1056 *J. Org. Chem.* 1983, *48*, 1056-1059

# Nitrocarbons. 3. Synthesis of Decanitrobiphenyl[1,2]

Arnold T. Nielsen,* William P. Norris, Ronald L. Atkins, and William R. Vuono

*Chemistry Division, Research Department, Naval Weapons Center, China Lake, California 93555*

*Received August 4, 1982*

The synthesis of 4,4′-diamino-2,2′,3,3′,5,5′,6,6′-octanitrobiphenyl and its peroxydisulfuric acid oxidation to decanitrobiphenyl are described.

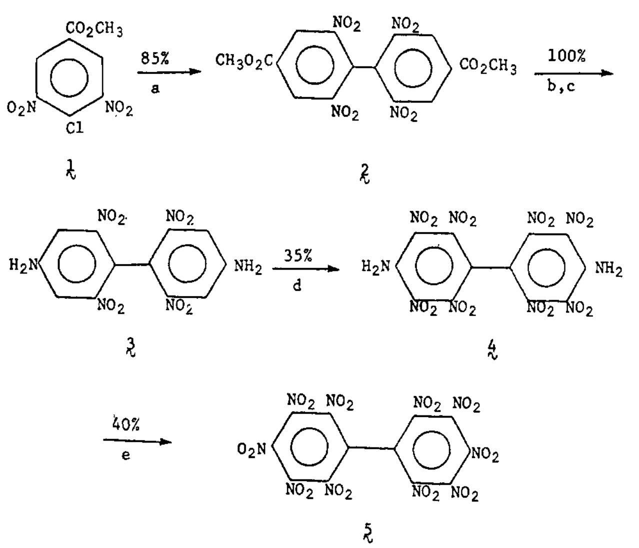
Three nitrocarbons, compounds $C_x(NO_2)_y$ composed only of nitro groups attached at nitrogen to carbon,[3] have been prepared: tetranitromethane,[4] hexanitroethane,[5] and hexanitrobenzene.[1,3] Tetranitroethylene and dinitroacetylene are known as their 9,10-anthracene adducts, but the pure nitrocarbons have not been isolated.[6] Calculations are said to show that octanitropropane is unstable and not preparable owing to a highly strained structure.[7]

In the present work we report the synthesis of a new nitrocarbon, decanitrobiphenyl (**5**), the fourth example of a compound of this type to be isolated. The synthesis of **5** proceeds from 4-chlorobenzoic acid in seven steps (overall yield ca. 10%; Scheme I). The first step is an improved nitration of the 4-chlorobenzoic acid with 90% nitric acid in 30% oleum at 95 °C which gives very pure 4-chloro-3,5-dinitrobenzoic acid in 90% yield; its methyl ester (**1**) was prepared in quantitative yield (methanol, $H_2SO_4$).

4,4′-Dicarbomethoxy-2,2′,6,6′-tetranitrobiphenyl (**2**) was prepared by the coupling of **1** with copper powder in refluxing *p*-xylene. The best yields (80–85%) require very efficient stirring. Two polymorphic forms of the substance were isolated (melting points at ca. 172 and 192 °C). The original procedure of Ullmann differs in that nitrobenzene was employed as the reaction solvent to produce the lower melting form (55% yield).[8] A similar procedure was employed by Mislow but gave the high-melting polymorph (yield not stated).[9] Methyl 4-bromo-3,5-dinitrobenzoate was employed by Castle and co-workers in a coupling reaction to produce an estimated 70% yield of pure **2**.[10] Castle's results appear similar to those of the present work with the chloro derivative wherein either polymorph of **2** could be isolated. 4,4′-Dicarboxy-2,2′,6,6′-tetranitrobiphenyl was readily prepared from **2** by hydrolysis in aqueous sulfuric acid (ca. 20% water) at 95 °C (100% yield).

4,4′-Diamino-2,2′,6,6′-tetranitrobiphenyl (**3**) was obtained in excellent yield (93–100%) by a Schmidt reaction on the dicarboxylic acid. The reaction employs sodium azide in fuming sulfuric acid (20% $SO_3$) at ca. 80 °C with added 1,2-dichloroethane to control the temperature and to dissolve unreacted hydrazoic acid, thereby providing a significant reduction in hazards. The present procedure for the **2** → **3** conversion is superior to those previously published which employ either a four-step Curtius rearrangement (<70% yield overall) or a three-step Hofmann reaction (<8–30% yield overall).[10]

Scheme I[a]



[a] (a) Cu, *p*-xylene, reflux; (b) 80% $H_2SO_4$, 95 °C; (c) $NaN_3$, 20% oleum, $ClCH_2CH_2Cl$, 80 °C; (d) $HNO_3$, $H_2SO_4$, 65-70 °C; (e) 95% $H_2O_2$, 30% oleum, 25 °C.

