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SYNTHESIS OF N,N'—BIS(2—NITRO—BENZODIFUROXANYL) —3,5—DINITRO—2,6—DIAMINOPYRIDINE

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ABSTRACT

N,N'—bis(2—nitro—benzodifuroxanyl)—3,5—dinitro—2,6—diaminopyridine has been synthesized from 2,6—diaminopyridine and trinitrotrichlorobenzene, Yields of 80 — 90% were obtained under extremely mild reaction conditions. For this end compound, The structure has been determined by elemental analysis, IR, ^{1}HNMR, and MS spectroscopies.

It has been believed that the replacement of nitro groups by furoxan groups can result in increase of density and detonation velocity of explosives[2], and the introduction of pyridine as well as amino groups in to the explosive molecules can result in an increase of density and heat resistance and a decrease of impact sensitivity. In order to utilize the advantanges of furoxan and pyridine as well as amino groups, the title compound with very low hydrogen content, high nitrogen content, high density, and good heat resistance was designed and has been synthesized.

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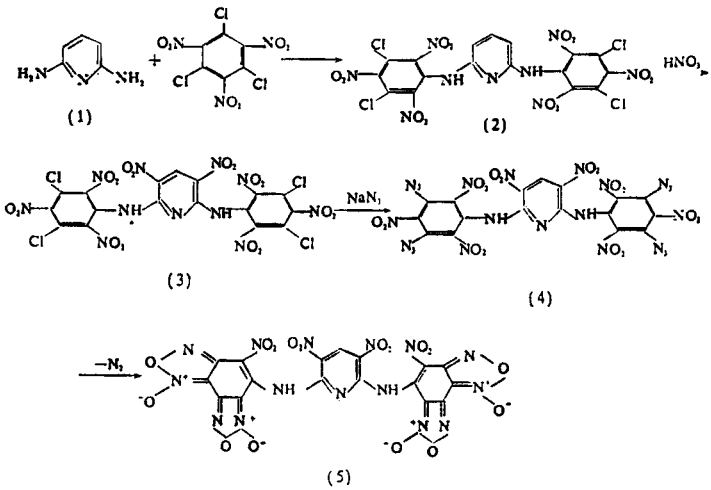
RESULTS

N,N'—bis(2—nitro—benzodifuroxanyl)—3,5—dinitro—2,6—diaminopyridine (5) has been synthesized by thermal degradation of N,N'—bis(2,4,6—trinitro—3,5—diazidophenyl)—3,5—dinitro—2,6—diaminopyridine(4), which was obtained by reaction of N,N'—bis(2,4,6—trinitro—3,5—dichlorophenyl)—3,5—dinitro—2,6—diaminopyridine(3) with NaN_3. Compound (3) was prepared by nitrating N,N'—bis(2,4,6—trinitro—3,5—dichlorophenyl)2,6—diaminopyridine(2). Compound (2) was synthesised by reaction of trinitrotrichlorobenzene (1) with 2,6—diaminopyridine. Our high yield preparation of (5) is shown in below:



Thermal degradation of (4) then generates the four furoxan ring of title compound(5) with accompanying loss of N_2. Compound(5) is a yellow solid, soluble in DMF and DMSO as well as acetone, and difficult to dissolve in other organic solvents. It has a molecular formula $C_{17}H_3N_{15}O_{16}$, molecular weight 673, density 1.91g/cm^3 (It was determined by the method of the density bottle). Melting point 231.5℃(dec), detonation velocity 8626. 7m · s^{-1} (Calculated). Compared with a moderately powerful heat resisting explosive 2,6—bis(picrylamino)—3,5—

dinitropyridine[3], compound (5) displays both a higher density and detonation velocity. In addition to being chemically inert, this energetic materials has better oxygen balance and increased energy. The compound is easily prepared in good yield. In the procedure for generating the furoxan rings and for thermal loss N_2, the use of propionic acid as solvent resulted in a substantial improvement in yield as well as a significant increase in particle size.

