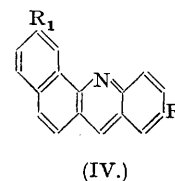
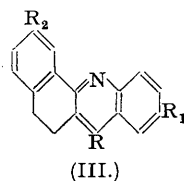
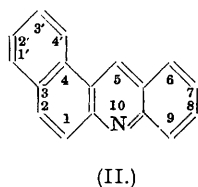
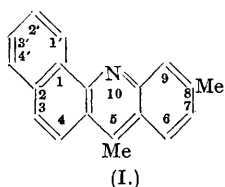


166. The Chemistry of Carcinogenic Nitrogen Compounds. New Derivatives of the Angular Benzacridines and of Some Related Nuclei.

By NG. PH. BUU-HOÏ.

In continuation of earlier work on the synthesis of carcinogenic nitrogen compounds (Buu-Hoï and Lecocq, *Compt. rend.*, 1944, **218**, 792), several methyl and halogen derivatives of 1:2- and 3:4-benzacridine have been prepared, by known methods, for examination of their physiological properties. In connexion with the same problem, some homologues of acridine, of 1:2:5:6- and 3:4:5:6-dibenzacridine, and of 1:2-benzcarbazole, mostly bearing substituents in the *meso*-position, have also been synthesised.

It has generally been observed that the replacement by nitrogen of a nuclear carbon atom in the molecules of carcinogenic hydrocarbons results in a significant lowering of their physiological activity. As a consequence of those earlier findings, it could hardly be expected that very potent carcinogens would be encountered among the group of polycyclic nitrogen compounds. Recently, however, report has been made of the very high activity displayed by some *meso*-substituted derivatives of 1:2-benzacridine (Buu-Hoï, Lacassagne, Lecocq, and Rudali, *Compt. rend. Soc. Biol.*, 1945, **139**, 955). For instance, 5:8-dimethyl-1:2-benzacridine (I) (Buu-



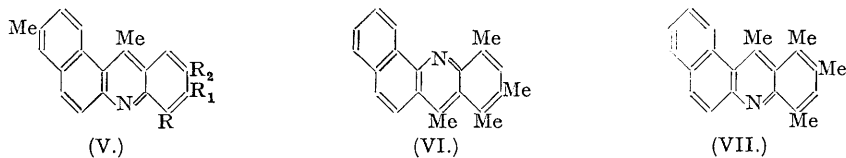
Hoï and Lecocq, *loc. cit.*) develops papilloma and epithelioma on the skin of mice in a proportion and with a rapidity approaching those characteristic of such a prominent carcinogenic hydrocarbon as 20-methylcholanthrene. On the other hand the isomeric 5:7- and 5:8-dimethyl-3:4-benzacridines, though derived from a similar ring system (II), are not active, or only very feebly so. These striking results make desirable a thorough investigation of the whole field of acridine derivatives. The present paper deals with the preparation and properties of some benzacridines of types (I) and (II), bearing methyl or halogen substituents in various positions.

7-Methyl-1-tetralone reacts with potassium isatate to give 2'-methyl-3:4-dihydro-1:2-benzacridine-5-carboxylic acid (III; R = CO₂H, R₁ = H, R₂ = Me) which retains tetrophan activity (cf. von Braun and Wolff, *Ber.*, 1922, **55**, 3685), and readily loses carbon dioxide on vacuum distillation to afford 2'-methyl-3:4-dihydro-1:2-benzacridine (III; R = R₁ = H, R₂ = Me); this is converted into 2'-methyl-1:2-benzacridine (IV; R = H, R₁ = Me) by heating either with chloranil in xylene solution (cf. Arnold and Collins, *J. Amer. Chem. Soc.*, 1939, **61**, 140; 1940, **62**, 983) or with lead monoxide at 300—320°. The aforementioned tetralone, condensed with potassium 5-bromoisatate, gives 7-bromo-2'-methyl-3:4-dihydro-1:2-benzacridine-5-carboxylic acid (III; R = CO₂H, R₁ = Br, R₂ = Me), the decarboxylation product of which, 7-bromo-2'-methyl-3:4-dihydro-1:2-benzacridine (III; R = H, R₁ = Br, R₂ = Me), loses bromine when heated with lead monoxide at high temperatures (cf. von Braun and Wolff, *loc. cit.*), but may undergo oxidation into 7-bromo-2'-methyl-1:2-benzacridine (IV; R = Br, R₁ = Me) on treatment either with bromine or better with chloranil in boiling

