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HEAT RESISTANT EXPLOSIVES, XI. AN UNUSUAL OXIDATION REACTION LEADING TO 3,3'-DIHYDROXY-2,2',4,4',6,6'-HEXANITROBIPHENYL (DIPICRIC ACID, DIPA) (C)

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NOLTR 62-32

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ABSTRACT: The oxidation of 3,3'-dimethyl-2,2',4,4',6,6'-hexanitrobiphenyl (I) with a dichromate-oleum-nitric acid mixture has been found to yield dipicric acid (III) rather than 3,3'-dicarboxy-2,2',4,4',6,6'-hexanitrobiphenyl (II) as reported by Adams and coworkers[2]. The replacement of a methyl group by hydroxyl under these oxidizing conditions appears to be general for trinitrotoluene derivatives but not for dinitrotoluenes or other alkyl trinitrobenzenes. The potentialities of DIPA as a high temperature explosive are discussed.

CHEMISTRY RESEARCH DEPARTMENT
U. S. Naval Ordnance Laboratory
White Oak, Silver Spring, Maryland

NOLTR 62-32 26 February 1962

This report describes an unusual oxidation reaction of trinitrotoluene derivatives and some interesting high temperature explosives derived therefrom. The work was done in an effort to show further relationships between molecular structure, high temperature resistance, and sensitivity of organic nitro compounds, (FR-44 and RUME-3E012). The examination of the materials for their explosive behavior was carried out under the "Explosive Properties" task, RUME 3E017

W. D. COLEMAN
Captain, USN
Commander

Albert Lightbody
ALBERT LIGHTBODY
By direction

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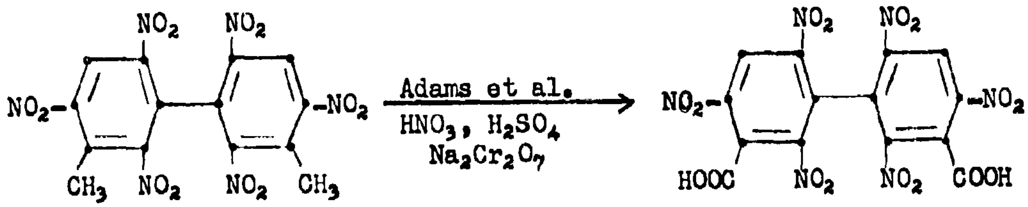
INTRODUCTION

In the course of their classic studies on optical activity due to restricted rotation in ortho-substituted biphenyls[1], Roger Adams and coworkers reported the synthesis and resolution of 3,3'-dicarboxy-2,2',4,4',6,6'-hexanitrobiphenyl (II)[2]. Their preparative method involved the oxidation of 3,3'-dimethyl-2,2',4,4',6,6'-hexanitrobiphenyl (I) with a mixture of oleum, nitric acid and sodium dichromate; the only departure from standard procedure involved the presence of the nitric acid in the oxidizing medium.



I

II

Oxidations of polynitrotoluenes to the correspondingly substituted polynitrobenzoic acids through the agency of dichromate and sulfuric acid are long-known and fairly routine. Such, for example, is the preferred method for the manufacture of 2,4,6-trinitrobenzoic acid from TNT[3,4]. Although not explicitly stated, it seems likely that the Adams group had first tried this routine method and found, as has been our own experience, that I is surprisingly unreactive under a wide variety of conditions.

Plagued by poor elemental analyses[5] and lacking the spectrophotometric tools now routinely used, Adams and coworkers had little reason to doubt that the product obtained on adding nitric acid to the dichromate-sulfuric oxidizing medium was the anticipated II. It was, as expected, a strong acid and readily resolvable into optical antipodes. The only evidence which in retrospect might have cast doubt on the structure assignment was the relative stability of the product to conditions wherein other trinitrobenzoic acid derivatives undergo ready decarboxylation[6].

HEAT RESISTANT EXPLOSIVES XI.

INTRODUCTION

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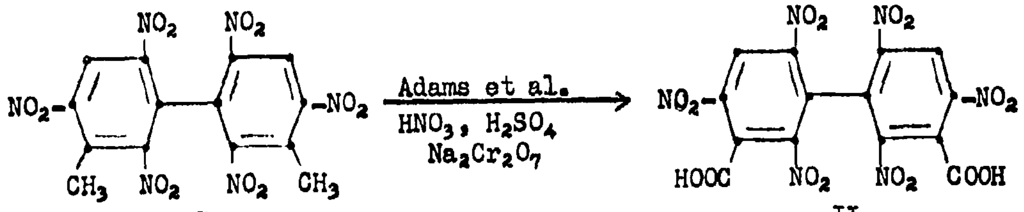

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DISCUSSION

Prompted by a continuing interest in polynitropolyphenyls for specialized high explosive applications[7] we repeated the Adams procedure[2]. This in our hands afforded 70-80% of a material whose properties resembled those described (colorless needles from benzene, turning yellow in moist air), but whose melting point, 311-312° (dec.) was somewhat higher than reported, 292-293° (dec.). The strong dependence of the decomposition point of our sample on minor amounts of impurities led us to believe that we were dealing with the same product as had been obtained by Adams et al.

Infrared and ultraviolet spectra furnished the first strong evidence that the assigned structure II was incorrect and that the product was instead 3,3'-dihydroxy-2,2',4,4',6,6'-hexanitrobiphenyl (dipicric acid, DIPA, III). The infrared spectrum was characterized by the complete absence of absorption in the carbonyl region; 2,4,6-trinitrobenzoic acid and 3-hydroxy-2,4,6-trinitrobenzoic acid, for comparison, show strong characteristic bands at 1722 and 1715 cm^{-1} respectively (Fluorolube mull).

