

CHEMICALS FROM CARBAZOLE BY REDUCTIVE PROCESSES

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Introduction: Carbazole was discovered in coal tar in 1872 (1). Synonyms for carbazole are dibenzopyrrole and diphenyleneimine. The numbering system used by Chemical Abstracts for the carbazole ring is shown in Figure 1.

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(1) Graebe and Glaser, Ber., 5, 12 (1872).

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Carbazole melts at 245.5°C. and sublimes readily. Its boiling point is 354°C./760 mm. It is sparingly soluble in most common solvents with the exception of acetone and pyridine. While most of the ring-substituted carbazole derivatives are also high melting, many N-substituted carbazole compounds melt below 100°C. Of course, all carbazole derivatives are high boilers.

The N-atom of carbazole is very weakly basic. Actually, the imino hydrogen is replaceable by alkali metals. Nevertheless, in aromatic substitution reactions the NH group exerts the same o, p-directing influence as in diphenylamine. Thus, in electrophilic substitution reactions, the 3- and 6- (i.e. p-) positions react primarily, with some o-substitution in the 1- or 8- positions.

In addition to being found in coal tar several good syntheses for making carbazole are also available. For example, the method of Tauber (2) involves the heating of 2,2'-diaminodiphenyl with a strong mineral acid to give excellent yields of carbazole (Figure 2).

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(2) Tauber, Ber., 24, 197 (1891)

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However, while synthesis will deliver a product of highest purity, it is believed that coal tar carbazole of 97% or better purity will always be cheaper than the synthetic product.

It is not intended to elaborate here on the methods of extracting carbazole from coal tar, but a brief general review may be useful. Dry coal tar contains 1-2% of carbazole. Of this amount, about 35% is industrially recoverable (3). Thus, the po-

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(3) Lowry, ed., "Chemistry of Coal Utilization", J. Wiley & Sons, N. Y. 1945

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tential U. S. capacity for coal tar carbazole is in excess of 50,000,000 lbs./yr. Generally, carbazole is recovered from coal tar by distillation and extraction. A coal tar distillate boiling at about 320-60°C., is allowed to cool whereupon crystalline solids deposit. These solids are recovered by centrifugation and contain 30-40% of anthracene, 20-25% of carbazole, and 10-40% of phenanthrene, their homologs, and impurities such as methyl fluorenes. Carbazole, anthracene, and phenanthrene can be isolated from this cake by fractional crystallization and/or extraction.

The commercial uses of carbazole have been mostly European developments. They include dyes such as Hydron Blue, pesticides, and vinylcarbazole polymers. In the U. S., the latter two have apparently never progressed beyond the pilot plant stage.

As a part of a wide-ranging utilization research program for the high boiling components of coal tar, the chemistry of carbazole was surveyed. These studies included reduction, oxidation, nitration-reduction, chlorination, alkylation, carboxylation, sulfonation, acetylation, pyridylethylation, and dye chemistry.

Scientifically and in their commercial prospects, the studies of the reduction of carbazole were perhaps the most fruitful. The present paper deals, for these reasons, with this aspect of carbazole chemistry.

In the past, the reduction of the carbazole nucleus by chemical agents or by catalytic hydrogenation has been difficult. Thus, compared with aromatics and certain other nitrogen heterocyclics such as acridine, indole, and phenylpyrrole, carbazole is much more resistant to catalytic hydrogenation. The first report (4) of the catalytic hydrogenation of carbazole claimed the formation of 2,3-diethylindole as the main product. However, none of the subsequent investigators were able to substantiate this claim. von Braun and Ritter (5) were actually unable to hydrogenate purified carbazole in the presence of a nickel catalyst at 260°C. and 450 psig., and obtained only fair yields of 9-methyl-1,2,3,4-tetrahydrocarbazole and 1,2,3,4,5,6,7,8-octahydro-9-methylcarbazole from 9-methylcarbazole. The perhydrogenation of carbazole in an organic solvent at 160-220°C. and 590-1200 psig., using a nickel catalyst, was reported

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(4) Padoa and Chiaves, *Atti R. Accad. Lincei*, 16, 762 (1908); *Gazz. chim. ital.* 38, 236 (1903).

(5) v. Braun and Ritter, *Ber.*, 55, 3792 (1922).

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in a 1930 German patent (6). The best data were obtained by Adkins and Coonradt (7) who hydrogenated carbazole in the presence of Raney nickel at 230°C. to obtain an 87%

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(6) German pat. 514,822 (1930).

(7) Adkins and Coonradt, *J. Am. Chem. Soc.*, 63, 1563 (1941).

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yield of dodecahydrocarbazole; when they used a copper chromite catalyst under these conditions, a 72% yield of 1,2,3,4-tetrahydrocarbazole was obtained. However, this procedure required rather high pressures (of 3600-4400 psig.) and highly purified materials.

