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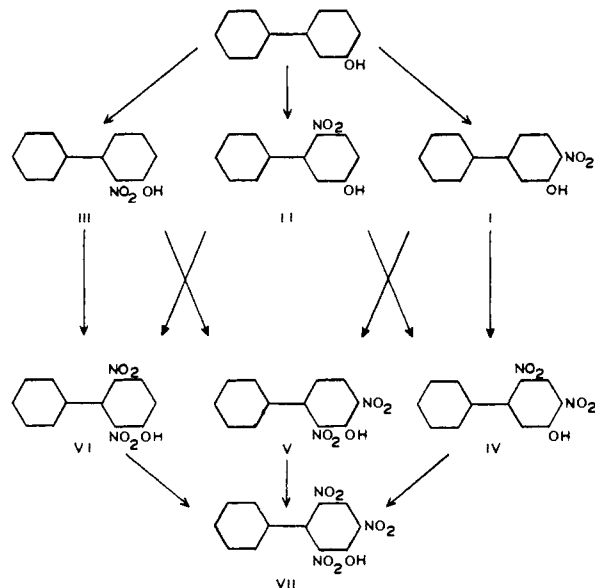
Nitration of 3-Hydroxybiphenyl¹

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The nitration of 3-hydroxybiphenyl has been carried out under a variety of conditions. Eight identifiable compounds resulted from each nitration. A chromatographic procedure for separation of these products has been developed. Tentative structures have been suggested and proofs presented for five of the nitrophenols not previously reported.

It has been known for some time² that the nitration of 3-hydroxybiphenyl results in the formation of 4-nitro-3-hydroxybiphenyl (I). Since directional influences in 3-hydroxybiphenyl should lead to formation of three mononitro derivatives I, II, III, three dinitro derivatives IV, V and VI and to one trinitro derivative VII, without considering the possible introduction of nitro groups into the non-phenolic ring, the preparation and separation of these derivatives is of interest. In addition to the formation of I through direct introduction of the nitro group into 3-hydroxybiphenyl, III has been obtained³ by the phenolation of *o*-nitrobiphenyl. The preparation of V has been reported^{2,3}; however, the present work does not support earlier claims.



When 3-hydroxybiphenyl was dissolved in either glacial acetic acid, dioxane or nitromethane, and either concd. or fuming nitric acid added, compounds I-VII were formed together with small quantities of a derivative isomeric with VII. The conditions of nitration such as temperature, concentration of acid and choice of solvent had a considerable effect upon the distribution of products

(1) Abstracted from a thesis submitted by Daniel W. Fox in partial fulfillment of requirements for the degree of Doctor of Philosophy and from a thesis submitted by Charles Matuszak in partial fulfillment of requirements for the degree of Master of Science at the University of Oklahoma. This research was made possible by a grant from the Office of Ordnance Research, Durham, N. C. Thanks are due the Dow Chemical Co. of Midland, Michigan, for supplying the 3-hydroxybiphenyl used in this research.

(2) J. C. Colbert, W. Meigs and R. L. Jenkins, *THIS JOURNAL*, **59**, 112 (1937).

(3) O. C. Dermer and L. S. Drucker, *Okla. Acad. Sci.*, **23**, 55 (1943).

but did not in any case completely eliminate any one of the eight finally isolated.

Chromatographic procedures on Magnesol⁴ using benzene as an eluant were developed which gave a satisfactory separation of the reaction mixtures resulting from the nitration of 3-hydroxybiphenyl. While I and III are of known structure II and IV-VII do not appear to have been reported. Structural proofs were obtained for these five derivatives and partial proof for an eighth derivative formed in small amount. The structure of 6-nitro-3-hydroxybiphenyl (II) was determined by the transformation of 4,6-dinitro-3-hydroxybiphenyl (IV) into II by methylation of IV, partial reduction, diazotization, deamination and demethylation. The nitro group in the 4-position is believed to have been reduced since it has been shown⁵ that in a dinitrophenol the nitro group *ortho* to the hydroxyl group is most readily attacked. Since the other two mononitro derivatives of 3-hydroxybiphenyl involved are of known structure and since II upon further nitration yields both IV and VI but not V the structure can be considered proved. Compounds IV-VII gave benzoic acid upon oxidation by chromic acid indicating all nitro groups to be in the phenolic ring.

