930 (s), 870 (m), 743 (s), 702 (s) cm^{-1}. The nmr spectrum in CCl_4 was consistent with the structural assignment.[23]

Anal. Calcd for $C_{10}H_{15}NO$: C, 72.69; H, 9.15; N, 8.48. Found: C, 72.53; H, 9.16; N, 8.51.

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[23] The τ values for the $ArCH_2$ and NCH_2O groups were incorrectly reversed in the earlier work.[1]

Registry No.—N,N-Dimethylbenzylamine, 103-83-3; II, 13657-14-2.

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Permanganate Oxidation of N-Aryl-2-naphthylamines

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The major crystalline products from permanganate oxidation of N-aryl-2-naphthylamines are 1,1′-coupling dimers. Structures were determined by instrumental methods and by degradation to known 7-aryldibenzo[*c,g*]carbazoles. Also formed are significant quantities of carbon–nitrogen coupling products, believed to be the *o*-semidines. 7-Aryldibenzo[*c,g*]carbazoles are formed in minor amounts. No evidence was found for stable symmetrical tetraarylhydrazines.

The oxidation of diarylamines to tetraarylhydrazines is well known from the classic work of Wieland and coworkers.[5] Wieland's views on the reversibility of

$$Ar_2NH \xrightarrow{\text{oxidn}} Ar_2NNAr_2 \rightleftharpoons 2Ar_2N\cdot \longrightarrow \text{decomposition products}$$

diarylamino radical formation and on the nature of the decomposition products have been modified by more recent work. Neugebauer and Fischer[6] have shown that no stable radicals are detected from tetraphenylhydrazine at temperatures as high as 90°. Diarylamino radicals were detected, however, when the benzene rings contained electron-supplying substituents. Contrary to Wieland's original results, the major decomposition product of tetraphenylhydrazine was shown not to be 5,10-diphenyl-5,10-dihydrophenazine.[7] The hydrazine decomposes irreversibly at 90° with a half-life of about 10 min.[8] Musso[9] recently showed the major decomposition product to be an oligomer containing an average of five diphenylamino units, formed by nitrogen–carbon coupling.

These several facets of the oxidation of diphenylamine may be considered reasonably well established. In contrast, no aspect of the oxidation of secondary naphthylamines is well understood at this time. N-Arylnaphthylamino radicals have not been identified unambiguously, and there seems to be no agreement on the products of oxidation of secondary naphthylamines.

Wieland and Süsser[10] showed that the permanganate oxidation of di-2-naphthylamine did not yield a hydrazine, and tentatively assigned to the crystalline product an *o*-semidine structure. An analogous structure was assigned by Rehner and coworkers to a crystalline product of the permanganate oxidation of N-phenyl-2-naphthylamine.[11] Somewhat later, Lieber and Somasekhara[12] oxidized a series of dinaphthylamines with potassium permanganate. Completely disregarding the previous work of Wieland[10] and Rehner,[11] and without any valid experimental evidence, they assigned symmetrical hydrazine structures to all crystalline products. The hydrazine structure has also been suggested for the oxidation product of N-phenyl-2-naphthylamine.[13] The oxidation of N-phenyl-1-naphthylamine and di-1-naphthylamine with a variety of oxidizing agents produces *p*-semidine polymers,[14] similar to those formed by decomposing tetraphenylhydrazine.[9]

The present work deals with the products resulting from permanganate oxidation of two N-aryl-2-naphthylamines.

Results and Discussion

The oxidation of N-phenyl-2-naphthylamine or di-2-naphthylamine by neutral potassium permanganate in acetone leads to the dehydrogenated 1,1′ dimer as the major crystalline product. Structure proof is shown in Scheme I.

