

Joseph C. Dacons and Michael E. Sitzmann (1)

Naval Surface Weapons Center, White Oak, Silver Spring, Maryland 20910

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The preparation of 2,4,6-trinitrophenyl (picryl) derivatives of triazine, pyrimidine, thiophene, furan, thiazole, 1,3,4-oxadiazole and 1,3,4-thiadiazole is described. The picryl derivatives are prepared by the Ullmann reaction and by cyclization reactions to form the heterocyclic ring.

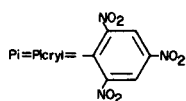
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Relatively few explosives are capable of withstanding high temperatures in the region of 230 to 300°C without melting or decomposing significantly. In a search for such explosives we explored the possibility of preparing picryl derivatives of heterocycles. Direct nitration of phenyl-heterocycles to the picryl compounds is not feasible. The phenyl ring is very difficult to nitrate to the trinitro stage unless a ring activating group is present. If an activating group is employed during the nitration step, the problem exists of how to replace this group with hydrogen to obtain the picryl compound. Hence a method for directly attaching a picryl group to a heterocyclic ring is preferred. One such method is the Ullmann biaryl synthesis (coupling of aromatic halides in the presence of copper).

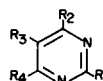
The Ullmann reaction occurs for both aromatic and heteroaromatic compounds (2). We have employed a mixed Ullmann reaction (picryl halides with heterocyclic halogen compounds) as a method for preparing picryl heterocycles. The picryl halides, being much more reactive than the heterocyclic substrates (3), will couple with themselves to form 2,2', 4,4', 6,6'-hexanitrobiphenyl faster than they will couple with the less reactive heterocyclic compounds. However, this self-coupling to form hexanitrobiphenyl can be minimized by slow addition of the picryl halide to the hot reaction mixture. This procedure allows the heterocyclic halide to be in large excess for most of the reaction and thus favors formation of the picryl heterocycle.

Water and other proton sources adversely affect the Ullmann reaction of picryl halides (formation of trinitrobenzene occurs). Hence the starting materials and solvent used must be free of proton sources in order to obtain the maximum yields of coupled product. Nitrobenzene was found to be a convenient solvent since it can be readily dried and its high boiling point (210°) allows a wide range of reaction temperatures.

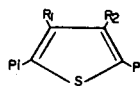
Picryl derivatives of triazine, pyrimidine, thiophene, furan and thiazole (compounds I, IIa, IIb, IIc, IIIa, IVa and Va) were prepared *via* the Ullmann reaction of picryl bromide with the appropriate heterocyclic halogen compounds. Nitration of IIIa, IVa and Va gave their higher nitrated derivatives (IIIb, IIIc, IVb, IVc and Vb) (4).



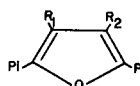
I



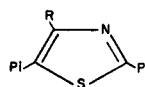
IIa  $R_1 = R_2 = R_4 = \text{Pi}, R_3 = \text{H}$   
 IIb  $R_2 = R_4 = \text{Pi}, R_3 = \text{NO}_2, R_1 = \text{H}$   
 IIc  $R_1 = R_2 = \text{Pi}, R_3 = \text{NO}_2, R_4 = \text{H}$



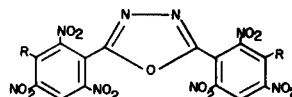
IIIa  $R_1 = R_2 = \text{H}$   
 IIIb  $R_1 = \text{NO}_2, R_2 = \text{H}$   
 IIIc  $R_1 = R_2 = \text{NO}_2$



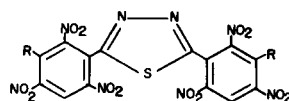
IVa  $R_1 = R_2 = \text{H}$   
 IVb  $R_1 = \text{NO}_2, R_2 = \text{H}$   
 IVc  $R_1 = R_2 = \text{NO}_2$



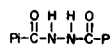
Va  $R = \text{H}$   
 Vb  $R = \text{NO}_2$