cumene. The same condensation, performed with potassium 5-chloroisatate, leads to chlorine analogues, the acid also showing some tetraphan activity.

Cyclodehydrogenation of *N-as-m-xylyl- α -naphthylamine* (Buu-Hoï and Lecocq, *Compt. rend.*, 1944, **218**, 648, 792) occurs on heating this base with lead monoxide at 320–350° (cf. Ullmann and La Torre, *Ber.*, 1906, **37**, 2924), the resulting 7-methyl-1 : 2-benzacridine (IV; R = Me, R₁ = H) being also obtained *via* the atophan-like 7-methyl-3 : 4-dihydro-1 : 2-benzacridine-5-carboxylic acid (III; R = CO₂H, R₁ = Me, R₂ = H) and the 7-methyl-3 : 4-dihydro-1 : 2-benzacridine (III; R = R₂ = H, R₁ = Me) through a Pfitzinger synthesis involving α -tetralone and potassium 5-methylisatate. None of these 1 : 2-benzacridines has been found to be carcinogenic (private communication from Prof. Lacassagne).

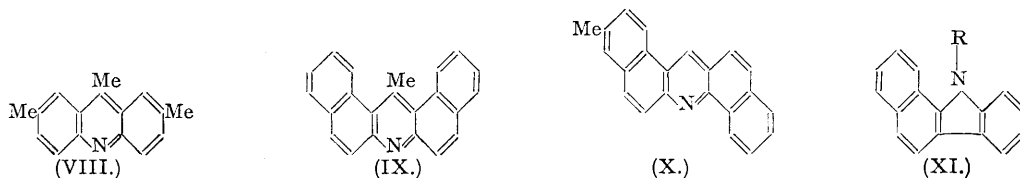
The modified Bernthsen reaction (cf. Buu-Hoï and Lecocq, *loc. cit.*) performed with *N-o-tolyl-6-methyl-2-naphthylamine* (Buu-Hoï, Hiong-Ki-Wei, and Royer, *Bull. Soc. chim.*, 1945, **12**, 904), acetic anhydride, and zinc chloride gives 2' : 5 : 9-trimethyl-3 : 4-benzacridine (V; R = Me, R₁ = R₂ = H) in rather poor yield. Using



N-m-tolyl- and *N-p-tolyl-6-methyl-2-naphthylamine*, 2' : 5 : 8- (V; R = R₂ = H, R₁ = Me) and 2' : 5 : 7-trimethyl-3 : 4-benzacridine (V; R = R₁ = H, R₂ = Me) are respectively obtained. 5 : 6 : 7 : 9-Tetramethyl-1 : 2- (VI) and -3 : 4-benzacridine (VII) were prepared in the same manner from *N- ψ -cumyl- α - and - β -naphthylamine* (Buu-Hoï and Lecocq, *loc. cit.*) respectively. Both are slowly active in the production of epithelioma. The picrate of (VI) melts considerably lower than that of (VII); this is consistent with a similar observation made by Senier and Austin (*J.*, 1907, **91**, 1240) regarding the picrates from 5 : 6 : 8-trimethyl-1 : 2- and -3 : 4-benzacridines.

The Bernthsen reaction may also be applied to the synthesis of halogenated *meso*-substituted benzacridines : thus, 8-chloro-5-methyl-3 : 4-benzacridine was obtained from *N-m-chlorophenyl- β -naphthylamine*, and the isomeric 9-chloro-compound from *N-o-chlorophenyl- β -naphthylamine*.