1,1′-Bis(N-phenyl-2-naphthylamine) (**2a**) was found by nmr and infrared spectroscopy to have one amino hydrogen per phenyl-2-naphthylamine residue, *i.e.*, two amino hydrogens per molecule. 1,1′-Bis(di-2-naphthylamine) (**2b**) was too sparingly soluble for accurate nmr integration of the amine hydrogen peak. However, its infrared spectrum indicated the presence of two N–H bonds per molecule. Both dimers gave diacetates (no N–H infrared absorption band and three acetate protons per amine residue). Each oxidative dimer was degraded in excellent yield to the corresponding 7-aryldibenzo[*c,g*]dibenzocarbazole (**3**), which was synthesized by standard methods.

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(5) (a) H. Wieland and S. Gambarjan, *Ber.*, **39**, 1499 (1906); (b) H. Wieland, *Ann.*, **381**, 200 (1911).

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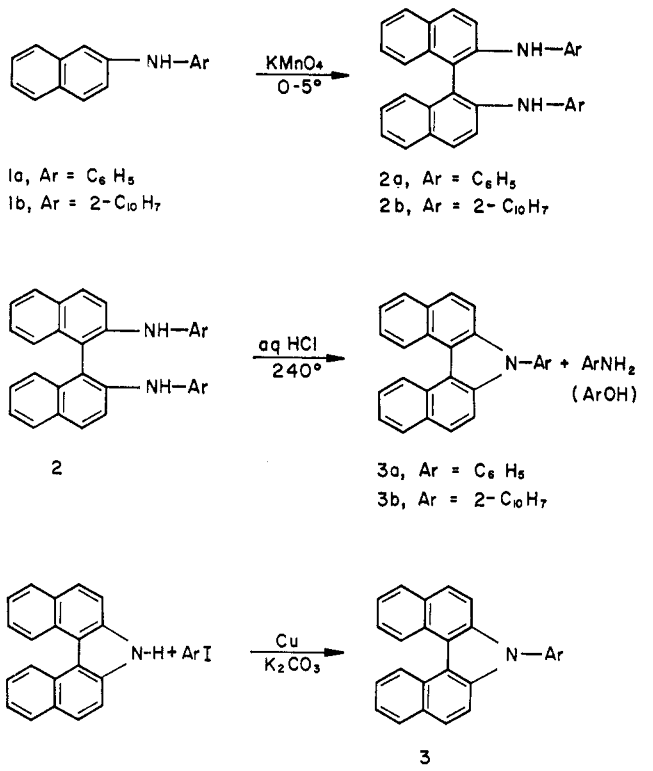
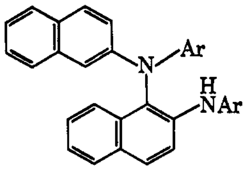
SCHEME I



Although Wieland and Süsser[10] had sound experimental evidence for eliminating a hydrazine structure for their crystalline dimer of di-2-naphthylamine (mp 273° *vs.* 282–283° in the present work), they also discarded structure **2b** without serious consideration in favor of the *o*-semidine **4b**. Rehner and coworkers[11] also favored an *o*-semidine structure, **4a**, for the crystalline dimer from N-phenyl-2-naphthylamine (mp 164–165° *vs.* 168° in the present work). Their experimental evidence included the formation of aniline on hydrolysis (see Experimental Section) and the formation of a dipicrate and a monoacetate (a gray-white powder, mp 170–175°). In contrast, using their experimental conditions, we were unable to obtain a picrate and obtained a crystalline diacetate (mp 283–284°). There seems no reason to doubt that the crystalline dimers found in the present work are the same as those previously isolated. The earlier structural assignments must therefore be considered incorrect.



4a, Ar = C_6H_5
b, Ar = 2-$C_{10}H_7$

With 1 equiv of permanganate the amount of **1a** unreacted varied from 4 to 25% in different experiments. The yield of **2a** was always about 63% based on the amount of **1a** consumed. Several methods were used to obtain a material balance on the crude product from the oxidation of **1a**.

