

POTENTIAL NITROGEN-HETEROCYCLE CARCINOGENS. VI. POLY-
SUBSTITUTED 1,2-BENZOCARBAZOLES, 1,2,5,6- AND 1,2,7,8-
DIBENZOCARBAZOLES¹

NG. PH. BUU-HOÏ, PAUL CAGNIANT, NG. HOÁN, AND NG. H. KHÔI

Received December 7, 1949

In continuation of the investigation which is being carried out in this Institute under Professor A. Lacassagne upon the relationship between chemical constitution and carcinogenicity in the carbazole series (1), the synthesis of a number of polysubstituted 1,2-benzocarbazoles, 1,2,5,6- and 1,2,7,8-dibenzocarbazoles is now reported. The method of preparation used throughout this work was the one already outlined in previous paper: cyclization of arylhydrazones of properly substituted 1-tetralones to polycyclic 3,4-dihydrocarbazoles, and dehydrogenation of the latter by chloranil; the introduction of methyl groups in position 9 was easily achieved by treatment with methyl sulfate of the organomagnesium compound corresponding to the non-methylated carbazole involved.

The substituted 1-tetralones used in this work were: 6,7-dimethyl-(I), 5,7-dimethyl- (II), 7-methoxy-(III), 6-methyl-7-methoxy-(IV), 8-methyl-5-methoxy- (V), and 6,7-dimethoxy-1-tetralone (VI). They were prepared from the appropriate hydrocarbons or phenol ethers by the routine succinic anhydride method (2). Among them, the ketones (IV) and (V) were unknown; the preparation of those already described has in some instances been greatly improved, and the many new substances prepared in connection with this are reported in the experimental part. The arylhydrazines used were: phenylhydrazine, *p*-tolylhydrazine, *p*-xylylhydrazine, *p*-chloro- and *p*-bromo-phenylhydrazine, and α - and β -naphthylhydrazine.

Among the substituents dealt with, methyl groups are known in the parent series (*viz.* 1,2-benzanthracene, 1,2- and 3,4-benzacridine, etc.) to enhance generally the carcinogenicity of the basic molecules (3); the influence of methoxyl groups is less known, but in a few definite instances they have been found to enhance the action (4), as has chlorine (5), whereas the effect of bromine has been to decrease carcinogenicity.

The new carbazoles reported are listed in the chart given below; they are at present under biological examination by Professor Lacassagne and Dr. Zajdela.

Acknowledgement. This work was carried out under a grant from the U. S. Public Health Service (Federal Security Agency); the authors wish to express their gratitude to the authorities concerned.

EXPERIMENTAL²

I. PREPARATION OF INTERMEDIATES

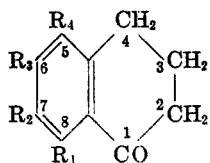
Friedel-Crafts reaction of succinic anhydride with hydrocarbons and phenol ethers. In all the cases considered here, the best yields of β -aroylpropionic acids (up to 95%) were ob-

¹ Paper V in this series: Buu-Hoï, Hoán, Khôi, and Xuong, *J. Org. Chem.*, **15**, 511 (1950).

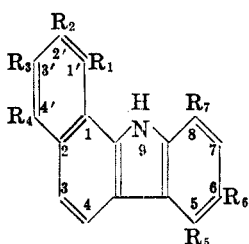
² All melting points are uncorrected and were taken with a Maquenne block.

tained when the reaction was performed in redistilled tetrachloroethane (b.p. 144-145°), the aluminum chloride (1.3 moles) being added in small portions to the ice-cooled and well-stirred solution of succinic anhydride (1 mole), the hydrocarbon or the phenol ether (1.5 to 2 moles), and the solvent. The mixture was kept at room temperature for 24 to 48 hours with occasional shaking, then poured into ice, the solvent and the hydrocarbon or the phenol