In view of the activity of some *meso*-substituted anthracenes, recently reported by several authors (Kenaway and Warren, 1941), 3 : 5 : 7-trimethylacridine (VIII) has now been prepared for examination, using di-*p*-tolylamine, acetic anhydride, and zinc chloride. The same route was found suitable for the preparation of 5-methyl-3 : 4 : 6 : 7-dibenzacridine (IX) from $\beta\beta$ -dinaphthylamine. An analogue of the feebly carcinogenic 3'-methyl-1 : 2 : 5 : 6-dibenzanthracene (Cook, *J.*, 1931, 489), 3'-methyl-1 : 2 : 6 : 7-dibenzacridine (X), was readily obtained on heating 6-methyl-2-naphthol (Dziewoński, Schoenówna, and Waldmann, *Ber.*, 1925, **58**, 1912) with α -naphthylamine and trioxymethylene, following the Ullmann-Fettvadjan procedure for the preparation of the non-methylated dibenzacridine (*Ber.*, 1903, **36**, 1029).



Since 1 : 2-benzcarbazole (XI; R = H) has been claimed (Schürch and Winterstein, *Z. physiol. Chem.*, 1935, **136**, 79) to produce epithelial growths, a series of *N-alkyl-1 : 2-benzcarbazoles* (XI) were synthesised by allowing various alkyl halides to react with the sodio-derivative of 1 : 2-benzcarbazole. None of them appears to be actively carcinogenic, thus indicating that *meso*-substitution is effective only in an aromatic ring.

Some of the new substances described in this paper are being examined for anticarcinogenic activity (cf. Lacassagne, Buu-Hoï, and Rudali, *Brit. J. Exp. Path.*, 1945, **26**, 5); the biological data will be published elsewhere. Some methyl derivatives of 3 : 4-benzacridine have been used with success for inhibition of tumour-growth by Badger *et al.* (*Proc. Roy. Soc.*, 1942, *B*, **130**, 265).

This investigation will be continued.

EXPERIMENTAL.

2'-Methyl-1 : 2-benzacridine.—A mixture of isatin (1.5 g.), 7-methyl-1-tetralone in slight excess (1.7 g.), and potassium hydroxide (1.7 g. in 15 c.c. of 70% ethyl alcohol) was gently boiled for 12 hours on the water-bath. The slightly brown solution was diluted with water (50 c.c.), and twice shaken with ether in order to remove traces of unreacted ketone. On acidification with a slight excess of 50% acetic acid, the aqueous solution gave 2'-methyl-3 : 4-dihydro-1 : 2-benzacridine-5-carboxylic acid (2.5 g.), which crystallised from nitrobenzene in yellowish silky needles, m. p. 276° (efferv.) (Found : N, 4.6; C₁₉H₁₅O₂N requires N, 4.8%). This (2.0 g.) was fused, and the residue subsequently distilled in a vacuum. The distillate was moistened with alcohol and kept overnight; 2'-methyl-3 : 4-dihydro-1 : 2-benzacridine then separated as long colourless needles (1 g.), m. p. 103–104°, readily soluble in benzene, sparingly in alcohol (Found : N, 5.4. C₁₈H₁₅N requires N, 5.7%). This base develops on heating a smell resembling that of tobacco; the alcoholic solutions exhibit a strong blue fluorescence; sulphuric solutions are greenish-yellow. The picrate crystallised from nitrobenzene in fine yellow needles, m. p. 218–219° (decomp.), which were almost insoluble in alcohol (Found : N, 12.4. C₁₈H₁₅N, C₆H₃O₇N₃

requires N, 12.6%). The dihydro-base (1 g.) was heated during $\frac{1}{2}$ hour at 300—320° with excess of lead monoxide (50 g.); the cooled mass was extracted twice with boiling alcohol, and the alcoholic extract boiled with charcoal and evaporated to small bulk. *2'-Methyl-1:2-benzacridine* separated on cooling in long, glittering, yellowish needles, m. p. 125°, which were readily soluble in benzene, sparingly in alcohol (Found: N, 5.5. $C_{18}H_{13}N$ requires N, 5.7%). The orange-yellow *picrate* crystallised from nitrobenzene in fine prismatic needles, m. p. 236—237° (decomp.) (Found: N, 12.5. $C_{18}H_{13}N, C_6H_3O_7N_3$ requires N, 12.7%).

