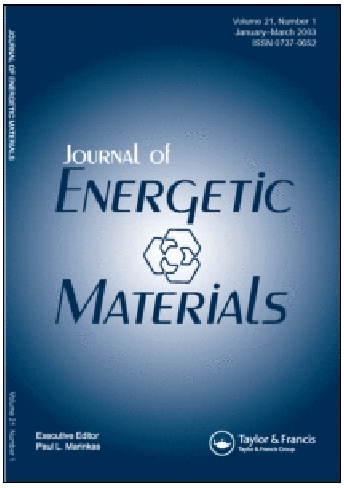

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An investigation of the shipp hexanitrostilbene (HNS) process

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AN INVESTIGATION OF THE SHIPP HEXANITROSTILBENE (HNS) PROCESS

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ABSTRACT

This report describes the separation, characterization, and analysis of products formed during the Shipp hexanitrostilbene (HNS) process. In this process, trinitrotoluene (TNT), dissolved in a mixture of tetrahydrofuran (THF) and methanol (MeOH), reacts with commercial bleach (NaOCl) to form HNS. The identified products include: hexanitrostilbene (HNS), hexanitrobibenzyl (HNBiB), trinitrobenzene (TNB), trinitrobenzoic acid (PiCOOH), trinitrobenzaldehyde (PiCHO), trinitrobenzyl chloride ($PiCH_2Cl$), picryl chloride (PiCl), picric acid (PiOH), trinitrobenzyl alcohol ($PiCH_2OH$), 4,6-dinitro

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[2,1]benzisoxazole (Anil), and trichloronitromethane (chloropicrin) as well as unreacted TNT. An additional study was made of the $PiCH_2Cl \rightarrow HNS$ reaction which was the source of the red tar components. Approximately 5-10% of the red tar fraction could not be identified. Solvent effects on the yield of several of the above cited by-products are also discussed.

INTRODUCTION

Since its discovery in the early 1960's by Kathryn G. Shipp, thermally stable 2,2',4,4',6,6'-hexanitrostilbene (HNS) has found numerous applications in military ordnance items[1] and throughout the aerospace industry[2,3,4].

HNS is currently prepared commercially[5] by reacting 2,4,6-trinitrotoluene (TNT) with a 5% aqueous sodium hypochlorite solution (household bleach) in the presence of tetrahydrofuran (THF) and methanol (MeOH) as solvents (Shipp Process[6,7]).

$$\text{TNT} \xrightarrow[\text{THF, MeOH}]{\text{NaOCl (0-5°C)}} \underset{(\sim 40\%)}{(\text{HNS} + \text{HNBiB})} + \underset{(\sim 60\%)}{\text{red-tar}}$$

It was proposed[6] that, under the alkaline conditions of the reaction, TNT forms trinitrobenzyl anion, which is chlorinated to yield trinitrobenzyl chloride. Subsequent reaction of the chloride with alkali produces a mixture of HNS and HNBiB as crystalline products in a combined yield of less than 50% with the remainder of the material forming a red-tar fraction.

The purpose of this study was two-fold: (1) to determine what by-products, other than HNBiB, are produced in the TNT-NaOCl reaction, and (2) to search for a way to reduce or eliminate the concurrent side reactions which decrease the yield of HNS. An investigation of the composition of the red-tar fraction was necessary to determine the nature of the competing side reactions. Approximately 90% of the compounds were isolated and characterized using thin layer chromatography (TLC) coupled with nuclear magnetic resonance spectroscopy (NMR), gas chromatography (GC), and/or high performance liquid chromatography (HPLC)[8,9,10]. Final product identification was achieved by comparison with known compounds.

To facilitate the second part of this study, the HNS reaction (TNT ⟶ HNS) was separated into two steps:

$$\text{(A)}\quad \mathrm{TNT} \xrightarrow[\text{THF, MeOH (exothermic)}]{\text{NaOCl (0-5°C)}} \underset{\substack{\text{stable intermediate} \\ (\sim 75\%\text{-}85\%)}}{\mathrm{PiCH_2Cl}}$$

$$\text{(B)}\quad \mathrm{PiCH_2Cl} \xrightarrow[\text{(non-exothermic)}]{\text{NaOH}} \underset{(\sim 35\%\text{-}40\%)}{\mathrm{HNS + HNBiB}} + \underset{(\sim 60\%)}{\text{red-tar}}$$

