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POLYNITROAROMATICS—I

REPLACEMENT OF METHYL BY HYDROXYL IN MONO- AND DIMETHYLHEXANITROBIPHENYL BY OXIDATION WITH DICHROMATE-SULFURIC ACID-NITRIC ACID

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Contribution from the Organic Chemistry Division, U.S. Naval Ordnance Laboratory

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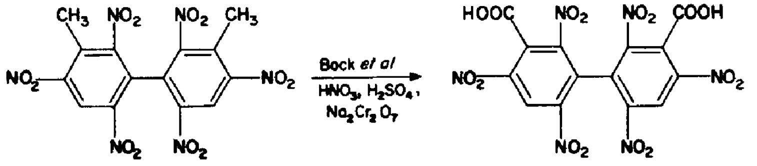
Abstract—The reaction product of 3,3′-dimethyl-2,2′,4,4′,6,6′-hexanitrobiphenyl (I) with a mixture of dichromate, nitric acid and sulfuric acid is shown from its I.R. and U.V. spectra and by independent synthesis to be dipicric acid (3,3′-dihydroxy-2,2′,4,4′,6,6′-hexanitrobiphenyl, III) rather than the 3,3′-dicarboxy-derivative (II) as had been suggested by earlier workers. 3-Hydroxy-2,2′,4,4′,6,6′-hexanitrobiphenyl (VI), a low-yield by-product in the aforementioned reaction, is obtained in satisfactory yield as the sole product of the oxidation of 3-methyl-2,2′,4,4′,6,6′-hexanitrobiphenyl with the dichromate–nitric acid–sulfuric acid mixture.

In the course of the original classic studies on optical isomerism due to restriction of rotation in *ortho*-substituted biphenyls,[2] Bock *et al.* described the synthesis and resolution of a compound to which had been assigned the structure 3,3′-dicarboxy-2,2′,4,4′,6,6′-hexanitrobiphenyl (II).[3] Their preparative method involved the oxidation of 3,3′-dimethyl-2,2′,4,4′,6,6′-hexanitrobiphenyl (I) with a mixture of oleum, sodium dichromate *and nitric acid.*



I   II

Dichromate–sulfuric acid oxidations of polynitrotoluenes to the corresponding polynitrobenzoic acids had been long known and fairly routine. Such, for example, was a preferred method for the conversion of T.N.T. into 2,4,6-trinitrobenzoic acid.[4,5] The method used by Bock *et al.* was unusual only in the presence of the nitric acid and, although not explicitly stated, it seems likely that they had first tried the standard procedure. They may have found, as has been our own experience, that I was quite unreactive under a variety of conditions but that, with the addition of nitric acid, oxidation took place fairly readily.

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[1] Temporarily detached from NOL. Present address: ONR–London, Navy 100, Box 39, FPO, New York, N.Y.

[2] L. Shriner, R. Adams and C. S. Marvel in H. Gilman, Editor, *Organic Chemistry* (2d Edition) Vol. I, pp. 347–382. John Wiley, New York (1943).

[3] L. H. Bock, W. W. Moyer and R. Adams, *J. Amer. Chem. Soc.* 52, 2054 (1930).

[4] T. L. Davis, *The Chemistry of Powder and Explosives* p. 134. John Wiley, New York (1943).

[5] H. T. Clarke and W. W. Hartman in H. Gilman and A. H. Blatt, Editors, *Organic Syntheses*, (2d Edition) Coll. Vol. I, p. 543. John Wiley, New York (1948).

With a wealth of analogy to guide them, lacking the spectrophotometric tools now routinely used, and plagued by difficulties in elemental analyses and the determination of neutral equivalents,[6] these workers had little reason to doubt that their oxidation product was the anticipated II. It was, as expected, a strong dibasic acid and resolvable into optical antipodes.[7]

We wish now to report that the above modified procedure 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 points of our samples on minor amounts of impurities led us to believe that we were dealing with the same product as had been obtained by the earlier workers. Routinely determined I.R. and U.V. spectra showed, however, that the assigned structure II was improbable and suggested that the product was instead 3,3′-dihydroxy-2,2′,4,4′,6,6′-hexanitrobiphenyl (dipicric acid, III).

