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Synthesis of Hexanitrostilbene (HNS) using a Kenics Static Mixer

Anthony J. Bellamy*

Cranfield University, Defence Academy of the United Kingdom, Shrivenham, Swindon SN6 8LA, U.K.

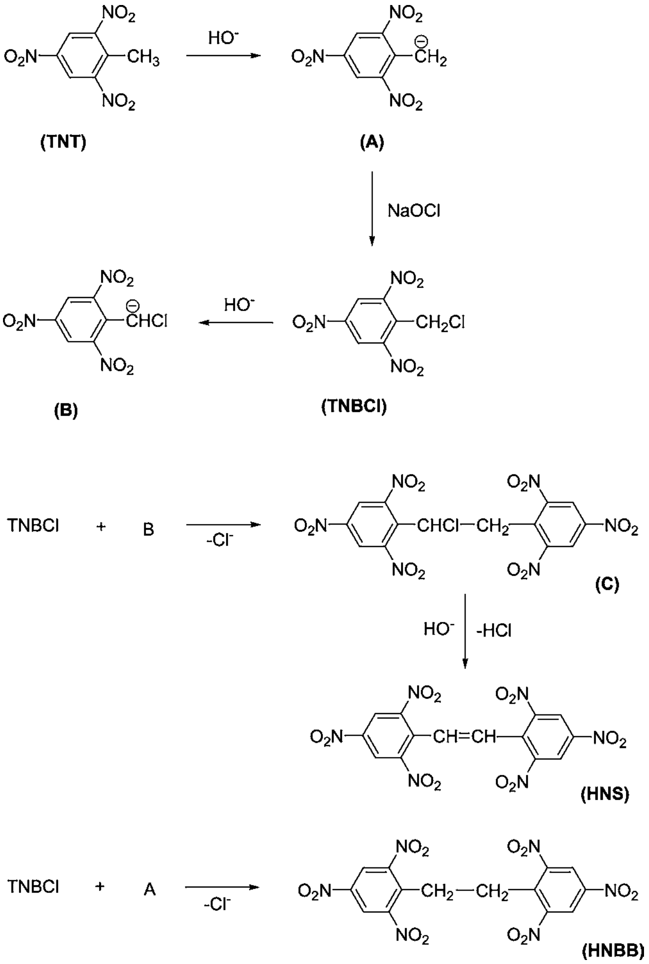
Abstract:

Previous work on a Shipp−Kaplan type synthesis of hexanitrostilbene (HNS) using a Kenics static mixer (ref 1, from Chemineer Ltd., Cranmer Road, West Meadows, Derby DE21 6XT, UK; www.chemineer.com) has been extended by using a larger mixer (9.5 mm vs 4.75 mm OD), enabling the scale to be increased from 2.5 g to 25 g of trinitrotoluene (TNT) for the same mixing time (<4 min). Various conditions for the after-reaction period (2 h) have been explored on the basis of previous work with a batch reactor, including (i) no pH control, (ii) pH control using aqueous H_2SO_4 and NaOH solutions, and (iii) pH control using aqueous RNH_3Cl and RNH_2 solutions. Other parameters that have been varied are the ratio of NaOCl to TNT (0.5−1.2) and the concentration of both reactants. The yields of crude HNS that have been achieved, whilst not outstanding, are an improvement over the conventional batch process. It has been demonstrated that the yield and selectivity of the HNS synthesis can be considerably increased if, during the after-reaction period, the reaction conditions are pH controlled. The yield and selectivity are also significantly enhanced by using more dilute reaction solutions.

1. Introduction

The synthesis of 2,2′,4,4′,6,6′-hexanitrostilbene (HNS) by reacting a solution of trinitrotoluene (TNT) with sodium hypochlorite (NaOCl) was first reported by Shipp and Kaplan[2,3] in 1964 and has been widely studied since.[4−7] As described by Shipp and Kaplan,[3] the reaction conditions may be varied so that the isolated product is either HNS (by adding TNT to NaOCl - yield normally 40−45%), hexanitrobibenzyl (HNBB, by adding NaOCl to TNT - yield normally ∼80%), or trinitrobenzyl chloride (TNBCl), the initially formed reaction intermediate (by quenching the reaction mixture in acid a short time after mixing - yield normally ∼85%). The likely reaction scheme is shown in Scheme 1. One can envisage that HNS is formed by self-condensation of TNBCl (reaction between TNBCl and its conjugate base B), via α-chlorohexanitrobibenzyl[7] (α-Cl·HNBB; C in Scheme 1), whilst HNBB is formed by cross condensation of TNBCl with the conjugate base of TNT (A), the mode of addition generating conditions which favor one or the other of these two products. In less controlled mixing regimes both products are likely to be formed.

Scheme 1. **Reaction scheme for NaOCl oxidation of TNT**



In the batch synthesis of HNS, the reaction occurs in essentially two stages. In stage one (mixing - duration = minutes), TNT reacts exothermically with NaOCl to form TNBCl. In stage two (ageing - duration ≈ 2 h), the TNBCl is allowed to react with the basic medium (NaOCl/NaOH) generating HNS which precipitates as a solid. The best selectivity in the reaction is achieved if the temperature on mixing is kept below 15 °C and the pH during the ageing period is maintained around 10.[4,9] Shipp and Kaplan[3] kept the mixing temperature low by precooling both solutions to 0 °C, but did

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* Author for correspondence. E-mail: banda.bellamy@btinternet.com.

(1) From Chemineer Ltd., Cranmer Road, West Meadows, Derby DE21 6XT, UK; www.chemineer.com.

