ATTEMPTS TO PREPARE OPTICALLY ACTIVE TRIVALENT NITROGEN COMPOUNDS.

SYNTHESIS OF 8:9-PHENYLENECARBAZOLE AND DERIVATIVES.

- THESIS -

presented by Helen Greig Dunlop, B.Sc., for the degree of Doctor of Philosophy in the Faculty of Science, University of Glasgow.

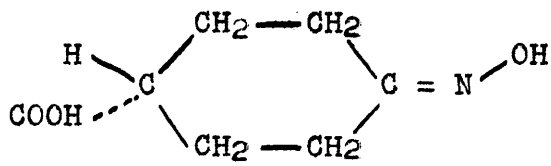
May 1936.

ProQuest LLC.
789 East Eisenhower Parkway
P.O. Box 1346
Ann Arbor, MI 48106 – 1346

The author wishes to express her gratitude to Dr. S. Horwood Tucker for his constant guidance and encouragement, and to the Carnegie Trust, the Chemical Society and the Renfrewshire Education Committee for grants.

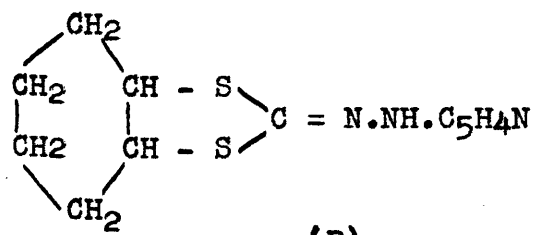
INDEX.

The Hantzsch-Werner hypothesis, that the valencies of the doubly linked trivalent nitrogen atom do not lie in one plane, but are directed along the three edges of a trihedral angle, has been fully substantiated in recent years by the researches of Mills and his co-workers. They have shown that, because of this non-planar configuration of the nitrogen valencies, the oxime (A), phenyl hydrazone and semicarbazone of a compound such as cyclohexanone-4-carboxylic acid can be isolated in optically active forms. (1) (2).

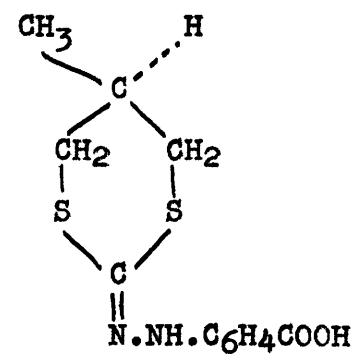


(A)

They have further extended the work and resolved the pyridyl-hydrazone of cyclohexylene dithiolcarbonate (B) (3), and the o-carboxyphenylhydrazone of β-methyltrimethylene dithiol-carbonate (C) (4).



(B)

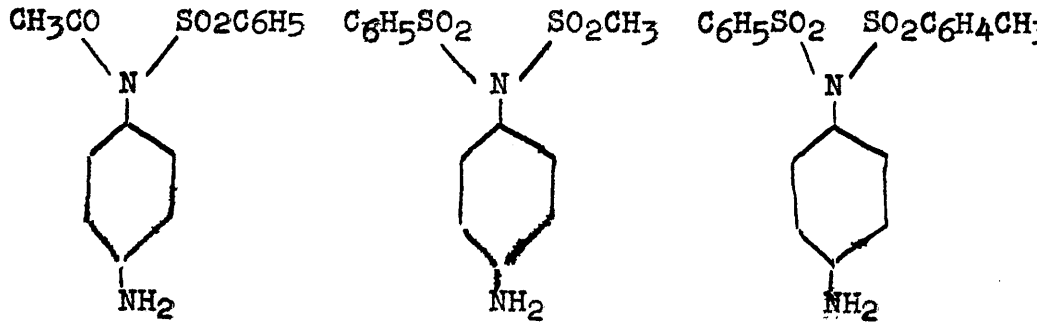


(C)

The applicability of the above hypothesis to compounds in

which three separate groups are attached to the nitrogen atom is open to some doubt. In 1924, Meisenheimer (5), after having critically reviewed, (6) (7) (8), the attempts to resolve compounds of the type Nabc, came to the conclusion that in compounds of this type, if the valencies are non-planar, the one form changes into its enantiomorph so readily that isomerism can only be detected under exceptional circumstances, such as when the nitrogen is linked into a multiple ring system in a special way.

Recently Schreiber and Schriner (9) investigated the possibility that the presence of heavy negative groups attached to the nitrogen atom might be effective in preventing racemisation, and thus allow the isolation of the optically active forms. They therefore attempted to resolve compounds such as (D) (E) and (F) below,

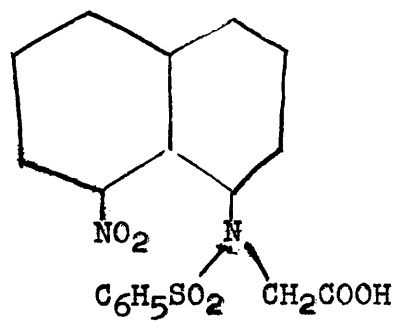


(D) (E) (F)

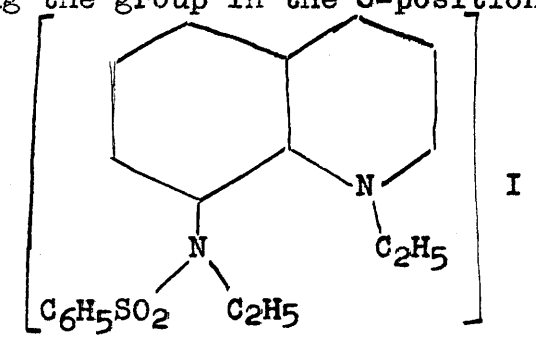
but the mutarotation of the solutions of the salts which these formed with d-camphor-10-sulphonic acid was traced to an equilibrium between the salt and a compound of the ketimine

type, formed by a reaction between the ketone group of the camphor-10-sulphonic acid and the primary amine.

In recent years compounds of the type Nabc, such as the benzenesulphonyl derivative of 8-nitro-1-naphthyl glycine (G), and 8-benzenesulphonylethylamino-1-ethylquinolonium iodide (H) have been resolved by Mills and his collaborators, (10) (11), but they have shown that in these cases asymmetry is due to restricted rotation of the complex radicles about the C-N bond, the obstruction being the group in the 8-position.



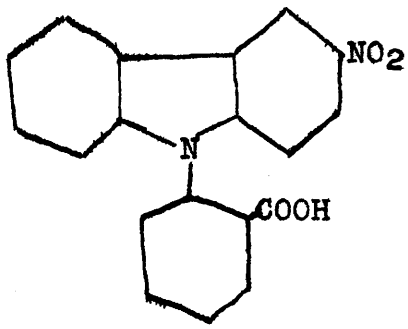
(G)



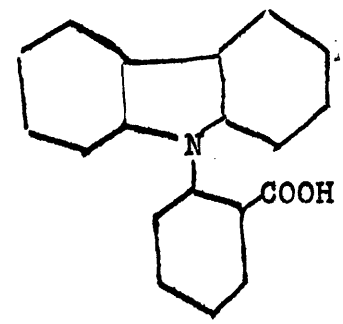
(H)

Substituted N-phenylpyrroles (12), N-N'-dipyrryls (13), and N-2'-carboxyphenyl-3-nitrocarbazole (14) have also been resolved, but in these cases too the evidence points to the asymmetry being dependent on restricted rotation due to the ortho substituents. For example, in the case of the last mentioned substance (J) (see page 4), if the rotation of the ortho substituted phenyl group attached to the pyrrole nitrogen atom is restricted by the two benzenoid rings, (J) should then give two stereoisomeric forms and might be resolvable, but (K),

which under these circumstances has a plane of symmetry, should not be resolvable. If however the asymmetry is due to the pyrrole nitrogen atom, then both (J) and (K) should be capable of resolution. Actually it has been found (14) that (J) but not (K) could be resolved.

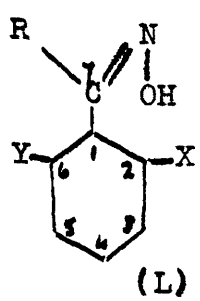


(J)

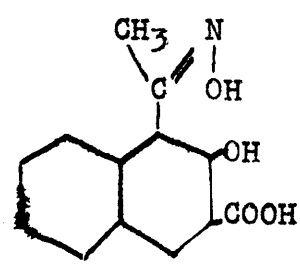


(K)

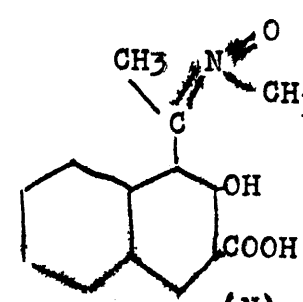
This theory of restricted rotation has been used by Meisenheimer, Theilacker and Beiswinger (15) to obtain further confirmation of the Hantzsch-Werner hypothesis, since if both hypotheses are true, a β-oxime of the type (L) should be resolvable, provided X and Y are sufficiently large to prevent rotation of the R.C:NOH about the axis C_1-C_7. The simple oxime (M) was not isolated in optically active form, but α-2-hydroxy-3-carboxy-1-naphthylmethylketoxime N-methyl ether (N) was successfully resolved.



(L)

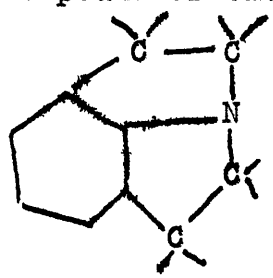


(M)

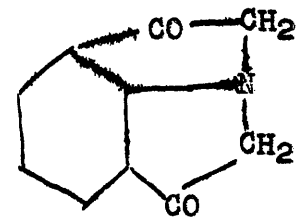


(N)

In 1928, Jackson and Kenner (16) reviewed the evidence in favour of a non-planar structure for trivalent nitrogen of the type Nabc, and considered that '' in general the non-planar readily passes into a planar form, from which the original or its enantiomorph may be regenerated, or else the normal configuration is plane''. They considered that positive evidence for this would be supplied by the formation of a compound in which the nitrogen atom is common to two ring structures which are at the same time plane and co-planar. Assuming (1) the Kekulé formula for benzene, and (2) the plane configuration of five membered ring structures, they sought a compound of the type (O), such as (P).

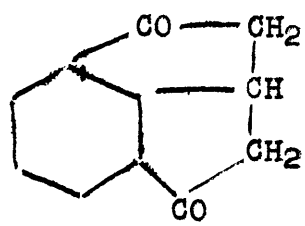


(O)



(P)

To test the validity of the former assumption (1) they attempted to prepare the compound (Q) analogous with (P), with carbon, whose stereochemical relationships are known to be closely similar to those postulated for nitrogen by the Hantzsch-Werner hypothesis, replacing nitrogen.



(Q)

No evidence of the formation of such a compound (Q) could be found. The authors therefore concluded that their assumption (1) was valid, and suggested that the non-existence of (Q) supported their contention that ''two five membered rings associated with a benzene nucleus in the manner contemplated must be co-planar''.

With regard to the formation of the nitrogen compound (P), only a minute quantity of a substance with constitution $C_{10}H_{10}O_2N_2$ was isolated from the fusion of sodium indoxyl-acetate with sodamide. This substance could only be isolated when the product was treated with methyl sulphate, although the authors seem to indicate that it had no specific action. They refer to this substance as ''a compound of the desired composition'', though clearly the composition of the compound (P) which they sought is $C_{10}H_7O_2N$. Private communications from Kenner and Jackson do not elucidate this discrepancy, which they admit.