The I.R. spectrum was characterized by the complete absence of absorption in the carbonyl region.[8]

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

As is shown in Table 1, 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. Completely inconsistent with structure II, these spectra gave a clue to the true nature of the product since they bore a relationship to the corresponding spectra of picric acid such as would be expected of structure III.

Other evidence corroborated that the supposed compound II had the structure III. Spectrophotometric measurements showed it to be a strong acid, half ionized in 5N hydrochloric acid; neutral equivalent determinations, albeit poor,[6] showed that it was dibasic. With pyridine in ethanol it yielded 91% of a dipyridinium salt which with phosphorus oxychloride[9] was transformed in 99% yield to a derivative analyzing well

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[6] In company with other high-melting explosives, elemental analyses of this material were generally quite poor as a consequence of its tendency to explode rather than burn smoothly in the combustion tube. Neutral equivalents of III also generally ran high as a consequence of contamination by VI (see text). Almost as if the fates had conspired to confound the earlier workers, typical recrystallized samples of III contained sufficient amounts of VI to raise neutral equivalents to the range calculated for II.

[7] The only evidence which might, in retrospect, have caused the earlier workers to doubt the structure assignment was the stability of their compound to conditions wherein II might be expected to undergo decarboxylation. Compare, for example, the reaction conditions required for the conversion of trinitrobenzoic acid to trinitrobenzene; H. T. Clarke and W. W. Hartman, ref. 5, p. 541.

[8] 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).

[9] M. Warman and V. I. Siele, *J. Org. Chem.* 26, 2997 (1961).

TABLE 1. ULTRAVIOLET ABSORPTION SPECTRA[e]

	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	4·23
		254	4·18
		340	3·62
Dipicric acid (III)	H_2O	255s	4·29
		368	4·29
		368	4·44
	MeOH	255s	4·34
		365	4·37
	MeCN	260	4·53
		331	3·99
Picramide	MeOH	240	4·21
		318	4·08
		407	3·90
Dipicramide (V)	MeOH, 4% MeCN	260	4·39
		330	4·35
		385s	4·11
3,3'-Dichloro-2,2',4,4',6,6'-hexanitrobiphenyl (IV)	MeOH, 4% MeCN	240	4·55
m-Picrylpicric acid (VI)	MeOH	367	4·20
	H_2O	365	4·19
m-Picrylpicramide (VIII)	MeOH, 4% MeCN	231	4·53
		330	4·08
		390s	3·80

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

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

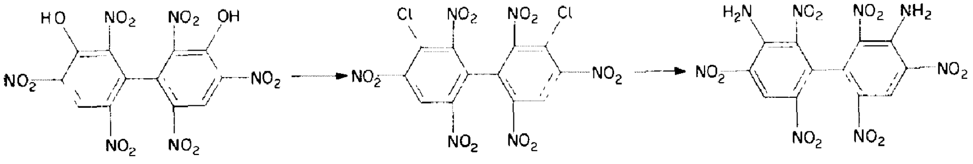
[c] J. D. Teresi, *J. Amer. Chem. Soc.* **72**, 3972 (1950).

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

[e] Spectra were determined on a Cary Model 14 recording spectrophotometer using 1 cm. quartz cells. s = shoulder or inflection.

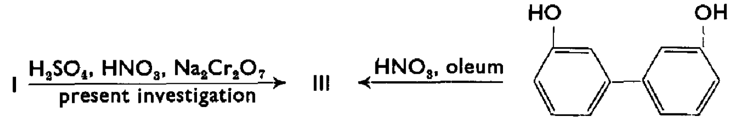
for 3,3'-dichloro-2,2',4,4',6,6'-hexanitrobiphenyl (IV). The latter, on treatment with ammonia in ethanol, afforded 92% of a compound for which elemental analyses were consistent with 3,3'-diamino-2,2',4,4',6,6'-hexanitrobiphenyl (dipicramide, V). With neither IV nor V was there a carbonyl band in the I.R. and the primary band in the U.V. spectrum of V showed the expected 12 mμ bathochromic shift in λ_{max} and approximately doubled ε_{max} relative to that of picramide (*vide supra* and Table 1).

