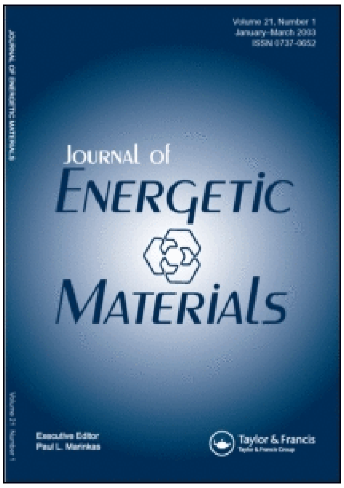

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Identification of α-Chloro-2,2′,4,4′,6,6′-Hexanitrobibenzyl as an Impurity in Hexanitrostilbene

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The final intermediate in the Shipp synthesis of 2,2′,4,4′,6,6′-hexanitrostilbene (HNS) from TNT, α-chloro-2,2′,4,4′,6,6′-hexanitrobibenzyl, has been extracted and characterized by nuclear magnetic resonance (NMR) spectroscopy, chlorine elemental analysis, and high-performance liquid chromatography (HPLC). It has also been shown that digestion in NMP of HNS containing α-chlorohexanitrobibenzyl generates another chlorine-containing by-product, 2-chloro-2′,4,4′,6,6′-pentanitrostilbene. This too has been characterized by NMR spectroscopy, chlorine elemental analysis, and HPLC.

Keywords: α-chloro-2,2′,4,4′,6,6′-hexanitrobibenzyl, 2,2′,4,4′,6,6′-hexanitrostilbene (HNS), 2-chloro-2′,4,4′,6,6′-pentanitrostilbene

Introduction

2,2′,4,4′,6,6′-Hexanitrostilbene (HNS) is widely used as a heat-resistant explosive [1,2]. It is normally manufactured by the oxidative coupling of 2,4,6-trinitrotoluene (TNT) in

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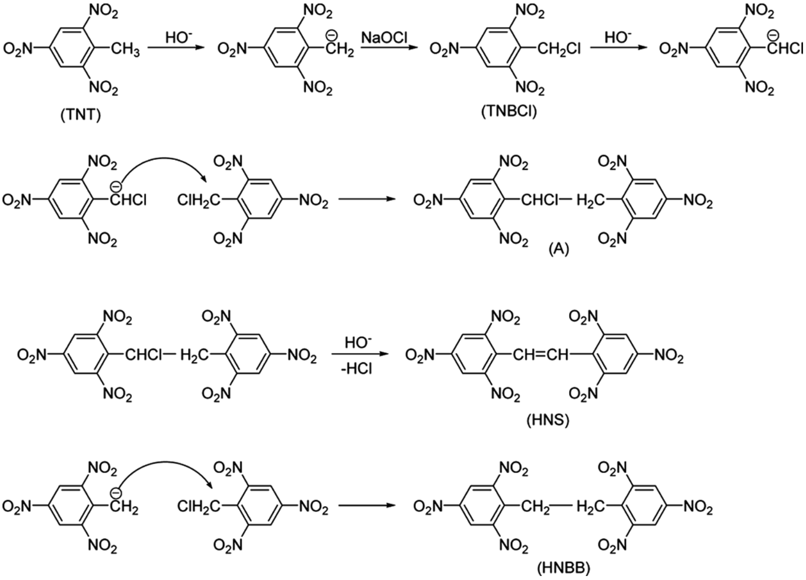
tetrahydrofuran (THF)-methanol (MeOH) solution using aqueous sodium hypochlorite (NaOCl), commonly referred to as the Shipp method [3,4], although other routes exist; for example, via 2,2′,4,4′,6,6′-hexanitrobibenzyl (HNBB) [5]. The characteristics of the Shipp route were extensively studied in the 1980s, and many of the by-products were identified [6–10]. Despite the poor yield (~40%), the low cost and availability of the starting reactants continue to make the Shipp process the preferred manufacturing route.

The reaction scheme for the formation of HNS is generally accepted [4,6] to be as shown in Scheme 1. TNT is initially deprotonated by hydroxide ion (NaOH) in the NaOCl solution and then chlorinated to give trinitrobenzyl chloride (TNBCl in Scheme 1). The trinitrobenzyl chloride is then deprotonated. It is the attack by this conjugate base on its parent, the unionised form, that leads to C-C bond formation. The intermediate from self-coupling of trinitrobenzyl chloride,



Scheme 1. Reaction of TNT with NaOCl.

