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4-Hydroxy-2,2',4',6,6'-pentanitrostilbene; a Major By-Product in the Oxidation of Hexanitrobibenzyl to Hexanitrostilbene using Oxygen

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Abstract: Oxidation of hexanitrobibenzyl to hexanitrostilbene using oxygen has been shown to produce 4-hydroxy-2,2',4',6,6'-pentanitrostilbene as a major by-product. The single crystal structure of this new product is reported.

Keywords: 4-hydroxy-2,2',4',6,6'-pentanitrostilbene, hexanitrobibenzyl, hexanitrostilbene

Introduction

Of the methods available for the preparation of hexanitrostilbene (HNS, **II**), those involving the oxidation of hexanitrobibenzyl (HNBB, **I**) generally give the cleanest product [1]. A range of oxidants for this reaction was explored by Gilbert

[1] and others [2]. These included bromine [1], copper(II) [1], various halogenating agents including hypochlorite [1], hydrogen peroxide [1], and oxygen in the presence of various promoters [1, 2]. We have examined the use of oxygen employing the conditions reported in reference 2, and found that whilst HNS is indeed formed, a significant proportion of the HNBB is converted to 4-hydroxy-2,2',4',6,6'-pentanitrostilbene (**III**, mole ratio of HNS to 4-hydroxypentanitrostilbene 1:0.43-0.49).

Experimental

Reaction of hexanitrobibenzyl with oxygen

HNBB (1.00 g) was dissolved in dimethylsulphoxide (DMSO, 30 mL) and sodium benzoate (0.34 g) was added. The solution became dark blue. Oxygen gas was then passed through the solution with rapid mechanical stirring during 90 min, by which time the solution was reddish-brown in colour. The solution was added to water (60 mL) containing conc. HCl (0.6 mL). The solid was filtered off after standing for 10 min and was washed thoroughly with water. ^{1}H NMR spectroscopic analysis indicated that the dried, brown, crude product (0.89 g) was largely a mixture of HNS and 4-hydroxy-2,2',4',6,6'-pentanitrostilbene in the molar ratio 1:0.43-0.49, with DMSO and minor amounts of other products.

The crude product was washed with methanol (3x10 mL) and dried to give a residue (0.58 g) which was a mixture of HNS and 4-hydroxypentanitrostilbene in the molar ratio 1:0.32 by ^{1}H NMR analysis. Evaporation of the methanol washings gave a red solid (0.29 g) which was predominantly 4-hydroxypentanitrostilbene, together with DMSO and other minor products, by ^{1}H NMR analysis.

The methanol washed product was then washed with acetone (3x10 mL) and dried to give a pale beige solid (0.39 g, 39%) which was predominantly HNS containing a small amount of 4-hydroxypentanitrostilbene (molar ratio 1:0.03-0.10) by ^{1}H NMR analysis. It exhibited melting (DSC/10 K min^{-1}) at 307 °C (onset). Evaporation of the acetone washings gave a light red solid (0.20 g) which was a mixture of HNS and 4-hydroxypentanitrostilbene, the latter predominating (molar ratio 1:5.0) by ^{1}H NMR analysis. A solution of crude 4-hydroxypentanitrostilbene in EtOAc, when washed with 1M NaOH gave a dark organic phase and a dark aqueous phase. Subsequent washing of the dark organic phase with 1M HCl removed the colour and gave back unchanged crude 4-hydroxypentanitro-stilbene. Thus 4-hydroxypentanitrostilbene is not extracted into water as its salt. Perhaps this is not unexpected, considering the size of the molecule and the anticipated low acidity of the hydroxyl group (3,5-dinitrophenol has pKa 6.73 [3]).

