27
7-13-77

25 to NTIS

MHSMP-77-12

Dist. Category UC-45

ALTERNATE HNS SYNTHESIS ROUTES

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JANUARY - MARCH 1977

For
Sandia Laboratories
Albuquerque, New Mexico
P.O. No. 05-1468

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Price: Printed Copy $3.50; Microfiche $2.25

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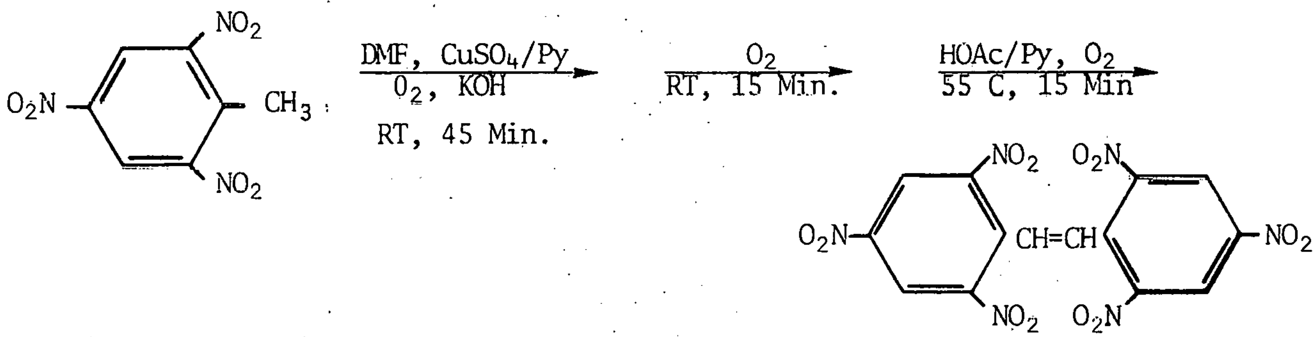
ABSTRACT

Process variations in the Hungarian patent procedure for production of hexanitrostilbene (HNS) through the air oxidation of TNT, with the primary objective the improvement of product yield, were not met with any degree of success. Investigation of the copper pyridinate/DMF route resulted in somewhat inconsistent and only approximate reproduction of the Hungarian results. Elimination of the 55 C process heating step results in curtailment of the production of HNS, and tends to favor the production of dipicrylethane (DPE). Variations thus far employed in the patent process in this study have produced no consistent yield improvement over the original procedure.

EXPERIMENTAL

The Hungarian process[a] for the preparation of hexanitrostilbene (HNS) essentially involves the catalytically induced air oxidation of an aprotic solvent solution of TNT, viz,



This study began by following the original procedure as described in the patent, with subsequent repetition of that procedure incorporating stepwise variations in the preparative steps. The following is a general description of that procedure.

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[a] *Hungarian Patent; T/9639 VE-719 (C 06 f 9/04).*

Weigh out 4.54 g (0.2 moles) of TNT in a 3-neck 125 mℓ flask. Add 25 mℓ of dimethylformamide. Stirring of the reaction mixture is effected through the bubbling of cylinder air through the liquid. Maintaining the system at 25 C (± 1 C), add 1 g of copper sulfate which is first mixed with 10 mℓ of pyridine and 25 mℓ of dimethylformamide and stirred for 30 minutes by means of a Teflon stirring bar[b]*. Over the next 45 minutes, 10 mℓ of a 2-molar methanolic potassium hydroxide solution is added in a dropwise manner. Air is continued to be introduced into the mixture at a 100 mℓ/min rate*[c]*. Following addition of the KOH, the system is air oxidized at room temperature for an additional 15 minutes. At this point, a buffer solution made up of 4 mℓ of alpha-picoline and 2.5 mℓ of glacial acetic acid is added. While continuing air oxidation and agitation, the temperature of the reaction system is raised to 55 C by means of a silicone bath. The system is maintained at this temperature for 15 minutes. The system is then allowed to cool to room temperature and 20 mℓ of a 10% acetic acid solution is added. The crude crystalline product is filtered off using a sintered glass Buchner funnel. The product is washed with hot water, then dilute ammonia water, and finally with methanol. The product is air dried.*

[b] *Product is probably* $[Cu(Py)_4]SO_4$.