In Step A the stable intermediate, 2,4,6-trinitrobenzyl chloride ($PiCH_2Cl$), was obtained in a 75% - 85% yield by quenching the reaction mixture in dilute aqueous hydrochloric acid (HCl) approximately one minute after the NaOCl addition was complete[6]. No evidence of appreciable amounts of by-products, other than unreacted TNT, was found by short stopping the reaction at this point. Since the red tar products are formed in Step B of the HNS reaction, this step was studied independently by investigating the $PiCH_2Cl$ reaction with base in various solvents. In addition, several by-products of the Shipp reaction, i.e., 1,3,5-trinitrobenzene (TNB), 4,6-dinitro [2,1] benzisoxazole (Anil), 2,4,6-trinitrobenzyl alcohol ($PiCH_2OH$), 2,4,6-trinitrobenzaldehyde (PiCHO), and 2,4,6-trinitrobenzoic acid (PiCOOH), were also treated with base under various conditions to observe the products formed.

EXPERIMENTAL

Reaction Conditions and Work-Up Procedures

To determine the by-products present in the red-tar fraction, twenty TNT-NaOCl reactions were carried out under the following conditions reported to maximize the yield of HNS[6,7].

1.0 gm (0.0044 moles) of TNT in (10 ml THF and 5 ml MeOH) was cooled to about 0°C then added quickly, with thorough mixing, to 10 ml of "Chlorox" (commercial bleach 5.25% NaOCl) which was chilled to 0°C. During the initial reaction period of about 2-3 minutes, the temperature of the mixture was held below 15°C in an ice-salt bath. The mixture was then allowed to stand at ambient temperature until precipitation of the HNS product was complete (approximately 20-30 minutes). The crystalline material (HNS-HNBiB) from each reaction was filtered from the reaction mixture, washed with methanol, dried and weighed. Further reactions of the by-products, in the remaining filtrate, were quenched by neutralization with aqueous HCl. After an initial extraction of the filtrate with benzene, both the extract and the remaining aqueous filtrate were evaporated to dryness and assayed by TLC and NMR for identifiable products. The organic components of the red-tar material contained in the benzene extract were separated using preparative TLC. After TLC separation, the compounds were characterized by NMR, GC, and HPLC. Structural confirmation was achieved by comparison with authentic compounds.

Several of the TNT-NaOCl reactions were carried out in a closed system to retain any gaseous by-products. Although several volatile materials were separated from both the benzene extract and the aqueous solution of the red-tar fraction, chloropicrin was the only such product, which was characterized and identified with GC and HPLC by comparison with the known compound.

A supplemental study of the reactions of TNT with several of the isolated by-products of the Shipp process (TNB, Anil, $PiCH_2OH$, $PiCH_2Cl$, PiCHO, and PiCOOH) was carried out at room temperature, with aqueous NaOH and NH_4OH, to observe the formation of any secondary products. Reaction times were arbitrarily set at 30 and 90 minutes. A 1:1 mole ratio of reactant to base[6] was used in each case, with MeOH, THF and dioxane as solvents. The work-up procedure for these reactions was identical to that described for the TNT-NaOCl reactions. The major reaction products were identified by NMR spectroscopy, and structural confirmation was achieved by comparison with authentic compounds.

Analysis Procedures

Organic components of the red-tar material (benzene extract) were separated using preparative TLC. The plates (1/4" thickness) were prepared using Brinkman Silica gel HF 254 as the absorbent with a calcium sulfate binder. As purchased, this material contains a fluorescent indicator which allows location of the developed spots with a 254 nm light. The TLC developing solvents used were either benzene or a benzene:ether:ethanol mixture (50:30:20 by volume) depending on material polarity.

Estimated yields for HNS, HNBiB, unreacted TNT and nine by-products were obtained with a Varian HA-100 NMR spectrometer using 2,3-dimethyl-2,3-dinitrobutane as an internal standard. The chemical shift values (δ) for the TNT and by-product protons were determined relative to the reference compound, tetramethylsilane (TMS). The NMR solvent was dimethyl sulfoxide-d_6 (min. isotopic purity 99.5 atom % D), which was the best general solvent found for the TNT-NaOCl reaction products.