In the ultraviolet it had been our experience that spectra of non-coplanar polynitropolyphenyls resemble summations of the monophenyl moieties with maxima shifted slightly to the red for reasons which will be detailed in a subsequent report. Thus, for example, I and 2,2',4,4',6,6'-hexanitrobiphenyl show λ_{max} 12 and 13 mμ higher than 2,4,6-trinitrotoluene and 1,3,5-trinitrobenzene respectively with ε_{max} in each case almost twice as large. Judging from $\lambda_{max} < 217$ for 2,4,6-trinitrobenzoic acid the primary band maximum for II would be expected to fall in the 225-240 mμ region with little absorption above 280 mμ.

As is shown in Table I, the oxidation product exhibited an intense longer-wavelength band with a maximum at 331 mμ in a non-ionizing solvent and at 365-368 mμ in ionizing solvents. although completely inconsistent with structure II, these spectra did give the first clue to the true nature of the oxidation product since they bore a relationship to the spectra of picric acid in ionizing and non-ionizing solvents such as would be expected of structure III.

TABLE I

ULTRAVIOLET ABSORPTION SPECTRA

	Solvent	λ_{max}, mμ	log ε
1,3,5-trinitrobenzene	EtOH[a]	225	4.41
2,2',4,4',6,6'-hexanitrobiphenyl	MeOH, 2% MeCN	238	4.64
2,4,6-trinitrotoluene	EtOH[b]	227	4.29
3,3'-dimethyl-2,2',4,4',6,6'-hexanitrobiphenyl (I)	MeOH	239	4.57
	MeCN	242	4.56
2,4,6-trinitrobenzoic acid	MeOH	<217	>4.33
picric acid	H_2O[c]	357.5	4.16
	EtOH, HCl[b]	335	3.73
	Isooctane[d]	230 254 340	4.23 4.18 3.62
dipicric acid (III)	H_2O	255s 368	4.29 4.44
	MeOH	255s 365	4.34 4.37
	MeCN	260 331	4.53 3.99

---

[a] P. Fielding and R. J. W. LeFevre, J. Chem. Soc., 1950, 2812.

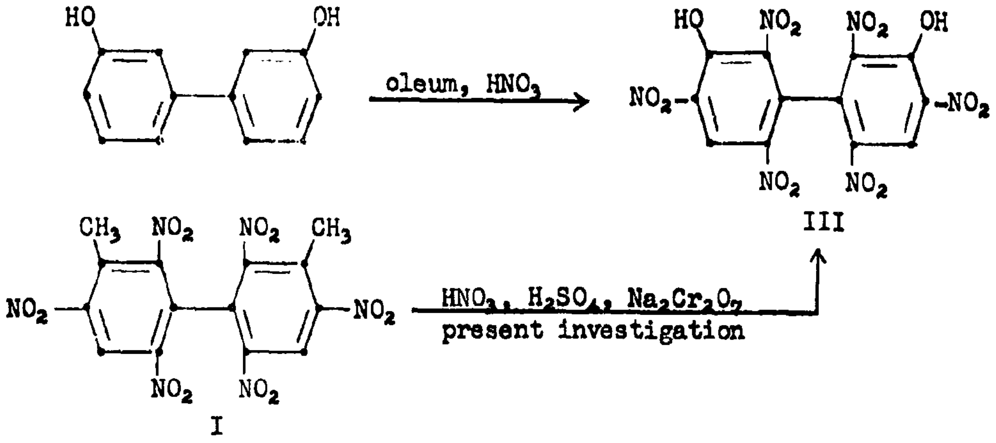
[b] W. A. Schroeder, P. E. Wilcox, K. N. Trueblood and A. O. Dekker, Anal. Chem., 23, 1740 (1951).

[c] J. D. Teresi, J. Am. Chem. Soc., 72, 3972 (1950).

[d] C. E. Moore and R. Peck, J. Org. Chem., 20, 673 (1955).

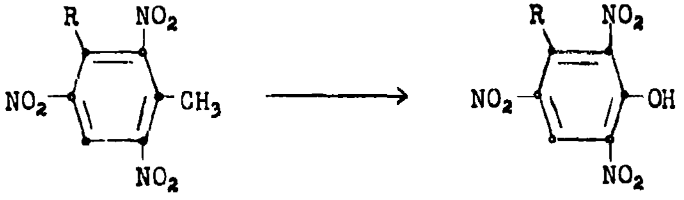
Other evidence corroborated that the dichromate-nitric-sulfuric oxidation product of I had the structure of dipicric acid. Spectrophotometric measurements showed it to be a strong acid, half-neutralized in 5N hydrochloric acid; neutralization equivalents, albeit poor[5], showed it to be dibasic. On treatment with pyridine in ethanol it yielded 91% of a dipyridinium salt which with phosphorus oxychloride was converted in 99% yield to a dichloro derivative. The dichloro derivative showed no carbonyl band in the infrared and gave elemental analyses which were consistent with 3,3'-dichloro-2,2',4,4',6,6-hexanitrobiphenyl (IV). The latter compound on treatment with excess ammonia in ethanol afforded 92% of a compound which similarly showed no carbonyl band in the infrared and whose elemental analyses and ultraviolet spectrum were consistent with 3,3'-diamino-2,2',4,4',6,6'-hexanitrobiphenyl (dipicramide, DIPAM, V). These transformations will be discussed in greater detail in a subsequent report[8].

