mixture had refluxed for 70 hr. it was cooled, diluted with water, and extracted with ether. Recrystallization of the residue left from evaporation of the ether afforded the anthrone. The yield of anthrone from *A* was 61%; with the added material from *B* the total yield amounted to 84%.

For comparison purposes 10-hydroxy-10-phenylanthrone was prepared by oxidation of 9-phenylanthracene by the procedure of Baeyer.[11] The purified product melted at 215–216° and gave a purple color with sulfuric acid as reported.[11] Baeyer reported a m.p. of 208°; Barnett and Cook,[12] a m.p. of 214°.

The 9-phenylanthracene was obtained by heating for 70 hr. 15 g. of 3,3-diphenylnaphthalide, 2.5 g. of red phosphorus, 50 g. of hydriodic acid, and sufficient acetic acid to give a homogeneous solution. Two recrystallizations of the organic product gave 5.0 g. (37%) of 9-phenylanthracene; m.p. 152–153°; lit. m.p. 152–153°.[11] The ultraviolet spectrum showed five peaks, as reported for 9-phenylanthracene: $\lambda_{max}^{ethanol}$ 2540 (log ϵ 5.16); 3295 (3.55); 3463 (3.90); 3638 (4.11); 3825 (4.07); reported[13]: λ_{max} 2555 (5.16); 3305 (3.56); 3465 (3.90); 3645 (4.10), and 3840 (4.08). Baeyer prepared 9-phenylanthracene by reduction of 3,3-diphenylphthalide with zinc dust in acid.[11]

Oxidation of ketone IV to anthrone X. Ketone IV (0.200 g.) was heated with a solution of 0.75 g. of potassium permanganate and 1.25 g. of potassium hydroxide in 25 ml. of water for 3.5 hr. at reflux. Dilution with water, acidification, treatment with sodium bisulfite, ether extraction, and recrystallization gave 0.10 g. (50%) of 10-hydroxy-10-phenylanthrone (identified by mixture m.p. and infrared spectrum); m.p. 213–216°.

EVANSTON, ILL.

(11) A. Baeyer, *Ann.*, **202**, 58 (1880).

(12) E. B. Barnett and J. W. Cook, *J. Chem. Soc.*, **123**, 2638 (1923).

(13) E. Clar and D. G. Stewart, *J. Am. Chem. Soc.*, **74**, 6235 (1952).

[CONTRIBUTION FROM THE VERONA RESEARCH CENTER OF KOPPERS CO., INC.]

The Reduction of the Carbazole Nucleus. Some Derivatives of Hydrocarbazoles[1]

HANS DRESSLER AND MELVIN E. BAUM

Received May 16, 1960

Improved methods for the preparation of tetrahydrocarbazole and dodecahydrocarbazole in high yields by the catalytic hydrogenation of carbazole are described. 3-Amino-1,2,3,4-tetrahydrocarbazole and 3-amino-9-methyldodecahydrocarbazole were made by the hydrogenation of the appropriate aminocarbazoles. The reduction of carbazole with lithium in *n*-propylamine gave a 90% yield of 1,2,3,4-tetrahydrocarbazole. The latter was resistant to further reduction by this reagent, as was 1,2,3,4,10,11-*cis*-hexahydrocarbazole. 9-Methylcarbazole was reduced by lithium in *n*-propylamine to 9-methyl-1,2,3,4,-10,11-hexahydrocarbazole in 71% yield. A number of new derivatives of the hydrocarbazoles, such as the pyridylethylation products, are described.