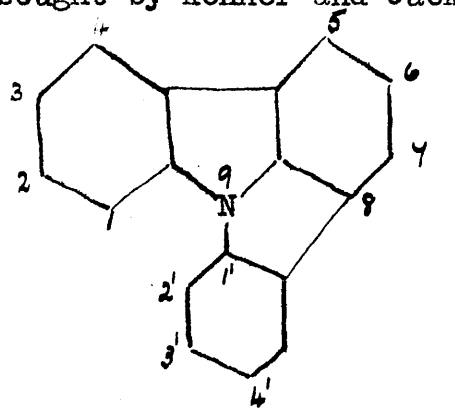
The authors suggest (16) that a possible explanation of their lack of success in isolating (P) in quantity, is that a valency angle of 120° in the case of nitrogen might be great enough to inhibit the formation of the ring system, and that ''though the outcome of the experimental work now described is thus in some respects indefinite, the mode of approaching the main problem on which it is based is not without value''.

In view of the non-formation of (P) it seems to us that

the non-existence of (Q) is no positive evidence for the assumption that the five membered ring structures are necessarily co-planar in a compound of the type (O), and as the authors produce no other evidence we consider the matter open to question.

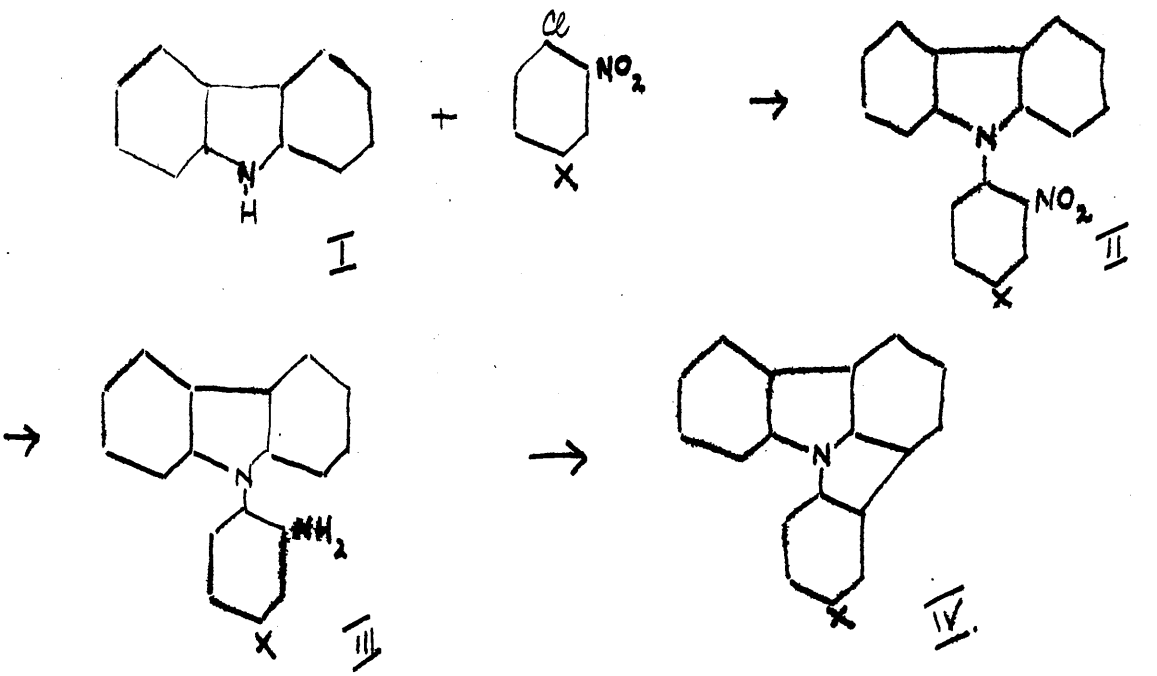
8:9-Phenylenecarbazole.

A compound such as (S), 8:9-phenylenecarbazole, is also of the type (O) sought by Kenner and Jackson, (see page 5).

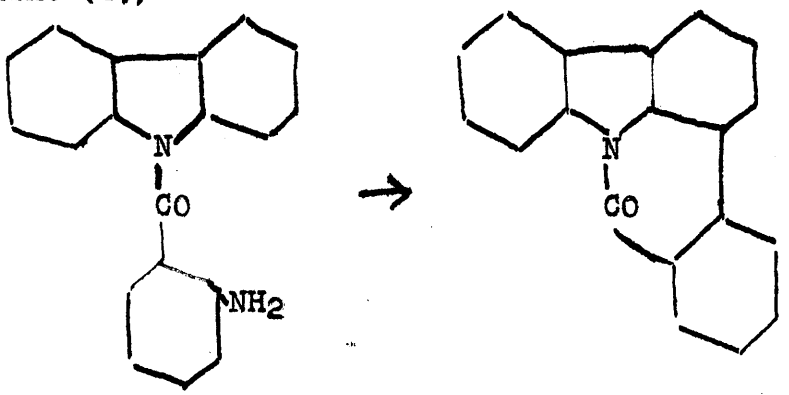


(S).

The synthesis of this compound was therefore attempted according to the following scheme:- (X = H).



Plant and Tomlinson (17) prepared 19-ketophenanthridine-docoline (T),



(T)

from N-o-aminobenzoylcarbazole by decomposing the diazonium sulphate solution of the amine in presence of methyl alcohol, but when N-2'-aminophenylcarbazole was treated in a similar manner only N-phenylcarbazole resulted. However replacement of the methyl alcohol with glacial acetic acid yielded in good amount a colourless crystalline compound of m.p. 40° above that of N-phenylcarbazole. Molecular weight determinations and analyses of the compound, its picrate and its trinitrobenzene derivative, all point to it being 8:9-phenylenecarbazole. The compound sublimes unchanged at 230°/15mm. and is quite stable.

A study of the structure of 8:9-phenylenecarbazole on models suggests that the least strained configuration is one in which the two five membered rings are not co-planar, (dee stereoscopic photographs on page 64), and we are therefore inclined to doubt the validity of Jackson and Kenner's assumption (2),

and to believe that this is a compound of the type suggested by Meisenheimer (5) (see page 2), in which the nitrogen valencies are linked into a multiple ring system so that they are held in a non-planar position.

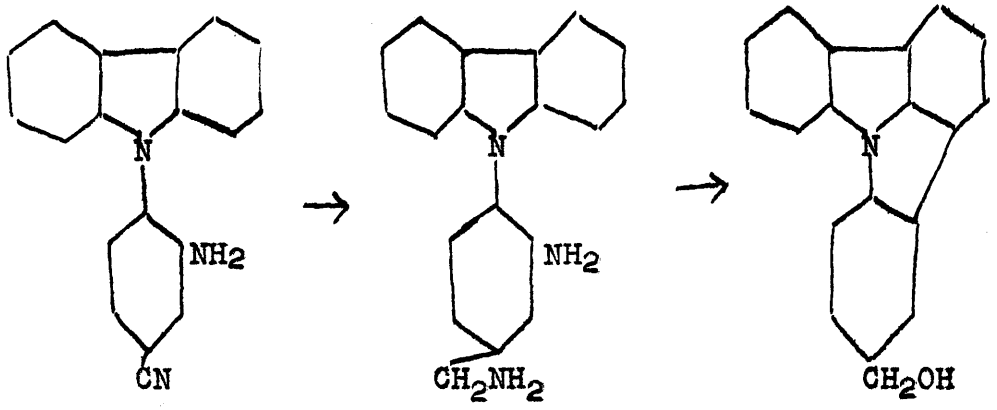
If this is so, mono-substituted derivatives of 8:9-phenylene-carbazole (except the derivatives in the 6-position, (see page 7), which have a plane of symmetry) should be capable of resolution.

The synthesis of 4'-carboxy-8:9-phenylenecarbazole, which should on our assumption be asymmetric, (see photographs, page 66) was therefore attempted according to the method found for the parent substance.

Commencing with 4-chloro-3-nitrobenzonitrile (X = CN) (see page 7) III to IV failed to give 4'-cyano-8:9-phenylene-carbazole, but the acid was eventually obtained by carrying the synthesis to stage III (X = CN), and hydrolysing this compound to N-2'-amino-4'-carboxyphenylcarbazole. When nitro-benzene was added to the diazonium sulphate solution of this compound before decomposition, 4'-carboxy-8:9-phenylenecarbazole was isolated. In the absence of nitrobenzene only brown insoluble products were obtained. The yield was very poor in the final stage of the synthesis, and another method of preparation was essential to allow of the substance being obtained in quantities sufficient for the work of resolution.

Attempts to reduce N-2'-amino-4'-cyanophenylcarbazole to

N-2'-amino-4'-aminomethylphenylcarbazole, from which 4'-hydroxymethyl-8:9-phenylenecarbazole (see below) might have been prepared, were completely unsuccessful.



4'-Acetyl-8:9-phenylenecarbazole (X = $COCH_3$) could not be prepared owing to failure to condense carbazole with 4-chloro-3-nitroacetophenone in presence of anhydrous potassium carbonate. At relatively low temperatures the last two substances formed a black insoluble product. The bromo- and iodo- compounds reacted similarly, and the same effect was produced using potassium carbazole.

4'-Methyl-8:9-phenylenecarbazole (X = CH_3) was prepared in fairly good yield, but efforts to oxidise the methyl to a carboxyl group were entirely unsuccessful with this compound and with the comparable N-4'-methylphenylcarbazole. It is significant, however, that no method of oxidising a methyl carbazole to the corresponding carboxy carbazole has yet been described.

Efforts to prepare 4'-chloro-8:9-phenylenecarbazole (X = Cl) met with little success. A minute quantity of a halogen-containing substance, which differed from N-4'-chlorophenyl-carbazole, was isolated.

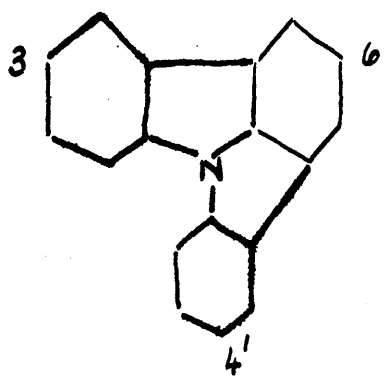
4'-Nitro-8:9-phenylenecarbazole (X = NO_2) could not be prepared owing to the fact that on partial reduction of N-2'-4'-dinitrophenylcarbazole (II to III, see page 7) it is the 4'- nitro, and not the 2'- nitro group, which is preferentially reduced. Elimination of the amino group from the nitro amine formed yielded N-2'-nitrophenylcarbazole. This result is in agreement with the findings of Storrie and Tucker (18). They have shown that on partial reduction of N-2:4-dinitro-methyldiphenylamine it is the 4- nitro group which is reduced, whereas with the unalkylated compound, 2:4-dinitrodiphenylamine, the 2- nitro group is preferentially reduced. They suggested that this is a steric effect due to the presence of the alkyl group, and it was deduced, as has been found above, that other N substituted compounds would behave similarly.