(2) Shipp, K. G. Reactions of α-substituted polynitrotoluenes. I. Synthesis of 2,2′,4,4′,6,6′-hexanitrostilbene. *J. Org. Chem.* **1964**, *29*, 2620–2623.

(3) Shipp, K. G.; Kaplan, L. A. Reaction of α-substituted polynitrotoluenes. II. The generation and reactions of 2,4,6-trinitrobenzyl anion. *J. Org. Chem.* **1966**, *31*, 857–861.

(4) Golding, P.; Hayes, G. F. A parametric study of the synthesis of 2,2′,4,4′,6,6′-hexanitrostilbene from trinitrotoluene and sodium hypochlorite. *Propellants, Explos., Pyrotech.* **1983**, *8*, 35–39.

(5) Singh, B.; Singh, H. Synthesis of 2,2′,4,4′,6,6′-hexanitrostilbene. *Def. Sci. J.* **1982**, *31*, 305–308.

(6) Singh, B.; Malhotra, R. K. Hexanitrostilbene and its properties. *Def. Sci. J.* **1983**, *33*, 165–176.

(7) Kayser, E. G. An investigation of the Shipp hexanitrostilbene (HNS) process. *J. Energ. Mater.* **1983**, *1*, 325–348.

10.1021/op1000644

not control the pH during the ageing period (initially 11−12, reducing to <7 during the ageing period due to elimination of HCl). Under these conditions the reaction temperature peaked at 24 °C after 2 min (10 g scale; see Table 3, Run F).

A batch HNS process as it was operated at the Royal Ordnance Factory, Bridgwater, UK, has been reported.[9] This involved mixing a 10% solution of TNT in tetrahydrofuran (THF)/methanol and 5% aqueous sodium hypochlorite at 13 °C before lowering the initial pH (11−12) to ∼10 with carbonate/bicarbonate buffer. After an ageing period of 2 h, the precipitated HNS was coagulated by acidification with dilute HCl, filtered off and washed sequentially with acetone and water. The yield of HNS was ∼45% and could be produced at the rate of ∼20 tonnes per annum. Both THF and methanol from the mother liquor and acetone from the washings were recycled. The plant was closed for economic reasons caused by environmental issues. At the present time HNS is produced via a batch process by Eurenco Bofors in Sweden and China.

In scaling up the batch process, one of the major problems is controlling the temperature at the point of mixing. This is also likely to be a problem if the reaction is performed as a semi-continuous flow system. Any excess temperature rise on mixing will cause HNS to form and precipitate prematurely in the mixing tube and result in blockage. In order to minimise this problem we have explored[10] the use of a Kenics static mixer[1] immersed in ice−water in the hope that any heat generated on mixing will be rapidly dissipated through the metal walls of the mixer into the surrounding bath.

This preliminary study[10] using a Kenics static mixer [37-03-075, material 316SS, length 190 mm, OD 4.75 mm, with 27 mixing elements] investigated the following aspects:

1.1. HNS vs HNBB Formation. The yield and composition of the product from a fixed amount of TNT (1.8 g) was investigated as the amount of NaOCl was varied from 0.5 to 1.8 equiv, with no attempt being made to control the pH in the ageing period. In theory only one equivalent of NaOCl is required to convert all of the TNT to TNBCl and thence to HNS. In practice, the highest material yield occurs in the region of 1 equiv of NaOCl, but the product in that case contains a high proportion of HNBB. The highest proportion of HNS (93−96%) occurs when 1.2−1.4 equiv of NaOCl are used, but by this stage the material yield has started to decrease. The proportion of HNBB in the product steadily decreases from 86% when 0.5 equiv of NaOCl is used and to ∼5% when >1.2 equiv are used.

1.2. pH Control. All experiments were conducted using 1.2 equiv of NaOCl (the amount that gave a low proportion of HNBB but without reducing the material yield excessively), and the pH during the ageing period was controlled by addition of aqueous H_2SO_4 and NaOH. Consistently higher material yields were obtained with pH control, compared to the uncontrolled reaction with 1.2 equiv of NaOCl. The material yield and composition of the product was not particularly sensitive to pH in the range 9.5−11.5, but slightly purer HNS was obtained in the lower part of this range. This is in agreement with Golding and Hayes' observations[4] from a series of batch reactions.

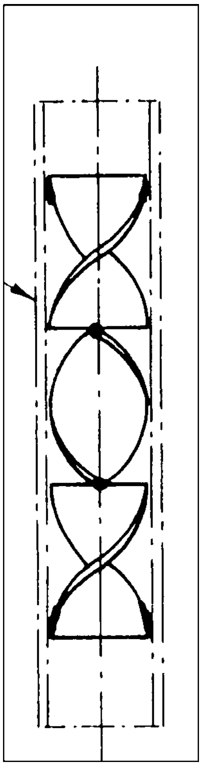

Figure 1. **Kenics static mixer (schematic) showing three mixing elements.**

1.3. Quenched reactions. One of the main objectives of our former study[10] was to prepare TNBCl using a flow reactor, quenching the reaction with HCl almost immediately after mixing. Since the highest selectivity for HNS formation most probably reflects efficient conversion of TNT to TNBCl, we chose those reactant proportions that gave the purest HNS, viz 1.2−1.4 equiv of NaOCl, for testing in quenched reactions. Reactions using 1.4 equiv of NaOCl gave high selectivity (∼95%) and high material yield (∼95%) of TNBCl. Indeed, these results are similar to those one obtains using the Shipp and Kaplan procedure,[3] viz ∼98% purity and 87% material yield.

Our earlier study has now been extended by using a larger Kenics static mixer.[1]

2. Experimental Section

Whilst both TNT and HNS are classed as relatively insensitive explosives, they should not be subjected to excessive impact, friction, or electrostatic discharge.