4,4′-Diamino-2,2′,3,3′,5,5′,6,6′-octanitrobiphenyl (**4**) was prepared by nitration of 4,4′-diamino-2,2′,6,6′-tetranitrobiphenyl (**3**) with nitric acid in 95–99% sulfuric acid at 10–70 °C. The initial reaction at 10–30 °C was conducted in 99% total acid concentration. The acid strength was subsequently reduced to 96% total acid by the addition of 50% $H_2SO_4$, followed by heating at 30–70 °C for 2 h. This procedure minimized the formation of a diazo oxide impurity (vide infra), thereby simplifying the purification procedure and improving the yield of the purified product. The optimum conditions found which produced the highest yield of crude product **4** (70–71%) were found to coincide closely with the optimum conditions for formation of the purest product (yields of pure, recrystallized **4** were 25–35%). In an alternate, more convenient, but less efficient procedure in which the acid concentration is held constant at 98–99% throughout the reaction, the yield of crude **4** is somewhat less (65–67%), and the product contains more of the undesirable diazo oxide impurity and is more difficult to purify. In a series of runs (70 °C, 1.5 h, 19.4 molar equiv of $HNO_3$), it was established that at a fixed acid concentration throughout the reaction the yield and purity of crude **4** dropped sharply at acid concentrations outside the range 97.5–99.5% (Figure 1).

Principal side reactions occurring during nitration of **3** are believed to include the formation of mono and bis nitramines (e.g., **6**) which are favored by use of a large

---

[1] Part 2: Nielsen, A. T.; Atkins, R. L.; Norris, W. P.; Coon, C. L.; Sitzmann, M. E. *J. Org. Chem.* **1980**, *45*, 2341.

[2] Presented at the Pacific Conference on Chemistry and Spectroscopy, San Francisco, CA, Oct 28, 1982.

[3] Nielsen, A. T.; Atkins, R. L.; Norris, W. P. *J. Org. Chem.*, **1979**, *44*, 1181.

[4] Schischkoff, L. *Justus Liebigs Ann. Chem.* **1861**, *119*, 247.

[5] Will, W. *Ber. Detsch. Chem. Ges.* **1914**, *47*, 961.

[6] (a) Griffin, T. S.; Baum,. K. *J. Org. Chem.* **1980**, *45*, 2880. (b) Baum, K.; Griffin, T. S. *Ibid.* **1981**, *46* 4811.

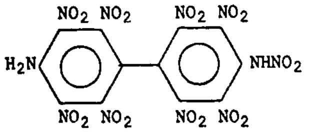
[7] Pivina, T. S.; Gritsaev, E. I.; Smirnov, B. B.; Shlyapochnikov, V, A,; Novikov, S. S. *Izv. Akad. Nauk SSSR* **1977**, 182.

[8] Ullmann, F.; Bielecki, J. *Ber. Detsch. Chem. Ges.* **1901**, *34*, 2174.

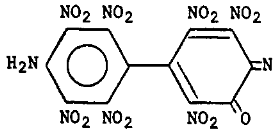
[9] Mislow, K.; Bolstad, R. *J. Am. Chem. Soc.* **1955**, *77*, 6712.

[10] Castle, R. N.; Guither, W. D.; Hübert, P.; Kempter, F. E.; Patel, N. R. *J. Heterocycl. Chem.* **1969**, *6*, 533.

0022-3263/83/1948-1056$01.50/0



**6**



**7**

excess of nitric acid. These compounds would be in equilibrium with 4 and are known precursors of diazo oxides such as 7.[11,12] Use of less nitric acid than the 15–20 molar equiv employed disfavors complete C-nitration and lowers the yield of 4. A larger excess of nitric acid not only favors nitramine formation but its derived degradation products as well, including the monodiazo oxide (7; suggested structure). (It is believed that similar side reactions are favored by reaction temperatures above 75 °C and total acid concentrations above 99%). A bis diazo oxide might be expected to form in small amounts.