Final confirmation of the structure was achieved by independent synthesis. Mixed acid nitration of 3,3'-dihydroxybiphenyl at 100°C. according to the procedure of Mascarelli and Visintin[9] yielded an authentic sample of III, m.p. 310-311° (dec.). Ultraviolet and infrared spectra were identical with those of the oxidation product of I and there was no depression in melting point on admixture of samples.



For reasons which will be discussed below and in a subsequent report[8] we had occasion to prepare a relatively large amount of DIPA. On working up mother liquors from purification of the oxidation product of 1082 g. I, small amounts ($<$ 1%) of a second reaction product were isolated. From its reactions (vide infra), neutralization equivalent, elemental analyses, infrared spectrum (no carbonyl) and ultraviolet spectrum which resembled a summation of the spectra of trinitrobenzene and picric acid, it was concluded that this second product had the structure 3-hydroxy-2,2',4,4',6,6'-hexanitrobiphenyl (m-picrylpicric acid, PIPA, VI). Whereas in the formation of III both methyl groups of I had been replaced by hydroxyl, in the formation of VI one had been replaced by hydroxyl, one by hydrogen.

The replacement of the methyl group in trinitrotoluene derivatives by hydroxyl through the agency of dichromate-nitric-sulfuric acids appears to be a fairly general reaction. Thus, under conditions similar to those used by Adams et al., TNT furnished 85% picric acid; 3-bromo-2,4,6-trinitrotoluene yielded 28% bromopicric acid, identified by comparison with an authentic sample prepared by nitration of m-bromophenol; 2,4,6-trinitro-m-cresol yielded 7% trinitroresorcinol with 40% recovery of starting material[10].



R = H, OH, Br

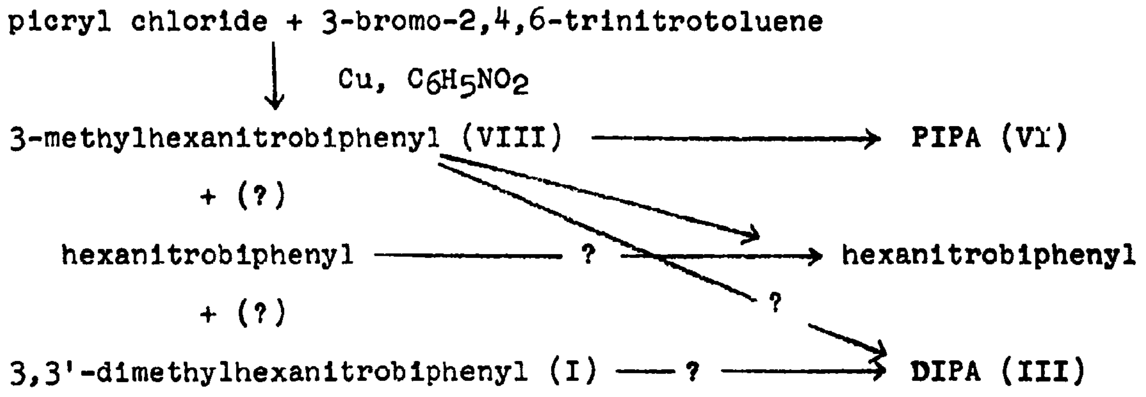
An exception was observed in the case of 1-t-butyl-3,5-dimethyl-2,4,6-trinitrobenzene (xylene musk), no phenolic species being isolated. This material furnished 20-25% of a still unidentified neutral compound, m.p. 210° (dec.) together with 1% 1-t-butyl-3,5-dicarboxy-2,4,6-trinitrobenzene (VII). The latter compound showed end absorption in the ultraviolet and in the infrared a split carbonyl band with maxima at 1700 and 1725 cm^{-1}. The identity of VII was confirmed by decarboxylation in boiling aqueous solution to form 1-t-butyl-2,4,6-trinitrobenzene identical with a sample prepared by the nitration of t-butylbenzene.

The oxidation of 3-methyl-2,2',4,4',6,6'-hexanitrobiphenyl (VIII) led to some interesting problems. This material, prepared by the mixed Ullmann reaction of 3-bromo-2,4,6-trinitrotoluene and picryl chloride with copper, gave satisfactory elemental analyses and a sharp melting point which did not change on repeated recrystallization. We were never quite sure, however, that it did not contain as contaminants approximately equal amounts of hexanitrobiphenyl and dimethylhexanitrobiphenyl (I).

The main oxidation product, isolated in about 53% yield, was 2,2',4,4',6,6'-hexanitrobiphenyl identified by comparison with an authentic sample from the Ullmann reaction of picryl chloride. Such a quantity was too great to have been carried over in the starting material and it is likely that it was formed by a reaction ($CH_3 \longrightarrow H$) such as led to the formation of the monohydroxy derivative VI as a by-product in the oxidation of the dimethyl derivative I.