2.1. Mixing System. The mixer−reaction system employed consisted of a Kenics Static Tube Mixer 37-06-110[1] [material 316SS, length 356 mm, OD 9.5 mm, ID 8.1 mm,] with 27 mixing elements (see Figure 1 - only 3 of the 27 mixing

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(8) Bellamy, A. J. Identification of α-chloro-2,2′,4,4′,6,6′-hexanitrobibenzyl as an impurity in hexanitrostilbene (HNS). *Proceedings of the 12th Seminar*; New Trends in Research of Energetic Materials, Pardubice, Czech Republic, 2009, pp 433−441. *J. Energ. Mater.* **2010**, *28*, 1−16.

(9) Gallo, A. E.; Tench, N. Commisioning of a production plant for hexanitrostilbene. *J. Hazard. Mater.* **1984**, *9*, 5–11.

(10) Bellamy, A. J., Lomax, V. Read, K. The use of a Kenics static mixer for the reaction of TNT with NaOCl. *Proceedings of the 9th Seminar*; New Trends in Research of Energetic Materials, Pardubice, Czech Republic, 2006, pp 491−499.

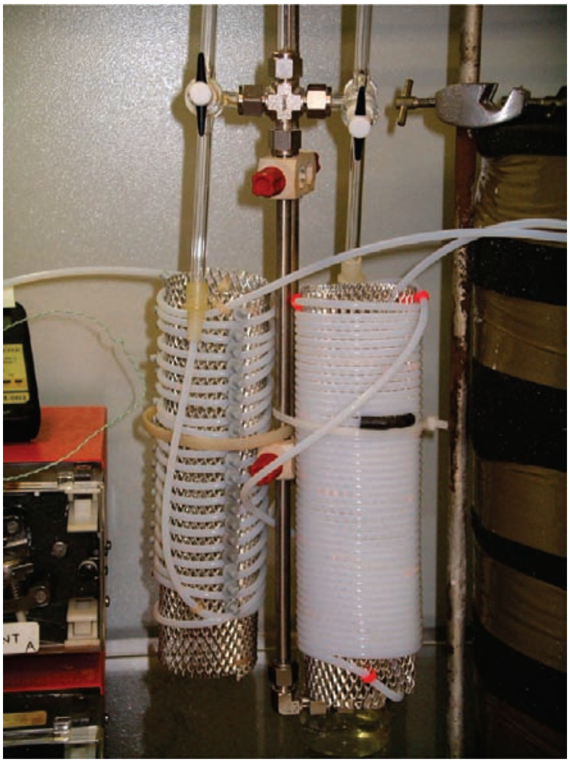

Figure 2. **Intercoiled inlet tubes (left), coiled exit tube (9 m, right), static mixer (vertical in centre).**

elements are shown), oriented vertically with the inlet at the top. The reactant solutions [TNT in THF/MeOH/water and aqueous NaOCl] were delivered by two peristaltic pumps [Watson Marlow model 302S, butyl tubing], via PTFE tubing [ID 3.2 mm, OD 4.8 mm] to the mixing tee [Swagelok SS-600-3, ID 7.1 mm, internal volume after mixing point ~0.55 cm^3] (or cross-piece [Swagelok SS-600-4] when it was required to monitor the internal temperature at the point of mixing). The mixing tee was directly attached to the top end of the static mixer. The outflow from the bottom of the static mixer was conveyed by PTFE tubing [ID 3.2 mm, OD 4.8 mm, variable length 0.8−9 m], also immersed in the ice−water bath, to the ageing or quenching vessel. Various parts of the system are shown in Figures 2−5. Before commencing a reaction, the whole of the system [inlet tubes (to ensure that the reactant solutions were precooled), mixing tee, static mixer, outlet tube] was immersed in ice−water contained in a stirred vessel (Figure 4, 5), and the inlet tubes were primed to within 2 cm of the mixing tee (Figure 6). The PTFE delivery tubes were partially coiled (diam ≈ 6 cm, total length of immersed coiled tube ≈ 2 m). This allowed precooling of the solutions from ambient to 1−2 °C before mixing. The exit tube was mainly in the form of a coil [diam ≈ 6 cm, total length of immersed coiled tube = 3−9 m].

2.2. Choice of Reaction Conditions (Table 1). The original Shipp−Kaplan procedure[3] (10-g scale) used TNT in THF/MeOH (150 mL; 2:1 by volume) and 1.53 equiv of 5 wt % NaOCl (volume equal to that of THF). The procedure adopted at Bridgwater[9] appears to mimic that of Shipp and Kaplan and that reported in a UK patent.[11] In the present work the TNT was dissolved in THF/MeOH/H_2O (60:30:10% by volume) - see Table 1 (all processes scaled to 25 g of TNT), since in a