The formation of diazo oxides by the thermal rearrangement of polynitroarylamines in sulfuric acid solution is frequently encountered in our nitration studies with polynitroarylamines.[11] The presence of diazo oxide (presumably 7) is readily detected in the infrared spectrum of crude reaction products by the appearance of a weak, characteristic absorption band at 2192 cm$^{-1}$. (Based on the intensity of this normally very intense band, as well as purification experiments, it is estimated that diazo oxide content in the crude samples in less than 5–10%.) Attempts to recover pure 7 from the reaction mixture by various techniques, including chromatography, were unsuccessful. Crude samples of 4 containing small amounts of diazo oxide could be purified by recrystallization. Other methods of purification were found to be less effective, including an initial reduction treatment with excess hypophosphorous acid in boiling ethanol which very effectively removed diazo oxide but also caused some decomposition of 4. Elution chromatography of crude 4 on silica or alumina, while removing major impurities, also resulted in some decomposition of product. A mechanism for diazo oxide formation from nitramines has been suggested;[12] the details of this intriguing rearrangement await further study.

Decanitrobiphenyl (5) was prepared by peroxydisulfuric acid oxidation of 4 in 30% oleum solution containing 6.7 vol % of $H_2O_2$. The oxidation proceeds very slowly (ca. 10–14 days at 25 °C) compared to previous oxidations on substances such as pentanitroaniline (to yield hexanitrobenzene) which were complete within 18–24 h.[1] In previous examples 100% $H_2SO_4$ or 20% oleum was used, but 4 is practically insoluble in these solvents containing added $H_2O_2$. In 30% oleum/$H_2O_2$ solution the amine 4 is believed to be highly protonated, and the solution probably contains a rather low concentration of the free amine required for oxidative attack, thereby slowing the rate. Similar observations were reported previously in certain analogous examples where rates were slower in 20% oleum than in 100% $H_2SO_4$.[1,3] The yield in the 4 → 6 conversion (39%) is somewhat lower than in previous oxidations of this type (56–96%).[1] For example, the oxidation of 3,3′-diamino-2,2′,4,4′,6,6′-hexanitrobiphenyl to 2,2′,3,3′4,4′,6,6′-octanitrobiphenyl proceeds in 96% yield in 20% oleum. The lower yields are usually associated with oxidative degradation of the reactants and may be a result, in part, in the case of 4, of the prolonged reaction time required.

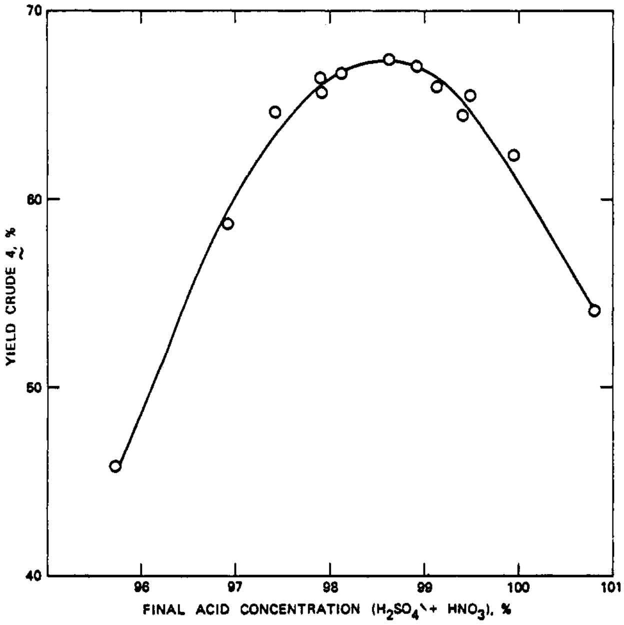


**Figure 1.** Plot of percentage yield of 4,4′-diamino-2,2′,3,3′,5,5′,6,6′-octanitrobiphenyl (4) vs. final acid concentration (% $H_2SO_4$ + $HNO_3$ constant throughout the reaction) from the nitration of 4,4′-diamino-2,2′,6,6′-tetranitrobiphenyl (3; 70 °C, 1.5 h, 19.4 molar equiv of $HNO_3$). Conditions were not optimum (see text).

Decanitrobiphenyl was isolated as pale yellow prisms, mp 243–248 °C dec. Its mass spectrum revealed a weak molecular ion peak. Chemically, it is similar to, but more reactive than, hexanitrobenzene, reacting readily with water or aqueous base to yield amorphous nitrophenol products. Suspended in benzene it reacts rapidly with ammonia to yield amorphous nitro amino products different from 4. This behavior is similar to that of hexanitrobenzene which gave trinitrophloroglucinol wiih aqueous base and 1,3,5-triamino-2,4,6-trinitrobenzene with ammonia in benzene. In reactions of hexanitrobenzene, however, the crystalline products were isolated from each reaction in nearly quantitative yield. Decanitrobiphenyl is much less soluble in organic solvents, including benzene and chloroform, than is hexanitrobenzene.

