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SYNTHESIS OF DIFLUORAMINOPOLYNITROAROMATIC COMPOUNDS
USING ELEMENTAL FLUORINE:
3-DIFLUORAMINO-2,2',4,4',6,6'-HEXANITROSTILBENE

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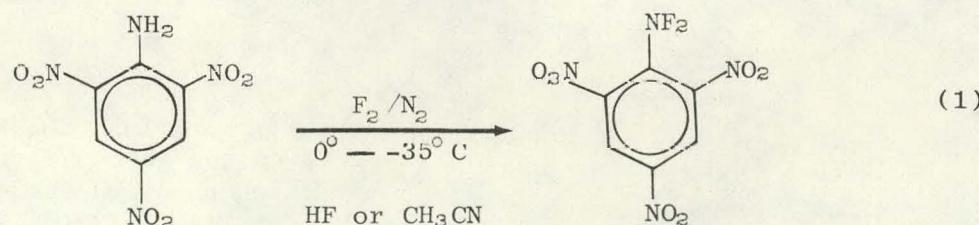
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A synthesis study is reported of difluoramino-polynitroaromatic compounds of the type (H or NF_2)Ar(NO_2)₃-R-Ar(NO_2)₃(NF_2), where R = -CH=CH- or -N=N-. 3-Difluoramino-2,2',4,4',6,6'-hexanitrostilbene was prepared and characterized. Attempts to prepare the corresponding bis(difluoramino)hexanitrostilbene and mono- and bis-difluoraminohexanitroazobenzene were unsuccessful for various reasons. The synthetic routes to the novel compounds and their physical constants are described.

Over the past several years, we have been investigating the synthesis, characterization, and evaluation of difluoraminopolynitroaromatic compounds. Recently, we reported that weakly basic amines could be successfully fluorinated using elemental fluorine (1), Reaction 1.



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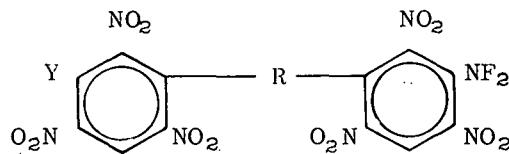
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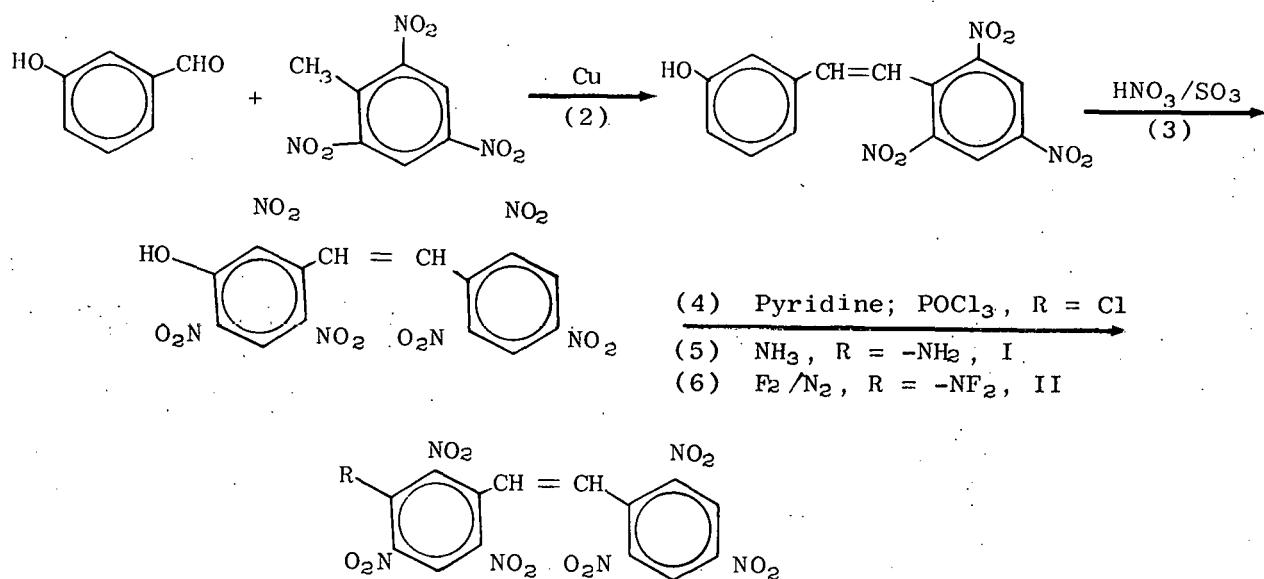
A portion of our earlier work on organic nitrogen-fluoride compounds has been reviewed by Freeman (5).

