[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY UNIVERSITY OF MICHIGAN]

The Reaction of Aryl Azides with Hydrogen Halides[1,2]

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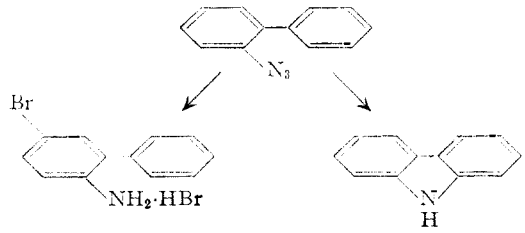
The reaction of aryl azides with hydrogen halides to form halogenated anilines with loss of nitrogen has been studied in the biphenyl series. For this purpose a number of *o*-azidobiphenyls substituted with bromo and nitro groups has been prepared. Base-weakening substituents have been found to retard the loss of nitrogen, and the ease of the reaction was observed to be qualitatively a function of the acid strength of the environment. The intermediate liberation of free halogen has been demonstrated in several ways, and a reaction sequence to account for the observed behaviors is proposed.

In connection with studies of the action of hydrogen azide on organic molecules,[3] it became of interest to examine further the chemistry of the aryl azides. Other classes of organic azides are more or less susceptible to rearrangement, frequently to the exclusion of alternate modes of decomposition. Since there is no reasonable path for the rearrangement of the aryl azides, they appeared to offer a convenient means of studying the interaction of the disrupting azido group with other functions. The interpretation of previous work with aryl azides[4,5] has been inconclusive by reason of the failure to distinguish clearly between acid-catalyzed reactions and energy-induced reactions, and also by the multiplicity of products frequently obtained under the conditions chosen.

The work reported here is concerned with the action of hydrogen bromide upon a series of *o*-azidobiphenyls, a class of compounds chosen because it offered the possibility of competitive reaction paths of ring halogenation[4] and cyclization[6]

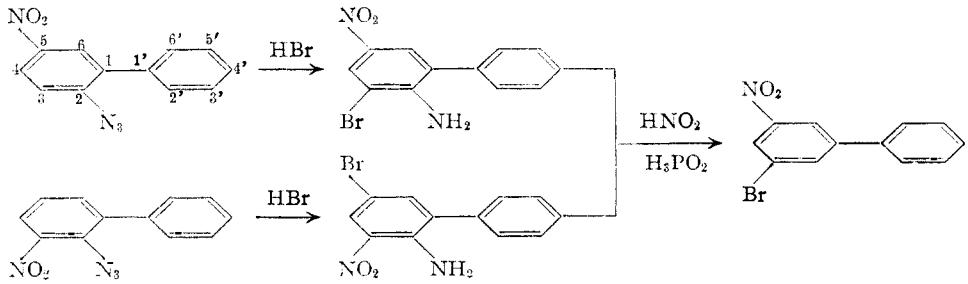


in the same molecule. The availability of solutions of hydrogen bromide in acetic acid provided an anhydrous reagent with excellent solvent powers for carrying out the decompositions, and did away with the long reaction periods and tar-formation characteristic of these reactions when carried out in aqueous media. The rate of reaction of the *o*-azidobiphenyls with hydrogen bromide ranged from great rapidity to complete inertness, and became slower as base-weakening substituents were accumulated.

Although the hydrogen bromide reaction was studied in greatest detail, qualitative results with the other halogen acids indicated the ease of reaction to be HI > HBr > HCl > HF, or in the same order as their reducing power and acid strength. *o*-Azidobiphenyl was completely inert in the presence of hydrogen fluoride, but showed a nearly instantaneous decomposition with hydrogen iodide, accompanied by the liberation of free iodine. The possibility that the reaction with hydrogen iodide might be adapted to quantitative determination of the aryl azide group is under investigation.