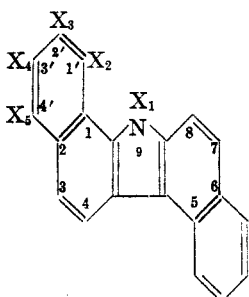
CHART I



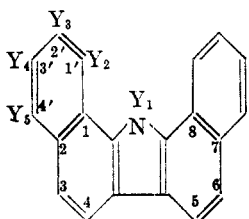
- I: $R_1 = R_4 = H, R_2 = R_3 = CH_3$
 II: $R_1 = R_3 = H, R_2 = R_4 = CH_3$
 III: $R_1 = R_3 = R_4 = H, R_2 = OCH_3$
 IV: $R_1 = R_4 = H, R_2 = OCH_3, R_3 = CH_3$
 V: $R_1 = CH_3, R_2 = R_3 = H, R_4 = OCH_3$
 VI: $R_4 = R = H, R_2 = R_3 = OCH_3$



- VII: $R_1 = R_3 = R_4 = R_5 = R_7 = H, R_2 = OCH_3, R_6 = CH_3$
 VIII: $R_1 = R_3 = R_4 = R_6 = H, R_2 = OCH_3, R_5 = R_7 = CH_3$
 IX: $R_1 = R_3 = R_4 = R_5 = R_7 = H, R_2 = OCH_3, R_6 = Br$
 X: $R_1 = R_2 = R_5 = R_6 = R_7 = H, R_3 = R_4 = CH_3$
 XI: $R_1 = R_3 = R_6 = H, R_2 = R_4 = R_5 = R_7 = CH_3$
 XII: $R_1 = R_3 = R_5 = R_7 = H, R_2 = R_4 = CH_3, R_6 = Cl$
 XIII: $R_1 = R_4 = R_5 = R_6 = R_7 = H, R_2 = OCH_3, R_3 = CH_3$
 XIV: $R_1 = R_4 = R_5 = R_7 = H, R_2 = OCH_3, R_3 = R_6 = CH_3$
 XV: $R_1 = R_4 = R_5 = R_7 = H, R_2 = OCH_3, R_3 = CH_3, R_6 = Cl$
 XVI: $R_1 = R_4 = R_5 = R_7 = H, R_2 = OCH_3, R_3 = CH_3, R_6 = Br$
 XVII: $R_1 = CH_3, R_2 = R_3 = R_5 = R_6 = R_7 = H, R_4 = OCH_3$



- XVIII: $X_1 = X_2 = X_4 = H, X_3 = X_5 = CH_3$
 XIX: $X_1 = X_3 = X_5 = CH_3, X_2 = X_4 = H$
 XX: $X_1 = X_2 = X_5 = H, X_3 = X_4 = CH_3$
 XXI: $X_1 = X_3 = X_4 = CH_3, X_2 = X_5 = H$
 XXII: $X_1 = X_3 = X_4 = H, X_2 = CH_3, X_5 = OCH_3$
 XXIII: $X_1 = X_2 = X_5 = H, X_3 = OCH_3, X_4 = CH_3$
 XXIV: $X_1 = X_2 = X_5 = H, X_3 = X_4 = OCH_3$



- XXV: $Y_1 = Y_2 = Y_4 = H, Y_3 = Y_5 = CH_3$
 XXVI: $Y_1 = Y_3 = Y_5 = CH_3, Y_2 = Y_4 = H$
 XXVII: $Y_1 = Y_2 = Y_5 = H, Y_3 = Y_4 = CH_3$
 XXVIII: $Y_1 = Y_3 = Y_4 = CH_3, Y_2 = Y_5 = H$
 XXIX: $Y_1 = Y_3 = Y_4 = H, Y_2 = CH_3, Y_5 = OCH_3$
 XXX: $Y_1 = Y_2 = Y_5 = H, Y_3 = OCH_3, Y_4 = CH_3$
 XXXI: $Y_1 = Y_2 = Y_5 = H, Y_3 = Y_4 = OCH_3$

ether in excess removed by steam-distillation, and the crude acid purified in the usual way by means of its sodium salt.

Reduction of β -aroylpropionic acids to γ -arylbutyric acids. The Clemmensen-Martin procedure (5) was found satisfactory in all instances, except that the time of refluxing had to be at least 72 hours. The following acids were prepared:

γ -(3,4-Dimethylphenyl)butyric acid (7): b.p. 192-193°/12 mm.; yield: 90%.