The structure of 4,6-dinitro-3-hydroxybiphenyl (IV) was proved by treating with urea to form 4,6-dinitro-3-aminobiphenyl, diazotizing and deaminating through use of hypophosphorous acid. 2,4-Dinitrobiphenyl was obtained in pure form by passing the reaction mixture in benzene solution through a Magnesol column. Properties of this substance agree with those previously⁶ reported. The formation of 2,4-dinitrobiphenyl from IV eliminates VI as a possible structure but does not differentiate IV from V since both of these dinitrophenols would yield 2,4-dinitrobiphenyl by removal of the hydroxyl group. Final differentiation between IV and V was made by conversion of IV to II as previously described and by further nitration of I, II and III as shown in Table I. It will be observed that upon further nitration both I and II gave high yields of IV while III failed to yield IV by any method of nitration attempted. The structure of 2,4-dinitro-3-hydroxybiphenyl (V) has been established by formation from both I and III and failure to obtain it by nitration of II. 2,6-Dinitro-3-hydroxybiphenyl (VI) was prepared by the nitration of both II and III but was not obtained when I was further nitrated. The structure of 2,4,6-trinitro-3-hydroxybiphenyl (VII) was established by its preparation through further nitration of compounds I-VI. A trinitro-

(4) Magnesol, a synthetic magnesium silicate, was obtained from Westvaco Chemical Division of the Food Machinery and Chemical Corporation.

(5) K. Auwers and H. Rohrig, *Ber.*, **30**, 995 (1897).

(6) H. C. Gull and E. E. Turner, *J. Chem. Soc.*, 496 (1929).

phenol isomeric with VII was obtained in small amount. Oxidation of this substance by chromic acid gave *p*-nitrobenzoic acid thereby establishing the 4'-position for one of the nitro groups. Efforts to assign positions to the remaining two nitro groups failed. This was in part due to the small quantity of material available. Infrared spectra have been determined for all nitrophenols obtained in the course of this investigation.⁷

The mono- and dinitrophenols obtained from 3-hydroxybiphenyl were all submitted to further nitration. The results of these nitrations are summarized in Table I.

TABLE I
PRODUCTS FROM THE NITRATION OF MONO- AND DINITRO-3-HYDROXYBIPHENYLS

Reactant	Nitrating agent	4,6-Di-nitro	2,4-Di-nitro	2,6-Di-nitro	2,4,6-Tri-nitro
4-Nitro	Concd. HNO ₃	34.8	32.2	..	4.5
	Fuming HNO ₃	4.0	50.0	..	4.0
6-Nitro	Concd. HNO ₃	36.0	38.0
	Fuming HNO ₃	49.0	..	38.0	..
2-Nitro	Concd. HNO ₃	..	29.7	35.8	17.8
	Fuming HNO ₃	..	19.0	3.0	28.0
4,6-Dinitro	Fuming HNO ₃	44.0
2,4-Dinitro	Fuming HNO ₃	37.0
2,6-Dinitro	Fuming HNO ₃	57.0

Experimental

Chromatographic Separations.—Columns for use in separating reaction mixtures resulting from the nitration of 3-hydroxybiphenyl were packed using benzene slurries of Magnesol. The capacity of a 2.5 × 50 cm. column varied from 3–5 g. of the mononitro- to as much as 25 g. of the trinitro derivatives of 3-hydroxybiphenyl. The reaction mixtures were adsorbed from benzene solutions and partially developed and eluted with the same solvent. After the bulk of the first mono-nitro compound, I, had been eluted petroleum ether was added to the eluant to slow the rate of elution. This was necessary to effect a clean separation of the mononitro compounds. When compounds I, III and II, in that order, were completely removed, the resulting column was void of color in the lower quarter. Above this point an orange-yellow zone was occupied by IV and a second void zone occurred immediately above. The remaining compounds were in the top half of the column. Removal from the column was accomplished in two ways. Continued elution with benzene slowly moved the lower zone down and out of the column, or the bottom support of the column could be removed and the lower zone extruded. In the latter case, the column support was replaced and elution continued after partial extrusion. The portion of the extruded column containing the adsorbed compound was placed in a sintered glass funnel and leached with 90–95% ethanol. Regardless of which of these two procedures was followed to remove compound IV, 0.5–1.0% acetic acid was added to the benzene eluant to move compounds V, VI and VII, in that order, down to the bottom of the column. The acetic acid addition was then discontinued to effect a slow removal of these three compounds. The bulk of V could be removed in a pure state, the trailing portion of the zone tending to overlap the leading portion of the zone containing compound VI. Eluate from the overlapping portion of the column was collected as a separate fraction. Addition of petroleum ether to a concentrated benzene solution of the mixture precipitated essentially all of the very insoluble VI, whereas compound V remained in solution. With continued benzene elution of the column the remainder of VI could be removed. Acetic acid up to 5% was then added to rapidly remove an eighth derivative, isomeric with VII, and to

