26
9-22-80

23 to NTIS

MHSMP-79-35

MASTER

SYNTHESIS OF HNS I VIA THE INTERMEDIATE DIPICRYLETHANE - 5 KG SCALE

Jacob Sandoval

DEVELOPMENT DIVISION

JUNE 1979

For
Sandia Laboratories
Albuquerque, New Mexico
(P.O. 13-3029)

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

Mason & Hanger-Silas Mason Co., Inc.
Pantex Plant

P. O. BOX 30020
AMARILLO, TEXAS 79177
806-335-1581

OPERATED FOR THE
Department of Energy
UNDER
U. S. GOVERNMENT CONTRACT DE-AC04-76DP-00487

SYNTHESIS OF HNS I VIA THE INTERMEDIATE DIPICRYLETHANE - 5 KG SCALE

Jacob Sandoval

DEVELOPMENT DIVISION
(June 1979)

For
Sandia Laboratories
Albuquerque, New Mexico
(P.O. 13-3029)

ABSTRACT

An alternate route for the synthesis of 2,2′,4,4′,6,6′-hexanitrostilbene has been successfully scaled to 5 kg quantities. The intermediate dipicrylethane was synthesized via the Shipp process and was subsequently oxidized into HNS through a Hungarian process.

DISCUSSION

The two-step, alternate synthesis route for the evaluation of HNS I in quantities of 0.010, 0.050 and 0.500 kg has been described and reported earlier(*1*,*2*). The synthesis of HNS I in 5 kg lots was undertaken to evaluate the merits and limitations, if any, of further scaling.

During these experiments, the reaction parameters and volume ratios established and reported earlier, were followed explicitly; however, minor changes in the introduction of reagents into the reaction vessel were incorporated to satisfy the reactor requirements or limitations.

The synthesis of dipicrylethane (DPE), from TNT via the Shipp process is simple and quite efficient. This process is described below:

> *"A solution of 10 g of TNT in 50 mℓ of THF and 100 mℓ of methanol was prepared in a 500 mℓ wide mouth erlenmeyer flask equipped with a mechanical stirrer and a 125 mℓ dropping funnel. A solution prepared by adding 35 mℓ of '5%' aqueous sodium hypochlorite to 0.5 g of sodium hydroxide dissolved in 65 mℓ of water was placed in the dropping funnel and added, with rapid stirring, during 5-10 minutes, to the TNT solution. The mixture turned dark red-brown and a crystalline product appeared after about one minute. Formation of the crystalline product was heavy by the end of addition*

---

(1) *Jacob Sandoval, Alternate HNS I Synthesis Via the Intermediate Dipicrylethane, MHSMP-78-56 (November 1978).*

(2) *Jacob Sandoval, Alternate HNS I Synthesis Via the Intermediate Dipicrylethane, MHSMP-79-18 (March 1979).*

> *of the hypochlorite solution and the temperature of the reaction mixture had risen to 35 C. The mixture was allowed to stand for 15 minutes, filtered with suction and the filter cake was washed thoroughly with methanol and dried. It weighed 7.9 g, 79% of theoretical...."(3).*

An 80% yield of DPE is promoted through the Shipp process. Thus, 10 kg of TNT would provide sufficient DPE with which to synthesize the desired 5 kg of HNS I. However, the ease and simplicity of the DPE synthesis prompted the decision to increase the reactants and convert 22.5 kg TNT into DPE. A portion of the DPE was utilized in the 5 kg HNS synthesis and the balance catalogued and stored for future use.

The synthesis of the DPE was conducted in a 760 litre (200 gallon) pilot plant glass-lined reactor. Into this vessel were introduced 120 litres of tetrahydrofuran (THF) and 235 litres of methanol (MeOH). After a nitrogen sweep was established, stirring of the reactor contents was initiated (150 rpm) and 22.7 kg of TNT were added.

Dissolution of 1.13 kg of sodium hydroxide in 18.2 litres was effected in a clean stainless steel kettle. This solution, along with an additional 130 litres of water and 75 litre of institutional grade Clorox, was introduced into a 375 litre glass-lined reactor. The lid was bolted in place and the vessel was pressurized with nitrogen to a maximum of 20 psig. The contents were then passed through a transfer line (10 litre/min) into the reactor containing the TNT solution.

The reaction was allowed to continue for an additional 45 minutes following the completion of the final addition. At no time during the DPE synthesis did the reaction temperature rise above 30 C.