Our present observations suggest that the storage stabilities of known nitrocarbons decrease in the order tetranitromethane > hexanitroethane > hexanitrobenzene > decanitrobiphenyl. Tetranitromethane is stable on storage at 25 °C and boils at 126 °C without decomposition. Hexanitroethane, although storable at 25 °C, begins to decompose at 75 °C and decomposes rapidly at its melting point (142 °C).[5] Hexanitrobenzene, (mp 246–262 °C) shows some lowering of melting point and slight decomposition on prolonged storage at 25 °C. Decanitrobiphenyl, on the other hand, on standing in a desiccator at 25 °C over calcium chloride in the dark, slowly evolves oxides of nitrogen and ultimately forms a dark oily solid after 3–4 months (storage at 0 °C produced no change within this time). The instability is believed associated with a facile >C–NO$_2$ → >C–ONO rearrangement (via radical pairs) and subsequent degradation (>C–ONO → >CO· + NO·).[13] Evidence for this sequence is seen in the mass spectrum of 5 which reveals a strong M − 30 peak at *m*/*e* 574. The dissociation is facilitated by accumulated electron-releasing groups at or near the carbon of the C–nitro bond and by

---

[11] Nielsen, A. T.; Henry, R. A.; Norris, W. P.; Atkins, R. L.; Moore, D. W.; Lepie, A. H. *J. Org. Chem.* **1979**, *44*, 2499.

[12] Mudge, P. R.; Salter, D. A.; Scilly, N. F. *J. Chem. Soc., Chem. Commun.* **1975**, 569.

[13] (a) Ketari, R.; Foucaud, A. *J. Org. Chem.* **1981**, *46*, 4498. (b) McCarthy, E.; O'Brien, K. *Ibid*, **1980**, *45*, 2086. (c) Hochstein, W.; Schöllkopf, U. *Justus Liebigs Ann. Chem.* **1978**, 1823.

steric repulsion which destroys the phenyl–nitro coplanarity. In **5** resonance energy is also lost owing to noncoplanarity of the rings.

## Experimental Section

**Caution!** The polynitro compounds described herein are powerful explosives and should be handled carefully. The reagent peroxydisulfuric acid in sulfuric acid solution is a very powerful oxidant which may react violently with many organic materials, especially when heated. New reactions in which it is employed should first be tested on small quantities (100 mg or less of substates) with adequate safety precautions. Used peracid solutions should be disposed of immediately after workup by cautiously flushing with plenty of water. Concentrated $H_2O_2$ (90–98%), a powerful oxidant, must be handled with extreme care.

**4-Chloro-3,5-dinitrobenzoic Acid.** 4-Chlorobenzoic acid (Aldrich, 250 g, 1.60 mol) is added slowly, with stirring, to a mixture of 90% $HNO_3$ (900 mL 19.2 mol) and 1000 mL of fuming sulfuric acid (30% $SO_3$) at such a rate that the reaction temperature is maintained at 25–30 °C (ice bath cooling). After the addition is complete, a reflux condenser is attached, and the reaction mixture is heated, with stirring, to 85 °C by means of a heating mantle. The mantle is then removed and the temperature allowed to rise to, but not exceed, 95 °C. The flask is alternately inserted into and removed from an ice bath at intervals so as to maintain the reaction temperature at 95 °C. During this period (about 30 min), most of the 4-chlorobenzoic acid dissolves, and oxides of nitrogen are vigorously evolved. Heating and stirring are continued, maintaining the temperature at 95 ±1 °C for 4 h, after which time the flask contents are cooled by inserting the flask into an ice bath and then pouring the contents onto 12 L of crushed ice. The product is removed by suction filtration, washed thoroughly with 2 L of cold water, and vacuum dried at 25 °C. The high-purity 4-chloro-3,5-dinitrobenzoic acid is obtained as a very pale yellow solid: 352.9 g (89.6% yield); mp 161–163 °C (lit. mp 158 °C,[8] 159 °C,[14] 161–163 °C[15]). Parallel runs gave yields of 87–90%. The product is suitable for conversion to its methyl ester without further purification.