Final confirmation of the structure was achieved by independent synthesis. Mixed acid nitration of 3,3'-dihydroxybiphenyl according to the procedure of Mascarelli and



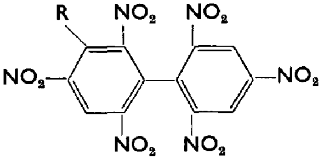
III IV V

Visintin[10] yielded an authentic sample of III, m.p. 310–311° (dec.). Ultraviolet and I.R. spectra were identical with those of the oxidation product of I and there was no depression in melting point on admixture of samples.



Neutral equivalents running several percent high on all samples of III prepared by the oxidation route, coupled with acceptable carbon and hydrogen analyses, led us to believe that our product was contaminated with a second species of generally similar physical properties and elemental composition. Repeated recrystallizations from a variety of organic solvents were not effective in separating this contaminant, but a pure sample of the by-product was eventually obtained in less than 1% yield by careful acidification of an aqueous sodium carbonate solution of the combined final crops from a number of large-scale oxidations.

Like III, this second product proved to be a strong acid, but with no carbonyl band in the infrared. From its neutral equivalent, elemental analyses and U.V. spectrum, which bore the appropriate relationship to a summation of the spectra of trinitrobenzene and picric acid (Table 1), it was concluded to have the structure 3-hydroxy-2,2′,4,4′,6,6′-hexanitrobiphenyl (*m*-picrylpicric acid, VI). For confirmation, its pyridinium salt was converted to 3-chloro- (VII) and subsequently to 3-amino-2,2′,4,4′,6,6′-hexanitrobiphenyl (VIII) by treatment first with phosphorus oxychloride and then with ethanolic ammonia.



VI, R = OH
VII, R = Cl
VIII, R = NH_2
IX, R = CH_3

It seems, therefore, that whereas in the formation of III both methyl groups of I had been replaced by hydroxyl, the concurrent formation of VI involved the replacement of one methyl group by hydroxyl, one by hydrogen. As will be shown in Paper II of this series,[11] it is likely that both products arose from a common intermediate with "reaction branching" in subsequent stages of the transformation.

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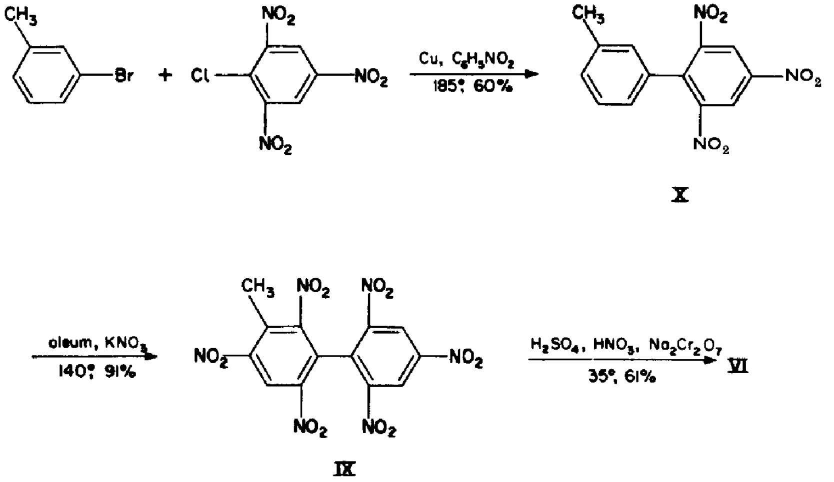
[10] L. Mascarelli and B. Visintin, *Gazz. Chim. Ital.* **62**, 358 (1932); *Chem. Abstr.* 26, 4809 (1932). It is of interest that these workers attempted unsuccessfully to resolve dipicric acid into optical antipodes whereas, unbeknownst to either group, Bock *et al.* had already described its resolution.