In the past, the reduction of the carbazole nucleus by chemical agents or by catalytic hydrogenation has been difficult. Thus, compared with aromatic compounds and certain other nitrogen heterocyclics such as acridine, indole, and phenylpyrrole, carbazole is much more resistant to catalytic hydrogenation. The first report[2] 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[3] were actually unable to hydrogenate purified carbazole in the presence of a nickel catalyst at 260° and 450 p.s.i.g., 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° and 590–1200 p.s.i.g., using a nickel catalyst, was reported in a 1930 German patent[4] with little detail. The best data were obtained by Adkins and Coonradt[5] who hydrogenated carbazole in the presence of Raney nickel at 230° to obtain an 87% 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 p.s.i.g.) 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.[6] Later it was shown that the product of this reaction is a mixture containing at least 50% of carbazole, tetrahydrocarbazole, plus unknowns.[7] Surprisingly, a 1950 publication again claimed the isolation of 1,4-dihydrocarbazole from this mixture.[8] 1,2,3,4-Tetrahydrocarbazole can indeed be prepared in fair

(1) Based upon a paper presented at the 137th National Meeting of the American Chemical Society, Cleveland, April 1960.

(2) M. Padoa and C. Chiaves, *Atti reale accad. Lincei*, **16**, 762 (1908); *Gazz. chim. ital.*, **38**, 236 (1903).

(3) J. v. Braun and H. Ritter, *Ber.*, **55**, 3792 (1922).

(4) German pat. **514,822** (1930).

(5) H. Adkins and H. L. Coonradt, *J. Am. Chem. Soc.*, **63**, 1563 (1941).

(6) J. Schmidt and R. Schall, *Ber.*, **40**, 3225 (1907).

(7) B. M. Barclay, N. Campbell, and R. S. Gow, *J. Chem. Soc.*, 997 (1946).

(8) G. Sanna, *Gazz. chim. ital.*, **80**, 572 (1950).

TABLE I

CATALYTIC HYDROGENATION OF CARBAZOLE

Catalyst[a]	Medium	Total Pressure (p.s.i.g.)	Hydrogen Partial Pressure (p.s.i.g.)	Temp.	Main Product[b]
5% Ru-C	Decalin	250	250	250	53% THC
5% Ru-C	Decalin	500	500	200	81% DHC
5% Rh-C	Water (*p*H 5.5)	1000	380	200	93% DHC
U.O.P.-Ni[c]	Water	1000	380	200	88% DHC
Sponge-Ni	Water	1000	380	200	90% DHC
U.O.P.-Ni[d]	Water (*p*H 12)	1000	320	250	87% THC
U.O.P.-Ni	Water (*p*H 10)	1000	320	250	67% THC

[a] U.O.P.-Ni = Prereduced and stabilized nickel on kieselguhr (55% Ni). [b] THC = 1,2,3,4-tetrahydrocarbazole; DHC = dodecahydrocarbazole. [c] The hydrogenation was stopped at the theoretical pressure drop calculated for tetrahydrocarbazole. [d] The hydrogen uptake practically stopped at the tetrahydro stage. The *p*H of the aqueous medium was adjusted with potassium hydroxide.

yield by the reduction of carbazole with sodium and alcohol.[9]

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.

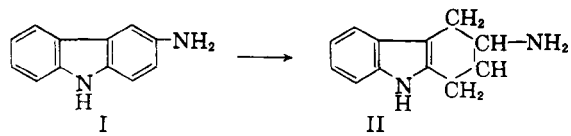
The hydrogenation of carbazole. Rhodium catalysts are effective for the hydrogenation of aromatic compounds and heterocyclics like pyrrole and pyridine at room temperature and atmospheric pressure while ruthenium catalysts are useful for the reduction of aromatic compounds at elevated temperature and pressure.[10] The use of these catalysts for the hydrogenation of condensed heterocyclic ring systems has apparently been little explored.

An investigation of the hydrogenation of carbazole revealed that 5% rhodium-carbon and 5% ruthenium-carbon were about equally effective, with reduction of the carbazole ring beginning at about 100° and 500 p.s.i.g. of hydrogen. Purification of materials was unnecessary. The use of a 5% palladium-carbon catalyst under similar conditions gave only about one fourth of the rate of hydrogenation realized with the rhodium or ruthenium catalysts. The reductions with ruthenium-carbon, rhodium-carbon, palladium-carbon, or nickel catalysts could be carried out in organic or aqueous media. The conditions for obtaining optimum yields of either tetrahydro- or dodecahydrocarbazole are summarized in Table I.