(7) Infrared spectra can be obtained from Samuel P. Sadtler Research Laboratories, 1517 Vine St., Philadelphia 2, Pa.

slowly remove VII. Several indistinct zones were frequently observed which were even more difficult to remove than VII. They were, however, never isolated and identified due to the large amount of silicic acid formed with increasing acetic acid concentrations.

In most cases, the phenolic compounds were recovered from the eluate by evaporation with a trace of added acetic acid. The acid was necessary since some salt formation resulted. The dried residues were taken up in benzene and re-evaporated to free them of inorganic material. An alternative procedure in those cases where the eluate was very dilute, with respect to phenolic compounds, was to pass it through a short calcium oxide column. This adsorbent effectively removed all of the phenols. Recovery of the desired compounds was effected by solution of the calcium oxide in dilute hydrochloric acid.

The general procedure of preparing the reaction mixtures for all chromatographic separations consisted of stopping the reactions by the addition of water and extraction of the products with benzene. When acetic acid was used as nitration solvent, the benzene extracts were concentrated several times with added benzene or petroleum ether to remove the acid azeotropically.

Mononitro Derivatives of 3-Hydroxybiphenyl.—One and seven-tenths g. (0.01 mole) of 3-hydroxybiphenyl was dissolved in 17 ml. of nitromethane and cooled to 2–4° in an ice-bath. Fuming nitric acid (0.34 ml., 0.008 mole) was added dropwise with stirring. The nitrating mixture remained in the cold bath 12 hours. Following addition of several volumes of water the reaction mixture was extracted with benzene and the extract washed with dilute hydrochloric acid and a small portion of water. The benzene extract was concentrated to near dryness several times with addition of toluene. The final solution was made up to 50 ml. with benzene and placed on a 3.5 × 60 cm. column of Magnesol.

4-Nitro-3-hydroxybiphenyl (I).—Upon elution of the Magnesol column the first band to move out was that containing 4-nitro-3-hydroxybiphenyl. Evaporation of the eluant left 0.65 g., yield 30%. Recrystallization from 95% alcohol gave m.p. 104–105°. This compound is difficultly volatile in steam; solubility⁸ at 25°, 2.98 mg./100 ml. water; 1.31 g./100 ml. abs. alcohol. While excellent results were obtained using fuming nitric acid in nitromethane the use of 0.011 mole of fuming nitric acid in dioxane, temperature 15°, lowered the yield to 20% and with 0.011 mole of fuming nitric acid in glacial acetic acid, temperatures 2–4°, the yield was 21.5%.

2-Nitro-3-hydroxybiphenyl (III).—This compound has not been previously reported from direct nitration of 3-hydroxybiphenyl. The second band to come from the chromatographic column was that containing 2-nitro-3-hydroxybiphenyl. Evaporation of the eluant left 0.60 g., yield 28%. Recrystallization from benzene gave m.p. 85–86°. This is higher by 2° than previously reported. We have observed that separation of isomers such as the mononitro derivatives of 3-hydroxybiphenyl through use of the Magnesol column often leads to purer products and slightly higher melting points than previously reported; solubility at 25° 2.42 mg./100 ml. water; 14.97 g./100 ml. abs. alcohol. Nitration in dioxane solution using 0.011 mole of fuming nitric acid, temperature 15°, lowered the yield to 11% while in glacial acetic acid using 0.011 mole of fuming nitric acid, temperature 2–4°, the yield was 10%. When nitromethane was used and the concentration of fuming nitric acid increased from 0.008 to 0.015 mole, temperature 2–4°, the yield fell to 21%.