[c] *Increased to approximately 250 mℓ/min to effect agitation of the mixture.*

Reagents Used in This Study

Air, dry (Cylinder)	Matheson
N,N-Dimethylacetamide*	Eastman
N,N-Dimethylformamide*	Eastman
Pyridine*	Eastman
Methanol**	MCB
Methanol*	Eastman
Triglyme	Eastman
Tetrahydrofuran*	Eastman
Dimethylsulfoxide*	Eastman
Alpha-picoline	Eastman
Ammonium Hydroxide (28%)*	Eastman
Acetic Acid (Glacial)***	MCB
Nitric Acid (c)	Baker
Copper Sulfate, Anhydrous	Pfaltz & Bauer

**Reagent grade ACS*
***Spectroquality*
****Reagent grade*

The following section lists the variations in the patent procedures and pertinent results. Where variations in the preparative steps are noted, it is understood that all other steps are as stated in the general preparative procedure (above). It should be noted that throughout the study, the use of the crude product washing procedure (as prescribed in the patent) resulted in little or no cleanup of the crude product. The ammonia water wash step consistently produced a clogging of the filter, resulting in an extremely slow filtration. A considerable way into the study it was found that a preliminary wash of the crude product with acetone prior to the water-ammonia-methanol wash sequence produced relatively good filtering and a reasonable product cleanup.

Run 1

1 gram of anhydrous copper sulfate was added without a DMF/pyridine premix. 1.064 g of crude product (23.6% yield). Dark chocolate brown material. Would not cleanup. DTA/m pt - indeterminate.

Run 2

$CuSO_4$/DMF/Py pre-mix (15 minutes), total slurry added. 2.1890 g of crude product (48.6% yield). Would not clean up. Used 5% ammonia wash.

Run 3

No variations. 2.3950 g of crude product (52.4% yield). Would not clean up.

Run 4

$CuSO_4$/DMF/Py - mixed and filtered. 3 g of solid added. 2.500 g of crude product (55.6% yield). Would not cleanup. DTA/m pt - indeterminate.

Run 5

3 g $[Cu(Py)]_4SO_4$ added. 2.001 g of crude product (44.4% yield). Would not clean up. DTA/ m pt - indeterminate.

Run 6

3 g $[Cu(Py)]_4SO_4$ added. 2.079 g of crude product (46.2% yield). Following procedural water/ammonia/methanol wash, used repeated acetone-methanol washes of crude product (33.9% yield). DTA/m pt ∿ 315 C.

Run 7

3 g $[Cu(Py)_4]SO_4$ added. Increased KOH addition time from 45 minutes to 90 minutes. Increased 55 C heating time from 15 to 30 minutes. Following procedural wash, used repeated acetone/methanol wash, then acetone wash. 29.5% Yield. DTA/m pt ∿ 316 C. Final material a dark brown.

Run 8

3 g $[Cu(Py)_4]SO_4$ added. No ammonia water wash. 2.868 g of crude product (59.7% yield). Nitric acid wash of crude product (31.8% yield). DTA/m pt ∿ 314 C. Final material a dark brown.

Run 9

Reverted to $CuSO_4$/DMF/Py premix, added slurry. No product.

Run 10

Added only the filtered solid from $CuSO_4$ premix. No ammonia water wash. 2.158 g of crude product (47.9% yield). Nitric acid wash (c). 29% yield. DTA/m pt ∿ 316 C. Liquid chromatograph results - 4.57% DPE, 95.43% HNS. Final material a brownish-yellow.

Run 11

Used 25 mℓ of dimethylacetamide as system solvent. $CuSO_4$/DMA/Py premix, filtered and added solid. 2.102 g of crude product (46.7% yield). No ammonia wash. Nitric acid wash. 23% yield. DTA/m pt ∿ 316 C. Brownish-yellow product.

Run 12

Used dimethylacetamide as solvent. $CuSO_4$/DMF/Py premix. Added filtered solid. 1.582 g of crude product (35.2% yield). Nitric acid wash (22.9%). DTA m pt ∿ 315 C. Brownish-yellow product.

Run 13

Used 25 mℓ of THF/DMA (50/50 V) as system solvent. $CuSO_4$/DMF/Py premix, added filtered solid. No ammonia wash. 3.129 g of crude product (69.5% yield). Nitric acid wash. 27.9% yield. DTA/m pt ∿ 307 - 311 C. Dark brown.

Run 14

25 mℓ DMA/Triglyme (50/50 V) as system solvent. Filtered solid from $CuSO_4$/DMF/Py premix added. No ammonia wash. 2.523 g of crude product (53.8% yield). Nitric acid wash, 27.9% yield. DTA/m pt ∿ 313 C.

Run 15

25 mℓ DMSO/THF (5/20 V) used as system solvent. Filtered $CuSO_4$/DMF/Py premix solid added. Tar-like product. Procedural wash sequence. 1.690 g of crude product (37.6% yield). Nitric acid wash 4.6% recovery. DTA/m pt ∿ 317 C. LC analysis 88.9% HNS, 11.1% Unknown material. (4.1% HNS yield.)