Reaction with hydrogen bromide gave rise to amines with or without bromination; in no case could any evidence of a cyclization product be found. When bromination occurred, the entering bromine atom was always found ortho or para to the original azido group; when those positions were blocked, conversion of the azide to an amine occurred with no bromination. The presence of two nitro groups in the molecule was in all cases sufficient to fortify the molecule against hydrogen bromide, even when one of the nitro groups was on a different ring from the azido group.

Decomposition of 2-azido-5-nitro- and 2-azido-3-nitrobiphenyl led to the previously unreported products, 2-amino-3-bromo-5-nitrobiphenyl and 2-amino-5-bromo-3-nitrobiphenyl. Although the position of the entering bromine atom was reasonably certain in both cases, since direct bromination of the corresponding aminonitrobiphenyls yielded products identical with those obtained from the azides and hydrogen bromide, an unequivocal proof of structure was obtained by conversion to the known bromonitrobiphenyl by means of the deamination procedure of Kornblum and Iffland.[7]



The only azide to yield a mixture of products upon decomposition was 2-azido-4′-nitrobiphenyl;

(1) Presented at the National Meeting of the American Chemical Society, San Francisco, March, 1949.

(2) From the doctoral dissertation of Bernard Beau Brown, 1949.

(3) P. A. S. Smith and J. P. Horwitz, THIS JOURNAL, **72**, 3718 (1950).

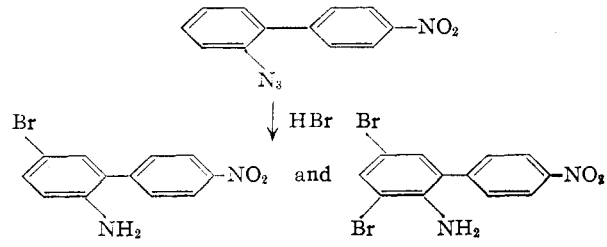
(4) E. Bamberger, *et al.*, *Ann.*, **424**, 252 (1921).

(5) A. Bertho, *J. prakt. Chem.*, **120**, 89 (1929).

(6) P. A. S. Smith and B. B. Brown, THIS JOURNAL, **73**, 2435 (1951).

(7) N. Kornblum and D. C. Iffland, *ibid.*, **71**, 2137 (1949).

2-amino-5-bromo-4′-nitrobiphenyl and 2-amino-3,5-dibromo-4′-nitrobiphenyl were obtained in a ratio of 3 to 1.



They were separated by extraction of the mixture with varied concentrations of hydrochloric acid, taking advantage of the difference of basicity between the mono- and dibrominated amines. The absence of unbrominated amine in the most dilute acid wash was in agreement with the nearly quantitative recovery of the brominated amines. The formation of dibrominated material appears to be due to free bromine, since its presence in solutions of hydrogen bromide in acetic acid which have been stored for some time in partly filled bottles can be demonstrated.

Our experience with these reactions suggests the following sequence of steps.

$$\text{Ar–N}_3 + \text{H}^+ \longrightarrow (\text{Ar–NH–N}_2)^+ \quad (1)$$

$$(\text{Ar–NH–N}_2)^+ + \text{Br}^- \longrightarrow \text{Ar–NH–Br} + \text{N}_2 \quad (2)$$

$$\text{Ar–NH–Br} + \text{HBr} \longrightarrow$$

$$\text{Br}_2 + \text{Ar–NH}_2 \left(\underset{\longleftarrow}{\overset{\text{HBr}}{\longrightarrow}} \text{Ar–NH}_3^+ + \text{Br}^-\right) \quad (3)$$

$$\text{Ar–NH}_2 + \text{Br}_2 \longrightarrow \text{Br–Ar–NH}_2\cdot\text{HBr} \quad (4)$$

Qualitative observation of the relative rates of nitrogen evolution from the respective azides indicates that step (2) is probably rate-determining. The rate of reaction should thus depend in part on the concentration of the conjugate acid of the azide, $(\text{Ar–NH–N}_2)^+$, supplied by step (1). Alternatively, step (1) might be rate-determining if step (2) is faster. Both possibilities are in accord with the observations that the rate increases with increasing acid strength of the medium, but is retarded by base-weakening substituents on the azide.