A filter press was employed to isolate the reaction product. The collected material was washed in hot water for 30 minutes. Following the extraction of the wash water the material was rinsed with 50 litres of methanol. Steam was circulated through the filter press and the product dried under vacuum over a 30 minute period.

The filter press was disengaged and the DPE removed. A sample of this material (SH-9047-a) was removed for evaluation before the product was slurry washed with 150 litres of fresh methanol for 30 minutes. During the final collection and drying of the DPE, vacuum was applied over a 60 minute period while steam was passed through the filter press plates.

After accounting for material losses in the reactor, transfer lines, and filter press, a DPE yield of 75% was calculated as compared to the 80% yield obtained repeatedly with smaller batch sizes. No cause has been established for the lower yield. The melting point and product properties of the synthesized DPE, Lot SH-9047-01 are listed in Table I.

A unique procedure for the synthesis of HNS from DPE has been developed and patented by Kompolthy and coworkers. This process, with minor modifications, was employed in the synthesis of HNS The Hungarian process, patented by Kompolthy, et.al., is given below:

> *"We weigh out 22.6 g (0.05 mole) of HNB* into a 500 mℓ round-bottomed flask equipped with a mechanical stirrer, thermometer and a separatory funnel; we then*

---

(3) K. G. Shipp and Lloyd Kaplan, Journal of Organic Chemistry, 31, 857 (1966).

Table I. Summary of Dipicrylethane Synthesis (Lot No. SH-9047-01)

TNT (kg)	22.7
THF (ℓ)	120
Methanol (ℓ)	235
Stirring Rate (rpm)	150
'A' Clorox (ℓ)	75
B Water with NaOH[a] (ℓ)	140
Addition Rate[b] A = B (ℓ/min)	20
Reaction Time (min)	45
Reaction Temperature (C)	20-30
Wash[c]	-
Color	Tan
Yield (%)	75
Melting Point (C)	208
Composition	
TNT (%)	0.09
DPE (%)	99.58
HNS (%)	0.33

[a] *1.13 kg NaOH in 140 litre water*

[b] *215 litre (Clorox - mild alkali mix) added over 10 min.*

[c] *Wash - (Clean-up process)*
DPE collected in filter press; washed with filtered hot water/30 min.
*Rinsed with 50 litre methanol; filtered. Sample SH-9047-a removed.**
Slurried with 150 litre methanol/30 min.
Vacuum applied 60 min./steam heat. Oven dried, 115 C.

**LC analysis of product at this point indicates superior product (TNT = 0.15, DPE = 99.49, HNS = 0.36).*

add to it 125 mℓ of dimethylformamide and follow it with dropwise addition of 5 mℓ of 2-molar methanolic potassium hydroxide solution. We start the stirring and after the dissolution of the HNB, we add 15 g of anhydrous copper sulfate, which we had previously finely ground with a mixture of 125 mℓ of dimethylformamide and 50 mℓ of pyridine. We warm the reaction mixture to 50 C and keep it at that temperature for 1 hour. Then we add dropwise to the system 100 mℓ of water, cool it to room temperature, filter off the precipitated product, wash it with hot water, then with diluted ammonia water until the wash solution is colorless. Finally, we cover it with methanol. We dry the product and obtain 19.6 g of HNS" (4).

**Hexanitrobibenzyl or dipicrylethane (DPE).*

All constituents in the HNS I synthesis, via the Hungarian process, were proportionately scaled to correspond to 11.4 kg DPE. For this size reaction a slurry consisting of 8.6 kg anhydrous copper sulfate in a solvent mixture of 70 litres DMF and 28.5 litres of pyridine is introduced into the DPE solution. The concern that difficulty might be encountered in the movement of this slurry through a 3.75 cm dia. transfer line prompted the decision to add the solution to the slurry as indicated below.

Into a clean glass-lined 190 litre (50 gallon) reaction vessel were introduced 70 litres of dimethylformamide (DMF). The stirring mechanism was activated at 150 rpm and a nitrogen sweep was established. This was followed by the addition of 11.4 kg DPE. Upon dissolution of the DPE a solution comprised of 319 g potassium hydroxide in 2.8 litres of methanol were introduced.

Into an adjoining 375 litre (100 gal) reactor were introduced 70 litres of DMF, 28.5 litres pyridine and 8.6 kg of copper sulfate. The above contents were stirred (150 rpm) for approximately 15 minutes and then the contents from the 190 litre reactor containing the DPE solution were emptied over the stirring copper sulfate slurry.