The organic components of the benzene extract were also characterized by High Pressure Liquid Chromatography (HPLC). A Model ALC 202 liquid chromatograph (Waters Associates, Milford, MA) equipped with the following (a) a model 6000 solvent delivery system, (b) a U6K high pressure loop injector, (c) a 254 nm UV detector, (d) a Whatman HPLC guard column containing CO:PELL ODS pellicular material, and (e) a Whatman Partisil-10 ODS-2 bonded C-18 reverse phase analytical column [25cm long, 4.6mm ID, 1/4" (6.350mm) OD] was used for these analyses. UV absorption signals were recorded on an Omniscribe strip chart recorder set at 0.5cm/minute. The mobile phase consisted of MeOH (Baker - HPLC grade) and distilled water in a ratio of 2:3 by volume. Pressure at the column head was approximately 2000 psi with a flow rate of 2 ml/minute. The column temperature was approximately 25°C. All solvents and samples were filtered prior to use in the HPLC. Material concentration was determined by manual integration of the chromatographic peak area. Dimethylsulfoxide (DMSO, Fisher Scientific, A.C.S. grade) was used as the sample solvent. All the compounds, except PiCOOH at relatively low concentrations (<50 ppm), were found to be stable in the sample solvent (DMSO). In dilute solutions, PiCOOH reacts in DMSO to form TNB (peak retention time, 6.9 minutes). However, a peak retention time of approximately 1.0 minute was obtained with more concentrated PiCOOH-DMSO solutions. This value agreed with that obtained for PiCOOH in MeOH.

RESULTS AND DISCUSSION

Since its discovery in the early 1960's by Kathryn G. Shipp, thermally stable 2,2'4,4'6,6'-hexanitrostilbene (HNS) has found numerous applications in military ordnance items[1] and throughout the aerospace industry[2,3,4]. HNS is used in rigid explosive transfer lines, commonly called shielded mild detonating cord (SMDC) which are used to initiate and sequence aircraft emergency crew escape systems. More than one million cords have been manufactured for fourteen various aircraft and spacecraft[5]. For this reason, an investigation of the by-products formed during the HNS commercial synthesis procedure was undertaken to determine the nature of the competing side reactions and also to search for a possible method to reduce or eliminate these reactions.

Eleven compounds (HNS, HNBiB, Anil, PiOH, $PiCH_2OH$, $PiCH_2Cl$, chloropicrin, PiCOOH, PiCl, PiCHO, and TNB) have been identified as reaction products of the Shipp Process. Approximately 98% of the nominal yield of HNS (35-45%) is recovered in the crystalline form; however, several by-products and/or unreacted TNT have been found trapped within the HNS crystals[6,9,10,12]. All twelve compounds were found in the red-tar fraction. NMR and TLC data of these materials (with the exception of chloropicrin) are summarized in Tables 1 and 2. HPLC data are given in Table 3 and Figure 1.

Deuterium exchange experiments carried out earlier[13] indicated the formation of 2,4,6-trinitrobenzyl anion from 2,4,6-TNT in alkaline THF/MeOH solutions. The results of a recent photodeuterium exchange study[14] of aqueous 2,4,6-TNT solutions also indicate the initial formation of 2,4,6-trinitrobenzyl anion. Previous work at this laboratory by Burlinson, Kaplan, Adams and Sitzmann[15,16] has shown that photolyzed aqueous solutions of TNT (using sunlight or a pyrex filtered Hg-lamp) contain several of the compounds isolated from the TNT-NaOCl reaction (e.g., TNB, PiCHO, Anil, and $PiCH_2OH$).

Estimated weight percentages, based on NMR analysis, are reported for eleven of the organic components recovered from the red-tar fraction (Table 4). At least two other compounds were formed during the reaction (as evidenced by peaks on the GC and HPLC), however, due to their volatility at room temperature and

TABLE 1. NMR DATA FOR COMPOUNDS ISOLATED FROM THE TNT-NaOCl REACTION

Compound	NMR Spectrum[(a)]
HNS	9.07 (s, 4 Ar-H) 7.11 (s, CH=CH)
HNBiB	9.05 (s, 4 Ar-H) 3.39 (s, CH_2-CH_2)
PiCH_2Cl	9.05 (s, 2 Ar-H) 4.98 (s, CH_2)
PiCH_2OH	8.95 (s, 2 Ar-H) 4.82 (s, CH_2)
PiCHO	9.14 (s, 2 Ar-H) 10.51 (s, CH)
PiCOOH	9.11 (s, 2 Ar-H)
PiCl	9.20 (s, 2 Ar-H)
TNB	9.14 (s, 3 Ar-H)
PiOH	8.56 (s, 2 Ar-H)
TNT	8.98 (s, 2 Ar-H) 2.53 (s, CH_3)
Anil	10.56 (d, Ar-H) 9.31 (q, Ar-H) 8.62 (d, Ar-H)

(a) s=singlet, d=doublet, q=quartet, Ar=aromatic protons. Chemical shifts are in δ units downfield from internal TMS with line multiplicity and relative intensity in parentheses. Spectra were determined on a Varian HA-100 in DMSO-d_6.

