sumed to be tetratriacontane; lit.[8] m.p., 72–73°. The filtrate was concentrated and the residue was distilled to give 40.5 g. of material which boiled at 200–218°/1 mm. This was shaken with four 25-ml. portions of concentrated sulfuric acid, washed with water, 5% potassium carbonate solution, again with water, and dried over anhydrous calcium sulfate. There was obtained 32.2 g. (23%) of product; b.p., 208–210°/1 mm., n_D^{25} 1.4511, m.p. 10–11°.

Anal. Calcd. for $C_{27}H_{56}$: C, 85.17; H, 14.83. Found: C, 85.07; H, 14.57.

COLUMBIA, MO.

---

[8] G. Egloff, *Physical Constants of Hydrocarbons*, Vol. V, Reinhold Publishing Corp., New York, 1953, p. 270.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF MICHIGAN]

Synthesis of Heterocyclic Compounds from Aryl Azides. IV. Benzo-, Methoxy-, and Chloro-carbazoles[1,2]

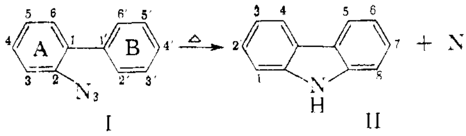
PETER A. S. SMITH, JOHN M. CLEGG,[3] AND J. H. HALL

Received September 3, 1957

1,2-Benzocarbazole(III) has been prepared in high yield from both 2-(2′-azidophenyl)naphthalene(IV) and 1-azido-2-phenylnaphthalene(V). The isomeric 2,4-benzocarbazole has been prepared from 1-(2′-azidophenyl)naphthalene. 1,4-Dimethoxycarbazole has been prepared from (*o*-azidophenyl)hydroquinone dimethyl ether, and 2-methoxy-, 2-hydroxy-, and 3-chloro-carbazole have been prepared from *o*-azidobiphenyls. 2-Azido-2′-cyanobiphenyl has been found to cyclize to tetrazolophenanthridine instead of to 4-cyanocarbazole, and 4-azidofluorene and 4-azidofluorenone to decompose on heating without apparent cyclization, to give intractable products.

o-Azidobiphenyl has been prepared from *o*-hydrazinobiphenyl and N^{15}-labeled potassium nitrite. Thermal decomposition gave carbazole with normal isotope content, while all the excess N^{15} was found in the evolved nitrogen.

The thermally or photochemically induced cyclization of *o*-azidobiaryls (I) to give carbazole derivatives has been shown in previous papers[2] to be a synthetically useful route to bromo- and nitro-carbazoles, and to certain heterocyclic analogs. From these studies, little could be concluded regarding the generality of the reaction or its mechanism, particularly since the substituents studied were all electron-withdrawing. In the work reported in this paper, an attempt has been made to fill some of these gaps in the knowledge of the reaction.



I II

The loss of nitrogen from the azido group might occur as the first stage in the reaction, unassisted by any sort of preliminary cyclization. In such a case, the ease with which nitrogen is lost should depend on the electronic condition of the ring holding the azido group, and be independent of the nature of the ultimate cyclization point on ring B, except insofar as ring B influences the condition of ring A. Furthermore, the outer two nitrogen atoms of the azido group would be those that appear as molecular nitrogen.

Alternatively, loss of nitrogen might accompany or follow cyclization to ring B. In such a case, the nature of the site of cyclization on ring B should profoundly influence the ease with which nitrogen is released from the azide. Furthermore, the structure of this cyclic intermediate or transition state, as the case may be, would determine which of the azide nitrogen atoms would be released.

o-Azidobiphenyls substituted in ring B with a hydroxy or methoxy group in the 4′-position, and with two methoxy groups in the 3′,6′-positions, have now been prepared. All give the expected carbazoles on heating. Qualitatively, no difference in ease of decomposition large enough to clearly show a concerted reaction was noticed, either among these compounds, or between them and the azidobiphenyls previously reported.[4] It thus appears that the synthesis of carbazoles by this reaction may be expected to succeed with most types of substituents.

A similar comparison is provided by the reactions leading to benzocarbazoles. 1,2-Benzocarbazole(III) was prepared from *β*-(*o*-azidophenyl)-naphthalene(IV), involving cyclization to the *α*-position of the naphthalene, and from *β*-phenyl-*α*-azidonaphthalene(V), involving cyclization to a simple benzene ring. The high yields were similar for the two cyclization paths, but the ease of nitrogen release was noticeably different, the azidophenyl isomer requiring at least a 10° higher temperature for comparably rapid decomposition. Complete selectivity was shown in cyclization to the naphthalene ring; cyclization to the 3-position, which would have led to 2,3-benzocarbazole, did not occur to a detectable extent. Another example

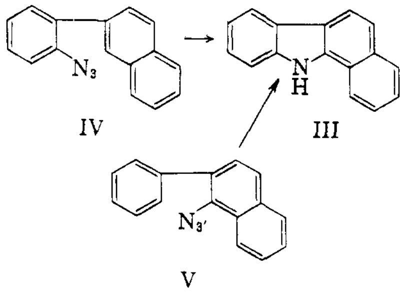
---

[1] The larger part of this work was supported by the Office of Ordnance Research, U. S. Army (D.O.R. Project No. 965).

