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HEAT RESISTANT EXPLOSIVES. XIV.
SYNTHESIS AND PROPERTIES OF 2,2',
4,4', 6,6'-HEXANITROSTILBENE,
HNST (C)

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UNITED STATES NAVAL ORDNANCE LABORATORY, WHITE OAK, MARYLAND

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HEAT RESISTANT EXPLOSIVES. XIV.
SYNTHESIS AND PROPERTIES OF 2,2',4,4',6,6'-HEXANITROSTILBENE,
HNST (C)

Prepared by: K. G. Shipp

ABSTRACT: The synthesis of 2,2',4,4',6,6'-hexanitrostilbene is described. A 40-45% over-all yield of the product is obtained in a five step procedure from TNT and meta-hydroxybenzaldehyde.

The hexanitrostilbene crystallizes in pale yellow needles which melt with decomposition at 316°C. It is thermally stable, 0.50 cc/g/hr at 260°C for two hours, and has an impact sensitivity comparable to that of tetryl. These properties indicate a potential use as an explosive booster.

Other methods for synthesizing hexanitrostilbene were investigated with but slight success. ~~The procedures are reported here~~ (C)

Approved by: Darrell V. Sickman, Chief
Organic Chemistry Division
CHEMISTRY RESEARCH DEPARTMENT
U. S. NAVAL ORDNANCE LABORATORY
White Oak, Silver Spring, Maryland

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15 June 1962

This report describes the preparation and properties of a new heat resistant explosive, 2,2',4,4',6,6'-hexanitrostilbene. The high melting point, thermal stability and sensitivity of this compound indicate possible use as an explosive booster. The work was carried out under Task FR-44.

W. D. COLEMAN
Captain, USN
Commander

Albert Lightbody
ALBERT LIGHTBODY
By direction

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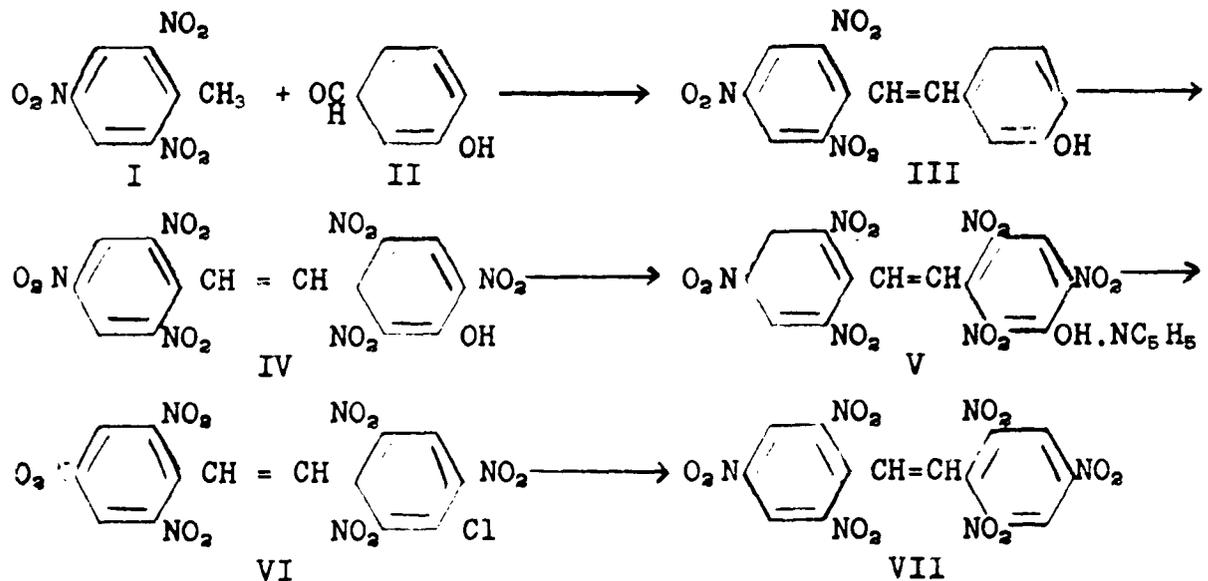
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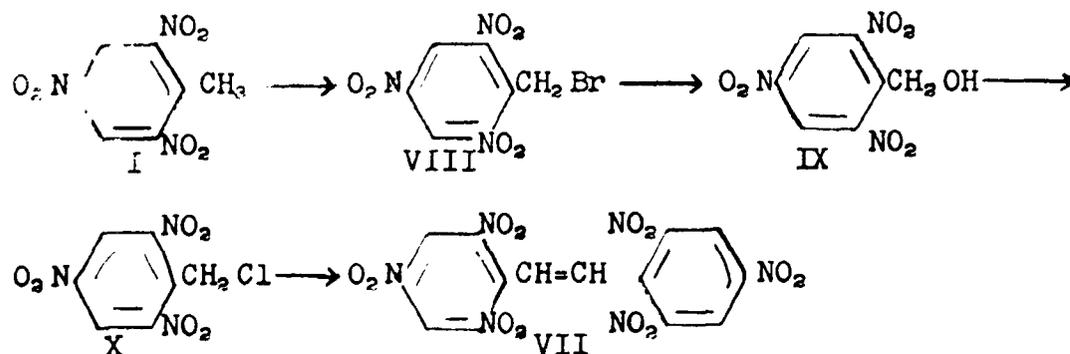
HEAT RESISTANT EXPLOSIVES. XIV.