γ -(2,4-Dimethylphenyl)butyric acid (7): b.p. 198°/16 mm.; yield: 87%.

γ -Anisylbutyric acid (6): b.p. 205–206°/13 mm.; yield: 90%.

γ -(3-Methyl-4-methoxyphenyl)butyric acid (8): b.p. 210°/14 mm.; yield: 87%.

γ -(5-Methyl-2-methoxyphenyl)butyric acid (8): b.p. 200°/12 mm.; yield: 85%.

γ -(3,4-Dimethoxyphenyl)butyric acid (9): b.p. 228–230°/14 mm.; yield: 70%.

γ -Arylbutyryl chlorides and amides. The foregoing acids were converted into their fluid, pale yellow, liquid chlorides by thionyl chloride in chloroform solution. The corresponding amides were prepared with cold aqueous ammonia. The following substances had not hitherto been isolated:

(a) γ -(3,4-Dimethylphenyl)butyryl chloride, b.p. 155–157°/15 mm.; the corresponding γ -(3,4-dimethylphenyl)butyramide formed glinting colorless prisms, m.p. 127° from benzene.

Anal. Calc'd for $C_{12}H_{17}NO$: N, 7.3. Found: N, 7.2.

(b) γ -(2,4-Dimethylphenyl)butyryl chloride, b.p. 153–155°/13 mm. γ -(2,4-dimethylphenyl)butyramide formed silky colorless needles m.p. 129° from benzene (Found: N, 7.1).

(c) γ -Anisylbutyryl chloride, b.p. 165°/13 mm.; γ -anisylbutyramide formed lustrous silky needles from benzene, m.p. 119°.

Anal. Calc'd for $C_{11}H_{15}NO_2$: N, 7.2. Found: N, 7.0.

(d) γ -(3-Methyl-4-methoxyphenyl)butyryl chloride, b.p. 170–172°/14 mm.; γ -(3-methyl-4-methoxyphenyl)butyramide crystallized from benzene in lustrous colorless leaflets, m.p. 125°.

Anal. Calc'd for $C_{12}H_{17}NO_2$: N, 6.9. Found: N, 7.0.

(e) γ -(5-Methyl-2-methoxyphenyl)butyryl chloride, b.p. 168–170°/11 mm.; γ -(5-Methyl-2-methoxyphenyl)butyramide formed fine glinting needles from benzene, m.p. 103°. (Found: N, 6.8).

(f) γ -(3,4-Dimethoxyphenyl)butyryl chloride underwent spontaneous cyclization during vacuum-distillation.

Substituted 1-tetralones. These were best prepared by cyclization of the corresponding γ -arylbutyryl chlorides (1 mole) with aluminum chloride (1.2 moles), either in benzene or in tetrachloroethane (at -10° during addition of the catalyst and then 24 hours at room temperature).

(a) 6-Methyl-7-methoxy-1-tetralone (IV). From 28 g. of γ -(3-methyl-4-methoxyphenyl)butyryl chloride, were obtained 20 g. of a ketone, b.p. 165° at 10 mm., which crystallized from ligroin in colorless prisms, m.p. 46°, giving a yellow coloration with sulfuric acid.

Anal. Calc'd for $C_{12}H_{14}O_2$: C, 75.7; H, 7.3.

Found: C, 75.4; H, 7.5.

The corresponding semicarbazone crystallized from ethanol in fine colorless needles, m.p. 220°.

(b) 8-Methyl-5-methoxy-1-tetralone (V). This ketone, b.p. 180–182° at 14 mm., crystallized from ligroin in colorless prisms, m.p. 108°, giving a yellow coloration with sulfuric acid.

Anal. Calc'd for $C_{12}H_{14}O$: C, 75.7; H, 7.3.

Found: C, 75.5; H, 7.5.

The semicarbazone crystallized from ethanol in fine colorless needles m.p. 200°.

II. 1,2-BENZOCARBAZOLES

The preparation of the arylhydrazones of the various 1-tetralones, their indolization by acetic acid saturated with hydrogen chloride, and the chloranil-treatment of the dihydrocarbazoles thus obtained, were performed in the way described previously (1); the yields at each step were also similar to those recorded.

