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HEAT RESISTANT EXPLOSIVES. XV. (U)

Alternate Synthetic Routes to 3,3'-Diamino-2,2',4,4',6,6'-hexanitrobiphenyl, DIPAM (C)

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NOL

UNITED STATES NAVAL ORDNANCE LABORATORY, WHITE OAK, MARYLAND

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HEAT RESISTANT EXPLOSIVES. XV. (U)
Alternate Synthetic Routes to 3,3'-Diamino-2,2',4,4',6,6'-hexanitrobiphenyl, DIPAM (C)

Prepared by: Robert E. Oesterling
Joseph C. Dacons
Lloyd A. Kaplan

ABSTRACT: DIPAM has been prepared from m-bromoanisole by a new three step synthesis involving the following reactions: m-bromoanisole to trinitro-m-bromoanisole which was in turn converted to dimethoxy hexanitrobiphenyl via the Ullmann reaction. Conversion of the dimethoxy derivative to DIPAM was readily achieved by treating it with ammonia in alcohol.

A second route, starting with m-bromoaniline via the sequence methyl m-bromophenylurethane to methyl trinitro-m-bromophenylurethane to the bis-methyl urethane of DIPAM to DIPAM was also attempted because of its simplicity. However the sole product isolated from this sequence was picramide. (C)

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

NOLTR 62-175 24 September 1962

This report describes a new method for the preparation of DIPAM, a new thermally stable high explosive which may be useful in mild detonating fuse for stage separation in advanced POLARIS missiles. This compound was previously described in NOLTR 62-82 which was Part XIII in the series Heat Resistant Explosives. The work described herein was carried out under Task FR-44.

R. E. ODENING
Captain, USN
Commander

Albert Lightbody
ALBERT LIGHTBODY
By direction

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HEAT RESISTANT EXPLOSIVES. XV.

INTRODUCTION

In a previous NOLTR (1) the preparation of a new, thermally stable high explosive 3,3'-diamino-2,2',4,4',6,6'-hexanitrobiphenyl, DIPAM, was described. This explosive was particularly interesting since not only was it relatively non-volatile at elevated temperatures and reduced pressures, but it was also found that its detonation would propagate in very small diameters and around corners. These latter two properties led to the testing of DIPAM for application in mild detonating fuse for use in stage separation in advanced Polaris missiles.

The preparation of DIPAM described previously (1) involved a six step synthesis which is described schematically in Fig. 1.