6-Nitro-3-hydroxybiphenyl (II).—The third band to come from the column contained 6-nitro-3-hydroxybiphenyl. Evaporation of the eluant gave 0.49 g., yield 23%. Recrystallization from benzene gave m.p. 57–58°; solubility at 25° 4.66 mg./100 ml. water; 24.37 g./100 ml. abs. alcohol. This substance crystallizes with extreme difficulty.

When the concentration of fuming nitric acid was increased to 0.033 mole and other conditions unaltered no 6-nitro-3-hydroxybiphenyl was isolated. When the concentration of fuming nitric acid was increased to 0.015 mole the yield of this compound increased to 30.75%.

6-Nitro-3-hydroxybiphenyl by Conversion of 4,6-Dinitro-3-hydroxybiphenyl.—Nine g. (0.033 mole) of 4,6-dinitro-3-methoxybiphenyl in 500 ml. of ethanol was treated with 11.0

(8) All solubility determinations were made by James A. Hanan.

g. (0.039 mole) of sodium disulfide.⁹ The reduction products were recovered by the following operations. The reduction mixture was filtered hot and evaporated to dryness under reduced pressure to obtain a residue which was partially taken up in benzene. The benzene extracts were shaken with concd. hydrochloric acid to form a slurry of the hydrochlorides. Excess 5% sodium hydroxide was added to the aqueous slurry and the amines extracted with benzene. Evaporation gave 4.5 g. of oil which could not be readily crystallized and was converted into a slurry with concd. hydrochloric acid. The ether was removed in a forced draft and 1.4 g. (0.02 mole) of sodium nitrite in 50 ml. of ice-water was added. A chilled (5°) 30% solution (50 ml.) of hypophosphorous acid¹⁰ was added to the diazotized amine. After standing at 5° for 24 hr. excess water was added to the deamination reaction and the solution extracted with benzene. The benzene solution was dried over anhydrous sodium sulfate and evaporated to an oil under reduced pressure. Demethylation to 6-nitro-3-hydroxybiphenyl was accomplished by heating this oil dissolved in 40 ml. of 1:1 acetic anhydride-48% hydrobromic acid for 48 hr. on a steam-bath. Following dilution with several hundred ml. of water benzene extraction removed both phenol and unhydrolyzed material. Extraction of the benzene extract with 5% sodium hydroxide removed the desired phenol. Acidification and reextraction with benzene, concentration and drying gave a solution suitable for chromatographing. The eluate from the central of three distinct zones on the column gave, upon evaporation, a pale, yellow, viscous, oil which crystallized after standing for several days; yield 0.50 g., 7% based upon 4,6-dinitro-3-methoxybiphenyl, m.p. 57-58°.

Anal. Calcd. for $C_{12}H_9O_2N$: N, 6.51. Found: N, 6.50.

4,6-Dinitro-3-hydroxybiphenyl (IV).—This is the most readily prepared and isolated of the dinitro-3-hydroxybiphenyls. Either fuming or concentrated nitric acid in acid:phenol ratio of 3:1 in the presence of 5 ml. of glacial acetic acid per gram of 3-hydroxybiphenyl will give yields of 30-40%. The bulk of the product separates from the reaction mixture as well formed crystals and the remainder is readily separated from the many other reaction products by passing through the Magnesol column using benzene as the eluant. On the column the band containing this substance is preceded and followed by a void zone meaning there is no admixture with either mononitro derivatives which precede it or with the dinitro derivatives which follow it further up the column. Ninety-four hundredths g. (0.015 mole) of concd. nitric acid in 3 ml. of glacial acetic acid was added to 0.85 g. (0.005 mole) of 3-hydroxybiphenyl in 5 ml. of glacial acetic acid. After one hour at room temperature an equal volume of water was added and the reaction mixture extracted with benzene. Twenty ml. of *n*-heptane was added and upon distillation acetic acid was removed as an azeotrope. The benzene solution was chromatographed after removal of crystalline 4,6-dinitro-3-hydroxybiphenyl. The amount obtained from the column plus crystals filtered off before chromatographing totalled 0.507 g. (39%), m.p. 176-178°, from benzene; solubility at 25° 0.88 mg./100 ml. water and in abs. alcohol 0.275 g./100 ml.

Anal. Calcd. for $C_{12}H_8O_3N_2$: N, 10.76. Found: N, 10.70.