The reality of step (3) is demonstrated by the elimination of step (4) when the reaction is carried out in the presence of an avid bromine acceptor. 2-Azido-5-nitrobiphenyl was "reduced" to 2-amino-5-nitrobiphenyl in 80% yield upon treatment with hydrogen bromide and two molar equivalents of phenol; in the absence of the phenol, the product is the 3-bromoamine. Step (4) is also prevented when the positions ortho and para to the azido group are already occupied, as in 2-azido-3,5-dibromophenyl. This azide was simply reduced to the amine by hydrogen bromide, and free bromine was identified by aspiration into potassium iodide solution.

Further demonstration of step (3) is given by the reactions with hydrogen iodide, in which step (4) does not occur because of the weakness of iodine as a halogenating agent, compared to bromine.

Liberation of nitrogen from aryl azides is also brought about by other strong acids, such as sulfuric, perchloric and boron trifluoride. In all these cases bright green substances were produced, possibly dyes of the indophenol type. Because of the difficulty of isolating and identifying the products from these more complicated reactions, they have not been further investigated at this time.

Experimental[8]

2-Amino-5-bromobiphenyl was prepared by the hydrolysis of 2-acetamido-5-bromobiphenyl[9] by means of a hydrochloric–acetic acid mixture; m.p. 55–56°. Scarborough and Waters[10] report 57.5°.

2-Amino-3,5-dibromobiphenyl was prepared by the bromination of 2-aminobiphenyl in acetic acid solution buffered with sodium acetate.[10]

2-Amino-5-nitrobiphenyl was prepared by the hydrolysis of 2-(*p*-toluenesulfonamido)-5-nitrobiphenyl with concentrated sulfuric acid as described by Ray and Barrick.[11] These authors prepared the above sulfonamide by nitration of 2-*p*-toluenesulfonamidobiphenyl in acetic acid at steam-bath temperature, but in several attempts to repeat their directions we obtained largely the 3,5-dinitro compound, m.p. 185–187°. The mononitration was successfully carried out, however, at a lower temperature. A solution of 17 g. of 2-*p*-toluenesulfonamidobiphenyl dissolved in 75 ml. of warm glacial acetic acid was slowly cooled to room temperature. A mixture of 3.5 ml. of nitric acid (sp. gr. 1.5) and 10 ml. glacial acetic acid was added at one time and the resulting solution swirled at room temperature. The reaction became slightly exothermic after about 10 minutes, but was kept at 25–30° by intermittent swirling under the tap; a yellow precipitate started to form a few minutes later. The suspension was allowed to stand for one hour at room temperature after all heat evolution had ceased and was then chilled in the refrigerator for several hours. The orange crystals were filtered off with suction and became pale yellow when washed with small amounts of cold 95% ethanol. The yield was 16.9 g. (87%), m.p. 166–167°. Recrystallization from ethanol gave pale yellow crystals, m.p. 167–168° (Ray and Barrick[11] 168–169°).

2-Amino-3,5-dinitrobiphenyl was prepared by the concentrated sulfuric acid hydrolysis of 2-*p*-(toluenesulfonamido)-3,5-dinitrobiphenyl, which was synthesized in 70% yield by the procedure described by Ray and Barrick[11] for 2-(*p*-toluenesulfonamido)-5-nitrobiphenyl using nitric acid (sp. gr. 1.5) at 90°. The small amount of mononitrated material that formed was leached from the crude product with hot ethanol.

