30
9-22-80
25 to NTIS

MHSMP-78-56

Dist. Category UC-45

ALTERNATE HNS I SYNTHESIS ROUTE VIA THE INTERMEDIATE DIPICRYLETHANE

MASTER

Jacob Sandoval

DEVELOPMENT DIVISION

NOVEMBER 1978

Process Development
Endeavor No. 107

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

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

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

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

Printed in the United States of America
Available from
National Technical Information Service
U. S. Department of Commerce
5285 Port Royal Road
Springfield, VA 22161 5— 3.50
Price: Printed Copy $~~4.00~~; Microfiche ~~$3.00~~

ALTERNATE HNS I SYNTHESIS ROUTE VIA THE INTERMEDIATE DIPICRYLETHANE

Jacob Sandoval

DEVELOPMENT DIVISION
(November 1978)

Process Development

ABSTRACT

A two step process for HNS synthesis consisting of the Shipp synthesis of dipicrylethane from TNT followed by the conversion of DPE to HNS by a Hungarian process was successfully demonstrated on a 50 g TNT scale. HNS yields of 60 percent and product purities of above 97 percent were obtained.

DISCUSSION

The thermal stability of 2,2′,4,4′,6,6′-hexanitrostilbene (HNS) has elicited pronounced interest and demand for this compound.

The preparation of HNS is normally promoted through procedures developed by Kathryn Shipp and Lloyd Kaplan(*1*). This involves treatment of a tetrahydrofuran-methanol solution of 2,4,6-trinitrotoluene (TNT) with an excessive amount of 5% aqueous sodium hypochlorite. The crude HNS is obtained in 42% yield. Reaction conditions can be modified to produce 2,2′,4,4′,6,6′-hexanitrobibenzyl-(dipicrylethane, DPE) rather than the nitrated stilbene. DPE was produced in this manner for the work described in this report.

A Hungarian patent[a] assigned to Tivadar Kompolthy and co-workers details procedures for production of HNS from TNT in solution. Briefly, this patent disclosed that TNT, or more precisely the 2,4,6-trinitrobenzyl anion, can be oxidized quite readily with molecular oxygen, or quite effectively with air to form DPE or HNS.

Experiments have been directed, both at this installation(*1*) and at Sandia Laboratories, Albuquerque, towards duplicating the procedure detailed in the patent for the synthesis of HNS. These experiments have involved repeating the procedures, as stated, as well as incorporating step-wise process variations. No appreciable success was experienced in attempting to duplicate this portion of the Hungariun patent.

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

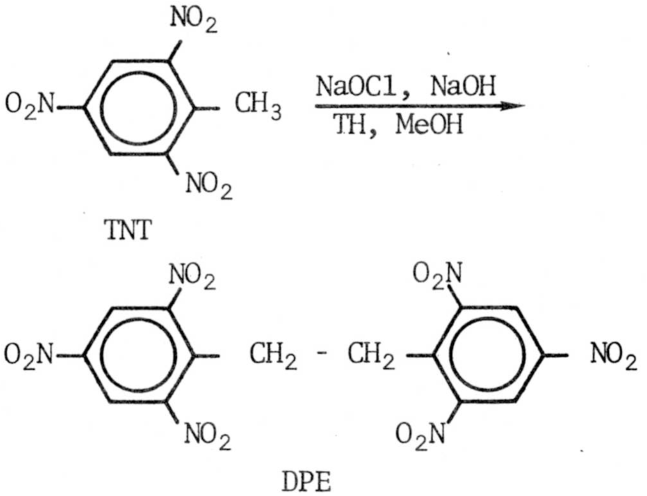
[a] *Tivadar Kompolthy, et.al.,* [*Hungarian Patent - T/9639 VE-719 (c 06 f 9/04)*].

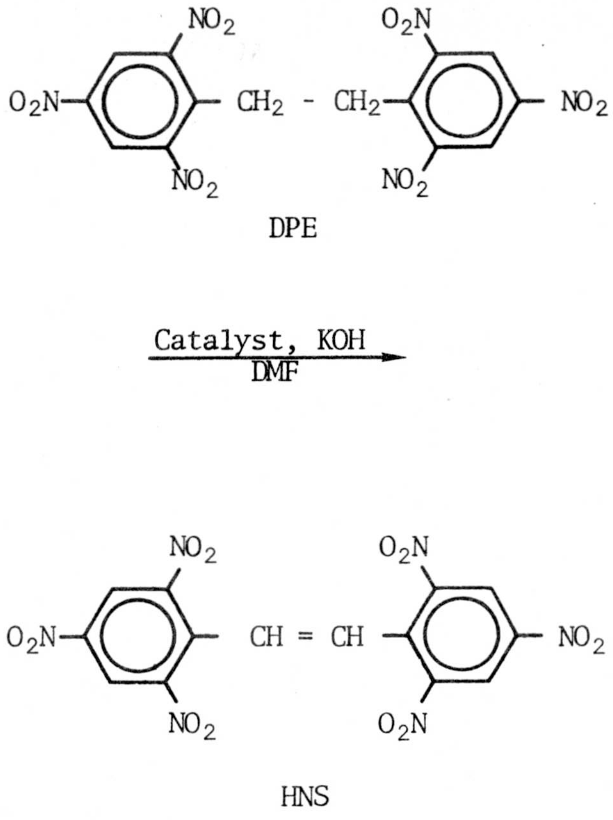
(*2*) *G. L. Clink, Alternate HNS Synthesis Routes, MHSMP-77-12 (June 1977).*