By utilizing the solubilities of the hydrochlorides of **1a** and **2a** in different solvents, it was possible to precipitate **2a** relatively free from the other components of the mixture by passing anhydrous hydrogen chloride through a benzene solution of the crude reaction mixture. After evaporation of the solvent, the mixture was dissolved in ether, and **1a** was likewise precipitated as the hydrochloride. The remaining material, after washing and drying, was an amorphous solid, which was found to contain a small amount of 7-phenyldibenzo[*c,g*]carbazole (**3a**) and a major fraction which will be designated as the semidine fraction **4a**. The quantities in the first column of Table I are based on crude yields of the isolated products.

TABLE I

PRODUCTS FROM THE PERMANGANATE OXIDATION OF N-PHENYL-2-NAPHTHYLAMINE

	% yield based on amine consumed	
Compd	Isolated	Nmr
2a	63	66
3a	0.5[b]	
4a[a]	32	34

[a] Semidine fraction; see text. [b] Determined by thin layer chromatography (tlc) and ultraviolet (uv) absorption.

After repeated chromatography, the semidine fraction remained amorphous. Analysis and molecular weight determination showed it to be isomeric with **2a**. The thin layer chromatogram gave a single spot with only traces of **1a**, **2a**, and **3a** discernible. A single proton resonance at τ 3.78 ($CDCl_3$) indicated one N–H bond per molecule, as did the infrared spectrum. Upon long standing, seed crystals of **4a** were finally obtained, and the amorphous material was converted (77% recovery) into a crystalline substance which had an infrared spectrum identical with that of the original amorphous fraction.

The results in the second column of Table I were obtained by integrating N–H peaks appearing at τ 4.52 (**1a**), 4.45 (**2a**), and 3.78 (**4a**) in the freeze-dried crude reaction mixture dissolved in chloroform-*d*. From the close agreement between the isolated percentages and the nmr results we conclude that no change occurred during the isolation procedure. Furthermore, the thin layer chromatograms of the crude reaction mixture and a sample reconstituted from the isolated fractions were identical.

The composition of the semidine indicates that it is a product of nitrogen–carbon coupling. The chemical shift of the amino proton—0.74 ppm downfield of **1a**—suggests an *o*-diamine structure, *i.e.*, the *o*-semidine **4a**. Attempts to synthesize **4a** by coupling **1a** with 1-iodo-N-phenyl-2-naphthylamine failed because the iodo compound could not be prepared by any of the standard methods.

The products of the oxidation of di-2-naphthylamine were isolated by crystallization, and the results in Table II probably include appreciable overlap between fractions. Again the semidine fraction **4b** was found to be isomeric with **2b** and was originally noncrystalline. By slow crystallization from benzene solution, it was possible to obtain a small quantity of a crystalline product from the semidine fraction (5% based on the semidine formed). The infrared spectra showed both the crude semidine and the crystalline product to have one N–H bond per molecule.

TABLE II

PRODUCTS FROM THE PERMANGANATE OXIDATION OF DI-2-NAPHTHYLAMINE

Compd	% yield based on amine consumed
2b	45
3b	6[b]
4b[a]	49

[a] Semidine fraction; see text. [b] By tlc and uv absorption; isolated yield 3%.

Although the structural assignments of **4a** and **4b** must be considered tentative at this point, it is evident that stable hydrazines are not formed from **1a** and **1b**. Since the thin layer chromatograms of freshly oxidized solutions give no indication of products other than **1–4**, we conclude that the half-lives of the tetraarylhydrazines must be much less than 1 hr at 25°.

The possibility of a hydrazine intermediate, however, remains. There is precedent[15] for formation of compounds **2** and **3** *via* a thermal benzidine rearrangement of a hydrazine intermediate. The yields of dibenzocarbazoles observed in the present work, however, are too low to consider this as a significant mode of reaction. The simplest rationalization of the major products appears to be formation by carbon–carbon and carbon–nitrogen radical coupling reactions.

Experimental Section

Infrared Spectra.—The frequencies and extinction coefficients (ϵ) of the fundamental N–H stretching band are given in Table III. Since all amine peaks were narrow and of equal half-width, the linear absorbance was used to calculate ϵ (M^{-1} cm^{-1}). Calculating the number of N–H bonds per molecule by $\epsilon/60$ seems well justified by the results for compounds **1a**, **2a**, and **1b**. All amine hydrogens exchanged in less than 1 min on shaking with D_2O.