2,4-Dinitro-3-hydroxybiphenyl (V).—This nitrophenol¹¹ can be prepared by either direct nitration of 3-hydroxybiphenyl or by further nitration of both 4-nitro- and 2-nitro-3-

(9) P. E. Verkade, C. P. van Dijk and W. Meerburg, *Rec. trav. chim.*, **65**, 346 (1946).

(10) Roger Adams and N. Kornblum, *This Journal*, **63**, 194 (1941).

(11) This compound has been reported formed by the nitration of I² and III.³ Both reports give melting points in the 169-173° range. In the present investigation a compound melting in this range was obtained by nitration of I but not from III. Both I and III yield a dinitrophenol melting at 126-127° which must be 2,4-dinitro-3-hydroxybiphenyl (V). When a mononitro derivative of 3-hydroxybiphenyl is further nitrated a number of higher nitration products are formed and no variation in conditions can shut out any one of the possibilities. We think that prior to use of the keen edged tool of chromatographic separation the "compounds" reported were impure and that this accounts for the differences in melting points reported for 2,4-dinitro-3-hydroxybiphenyl. We dissolved a sample of the so-called V, prepared by one of us in 1937, in benzene and placed it on the Magnesol column. At least three bands appeared, indicating a mixture.

hydroxybiphenyl. To 0.85 g. (0.005 mole) of 3-hydroxybiphenyl dissolved in 8 ml. of glacial acetic acid there was added dropwise 0.42 ml. (0.010 mole) of concd. nitric acid. The reaction mixture stood at room temperature for one hour before being prepared for the chromatographic column. In addition to I-IV and VI, VII, 0.163 g. (12.5%) of 2,4-dinitro-3-hydroxybiphenyl was obtained, m.p. 126-127°, from benzene; solubility 1.0 mg./100 ml. water at 25° and in abs. alcohol 1.78 g./100 ml.

Anal. Calcd. for $C_{12}H_8O_3N_2$: N, 10.76. Found: N, 10.75.

Substitution of nitromethane and fuming nitric acid for glacial acetic acid and concd. nitric acid did not improve the yield of 2,4-dinitro-3-hydroxybiphenyl. When 4-nitro-3-hydroxybiphenyl was nitrated in glacial acetic acid using fuming nitric acid, 2,4-dinitro-3-hydroxybiphenyl was obtained in 50% yield. Nitration of 2-nitro-3-hydroxybiphenyl in glacial acetic acid solution using concd. nitric acid gave 29.7% yield of 2,4-dinitro-3-hydroxybiphenyl.

2,6-Dinitro-3-hydroxybiphenyl (VI).—Optimum conditions for the preparation of this nitrophenol are an acid:phenol ratio of 2.5 to 1, concd. nitric acid, and glacial acetic acid as solvent in the ratio of 7.5 ml. to 1 g. of 3-hydroxybiphenyl. Under these conditions maximum yields of 40% were obtained. Eighty-five hundredths g. (0.005 mole) of 3-hydroxybiphenyl in 6.4 ml. of glacial acetic acid when treated at room temperature with 0.64 g. (0.012 mole) of concd. nitric acid gave a mixture containing I-VII, and a trace of a compound isomeric with VII. When separated on the Magnesol column there was obtained by evaporation of the benzene eluant 0.52 g. of 2,6-dinitro-3-hydroxybiphenyl, m.p. 214°, yield 40%; solubility 4.54 mg./100 ml. water at 25° and in abs. alcohol 10.54 g./100 ml.

Anal. Calcd. for $C_{12}H_8O_3N_2$: N, 10.76. Found: N, 10.70.

Substitution of fuming nitric acid in this preparation lowered the yield to 36%. Upon further nitration using fuming nitric acid 2-nitro-3-hydroxybiphenyl gave 35.8% and 6-nitro-3-hydroxybiphenyl a 38% yield of 2,6-dinitro-3-hydroxybiphenyl.

2,4,6-Trinitro-3-hydroxybiphenyl (VII).—This is the only nitration product of 3-hydroxybiphenyl which can be obtained in high yield and pure condition without use of the chromatographic column. Ten grams of 3-hydroxybiphenyl in 200 ml. of glacial acetic acid was treated dropwise with 12 ml. of fuming nitric acid (4:1 acid to phenol ratio) in 30 ml. of glacial acetic acid. The solution was kept just short of boiling during the addition. The reaction mixture stood two hours at room temperature and was heated on a steam-bath for an additional two hours. The reaction mixture was poured into an equal volume of boiling water to give a semi-gelatinous mass. The crude product gave from 95% alcohol 14.3 g. (80%), m.p. 165-167°. A second crystallization gave 168-170°; solubility 80.8 mg./100 ml. water at 25° and from abs. alcohol 5.3 g./100 ml.