As expected, 9-alkylcarbazoles were also easily reducible. For example, 9-methylcarbazole could be hydrogenated in decalin solution at 500 p.s.i.g. of hydrogen and 150–200°, using a 5% palladium-carbon 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. The hydrogenation of 0.135 mole of this compound in water containing 0.27 mole of hydrochloric acid in the presence of 5% rhodium-carbon catalyst at 50–100° and 800–350 p.s.i.g. gave a 72% yield of 3-amino-9-methyldodecahydrocarbazole.

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-aminocarbazole (I) which gave a 38% yield of unchanged starting material and an 11% yield of the hitherto unknown 3-amino-1,2,3,4-tetrahydrocarbazole (II), identified by its neutralization equivalent and ultraviolet spectrum (Table II). Compound II is structurally similar to the biologically active indole derivative tryptamine. Tests of 3-amino-1,2,3,4-tetrahydrocarbazole for its ability to inhibit (serotonin) monoamine oxidase showed it to be moderately active but not as effective as



I II

TABLE II

COMPARATIVE ULTRAVIOLET SPECTRAL DATA

	$\lambda_{max}^{C_2H_5OH}$	log ε
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-hexahydrocarbazole	244, 294–5	3.8, 3.3

(9) C. U. Zanetti, *Ber.*, **26**, 2006 (1893).

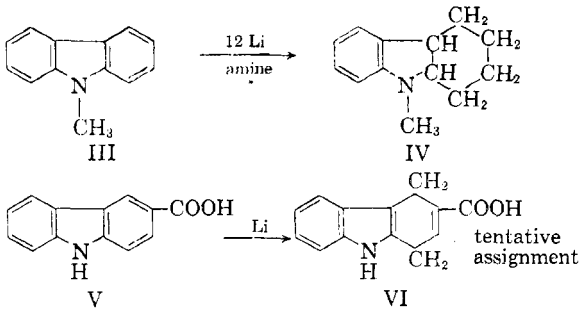
(10) G. Gilman and G. Cohn, *Advances in Catalysis*, Vol. IX, A. Farkas, ed., Academic Press, Inc., New York, N. Y., 1957, p. 733.

other compounds such as Marsilid and harmine for this purpose.[11]

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.[12,13] The reduction of carbazole compounds with this reagent was investigated. It was hoped that 1,4-dihydrocarbazole might be obtained by 1,4-addition of lithium to one of the benzenoid rings of carbazole. However, when carbazole dissolved in *n*-propylamine was treated with two moles of lithium per mole of carbazole, a product, m.p. 137–45°, was obtained which could not be purified. When four 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. *cis*-Hexahydrocarbazole was also resistant to reduction by lithium in amine yielding an 82% recovery of starting material.[14]

Surprisingly, in view of the carbazole reduction stopping at the tetrahydro stage, the reduction of 9-methylcarbazole (III) with twelve moles of lithium per mole of carbazole derivative in *n*-propylamine proceeded to give 9-methyl-1,2,3,4,10,11-hexahydrocarbazole (IV) in good yield.[15]

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 (V) gave a 24% yield of a product tentatively identified as 1,4-dihydrocarbazole-3-carboxylic acid (VI) plus a 35% yield of an unidentified nonacidic product.



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.[16] Subsequently, this reaction, using alkali metal or acid catalysts, was applied to aromatic amines such as *N*-methylaniline,[17] and nitrogen heterocyclics such as pyrrole[17] and indole.[18] The literature mentions that diphenylamine and dicyclohexylamine, which are structurally related to carbazole and dodecahydrocarbazole, respectively, could not be pyridylethylated.[17]

Carbazole and the hydrocarbazoles, which had not been pyridylethylated before, have now been allowed to react with 2- and/or 4-vinylpyridine to give excellent to fair yields of the corresponding *N*-pyridylethylation products as listed in Table III. Carbazole itself and 1,2,3,4-tetrahydrocarbazole, which are very weak bases, were allowed to react 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 thirty 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.[5] The new derivatives of dodecahydrocarbazole are tabulated in Table IV.