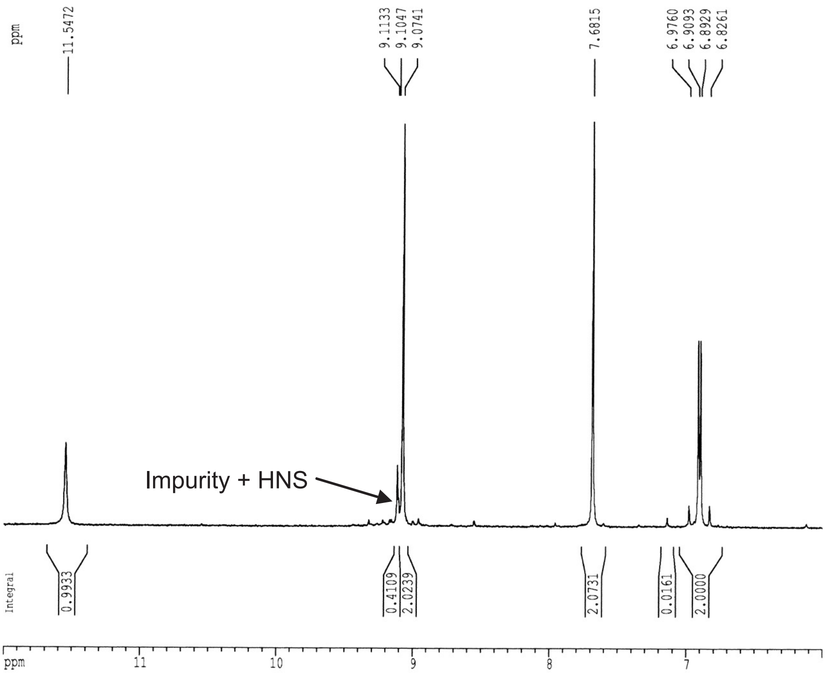


Figure 1. ^{1}H NMR spectrum (250 MHz, DMSO-d_6) of 4-hydroxy-2,2',4',6,6'-pentanitrostilbene

The residue from the acetone washings (~150 mg) was recrystallised by dissolving it in EtOAc (2.0 mL), filtering off the undissolved HNS (identified as 80% HNS and 20% 4-hydroxypentanitrostilbene by ^{1}H NMR), washing the undissolved material with EtOAc (1.0 mL) and then slowly adding heptane (20 mL at 10 mL h^{-1}) with stirring to the combined EtOAc solutions. The dark coloured material which separated after 3-4 mL heptane had been added adhered to the wall of the flask. This was left undisturbed. Thereafter more light-coloured material separated and remained in suspension. This was filtered off, washed with heptane (3x) and dried to give a beige solid (95 mg). ^{1}H NMR analysis revealed this material to be free of HNS, but implied that it contained some aromatic absorption (in addition to that of 4-hydroxypentanitrostilbene) at 9.11 and heptane.

DSC (10 K min^{-1}) of the recrystallised material: endotherm at 76 °C (loss of heptane?), endotherm at 190 °C (not melting), endotherm at 236 °C (onset 226 °C, melting), exotherm 338 °C (onset 285 °C, decomposition).

NMR (DMSO-d_6): ^{1}H (250 MHz, Figure 1) 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. NMR (acetonitrile-d_3): ^{1}H 6.91 and 6.85 (AB system, 2.00H, CH=CH, J = 20Hz), 7.64 (s, 2.02H, H-3 and H-5), 8.58 (br s, 1.09H, OH), 8.91 ppm (s, 1.95H, H-3' and H-5'). For comparison, the NMR data for HNS (DMSO-d_6) is ^{1}H (DMSO-d_6): 7.14 (s, 2.00H, CH=CH), 9.11 ppm (s, 3.84H, H-3, H-3', H-5 and H-5'); ^{13}C 123.1 (CH, C-3, C-3', C-5 and C-5', correlates with 9.11), 126.1 (CH, CH=CH, correlates with 7.14), 130.5, 147.0, 149.4 ppm. 3,5-Dinitrophenol is reported [4] to exhibit (acetonitrile-d_3): ^{1}H 7.96 ppm (d, H-2 and H-6).

The oxidation of HNBB in dimethylformamide (DMF) gave almost identical results to those in DMSO. The molar ratio of HNS to 4-hydroxypentanitrostilbene (by ^{1}H NMR analysis of the crude product – unwashed with MeOH or acetone) was 1 : 0.45.

Reaction of hexanitrobibenzyl with hydrogen peroxide

The oxidation of HNBB (1.00 g, 2.2 mmol) was performed as with oxygen (*i.e.* with PhCOONa present) except that 30% H_2O_2 (0.45 mL, 0.50 g, 4.4 mmol) was added instead of oxygen. After stirring for 2 h the reaction mixture was added to water (60 mL) containing conc. HCl (0.60 mL) and the product was isolated as before. The reaction in DMSO gave a brown solid (0.96 g) which contained HNS (84%), 4-hydroxypentanitrostilbene (16%), DMSO and other minor components (by ^{1}H NMR). The reaction in DMF gave a brown solid (0.90 g) which contained HNS (83%), 4-hydroxypentanitrostilbene (17%), DMF and other minor components (by ^{1}H NMR).