Synthetic methods having failed to yield 4'-carboxy-8:9-phenylenecarbazole in good amount, attempts were made to prepare it by direct substitution in 8:9-phenylenecarbazole. Chlorination experiments failed, and iodination in presence of nitric acid gave a trinitro-iodo compound. Bromination however was effected - both the mono- and dibromo- compounds

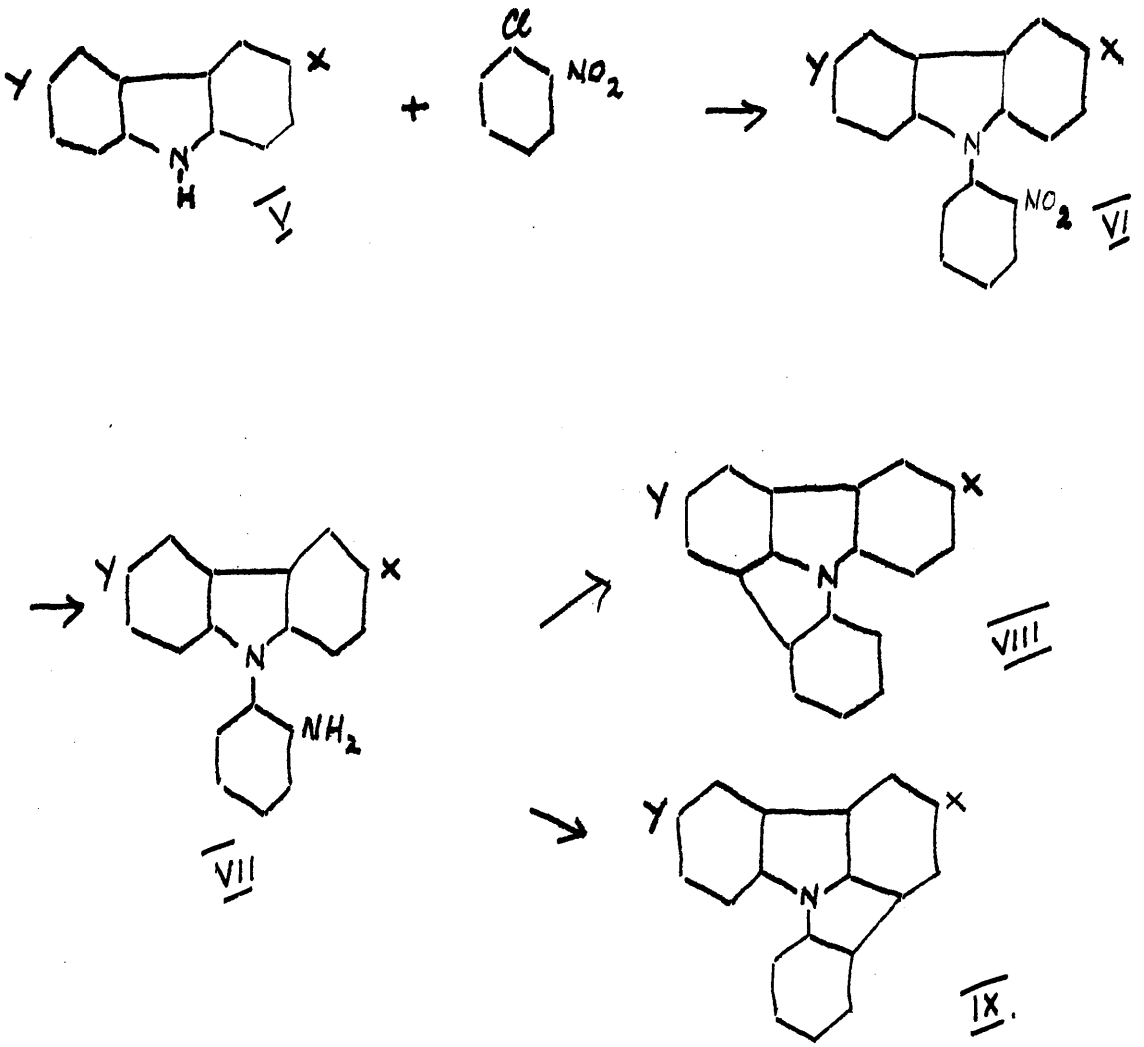
being isolated. The mono- halogen derivative, however, could not be induced to react with magnesium to form a Grignard compound from which the acid might have been prepared by the action of carbon dioxide.

The method found by Dr. S. H. Tucker (unpublished work) for the preparation of 3-carboxycarbazole by the action of trichloracetonitrile, aluminium chloride, and dry hydrogen chloride in presence of a suitable solvent, was therefore employed in an attempt to introduce a carboxyl group into 8:9-phenylenecarbazole. A monocarboxy acid m.p. 305°, which is 35° below that of 4'-carboxy-8:9-phenylenecarbazole, resulted. This substance appeared to be more acidic than 4'-carboxy-8:9-phenylenecarbazole, and it was more easily decarboxylated.

Since in the carbazole molecule substitution takes place most readily in the 3- position, it seems probable that a substituent group entering the 8:9-phenylenecarbazole molecule will take the 6- position, which is the active position common to the two carbazole structures (see below), rather than the 3 (or 4') position.



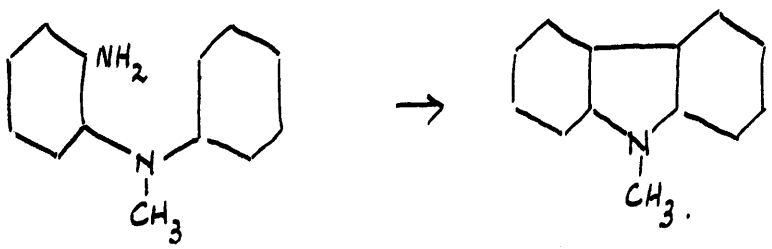
In view of these results a further attempt was made to prepare 4'-carboxy-8:9-phenylenecarbazole by synthesis, according to the following scheme:-



In this synthesis there are two possible end products as shown. The synthesis was carried out using 3-carbethoxycarbazole V (Y =H) (X = $COOC_2H_5$), and on hydrolysis of the product, an acid was isolated which was different from 4'-carboxy-8:9-phenylene-carbazole VIII, but identical with the acid obtained by direct

substitution of 8:9-phenylenecarbazole. This is therefore 6-carboxy-8:9-phenylenecarbazole IX (see previous page, X = COOH, Y = H). This compound however has a plane of symmetry, (see page 9), and therefore will not be optically active. In view of these results, it seems that, for purposes of resolution, a substituted derivative of 6-carboxy-8:9-phenylenecarbazole will be a more readily accessible compound than 4'-carboxy-8:9-phenylenecarbazole. This may be obtained by introducing a substituent directly into 6-carboxy-8:9-phenylenecarbazole or, since the stage VII to IX (see previous page) proceeded successfully (X = $COOC_2H_5$, Y = H), by synthesis from 3-6-dicarbethoxycarbazole V (see previous page, X = Y = $COOC_2H_5$).

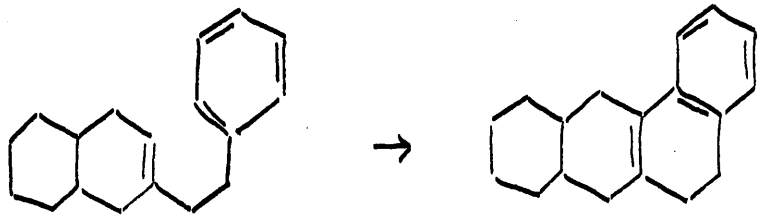
The possibility of preparing 8:9-phenylenecarbazole and its derivatives by other methods has also been considered. Storrie and Tucker (18) converted o-amino-N-methyldiphenylamine into N-methylcarbazole,



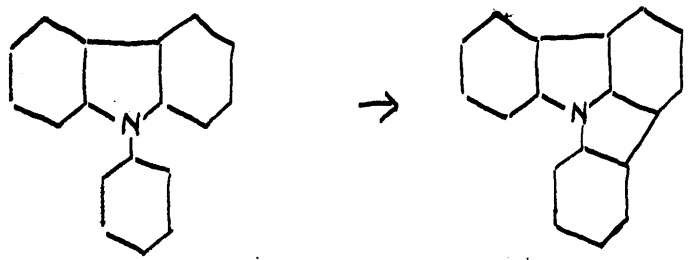
by warming the diazonium sulphate solution of the amine with dilute sodium hydroxide solution. When N-2'-aminophenylcarbazole

III (see page 7, X ≠ H) or its 4'- derivatives were treated in a similar manner unworkable tars resulted.

The formation of dodecahydro-1:2-benzanthracene from 2-β-phenyl-$\Delta^{2:3}$-ethyloctalin

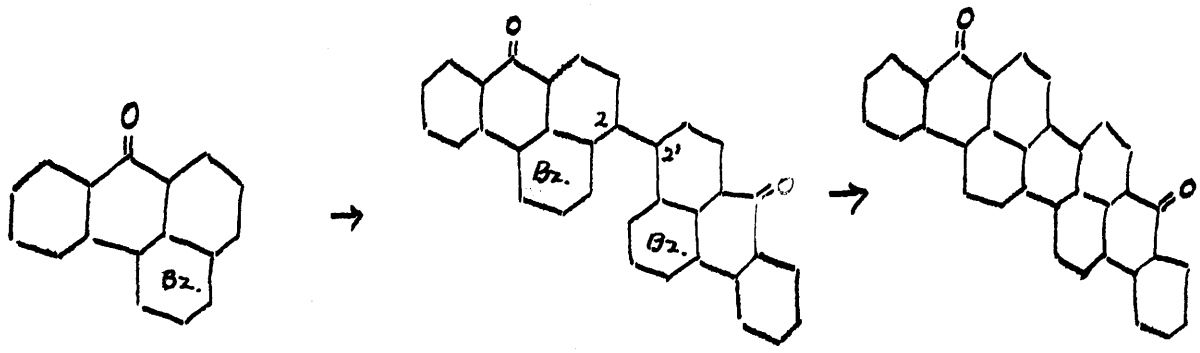


by the action of aluminium chloride in carbon disulphide solution (19) suggested that in like manner 8:9-phenylene-carbazole might be prepared from N-phenylcarbazole.



The N-phenylcarbazole was recovered unchanged from the carbon disulphide, and when anhydrous ether, in which the aluminium chloride is soluble, was used as a solvent the same result was obtained. When nitrobenzene was employed a black tar resulted.