SUMMARY OF RESULTS

2,2',4,4',6,6'-Hexanitrostilbene has been synthesized from TNT and meta-hydroxybenzaldehyde as follows:



The over-all yield of the hexanitrostilbene VII is 40-45% of recrystallized product. With the exception of a 60-65% yield in the nitration reaction the yields are better than 85% and, also with the exception of the nitration product IV the crude products can be used in subsequent reactions without further purification. The hexanitrostilbene VII has also been prepared by the following series of reactions:



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This method, however, was not satisfactory since yields were low, the hydrolysis reaction was tedious and the final reaction showed varying reproducibility of results.

Other routes to the hexanitrostilbene were investigated and also found to be impractical but did add information as to the structure of the compound obtained.

Properties of 2,2',4,4',6,6'-Hexanitrostilbene

Crystal form	Pale yellow needles
Melting point	316°C
Crystal density	1.74
Thermal stability	0.50 cc/g/hr (260°C for 2 hrs)
Impact sensitivity	39 cm (ERL machine Tetryl = 32 cm)

INTRODUCTION

The need for thermally stable explosives to meet the requirements of aerodynamic heating created by the speed of modern weapons has been recognized for some time. DATB (1) and TATB (2), explosive compounds which have been developed at the Naval Ordnance Laboratory, can be applied to fill this need in the high explosive field.

Along with the need for thermally stable high explosives there is the need for boosters, i.e. more sensitive explosives which will withstand high temperature also. NONA (3) and DIPAM (4), more recent developments at NOL, are possible answers to this problem. DIPAM is now being evaluated for use.

2,2',4,4',6,6'-Hexanitrostilbene, VII, the synthesis of which is reported here, has also been found to have properties which place it among compounds with potential use as heat resistant explosive boosters. It is high melting, 316°C, its thermal stability is 0.50 cc/g/hr at 260°C and it has an impact sensitivity comparable to that of tetryl.

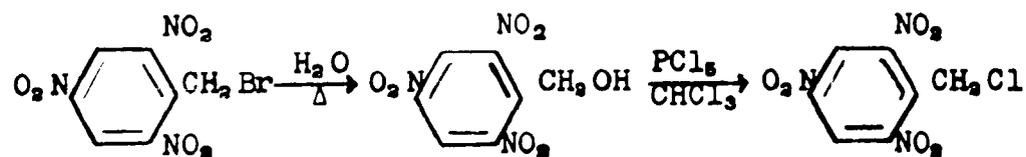
Originally the synthesis of 2,2',4,4',6,6'-hexanitrostilbene, VII, in this laboratory was proposed because information about this member of the polynitroaromatic compounds would be useful in connection with the work of the laboratory on the

relationship of structure to thermal stability of explosives (5). Interest in the hexanitrostilbene was enhanced, however, when its properties, as determined by the usual tests applied to explosive compounds showed such desirable characteristics. The original method of synthesis was not considered suitable for producing the stilbene on a large scale, but a feasible method has been developed and the hexanitrostilbene can now be considered available for testing in explosive applications.