Run 16

25 mℓ DMSO/THF (5/20 V). Filtered solid from $CuSO_4$/DMF/Py premix added. No ammonia wash. 2.695 g of crude product (59.9% yield). DTA/m pt - indeterminate.

Run 17

25 mℓ DMF as system solvent. $CuSO_4$ premix solid added. No ammonia wash. 1.989 g of crude product (44.2% yield). Water, methanol washes. 20.5% yield. DTA/m pt - indeterminate.

Run 18

Standard procedure, but used a 2-1/2% ammonia water wash. Very slow filtration. 1.630 g of crude product (36.2% yield). Repeatedly washed with methanol and acetone. 28.1% yield. DTA/m pt ∿ 312 - 316 C.

Run 19

Same procedure as Run 18 but used a 10% ammonia water wash. 2.045 g of crude product (45.4% yield). Methanol-acetone cleanup yield 10.9%. DTA/m pt - indeterminate.

Run 20

Same as Runs 18 and 19 but used a 20% ammonia water wash. 1.935 g of crude product (43% yield). Methanol-acetone cleanup 14.2% yield. DTA/m pt - indeterminate.

Run 21

Standard procedure, but used 20 mℓ of 20% acetic acid addition rather than 20 mℓ of 10% solution. Very low yield. DTA/m pt ∿ 317 C.

Run 22

$CuSO_4$/DMF/Py premix slurry added. Used 20 mℓ of 20% acetic acid. 1.063 g of crude product (23.6% yield) DTA/m pt ∿ 312 -316 C.

Run 23

$CuSO_4$/DMF/Py Filtered solid added. Used a 1-1/2% ammonia water wash. Methanol wash of crude material. Recrystallized from DMF. 5.5% yield. DTA/m pt ∿ 315 C.

Run 24

Same as run 22 except $CuSO_4$ premix filtered solid used. 3.386 g of crude product (75.2% yield). Acetone, methanol wash 26.6% yield DTA/m pt - indeterminate.

Run 25

Standard (general) procedure, but air oxidation time at room temperature doubled (2 hours) and 15 minutes at 55 C. 1.888 g of crude product (42% yield). DTA/m pt - indeterminate.

Run 26

Standard (general) procedure, but air oxidation time in the 55 C step doubled to 30 minutes. 2.051 g of crude product (45.6% yield) DTA/m pt - indeterminate.

Run 27

Standard (general) procedure. 1.794 g of crude product (39.9% yield). Nitric acid (c) wash. (24.3% yield) DTA/m pt ∿ 315 C. LC analysis 93.2% HNS, 5.8% DPE.

Run 28

Standard procedure, but air oxidation time at RT doubled (2 hours) and at 55 C doubled (30 minutes). 2.049 g of crude product (45.5% yield). Repetitive acetone washing (19.4% yield). DTA/m pt ∿ 312 C.

Run 29

Standard procedure, but KOH addition cut in half to a 5 mℓ addition. Product very sticky, tar-like. After a difficult filtration, product was quite hard, difficult to break up. 1.425 g of crude product (31.7% yield). Acetone wash (12.8% yield) DTA/m pt ∿ 313 C. LC analysis 81.7% HNS, 16.9% DPE.

Run 30

Standard procedure, but KOH addition 7.5 mℓ. 2.216 g of crude product (49.2% yield). Nitric acid (c) wash. (18.2% yield). DTA/m pt - indeterminate. LC analysis 79.8% HNS, 18.2% DPE.

Run 31

Standard procedure, but KOH addition 15 mℓ. 1.998 g of product (44.4% yield) DTA/m pt - indeterminate.

Run 32

Standard procedure, but amount of alpha-picoline/acetic acid buffer cut to 50%. 2.192 g of crude product (48.7% yield). DTA/m pt - indeterminate.

Run 33

Standard procedure, but amount of buffer increased to 150%. 1.813 g of crude product (40.3% yield). DTA/m pt - indeterminate.

Run 34

1 g $CuSO_4$ and 10 mℓ of pyridine/25 mℓ DMF mixed for 50 minutes, then 4.54 g of TNT added to mixture. Standard wash sequence. 2.519 g of crude product (56% yield). Acetone wash of crude material-28.2% yield. DTA/m pt ∿ 313 C.

Run 35

Standard procedure, but no heat (55 C) applied to system. 2.110 g of crude product (46.9% yield). Acetone wash (12.8% yield). DTA/m pt indeterminate. LC analysis 85.1% HNS, 10.7% DPE.