Anal. Calcd. for $C_{12}H_7O_7N_3$: N, 13.77. Found: N, 14.00.

Concentrated nitric acid yields only 2.7% of this derivative using an acid-phenol ratio of 1:1 and 7.7% when the ratio is 3.25:1.0. Preparation of 2,4,6-trinitro-3-hydroxybiphenyl by the nitration of the mono- and dinitro derivatives is possible in all six cases; however, the yields are less than by the direct nitration already described: 4-nitro yields 4.5%, 2-nitro 17.8%, 6-nitro 38%, 4,6-dinitro 44%, 2,4-dinitro 37%, and from 2,6-dinitro 57%.

4',X,X-Trinitro-3-hydroxybiphenyl.—This compound was formed in trace yields in all of the nitrations of 3-hydroxybiphenyl. At the conclusion of the investigation all unidentified material was collected and rechromatographed and this substance isolated by evaporation of the eluant. This compound was observed on chromatographic columns as ill defined bands and as scarlet spots. The sodium, potassium and magnesium salts are less soluble in water than are similar salts of the other nitrophenols obtained in this investigation. Well over twenty nitrations of 3-hydroxybiphenyl gave only enough of this substance for the oxidation study mentioned earlier and for a nitrogen analysis; m.p. 212°.

Anal. Calcd. for $C_{12}H_7O_7N_3$: N, 13.77. Found: N, 14.11.

Chromic Acid Oxidation of the Dinitro-3-hydroxybiphenyls.—One and nine-tenths g. of 4,6-dinitro-3-hydroxybi-

TABLE II
 DERIVATIVES OF THE NITRO-3-HYDROXYBIPHENYLS

Derivative	Formula	Yield, %	M.p., °C.	Nitrogen, %	
				Calcd.	Found
<i>p</i> -Nitrobenzoate of I	C ₁₃ H ₁₂ O ₆ N ₂	47	157	7.69	7.87
3,5-Dinitrobenzoate of I	C ₁₃ H ₁₁ O ₈ N ₃	79	199	10.26	10.28
<i>p</i> -Nitrobenzoate of 6-nitro-3-hydroxybiphenyl (II)	C ₁₃ H ₁₂ O ₆ N ₂	59	135	7.69	7.43
3,5-Dinitrobenzoate of (II)	C ₁₃ H ₁₁ O ₈ N ₃	32	171	10.26	10.40
2,4-Dinitrophenyl ether of II	C ₁₈ H ₁₁ O ₇ N ₃	56	131	11.02	10.67
<i>p</i> -Nitrobenzoate of III	C ₁₃ H ₁₂ O ₆ N ₂	41	196	7.69	7.75
2,4-Dinitrophenyl ether of 2-nitro-3-hydroxybiphenyl (III)	C ₁₈ H ₁₁ O ₇ N ₃	68	165	11.02	11.03
Benzoate of 4,6-dinitro-3-hydroxybiphenyl (IV)	C ₁₃ H ₁₂ O ₆ N ₂	44	157	7.69	7.70
Benzoate of 2,4-dinitro-3-hydroxybiphenyl (V)	C ₁₃ H ₁₂ O ₆ N ₂	65	127	7.69	7.74
Benzoate of 2,6-dinitro-3-hydroxybiphenyl (VI)	C ₁₃ H ₁₂ O ₆ N ₂	90	162	7.69	7.59
<i>p</i> -Nitrobenzoate of 2,4,6-trinitro-3-hydroxybiphenyl (VII)	C ₁₃ H ₁₀ O ₁₀ N ₄	70	145	12.33	12.50
2,4-Dinitrophenyl ether of VII	C ₁₈ H ₉ O ₁₁ N ₆	25.8	212	14.86	14.70