The reactor contents were then heated to 50 ± 5 C and this temperature and stirring rate were maintained throughout the 60 minute reaction period. At the end of the reaction period 75 litres of distilled water were added to the vessel contents. Cooling water was circulated through the vessel jacket and the contents cooled to 25 C before collection.

The reactor contents were drawn into the filter press and the crude HNS was collected by filtration. The washing procedure for isolation of the HNS, as prescribed by Kompolthy(4), was bypassed and the following washing technique was employed:

After collection in the filter press, the crude HNS was rinsed with 50 litre acetone. The rinse solvent was extracted from the product by application of vacuum over a 30 minute period while steam heat was applied to the filter frames. While still in the press the HNS was subjected to a hot water rinse before it was refiltered, gathered and returned to the reactor for additional treatment.

In the reaction vessel the HNS was slurried over a 30 minute period in 75 litre of a dilute ammonium hydroxide solution (200 mℓ reagent/litre). The precipitated HNS was rinsed copiously in hot water in the filter press.

---

(4) Tivadar Kompolythy, et.al., [Hungarian Patent - T/9639 VE-719 (c 06 f 9/04)].

Visual examination of the material at this time revealed the presence of minute black particles dispersed throughout the product. Earlier investigation had disclosed similar particles to be a copper complex; thus the HNS was returned to the reactor for additional treatment.

The product was slurried for 30 minutes in 75 litres of dilute (3% by wt.) hydrochloric acid. After filtering, the product was rinsed with 38 litres of acetone followed by an extensive hot water rinse. The contents on the filter press were kept under vacuum for 60 minutes while steam was being passed through the frames.

The HNS was once more returned to the reaction vessel and reslurried in 50 litres of acetone for 30 minutes. After filtering, the HNS was again rinsed extensively in hot water. Vacuum and heat were applied to the press for 180 minutes. Additional drying of the HNS was continued in a forced-air oven at 115 C for approximately 12 hours.

A summary of the HNS I, Lot SH-9052-01 synthesis and reaction parameters, reaction yield and product properties is found in Table II.

In addition to researching the feasibility of 5 kg synthesis of HNS I via the two-step alternate route, a complementary objective was to establish an efficient clean-up procedure for the crude HNS crop. Product compliance with HNS I specification requirements, SLA-5003 (Table III) was evaluated. The crude HNS I (Lot SH-9052-01) was subjected to extensive cleansing studies. Ten gram quantities of the HNS were washed and/or slurried in water (basic, acidic), organic solvents or solvent systems for predetermined periods of time. None of the slurry or washing studies proved useful; however, an effective purification of the crude HNS I can be promoted by dissolution of the reaction product in hot DMF followed by crash precipitation of the HNS. This is affected by addition of a diluent (water, methanol) to the hot solution. Upon filtration, most of the contaminants remain in solution and are carried away with the filtrate. The procedure is described below.

The solubility curve of HNS in DMF (g solute/mℓ solvent), as a function of temperature, has been established from ambient to 115 C(*5*). Dimethylformamide boils at 153 C; however, at approximately 120 C decomposition accompanied by intense discoloration commences. In an HNS/DMF solution the discoloration is transmitted to the solute; consequently most DMF applications are conducted at 105 C. At this temperature a saturated HNS/DMF solution contains 8.8 g solute/100 mℓ solvent(*5*).

HNS I Cleaning Technique

> *Five grams of HNS I (Lot SH-9052-01) and 65 mℓ DMF were introduced into a 125 mℓ erlenmeyer flask, positioned over an oil bath. Application of heat to the flask contents, with stirring (150 rpm), was commenced, and the temperature raised to 105 C. Upon dissolution of the HNS, 9.5 mℓ of cold-distilled water was added. Precipitation of the HNS*

---

(5) Jacob Sandoval, HNS Crystallization Studies, MHSMP-75-24H (April-June 1975).