2-Amino-4′-nitrobiphenyl.—A solution of 5.0 g. (0.033 mole) of 2-aminobiphenyl dissolved in 50 ml. of concentrated sulfuric acid was cooled to −6° in an ice–salt-bath. A mixture of 1.2 ml. of nitric acid (sp. gr. 1.5) and 3.0 ml. of concentrated sulfuric acid was added dropwise to the mechanically stirred solution at such a rate as to maintain the temperature at −4 to −6°. After one-half hour at this temperature, the orange solution was poured into 300 ml. of cold water and the insoluble material was quickly filtered off. When the filtrate was neutralized with sodium carbonate, an orange precipitate formed; this was filtered, washed with water, pressed as dry as possible and kept in a vacuum desiccator overnight. The weight of crude material was 5.4 g. (86%); m.p. 149–153°. Recrystallization from 95% ethanol gave 4.5 g. (71%) of brownish-red needles; m.p. 152–154° (Scarborough[10] 158°).

2-Amino-3-nitrobiphenyl was prepared by the nitration of 2-acetamidobiphenyl followed by hydrolysis with hydrochloric–acetic acid. The partially crystalline product, which has been reported as an oil[9] was used without further purification; m.p. *ca.* 25°.

2-Amino-5,4′-dinitrobiphenyl.—2-Acetamido-4′-nitrobiphenyl (10 g.) dissolved in 15 ml. of glacial acetic acid and 30 ml. of concentrated sulfuric acid was kept at 5–10° and swirled while a mixture of 8.0 ml. of nitric acid (sp. gr. 1.5) and 10 ml. of glacial acetic acid was added dropwise. After standing at room temperature for one-half hour, the reaction mixture was slowly poured into an ice slurry; a yellow

(8) Melting points are uncorrected.

(9) S. Sako, *Bull. Chem. Soc. Japan*, **9**, 55 (1934).

(10) H. A. Scarborough and W. A. Waters, *J. Chem. Soc.*, **130**, 89 (1927).

(11) F. E. Ray and J. G. Barrick, THIS JOURNAL, **70**, 1492 (1948).

TABLE I

o-AZIDOBIPHENYLS

Substituted 2-azidobiphenyl	Method of prepn.	Yield, %	M.p., °C.	Formula	Analyses, %[b] Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found
(*o*-Azidobiphenyl)	A	88	49–50	$C_{12}H_9N_3$	73.84	73.60	4.65	4.78
5-Bromo	A	93	49–50	$C_{12}H_8N_3Br$	52.63	52.60	2.94	3.12
3,5-Dibromo	A	97	89–89.50	$C_{12}H_7N_3Br_2$	40.82	41.04	2.00	2.14
5-Nitro	A	93	86–87	$C_{12}H_8O_2N_4$	60.00	60.08	3.35	3.31
4′-Nitro	A	96	92.5–93.5	$C_{12}H_8O_2N_4$	60.00	60.60	3.35	3.27
5,4′-Dinitro	B	78	174–175	$C_{12}H_7O_4N_5$	50.53	60.65	2.48	2.64
4,4′-Dinitro	B	91	177–178	$C_{12}H_7O_4N_5$	50.53	50.45	2.48	2.51
3-Nitro	A	89	62.5–63.5	$C_{12}H_8O_2N_4$	60.00	60.18	3.35	3.30
3,5-Dinitro	B	74	118–119	$C_{12}H_7O_4N_5$	50.53	51.54	2.48	2.51
2′-Nitro	A	33[a]	80.5–81.5	$C_{12}H_8O_2N_4$	60.00	60.05	3.35	3.46

[a] Yield based on 2,2′-dinitrobiphenyl. [b] Microanalyses by Microtech Labs., Skokie, Ill.

precipitate formed instantly. After two hours the suspension was filtered with suction and pressed as free of water as possible. The crude product was triturated with 10% sodium carbonate solution, filtered, washed with water and dried in an oven at 110°; weight 8.5 g. (73%), m.p. 199–204°. Recrystallization from benzene gave 6.0 g. (51%) of shiny, yellow crystals, m.p. 205–206°. Scarborough and Waters[10] reported 208° (in our hands their nitration procedure starting with 2-acetamidobiphenyl gave 2-acetamido-4′-nitrobiphenyl as the major product). Hydrolysis of the above material with alcoholic hydrochloric acid gave 2-amino-5,4′-dinitrobiphenyl in 93% yield, m.p. 234–235° (Scarborough and Waters[10] 238°).