To relate structure to physical properties in this class of compounds, it was necessary to prepare additional representative structures. Thus, to determine the scope of Reaction 1, we prepared a number of novel aromatic difluoramines by fluorination of the corresponding amines. The present paper describes the synthesis of the intermediates



and the structures where Y is -H or -NF₂ and R is -CH=CH-, i.e., the stilbenes, or -N=N-, i.e., the azobenzenes. In succeeding papers of this series, we discuss the synthesis of difluoroamino compounds where R is zero, i.e., and biphenyls (10) and where R is a nitroaromatic group, i.e., the terphenyls (12).

The synthesis of the difluoramino compound in which R = -CH=CH-, 3-amino-2,2',4,4',6,6'-hexanitrostilbene, I, was completed by the following route, Reactions 2 through 6.



Reactions 2 through 5 were repeated according to Shipp (14, 15), and I was obtained in 10% overall yield.

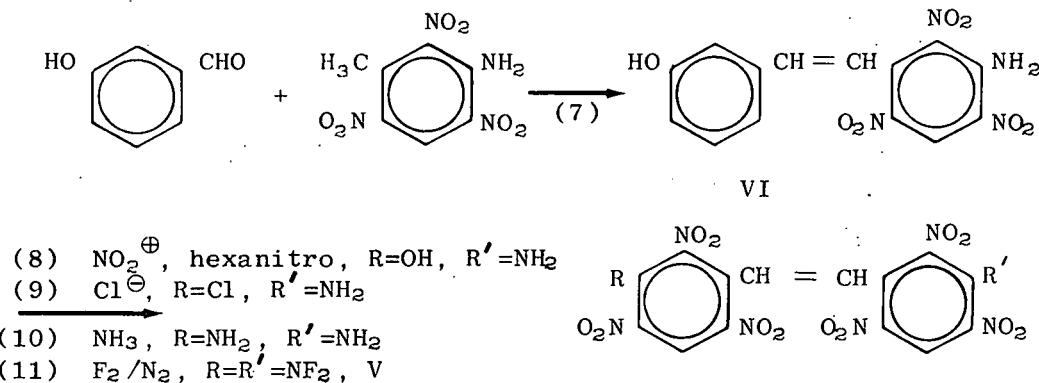
Compound I was then fluorinated, Reaction 6, under a variety of experimental conditions, i.e., anhydrous hydrogen fluoride, 96% sulfuric acid, and acetonitrile as solvents, at temperatures from 0° to -35°C, and for 1.5 to 15 hours. The best results were obtained by fluorination of a suspension of I in acetonitrile for 5 to 8 hours at -10 to -15°C; 3-difluoramino-2,2',4,4',6,6'-hexanitrostilbene, II, was obtained in 35-45% yield.

Because of low solubility of I in acetonitrile and the only fair yield of II, we attempted to prepare the acetamido derivative of I, which should be more soluble than I in solvents such as acetonitrile or anhydrous hydrogen fluoride. I was treated with acetic anhydride and a catalytic amount of sulfuric acid. The desired -NHCOCH₃ group was formed but apparently acetic anhydride also attacked the connecting vinyl group; this reaction has been observed in other unsaturated systems (8, 13).

Two compounds were isolated and characterized; one was assigned a diacetyl

structure, III; the other was tentatively assigned a triacetyl structure, IV, based on the available physical measurements. The elemental analysis of IV was probably in error due to the inherent instability of these vinyl-diacetyl structure and the loss of acetic acid, as has been observed in other systems (13). Thus, rate of reaction of acetic anhydride with the olefinic bond of I appears to be at least as fast as N-acetylation.

The synthesis of a second difluoramino compound where $R = -CH=CH-$, 3,3'-bis (difluoramino)-2,2',4,4',6,6'-hexanitrostilbene, V, was attempted by a number of routes. A discussion of the routes is given, and the steps are outlined in Reactions 7 through 11.



We obtained 3-amino-3'-hydroxy-2,4,6-trinitrostilbene, VI, in 66% yield from the condensation of trinitro-m-toluidine with m-hydroxybenzaldehyde, Reaction 7. Attempts to nitrate VI, by a variety of methods, to 3-amino-3'-hydroxy-2,2',4,4',6,6'-hexanitrostilbene were unsuccessful, Reaction 8. The nitration reactions included use of sulfonation with 30% oleum followed by commercial 70% nitric acid, specially prepared 70% nitric acid containing no nitrous acid, sodium nitrate in oleum, and 100% nitric acid, at various temperatures. In all the reactions, a dark