TABLE 2. TLC DATA[a] OF IDENTIFIED COMPOUNDS FROM THE HNS REACTION

Compound	R_f (benzene)
TNT	.86
PiCl	.89
PiOH	.17[b]
PiCOOH	0.0 (origin)
$PiCH_2Cl$	.83
TNB	.74
PiCHO	.56
Anil	.64
$PiCH_2OH$	.20
HNS	.38
HNBiB	.58
Red-Tar (unidentified)	0.0 (origin)

Compound	R_f (benzene:ether:ethanol) 50 : 30 : 20
PiOH	.90
PiCOOH	.73
Red-Tar (unidentified)	0.0 - 0.05

(a)Thin layer plates prepared with Brinkman Silica gel - HF 254. Spot visualization by UV lamp. R_f taken from leading edge of spot.

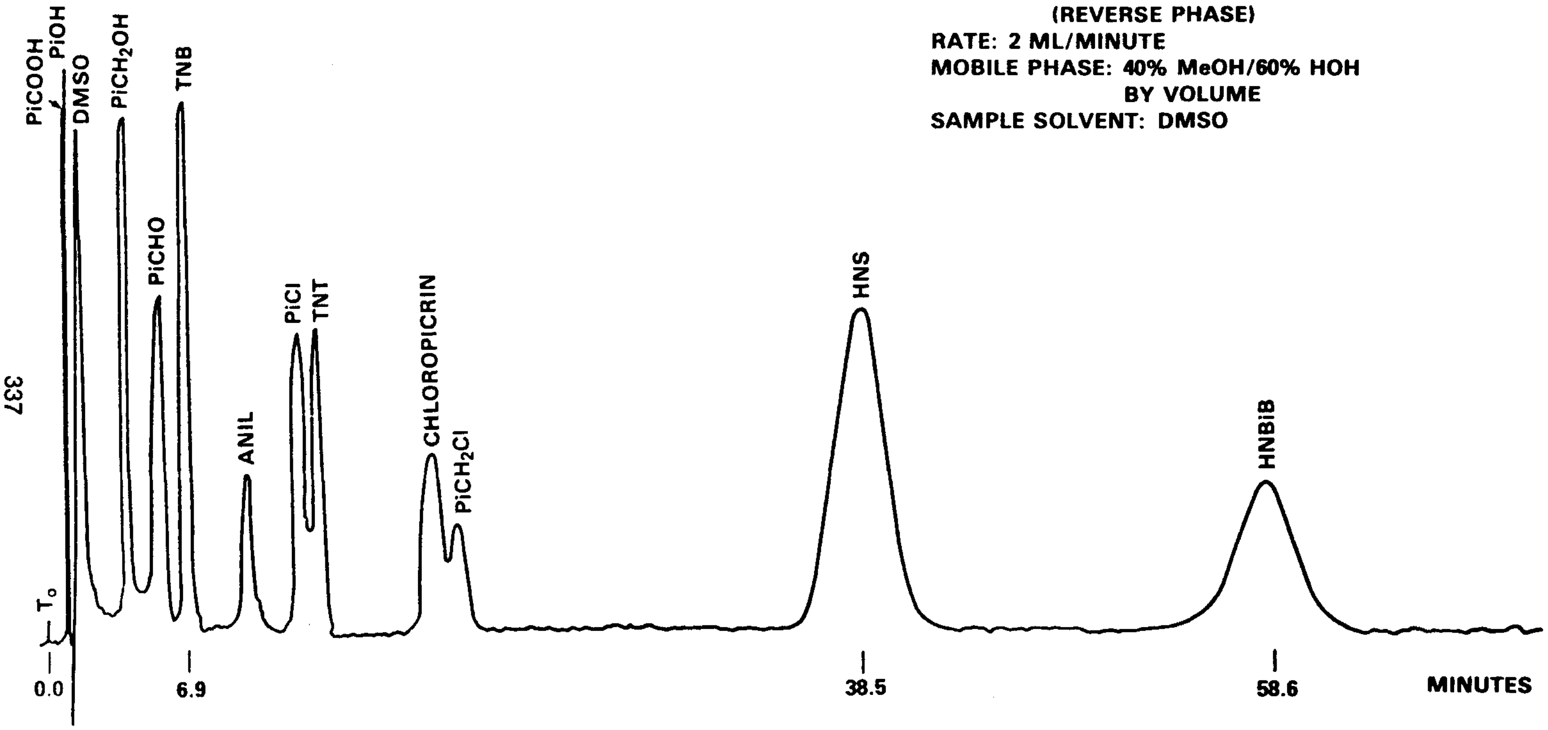
(b)Streaking from .17 to origin.