2-Amino-4,4′-dinitrobiphenyl was prepared by the nitration of 5.0 g. of 2-amino-4′-nitrobiphenyl dissolved in 50 ml. of concd. sulfuric acid with 1.2 ml. of nitric (density 1.5) in 3.0 ml. of concd. sulfuric acid, at −4°. After one-half hour, 2-amino-4,4′-dinitrobiphenyl was precipitated by pouring the mixture into water and neutralizing with sodium carbonate; wt. 5.4 g., m.p. 145–151°. Recrystallization from ethanol gave 4.5 g. (83%), m.p. 152–154°. This compound has been prepared before by nitration with ethyl nitrate.[12]

2-Amino-2′-nitrobiphenyl.—2,2′-Dinitrobiphenyl was prepared by the Ullmann reaction with *o*-nitrochlorobenzene.[13] 2-Amino-2′-nitrobiphenyl was prepared from it by reduction with sodium polysulfide as described by Purdie[14] but was not isolated; an aqueous solution of the amine hydrochloride was directly converted to 2-azido-2′-nitrobiphenyl (Procedure A).

All of the azides reported in this paper were prepared by one of two general procedures involving the addition of hydrazoic acid to the corresponding diazotized aminobiphenyls. The basicity of the amine determined the method used; an example of each method follows.

Procedure A (for the more basic amines).—Five grams (0.033 mole) of 2-aminobiphenyl (Eastman Kodak Co.) was dissolved in a warm (40–50°) solution of 6 ml. of concentrated sulfuric acid in 35 ml. of water; the resulting solution was cooled in an ice–water-bath, which caused some of the amine sulfate to precipitate. The amine was diazotized with a solution of 2.75 g. of sodium nitrite (0.04 mole) in 25 ml. of distilled water, the excess nitrous acid was removed with urea and 0.5 g. of Norit was added to the stirred solution. After one-half hour the charcoal was filtered off and a solution of 3.6 g. of sodium azide (0.056 mole) in 20 ml. of water was added dropwise to the cold, stirred filtrate. Nitrogen was immediately evolved, the solution became turbid and a light tan precipitate formed in a few minutes. The suspension was kept in the ice-bath and stirred for one hour after the final addition of the sodium azide, and was then allowed to stand overnight in a hood at room temperature. The solid was filtered off with suction, washed first with a 10% sodium carbonate solution and then with water. The precipitate was pressed as free of water as possible and dried in a vacuum desiccator overnight. The weight of crude material was 5.0 g. (88%); m.p. 47–49°. Recrystallization from aqueous methanol gave 4.8 g. of very light tan, shiny plates, m.p. 49–50°. Sublimation at about 70° and 0.5 mm. pressure gave colorless crystals, m.p. 49–50°.

Procedure B (for the less basic amines).—One gram (0.0039 mole) of 2-amino-5,4′-dinitrobiphenyl was dissolved in 20 ml. of glacial acetic acid containing 4 ml. of concentrated sulfuric acid. The solution was cooled to 5–10° and diazotized with 0.5 g. (0.0042 mole) of fresh amyl nitrite. After one hour of stirring, 50 ml. of ice-water was added; the absence of turbidity indicated that diazotization was complete. Enough urea was added to destroy the excess nitrous acid, and 0.5 g. of Norit was then added. The cold suspension was stirred for 15–20 minutes and was then rapidly filtered into a flask immersed in an ice-bath. The clear, yellow filtrate was treated with a solution of 0.5 g. (0.0077 mole) of sodium azide in 10 ml. of water, after which the preparation was worked up as in Procedure A. The weight of crude 2-azide-5,4′-dinitrobiphenyl was 0.85 g. (78%); m.p. 170–174°. Recrystallization from ethanol–acetone gave 0.75 g. of yellow needles, m.p. 174–175°.