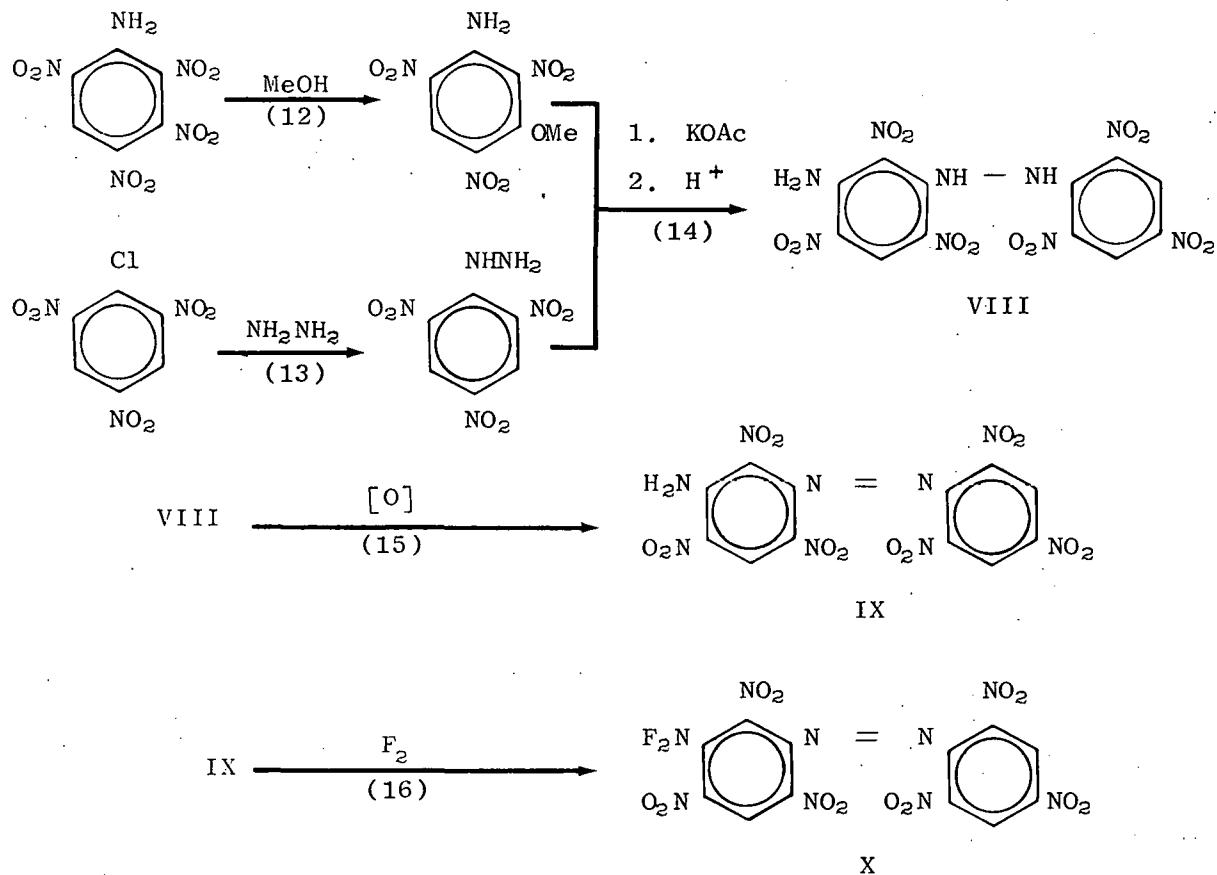
red-colored solution was obtained from which the starting material disappeared, gases were evolved, and black tars were obtained, but no V could be isolated.

The difficulties encountered in the nitration of VI can undoubtedly be attributed to the presence of the free hydroxyl and amino groups in the same molecule. There is reason to believe that phenols can be nitrated only with nitric acid containing a small amount of nitrous acid (11). However, since the amino group of VI would be expected to react with nitrous acid, the literature procedure for the nitration of VI to give VII was not considered further.

An amino group can be blocked from the action of nitric acid by acylation (9); however, Compound VI could also undergo acylation of the ring as well as of the ethylenic linkage. An alternative method would be N-acylation before the condensation reactions. Therefore, we prepared ethyl N-(3-methyl-2,4,6-trinitrophenyl)carbamate, VII, but we were unable to condense it with m-hydroxybenzaldehyde to obtain 3'-hydroxy-3-carbethoxyamino-2,4,6-trinitrostilbene. The amine catalysts used, piperidine and pyridine, apparently reacted with the carbamate by trans-amidination.

A number of other attempted routes to precursors of V included nitration of 3,3'-dimethoxystilbene, nitration of 3-amino-3-methoxy-2,4,6-trinitrostilbene, and condensation of m-hydroxybenzaldehyde with 2,4,6-trinitro-m-cresol. However, none of these reactions was successful, and we were unable to prepare V because the intermediates could not be synthesized.

The chemical equations below show our approach to the synthesis of 3-difluoramino-2,2',4,4',6,6'-hexanitroazobenzene, X.



Approaches to this synthesis were guided by the methods reported to prepare 2,2',4,4',6,6'-hexanitrohydrazobenzene and 2,2',4,4',6,6'-hexanitroazobenzene (7).