phenyl in 20 ml. of glacial acetic acid was treated with 14.4 g. of chromic acid in 25 ml. of glacial acetic acid and 12 ml. of water. Addition was made over a 25-minute period. Refluxing occurred spontaneously for 30 minutes after which refluxing was continued to a total of two hours. Fifteen ml. of 40% formaldehyde made up to 25 ml. with glacial acetic acid was added slowly. The reaction mixture was diluted with an equal volume of concd. hydrochloric acid and extracted four times with 25-ml. volumes of ether. The ether extracts were combined, washed with 200 ml. of 5% hydrochloric acid and evaporated to dryness. Benzoic acid was obtained, 0.747 g. (84%). Repetition of this procedure gave from 1.0 g. of 2,4-dinitro-3-hydroxybiphenyl 0.32 g. of benzoic acid (69%), from 2.0 g. of 2,6-dinitro-3-hydroxybiphenyl 0.37 g. of benzoic acid (39.7%), from 2.0 g. of 2,4,6-trinitro-3-hydroxybiphenyl 0.21 g. of benzoic acid (26%) and from 0.10 g. of 4',X,X-trinitro-3-hydroxybiphenyl 15 mg. (27%) of *p*-nitrobenzoic acid.

4,6-Dinitro-3-methoxybiphenyl.—Fourteen grams of *N*-methyl-*N*-nitroso-*N'*-nitroguanidine was treated with 13 g. of 4,6-dinitro-3-hydroxybiphenyl in potassium hydroxide solution using the method of McKay.¹² Thirteen grams (90%) of 4,6-dinitro-3-methoxybiphenyl was obtained, melting after sublimation at 148°.

Anal. Calcd. for C₁₃H₁₀O₅N₂: N, 10.21. Found: N, 10.28.

4,6-Dinitro-3-aminobiphenyl.—Two grams (0.008 mole) of 4,6-dinitro-3-hydroxybiphenyl was heated in a sealed tube with 5.0 g. (0.08 mole) of urea for 25 hours at 180°. The contents of the tube were flushed into a sintered glass funnel with hot water. Repeated hot water washings removed urea and condensation products, unchanged phenol being removed by washing with alkali; yield 1.24 g. (62.5%). 4,6-Dinitro-3-aminobiphenyl sublimes at 110° forming pale yellow to colorless needles, m.p. 137°.

Anal. Calcd. for C₁₂H₉O₄N₃: N, 16.21. Found: N, 15.88.

(12) A. F. McKay, *This Journal*, **70**, 1974 (1948).

(13) O. Kym, *J. prakt. Chem.*, **75**, 323 (1907).

Conversion of 4,6-Dinitro-3-aminobiphenyl to 2,4-Dinitro-biphenyl.—Twenty-five hundredths gram (0.001 mole) of 4,6-dinitro-3-aminobiphenyl in 3 ml. of glacial acetic acid was added to 0.07 g. (0.001 mole) of sodium nitrite in 3 ml. of concd. sulfuric acid. No precipitation occurred and after standing at room temperature for two hours diazotization was assumed to be complete. It was found that reverse addition of the solutions described above resulted in precipitation without diazotization, also that diazotization failed using either the sulfate or the hydrochloride of the amine. Deamination was accomplished by adding 2 ml. of hypophosphorous acid cooled to 10° to the previously described diazonium solution. The reaction flask was loosely stoppered and stored at 10° for 24 hours. The product separated as a dark oil when several volumes of water were added. The supernatant aqueous layer was decanted; the oil was washed several times with water and taken up in benzene. After drying over anhydrous sodium sulfate the benzene solution was passed through a 1 × 6 cm. column of Magnesol (benzene slurry). A deep red zone was retained by the column and a yellow zone (2,4-dinitrobiphenyl) was readily eluted with benzene. The benzene eluate was evaporated to a pale yellow oil which crystallized after several days standing. After washing the oily, crystalline solid with cold heptane it was recrystallized from methanol; yield 0.06 g. (25%), m.p. 110°. The m.p. has been reported⁶ as 110°.

Derivatives of the Nitro-3-hydroxybiphenyls.—Twelve derivatives involving the -OH group in compounds I-VII were prepared. All were prepared by well known methods. In general the phenol was dissolved in pyridine and the acid chloride added in slight excess. Refluxing for from 30 minutes to two hours was followed by pouring the reaction mixture over ice or into cold water. The precipitate was dissolved in a suitable solvent such as alcohol or in chloroform followed by addition of petroleum ether to obtain a crystalline product.

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