The azides prepared according to these procedures were in general stable enough to retain the reported melting points on storage for several months. However, 3,5-dinitro-2-azidobiphenyl, which undergoes thermal decomposition at a lower temperature than do the other azides, could not be obtained in a state of analytical purity.

The Reaction with Hydrogen Bromide.—The following examples are typical of the reactions carried out. The data for the entire series of azides are recorded in Table II.

TABLE II

REACTION OF *o*-AZIDOBIPHENYLS WITH HYDROGEN BROMIDE

Substituted 2-azidobiphenyl	Product Substituted 2-aminobiphenyl	M.p., °C.	Yield, %
(2-Azidobiphenyl)	5-Bromo-	55–56[a]	82[b]
5-Bromo	3,5-Dibromo-	50–52[c]	88[b]
3,5-Dibromo	3,5-Dibromo-	51–52[c]	97[b]
5-Nitro	3-Bromo-5-nitro-	139–140[d]	87
3,5-Dinitro-	Recovered azide		90
5,4′-Dinitro-	Recovered azide		95
4,4′-Dinitro-	Recovered azide		95
3-Nitro-	3-Nitro-5-bromo-	117–118[e]	57
4′-Nitro-	5-Bromo-4′-nitro	146–148[f]	75
	and 3,5-Dibromo-4′-nitro	185–187[g]	24

[a] Reported 57.5°.[10] [b] Based on hydrobromide. [c] Reported 51–52.°[10] [d] *Anal.* Calcd. for $C_{12}H_9O_2NBr$: C, 49.15; H, 3.07. Found: C, 49.31; H, 3.10. [e] *Anal.* Calcd. for $C_{12}H_9O_2NBr$: C, 49.15; H, 3.07. Found: C, 49.17; H, 3.01. [f] Reported 152°.[17] [g] Reported 189°.[18]

Reactive Azides.—One gram (0.0036 mole) of 2-azido-5-bromobiphenyl was dissolved in 15 ml. of glacial acetic acid, and an equal volume of a 30% solution of hydrogen bromide in acetic acid (Eastman Kodak Co.) was slowly added. The mixture was warmed to 50–60°, whereupon a vigorous decomposition took place accompanied by about a 30° rise in temperature. The orange solution was kept at room temperature until the nitrogen evolution ceased, about 24 hours, and was then evaporated in a dry air stream to a thin paste. Trituration of the paste with 10 ml. of dry ether

(12) C. Finzi and V. Bellavita, *Gazz. chim. ital.*, **68**, 77 (1938).
(13) R. C. Fuson and E. A. Cleveland, *Org. Syntheses*, **20**, 45 (1940).
(14) D. Purdie, THIS JOURNAL, **63**, 2276 (1941).

to remove residual acetic acid and unreacted azide gave 1.31 g. (88%) of white, crystalline 2-amino-3,5-dibromobiphenyl hydrobromide; m.p. 188–193°. Addition of all the material to 20 ml. of a 10% sodium carbonate solution followed by ether extraction, drying over sodium sulfate and removal of the solvent yielded 1.00 g. of a pale yellow oil. Crystallization from aqueous ethanol gave 0.85 g. (72%) of 2-amino-3,5-dibromobiphenyl as pale yellow needles; m.p. 50–52°. A mixed melting point with a sample obtained by the method of Scarborough,[10] m.p. 51–52°, showed no depression.

Non-reactive Azides.—2-Azido-3,5-dinitrobiphenyl (0.5 g.) was treated with 30% hydrogen bromide in acetic acid as described above. Even at 70°, only a very slow gas evolution could be seen. On working up as described above, there was obtained 0.45 g. of residue, m.p. 115–118° (bubbles). Recrystallization from an ethanol–acetone mixture raised the melting point to 117–118°, undepressed when mixed with the starting material.