DISCUSSION AND RESULTS

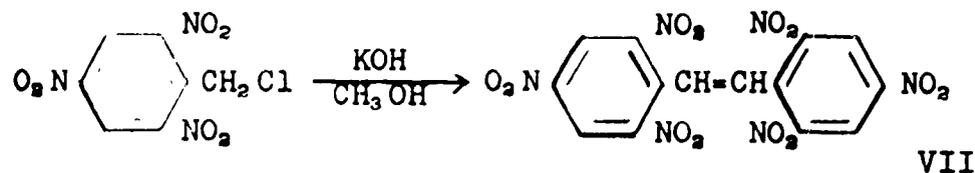
The synthesis of 2,2',4,4',6,6'-hexanitrostilbene, VII, was reported in 1912 by Reich, Wetter and Widmer (6). From the reaction of alcoholic potassium hydroxide with trinitrobenzyl bromide, VIII, these authors reported a 40% yield of a product which crystallized from nitrobenzene in beautiful yellow needles melting at 211°C. More recently A. D. Little, Inc., (7) reported that their attempts to repeat the work of Reich, Wetter and Widmer were unsuccessful. When the reported procedures were repeated in these laboratories the results obtained were also at variance with those described by Reich et al (6). With methanol or ethanol as solvent and varying the parameters of the reaction, i.e. the temperature of the reaction, concentration of reactants, rate of addition of reactants and the aqueous concentration of the alcoholic solvent no product similar to the one reported (6) was obtained. If any precipitate formed in the reactions it was highly colored and usually water soluble, although in one case a few milligrams of material were isolated which, when recrystallized from nitrobenzene, melted above 275°C.

Since there are examples of nitrobenzyl chlorides such as p-nitrobenzyl chloride (8) and 2,4-dinitrobenzyl chloride (9) which form the corresponding stilbenes by reaction with alcoholic potassium hydroxide, 2,4,6-trinitrobenzyl chloride, X, was prepared (10):



It was hoped that the difference in the reactivity of the chloride as opposed to that of the bromide would be favorable to the stilbene formation in this case.

The following reaction was then carried out:



A scintillating crystalline precipitate formed, which crystallized from nitrobenzene in beautiful pale yellow needles. This product, however, melted at 316°C instead of 211°C as reported by Reich et al (6). In addition to the difference in melting points there was also a discrepancy in the solubility of the product in acetone. Reich reported ready solubility of the stilbene, VII, in acetone at ordinary temperature. We found the product to be only slightly soluble in acetone even at the boiling point of the solvent.

Since we were unable to repeat the preparation as described in the literature, we were unable to resolve the question of the structure of Reich's compound. Stilbenes do form cis and trans isomers and it is conceivable that the two products, mp 211°C and 316°C, are isomeric. It is also conceivable that the mp 211°C could be a typographical error but no correction was found on searching errata reported in later issues of the Berichte.

Elemental analysis of the nitrostilbene, mp 316°C, obtained in these laboratories was satisfactory for hexanitrostilbene:

Calc'd. for C ₁₄ H ₆ O ₁₂ N ₆ :	C, 37.33;	H, 1.33;	N, 18.67
Found:	C, 37.24;	H, 1.83;	N, 18.52
	37.43	1.88	18.73

Also the molecular weight of the product, mp 316°C, determined by unit cell dimensions and measured density was 448 which agreed to within 1% of the calculated molecular weight, 450.3, of hexanitrostilbene. Furthermore the same product, as determined by mp 316°C and X-ray powder diffraction pattern, has been synthesized by three other independent methods (see below). These facts were deemed sufficient proof that the product, mp 316°C, was indeed the desired 2,2',4,4',6,6'-hexanitrostilbene, VII.

After obtaining hexanitrostilbene from 2,4,6-trinitrobenzyl chloride, the use of 2,4,6-trinitrobenzyl bromide, VIII, in the

preparation of VII was reinvestigated. By using acetonitrile as a solvent for VIII a 10-15% yield of VII was obtained.

The synthesis of the hexanitrostilbene, VII, from either trinitrobenzyl chloride or trinitrobenzyl bromide was only suitable for the preparation of laboratory samples of the compound. Yields were low and reproducibility of results was poor. Since interest in the product had been enhanced after characterizing the compound obtained by the above methods, other routes to the synthesis of the hexanitrostilbene, were investigated.