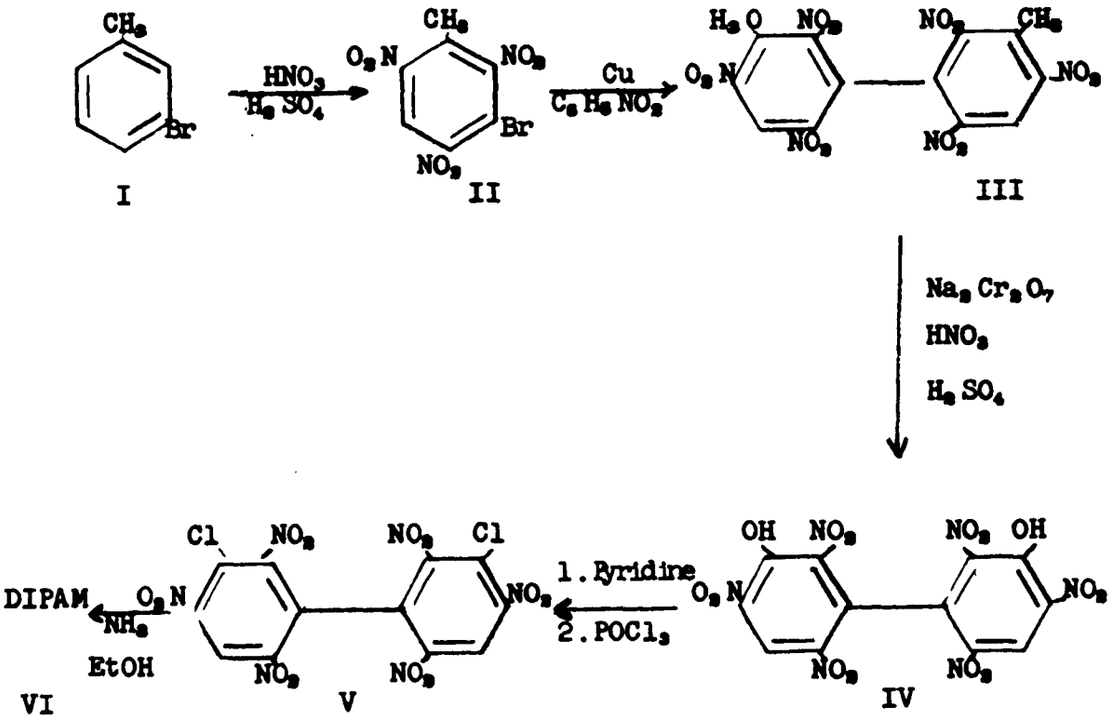

Figure 1

m-Bromotoluene was nitrated in a one step nitration with ninety percent nitric acid and 30 percent oleum by heating at reflux for several hours after first maintaining the mixture at 55° for several hours. The product II, generally obtained in recrystallized yields of 86 percent, was isolated by drowning in ice.

The conversion of the trinitro derivative II to 3,3'-dimethyl-2,2',4,4',6,6'-hexanitrobiphenyl, III, was accomplished by the Ullmann method which consists of heating a halogenated benzene derivative at about reflux temperatures in nitrobenzene with "activated" copper powder. In this instance, the procedures of Moyer, Bock, and Adams (2) were followed. The biphenyl III was generally isolated in yields of 77 percent after crystallization.

Oxidation of the biphenyl III to dipicric acid, IV, was accomplished by the procedure of Moyer, Bock, and Adams (2) utilizing a mixture of sodium dichromate, nitric and sulfuric acids. This procedure was shown (3) to yield dipicric acid and not the reported (2) 3,3'-dicarboxy-2,2',4,4',6,6'-hexanitrobiphenyl. The yields of IV obtained by this procedure were generally about 75 percent.

Conversion of IV to the dichloro derivative V was accomplished by reacting the dipyridinium salt of IV with phosphorus oxychloride. This technique involved treating IV with pyridine to form the dipyridinium salt which was isolated as a crystalline material in yields of 89 percent. The dipyridinium salt was then added to an excess of phosphorus oxychloride, after which the mixture was drowned in ice. This procedure afforded the dichloro derivative V in average yields of 99 percent from the dipyridinium salt.

Finally, conversion of the dichloro derivative V to DIPAM, VI, was readily accomplished by adding the dichloro derivative to a solution of ammonia in ethanol at 10°. A 90 percent yield of DIPAM was obtained upon recrystallization from acetone-ethanol.

The above sequence gave an overall yield of DIPAM of 39.4 percent. Although this synthesis was attractive from the standpoint of the rather excellent yields obtained in most of the steps, the multiplicity of procedures involved in the sequence is not only somewhat time consuming but also tends to reduce the overall yield of DIPAM obtained. Thus, it appeared reasonable to look at some other possible synthetic routes to DIPAM which would involve fewer steps.

DISCUSSION

Two possible alternate routes presented themselves for consideration. The first of these started with m-bromoaniline which was converted to the methyl urethane VII. Nitration of VII with mixed acid would yield the trinitro derivative VIII. Reacting VIII under Ullmann conditions, hopefully, would afford the bis-methyl urethane of DIPAM, IX, which could be readily hydrolyzed to DIPAM with sulfuric acid. This sequence is described in Figure 2.