TABLE 3. HPLC DATA OF COMPOUNDS ISOLATED FROM THE TNT - NaOCl REACTION(a)

Compound	Peak Retention Time in Minutes
PiCOOH	1.0
PiOH	1.1
DMSO(b)	1.7
$PiCH_2OH$	3.9
PiCHO	5.8
TNB	6.9
Anil	9.2
PiCl	12.0
TNT	12.8
Chloropicrin	18.5
$PiCH_2Cl$	19.8
HNS	38.5
HnBiB	58.6

(a)Column: Partisil-01-ODS-2 (reverse phase)
Mobile Phase: 40% MeOH/60% HOH by volume.
Flow Rate: 2 mls/minute.

(b)Sample Solvent: DMSO.



CONDITIONS

COLUMN: PARTISIL-10-ODS-2
(REVERSE PHASE)
RATE: 2 ML/MINUTE
MOBILE PHASE: 40% MeOH/60% HOH
BY VOLUME
SAMPLE SOLVENT: DMSO

FIGURE 1

HPLC Trace of Compounds Isolated From the TNT-NaOCl Reaction

TABLE 4.

COMPOUNDS IDENTIFIED AS PRODUCTS OF THE TNT-NaClO REACTION

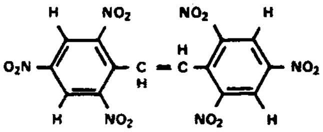
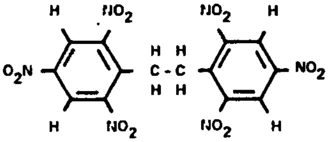
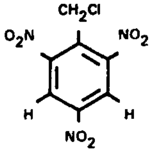
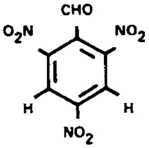
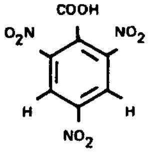
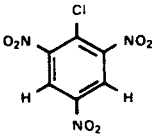
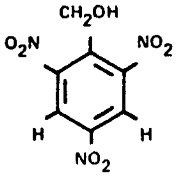
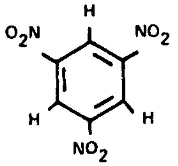
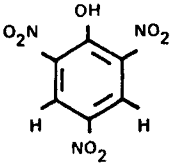
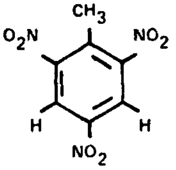
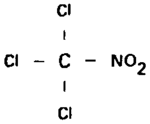
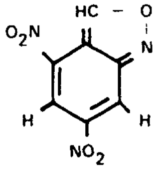
COMPOUND STRUCTURE		MOLECULAR WEIGHT	WEIGHT PERCENT [a]
	2,2',4,4',6,6'-HEXANITROSTILBENE (HNS)	450	30-45
	2,2',4,4',6,6' – HEXANITROBIBENZYL (HNBiB) DIPICRYLETHANE (DPE)	452	5-10
	2,4,6 – TRINITROBENZYL CHLORIDE ($\mathrm{PiCH_2Cl}$)	261	5-10
	2,4,6 – TRINITROBENZALDEHYDE (PiCHO)	241	~5-10
	2,4,6 – TRINITROBENZOIC ACID (PiCOOH)	257	~2-5
	PICRYL CHLORIDE (PiCl)	247	0-TRACE [b]

TABLE 4. (CONTINUED)

COMPOUND STRUCTURE		MOLECULAR WEIGHT	WEIGHT PERCENT (a)
	2,4,6 – TRINITROBENZYL ALCOHOL ($PiCH_2OH$)	243	5-10
	2,4,6 – TRINITROBENZENE (TNB)	213	5-10
	2,4,6 – TRINITROPHENOL (PiOH) PICRIC ACID	229	$\sim$0-2
	2,4,6 – TRINITROTOLUENE (TNT)	227	5-10
 $Cl_3C{-}NO_2$	CHLOROPICRIN (c)	164	> 1
	4,6 – DINITROANTHRANIL (ANIL) 4,6-DINITRO (2,1) BENZISOXAZOLE	209	< 1-5
RED-TAR (d)			5 10