EXPERIMENTAL

All melting and boiling points are uncorrected.

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

(11) Private communication from Dr. Bernard Witkop, Chief, Laboratory of Chemistry, National Institute of Arthritis and Metabolic Diseases.

(12) R. A. Benkeser, R. E. Robinson, D. M. Sauve, and O. H. Thomas, *J. Am. Chem. Soc.*, **77**, 3230 (1955).

(13) L. Reggel, R. A. Friedel, and I. Wender, *J. Org. Chem.*, **22**, 891 (1957).

(14) This result was unexpected since R. A. Benkeser, R. F. Lambert, P. W. Ryan, and D. G. Stoffey, *J. Am. Chem. Soc.*, **80**, 6573 (1958), report that *N*-methylaniline is reduced by this reagent. However, R. A. Benkeser, J. J. Hazdra, R. F. Lambert, and P. W. Ryan, *J. Org. Chem.*, **24**, 854 (1959), indicate that large substituents may have an unfavorable effect on the ease of reduction.

(15) The overall results are not easily accommodated by Benkeser's proposed mechanisms (references in footnote 14). However, no definitive work has been reported on the lithium reduction of more closely related compounds such as pyrrole or indole.

(16) W. E. Doering and R. A. N. Weil, *J. Am. Chem. Soc.*, **69**, 2461 (1947).

(17) H. E. Reich and R. Levine, *J. Am. Chem. Soc.*, **77**, 4913 (1955).

(18) A. P. Gray and W. L. Archer, *J. Am. Chem. Soc.*, **79**, 3554 (1957).

TABLE III

PYRIDYLETHYLATION OF CARBAZOLE AND HYDROCARBAZOLES

Nucleophile[a]	Vinylpyridine (VP)	Catalyst	Solvent	% Yield of Adduct	M.P. or B.P.
Carbazole[b]	2-VP	K	Pyridine	98	m. 77–78
Carbazole[b]	4-VP	Na	Pyridine	97	m. 173–174
THC	2-VP	Na	Pyridine	29	b. 194–201/3 mm.
THC	4-VP	Na	Pyridine	55	m. 83–84
HHC	2-VP	Acetic acid	Methanol	80	b. 175–180/1 mm.
DHC	4-VP	Acetic acid	None	65	b. 174–182/2 mm.

[a] THC = 1,2,3,4-tetrahydrocarbazole; HHC = 1,2,3,4,10,11-*cis*-hexahydrocarbazole; DHC = dodecahydrocarbazole. [b] An alternate and unequivocal synthesis of two pyridylethylated carbazoles is described in Brit. pat. 822,592 [*Chem. Abstr.*, 54, 4628 (1960)]. The reaction of carbazole with sodium amide in xylene, followed by reaction with the appropriate haloalkylpyridine gave 9-[2-(2-pyridyl)ethyl]carbazole, m.p. 77°, and 9-[2-(4-pyridyl)ethyl]carbazole, m.p. 171–173°.

TABLE IV

DERIVATIVES OF DODECAHYDROCARBAZOLE

Dodecahydrocarbazole Treated with	Product[a] (% Yield)	Physical Properties
Lauroyl chloride	9-Dodecoyl DHC (87)	Pale yellow oil, b.p. 247–252°/3 mm.
KCNO	DHC-9-carboxamide (74)	Colorless crystals; m.p. 167–170° (benzene), 178–180° (ethanol)
Urea	DHC-9-carboxamide (88)	M.p. 180–182° (dil. ethanol)
CS_2	*N,N*-(Perhydro-*o,o'*-biphenylene) dithiocarbamate (100)	Almost colorless solid; m.p. 184–191° (ethanol)
$HCOOCH_3$	9-Formyldodecahydrocarbazole (90)	Colorless liquid, b.p. 157–159°/4 mm.
$CH_2{=}CH_2CN$	9-(2-Cyanoethyl) DHC (89)	Colorless oil, b.p. 157–161°/2 mm.
Cyclohexanone	9-(1-Cyclohexenyl) DHC (62)	Pale yellow oil, b.p. 155–160°/1 mm.
Succinic anhydride	9-(3-Carboxypropionyl) DHC (68)	Colorless solid, m.p. 111–115°
Phthalic anhydride	9-(2-Carboxybenzoyl) DHC (74)	Colorless solid, m.p. 182–187°
Maleic anhydride	9-(ω-Carboxyacrylyl) DHC (65)	Colorless solid, m.p. 124–129°
HNO_2	Nitrous salt of DHC (68)	Colorless solid, m.p. 150–155°
BF_3	BF_3 adduct of DHC (89)	Colorless solid, m.p. 212–214°