2-Amino-3-bromo-5-nitrobiphenyl.—To 0.50 g. of 2-amino-5-nitrobiphenyl (0.0021 mole) dissolved in 10 ml. of glacial acetic acid was added a solution of 0.35 g. of bromine (0.0022 mole) in 5 ml. of glacial acetic acid. The reddish solution was heated on the steam-bath at 80–90° for 10–15 minutes and then slowly diluted with water until a turbidity persisted for a few seconds. The cooled solution deposited 0.60 g. (90%) of orange-red needles; m.p. 139°. Recrystallization from aqueous ethanol raised the melting point to 139–140°. A mixed melting point determination with the product of the hydrogen bromide decomposition of 2-azido-5-nitrobiphenyl showed no depression.

Deamination.—Cold 50% hypophosphorous acid (1 ml.) was added slowly to a cold solution of 0.30 g. of sodium nitrite in 10 ml. of concentrated sulfuric acid. To the above solution was added slowly, with stirring, a solution of 0.40 g. of 2-amino-3-bromo-5-nitrobiphenyl in 15 ml. of glacial acetic acid; the temperature of the reaction mixture was not allowed to rise above 0°. The addition took about an hour, during which nitrogen was evolved copiously. After another hour of stirring, the yellow solution was placed in the refrigerator for 24 hours. The mixture was filtered from small amounts of solid, poured into 50 ml. of cold water and then extracted five times with 10-ml. portions of benzene and three times with 10-ml. portions of 85% ethyl acetate. The extracts were concentrated to a volume of 15–20 ml. and washed with 10-ml. portions of 10% sodium carbonate solution until the water layer was colorless; about fifteen such washings were required. This was followed by a single washing with 10 ml. of 10% hydrochloric acid. The remainder of the solvent was removed in a dry air stream and the residual viscous oil was crystallized from aqueous ethanol (after treatment with Norit) to give 0.10 g. (26%) of yellow crystals; m.p. 68.5–69.5°. Recrystallization gave small needles, m.p. 69.5°. A mixed melting point with an authentic sample of 3-bromo-5-nitrobiphenyl,[15] m.p. 69–70°, showed no depression.

2-Amino-3-nitro-5-bromobiphenyl.—Bromination of 1 g. of 2-amino-3-nitrobiphenyl in a manner similar to that used with 2-amino-5-nitrobiphenyl gave 1.10 g. (90%) of 2-amino-3-nitro-5-bromobiphenyl; m.p. 118–119°. Recrystallization from aqueous ethanol or sublimation did not raise the melting point. A mixed melting point determination with the product of the hydrogen bromide decomposition of 2-azido-3-nitrobiphenyl showed no depression.

Deamination of 2-amino-3-nitro-5-bromobiphenyl to the known 3-bromo-5-nitrobiphenyl[16] (25% yield) was carried out in a manner similar to that for 2-amino-3-bromo-5-nitrobiphenyl.

Hydrogen Bromide Decomposition of 2-Azido-4′-nitrobiphenyl.—2-Azido-4′-nitrobiphenyl (5.00 g.) was decomposed with hydrogen bromide in acetic acid in the manner described to give 6.40 g. of orange crystals; m.p. 125–135°. Recrystallization from benzene yielded stout, orange needles; m.p. 133–138°. Further recrystallization from benzene or ethanol did not narrow or shift the melting range.

0.80 g. of the above mixture, dissolved in 20 ml. of reagent benzene, was extracted with 10-ml. portions of 1:1 hydrochloric acid until the acid layer showed no turbidity on neutralization. The combined acid washings were made slightly basic with sodium hydroxide and extracted with three 20-ml. portions of benzene. The benzene extracts were dried by distillation and evaporated to dryness; crystallization from benzene–petroleum ether gave 0.55 g. of yellow-orange crystals; m.p. 146–148°. A mixed melting point with a sample of 2-amino-5-bromo-4′-nitrobiphenyl, m.p. 146–147°, prepared according to the method of Case,[17] showed no depression.