**Methyl 4-Chloro-3,5-dinitrobenzoate (1).** Concentrated (96%) $H_2SO_4$ (30 mL) is slowly added to 4-chloro-3,5-dinitrobenzoic acid (70.0 g, 0.284 mol) and 160 mL of methanol, and the mixture is gently heated to reflux with the aid of a heating mantle. As refluxing starts, crystallization of the product is observed, and the mantle is removed (heat released from crystallization of the product may cause vigorous boiling, and cooling of the flask may be required). After the exothermic crystallization has subsided (about 10 min), heating under reflux is continued for 4 h; then, the flask is allowed to cool to 25 °C for 12–15 h. The condenser is removed and the mixture stirred mechanically to break up the lumps of precipitate. The product is removed by suction filtration and washed with two 30-mL portions of methanol to yield, after drying in air, 71.0 g (95.9%) of methyl 4-chloro-3,5-dinitrobenzoate as very pale yellow prisms, mp 104–106 °C (lit.[8,14] mp 105 °C). Dilution of the filtrate with water deposits additional product (ca. 3 g, mp 103–105 °C) which is recrystallized from methanol to yield 2.4 g of ester (mp 104–105 °C), raising the total yield to 73.4 g (99.2%). Parallel runs provide yields of 97–100%.

**4,4′-Dicarbomethoxy-2,2′,6,6′-tetranitrobiphenyl (2).** Methyl 4-chloro-3,5-dinitrobenzoate (20.0 g, 0.77 mol) and dry xylene (80.0 mL) are introduced into a three-necked flask provided with a reflux condenser, thermometer, and a wide-center neck (ball joint) to accommodate a stainless steel, four-bladed propeller on a shaft to fit the motor chuck. The mixture is stirred vigorously by means of a high-speed, high-torque, variable-speed stirring motor, maintaining a stirring speed of at least 600–800 rpm. Copper powder (4.8 g, 0.0755 mol, of fine copper powder, no. 44, from American Bronze Powder Co.) is added and the stirred mixture heated to reflux by means of a heating mantle (135–140 °C, 30–40 min). There is a slight exothermic reaction with a color change to dark brown during the heating. Gentle refluxing (pot temperature 137 °C) and vigorous stirring are continued for 1.5 h. A second portion of copper powder (2.4 g) is added, and refluxing and vigorous stirring are continued for an additional hour. The hot solution is filtered by suction through a 1-cm bed of Celite filter aid and the solid extracted three times by stirring with 40-mL portions of boiling methylene chloride. The filtrate and the extracts are treated with Darco decolorizing charcoal, heated, and filtered hot into a round-bottomed flask; complete removal of solvent on a rotary evaporator (hot water bath heating) gave 15.9 g of crude product as a tan powder. The crude product is dissolved in a minimum volume of boiling benzene, followed by addition of methanol (twice the volume of benzene), and allowed to cool to 0 °C for several hours. Filtration by suction, followed by washing with cold methanol, yields 4,4′-dicarbomethoxy-2,2′,6,6′-tetranitrobiphenyl (**2**): 14.6 g (84.6% yield); flat needles; mp 189–191 °C (lit. mp 187–189 °C,[10] 192–192.5 °C[9]). Another crystalline form has been reported as flakes, mp 171–172 °C,[10] 173 °C.[8] In parallel runs, yields of 80–85% are obtained. Occasionally, the lower melting polymorph is obtained by the above procedure; mp 170–172 °C.

**4,4′-Dicarboxy-2,2′,6,6′-tetranitrobiphenyl.** 4,4′-Dicarbomethoxy-2,2′,6,6′-tetranitrobiphenyl (15.0 g, 0.033 mol) is added to 100 mL of concentrated $H_2SO_4$ (96%), and the mixture is heated by a heating mantle, with stirring, to ca. 70 °C to produce a dark-colored solution. The mantle is then removed, and water (20 mL) is added dropwise at a rate to keep the reaction temperature at 95 ± 5 °C; after the water addition is complete, the mantle is replaced, and heating at 95 °C is continued for 1 h. The mixture is then poured over 300 g of ice with stirring. The precipitated product is filtered, washed with cold water, and dried under vacuum at 25 °C to yield 14.1 g (100%) of 4,4′-dicarboxy-2,2′,6,6′-tetranitrobiphenyl as a white powder, mp 325–338 °C dec (lit. mp 350–352 °C,[10] 338–342 °C.[9] Parallel runs gave 99.5–100% yields of product. The unrecystallized material is suitable for conversion to 4,4′-diamino-2,2′,6,6′-tetranitrobiphenyl without further purification. A sample recrystallized from acetonitrile yields prisms, mp 345–355 °C dec (85% recovery).