VIa  $R = \text{H}$   
 VIb  $R = \text{OCH}_3$   
 VIc  $R = \text{NH}_2$



VIIa  $R = \text{H}$   
 VIIb  $R = \text{OCH}_3$   
 VIIc  $R = \text{NH}_2$



VIII

Another possible approach for preparation of picryl heterocycles is to employ a picryl precursor which can be cyclized to give the desired heterocyclic ring with picryl groups attached. This approach was used for the preparation of picryl derivatives of oxadiazole and thiadiazole because the necessary halogen compounds for the Ullmann reaction are not available. Thus cyclization of *N,N'*-bis-(2,4,6-trinitrobenzoyl)hydrazine (VIII) with phosphorus

pentoxide or phosphorus pentachloride gave 2,5-dipicryl-1,3,4-oxadiazole (VIa) (5). However, attempted cyclization of VIII with phosphorus pentasulfide to give the corresponding dipicrylthiadiazole (VIIa) was not successful. Deamination of the aminopicrylthiadiazole (VIIc) gave VIIa in low yield. The aminopicryloxadiazole and thiadiazole (VIc and VIIc) were formed by reaction of ammonia with the methoxyl compounds (VIb and VIIb) which in turn were prepared by direct nitration of the respective 2,5-bis(3-methoxyphenyl)oxadiazole and thiadiazole.

## EXPERIMENTAL

### General.

**CAUTION! THE COMPOUNDS DESCRIBED HEREIN ARE EXPLOSIVES AND SHOULD BE HANDLED WITH CARE.** Elemental analyses were performed by Dr. Mary Aldridge, American University. The nmr spectra were determined on a Varian HA100 spectrometer. The melting points are uncorrected.

The Ullmann reactions were carried out in a 3 neck round bottom flask equipped with a mechanical stirrer, thermometer and addition funnel. Heating control was obtained by using a hot oil bath on a lab jack. To start the Ullmann reaction approximately 10% of the picryl bromide solution was added to the hot reaction mixture. After the reaction started (copper changed color) the remainder of the picryl bromide solution was added over the period of time given in the experimental procedure. The copper used was Venus Natural Copper Fine No. 44-F, U.S. Bronze Powders, Inc., Flemington, New Jersey. Dry nitrobenzene was obtained by distilling a small forerun from reagent grade material and using the pot fraction.

The finely divided copper salts obtained from the Ullmann reaction cause any subsequent filtration to be slow and difficult. These copper salts can be separated from the organic products by treating the reaction product with 20% hydrochloric acid at 50-60°. The acid insoluble material is then washed with dilute hydrochloric acid, water and methanol before being dissolved in the crystallizing solvent (the unreacted copper remains insoluble).

The picryl bromide used in this study was prepared as follows: 355 g. of potassium nitrate was added to 800 ml. of 30% fuming sulfuric acid with stirring and cooling below 60°; bromobenzene (79 g.) was slowly added keeping the temperature below 50°; the reaction mixture was heated at 125° for 4 hours, then was cooled and poured onto ice; the precipitated product was crystallized to give a total of 104.7 g. (71.6%), m.p. 120-122°.

Many of the picryl heterocycles were crystallized using an acetone-methanol procedure. The procedure involves dissolving the compound in the minimum amount of boiling acetone (large volumes of acetone are often required and the product will not reprecipitate upon cooling the acetone solution). The acetone solution is treated with Darco G60, filtered, and the filtrate concentrated by distillation until appreciable crystallization occurs (often requires removing 75% of the original volume of acetone). Methanol is then added with continued distillation (keeping the volume of crystallizing solvent approximately constant) until the distillate temperature reaches 61-62°. The crystals are removed and washed with methanol. Acetone-methanol was often used as the crystallizing solvent because many of the picryl heterocycles form solvates. The acetone solvates can be readily broken up by heating.

### 2,4,6-Tripicryl-s-triazine (I).

A mixture of 18.5 g. (0.1 mole) of cyanuric chloride and 89.0

g. (1.4 moles) of copper in 100 ml. of dry nitrobenzene was vigorously stirred at 140-146° during the addition of 118 g. (0.4 mole) of picryl bromide in 150 ml. of dry nitrobenzene over a 40 minute period. The cooled reaction mixture was poured into 700 ml. of methanol and then cooled to 5°. The insoluble material was washed with methanol and then treated to remove copper salts (see general experimental section) before it was dissolved in 3 liters of hot acetone. Work up according to the acetone-methanol procedure gave 60.7 g. of yellow crystals, m.p. 350-351° after sintering at 140°. Recrystallization from acetone-methanol gave 55.5 g. of product which after drying overnight at 140° lost acetone of crystallization to yield 50.4 g. (72%) of crystals, m.p. 352-353°; nmr (DMSO):  $\delta$  9.24 (s); Mol. wt. Calcd: 714. Found: 710.