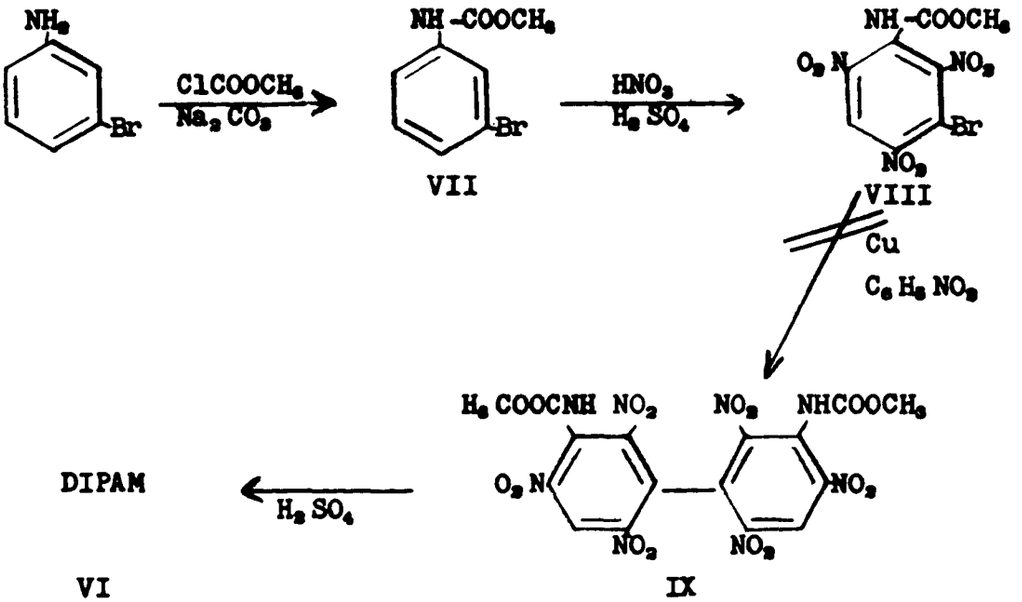

Figure 2

The interesting features of the above sequence are that it starts with the readily available m-bromoaniline* and all of the steps with the exception of the Ullmann reaction leading to the

* m-Bromoaniline can be readily prepared from m-bromonitrobenzene; the corresponding chloro compounds are available in commercial quantities.

biphenyl derivative IX have been carried out previously (4). Its disadvantage lies in the fact that the Ullmann reaction, when carried out with compounds containing "active hydrogen atoms", viz. carboxylic acids, phenols, etc., is reported to yield reduction products (5). Thus the reaction of the trinitro derivative VIII under Ullmann conditions might yield the methyl urethane of picramide as the sole product. This would perhaps occur by reaction of the "organo-copper" intermediate with the acidic hydrogen atom of the amine function of a second molecule. Hydrolysis of this reduction product with sulfuric acid would in turn afford picramide instead of DIPAM.

Conversion of m-bromoaniline to the methyl urethane VII was accomplished in 82 percent yield by refluxing the amine and methyl chloroformate in benzene with sodium carbonate. Nitration of the methyl urethane VII to the trinitro derivative VIII was readily effected in 66 percent yield by a modification of the procedure of de Monchy (4). When the trinitro derivative was subjected to Ullmann conditions, it was observed that reaction set in at about 150° as evidenced by the disappearance of the bright copper color in the reaction mixture. The reaction proceeded smoothly at this temperature and the solid material at the end of the reaction was found to consist of unreacted copper and cuprous halide. The organic product from this reaction, obtained in low yield, could not be crystallized to yield a sharp melting product. Therefore it was hydrolyzed directly with sulfuric acid to remove the urethane function. Workup of the hydrolysis mixture yielded picramide and not DIPAM, thus indicating that the Ullmann reaction did not take the normal path, but instead effected reduction of the trinitro-m-bromophenylurethane, VIII.

