The reaction mixture was cooled under nitrogen, filtered, and the filter cake washed with three 10-ml. portions of Cellosolve. To the combined filtrate and washings were added 2.33 g. (0.025 mole) of aniline and 12.0 g. (0.125 mole) of anhydrous magnesium chloride, washed into the flask with 15 ml. of Cellosolve. After heating under reflux in an atmosphere of nitrogen for 4 hr. the solution was cooled and allowed to run slowly into a stirred mixture of 100 ml. of concd. hydrochloric acid and 250 g. of cracked ice. After standing overnight, the mixture was filtered and washed with dilute hydrochloric acid, water, and twice with 50% aqueous ethanol. After drying in a vacuum desiccator, the crude *tetrahydrocarbazole* weighed 7.29 g. (85%) and melted at 110–116°.

Dehydrogenation of 2.50 g. of this material in the usual manner gave 2.12 g. (74%, based on 2-chlorocyclohexanone) of XXVII, white plates, m.p. 244–246.5°.

By a similar procedure *1-methylcarbazole* was obtained in 83% yield (crude product, m.p. 118–121°; the yield of purified XXVIII, m.p. 120–121°, was 65%) and *3,4-benzocarbazole* in 40% yield (m.p. 133–134.5°), based on 2-chlorocyclohexanone.

BLOOMINGTON, IND.

[CONTRIBUTION NO. 873 FROM THE CHEMISTRY LABORATORY OF INDIANA UNIVERSITY]

Syntheses of Some Methyl Substituted 3,4-Benzocarbazoles[1,2]

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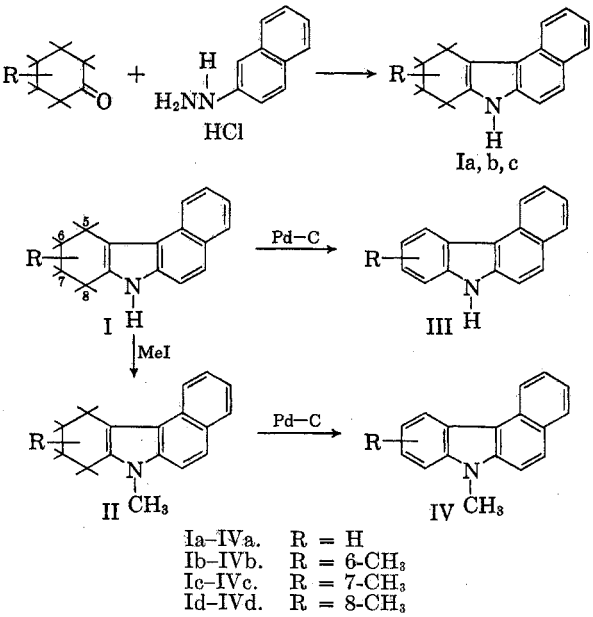
A series of methyl and dimethyl 3,4-benzocarbazoles were prepared by dehydrogenation of the respective 5,6,7,8-tetrahydro-3,4-benzocarbazoles. The latter compounds were obtained by a modified Fischer-Borsche reaction. The product of the reaction of 3-methylcyclohexanone and β-naphthylhydrazine was proved to be 7-methyl-5,6,7,8-tetrahydro-3,4-benzocarbazole, rather than the alternate possible 5-methyl isomer.

The fact that the dibenzocarbazoles are carcinogenic[6–8] has stimulated interest in the synthetic[9,10] and theoretical[11] study of carbazoles. It is known that the tumor producing activity of 1,2,5,6-dibenzanthracene is inhibited by 1,2,5,6-dibenzocarbazole.[12] Partially hydrogenated carbazoles are also of interest because of potential anticarcinogenic activity.[13]

Accordingly, we have undertaken the synthesis of a series of methyl substituted 3,4-benzocarbazoles and 5,6,7,8-tetrahydro-3,4,benzocarbazoles, for use in biological experiments. (Table I). As a result, an extremely convenient technique, involving a modified Fisher-Borsche synthesis,[14] has been developed for the preparation of 5,6,7,8-



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(2) Taken in part from the thesis of R. D. Lake, presented in partial fulfillment of the requirements for the degree Doctor of Philosophy at Indiana University, September, 1956.