*Anal.* Calcd. for  $C_{21}H_6N_{12}O_{18}$ : C, 35.30; H, 0.85; N, 23.53. Found: C, 35.41; H, 0.91; N, 22.78.

### 2,4,6-Tripicrylpyrimidine (IIa).

A vigorously stirred mixture of 22.0 g. (0.12 mole) of 2,4,6-trichloropyrimidine (6) and 106.7 g. (1.68 moles) of copper in 120 ml. of dry nitrobenzene was heated at 145-150° during the addition of 140.2 g. (0.48 mole) of picryl bromide in 210 ml. of dry nitrobenzene over a 25 minute period. The cooled reaction mixture was poured into 1300 ml. of methanol and then cooled to 10°. The insoluble material was washed with methanol, the copper salts were removed (see general experimental reaction) and the product dissolved in 280 ml. of dimethylsulfoxide at 100°. The dark solution was treated with Darco G60, filtered, and the filtrate poured into 1500 ml. of methanol (followed by cooling to 10°) to precipitate 52.6 g. of a tan product, m.p. 335-340°. Two recrystallizations from nitrobenzene gave 45.6 g. of yellow crystals which after drying at 145-150° for 4.5 hours under vacuum (loses nitrobenzene of solvation) yielded 38.9 g. (45.4%) of cream colored crystalline product, m.p. 341-342°; nmr (DMSO):  $\delta$  9.24 (s, 4H, picryl-H), 9.17 (s, 2H, picryl-H), 8.50 (s, 1H, pyrimidine-H).

*Anal.* Calcd. for  $C_{22}H_7N_{11}O_{18}$ : C, 37.04; H, 0.99; N, 21.60. Found: C, 37.02; H, 1.04; N, 21.59.

### 4,6-Dipicryl-5-nitropyrimidine (IIb).

A vigorously stirred mixture of 23.3 g. (0.12 mole) of 4,6-dichloro-5-nitropyrimidine (6) and 71.1 g. (1.12 moles) of copper in 100 ml. of dry nitrobenzene was heated at 145-150° during the addition of 93.5 g. (0.32 mole) of picryl bromide in 140 ml. of dry nitrobenzene over a 25 minute period. The cooled mixture was poured into one liter of methanol, cooled to 10°, and the insoluble material was washed with methanol and then stirred with 1500 ml. of boiling acetone. The hot mixture was filtered and the product was crystallized from the acetone filtrate by the acetone-methanol procedure to give 31.0 g. (47.3%) of cream colored crystals, m.p. 349-350°; nmr (DMSO):  $\delta$  9.76 (s, 1H, pyrimidine-H), 9.39 (s, 4H, picryl-H).

*Anal.* Calcd. for  $C_{16}H_5N_9O_{14}$ : C, 35.12; H, 0.92; N, 23.03. Found: C, 35.37; H, 1.26; N, 22.73.

### 2,4-Dipicryl-5-nitropyrimidine (IIc).

A solution of 23.4 g. (0.08 mole) of picryl bromide in 40 ml. of dry nitrobenzene was added over a 25 minute period to a mixture of 5.28 g. (0.03 mole) of 2,4-dichloro-5-nitropyrimidine (7) and 17.6 g. (0.28 mole) of copper in 20 ml. of dry nitrobenzene vigorously stirred at 145-150°. The cooled mixture was poured into 500 ml. of methanol and then cooled to 10°. The insoluble material was washed with methanol and then treated to remove copper salts (see general experimental section) before it was dissolved in 50 ml. of dimethyl sulfoxide at 80°. The dark solution was treated with Darco G60, filtered, and the product (9.25 g. of light brown crystals, m.p. 325-326°) was precipitated by adding 300 ml. of methanol to the filtrate. Crystallization from nitro-

benzene gave 8.0 g. of yellow crystals, m.p. 327-328°. A second crop (0.95 g., m.p. 327-328°) obtained by adding methanol to the nitrobenzene mother liquor raised the yield to 54.6%; nmr (DMSO):  $\delta$  10.07 (s, 1H, pyrimidine-H), 9.32 (s, 2H, picryl-H), 9.24 (s, 2H, picryl-H).

*Anal.* Calcd. for  $C_{16}H_5N_9O_{14}$ : C, 35.12; H, 0.92; N, 23.03. Found: C, 35.36; H, 1.20; N, 22.90.