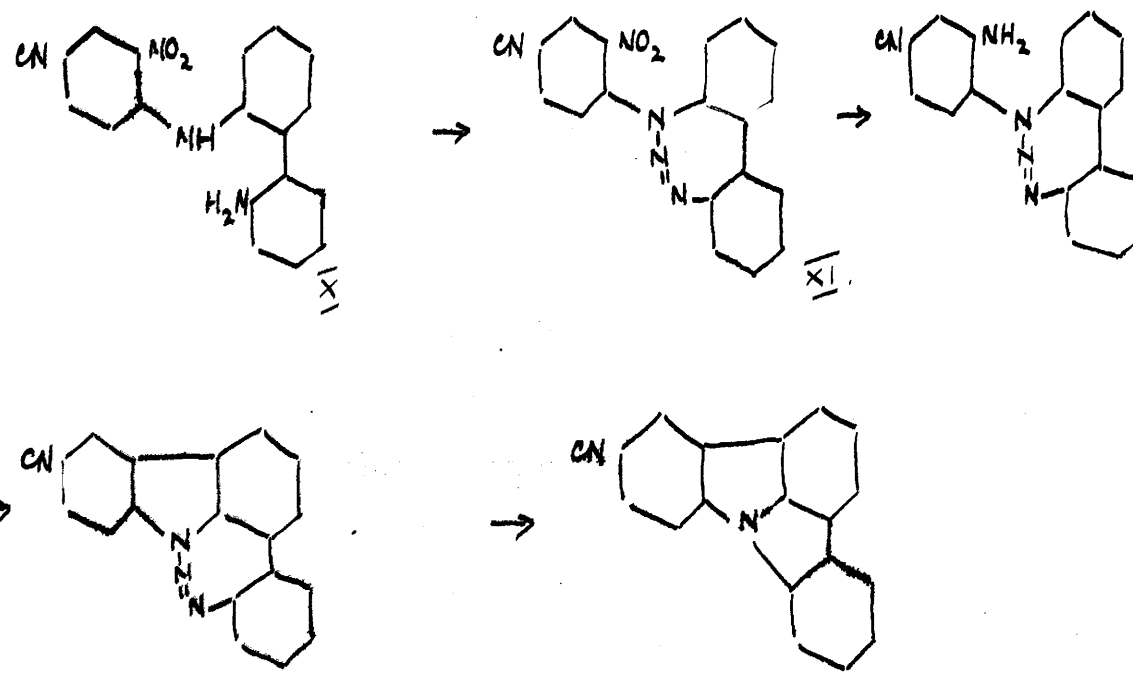
The formation of dibenzanthrones from benzanthrone through the 2-2'-dibenzanthronyl (20) (see following page) suggested that ring closure of N-phenylcarbazole might be effected by potash fusion.



Benzanthrone. 2-2'-Dibenzanthronyl. Dibenzanthrone.

Attempts were made using N-4'-methylphenylcarbazole, but in vain.

Since a supply of 2-(2''-nitro-4''-cyanophenylamino)-2'- amino-diphenyl (21) (X below) was available, a synthesis of 4'-cyano-8:9-phenylenecarbazole seemed possible if a triazole compound 1-(2-nitro-4-cyanophenyl)-diphenyltriazole (XI below) could be formed from it.



The substance isolated in the first stage of the synthesis, contained only 75% of the nitrogen required for 1-(nitro-4-cyanophenyl)-diphenyltriazole. The percentage of nitrogen found agreed with that required for the corresponding carboxy compound, but the substance showed no acidic properties. The proposed synthesis was abandoned.

In the determination of the constitution of the various 8:9-phenylenecarbazole compounds prepared, it was desirable to prepare the corresponding N-phenylcarbazole derivatives for purposes of comparison, since these differ in constitution by only two hydrogen atoms. The method employed hitherto for preparing compounds of the latter type necessitated the use of potassium carbazole (22), or condensation in nitrobenzene in presence of potassium hydroxide (23) (24). It has now been found that iodo compounds, (p-iodo--benzene, -toluene, -chloro-benzene, -ethylbenzoate), condense readily with carbazole in presence of anhydrous potassium carbonate and a trace of copper bronze. When a suitable group is present to activate the halogen, chloro compounds, (o-nitrochlorobenzene, 1:4-dichloro-2-nitrobenzene, 4-chloro-3-nitrobenzonitrile and 1-chloro-2:4-dinitrobenzene), condense with carbazole in presence of anhydrous potassium carbonate. N-Benzoyl carbazole (cf. (25) (26)) can be readily prepared in a similar manner.

The presence of copper bronze in small quantity in the condensations of carbazole with the various halogen compounds used in the course of the work has been examined. Its presence has been beneficial to varying extents in all cases except those of 1-chloro-2:4-dinitrobenzene and 4-chloro-3-nitrobenzonitrile. In the former case it seems to have no effect, but in the latter case the effect is definitely detrimental, and an unworkable tar results from the presence of copper. The beneficial effect is greatest in the case of o-nitrochlorobenzene, when the presence of 0.2-0.3 g. of copper bronze increases the yield of product from 10% to 50-60%. This seemed to be the optimum amount of copper in each case. Copper has already been used in analogous reactions by Cassella (22), and Rule and Turner (27) have also employed it in the reactions between the halogen atom of 8-bromo-1-naphthoic acid and various compounds. They describe the action as catalytic, and indeed it seems to be so in the condensations described in the course of this work, since it is recovered unchanged from the reaction products.

Brewin and Turner (28) found that 4-chloro-3-nitrobenzonitrile and 1-chloro-2:4-dinitrobenzene have practically equal reactivity towards piperidine. Dunlop, Macrae, and Tucker (21) found that the former was less reactive than the latter

towards 2-2'-diaminodiphenyl. This has also been found to be so in their reactions with carbazole, for whereas N-2:4-dinitrophenylcarbazole is formed at 170-180° in 50% yield, N-2'-nitro-4'-cyanophenylcarbazole requires a temperature of 180-190° and is obtained in only 40% yield. This adds weight to the suggestion (21) that towards piperidine the reactivities are different, but that the velocity of this reaction is too great to allow this difference to be measured.

In the course of the work a quantity of 3-carbethoxycarbazole was required (see page 13). Plant and Williams (29) found that on heating with aluminium chloride, N-acetyl carbazole was converted into 3-acetyl carbazole. Later (30) they found that the reaction is best carried out in nitrobenzene, and Meitzner (31) has recently improved the method slightly. It was therefore hoped that a similar migration of the carbethoxy group of N-carbethoxycarbazole might take place under similar circumstances. However it was found that at 100° no migration occurred, and at higher temperatures a black insoluble product was formed.

EXPERIMENTAL.

Note. Footnotes (numbered in red) are given immediately after the preparation with which they deal. Compounds which are not described in the literature are typed in red and underlined.

EXPERIMENTAL.

SYNTHESIS OF 8:9-PHENYLENECARBAZOLE.

N-2'-Nitrophenylcarbazole:- A mixture of carbazole (20 g.), o-nitrochlorobenzene (40 g.), anhydrous potassium carbonate (20 g.), and copper bronze[1] (0.2-0.3 g.) was boiled gently with frequent shaking for 3[2] hours, and then steam distilled to remove the excess of o-nitrochlorobenzene. The brown residue was dissolved in acetic acid, (250 c.c.: charcoal), and the product therefrom extracted several times with alcohol. The first extract contained a small amount of carbazole. N-2'-nitrophenylcarbazole crystallised in yellow needles m.p. 153-156° from the other extracts. (15-18 g.: yield 50-60%). cf. (32). The improved yield is due entirely to the addition of copper bronze.

(1) 0.3 g. is the optimum quantity of copper bronze. Replacement of the potassium carbonate with copper (1 g.) gave an unworkable tarry product.

(2) 3 hours is the optimum period of heating: 2 hours yielded much unchanged carbazole and 4 hours a tarry product.

N-2'-Aminophenylcarbazole:- The above nitro compound can be reduced simply by boiling with tin and hydrochloric acid, but this is a slow process, or

(I). The nitro compound (10 g.), stannous chloride (40 g.), and glacial acetic acid saturated with dry hydrogen chloride (150 c.c.) were boiled together. The colour of the solution

changed to green almost immediately. After pouring into a large excess of sodium hydroxide solution the product was filtered. The solid matter was extracted with benzene, and when the extract was dried and concentrated almost to dry--ness, N-2'-aminophenylcarbazole crystallised out. Recryst--allisation from alcohol (charcoal) yielded colourless crystals, m.p. 117-119°. (7g.: yield 75%). (Found N, 10.72; $C_{18}H_{14}N_2$ requires N, 10.85%).

(II). N-2'-Nitrophenylcarbazole (10g.) was dissolved in glacial acetic acid (50 c.c.) and tin was added to the hot solution. After the first vigorous reaction had subsided, concentrated hydrochloric acid (25 c.c.) was added and the mixture boiled until the solution became faintly yellow (10 minutes). It was then decanted from the tin into hot concentrated potassium hydroxide solution and cooled. The crystalline product was dissolved in ligroin, from which pink crystals separated after the mother liquor had been poured off from a small amount af oil. On sublimation these crystals gave a white powder which crystallised from alcohol m.p. 119-121° corr. (4.5g.: yield 50%).

8:9-Phenylenecarbazole:- N-2'-Aminophenylcarbazole (5 g.) was dissolved in glacial acetic acid (50 c.c.), and concentrated sulphuric acid (11 c.c.) was added. The solution was diazotised at 0° with sodium nitrite[1] solution (1.35g. in 30 cc. water). After standing for a short time, the deep red solution was

boiled gently[2] for ½ hour, and a reddish brown crystalline solid separated. Recrystallisation from alcohol[3] (charcoal) yielded colourless silky needles m.p. 135-137°. (2.6 g.: yield 56%). (Found; C, 89.66; H, 4.73; N, 5.97; M.W. (Rast's method) 248. $C_{18}H_{11}N$ requires C, 89.63; H, 4.56; N, 5.81%; M.W. 241).

(1). Excess of sodium nitrite gave a diminished yield.

(2). Heating may be carried out on the water bath, but the reaction is slower and the yield is not improved. Vigorous boiling caused the formation of a tarry product.

(3). A quicker and more efficient way of purifying small quantities of the substance is that of sublimation (250°/15mm.). The substance crystallises also from acetic acid and from acetic anhydride, but the latter should not be used with very crude material. It is very soluble in cold benzene and carbon tetrachloride, and sparingly soluble in ligroin.

Picrate of 8:9-Phenylenecarbazole:- This was prepared by dissolving equal weights of the component substances in ether, and mixing the solutions. Red needles, which crystallised from acetic acid, were obtained, m.p. 165-169° with preliminary softening. (Found; C, 61.31; H, 3.03; N, 11.74; $C_{18}H_{11}N.C_6H_3O_7N_3$ requires C, 61.28; H, 2.98; N, 11.91%).

Trinitrobenzene compound of 8:9-phenylenecarbazole:- This was prepared in alcoholic solution, and crystallised from acetic acid solution in long yellow needles m.p. 192-194°. (Found;

C, 63.54; H, 3.17; N, 12.43. $C_{18}H_{11}N$. $C_6H_3O_6N_3$ requires C, 63.44; H, 3.08; N, 12.33%).

N-Phenylcarbazole:- A mixture of carbazole (5 g.), iodobenzene (12 g.), anhydrous potassium carbonate (5 g.), and copper bronze (0.3 g.) was heated in an air bath at 190-200° for 6 hours. On cooling the product was washed with warm water, and the residue crystallised from alcohol in colourless crystals m.p.91-93° after 3 crystallisations. (4.5 g.: yield 65%). (cf. (22) (24) (33)).

Trinitrobenzene compound of N-phenylcarbazole:- This was prepared in alcoholic solution and crystallised from alcohol, and then from acetic acid in orange needles m.p. 132-134°. (Found; N, 12.13; $C_{18}H_{13}N$. $C_6H_3O_6N_3$ requires N, 12.28%).

SYNTHESIS OF 4'-CARBOXY-8:9-PHENYLENECARBAZOLE.

4-Chloro-3-nitrobenzonitrile was prepared by Mattaar's method (34) slightly modified. p-Chloraniline gave p-chlorobenzonitrile in 65-70% yield. The latter (10 g.) was added to fuming nitric acid (50 c.c.: d 1.51). Heat was evolved, and the solution was poured into water after 20 minutes. Pure 4-chloro-3-nitrobenzonitrile was precipitated in theoretical yield. m.p. after crystallisation from alcohol 101°. (Mattaar gives 110°).