It will also be shown[11] that with the addition of nitric acid the dichromate–sulfuric acid mixture becomes effective in oxidizing T.N.T. and a variety of its ring- substituted derivatives to the correspondingly substituted picric acids. This afforded a more convenient method for the synthesis of VI from 3-methyl-2,2′,4,4′,6,6′-hexanitrobiphenyl (IX).

Original attempts at the preparation of IX by the mixed-Ullmann reaction of picryl chloride with 3-bromo-2,4,6-trinitrotoluene and copper in nitrobenzene yielded, under a variety of conditions, not-readily-separable mixtures of I, IX and 2,2′,4,4′,6,6′-hexanitrobiphenyl. From these on oxidation were obtained mixtures of hexanitrobiphenyl, III and VI, from which VI could be separated in about 20% yield on account of its intermediate water solubility.

Still more satisfactory from considerations of convenience and yields was the mixed-Ullmann reaction of picryl chloride and *m*-bromotoluene which yielded almost exclusively the desired unsymmetrical product, 3-methyl-2′,4′,6′-trinitrobiphenyl (X). Although attempts by the earlier workers[3] to hexanitrate 3,3′-dimethylbiphenyl had not met with success, X was converted to IX smoothly and in good yield by reaction with potassium nitrate in 30% oleum. Pure IX, thusly prepared, was readily oxidized to VI in 60% yield. Pure VI, prepared by both methods, was identical in all properties with the by-product from the oxidation of I.



The behavior of the aryl and nitroaryl halides in attempted mixed-Ullmann reactions is comment-worthy. Our finding that picryl chloride gave a mixture of the three possible normal Ullmann products with 3-bromo-2,4,6-trinitrotoluene, but primarily the desired unsymmetrical product with 3-bromotoluene conforms with Forrest's suggestion[12] that the greater the difference in electronegativity of substituents on the two aryl halides, the greater will be the difference in reactivity toward copper and the proportion of unsymmetrical Ullmann product formed.

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[11] H. G. Adolph, J. C. Dacons and M. J. Kamlet, *Tetrahedron* **19**, 801 (1963).

[12] J. Forrest, *J. Chem. Soc.* 595 (1960).

EXPERIMENTAL[13] (CAUTION[14])

3-*Bromo*-2,4,6-*trinitrotoluene*. Previously described methods for the preparation of this compound involve a two-step nitration with separation of the intermediate 3-bromo-4,6-dinitrotoluene.[15] We have found that the trinitration may be carried out conveniently in a single operation and in excellent yield.

To a well-stirred mixture of 150 ml 30% oleum and 180 ml 90% nitric acid at 55° was added dropwise over a 50 min period 58·8 g *m*-bromotoluene. The resulting clear orange solution was stirred an additional 75 min at 55°, then heated to the reflux whereupon a mildly exothermic reaction which was self-sustaining for about 15 min ensued. The solution was kept at the reflux for a total of 2 hr, then allowed to cool slowly with vigorous agitation (to prevent the precipitating product from forming a hard cake at the surface).

The cooled reaction mixture was drowned with stirring in ice-water, filtered and the filter cake washed with water and air-dried overnight to yield 98·5 g (93%) of crude bromotrinitrotoluene, m.p. 134–137°. A single recrystallization from 400 ml acetone furnished 3 crops, totalling 89·8 g, m.p. 142–144° and a further crop, 3 g, m.p. 141–143°. The yield of recrystallized material was 88%.

3,3′-*Dimethyl*-2,2′,4,4′,6,6′-*hexanitrobiphenyl* (I). The procedure was a modification of that of Bock *et al.*,[3] but with substantially reduced amounts of nitrobenzene and copper. As a consequence of the smaller amount of solvent it was found desirable to filter the reaction mixture hot and to wash the filter cake thoroughly with acetone. From 440 g bromotrinitrotoluene, 280 g copper dust[16] and 500 ml dry nitrobenzene there was obtained 260 g (80%) of recrystallized (from acetone) dimethylhexanitrobiphenyl.