#### 2,5-Dipicrylthiophene (IIIa).

A well-stirred mixture of 19.4 g. (0.08 mole) of 2,5-dibromothiophene and 45.7 g. (0.72 mole) of copper in 80 ml. of dry nitrobenzene was heated at 145-150° during the slow addition of a solution containing 58.4 g. (0.20 mole) of picryl bromide in 150 ml. of dry nitrobenzene over a 35 minute period. The dark reaction mixture (cooled to 100°) was poured into 300 ml. of toluene and then cooled to 10°. The insoluble material was washed with methanol and the copper salts were removed (see general experimental section). The resulting product (37.6 g.) was dissolved in 300 ml. of dimethylsulfoxide at 100°, the dark solution treated with Darco G60, filtered, and the filtrate added to 700 ml. of methanol. After cooling to 5°, filtration gave 31.1 g. (76.8%) of yellow crystals, m.p. 359-360°; nmr (DMSO):  $\delta$  9.19 (s, 4H, picryl-H), 7.29 (s, 2H, thiophene-H).

*Anal.* Calcd. for  $C_{16}H_6N_6O_{12}S$ : C, 37.95; H, 1.19; N, 16.60; S, 6.33. Found: C, 38.09; H, 1.40; N, 16.62; S, 6.24.

#### 2,5-Dipicryl-3-nitrothiophene (IIIb).

To a stirred volume of 250 ml. of 90% nitric acid was added 25.3 g. of 2,5-dipicrylthiophene. The temperature was raised to 45° to effect complete solution and after 2 minutes at 45° the solution was poured into 1 liter of ice water. The precipitated product was washed with water and methanol to give 27.1 g. (98.4%) of yellow solid, m.p. 285-286°. Crystallization from acetone-methanol gave 26.3 g. of yellow crystals, m.p. 287-288°; nmr (DMSO):  $\delta$  9.28 (s, 2H, picryl-H), 9.23 (s, 2H, picryl-H), 8.08 (s, 1H, thiophene-H).

*Anal.* Calcd. for  $C_{16}H_5N_7O_{14}S$ : C, 34.86; H, 0.91; N, 17.78; S, 5.82. Found: C, 34.91; H, 1.03; N, 18.10; S, 5.88.

#### 2,5-Dipicryl-3,4-dinitrothiophene (IIIc).

A quantity of 39.5 g. of 2,5-dipicrylthiophene was added to 500 ml. of 90% nitric acid with stirring and the mixture was heated to 60° to dissolve all material. The solution was kept at 60° for 5 minutes before 200 ml. of 30% fuming sulfuric acid was slowly added with external cooling to maintain the temperature at 60-65°. The reaction mixture was heated at 60-65° for 5 hours, then was cooled and poured onto ice. The precipitated product was washed with water and methanol to give 44.8 g. of yellow solid, m.p. 299°. Crystallization from acetone-methanol yielded 40.3 g. (86.7%) of yellow crystals, m.p. 305-306°; nmr (DMSO):  $\delta$  9.31 (s).

*Anal.* Calcd. for  $C_{16}H_4N_8O_{16}S$ : C, 32.23; H, 0.67; N, 18.79; S, 5.38. Found: C, 32.35; H, 1.07; N, 18.76; S, 5.39.

Compound IIIc was also prepared in 32% yield by the Ullmann reaction of picryl chloride with 2,5-dibromo-3,4-dinitrothiophene. The compound obtained was identical in all respects to that obtained from nitration of IIIa in the procedure described above.

#### 2,5-Dipicrylfuran (IVa).

A well-stirred mixture of 137.4 g. (2.16 moles) of copper and 54.4 g. (0.24 mole) of 2,5-dibromofuran (8) in 220 ml. of dry nitrobenzene was heated at 145-150° during the addition of a solution of 175.2 g. (0.6 mole) of picryl bromide in 270 ml. of dry nitrobenzene over a 30 minute period. The cooled reaction mixture was poured into 1500 ml. of methanol and then cooled to 10°. The insoluble material was stirred with 3500 ml. of boiling

acetone, the mixture was filtered and the acetone filtrate worked up according to the acetone-methanol crystallization procedure to give 101.8 g. of crystals, m.p. 271-274°. Recrystallization from acetone-methanol gave 99.2 g. (84.4%), m.p. 274-275°; nmr (DMSO):  $\delta$  9.19 (s, 4H, picryl-H), 7.13 (s, 2H, furan-H).

*Anal.* Calcd. for  $C_{16}H_6N_6O_{13}$ : C, 39.20; H, 1.23; N, 17.14. Found: C, 38.92; H, 1.50; N, 17.18.