Prior work on the chemical reduction of carbazole was limited to the sodium-alcohol system. In 1907, the preparation of 1,4-dihydrocarbazole from carbazole by this reagent was reported (8). Later it was shown that the product of this reaction is a mixture containing at least 50% of carbazole, tetrahydrocarbazole, plus unknowns (9). Surprisingly, a 1950 publication again claimed the isolation of 1,4-dihydrocarbazole from this mixture (10). 1,2,3,4-Tetrahydrocarbazole can indeed be prepared in fair yield by the reduction of carbazole with sodium and alcohol (11).

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- (8) Schmidt and Schall, Ber., 40, 3225 (1907).  
(9) Barclay, Campbell, and Gow, J. Chem. Soc., 1946, 997.  
(10) Sanna, Gazz. chim. ital., 80, 572 (1950).  
(11) Zanetti, Ber., 26, 2006 (1893).
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The present paper concerns (1) a reinvestigation of the catalytic hydrogenation of carbazole, (2) a study of the chemical reduction of carbazole and derivatives with lithium metal in amine, and (3) some new N-substituted derivatives of carbazole and its hydrogenation products.

#### 1) The Hydrogenation of Carbazole

Rhodium catalysts are effective for the hydrogenation of aromatic compounds and heterocyclics like pyrrole and pyridine at room temperature and atmospheric pressure while ruthenium catalysts are useful for the reduction of aromatic compounds at elevated temperature and pressure (12). The use of these catalysts for the hydrogenation of condensed heterocyclic ring systems has apparently been little explored.

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- (12) Gilman and Cohn, in "Advances in Catalysis", IX, 733 (1957), Academic Press, Inc., New York, N. Y.
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An investigation of the hydrogenation of carbazole revealed that 5% Rh-C and 5% Ru-C were about equally effective, with reduction of the carbazole ring beginning at about 100°C. and 500 psig. of hydrogen. Purification of materials was unnecessary. The use of a 5% Pd-C catalyst under similar conditions gave only about one fourth of the rate of hydrogenation realized with the rhodium or ruthenium catalysts. The conditions for obtaining optimum yields of either tetrahydro- or dodecahydrocarbazole are summarized in Table I. Thus, in the decalin medium the reduction of carbazole with a 5% Ru-C catalyst at 250 psig. of hydrogen and 250°C., when stopped at the pressure drop calculated for tetrahydrocarbazole, gave a 53% yield of tetrahydrocarbazole plus a 15% recovery of carbazole, the remainder of the product being higher hydrogenation products. The reduction of carbazole in decalin solution at 500 psig. and 200°C. in the presence of 5% Ru-C gave an 81% yield of dodecahydrocarbazole. Surprisingly, carbazole could be reduced in water suspension (pH 5.5) at 1000 psig. (320 psig. hydrogen partial pressure) and 200°C., using a 5% Rh-C catalyst, to obtain a 93% yield of dodecahydro-

carbazole. Both U.O.P. prereduced and stabilized nickel-on-kieselguhr and sponge nickel catalysts worked equally well under these conditions, to give 88-90% yields of dodecahydrocarbazole. In all of these systems the yields of tetrahydrocarbazole were only fair when the hydrogenation of carbazole was stopped at the theoretical hydrogen uptake for tetrahydrocarbazole. When carbazole was hydrogenated in an aqueous suspension, adjusted to pH 12 with potassium hydroxide, at 1000 psig. (320 psig. hydrogen partial pressure) and 250°C., the hydrogen uptake practically stopped at the tetrahydro stage and an 87% yield of 1,2,3,4-tetrahydrocarbazole could be isolated. The same experiment carried out in a water medium adjusted to pH 10 gave only a 67% yield of tetrahydrocarbazole.

As expected, 9-alkylcarbazoles were also easily reducible. For example, 9-methylcarbazole could be hydrogenated in decalin solution at 500 psig. of hydrogen and 150-200°C., using a 5% Pd-C catalyst, to give an 88% yield of N-methyldodecahydrocarbazole.

The facile perhydrogenation of ring-substituted carbazoles was demonstrated by the example of 3-amino-9-methylcarbazole (I). The hydrogenation of 0.135 m. of this compound in water containing 0.27 m. of hydrochloric acid in the presence of 5% Rh-C catalyst at 50-100°C. and 800-350 psig. gave a 72% yield of 3-amino-9-methyldodecahydrocarbazole (II, fig. 3).

It is known that partial hydrogenation of ring-substituted carbazoles is difficult to stop at a specific stage of reduction. In addition, the ring containing the substituent and/or the unsubstituted ring may be exclusively or simultaneously hydrogenated. The only such example investigated by us was 3-amino-carbazole (III) which gave a 38% yield of unchanged starting material and an 11% yield of 3-amino-1,2,3,4-tetrahydrocarbazole (IV) as the only identified product. The latter compound is structurally similar to the indole derivative tryptamine. 3-Amino-1,2,3,4-tetrahydrocarbazole was tested for its ability to inhibit (serotonin) monoamine oxidase and found to be moderately active but not as effective as Marsilid, amphetamine hydrazine, harmine, and harmaline for this purpose\*.