The second route selected did not suffer from the possibility that the Ullmann reaction would yield reduction products. This sequence, Figure 3, starts with the conversion

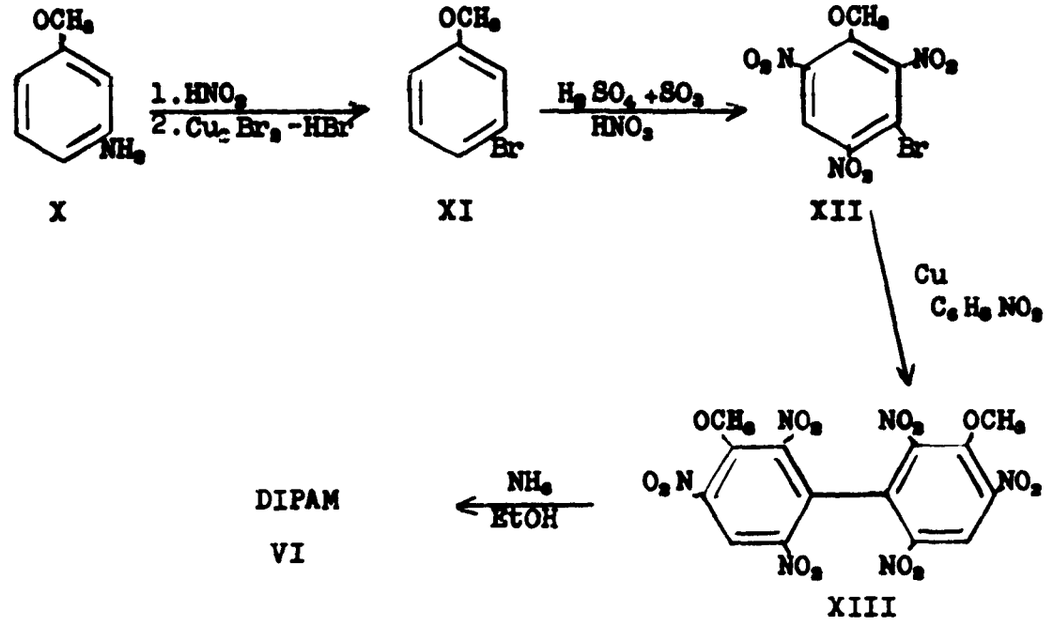

Figure 3

of m-anisidine, X, to m-bromoanisole, XI*, by means of the usual Sandmeyer reaction. In this instance, in a 75 percent yield. Nitration of XI to the trinitro derivative XII was effected in 74 percent yield (recrystallized, 88 percent crude) by a modification of the procedure of de Monchy (4). Reacting the trinitro derivative XII with activated copper powder under Ullmann conditions afforded a 78 percent recrystallized yield of the expected 3,3'-dimethoxy-2,2',4,4',6,6'-hexanitrobiphenyl, XIII. Finally, the dimethoxy derivative XIII was readily converted to DIPAM in 91 percent yield by treating it with alcoholic ammonia. The DIPAM so obtained melted at 295-96° without recrystallization; an authentic sample melted at 296-97° (simultaneous determination) and gave no depression on admixture with the product obtained by the above sequence of reactions.

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*m-Bromoanisole can also be prepared in 75 percent yield by the methylation of m-bromophenol (6). However, m-bromophenol is about four times more expensive than m-anisidine.

Thus, it was possible to prepare DIPAM by a four-step synthesis starting from m-anisidine* in a 39.4 percent overall yield.

It should be noted that the above sequence leading to DIPAM was carried out in such a manner as to test the feasibility of the method. No attempt was made to optimize reaction conditions so as to obtain the maximum possible yields in each of the steps in the synthetic path. Undoubtedly, higher yields could be obtained in the nitration of m-bromoanisole to the trinitro derivative XII as evidenced by the 14 percent loss on purification of the nitration product. It is also probable that the yields obtained in the conversion of m-anisidine to m-bromoanisole and the coupling of the trinitro derivative XII to the biphenyl XIII could be increased somewhat by optimizing these reaction conditions.