Attempted oxidation of I *with dichromate in sulfuric acid.* A mixture of 1·85 g I, 30 ml conc sulfuric acid and 8 g sodium dichromate was stirred 18 hr at room temp after which time apparently little or no reaction had occurred as judged from the color. After an additional 5 hr stirring at 75° the dark green mixture was poured on ice and the precipitate triturated with dil sodium bicarbonate solution. No carboxylic acid could be detected in the bicarbonate extract. Stirring a mixture of 5 g I, 100 ml conc sulfuric acid, 25 ml 30% oleum and 22 g sodium dichromate for 1 week at 40° likewise did not yield any acidic product. Only 2 g starting material could be recovered.

Dipicric Acid (III). The oxidation procedure was also a modification of that described by Bock *et al.*[3] To 260 g I in a 5 l. 3-neck flask fitted with stirrer and thermometer were added with stirring 2600 ml 90–100% nitric acid (no rise in temp) and sufficient of a total of 905 ml 30% oleum to raise the temp to 50° and to hold the mixture at this temp 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 temp at about 25° (not above 30°), 700 g sodium dichromate dihydrate was added portionwise over a several hr period whereupon the mixture turned greenish-black. Cooling was necessary for an additional several hr after which time the mixture could be left unattended at room temp. Total stirring time was about 25 hr.

Crude dipicric acid was obtained as a yellow amorphous product by pouring the reaction mixture on about 10 l. cracked ice, allowing the precipitate to settle, 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 extracted with an additional 750–1000 ml hot ethanol and the solution again filtered. Conc hydrochloric acid was then added to the combined filtrates until the mixture appeared to be almost colorless.

After chilling for several hr, the mixture was filtered and the product air-dried overnight 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.

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[13] M.P. are uncorrected. Microanalyses were performed by Prof. Mary Aldridge, Dept. of Chemistry, American University, Washington, D.C.

[14] Many of the compounds herein described are explosive in nature. Appropriate precautions should be taken in their handling.

[15] E. A. Grete, *Liebigs Ann.* **177**, 258 (1875); W. B. Bentley and W. H. Warren, *Amer. Chem. J.* **12**, 4 (1890).

[16] Electrolytic dust from Fisher Scientific Co. was activated by stirring with concentrated hydrochloric acid, filtering, washing with water, methanol and ether and drying in the oven.

The organic phase was then dried over Drierite and concentrated to yield two successive crops of III. The first crop, washed with benzene and then with hexane and dried for 24 hr at 60°/1 mm, weighed 167 g and melted with decomposition at 311°. The second crop, treated similarly, amounted to 41 g, m.p. 301° (dec), total yield 79% of theory.

By recrystallizing the higher melting material several times from benzene the analytical sample of dipicric acid was obtained as fine white needles, turning yellow on standing in air, m.p. 311–312° (dec). (Found:[6] C, 32·00, 31·53, 31·90; H, 0·98, 0·73, 0·76; N, 17·73, 16·36, 17·58; neut. equiv., 241. Calc. for $C_{12}H_4N_6O_{14}$: C, 31·80; H, 0·88; N, 18·40%; neut. equiv. 228).

Isolation of 3-*hydroxy*-2,2′,4,4′,6,6′-*hexanitrobiphenyl* (VI) *as a by-product in the oxidation of* I. In this separation advantage was taken of the fact that III is considerably more soluble than VI in mildly acidic aqueous solutions. The combined mother liquors from recrystallization of the crude oxidation product from 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 l. hot water and 20 g sodium carbonate was slowly added till a color change to deep orange persisted. The solution was filtered, acidified with 31·3 ml conc hydrochloric acid, the precipitate filtered off and the procedure repeated with 1 l. hot water, 10 g sodium carbonate and 15·7 ml hydrochloric acid. The precipitate from this treatment was recrystallized from acetone-benzene and then several times from benzene to give 3·0 g VI, m.p. 274–275°, no depression on admixture with sample prepared as below. Several further recrystallizations from benzene afforded the analytical sample, m.p. 275·5–276·5°. (Found: C, 32·85, 32·51; H, 0·93, 0·67; N, 18·64, 19·12; neut. equiv., 436. Calc. for $C_{12}H_4N_6O_{13}$: C, 32·74; H, 0·92; N, 19·09%; neut. equiv., 440).