TABLE III

INFRARED SPECTRA OF AROMATIC AMINES

Compd	N–H[a]	ϵ, M^{-1} cm^{-1}	N–H per molecule, $\epsilon/60$	N–D[b]
1a	3440	60.0	1.0	2540
2a	3420	122	2.0	2530
4a	3410	67	1.1	2520
1b	3440	60.7	1.0	2550
2b	3410	123	2.0	2530
4b	3400	59.6	1.0	2520

[a] Positions are given in cm^{-1}; solutions 1.25% w/v in $CDCl_3$. [b] Positions are in cm^{-1} after exchange with D_2O.

Ultraviolet Spectra.—Only minor differences were observed among the spectra of **1a**, **2a**, and **4a**. The spectra of **1b**, **2b**, and **4b** are similar also. The spectra of **3a** and **3b** are nearly identical and agree with the published[11] spectrum of **3a**. The extinction coefficient at 365 nm (2.7 × 10^4, 95% ethanol) was found to be somewhat higher than the published value.

Nuclear Magnetic Resonance (Nmr) Spectra.—Peak positions and integrations are summarized in Table IV. Chloroform-*d* was used as solvent. Crude reaction mixtures of **1a**, **2a**, and **4a** were analyzed by direct integration when the quantity of unreacted **1a** was small. For larger amounts of **1a** overlap between **1a** and **2a** was appreciable, and analysis was done by expanding the N–H region of the spectrum and integrating by plainimeter. Comparison with synthetic mixtures and independent determination of **1a** by gc showed a simple graphical correction to be sufficiently accurate. All peaks assigned to amine protons disappeared on shaking with D_2O and were immediately regenerated on adding H_2O.

TABLE IV

NMR OF AROMATIC AMINES AT 60 MC

Compd	N–H, τ^a	Area of N–H/ area of C–H	N–H per molecule
1a	4.52	0.0826	1.1
2a	4.45	0.0820	2.0
4a	3.78	0.0430	1.0

[a] *Ca.* 40% w/v in $CDCl_3$.

Chromatography.—Thin layer chromatograms on silica gel plates were developed with carbon tetrachloride or carbon tetrachloride–cyclohexane mixtures and were visualized with 260-nm light. Compounds **3a** and **3b** were determined quantitatively from reaction mixtures by removing the spot, washing out the product with ethanol, and measuring the ultraviolet absorbance at 365 nm.

Woelm neutral aluminum oxide of activity grade I was used for column chromatography with benzene as eluent unless otherwise specified. A 2-ft silicone gum rubber column was employed for gas phase chromatography.

Molecular Weights.—When solubility and availability of sample permitted, molecular weights were measured by vapor pressure osmometry (vpo). A vapor pressure osmometer, Model 302, Mechrolab, Inc., was used at 37° with benzene as solvent. Because of the low solubility of **2b**, its molecular weight was determined in toluene at 90°. Values of *m/e* were determined by mass spectrometry at 7 eV.

Materials.—N-Phenyl-2-naphthylamine (Matheson Coleman and Bell) was vacuum distilled, mp 108–109°. Di-2-naphthylamine (Aldrich Chemical Co., Inc.) was purified by chromatography over alumina, followed by recrystallization from benzene, mp 171.5–172.5°. Acetone was refluxed overnight with $KMnO_4$ and distilled prior to use as a solvent for oxidations.

