SYNTHESIS OF N^3, N^4-BIS (2,4-DINITROBENZOFUROXAN) -N^3, N^4-DINITRO-1, 2, 5-OXADIAZOLE-3, 4-DIAMINE

Wu-Wei Wang[a], Nai-Xing Wang[a, b]* Ya-Lan Xing[b], Rui long Sheng[a] , Jia Zhao[a]
[a]Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, 100101, Beijing, China
[b]Beijing University of Chemical Technology, 100029, Beijing, China

Abstract: Investigation of new energetic materials, especially those bearing no hydrogen atoms or with low hydrogen content, has attracted considerable interest recently. Herein the synthesis of a new kind of benzenefuroxan compound by two different methodologies was reported. The structure of the compound was characterized by IR, MALDI-TOF-MS, ^{1}H-NMR, ^{13}C-NMR.

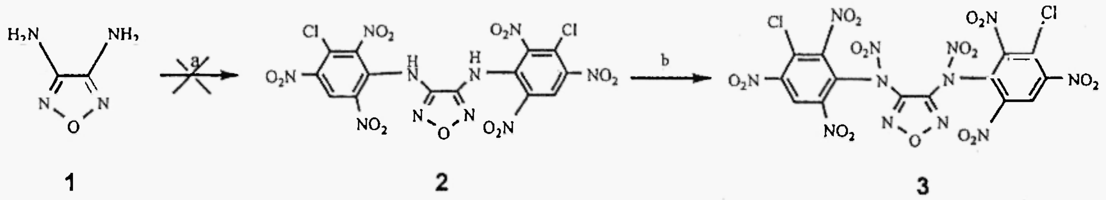
Introduction

Investigation of new energetic materials with excellent properties has attracted considerable interest recently; especially synthesis of energetic molecules bearing no hydrogen atoms or with low hydrogen content is a focused area. Recently, scientists had synthesized some of the energetic materials such as hexaazaisowutaitane[1], 3,3'-dinitroazetidine [2] and octanitrocubane [3], whose hydrogen content are very low and have a prominent performance as energetic materials.

Being useful structures to the synthesis of explosives and other functional materials[4], furazan rings (1,2,5-oxadiazole) and furoxan groups (N oxides of furazan) have been attracting many attentions in synthetic chemical field. It has been proved that furoxan groups can result in the increase of densities of the materials and detonation velocities of the explosives compared to nitro groups [5].The aromatic rings or fused rings were introduced into energetic molecules usually can improve heat resistance of energetic materials and decrease their sensibility to mechanical collision. Considering of the advantages of furazan groups and aromatical rings, we synthesized the title compound, which has six nitro groups, two furoxan rings and one furazan ring. The compound, with symmetrical structure, has very low hydrogen content (only has two hydrogen atoms, H%=0.31%) and high nitrogen content (N%=30.72%), which makes it could be utilized as new energetic material.