6-Methyl-2'-methoxy-3,4-dihydro-1,2-benzocarbazole. Obtained from the *p*-tolylhydrazone of ketone III, it formed (from benzene) pale yellow prisms m.p. 159°, giving with sulfuric acid an orange-yellow coloration.

Anal. Calc'd for $C_{13}H_{17}NO$: N, 5.3. Found: N, 5.2.

6-Methyl-2'-methoxy-1,2-benzocarbazole (VII). Crystallized from benzene in colorless needles m.p. 207°, also giving with sulfuric acid an orange-yellow coloration.

- Anal.* Calc'd for $C_{18}H_{15}NO$: N, 5.4. Found: N, 5.2.
- 5,8-Dimethyl-2'-methoxy-3,4-dihydro-1,2-benzocarbazole.* Obtained from the *p*-xylylhydrazone of ketone III; it formed pale yellow needles, m.p. 157° from benzene; yellow coloration with sulfuric acid.
- Anal.* Calc'd for $C_{19}H_{19}NO$: N, 5.0. Found: N, 4.9.
- 5,8-Dimethyl-2'-methoxy-1,2-benzocarbazole* (VIII). Formed yellowish microcrystals, m.p. 216° from benzene, giving with sulfuric acid the same coloration as the above.
- Anal.* Calc'd for $C_{19}H_{17}NO$: N, 5.0. Found: N, 4.9.
- 6-Bromo-2'-methoxy-3,4-dihydro-1,2-benzocarbazole.* From the *p*-bromophenylhydrazone of ketone III; crystallized from benzene in colorless needles, m.p. 136°.
- Anal.* Calc'd for $C_{17}H_{14}BrNO$: N, 4.2. Found: N, 4.0.
- 6-Bromo-2'-methoxy-1,2-benzocarbazole* (IX). Cream-yellow microcrystals (from benzene) m.p. 220°; orange coloration with sulfuric acid.
- Anal.* Calc'd for $C_{17}H_{12}BrNO$: N, 4.2. Found: N, 4.0.
- 2',4'-Dimethyl-3,4-dihydro-1,2-benzocarbazole.* From the phenylhydrazone of ketone II; formed (from benzene) colorless needles m.p. 186°, giving a yellow coloration with sulfuric acid.
- Anal.* Calc'd for $C_{18}H_{17}N$: N, 5.6. Found: N, 5.4.
- 2',4'-Dimethyl-1,2-benzocarbazole* (X). Glistening slightly gray-tinged needles (from benzene), m.p. 229°, giving with sulfuric acid a yellow coloration.
- Anal.* Calc'd for $C_{18}H_{15}N$: N, 5.7. Found: N, 5.6.
- 2',4',9-Trimethyl-1,2-benzocarbazole.* Prepared from the magnesium compound of X with methyl sulfate (1b); formed (from methanol) glistening colorless needles m.p. 175°.
- Anal.* Calc'd for $C_{19}H_{17}N$: N, 5.4. Found: N, 5.1.
- 5,8,2',4'-Tetramethyl-3,4-dihydro-1,2-benzocarbazole.* From the *p*-xylylhydrazone of ketone II; colorless needles (from benzene) m.p. 178°; yellow coloration with sulfuric acid.
- Anal.* Calc'd for $C_{20}H_{21}N$: N, 5.0. Found: N, 5.2.
- 5,8,2',4'-Tetramethyl-1,2-benzocarbazole* (XI). Slightly gray-tinged needles (from benzene), m.p. 224°.
- Anal.* Calc'd for $C_{20}H_{19}N$: N, 5.0. Found: N, 4.9.
- 2',4'-Dimethyl-6-chloro-3,4-dihydro-1,2-benzocarbazole.* From the *p*-chlorophenylhydrazone of ketone II; colorless needles (from ligroin) m.p. 205°; yellow coloration with sulfuric acid.
- Anal.* Calc'd for $C_{18}H_{16}ClN$: N, 4.9. Found: N, 4.8.
- 2',4'-Dimethyl-6-chloro-1,2-benzocarbazole* (XII). Gray-tinged glinting needles (from benzene) m.p. 239-240°.
- Anal.* Calc'd for $C_{18}H_{14}ClN$: N, 4.9. Found: N, 4.6.
- 3'-Methyl-2'-methoxy-1,2-benzocarbazole* (XIII). From the phenylhydrazone of ketone IV; formed (from benzene) colorless needles m.p. 222°, giving a yellow coloration with sulfuric acid.
- Anal.* Calc'd for $C_{18}H_{15}NO$: N, 5.4. Found: N, 5.1.
- 3',6-Dimethyl-2'-methoxy-3,4-dihydro-1,2-benzocarbazole.* From the *p*-tolylhydrazone of ketone IV; formed (from benzene) fine yellowish prisms m.p. 192°.
- Anal.* Calc'd for $C_{19}H_{19}NO$: N, 5.0. Found: N, 5.1.
- 3',6-Dimethyl-2'-methoxy-1,2-benzocarbazole* (XIV). Slightly gray-tinged microcrystals, m.p. 237°, giving a yellow coloration with sulfuric acid.
- Anal.* Calc'd for $C_{19}H_{17}NO$: N, 5.0. Found: N, 4.8.
- 3'-Methyl-2'-methoxy-6-chloro-3,4-dihydro-1,2-benzocarbazole.* From the *p*-chlorophenylhydrazone of ketone IV; fine colorless needles (from benzene) m.p. 198°.
- Anal.* Calc'd for $C_{18}H_{16}ClNO$: N, 4.7. Found: N, 4.8.
- 3'-Methyl-2'-methoxy-6-chloro-1,2-benzocarbazole* (XIV). Fine colorless needles (from benzene) m.p. 220°; orange-yellow coloration with sulfuric acid.
- Anal.* Calc'd for $C_{18}H_{14}ClNO$: N, 4.7. Found: N, 4.6.
- 3'-Methyl-2'-methoxy-6-bromo-3,4-dihydro-1,2-benzocarbazole.* From the *p*-bromophenylhydrazone of ketone IV; almost colorless microcrystals (from benzene) m.p. 209°.