[2] Part III, *J. Am. Chem. Soc.*, **75**, 6335 (1953).

[3] In part from the doctoral thesis of John M. Clegg.

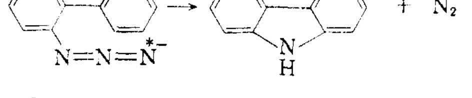
[4] P. A. S. Smith and B. B. Brown, *J. Am. Chem. Soc.*, **73**, 2438 (1951).

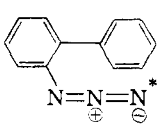


of internal selectivity is given by the example of α-(*o*-azidophenyl)naphthalene, which cyclized entirely to the 2-position, giving 3,4-benzocarbazole, and not to a detectable extent to the 8-position, which would have given a benzacridine. β-(*o*-Azidophenyl)pyridine, reported previously,[5] shows little selectivity, however, and cyclizes to both the α- and the γ-positions, but in this case the two sites are electronically similar.

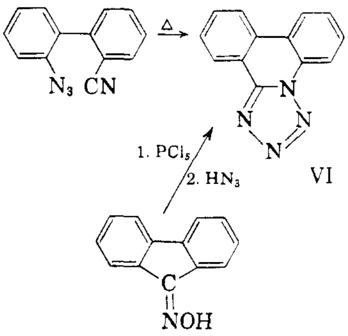
These observations are insufficient to determine the mechanism of the reaction, but they do imply that regardless of whether the loss of nitrogen is concerted or not, the formation of the new bond to nitrogen can be a highly selective process. Therefore, if the rate-determining step is the unassisted breakdown of the azido group to give molecular nitrogen and an arylnitrogen, Ar-N:, the latter species either has a half-life appreciably longer than the time for rotation about the aryl-aryl bond, or it is able by polarization to accelerate such rotation in a selective manner. To help resolve these questions, kinetic investigations have recently been begun.

Further information about the nature of the breakdown of the azido group was obtained from *o*-azidobiphenyl in which the terminal nitrogen was isotopically labeled. This was obtained by treatment of the hydrazine with isotopic nitrite, according to the method developed by Clusius.[6] On heating, all of the excess isotopic nitrogen was found in the evolved gas, which showed that it is almost certainly the carbon-attached nitrogen atom that is retained in the carbazole (retention of the central nitrogen can be safely ignored on the grounds of mechanistic improbability). A cyclic intermediate or transition state involving the outer azide nitrogen is therefore very unlikely.





2-Azido-2′-cyanobiphenyl, prepared in a series of steps through the half-nitrile of diphenic acid, was studied in order to see whether the difficultly accessible carbazole-4-carbonitrile could be made by this reaction, and if it could not, to learn in what way the cyano group would interfere. This azide was found to undergo a change in melting point from 57° to 223.5° as a result of heating, but no loss of nitrogen occurred. The alteration product was found to be tetrazolophenanthridine(VI), whose structure was confirmed by independent synthesis in the form of the von Braun-Rudolph reaction applied to 9-chlorophenanthridine, obtained by the Beckmann rearrangement of fluorenone oxime.



This is the first authenticated case of an azide other than hydrogen azide adding to a nitrile (an isolated patent claim of a similar reaction in the aliphatic series has been disputed).[7] Tetrazolophenanthridine was found to have exceptional stability to heat; unlike most tetrazoles, which lose nitrogen at slightly above 200°, this substance required 300° for decomposition, at which temperature it was converted to a black glass, from which nothing could be characterized.

4-Azidofluorene and 4-azidofluorenone were prepared from the amines obtained by degradation of the corresponding carboxylic acids, with the intention of seeing whether the energy of the azido group would enable them to be converted to the strained carbazoles with, respectively, a 4,5-methylene or 4,5-carbonyl bridge. Such cyclization of an azide between two benzene rings held coplanar by the bridging group might be feasible if the cyclization proceeded through abstraction of the 5-hydrogen by the aryl nitrogen, followed by N-C bond formation. If, on the other hand, it should be necessary for N-C bond formation to occur first, with subsequent hydrogen migration, the nitrogen would have to approach the 5-carbon partly from one side, to avoid having the 5-hydrogen between it and the carbon, and the coplanarity enforced by the bridging group should interfere with the cyclization. Furthermore, by either path followed, the final tetracyclic system would be highly strained, and ring closure might not occur for this reason alone.

---

[5] P. A. S. Smith and J. H. Boyer, *J. Am. Chem. Soc.*, **73**, 2626 (1951).

[6] K. Clusius and H. R. Weisser, *Helv. Chim. Acta*, **35**, 1548 (1952).

[7] J. H. Boyer and F. C. Canter, *Chem. Revs.*, **54**, 44 (1954).