The patent also describes a method whereby DPE in solution with an aprotic solvent can be oxidized to HNS. This is accomplished using anhydrous cupric sulfate as the oxidizing agent. Oxidation of DPE to HNS, as disclosed, was accomplished in the experiment reported herein.

The current investigation was pursued in collaboration with Sandia Laboratories, Albuquerque. Sandia was largely responsible for establishing the reaction parameters involved in the production of DPE and HNS. Efforts were coordinated in the evaluation of those parameters which would enhance the product yields and purities. Endeavor priorities were established with the initial product scale-up involving 50 g of TNT to be undertaken at Mason & Hanger, Pantex.

The synthesis of DPE from TNT via the Shipp process is simple and fairly efficient. Conversion of DPE into HNS by the Hungarian Patent can be promoted in good yields with minimal difficulty. Consequently, a procedure which encompasses both the Shipp and the Hungarian processes was considered as an alternate experiment for the synthesis HNS I.





EXPERIMENTAL

10 Gram TNT Scale

Dipicrylethane was synthesized by the procedure developed by Shipp. 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 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...."(1).*

Commercial 'Chlorox,' as obtained from the manufacturer, was employed rather than 5% aqueous sodium hypochlorite. Efforts to improve the product yield and/or product composition by stepwise altering the reactant ratios proved fruitless; thus the Shipp process was followed explicity in the synthesis of DPE.

One of the goals of this study was that a continuous HNS synthesis route could be developed. Consequently, for a portion of the 10 gram batches the crude DPE was treated with various washes and transferred to the HNS reaction in the damp state. The DPE reaction product was collected over a fine-porosity glass filter using either a water or methanol chase in transfering the product from the reactor to the filter. The filter cake was then suction-filtered to extract the wash solvent and transferred in the damp state to the HNS reactor. In other batches the DPE after washing was dried before conversion into HNS.

The Hungarian process for DPE synthesis to HNS is found below. This process with minor parameter variations was employed in this study.

> *"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 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."*

Extensive parameter evaluation was made by incorporating step-wise variations in the reaction process to establish whether these variations would improve product yield and composition. Taking TNT at unity, all process reactants were increased by 14% over those specified in the patent. The reaction temperature and time remained unchanged.

The DPE from the Shipp process was added to 50 mℓ dimethylformamide followed by dropwise addition of 2 mℓ of 2 molar methanolic potassium hydroxide solution. After solution 6 g anhydrous $CuSO_4$ in 50 mℓ pyridine

---

**Hexanitrobibenzyl or dipicrylethane.*

which had been stirred 10 minutes just prior to introduction was added. The reaction mixture was heated to 50 C and held at this temperature for 60 minutes. Fifty mℓ of water was then added dropwise and the mixture was cooled to ambient and filtered.

The HNS product was given 4 successive washes (20 mℓ/wash) with each of the following: acetone, dilute ammonia (200 mℓ/ℓ), hot water and acetone. The product was then dried and compositional analysis determined using liquid chromatography.

A summary of results from the 10 g batches is given in Table I. Run 17 was not converted into HNS. The other batches are divided into those runs which involved the transfer of damp DPE to the HNS reactor and those in which the DPE was dried prior to conversion. The DPE samples contained unreacted TNT ranging from trace quantities up to 8.1%. The final HNS products contained DPE contamination. DPE contaminations appear to be reduced by methanol washing of the DPE intermediate and drying the DPE prior to conversion into HNS.

50 Gram TNT Scale

For 50 g TNT reactions all reagent volumes were increased proportionately. However, the increased 175 mℓ Chlorox and 325 mℓ sodium hydroxide solution combination was added at approximately 120 mℓ/minute. The reaction time was varied from 15 to 60 minutes before the precipitated product was filtered. Table II lists the reaction times, yields, melting points and compositions of the products of the DPE synthesis reactions. Four of the DPE products were washed with methanol, filtered and dried prior to conversion into HNS. The other sets of DPE products were copiously washed in distilled water, filtered and dried prior to conversion.

The DPE products were converted to HNS by the procedure used for the 10 gram TNT scale. The reagent volumes were increased proportionately, i.e. 250 mℓ dimethylformamide, 10 mℓ of 2 molar methanolic potassium hydroxide solution and 30 g anhydrous $CuSO_4$ in 250 mℓ pyridine. The reaction times and temperatures, volumes of water added, yields, melting points and compositions of the products are given in Table III.