α-chloro-2,2′,4,4′,6,6′-hexanitrobibenzyl (A in Scheme 1), finally undergoes base-catalyzed elimination of hydrogen chloride (HCl) to form the C=C bond of HNS.

The attack of the conjugate base of TNT on trinitrobenzyl chloride also leads to C-C bond formation, but the product, hexanitrobibenzyl (HNBB), cannot react further and is one of the major by-products in the process. In order to minimize this side reaction, the normal procedure is to slowly add the TNT solution to the NaOCl solution, thereby reducing the possibility of the trinitrobenzyl chloride reacting with the conjugate base of TNT because the conjugate base of trinitrobenzyl chloride will be in large excess. An alternative strategy is to effect the mixing at low temperature and thus slow the coupling reaction until all of the TNT has been converted into trinitrobenzyl chloride.

The proposed reaction scheme is supported by the identification and quantification of some of the reaction intermediates, viz. trinitrobenzyl chloride and products derived from its hydrolysis and oxidation (trinitrobenzyl alcohol, trinitrobenzaldehyde, trinitrobenzoic acid, trinitrobenzene [TNB]), and hexanitrobibenzyl (HNBB), in both the mother liquor [7] and the isolated crude HNS [11,12]. However, the final intermediate, α-chloro-2,2′,4,4′,6,6′-hexanitrobibenzyl, has not previously been identified. By choosing conditions that enhance the amount of this impurity in the crude HNS, we have now been able to extract, concentrate, and characterize this intermediate.

Experimental

Product Analysis

^{1}H NMR (10 mg/1.0 mL DMSO-d_6) was used to confirm product identity and distribution in HNS samples. An illustrative NMR spectrum is shown in Fig. 1.

TNT: 2.56 (s, CH_3), 9.03 ppm (s, 2H, Ar)
TNBCl: 5.00 (s, CH_2Cl), 9.09 ppm (s, 2H, Ar)
HNS: 7.14 (s, 2H, CH=CH), 9.11 ppm (s, 4H, Ar)

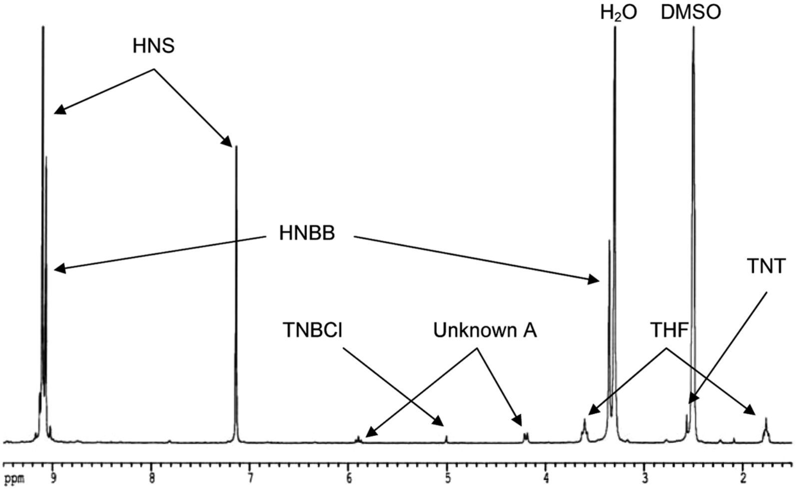


Figure 1. ^{1}H NMR spectrum (DMSO-d_6) of crude HNS (illustrative example).

HNBB: 3.35 (s, 4H, CH_2), 9.08 ppm (s, 4H, Ar)
TNB: 9.17 ppm (s, 3H, Ar)
Unknown A (α-chloro-2,2′,4,4′,6,6′-hexanitrobibenzyl): 4.20 (d, 2H, J = 6.9 Hz), 5.90 ppm (t, 1H, J = 6.8 Hz). Due to the low abundance of this product the aromatic peaks were not visible in the original HNS sample.
Unknown B (2-chloro-2′,4,4′,6,6′-pentanitrostilbene): 6.94 (d, J = 17 Hz, 1H, CH=), 7.29 (d, J = 17 Hz, 1H, CH=), 8.69 (d, J = 2.3 Hz, 1H, Ar), 8.78 (d, J = 2.3 Hz, 1H, Ar), 9.13 ppm (s, 2H, Ar).