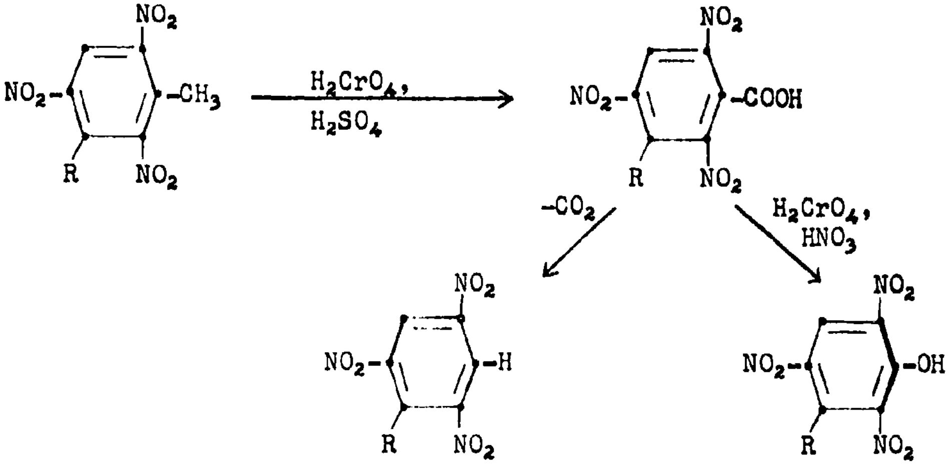
The expected product, PIPA, (VI, _vide supra_) was recovered in 16% yield. Its identification has already been discussed. The conversion of this material to a pyridinium salt and thence to 3-chloro-2,2',4,4',6,6'-hexanitrobiphenyl and the Ullmann reaction of the latter compound to form 3,3'-bis(2,4,6-trinitrophenyl)-2,2',4,4',6,6'-hexanitrobiphenyl (dodecanitroquaterphenyl) will be the subject of a separate report[11].

A third product, which came as somewhat a surprise was dipicric acid (III). From the amount isolated, 2%, we cannot state with certainty whether it derived from dimethylhexanitrobiphenyl which was present as an impurity in the starting material or whether a reaction took place wherein hydrogen in an unsubstituted position was replaced by hydroxyl. We have observed no other unambiquous instances of the latter type of reaction under such conditions, but from the care expended in purifying VIII we feel that it is the most likely possibility. The reactions which may have taken place are detailed below:



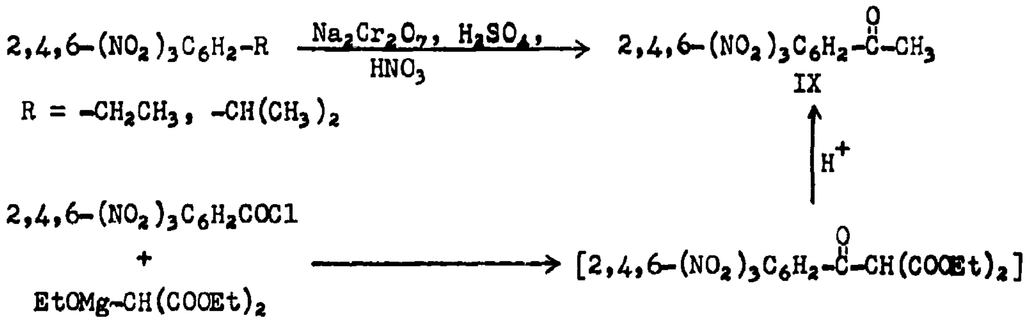
In the simpler cases mentioned above, the nitric acid:sulfuric acid ratio could be varied over a rather wide range with apparently little effect on the course of the reaction. Using trinitrotoluene as substrate the yields of picric acid ranged from 60 to 85% as this ratio was changed from 1:3 to 30:1. In the complete absence of sulfuric acid, however, the oxidation rate dropped sharply and no picric acid could be isolated. In the complete absence of nitric acid we of course had the classical conditions for oxidation to the carboxylic acid[3,4] and trinitrobenzoic acid was, indeed, the only product.

Although we cannot yet offer a detailed mechanism, some insight into the course of this unusual replacement of the methyl group by hydroxyl is given by the fact that trinitrobenzoic acid, dissolved in strong nitric acid or in a mixture of nitric acid with oleum, on treatment with sodium dichromate reacted smoothly to give an 85-87% yield of picric acid, the dichromate being reduced to chromium-III. The reaction did not take place in the absence of dichromate nor was potassium permanganate or potassium chlorate an effective substitute. It is therefore quite likely that the carboxylic acid is an intermediate and that chromic and nitric acids convert it to the phenol. This would explain the formation of PIPA (VI) concurrently with DIPA (III) and of hexanitrobiphenyl concurrently with PIPA. The demethylated products might arise from decarboxylation rather than oxidation of the common intermediate.



The dinitrotoluenes furnished the same products with dichromate-nitric-sulfuric acid mixtures as with dichromate-sulfuric acid alone, the 2,4- and 2,6-isomers being converted to the correspondingly substituted benzoic acids in 57 and 34% yields respectively[12]. Nor were phenolic products obtained with the higher alkyl homologs of TNT. 1-Ethyl-2,4,6-trinitrobenzene yielded 85% of a non-acidic species (IX); the same species was obtained in 35% yield together with small amounts of a product of as yet unidentified structure from 1-isopropyl-2,4,6-trinitrobenzene. The presence in the infrared of a strong carbonyl band at 1710 cm^{-1} together with excellent elemental analyses were consistent with IX having the structure of 2,4,6-trinitroacetophenone, but physical properties did not correspond with those reported for the latter compound by Sonn and Bulow[13].