3'-Amino-2,2',4,4',6,6'-hexanitrohydrazobenzene, VIII, was obtained in about 40% crude yield by boiling 3-methoxy-2,4,6-trinitroaniline with picrylhydrazine and potassium acetate in ethanol. Crude VIII could not be purified by column chromatography or crystallization. It appeared to decompose rapidly, possibly due to the sensitivity of the compound to

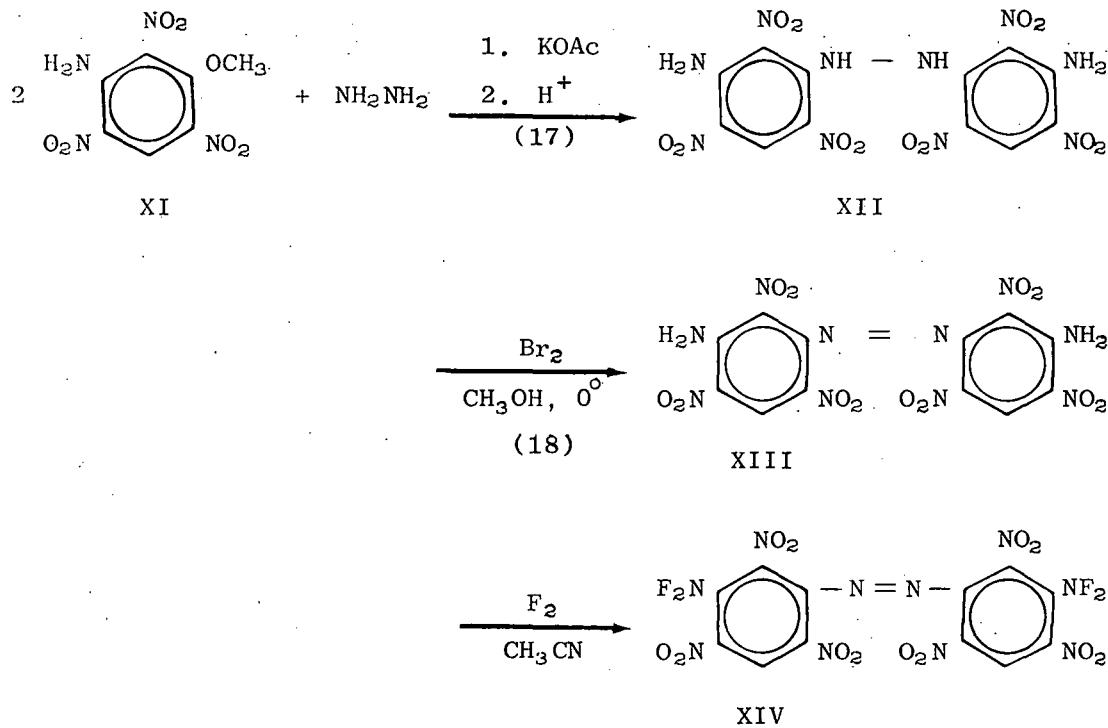
basic conditions or to air oxidation, or to an intramolecular redox reaction that was described for similar compounds by Giua (6).

We treated VIII with a variety of oxidizing agents, Reaction 15, to obtain 3-amino-2,2',4,4',6,6'-hexanitroazobenzene, IX. The first choice was 70% nitric acid, since hexanitrohydrazobenzene had been oxidized to hexanitroazobenzene (7) by this reagent. A material was obtained whose infrared spectrum corresponded to a diazonium salt rather than to VIII. The same material was obtained even after treating the nitric acid with a large excess of urea to remove nitrous acid. Apparently, the nitrous acid generated by the nitric acid oxidation of $-\text{NH}_2\text{NH}-$ attacked the neighboring $-\text{NH}_2$ more quickly than it attacked urea. A small amount of colorless gas, probably nitrogen and carbon dioxide, was observed as small bubbles in the reaction mixture during the nitric acid oxidation.

We found that bromine oxidation successfully produced IX. Frankel and Klager's method (4) for oxidizing bis- $\text{N},\text{N}'-(2,2\text{-dinitropropyl})$ hydrazine was adapted for our work, and IX was produced as a rust-colored solid in 66% yield. Other oxidizing agents that were used on VIII included NaOCl , $\text{Hg}(\text{OAc})_2$, Pd/C , MnO_2 , and O_2 , and the reactions were followed by thin layer chromatography (TLC). A product common to all of the reactions was observed by TLC; it was isolated from the air oxidation reaction and tentatively identified as IX in 50-70% crude yields. However, on further examination it was found not to be IX.