#### 2,5-Dipicryl-3-nitrofurane (IVb).

To 250 ml. of 90% nitric acid was added 35 g. of 2,5-dipicrylfuran rapidly in portions with stirring. The temperature rose to 40°, the solution was kept at 40° for 10 minutes and then poured into 1 liter of ice water. The precipitated product was washed with water and methanol and then crystallized from acetone-methanol to give 34.3 g. (89.8%) of bright yellow crystals, m.p. 240° with resolidification and remelting at 268-269°. The crystals were dissolved in hot acetonitrile, the solution concentrated and benzene added to give 36 g. of yellow crystals, m.p. 268-269° with no prior melting at 240°. Drying at 130-135° under vacuum for 4 hours removed solvent of crystallization to give 31.7 g. (83.0%) of pale yellow crystals, m.p. 268-269°; nmr (DMSO):  $\delta$  9.31 (s, 2H, picryl-H), 9.25 (s, 2H, picryl-H), 7.90 (s, 1H, furan-H).

*Anal.* Calcd. for  $C_{16}H_5N_7O_{15}$ : C, 35.90; H, 0.94; N, 18.32. Found: C, 36.14; H, 1.24; N, 18.15.

#### 2,5-Dipicryl-3,4-dinitrofurane (IVc).

To 250 ml. of 90% nitric acid was added 35 g. of 2,5-dipicrylfuran rapidly in portions with stirring. The temperature rose to 38° and the clear yellow solution was stirred for 2 minutes before 125 ml. of 30% fuming sulfuric acid was slowly added with the temperature maintained below 60° by external cooling. The mixture was stirred at 55-60° for 1 hour, then cooled to 25° and poured onto ice. The product was washed with water and methanol to give 37.3 g. of bright yellow solid, m.p. 324-325°. Crystallization from acetone-methanol gave bright yellow crystals which after drying at 130° for 3 hours reached a constant weight of 35.9 g. (86.9%), m.p. 327-328°; nmr (DMSO):  $\delta$  9.34 (s).

*Anal.* Calcd. for  $C_{16}H_4N_8O_{17}$ : C, 33.12; H, 0.69; N, 19.31. Found: C, 33.34; H, 1.00; N, 19.01.

#### 2,5-Dipicrylthiazole (Va).

To a well-stirred mixture of 58.4 g. (0.24 mole) of 2,5-dibromothiazole (9) and 137.4 g. (2.16 moles) of copper in 210 ml. of dry nitrobenzene at 145-150° was added a solution of 175.2 g. (0.6 mole) of picryl bromide in 270 ml. of dry nitrobenzene over a 20 minute period. The cooled reaction mixture was filtered and the insoluble material washed with warm acetone until the washings were nearly colorless. Steam distillation removed the solvents from the filtrate leaving a dark insoluble residue which was washed with hot methanol and then dissolved in hot acetone. The acetone solution was worked up according to the acetone-methanol procedure to give 79.0 g. of product, m.p. 324-326°. Recrystallization from acetone-methanol gave 72.1 g. (59.2%) of yellow crystals, m.p. 329-330°; nmr (DMSO):  $\delta$  9.22 (s, 1H, picryl-H), 9.21 (s, 1H, picryl-H), 8.08 (s, 1H, thiazole-H).

*Anal.* Calcd. for  $C_{15}H_5N_7O_{12}S$ : C, 35.51; H, 0.99; N, 19.33; S, 6.32. Found: C, 35.57; H, 1.30; N, 19.23; S, 6.12.

#### 2,5-Dipicryl-4-nitrothiazole (Vb).

Potassium nitrate (42 g., 0.375 mole) was added in portions with stirring to 100 ml. of 30% fuming sulfuric acid cooled below 60°. To this mixture was added 38.0 g. (0.075 mole) of 2,5-dipicrylthiazole rapidly in portions. The mixture was heated at 120-125° for 6.5 hours, then cooled to 40° and poured onto ice. The precipitate was washed with water and methanol to give 37.2 g. of product, m.p. 263-266°. Crystallization from acetone-

methanol gave 30.3 g. (73.2%) of yellow crystals, m.p. 269-270°; nmr (DMSO):  $\delta$  9.33 (s, 2H, picryl-H), 9.28 (s, 2H, picryl-H).

*Anal.* Calcd. for  $C_{15}H_4N_8O_{14}S$ : C, 32.62; H, 0.73; N, 20.29; S, 5.80. Found: C, 32.64; H, 1.00; N, 20.34; S, 5.61.