N-2-Nitro-4'-cyanophenylcarbazole:- A mixture of carbazole (10 g.), 4-chloro-3-nitrobenzonitrile (25 g.), and anhydrous potassium carbonate (10 g.) was heated in an oil bath at 180-190° for 12 hours with frequent shaking, and on cooling

was extracted with acetic acid (charcoal). The product which crystallised therefrom contained carbazole and 4-chloro-3-nitrobenzonitrile. Washing with warm alcohol removed the latter, and the residue was crystallised from xylene and then from acetic anhydride. Most of the carbazole remained in solution in these solvents. (7.5 g. : yield 40%). N-2'-nitro-4'-cyanophenylcarbazole crystallises from alcohol in small yellow needles, s.p. 155-160°, m.p. 171-173°. From acetic anhydride, anisole and xylene however it crystallises in clusters of needles, m.p. 172-174° without preliminary softening. (Found, C, 72.95; H, 3.44; N, 13.32. $C_{19}H_{11}O_2N_3$ requires C, 72.48; H, 3.51; N, 13.42%).

The addition of copper-bronze was found to be detrimental to the condensation.

(1) When potassium carbonate was replaced by barium carbonate no condensation took place. cf. (35).

(2) Temperature 190-200° gave a tarry product, and above 200° the reaction was violent and only a charred mass resulted.

(3) Heating for 18 hours gave a tar.

N-2'-Amino-4'-cyanophenylcarbazole:- The above nitro-compound (5 g.), stannous chloride (25 g.), and glacial acetic acid saturated with dry hydrogen chloride (100 c.c.) were boiled together. The colour of the solution changed almost immediately to brownish green and was then poured into a large excess of cold concentrated sodium hydroxide solution. The white solid

thus obtained was filtered and crystallised from alcohol. Colourless plate crystals, m.p. 186-188°. (3 g, : yield 70%). (Found, N, 14.75; $C_{19}H_{13}N_3$ requires N, 14.84%).

The acetyl derivative of N-2'-amino-4'-cyanophenylcarbazole, which was formed by boiling the amine with acetic anhydride for a few minutes, crystallised from methyl alcohol in nacreous plate crystals, m.p. 241-243°.

Attempted preparation of 4'-cyano-8:9-phenylenecarbazole. The above amine (1 g.) was dissolved in glacial acetic acid (10 c.c.), and concentrated sulphuric acid (2.2 c.c.), and after cooling in ice the solution was diazotised with sodium nitrite solution (0.25 g. in 5 c.c. water). After standing for a short time the deep red solution was gently boiled. A brown solid separated and was extracted with alcohol. Attempts to purify the substance by treatment with animal charcoal failed owing to the adsorption of the compound by the charcoal. Efforts to crystallise the original brown solid from various solvents were unsuccessful. The solid was sublimed with difficulty. The pink sublimate was resublimed and the pale yellow product crystallised from alcohol m.p. 186-196°. Only a minute quantity of this pro-duct was isolated.

<u>N-2'-Amino-4'-carboxyphenylcarbazole hydrochloride</u>:- N-2'-Amino-4'-cyanophenylcarbazole (4.2 g.) was boiled for 1 hour with a mixture of glacial acetic acid (30 c.c.) and concen-

trated hydrochloric acid (75 c.c.). A crystalline solid separated m.p. 210-220°. Attempts to further purify the substance met with no success.

On the addition of sodium hydroxide to a slightly acid solution of the substance in water, a white precipitate of N-2'-amino-4'-carboxyphenylcarbazole was formed when the solution was just acid, and this redissolved when the solution was made alkaline.

4'-Carboxy-8:9-phenylenecarbazole:- The above hydrochloride (1.5 g.) dissolved in glacial acetic acid (11.4 c.c.) and concentrated sulphuric acid (2.5 c.c.) was cooled in ice. The solution was diazotised with sodium nitrite solution (0.307 g.) in water (7 c.c.), and after standing for a few minutes it was gently boiled. A colourless compound seemed to be formed in the course of the decomposition, but it was quickly changed into a brown compound. This substance could not be crystallised. It was soluble in alkali, but attempts to purify it by repeated solution in alkali and precipitation with acid were unsuccessful.

The above procedure was therefore repeated, ligroin (80-100°) (150 c.c.) being added to the diazonium solution before heating, in an attempt to isolate the first product formed. The ligroin was separated off and concentrated almost to dryness. A minute quantity of a brownish substance which crystallised from nitrobenzene, m.p. above 280°, was obtained.

Using 3 g. of N-2'-amino-4'-carboxyphenylcarbazole hydro--chloride the method was repeated, the ligroin being replaced by nitrobenzene (25 c.c. redistilled). The mixture was heated for 10 minutes and then allowed to cool. A brownish-white crystalline solid, soluble in ammonia and reprecipit--ated on acidification, separated. (0,45 g. : yield 18%). Crystallisation from nitrobenzene or glycol monomethyl ether did not remove the brown colouration. The acid sublimed without decomposition at 300-350°/15 mm. and crystallisation thereafter yielded pink prisms m.p. 340° (blackening 320°). (Found, C, 79.99; H, 3.94. $C_{19}H_{11}O_2N$ requires C, 80.00; H, 3.86%).

Esterification of 4'carboxy-8:9-phenylenecarbazole.

The above acid was boiled for 12 hours with excess of specially dried methyl alcohol containing dry hydrogen chloride. The residual solid and the product obtained by pouring the alcohol solution into water were quite insoluble in ammonia. Repeated crystallisation from aqueous dioxane gave a faintly pink product, m.p. 155-162°.

Decarboxylation of 4'carboxy-8:9-phenylenecarbazole.

Attempts to decarboxylate the acid by boiling it with copper bronze in dry quinoline were quite unsuccessful, nor was it decarboxylated by heating to 300° with copper.

The acid was therefore mixed with copper-bronze and heated in a metal bath until it decomposed, and the product sublimed

on to a water cooled tube. The substance crystallised from alcohol in colourless silky needles m.p. 130°, and showed no depression of m.p. on admixture with 8:9-phenylene-carbazole. A trinitrobenzene derivative was readily formed, and it was identical with that formed by 8:9-phenylene-carbazole.

SYNTHESIS OF N-4'-CARBOXYPHENYLCARBAZOLE.

p-Iodobenzoic acid:- p-Iodotoluene (35 g.), glacial acetic acid (300 c.c.), and concentrated sulphuric acid (50 c.c.) in water (50 c.c.) were boiled together, and a solution of sodium dichromate (60 g.) in water (100 c.c.) was added during ½ hour with frequent shaking. The whole was then boiled for a further ½ hour. On cooling p-iodobenzoic acid separated. It was washed with water and crystallised from acetic acid, m.p. 265-266°. (25 g.: yield 63%). (cf. (36) (37)).

The acid was esterified by boiling for 12 hours with absolute alcohol into which dry hydrogen chloride had been passed. (38). Colourless liquid b.p. 157°/24 mm.

N-4'-Carbethoxyphenylcarbazole:- A mixture of carbazole (4 g.), p-iodoethyl benzoate (13 g.), anhydrous potassium carbonate (4 g.), and copper bronze (1) (0.15 g.) was heated in an air bath at 220-230° for 6 hours with frequent shaking. The excess p-iodoethyl benzoate was removed by steam distillation. The residue crystallised from alcohol in colourless glistening plates m.p. 97-100°. (6 g.: yield 80%).

(Found C, 79.96; H, 5.36; N, 4.5. $C_{21}H_{17}O_2N$ requires C, 80.0; H, 5.4; N, 4.44%).

(1). In the absence of copper bronze only a very small quantity of N-4'-carbethoxyphenylcarbazole was formed at the above temperature.

N-4'-Carboxyphenylcarbazole:- The above ester was boiled with alcoholic potassium hydroxide for 20 minutes, and the product was poured into dilute hydrochloric acid. The solid obtained crystallised from glacial acetic acid in colourless prisms, m.p. 215-219°. The substance was completely soluble in ammonia, but repeated crystallisation gave no sharper m.p. than that recorded. (Found:C, 79.3, H, 4.52. $C_{19}H_{13}O_2N$ requires C, 79.43, H, 4.53%).

Decarboxylation of N-4'-carboxyphenylcarbazole.

The acid was not decarboxylated by boiling with copper bronze in dry quinoline, nor on heating to 300° with copper bronze for 15 minutes. On heating with copper bronze to a much higher temperature however, decomposition took place, and the product sublimed on to a water cooled tube. The sublimate crystallised from alcohol m.p. 91-93° and showed no depression of m.p. on admixture with N-phenylcarbazole.

ATTEMPTS TO PREPARE N-2'-AMINO-4'-AMINOMETHYLPHENYLCARBAZOLE.

(1). N-2'-Amino-4'-cyanophenylcarbazole (1 g.) dissolved in glacial acetic acid saturated with dry hydrogen chloride (35 c.c.) was boiled with zinc dust for ½ hour, and then cooled and poured into concentrated sodium hydroxide solution. The only product isolated on crystallising the solid thus obtained was starting material.

(2). The above procedure was repeated, using stannous chloride (10 g.) in place of zinc dust, and boiling was continued for 1 hour. A result similar to that of (1) was obtained.

(3). cf. (39) To N-2'-amino-4'-cyanophenylcarbazole (1 g.) dissolved in methyl alcohol (boiling) (40 c.c.) magnesium (1.5-2 g.) was added. After boiling for 2 hours the solution was allowed to cool, and the white solid product was removed by filtration. Evaporation of the methyl alcohol yielded a white solid which was washed with very dilute hydrochloric acid. The residue crystallised from alcohol and was identical with the original material.

(4). To a solution of the above substance (2 g.) in boiling absolute alcohol (70 c.c.), sodium (2.5 g.) was added in small pieces. Boiling was continued for ½ hour and the cooled solution was then poured into water. Attempts to crystallise the gum-like product met with little success, so it was treated with acetic anhydride. The product therefrom was identical with N-2'-acetamino-4'-cyanophenylcarbazole, m.p.

241-243°. see page 26).

(5) The procedure in (4) was repeated using sodium (6 g.). On acetylating the product a crystalline solid m.p. 215°, which was not N-2'-acetamino-4'-cyanophenylcarbazole was obtained in very small amount.

(6). The procedure in (4) was repeated using n-butyl alcohol (30 c.c.) in place of ethyl alcohol. Much frothing occurred and a white solid separated. On treatment with water the solid matter dissolved, allowing the butyl alcohol to be separated off and concentrated almost to dryness. A small quantity of a tarry substance separated, but attempts to crystallise it failed.

(7). Palladium hydroxide (0.1 g.) was dissolved in glacial acetic acid (25 c.c.) and shaken with hydrogen until absorption was complete. N-2'-Amino-4'-cyanophenylcarbazole (2 g.) dissolved in glacial acetic acid (40 c.c.) was added to the colloidal palladium and shaken with hydrogen. The latter seemed to be absorbed during 2 days (the catalyst was reactivated after the first day's shaking). The palladium was removed, and the solution was concentrated to half bulk, and poured into water. Efforts to crystallise the product were unsuccessful, so it was sublimed under reduced pressure. The sublimate crystallised readily and was found to be identical with the original product.

ATTEMPTED SYNTHESIS OF N-2'-NITRO-4'-ACETYLPHENYLCARBAZOLE.

p-Chloroacetophenone (40) was prepared from chlorobenzene using 1/5 of the quantities recommended. (30 g.: Yield 50% calculated on the acetic anhydride used). The authors claim to obtain 285-300 g. product from 281 g. (2½ mols.) of chlorobenzene and 205 g. (2 mols.) of acetic anhydride. They describe this as a 70-75% yield. Calculated on the chlorobenzene this is so, but calculated on the acetic anhydride, which is the constituent present in theoretical amount, it is a 92-97% yield.