**4,4′-Diamino-2,2′,6,6′-tetranitrobiphenyl (3).** 4,4′-Dicarboxy-2,2′,6,6′-tetranitrobiphenyl (12.0 g, 0.028 mol) is added, with stirring, to 73 mL of oleum (20% $SO_3$). After a clear solution is obtained, 1,2-dichloroethane (64 mL) is added and the mixture heated to 45 °C with a heating mantle. The mantle is then removed, and sodium azide (5.2 g, 0.080 mol) is slowly added in small portions with stirring, keeping the temperature below 47 °C by ice bath cooling. The addition funnel is replaced by a reflux condenser, and the mixture is heated to 65–67 °C, whereupon the heating mantle is removed; vigorous gas evolution occurs during a period of 5–10 min. After the gas evolution subsides, the mixture is heated under reflux, with stirring, for 3 h. The mantle is removed, the mixture cooled to 45 °C, and additional sodium azide (2.0 g, 0.031 mol) is added in small portions, keeping the temperature at 45 ± 2 °C. The mixture is then heated under reflux, with stirring, for an additional 2 h. After cooling to 25–40 °C, the solution is poured into a separatory funnel, and the bottom acid layer is drained, with stirring, onto 500 mL of ice cubes. The mixture, containing a yellow precipitate, is warmed to 60 °C and then allowed to cool to 25 °C for 12–20 h (overnight) to increase particle size and facilitate filtration. (Alternatively, the mixture may be filtered directly, but the filtration is slow.) Filtration of the product, followed by washing with 300 mL of cold water, gave 1,4-diamino-2,2′,6,6′-tetranitrobiphenyl (**3**); 10.2 g, 98.8%) as a bright yellow powder (vacuum dried at 25 °C), mp 340–350 °C dec (lit.[10] mp 300 °C dec). Parallel runs gave yields of 93–100% (in 14–24% $SO_3$ oleum solvent). A sample, recrystallized from acetonitrile, had a melting point of 345–355 °C dec (71% recovery). The unrecrystallized material is very pure and suitable for conversion to 4,4′-diamino-2,2′,3,3′,5,5′,6,6′-octanitrobiphenyl: $^1H$ NMR ($(CD_3)_2SO$) $\delta$ 7.38 ($(CD_3)_2C{=}O$) 7.70 (s, CH), 4.6 (br s, $NH_2$); IR (KBr) 3450, 3350 ($NH_2$ doublet), 1630, 1525 (s), 1430 (w), 1340, 1300, 922, 865, 810, 775, 730 $cm^{-1}$.

**4,4′-Diamino-2,2′,3,3′,5,5′,6,6′-octanitrobiphenyl (4).** 4,4′-Diamino-2,2′,6,6′-tetranitrobiphenyl (5.0 g, 0.014 mol) is added with stirring to 150 mL of 99% $H_2SO_4$ (100 mL of concentrated 96% $H_2SO_4$) and 50 mL of 22% $SO_3$ oleum (the oleum concentration was checked with a hydrometer). The mixture is stirred until all of the reactant has dissolved (about 10 min). It is then cooled to 10–15 °C by means of an ice bath, and a mixture of 90%

---

[14] Ullmann, F.; Wosnessensky, N. *Justus Liebigs Ann. Chem.* **1909**, *366*, 79, 92.

[15] Berkenheim, A. M.; Lur'e, S. I. *Zh. Obshch. Khim.* **1936**, *6*, 1043.