Anal. Calc'd for $C_{13}H_{13}BrNO$: N, 4.1. Found: N, 4.0.

3'-Methyl-2'-methoxy-6-bromo-1,2-benzocarbazole (XV). Colorless lustrous leaflets (from benzene) m.p. 222°, giving an orange coloration with sulfuric acid.

Anal. Calc'd for $C_{13}H_{13}BrNO$: N, 4.1. Found: N, 4.0.

1'-Methyl-4'-methoxy-3,4-dihydro-1,2-benzocarbazole. From the phenylhydrazone of ketone V; formed (from benzene) colorless microcrystals, m.p. 189°.

Anal. Calc'd for $C_{13}H_{13}NO$: N, 5.3. Found: N, 5.3.

1'-Methyl-4'-methoxy-1,2-benzocarbazole (XVII). Colorless microcrystals (from benzene) m.p. 232°, giving an orange-yellow coloration with sulfuric acid.

Anal. Calc'd for $C_{13}H_{13}NO$: N, 5.4. Found: N, 5.3.

III. 1,2,5,6-DIBENZOCARBAZOLES

2',4'-Dimethyl-3,4-dihydro-1,2,5,6-dibenzocarbazole. Obtained from the β -naphthylhydrazone of ketone II; formed (from benzene) colorless needles m.p. 240°, giving a deep red coloration with sulfuric acid.

Anal. Calc'd for $C_{22}H_{19}N$: N, 4.7. Found: N, 4.5.

2',4'-Dimethyl-1,2,5,6-dibenzocarbazole (XVIII). Crystallized from benzene in gray-tinged prisms, m.p. 273°, giving a deep brownish-red coloration with sulfuric acid.

Anal. Calc'd for $C_{22}H_{17}N$: N, 4.7. Found: N, 4.5.

2',4',9-Trimethyl-1,2,5,6-dibenzocarbazole (XIX). Obtained from the magnesium-compound of XVIII with methyl sulfate; crystallized from methanol in colorless needles, m.p. 210°.