4-Chloro-3-nitroacetophenone was obtained by nitration of p-chloroacetophenone by Le Fèvre's method (41).

Attempts to condense carbazole with 4-chloro-3-nitroacetophenone in presence of anhydrous potassium carbonate were completely unsuccessful, since when the two latter substances are heated together for 5 minutes at 120° a black solid mass results. An account of the various attempts to obviate this difficulty is given in the table. (page 35).

p-Bromoacetophenone (40) was prepared and from it 4-bromo-3-nitroacetophenone. (41). It showed a similar blackening with potassium carbonate.

p-Iodoacetophenone (42) was prepared.

4-Iodo-3-nitroacetophenone:- p-Iodoacetophenone (1 g.) was slowly added to fuming nitric acid (d. 1.5. 6 c.c.) cooled in ice. After standing for 5 minutes the solution was poured

into water, and the precipitated solid recrystallised from alcohol; pale yellow needles m.p. 112-115°. (Found: N, 4.81; I, 44.2. $C_8H_6O_3NI$ requires N, 4.81; I, 43.64%).

When heated with anhydrous potassium carbonate 4-iodo-3-nitroacetophenone forms a black mass.

Note:- The blackening is not due to an impurity in the potassium carbonate since an analytically pure specimen gave the same effect.

Potassium carbazole (0.2 g.) and 4-chloro-3-nitroacetophenone (0.4 g.) were heated together. At 100° the mixture melted, blackened, and frothed up, finally leaving a black mass.

ATTEMPTED CONDENSATION OF CARBAZOLE WITH 4-CHLORO-3-NITRO-ACETOPHENONE.

In each case 5 g. carbazole and 12 g. 4-chloro-3-nitro-acetophenone were used.

Condensing agent.	Temp.	Time.	Result.
Anhyd. K_2CO_3 (5 g.).	170°.	-	No effervescence - black mass.
	190°.	-	Vigorous reaction - yellow fumes emitted - charred mass.
Anhyd. K_2CO_3 (5 g.) in diethylaniline (25 c.c.)	170°	2 hrs.	Slight effervescence - darkening in colour.
	180°	8 hrs.	Mass poured into water - solid crystallised from acetic acid - carbazole. Filtrate poured into water - tar - crystallised from ligroin - 4-chloro-3-nitroacetophenone.
Anhyd. K_2CO_3 (5 g.), Cu (0.2 g.), diethylaniline (10 c.c.)	190°	10 hrs.	Mass became very dark in colour. Only starting materials isolated.
Anhyd. K_2CO_3 (5 g.) in diethylaniline (20 c.c.)	210°	9 hrs.	Mass blackened during first hour. Some carbazole recovered but product was mostly a black insol. mass.
$BaCO_3$ (5 g.).	180°	9 hrs.	Starting materials recovered.
$BaCO_3$ (5 g.).	230°	5 hrs.	Effervescence at first - after 4 hrs. mixture very dark in colour. Product was carbazole and a black insol. residue.
Quinoline (20 c.c.)	230°	5 hrs.	Starting materials recovered.

SYNTHESIS OF 4'-METHYL-8:9-PHENYLENECARBAZOLE.

4-Chloro-3-nitrotoluene was prepared from p-toluidine by nitration to m-nitro-p-toluidine (43), followed by a Sandmeyer reaction (44).

N-2'-Nitro-4'-methylphenylcarbazole:- Carbazole (10 g.), 4-chloro-3-nitrotoluene (22 g.), anhydrous potassium carbonate[1] (10 g.), and copper bronze[2] (0.1 - 0.2 g.) were heated together in an air bath at 220-230° for 3 hours. The product was steam distilled to remove excess of 4-chloro-3-nitrotoluene, and the residue was dissolved in acetic acid (charcoal). The mother liquor was decanted from the brown tar which separated on cooling. A quantity of a yellow substance, N-2'-nitro-4'-methylphenylcarbazole, then crystallised from the acetic acid solution. On extracting the tar with alcohol a further quantity of product was obtained. N-2'-Nitro-4'-methylphenylcarbazole crystallises from alcohol in yellow needles m.p. 104-106°. (6 g.: yield 35%.) (Found, N, 9.4. $C_{19}H_{14}O_2N_2$ requires N, 9.3%).

(1). When potassium carbonate was replaced by barium carbonate no condensation took place under the above conditions.

(2). In the absence of copper bronze a poorer yield resulted.

N-2'-amino-4'-methylphenylcarbazole:- The above nitro compound (5 g.), stannous chloride (25 g.), and glacial acetic acid saturated with hydrogen chloride (100 c.c.) were boiled together for ½ hour passing in hydrogen chloride. A further

quantity of stannous chloride (10 g.) and acetic acid (25 c.c.) was added, and boiling was continued until a white solid separated. The mixture was then poured into a large excess of sodium hydroxide solution, and after filtering, the solid was extracted with cold benzene. On concentrating the solution almost to dryness N-2'-amino-4'-methylphenylcarbazole separated, and crystallised from alcohol in colourless prisms, m.p. 117-119°. (3 g.: yield, 75%). (Found, N, 10.3. $C_{19}H_{16}N_2$ requires N, 10.29%).

The reduction may be carried out with tin and hydrochloric acid, but the reaction is slow and a black tar separates.

4'-Methyl-8:9-phenylenecarbazole:- N-2'-Amino-4'-methylphenylcarbazole (5 g.) was dissolved in glacial acetic acid (45 c.c.) and concentrated sulphuric acid (10.5 c.c.), and cooled in ice. The solution was diazotised with sodium nitrite solution (1.3 g. in 30 c.c. water), allowed to stand for a few minutes, and then gently boiled for 10 minutes. The deep red colour of the solution changed to brown and a black tar separated. This solidified on cooling in ice. Extraction with alcohol and precipitation of the extracts with water yielded a brownish white solid . It was crystallised fromalcohol, and then purified by sublimation (210 - 270°/15 mm.), and a soft white sublimate which slowly became brittle was obtained. On crystallisation from ligroin, methyl alcohol, or glacial acetic acid it gave tufts of long colourless needles, which on dry-

ing were matted thickly together like felt; m.p. 108-110°. (Found: C, 89.4: H, 5.06. $C_{19}H_{13}N$ requires C, 89.42: H, 5.098%).

The substance is very soluble in carbon tetrachloride, ethyl acetate, benzene or chlorobenzene; less soluble in ether. Solutions seem to have a very faint violet fluorescence.

Picrate of 4'-methyl-8:9-phenylenecarbazole:- This was prepared in ether solution and crystallised from alcohol in red needles m.p. 145-150°. (Found, C, 61.96; H, 3.42; N, 11.49. $C_{19}H_{13}N.C_6H_3O_7N_3$ requires C, 61.98; H, 3.31; N, 11.57%.)

Trinitrobenzene compound of 4'-methyl-8:9-phenylenecarbazole:- This was prepared in alcoholic solution and crystallised from acetic acid in yellow needles m.p. 170-172°. (Found, C, 63.88; H, 3.4; N, 11.98. $C_{19}H_{13}N.C_6H_3O_6N_3$ requires C, 64.1; H, 3.42; N, 11.96%.)

N-4'-Methylphenylcarbazole:- A mixture of carbazole (5 g.), p-iodotoluene (15 g.), anhydrous potassium carbonate (5 g.), and copper bronze[1] (0.3 g.) was heated in an air bath at 180-200° for 6[2] hours. On cooling, the product was washed with warm water, and the insoluble residue recrystallised from alcohol. N-4'-Methylphenylcarbazole crystallised in colourless needles m.p. 105-107°. (5 g.; yield 66%). (Found N, 5.64. $C_{19}H_{15}N$ requires N, 5.45%.)

(1) In the absence of copper bronze a poorer yield (3 g.: 40%) was obtained.

(2) Shorter heating (3 hours) resulted in a poor yield.

N-4'-Methylphenylcarbazole may also be prepared by heating potassium carbazole (5 g.), p-iodotoluene (7 g.), and copper bronze (0.3 g.) in an air bath at 180-200° for 6 hours. The product was washed with warm water and the residue crystallised from alcohol. The N-4'-methylphenylcarbazole prepared thus had a brown colour, and the yield (50%) was poorer than in the previous method.

Trinitrobenzene compound of N-4'-methylphenylcarbazole:- This was prepared in alcoholic solution, and crystallised from alcohol in long red needles (powdered yellow) m.p. 106-108°. (Found: N, 12.1. $C_{19}H_{15}N.C_6H_3O_6N_3$ requires N, 11.9%).

ATTEMPTED OXIDATION OF N-4'-METHYLPHENYLCARBAZOLE TO N-4'-CARBOXYPHENYLCARBAZOLE.

I. With potassium permanganate.

1) in acetone:- N-4'-Methylphenylcarbazole (2 g.) was dissolved in pure acetone (30 c.c.) and potassium permanganate (powdered, 1 g.) was added. After boiling for 1 hour, a further quantity of permanganate (1 g.) was added, and boiling was continued for 3 hours. On cooling, the solution was poured into sulphurous acid, and a white solid m.p. 105° was obtained. This showed no depression of m.p. on admixture with N-4'-methylphenylcarbazole. The solid was extracted with sodium hydroxide solution, but on acidifying the extract no acid product was precipitated.

2) in pyridine:- The above compound (2 g.) dissolved in pyridine (10 c.c.) was boiled for 1½ hours while potassium permanganate (2 g.) in pyridine (70 c.c.) was added. The product was isolated by treatment with sulphurous acid as before, but no trace of an acidic substance was detected.

3) in acetone with aqueous potassium permanganate solution:- 1) was repeated using potassium permanganate (2 g.) in water (75 c.c.). A vigorous and sometimes violent reaction took place, and a brown precipitate formed in the solution. On pouring into sulphurous acid only a portion of the starting material was recovered, and no trace of N-4'-carboxyphenylcarbazole could be found.

4) in acetone in presence of sodium bicarbonate:- 1) was repeated with the addition of a quantity of solid sodium bicarbonate, but a result similar to that of 1) was obtained.

II. With sodium dichromate.

1) To a boiling solution of N-4'-methylphenylcarbazole (2 g.) in acetic acid (33 c.c.) and concentrated sulphuric acid (2.5 c.c.) in water (2.5 c.c.), sodium dichromate (3 g.) in water (5 c.c.) was added gradually with shaking. The solution was boiled for 30 minutes. A black tarry product which could not be purified resulted.

2) The above substance (2 g.) was dissolved in glacial acetic acid (100 c.c.) and concentrated sulphuric acid (2.5 c.c.), and the solution was cooled in ice. Sodium dichromate (3 g.)

in the smallest possible amount of water was added during 1 minute. After 10 minutes the solution was poured into an equal bulk of concentrated sodium bisulphite solution, and heated on the water bath. A brown solid precipitated and was removed by filtration, leaving a green solution. Extraction with benzene and addition of ligroin to the concentrated solution yielded a brown solid m.p. above 180°. This solid was completely insoluble in sodium hydroxide. It was soluble in anisole and acetic anhydride, but did not crystallise from these solvents. It was not investigated further owing to its non-acidic character.