[a] DHC = dodecahydrocarbazole.

The insoluble material was 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. 124–125°/10 mm.[19]

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 mole) of carbazole, 1000 ml. of water adjusted to *p*H 12 with dilute potassium hydroxide, and 85 g. of a prereduced nickel-on-kieselguhr catalyst, was stirred and heated to 250°. A pressure of 680 p.s.i.g. was reached. The autoclave was then pressured to 1000 p.s.i.g. with hydrogen. A fast reaction ensued. The autoclave was repressured to 1000 p.s.i.g. with hydrogen when the pressure fell to 800 p.s.i.g. 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 insoluble material was 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, 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. 115–118°; after one recrystallization from 95% ethanol, m.p. 118–119°.[19]

3-Amino-9-methyldodecahydrocarbazole. A 1-gal. stirring autoclave was charged with 26.0 g. (0.135 mole) of 3-amino-9-methylcarbazole, 1.0 l. of water, 23.8 g. (0.27 mole) of concd. hydrochloric acid, and 4.0 g. of 5% rhodium-on-carbon catalyst. The mixture was hydrogenated at 50–100° and 800–350 p.s.i.g. of hydrogen pressure during 4 hr. 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. 115–125°/3 mm. Redistillation gave a center cut of b.p. 115–119°/3.5 mm.

Anal. Calcd. for $C_{13}H_{24}N_2$: Neut. equiv., 104; N, 13.4. Found: Neut. 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 mole) of carbazole in 100 ml. of *n*-propylamine was added 1.46 g. (0.21 mole) of lithium ribbon in small pieces during 5 hr. The mixture was stirred at room temperature overnight. Thereafter, 17 g. (0.32 mole) 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

(19) Adkins and Coonradt, *J. Am. Chem. Soc.*, 63, 1563 (1941), reported b.p. 124–125°/10 mm. for dodecahydrocarbazole and m.p. 115–115.5° for 1,2,3,4-tetrahydrocarbazole.

water and dried over anhydrous sodium sulfate. Evaporation of the ethereal filtrate to dryness gave 8.6 g. (100% yield) of solids, m.p. 115–119°. One gram of this product was recrystallized from 5 ml. of cyclohexane to give 0.9 g. (90% yield) of tetrahydrocarbazole, m.p. 119–120°.

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 mole) of 3-aminocarbazole in 200 ml. (0.2 mole) 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% ruthenium-on-carbon catalyst at 100° and 820 p.s.i.g. of hydrogen for 12 hr. The catalyzate was then filtered to remove 17 g. of insoluble material, *i.e.* a 38% recovery of 3-aminocarbazole (corrected for catalyst weight). Extraction of the insoluble material with ethanol and concentration of the extract gave 3-aminocarbazole, m.p. 238–241°. The aqueous filtrate was alkaline (*p*H 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. 116–170°. After recrystallization from ethanol, m.p. 170–172°. 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 $C_{12}H_{14}N_2$: Neut. equiv. 186. Found: Neut. equiv. 184.

Since hexahydrocarbazole was titratable, the alternate structure, 3-aminohexahydrocarbazole $\cdot C_{12}H_{16}N_2$, would have a neutralization equivalent of 94. 6-Aminotetrahydrocarbazole 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 II).