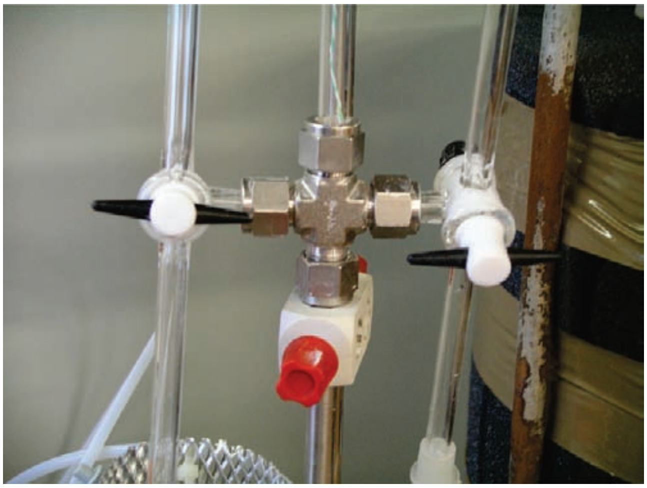

Figure 3. **Top of static mixer and inlet system.**

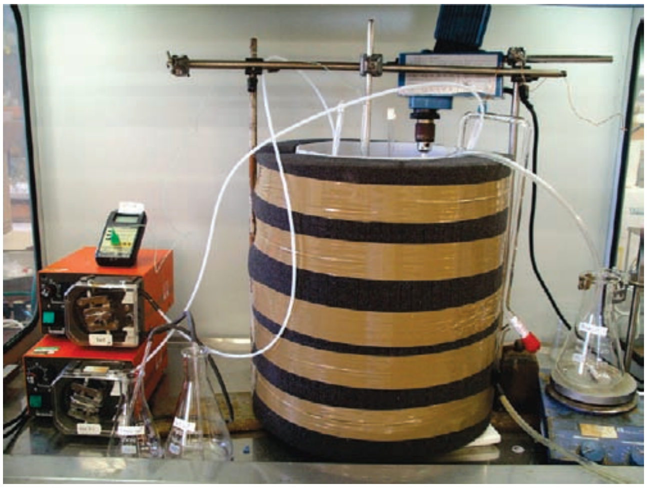

Figure 4. **Complete system in ice−water bath.**

Figure 5. **Mixing system in ice−water bath.**

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(11) Jones, R. H.; Pryde, A. W. H. Production of hexanitrostilbene, GB 1570569, 1980.

Table 1. **Reagent proportions for the NaOCl oxidation of TNT**

	TNT, g	THF, mL	MeOH, mL	H_2O, mL	NaOCl, mL	NaOCl, % wt/vol	NaOCl, equiv	comments
Batch Processes[a]								
Shipp−Kaplan[b]	25	250	125	0	250	5.0	1.53	batch process for HNS (10 g scale)
GB 1570569[c]	25	213	107	0	225	4.4	1.2	batch process for HNS (500 g scale)
present work	25	180	90	30	90	8.2−11.8	0.9−1.3	optimisation of a batch recipe (50 g scale)
static mixer								
present work	25	180	90	30	200	11.6	1.32	HNS synthesis (example)
present work	25	180	90	30	200	11.6	1.37	TNBCl synthesis (example)
present work	25	180	90	30	200	2.5	0.86	HNBB synthesis; blocked tube

[a] Scaled to 25 g TNT. [b] Reference [3] [c] Reference [11]

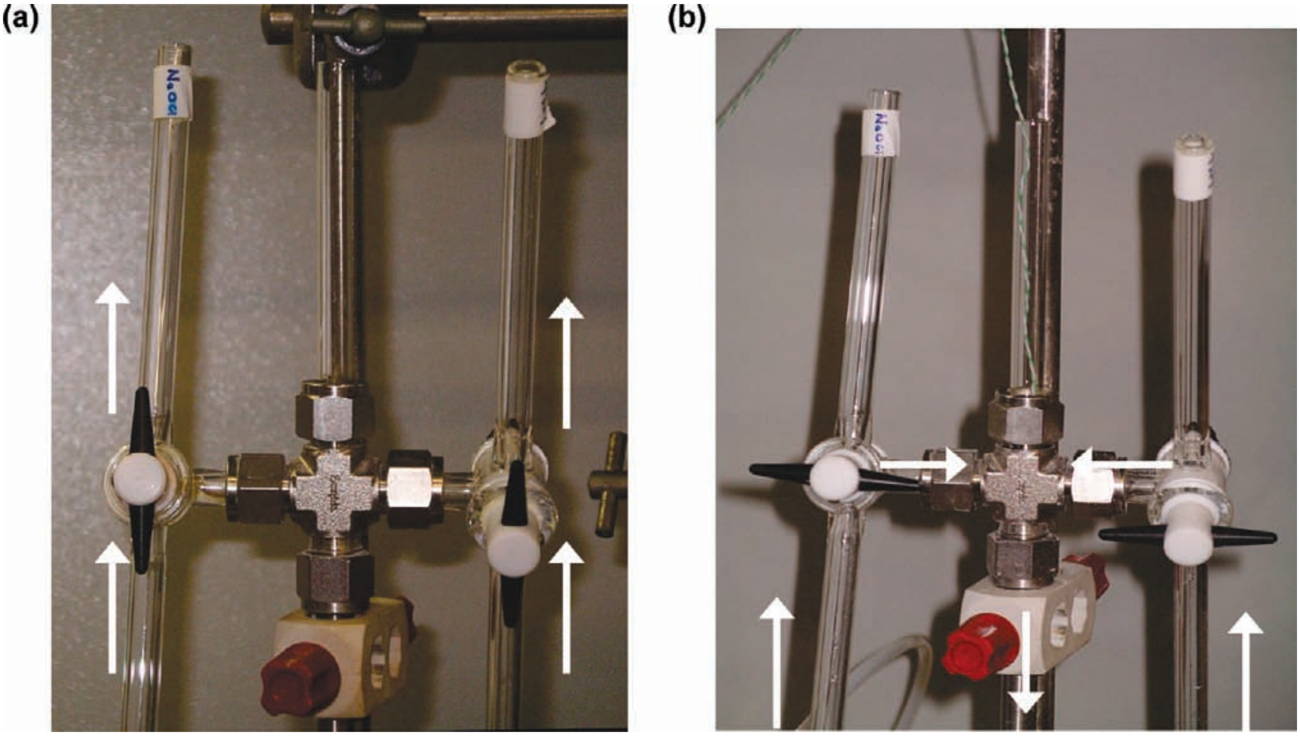

Figure 6. **(a) Tap positions for priming of inlet tubes (b) Tap positions for mixing (arrows indicate flow direction).**

commercial process the solvent is recovered (as a mixture by distillation) from a previous run and often contains 10−12 wt % H_2O.