7-Phenyldibenzo[*c,g*]carbazole (3a).—The standard procedure[16] was modified slightly. 7H-Dibenzo[*c,g*]carbazole[17] (1.00 g), finely divided potassium carbonate (0.54 g), iodobenzene (3.64 g), and freshly prepared[18] copper powder (0.05 g) were refluxed in 10 ml of nitrobenzene with vigorous stirring for 18 hr. After removal of nitrobenzene by steam distillation, the residue was dissolved in a minimum amount of benzene and eluted from alumina with 1:1 benzene–petroleum ether (bp 30–60°). A pale yellow glassy solid was obtained which crystallized upon stirring with a small amount of diethyl ether. Recrystallization from a diethyl ether–alcohol mixture yielded 1.11 g (87%) of 7-phenyldibenzo[*c,g*]carbazole, mp 142.5–143° (lit.[19] mp 144°).

7-(2-Naphthyl)dibenzo[*c,g*]carbazole (3b) was prepared from 7H-dibenzo[*c,g*]carbazole (0.963 g) and 2-iodonaphthalene (1.37 g) by the procedure described above. After two treatments with alumina and recrystallization from heptane–benzene the yield of **3b** was 0.766 g (54%), mp 216–217°.

Anal. Calcd for $C_{30}H_{19}N$: C, 91.57; H, 4.87; N, 3.56; mol wt, 393.5. Found: C, 91.62; H, 4.89; N, 3.50; mol wt (*m/e*), 393.

Oxidation of N-Phenyl-2-naphthylamine (1a) with Potassium Permanganate.—A solution of **1a** (0.5 mol, 109 g) in 1 l. of acetone was cooled to 0°. $KMnO_4$ (26.3 g, 1 equiv) was added in small portions during a 5-hr period to the cooled solution under a blanket of nitrogen. The solution was allowed to warm to room temperature and stand overnight. Filtration to remove MnO_2 produced a colorless solution, which was evaporated at reduced pressure. The residue was dissolved in benzene, washed with water, dried over K_2CO_3, filtered, and finally freeze dried from benzene. The freeze-dried crude mixture (101 g) was used for the operations described below.

A. **1,1′-Bis(N-phenyl-2-naphthylamine) (2a).**—To a benzene solution (200 ml) of the crude reaction mixture (11.9 g) anhydrous HCl was introduced with stirring for 20 min. The white precipitate (6.6 g) was collected by filtration and hydrolyzed by stirring in a mixture of 100 ml of benzene and 100 ml of water for 30 min. Upon evaporation of the benzene and drying, the crude yield of **2a** was 5.65 g (44% yield), mp 160–167° (oil bath).

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(17) J. Meisenheimer and K. Witte, *Ber.*, **36**, 4153 (1903).

(18) R. Q. Brewster and T. Groening, "Organic Syntheses," Coll. Vol. II, John Wiley & Sons, Inc., New York, N. Y., 1961, p 445.

(19) H. Walder, *Ber.*, **15**, 2166 (1882).

After two recrystallizations from diethyl ether, the melting point was 167.5–8.0.

Anal. Calcd for $C_{32}H_{24}N_2$: C, 88.04; H, 5.54; N, 6.42; mol wt, 436.5. Found: C, 88.13; H, 5.51; N, 6.37; mol wt (vpo), 442, (*m/e*), 436.

B. **N-Phenyl-2-naphthylamine (1a).**—The remaining benzene solution from the HCl treatment was evaporated, and the residue was dissolved in 200 ml of diethyl ether. Anhydrous HCl was introduced with stirring for 20 min to yield 3.6 g of hydrochloride, which was hydrolyzed as before to give 3.0 g (25% yield) of **1a**, identified by mixture melting point and comparison of infrared spectrum with that of an authentic specimen.

C. **Semidine Fraction 4a.**—The remaining ether solution described above was washed, dried, and evaporated to give 2.9 g (24% yield) of the amorphous semidine fraction. Seed crystals were obtained by treating 0.3 g of amorphous **4a** with diethyl ether, allowing the solution to evaporate at room temperature, and leaving the residue in an open flask for 35 days. Crystallization of a larger quantity was induced by seeding 6.9 g of amorphous **4a** in the presence of 2 ml of diethyl ether for 48 hr. The resulting solid was triturated with ether and filtered to give 3.4 g of crystalline **4a**, mp 134–136°. After evaporation of the filtrate, the residue was crystallized from absolute ethanol to yield an additional 1.9 g (77% recovery) of crystalline **4a**. The infrared spectra and elemental analyses of the crystalline and amorphous materials were identical.