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- Private communication from Dr. Bernard Witkop, Chief, Laboratory of Chemistry, National Institute of Arthritis and Metabolic Diseases.
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Tetrahydrocarbazole itself should be a versatile intermediate useful in fields such as dyes, pharmaceuticals, and plastics. For example, the monomer 9-vinyl-1,2,3,4-tetrahydrocarbazole is made in excellent yield by vinylating carbazole with acetylene (13).

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(13) W. Reppe, Ann., 601, 133 (1956).

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Dodecahydrocarbazole possesses antioxidant activity in gasoline and should have anticorrosive action. These combined properties may make dodecahydrocarbazole a useful low-cost additive to fuels and lubricants. Dodecahydrocarbazole should also be useful in dye chemistry as a component of certain dye salts.

## 2) The Reduction of Carbazole Compounds with Lithium in Amine

The chemical reduction of benzenoid rings to the tetrahydro (cyclohexene) and hexahydro (cyclohexane) stage by means of the lithium in amine reagent has been reported recently (14, 15). The reduction of carbazole compounds with this reagent was investigated (Figure 4). It was hoped that 1,4-dihydrocarbazole might be obtained by

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(14) Benkeser, Robinson, Sauve, and Thomas, J. Am. Chem. Soc., 77, 3230 (1955).

(15) Reggel, Fridel, and Wender, J. Org. Chem., 22, 891 (1957).

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1,4-addition of lithium to one of the benzenoid rings of carbazole. However, when carbazole dissolved in n-propylamine was reacted with 2 moles of lithium per mole of carbazole, a product of m.p. 137-45°C. was obtained which could not be purified by recrystallization. When 4 moles of lithium per mole of carbazole were employed for the reduction, a 90% yield of 1,2,3,4-tetrahydrocarbazole was obtained. The latter was resistant to further reduction by lithium in amine. This result was unexpected, since aromatic amines such as N-methylaniline have been readily reduced by this reagent (16).

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(16) Benkeser, Lambert, Ryan, and Stoffey, J. Am. Chem. Soc., 80, 6573 (1958).

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Presumably, tetrahydrocarbazole, which is more basic than carbazole, formed a N-lithium compound and was thus stabilized against further reduction. This presumption was strengthened by the reduction of 9-methylcarbazole to 9-methyl-1,2,3,4,10,11-cis-hexahydrocarbazole with 12 moles of lithium per mole of carbazole in n-propylamine in good yield. The intermediate 9-methyl-1,2,3,4-tetrahydrocarbazole no longer has a hydrogen atom on the nitrogen atom and was therefore reduced further. This is the first synthesis of a hexahydrocarbazole directly from carbazole. cis-Hexahydrocarbazole itself was also resistant to further reduction by lithium in amine, yielding an 82% recovery of hexahydrocarbazole.

The reduction of ring-substituted carbazoles was briefly investigated and proved to be more complex. Thus, the reduction of 3-aminocarbazole with lithium metal in ethylene diamine gave a 27% recovery of starting material as the only identified product. A similar reduction of carbazole-3-carboxylic acid gave a 24% yield of a product tentatively identified as 1,4-dihydrocarbazole-3-carboxylic acid plus a 35% yield of an unidentified nonacidic product.

## 3) Some New N-Substituted Carbazole Derivatives

The noncatalytic reaction of 2- and 4-vinylpyridines with nucleophilic reagents such as sodiomalonic ester, piperidine, diethylamine, and sodium bisulfite was first recognized by Doering and Weil (17). Subsequently, this reaction, using alkali metal or acid catalysts, was applied to aromatic amines such as N-methylaniline (18),

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(17) Doering and Weil, J. Am. Chem. Soc., 69, 2461 (1947).

(18) Reich and Levine, J. Am. Chem. Soc., 77, 4913 (1955).

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and nitrogen heterocyclics such as pyrrole (18) and indole (19). The literature mentions that diphenylamine, which is structurally similar to carbazole, could not be pyridylethylated (18).

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(18) Reich and Levine, J. Am. Chem. Soc., 77, 4913 (1955).

(19) Gray and Archer, *ibid.*, 72, 3554 (1957).

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Carbazole and the hydrocarbazoles, which had not been pyridylethylated before, have now been reacted with 2- and/or 4-vinylpyridine to give excellent to fair yields of the corresponding N-pyridylethylation products (Fig. 5 shows an example) as listed in Table II. Carbazole itself and 1,2,3,4-tetrahydrocarbazole, which are very weak bases, were reacted in pyridine solution with vinylpyridine in the presence of alkali metal catalysts. 1,2,3,4,10,11-cis-Hexahydrocarbazole and dodecahydrocarbazole, which are relatively strong bases, were pyridylethylated using acid catalysts. Pyridylethylated carbazole has fungicidal properties which will be reported in detail elsewhere.

