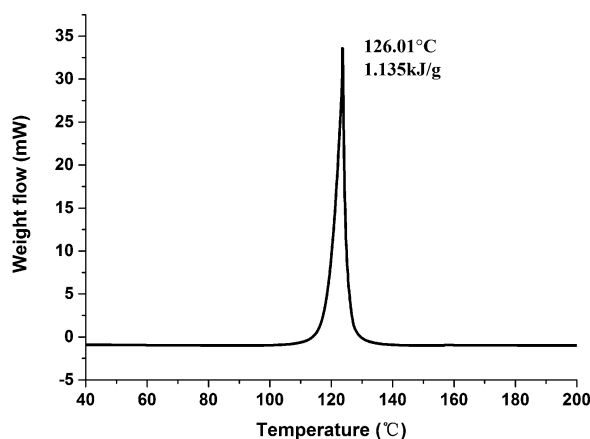


Fig. 1. DSC curve of **4**.

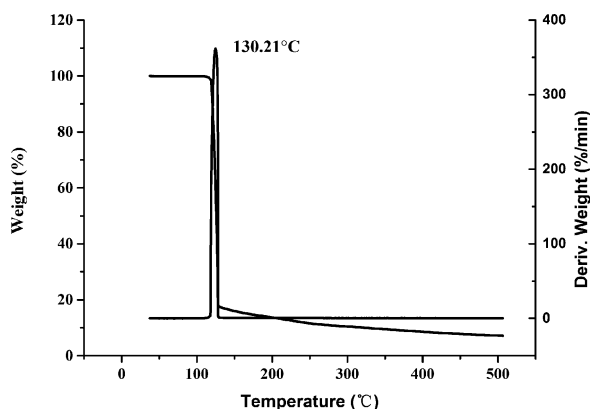


Fig. 2. TG curve of **4**.

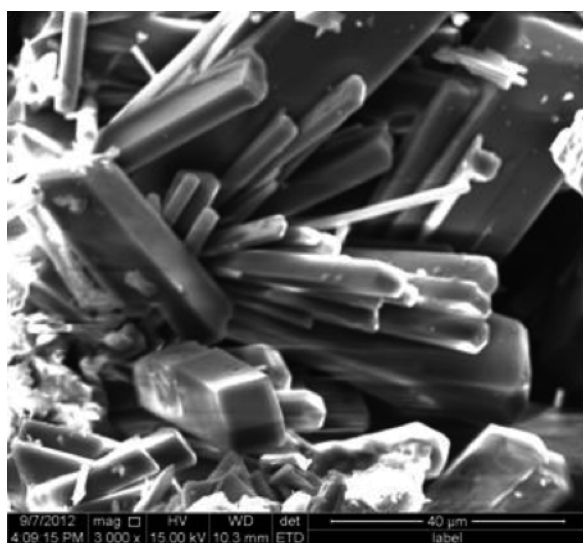
Compounds	O. B. (%)	$\rho$ (g·cm <sup>-3</sup> )	VOD (km·s <sup>-1</sup> )	ET (K)	$P_{C-J}$ (GPa)
<b>4</b> , C <sub>4</sub> H <sub>5</sub> N <sub>5</sub> O <sub>6</sub>	-32.87	1.83	8.69	5330	36.04
TACOT, C <sub>12</sub> H <sub>4</sub> N <sub>8</sub> O <sub>8</sub>	-74.18	1.81	7.05	3900	18.1
HNS, C <sub>14</sub> H <sub>6</sub> N <sub>6</sub> O <sub>12</sub>	-67.51	1.74	6.82	3300	20.0
TATB, C <sub>6</sub> H <sub>6</sub> N <sub>6</sub> O <sub>6</sub>	-55.78	1.93	7.86	2100	24.40
RDX, C <sub>3</sub> H <sub>6</sub> N <sub>6</sub> O <sub>6</sub>	-21.61	1.81	8.69	3234	33.39

Table 1. Comparison of the theoretical performance of **4** with other energetic materials.

Compounds	Friction force (N)	Impact sensitivity $H_{50}^a$ (cm)	Spark sensitive $E_{50}$ (J)
<b>4</b>	162	9.62	< 0.11
HMX <sup>b</sup>	118	24.50	2.92
RDX <sup>b</sup>	118	28	2.49

Table 2. The experimentally determined sensitivity to external stimuli of **4** compared with other energetic materials.

<sup>a</sup> Drop weight:  $5 \pm 0.005$  kg; <sup>b</sup> values from ref. [42].

