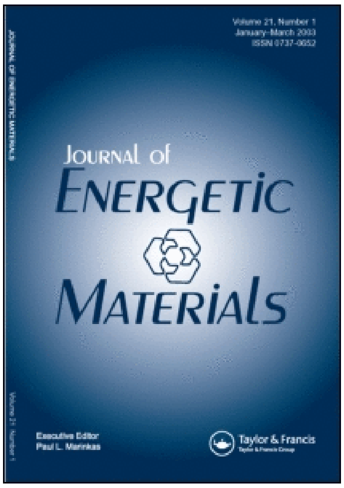

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Feng Zengguo[a]; Chen Boren[a]
[a] Department of Chemical Engineering Beijing, Institute of Technology, Beijing, People's Republic of China

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STUDIES ON REACTIONS OF POLYNITROSTILBENES WITH SODIUM AZIDE

Feng Zengguo   Chen Boren
Department of Chemical Engineering
Beijing Institute of Technology, Beijing 100081
People's Republic of China

ABSTRACT

Three polyazidonitrostilbenes were prepared via the reaction of polynitrostilbenes with sodium azide. Addition of 2 mole of this nucleophile to a solution of 3-chloro-2,2',4,4',6,6'-hexanitrostilbene in DMF results in the substitution of azido groups for one nitro group and the chlorine in the same benzene ring. The reactions of 2,2',4,4',-6,6'-hexanitrostilbene with 2 and 4 mole of NaN_3 exhibit a different reactivity and selectivity and produce symmetrically substituted azido polynitrostilbenes.

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INTRODUCTION

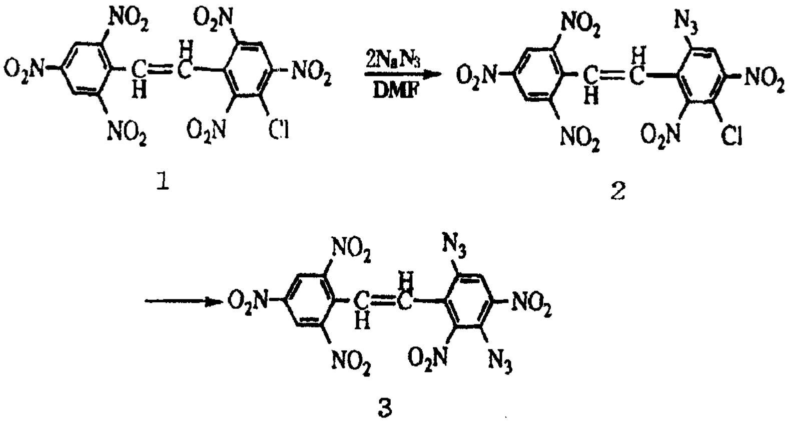
Among today's most spectacular energetic materials, special attention has been given to aliphatic azides which are stable and not sensitive to mechanical stimuli. Unfortunately, aromatic azides are so unstable and sensitive to impact or friction that their applications to detonation purposes are extremely limited. Of particular interest recently has been the study of the synthesis of 3-azido-2,4,6-trinitroaniline and pentanitrophenyl azide, the key intermediates to new explosives of substituted amino benzofuroxans[1,2].

As part of continuing program to study the synthesis and reactivity of polynitrostilbenes, three new polyazidonitrostilbenes were prepared from the reaction of polynitrostilbenes with sodium azide. These products are highly energetic and comparable to HNS. This paper describes briefly the reactivity and selectivity observed in the reaction of