A modification of the synthetic path described in Figure 3 starts with the more readily available resorcinol monomethyl ether. Nitration of the monomethyl ether of resorcinol under the appropriate conditions ** would afford 3-methoxy-2,4,6-trinitrophenol. Conversion of 3-methoxy-2,4,6-trinitrophenol to the chlorine analog of the trinitro derivative XII could probably be accomplished by means of the pyridine-phosphorus oxychloride method previously described (1). The chlorine analog of XII, 3-chloro-2,4,6-trinitroanisole, would then be reacted with copper powder under Ullmann conditions to yield the biphenyl XIII which in turn would be aminated to DIPAM with ammonia in alcohol.

Although this sequence requires the same number of steps as the route starting with m-anisidine, resorcinol monomethyl ether costs about one half as much as m-anisidine in research quantities***. Therefore, the per pound cost of DIPAM

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* m-Anisidine is currently available in research quantities at a price of $16.00 per 100 grams. It could undoubtedly be made more cheaply on a larger scale by the sequence: m-nitroaniline to m-nitrophenol to m-nitroanisole which can be reduced in 80 percent yield to m-anisidine (7).

**The conditions used for this nitration would undoubtedly be similar to those used in the nitration of phenol to picric acid or resorcinol dimethyl ether to trinitroresorcinol dimethyl ether (8).

***In large scale production, the cost of resorcinol monomethyl ether would be reduced even more than that of m-anisidine since its preparation involves a one-step reaction starting with $0.75 a pound resorcinol.

prepared by this route would be less than that prepared by the sequence described in Figure 3. This proposed synthesis will be tested in the future and the results will be the subject of a forthcoming NOLTR.

EXPERIMENTAL

m-Bromoanisole (XI) was prepared by a modification of the method used for the preparation of p-bromotoluene from p-toluidine (9). In the preparation of XI an equivalent amount of hydrobromic acid was used in place of sulfuric acid for the diazotization of m-anisidine. From 0.32 mole of m-anisidine there was obtained 0.24 mole (45 g - 75%) of m-bromoanisole; b. 209-12°.

3-Bromo-2,4,6-trinitroanisole (XII) was prepared by adding 0.1 mole (18.7 g) of m-bromoanisole dropwise to a stirred mixture of forty grams of 100% nitric acid and 50 ml of 30% oleum at 35 to 45°. During the addition of the anisole, the yellow trinitro derivative XII separated as a solid from the nitrating medium. After the addition of the anisole was completed, the mixture was stirred for an additional 20 minutes at 30 to 40°.

The reaction mixture was then poured into 500 ml of ice and water and the yellow granular solid that separated was filtered off with suction after all of the ice had melted. The crude product was washed several times with water and then dried in air to give 28.5 g (88%) of crude XII. Recrystallization from hexane-benzene gave 23.5 g (74%) bright yellow-orange crystals; m. 96-7° (lit. (10) 97°).

Anal. calc'd for $C_7H_4BrN_3O_7$; C, 26.08; H, 1.24; N, 13.04.

Found; C, 26.30; H, 1.34; N, 12.81 λ_{max}^{MeOH} (ε), 247 (13,880).

3,3'-Dimethoxy-2,2',4,4',6,6'-hexanitrobiphenyl (XIII) was prepared by heating a solution of 0.05 mole (16.1 g) of 3-bromo-2,4,6-trinitroanisole in 50 ml of nitrobenzene to 155°. After this temperature had been reached, 7 g of activated copper powder (1) was added in small portions with continual stirring over a period of 30 minutes while maintaining the temperature at 160-65°. The dark brown reaction mixture was stirred for an additional 15 minutes at this temperature after the addition of the copper was completed.

At the end of this time, the mixture was filtered with suction while hot and the solids washed thoroughly with acetone. The combined filtrates and washings were steam distilled until nitrobenzene could no longer be detected in the distillate.