7-Bromo-2'-methyl-1:2-benzacridine.—5-Bromoisatin (2.3 g.), condensed with 7-methyl-1-tetralone (1.8 g.) in the presence of alcoholic potassium hydroxide (1.7 g.) during 12 hours, gave almost quantitatively *7-bromo-2'-methyl-3:4-dihydro-1:2-benzacridine-5-carboxylic acid* (4 g.), which crystallised from acetic acid in silky yellowish needles, m. p. 239—240° (decomp.) (Found: N, 3.7. $C_{19}H_{14}O_2NBr$ requires N, 3.9%). This acid strongly retains solvent, which it loses above 160°. Decarboxylation gave a viscous resin which did not solidify spontaneously, and was therefore converted into a *picrate* (4 g.) which crystallised from nitrobenzene in silky yellow needles, m. p. 241—242° (decomp.) (Found: N, 10.2. $C_{18}H_{14}NBr, C_6H_3O_7N_3$ requires N, 10.1%). *7-Bromo-2'-methyl-3:4-dihydro-1:2-benzacridine*, regenerated from this *picrate* by treatment with aqueous ammonia, gave long colourless needles, m. p. 98—99°, on recrystallisation from alcohol (Found: N, 4.2. $C_{18}H_{14}NBr$ requires N, 4.3%). A solution of this dihydro-base in boiling cumene was treated dropwise with excess of bromine, heating being continued until evolution of hydrogen bromide had ceased. The orange-yellow precipitate was collected, washed with ether, and decomposed by aqueous ammonia. *7-Bromo-2'-methyl-1:2-benzacridine* formed clumps of yellowish needles (1.8 g.) from alcohol (Found: N, 4.2. $C_{18}H_{12}NBr$ requires N, 4.4%); its *picrate*, which formed silky, glistening, orange needles from nitrobenzene, darkened and charred above 228—230° (Found: N, 10.1. $C_{18}H_{12}NBr, C_6H_3O_7N_3$ requires N, 10.2%). The base regenerated from the *picrate* had m. p. 108°.

7-Chloro-2'-methyl-3:4-dihydro-1:2-benzacridine.—5-Chloroisatin (3 g.), 7-methyl-1-tetralone (3 g.), and potassium hydroxide (3 g.) yielded *7-chloro-2'-methyl-3:4-dihydro-1:2-benzacridine-5-carboxylic acid* (4.8 g.) as faintly yellowish needle rosettes, m. p. 230—231° (from alcohol) (Found: N, 4.2. $C_{19}H_{14}O_2NCl$ requires N, 4.3%). The corresponding *7-chloro-5'-methyl-3:4-dihydro-1:2-benzacridine* formed long silky yellowish needles (from alcohol) (Found: N, 5.2. $C_{18}H_{14}NCl$ requires N, 5.0%), and gave a *picrate* which crystallised from nitrobenzene in flimsy orange-yellow needles, m. p. 229—230° (decomp.) (Found: N, 10.8. $C_{18}H_{14}NCl, C_6H_3O_7N_3$ requires N, 11.1%).