TABLE I

NEW AZIDOBIARYLS

	Yield, %	M.P., C.°	Empirical Formula	Anal. Calcd. C	Anal. Calcd. H	Anal. Found C	Anal. Found H
2-Azido-4′-hydroxybiphenyl	57.5	117–119.2	$C_{12}H_9ON_3$[13]	68.23	4.30	68.25	4.31
2-Azido-2′,5-dimethoxybiphenyl	61[a]	81.5–83.5	$C_{14}H_{13}O_2N_3$[14]	65.87	5.13	66.07	5.24
1-Azido-2-phenylnaphthalene	43[b]	44–45	$C_{16}H_{11}N_3$[16]	78.34	4.52	78.70	4.20
2-(2′-Azidophenyl)naphthalene	72[c]	46–47	$C_{16}H_{11}N_3$[16]	78.34	4.52	77.64	4.30
1-(2′-Azidophenyl)naphthalene	95[d]	101–102	$C_{16}H_{11}N_3$[16]	78.34	4.52	78.40	4.57
2-Azido-2′-cyanobiphenyl	16[e]	55.5–57	$C_{13}H_8N_4$[17]	70.89	3.66	70.84	3.72
4-Azidofluorenone	96.5[f]	118.5–120	$C_{13}H_7ON_3$[17]	70.58	3.19	70.77	3.32
4-Azidofluorene[g]	83.5	78–81	$C_{13}H_9N_3$[17]	75.34	4.38	75.41	4.42

[a] From 2-amino-2′,5′-dimethoxybiphenyl in aqueous hydrochloric acid. [b] From 2-phenyl-1-naphthylamine in aqueous hydrochloric acid. [c] From 2-(2′-aminophenyl)naphthylamine[15] in aqueous hydrochloric acid. [d] From 1-(2′-aminophenyl)-naphthalene with hydrochloric acid in water; crude product m.p. 98–101°. [e] From 2-amino-2′-cyanobiphenyl hydrochloride with hydrochloric acid in aqueous acetic acid; crude product m.p. 55.5–58°. [f] From 4-aminofluorenone,[18] with sulfuric acid in water-ethanol; crude product m.p. 110–115°. [g] From 4-aminofluorene with sulfuric acid in water-ethanol; crude product m.p. 75–79°.

The two azides lost nitrogen as usual, at about 180°, and gave solid products. However, the products were apparently amorphous and polymeric, having high, indefinite melting points and a general insolubility in organic solvents. It was apparent that cyclization did not take place, and one cannot conclude whether it is strain in the product of cyclization or the availability of only an unfavorable path that is responsible.

In the course of this work, the known 3-chlorocarbazole was prepared by the new route of cyclization of 2-azido-5-chlorobiphenyl. In connection with this synthesis, a route of synthetic value has been developed for 2-amino-5-chlorobiphenyl; direct chlorination of 2-benzamidobiphenyl gives the 5-chloro derivative in 65% yield, whereas attempts to chlorinate 2-acetamidobiphenyl are reported[8] to give tarry, nearly inseparable mixtures. In addition, the preparation of some biphenyl intermediates by synthetically practicable paths has been developed, in cases where the only published procedures are not of preparative value.

EXPERIMENTAL

2-Acetamido-4′-aminobiphenyl dihydrochloride. 2-Acetamido-4′-nitrobiphenyl (25.6 g., 0.1 mole) was hydrogenated[9] in 200 ml. of methanol with platinum oxide at an initial hydrogen pressure of 49 p.s.i. When the calculated amount of hydrogen had been absorbed, the mixture was filtered, concentrated, diluted with ether, and dried over magnesium sulfate. Passing in hydrogen chloride then precipitated 21.74 g. (71.2%) of 2-acetamido-4′-aminobiphenyl dihydrochloride as a white solid, m.p. 185° (dec.).

Anal.[10] Calcd. for $C_{14}H_{16}ON_2Cl_2$: C, 56.18; H, 5.39; Cl, 23.15. Found: C, 56.25; H, 5.38; Cl, 23.7.

2-Acetamido-4′-hydroxybiphenyl. A diazonium solution prepared from 19.42 g. (0.065 mole) of 2-acetamido-4′-aminobiphenyl dihydrochloride in 120 ml. of *N* sulfuric acid and 5.17 g. of sodium nitrite in 30 ml. of water was freed of excess nitrous acid with urea, and further acidified with 200 ml. of *N* sulfuric acid and overlaid with 75 ml. of toluene. The mixture was heated on a steam bath until the color lightened, chilled overnight, and the solid collected. The solid was dissolved in 150 ml. of 10% sodium hydroxide, decolorized with charcoal, and reprecipitated with hydrochloric acid, to give 11.56 g. (78%) of 2-acetamido-4′-hydroxybiphenyl, m.p. 177–182° (reported,[11] 185–186°).

2-Amino-4′-hydroxybiphenyl. 2-Acetamido-4′-hydroxybiphenyl (3.74 g.) was hydrolyzed by refluxing for 16 hr. with 30 ml. of concd. hydrochloric acid and 70 ml. of glacial acetic acid. Dilution with water and neutralization with sodium hydroxide precipitated 2.85 g. (93.5%) of 2-amino-4′-hydroxybiphenyl, m.p. 161–163.5°. Recrystallization from aqueous ethanol gave an analytical sample, m.p. 163.5–165.5° (reported,[12] 164–165°).