Fig. 3. Scanning electron micrograph of **4**.

130.21 °C, indicating that **4** is unstable at high temperature.

The SEM image of **4** showed its cuboid-type crystal morphology (Fig. 3). The column-like crystals were arranged loosely with large cavities.

#### Explosive performance

##### Theoretical explosive performance

The explosive performance of **4** was predicted by the VLW equation (an equation of state of detonation products as proposed by Wu based on the virial theory [38]) as shown in Table 1. The calculated velocity of detonation (VOD), pressure of detonation ( $P$ ) and explosive temperature (ET) of **4** were superior as compared to those of HNS, TACOT and RDX.

#### Experimental explosive performance

Density is one of the most important properties of an energetic compound because it directly affects the main detonation performance according to the Kamlet-Jacobs equations [39–41], in which the detonation pressure is dependent on the square of the density and the detonation velocity is proportional to the density. The incorporation of nitro groups in **4** could increase the energy as well as the density of the molecule compared to those of its parent compounds, whereas the sensitivity usually is increased due to a better oxygen balance. However, the density of **4** measured by a gas pycnometer was  $1.79 \text{ g} \cdot \text{cm}^{-3}$ , lower than the crystal value ( $1.83 \text{ g} \cdot \text{cm}^{-3}$ ). Experimental results in Table 2 indicate that **4** was friction insensitive, but impact and spark sensitive compared to other nitramine explosives, such as RDX and HMX.

#### Conclusion

A FOX-7 derivative, 2-(dinitromethylene)-1-nitro-1,3-diazacyclopentane (**4**), was synthesized in a more efficient way using  $\text{Mg}(\text{OAc})_2$  as catalyst and a modified nitration method. The crystal density was experimentally determined as  $1.79 \text{ g} \cdot \text{cm}^{-3}$ , and the experimental results indicated that **4** was sensitive towards impact and spark stimuli, but insensitive to friction. These results complement the existing data of **4**, but also give an insight into its possible thermal decomposition mechanism. This study could warrant the further in-depth studies on performance parameters of **4**, which is now a popular precursor for nitrogen-rich energetic compounds.

## Experimental Section

### Materials and instruments

FOX-7 was provided by Xi'an Modern Chemistry Research Institute with a purity of 98%, and magnesium acetate ( $\text{Mg}(\text{OAc})_2$ ) was prepared as reported [43]. The other reagents were purchased with AR grade and used directly. The reaction was monitored by TLC and the purity of the product was confirmed by HPLC (Shimadzu LC-20AT) with a C18 column (4.6 mm  $\times$  250 mm, 5  $\mu\text{m}$ , Agela). The melting point of **4** was measured on an X-5 microscope melting point apparatus. IR spectra were recorded on a Thermo Nicolet FTIR-Nexus 870 spectrophotometer with KBr pellets. Mass spectra were obtained from a HP5989B mass spectrometer. NMR spectra were obtained from a 500 MHz Bruker AV500 spectrometer with tetramethylsilane (TMS) as an internal standard. Elemental analysis was carried out on an Elementar Vario EL III instrument. DSC experiments were performed on a Perkin-Elmer DSC-7 with a heating rate of 5  $^\circ\text{C min}^{-1}$ , with the baseline corrected and indium and zinc used as standards for calibration. The thermogravimetric (TG) study on **4** was carried out on a Nano SIITG-DTA 6200 system. The impact sensitivity was determined by applying a standard staircase method with a 5 kg drop weight, and the results are reported in terms of the height for 50% probability of explosion ( $H_{50}$ ) of the sample [44]. The results for impact and friction sensitivity have the uncertainty limits of  $\pm 5$  cm and  $\pm 0.2$  kg, respectively. The crystal morphology was studied on a Philips SEM (FEI XL-30). Explosive performances of **4** were predicted with the VLW equation. In addition, the density was measured experimentally on a Contador Ultra PYC 1200e.