Although dodecahydrocarbazole has been known for more than 30 years, only a few derivatives have been prepared from it. A survey of the reactions of dodecahydrocarbazole revealed that it undergoes, as expected, all the usual transformations of a secondary cycloaliphatic amine. The melting points of the solid derivatives were not too sharp which was not surprising since the dodecahydrocarbazole was a mixture of stereoisomers. The new derivatives of dodecahydrocarbazole are tabulated in Table III.

The potential uses of these derivatives lie in the areas of corrosion inhibitors, fungicides, solvents, antioxidants, plasticizers, textile chemicals, resin curing agents and catalysts, and ore flotation agents. For example, the nitrous salt of dodecahydrocarbazole was found to be a good vapor phase corrosion inhibitor; and 9-dodecoyldodecahydrocarbazole might find application as a plasticizer with mild antioxidant properties.

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#### Experimental

All melting and boiling points are uncorrected.

Dodecahydrocarbazole. - A 1-gal. stainless steel autoclave (stirring-type) was charged with 167 g. (1.0 m.) of 97% carbazole, 85 g. of a prereduced, stabilized nickel-on-kieselguhr catalyst (55% Ni), and 1000 ml. of water. The autoclave was sealed, the mixture was stirred and heated to 200°C., at which temperature the autogeneous pressure was 630 psig. The autoclave was pressured to 1000 psig with hydrogen, and repressured to 1000 psig. whenever the pressure fell to 700 psig. After 6 hrs., no further pressure drop occurred. The catalyate

was filtered. The insolubles were extracted with 500 ml. of benzene. The benzene extract was then used to extract the filtrate. The organic phase was distilled through a 4-in. Vigreux column to give 157 g. (88% yield) of dodecahydrocarbazole, b.p. 124-5°C./10 mm. (20).

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(20) Adkins and Coonradt, J. Am. Chem. Soc., 63, 1563 (1941), report b.p. 124-125°C./10 mm.

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The other perhydrogenations of carbazole were carried out similarly. The amount of catalyst used in the case of 5% rhodium-on-carbon or 5% ruthenium-on-carbon was 2-5% by wt. of the carbazole charge.

1,2,3,4-Tetrahydrocarbazole by the Hydrogenation of Carbazole. - A 1-gal. autoclave, charged with 167 g. (1.0 m.) of carbazole, 1000 ml. of water adjusted to pH 12 with dilute potassium hydroxide, and 85 g. of a prereduced nickel-on-kieselguhr catalyst, was stirred and heated to 250°C. A pressure of 680 psig. was reached. The autoclave was then pressured to 1000 psig. with hydrogen. A fast reaction ensued. The autoclave was repressured to 1000 psig. with hydrogen when the pressure fell to 800 psig. In 60 min., the hydrogen absorption had practically stopped. The mixture was allowed to cool, the autoclave was vented, and the catalyzate was filtered. The insolubles were extracted with a 500-ml. and a 200-ml. portion of benzene. The combined benzene extract was shaken with three 200-ml. portions of 30% hydrochloric acid, in which carbazole is insoluble. Dilution of the combined acid extracts with water to give a 15% hydrochloric acid concentration precipitated tetrahydrocarbazole. The precipitate was filtered off, washed with water, a little ammonia, and again with water, then dried to give 134 g. (87% yield) of 1,2,3,4-tetrahydrocarbazole, m.p. 115-8°C.; after one recrystallization from 95% ethanol, m.p. 118-9°C. (21).

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(21) Adkins and Coonradt, loc. cit., report m.p. 115-115.5°C.

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3-Amino-9-methyldodecahydrocarbazole. A 1-gal. stirring autoclave was charged with 26.0 g. (0.135 m.) of 3-amino-9-methylcarbazole, 1.0 l. of water, 23.8 g. (0.27 m.) of concentrated hydrochloric acid, and 4.0 g. of 5% Rh-C catalyst. The mixture was hydrogenated at 50-100°C. at 800-350 psig. of hydrogen pressure during 4 hrs. after which time no further pressure drop was observed. The catalyzate was filtered through a Celite filter. The clear filtrate was boiled for a short time and filtered again to remove solids which had formed. The filtrate was concentrated to 160 ml. volume, made alkaline with 28% ammonium hydroxide, and extracted with two 100-ml. portions of ether. The extract was dried over anhydrous sodium sulfate, concentrated, and the residual oil was distilled through a 4-in. Vigreux column to give 20.0 g. (72% yield) of a colorless mobile liquid, b.p. 115-25°C./3 mm. Redistillation gave a heart cut of b.p. 115-9°C./3.5 mm.