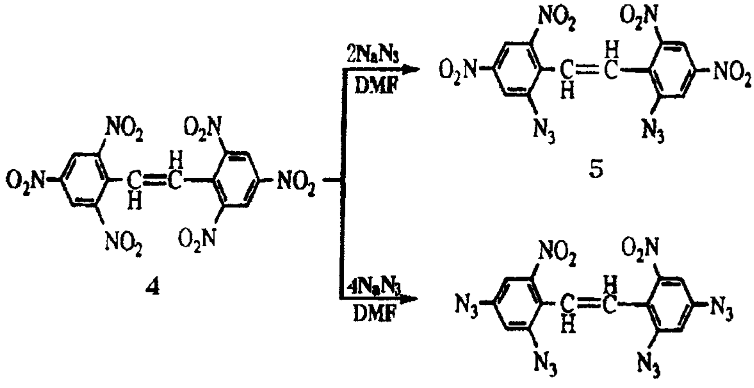
3-chloro-2,2',4,4',6,6'-hexanitrostilbene(3-CHNS) and 2,2',4,4',6,6'-hexanitrostilbene(HNS) with sodium azide.

RESULTS AND DISCUSSION

In 1967, Grieco and Mason[3] reported that the reaction of 1,3,5-trinitrobenzene(TNB) with NaN_3 in DMSO at elevated temperature gave 1-azido-3,5-dinitrobenzene. Although 2 mole of the nucleophile was added, only a substituted monoazido benzene was obtained. However, a high reactivity and selectivity has been found in the reaction of 3-CHNS with two mole of NaN_3 in DMF at room temperature. Two azide ions prefer to attack at its C-6 and C-3 in the same benzene ring to form 2,5-diazido-2',4,4',-6,6'-pentanitrostilbene(3). The evidence for this product's structural assignment is provided by its ^1H NMR spectrum which show four distinct peaks due to five protons. The peak at $\delta 9.11$(s) is consistent with two aromatic protons which is close to that of the C-3 or C-3' hydrogens of HNS or BHNS[4]. Taking into account of the ^1H NMR of diazidotetranitro- and tetraazidodinitrostilbene(5 and 6), a peak at δ8.31 (s) is attributed to a C-3 proton in 3. The two other peaks at δ7.05-7.23 and 6.78-6.96 are in accord with the two trans double bond hydrogens. Therefore, we proposed that a reaction sequence of 3-CHNS with 2 mole of NaN_3 might occur via a nucleophilic attack of the first azide ion at the C-6 nitro group, then the second ones at the C-3 chlorine as shown in Scheme I.



Scheme I Proposed reaction route of 3-CHNS with NaN_3



4

5

6

Scheme II Reaction of HNS with NaN_3

This above-stated observation has promoted us to make another study of the reaction of HNS with NaN_3. Because of a very low solubility of HNS in DMF at room temperature, the reaction is required to be carried out at 65-70 °C. Addition of 2 mole of NaN_3 leads to the substitution of both 2- and 2'-nitro groups. When 4 mole of NaN_3 is used, a symmetrical tetraazidodinitrostilbene(6) is obtained as shown in Scheme II. Even though a nitrogen elemental analysis is unsatisfactory in identifying the product, it is believed to be 6 owing to the facts that its ^1H NMR spectrum shows only three single peaks and field desorption(FD) mass spectrum indicates the $[M-1]^+$ ion peak.

TABLE 1 PROPERTIES OF POLYNITROAZIDOSTILBENES

Properties	3	5	6	HNS
nitrogen content (%)	31.62	31.67	45.15	18.67
heat of formation[a] (kJ/mol)	648	667	1312	-67
decomp. temperature[b] (°C)	166	160,178 226	182	352
detonation velocity[c] (km/s)	7.40	6.89	6.91	6.84
detonation pressure[c] (kb)	234.2	187.0	189.0	181.5

a calculated by method in literature[5]
b recorded with DSC
c calculated by method in literature[6]

Owing to the vigorous decomposition on melting, the polyazionitrostilbenes prepared above would not be suitable for thermo-stable explosives. The differential scanning calorimeter(DSC) recorded at a heating rate of 5 °C/min show no obvious melting processes in them. Compound **3** decomposes dramatically at 166°C. Meanwhile, three decomposition peaks are observed in **5**. A maximum decomposition peak is at 182°C in **6** with a relatively low decomposition speed compared with **3** and **5**.