These workers had reported 2,4,6-trinitroacetophenone as a reaction product of trinitrobenzaldehyde and diazomethane, giving as evidence for its structure a nitrogen analysis and the formation of a phenylhydrazone. Although they reported that their product was orange-red, an improbable color for trinitroacetophenone, it appeared that confirmation of the structure of IX required independent synthesis. This was accomplished by reacting trinitrobenzoyl chloride with ethoxymagnesium malonic ester[14] to form trinitrobenzoylmalonic ester. This was not isolated. Hydrolysis of the reaction mixture with propionic and sulfuric acids furnished 20% of a product whose infrared spectrum and melting point were identical with those of IX and which gave no depression in melting point on admixture with IX.



$$2,4,6\text{-}(NO_2)_3C_6H_2\text{-}R \xrightarrow[HNO_3]{Na_2Cr_2O_7,\ H_2SO_4,} 2,4,6\text{-}(NO_2)_3C_6H_2\text{-}\overset{O}{\overset{\|}{C}}\text{-}CH_3$$

IX

$R = -CH_2CH_3,\ -CH(CH_3)_2$

$$2,4,6\text{-}(NO_2)_3C_6H_2COCl + EtOMg\text{-}CH(COOEt)_2 \longrightarrow [2,4,6\text{-}(NO_2)_3C_6H_2\text{-}\overset{O}{\overset{\|}{C}}\text{-}CH(COOEt)_2] \xrightarrow{H^+} IX$$

1-t-Butyl-2,4,6-trinitrobenzene reacted less readily with the oxidizing mixture. On prolonged treatment it was mainly degraded to not readily isolable fragments.

DIPA, A THERMALLY STABLE BOOSTER EXPLOSIVE

Dipicric Acid (III) has been known for over forty-five years, but has not to our knowledge previously been considered for explosives applications. It was first prepared by Borsche[15] by the mixed acid nitration of 3,3'-dihydroxybiphenyl; Mascarelli and Visintin improved the procedure by first sulfonating then nitrating, but yields were still poor[9]. A primary drawback to this method of preparation of III was the relative difficulty in obtaining the dihydroxybiphenyl. Three routes to the latter compound have been described[9] beginning respectively with o-bianisidine, 3,3'-dinitrobenzidine and benzidine-3,3'-disulfonic acid. All were tedious and suffered extremely poor yields.

The present method from dimethylhexanitrobiphenyl (I) is far more convenient and makes DIPA for the first time a practicably obtainable material. Preparation of I involves the sequence:

p-toluidine → p-acetotoluidide → 4-acetylamino-3-bromotoluene

→ 4-amino-3-bromotoluene → m-bromotoluene $\xrightarrow[\text{nitration}]{\text{mixed acid}}$

2,4,6-trinitro-m-bromotoluene (88%) $\xrightarrow[\text{Cu, } C_6H_5NO_2]{\text{Ullmann Reaction}}$

3,3'-dimethyl-2,2',4,4',6,6'-hexanitrobiphenyl (I, 81%)

The steps through m-bromotoluene are reported in an "Organic Syntheses" procedure[16]; overall yields are fair. m-Bromotoluene is offered by the Distillation Products Industries Division of Eastman Kodak Company at $11.00 per 100 g. Improved methods for the conversion of m-bromotoluene to I will be detailed in a subsequent report[8].

In any consideration of DIPA as an explosive material it is necessary first to emphasize its one primary disadvantage. It is a strong acid of pK_a = ca. -0.5. Coupled with its high solubility in water, this suggests that DIPA would be corrosive with metals. It is further likely that the DIPA metal salts formed as a consequence of this corrosion process would, in common with the metal salts of picric acid, be extremely sensitive. Contact with metals would need to be stringently excluded as, for example, by enclosing the DIPA in a Teflon or other plastic liner.

TABLE II

PROPERTIES OF DIPA

Molecular Formula: $C_{12}H_4N_6O_{14}$

Oxidant Balance: $OB_{100} = 0.0$ (balanced to CO and H_2O)

Heat of Detonation: For compounds balanced at or near the carbon monoxide level, performance is a strong function of loading density[17]. Using the H_2O, CO, CO_2 arbitrary for calculation, DIPA would be expected to have a heat of detonation about like TNT.

Melting Point: 311-312° (dec.)

Thermal Stability:

At 260°C. gas evolved = 5.6 cc. per g. per hr.
At 230°C. gas evolved = 1.8 cc. per g. per hr.

Impact Sensitivity[18]: 42 cm., $\sigma = 0.12$

Crystal Density: 1.82 g./cc.

Solubility:

Very soluble: H_2O, ethanol, acetone, acetic acid
Difficultly soluble: ether, benzene, chloroform, conc. HCl

These properties suggest that, in company with NONA[7], KHND[19], hexanitrostilbene[20] and dodecanitroquaterphenyl[21], DIPA merits evaluation as a thermally stable booster explosive. Its disadvantages relative to the other candidates have already been detailed; its advantages are, relative to KHND a somewhat higher heat of detonation, relative to NONA, hexanitrostilbene and dodecanitroquaterphenyl a somewhat more ready availability.

EXPERIMENTAL[22]

Preparation of Dipicric Acid (III). The procedure is a modification of that of Bock, Moyer and Adams[2]. To 260 g 3,3'-dimethyl-2,2',4,4',6,6'-hexanitrobiphenyl (I) in a 5-liter three-neck flask fitted with stirrer and thermometer were added with stirring 2600 ml 90-100% nitric acid (no rise in temperature) and sufficient of a total of 905 ml 30% oleum to raise the temperature to 50° and to hold the mixture at this temperature until all or most of the I had dissolved. The remaining oleum was then added while cooling the mixture with an ice bath.