Fluorination of IX to 3-difluoramino-2,2',4,4',6,6'-hexanitroazobenzene, X, under a number of experimental conditions was unsuccessful, Reaction 16. These fluorination reactions are discussed at the end of the paper for both compounds where $\text{R} = -\text{N}=\text{N}-$,

The proposed synthesis of a second difluoramino compound where R = -N=N-, 3,3'-bis(difluoramino)-2,2',4,4',6,6'-hexanitroazobenzene, XIV, is shown below in Reactions 17-19. 3-Methoxy-2,4,6-trinitroaniline, XI,



was obtained according to Flürsheim (3) in 60% yield from 2,4,5,6-tetranitroaniline. Crude 3,3'-diamino-2,2',4,4',6,6'-hexanitrohydrazobenzene, XII, was prepared in 85% yield by treating 3-methoxy-2,4,6-trinitroaniline and hydrazine with potassium acetate in refluxing ethanol and acidifying the potassium salt that precipitated, Reaction 17. XII was converted immediately to 3,3'-diamino-2,2',4,4',6,6'-hexanitroazobenzene, XIII, in 63% yield by oxidation with bromine (3), Reaction 18. Attempts to obtain the diacetyl derivative of XIII by direct acylation and by a number of other routes were unsuccessful.

The fluorination of IX to X and XIII to XIV was attempted under a variety of conditions using anhydrous hydrogen fluoride and acetonitrile at 0° to -35° C. for 1 to 8 hours; however, only trace amounts of NF products were produced, which were detected by TLC and ¹⁹F NMR analysis.

During the fluorinations, TLC analysis of aliquots taken from the reaction mixtures showed that the major products did not contain the NF group. The products formed rapidly, and complete consumption of the starting materials occurred within two hours. When the crude products were freshly isolated by extracting with ether or washing with water, they evolved oxidizing and acidic gases. The fluorination of XIII in acetonitrile required a long period of time due to its low solubility. In one instance, a large sample of XIII was fluorinated, and about half of the starting material was recovered.

From the results of the experiments, we conclude that the azo group is unstable to the fluorination conditions in acetonitrile. The fluorination method was the same as that used in the successful preparation of other aromatic difluoramines from their corresponding amino derivatives (10, 12). In the fluorination of the azobenzene series, the two probable competing reactions are the attack of fluorine on the azo group and the fluorination of the amino group. The fluorinations consistently resulted in rapid formation of non-NF products and slow formation of traces of NF products. These results strongly indicate that fluorine attacks the azo group first to give unstable intermediates, which then decompose to non-NF products. To show that the azo group reacted faster than the amino group, fluorinations were conducted at lower temperatures so that the faster reaction would be favored. At the lower temperatures, it

appeared by ^{19}F NMR that smaller amounts of NF products formed. However, no NF azobenzene products could be isolated. We examined the fluorination of 2,2',4,4',6,6'-hexanitroazobenzene and found that the starting material also rapidly disappeared; therefore, we concluded that this $-\text{N}=\text{N}-$ linkage was being destroyed by fluorine as we had observed in X and XIV.

EXPERIMENTAL

Fluorine was obtained from the General Chemical Division of the Allied Chemical Corp. and was always diluted in a stream with nitrogen prior to fluorination. Unless otherwise noted, chemicals were used as received from the manufacturer.

Melting points reported are uncorrected and were obtained in a capillary using a Mel-Temp melting point apparatus or a melting point block. Elemental analyses were determined by Stanford University Analytical Laboratory and by Miss E. McCarthy, SRI Analytical Services. NMR data were obtained by Mrs. L. Stietzel using a Varian HA-100 NMR spectrometer. Values for ^1H chemical shifts are given in δ units with respect to tetramethylsilane as internal reference, and values for the ^{19}F chemical shifts are given in ψ^* units (2) with respect to trichlorofluoromethane as an internal reference. In NMR descriptions, s = singlet, d = doublet, t = triplet, q = quadruplet, m = multiplet, b = broad. Infrared spectra were run on a Perkin-Elmer Model 137 Infracord spectrometer. In IR descriptions, s = strong, m = medium, w = weak, b = broad.

Thin-layer chromatography was carried out on Eastman Chromagram sheets of silica gel with fluorescent indicator. Anhydrous magnesium sulfate was added to reaction mixtures from fluorinations in acetonitrile

to remove residual hydrogen fluoride. Since magnesium sulfate is slightly soluble in acetonitrile, addition of methylene chloride to the acetonitrile solution reduces this solubility. However, a small amount of magnesium sulfate that is present in the isolated crude product is removed by dissolving the crude product in methylene chloride or ethyl acetate and filtering off the insoluble magnesium sulfate. Elution of difluoraminonitroaromatic compounds in column chromatography was detected by spraying a spot of the eluate on filter paper with a 0.2% solution of N,N,N',N' -tetramethyl-p-phenylenediamine dihydrochloride in 50% methylene chloride and ethanol (TMPDA reagent); thin-layer chromatograms were also sprayed with TMPDA reagent. The reagent turned blue in the presence of strong oxidizers such as NF_2 -nitroaromatic compounds. Often the blue color changed to yellow at or above ambient temperature. Densities were determined using a Fisher-Davidson gravitometer.