Results and Discussions

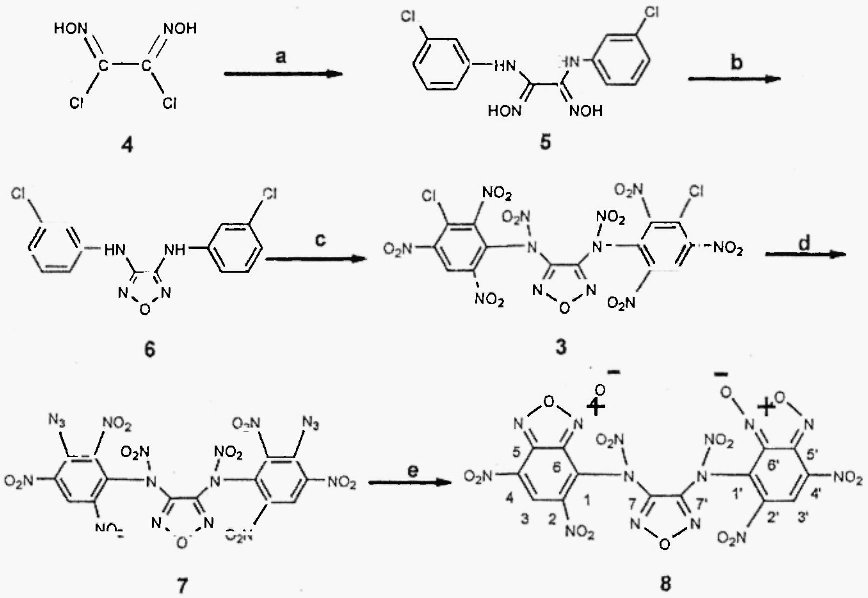
To synthesize the compound, we designed two different routes, as illustrated in scheme 1 and 2. Scheme 1 shows that 3,4-diaminefurazan, a useful precursor for synthesizing the construction of high energetic furazan derivations [6, 7], was used to react with 2,4,6-trinitro-1, 3-dichlorobenzene trying to obtain the key intermediate 3. However we found the reaction did not proceed in this experiment. It was believed that the furazan ring of 3,4-diaminefurazan disperses the election density of the two-amine groups and decreases the nucleophilicity of two the nitrogen atoms[8]. Therefore the chlorine atoms of 2,4,6-trinitro-1, 3-dichlorobenzene couldn't be replaced by 3,4-diaminofurazan.



Regents: a. 2,4,6-trinitro-1, 3-dichlorobenzene, $NaHCO_3$,THF, reflux, 3h; b. fuming H_2SO_4 ,fuming HNO_3

Scheme-1

As shown in scheme 2, the target compound was obtained in five steps from dichloroglyoxime. Dichloroglyoxime, **4**, was synthesized according to previously reported methods .It was obtained from the chlorination of glyoxime, which was synthesized from the reaction of commercially available aqueous glyoxal with hydroxylamine hydrochloride.



Regents: a. 3-chloroaniline $NaHCO_3$-THF, reflux, 3 h; b. NaOH-$OHCH_2CH_2OH$, 140□, 3 h; c. Fuming H_2SO_4, 90□, 2 h, then fuming HNO_3, 90□, 12 h; d. NaN_3, room temperature, 3 h; e. CH_3CH_2COOH , reflux, 1.5 h.

Scheme-2

Treatment of **4** with two equivalents of 3-chloroaniline in present of sodium bicarbonate in tetrahydrofuran gave N^3, N^4-bis (3-chlorophenyl)-N^3, N^4-diaminoglyoxime, **5**. **5** was dehydrated at 140 ^{0}C to gave N^3, N^4-bis (3-chlorophenyl)-N^3, N^4-diaminofurazan , **6**. The key intermediate **3** was prepared from **6** by nitration with fuming H_2SO_4 and fuming HNO_3. Then it was converted into **7** by treatment with sodium azide. To synthesize the furoxan ring, **7** was refluxed in propionic acid for 1~2 hours until no more nitrogen gas was evaporated, then the title product was obtained by further working up[10].

Experimental

All melting points were determined on a X4 digital microscopical melt-point instrument and were uncorrected. IR spectra were recorded on a BIO-RAD FTS 165 infrared spectrometer.^{1}H NMR and ^{13}C NMR spectra were obtained on a Varian Gemini 300 and Bruker 400MHz NMR spectrometer. EI-MS was obtained on TRIO 2000 MS spectrometer. MALDI-TOF mass spectra (positive ion mode) were recorded on BIFLEX III.