With continued cooling to maintain the temperature at about 25° (not above 30°), 750 g sodium dichromate dihydrate was added portionwise over a several hour period to the well stirred mixture which turned greenish-black. Cooling was necessary for an additional several hours after which time the mixture could be left unattended at room temperature. Total stirring time was about 25 hours.

Crude dipicric acid was obtained as a yellow amorphous product by drowning the reaction mixture on about 10 liters of cracked ice, allowing the precipitate to settle[23], filtering through a coarse sintered glass funnel and washing the filter cake twice with 20% hydrochloric acid. For preliminary purification this material was digested with 500 ml ethanol, the solution filtered off through a coarse sintered glass funnel, the residue digested with an additional 750-1000 ml ethanol and the mixture again filtered. Concentrated hydrochloric acid was then added to the combined filtrates until the mixture appeared to be almost colorless.

The mixture was then chilled for several hours, filtered and the product air dried for several hours after which time it still retained considerable water. Taking this material up in acetone and adding an equal volume of benzene caused most of the water to separate as a lower phase which was removed. The organic phase was then dried over Drierite and concentrated to yield two successive crops of III. The first crop, washed first with benzene and then with hexane and dried for 24 hours at 60°/1mm, weighed 167 g and melted with decomposition at 311°. The second crop, treated similarly, amounted to 41 g, m.p. 301° (dec.). The total yield of DIPA was 79% of theory.

The analytical sample was obtained as fine white needles, turning yellow on standing, m.p. 311-312° (dec.), by recrystallizing material from a similar but smaller scale run three times from benzene.

Anal. Calc'd. for $C_{12}H_4N_6O_{14}$: C, 31.80; H, 0.88; N, 18.40; neutral equiv., 228.
Found[5]: C, 32.80, 32.25, 32.00, 31.53, 31.90; H, 1.71, 1.39, 0.93, 0.73, 0.76; N, 17.73, 16.36, 17.58; N.E., 241, 256.

Authentic Dipicric Acid. An authentic sample was prepared by a modification of the procedure of Mascarelli and Visintin[9]. Fifty grams of 3,3'-dimethoxybiphenyl in 326 g hydriodic acid (D = 1.7) was refluxed three hours and the evolved methyl iodide, ca 30 ml, collected in a Dean-Stark trap. The clear solution was then chilled to give an essentially quantitative yield of 3,3'-dihydroxybiphenyl, m.p. 123-125° (lit.[9] 125.5-126°).

Ten grams of the latter material was heated 40 minutes on the steam bath with 25 ml 30% oleum and 25 ml concentrated sulfuric acid, cooled to room temperature, 30 ml 100% nitric acid and 30 ml oleum added, stirred one hour at room temperature, one hour at 100° and overnight at room temperature. The mixture was drowned in excess ice, filtered, the crude product dissolved in aqueous sodium hydroxide, the solution filtered and the product reprecipitated with concentrated hydrochloric acid. There was thus obtained 12 g (49%) of dipicric acid, m.p. 308-310° (dec).which showed identical infrared and ultraviolet spectra (Table I) with material prepared as above. There was no depression in melting point on admixture of samples.

3-Hydroxy-2,2',4,4',6,6'-hexanitrobiphenyl (m-picrylpicric acid, PIPA, VI) as a By-product in the Oxidation of I. The combined organic mother liquors from the oxidation of 1082 g I were mixed with an excess of hexane and the precipitated material was filtered off and air dried. This was then added to 2 liter hot water and sodium carbonate, 20 g, was slowly added till a color change to deep orange persisted for several minutes. The solution was filtered, acidified with 31.3 ml concentrated hydrochloric acid, the precipitate filtered off and the procedure repeated with 1000 ml water, 10 g sodium carbonate and 15.7 ml concentrated hydrochloric acid. The precipitate from this treatment was recrystallized from acetone-benzene and then several times from benzene to give 3.0 g PIPA, m.p. 274-275°, no depression on admixture with sample prepared as below.

Neutral Equiv. Calc'd. for $C_{12}H_4N_6O_{13}$: 440. Found: 436.

In the above separation advantage was taken of the fact that DIPA is considerably more soluble than PIPA in mildly acidic aqueous solutions.

3-Methyl-2,2',4,4',6,6'-hexanitrobiphenyl (VIII). This material was prepared by the mixed Ullmann reaction of picryl chloride and 3-bromo-2,4,6-trinitrotoluene with copper in nitrobenzene at 178-184°. The method is insufficiently well-worked-out to merit describing at this time; an improved procedure will be detailed in a subsequent report[11]. The product used in the following experiments melted at 180-183° and its X-ray pattern did not show discernable amounts (at least five percent) of either I or hexanitrobiphenyl. The analytical sample, light tan platelets from methylene chloride-carbon tetrachloride, melted at 182-183°.

Anal. Calc'd. for $C_{13}H_6N_6O_{12}$: C, 35.64; H, 1.37; N, 19.18. Found: C,36.06, 35.70; H, 1.59, 2.16; N, 18.92, 19.04.

Oxidation of VIII. Monomethylhexanitrobiphenyl (27.5 g) was oxidized as above, using 150 ml 97% nitric acid, 39 ml 30% oleum, 21 ml 96% sulfuric acid and 49.8 g sodium dichromate dihydrate. The product obtained after drowning, filtering and washing with ca 200 ml water was suspended in 1000 ml water, the mixture was heated, and 3.0 g sodium bicarbonate was added. After standing 30 minutes, the mixture was filtered; residue = Fraction A, filtrate = Fraction B.