$HNO_3$ (10 mL) and concentrated $H_2SO_4$ (96%, 25 mL), previously cooled to 25 °C, is added, with the temperature maintained below 20 °C during the addition. The addition funnel is replaced by a gas-exit tube, and the mixture is stirred and heated at 30–35 °C for 1.5 h; 50% aqueous $H_2SO_4$ (12.5 mL) is then added to lower the acid concentration to 96%. The mixture is then heated to 65 °C during 30 min. Stirring and heating are continued at 70 ± 2 °C for 1.5 h. The heating mantle is removed and replaced by an ice bath and the mixture stirred to cool the flask contents below 25 °C. The product is removed by filtration and washed, successively, with concentrated sulfuric acid, 50% aqueous sulfuric acid, and finally 1 N aqueous hydrochloric acid. After being vacuum dried, the crude product weighs 5.3 g (71%). Parallel runs provide yields of crude product of 70–72%. The IR (KBr) was similar to that of pure **4** except for a weak diazo oxide band at 2192 $cm^{-1}$ and slight broadening of other bands. For purification, the crude product is dissolved in 90 mL of dry acetonitrile at 35–40 °C, Darco decolorizing charcoal (1.0 g) and anhydrous $MgSO_4$ (1.0 g) are added, and the mixture is stirred magnetically for 1 h ($CaCl_2$ tube attached) at 25 °C. The mixture is then filtered and the filtrate concentrated under reduced pressure to a volume of ca. 10 mL (bath temperature 30–40 °C). Some dark red crystals of an acetonitrile solvate of **4** are deposited. Dry 1,2-dichloroethane (25 mL) is then added and the mixture chilled at 0 °C for several hours. Filtration yields 2.2 g (30%) of **4** as yellow-orange crystals: mp 310 °C dec; IR (KBr) 3467, 3350 ($NH_2$ doublet), 1640, 1520 (s), 1420, 1320, 1270, 890, 880, 833, 825, 800, 785 (w) $cm^{-1}$. Parallel runs gave 25–35% yields of pure **4**. The compound may be recrystallized from heated dry acetonitrile, followed by concentration to a small volume: 75–85% recovery; bright yellow or yellow-orange prisms; mp 310 °C dec. Anal. Calcd for $C_{12}H_4N_{10}O_{16}$: C, 26.46; H, 0.74; N, 25.74. Found: C, 26.49; H, 0.80; N, 25.58. Other solvents for crystallization of crude **4** were examined. Ethyl acetate is nearly as efficient as acetonitrile, but acetone, ethanol, dioxane, and acetic acid were less efficient. The crude **4** is very insoluble in most other common solvents.

The dried, crude reaction product (5.0 g) is added to a mixture of 50 mL of 95% ethanol and 5.0 mL of 50% aqueous hypophosphorous acid. The mixture is heated rapidly on a steam bath with swirling, maintaining a temperature of 65–75 °C for 5 min; gas is evolved during the heating period. The solution is then rapidly cooled to 30 °C in an ice bath, with swirling, and then concentrated under reduced pressure to near dryness (bath temperature 30–40 °C). Aqueous hydrochloric acid (200 mL of a 1 N solution) is then added to the residue, and the resulting precipitate is removed by suction filtration (yield 4.8 g, 96% recovery). The infrared spectrum of this treated, crude product reveals the absence of diazo oxide impurity. The treated, crude product is dissolved in 20 mL of hot ethyl acetate by warming it on a steam bath and then concentrated under reduced pressure to a volume of 7–8 mL. 1,2-Dichloroethane (5 mL) is then added and the mixture stored at 0 °C for several hours. The purified, precipitated product **4** is removed by suction filtration followed by washing with a cold solution of mixed ethyl acetate/1,2-dichloroethane (1:4 by volume) to yield 1.75 g of pure **4** (23.4% yield of **4** from **3**, 35% recovery from crude) as a yellow powder, mp 310 °C dec. Parallel runs gave 20–25% yields. Use of dioxane to replace ethanol in the above procedure gives a product contaminated with oxygenated impurities (as indicated from examination of infrared spectra). Several other methods were examined for purification of crude **4**. Trituration with sulfuric acid or oleum at 25–50 °C for several hours gives a product containing less diazo oxide. However, owing to the very low solubility of the sample in this medium, very little reaction occurred. Heating with acetic acid or with solvents containing acetic acid or other acids usually decomposes some of the desired product.

A 1.0-g sample of crude reaction product dissolved in 5 mL of acetonitrile is placed on a 2 × 28 cm column of silica gel (Woelm, dry column chromatography). Elution with a solution of methylene chloride/acetonitrile (3:1 by volume) gives a fast-moving band removed in the first 50 mL of eluate. Removal of solvent from this fraction by concentration under reduced pressure gives 0.35 g (23.4% yield from **3**; 35% recovery) of an orange, crystalline product containing principally **4**. Its infrared spectrum reveals the absence of the diazo oxide band and the appearance of new, weak signals at 905, 1120, 1150, and 1215 $cm^{-1}$ which are absent in the pure product. Further elution with the same solvent mixture (350 mL) gives ca. 0.1 g of dark red, gummy, unidentified material. A final elution with 175 mL of acetonitrile gives 0.48 g of a red, unidentified grease; its infrared spectrum resembles that of the crude reaction product (broad $NH_2$ doublet; diazo oxide bands were present). Recrystallization of fraction 1 from ethyl acetate/dichloroethane gives 0.22 g of crude **4** (63% recovery), which reveals the extraneous infrared peaks present in the unrecystallized, chromatographed sample and absent in pure **4**. Chromatography of a pure sample of **4** on silica gel by the above procedure results in 88% recovery of a product containing some impurities as indicated by its infrared spectrum.