Warning. 4-Hydroxypentanitrostilbene, HNBB and HNS are potentially explosive and should be treated with appropriate precautions.

X-ray single crystal determination of 4-hydroxypentanitrostilbene

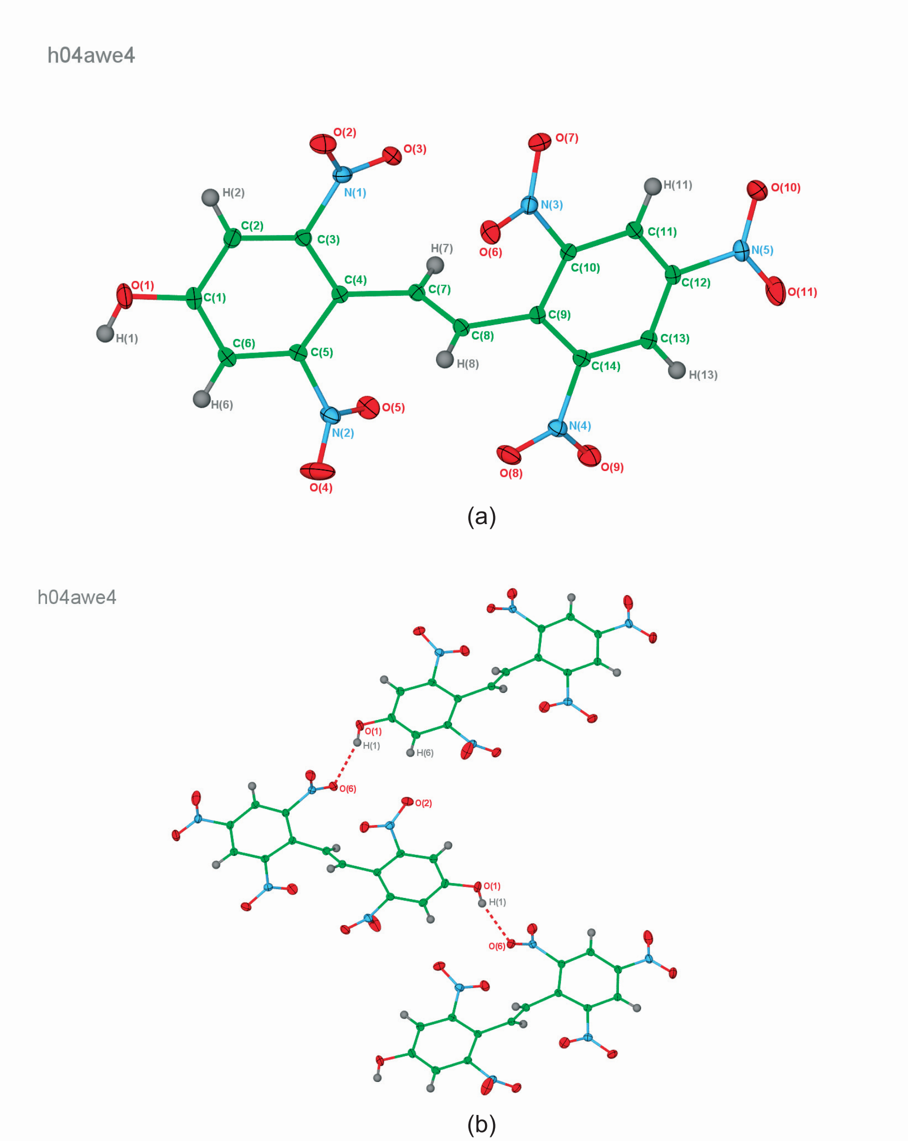
Crystals for X-ray analysis were obtained by dissolving a flash chromatographically purified sample (14 mg; contained some impurity and solvent by ^{1}H NMR) in EtOAc-heptane solution (2-3 by volume), and allowing it to crystallise by evaporation of the EtOAc. Observation by eye revealed that the product had two crystalline forms, one of which (long needles) was a mono-hydrate (presumably moisture was absorbed during the period in which EtOAc was allowed to evaporate – several weeks). The DSC (10 K min^{-1}) of these hydrated crystals exhibited: endotherm (loss of water) 70-110 °C, endotherm (melting) 244 °C, followed by a broad exotherm (decomposition). The non-hydrated crystals exhibited: endotherm (melting) 249 °C, followed by a broad exotherm (decomposition).