2,5-Dipicryl-1,3,4-oxadiazole (VIa) (5).

A mixture of 12.7 g. (0.025 mole) of *N,N'*-bis(2,4,6-trinitrobenzoyl)hydrazine (VIII) (see preparation below) and 24.8 g. (0.175 mole) of phosphorus pentoxide in 180 ml. of nitrobenzene was heated at 115-120° for 1 hour. The cooled mixture was combined with water and the nitrobenzene was removed by steam distillation. The residue was washed with water and methanol and then crystallized by the acetone-methanol procedure to yield 4.5 g. of yellow crystals, m.p. 326°. Recrystallization from acetone-methanol gave 4.1 g. (33%), m.p. 331° with violent decomposition; nmr (DMSO):  $\delta$  9.36 (s).

*Anal.* Calcd. for  $C_{14}H_4N_8O_{13}$ : C, 34.16; H, 0.82; N, 22.76. Found: C, 33.87; H, 1.14; N, 22.71.

An alternate method of preparation is as follows: phosphorus pentachloride (0.83 g., 0.004 mole) was added to 1.02 g. (0.002 mole) of *N,N'*-bis(2,4,6-trinitrobenzoyl)hydrazine stirred in 7 ml. of nitrobenzene at 80-90°; after 10 minutes at 80-90° the cooled mixture was poured into methanol to precipitate 0.4 g. of 2,5-dipicryloxadiazole.

2,5-bis(3-Methoxy-2,4,6-trinitrophenyl)-1,3,4-oxadiazole (VIb).

Nitric acid (90%) (40 ml.) was added to 80 ml. of 30% fuming sulfuric acid with cooling. To this well-stirred mixture was added 10.8 g. of 2,5-bis(3-methoxyphenyl)-1,3,4-oxadiazole (10) in portions at 10-15°. The reaction mixture was allowed to warm to 25° and then was heated at 45-50° for 30 minutes. The cooled mixture was poured onto ice and the product was removed by filtration and washed with water and dried. Tlc analysis showed the product was a complex mixture of compounds (presumably the tetranitro isomers) and that none of the hexanitro derivative (VIIb) was present. The weight of the product (16.5 g.) is 93% of the theoretical amount for nitration to the tetranitro stage. The product was added to a mixture of 50 ml. of 90% nitric acid and 150 ml. of 30% fuming sulfuric acid. Heating at 98° for 1.5 hours followed by cooling and pouring on ice yielded a solid which was crystallized by the acetone-methanol procedure to give 5.9 g. (27.8%) of yellow crystals, m.p. 205-206° dec. Two additional crystallizations from acetone-methanol gave the analytical sample, m.p. 211-212° dec.

*Anal.* Calcd. for  $C_{16}H_8N_8O_{15}$ : C, 34.79; H, 1.46; N, 20.28. Found: C, 34.87; H, 1.56; N, 20.26.

2,5-bis(3-Amino-2,4,6-trinitrophenyl)-1,3,4-oxadiazole (VIc).

To an ice cold solution of 1.7 g. of ammonia gas in 100 ml. of methanol was added 4.3 g. of 2,5-bis(3-methoxy-2,4,6-trinitrophenyl)-1,3,4-oxadiazole. The stirred mixture was slowly heated to the boiling point and methanol was distilled until the excess ammonia was expelled (when the vapors were only slightly basic to wet litmus paper). Methanol was added during the distillation to keep the volume of solvent approximately constant. The warm mixture was filtered to give 3.9 g. of yellow solid, m.p. 286° (violent dec.). The yellow solid was crystallized three times by dissolving in hot dimethylformamide, then adding methanol and cooling. The yield was 2.4 g. of bright yellow crystals, m.p. 317° (violent dec.); nmr (DMSO):  $\delta$  9.05 (s, 2H, picryl-H), 8.75 (s, 4H, NH<sub>2</sub>).

*Anal.* Calcd. for  $C_{14}H_6N_{10}O_{13}$ : C, 32.19; H, 1.16; N, 26.81. Found: C, 32.16; H, 1.31; N, 26.72.