Anal. Calcd for $C_{32}H_{24}N_2$: C, 88.04; H, 5.54; N, 6.42; mol wt, 436.5. Found: C, 87.99; H, 5.52; N, 6.35; mol wt (vpo), 440, (*m/e*), 436.

D. **7-Phenyldibenzo[*c,g*]carbazole (3a).**—During column chromatography of semidine fraction **4a**, early fractions eluted with 1:1 benzene–petroleum ether were fairly rich in **3a** as shown by the uv absorption at 365 nm. Efforts to crystallize **3a** from these fractions were unsuccessful. The yield in Table I was obtained by tlc and uv absorption.

Acetylation of 1,1′-Bis(N-phenyl-2-naphthylamine) (2a).—The dimer (1.0 g) was refluxed overnight with acetic anhydride (10 ml) in acetic acid (20 ml). The cooled solution was poured into aqueous methanol, and the resulting emulsion was coagulated with calcium chloride (1.0 g). The precipitate was dried and recrystallized from benzene–hexane to give **1,1′-bis(N-phenyl-2-naphthylamine) diacetate** (0.9 g) as cubes, mp 284–285°.

Anal. Calcd for $C_{36}H_{28}N_2O_2$: C, 83.05; H, 5.42; N, 5.38. Found: C, 82.86; H, 5.25; N, 5.35.

Oxidation of Di-2-naphthylamine (1b) with Potassium Permanganate.—$KMnO_4$ (1.2 equiv, 2.4 g) was added in small quantities during 3 hr to a solution of **1b** (0.037 mol, 10 g) in 400 ml of acetone at 0° under nitrogen. At the end of the addition, the reaction mixture was allowed to warm to room temperature and stand for 1 hr. The precipitated MnO_2 was removed by filtration to give a colorless solution. Isolation of products is described below.

A. **1,1′-Bis(di-2-naphthylamine) (2b).**—The acetone solution was successively reduced in volume and filtered until no more **2b** precipitated. The crude yield of **2b** was 2.8 g (28% yield). Once isolated, **2b** was sparingly soluble in most solvents. Recrystallization from xylene (1 g/25 ml, recovery 70–80%) gave colorless **2b**, mp 282–283°.

Anal. Calcd for $C_{40}H_{28}N_2$: C, 89.52; H, 5.26; N, 5.22; mol wt, 536.6. Found: C, 89.58; H, 5.32; N, 5.11; mol wt (vpo), 550, (*m/e*), 536.

B. **Di-2-naphthylamine (1b).**—The acetone filtrate described above was evaporated, and the residue was dissolved in benzene. The benzene solution was successively evaporated and filtered until no **1b** could be detected in the solution by gc. The yield of recovered **1b** was 3.7 g, identified by mixture melting point and infrared spectrum.

C. **Semidine Fraction 4b.**—Upon evaporation of the benzene filtrate described above, 3.4 g of amorphous **4b** was obtained. This was later shown to contain about 0.3 g of **3b**. Crystalline material was obtained from the semidine fraction of a large-scale run (30 g of **1b**). The semidine fraction (9.7 g) was chromatographed twice, and the center fractions (8.0 g) were stored in benzene (15 ml) under nitrogen for 2 months. White crystals (1.17 g) were removed by filtration and washed with boiling chloroform to give 0.55 g of crystalline **4b**, mp (sealed tube) 287–289° (depressed on admixture of **2b**).

Anal. Calcd for $C_{40}H_{28}N_2$: C, 89.52; H, 5.26; N, 5.22; mol wt, 536.6. Found: C, 89.56; H, 5.26; N, 5.13; mol wt (*m/e*), 536.

The crystalline substance obtained was apparently identical with the amorphous material. The amorphous fraction gave a satisfactory elemental analysis and a molecular weight of 560 by vpo and *m/e* 536. Both crystalline and amorphous materials had identical infrared spectra.