After decanting the water from the residue remaining in the flask, it was dissolved in 200 ml of acetone, treated with Darco charcoal, and evaporated to a volume of about 50 ml. Water was added to the hot concentrate till the cloud point and the solution cooled to 0°. The yellow solid that separated was filtered and dried in air. It was purified further by redissolving it in 50 ml of acetone, treating with Darco, and adding 50 ml of ethanol. The resulting solution was concentrated by boiling until precipitation begins. The mixture was then cooled to 0° and filtered to yield 9.5 g (78%) of 3,3'-dimethoxy-2,2',4,4',6,6'-hexanitrobiphenyl; m. 187-90°. Recrystallization from benzene gave pale yellow crystals; m. 194-95°. The product melting at 190° was considered sufficiently pure for the amination step which follows.

Anal. calc'd. for $C_{14}H_8N_6O_{14}$; C, 34.71; H, 1.65; N, 17.4.

Found; C, 34.92; H, 2.98; N, 17.9. λ_{max}^{MeOH} (ε), 243 (28,900).

Amination of 3,3'-dimethoxy-2,2',4,4',6,6'-hexanitrobiphenyl (XIII) to DIPAM (VI). Dry, gaseous ammonia was passed into a stirred mixture of 0.00414 mole (2.00 g) of the dimethoxy derivative XIII in 25 ml of absolute ethanol at room temperature. The mixture became dark red at first and then an orange product separated out. When an excess of ammonia was apparently present, the ammonia flow was stopped and the mixture boiled for ten minutes and then cooled to 0° in ice. The material which separated was filtered off with suction to yield 1.7 g (91%) of a yellow granular solid. After washing with ethanol, it was dried in vacuo at 100°; m. 295-96°. Authentic sample of DIPAM; m. 296-97° (simultaneous determination). The DIPAM obtained in this experiment gave no depression in melting point when mixed with an authentic sample.

Methyl 3-bromophenylurethane (VII) was prepared by refluxing a mixture of 0.22 mole (20.8 g) of methyl chloroformate, 0.20 mole (34.4 g) of m-bromoaniline, and 0.4 mole (42.2 g) of anhydrous sodium carbonate in 500 ml of benzene for 2.5 hours. The mixture was initially quite thick (amine hydrochloride) and as the reaction proceeded, thinned out to a suspension of inorganic salts in benzene. After the requisite time under reflux, the mixture was filtered hot and the filtrates were evaporated to dryness in vacuo. The residue was recrystallized from methanol-hexane to yield 37.7 g (82%) of white plates melting at 86-6.5° (lit. (4) 84°).

Methyl 3-bromo-2,4,6-trinitrophenylurethane (VIII) was prepared by a modification of the procedure of de Monchy (4). One tenth of a mole (23 g) of methyl 3-bromophenylurethane was dissolved in 50 ml of concentrated sulfuric acid while maintaining the temperature at 10° or lower. There was apparently no hydrolysis of the urethane function during this step as evidenced by the lack of carbon dioxide evolution from the solution. The resulting solution was added to a previously prepared mixture of 138 ml of concentrated sulfuric acid and 138 ml of 100% nitric acid which had been cooled to 0-10° in ice. The rate of addition of the urethane solution was such that the temperature was maintained between 5 and 10° during the addition. Following the completion of the addition, the resulting orange solution was stirred at 15-20° for 0.75 hour. During this period, a white solid separated (trinitro derivative VIII) and the mixture turned progressively yellower.

At the end of this time, the mixture was poured onto an excess of ice with stirring, and after the ice had melted, the solid which had separated was collected on a sintered glass funnel. The pale yellow solid was washed with water until neutral and recrystallized from methanol. There was obtained 24.1 g (66%) of an almost white solid; m. 226-228° uncorr. (lit. (4) 230°).