Anal. Calcd. for  $C_{13}H_{24}N_2$ : Neutral equiv., 104; N, 13.4  
Found: Neutral equiv., 108; N, 12.8

1,2,3,4-Tetrahydrocarbazole by Reduction of Carbazole with the Lithium in Amine Reagent. - To a solution of 8.35 g. (0.05 m.) of carbazole in 100 ml. of n-propylamine was added 1.46 g. (0.21 m.) of lithium ribbon in small pieces during 5 hrs. The mixture was stirred at room temperature overnight. Thereafter, 17 g. (0.32 m.) of ammonium chloride was added to the solution, the mixture was evaporated to dryness under vacuum, and the solid residue was taken up in 100 ml. of water. The resultant slurry was extracted with two 100-ml. portions of ether. The extract was washed with water and dried over anhydrous sodium sulfate. Evaporation of the ethereal filtrate to dryness gave 8.6 g. (100% yield) of solids, m.p. 115-19°C. One gram of this product was recrystallized from 5 ml. of cyclohexane to give 0.9 g. (90% yield) of tetrahydrocarbazole, m.p. 119-20°C.

A similar reduction of carbazole in ethylenediamine at 85-100° with lithium gave a 87% yield of tetrahydrocarbazole.

3-Amino-1,2,3,4-Tetrahydrocarbazole. - A solution of 36.4 g. (0.2 m.) of 3-aminocarbazole in 200 ml. (0.2 m.) of 1 N hydrochloric acid and 800 ml. of water was hydrogenated in a 1-gal. stirring autoclave in the presence of 3.0 g. of 5% Ru-C catalyst at 100°C. and 820 psig. of hydrogen for 12 hrs. The catalyze was then filtered to remove 17 g. of insolubles, i.e. a 38% recovery of 3-aminocarbazole (corrected for catalyst wt.) was made. Extraction of the insolubles with ethanol and concentration of the extract gave 3-aminocarbazole, m.p. 238-41°C. The aqueous filtrate was alkaline (pH 8) due to the formation of higher hydrogenated carbazoles. It was concentrated to 200 ml. volume, made strongly alkaline with ammonium hydroxide, and extracted with ether. The extract was evaporated to dryness to give 4.2 g. (11% yield) of solids, m.p. 116-70°C. After recrystallization from ethanol, m.p. 170-2°C. A sample was titrated in acetic acid with perchloric acid. The calculated neutralization equivalent for the title compound is based on the fact that tetrahydrocarbazole was found to be too weakly basic to be titratable.

Anal. Calcd for  $C_{12}H_{14}N_2$ : N. E. 186; Found, N. E. 184.

Since hexahydrocarbazole was titratable, the alternate structure, 3-aminohexahydrocarbazole  $C_{12}H_{16}N_2$ , would have a neutralization equivalent of 94. 6-Amino-tetrahydrocarbazole is eliminated on the basis of its m.p. 152°. The ultraviolet spectrum of the product was similar to that of tetrahydrocarbazole but different from that of hexahydrocarbazole (Table IV).

9-Methyl-1,2,3,4,10,11-cis-hexahydrocarbazole. - A solution of 9.1 g. (0.05 m.) of 9-methylcarbazole in 200 ml. of n-propylamine was treated with 4.3g. (0.62 m.) of lithium ribbon in small pieces during 5 hrs. at 25°C. After stirring for an additional 1.5 hrs., some unreacted lithium pieces were removed with forceps. Finally, 33.2 g. (0.62 m.) of ammonium chloride was added to the solution. The solvent was evaporated. The residue was taken up in water and extracted with two 100-ml. portions of ether. The extract was dried over Drierite, filtered, and the filtrate was evaporated to give 9.8 g. of residue. This crude product was distilled through a semimicro Vigreux column to give 6.5 g. (71% yield) of 9-methylhexahydrocarbazole, b.p. 125-35°C./1 mm., 98 mole % pure by nonaqueous titration with perchloric acid in acetic acid. An authentic sample of 9-methyl-1,2,3,4-tetrahydrocarbazole was too weakly basic to be titrated by this method.

Anal. Calcd. for  $C_{13}H_{17}N$ : Neutral. equiv., 187  
Found: Neutral. equiv., 190

The ultraviolet spectrum of the product was similar to that of 1,2,3,4,10,11-cis-hexahydrocarbazole itself except that the absorption maxima were shifted to slightly higher wavelengths. This corroborates the proposed structure of the product further, since a similar slight shift to higher wavelength was observed in the ultraviolet spectra of 9-methyl-1,2,3,4,-tetrahydrocarbazole vs. 1,2,3,4-tetrahydrocarbazole. The comparative spectral data are given in Table IV.