Fraction A was extracted with a further 1000 ml hot water containing 1.0 g sodium bicarbonate and filtered again to yield 14.5 g crude 2,2',4,4',6,6'-hexanitrobiphenyl, m.p. 225-230°, no depression with authentic hexanitrobiphenyl, m.p. 240°, X-ray diffraction pattern identical with authentic hexanitrobiphenyl[7]. Two recrystallizations from acetone-hexane raised the melting point only to 228-232° so that it is likely that this product was contaminated with some not readily separable impurity.

Fraction B was treated with 4.6 ml concentrated hydrochloric acid (equivalent to sodium bicarbonate previously added) and cooled; the precipitate was separated. Precipitate = Fraction C, filtrate = Fraction D.

Fraction C was extracted with 600 ml hot water, leaving 1.8g of a residue which was recrystallized from benzene-hexane to yield 1.7 g, m.p. 274-275°. Concentration and acidification of the aqueous solution yielded three crops, totalling 3.5 g, which on recrystallization from benzene-hexane proved to be the same product and had m.p. 274-275°. The combined products, recrystallized again from benzene-hexane, melted at 275-276° (dec) and amounted to 4.5 g (16.4%). Neutral equivalent, elemental analyses and ultraviolet spectrum confirmed that this product had the structure of m-picrylpicric acid (VI).

Anal. Calc'd. for $C_{12}H_4N_6O_{13}$: C, 32.7; H, 0.9; N, 19.1; neutral equiv., 440. Found: C, 32.51, 32.85; H, 0.67, 0.93; N, 18.64, 19.12; N.E., 431.

Ultraviolet: λ_{max}^{MeOH} (log ϵ) = 367 mμ (4.20); $\lambda_{max}^{H_2O}$ (log ϵ) = 233 (4.53), 365 (4.19).

Fraction D, concentrated to 400 ml and further acidified, yielded 3.1 g of a material which on recrystallization from benzene-hexane afforded two crops, 1.6 g, m.p. 285-286° (dec) and 0.7 g, m.p. 281° (dec). The combined crops were extracted with successive portions of boiling water and the solutions were combined, concentrated and acidified to yield 0.7 g, m.p. 300° (dec). Recrystallization from benzene-hexane raised the decomposition point to 305°; there was no depression on admixture with dipicric acid prepared as above.

Oxidations of TNT. To a mixture of 2.57 g TNT, 30 ml 97% nitric acid, 7.9 ml 30% oleum and 3.6 ml concentrated sulfuric acid was added over a 20 minute period 11.6 g sodium dichromate dihydrate. The mixture was stirred two hours at 0° and three hours at room temperature and drowned on ice to yield 1.3 g picric acid, m.p. >115°, no depression with authentic sample, m.p. 122-123°.

A trial using similar quantities of TNT and sodium dichromate with 10 ml 97% nitric acid and 35 ml concentrated sulfuric acid yielded 1.0 g picric acid. A trial using 30 ml nitric acid and 1 ml sulfuric acid yielded 1.1 g picric acid. In each instance an additional 0.6-0.8 g picric acid could have been recovered by extracting the drown liquors with methylene chloride.

A trial using 30 ml 100% nitric acid and no sulfuric acid yielded no picric acid.

Oxidations of 2,4,6-Trinitrobenzoic Acid. A solution of 2.91 g trinitrobenzoic acid in 30 ml 97% nitric acid was treated with 11.6 g sodium dichromate dihydrate and 5 ml oleum while being cooled in an ice bath. The mixture was allowed to stir overnight at room temperature, then drowned on ice to yield 1.45 g picric acid. The drown liquors, extracted several times with methylene chloride and the latter solution concentrated, yielded an additional 0.75 g; both crops melted at 118-120° and showed no carbonyl band in the infrared.

A similar trial but without the addition of the oleum yielded on drowning 1.55 g and from the methylene chloride extract 0.7 g, both crops of picric acid melting at 115-118° and showing no carbonyl band.

From 5 g trinitrobenzoic acid, dissolved in 50 ml nitric acid and drowned after 43 hours at room temperature, there was obtained only 3.5 g starting material. No picric acid had been formed as evidenced by absence of coloration of aqueous solutions.

Oxidation of 1-Ethyl-2,4,6-trinitrobenzene. In a typical oxidation procedure 27.3 g of ethyltrinitrobenzene was treated with 300 ml 97% nitric acid, 116 g sodium dichromate dihydrate and, with cooling, 50 ml oleum, stirred five hours and drowned on ice. The air dried product, 24 g, was digested with potassium bicarbonate solution, then recrystallized from chloroform to yield as a first crop 17.0 g of *2,4,6-trinitroacetophenone (IX)*, long colorless needles, m.p. 135-136°, as a second crop 4.5 g of the same product, m.p. 133.5-135.5°, and as a third crop a further 0.5 g. The analytical sample, m.p. 135.5-136.5°, was obtained on a single further recrystallization from chloroform.

Anal. Calc'd. for $C_8H_5N_3O_7$: C, 37.66; H, 1.98; N, 16.47. Found: C, 37.89, 37.91; H, 1.96, 2.09; N, 15.75, 15.91, 16.46.