Crystallography

The crystal structure of anhydrous 4-hydroxy-2,2',4',6,6'-pentanitrostilbene is shown in Figure 2. The supramolecular array is dominated by 1-dimensional hydrogen-bonded polymers that propagate along the *b* axis, as a consequence of the interaction between the hydroxyl hydrogen atom and a nitro group oxygen in the adjacent lattice neighbour [H(1)…O(6), 2.081 Å]. Moreover, intermolecular distances suggest the possibility of pi-stacking interactions between the centrosymmetrically related rings from pairs of proximate molecules in the lattice. In particular, the distances between the atoms of the ring based on C(1) and the least squares plane of a ring based on C(9) in a neighbouring molecule fall within the range of 3.49-4.06 Å.

Crystal data: $C_{14}H_7N_5O_{11}$, $M = 421.25$, 0.25x0.20x0.15 mm^3, monoclinic, space group $C2/c$, $a = 9.5020(1)$, $b = 13.8850(2)$, $c = 12.9460(2)$ Å, $\beta = 110.706(1)°$, $V = 1597.71(4)$ Å^3, $Z = 4$, $D\mathrm{c} = 1.751$ g cm^{-3}, $F(000) = 856$, MoKα radiation, $\lambda = 0.71073$ Å, T = 150(2) K, $2\theta\mathrm{max} = 60°$, 30937 reflections collected, 4645 unique (Rint = 0.0370). Goodness of Fit = 1.035, R1 = 0.0440, wR2 = 0.1148, [R indices based on 3645 reflections with $I > 2\sigma(I)$ (refinement on F^2)], 274 parameters, 1 restraint, $\mu = 0.155$ mm^{-1}.

Figure 3 denotes the crystal structure of hydrated 4-hydroxy-2,2',4',6,6'-pentanitrostilbene. As in the non-solvated case above, the gross structure in this compound is also dominated by hydrogen-bonding. However, in the latter instance, the 4-hydroxy-2,2',4',6,6'-pentanitrostilbene molecules stack in a head to head arrangement, a consequence of the hydroxyl group being located near to a crystallographic inversion centre. The presence of a water molecule close to this hydroxyl group facilitates formation of a hydrogen bonded ring motif, involving the hydroxyl atoms [O(1), H(1)], the water oxygen [O(12)] and one of the water hydrogens [H(12B)]. The remaining water hydrogen, H(12A) links to O(8) of another 4-hydroxypentanitrostilbene molecule, while H(12B) exhibits a second hydrogen bond to O(4) in the same molecule. The combined effect of these interactions is the formation of 2-dimensional hydrogen-bonded sheets within the structure, [H(1)…O(12) 1.79, H(12B)…O(1) 2.27 H(12B)…O(4) 2.29, H(12A)…O(8) 2.29 Å].



(a)

(b)

Figure 2. Crystal structure of anhydrous 4-hydroxy-2,2’,4’,6,6’-pentanitrostilbene (a) single molecule (b) showing interactions with neighbouring molecules.