### Synthesis of 2-(dinitromethylene)-1,3-diazacyclopentane (**1**)

Ethylenediamine was added dropwise to a solution of FOX-7 (2.96 g, 0.02 mmol) and  $\text{Mg}(\text{OAc})_2$  (1.46 g, 0.006 mmol) in *N*-methyl-2-pyrrolidone (NMP, 12.0 mL) at 110  $^\circ\text{C}$ . The mixture was stirred at 110  $^\circ\text{C}$  for 5.5 h. After the mixture was cooled to room temperature, cold water was added, and a light-yellow solid was formed immediately. Then the precipitate was filtered and washed with water to give **1** with a yield of 83.9%. Purity, 99% (HPLC). M. p. 261–262  $^\circ\text{C}$ . – IR (KBr):  $\nu = 3350$  (NH), 1568 (C=C), 1505, 1335 ( $\text{NO}_2$ ), 1173, 1122, 994  $\text{cm}^{-1}$ . –  $^1\text{H}$  NMR (500 MHz,  $[\text{D}_6]\text{DMSO}$ ):  $\delta = 8.97$  (s, 2 H, NH), 3.75 (s, 4 H,  $\text{CH}_2$ ). –  $^{13}\text{C}$  NMR (125 MHz,  $[\text{D}_6]\text{DMSO}$ ):  $\delta = 155, 43.7$ . –  $\text{C}_4\text{H}_6\text{N}_4\text{O}_4$  (174.11): calcd. C 27.59, H 3.45, N 32.16; found C 27.72, H 3.51, N 32.58. – MS ((+)-ESI):  $m/z = 175$   $[\text{M}+\text{H}]^+$ .

### Synthesis of 3-nitro-2-(trinitromethyl)-1,3-diazacyclopent-1-ene (**2**)

Nitric acid (98%, 100.0 mL) was added to a mixture of acetic anhydride (50.0 mL) and methylene chloride (300.0 mL) at 0  $^\circ\text{C}$ . After the mixture was stirred for 5 min, **1** (10.0 g) was dropped into the solution over 10 min, and the mixture was stirred for another 1 h at 0  $^\circ\text{C}$ . Then ice water (100 mL) was added to the solution slowly in order to keep the temperature at 5–10  $^\circ\text{C}$ . The organic layer was washed with water (3  $\times$  70 mL) and brine (50 mL) and dried with anhydrous  $\text{MgSO}_4$ . The solvent was removed under vacuum, and the residue was recrystallized from methylene chloride-hexane to give 10.9 g (yield 70%) of **2** as a colorless solid. M. p. 112  $^\circ\text{C}$ . – IR (KBr):  $\nu = 2877$  ( $\text{CH}_2$ ), 1617 (C=N), 1553 ( $\text{NO}_2$ ), 1275  $\text{cm}^{-1}$  ( $\text{NO}_2$ ). –  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ),  $\delta = 4.32 \sim 4.52$  (m, 4 H,  $\text{CH}_2$ ). –  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ),  $\delta = 50.10, 54.08, 120.07, 143.61$ . –  $\text{C}_4\text{H}_4\text{N}_6\text{O}_8$  (264.11): calcd. C 18.19, H 1.53, N 31.82; found C 18.55, H 1.59, N 31.41. – MS ((+)-ESI):  $m/z = 265$   $[\text{M}+\text{H}]^+$ .

### Synthesis of the potassium salt of 2-(dinitromethylene)-3-nitro-1,3-diazacyclopent-1-ene (**3**)

A mixture of **2** (4.0 g, 15.2 mol), potassium iodide (8.0 g, 48 mmol) and 18-crown-6 (4.0 g) in 200 mL of dry tetrahydrofuran was stirred at room temperature for 16 h. The solid product was isolated by filtration, washed with tetrahydrofuran, and recrystallized from water-methanol-ether to give 2.82 g (yield 73%) of **3** as a colorless solid. M. p. 205  $^\circ\text{C}$ . – IR (KBr):  $\nu = 2957$  ( $\text{CH}_2$ ), 1643 (C=C), 1496 ( $\text{NO}_2$ ), 1265  $\text{cm}^{-1}$  ( $\text{NO}_2$ ). –  $^1\text{H}$  NMR (500 MHz,  $[\text{D}_6]\text{DMSO}$ ):  $\delta = 3.94 \sim 4.20$  (m, 4 H,  $\text{CH}_2$ ). –  $^{13}\text{C}$  NMR (125 MHz,  $[\text{D}_6]\text{DMSO}$ ):  $\delta = 47.97, 51.41, 125.44, 148.14$ . –  $\text{C}_4\text{H}_5\text{N}_5\text{O}_6\text{K}$  (258.21): calcd. C 18.61, H 1.95, N 27.12; found C 18.45, H 1.58, N 28.41. – MS ((+)-ESI):  $m/z = 259$   $[\text{M}+\text{H}]^+$ .