Table II. Summary of HNS I Synthesis (Lot No. SH-9052-01)

DPE (kg)	11.4
DMF[a] (ℓ)	70.0
2M Methanolic Potassium Hydroxide[b] (ℓ)	2.8
Slurry	
Anhy. Cupric Solfate (kg)	8.6
DMF (ℓ)	70
Pyridine (ℓ)	28.5
Reaction Time (min)	60
Reaction Temperature (C)	50
Water (ℓ)	75
Addition Rate[c] (ℓ/min)	-
Wash*	-
Color	Tan
Yield (%)	67
Melting Point (C)	315
Composition	
TNT (%)	-
DPE (%)	1.65
HNS (%)	98.35

[a] *Start agitation (150 rpm); establish nitrogen sweep.*

[b] *318 g KOH in 2.8 litre methanol.*

[c] *Valve (1/2 inch line) completely open, flow not measured.*

**Wash - Crude HNS collected in filter press.*

Chase with 50 litres acetone; apply vacuum 30 min/steam heat; rinse with hot water.

Slurry in 75 litres dilute NH_4OH (5.6%); filter; rinse with hot water; apply vacuum 30 min/steam heat.

Slurry in 75 litres dilute HCl (3%); filter; rinse with 38 litres acetone.

Hot water rinse. Apply vacuum 60 min with steam.

Slurry in 50 litres acetone/30 min. Filter, rinse with hot water.

Apply vacuum 180 min/steam heat. Oven dry (115 C).

Table III. Physical and Chemical Requirements (SLA 5003A)

Requirement	Value		Test Procedure (Para No)
	HNS I	HNS II	
Melting Point(1,2)	Shall not be less than -2 C of MP of "SCS"		4.5.1.1
Melting Range(1,3)	Shall not exceed that of "SCS"		4.5.1.1
Vacuum Stability:(4)			
a. mℓ/g for first 20 min	3.0, Max	0.6, Max	4.5.1.2
b. mℓ/g/hr for additional 2 hrs	1.1, Max	0.6, Max	
Surface Moisture & Volatiles (% by Wt)	0.5, Max	0.05, Max	4.5.1.3
Water-Soluble Material (% by Wt)	0.03, Max	0.05, Max	4.5.1.4
Insoluble Material (% by Wt)	0.03, Max	0.03, Max	4.5.1.5
Insoluble Particles			4.5.1.6
a. Retained on 60 mesh Screen	5 Max (Avg)	5 Max (Avg)	
b. Retained on 40 Mesh Screen*			
Conductivity Test**			4.5.1.7
Bulk Density (g/cc)(5)	Information Only	0.45, Min	4.5.1.8
Pressure Density Test			4.5.1.9
a. Density at 3 Kpsi	Information Only		
b. Density at 16 Kpsi			
c. Density at 32 Kpsi			

**The average of results must be less than 1.*

***Must be less than the equivalent conductivity of 1 ppm NaCl (conductivity of 1 ppm NaCl approximately 3.2 x 10^{-6} mhos).*

NOTES: (1) *This requirement shall be determined by comparison with a standard comparison sample which is referred to as "SCS" in Table I. A standard comparison sample is supplied by the Quality Evaluation Laboratory (QEL), Naval Ammunition Depot (NAD), Crane, Indiana.*

(2) *The melting point is the lowest temperature at which complete liquefaction occurs.*

(3) *The melting range is the temperature span between the first appearance of liquid until complete liquefaction.*

(4) *Specified values are volumes of gas at 0 C and 760 mm pressure, after evolution at 260 ± 0.5 C.*

(5) *HNS II must be prepared by recrystallization from DMF or by extraction with acetonitril-toluene.*

> *was almost spontaneous. The flask was removed from the oil bath and moved over a cold water bath, where cooling to room temperature took place. The precipitated HNS was subsequently collected by filtration. The product was rinsed with methanol and dried. A light yellow crop was obtained (recovery 94.0%, melting point 317.5).*

Employing the clean-up procedure described above, 30 g of the crude HNS I, Lot SH-9052-01, were dissolved in 390 mℓ of DMF at 105 C. The dissolved HNS was precipitated by the addition of 57 mℓ of cold-distilled water to the hot solution. After the product was filtered, rinsed as specified, collected and dried, a 96.9% recovery was obtained. The yellow crystalline crop had a melting point of 317.5 C.

The precipitated HNS, sample SH-9054-01 was subjected to extensive testing to evaluate the merits of the purification procedure. The HNS was analyzed as specified in SLA-5003A for physical and chemical material specification requirements. The results of all tests are tabulated in Table IV. The effectiveness of the cleaning technique can be appreciated by comparison of the test results from the treated HNS (SH-9054-01) with the values obtained from the crude HNS (SH-9052-01) (Table IV). The increased reactant quantities involved in the scaled-up reaction precluded following the drop-wise addition of liquid components prescribed in both the DPE (Shipp) and HNS (Kompolthy) processes. The accelerated solvent introduction neither enhanced nor abated the reaction product properties of either DPE or HNS. At no time during the course of this study was any extraneous reaction behavior noted.