Pi = 2,4,6 - TRINITROPHENYL

(a) PERCENT OF COMPOUNDS FORMED IS DEPENDENT ON REACTION CONDITIONS

(b) TRACE ≤ 1%

(c) DETERMINED BY GAS CHROMATOGRAPHY (GC). ALL OTHER COMPOUNDS DETERMINED BY NMR.

(d) UNIDENTIFIED MATERIAL. HIGH MOLECULAR WEIGHT AND OR POLAR MATERIAL low yield these materials could not be identified. The British (PERME Group at Waltham Abbey) have identified methyl nitrite as a volatile component of this reaction.

Approximately 5-10% of the red-tar fraction that remained in the aqueous filtrate after removal of the HNS/HNBiB crystals and extraction with benzene could not be identified. This material probably contains high molecular weight and/or polar compounds, since most of the unidentifiable segment (>50%) remained at the origin when chromatographed with methanol.

Results of investigations of (a) the non-exothermic base reactions with aqueous sodium hydroxide (NaOH) and aqueous ammonium hydroxide (NH_4OH) in various solvents, and (b) the reactions of TNT with NaOCl in various solvents are summarized in Tables 5 and 6. In general, the base study indicated a greater degree of product reactivity in the aqueous NaOH system than in the aqueous NH_4OH system. As expected, the reactions of $PiCH_2OH$, $PiCH_2Cl$, and TNT with NaOH formed highly colored species and resulted in the greatest number of reaction products. However, most of the products resulting from the reaction of TNT with NaOH could not be separated or identified and remained at the origin when chromatographed with the relatively polar solvent mixture, benzene:ether:ethanol (50:30:20 by volume). Approximately 5-15% HNBiB was isolated from the TNT-NaOH reaction mix. Both TNB and Anil proved to be stable end products under these reaction conditions. Trinitrobenzoic acid (PiCOOH) decarboxylates to TNB in the presence of base. This reaction also occurs quite rapidly in DMSO (without added base) at PiCOOH concentrations of less than 50 ppm. TNB is also the final product from trinitrobenzylaldehyde (PiCHO). This reaction[17,18] proved to be quantitative in several of the solvents investigated.

As expected, the reaction of trinitrobenzyl chloride ($PiCH_2Cl$) with NaOH produced the highest yield of HNS (35-45%) in the THF-MeOH (2:1) and the THF solvent systems (Table 5). This is also true of the TNT-NaOCl reactions (Table 6). None of the other solvents examined exhibited the apparent specificity of THF for this reaction.

Sollott[19] has reported HNS yields of approximately 70% obtained from TNBzCl and certain nitrogen bases (e.g. isopropylamine and triethylamine). A 57% yield of HNS was also obtained with a 2.4:1 molar ratio of NH_4OH to TNBzCl. For these studies[19], the TNBzCl was dissolved in THF and MeOH and the bases were dissolved in water.

CONCLUSIONS

The by-products isolated from the Shipp Hexanitrostilbene (HNS) Process are: hexanitrobibenzyl (HNBiB), trinitrobenzene (TNB), trinitrobenzoic acid (PiCOOH), 4,6-dinitro [2,1]