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TABLE I

BENZOCARBAZOLE DERIVATIVES

A. 5,6,7,8-TETRAHYDRO-3,4-BENZOCARBAZOLES

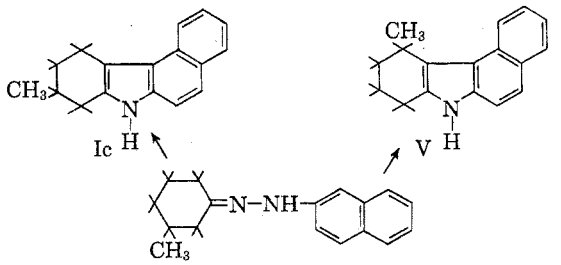
No.	Substituents	Yield, %	M.P.[a] °C	Empirical Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found
Ia	None	75	136–137[b]	$C_{16}H_{15}N$	86.84	86.22	6.83	6.79	6.33	6.29
Ib	6-methyl	60	129–130[c]	$C_{17}H_{17}N$	86.76	86.67	7.28	7.18	5.95	5.90
Ic	7-methyl	20	137–138	$C_{17}H_{17}N$	86.76	86.55	7.28	7.28	5.95	5.89
Id	8-methyl	17	114–115[d]	$C_{17}H_{17}N$	86.76	86.57	7.28	7.18	5.95	6.29
IIa	9-methyl	68	107–108	$C_{17}H_{17}N$	86.76	87.45	7.28	7.34	5.95	5.95
IIb	6,9-dimethyl	73	102–103	$C_{18}H_{19}N$	86.70	86.41	7.68	7.53	5.62	5.50
IIc	7,9-dimethyl	83	114–115	$C_{18}H_{19}N$	86.70	86.46	7.68	7.55	5.62	5.73
IId	8,9-dimethyl	78	95–97	$C_{18}H_{19}N$	86.70	86.48	7.68	7.64	5.62	5.75
				B. 3,4-BENZOCARBAZOLES						
IIIa	None	73	135–136[b]	$C_{16}H_{11}N$	88.45	88.24	5.10	5.09	6.45	6.39
IIIb	6-methyl	93	181–182[c]	$C_{17}H_{13}N$	88.28	88.26	5.66	5.65	6.06	6.00
IIIc	7-methyl	68	139–140	$C_{17}H_{13}N$	88.28	88.15	5.66	5.72	6.06	6.00
IIId	8-methyl	88	146–147[d]	$C_{17}H_{13}N$	88.28	88.27	5.66	5.51	6.06	6.04
IVa	9-methyl	80	118–119[e]	$C_{17}H_{13}N$	88.28	88.63	5.66	5.79	6.06	6.09
IVb	6,9-dimethyl	70	158–159	$C_{18}H_{15}N$	88.13	87.65	6.16	6.05	5.71	5.68
IVc	7,9-dimethyl	60	133–134	$C_{18}H_{15}N$	88.13	88.15	6.16	6.39	5.71	5.76
IVd	8,9-dimethyl	55	164–165	$C_{18}H_{15}N$	88.13	87.99	6.16	6.19	5.71	5.78

[a] Melting points are uncorrected. [b] S. H. Oakeshott and S. G. P. Plant, *J. Chem. Soc.*, 1840 (1928). [c] Ng. Ph. Buu-Hoï, Ng. Hoan, and Ng. H. Khoi, *Rec. trav. chim.*, 69, 1053 (1950). [d] S. A. Bryant and S. G. P. Plant, *J. Chem. Soc.*, 93 (1931). [e] F. R. Japp and W. Maitland, *Proc. Chem. Soc.*, 174 (1901).

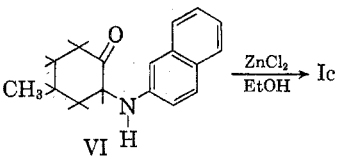
tetrahydro-3,4-benzocarbazole (Ia) and its 6- and 7-methyl derivatives (Ib, Ic). The method failed for 8-methyl-5,6,7,8-tetrahydro-3,4-benzocarbazole (Id), however, apparently due to steric hindrance.

The 5,6,7,8-tetrahydro-3,4-benzocarbazoles (I) were readily methylated by treatment with methyl iodide in the presence of alkali,[9,15] and were dehydrogenated to the corresponding carbazoles (III, IV) with palladium on carbon, a procedure found more convenient than the chloranil method.[16]

The Fischer-Borsche reaction of 3-methylcyclohexanone and β-naphthylhydrazine hydrochloride could produce either or both of the two isomers, 5- or 7-methyl-5,6,7,8-tetrahydro-3,4-benzocarbazole, V or Ic. When these compounds were reacted



as described in the experimental part, an 83% yield of crude product was obtained, which after several recrystallizations from methanol gave only one substance melting sharply at 138°. This product was unequivocally proved to be Ic by its independent synthesis *via* cyclization of 4-methyl-2-β-naphthylaminocyclohexanone (VI).



Although ring-closures of aminoketones may lead to rearrangements,[17] in this case the possible isomer would be 6 methyl-5,6,7,8-tetrahydro-3,4-benzocarbazole (Ib) previously prepared and melting at 129–130°. No rearrangement occurred on ring closure of VI, since a product melting at 137–138° was obtained, identical to the Fischer-Borsche product Ic. Each of these products was independently dehydrogenated to the same sharp-melting 7-methyl-3,4-benzocarbazole, IIIc.

EXPERIMENTAL[18]

5,6,7,8-Tetrahydro-3,4-benzocarbazole (Ia). Five g. (0.026 mole) of β-naphthylhydrazine hydrochloride were suspended in 60 ml. of methanol and 20 ml. of water added. The mixture was stirred for about 5 min. to achieve maximum solution and 2.85 g. (0.028 mole) of cyclohexanone added. Vigorous stirring was continued for about 1 hr. at room temperature and then the mixture was cooled in an ice bath and filtered. The crude yield of tetrahydrobenzocarbazole was 5.2 g. (90%). After decolorizing with Norit, and recrystallizing from methanol, colorless needles of 5,6,7,-8-tetrahydro-3,4-benzocarbazole, melting at 136–137°, were obtained.