Reduction of Carbazole-3-carboxylic Acid with Lithium in Amine. -

To a solution of 3.4 g. (0.016 m.) of carbazole-3-carboxylic acid in 100 g. of ethylamine was added at 25°C. during 40 min. 0.78 g. (0.112 m.) of lithium ribbon in small pieces. After stirring for 2 additional hrs. at 25°C., 5.95 g. (0.112 m.) of ammonium chloride was added. The mixture was evaporated to dryness under vacuum. The residue was digested in water and the mixture was extracted with ether. The extract was evaporated to dryness to give 1.8 g. of a nonacidic solid. This solid was distilled through a Bantamware column to give 1.2 g. (35 wt. % yield) of low-melting yellow solids, b.p. 220-70°C. (bath)/2 mm., which were not further investigated. The alkaline aqueous solution obtained above was acidified and extracted with ether. The ether extract was evaporated to dryness to give 0.8 g. (24 wt. % yield) of solids, m.p. 215-9°C; after vacuum sublimation, m.p. 220-1°C., colorless crystals. While carbazole-3-carboxylic acid has a -CO-absorption peak at 1660  $\text{cm}^{-1}$ , the product showed -CO-absorption at 1685  $\text{cm}^{-1}$ . This indicated that the carboxyl group of the product was in conjugation with a double bond (22) and that the product was probably 1,4-dihydrocarbazole-3-carboxylic acid.

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(22) L. J. Ballamy, "The Infra-red Spectra of Complex Molecules", 2nd Ed., John Wiley & Sons, New York 1958, p. 168

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Pyridylethylation of Carbazole and 1,2,3,4-Tetrahydrocarbazole. - A stirred mixture of 167 g. (1.0 m.) of carbazole, 115 g. (1.1 m.) of 2-vinylpyridine, 2.0 g. (0.05 m.) of small pieces of metallic potassium, and 1000 ml. of pyridine was refluxed for 3 hrs., then cooled to 60°C., and stirred for 0.5 hr. with 15 ml. of absolute ethanol. The solution was concentrated to ca. 250 ml. volume and poured into 2 l. of ice-water. An oil separated which solidified quickly. The solid was filtered off, washed with water, and air-dried to give 265 g. (98% yield) of crude product, m.p. 73-5°C. After recrystallization from 95% ethanol, m.p. 77-8°C., 99 mole % pure by nonaqueous titration with perchloric acid in acetic acid (only the pyridine N is basic enough to be picked up by this method).

Anal. Calcd. for  $\text{C}_{18}\text{H}_{16}\text{N}_2$ : Neutral. equiv., 272  
Found: Neutral. equiv., 275

The infrared spectrum of the product showed no NH absorption peak, indicating the formation of a 9-substituted carbazole.

The reactions of carbazole with 4-vinyl pyridine and of 1,2,3,4-tetrahydrocarbazole with 2- and 4-vinylpyridine were carried out in similar fashion.

Pyridylethylation of 1,2,3,4,10,11-cis-Hexahydro- and Dodecahydrocarbazole. - A mixture of 17.3 g. (0.1 m.) of cis-hexahydrocarbazole, 10.5 g. (0.1 m.) of 2-vinylpyridine, 6.0 ml. (0.1 m.) of glacial acetic acid, and 50 ml. of methanol was stirred and refluxed for 8 hrs. The alcohol was then stripped off and the concentrate was poured over 500 g. of crushed ice. A sticky gum formed. The mixture was made alkaline by the addition of 100 ml. of 10% sodium hydroxide and extracted with two 250-ml. portions of ether. The combined extracts were dried over Drierite, filtered, and concentrated. The residue (27.0 g., 97% yield) was distilled through a 4-in. Vigreux column to give 22.4 g. (80% yield) of a fraction of b.p. 175-80°C./1 mm., 98 mole % pure 9-[omega-(2-pyridyl) ethyl] - 1,2,3,4,10,11-cis-hexahydrocarbazole by nonaqueous titration with perchloric acid in acetic acid (both nitrogen atoms are basic enough to be picked up by this method).

Anal. Calcd. for  $C_{19}H_{23}N_2$ : Neutral. equiv., 139.5  
Found: Neutral. equiv., 142.4

Dodecahydrocarbazole was reacted with 4-vinylpyridine in the same manner, except that no solvent methanol was used.

Table I  
Catalytic Hydrogenation of Carbazole

<u>Catalyst</u> <sup>a)</sup>	<u>Medium</u>	<u>Total Pressure (psig.)</u>	<u>Hydrogen Partial Pressure (Psig.)</u>	<u>Temp. °C.</u>	<u>Main Product</u> <sup>b)</sup>
5% Ru-C	Decalin	250	250	250	53% THC
5% Ru-C	"	500	500	200	81% DHC
5% Rh-C	Water (pH 5.5)	1000	380	200	93% DHC
U.O.P.-Ni	"	"	"	"	86% DHC
Sponge-Ni	"	"	"	"	90% DHC
U.O.P.-Ni	Water (pH 12)	"	320	250	87% THC
U.O.P.-Ni	Water (pH 10)	"	"	"	67% THC

a) Ru-C = Ruthenium on carbon; Rh-C = rhodium on carbon; Universal Oil Products Ni catalyst = Prerduced and stabilized nickel on kieselguhr (55% Ni).

b) THC = 1,2,3,4-tetrahydrocarbazole; DHC = dodecahydrocarbazole.