Anal.[10] Calcd. for $C_{12}H_{11}ON$: C, 77.81; H, 5.99. Found: C, 77.70; H, 5.91.

Azides. The azides prepared are summarized in Table I. All were prepared from diazonium salts and sodium azide, with minor variations as noted, in a manner analogous to the following example.

2-Azido-4′-hydroxybiphenyl. A solution of 2.85 g. (0.0154 mole) of 2-amino-4′-hydroxybiphenyl in 40 ml. of water and 8 ml. of concd. sulfuric acid was diazotized at 0° with 1.17 g. (0.017 mole) of sodium nitrite, the excess nitrous acid was destroyed with urea, and a solution of 1.17 g. (0.018 mole) of sodium azide in 10 ml. of water was added. After two hours at 0°, the azide, wt. 1.87 g. (57.5%), m.p. 113–119°, was filtered off. Recrystallization from aqueous methanol gave an analytical sample, m.p. 117–119.2°.

2-Nitro-2′,5′-dihydroxybiphenyl. A diazonium solution prepared from 13.8 g. (0.1 mole) of *o*-nitroaniline in excess

---

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

(9) C. K. Bradsher and L. J. Wissow, *J. Am. Chem. Soc.*, **68**, 404 (1946).

(10) Analysis by Mrs. Anna Griffin, University of Michigan.

(11) F. C. Copp and L. P. Walls, *J. Chem. Soc.*, 313 (1950).

(12) W. H. von Glahn and B. W. Rottschaefer, U. S. Pat. **2,363,819**; *Chem. Abstr.*, **39**, 3675[4] (1945).

(13) Analysis by Clark Microanalytical Laboratories, Champaign, Ill.

(14) Analysis by Microtech Laboratories, Skokie, Ill.

(15) D. H. Hey and S. E. Lawton, *J. Chem. Soc.*, **374** (1940).

(16) Analysis by Spang Microanalytical Laboratory, Ann Arbor, Mich.

(17) Analysis by Dr. Goji Kodama, University of Michigan.

(18) C. Graebe and P. Schestakow, *Ann.*, **284**, 312 (1895).

25% sulfuric acid was added dropwise with stirring to a solution of 22 g. (0.2 mole) of hydroquinone in 1100 ml. of water at room temperature. After several hours of stirring, the mixture was filtered and the filtrate extracted with ether. The extracts were in turn extracted with 10% sodium hydroxide solution containing some sodium bisulfite, and the alkaline extract was neutralized with hydrochloric acid and allowed to cool. The orange needles of 2-nitro-2′,5′-dihydroxybiphenyl that separated had m.p. 163–167° (reported,[19] 167°), and the yield varied between 11.5 and 13.5% in four trials.

2-Nitro-2′,5′-dimethoxybiphenyl. This compound was prepared by treating the foregoing substance with dimethyl sulfate in aqueous sodium hydroxide solution. It could be obtained more expeditiously, however, by evaporating the ether extracts containing the crude dihydroxy compound, dissolving the residue in 4% sodium hydroxide solution, and treating with a large excess (4 moles per mole of *o*-nitroaniline) of dimethyl sulfate at 60–70° with stirring. When the mixture is heated overnight, the contaminating hydroquinone dimethyl ether sublimes, and on cooling, 2-nitro-2′,5′-dimethoxybiphenyl separates as a brown solid, m.p. 100–105°, in 10.5% yield.

The crude product was purified by washing its ether solution with *N* sodium hydroxide until the washings were colorless, drying over magnesium sulfate, and evaporating to a small volume. There was obtained from 4.54 g. of crude material two crops of light yellow crystals: 3.18 g. of m.p. 100–102°, and 0.45 g. of m.p. 96–101°.

Anal.[14] Calcd. for $C_{14}H_{13}O_4N$: C, 64.86; H, 5.05. Found: C, 65.17; H, 4.91.

2-Amino-2′,5′-dimethoxybiphenyl. In a Parr bottle was placed 3.33 g. (0.0128 mole) of 2-nitro-2′,5′-dimethoxybiphenyl with about 200 ml. of methanol and a small amount of platinum dioxide. It was shaken with hydrogen until the pressure reading on the gage was constant (about 16 hr.). The solution was filtered, the methanol evaporated, the residues taken up in acetone, and water added. The crude, brownish product weighed 1.60 g. (56.5%), m.p. 65–68°. It was recrystallized once from acetone-water, and once from methanol-water, to obtain an analytical sample as fine, white needles, m.p. 68–69°.

Anal.[14]: Calcd. for $C_{14}H_{15}O_2N$: C, 73.34; H, 6.59. Found: C, 74.16; H, 6.54.

2-Benzamido-5-chlorobiphenyl. Chlorine was passed through a sintered glass inlet tube into a solution of 27.3 g. (0.1 mole) of 2-benzamidobiphenyl in 250 ml. of dry ether until the mixture was bright yellow and crystals began to form. The solvent was partially evaporated and the product, 20.1 g. (65.5%), m.p. 137–143°, was filtered off. 2-Benzamido-5-chlorobiphenyl prepared by benzoylation of the amine has reported m.p. 142–143°.[8]

2-Amino-5-chlorobiphenyl. Hydrolysis of 4.0 g. (0.013 mole) of 2-benzamido-5-chlorobiphenyl by refluxing for 12 hr. with 25 ml. of concentrated hydrochloric acid and 75 ml. of glacial acetic acid gave 2.0 g. (75.5%) of the amine, m.p. 47–50° (reported, 48°,[20] 54°[21]).