The reactant proportions adopted for the flow mixer system, both in previous work[10] and the present work, are based on a commercial recipe (see Table 1).

2.3. Standard Procedure. TNT solution: TNT (25 g) was dissolved in THF (180 mL) and then diluted with MeOH (90 mL) and H_2O (30 mL). Total volume after dissolution ~320 mL (0.078 g/mL, 0.344 mmol/mL). Pump: 4.8 mm ID butyl tubing, pump operating at 40% of its maximum flow i.e. ~1.20 mL/s.

NaOCl solution: the appropriate volume of concentrated NaOCl solution (14.89 g/100 mL) was diluted with H_2O to 200 mL to give the required equivalents of NaOCl. For example, for 1.2 equiv of NaOCl, 137 mL of the original NaOCl solution (0.1489 g/mL) diluted to 200 mL (0.102 g/mL, 1.37 mmol/mL). Pump: 3.2 mm ID butyl tubing, pump operating at 27.5% of its maximum flow i.e. ~0.36 mL/s.

The combined flow rate of the two solutions lies within the turbulent flow regime of the Kenics static mixer.[1]

(1) Weigh both reagent solutions.

(2) Both T-taps set for vertical flow (see Figure 6a), pump until the reagents are just above the taps, then switch pumps off.

(3) Turn both T-taps to allow flow into the mixer (see Figure 6b).

(4) Switch on both pumps simultaneously. Collect the reaction solution leaving the exit tube in a magnetically stirred, uncooled flask. Switch off both pumps when the last of the TNT solution or NaOCl solution leaves the reservoir. Cease collection at this point (normally <4 min).

(5)Turn both T-taps back to vertical flow.

(6) Reverse pumps and draw back reagents in the tubes. Then reweigh both reagent solutions.

(7) Flush system, via the TNT inlet system, with MeOH/THF/H_2O (50 mL).

Table 2. **Data sheet for each experiment**

run: 10
experiment: standard, 9 m exit tube
conditions:
TNT (25 g) in THF (180 mL) +
MeOH (90 mL) + H_2O (30 mL); pump: 4.8 mm i..d.; 40% maximum flow
NaOCl (19.95 g) in H_2O (200 mL);
1.19 equiv; pump: 3.2 mm ID; 27.5% maximum flow
mixing time:
4 min 00 s (240 s)

mass (g)	TNT solution		NaOCl solution	total
initial + flask	443.1		343.1	
flask	158.4		109.6	
initial	284.7		233.5	
final + flask	195.1		243.2	
flask	158.4		109.6	
final	36.7		133.6	
introduced (used)	248.0	+	99.9	= 347.9
collected + flask			455.2	
flask			197.2	
collected			258.0	
lost in system	347.9	−	258.0	= 89.9 (−25.8%)

(8) Flush system, via the NaOCl inlet system, with H_2O (100 mL).

(9) Flush system, via the NaOCl inlet system, with NMP (50 mL).

(10) Flush system, via the NaOCl inlet system, with H_2O (100 mL).

(11) Flush system, via the TNT inlet system, with MeOH (50 mL).

(12) Leave both reagent systems empty (by reversing the pumps) and remove tubing from pumps.

(13) Weigh the contents of the receiver before filtering off the product.

At the end of the reaction period the product was filtered off on a preweighed sintered glass funnel (No. 4, 6.5 cm diam), applying suction until the filtrate flow had almost ceased. It was then washed with (i) methanol (50 mL) - the funnel walls were washed down 3× before adding the bulk of the methanol - and (ii) water (50 mL). The product was dried in a vacuum desiccator over silica gel. The results are tabulated as shown in Table 2 (typical entry).

Calculation of conditions actually used (using data in Table 2):

284.7 g of TNT solution contains 25 g of TNT ∴ the 248.0 g of TNT solution used contains 21.8 g (96 mmol) TNT.

233.5 g of NaOCl solution contains 19.95 g of NaOCl ∴ the 99.9 g of NaOCl solution used contains 8.54 g (115 mmol) of NaOCl.

Ratio of reactants (NaOCl/TNT) = 115/96 = 1.19 equiv.

The material remaining in the mixer and exit tube when the pumps were switched off (this material could neither be pumped into the receiver vessel nor withdrawn into the reagent storage flasks due to the geometry of the system) was calculated by subtracting the mass of the collected solution (measured at the end of the reaction period) from the sum of the TNT solution and the NaOCl solution delivered into the mixing chamber. It was assumed that, had this portion been pumped into the collection vessel, it would have increased the mass of the product proportionately.