HPLC was also used to analyze the product mixtures. Conditions: Inertsil 5 m ODS-2 (250 × 4.6 mm), mobile phase 45% water 55% acetonitrile, flow rate 1.0 mL/min. The retention times were TNT 6.61, TNB 6.61, TNBCl 9.45, HNS 12.84, HNBB 15.27, unknown A 17.62, unknown B 18.35 min. HPLC analyses of extracts of unknown A and unknown B are shown in Figs. 2 and 3, respectively.

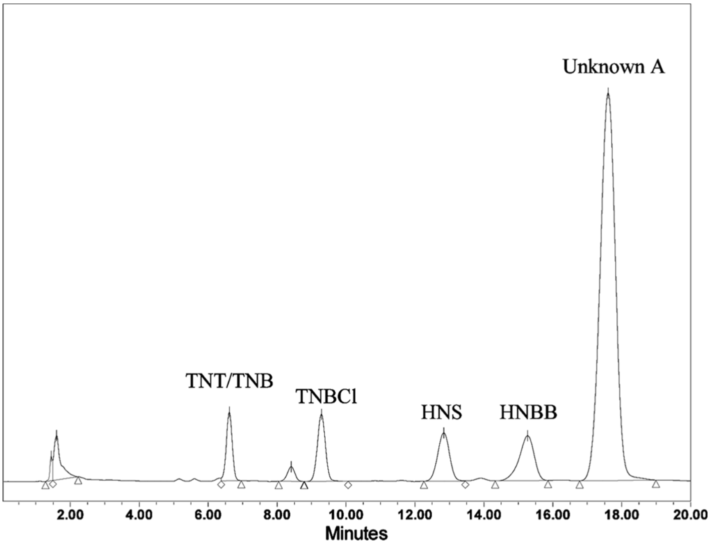


Figure 2. HPLC of extracted unknown A.

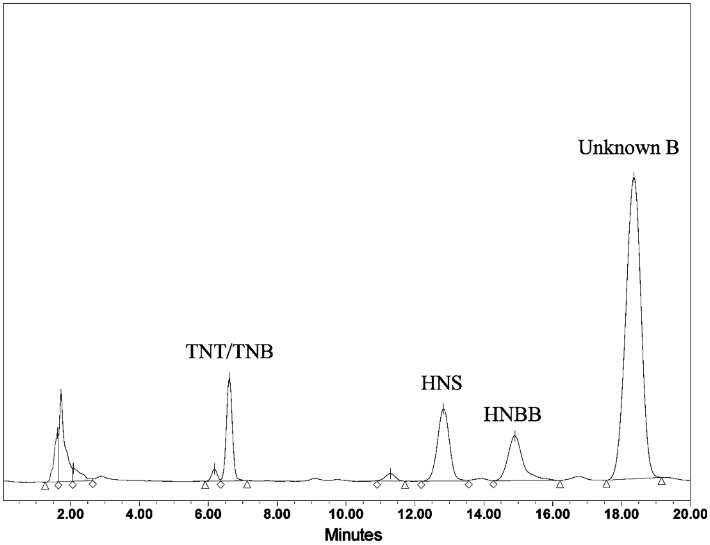


Figure 3. HPLC of extracted unknown B.

Synthesis of HNS

HNS was synthesized from TNT by the Shipp process using a Kenics® Static Tube Mixer 37-06-110 (Chemineer Ltd., Derby, UK) [13] (material 316SS, length 356 mm, OD 9.5 mm, ID 8.1 mm), with 27 mixing elements, oriented vertically with the inlet at the top, as described previously for a smaller mixer unit [12]. The reactant solutions (TNT in THF-MeOH-water [60:30:10 by volume, 0.039 g/mL, 0.172 mmol/mL] and aqueous NaOCl [0.051 g/mL, 0.69 mmol/mL]), both precooled to ~0°C, were delivered by two peristaltic pumps (Watson Marlow model 302S, butyl tubing), operating at ~1.20 and ~0.36 mL/s respectively (~1.2 equivalents of NaOCl). Full details of the mixing system will be described in a separate publication.