2-(2′-Nitrophenyl)naphthalene. A mixture of 2′- and 4′-nitro-2-phenylnaphthalene, b.p. 230–270°/0.8 mm., was prepared from 76.7 g. (0.415 mole) of 2-acetamidonaphthalene by the method of Hey and Lawton.[15] This mixture, a red sirup, was dissolved in 200 ml. of benzene and allowed to stand overnight. The crystals which separated melted at 167–175° and were primarily the 4′-nitro isomer. The filtrate was chromatographed on alumina using benzene for development and elution. Two bands were seen under ultraviolet light; the lower fluoresced deep purple and the upper fluoresced tan. The eluted lower band gave 12.2 g. (12%) of 2-(2′-nitrophenyl)naphthalene, m.p. 93–98° (m.p. 101° after recrystallization from ethanol); the upper band was found to contain the 4′-nitro isomer.

1-(2′-Nitrophenyl)naphthalene. Ten grams of copper-bronze powder was added over a period of 15 min. to a mixture of 14.9 g. (0.06 mole) of 1-iodo-2-nitrobenzene and 15.2 g. (0.06 mole) of 1-iodonaphthalene heated to 240°. After 3 hr. at 235–240°, the mixture was cooled and the mass extracted with three 30 ml. portions of benzene. Chromatography of the extracts on an alumina column, using benzene for development, gave three bands visible under ultraviolet light. The lowest fluoresced bright blue and contained α,α′-binaphthyl along with some other material, presumably 1-iodo-2-nitrobenzene. The middle band fluoresced grey-brown and contained 1-(2′-nitrophenyl)naphthalene and 1-iodonaphthalene. The upper band fluoresced purple and was 2,2′-dinitrobiphenyl. The middle band was washed out with benzene to give an oil after evaporation, which after crystallization from 70 ml. of 95% ethanol gave 3.41 g. (21%) of 1-(2′-nitrophenyl)naphthalene, m.p. 88–90° (reported m.p. 88–90°[22]). The upper band on similar treatment gave 2.70 g. of 2,2′-dinitrobiphenyl.

Carbazoles. The carbazoles prepared are summarized in Table II. All were prepared by heating dilute solutions of azides in kerosine, according to the method described for the following example.

3,4-Benzocarbazole from 1-(2′-azidophenyl)naphthalene. A solution of 0.5012 g. of 1-(2′-azidophenyl)naphthalene in 50 ml. of kerosine (washed by extraction with sulfuric acid) was quickly heated to 180–200°. After five minutes, the solution was allowed to cool and was eventually chilled to −10°. Filtration then gave 0.272 g. (61%) of 3,4-benzocarbazole, m.p. 132.5–134.5° after washing with petroleum ether (b.p. 30–40°). The filtrates were passed through an alumina column, the kerosine was removed by eluting with petroleum ether (b.p. 40–60°), and the column was devel-

TABLE II

CARBAZOLES PREPARED FROM AZIDOBIARYLS

	Yield	Crude M.P., C°.	Pure M.P., C.°
2-Hydroxycarbazole	87.5	255–260	266.5–269.5[a]
2-Methoxycarbazole	71.8[b]	227–234	234–235.5[c]
1,4-Dimethoxycarbazole	71	109–112	111.5–112.8[d]
3-Chlorocarbazole	60.5[e]	188–191	195.8–197[f]
1,2-Benzocarbazole[g]	94	226–228	229–230[h]
1,2-Benzocarbazole[i]	94	228–230	230–231
3,4-Benzocarbazole	100	132.5–134.5	135–136[j]

[a] Reported[24] m.p. 276°. *Anal.*[13] Calcd. for $C_{12}H_9ON$: C, 78.67; H, 4.95. Found: C, 78.78; H, 4.95. [b] Based on 2-amino-4′-methoxybiphenyl;[11] azide not isolated. [c] Reported[25] m.p. 235–236°. *Anal.*[14] Calcd. for $C_{13}H_{11}ON$: C, 79.6; H, 5.62. Found: C, 79.47; H, 5.73. [d] *Anal.*[14] Calcd. for $C_{14}H_{13}O_2N$: C, 73.99; H, 5.77. Found: C, 74.03; H, 5.83. [e] From 2-amino-5-chlorobiphenyl; azide not isolated. [f] Reported[26] m.p. 199°. [g] From 1-azido-2-phenylnaphthalene. [h] Reported[27] m.p. 225°; undepressed when mixed with 1,2-carbazole from 2-(2′-azidophenyl) naphthalene. Picrate, m.p. 186–188° (reported 185°). [i] From 2-(2′-Azidophenyl)-naphthalene. [j] Reported[23] m.p. 134–135°.