EXPERIMENTAL

Melting points were measured on a PCR—1 hot—stage apparatus, and elemental analyses were obtained by using on Carlo Erba 1102 Instrument. IR spectra were recorded on a Shimadzu IR—408 spectrophtometer. Mass spectra were obtained on a 80 RFA spectrometer, and ^{1}HNMR spectra were obtained on a LX—120 spectrometer (TMS as internal standard).

N,N^1-bis(2, 4, 6-trinitro-3, 5-dichlorophenyl)-2, 6-diaminopyridine (2) Trinitrotrichlorobenzene (5. 1g, 0. 016mol) and 2,6—diaminopyridine (0. 873g, 0. 008mol) were refluxed in 60 ml of polar aprotic solvent for 3h. Then product was poured into 800 ml of water with rapid stirring. The precipitated solid was collected by suction filtration through a coarse fritted disc funnel, washed first with cold water then with methanol, and finally dried. The yield of compound (2) is 4. 75g(88. 7%). mp247℃, IR(KBr): 3350(—NH—), 1540, 1320(—NO_2). 910(Ar—Cl)cm^{-1}. Anal calcd for $C_{17}H_5N_9O_{12}C_{l4}$: C, 30. 49; H, 0. 747; N, 18. 83; Cl, 21. 23. Found: C, 30. 52; H, 0. 713; N, 18. 87; Cl, 21. 31.

N,N^1—bis(2,4,6-trinitro-3,5-dichlorophenyl)-3,5-dinitro-2,6-diaminopyridine (3) To 80ml of fuming nitric acid (98% HNO_3), compound (2) (4. 7g, 7. 025mmol) was added with stirring in small portions. The resulting mixture was stirred at 50℃ for 0. 5h, then refluxed for 3h. The mixture is chilled to 0℃ by immersing the flask in an ice bath, then some crushed ice with cold water was added into the mixture without stirring. The precipitated solid was collected by filitration. The product was soaked in hot water at 90℃ for 1h. The precipitate, a yellow solid, was collected by filtration, and the residue was washed thoroughly with water and dried, giving 3. 8g (71. 3%) product. mp274℃. IR(KBr) 3450(—NH—), 1540, 1320(—NO2), 910 (Ar—Cl)cm^{-1}. Anal caled for $C_{17}H_3N_{11}O_{16}C_{l4}$: C, 26. 87; H, 0. 395; N, 20. 29; Cl, 18.

71. Found: C, 26. 81; H. 0. 390; N, 20. 25; Cl, 18. 69.

N,N'-bis(2, 4, 6-trinitro-3, 5-diazidophenyl)-3, 5-dinitro-2, 6-diaminopyridine (4) Sodium azide (1. 49g 21. 67mmol) in 10ml of water was added dropwise with stirring to a solution of 2. 0g (2. 63mmol) of compound (3) in 50ml DMSO. After having been stirred at 35℃ for 2h, the mixture was poured into cold water. The resulting yellow precipiate was collected by filitration and washed with water, giving 1. 63g (78. 8%) of compound (4). IR(KBr): 3400(—NH—), 2100($—N_3$), 1540, 1320($—NO_2$).

N,N'-bis(2-nitro-benzodifuroxanyl)-3, 5-dinitro-2, 6-diaminopyridine (5) Compound (4)(0. 98g, 1. 248mmol) was added to 35ml of propionic acid, and the mixture was heated to 125℃, and then kept at 125℃—130℃ for about 1h until the evolution of nitrogen gas was completed[4]. After being colded to room temperature, the mixture was poured into water. The precipitate was separated by filtration, washed thoroughly with water, and dried, giving 0. 688g (82%) of compound (5). Differental thermal analysis indicates that the product is stable to 231. 5℃. Thermal gravimetric analysis showed no weight loss for 48h at 100℃. IR(KBr): 3400(—NH—), 3000(Ar—H), 1615(—ONO—), 1540, 1320($—NO_2$)cm^{-1}. ^{1}HNMR(DMF—D_6): 9. 25(H, Ar—H), 3. 21(2H —NH—), ppm. MS(FAB) 675$(M+1)^+$. Anal Caled for $C_{17}H_3N_{15}O_{16}$: C, 30. 31; H, 0. 445; N, 31. 20. Found: C, 30. 40; H, 0. 437; N, 31. 23.

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