7-Methyl-1:2-benzacridine.—(a) *Ullmann and La Torre's reaction*. *N-as-m-Xylyl-β-naphthylamine* (3 g.) was heated at 325° in a metal-bath for $\frac{1}{2}$ hour; the temperature was then raised until distillation occurred, and the thick jelly thus obtained was treated with excess of an alcoholic solution of picric acid. After recrystallisation from nitrobenzene, the *picrate* formed yellow needles, m. p. 226—227°, insoluble in cold alcohol, slightly soluble in benzene (Found: N, 12.3. $C_{18}H_{13}N, C_6H_3O_7N_3$ requires N, 12.7%). The free base, liberated from the *picrate* by treatment with aqueous ammonia, separated from alcohol in long almost colourless prismatic needles, m. p. 131° (Found: N, 5.4. $C_{18}H_{13}N$ requires N, 5.7%). The hydrochloride formed silky yellow needles from water, and gave solutions showing an intense green fluorescence.

(b) *Pfizinger's reaction*. 5-Methylisatin (2.8 g.) was allowed to react with α -tetralone (2.8 g.) in the presence of potassium hydroxide (3 g.) in alcohol (25 c.c.), thus giving *7-methyl-3:4-dihydro-1:2-benzacridine-5-carboxylic acid* (4.8 g.), which crystallised from alcohol in almost colourless needles, m. p. 286—288° (Found: N, 4.7. $C_{19}H_{15}O_2N$ requires N, 4.8%). Decarboxylation gave *7-methyl-3:4-dihydro-1:2-benzacridine*, which separated from alcohol in colourless silky needles, m. p. 72°, very soluble in hot alcohol and benzene (Found: N, 5.5. $C_{18}H_{13}N$ requires N, 5.7%). This dihydro-base gave a *picrate* crystallising from much alcohol in yellow prisms, m. p. 211—212° (Found: N, 12.4. $C_{18}H_{15}N, C_6H_3O_7N_3$ requires N, 12.7%), and was easily converted into *7-methyl-1:2-benzacridine* (m. p. 127—128° after two recrystallisations from alcohol) by heating with lead monoxide at 300—320°. The same oxidation took place when a solution of the dihydro-base in cumene was boiled during 6 hours with a slight excess of chloranil.

2:5:9-Trimethyl-3:4-benzacridine.—*N-o-Tolyl-6-methyl-2-naphthylamine* (2 g.) was heated with freshly fused zinc chloride (2 g.) and acetic anhydride (6 c.c.) during 18 hours at 190—200° (extensive charring occurred above 200°). The sticky greenish fluorescent mass thus obtained was treated with a hot 40% aqueous solution of potassium hydroxide in the presence of benzene; the benzene layer was decanted and dried (Na_2SO_4). After removal of the solvent and vacuum distillation of the thick brown residue, the crude benzacridine was converted into its *picrate* (1 g.); silky yellow needles (from nitrobenzene), m. p. 223—224° (decomp.), almost insoluble in alcohol (Found: N, 10.9. $C_{20}H_{17}N, C_6H_3O_7N_3$ requires N, 11.2%). The base (0.6 g.), freed by aqueous ammonia, crystallised from alcohol in almost colourless needles, m. p. 118°, giving an intense yellow colour with sulphuric acid (Found: N, 5.1. $C_{20}H_{17}N$ requires N, 5.2%).

2':5:8-Trimethyl-3:4-benzacridine.—This base was obtained in a similar manner, but in far better yield (1 g.), from *N-m-tolyl-6-methyl-2-naphthylamine* (2 g.). It crystallised from alcohol-benzene in long silky yellowish needles, m. p. 198° (Found: N, 5.2. $C_{20}H_{17}N$ requires N, 5.2%). The *picrate* formed yellow silky needles (from nitrobenzene), m. p. 261—262° (efferv.) (Found: N, 11.4. $C_{20}H_{17}N, C_6H_3O_7N_3$ requires N, 11.2%).

2':5:7-Trimethyl-3:4-benzacridine.—This base formed very slightly yellowish needles (from alcohol), m. p. 135—136°, readily soluble in ether (Found: N, 5.1. $C_{20}H_{17}N$ requires N, 5.2%). The *picrate* formed short yellow prisms (from nitrobenzene), m. p. 243—244° (efferv.) (Found: N, 10.8. $C_{20}H_{17}N, C_6H_3O_7N_3$ requires N, 11.2%).