9-Methyl-1,2,3,4,10,11-hexahydrocarbazole. A solution of 9.1 g. (0.05 mole) of 9-methylcarbazole in 200 ml. of *n*-propylamine was treated with 4.3 g. (0.62 g.-atom) of lithium ribbon in small pieces during 5 hr. at 25°. After stirring for an additional 1.5 hr., some unchanged lithium pieces were removed with forceps. Finally, 33.2 g. (0.62 mole) 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. 125 135°/1 mm., analyzed 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 $C_{13}H_{17}N$: Neut. equiv., 187. Found: Neut. 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 wave lengths (Table II). The crystalline picrate reported for 9-methyl-1,2,3,4-cis-hexahydrocarbazole[8] could not be obtained from our product. The neutralization equivalent, ultraviolet spectrum, and the formulation of a noncrystalline picrate indicate that our product was a mixture of *cis*- and *trans*-hexahydrocarbazole isomers.

Reduction of carbazole-3-carboxylic acid with lithium in amine. To a solution of 3.4 g. (0.016 mole) of carbazole-3-carboxylic acid in 100 g. of ethylamine was added at 25° during 40 min. 0.78 g. (0.112 g.-atom) of lithium ribbon in small pieces. After stirring for 2 additional hr. at 25°, 5.95 g. (0.112 mole) 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. 220–270° (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 solid, m.p. 215–219°; after vacuum sublimation, m.p. 220–221°, colorless crystals. While carbazole-3-carboxylic acid has a —CO absorption peak at 1660 cm.$^{-1}$, the product showed —CO absorption at 1685 cm.$^{-1}$ This indicated that the carboxyl group of the product was in conjugation with a double bond[20] and that the product was probably 1,4-dihydrocarbazole-3-carboxylic acid.

Pyridylethylation of carbazole and 1,2,3,4-tetrahydrocarbazole. A stirred mixture of 167 g. (1.0 mole) of carbazole, 115 g. (1.1 moles) of 2-vinylpyridine, 2.0 g. (0.05 g.-atom) of small pieces of metallic potassium, and 1000 ml. of pyridine was refluxed for 3 hr., then cooled to 60°, 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, washed with water, and air-dried to give 265 g. (98% yield) of crude product, m.p. 73–75°. After recrystallization from 95% ethanol, 9-[2-(2-pyridyl)-ethyl]carbazole, m.p. 77–78°, was obtained; it was analyzed by nonaqueous titration with perchloric acid in acetic acid (only the pyridine nitrogen is basic enough to be picked up by this method).

Anal. Calcd. for $C_{19}H_{16}N_2$: Neut. equiv., 272. Found: Neut. 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 mole) of *cis*-hexahydrocarbazole,[21] 10.5 g. (0.1 mole) of 2-vinylpyridine, 6.0 ml. (0.1 mole) of glacial acetic acid, and 50 ml. of methanol was stirred and refluxed for 8 hr. The alcohol was then stripped 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, b.p. 175–180°/1 mm., 9-[2-(2-pyridyl)ethyl]-1,2,3,4,10,11-*cis*-hexahydrocarbazole; it was analyzed by nonaqueous titration with perchloric acid in acetic acid (both nitrogen atoms are sufficiently basic to be picked up by this method).

Anal. Calcd. for $C_{19}H_{22}N_2$: Neut. equiv., 139.5. Found: Neut. equiv., 142.4.

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

9-Dodecoyldodecahydrocarbazole. A mixture of 251 g. (1.4 moles) of dodecahydrocarbazole, 1600 ml. of xylene, and 154 g. (0.7 moles) of lauroyl chloride was stirred and refluxed for 4 hr. After cooling to 25°, the mixture was filtered. The solid was washed with 300 ml. of xylene and dried to give 99.2 g. (69% yield) of dodecahydrocarbazole hydrochloride. The filtrate was concentrated to 1 l. volume, cooled to 20°, and filtered to give an additional 55.5 g. (39% yield) of crude dodecahydrocarbazole hydrochloride.

(20) L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, 2nd ed., John Wiley & Sons, New York, 1958, p. 168.