Table II

Pyridylethylation of Carbazole and Hydrocarbazoles

<u>Nucleophile<sup>a)</sup></u>	<u>Vinylpyridine (VP)</u>	<u>Catalyst</u>	<u>Solvent</u>	<u>% Yield of Adduct</u>	<u>Melting or Boiling Point, °C.</u>
Carbazole	2-VP	K	Pyridine	98	m. 77-8
"	4-VP	Na	"	97	m. 173-4
THC	2-VP	"	"	29	b. 194-201/3 mm.
"	4-VP	"	"	55	m. 83-4
HHC	2-VP	Acetic Acid	Methanol	80	b. 175-80/1 mm.
DHC	4-VP	"	None	65	b. 174-82/2 mm.

a) THC = 1,2,3,4-tetrahydrocarbazole; HHC = 1,2,3,4,10,11-cis-hexahydrocarbazole;  
DHC = dodecahydrocarbazole

Table III

## Derivatives of Dodecahydrocarbazole

Dodecahydrocarbazole Reacted With	Product <sup>a</sup> (% Yield)	Physical Properties
Lauroyl Chloride	9-Dodecoyl DHC (87)	pale yellow oil, b.p. 247-52°C./3 mm.
KCN	DHC-9-carboxamide (74)	colorless crystals; m.p. 167-70°C. (f. EtOH)
Urea	" (88)	m.p. 180-2°C. (f. dil. EtOH)
CS <sub>2</sub>	N,N-(Perhydro-o,o'-biphenylene) dithiocarbamate (100)	almost colorless solid; m.p. 184-91°C. (f. EtOH)
HCOOCH <sub>3</sub>	8-Formyldodecahydrocarbazole (90)	colorless liquid, b.p. 157-9°C./4 mm.
CH <sub>2</sub> = CH <sub>2</sub> CN	9-(2-Cyanoethyl) DHC (89)	colorless oil, b.p. 157-61°C./2 mm.
Cyclohexanone	9-(1-Cyclohexenyl) DHC (62)	pale yellow oil, b.p. 155-60°C./1 mm.
CH <sub>2</sub> O + alpha-methylstyrene	1-(9-dodecahydrocarbazolyl)-3-phenyl-butene-3 (12)	colorless liquid, b.p. 169-80°C./1 mm.
Succinic Anhydride	9-(3-Carboxypropionyl) DHC (68)	colorless liquid, m.p. 111-5°C.
Phthalic Anhydride	9-(2-Carboxybenzoyl) DHC (74)	colorless solid, m.p. 182-7°C.
Maleic Anhydride	9-(omega-Carboxyacrylyl) DHC (65)	colorless solid, m.p. 124-9°C.
HNO <sub>2</sub>	Nitrous salt of DHC (68)	colorless solid, m.p. 150-5°C.
CH <sub>3</sub> COOH	Acetate of DHC (96)	colorless solid, m.p. 148-53°C.
BF <sub>3</sub>	BF <sub>3</sub> Adduct of DHC (89)	colorless solid, m.p. 212-4°C.

a) DHC = dodecahydrocarbazole

Table IV  
Comparative Ultraviolet Spectral Data

<u>Compound</u>	<u><math>\lambda</math> max (EtOH)</u>	<u>log E</u>
1,2,3,4-Tetrahydrocarbazole	227.5, 283, 291	4.5, 3.9, 3.8
9-Methyl-1,2,3,4-tetrahydrocarbazole	230, 287, 293.4	4.6, 3.8, 3.8
3-Amino-1,2,3,4-tetrahydrocarbazole	225, 283	4.5, 3.8
1,2,3,4,10,11-cis-Hexahydrocarbazole	241, 292	3.9, 3.4
9-Methyl-1,2,3,4,10,11-cis-hexahydrocarbazole	244, 294-5	3.8, 3.3