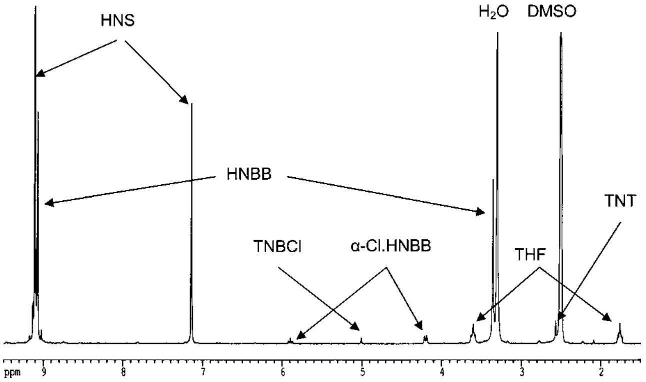

Figure 7. **^{1}H NMR spectrum (DMSO-d_6) of crude HNS (illustrative example). Data: TNT 2.56 (s, CH_3), 9.03 ppm (s, 2H, Ar); TNBCl 5.00 (s, CH_2Cl), 9.09 ppm (s, 2H, Ar); HNS 7.14 (s, 2H, CH=CH), 9.11 ppm (s, 4H, Ar); HNBB 3.35 (s, 4H, CH_2), 9.08 ppm (s, 4H, Ar); α-Cl·HNBB[8] 4.20 (d, 2H, J = 6.9 Hz), 5.90 ppm (t, 1H, J = 6.8 Hz); due to the low abundance of this product, the aromatic peaks were not visible.**

Thus, the yield of product = mass of product + % lost in mixer and exit tube (see Table 2).

Percentage yield (assuming all product is HNS) = 100 × [mass of product isolated + % lost in mixer and exit tube] × [2 × molecular mass of TNT]/[mass of TNT consumed] × [molecular mass of HNS].

2.4. Product Analysis. ^{1}H NMR (10 mg/1.0 mL DMSO-d_6) was used to confirm product identity and distribution. An illustrative NMR spectrum is shown in Figure 7.

HPLC may also be used to analyse the product mixture but was not used in the present work. Conditions: μ-Bondapak C-18 10 μm; 3.9 mm × 150 mm; mobile phase: 52.5% water/47.5% acetonitrile; flow rate 1.0 mL/min. The retention times were: TNT 5.6 min, TNBCl 6.4 min, HNS 11.6 min, HNBB 13.8 min, α-Cl·HNBB 16.4 min.

2.5. pH-Controlled Reactions. The mixing stage was as above. When mixing was complete, the pH of the reaction mixture was reduced from 12−13 to the desired pH e.g. 10, by the addition of 25 wt % H_2SO_4 (or to pH 9.7 by the addition of aqueous 4 M aqueous ethanolamine hydrochloride[12]), and the pH was then controlled at the desired pH by automatic addition of 6 wt % NaOH (alternatively neat ethanolamine[12]). Control equipment: combination glass electrode (Thermo Scientific CW757/A = 300 mm), Radiometer Copenhagen PMH 82 standard pH meter with a TTT titrator). The filtered product was washed with MeOH (50 mL) and water (2 × 50 mL).

2.6. Quenched Reactions. The mixing stage was as above. However, the mixture leaving the exit tube was added to a solution of conc HCl (25.4 mL) in H_2O (1250 mL). This caused precipitation of the products. The resultant mixture was stirred at ambient temperature during 1 h before the product was filtered off and washed with water.

2.7. Shipp−Kaplan Conditions (Run F, Table 3). A solution of TNT (10 g) in THF (100 mL) + MeOH (50

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(12) Sollott, G. P. Conversion of 2,4,6-trinitrobenzyl chloride to 2,2′,4,4′,6,6′-hexanitrostilbene by nitrogen bases. *J. Org. Chem.* **1982**, *47*, 2471–2474.

Table 3. **Results of reaction of TNT with NaOCl**

					product composition by ^{1}H NMR (mol %)						
run[a]	TNT consumed, g	yield, g	yield, %	NaOCl, equiv	HNS	HNBB	TNBCl	TNT	α-Cl·HNBB	THF	conditions
A	50.0	18.0	36.3	1.36	93.5	1.5	0.8	0.0	4.2	3.9	batch reactor
B	50.0	21.9	44.2	1.00	87.2	6.4	1.3	0.0	5.1	5.8	batch reactor
C	50.0	28.2	57.0	1.00	83.8	3.2	1.9	1.8	9.4	3.7	batch reactor; pH 10.2 controlled with H_2SO_4 and NaOH
D	50.0	30.8	62.1	1.00	85.6	2.0	1.3	1.7	9.4	3.6	batch reactor; pH 10.4 controlled with H_2SO_4 and NaOH
E	50.0	29.6	59.7	1.36	94.2	0.9	1.4	0.0	3.5	3.8	batch reactor; pH 9.7 controlled with ethanolamine buffer
F	10.0	3.5	35.3	1.55	93.8	0.0	1.0	0.0	5.2	6.0	Shipp−Kaplan synthesis[b]maximum temp. 24 °C
1	17.6	7.16	41.0	1.22	88.1	6.6	1.3	0.0	4.0	6.2	standard; 80 cm exit tube
2	21.9	9.20	42.4	1.13	78.9	14.6	1.7	0.0	4.8	7.6	standard; 300 cm exit tube
3	21.9	30.15		1.26			70.1	29.9			standard; 300 cm exit tube; quenched after mixing
4				(0.56)							standard, but NaOCl equiv halved; 300 cm exit tube; blocked
5	15.5	4.18	27.2	1.66	95.3	0.0	0.8	0.0	4.0	5.4	standard, but NaOCl undiluted; 300 cm exit tube
6	21.7	9.57	44.5	1.15	90.0	4.4	1.1	0.0	4.5	6.3	standard, but both concentrations halved; 300 cm exit tube
7	22.0	10.3	47.2	0.79	26.6	67.3	0.0	6.1	0.0	2.3	standard, but pumps at half speed; 300 cm exit tube
8	7.33	1.25		0.86	12.7	78.1	0.0	9.2	0.0	1.2	standard, but NaOCl halved and both concentrations halved; 300 cm exit tube; blocked
9	16.3	7.15	44.3	1.02	74.6	19.8	1.3	0.0	4.3	6.7	standard; 300 cm exit tube
10	21.8	8.54	39.5	1.19	73.0	20.2	1.7	0.0	5.2	7.2	standard; 900 cm exit tube
11	21.4	20.1	81.5	1.37			94.5	5.5			standard; 900 cm exit tube; quenched after mixing
12	21.5	7.93	37.2	1.32	86.1	7.3	1.5	0.0	5.1	6.5	standard; 900 cm exit tube
13	23.1	9.77	42.7	1.27	93.9	0.0	1.2	0.0	4.9	5.6	standard, but both concentrations halved; 900 cm exit tube
14	23.1	23.3	87.6	1.25			87.4	12.6			standard, but both concentrations halved; 900 cm exit tube; quenched after mixing
15	21.6	11.8	55.1	1.21	81.4	9.2	2.6	0.0	6.8	5.2	standard; 900 cm exit tube; pH 10.0
16	21.4	8.6	40.5	1.20	74.7	18.9	1.6	0.0	4.8	7.6	standard, but both concs halved (as run 15; but no pH control); 900 cm exit tube
17	21.4	10.4	49.0	1.24	89.1	1.5	1.9	0.0	7.5	5.6	standard; 900 cm exit tube; pH 10.0,
18	21.3	10.7	50.7	1.02	64.6	21.6	2.6	3.2	8.1	5.2	standard; 900 cm exit tube; pH 10.2
19	22.9	11.7	51.5	1.03	74.2	13.9	2.4	1.6	7.9	5.9	standard, but both concentrations halved; 900 cm exit tube; pH 10.2
20	21.3	11.8	55.9	1.16	76.9	12.0	2.7	2.2	6.3	5.7	standard; 900 cm exit tube; pH 9.7 controlled by ethanolamine buffer
21	23.1	13.3	58.1	1.19	89.6	3.2	1.9	0.7	4.7	5.7	standard, but both concs halved; 900 cm exit tube; pH 9.7 by ethanolamine buffer
22	20.9	5.9	28.5	1.55	94.2	0.0	0.9	0.0	4.9	6.3	standard; Shipp−Kaplan proportions; 900 cm exit tube