D. **7-(2-Naphthyldibenzo[*c,g*]carbazole (3b).**—During chromatography of the 3.4 g of amorphous **4b** described above, the first two fractions (0.62 g) eluted with 1:1 benzene–petroleum ether were found to contain about 50% **3b** by uv absorption. Boiling with diethyl ether for 5 min and cooling gave **3b** in 1.9% yield (0.14 g), mp 215–216° undepressed on admixture with an authentic sample. Determination of **3b** in the crude oxidation mixture by tlc and uv absorption indicated a 6% yield based on the amount of **1b** consumed.

Acetylation of 1,1′-Bis(di-2-naphthylamine) (2b).—Under the conditions described for **2a** above, **2b** gave a diacetate (nmr) which could not be crystallized and was obtained as a gray-white powder from aqueous acetone, softening at 90–95°. The analysis suggests that it may contain a molecule of water.

Anal. Calcd for $C_{44}H_{32}N_2O_2 \cdot H_2O$: C, 82.73; H, 5.37; N, 4.38. Found: C, 82.36; H, 5.59; N, 4.40.

Reaction of 1,1′-Bis(N-phenyl-2-naphthylamine) (2a) with Concentrated Hydrochloric Acid.—The amine (2.5 g) and 10 ml of concentrated hydrochloric acid were sealed in a heavy-walled Pyrex tube. The tube was enclosed in a stainless steel pipe which was securely capped at both ends and placed in an autoclave at an initial nitrogen pressure of 1200 psi.[20] The autoclave was rocked for 6 hr at 240–250°. When cooled, the contents of the tube had separated into a brown mass and a clear acid layer, which were separated by decantation. The acid layer was neutralized, and aniline was extracted with a known volume of ether. The yield determined by gas chromatography was 98%. After drying, the solvent was evaporated to give 0.47 g of aniline (88% yield), identified by its infrared spectrum. The brown mass was dissolved in a minimum amount of ether, washed with water, and diluted to a known volume with ethanol. The ultraviolet absorption at 365 mm indicated a 94% yield of 7-phenyldibenzo[*c,g*]carbazole (**3a**). In a separate experiment the product was purified by eluting from alumina with 1:1 benzene–petroleum ether to give 86.5% yield of **3a**, identified by comparison of melting point (143.5–144°), mixture melting point (143–144°), ultraviolet spectrum, and infrared spectrum with those of the authentic specimen described above.

From three previous attempts, a product melting at 122–123° was obtained. The mass, nmr, infrared, and ultraviolet spectra were identical with those of authentic 7-phenyldibenzo[*c,g*]carbazole. Elemental analysis and ultraviolet extinction coefficients revealed the low-melting material to be pure. The mixture melting point was 142.5–143°. The low-melting form could be converted into a solid melting at 143–144° by equilibrating the melt at 125° for 1 hr. This behavior is similar to that reported by Shine and Trisler for 7H-dibenzo[*c,g*]carbazole.[15]

Reaction of 1,1′-Bis(di-2-naphthylamine) (2b) with Hydrochloric Acid.—The procedure described above yielded 92% of **3b** as determined by uv spectroscopy. The isolated yield of **3b** was 70%, mp 214–216° undepressed on admixture with authentic **3b**. Infrared and uv spectra were identical with those of the authentic specimen. The 2-naphthylamine formed in the reaction did not survive, but was converted into 2-naphthol—60% by gc, 30% isolated and identified by mixture melting point and infrared spectrum.

Registry No.—**1a**, 135-88-6; **1b**, 532-18-3; **2a**, 17704-02-8; **2a**, diacetate, 17704-09-5; **2b**, 17704-01-7; **2b**, diacetate, 17704-10-8; **3b**, 17704-03-9; **4a**, 17704-04-0; **4b**, 17704-05-1.

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(20) This procedure helps to avoid shattering of the tube, which was observed on occasion.