---

(19) J. Dobáš, *Chem. listy*, **46**, 277 (1952); *Chem. Abstr.*, **47**, 8669d (1953).

(20) H. Hübner and H. Lüddens, *Ann.*, **209**, 349 (1881).

(21) Th. De Crauw, *Rec. trav. chim.*, **50**, 776 (1931).

(22) J. Forrest and S. H. Tucker, *J. Chem. Soc.*, 1137 (1948).

(23) F. R. Japp and W. Maitland, *J. Chem. Soc.*, **83**, 270 (1903).

(24) F. Baullauf, F. Muth, and A. Schmelzer, U. S. Patent **1,807,682**; *Chem. Abstr.*, **25**, 4412 (1931).

(25) C. K. Bradsher, F. C. Brown, and P. H. Leake, *J. Org. Chem.*, **22**, 500 (1957).

(26) O. Süs, *Ann.*, **557**, 240 (1947).

(27) S. H. Oakeshott and S. G. Plant, *J. Chem. Soc.*, 1843 (1928); W. Borsche, *Ann.*, **359**, 79 (1908).

oped with benzene. A single, bright blue, fluorescent band was visible under ultraviolet light. Elution with benzene gave 0.176 g. of a solid, m.p. 127–134°, which gave no m.p. depression with the 3,4-benzocarbazole first isolated; total yield 0.448 g. (100%). Recrystallization from 30 ml. of petroleum ether (b.p. 90–100°) raised the m.p. to 135–136° (reported,[23] 134–135°).

2-Methoxycarbazole from 2-Hydroxycarbazole. To a solution of 0.32 g. (0.00175 mole) of 2-hydroxycarbazole in 20 ml. of sodium hydroxide was added slowly 0.25 g. (0.002 mole) of dimethyl sulfate, and the resulting mixture was heated on the steam bath for one hour. The yield of crude 2-methoxycarbazole obtained upon filtration of the cooled solution was 0.28 g. (81%), m.p. 231.5–234.5°. Upon recrystallization from acetone-water, 0.15 g., m.p. 231.5–234.5°, and 0.06 g., m.p. 224–230° was obtained. A mixed melting point with material prepared from 2-azido-4′-methoxybiphenyl gave no depression.

2-Biphenylyl azide-3′-N^{15}. 2-Biphenylylhydrazine chlorostannite[28] (2.99 g., 0.00473 mole) was slurried with 7 ml. of concentrated hydrochloric acid in 25 ml. of water, and 1.00 g. of potassium nitrite (about 2% enriched in N^{15}) in 5 ml. of water was added dropwise to the solution at 0–5°. After 30 min., the precipitated azide was filtered off; wt. 1.77 g. (96%), m.p. 48–50°. It was recrystallized for use by chilling its solution in methanol to −20°.

Decomposition of labeled azide. The apparatus used for the collection of nitrogen from the decomposition of the N^{15}-labeled azide was that described by Vaughan, Boyd, McCane, and Sloan.[29] In the reaction vessel was placed 25 ml. of kerosine (extracted with sulfuric acid, sodium hydroxide solution, dried and distilled) along with 0.3–0.4 g. of the azide. The reaction vessel was connected to a nitrometer tube filled with 50% potassium hydroxide solution. Air was removed from the system by a stream of carbon dioxide, obtained from Dry Ice and found to contain only a slight trace of air. The reaction vessel was heated to 195° for 30 min. by means of an oil bath, and then cooled to room temperature. The nitrogen was swept into the nitrometer tube with carbon dioxide, and collected over 50% potassium hydroxide solution; the yield was quantitative. The nitrogen was drawn from the nitrometer through Ascarite and Dehydrite into an evacuated sample tube, and samples were analyzed on a Nier-type isotope-ratio mass spectrometer. (See Vaughan *et al.*[29] for details of the procedure.)

Assay of potassium nitrite. The labeled potassium nitrite was assayed by heating it with an equivalent of ammonium chloride in aqueous solution.[29] The nitrogen obtained was collected in the same way as described above.

TABLE III

RESULTS OF N^{15} EXPERIMENTS

Source of N_2	Isotope Ratio (29/28)	Atom % N^{15} in N_2	Excess Atom % N^{15} in N_2
"Pure" tank N_2	0.00735	0.365	0.000
$KN^*O_2 + NH_4Cl$	0.02617	1.291	0.926
Ordinary 2-azidobiphenyl	0.00738	0.368	0.003
Labeled 2-azidobiphenyl	0.02640	1.303	0.935

Atom % N^{15} in KN^*O_2, 2.217%.
Maximum possible atom percent of N^{15} in N_2 from labeled azide, 1.292%.
Maximum possible atom percent of N^{15} in N_2 from labeled azide over that from ordinary azide, 0.924%.

$$\frac{0.935}{0.924} \times 100 = 101\%$$

Thus, 101 ± 3% of the isotropic (terminal) nitrogen atoms of the azide appeared in the evolved nitrogen.

2-Carboxy-2′-cyanobiphenyl. Phenanthrenequinone monoxime was subjected to the Beckmann rearrangement "of the second kind" essentially according to Werner and Piguet,[30] except that the benzenesulfonyl chloride was added to the pyridine solution of the oxime at ice-bath temperature, followed by refluxing for 1.5 hr. The yield was 31%.