Anal. Calc'd for $C_{23}H_{19}N$: N, 4.5. Found: N, 4.4.

2',3'-Dimethyl-3,4-dihydro-1,2,5,6-dibenzocarbazole. From the β -naphthylhydrazone of ketone I; formed (from benzene) colorless needles, m.p. 223°, giving with sulfuric acid a deep brown-red coloration.

Anal. Calc'd for $C_{22}H_{19}N$: N, 4.7. Found: N, 4.4.

2',3'-Dimethyl-1,2,5,6-dibenzocarbazole (XX). Formed (from xylene) fine colorless needles, m.p. 285°; same coloration with sulfuric acid as the above.

Anal. Calc'd for $C_{22}H_{17}N$: N, 4.7. Found: N, 4.5.

2',3',9-Trimethyl-1,2,5,6-dibenzocarbazole (XXI). Crystallized from methanol in colorless lustrous needles m.p. 226°.

Anal. Calc'd for $C_{23}H_{19}N$: N, 4.5. Found: N, 4.5.

1'-Methyl-4'-methoxy-3,4-dihydro-1,2-dibenzocarbazole. From the β -naphthylhydrazone of ketone V; formed (from benzene) colorless microcrystals, m.p. 231°, giving with sulfuric acid a deep red coloration.

Anal. Calc'd for $C_{22}H_{19}NO$: N, 4.5. Found: N, 4.4.

1'-Methyl-4'-methoxy-1,2,5,6-dibenzocarbazole (XXII). Gray-tinged microcrystals (from benzene) m.p. 268°; deep red coloration with sulfuric acid.

Anal. Calc'd for $C_{22}H_{17}NO$: N, 4.5. Found: N, 4.3.

3'-Methyl-2'-methoxy-3,4-dihydro-1,2,5,6-dibenzocarbazole. From the β -naphthylhydrazone of ketone IV; colorless prisms (from benzene) m.p. 219°, giving with sulfuric acid a deep brown-red coloration.

Anal. Calc'd for $C_{22}H_{19}NO$: N, 4.5. Found: N, 4.4.

3'-Methyl-2'-methoxy-1,2,5,6-dibenzocarbazole (XXIII). Formed (from xylene) a grayish microcrystalline powder, m.p. 283°.

Anal. Calc'd for $C_{22}H_{17}NO$: N, 4.5. Found: N, 4.3.

2',3'-Dimethoxy-3,4-dihydro-1,2,5,6-dibenzocarbazole. From the β -naphthylhydrazone of ketone VI; crystallized from xylene in colorless needles, m.p. 275°.

Anal. Calc'd for $C_{22}H_{19}NO_2$: N, 4.2. Found: N, 4.2.

2',3'-Dimethoxy-1,2,5,6-dibenzocarbazole (XXIV). Crystallized from xylene in fine colorless needles m.p. 307°.

Anal. Calc'd for $C_{22}H_{17}NO_2$: N, 4.2. Found: N, 4.3.

IV. 1,2,7,8-DIBENZOCARBAZOLES

2',4'-Dimethyl-3,4-dihydro-1,2,7,8-dibenzocarbazole. From the α -naphthylhydrazone of ketone II; formed (from benzene) colorless microcrystals, m.p. 107–108°, giving with sulfuric acid an orange coloration.

Anal. Calc'd for $C_{22}H_{19}N$: N, 4.7. Found: N, 4.8.

2',4'-Dimethyl-1,2,7,8-dibenzocarbazole (XXV). Crystallized from benzene in colorless needles, m.p. 182°.

Anal. Calc'd for $C_{22}H_{17}N$: N, 4.7. Found: N, 4.6.

2',4',9-Trimethyl-1,2,7,8-dibenzocarbazole (XXVI). From the magnesium-compound of XXV with methyl sulfate; colorless needles (from methanol) m.p. 206°, giving an orange coloration with sulfuric acid.

Anal. Calc'd for $C_{23}H_{19}N$: N, 4.5. Found: N, 4.2.

2',3'-Dimethyl-3,4-dihydro-1,2,7,8-dibenzocarbazole. From the α -naphthylhydrazone of ketone I; iridescent colorless leaflets (from ligroin) m.p. 193°, giving a deep brown-red coloration with sulfuric acid.