Authentic dipicric acid (III). Following essentially the procedure of Mascarelli and Visintin,[10] 50 g 3,3′-dimethoxybiphenyl in 326 g hydriodic acid (*d.* 1·70) was refluxed 3 hr 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. 125·5–126°).

Ten grams of the latter material was heated 40 min on the steam bath with 25 ml conc sulfuric acid and 25 ml 30% oleum, cooled to room temp, 30 ml 100% nitric acid and 30 ml oleum added, stirred 1 hr at room temp, 1 hr at 100° and overnight at room temp. The mixture was poured onto excess ice, filtered, the crude product dissolved in aqueous sodium hydroxide, the solution filtered and the product reprecipitated with conc hydrochloric acid. There was thus obtained 12 g (49%) dipicric acid, m.p. 308–310° (dec), which showed identical I.R. and U.V. spectra (Table 1) with material prepared as above and no depression in m.p. on admixture.

3,3′-*Dichloro*-2,2′,4,4′,6,6′-*hexanitrobiphenyl* (IV). A published procedure[9] for the conversion of styphnic acid to dichlorotrinitrobenzene was readily adapted for the present purpose. Dipyridinium dipicrate, 183 g (91%), bright yellow crystals, m.p. 256–258° (dec) resulted from the slow addition of 75 ml pyridine to a well-stirred solution of 150 g III in 1500 ml methanol.

A mixture of 118 g dipyridinium salt with 236 ml phosphorus oxychloride was warmed on a steam bath, the salt dissolving nearly completely when the temp reached 60°, at which time the product began to precipitate. After heating for an additional ½ hr the reaction mixture was cooled to below 40° and drowned slowly with stirring, starting with 500 ml water and adding the reaction mixture and ice at a rate sufficient to keep the drowning mixture at about 30°(CAUTION[17]). When the exotherm had ceased the product was recovered by filtration and washed with 2 l. of cold water. It was then suspended in 500 ml methanol and warmed almost to the b.p. with stirring, then filtered and dried. The yield of dichlorohexanitrobiphenyl, m.p. 275–277° (dec) was 94 g (99·5%). The analytical sample, m.p. 276–278°(dec), was obtained by recrystallization from chloroform–acetone. (Found: C, 29·46, 29·43; H, 0·65, 0·45; N, 17·44, 17·35; Cl, 14·66. Calc. for $C_{12}H_2Cl_2N_6O_{12}$: C, 29·23; H, 0·41; N, 17·04; Cl, 14·38%).

3,3′-*Diamino*-2,2′,4,4′,6,6′-*hexanitrobiphenyl* (V). To 2200 ml absolute ethanol saturated with dry ammonia in a 5 l. 3-neck flask fitted with thermometer, stirrer and condenser was added portionwise during 1 hr and at a temp below 12° 226 g of IV. It dissolved as added to form a blood-red solution. Anhydrous ammonia was then slowly bubbled in for an additional 15 min and the solution then slowly heated to the reflux. At about 30–35° an orange solid began to precipitate and

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[17] It is not advisable on a larger scale to drown the reaction mixture directly on ice. The excess phosphorus oxychloride is not readily hydrolyzed in the cold, but when the ice melts and the mixture warms, it reacts vigorously and exothermally. In the presence of an insoluble phase comprised primarily of energetic materials, this may be quite hazardous.

the solution lightened in color. The mixture was refluxed ½ hr and then 500 ml ethanol boiled off carrying with it the excess ammonia.

The reaction mixture was cooled to 10° and filtered and the product washed with 3% aqueous hydrochloric acid, ethanol and ether and dried overnight at 80°/30 mm, yielding 197·5 g (95%) of an orange-brown powder, m.p. 296° (dec).