(21) J. Gurney, W. H. Perkin, and S. G. P. Plant, *J. Chem. Soc.*, 2678 (1927).

The filtrate was stripped of xylene and the residue was distilled through a 4-in. Vigreux column to give 220 g. (87% yield) of a pale yellow oil, b.p. 247–252°/3 mm.

Anal. Calcd. for $C_{24}H_{43}NO$: N, 3.88. Found: N, 3.84.

Dodecahydrocarbazole-9-carboxamide. The hydrochloride of dodecahydrocarbazole was formed by adding 25 ml. of 2*N* hydrochloric acid (0.05 mole) to 9.0 g. (0.05 mole) of dodecahydrocarbazole. The mixture was cooled to 25° and mixed with 4.1 g. (0.05 mole) of potassium cyanate. After standing for 2 hr. with occasional stirring, the oil which had formed initially solidified. The crystals were filtered, washed with 50 ml. of water and 25 ml. of ether, then dried to give 8.1 g. (74% yield) of crude product, m.p. 144–147°. Crystallization from benzene raised the m.p. to 167–170°, while crystallization from dilute ethanol gave a product, m.p. 178–180°. The product, m.p. 167–170° (from benzene) was analyzed by nitrogen analysis.

Anal. Calcd. for $C_{13}H_{22}N_2O$: N, 12.6. Found: N, 12.2.

As an alternate preparation, a melt of 18 g. (0.1 mole) of dodecahydrocarbazole and 12.0 g. (0.2 mole) of urea was stirred at 160° for 5 hr. (ammonia was evolved). The mix was then poured onto 100 g. of crushed ice, filtered, and the solid was washed with water to remove excess urea. The gummy insoluble material was ground under ether and filtered to give 19.6 g. (88% yield) of the crude *N*-carboxamide of dodecahydrocarbazole, m.p. 134–136°; after three recrystallizations from aqueous ethanol it melted at 180–182°. Mixture melting point with the corresponding products from the reaction of dodecahydrocarbazole with potassium cyanate was undepressed.

N,N-(Perhydro-o,o'-biphenylene)dithiocarbamate. Into a solution of 8.95 g. (0.05 mole) of dodecahydrocarbazole in 20 ml. of ether was stirred a solution of 3.8 g. (0.05 mole) of carbon disulfide in 10 ml. of ether at 20°. The solvent was evaporated to leave a pale yellow residue, 11.0 g. (102% yield) of crude dithiocarbamate of dodecahydrocarbazole, m.p. 180–190°; after recrystallization from 95% ethanol, m.p. 184–191°.

Anal. Calcd. for $C_{26}H_{42}N_2S_2$: N, 6.45; S, 14.75. Found: N, 6.20; S, 13.6.

9-Formyldodecahydrocarbazole. A mixture of 36 g. (0.20 mole) of dodecahydrocarbazole and 15 g. (0.25 mole) of methyl formate was refluxed on the steam bath for 1 hr. The methanol and the excess methyl formate were then distilled to give 46 g. of a clear yellow residue. This concentrate was distilled through a 4-in. Vigreux column to give 37.3 g. (90% yield) of crude product, b.p. 112–142°/2 mm. Redistillation of this fraction gave 21.8 g. (53% yield) of a center cut, b.p. 157–159°/4 mm.

Anal. Calcd. for $C_{13}H_{21}NO$: N, 6.77. Found: N, 6.51.

9-(2-Cyanoethyl)dodecahydrocarbazole. A mixture of 270 g. (1.5 moles) of dodecahydrocarbazole, 89 g. (1.7 moles) of acrylonitrile, and 8.0 ml. (0.13 mole) of glacial acetic acid was stirred and refluxed for 6 hr. The product was then distilled through a 4-in. Vigreux column to give 310 g. (89% yield) of a colorless oil, b.p. 157–161°/2 mm.

Anal. Calcd. for $C_{15}H_{24}N_2$: Neut. equiv., 232. Found: Neut. equiv., 243.