TABLE 5. BY-PRODUCT REACTIONS WITH BASE IN SEVERAL SOLVENTS

					% REACTION PRODUCTS									
BY-PRODUCT REACTANT	BASE	SOLVENT SYSTEM	REACTION TIME (IN MINUTES)	TEMPERATURE °C	$PiCH_2OH$	PiCHO	ANIL	TNB	PiOH	TNT	PiCOOH	$PiCH_2Cl$	HNS	HNBiB
$PiCH_2OH$	NaOH	THF/MeOH (2:1)	30	22.5°-25°	28	12	19	17	2					
$PiCH_2OH$	NaOH	THF/MeOH (2:1)	90	22.5°-25°	17	21	16	12	2					
$PiCH_2OH$	NaOH	MeOH	90	22.5°-25°	15	2	14	30						
$PiCH_2OH$	NaOH	DIOXANE	90	22.5°-25°	19	5	5	3	26					
$PiCH_2OH$	NaOH	DIOXANE	90	22.5°-25°	19	2	2	5	28					
$PiCH_2OH$	NaOH	DIOXANE (DISTILLED)	90	22.5°-25°	22	10	6	20						
$PiCH_2OH$	NaOH	THF	90	22.5°-25°	19	25	10	9						
$PiCH_2OH$	NH_4OH	THF/MeOH (2:1)	90	22.5°-25°	71									
$PiCH_2OH$	NH_4OH	DIOXANE	90	22.5°-25°	45									
$PiCH_2OH$	NH_4OH	MeOH	90	22.5°-25°	73									
$PiCH_2Cl$	NaOH	THF/MeOH (2:1)	30	22.5°-25°	5	9	~1	2				28	36	~10
$PiCH_2Cl$	NaOH	THF/MeOH (2:1)	90	22.5°-25°	5	6	~1	2	~1			17	46	~3
$PiCH_2Cl$	NaOH	MeOH	90	22.5°-25°	5			11				24	10	
$PiCH_2Cl$	NaOH	DIOXANE	90	22.5°-25°	2	5		<1	15			26	17	~1
$PiCH_2Cl$	NaOH	DIOXANE (DISTILLED)	90	22.5°-25°	6	7	2	4				15	15	
$PiCH_2Cl$	NaOH	THF	90	22.5°-25°	4	7		~4	~1			15	40	~5
$PiCH_2Cl$	NH_4OH	THF/MeOH (2:1)	90	22.5°-25°	3	5		2				51	16	5
$PiCH_2Cl$	NH_4OH	DIOXANE	90	22.5°-25°	2							52		
$PiCH_2Cl$	NH_4OH	MeOH	90	22.5°-25°	5	3		5				47	~1	
PiCHO	NaOH	THF/MeOH (2:1)	30	22.5°-25°		40		18						
PiCHO	NaOH	THF/MeOH (2:1)	90	22.5°-25°		22		68						
PiCHO	NaOH	MeOH	90	22.5°-25°		<5		85						
PiCHO	NaOH	MeOH	90	22.5°-25°		~2		95						
PiCHO	NaOH	DIOXANE	90	22.5°-25°		45		31						
PiCHO	NaOH	THF	90	22.5°-25°		55		40						
PiCHO	NH_4OH	THF/MeOH (2:1)	90	22.5°-25°		60		20						
PiCHO	NH_4OH	DIOXANE	90	22.5°-25°		88								
PiCHO	NH_4OH	MeOH	90	22.5°-25°				98						

TABLE 5. BY-PRODUCT REACTIONS WITH BASE IN SEVERAL SOLVENTS (CONTINUED)

BY-PRODUCT REACTANT	BASE	SOLVENT SYSTEM	REACTION TIME (IN MINUTES)	TEMPERATURE °C	% REACTION PRODUCTS									
					$PiCH_2OH$	PiCHO	ANIL	TNB	PiOH	TNT	PiCOOH	$PiCH_2Cl$	HNS	HNBiB
PiCOOH	NaOH	THF/MeOH (2:1)	30	22.5°-25°				15			59			
PiCOOH	NaOH	THF/MeOH (2:1)	90	22.5°-25°				15			53			
PiCOOH	NaOH	MeOH	90	22.5°-25°				6			80			
PiCOOH	NaOH	DIOXANE	90	22.5°-25°				19			41			
PiCOOH	NaOH	THF	90	22.5°-25°				8			47			
PiCOOH	NH_4OH	THF/MeOH (2:1)	90	22.5°-25°				40			48			
PiCOOH	NH_4OH	DIOXANE	90	22.5°-25°				11			61			
PiCOOH	NH_4OH	MeOH	90	22.5°-25°				~1			90			
TNB	NaOH	THF/MeOH (2:1)	90	22.5°-25°				90						
TNB	NaOH	MeOH	90	22.5°-25°				95						
TNB	NaOH	THF	90	22.5°-25°				89						
TNB	NH_4OH	THF/MeOH (2:1)	90	22.5°-25°				85						
TNB	NH_4OH	THF	90	22.5°-25°				90						
TNB	NH_4OH	MeOH	90	22.5°-25°				96						
ANIL	NaOH	THF/MeOH (2:1)	90	22.5°-25°			75							
ANIL	NaOH	MeOH	90	22.5°-25°			80							
ANIL	NaOH	DIOXANE	90	22.5°-25°			15							
ANIL	NaOH	THF	90	22.5°-25°			68							

BY-PRODUCT/BASE REACTION MIXTURES:
TO A SOLUTION OF 0.0042 MOLES OF REACTANT IN 16.92 ML THF AND 8.46 ML MeOH (AT AMBIENT TEMPERATURE) IS ADDED 16.92 ML OF WATER CONTAINING 0.0042 MOLES OF EITHER NaOH OR NH_4OH.