Anal. Calc'd for $C_{22}H_{19}N$: N, 4.7. Found: N, 4.6.

2',3'-Dimethyl-1,2,7,8-dibenzocarbazole (XXVII). Crystallized from benzene in colorless needles, m.p. 247°.

Anal. Calc'd for $C_{22}H_{17}N$: N, 4.7. Found: N, 4.6.

2',3',9-Trimethyl-1,2,7,8-dibenzocarbazole (XXVIII). Formed (from methanol) colorless microcrystals, m.p. 184°, giving a deep brown-red coloration with sulfuric acid.

Anal. Calc'd for $C_{23}H_{19}N$: N, 4.5. Found: N, 4.4.

1'-Methyl-4'-methoxy-3,4-dihydro-1,2,7,8-dibenzocarbazole. From the α -naphthylhydrazone of ketone V; colorless microcrystals (from benzene), m.p. 178°, giving a deep red coloration with sulfuric acid.

Anal. Calc'd for $C_{22}H_{19}NO$: N, 4.5. Found: N, 4.3.

1'-Methyl-4'-methoxy-1,2,7,8-dibenzocarbazole (XXIX). Formed (from benzene) fine gray-tinged needles, m.p. 253°.

Anal. Calc'd for $C_{22}H_{17}NO$: N, 4.5. Found: N, 4.6.

3'-Methyl-2'-methoxy-3,4-dihydro-1,2,7,8-dibenzocarbazole. From the α -naphthylhydrazone of ketone IV; fine colorless needles (from benzene), m.p. 189°, giving with sulfuric acid a deep brown-red coloration.

Anal. Calc'd for $C_{22}H_{19}NO$: N, 4.5. Found: N, 4.4.

3'-Methyl-2'-methoxy-1,2,7,8-dibenzocarbazole (XXX). Formed (from xylene) fine colorless needles, m.p. 225°; the violet-red *picrate* had m.p. 200°.

Anal. Calc'd for $C_{22}H_{17}NO$: N, 4.5. Found: N, 4.3.

2',3'-Dimethoxy-1,2,7,8-dibenzocarbazole (XXXI). Formed (from benzene) colorless needles, m.p. 274°, giving with sulfuric acid a deep brown-red coloration. The dark violet *picrate* had m.p. 252°.

Anal. Calc'd for $C_{22}H_{17}NO$: N, 4.2. Found: N, 3.9.

SUMMARY

A large number of new polysubstituted 1,2-benzocarbazoles, and 1,2,5,6- and 1,2,7,8-dibenzocarbazoles have been synthesized by known methods for biological studies.

PARIS V^e, FRANCE

REFERENCES

- (1) (a) BUU-HOÏ, HOÁN, AND KHÔI, *J. Org. Chem.*, **14**, 492 (1949); (b) BUU-HOÏ, HOÁN, KHÔI, AND XƯƠNG, *J. Org. Chem.*, **14**, 802 (1949).
- (2) See BERLINER, *Org. Reactions*, **5**, 229 (1949).
- (3) See FIESER, *Am. J. Cancer*, **34**, 37 (1934); LACASSAGNE, BUU-HOÏ, LECOCQ, AND RUDALI, *Bull. assoc. franc. étude cancer*, **33**, 48 (1946); **34**, 22 (1947).

- (4) SHEAR AND LEITER, *J. Natl. Cancer Inst.*, **1**, 303 (1940).
- (5) FIESER AND HERSHBERG, *J. Am. Chem. Soc.*, **59**, 1028 (1937).
- (6) MARTIN, *J. Am. Chem. Soc.*, **58**, 1438 (1936).
- (7) KROLLPFEIFFER AND SCHÄFER, *Ber.*, **56**, 627 (1923); DEBARRY BARNETT AND SANDERS, *J. Chem. Soc.*, 434 (1933).
- (8) DESAI AND WALI, *Proc. Indian Acad. Sci.*, **6** [A], 144 (1937).
- (9) HAWORTH AND MAVIN, *J. Chem. Soc.*, 1945 (1932).