Sodium nitrite (9 g.) was added to a solution of 100 ml. of acetic acid and 55 ml. of concentrated sulfuric acid cooled to -5°. Hypophosphorus acid (50%) (20 ml.), precooled to -5°, was added followed by 2.7 g. of 2,5-bis(3-amino-2,4,6-trinitrophenyl)-1,3,4-thiadiazole (VIIc) (see preparation below). The mixture was stirred at 0° for 48 hours and then poured into water but the precipitated product after crystallization from acetone-methanol still contained some unreacted starting material (by tlc analysis). The 1.2 g. of crystallized product (m.p. 235-247°) was treated as described above for an additional 7 hours. The product obtained (0.95 g., m.p. 245-250°) was crystallized twice from acetone-methanol to give 0.5 g. (20%) of a cream colored solid, m.p. 270-274°. An additional crystallization raised the melting point to 274-276°.

*Anal.* Calcd. for  $C_{14}H_4N_8O_{12}S$ : C, 33.08; H, 0.79; N, 22.05; S, 6.31. Found: C, 32.88; H, 0.94; N, 21.76; S, 6.52.

2,5-bis(3-Methoxy-2,4,6-trinitrophenyl)-1,3,4-thiadiazole (VIIb).

Nitric acid (90%) (160 ml.) was slowly added to 350 ml. of 30% fuming sulfuric acid with stirring and cooling. The nitric-sulfuric acid mixture was stirred at 10° during the addition of 25.6 g. of 2,5-bis(3-methoxyphenyl)-1,3,4-thiadiazole (11) in small portions. The mixture was allowed to warm to 20°, then was heated at 97-98° for 2 hours, cooled to 30°, and poured onto ice. The precipitated solid was washed with water and crystallized from acetone-methanol to give 26.2 g. (53.6%) of yellow crystals which softened and slowly decomposed above 220°. A sample repeatedly crystallized from acetone-methanol gave the same melting point behavior. Tlc analysis (silica gel) using benzene (90%)-ethyl acetate (10%) as developer showed only one spot.

*Anal.* Calcd. for  $C_{16}H_8N_8O_{14}S$ : C, 33.81; H, 1.42; N, 19.72; S, 5.64. Found: C, 33.82; H, 1.57; N, 19.75; S, 5.48.

2,5-bis(3-Amino-2,4,6-trinitrophenyl)-1,3,4-thiadiazole (VIIc).

An ice-cold solution of 4.0 g. of ammonia gas in 50 ml. of methanol was added all at once to a solution of 29.0 g. of 2,5-bis(3-methoxy-2,4,6-trinitrophenyl)-1,3,4-thiadiazole in 350 ml. of tetrahydrofuran stirred at ambient temperature. A precipitate quickly forms and after 15 minutes the mixture was heated to boiling and solvent distilled until the excess ammonia was removed (when the vapors were only slightly basic to wet litmus paper). Methanol was added during the distillation to keep the volume of solvent nearly constant. The reaction mixture was cooled to room temperature and the insoluble material (24.8 g., m.p. 340°, violent dec.) was dissolved in 300 ml. of dimethylsulfoxide at 100°. The solution was filtered and methanol (500 ml.) was added to the filtrate to precipitate 27.6 g. of bright yellow solid (m.p. 352° with violent decomposition, solvate with DMSO). The yellow solid was digested in one liter of boiling acetone for 2 hours, the mixture was cooled and the crystals removed. The acetone digestion was repeated to give 25.9 g. of bright yellow crystals which after drying 2 hours at 110° lost acetone of crystallization to yield 22.1 g. (80.2%) of crystals, m.p. 357° (violent dec.); nmr (DMSO):  $\delta$  9.04 (s, 2H, picryl-H), 8.58 (s, 4H, NH<sub>2</sub>).

*Anal.* Calcd. for  $C_{14}H_6N_{10}O_{12}S$ : C, 31.23; H, 1.12; N, 26.01; S, 5.96. Found: C, 31.41; H, 1.27; N, 26.00; S, 6.01.

*N,N'*-bis(2,4,6-Trinitrobenzoyl)hydrazine (VIII) (5).

A solution of 14.6 g. (0.255 mole) of 85% hydrazine hydrate in 75 ml. of methanol was added dropwise over a 40 minute period to 45.7 g. (0.166 mole) of 2,4,6-trinitrobenzoyl chloride stirred in 300 ml. of methanol at 25-30° (12). The mixture was neutralized with concentrated hydrochloric acid and the gray insoluble product was stirred with warm water (60°) for 15 minutes. The water-insoluble product was washed with methanol and then di-

solid, m.p. 262° dec. A sample (0.5 g.) of the cream colored solid was dissolved in boiling acetone (requires 150 ml.) and crystallized by the acetone-methanol procedure to give 0.4 g. of crystals, m.p. 263° dec.; nmr (DMSO):  $\delta$  12.13 (s, 2H, hydrazine-H), 9.15 (s, 4H, picryl-H).