When the mixing was complete (435 s; temperature in aging vessel 5.5°C), the pH of the solution was reduced from ~12 to 10.0 by the addition of 25 wt% H_2SO_4 (10.8 g) and then maintained at this pH by the addition of 6 wt% NaOH (39.2 g, pH-stat control). The temperature was allowed to rise slowly to 20°C during 2 h. The solid was filtered off and washed with MeOH (50 mL) until the washings were colorless and water (50 mL) to remove water-soluble salts and products. The product was then dried in vacuo over silica gel. Yield of crude HNS from 21.4 g TNT was 10.4 g (49% assuming all HNS).

Analysis of the product by ^{1}H NMR spectroscopy indicated that it consisted of HNS (89.1), HNBB (1.5), TNBCl (1.9), TNT (0.0), unknown A (7.5 mol%), plus some THF.

A reaction in which the pH was not controlled during the after-reaction period gave 9.77 g HNS (39% assuming all HNS; from 23.1 g TNT). Composition (by ^{1}H NMR): HNS (93.9), HNBB (0.0), TNBCl (1.2), TNT (0.0), unknown A (4.9 mol%), plus some THF.

Extraction of Unknown A

A sample of crude HNS (2.00 g) consisting of HNS (89.8), HNBB (trace), TNBCl (1.8), TNT (0.0), unknown A (9.0 mol%), plus some THF was refluxed with ethyl acetate (EtOAc, 200 mL) during 20 h. The undissolved material was filtered off after cooling and the filtrate was evaporated to give a residue (330 mg). The residue was triturated with acetone (2.0 mL) to remove most of the HNS (undissolved), filtered, and washed with acetone (3 × 1.0 mL). The filtrate and washings were evaporated to give a brittle foam (267 mg) consisting of (by ^{1}H NMR) HNS (3.6), HNBB (6.8), TNBCl (12.0), TNB (7.6), unknown A (58.4), plus N-methylpyrrolidinone (NMP, 7.6) and EtOAc (4.0 mol%).

NMR spectra (acetone-d_6) assigned to unknown A: ^{1}H (Fig. 4) 4.43 (d, J = 6.7 Hz, 2.00H, CH_2), 6.06 (t, 0.96H, 6.7 Hz, CHX), 9.06 (s, 1.82H, Ar), 9.10 ppm (s, 1.88H, Ar); ^{13}C 35.6 (CH_2), 53.1 (CHX), 124.5 and 124.7 (Ar, C-3 and C-3′), 131.9 and 132.3 (Ar, C-1 and C-1′), 148.5 and 149.3 (Ar, C-4 and C-4′), 151.9 and 152.8 ppm (Ar, C-2 and C-2′).

For comparison, the NMR spectra (acetone-d_6) for HNBB are ^{1}H 3.63 (s, 4H, CH_2), 9.05 ppm (s, 4H, Ar); ^{13}C 28.3 (CH_2), 124.1 (CH, picryl), 135.1 (C), 148.0 (C), 152.5 ppm (C).

The concentrate of unknown A gave a +ve Lassaigne test for Cl. Elemental chlorine analysis of the concentrate (composition from ^{1}H NMR spectrum: unknown A [73.1], TNBCl [8.1],

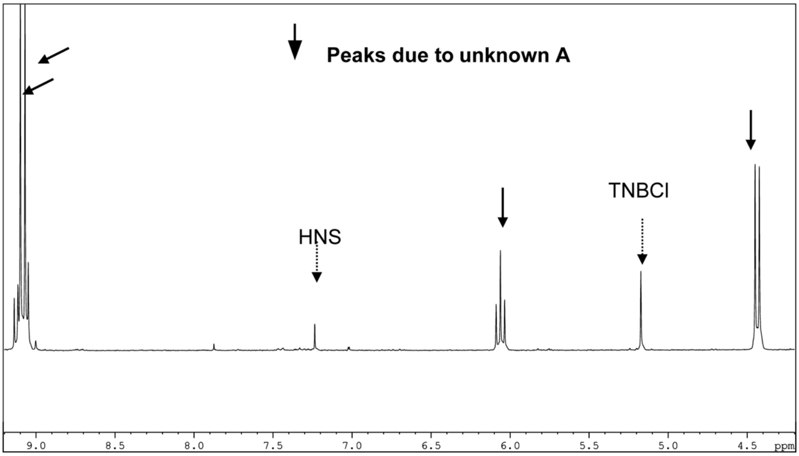


Figure 4. ^{1}H NMR spectrum (acetone-d_6) of extracted unknown A.