Independent Synthesis of 2,4,6-Trinitroacetophenone. To a solution of ethoxymagnesium malonic ester prepared by the procedure of Bowman[14] from 1.4 g magnesium and 16 g diethylmalonate was added a solution of 14 g 2,4,6-trinitrobenzoyl chloride in a minimal amount of benzene. The addition, with cooling to hold the temperature at 25°, required 30 minutes; the mixture was stirred an additional hour at room temperature. Several milliliters of propionic acid were added, the benzene was removed in vacuo, an additional 50 ml propionic acid and 1 ml concentrated sulfuric acid were added, the mixture was refluxed three hours, a further 5 ml dilute sulfuric acid was added, the mixture was refluxed 40 minutes.

Drowning the mixture on ice caused the separation of an oil. After neutralizing the drown-mixture with sodium bicarbonate and allowing to stand over the week-end, this oil solidified. This material was filtered, washed with water, air dried and dissolved in chloroform. Concentration of the chloroform solution and addition of hexane caused the separation first of a black tarry material, then of ca 5 g of brown crystalline material which was reserved, and finally of further tarry material. The tarry fractions were combined, dissolved in methylene chloride and filtered through a column of silicic acid. The slightly colored eluate on evaporation left a pale brown oil, ca 2 g, which solidified on standing. This was combined with the previous 5 g and recrystallized from chloroform to yield: first crop, 3.1 g, m.p. 130-134°; second crop, 1.3 g, m.p. 100-110°; final crop, 2.0 g, half oil-half solid.

The first crop, further recrystallized from chloroform, yielded 2.5 g <u>2,4,6-trinitroacetophenone (IX)</u>, m.p. 135-136°, mixture m.p. with material from oxidation of ethyltrinitrobenzene, 135-136°. Infrared spectra of the two samples were identical, carbonyl band at 1710 cm^{-1}.

<u>Oxidation of 1-Isopropyl-2,4,6-trinitrobenzene</u>. An oxidation mixture from 4.75 g isopropyltrinitrobenzene, 50 ml 97% nitric acid, 19.0 g sodium dichromate dihydrate and 8.5 ml oleum, stirred two hours below 10°, allowed to warm to room temperature over a two hour period and stirred at room temperature for an additional hour, yielded on drowning 2.5 g of an orange-brown product. Recrystallization of this material from chloroform gave 1.4 g <u>2,4,6-trinitroacetophenone, IX</u>, m.p. 135-136°, identical with material prepared as above.

A work-up of the combined recrystallization mother liquor and methylene chloride extract of the drown-liquor afforded an additional 0.45 g IX, m.p. 134-136° together with ca 50 mg of a higher melting red crystalline product. The latter compound showed some interesting physical and spectral properties; an attempt to characterize it is currently under way.

<u>Oxidation of 2,4-Dinitrotoluene</u>. The routine procedure, involving 6.2 g dinitrotoluene, 30 ml 97% nitric acid, 20 g sodium dichromate dihydrate and 5 ml oleum, yielded on drowning 0.45 g of insoluble material which softened at 75-80°, melted partially at about 120° and did not melt completely below 200°. This material was insoluble in bicarbonate solution. On standing over the week-end in the refrigerator, there crystallized from the drown mother liquors 4.15 g of nicely crystalline <u>2,4-dinitrobenzoic acid</u>, m.p. 178-181° (lit. 180°).

When a similar procedure was attempted with 3.1 g 2,6-dinitrotoluene the product (1.85 g) which was insoluble in the drown liquors was unreacted starting material. Exhaustive extraction of the mother liquor with chloroform and concentration of the latter gave 0.5 g 2,6-dinitrobenzoic acid, m.p. 204-206° (lit. 202°).

Oxidation of 3-Bromo-2,4,6-trinitrotoluene. An oxidation involving 3.6 g Bromo-TNT, 30 ml 97% nitric acid, 3.6 ml concentrated sulfuric acid, 7.9 ml oleum and 11.6 g sodium dichromate dihydrate, stirred 4 hours at 0.5° and overnight at room temperature, yielded on drowning 1.5 g of crude product. Digestion with dilute bicarbonate solution left ca 0.5 g insoluble. Acidification of the solution afforded 1.0 g bromopicric acid, m.p. 147-149°, no depression on admixture with authentic sample, m.p. 150-151°, prepared by the nitration of m-bromophenol. In this as in the previous instances, no attempt was made to optimize yields.

A similar reaction, starting with 2.75 g 2,4,6-trinitro-m-cresol, yielded on drowning 1.1 g unreacted starting material. By extracting the drown liquor with methylene chloride there was obtained 200 mg styphnic acid, m.p. 177-180°, no depression with authentic sample, m.p. 180°, ultraviolet spectrum identical with authentic sample.

The oxidation of 1-t-butyl-3,5-dimethyl-2,4,6-trinitrobenzene yielded as a main product a compound of as yet unascertained structure. Details of this oxidation will be deferred to a subsequent communication.

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18. Impact sensitivities were determined on an ERL machine as modified at NOL using type 12 tools. On this machine TNT shoots at 160 cm, Comp. A at 70 cm, Tetryl at 32 cm, RDX at 24 cm, BTNEC at 16 cm.

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22. Microanalyses were by Prof. Mary H. Aldridge, Department of Chemistry, American University, Washington, D. C. Ultraviolet spectra were determined on a Cary Model 14 recording spectrophotometer.

23. This material occasionally precipitates in a very fine form and passes quite slowly through the filter. When this occurs filtration time may be shortened appreciably by allowing the material to settle and first passing the supernatant liquor through the sintered glass funnel.

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