Attempted preparation of 2,2',4,4',6,6'-hexanitro-3,3'-di(carbamylmethyl)biphenyl (IX). In a one-liter flask fitted with a thermometer, stirrer, and solids addition funnel was placed 0.04 mole (14.6 g) of methyl 3-bromo-2,4,6-trinitrophenylurethane and 100 ml of nitrobenzene. The mixture was heated to 120° and a water pump vacuum was applied to distill off part (5 to 10 ml) of the nitrobenzene. This operation was carried out to "dry" the reaction mixture.

The solids addition funnel was placed back in the flask and a one gram portion of activated copper (1) from the total amount, 0.16 mole (10.16 g), was added. The temperature of the reaction mixture was raised slowly until evidence that reaction was occurring was observed (150°). At this point the remainder of the copper was added portionwise while keeping the temperature at 150°. After the addition was complete, the mixture was held at this temperature for an additional fifteen minutes.

At the end of this time the mixture was filtered hot with suction and the collected solids were washed thoroughly with acetone. The combined washings and filtrate were evaporated

in vacuo to remove the solvent and the solids remaining were taken up in acetone and treated with Norit to yield a dark red solution. The solution was evaporated to dryness and the residue titrated with ether. On filtering the slurry there was obtained about four grams of a tan amorphous solid; m. 169-72°. This product could not be purified by recrystallization.

The tan product was therefore hydrolyzed directly by heating it with 30 ml of concentrated sulfuric acid. At about 120° gas evolution (carbon dioxide) commenced. The mixture was heated at 120-40° until gas evolution ceased and then poured onto ice after cooling to about 50°. The yellow-brown product which separated was recrystallized from ethanol (Norit) to yield a yellow crystalline solid; m. 188-89.5°. No depression on admixture with an authentic sample of picramide.

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DESCRIPTORS	CODES	DESCRIPTORS	CODES	DESCRIPTORS	CODES
Heat-resistant	HEAA	Derivative	DERI		
Explosives	EXPL	Ammonia	AMMO		
Diamino	DIAM	Alcohol	ALCO		
Hexa	HEXA	Aniline	ANIL		
Nitro	NITRO	Methyl	METY		
Diphenyl	DIPH	Phenyl	PHEY		
Synthesis	SYNS	Urethane	URET		
Bromo	BROO	Bis	BISE		
Anisole	ANSL	Picramide	PCRM		
Trinitro	TRIT				
Dimethoxy	DIMH				
Conversion	CNVE				

PRNC-NOL-5070/28 (5-62)

Naval Ordnance Laboratory, White Oak, Md.
(NOL technical report 62-175)
HEAT RESISTANT EXPLOSIVES. XV. (U) ALTERNATE SYNTHETIC ROUTES TO 3,3'-DIAMINO-2,2',4,4',6,6'-HEXANITROBIPHENYL, DIPAM (C), by Robert E. Oesterling and others. 24 Sept. 1962. 11p. diagr. NOL task FR-44 CONFIDENTIAL

DIPAM has been prepared from m-bromoanisole by a new three step synthesis involving the following reactions: m-bromoanisole to trinitro-m-bromoanisole which was in turn converted to dimethoxy hexanitrobiphenyl via the Ullmann reaction. Conversion of the dimethoxy derivative to DIPAM was readily achieved by treating it with ammonia in alcohol.

Abstract card is confidential

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1. Explosives, Heat resistant
2. 3,3'-Diamino-2,2',4,4',6,6'-hexanitrobiphenyl
3. Explosives-Production

I. Title
II. Title: Alternate synthetic routes to DIPAM
III. Oesterling Robert E.
IV. Project

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(NOL technical report 62-175)
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Abstract card is confidential

DOWNGRADED AT 3 YEAR INTERVALS: DECLASSIFIED AFTER 12 YEARS DOD DIR 5200.10.

1. Explosives, Heat resistant
2. 3,3'-Diamino-2,2',4,4',6,6'-hexanitrobiphenyl
3. Explosives-Production

I. Title
II. Title: Alternate synthetic routes to DIPAM
III. Oesterling Robert E.
IV. Project

Naval Ordnance Laboratory, White Oak, Md.
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