HNBB [7.9], HNS [4.2], TNB [4.2], NMP [1.7], EtOAc [0.9 wt%]; Butterworth Laboratories Ltd., Teddington, UK): Found 5.85 and 5.88 wt%, calculated for concentrate of unknown A 6.42 wt% if X=Cl (Cl from unknown A + TNBCl), 1.13 wt% if X=OH (Cl from TNBCl alone). The ^{1}H NMR analysis for calculation of the Cl content did not include possible moisture and other minor impurities, although the sample was dried.

Digestion of HNS in N-*Methylpyrrolidinone, Extraction of Unknown B*

A sample of crude HNS (8.5 g) consisting of HNS (89.3), HNBB (trace), TNBCl (1.8), TNT (0.0), unknown A (8.9 mol%), plus some THF was mixed with *N*-methylpyrrolidinone (NMP, 70 g). The temperature was cycled seven times, with stirring, between 50 and 100°C, and then cooled. The HNS was filtered off, washed with MeOH (50 mL), and dried to give pure HNS (5.72 g).

The washings plus more MeOH (50 mL) were added to the filtrate and the precipitated solid was filtered off after 1 h. The solid was washed with MeOH (50 mL) and dried. Yield of impure HNS was 2.06 g. ^{1}H NMR analysis indicated that it consisted of HNS (84.4), NMP (5.3), and unknown B (10.3 mol%). Unknown A was absent.

The filtrate was concentrated to remove MeOH and then H_2O (210 mL) was added. The precipitate was coagulated with saturated aqueous $Al(NO_3)_3$ solution (30 drops), filtered off, and washed with H_2O. The recovered material was impure HNS (0.75 g). ^{1}H NMR analysis indicated that it consisted of HNS (82.7), NMP (6.9), and unknown B (10.3 mol%). Again, unknown A was absent.

The above first crop of impure HNS (1.90 g) was refluxed with EtOAc (190 mL) for 72 h. The undissolved material was filtered off after cooling and the filtrate was evaporated. The residue was triturated with acetone (2.0 mL) to remove most of the HNS (undissolved), filtered, and washed with acetone (3 × 1.0 mL). The filtrate and washings were evaporated to give a beige solid (93 mg) consisting of (by ^{1}H NMR) HNS (11.2), TNB (13.7), unknown B (51.8), plus NMP (17.5) and acetone (5.8 mol%).

Similar digestion of HNS II (5.32 g) in NMP (44 g) gave pure HNS (4.19 g) and impure HNS (0.96 g) recovered from the mother liquor. The latter contained 0.77 mol% unknown B. The starting HNS II contained no unknown A or B.

NMR spectra (DMSO-d_6) assigned to unknown B: ^{1}H (Fig. 5) 6.94 (d, J = 17.0 Hz, 0.97H, CH=), 7.29 (d, J = 17.0 Hz, 1.00H, CH=), 8.69 (d, J = 2.3 Hz, 0.84H, Ar), 8.78 (d, J = 2.3 Hz, 0.78H, Ar), 9.13 ppm (s, 1.74H, Ar); ^{13}C 118.3 (CH, Ar, correlates with CH doublet at 8.78), 122.9 (CH, picryl, correlates with CH singlet at 9.13), 127.5 (CH=), 127.8 (CH=), 128.1 (CH, Ar, correlates with doublet at 8.69), 130.8 (C, Ar), 134.2 (C, Ar), 135.0 ppm (C, Ar). The carbon atoms bearing NO_2 groups were not observed, probably due to the normally low intensity of aromatic C-nitro groups.

For comparison, the NMR spectra (DMSO-d_6) for HNS are ^{1}H 7.14 (s, 2H, CH=), 9.11 ppm (s, 4H, Ar); ^{13}C 123.1 (CH, picryl), 126.1 (CH=), 130.5 (C), 147.0 (C), 149.4 ppm (C),