III. With chromyl chloride. cf. (45)

To chromyl chloride (3 g.) in redistilled carbon tetrachloride (7 c.c.) was added N-4'-methylphenylcarbazole (2 g.) in carbon tetrachloride (60 c.c.), and the mixture was allowed to stand for 2 days. It was then poured into water and saturated with sulphur dioxide. The solid formed was washed with sodium bicarbonate solution, and then crystallised from alcohol. The product left a large inorganic residue when heated on a nickel spatula, and seemed to contain chromium. The bicarbonate washings were acidified, but no trace of an acidic product was found.

IV. With nitric acid.

1) N-4'-Methylphenylcarbazole (0.5 g.) was added to boiling nitric acid (10 c.c. concentrated acid to 10 c.c. water).

A brown product was formed. This was insoluble in sodium hydroxide solution, and had m.p. above 200°.

2). The above substance (0.5 g.) was added to nitric acid (5 c.c. concentrated acid to 15 c.c. water) and the solution was boiled. A brown product similar to that obtained in 1) was formed.

V. With mercuric oxide in acetic acid.

N-4'-Methylphenylcarbazole (1 g.), mercuric oxide (4 g.), and glacial acetic acid (20 c.c.) were boiled together for 2 hours, and the solution was allowed to cool. A minute quantity of a white product separated, but this was mainly inorganic material. Dilution of the original solution with water yielded a white precipitate which dissolved in ammonium hydroxide, and was reprecipitated on making the solution acid. It was extracted with benzene, and the extract was concentrated. Only a trace of product was recovered on evaporating to dryness.

VI. With potassium hydroxide.

Potassium hydroxide (50 g.) was fused in a nickel basin, and N-4'-methylphenylcarbazole (5 g.) was added in small quantities - temperature 240° approx. On cooling, the melt was extracted with water. The insoluble matter was removed, and was found to be unchanged starting material. Acidification of the potassium hydroxide solution caused only a slight turbidity.

Attempts to oxidise 4'-methyl-8:9-phenylenecarbazole to the corresponding carboxy compound by methods I 1) and V gave similar results to those detailed in the foregoing pages.

ATTEMPTED SYNTHESIS OF 4'-CHLORO-8:9-PHENYLENECARBAZOLE.

N-2'-Nitro-4'-chlorophenylcarbazole:- A mixture of carbazole (10 g.), 1-4-dichloro-2-nitrobenzene (22 g.), anhydrous potassium carbonate (10 g.), and copper bronze[1] (0.2g.) was heated in an air bath at 220-230° for 4 hours. The brown mass was then steam distilled[2] to remove the excess 1-4-dichloro-2-nitrobenzene, and on crystallising the residue from alcohol (charcoal), orange yellow prisms m.p. 134-136° were obtained. (6.6 g.: yield, 35%). (Found, Cl, 10.9. $C_{18}H_{11}O_2N_2Cl$ requires Cl, 11.0%).

N-2'-Nitro-4'-chlorophenylcarbazole crystallises readily from methyl or ethyl alcohol. It is only slightly soluble in ligroin, but is very soluble in benzene and carbon tetrachloride.

(1) No condensation product was obtained at this temperature in the absence of copper, even after heating for 7 hours. At 230-240° a very small quantity of product was detected among much unchanged carbazole.

(2) If the excess 1-4-dichloro-2-nitrobenzene is not removed at this stage a tarry product is obtained, and this is very difficult to crystallise.

N-2'-Amino-4'-chlorophenylcarbazole:- The above nitro compound (5 g.), stannous chloride (25 g.), and glacial acetic acid

saturated with dry hydrogen chloride (100 c.c.) were boiled together for a few minutes, until the colour of the solution was a pale yellowish green. It was then poured into concentrated sodium hydroxide solution. The solid product was filtered and extracted with benzene. After drying and concentrating considerably, the solution was saturated with dry hydrogen chloride, and the hydrochloride of the base was precipitated by adding ligroin. The hydrochloride was decomposed with ammonia, and the amine crystallised from methyl alcohol. An oil separated first, but when the mother liquor was decanted off crystals separated from it, m.p. 84-86°. (4 g. hydrochloride: yield, 80%). (Found, N, 9.49. $C_{18}H_{13}N_2Cl$ requires N, 9.57%).

Attempted preparation of 4'-chloro-8:9-phenylenecarbazole. The above amine hydrochloride (2.5 g.) was dissolved in glacial acetic acid (20 c.c.). Almost immediately a white crystalline solid separated, but it redissolved on the addition of concentrated sulphuric acid (4.4 c.c.). The solution was cooled in ice, and diazotised with sodium nitrite solution (0.54 g. in 12 c.c. water). A deep crimson coloured solution was obtained. After standing for 10 minutes it was decomposed by heating to 80° for ½ hour. A black tar which solidified readily on cooling resulted. Attempts to crystallise the black solid from various solvents were quite unsuccessful, and on treatment with animal charcoal it was

completely absorbed. Finally it was sublimed (230-250°/15 mm.). A yellowish white product, which crystallised in colourless needles from alcohol or acetic acid, was obtained m.p. 138-140°.

N-4'-Chlorophenylcarbazole:-

p-Chloriodobenzene was prepared from p-chloraniline (46). Colourless glistening plates m.p. 56-57°.

A mixture of carbazole (5 g.), p-chloriodobenzene (14 g.), anhydrous potassium carbonate (5 g.), and copper bronze (0.2 g.)(1) was heated in an air bath at 200° for 6 hours with frequent shaking. The excess p-chloriodobenzene was removed in steam, and the residual brownish white solid crystallised readily from ethyl acetate in colourless prisms m.p. 140-143°. (6 g.: yield 70%). (Found Cl, 13.0%. $C_{18}H_{12}NCl$ requires Cl, 12.8%). Guillaume and Marcel de Montmollin, (23) give m.p. 146°.

(1) In the absence of copper bronze the solid which crystallised from the ethyl acetate extract was carbazole. A quantity of N-4'-chlorophenylcarbazole was isolated from the mother liquor. (1.5 g.: yield, 17%).

The product from the attempt to prepare 4'-chloro-8:9-phenylenecarbazole gave a depression of m.p. of 20° when mixed with N-4'-chlorophenylcarbazole.

ATTEMPTED CHLORINATION OF 8:9-PHENYLENECARBAZOLE.

1) 8:9-Phenylenecarbazole (1 g.) was dissolved in warm glacial acetic acid (75 c.c.). Chlorine (approx. 0.4 g.) dissolved in glacial acetic acid (10 c.c.) was added, and the whole was cooled in ice. After boiling for 10 minutes the solution was concentrated. Only unchanged starting material was obtained.

2) The compound (0.4 g.) was dissolved in chloroform (15 c.c.), and chlorine was passed into the solution. On removing the solvent only 8:9-phenylenecarbazole was isolated.

3) The compound (0.5 g.) was dissolved in ligroin (b.p. above 120°) (25 c.c.) and dry chlorine was passed into the solution for 15 minutes. The white product which crystallised from the solution on concentrating, was unchanged starting material, and no trace of a substituted product was detected.

IODINATION OF 8:9-PHENYLENECARBAZOLE. cf. (47).

8:9-Phenylenecarbazole (2 g.), iodine (1 g.), and glacial acetic acid (50 c.c.) were boiled together, and concentrated nitric acid (6 c.c.) was added drop by drop. The violet colour changed to red and a solid separated. After washing with sodium bisulphite solution the solid was grey in colour. It was soluble only in nitrobenzene, aniline, quinoline, anisole and ethyl benzoate. It separated from the last as a pale yellow powder m.p. above 340°. (Found I, 24.8: 24.8. $C_{18}H_7O_6N_4I$ requires I, 25.3%).

BROMINATION OF 8:9-PHENYLENECARBAZOLE.

3:6?-Dibromo-8:9-phenylenecarbazole:- 8:9-Phenylenecarbazole (1.5 g.) was dissolved in warm chloroform (10 c.c.), and to it was added bromine (0.35 c.c.) in chloroform (5 c.c.). A vigorous evolution of hydrogen bromide took place. Removal of the solvent yielded a brominated product mixed with starting material. The above procedure was therefore repeated using an excess of bromine (0.66 c.c.), and the solution was finally boiled for 1 minute when the evolution of hydrogen bromide seemed to have ceased. The solid which separated had m.p. 175-195°. It was washed with hot alcohol, and then with a little hot acetic acid. The residue was crystallised from acetic acid and finally from glycol monomethyl ether, m.p. 202-205° (turbid melt). (Found, Br, 41.2. $C_{18}H_9NBr_2$ requires Br, 40.1%).

Further efforts to purify the substance by crystallisation from anisole, pyridine, ethyl acetate etc. gave a powder m.p. 202-209° (turbid melt clearing at 214°). Attempts to purify by sublimation were unsuccessful.

6?-Bromo-8:9-phenylenecarbazole:- 8:9-Phenylenecarbazole (4.5 g.) was dissolved in cold chloroform (75 c.c.), and the solution was cooled in ice and mechanically stirred. Bromine (1 c.c.) in chloroform (30 c.c.) was added during 3 hours. The solid which separated, 'A', was removed by filtration, and the filtrate on evaporation to dryness yielded a further

quantity of solid,'B'. The latter contained some unchanged starting material which was washed out with hot alcohol. The residue from 'B' and 'A' then crystallised from acetic acid as colourless needles m.p. 195-205°. After repeated recrystallisation from acetic acid and amyl ether m.p. 205-210°. On admixture with the other bromo-derivative isolated (see previous page) the m.p. was depressed about 20°.

(Found Br, 25.4. $C_{18}H_{10}NBr$ requires Br 25.0%.)

To the above compound (0.5 g.) in chloroform (20 c.c.) bromine (1c.c. in 12 c.c. chloroform - 4 c.c. of this solution taken) was added. Since there was no evidence of a reaction taking place the solution was boiled for ½ hour. Removal of the solvent, and crystallisation from acetic acid yielded a product m.p. 200-207°, which differed from 6?-bromo-8:9-phenylene-carbazole and was identical with 3:6?-dibromo-8:9-phenylene-carbazole.

Attempts to form a Grignard compound from 6?-bromo-8:9-phenyl-enecarbazole.

The halide was too insoluble in ether to permit of its use as a solvent.

6?-Bromo-8:9-phenylenecarbazole (3.5 g.), magnesium turnings (0.25 g.), and dry amyl ether (25 c.c.) were stirred together. No reaction took place even on heating, nor on the addition of a trace of iodine or activated magnesium (48).

An attempt was also made using sodium dried xylene in place

of amyl ether, but this also failed.

Efforts to form the Grignard compound by heating the halide with magnesium powder in an inert atmosphere resulted in decomposition. (49).

6-Carboxy-8:9-phenylenecarbazole:- 8:9-Phenylenecarbazole (2 g.), trichloracetonitrile (1 c.c.), and powdered $AlCl_3$ (4 g.) were mixed together in chlorobenzene (5 c.c.), and dry hydrogen chloride was passed into the mixture. The product was allowed to stand for 3 weeks. On treatment with water the red mass became yellow in colour. The insoluble matter was boiled for 1 minute with potassium hydroxide solution and then filtered. The solid which separated from the filtrate (probably the K salt of the acid) was soluble in hot water, and on acidifying the solution a gelatinous precipitate was obtained. Filtration yielded a brown solid which was quite soluble in ammonia. Purification was difficult and the best method found was that of sublimation at 300°/15 mm., followed by crystallisation from a mixture of nitrobenzene and acetic anhydride. 6-Carboxy-8:9-phenylenecarbazole separated in pale brown micro crystals s.p. 270°. m.p. 305°. (Found C, 80.04: H, 3.93. $C_{19}H_{11}O_2N$ requires C, 80.00:H, 3.86%).

