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Synthesis of 3,4-Dinitrofuroxan

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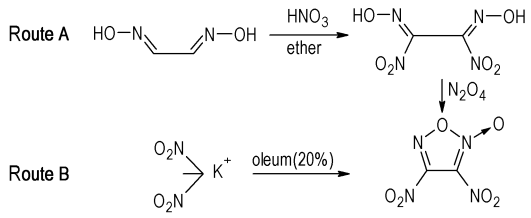
Furoxan derivatives[1-2], which have both high enthalpy of formation, high density and high oxygen balance, lead to an obvious increase in specific impulse of propellant compared to a composition of the same type containing RDX. Especially, 3, 4-dinitrofuroxan is a powerful energetic compound first reported in 1993[3]. In addition, it would serve as an intermediate in the synthesis of other furoxan derivatives. Godovikova et al[3-4] reported the synthetic method from glyoxime via two steps of nitration and oxidation (Route A). Furthermore, 3,4-dinitrofuroxan was aslo obtained by treating dinitromethane potassium salt with concentrated H_2SO_4 or oleum (Route B)[5]. But details of two methods were incomplete. In this paper, two approaches of the synthesis of 3, 4-dinitrofuroxan were carried out on the basis of literature (scheme 1), the post-processing method for dinitroglyoxime was improved. The structure of ultimate product was well confirmed by ^{13}C NMR, ^{14}N NMR, ^{15}N NMR, IR, MS and elemental analysis, and its ^{15}N NMR and MS spectra were obtained firstly.



Scheme 1 Two synthetic routes of 3, 4-dinitrofuroxan

Route A: To a suspension of 6.6g (0.075 mol) glyoxime and 0.15 g(0.002 mol) $NaNO_2$ in 90mL ether, 56.7 g 25% HNO_3 (0.225mol) was added dropwise at 15 ℃, then the resulting solution was stirred at 15 ℃ for 2.5 h. The organic layer was separated off, washed with water and dried over anhydrous magnesium sulfate, then filtered and the solvent was removed to give a yellow residue. 20 mL trifluoroacetetic acid was added to the residue. After the solution was cooled to −10 ℃, the yellow precipitate was filtered and dried in air to obtain 7.1 g of solid with yield of 53.2%. ^{13}C NMR (CD_3COCD_3, 500 MHz), δ: 148.34; ^1H NMR (CD_3COCD_3, 500 MHz), δ: 13.95; IR (KBr, cm^{-1}), ν: 3342, 1665, 1570, 1352 and 835; Anal. Calcd for $C_2H_2N_4O_6$ (%): C 13.49, H 1.13, N 31.47; found C 13.78, H 1.13, N 30.19.

A solution of 1.5 mL(25 mmol) N_2O_4 in 10 mL CCl_4 was added dropwise to a suspension of 0.89 g(5 mmol) dinitroglyoxime in 20 mL CCl_4 at 0 ℃. After 3.5 h the solvent was removed and the residue was purified by column chromatography on silica gel using a mixture of hexane and ethyl acetate (R_f =0.7, 10: 1, *V/V*) as the eluent, and 0.6 g 3, 4-dinitrofuroxan was afforded with yield of 67.4% . ^{13}C NMR ($CDCl_3$, 500 MHz), δ: 119.54, 150.65; ^{14}N NMR($CDCl_3$, 500 MHz), δ: −40.54 (4—NO_2), −45.63 (3—NO_2); IR (KBr, cm^{-1}), ν: 1675, 1581, 1558, 1508, 1461, 1328, 1030, 835; MS (EI) *m/z* (%): 193 (M + OH, 22), 146 (M—NO, 24), 130 (M—NO_2, 100); Anal. Calcd for $C_2N_4O_6$ (%): C 13.60, H 0.00, N 31.80; found C 13.48, H 0.00, N 30.79.

Route B: 2.9 g dinitromethane patassium salt was added to 50 mL oleum(20%) at room temperature, and was stirred for 1 h at 100 ℃, then poured to 100 mL ice-water. The mixture was extracted with ether 50 mL × 5. The organic layers were washed with water and dried over anhydrous magnesium sulfate, then filtered and the solvent was removed to give a yellow residue. The title compound was purified by column chromatography on silica gel using a mixture of hexane and ethyl acetate (R_f = 0.7, 10: 1, *V/V*) as the eluent, and 0.6 g the title compound was obtained with yield of 17.1%. The analysis show that the compound same as route A.

The structure of 3, 4-dinitrofuroxan was determined by ^{13}C NMR, ^{14}N NMR, ^{15}N NMR, IR, MS as well as elemental analysis. In the ^{13}C spectra of 3, 4-dinitrofuroxan, the resonance bands appear at 119.54 and 150.65. The ^{14}N spectra was showed in Fig.1, where two signals of N4 and N3 were observed at −40.54 and −45.63 respectively. The ^{15}N spectra of 3, 4-dinitrofuroxan (Fig.2) was depicted with four signals at −10.49 (N1), −24.55 (N2), −43.53 (N4) and −48.60 (N3). The signals of N2, which has a ligand oxygen atom as a neighbor in the furoxan ring, appear as expected at higher field (−24.55) compared with N1(−10.49). In the IR spectra, several main absorption bands around 1675, 1581, 1508, 1461, 1030, 835 cm^{-1} were attributed to the furoxan ring, and strong absorption bands around 1558, 1328 cm^{-1} could be assigned to the nitro group.

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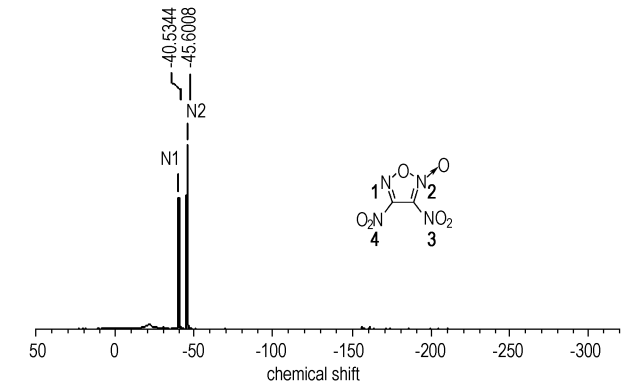

Fig. 1 ^{14}N spectra of 3, 4-dinitrofuroxan

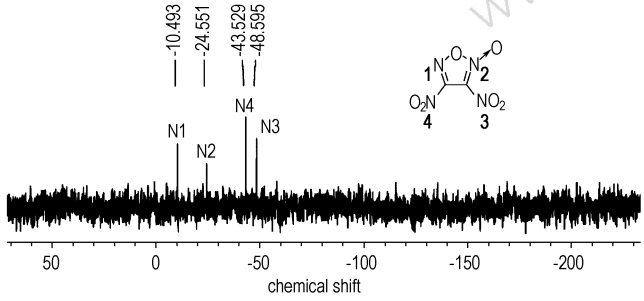

Fig. 2 ^{15}N spectra of 3, 4-dinitrofuroxan

3, 4-Dinitrofuroxan was synthesized from two different routes. Compared with route B the route A allowed the synthesis of 3, 4-dinitrofuroxan from accessible initial compounds with a high yield of 35.9%, and its structure was well confirmed by ^{13}C NMR, ^{14}N NMR, ^{15}N NMR, IR, MS and elemental analysis.

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