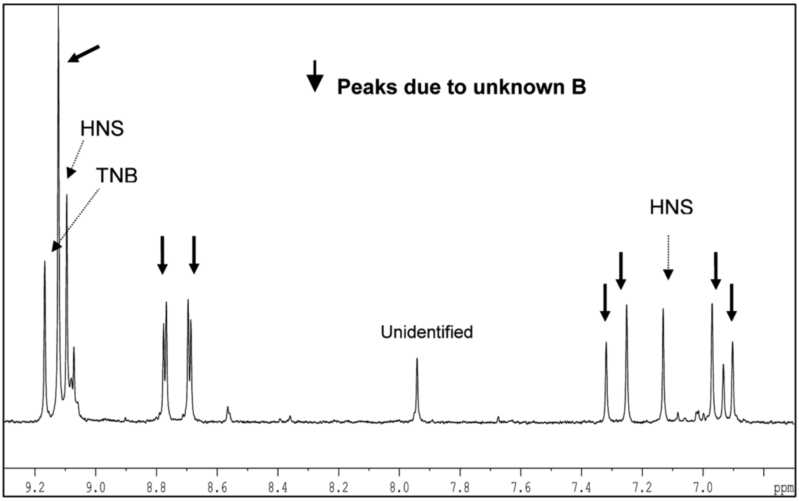


Figure 5. ^{1}H NMR spectrum (DMSO-d_6) of extracted unknown B.

and the NMR (DMSO-d_6) for 4-hydroxy-2,2-′,4′,6,6′-pentanitrostilbene are ^{1}H 6.92 and 6.88 (AB system, 2.00H, CH=CH, J = 17 Hz), 7.68 (s, 2.07H, H-3 and H-5), 9.07 (s, 2.02H, H-3′ and H-5′), 11.55 ppm (br s, 0.99H, OH); ^{13}C 115.5 (CH, C-3 and C-5), 123.3 (CH, C-3′ and C-5′), 124.2 (=CH, correlates with high field doublet in AB system), 128.2 (=CH, correlates with low field doublet in AB system), 131.1, 133.2, 147.2, 149.9, 150.5, 158.6 ppm.

FTIR spectrum (KBr) of a sample of the concentrate of unknown B (composition from ^{1}H NMR spectrum: unknown B [47], HNS [13], TNB [12], NMP [20], acetone [8 mol%]) was very similar to that of HNS: 1618(m), 1601(m), 1538(s), 1403(w), 1347(s), 1081(m), 955(w), 921(m), 810(w), 773(w), 756(w), 722(m) cm^{-1}. For comparison, 2,2′,4,4′,6,6′-hexanitrostilbene exhibits: 1618(m), 1601(m), 1540(s), 1403(w), 1347(s), 1265(w), 1183(w), 1084(m), 957(m), 921(m), 825(w), 808(w), 781(w), 740(m), 724(m), 714(m) cm^{-1}.

The concentrate of unknown B gave a +ve Lassaigne test for Cl. Chlorine analysis of the concentrate (composition from ^{1}H NMR spectrum: unknown B [69.4], HNS [15.4], TNB [8.9], NMP [5.3], acetone [1.0 wt%]; Butterworth Laboratories Ltd.,Teddington, UK): Found 4.59 and 4.73 wt%, calculated for concentrate of unknown B 5.61 wt%. The ^{1}H NMR analysis for calculation of the Cl content did not include two unassigned singlets at 3.97 and 7.94 ppm (integrals 0.36 and 0.29), respectively, relative to 1.00H for each aromatic proton in unknown B. The water content was also unknown although the sample was dried.

NMP Treatment of Unknown A

Unknown A (16 mg, HNS [3.6], HNBB [6.8], TNBCl [12.0], TNB [7.6], unknown A [58.4], NMP [7.6], and EtOAc [4.0 mol%]) was dissolved in NMP (130 mg) and the temperature was cycled seven times between 50 and 100°C. Some crystals had separated before water (1.5 mL) was added. The solid was filtered off, washed with water (3X), and dried. The product (13 mg) consisted (by ^{1}H NMR) of predominantly HNS

(87 mol%), plus some unknown B (13 mol%) and NMP. No unknown A remained.

HCl/NMP Treatment of HNS

Pure HNS (32 mg) was mixed with HCl/NMP (260 mg; from 34 mg 35% HCl + 1.30 g NMP; approximately the amount of HCl liberated by elimination from α-chlorohexanitrobibenzyl to form HNS) and the temperature was cycled seven times between 50 and 100°C. Water (3.0 mL) was added. The solid was filtered off, washed with water (3X), and dried. The product (28 mg) consisted (by ^{1}H NMR) of HNS (94 mol%) and unknown B (6 mol%) plus a small amount of NMP.