Nitration of stilbene or nitrostilbenes to the hexanitrostilbene appeared an obvious route to the synthesis. 2,4,6-Trinitrostilbene has been obtained in good yield from the condensation of TNT and benzaldehyde (11). Nitration of this product with concentrated nitric acid and concentrated sulfuric acid produced 2,2',4,4',6-pentanitrostilbene (12). Further treatment with nitric acid oxidized the ethylenic linkage (12). Since nitration of tetranitrobiphenyl with potassium nitrate in oleum solution at high temperature had been drastic enough to achieve nitration to hexanitrobiphenyl without cleaving the ethane bond (13) this method was tried in these laboratories with nitrostilbenes. With both 2,2',4,4'-tetranitrostilbene and 2,2',4,4',6-pentanitrostilbene, however, nitration to hexanitrostilbene, VII, was unsuccessful.

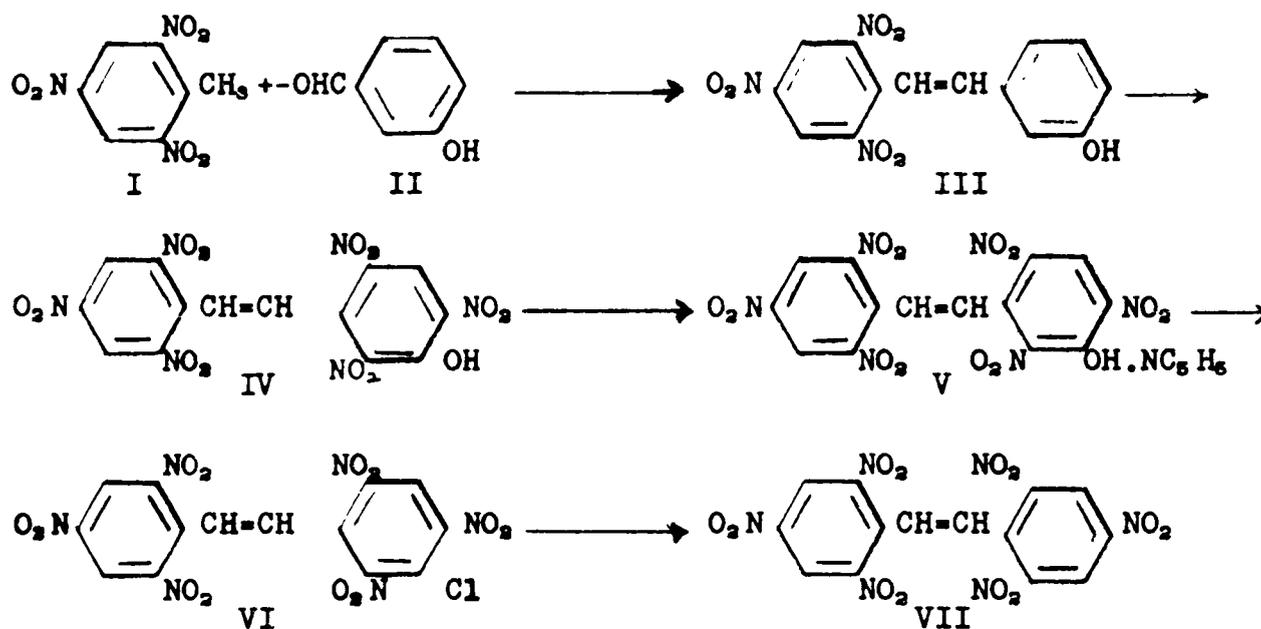
The classic synthetic route to nitrostilbenes, the condensation of the nitrated toluene with the appropriate nitrobenzaldehyde was most attractive also. Although there are many preparations reported in the literature (14) using mononitroaldehydes there are none for di- or trinitroaldehydes.

A. D. Little, Inc. (?) reported recovery of unchanged starting materials from refluxing benzene or toluene solutions of TNT and trinitrobenzaldehyde with piperidine added as catalyst. Therefore other solvents were tried in the reaction. In acetonitrile solution a very small amount, only enough to identify by the X-ray diffraction pattern, of the hexanitrostilbene, VII, was isolated from the reaction mixture. Attempts to improve the yield by varying the concentration of piperidine or by prolonged heating were unsuccessful.

Unchanged starting materials were recovered from heating TNT and trinitrobenzaldehyde together without solvents. If piperidine or pyridine was added to the melt a very dark colored tar resulted.

2,2',4,4'-Tetranitrostilbene had been reported by Green and Baddiley (15) in 70% yield from the reaction of concentrated alcoholic solution of potassium hydroxide on 2,4-dinitrotoluene in pyridine solution containing iodine. If this reaction could be adapted to the formation of hexanitrostilbene, VII, from TNT it would mean a simple one-step procedure from an inexpensive, readily available starting material. Hexanitrostilbene was, indeed, prepared in this way, but in maximum yield of 4%.