Run 36

Standard procedure but changed crude product washing procedure: methanol, ammonia water, hot water, methanol. 1.887 g of crude product (41.9% yield). Acetone/methanol (50/50) wash (10.6% yield) DTA/m pt - indeterminate.

Run 37

Standard procedure, but acetic acid added while system still at 55 C. 2.087 g of crude product (46.4% yield). Recrystallized from DMF by adding acetonitrile (8.7% yield). DTA/m pt ∿ 317 C. LC analysis 99% HNS, 1% DPE.

Run 38

Standard procedure, but rather than the portion of preparation run at room temperature, system was maintained in an ice bath for 1 hour and then raised to 55 C for 15 minutes. 0.444 g of crude product (9.9% yield). DTA/m pt - indeterminate.

Run 39

Standard procedure. 2.085 g of crude product (46.3% yield). Acetone/methanol (50/50 V) wash. 40.1% yield. DTA/m pt ∿ 317 C. LC analysis 86.4% HNS, 13.7% DPE.

Run 40

TNT mixed with $CuSO_4$/DMF/Py slurry. 1.337 g of crude product (29.7% yield). DTA/m pt ∿ 316 C. LC analysis 94.5% HNS, 5.47% DPE.

Run 41

No 55 C heating, no buffer added. 12.2% yield. DTA/m pt indeterminate. LC analysis 44.9% HNS, 55.1% DPE.

Run 42

Increased DMF solvent volume from 25 → 50 mℓ. Recovered 0.043 g. DTA/m pt - indeterminate.

Run 43

Standard procedure, but no heat applied. 2.835 g of crude product (63% yield). Acetone/methanol (50/50 V) wash (31.1% yield). DTA/m pt - indeterminate. LC analysis 31.1% HNS, 65.2% DPE.

Run 44

Standard procedure, but initial cleanup wash of crude product with acetone, followed by ammonia, hot water and methanol. 1.380 g of crude product (30.7% yield). DTA/m pt ∿ 316 C. LC analysis 79.9% HNS, 20.1% DPE.

Run 45

Standard procedure, but system maintained in 0 C cold bath. Buffer added at 0 C, then warmed up to room temperature. No 55 C heating. Initial acetone wash. 0.564 g (12.4% yield) DTA/m pt - indeterminate. LC analysis 63.1% HNS, 36.9% DPE.

Run 46

Same as Run 45 but system warmed to 55 C for 15 minutes after buffer addition at 0 C. Initial acetone wash. 0.750 g of crude product (16.7% yield). DTA/m pt ∿ 313 C. LC analysis 82.8% HNS, 16.6% DPE.

Run 47

Copper sulfate increased 20% (→ 1.2 g). Acetic acid added while system at 45 C (after 55 C heating period), initial acetone wash. 1.568 g (34.8% yield). DTA/m pt ∿ 313 C. LC analysis: 86.5% HNS, 13.5 DPE.

Run 48

30 mℓ DMF as system solvent. 1.2 g $CuSO_4$. Initial acetone wash. 1.300 g (28.9% yield). DTA/m pt ∿ 315 C. LC analysis: 86.1% HNS, 13.9% DPE.

Run 49

35 mℓ DMF as solvent. Initial acetone wash. 1.525 g (33.9% yield). Recrystallized from hot DMF using acetonitrile. (29.3% yield). DTA/m pt ∿ 316 C. LC analysis: crude 78.5% HNS, 21.1% DPE, recrystallized: 87.9% HNS, 12.1% DPE.

Run 50

1.2 g $CuSO_4$/DMF/Py premix. Wash sequence of crude product; hot methanol, hot water, acetone, ammonia water. 1.557 g (34.6% yield). DTA/m pt (crude) 310-316 C. LC analysis; 78.9% HNS, 21.1% DPE.

Run 51

Increase $CuSO_4$ by 40% (1.4 g). Cut reaction time down; RT from 1 hour → 30 min, 55 C; 15 minutes. 1.485 g (33.0% yield). DTA/m pt ∿ 315 C. LC analysis: 75.8% HNS, 23.6% DPE.

Run 52

Standard run, no heat. 0.660 g (14.7% yield). DTA/m pt - indeterminate.

Run 53

Total procedure standard except ran at 55 C. Wash sequence; hot water, methanol, acetone. Acetone portion of wash sequence dissolved all of product.

Run 54

Copper sulfate increased 20% (1.2 g). Reaction time decreased to 30 minutes at room temperature and to 10 minutes at 55 C. Wash sequence; hot water, methanol, acetone, ammonia. hot water, acetone/methanol. 1.555 g (34.6% yield). DTA/m pt ∿ 317 C.