CONCLUSIONS AND COMMENTS

This investigation involved two objectives: (1) to establish the feasibility of 5 kg HNS synthesis through an alternate route, and (2) to develop an efficient cleaning procedure for the crude HNS reaction product.

It has been demonstrated that HNS I can be successfully synthesized through an alternate route consisting of the Shipp process for conversion of TNT to DPE followed by a Hungarian process for conversion of the DPE to HNS. HNS yields are increased with the demonstrated two-step process over previous HNS synthesis routes, i.e. 48.7% versus 40%.

A simple and inexpensive cleaning process for the crude HNS has been established, wherein HNS is dissolved in DMF and precipitated from the hot solution by introduction of water. Upon filtration most of the impurities are removed in the filtrate.

One of the drawbacks which may be encountered in HNS process via the intermediate dipicrylethane is associated with equipment. The time involved for the introduction or transfer of reagents and for the HNS washing and slurry processes is directly proportional to equipment availability and versatility.

ACKNOWLEDGEMENT

The author wishes to thank Greg Locke for his expertise in writing a safety oriented operational procedure, James Bradshaw and Ray Heckman for their contribution to this study, and to Bill Allen for his assistance in gathering and documenting of data relevant to this evaluation.

Table IV. Sample Analysis of HNS I

(Physical/Chemical Requirements, HNS Specification SLA-5003A)

Requirement	Procedure	HNS SH-9052-01[a]	HNS SH-9054-01[b]
Melting Point (C)	4.5.1.1	315.0	317.5
Melting Range (C)	4.5.1.1	0.8	0.5
Vacuum Stability	4.5.1.2		
a. 1st 20 min (mℓ/g)		3.70	1.09
b. Add. 2 hrs (mℓ/g/hr)		1.95	0.20
Surface Moisture (Wt %)	4.5.1.3	0.008	0.008
Water Solubles (Wt. %)	4.5.1.4	0.076	0.023
Insolubles, DMF (Wt %)	4.5.1.5	0.12	0.11
Conductivity (mhos x 10^{-6})	4.5.1.7	4.10[c]	2.80[c]
Bulk Density (g/cc)	4.5.1.8	0.20	0.19
Pressure-Density (g/cc)	4.5.1.9		
a. 3 Kpsi		1.153	-
b. 16 Kpsi		1.489	-
c. 32 Kpsi		1.597	-
Additional Tests*			
Surface Area (M^2/g)		2.40	2.46
Copper (Wt %)		0.01	T
Compositional Analysis (%) (Liquid Chrom)			
TNT		-	-
DPE		1.65	0.55
HNS		98.36	99.45

**Not part of SLA 5003A*

[a] *Crude HNS, as synthesized (SH-9052-01)*

[b] *Treated HNS (SH-9054-01)*

[c] *Conductivity of 1 ppm NaCl (3.9 x 10^{-6} mhos)*

DISTRIBUTION

DOE

Ralph E. Caudle
Assistant Director of Operations
Military Application
Attn: Robert E. Clough
Washington, DC

ALO

H. N. Meyer, Director
Weapons Development Division

R. R. Fredlund, Jr., Director
Classification & Technical Information

AAO

G. W. Johnson, Chief
Operations Branch

Mound Facility

R. T. Braun

SLL

R. D. Cozine - Org. 8180

LLL

G. L. Dittman (15 Copies)
Attn: A. C. Van Dyk

C. T. Brockett, Technical Information Dept.

LASL

E. H. Eyster - WX-DO
Attn: J. J. Wechsler

R. N. Rogers - WX-2
J. Aragon - WX-3
Report Library - ISD-4

SLA

B. E. Arthur - Org. 4370
J. C. Crawford - Org. 2500/
  D. H. Anderson - Org. 2510
J. C. King - Org. 2300
Central Technical Files - Org. 3141

TIC

Technical Information Center (27 Copies)
Oak Ridge, TN

PX

Division Manager, Mfg. Engineering
Division Manager, Quality
Division Manager, Development
Division Manager, Manufacturing
Division Manager, Safety & Fire Protection
Education & Training Center (5 Copies)
Technical Library (5 Copies)

Circulation Copy:

(1) Asst. Plant Manager
(2) Plant Manager
(3) M&H-SM Co., Inc., Lexington, KY