A different approach to the synthesis of hexanitrostilbene, VII, was then attempted (16).

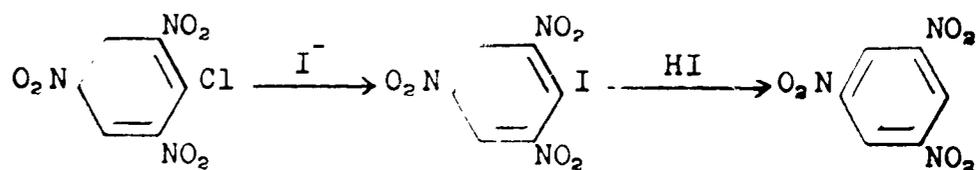


The condensation of TNT and meta-hydroxybenzaldehyde proceeded well in benzene solution with piperidine as catalyst and removal of the water formed by azeotropic distillation. The hydroxy-trinitrostilbene, III, crystallized from the reaction mixture in 90% yield and could be nitrated without further purification. The hydroxyl group present in the un-nitrated benzene ring of III both activated the ring and directed the entry of the nitro groups during the nitration procedure.

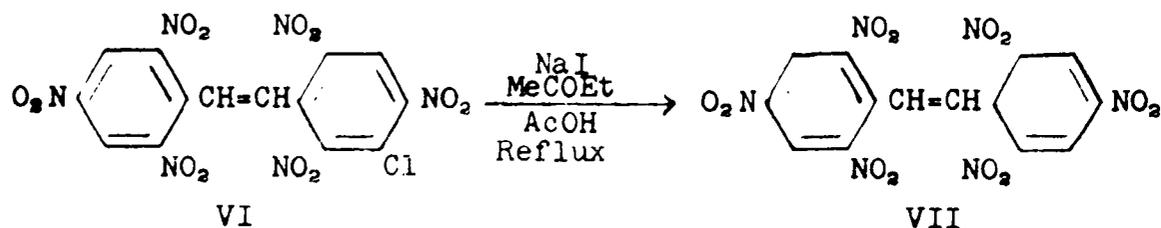
The comparatively low yield of nitration product, IV, may be accounted for by an oxidative side reaction which would be expected with nitration of a phenol. An attempt to minimize the oxidation reaction was made by nitration of III at low temperature with anhydrous nitric acid. However, the best yield obtained under these conditions was 30% and the reaction was accompanied by a great deal of foaming. By the addition of a

sulfuric acid solution of III, presumably the sulfonated stilbene, to a nitrating mixture of commercial concentrated nitric and sulfuric acids at 55°-60°C the yield was raised to 60-65%, and the foaming was eliminated. The crude product from the nitration procedure required purification for use in subsequent reactions and one crystallization from acetonitrile provided an excellent purity of 3-hydroxy-2,2',4,4',6,6'-hexanitrostilbene, IV.

The removal of the hydroxyl group was achieved by an adaptation of a method reported by Blatt and Gross (17), and Blatt and Tristram (18) for the reduction of picryl chloride to trinitrobenzene:



In order to apply this reduction procedure the hydroxy-hexanitrostilbene, IV, was converted to 3-chloro-2,2',4,4',6,6'-hexanitrostilbene, VI, by treating the pyridine salt of 3-hydroxy-2,2',4,4',6,6'-hexanitrostilbene, V, with phosphorus oxychloride (19). The crude chloride, VI, obtained 95% yield, was used in the reduction procedure without further purification:



This reduction reaction afforded an 85% yield of a light tan crystalline solid which was recrystallized from nitrobenzene. The purified product was obtained in 75% yield, and consisted of pale yellow needles which melted at 316°C and had an X-ray powder diffraction pattern identical with the product obtained from trinitrobenzyl chloride and alcoholic potassium hydroxide.

The foregoing synthesis is a feasible route for the preparation of 2,2',4,4',6,6'-hexanitrostilbene, VII, in an over-all yield of 40-45%.

PROPERTIES OF 2,2',4,4',6,6'-HEXANITROSTILBENE

Melting Point	316°C (a)
Crystal Density	1.74
Impact Sensitivity	39 cm ERL machine (Tetryl=32 cm)
Thermal Stability	0.5 cc/g/hr at 260°C (2 hrs)
Solubility	Soluble in hot nitrobenzene, dimethylformamide, almost insoluble cold. Slightly soluble in hot glacial acetic acid, acetone or methyl ethyl ketone. Insoluble in methanol and hexane.