Caution: The difluoraminonitroaromatic compounds and their intermediates described in this paper are explosives and sensitive to initiation by impact, shock, friction, rapid heating, or other means. Many difluoramino and aromatic compounds are toxic in varying degrees and will cause stains and burns when brought into contact with the skin. Therefore, care should be taken when handling compounds I-XIV.

3-Difluoramino-2,2',4,4',6,6'-hexanitrostilbene, II

A mixture of 6.0 grams of finely divided I and 300 ml. acetonitrile (Nanograde) was boiled for 15 minutes for dispersion and partial solution (~1-2 grams), and placed in a Kel-F reactor. The system was flushed with nitrogen and immersed in a $-10^{\circ}C$. bath. Suspension of the I was maintained

by a magnetic stirrer. A 60-ml. minute stream of fluorine/nitrogen (30/70) was bubbled through the reaction mixture using a 2-mm. i.d. Kel-F tubing. During the first three hours, the suspension darkened from green-yellow to red-brown. At the fourth hour the reaction mixture was orange and nearly clear. The fluorine was stopped when the liquid was clear and yellow; the total fluorination time was five hours. Residual fluorine was swept from the system with nitrogen while the reaction mixture was warmed with a 25° C. bath. The liquid, which darkened slightly on warming to 25°, was poured into 300 ml. of methylene chloride. Removing residual hydrogen fluoride was difficult; however, approximately 50 grams of silica gel and 100 grams of anhydrous magnesium sulfate were added, and the mixture was stirred at least 1 hour. Crystallization was accomplished by dissolving the isolated crude II in 50 ml. of warm ethyl acetate, filtering to remove a trace of solid, and adding 100 ml. of hot chloroform to the filtrate. After cooling the mixture to 0°, the light tan solid was collected, washed with chloroform, and dried in vacuo. 2.7 grams (42% yield); m.p. 190°-197° C. (dec.). The melting point was determined by placing the solid on a melting point block, starting at 180°.

Using column chromatography, 0.5 grams of II, m.p. 175°-190° C. dec., was obtained from the dark oil in the combined mother liquors of two runs. Silica gel alone was not as effective an absorbent; however, a short band of acid-washed alumina placed near the top of the column gave satisfactory results. The lengths of material in the 2.6-cm. i.d. column were, from top to bottom, 20 cm. of silica gel, 2 cm. of acid-washed

alumina, and 50 cm. of silica gel. Elution with ethyl acetate/chloroform (1/3, v/v) was rapid because II decomposed on acid-washed alumina. Recrystallization of a portion from nitromethane/chloroform (1/3, v/v), m.p. 205°-208° C. (dec.) (placed on 200° melting point block); d^{25} 1.76; IR (fluorolube) 3106 (w, C=C), 1618 (w, CNO₂), 1586 (s, CNO₂), 1548 cm⁻¹ (s, CNO₂); NMR (CH₃CN) φ^* 61.9 (s, NF₂).

Anal. Calcd. for C₁₄H₅F₂N₇O₁₂: C, 33.55; H, 1.01; F, 7.58; N, 19.56

Found: C, 33.86; H, 1.15; F, 7.50; N, 19.09

Diacetyl, III, and Triacetyl, IV, Derivatives of 3-Amino-2,2',4,4',6,6'-hexanitrostilbene

A mixture of 2.0 grams of I, 65 ml. of acetic anhydride, and 6 drops of 96% sulfuric acid was heated at 85° C. for 2 hours. I did not dissolve and no reaction was apparent. However, when heated to 110° C., all of the solid dissolved immediately. This temperature was maintained for 40 minutes before the hot liquid was poured into 200 ml. of water at 25°. The mixture was stirred at 50° for 15 minutes. A yellow solid weighing 1.9 grams was obtained by extraction with ethyl acetate and recrystallized from ethyl acetate and n-hexane to give 0.3 gram of IV, m.p. 204°-205° C. (dec.); IR (fluorolube) 3380 (w, NH), 3086 (w, CH₃), 1730 (m, C=O), 1600 (m, CNO₂), 1698 (m, C=O), 1543 cm⁻¹ (s, CNO₂). Anal. Calcd. for C₂₀H₁₅N₇O₁₆: C, 39.40; H, 2.48; N, 16.09. Found: C, 37.70; H, 2.00; N, 17.89.

The mother liquor gave 0.9 gram of III; m.p. 183°-186° C.; IR (fluorolube) 3096 (w, CH₃), 1739 (m, C=O), 1709 (m, C=O), 1608 (m, CNO₂), 1555 (s, CNO₂), 1540 (s, CNO₂). Anal. Calcd. for C₁₈H₁₁N₇O₁₄: C, 39.36; H, 2.02; N, 17.85. Found: C, 39.40; H, 2.05; N, 17.96.