9-(1-Cyclohexenyl)dodecahydrocarbazole. A mixture of 17.1 g. (0.1 mole) of dodecahydrocarbazole, 9.8 g. (0.1 mole) of cyclohexanone, and 50 ml. of benzene was refluxed for 6 hr. During this time, 1.25 ml. (70%) of water was removed *via* a Dean-Stark trap. The mixture was then concentrated to remove the benzene and the residue was distilled through a 4-in. Vigreux column to give 16 g. (62% yield) of a pale yellow mobile oil, b.p. 155–160°/1 mm.

Anal. Calcd. for $C_{18}H_{29}N$: Neut. equiv., 259.5; N, 5.40. Found: Neut. equiv., 260; N, 5.25.

Reaction of dodecahydrocarbazole with acid anhydrides. A solution of 18 g. (0.1 mole) of dodecahydrocarbazole, 10 g. (0.1 mole) of succinic anhydride, and 25 ml. of ethyl acetate was refluxed for 1 hr., then kept at 5° overnight. The product was filtered to give 19 g. (68% yield) of colorless crystals, m.p. 109–114°. After recrystallization from ethyl acetate, it melted at 111–115°.

Anal. Calcd. for $C_{16}H_{25}NO_3$: Neut. equiv., 279. Found: Neut. equiv., 271.

A similar reaction of dodecahydrocarbazole with an equimolar amount of phthalic anhydride gave a 74% yield of crude 9-(2-carboxybenzoyl)dodecahydrocarbazole, m.p. 182–187°; after recrystallization from 50% aqueous ethanol, it melted at 207–209°.

Anal. Calcd. for $C_{20}H_{25}NO_3$: Neut. equiv., 327. Found: Neut. equiv., 337.

Similarly, the reaction of equimolar quantities of dodecahydrocarbazole and maleic anhydride gave a 50% yield of crude 9-(ω-carboxyacrylyl)dodecahydrocarbazole, m.p. 122–126°; after recrystallization from ethyl acetate it melted at 124–129°.

Anal. Calcd. for $C_{16}H_{23}NO_3$: Neut. equiv., 277. Found: Neut. equiv., 270.

The product showed a strong absorption band at 6.15 μ believed to be due to a conjugated *cis* CH=CH group. Apparently, no isomerization took place during the reaction.

Nitrous salt of dodecahydrocarbazole. A solution of 18 g. (0.1 mole) of dodecahydrocarbazole in 400 ml. of water and 20 ml. (0.25 mole) of concd. hydrochloric acid was neutralized with ammonium hydroxide to *p*H 8.0. To this solution was added 69 g. (1.0 mole) of sodium nitrate, the mixture was heated to 60°, filtered, and the filtrate was cooled to 5–10° for 1 hr. After filtration, there were obtained 11.3 g. (50% yield) of a colorless solid, m.p. 150–155° dec.; after recrystallization from *n*-butyl alcohol it melted at 157–158° dec. The product was characterized by nitrogen analysis and by titration for nitrite with an excess of a standard permanganate solution, followed by back titration with standard ferrous ammonium sulfate.

Anal. Calcd. for $C_{12}H_{22}N_2O_2$: N, 12.38; HNO_2, 8.87 meq./g. Found: N, 12.08; HNO_2, 9.04 meq./g.

To the final filtrate was added another 69 g. (1.0 mole) of sodium nitrite and the mixture was stirred for 1 hr., then filtered to give an additional 4.0 g. (18% yield) of product, m.p. 145–155° dec.

Boron trifluoride adduct of dodecahydrocarbazole. To a stirred solution of 10 g. (0.056 mole) of dodecahydrocarbazole in 50 ml. of ether was added dropwise 10 ml. of boron trifluoride etherate during 15 min. The exothermic reaction brought the ether to boil and a solid precipitated. The mixture was cooled to 5° and filtered. After washing the solid with 50 ml. of ether there were obtained 12.2 g. (89% yield) of a colorless material, m.p. 212–214°.

Anal. Calcd. for $C_{12}H_{21}BF_3N$: N, 5.67. Found: N, 5.15.

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