Compound 5: Dichloroglyoxime (4.0 g, 0.026 mol), 3-chloroaniline (10.7 ml, 0.107 mol), sodium bicarbonate (4.3 g, 0.052 mol) were dissolved in 50 ml of tetrahydrofuran and the resulting solution was refluxed for 3h. The solid was filtrated and the solvent was removed. The concentrated solution was diluted with chloroform until no more product precipitated. The solid was isolated by filtration and washed well with large amount of chloroform. The crude material recrystallized from ethanol-water gave 6.5 g of pure product. Yield: 73%. m.p. 208~210 ^{0}C (lit. [11] m.p.206~208 ^{0}C). IR (KBr) cm^{-1}: 3377(N-H), 3198~2810(O-H), 1643(C=N), 1595,1481(C=C), 1078(C-Cl). EI-MS: m/z 338, 321, 286, 152, 127, 99, 75. ^{1}H NMR(acetone-d$_6$) δ ppm: 10.27(s, 2H, N-OH), 7.82 (s,2H, -NH), 6.75~7.14(m,8H, -C_6H_4-).

Compound 6: compound **5** (3.6 g 0.0106 mole)was added to the solution of 0.120 g sodium hydroxide in 10 ml of ethylene glycol and the resulting mixture was heated to 140 ^{0}C for 3h. Then, the solution was cooled to 0 ^{0}C and the precipitated solid was collected by filtration. Recrystallization from ethanol-water gave 1.5 g of product. Yield: 45% m.p. 190~192 ^{0}C (lit. [11] m.p.191~192 ^{0}C. IR (KBr) cm^{-1}: 3333(N-H), 1624(C=N), 1594, 1482(C=C). EI-MS: m/z 320, 153,127,75. ^{1}H NMR (acetone-d$_6$) δ ppm: 8.02 (s, 2H, -NH-), 7.02~7.72(m, 8H, -C_6H_4-).

Compound 3: compound **6** (1.0 g, 3.11 mmole) was added in small portions to 12 ml fuming sulfuric acid and the temperature was allowed lower than 40 ^{0}C. The resulting mixture was heated to 90 ^{0}C and stirred at 90 ^{0}C for 2 h. The mixture was cooled to room temperature and 18 ml fuming nitric acid was added slowly, the temperature was kept lower than 30 ^{0}C. The resulting mixture was heated to 90 ^{0}C and held at this temperature for 12h. The mixture was cooled down again and poured into 100g of crushed ice. The resulting yellow solid was collected by filtration and gave 0.2 g of product. Yield: 10%. IR (KBr) cm^{-1}: 3093(C-H), 1586, 1498(C=C), 1553,1347(-NO_2). MOLDI-TOF-MS: m/z 590,681.

Compound 7: Sodium azide (0.200 g, 3.07 mmole) in 1ml of water was added with stirring to the solution of compound **6** (0.420 g.0.62 mmole) in 3ml of ethanol. After being stirred at room temperature for 3 h, the mixture was poured into small amount of ice water. The resulting yellow solid was collected by filtration and washed well with water to give 0.345 g of product. Yield: 80%. IR (KBr) cm^{-1}: 3091(C-H), 2161(-N_3), 1607,1576, (C=C), 1554,1339(-NO_2).

Compound 8: compound 7 (0.300 g, 0.45 mmole) was added to 2ml of propionic acid and refluxed for 1.5h. The mixture was cooled down and poured into small amount of ice water. The yellow precipitate was collected by filtration and well washed with water. Recrystallization from ethanol-chloroform gave 0.226 g of product. Yield: 75%. m.p. 159~161 ^{0}C. IR (KBr) cm^{-1}: 3070(Ar-H), 1660,1623, (-ONO-), 1598,1564, (C=C). ^{1}H-NMR(acetone-d6) δ ppm: 8.79(s, 2H, -C_6H_1-). ^{13}C-NMR(acetone-d6) δ ppm: 145.9(C-1,C-1'), 140.6(C-5,C-5'), 137.8(C-2,C-2' C-4,C-4'), 121.5(C-3,C-3'), 110.0(C-6,C-6'), 104.2(C-7,C-7'). MOLDI-TOF-MS: m/z 588.2, 637.1, 659.1(M+Na), 675.1(M+K).

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