3-Amino-3'-hydroxy-2,4,6-trinitrostilbene, VI

To a warm solution of 60 ml. of benzene, 11.27 grams (0.047 mole) of 2,4,6-trinitro-m-toluidine and 5.72 grams (0.047 mole) of m-hydroxybenz-aldehyde (Aldrich Chemical Co.) in a 250-ml. single-neck flask was added 1 ml. of piperidine. The resulting mixture was heated to reflux using a condenser connected through a Dean Stark trap. After about 1 hr. the product separated from the dark liquid as a brown solid. The reaction mixture was heated under reflux an additional hour or until the theoretical yield of water had collected in the Dean Stark trap (ca. 0.9 ml.). Crude VI was filtered from the hot liquid, washed with benzene, and dried. When crystallized from 300 ml. of hot acetonitrile, the product gave yellow-brown crystals melting at 228° to 232° C. with decomposition and weighing 10.55 grams, 66% of the theoretical yield.

A pure sample of VI was prepared for analyses by treating a 4-gram sample with Norit in hot acetone and recrystallizing the material from a mixture of 50 ml. of acetone and 20 ml. of hexane. Small yellow crystals were collected as VI: 2.0 grams; m.p. 231°-232° C. (dec.); IR (fluorolube), 3460 (m, COH), 3367 (m, NH), 1639 (s), 1634 (s), 1608 (s, CNO₂), 1585 (s, CNO₂), 1538 cm.⁻¹ (s); NMR (acetone-d₆), δ 7.30 to 6.46 (complex m, 6, 2', 4', 5', 6' and CH=CH protons), 8.28 (bs, 2 NH₂), 8.80 (s, 1, 5 proton), 8.49 (bs, COH). Anal. Calcd. for C₁₄H₁₀N₄O₇: C, 48.56; H, 2.91; N, 16.18. Found: C, 48.73; H, 3.08; N, 16.09.

Ethyl N-(3-Methyl-2,4,6-trinitrophenyl)carbamate, VII

Ethyl N-(m-tolyl)carbamate, b.p. 122° C. (3 mm.), was prepared in 73% yield from m-toluidine, ethyl chloroformate, and sodium carbonate in

benzene at reflux temperature. A solution of 1.8 grams (0.01 mole) of the carbamate in 7 ml. of 96% sulfuric acid was added dropwise during a 15-min. period to a stirred solution of 11 ml. of 100% nitric acid and 11 ml. of 96% sulfuric acid at 0°C. The clear yellow reaction mixture was stirred for 2 hr. at 25°C. and was then poured into 200 ml. of crushed ice. A white gum separated. Crude, yellow oil (2.7 grams) was isolated by ethyl acetate extraction. Crystallization from methanol-chloroform gave 0.9 gram (30% yield) of product as white crystals, m.p. 154°-155°C.; IR (fluorolube) 3226 (m, NH), 1733 (s, C=O), 1610 (w, CNO₂), 1536 (s), 1511 cm.⁻¹ (s); NMR (DMSO-d₆), δ 10.48 (bs, NH), 8.80 (s, 1, 5-proton), 4.08 (q, 2, J = 6.8 Hz, CH₂CH₃), 2.44 (s, 3 ArCH₃), 1.20 (t, 3, J = 6.8 Hz, CH₂CH₃). Anal. Calcd. for C₁₀H₁₀N₄O₈: C, 38.22; H, 3.21; N, 17.83. Found: C, 38.01, H, 3.25; N, 18.01.

An attempt to carry out this nitration with commercial grade 90% nitric acid which had not been freed of nitrous acid and oxides of nitrogen resulted in evolution of first, a brown gas and then, a colorless gas. The amide N-H was rapidly attacked by impurities in the nitric acid.

3-Amino-2,3',4,4',6,6'-hexanitrohydrazobenzene, VIII

A solution of 0.98 gram of potassium acetate in 30 ml. of ethanol was added all at once to a stirred, boiling solution of 2.58 grams of 3-methoxy-2,4,6-trinitroaniline and 2.43 grams of picrylhydrazine in 250 ml. of ethanol. The color of the reaction mixture changed instantly from clear amber to deep purple. Boiling was stopped after 20 minutes, and the mixture of dark liquid and dark precipitate was stirred overnight at ambient temperature. The solid was collected, washed with ethanol,

and dried, giving 2.53 grams. Ignition of the solid on platinum foil gave the characteristic potassium flame and a water-soluble residue.