### Synthesis of 2-(dinitromethylene)-1-nitro-1,3-diazacyclopentane (**4**)

An aqueous solution of **3** (3.25 g, 12.6 mmol) in 150 mL water was cooled to 0  $^\circ\text{C}$ , and conc. HCl (35.0 mL) was added dropwise. After 15 min the precipitate was washed with water and recrystallized from acetone-hexane to produce 1.87 g of **4** (yield 69%) as a bright-yellow solid. M. p. 121  $^\circ\text{C}$ . – IR (KBr):  $\nu = 3300$  (NH), 1619 (C=C), 1574, 1520 ( $\text{NO}_2$ ), 1265  $\text{cm}^{-1}$  ( $\text{NO}_2$ ). –  $^1\text{H}$  NMR (500 MHz,  $[\text{D}_6]\text{DMSO}$ ):  $\delta = 3.97$  (t, 2 H), 4.37 (t, 2 H), 10.01 (br s, 1

H). –  $^{13}\text{C}$  NMR (125 MHz,  $[\text{D}_6]\text{DMSO}$ ):  $\delta = 48.57, 49.34, 128.20, 150.29$ . –  $\text{C}_4\text{H}_5\text{N}_5\text{O}_6$  (219.11): calcd. C 21.93, H 2.30, N 31.96; found C 22.30, H 2.36, N 31.86. – MS (–ESI):  $m/z = 218$   $[\text{M}-\text{H}]^-$ .

#### Acknowledgement

The authors thank Xi'an Modern Chemistry Institute for the structure analysis and thermal analysis experiments.