The estimated detonation properties of the new polyazidonitrostilbenes are summarized in Table 1. As can been seen, they are highly energetic and comparable to HNS. Moreover, azide groups attached to the benzene render the nitration reaction easy to carry out[7] and the more powerful benzofuroxan explosives would be available with these new azide compounds.

EXPERIMENTAL SECTION

All starting materials were obtained from commercial sources or prepared from the referenced literature. Melting points were determined on a WC-1 hot stage and presented uncorrected. ^1H NMR spectra were recorded with a WH-90 spectrometer (tetramethylsilane as an internal standard), mass spectra on a Hitachi M-80 spectrometer and infrared spectra on a Perkin-Elmer 599B instrument in KBr pellets. Elemental analyses were made by Institute of Chemistry, Academia Sinica, Beijing.

3.1 2,5-diazido-2',4,4',6,6'-pentanitrostilbene(3)

To 0.50g(1.1mmol) of 3-ClHNS dissolved in 15ml of DMF was added 0.14g(2.2mmol) of sodium azide in 1.5ml of water. After the resulting mixture was stirred for 15 minutes at room temperature, the yellow precipitate was formed. The reaction was continued for one hour. The product was filtered and washed with water. An additional portion of the product was obtained by adding 50ml of water into the filtration and collecting the precipitate. The combined product weighed 0.47g(94% of theoretical). Recrystallization from a mixture of acetone and ethanol yielded yellow platelets with melting point 171-73°C(dec.).

IR: 3100(w), 2150(s), 1604(m), 1545(s), 1352(s) cm^{-1}. MS(EI):m/e=487($[M]^+$). ^1H NMR(Me_2CO-d_6):δ9.11

(s, 2H), 8.31(s,1H), 7.05-7.23(d,1H,J=17Hz), 6.78-6.96(d,1H,J=17Hz)ppm. Anal. calcd. for $C_{14}H_5N_{11}O_{10}$: C, 34.51; H,1.03; N,31.62. Found: C,34.21; H, 1.06; N, 31.38.

3.2 2,2'-diazido-4,4',6,6'-tetranitrostilbene(5)

To 0.25g(0.55mmol) of HNS dissolved in 20ml of warm DMF was added 0.07g(1.1mmol) of sodium azide in 1ml of water. The reaction was discontinued after stirring 1.5 hours at 65-70°C. The mixture was poured into 150ml of water and the yellow precipitate was formed. The product was filtered and washed with water. After drying it weighed 0.22g (88% of theoretical). Recrystallization from acetone gave yellow needles with melting point 183-85°C(dec.)

IR: 3100(w), 2140(s), 1610(m), 1534(s), 1346 (s)cm^{-1}. ^1H NMR(Me_2SO-d_6): δ8.56(d, 2H, J=3Hz), 8.39(d, 2H, J=3Hz), 7.14(s,2H)ppm. Anal. calcd. for $C_{14}H_6N_{10}O_8$: C, 38.02; H, 1.37; N, 31.67. Found: C, 38.00; H, 1.42; N, 31.86.

3.3 2,2',4,4,'-tetraazido-6,6'-dinitrostilbene(6)

To 0.25g(0.55mmol) of HNS dissolved in 20ml of warm DMF was added 0.14g(2.2mmol) of sodium azide in 1.5ml of water. After stirring for two hours at 65-70°C the reaction was discontinued. The mixture was poured into 150ml of water. The yellow precipitate was formed, filtered, washed with water and dried to yield 0.18g of the product (76% of theoretical). Recrystallization from acetone yielded yellow needles with melting point 185 °C(dec.)

IR: 3040(w), 2140(s), 1604(m), 1580(s), 1340(s) cm^{-1}. MS(FD):m/e=433($[M-1]^+$). ^1H NMR($MeCN-d_3$):δ8.38 (d, 2H, J=3Hz), 8.20(d, 2H, J=3Hz), 7.09 (s,2H)ppm. Anal. calcd. for $C_{14}H_6N_{14}O_4$: C, 38.72; H,1.39; N, 45.15. Found: C, 38.46; H, 1.47; N, 44.17.

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