(a) Mp determined on microscope hot stage

IMPACT SENSITIVITIES OF INTERMEDIATES

Intermediate	I.S. (ERL machine)	Sigma
3'-Hydroxy-2,4,6-trinitro-stilbene	222 cm	0.31
3-Hydroxy-2,2',4,4',6,6'-hexanitrostilbene	37 cm	0.19
Pyridine salt of 3-hydroxy-2,2',4,4',6,6'-hexanitrostilbene	97.4 cm	0.23
3-Chloro-2,2',4,4',6,6'-hexanitrostilbene	61 cm	0.28

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UNIT CELL DIMENSIONS
AND MOLECULAR WEIGHT OF HEXANITROSTILBENE

X-ray diffraction measurements on a single crystal of hexanitrostilbene showed that it had orthorhombic symmetry and the following unit cell dimensions: $a = 20.93 \text{ \AA}$; $b = 5.57 \text{ \AA}$; $c = 14.67 \text{ \AA}$. The unit cell volume is therefore 1710 \AA^3 . The crystal density was measured by flotation to be 1.740 gm/cm^3 . The unit cell weight is therefore $2975 \times 10^{-24} \text{ gm}$ or 1792 molecular weight units. Since the unit cell must contain an integral number of molecules and orthorhombic symmetry indicates that the number is 2, 4 or 8; the most probable molecular weights are 896, 448 and 224. The calculated molecular weight of hexanitrostilbene, 450.3, agrees to within one percent of the observed value corresponding to 4 molecules per unit cell.

Powder Diffraction Pattern

Interplanar Spacing Angstroms	Relative Intensity	2 θ Cu K Radiation Degrees
6.06	23	14.6
5.27	37	16.8
4.98	58	17.8
4.46	27	19.9
4.33	13	20.5
4.27	12	20.8
4.11	20	21.6
3.85	97	23.1
3.78	100	23.5
3.69	73	24.1
3.64	60	24.4
3.52	25	25.3
3.42	8	26.0
3.28	15	27.2
3.23	17	27.6
3.13	48	28.5
2.99	28	29.9
2.92	27	30.6
2.88	15	31.0
2.79	37	32.0
2.78	35	32.2
2.63	47	34.0
2.49	17	36.0
2.38	17	37.7
2.24	13	40.2
2.16	5	41.7
2.14	3	42.2
2.05	10	44.1
2.02	8	44.8

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ACKNOWLEDGMENTS

The author is grateful to other members of the Organic Chemistry Division for their assistance in this project: to H. T. Simmons for determining crystal density and thermal stability values; to Dr. J. R. Holden for determination of X-ray powder diffraction patterns and molecular weight by unit cell volume; to Dr. J. M. Rosen for determination of melting point and to Drs. D. V. Sickman, T. N. Hall and M. J. Kamlet for many helpful discussions and suggestions.

Impact sensitivities were determined by Mrs. Sarah Duck.

EXPERIMENTAL

3'-Hydroxy-2,4,6-trinitrostilbene, III:

To a mixture of 100 g, 0.44 mole, of 2,4,6-trinitrotoluene, 50 g, 0.41 mole, of meta-hydroxybenzaldehyde and 750 ml of benzene in a one-liter round bottom flask was added 5 ml of piperidine and the resulting mixture was heated to reflux using a condenser connected through a Dean Stark trap. The reaction mixture was an homogeneous solution at reflux temperature, initially a light orange color which gradually deepened to dark red-brown during the heating period. After 4½-5 hours at reflux, when nearly the theoretical volume of water had collected in the Dean Stark trap, i.e. ca 7 ml, heating was discontinued and the solution was cooled. The yellow crystalline product which formed was filtered off, washed with benzene and then hexane and dried. It weighed 135 g, or 90% of the theoretical yield, and melted at 156-158°C. Recrystallized from methanol it formed bright yellow needles which melted at 160°C.

Anal: Calc'd. for C₁₄H₉O₇N₃: C, 50.76; H, 2.73; N, 12.68.

Found: C, 51.11, 51.37; H, 2.82, 2.96; N, 12.99, 12.56.