5:6:7:9-Tetramethyl-3:4-benzacridine.—From *N-ψ-cumyl-β-naphthylamine* (4 g.), zinc chloride (4 g.), and acetic anhydride 10 c.c., heated for 12 hours at 200—220°, the crude base (2.8 g.) was obtained. This spontaneously solidified after distillation (b. p. 272—275°/18 mm.), and crystallised from alcohol in faintly yellowish prismatic needles, m. p. 189—190°, extremely soluble in benzene, slightly in alcohol or acetone (Found: N, 5.1. $C_{21}H_{19}N$ requires N, 4.9%). The hydrochloride formed deep yellow needles, very sparingly soluble in water; the *picrate* crystallised from nitrobenzene in short glistening orange prisms, m. p. 252—253° (Found: N, 10.7. $C_{21}H_{19}N, C_6H_3O_7N_3$ requires N, 10.9%).

5:6:7:9-Tetramethyl-1:2-benzacridine.—This base was still more soluble in benzene than the previous isomer; it formed faintly yellowish needles, m. p. 154° (from alcohol), and gave a *picrate* crystallising from benzene in elongated orange-yellow prisms, m. p. 169—170°, easily soluble in alcohol and benzene (Found: N, 5.0. $C_{21}H_{19}N$ requires N, 4.9%).

7-Chloro-5-methyl-3:4-benzacridine.—*N-m-Chlorophenyl-β-naphthylamine* (Knoevenagel, *J. pr. Chem.*, 1914, 89, 17) (2 g.) was heated with zinc chloride (3 g.) and acetic anhydride (6 c.c.) during 24 hours at 220—230°. The base thus obtained could be distilled in a high vacuum without decomposition, and crystallised from benzene in long, prismatic, almost colourless needles, m. p. 183°, which were very sparingly soluble in alcohol (Found: N, 5.1. $C_{18}H_{12}NCl$ requires N, 5.0%). The *picrate* formed deep yellow needles, m. p. 197°, from nitrobenzene (Found: N, 11.0. $C_{18}H_{12}NCl, C_6H_3O_7N_3$ requires N, 11.2%).

9-Chloro-5-methyl-3:4-benzacridine.—After two recrystallisations from alcohol-benzene, this base formed yellowish silky needles, m. p. 129° (Found: N, 5.3. $C_{18}H_{12}NCl$ requires N, 5.0%). It gave a *picrate* which crystallised from nitrobenzene in short yellow prisms which decomposed above 216—217° (Found: N, 11.4. $C_{18}H_{12}NCl, C_6H_3O_7N_3$ requires N, 11.2%).

3:5:7-Trimethylacridine.—Di-*p*-tolylamine (5 g.) was heated with zinc chloride (7 g.) and acetic anhydride (5 c.c.)

during 18 hours at 230—250°; the base (3 g.) was conveniently purified by distillation in a high vacuum (b. p. 195°/2.5 mm.); it separated from aqueous acetone in feebly yellowish silky needles, m. p. 84°, extremely soluble in alcohol and benzene (Found: N, 6.4. $C_{16}H_{15}N$ requires N, 6.3%). The picrate formed glistening yellow needles, m. p. 219—220° (from nitrobenzene) (Found: N, 12.3. $C_{16}H_{15}N, C_6H_3O_7N_3$ requires N, 12.4%).

3-Methyl-1 : 2 : 6 : 7-dibenzacridine.—A mixture of 6-methyl-2-naphthol (2 g.) and α -naphthylamine (2 g.) was fused at 160—170° and carefully treated with paraformaldehyde (0.4 g.); a violent reaction took place with evolution of steam and considerable frothing. The temperature was subsequently raised to 260°, and the reaction product vacuum distilled; after two recrystallisations from benzene, the acridine (3.2 g.) was obtained as silky yellowish needles, m. p. 195°, very sparingly soluble in alcohol (Found: N, 4.9. $C_{22}H_{15}N$ requires N, 4.7%). The picrate crystallised from nitrobenzene in orange-yellow needles which decomposed above 250° (Found: N, 10.4. $C_{22}H_{15}N, C_6H_3O_7N_3$ requires N, 10.7%).