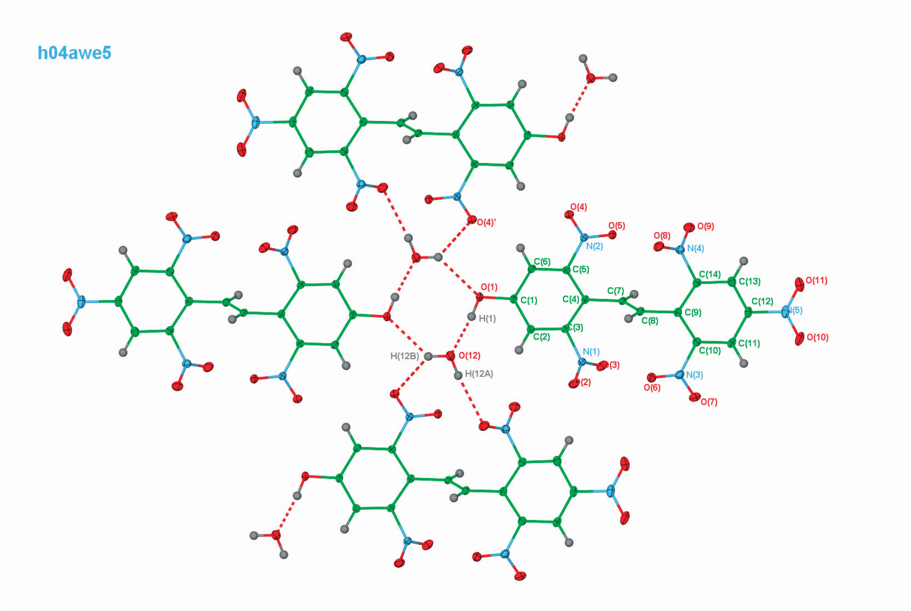


Figure 3. Crystal structure of 4-hydroxy-2,2’,4’,6,6’-pentanitrostilbene monohydrate.

Crystal data: $C_{14}H_9N_5O_{12}$, $M = 439.26$, 0.15x0.08x0.05 mm^3, triclinic, space group P-1, $a = 9.3770(2)$, $b = 9.6200(2)$, $c = 10.0500(3)$ Å, $\alpha = 82.131(1)°$, $\beta = 85.0820(1)°$, $\gamma = 70.726(1)°$, $V = 846.91(4)$ Å^3, $Z = 2$, Dc = 1.723 g cm^{-3}, $F(000) = 448$, MoKα radiation, $\lambda = 0.71073$ Å, $T = 150(2)$ K, 2θmax = 55°, 15983 reflections collected, 3839 unique (Rint = 0.0333). Goodness of Fit = 0.997, R1 = 0.0389, wR2 = 0.1026, [R indices based on 2914 reflections with $I > 2\sigma(I)$ (refinement on F2)], 290 parameters, 1 restraint, $\mu = 0.155$ mm^{-1}.

CCDC 266708 contains the supplementary crystallographic data for 4-hydroxy-2,2’,4’,6,6’-pentanitrostilbene and CCDC 266709 contains the supplementary crystallographic data for the monohydrate form. These data can be obtained free of charge *via* www.ccdc.cam.ac.uk/conts/retrieving.html (or from Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-366033; or deposit@ccdc.cam.ac.uk.

Results and Discussion

The oxidation of HNBB (I) in dimethylsulphoxide (DMSO) using oxygen as described in Examples 1, 11 and 12 of reference 2 was reported to give crude HNS in 96% yield and reasonably pure HNS (m.p. 315 °C, after methanol and acetone washing) in 64-91% yield. Other than unoxidized HNBB, no other water-insoluble products were detected. However, when we repeated this procedure according to Example 1 we found that the crude product was a mixture consisting mainly of HNS (II) and a new compound which was identified as being 4-hydroxy-2,2',4',6,6'-pentanitrostilbene (III, mole ratio 1:0.43-0.49; Figure 4), plus other minor components.

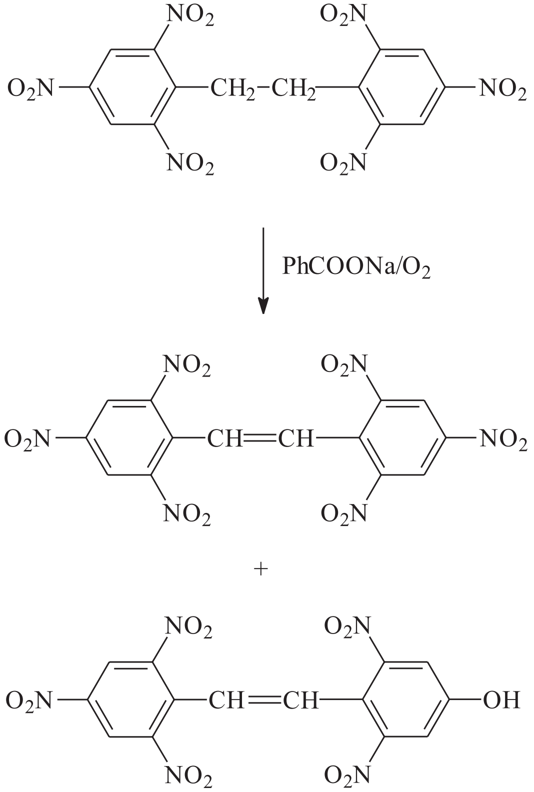


Figure 4. Oxidation of hexanitrobibenzyl (I)