[a] A−E: batch reactions in a stirred reactor (50 g scale); F: Shipp−Kaplan batch reaction (10 g scale); 1−22: static mixer reactions (25 g scale). [b] Reference 3.

mL) was cooled to ∼0 °C and was then added with rapid mixing to 5% NaOCl (100 mL; also precooled to ∼0 °C). The ensuing exothermic reaction caused the temperature to rise to a maximum temperature of 24 °C within 2 min. The very dark-coloured solution was then cooled to 15 °C and left for 2 h, during which time the temperature rose slowly to 20 °C. The precipitated HNS was isolated as described above. Yield of crude HNS 3.5 g (35%): see Table 3, Run F.

2.8. Reactions with <1 equiv of NaOCl. Attempts were made to synthesise hexanitrobibenzyl (HNBB) by reducing the equivalents of NaOCl to ∼0.5, but in general these failed due to unreacted TNT separating from the reaction mixture (due to the increased water content after mixing).

3. Results and Discussion

The complete set of results for reactions (runs 1−22) utilising the Kenics static mixer system as described above (arranged chronologically), and comparable batch reactions (runs A−F) mixed by adding the NaOCl solution to the TNT solution in a stirred reactor, are presented in Table 3.

Runs 1−11 were essentially exploratory in nature to ascertain the proper functioning of the system and to make any adjustments that were deemed necessary.

Runs A and B were normal batch reactions (essentially commercial conditions) with different equivalents of NaOCl (1.36 and 1.00 equiv, respectively). The yields of crude HNS were 36 and 44%, respectively, the HNS contents were 93 and 87%, respectively, and the HNBB contents were 1.5 and 6.4%, respectively. As observed previously (see Introduction 1.1) the proportion of HNBB decreases as the number of NaOCl equivalents is increased.

Runs 3, 11, and 14 were quenched reactions performed to measure the extent of reaction before the reaction mixture left the exit tube. In Run 3 the exit tube was ∼3 m long; in Runs 11 and 14 it was ∼9 m long. From the amount of TNT remaining in the quenched product, it was clear that the 9 m exit tube was necessary for an almost complete reaction. With only a 3 m exit tube, 30% TNT remained unreacted. If a significant proportion of the TNT was still present at this point, its continued reaction with NaOCl would generate heat in the ageing vessel, giving less control over the after-reaction conditions. This was observed as a more rapid temperature rise (22 °C vs 13.5 °C after 30 min, respectively) in the collection vessel in later runs. Run 11 indicated that moderately pure TNBCl could be synthesised by this method, the only impurity being TNT.

Run F was a standard (10-g scale) Shipp−Kaplan HNS synthesis,[3] and Run 22 was a static mixer run utilising the same reactant concentrations and proportions as those in the Shipp−Kaplan synthesis. Whilst the selectivity was high in both cases, the yield of crude HNS was lower in the flow system (28 vs 35%).

Runs 12 and 13 used the same number of equivalents of NaOCl (∼1.3), but Run 13 used halved concentrations of both reactants. The yield (37 vs 43%, respectively) and selectivity (86 vs 94 mol % HNS, respectively) were better in the diluted system.