A pure sample of diaminohexanitrobiphenyl, microcrystalline yellow powder, m.p. 299° (dec), was obtained by treating a hot acetone solution of the above material with charcoal, adding hot ethanol and concentrating to a small volume. (Found:[6] C, 32·09, 32·50; H, 1·12, 1·24; N, 22·86, 24·20. Calc. for $C_{12}H_6N_8O_{12}$: C, 31·80; H, 1·33; N, 24·70).

3-Methyl-2,2′,4,4′,6,6′-hexanitrobiphenyl (IX) *by the mixed Ullmann reaction.* A solution of 60 g 3-bromo-2,4,6-trinitrotoluene and 48·6 g picryl chloride in 300 ml dry nitrobenzene was heated to 130° and 1 g copper[16] was added. Heating was continued and an exothermic reaction occurred at about 140°. With the temp maintained at 140–142° a further 58·2 g copper was then added over a ½ hr period. After stirring the mixture an additional hr at the same temp it was allowed to cool, filtered and the filter cake washed with acetone.

The solvents were removed from the combined filtrate and washings by steam distillation and the dark solid residue was dried, dissolved in acetone, treated with 5 g charcoal, refluxed and filtered. Addition of chloroform and concentration yielded 61·3 g crude material which was recrystallized twice from acetone–chloroform to give 29·8 g, m.p. 176–182° and 10·6 g, m.p. 163–175°.

Similar results were obtained when the reaction was carried out at 150° or 180° and when the relative amounts of bromotrinitrotoluene, picryl chloride and copper were varied.

Several samples melting above 175° were oxidized with varying amounts of sodium dichromate, nitric acid and sulfuric acid according to the procedure outlined above for the conversion of I to III. By extracting the crude oxidation product with hot dil. sodium bicarbonate solution, about 20% of 3-hydroxy-2,2′,4,4′,6,6′-hexanitrobiphenyl (VI), contaminated by dipicric acid, was isolated in all instances. After purification as above, this material melted at 275–276° and showed no depression on admixture with samples of VI prepared as above and below.

3-Methyl-2′,4′,6′-trinitrobiphenyl (X) . A solution of 100 g picryl chloride in 200 ml *m*-bromotoluene at 182–185° was treated portionwise over a 15 min period with 150 g copper[16]. The mixture was stirred an additional 15 min at 183–185°, then allowed to cool. Copper and salts were filtered off and washed thoroughly with acetone. Concentration of combined filtrate and washings, addition of hexane and cooling furnished 84·1 g crude X (68·7% based on picryl chloride). Most of the excess *m*-bromotoluene could be recovered from the mother liquors by fractional distillation.

A single recrystallization of the above material from chloroform (charcoal) gave 73·3 g (60%) yellow crystals, m.p. 143–146°. The analytical sample (from chloroform) melted at 144·5–146°. (Found: C, 51·31, 51·66; H, 3·42, 3·48; N, 13·73, 14·05. Calc. for $C_{13}H_9N_3O_6$: C, 51·49; H, 2·99; N, 13·86).

3-Methyl-2,2′,4,4′,6,6′-hexanitrobiphenyl (IX) *by nitration of* X. Gradual addition of 132·8 g X at 30–35° to a mixture of 1500 ml 30% oleum and 405 g potassium nitrate resulted in a slightly exothermic reaction requiring some cooling with ice-water. After stirring the mixture without cooling for about 1 hr, during which time the temp dropped a few degrees, the mixture was gradually heated (3–4 hr) to and kept at 120° (a clear solution results around 100°) for 18 hr with efficient stirring.

The cooled reaction mixture was poured onto crushed ice, filtered, washed thoroughly with water and the crude damp product digested 4 times with 800 ml portions hot ethanol, leaving 157·2 g crude IX, m.p. 150–170°. One recrystallization from glacial acetic acid furnished 90·9 g, m.p. 186–190° and 5·9 g, m.p. 184–187°.