3-Hydroxy-2,2',4,4',6,6'-hexanitrostilbene, IV:

The addition of 100 g of 3'-hydroxy-2,4,6-trinitrostilbene, III, to 100 ml of 96% sulfuric acid in a 400 ml beaker produced a dark green colored slurry. This slurry was chilled in an ice and water bath and 150 ml of 30% oleum was added slowly with stirring, keeping the temperature of the mixture under 30°C. The resulting dark red-brown viscous solution was allowed to stand at room temperature for 15 minutes, then heated to 85°C on the steam bath and held at that temperature for one hour. After cooling to room temperature this solution was added slowly, with rapid stirring, during ¾ hour, to a mixture of 100 ml of 70% nitric acid and 50 ml of 96% sulfuric acid at 55°-60°C accompanied by the addition of 200 ml of 70% nitric acid in 25 ml portions. Initially the reaction mixture was an homogeneous red-brown solution but after about 5 minutes a crystalline product appeared in the mixture and the color lightened to a light brown. The mixture was stirred for 10-15 minutes after the addition of the stilbene-sulfuric acid solution was completed and then drowned in ca 2 l flaked ice and water. The product was filtered off, washed with water and dried. The light tan filter cake weighed 140 g. Recrystallization from 2½ liter of acetonitrile, Celite and Norite yielded 87.5 g, 62% of theoretical, of fine colorless needles which melted

at 274-275°C. An additional 5 g of product could be obtained by evaporating the acetonitrile filtrate to ca 200 ml and chilling. Combined yield was 65.5%.

Anal: Calc'd. for $C_{14}H_6O_{13}N_6$: C, 36.06; H, 1.30; N, 18.03.

Found: C, 36.53, 36.56; H, 1.60, 1.59; N, 17.33, 17.95.

Pyridine salt of 3-hydroxy-2,2',4,4',6,6'-hexanitrostilbene, V:

A suspension of 25 g of 3-hydroxy-2,2',4,4',6,6'-hexanitrostilbene, IV, in 250 ml of methanol was placed in a one liter creased round bottom flask equipped with a mechanical stirrer and heated in a water bath at 50°C. To this slurry was added 10 ml of pyridine and the mixture was stirred rapidly for one hour. There was an immediate formation of a yellow solid product replacing the colorless hydroxy stilbene. After cooling the mixture the product was filtered off, washed with methanol and dried. It weighed 28.5 g, 97.5% of the theoretical yield. It could be used as obtained from the reaction for preparing the chloride. Recrystallized from acetone it formed fine lemon yellow needles which melted at 205°C.

Anal: Calc'd. for $C_{19}H_{11}O_{13}N_7$: C, 41.85; H, 2.03; N, 17.98.

Found: C, 42.13, 42.69; H, 2.58, 2.52; N, 17.6, 17.9.

3-Chloro-2,2',4,4',6,6'-hexanitrostilbene, VI:

A mixture of 100 g of the pyridine salt of 3-hydroxy-2,2',4,4',6,6'-hexanitrostilbene, V, in 300 ml of phosphorus oxychloride was heated on the steam bath. The pyridine salt dissolved to form a light yellow solution from which a colorless crystalline precipitate began to separate almost immediately. The mixture rapidly became colorless and thick with product. Heating on the steam bath was continued for 15 minutes then the mixture was added slowly, with stirring, to iced water keeping the temperature under 30°C by the rate of addition and addition of more ice. The colorless crystalline product was filtered off with suction, washed with water until the washings were neutral to acid test paper, and dried. It weighed 85 g, 95% of the theoretical yield. Recrystallized from methyl ethyl ketone it formed fine colorless needles which melted with decomposition at 250°C-251°C.

Anal: Calc'd. for $C_{14}H_5O_{12}N_6Cl$: C, 34.70; H, 1.01; N, 17.3.

Found: C, 34.88, 35.01; H, 1.21, 0.99; N, 16.92, 17.41.

2,2',4,4',6,6'-Hexanitrostilbene, VII:

A. From 3-chloro-2,2',4,4',6,6'-hexanitrostilbene, VI:

A mixture of 100 g of 3-chloro-2,2',4,4',6,6'-hexanitrostilbene, VI, 200 g of sodium iodide, 1500 ml of methyl ethyl ketone and 375 ml of glacial acetic acid was heated to reflux for 20 hours in a creased 3 liter round bottom flask with mechanical stirring. Originally almost colorless, the reaction mixture rapidly became dark red-brown during heating. Complete solution was not attained at this concentration but the character of the undissolved material was observed to change rapidly to fairly large needles which, on longer heating gradually became a very fine crystalline product. At the end of the heating period this product was filtered off with suction, slurried with hot water to remove inorganic salts, washed well with methanol and dried. It weighed 86 g, or 92% of the theoretical yield. Recrystallized from nitrobenzene, 50 g/l it yielded 71 g, 76.5%, of pale yellow needles, mp 315°-316°C.