*Anal.* Calcd. for  $C_{14}H_6N_8O_{14}$ : C, 32.95; H, 1.18; N, 21.96. Found: C, 33.10; H, 1.40; N, 21.99.

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#### REFERENCES AND NOTES

- (1) Author to whom correspondence should be addressed.
- (2) P. E. Fanta, *Chem. Rev.*, **38**, 139 (1946).
- (3) The nitro group activates a halogen atom toward the Ullmann reaction (reference 2).
- (4) Instances of direct nitration of 2,5-disubstituted furans to give 3,4-dinitro derivatives such as IVc are very rare. The furan ring is usually susceptible to oxidation by the nitrating medium unless stabilizing negative substituents are in the  $\alpha$ (2,5) positions. However, the negative substituents in the  $\alpha$  positions usually decrease the activity of the furan ring to the extent that dinitration will not occur. (F. N. Peters and A. P. Dunlop, "The Furans", Reinhold Publishing Corp., New York, N. Y., 1953, pp. 141-148).
- (5) G. P. Sharnin, B. I. Buzykin and R. Kh. Fassakhov, U.S.S.R. Patent 233,671; December 24, 1968, prepare VIa by subjecting VIII to cyclization in the presence of phosphorus oxychloride at the b.p. of the reaction mixture [*Chem. Abstr.*, **70**, 115162s (1969)]. Our attempts to prepare VIa from VIII employing refluxing phosphorus oxychloride or phosphorus oxychloride in high boiling solvents gave only trace amounts of VIa (by tlc analysis) even after prolonged reaction times. The Russian authors describe a preparation of VIII by treating 2,4,6-trinitrobenzoyl hydrazide with 2,4,6-trinitrobenzoyl chloride in dioxane at 50-60° [U.S.S.R. Patent 248,697, July 18, 1969] [*Chem. Abstr.*, **72**, 90089z (1970)]. The physical properties and yields of VIa and VIII are not given.
- (6) Aldrich Chemical Co.
- (7) N. W. Whittaker, *J. Chem. Soc.*, 1565 (1951).
- (8) 2,5-Dibromofuran was reported as a by-product in the preparation of 2-bromofuran from furan and *N*-bromosuccinimide [J. D. Prugh, A. C. Huitric and W. C. McCarthy, *J. Org. Chem.*, **29**, 1993 (1964)]. To favor formation of the desired 2,5-dibromofuran the ratio of *N*-bromosuccinimide to furan was increased. A mixture of 0.5 g. of *p*-toluenesulfonic acid, 37.4 g. (0.55 mole) of furan and 178 g. (1.0 mole) of *N*-bromosuccinimide in 335 ml. of dry benzene was cautiously heated to reflux temperature. An exothermic reaction began and cooling in ice was necessary to control the vigorous refluxing. Heating at gentle reflux was maintained for 30 minutes thereafter. The cooled mixture was filtered, extracted with aqueous sodium bicarbonate, dried over magnesium sulfate and then distilled to give 76.2 g. (67.4%) of 2,5-dibromofuran, b.p. 50-52° (10 mm).
- (9) H. C. Beyerman, P. H. Berben, and J. S. Bontekoe, *Rec. Trav. Chim.*, **73**, 329 (1954).
- (10) Treatment of an ether solution of 3-methoxybenzoyl chloride with 85% hydrazine hydrate gave *N,N'*-bis(3-methoxybenzoyl)-hydrazine, m.p. 191-193° (74% yield). Refluxing the hydrazine derivative in phosphorus oxychloride for 5 hours gave an 88% yield of 2,5-bis(3-methoxyphenyl)-1,3,4-oxadiazole, m.p. 98-100°, lit. m.p. 98-99°, Ya. A. Levin, M. S. Skorobogatova, *Khim. Ceterotsikl. Soedin.*, 1114 (1967); *Chem. Abstr.*, **69**, 59163h (1968).
- (11) CIBA Ltd., British Patent 899,842, June 27, 1962; *Chem. Abstr.*, **57**, 13767f (1962).
- (12) Other solvents (ether, tetrahydrofuran, and acetonitrile) were tried but methanol gave the best yields even though an obvious side reaction of the acid chloride with methanol can occur.