2-Amino-2′-cyanobiphenyl. A mixture of 13.5 g. (0.061 mole) of 2-carboxy-2′-cyanobiphenyl and 14.3 g. (0.12 mole) of thionyl chloride was heated under reflux on a steam bath for 2 hr., and the excess thionyl chloride was removed under aspirator vacuum. A solution of 7.8 g. (0.12 mole) of sodium azide in 30 ml. of water was added dropwise with stirring to the residual dark oil dissolved in 50 ml. of acetone, kept at 0–5° with an ice-salt bath. After several hours, 40 ml. of water was added and the suspension was allowed to stand overnight. The solid azide was collected, dissolved in toluene to a total volume of 294 ml., and dried over magnesium sulfate. The resulting amber solution was heated until nitrogen evolution ceased. A small portion of the resulting purple solution was reserved for other work, and the main portion, 245 ml., was cooled and added dropwise with stirring to 500 ml. of concentrated hydrochloric acid that had been additionally saturated with hydrogen chloride near 0°; some frothing occurred. The mixture was then allowed to come to room temperature overnight with continuous stirring, after which the layers were separated and the aqueous phase was neutralized with sodium carbonate. The mixture was extracted with ether, the extracts were dried over magnesium sulfate, and hydrogen chloride was passed in until precipitation appeared complete. There was obtained 4.41 g. (40%) of *2-amino-2′-cyanobiphenyl hydrochloride*, m.p. 307–310°, which, from the analytical figures, may have lost a small amount of hydrogen chloride during drying.

Anal.[18]: Calcd. for $C_{13}H_{11}N_2Cl$: C, 67.68; H, 4.81. Found: C, 67.90, 67.88; H, 5.25, 5.30.

The free base was obtained as a brown oil when the hydrochloride was dissolved in sodium carbonate solution. Taking it up in ether, drying over magnesium sulfate, concentration and crystallization from chilled aqueous ethanol gave fine, white needles, m.p. 61–63°.

Anal.:[13] Calcd. for $C_{13}H_{10}N_2$: C, 80.38; H, 5.19. Found: C, 80.12; H, 5.01.

The N-carboethoxy derivative was obtained from an experiment in which the hydrochloric acid hydrolysis step following the Curtius rearrangement was largely incomplete. From 14.13 g. of 2-carboxy-2′-cyanobiphenyl, there was obtained in the manner described only 0.396 g. (2.7%) of 2-amino-2′-cyanobiphenyl hydrochloride. Evaporation of the toluene layer and addition of ethanol to the residual oil gave 8.83 g. (33%) of 2-carboethoxyamino-2′-cyanobiphenyl, light tan solid from aqueous ethanol, m.p. 91–96°. An analytical sample from one further crystallization melted at 94.5–96.5°.

Anal.:[18] Calcd. for $C_{16}H_{14}N_2O_2$: C, 72.16; H, 5.30; N, 10.52. Found: C, 71.74; H, 5.42; N, 10.44.

9,10-Tetrazolophenanthridine. A. From 2-Azido-2′-cyanobiphenyl. In an attempt to bring about cyclization to 4-cyanocarbazole, 0.1 g. of 2-azido-2′-cyanobiphenyl in 20 ml. of kerosine was heated near 180° for 0.5 hr. and allowed to cool; a few bubbles were noticed during the heating. The tan solid that formed was collected by centrifugation, washed with petroleum ether, and treated with charcoal in hot absolute alcohol. Dilution with water produced a crystalline solid, wt. 0.0718 g. (71.8%), m.p. 220–222°, which proved to be 9,10-tetrazolophenanthridine. An analytical sample recrystallized from ethanol had m.p. 221.5–223.5°.

---

(28) C. Graebe and A. Sc. Rateanu, *Ann.*, **279**, 267 (1894).

(29) W. R. Vaughan, W. T. Boyd, D. L. McCane, and G. J. Sloan, *Anal. Chem.*, **23**, 508 (1951).

(30) A. Werner and A. Piguet, *Ber.*, **37**, 4311 (1904).

Anal.:[10] Calcd. for $C_{13}H_8N_4$: C, 70.89; H, 3.66. Found: C, 70.65; H, 3.77.

B. From fluorenone oxime. To a mixture of 10 g. (0.05 mole) of fluorenone oxime and 15 g. (0.07 mole) of phosphorus pentachloride was cautiously added 100 ml. of phosphorus oxychloride; a vigorous reaction began at once. After two hours of refluxing, the mixture had turned black. The phosphorus oxychloride was removed by distillation after the addition of 25 ml. of xylene as diluent and chaser, and a solution of *ca.* 0.1 mole of hydrogen azide in 200 ml. of dry benzene was added to the cold residue. After one week at room temperature, the solution was heated for 0.5 hr., cooled and washed thoroughly with 20% sodium carbonate solution. The dried (magnesium sulfate) and filtered solution was concentrated to near dryness, heated with absolute alcohol, filtered from some insoluble matter, and crystallized by the addition of water to give 2.06 g. (18.4%), m.p. 208–218°. A sample recrystallized from aqueous ethanol gave no depression of melting point when mixed with the compound obtained from 2-azido-2′-cyanobiphenyl.