In a further experiment in which the HCl concentration was increased 10-fold, the product was predominantly HNS (31 mg) with only 0.5 mol% of unknown B. When HNS was subjected to similar treatment but in the absence of HCl, no unknown B was formed.

Results and Discussion

Isolation of an Unidentified Impurity in Crude HNS

Previous work [11,12] has shown that control of the pH of the reaction solution during the after-reaction period of the Shipp process has a significant effect on the yield and selectivity of the reaction. Most importantly for the purpose of the present work, the proportion of α-chloro-2,2′,4,4′,6,6′-hexanitrobibenzyl in the crude HNS is increased by holding the pH at 10 and above. A typical reaction without pH control gives HNS containing <5 mol% of α-chlorohexanitrobibenzyl, whereas a reaction at pH 10 gives 7.5–9.0 mol% α-chlorohexanitrobibenzyl. The presence of α-chlorohexanitrobibenzyl in the product (referred to as unknown A in the Experimental section) is readily established by the appearance of a characteristic doublet (4.2 ppm) and triplet (5.0 ppm) in the ^{1}H NMR spectrum (DMSO-d_6) of the crude HNS (Fig. 1).

Batches of HNS containing an increased amount of α-chlorohexanitrobibenzyl (unknown A) were prepared using a flow mixer as described previously [12]. The HNS was then extracted by boiling with EtOAc. This gave a mixture containing the desired impurity plus significant amounts of HNS, trinitrobenzyl chloride, trinitrobenzene, hexanitrobibenzyl, and solvents THF and *N*-methylpyrrolidinone (NMP). Most of the HNS was removed from the mixture by trituration with acetone in which the HNS is only slightly soluble. The resultant concentrated mixture enabled the complete NMR characterization of unknown A.

The ^{1}H NMR spectrum (Fig. 4) exhibited two aromatic singlets, 2H each, indicative of two different picryl groups, and this was supported by the ^{13}C spectrum that exhibited duplicate pairs of the four picryl carbons. The CH_2CHCl group exhibited ^{1}H absorptions (doublet and triplet) and ^{13}C absorptions, which were shifted downfield from the CH_2CH_2 absorptions of hexanitrobibenzyl due to the α and β effects of the Cl atom (2.43 and 0.80 ppm, respectively, for ^{1}H and 24.8 and 7.3 ppm, respectively, for ^{13}C).

Initially, it was unclear whether A was the proposed reaction intermediate α-chlorohexanitrobibenzyl or its hydrolysis product, α-hydroxyhexanitro-bibenzyl, both of which would exhibit similar NMR spectra. In fact the hydrolysis product was favored due the formation of A at higher pH conditions. However, the concentrated mixture gave a positive test for chlorine and a quantitative elemental analysis for chlorine in the mixture gave a value within 10% of that calculated from the observed composition of the mixture assuming that A was α-chlorohexanitrobibenzyl and much higher than would have been the case had A been the hydroxyl derivative. The unknown A is therefore identified as α-chloro-2,2′,4,4′,6,6′-hexanitrobibenzyl.

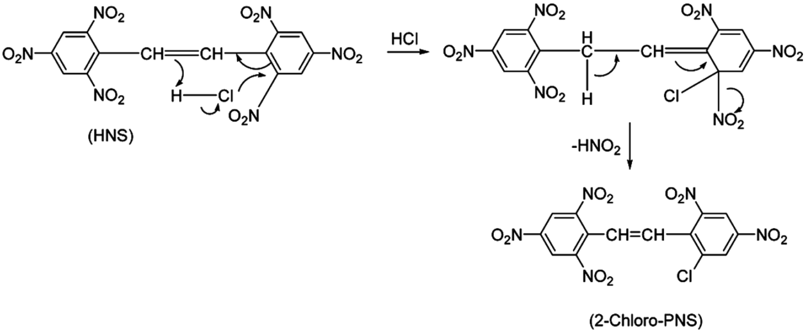
Identification of a New Impurity in Purified HNS