The hexanitrostilbene, VII, was slightly soluble in hot acetone, methyl ethyl ketone and glacial acetic acid. It could be recrystallized from dimethyl formamide.

Anal: Calc'd. for $C_{14}H_6O_{12}N_6$: C, 37.33; H, 1.33; N, 18.67

Found: C, 37.24, 37.43; H, 1.83, 1.88; N, 18.52, 18.73.

B. From 2,4,6-trinitrobenzyl chloride, X:

A solution of 2.6 g, 0.01 mole, of 2,4,6-trinitrobenzyl chloride in 25 ml of methanol was heated on the steam bath and 12 ml of methanol containing 0.01 mole of potassium hydroxide was added 2-3 drops at a time during 15 minutes with vigorous shaking after each addition. A dark red color appeared after each addition. The color disappeared after shaking the first few times, but persisted after the addition of 3-4 ml of the alkali solution. A scintillating crystalline product appeared in the reaction mixture about the time the color persisted. After the addition of the alkali solution was completed the mixture was allowed to stand 15 minutes and then the product was filtered off, washed well with methanol and dried. It weighed 0.7 g, or 30% of theoretical yield. Recrystallization from nitrobenzene yielded pale yellow needles melting at 315°-316°C.

C. From 2,4,6-trinitrobenzyl bromide, VIII:

Dropwise addition of 10 ml of methanol containing 0.5 g of potassium hydroxide to a solution of 2.0 g of 2,4,6-trinitrobenzyl bromide in 10 ml of acetonitrile at 65°C was carried out accompanied by vigorous shaking after each addition of the alkali solution. The dark red color which appeared immediately on addition of the alkali disappeared on shaking at first but persisted after the addition of several drops. A crystalline product also appeared during the addition of the potassium hydroxide solution. After the addition was completed the reaction mixture was held at 60°-65°C for ten minutes, then allowed to stand at room temperature for an hour. The product was filtered off, washed with water and methanol and dried. It was dark red in color and weighed 0.25 g, 15% of theoretical yield. Recrystallized from nitrobenzene it yielded 0.2 g of pale yellow needles, mp 315°-316°C.

D. From 2,4,6-trinitrotoluene and potassium hydroxide:

A solution of 4.5 g, 0.02 mole, of 2,4,6-trinitrotoluene in 25 ml of pyridine was prepared in a 300 ml 3-neck round bottom flask equipped with a thermometer and a mechanical stirrer. A solution of 8 g of iodine in 75 ml of methanol was added to the pyridine solution of TNT and the mixture was chilled to -10°C in an ice salt bath. A heavy red-gold precipitate formed which was replaced by a red-brown finely divided precipitate suspended in a blood-red solution during the 1/2 hour addition of 17 ml of a 33% methanolic potassium hydroxide solution. After the addition of the alkali was completed the reaction mixture was allowed to stir in the ice salt bath for 1/2 hour, then for 15 minutes after removal of the bath. The product was filtered off, slurried with hot methanol, then with hot water, washed with methanol and dried. The dark red-brown material weighed 0.5 g, 10% of the theoretical yield. Recrystallized from nitrobenzene it yielded 0.2 g of pale yellow needles, mp 315°-316°C.

E. From 2,4,6-trinitrotoluene and 2,4,6-trinitrobenzaldehyde:

To a solution of 0.5 g of 2,4,6-trinitrotoluene and 0.5 g of 2,4,6-trinitrobenzaldehyde in 5 ml of dry acetonitrile was added one drop of piperidine. A dark red brown color appeared immediately. The solution was allowed to stand at room temperature for several days, then diluted with an equal volume of methanol and chilled. A scintillating crystalline product was filtered off, washed with methanol and recrystallized from

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nitrobenzene to yield only a few mg of pale yellow needles which were identified as 2,2',4,4',6,6'-hexanitrostilbene, VII, by X-ray powder diffraction pattern.

Heating the reaction mixture to reflux for a few minutes or for a prolonged period did not improve the yield of hexanitrostilbene.

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