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(17) E. Campaigne and R. D. Lake, *J. Org. Chem.* **24**, 478 (1959).

(18) Melting points are uncorrected. Microanalyses by Miss J. Dickey.

6-, 7- and 8-Methyl-5,6,7,8-tetrahydro-3,4-benzocarbazoles (Ib, Ic, Id). The 6- and 7-methyl derivatives were prepared from 4-methyl- and 3-methylcyclohexanone respectively, as described above for Ia. The 8-methyl isomer (Id) was synthesized by the method of Bryant and Plant.[19]

Proof of structure of Ic. *4-Methyl-2-(2-naphthylamino)-cyclohexanone.* (VI). A mixture of 14.8 g. (0.100 mole) of 2-chloro-4-methylcyclohexanone,[17] 14.4 g. (0.100 mole) of 2-naphthylamine, 2.6 g. (0.020 mole) of quinoline, 20 g. of anhydrous sodium carbonate and 75 ml. of cellosolve were heated and stirred under reflux for 1 hr. The cooled reaction mixture was filtered and the solid material washed with a little methanol. Solvent was removed at reduced pressure and the residual slurry diluted with an equal volume of methanol and allowed to stand overnight. Filtration and washing with cold methanol provided 8.8 g. (35%) of 4-methyl-2-(2-naphthylamino)cyclohexanone, m.p. 116–117°. Crystallization from cyclohexane gave colorless crystals of unchanged melting point.

Anal. Calcd. for $C_{17}H_{19}NO$: C, 80.59; H, 7.56; N, 5.53. Found: C, 80.75; H, 7.54; N, 5.65.

7-Methyl-5,6,7,8-tetrahydro-3,4-benzocarbazole (Ic). A solution of 5.00 g. (0.0198 mole) of 4-methyl-2-(2-naphthylamino)cyclohexanone in 100 ml. of 20% absolute ethanolic zinc chloride was refluxed for 18 hr. under nitrogen. The cooled, deep red solution was poured into a mechanically stirred mixture of 150 ml. of concentrated hydrochloric acid and 350 ml. of ice. Filtration, washing with dilute hydrochloric acid and water and drying *in vacuo* gave 4.56 g. of crude product, m.p. 128–135°. Decolorization with Norit and crystallization from ethanol provided 3.51 g. (76%) of colorless needles, m.p. 136.5–138°. A second crystallization raised the melting point to 137–138°. A mixed melting point with a sample prepared as described above showed no depression and the infrared spectra were identical.

The *9-methyl derivatives* (IIa–IId) were prepared by methylation of Ia–Id with methyl iodide in acetone in the presence of concentrated alkali.[9]

Dehydrogenation was carried out as follows: The tetrahydro compound (2 g.), 30% palladium on carbon (0.8 g.) and 25 ml. of xylene were heated at vigorous reflux for 8 to 48 hr. The cooled reaction mixture (diluted with ethyl acetate, when necessary to dissolve precipitated product) was then filtered and evaporated to a thick slurry by heating on the steam bath in a stream of air. The slurry was diluted with hexane, filtered, and crystallized from methanol.

8,9-Dimethyl-3,4-benzocarbazole (IVd) was obtained in impure form by the above treatment. A second dehydrogenation, using *p*-cymene as solvent, followed by crystallization from an ethanol-ethyl acetate mixture gave pure IVd.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF BUFFALO]

Studies in Organosilicon Chemistry. XXXV. Preparation of Certain Olefinic and Alkylsilanes

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Several olefinic silanes have been prepared from appropriate Grignard reagents and their infrared spectra are recorded. Hexamethylbis(1,5-chloromethyl)trisiloxane and dimethylallylethoxysilane have also been prepared.

By the action of allylmagnesium bromide on the appropriate chlorosilane, dimethyldiallylsilane, methylphenyldiallylsilane, and diphenyldiallylsilane have been prepared. Similarly, from β methallylmagnesium chloride, dimethylbis(β-methallyl)-silane, methylphenylbis(β-methallyl)silane, and diphenylbis(β-methallyl)silane have been prepared. Cohydrolysis of one molar part of dimethyldichlorosilane and two of dimethylchloromethylchlorosilane yielded hexamethylbis(1,5-chloromethyl)trisiloxane. Dimethylallylethoxysilane has been prepared by the action of allylmagnesium bromide on dimethyldiethoxysilane. Infrared absorption curves are presented for the first three compounds above.

Discussion. The compounds herein described were needed for the carrying out of certain experiments in the formation of polymeric silicon compounds containing sulfur and reported elsewhere in this journal.[1] In general, the principles involved are not novel, but certain modifications in procedure have been developed which are deemed of value. These modifications are based on procedures already in the literature.[2–9] Two compounds are

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