REACTION TIME: 30 AND/OR 90 MINUTES

MAJOR IDENTIFIABLE REACTION PRODUCTS: DETERMINED BY NMR SPECTROSCOPY

NMR SAMPLE SOLVENT: DMSO

TABLE 6. TNT REACTIONS

REACTANT	NaOCl	BASE	SOLVENT SYSTEM	REACTION TIME IN MINUTES	TEMPERATURE °C	% REACTION PRODUCTS			
						TNT	TNB	HNS	HNBiB
TNT		NaOH	THF/MeOH (2:1)	30	22.5°-25°	53	<1	TRACE	6
TNT		NaOH	MeOH	90	22.5°-25°	37			6
TNT		NaOH	DIOXANE	90	22.5°-25°	16			16
TNT		NaOH	THF	90	22.5°-25°	29			18
TNT		NH_4OH	THF/MeOH (2:1)	90	22.5°-25°	74			
TNT		NH_4OH	DIOXANE	90	22.5°-25°	39			
TNT		NH_4OH	MeOH	90	22.5°-25°	65			
TNT	NaOCl		THF/MeOH (2:1)	2-3	<15°				
				20	22.5°-25°			43	8
TNT	NaOCl		THF/MeOH (2:1)	5	<15°				
				30	22.5°-25°			38	10
TNT	NaOCl		THF/MeOH (2:1)	2-3	<15°				
				20	22.5°-25°			35	7
TNT	NaOCl		THF	2-3	<15°				
				20	22.5°-25°			41	6
TNT	NaOCl		DIOXANE	2-3	<15°				
				20	22.5°-25°			~12	<5
TNT	NaOCl		MeOH	2-3	<15°				
				20	22.5°-25°			~2	
TNT	NaOCl		ACETONE	2-3	<15°				
				20	22.5°-25°			<2	~2
TNT	NaOCl		ACETONITRILE	2-3	<15°				
				20	22.5°-25°			1-2	

TNT/BASE REACTION MIXTURES:

TO A SOLUTION OF 0.0042 MOLES OF TNT IN 16.92 ML THF AND 8.46 ML MeOH (AT AMBIENT TEMPERATURE) IS ADDED 16.92 ML OF WATER CONTAINING 0.0042 MOLES OF EITHER NaOH OR NH_4OH.
REACTION TIME: 30 AND/OR 90MINUTES

TNT/NaOCl REACTION MIXTURES:

1.0 GM (0.0044 MOLES) OF TNT IN (10 ML THF AND 5 ML MeOH) IS CHILLED TO ABOUT 0°C THEN ADDED QUICKLY, WITH THOROUGH MIXING, TO 10 ML OF "CHLOROX" (COMMERCIAL BLEACH - 5.25%) WHICH IS ALSO CHILLED TO 0°C. DURING THE INITIAL REACTION PERIOD OF ABOUT 2-3 MINUTES, THE TEMPERATURE OF THE MIXTURE IS HELD BELOW 15° C BY CHILLING IN AN ICE-SALT BATH. THE MIXTURE IS THEN ALLOWED TO STAND AT AMBIENT TEMPERATURE UNTIL PRECIPITATION OF THE HNS PRODUCT IS COMPLETE (APPROXIMATELY 20-30 MINUTES).

MAJOR IDENTIFIABLE REACTION PRODUCTS: DETERMINED BY NMR SPECTROSCOPY
NMR SAMPLE SOLVENT: DMSO

benzisoxazole (Anil), trinitrobenzaldehyde (PiCHO), trinitrobenzyl chloride ($PiCH_2Cl$), picryl chloride (PiCl), picric acid (PiOH), trinitrobenzyl alcohol ($PiCH_2OH$), and trichloronitromethane (chloropicrin). Unreacted TNT (5-10%) was also isolated from the red-tar fraction. Investigations of the reactions of all of the above polynitroaromatic compounds with base furnished additional information, but no method was found to either reduce the side reactions or increase the yield of HNS. None of the solvents investigated displayed the pronounced specificity of tetrahydrofuran (THF) for this reaction.

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