5-Methyl-3 : 4 : 6 : 7-dibenzacridine.—Knoevenagel (*loc. cit.*) claimed that he had obtained pure $\beta\beta$ -dinaphthylamine by heating a solution of β -naphthylamine in aniline with traces of iodine. However, when a sample thus prepared was submitted to a Berthsen synthesis with acetic anhydride and zinc chloride, 5-methyl-3 : 4-benzacridine (Posadowski and Lundin, *Centr.*, 1940, II, 205) (almost colourless silky needles, b. p. 250°/2 mm., m. p. 144°) was isolated from the reaction mixture; the picrate of this base had m. p. 237° after recrystallisation from nitrobenzene. Hence, it is clear that Knoevenagel's $\beta\beta$ -dinaphthylamine was contaminated by *N*-phenyl- β -naphthylamine. A purer product was obtained by heating β -naphthol with β -naphthylamine in the presence of iodine; by Berthsen's reaction this yielded only 5-methyl-3 : 4 : 5 : 6-dibenzacridine (IX), which distilled above 300°/2 mm. and formed straw-coloured silky needles, m. p. 184—185° after repeated crystallisation from alcohol-benzene (Found: N, 4.5. $C_{22}H_{15}N$ requires N, 4.7%). The benzene solutions showed a strong violet fluorescence and the sulphuric solutions were intensely yellow. The picrate formed silky yellow-orange needles (from nitrobenzene) which decomposed above 278—280°.

N-Alkyl-1 : 2-benzcarbazoles.—These were prepared by the following procedure: a solution of 1 : 2-benzcarbazole in dry toluene or xylene (Bucherer and Sonnenburg, *J. pr. Chem.*, 1910, 81, 3, 18) was heated under reflux with a slight excess of finely powdered sodamide until evolution of ammonia had ceased. After cooling, a large excess of an alkyl halide (2 mols.) was added, and the mixture heated again for 2 or 3 hours. The product was poured into iced water, and the toluene (or xylene) layer was collected, washed with water, and dried (Na_2SO_4). After removal of the solvent, the solid residue was crystallised several times from alcohol-benzene (yield, 40—60%). As a rule, the *N*-alkyl-1 : 2-benzcarbazoles were much more soluble in benzene than the non-alkylated product, and like the latter, gave with sulphuric acid a yellow coloration which rapidly became greenish-blue by oxidation in air. The deep red picrates and 1 : 3 : 5-trinitrobenzene complexes were very sparingly soluble in alcohol. The new compounds are listed below:

	Crystal form.	M. p.	Formula.	N, %.	
				Found.	Required.
1 : 2-Benzcarbazoles.					
<i>N</i> -Methyl	Yellowish glinting prisms	168°	$C_{17}H_{13}N$	5.8	6.0
<i>N</i> -Ethyl	Long needles	146	$C_{18}H_{15}N$	5.4	5.7
<i>N</i> -Propyl	Glistening plates	90	$C_{19}H_{17}N$	5.3	5.4
Picrates.					
<i>N</i> -Methyl	Brown-red silky needles	162			
<i>N</i> -Ethyl	Deep reddish-brown prisms	135			
<i>N</i> -Propyl	Short brown needles	106			
1 : 3 : 5-Trinitrobenzene complexes.					
1 : 2-Benzcarbazole	Blood-red needles	190			
<i>N</i> -Methyl	Clumps of red silky needles	187			
<i>N</i> -Ethyl	Vermilion-red needles	157			
<i>N</i> -Propyl	Long silky needles	125			

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