Pyrolysis of 4-Azidofluorenone. When 1.0 g. samples of 4-azidofluorenone were heated in kerosine or resorcinol dimethyl ether solution, nitrogen was evolved at about 175° and the solutions turned nearly black. On cooling, a brown, amorphous solid separated, insoluble in benzene or ethanol, but soluble in nitrobenzene. Attempts at crystallization, with and without chromatography, failed, as did attempts to prepare a picrate and an oxime.

4-Aminofluorene. A mixture of 5.00 g. (0.0238 mole) of fluorene-4-carboxylic acid[31] and 5.95 g. (0.05 mole) of thionyl chloride was heated on a steam bath for one hour and the excess thionyl chloride was distilled off. A solution of 3.25 g. (0.05 mole) of sodium azide in 15 ml. of water was added with stirring to a solution of the resulting acid chloride in 25 ml. of acetone. The light orange-brown, crude, solid azide was collected after the addition of 50 ml. of water, and was pressed dry and promptly dissolved in 60 ml. of benzene. After 0.5 hr. of refluxing, nitrogen evolution had stopped, and 25 ml. of 50% potassium hydroxide solution was added and the refluxing continued for several hours. Hydrogen chloride was passed into the separated and dried benzene layer, precipitating 3.28 g. (63.5%) of 4-aminofluorene hydrochloride, m.p. 240° (dec.). A purer sample was prepared by releasing the free base with aqueous ammonia, taking it up in benzene, and reprecipitating with hydrogen chloride, which gave a white solid, m.p. 283–288°.

Anal.[14]: Calcd. for $C_{13}H_{12}NCl$: C, 71.69; H, 5.56. Found: C, 71.82; H, 5.70.

The free base was obtained by decomposing the salt with aqueous ammonia and crystallizing from benzene. It formed pale yellow needles, m.p. 112.5–114°.

Anal.[14]: Calcd. for $C_{13}H_{11}N$: C, 86.16; H, 6.12. Found: C, 86.02; H, 6.09.

Pyrolysis of 4-azidofluorene. Attempted thermal cyclization of 4-azidofluorene in the same manner as described for 4-azidofluorenone gave an amorphous, brown solid of similar characteristics, that resisted all attempts at crystallization.

ANN ARBOR, MICH.

---

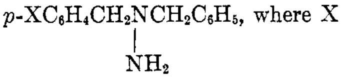
[31] W. E. Bachmann and J. C. Sheehan, *J. Am. Chem Soc.*, 62, 2689 (1940).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STATE UNIVERSITY OF IOWA]

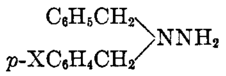
Synthesis of Some 1,1-Dibenzylhydrazines[1]

R. L. HINMAN[2] AND KENNETH L. HAMM

Received June 28, 1957

A series of unsymmetrically substituted dibenzylhydrazines,  $p\text{-}XC_6H_4CH_2\underset{NH_2}{\underset{|}{N}}CH_2C_6H_5$, where X = CH_3O—, $(CH_3)_2N$—, CH_3—, and Cl—, have been prepared by reduction of the corresponding nitrosamines with lithium aluminum hydride. 1-Benzyl-1-furfurylhydrazine was also prepared by this method. Attempts to prepare other hydrazines of this type are discussed.

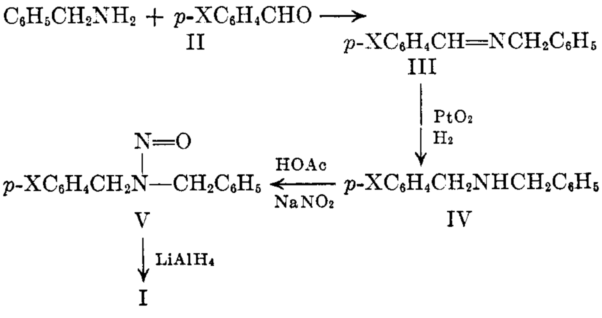
In connection with a current investigation of the oxidation of 1,1-dibenzylhydrazines, it was necessary to prepare a number of disubstituted hydrazines of the general formula I.



$C_6H_5CH_2\backslash NNH_2$, $p\text{-}XC_6H_4CH_2/$

I

The hydrazines were all prepared by the same general route. Benzylamine and a suitably substituted benzaldehyde (II) were condensed to give a Schiff base (III). III was reduced in absolute ethanol in the presence of platinum oxide to a secondary amine (IV) which was then nitrosated in dilute acetic acid solution to give a nitrosamine (V). The latter was reduced with lithium aluminum hydride to the corresponding 1,1-dibenzylhydrazine (I). The properties of the products are listed in Tables I–V.



---

[1] Presented before the Organic Division of the American Chemical Society at the Atlantic City Meeting, September 16, 1956.

[2] Present Address: Union Carbide Research Institute, 32 Depot Plaza, White Plains, N. Y.