Run 55

25 mℓ of dimethylacetamide as system solvent. 1.2 g $CuSO_4$. Wash sequence;

water, methanol, acetone, methanol, ammonia, water. 1.298 g (28.8% yield). DTA/m pt ∿ 313 C.

Table I is a list of selected preparative runs, chosen and listed to depict an increasing level of yield in the HNS product, would seem to indicate the following effects due to changes in the described patent steps:

1. Maintaining the system at 0 C rather than at room temperature during that portion of the preparation significantly decreases the yield of HNS, with or without the 55 C heating step.

2. Elimination of the 55 C heating step in the process significantly decreases the yield of HNS.

3. Reduction of the prescribed amount of KOH added to the system significantly curtails the TNT anion formation and subsequently the HNS yield.

4. An increase in the amount of copper complex to the system did not conclusively indicate any appreciable change in the yield.

Table II is a list of selected preparative runs, chosen and listed to depict an increasing ratio of dipicrylethane yield to hexanitrostilbene yield (DPE/HNS) strongly suggests that the elimination of the heat step in the preparative process not only curtails the production of HNS, but favors the formation of DPE. Although Run 35 (no heat) shows a significantly lower amount of DPE than Run 43 (no heat), the initial crude product wash in Run 35 was with acetone alone, washing out a substantial amount of DPE contained in the product. It should be pointed out that the analytical results presented here are on the purified product(s), and the amount of DPE contained in the crude product(s) is probably considerably higher, losses occurring as a result of washing processes employing predominately polar solvents.

Proton NMR analyses of the washed HNS products produced spectra which, within the limits of detection, indicated the presence of only HNS and DPE.

COMMENTS

Process variations in the patent process, thus far investigated, have not produced any improvement in the yield of HNS over that reported in the patent. An appreciable amount of laboratory time was spent due to the ineffectivness of the patent procedure for the cleanup of the crude product, obviously needed to determine product yield. The initial crude product wash with acetone has greatly facilitated the process variation study.

Table I

HNS Yield (% Theoretical)	Run	System Process Comments
4.1	15	DMSO/THF solvent system; crude product wash/nitric acid (c)
4.4	41	Deleted 55 C heating step, no buffer added
7.9	45	System maintained at 0 C, warmed to room temperature after buffer addition, no 55 C heating
8.6	37	Acetic acid added while system is at 55 C
9.7	43	No heat
10.5	29	KOH addition decreased to 50% of standard process amount
10.9	35	No heat
11.6	30	KOH addition decreased to 75% of standard process amount
13.8	46	System at 0 C until buffer addition then, heating at 55 C for 15 minutes
24.5	44	Initial crude product wash with acetone; 72 hour cooling period
24.9	48	30 mℓ DMF, 20% increase in $CuSO_4$ (1.2 g)
25.0	51	40% increase in $CuSO_4$ (1.4 g)
25.8	49	35 mℓ DMF
27.3	50	20% increase in $CuSO_4$ (1.2 g)
29.6	10	No ammonia wash, crude product wash with nitric acid (c)
30.1	47	20% increase in $CuSO_4$ (1.2 g), acetic acid added at 45 C
34.9	39	12 hour cooling period

Table II

HNS Yield (% Theoretical)	DPE/HNS Ratio (%)	Run	System Process Comments
8.6	0.012	37	Acetic acid added at 55 C
29.6	0.048	10	No ammonia wash, crude product wash with nitric acid (c)
10.9	0.110	35	No heat, initial crude product wash with acetone
25.8	0.136	49	35 mℓ DMF, product recrystallized from hot DMF with acetonitrile
34.9	0.149	39	Standard process
30.1	0.156	47	$CuSO_4$ increased by 20%, acetic acid added at 45 C, initial crude product wash with acetone
24.9	0.161	48	$CuSO_4$ increased by 20%, 30 mℓ DMF, initial crude product wash with acetone
13.8	0.203	46	System maintained at 0 C prior to 55 C warm-up
10.5	0.210	29	KOH addition cut to 50% of standard process amount
11.6	0.224	30	KOH addition cut to 75% of standard process amount
24.5	0.253	44	Standard process, initial crude product wash with acetone
27.3	0.267	50	$CuSO_4$ increased 20% (1.2 g), initial crude product wash with methanol
25.0	0.280	51	$CuSO_4$ increased 40% (1.4 g), RT reaction time cut to 30 minutes (50%)
7.9	0.582	45	System maintained at 0 C, buffer added, warmed to room temperature, no 55C heating
4.4	1.705	41	No buffer added, no 55 C heating
9.7	2.093	43	No heat, initial crude product wash with acetone/methanol (50/50 V)