It had been observed by HPLC [11] that when HNS was digested/recrystallized in NMP, the impurity identified above as α-chlorohexanitro-bibenzyl did not appear to be removed. However, on closer examination by ^{1}H NMR spectroscopy of HNS recovered after similar treatment of crude HNS containing enhanced amounts of α-chlorohexanitrobibenzyl, it was observed that α-chlorohexanitrobibenzyl was indeed removed but appeared to be replaced by another unidentified impurity (referred to as unknown B in the Experimental section) with a similar HPLC retention time (α-chlorohexanitrobibenzyl 17.62, unknown B 18.35 min) but completely different NMR spectra. This impurity was extracted and concentrated in the same manner as employed for α-chlorohexanitrobibenzyl. ^{1}H and ^{13}C NMR spectroscopy indicated that unknown B was a 2-substituted 2′,4,4′,6,6′-pentanitrostilbene. The ^{1}H spectrum (Fig. 5) exhibited two pairs of doublets, one assigned to the alkene protons, at 6.94 and 7.29 ppm ($J = 17.0$ Hz; cf. $J = 16.2$ Hz for HNS from the ^{13}C side-bands), either side of the corresponding singlet for HNS at 7.14 ppm, and the other pair of doublets, assigned to the three and five protons in the dinitrophenyl group, at 8.69 and 8.78 ppm ($J = 2.3$ Hz meta coupling; cf. $J = 2.3$ Hz for HNS from the ^{13}C side-bands). The singlet due to the two picryl protons appeared at 9.13 ppm (cf. HNS 9.11 ppm). The ^{13}C spectrum and the H-C correlation spectrum supported this structure (see Experimental section).

A somewhat analogous structure 4-hydroxy-2,2′,4′,6,6′-pentanitrostilbene was recently reported by us [14]. This also exhibited two doublets for the alkene protons ($J = 17$ Hz), but the chemical shift difference between them was much smaller (6.88 and 6.92 ppm). The two picryl protons appeared at 9.07 ppm. No analogous 4-substituted 2,2′,4′,6,6′-pentanitrostilbene was observed in the present study.

The FTIR spectrum (KBr) of unknown B was extremely similar to that of hexanitrostilbene, with only minor shifts in the frequencies of some of the peaks in the region 700–1700 cm^{-1}.

The concentrated mixture containing unknown B gave a positive test for chlorine and a quantitative elemental analysis for chlorine in the mixture gave a value within 20% of that calculated from the observed composition of the mixture assuming that B was 2-chloro-2′,4,4′,6,6′-pentanitrostilbene. The unknown



Scheme 2. Formation of 2-chloro-2′,4,4′,6,6′-pentanitrostilbene.

B is therefore identified as 2-chloro-2′,4,4′,6,6′-pentanitrostilbene (2-chloro-PNS in Scheme 2). The corresponding 4-chloro isomer was not detected.

Further proof that unknown A was α-chlorohexanitrobibenzyl was obtained when a concentrated sample of unknown A (unknown A [58.4] + HNS [3.6], HNBB [6.8], TNBCl [12.0], TNB [7.6], NMP [7.6], and EtOAc [4.0 mol%]) was dissolved in NMP and the temperature cycled between 50 and 100°C. The solid that was isolated was found to be predominantly HNS (87 mol%), plus some unknown B (13 mol%) but no unknown A. The α-chlorohexanitrobibenzyl had thus undergone elimination of HCl, accompanied by the formation of some unknown B.

The formation of unknown B, 2-chloro-2′,4,4′,6,6′-pentanitrostilbene, is probably not directly by rearrangement/elimination of α-chlorohexanitrobibenzyl on heating in NMP, because it was shown to be for from HNS on similar treatment in the presence of that amount of HCl that would be eliminated during the formation of HNS from α-chlorohexanitrobibenzyl. Scheme 2 suggests a cyclic mechanism that would generate the 2- but not the 4-chloro derivative. No 2-chloro-2′,4,4′,6,6′-pentanitrostilbene is formed when HCl is absent.

Conclusions

The final intermediate in the Shipp synthesis of HNS from TNT, α-chloro-2,2′,4,4′,6,6′-hexanitrobibenzyl, has been extracted and characterized by NMR spectroscopy, chlorine elemental analysis, and HPLC. It has also been shown that digestion in NMP of HNS containing α-chlorohexanitrobibenzyl generates another chlorine-containing by-product 2-chloro-2′,4,4′,6,6′-pentanitrostilbene. This too has been characterized by NMR spectroscopy, chlorine elemental analysis, and HPLC. It appears that 2-chloro-2′,4,4′,6,6′-pentanitrostilbene is not formed directly from α-chloro-2,2′,4,4′,6,6′-hexanitrobibenzyl but via the HCl liberated during the conversion of the latter into HNS.

Acknowledgments

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