Figure 1

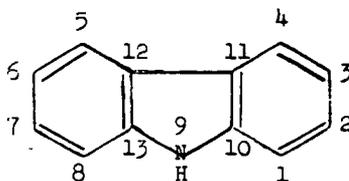


Figure 2

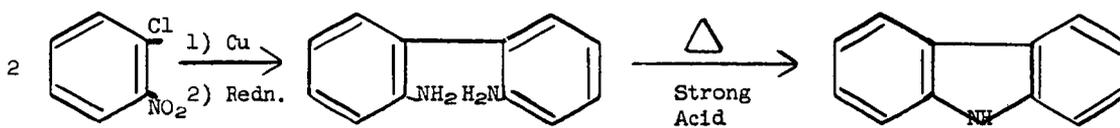


Figure 3

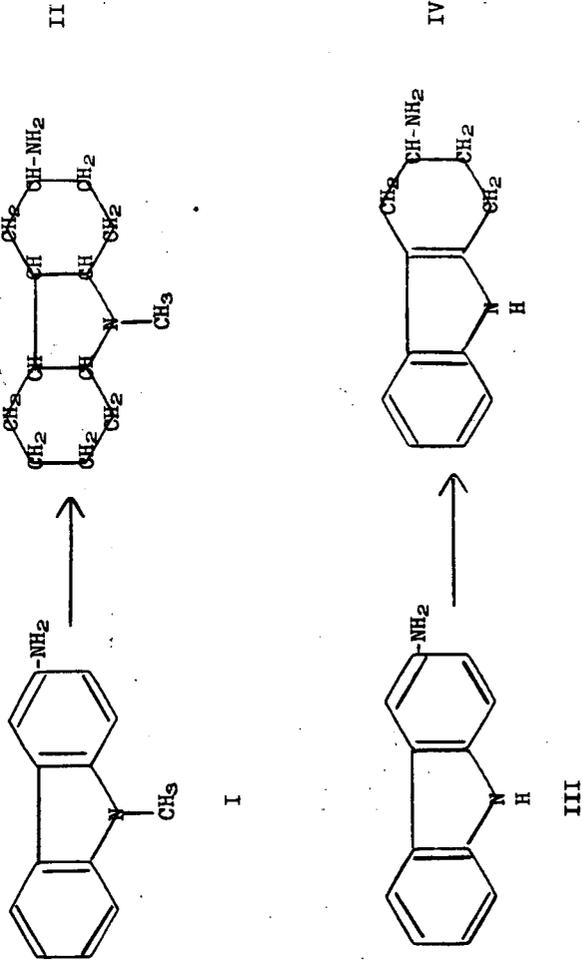


Figure 4

Lithium in Amine Reductions

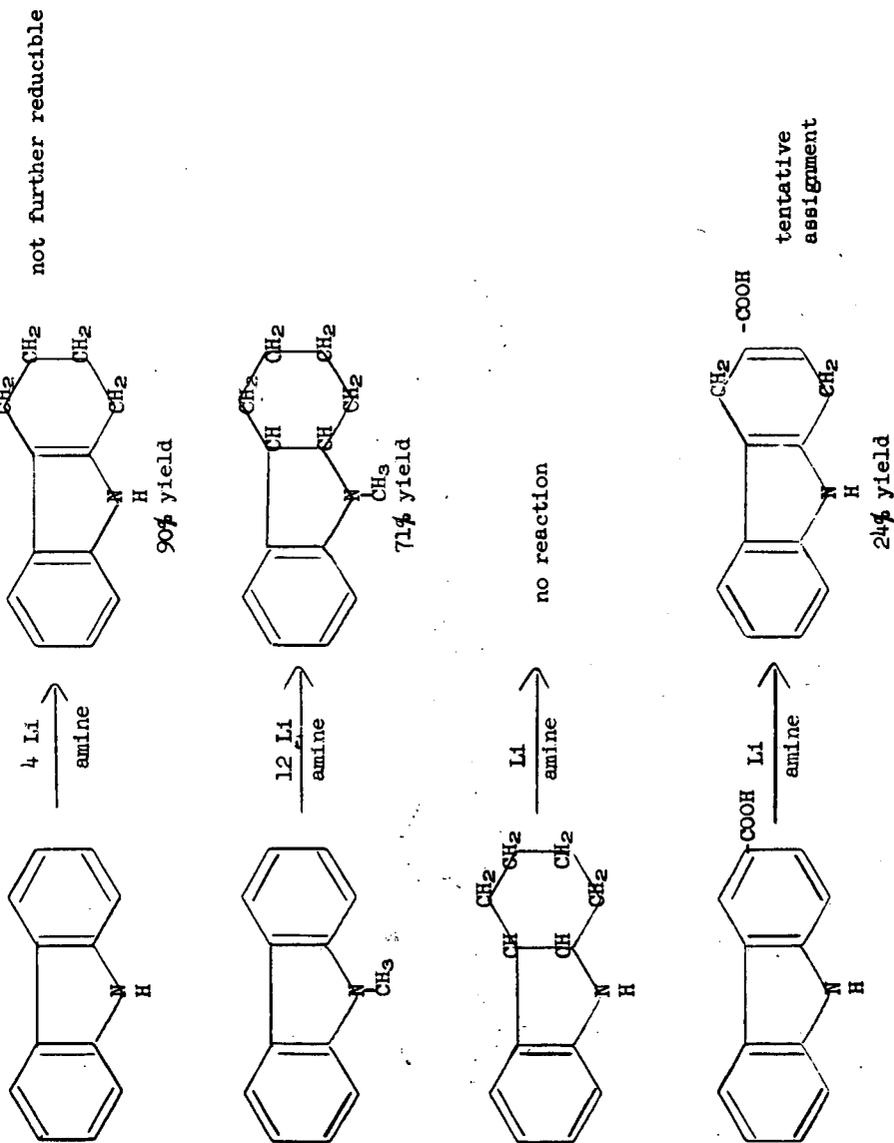


Figure 5