The methyltetra- and pentanitrobiphenyls were renitrated as follows: The recrystallization mother liquors and the ethanolic solutions from the digestions were combined and sufficient water added to precipitate all dissolved material (80·5 g dried). This was then added at about 40° to a mixture of 700 ml 30% oleum and 225 g potassium nitrate, heated for 16 hr at 130–140°, cooled, poured on ice and filtered. The product was digested once with 500 ml warm ethanol, leaving 78·7 g, m.p. 182–187°. The overall yield of methylhexanitrobiphenyl, m.p. above 182° was 175·5 g (91·5%).

The analytical sample (from acetic acid) m.p. 189·5–190·5°. (Found: C, 36·24; H, 1·73; N. 19·34, 19·24. Calc. for $C_{13}H_6N_6O_{12}$: C, 35·63; H, 1·38; N, 19·18).

3-Hydroxy-2,2′,4,4′,6,6′-hexanitrobiphenyl (VI) *by oxidation of* IX. To a solution of 153 g IX in 1050 ml 90% nitric acid was added with cooling (below 40°) 525 ml 30% oleum.

Sodium dichromate dihydrate, 210 g, was then added (½ hr) with the temp maintained at 25–30°; the temp was then allowed to rise to 35°. After 2 hr the cooling bath was removed and the mixture stirred an additional 14 hr. The mixture was then poured on crushed ice, the precipitate filtered through a large coarse sintered glass funnel, the damp product which retained a considerable amount of water triturated with 400 ml cold acetone and the solid residue separated (filtrate *A*). This was dissolved in warm acetone, an equal volume of benzene added and the organic layer separated from the water phase, dried over Drierite and concentrated. When crystallization started, a further equal volume of benzene was added and the mixture cooled and filtered (filtrate *B*) to yield 113 g, m.p. 265–273° (dec). Recrystallization from benzene–acetone (filtrate *C*) afforded 75·5 g pure VI, neutral equivalent 443 (calc. 440), m.p. 275–276°, no depression on admixture with samples prepared as above.

An additional 18 g, m.p. 273–275°, was obtained as follows, bringing the total yield to 61%: Combined filtrates *A*, *B* and *C* were concentrated to give about 20 g material (filtrate *D*) which on recrystallization yielded about 10 g, m.p. from 250° (crop *E* and filtrate *F*). Filtrates *D* and *F* were combined and sufficient hexane was added to precipitate most of the dissolved material. After drying and powdering, this was extracted with 2 l. boiling water, adding just enough sodium bicarbonate to keep the solution neutral. The extract was acidfied with conc hydrochloric acid whereupon 18 g, m.p. from 250°, precipitated. Finally the latter product and crop *E* were combined and recrystallized twice from acetone–benzene.

3-*Amino*-2,2′,4,4′,6,6′-*hexanitrobiphenyl* (V). The pyridinium salt of VI, 4·8 g, was added slowly with stirring to 20 ml phosphorus oxychloride and the mixture heated on a steam bath for ½ hr, during which time the salt dissolved. The solution was allowed to cool and poured into ca. 200 ml ice-water with vigorous stirring. The product was recovered by filtration, thoroughly washed with water, and dried; 5·1 g crude 3-chloro-2,2′,4,4′,6,6′-hexanitrobiphenyl (no carbonyl band in the IR-spectrum) was thus obtained and converted to the amino derivative without further purification: it was added portionwise to 50 ml saturated solution of ammonia in ethanol at 0°. After all of the chloro compound had dissolved, the excess ammonia was boiled off, the mixture cooled to 0° and the product collected on a funnel. It was washed with a small vol. cold ethanol, then with dil. hydrochloric acid and with water. Yield 4·1 g (93% from VI); m.p. after a single recrystallization from acetone–ethanol 217·5–218·5°. (Found: C, 33·20, 33·21; H, 1·45, 1·41; N, 22·55, 22·46. Calc. for $C_{12}H_5N_7O_{12}$: C, 32·81; H, 1·15; N, 22·33).