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ALTERNATE HNS I SYNTHESIS ROUTES

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DEVELOPMENT DIVISION

JULY - SEPTEMBER 1976
(P.O. NO. 05-1468)

Normal Process Development
Endeavor No. 107

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For
Sandia Laboratories
Albuquerque, New Mexico

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ABSTRACT

NMR analysis of several Sandia samples of HNS, prepared through air oxidation of DMF solutions of TNT, show the material to be predominantly HNS, with dipicrylethane the major impurity. Work in this area, to be done at Pantex, has been delayed due to late receipt of reagents mandatory to this investigation.

DISCUSSION

As a result of the recently reported preparation of 2,2', 4,4', 6,6'-hexanitrostilbene (HNS) through catalytic-induced air oxidation of 1,3,5-trinitrotoluene (TNT) and some of its hydrocarbon derivatives(1), some work in this area has been done at Sandia Laboratories, Albuquerque, with additional work which will parallel these efforts, to be done at Pantex.

Although a copy of the Hungarian Patent that describes this synthesis route has just recently been obtained, a translation of the article has not yet been effected. Work which has thus far been done in this area has been generally guided by the published notes in Chemical Abstracts, which are somewhat nebulous in content.

Basically, the process involves air oxidation of a dimethylformamide solution of TNT, to which has been added a solution of cobalt naphthenate which reportedly acts as a catalyst. The solvent system is not restricted to DMF, and in addition to TNT, air oxidation of some of its aryl derivatives to produce HNS are reported in the study. Much of the work thus far done at Sandia has involved the air oxidation of DMF solutions of TNT, to which were added pyridinic solutions of cobalt naphthenate, at various concentrations. In other attempted preparations, selected potential catalysts other than the cobalt naphthenate were used. Some variation of reaction system temperature was also investigated.

NMR analysis of the products of several of these experimental runs were performed at Pantex, basically to identify the product as HNS, and to obtain some idea of the purity level. Table I presents the results of NMR analysis, as well as the preparation data of the materials. NMR analysis was effected by dissolving the product(s) in deuterated (d-7) dimethylformamide (99.5 atom percent, MERCK), to a concentration of 12 mg/ml, and using the formyl proton impurity resonance as the internal quantitative standard. Tetramethylsilane (TMS) was used as the internal reference. The samples were run on a Varian HA-100, utilizing routine integration techniques. Fig. 1 presents spectra of HNS produced by use of (A) cobalt naphthenate and (B) sodium palladium chloride. Spectrum 1-C is that of d-7 DMF.

(1) Kompolthy, et al, Hung. Teljes, 9,639 (April 1975).

The spectral results presented in Fig. 1 (spectra A, B, C) are given the following assignments:

<u>Resonance (Hz, TMS)</u>	<u>Assignment</u>
280 (2)	d-5 dimethyl of DMF
335	Water
355	Ethane of dipicrylethane (Spectrum A)
730	Trans-ethylene of HNS (Spectrum A, B)
803	Formyl proton impurity of d-7 DMF
815	Aromatic of dipicrylethane (Spectrum A, B)
824	Aromatic of HNS (Spectrum A, B)

The presence of varying amounts of dipicrylethane in the HNS product is quite evident, especially so in the samples prepared by use of cobalt naphthenate. Of the five samples analyzed, the purity of the HNS was at its highest when TNT in DMF was air oxidized without the addition of "catalyst", although the percentage yield was the lowest.

COMMENTS

At this writing no work other than the NMR analysis of the Sandia samples has been undertaken, due to delays in receipt of reagents mandatory to this work. Pending information obtained upon translation of the Hungarian patent, it is planned at this time to investigate the air oxidation of TNT solutions containing catalytic potential additives at various concentrations and reaction system temperatures. Analysis of these systems and their products will be done for the most part through NMR methods. These catalytic potential materials will include, but not be limited to, cobalt naphthenate. Naphthenates of several of the transition metals have been obtained, and if time permits, at least a cursory investigation of their catalytic properties in the air oxidation of the TNT/DMF system will be investigated. At the present time approximately 100 g of high purity TNT is being prepared through repeated recrystallization from toluene.

Table I. Preparation Data and NMR Analysis Results

<u>Sandia Sample Number</u>	<u>Catalyst</u>	<u>Weight (mg)</u>	<u>Pyridine (ml)</u>	<u>Yield (%)</u>	<u>Sample Purity HNS (%, NMR)</u>	<u>Dipicrylethane (%, NMR)</u>
4157-17	Cobalt Naphthenate	100	1.0	27.2	77	8
4157-20	Cobalt Naphthenate	200	1.0	26.6	81	10
4157-28	None	-	None	2.7	97	*
4157-29	PdI ₂	53	None	9.4	95	*
4157-34	Na ₂ PdCl ₄	52	None	16.7	86	4.0

* *Resonance intensity too low to integrate*

(A) HNS SAMPLE 4157-20

(B) HNS Sample 4157-34

(C) d-7 Dimethylformamide

Fig. 1. HA-100 Spectra of HNS Analysis System