The potassium salt was acidified by first suspending it in 25 ml. of warm acetic acid, adding 50 ml. of 37% hydrochloric acid, and heating the mixture at 75° C. for 10 minutes. The dark mixture turned bright orange when the hydrochloric acid was added. An orange precipitate was collected after the hot mixture was poured into 500 ml. of cold water. The solid was washed with water and dried to give 1.98 grams, m.p. 136°-150° C. (dec.). Attempted recrystallization from acetic acid and hexane or nitrobenzene and benzene was not successful. One gram of VIII was dissolved in 20 ml. of warm, dry ethyl acetate. The solution was filtered warm, and 40 ml. of hot chloroform was added. Because crystallization was fast it was necessary to allow the liquid to cool slowly to room temperature. The red plates were filtered and washed with chloroform after 2 hours. The dried crystals weighted 0.85 gram and melted with decomposition at 198°-200° C. Oxidation of the hydrazo group by air or by an ortho nitro group may occur during the heating period of recrystallization. Because of the difficulties of isolation, proof of structure of VIII was limited to TLC and IR analyses: 3590 (m, NH), 3350 (m, NH), 3300 (m, NH), 3100 to 3220 cm.^{-1} (b, NH_2) and oxidation to IX.

3-Amino-2,2',4,4',6,6'-hexanitroazobenzene, IX

A 2.45-gram (0.005 mole) sample of crude VIII was dissolved in 500 ml. of methanol at 40° C. The resulting clear, maroon-colored solution was cooled at 0° C. An equivalent of bromine, 0.85 gram (0.005 mole),

in 25 ml. of methanol was added in one portion with stirring; the color lightened. Thin-layer chromatography (ethyl acetate, silica gel) showed only product after 5 min.: VIII, R_f 0.04, red-brown; IX, R_f 0.74, amber. The reaction mixture was stirred 1 hour at 0°C . and stored at 4°C . overnight to allow crystallization of the product. The rust-colored IX was filtered, washed with chloroform, and dried in vacuo to give 1.60 grams, 66% of theory. The last traces of methanol were removed from a sample for analysis by drying for 18 hours at 0.5 mm. pressure and 56°C . (refluxing acetone). The sample melted with decomposition at 205° - 206°C .; IR (fluorolube) 3378 (m, NH), 1631 (s, CNO_2), 1550 (s, CNO_2) 1348 (s), 1287 cm.^{-1} (s). Anal. Calcd. for $\text{C}_{12}\text{H}_5\text{N}_9\text{O}_{12}$: C, 30.71; H, 1.60; N, 26.86. Found: C, 30.81; H, 1.54; N, 26.77.

3,3'-Diamino-2,2',4,4',6,6'-hexanitrohydrazobenzene, XII

A solution of 0.17 gram of 95% aqueous hydrazine in 25 ml. of ethanol was added in one portion to a stirred solution of 3-amino-2,4,6-trinitroanisole in 50 ml. of ethanol at 75°C . Next, 0.98 gram of potassium acetate dissolved in 25 ml. of ethanol was added all at once, with stirring. The resulting dark liquid was heated to reflux temperature for 15 minutes and stirred overnight at ambient temperature. The potassium salt of XII was filtered, washed with ethanol, and dried to give 2.65 grams, 100% of theory.

The dark potassium salt of XII (2.65 grams) was stirred to a fine suspension in 25 ml. of acetic acid, and 50 ml. of 37% hydrochloric acid was then added. After the light mixture was heated at 60° - 65°C . for 10 minutes, it was poured into 250 ml. of water at 15°C . and stirred for

15 minutes. A yellow solid XII was filtered, washed with water, and dried to give 2.05 grams, 85% of theory, m.p. 159°-175°C. (dec.). IR (fluorolube) 3460 (m, NH), 3344 (m, NH), 3247 (m, NH), 1631 (s, CNO₂), 1582 (s, CNO₂), 1534 (m), 1479 cm.⁻¹ (m).

3,3'-Diamino-2,2',4,4',6,6'-hexanitroazobenzene, XIII

A 5.4 gram (0.011 mole) sample of XII was dissolved in 1900 ml. of hot methanol. After the clear, red solution was cooled to 0°C., 1.8 grams (0.011 mole) of bromine in 110 ml. of methanol was added in one portion, with stirring. A red solid separated within 2 minutes. The reaction mixture was stirred 1 hour at 0°C. and stored overnight in a refrigerator. XIII was filtered, washed with chloroform, and dried in vacuo, giving 3.4 grams, 63% of theory, m.p. 257°-259°C. (dec.); IR (fluorolube) 3460 (w, NH), 3367 (m, NH), 1623 (s, CNO₂), 1572 (m, CNO₂), 1515 cm.⁻¹ (s). Anal. Calcd. for C₁₂H₆N₁₀O₁₂: C, 29.89; H, 1.25; N, 29.05. Found: C, 29.92; H, 1.47; N, 28.77.

Acknowledgement

The authors wish to thank Dr. John Dick of the Sandia Laboratories Albuquerque, New Mexico, for many helpful discussions concerning this research.

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Received for review _____, 1971. Accepted _____

This paper is based on work performed under Contract Nos. 58-0883, 58-3246, and 58-5131, for the U.S. Atomic Energy Commission. Technical direction was provided by the Sandia Laboratories, Albuquerque, New Mexico, with Dr. John Dick as contract monitor.