The acid-washed benzene layer was dried by distillation and evaporated to dryness. Crystallization of the residue from benzene–petroleum ether gave 0.22 g. of brownish-yellow needles, m.p. 182–186°. Recrystallization raised the melting point to 185–187°. A mixed melting point with a sample of 2-amino-3,5-dibromo-4′-nitrobiphenyl,[18] m.p. 188–189°, melted at 187°.

The combined weight of the mono- and dibrominated compounds, 0.77 g., represents 96% of the original mixture (0.80 g.). The ratio of 0.0018 mole/0.00059 mole of monobromo to dibromo compound indicates the 6.40 g. of original crude product to be a 98% yield of amines from the azide.

Hydrogen Bromide Decomposition of 2-Azido-3,5-dibromobiphenyl.—One gram of 2-azido-3,5-dibromobiphenyl, dissolved in 10 ml. of glacial acetic acid, was decomposed at 50° with hydrogen bromide in acetic acid in the manner described to yield 1.10 g. (97%) of white, crystalline 2-amino-3,5-dibromobiphenyl hydrobromide; m.p. 185–190°. Addition of all of the salt to 15 ml. of a 20% sodium carbonate solution, followed by ether extraction, drying over sodium sulfate and evaporation of the solvent yielded 0.82 g. (87%) of a pale yellow oil. Crystallization of the oil from aqueous ethanol gave 0.70 g. (76%) of colorless needles; m.p. 51–52°. A mixed melting point with a sample of 2-amino-3,5-dibromobiphenyl,[10] m.p. 51–52°, showed no depression. Benzoylation of the amine with benzoyl chloride in pyridine solution and recrystallization of the product from ethanol yielded colorless crystals, m.p. 214–215° (reported 218°).[10]

In another experiment, one gram of the same azide was dissolved in 15 ml. of glacial acetic acid contained in a small gas-washing bottle. The system was swept with dry nitrogen for five minutes, the top quickly lifted and 15 ml. of a fresh 30% hydrogen bromide–acetic acid solution poured in. As the decomposition progressed, a stream of dry nitrogen was bubbled through the solution and into carbon tetrachloride overlaid with a potassium iodide solution. After one hour the carbon tetrachloride layer became violet due to free iodine. A blank run carried out under the same conditions and for the same length of time gave only a very light brown coloration to both the aqueous and the carbon tetrachloride layers. In experiments in which hydrogen iodide was substituted for hydrogen bromide, approximately one mole of I_2 was liberated per mole of azide, as determined by titration with sodium thiosulfate solution.

Decomposition of 2-Azido-5-nitrobiphenyl in the Presence of Phenol.—2-Azido-5-nitrobiphenyl (0.50 g., 0.0021 mole) and 0.37 g. of phenol (0.0042 mole) were dissolved in 10 ml. of glacial acetic acid. Decomposition was carried out in the usual manner by the addition of 10 ml. of the 30% hydrogen bromide–acetic acid reagent. Recrystallization of the solid residue after evaporation of the solvent gave 0.37 g. (84%) of orange crystals, m.p. 122–123°. A mixed melting point with a sample of 2-amino-5-nitrobiphenyl, m.p. 123–124°, showed no depression.

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(15) Kindly supplied by Dr. F. H. Case of Temple University.

(16) F. H. Case, THIS JOURNAL, **61**, 3487 (1939).

(17) F. H. Case, *ibid.*, **67**, 116 (1945).

(18) V. Bellavita, *Atti V. Congr. Natl. Chim. pura applicata*, Rome 1935, Pt. 1, 290, 296 (1936); *cf. C. A.*, **31**, 3901 (1937), and *Gazz. chim. ital.*, **67**, 574 (1937).