Runs C and D were batch reactions run with pH control (H_2SO_4, NaOH) during the after-reaction period, Run C at pH 10.2 and Run D at pH 10.4. Both used 1.0 equiv of NaOCl. The yields of crude HNS were 57 and 62%, respectively. Flow mixing, Run 17 (1.24 equiv of NaOCl) and Run 18 (1.02 equiv of NaOCl), followed by control (H_2SO_4, NaOH) at pH 10.0 and 10.2, respectively, gave yields of ∼50% in both cases, but selectivity was much higher with the greater proportion of NaOCl (Run 17). A repeat of Run 18 with halved concentrations (Run 19), gave essentially the same yield, but slightly better selectivity.

Run E was a batch reaction run with pH control (pH 9.70) using an ethanolamine buffer. The yield of crude HNS was 60% with high selectivity. A corresponding static mixer run (Run 20), but with lower NaOCl (1.16 equiv; Run E used 1.36 equiv), gave a 56% yield with reduced selectivity. However a similar run (Run 21) with halved concentrations gave 58% yield with high selectivity.

From previous work[10,13] it is known that the byproduct α-chloro-2,2′,4,4′,6,6′-hexanitrobibenzyl (α-chloro•HNBB) in crude HNS is converted by recrystallisation from NMP into 2-chloro-2′,4,4′,6,6′-pentanitrostilbene, which remains in the recrystallised HNS. It is therefore important to reduce the production of this byproduct as much as possible, even at the expense of increasing the HNBB content since the latter is lost on recrystallisation. In the present flow runs, the isolated HNS contained 4−8 mol % of this byproduct. Other results from batch experiments[10,13] indicate that a higher pH level during the after-reaction period favors the formation of α-chloro•HNBB.

Attempts to synthesise hexanitrobibenzyl (HNBB), by reducing the equivalents of NaOCl to ∼0.5, failed due to unreacted TNT separating from the reaction mixture (due to the increased water content after mixing). This blocked the static mixer (Runs 4 and 8).

Further observations relate to the observed temperatures, at or after mixing. With water being pumped through both inlet systems the observed temperature at the mixing point was 3.5 °C (pump settings 40% and 27.5%). Thus, even though both liquids had passed through 2 m of PTFE tubing immersed in ice−water, the temperature of the liquid had only been reduced from ambient to 3.5 °C. It is suggested that SS tubing, with its better thermal conductivity, should be substituted for PTFE in the inlet tubing coils in order to achieve better cooling of the inlet solutions. That this temperature is the same as that observed during an actual HNS run suggests that the present positioning of the temperature sensor does not record the temperature generated by the exothermic reaction on mixing. A temperature sensor positioned at the bottom of the static mixing tube should be explored.

The temperature in the collecting vessel during an actual HNS run was never lower than 5.5 °C. This suggests that the exothermic reaction may not be complete when the reaction solution leaves the exit tube. This is supported by the observation in Runs 11 and 14 that some TNT remains unreacted at this stage. Replacement of the PTFE exit tubing by SS tubing should enhance the efficiency of cooling the reaction mixture. This, of course, would reduce the rate of reaction further, necessitating an extension (or broadening) of the exit tube in order to achieve the same or increased extent of reaction at this stage. Both changes would certainly be required if the pump rate were to be increased in order to increase the scale of the reaction.

In the present work, PTFE cooling coils were used both before and after the mixer because they were more flexible to work with. It was appreciated at the outset that SS coils would give more efficient cooling. However, without experimental data using the PTFE coils, it was not possible to say whether they would have been of sufficient length to achieve the necessary cooling.

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(13) Bellamy A. J. Unpublished work.

4. Conclusions

Previous work[10] on a Shipp−Kaplan type synthesis of hexanitrostilbene (HNS) using a small Kenics static mixer[1] has been extended to the use of a larger mixer (9.5 mm vs 4.75 mm OD) enabling the scale to be increased from 2.5 g to 25 g of TNT for the same mixing time (<4 min). In order to allow almost complete initial reaction between the TNT and the NaOCl before exiting the system (conversion to trinitrobenzyl chloride TNBCl) the exit tube connected to the end of the mixer, also cooled in ice−water, had to be extended from 3 m to >9 m. This was studied by quenching the reaction on exiting the tube and measuring the consumption of TNT. The PTFE inlet tubes to the mixer (length ∼2 m, also cooled in ice−water) and the PTFE exit tube were configured as coils (6 cm diam). Various conditions for the after-reaction period (2 h) have been explored on the basis of previous work with a batch reactor (50-g scale of TNT), including (i) no pH control, (ii) pH control using aqueous H_2SO_4 and NaOH solutions, and (iii) pH control using aqueous RNH_3Cl and RNH_2 solutions. Other parameters that have been varied are the ratio of NaOCl to TNT (0.5−1.2) and the concentration of both reactants. Attempts to synthesise HNBB by using a low NaOCl/TNT ratio failed due to blockage in the mixer from precipitation of TNT.

The yields of crude HNS that have been achieved, whilst not outstanding, are an improvement over the conventional batch process. It has been demonstrated that the yield and selectivity of the HNS synthesis can be considerably increased if, during the after-reaction period, the reaction conditions are pH controlled. The yield and selectivity are also significantly enhanced by using more dilute reaction solutions.

The same mixer should be capable of mixing on a larger scale by increasing the flow rate of the two solutions, but this would necessitate an extension (or broadening) of the exit tube to give sufficient reaction time before the reaction solution leaves the system. Both the inlet PTFE cooling coils and the exit PTFE cooling coil should be replaced by SS coils in order to achieve more efficient cooling.

The use of larger, preferably jacketed Kenics static mixers[1] for contacting the NaOCl and TNT solutions would enable the temperature during the short period after contact, during which the exothermic reaction to give trinitrobenzyl chloride occurs, to be better controlled. This should lead to better selectivity in the process. The control of conditions during the after-reaction period merits further investigation.

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