Table I. Summary of 10 Gram TNT Reactions

DPE							HNS				
			% Composition							% Composition	
Run	% Yield	Melting Point (C)	TNT	DPE	HNS	Treatment	Run	% Yield	Melting Point (C)	DPE	HNS
17	79.8	203	1.8	98.2	T	-	-	-	-	-	-
18	80.7	207	1.7	98.3	T	-	-	-	-	-	-
						(Damp Transfer)					
19	-	-	-	-	-	Water Chase, Water Wash	20	44.9	308	20.8	79.2
21	-	207	-	99.0	1.0	↓	22	64.2	312	14.3	85.7
23	-	209	-	99.2	0.8	↓	24	62.3	311	18.5	81.5
25	-	208	-	99.0	1.0	↓	26	53.5	316	12.8	87.2
28	-	219	-	99.4	0.6	↓	29	61.0	308	14.1	85.8
33	-	212	2.2	97.4	0.4	Water Chase, No Wash	34	62.2	308	13.0	86.9
35	-	207	4.0	95.5	0.6	Water Chase, No Wash	36	55.7	307	16.7	83.3
39	-	205	8.1	91.6	0.3	Water Chase, MeOH Rinse	40	-	315	7.8	92.7
42	-	204	6.8	92.8	0.4	Water Chase, No Wash	43	62.5	315	8.2	91.7
44	-	208	4.8	94.4	0.3	↓	45	61.9	313	7.4	92.6
46	-	205	6.3	93.5	0.2	↓	47	59.6	312	10.2	89.8
52	-	-	3.3	96.5	-	↓	53	64.4	309	8.4	91.6
54	-	205	2.1	97.9	-	↓	55	64.5	314	6.1	93.9
56	-	-	-	-	-	MeOH Chase, No Wash	57	62.1	317	3.0	97.0
58	-	208	2.8	97.2	-	MeOH Chase, No Wash	59	61.1	315	3.1	96.9
						(Dry Transfer)					
18	80.7	207	1.7	98.3	T	Water Chase	27	64.1	315	5.7	94.3
30	78.7	203	-	98.4	1.6	Water Chase, MeOH Wash	31	60.5	317	5.5	94.5
48	74.0	213	2.7	97.0	0.2	Water Chase, MeOH Wash	50	46.7	317	2.3	97.7
49	80.7	206	6.0	93.9	T	Water Wash MeOH Wash	51	55.3	317	2.8	97.1

T = Trace

Table II. Summary of 50 Gram TNT Reactions DPE Synthesis

Run	Reaction Time (min)	% Yield	Melting Point (C)	% Composition TNT	DPE	HNS	DPE Treatment
61	15	78.0	205	3.6	96.6	-	MeOH Wash
63	15	74.0	204	3.5	96.5	-	↓
65	30	76.6	205	2.8	97.2	-	↓
66*	60	80.0	203	2.9	97.1	-	↓
69	25	77.0	205	3.2	96.8	-	Copious Water Washes
70	25	76.6	208	2.1	97.9	-	↓
73	25	79.6	207	4.4	95.6	-	↓

**Chlorox + NaOH added over 25 minute period.*

Table III. Summary of 50 Gram TNT Reactions HNS Synthesis

DPE Run	HNS Run	Reaction Temperature (C)	Reaction Time (min)	Water Additional (mℓ)	% Yield	Melting Point (C)	% Composition DPE	HNS
61	62	50	120	50	-	315	3.0	97.0
63	64	50	120	50	59.0	317	2.7	97.3
65	67	50	60	250	60.4	315	2.1	97.9
66	68	50	60	250	60.2	316	2.1	97.9
69	71	60	120	50	65.2	315	0.6	99.4
70	72	45	120	50	61.2	316	1.3	98.7
73	74	55	120	50	53.6	316	0.7	99.3

Purer HNS products based on DPE content were produced with (1) reaction temperatures of 55 and 60 C than at 50 C and (2) with DPE reactants that were washed with large amounts of water than reactants washed with methanol. The effects of reaction conditions on yield are not pronounced.

CONCLUSIONS

An alternate synthesis route for HNS consisting of the Shipp process for conversion of TNT to DPE followed by a Hungarian process for conversion of DPE to HNS was successfully demonstrated by the experiment.

Superior results were obtained by drying the DPE intermediate prior to conversion to HNS. Both yield and HNS purity were increased with dried DPE.

HNS yield is increased with the demonstrated two-step process over previous HNS synthesis routes.

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

P. M. Ramey, Chief
Operations Branch

Mound Facility

R. T. Braun

SLL

R. D. Cozine - Org. 8180

LLL

G. L. Dittman (10 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. 1570
J. C. Crawford - Org. 2500/
D. H. Anderson - Org. 2510
J. C. King - Org. 2300/
C. B. McCampbell - Org. 2310
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