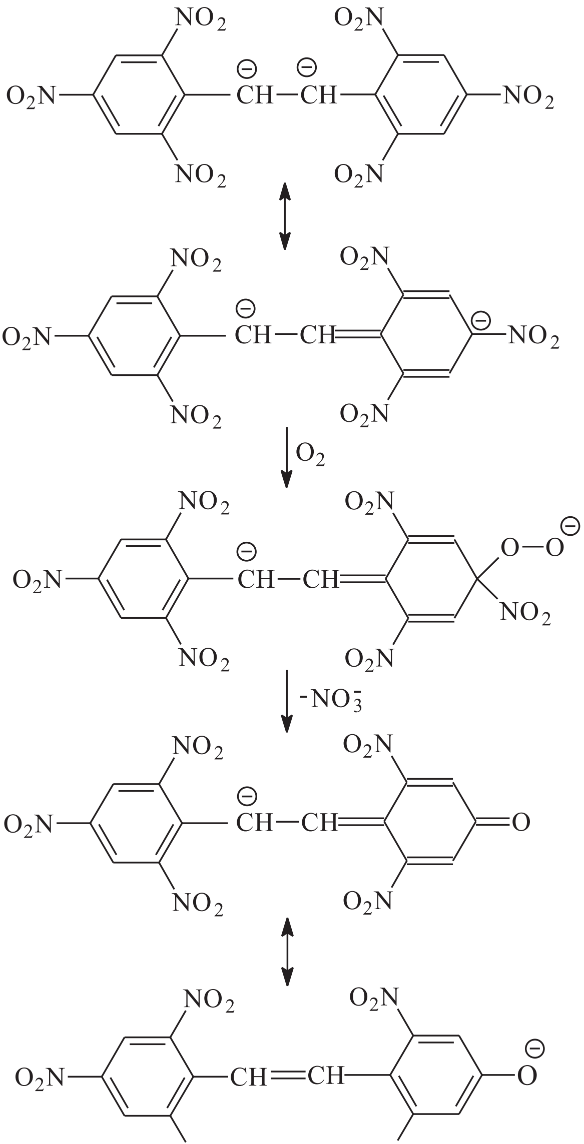


Figure 5. Possible rationalisation for the formation of 4-hydroxy-2,2’,4’,6,6’-pentanitrostilbene.

After washing with methanol and acetone, as described in reference 2, the purified material (39% yield) had an onset of melting (DSC) of only 307 °C, and ^{1}H NMR analysis indicated that it was largely HNS but that it still contained some 4-hydroxypentanitrostilbene (3-9 mol%). The structure of 4-hydroxypentanitrostilbene was determined by X-ray single crystal analysis (see Experimental and Figures 2 and 3). A similar oxidation in dimethylformamide (DMF) instead of DMSO gave almost identical results.

A possible rationalization for the formation of 4-hydroxypentanitrostilbene from HNBB in the presence of oxygen is shown in Figure 5. It is assumed that the base (PhCOONa) deprotonates HNBB to generate a resonance stabilised di-anion. A blue coloration has been reported to be due to the formation of the di-anion when HNBB reacts with aliphatic amines in DMSO [5]; no mono-anion was detected under those conditions. In the present case the di-anion appears to react with O_2 at either of two sites: (i) at the original sites of deprotonation, this mode presumably leading to HNS [5a, 6], or (ii) at position C-4 in the aromatic ring. In the latter case, initial formation a hydroperoxide anion followed by elimination of NO_3^- would leave a carbonyl group at C-4. Protonation of this intermediate at the oxygen atom would generate III and restore the aromaticity of the ring. An analogous series of reactions can be envisaged involving the mono-anion, but from the available evidence the di-anion route appears more likely.

4-Hydroxypentanitrostilbene was also formed, but to a lesser degree (mole ratio 1 : 0.2), when hydrogen peroxide was used as the oxidant instead of oxygen.

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