- [1] N. V. Latypov, J. Bergman, A. Langlet, U. Wellmar, U. Bemm, *Tetrahedron* **1998**, *54*, 11525–11536.
- [2] K. Baum, N. V. Nguyen, R. Gilardi, J. L. Flippen-Anderson, C. George, *J. Org. Chem.* **1992**, *57*, 3026–3030.
- [3] V. Venkatesan, B. G. Polke, A. K. Sikder, *Comp. Theor. Chem.* **2012**, *995*, 49–54.
- [4] L. Simkova, F. Liska, J. Ludvik, *Curr. Org. Chem.* **2011**, *15*, 2983–2995.
- [5] V. Thottempudi, J. N. M. Shreeve, *J. Am. Chem. Soc.* **2011**, *133*, 19982–19992.
- [6] V. Thottempudi, H. X. Gao, J. N. M. Shreeve, *J. Am. Chem. Soc.* **2011**, *133*, 6464–6471.
- [7] U. R. Nair, S. N. Asthana, *Def. Sci. J.* **2010**, *60*, 137–151.
- [8] T. M. Klapötke, P. Mayer, C. M. Sabate, J. M. Welch, N. Wiegand, *Inorg. Chem.* **2008**, *47*, 6014–6027.
- [9] M. B. Talawar, R. Sivabalan, M. Anniyappan, G. M. Gore, S. N. Asthana, B. R. Gandhe, *Comb. Explor. Shock Waves* **2007**, *43*, 62–72.
- [10] Q. B. Fu, Y. J. Shu, Y. G. Huang, J. H. Zhou, Y. X. Zhang, *Chin. J. Expl. & Propel.* **2009**, *32*, 6–9.
- [11] A. J. Bellamy, *Struct. Bond.* **2007**, *125*, 1–33.
- [12] A. V. Kimmel, P. V. Sushko, A. L. Shluger, M. M. Kuklja, *J. Phys. Chem. A* **2008**, *112*, 4496–4500.
- [13] A. V. Kimmel, P. V. Sushko, A. L. Shluger, *J. Chem. Phys.* **2007**, *126*, 1–10.
- [14] K. Z. Xu, X. G. Zuo, J. R. Song, F. Wang, J. Huang, C. R. Chang, *Chem. J. Chin. Univ.* **2010**, *31*, 638–643.
- [15] J. N. Luo, K. Z. Xu, M. Wang, J. R. Song, X. L. Ren, Y. S. Chen, F. Q. Zhao, *Bull. Korean Chem. Soc.* **2010**, *31*, 2867–2872.
- [16] K. Z. Xu, X. G. Zuo, H. Zhang, B. Yan, J. Huang, H. X. Ma, B. Z. Wang, F. Q. Zhao, *J. Therm. Anal. Calorim.* **2012**, *110*, 585–591.
- [17] P. Gilinsky-Sharon, H. E. Gottlieb, D. E. Rajsfus, K. Keinan-Adamsky, V. Marks, P. Aped, A. A. Frimer, *Magn. Reson. Chem.* **2012**, *50*, 672–679.
- [18] M. Wang, K. Z. Xu, F. He, H. Zhang, Y. S. Chen, J. R. Song, F. Q. Zhao, *Chem. Res. Chin. Univ.* **2012**, *28*, 716–720.
- [19] J. H. Song, Z. M. Zhou, H. F. Huang, D. Cao, L. X. Liang, K. Wang, J. Zhang, F. Q. Zhao, *Z. Anorg. Allg. Chem.* **2012**, *638*, 957–964.
- [20] J. He, B. Jin, R. F. Peng, S. J. Chu, H. S. Dong, *Chin. J. Org. Chem.* **2011**, *31*, 1643–1647.
- [21] K. Z. Xu, F. Q. Zhao, F. Wang, H. Wang, J. A. Luo, R. Z. Hu, *Chin. J. Chem. Phys.* **2010**, *23*, 335–341.
- [22] K. Z. Xu, F. Wang, Y. H. Ren, W. H. Li, F. Q. Zhao, C. R. Chang, J. R. Song, *Chin. J. Chem.* **2010**, *28*, 583–588.
- [23] C. R. Chang, K. Z. Xu, J. R. Song, B. Yan, H. X. Ma, H. X. Gao, F. Q. Zhao, *Acta Chim. Sinica* **2008**, *66*, 1399–1404.
- [24] M. Anniyappan, M. B. Talawar, G. M. Gore, S. Venugopalan, B. R. Gandhe, *J. Hazard. Mater.* **2006**, *137*, 812–819.
- [25] J. H. Song, Z. M. Zhou, D. Cao, H. F. Huang, L. X. Liang, K. Wang, J. Zhang, *Z. Anorg. Allg. Chem.* **2012**, *638*, 811–820.
- [26] P. Liu, Z. B. Xu, B. Z. Wang, *Chin. J. Energ. Mater.* **2013**, *21*, 222–225.
- [27] R. J. Wehmschulte, B. Twamley, M. A. Khan, *Inorg. Chem.* **2001**, *40*, 6004–6008.
- [28] X. X. Zhang, W. D. Li, *Chin. J. Org. Chem.* **2003**, *23*, 1185–1197.
- [29] C. Blomberg, F. A. Hartog, *Syn.* **1977**, *1*, 18–30.
- [30] Y. Ohnishi, K. Masayuki, A. Ohno, *J. Am. Chem. Soc.* **1975**, *97*, 4766–4768.
- [31] G. Righi, G. Pescatorea, F. Bonadiesa, C. Boninib, *Tetrahedron* **2001**, *57*, 5649–5656.
- [32] G. Righi, T. Franchinia, C. Boninib, *Tetrahedron Lett.* **1998**, *39*, 2385–2388.
- [33] S. Yamaguchi, M. Nedachi, H. Yokoyama, Y. Hirai, *Tetrahedron Lett.* **1999**, *40*, 7363–7365.
- [34] T. Wirth, *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 61–63.
- [35] D. S. Rawat, M. Jeffrey, *J. Am. Chem. Soc.* **2001**, *123*, 9675–9676.
- [36] E. J. Corey, I. Kazuaki, *Tetrahedron Lett.* **1992**, *33*, 6807–6810.
- [37] G. Desimoni, G. Faita, A. Mortoni, P. P. Righetti, *Tetrahedron Lett.* **1999**, *40*, 2001–2004.
- [38] X. Wu, X. P. Long, B. He, X. H. Jiang, *Sci. China Ser. B* **2009**, *52*, 605–608.
- [39] M. J. Kamlet, S. J. Jacobs, *J. Chem. Phys.* **1968**, *48*, 23–35.
- [40] M. J. Kamlet, J. E. Ablard, *J. Chem. Phys.* **1968**, *48*, 36–42.

- [41] M. J. Kamlet, C. Dickinson, *J. Chem. Phys.* **1968**, *48*, 43–50.
- [42] S. Zeman, P. Valenta, V. Zeman, J. Jakubko, Z. K. Kamensky, *Chin. J. Energ. Mater.* **1988**, *6*, 188–122.
- [43] G. L. Shen, C. B. Xu, C. B. Fu, Y. F. Ban, Y. N. Chen, *Mod. Chem. Ind.* **2009**, *29*, 222–225.
- [44] Z. L. Yu, X. Q. Wu, *Anhui Chem. Ind.* **2003**, *29*, 20–22.