**Decanitrobiphenyl (5).** 4,4′-Diamino-2,2′,3,3′,5,5′,6,6′-octanitrobiphenyl (**4**; 2.18 g, 4.0 mmol; recrystallized pure sample) is added to 300 mL of oleum (30% $SO_3$); a calcium chloride tube is attached to the flask. After magnetic stirring for 5 min at 25 °C, all of the diamine is dissolved, providing a clear yellow solution. The solution is cooled with an ice bath to 5 °C, and hydrogen peroxide (20 mL of 98%) is cautiously added dropwise with stirring during 1 h, keeping the temperature at 8–12 °C. The stirring is stopped, and the red-orange, clear solution is warmed slowly to 25 °C by allowing the ice to melt. The solution gradually becomes orange and turbid after 3 or 4 days; after 6–7 days the color changes to yellow, and a precipitate appears. After 2 weeks at 25 °C the mixture is filtered and washed successively with concentrated $H_2SO_4$, 50% $H_2SO_4$, and 1 N aqueous HCl; vacuum drying gives 0.94 g (38.6%) of **5** as small yellow prisms: mp 243–248 °C dec; IR (KBr) 1550, 1315, 885, 828 $cm^{-1}$, $NH_2$ and OH bands absent; mass spectrum, *m/e* 605 ($M^{+\cdot} + 1$), 604 ($M^{+\cdot}$), 574, 529, 326, 46 (base). (Parallel runs give similar results.) The compound is not measurably soluble in boiling $CH_2Cl_2$, $C_6H_6$, or $CHCl_3$. It dissolves in boiling acetonitrile or 1,2-dichloroethane, but with some decomposition. Attempts to purify the compound by recrystallization from these solvents result in rather large losses and formation of a less pure product. For example, a 20-mg sample of the crude material dissolved in 20 mL of boiling 1,2-dichloroethane is concentrated under nitrogen at 25 °C to yield small yellow prisms having a lower melting point (238–248 °C dec) and giving elemental analyses less satisfactory than those of the crude product. Owing to low solubility and/or decomposition in solution, it was not possible to secure a satisfactory $^{13}C$ NMR spectrum of **5**. Elemental analysis of a sample of unrecrystallized material gave the following. Anal. Calcd for $C_{12}N_{10}O_{20}$: C, 23.86; N, 23.18. Found: C, 24.01; H, 0.36; N, 20.53. We have found low nitrogen analyses to be a persistent problem with polynitro compounds such as hexanitrobenzene.[3] The filtrate from removal of **5** is extracted with six 40-mL portions of methylene chloride; the extracts are combined and poured through a short column of anhydrous $MgSO_4$. Concentration to dryness gives 0.1 g of amorphous yellow powder (mp 100–120 °C) from which no **5** could be isolated.

Reactions of **5** with aqueous m sodium hydroxide and (separately) ammonia gas are performed by the procedures employed with hexanitrobenzene.[3] With aqueous NaOH a yellow amorphous solid is formed (mp 75–140 °C), revealing a strong OH band at 3350 $cm^{-1}$ in its infrared spectrum. Dry $NH_3$ bubbled through a suspension of **5** in dry benzene gives an instantaneous formation of a red gummy solid. Trituration of the solid with acetonitrile gives a yellow amorphous product (mp 190–200 °C dec), revealing a strong $NH_2$ doublet at 3300, 3200 $cm^{-1}$ and $NO_2$ bands at 1570 and 1370 $cm^{-1}$. Crystalline material could not be isolated from these reaction products.

**Acknowledgment.** This work was performed under Naval Weapons Center Independent Research and Naval Sea Systems Command funds. The support of L. A. Roslund is gratefully acknowledged.

**Registry No.** **1**, 2552-45-6; **2**, 24059-53-8; **3**, 23938-91-2; **4**, 84642-53-5; **5**, 84647-88-1; 4-chlorobenzoic acid, 74-11-3; 4-chloro-3,5-dinitrobenzoic acid, 118-97-8; 4,4′-dicarboxy-2,2′,6,6′-tetranitrobiphenyl, 84642-54-6.