Esterification of 6-carboxy-8:9-phenylenecarbazole.

The acid was boiled for 12 hours with specially dried methyl alcohol containing dry hydrogen chloride. The insoluble product which resulted was washed with ammonium hydroxide,

, but only a trace of unchanged acid was precipitated on acidifying the alkaline solution. The ester, which was brown in colour, sublimed at 250°/15 mm., and the colourless sublimate crystallised from aqueous dioxane m.p. 210 -220° (turbid melt which cleared at 225°).

Decarboxylation of 6-carboxy-8:9-phenylenecarbazole.

The substance was boiled with copper bronze in dry quinoline for ¾ hour. On pouring the product into dilute hydrochloric acid a solid, soluble in alcohol, was precipitated. The product from the alcoholic extract sublimed at 250°/15 mm., and the sublimate crystallised from methyl alcohol in tufts of needles m.p. 130°. The m.p. of this substance was not depressed on admixture with 8:9-phenylenecarbazole.

SYNTHESIS OF 6-CARBOXY-8:9-PHENYLENECARBAZOLE.

N-Carbethoxy[redacted]carbazole:- (50). To methyl magnesium iodide (10 g. approx.) prepared in dry ether (12 c.c.), carbazole (10 g.) was added gradually. A brisk effervescence took place, and after the addition of the last of the carbazole the contents of the flask suddenly became solid. Ether (40 c.c.) was added, and then chloroformic ester (7 g.) in ether (10 c.c.) drop by drop. The product was heated on a water bath for a few minutes and then it stood overnight. The addition of water caused a red solid to be precipitated. This was removed by filtration. The ether filtrate was washed with water, dilute hydrochloric

acid, water again, dried and concentrated. A yellowish white solid separated and was recrystallised from alcohol, m.p. 75-77°. (11 g.: yield 80% approx.).

Attempts to prepare 3-carbethoxycarbazole from N-carbethoxycarbazole.

To N-carbethoxycarbazole (3 g.) dissolved in nitrobenzene (redistilled, 25 c.c.) powdered $AlCl_3$ (2.5 g.) was added, the whole being water cooled. The solution was allowed to stand for 24 hours and then heated to 110°, and maintained at that temperature for 15 minutes. After removing the nitrobenzene in steam a black solid was obtained, and this was recrystallised from alcohol (charcoal). The resulting product m.p. 70-75° gave no depression of m.p. on admixture with N-carbethoxycarbazole.

The above procedure was repeated heating to 120-130° for 25 minutes. The black solid which resulted from the removal of the nitrobenzene was completely insoluble in alcohol or acetic acid. Since 3-carbethoxycarbazole is soluble in both these solvents this product was not investigated further.

This same insoluble product was obtained by heating the substances to 120° for 15 minutes immediately after mixing.

3-Carboxycarbazole was prepared from N-acetyl carbazole (51) by conversion to 3-acetylcarbazole, [(30) and later (31)], and fusion of this with potassium hydroxide (29).

The ethyl ester m.p. 165° was obtained by boiling the acid for 6 hours with absolute alcohol containing concentrated sulphuric acid (1 c.c. acid to 20 c.c. alcohol). (29).

N-2'-Nitrophenyl-3-carbethoxycarbazole:- A mixture of 3-carbethoxycarbazole (5 g.), o-nitrochlorobenzene (10 g.), anhydrous potassium carbonate (5 g.) and copper bronze (0.2 g.) was heated in an air bath at 200-210°(1) for 5 hours. After removing the excess o-nitrochlorobenzene in steam, the residue was dissolved in acetic acid (charcoal). The solution was poured into water. The resulting solid crystallised from methyl alcohol in small yellow needles m.p. 120-122.° (5 g.: yield 66%). (Found N, 7.9. $C_{21}H_{16}O_4N_2$ requires N, 7.8%).

(1) Boiling the mixture for a shorter time (cf. condensation of carbazole with o-nitrochlorobenzene, page 21) caused the formation of a tar from which the desired product was isolated in poor yield.

N-2'-Aminophenyl-3-carbethoxycarbazole:- The above nitro compound (4 g.), stannous chloride (10 g.), and glacial acetic acid saturated with dry hydrogen chloride (40 c.c.) were boiled together for a few minutes until the colour of the solution was greenish - yellow. It was then poured into concentrated sodium hydroxide solution. The solid matter was separated by filtration and dissolved in benzene. After drying, the solution was concentrated considerably and the

~~and the~~ amine was precipitated by the addition of ligroin. N-2'-Aminophenyl-3-carbethoxycarbazole separated from methyl alcohol as colourless prisms m.p. 140-142° (2.4 g.: yield 70%.) (Found: N, 8.3. $C_{21}H_{18}O_2N_2$ requires N, 8.5%).

6-Carboxy-8:9-phenylenecarbazole:- N-2'-Aminophenyl-3-carbethoxycarbazole (1.5 g.) was dissolved in glacial acetic acid (12 c.c.) and concentrated sulphuric acid (2.7 c.c.), and the solution was cooled in ice. It was then diazotised with sodium nitrite solution (0.3 g. in 12 c.c. water). After standing for 10 minutes the red solution was gently heated until decomposition was complete. A black tar, which solidified on cooling, was obtained. The resulting solid was dissolved in dioxane, and on pouring the solution into water a yellow solid was precipitated. This product was hydrolysed by boiling for ½ hour with alcoholic potassium hydroxide solution. The solution was then poured into dilute hydrochloric acid. The resulting solid was quite soluble in ammonia and was reprecipitated on acidifying the solution, After drying it was sublimed at 300°/15 mm. The white sublimate crystallised with difficulty from nitrobenzene in micro crystals m.p. 305°.

The methyl ester of the acid was prepared, (as in page 49) and was found to be identical with the methyl ester of the acid obtained by direct substitution of 8:9-phenylene-carbazole.

ATTEMPTS TO PREPARE 8:9-PHENYLENECARBAZOLE AND ITS DERIVATIVES BY OTHER METHODS.

I. cf. Plant and Tomlinson (17).

To N-2'-aminophenylcarbazole (2 g.) dissolved in methyl alcohol (130 c.c.), concentrated sulphuric acid (4.4 c.c.) was added. The solution was cooled in ice, and diazotised with sodium nitrite solution (0.54 g. in 12 c.c. water). After ½ hour the solution was boiled for ½ hour. A small quantity of an insoluble dark red compound separated. The mother liquor was poured into water, and the reddish yellow substance obtained was dissolved in benzene. After drying, the solution was concentrated considerably. The resulting solid was crystallised twice from methyl alcohol (charcoal), and a colourless product m.p. 87-89°, which showed no depression of m.p. on admixture with N-phenylcarbazole, was obtained. The picrate was formed and was identical with the picrate of N-phenylcarbazole, m.p. 126-129° (24).

The above procedure was repeated using N-2'-amino-4'-cyanophenylcarbazole (1 g.), methyl alcohol (120 c.c.), concentrated sulphuric acid (2 c.c.), and sodium nitrite (0.25 g.). After the decomposition of the diazonium solution, most of the alcohol was distilled off, and a reddish crystalline solid separated. Recrystallisation from alcohol and then from acetic anhydride gave a colourless compound m.p. 176°, which was not N-2'-amino-4'-cyanophenylcarbazole.

N-4'-Cyanophenylcarbazole (23) was prepared from N-4'-aminophenylcarbazole (32) by the action of cuprous cyanide solution on the diazonium chloride solution. The crude product had m.p. 165° as described by de Montmollin (23), but crystallisation from alcohol and then acetic anhydride gave colourless crystals m.p. 175-177°.

On admixture with N-4'-cyanophenylcarbazole, the product from the attempted ring closure showed no depression of m.p.

II. cf. Storrie and Tucker, (18).

N-2'-Amino-4'-cyanophenylcarbazole (1 g.) in concentrated hydrochloric acid (15 c.c.) was diazotised with sodium nitrite solution (0.5 g. in 10 c.c. water). Excess of sodium hydroxide solution was added and the mixture was boiled. A brown sludge which could not be crystallised separated out. On acidifying the filtrate, a minute quantity of a brownish white solid was precipitated. The amount of the product was insufficient for further work.

III. The action of $AlCl_3$ on N-phenylcarbazole. cf. Cook and Hewett (19).

(1) N-Phenylcarbazole (2.5 g.) was dissolved in dry carbon disulphide (distilled over $AlCl_3$) (25 c.c.), and the solution was cooled in ice. Powdered $AlCl_3$ (3 g.) was added and the mixture was allowed to stand in ice for 3 hours, and then overnight at room temperature. Most of the carbon disulphide was removed, and the $AlCl_3$ was decomposed by adding water

and dilute hydrochloric acid. The solid obtained was extracted with ether, and the extract was dried and concentrated almost to dryness. The colourless product which separated crystallised from alcohol, m.p. 90°, and showed no depression of m.p. on admixture with N-phenylcarbazole.

(2). To N-phenylcarbazole (1.25 g.) dissolved in dry ether (50 c.c.), powdered $AlCl_3$ (1.5 g.) was added. Since no colour change took place on allowing the solution to stand, it was boiled for 1 hour. There was still no colour change, so the solution was concentrated considerably and allowed to stand for several days. After removing the ether, the solid product was decomposed with dilute acid, and the substance obtained was crystallised from alcohol. It had m.p. 90° and was identical with N-phenylcarbazole.

(3). To N-phenylcarbazole (1.25 g.) dissolved in nitrobenzene (8 c.c.), powdered $AlCl_3$ (1.5 g.) was added. The solution darkened in colour and finally became black, and a certain amount of heat was evolved. The solution was allowed to stand overnight, and then the nitrobenzene was removed by steam distillation. An unworkable black tar was obtained.

IV. The action of potassium hydroxide melts on N-4'-methylphenylcarbazole. cf. Luttringhaus and Neresheimer (20).

(1). Potassium hydroxide (10 g.) and methyl alcohol (10 c.c.) were heated together. N-4'-Methylphenylcarbazole (2 g.) was

added, and the temperature was maintained at 115-120° for 1½ hours. On treating the cooled mass with water only the starting material (1.75 g.) was obtained. Acidification of the alkaline solution yielded no product.

(2). Potassium hydroxide (8 g.) and ethyl alcohol (5 c.c.) and the above substance (2 g.) were heated together in an oil bath at 180° for 2-3 hours. On treating the product with water N-4'-methylphenylcarbazole was recovered in almost theoretical amount.

(3). N-4'-Methylphenylcarbazole (2 g.) was fused with potassium hydroxide (10 g.) containing a few drops of water at 220° for 1 hour. A small amount of the starting material was recovered, but only a trace of a product soluble in alkali, and no 4'-methyl-8:9-phenylenecarbazole was obtained.

(4) Fusion of the substance (2 g.) with potassium hydroxide (40 g.) and sodium acetate (3 g.) at 240° for 1¼ hours yielded an amount of an acidic product insufficient for further work.

V. Attempted preparation of 1-(2-nitro-4-cyanophenyl)-diphenyl-triazole.

2-(2''-Nitro-4''-cyanophenylamino)-2'-aminodiphenyl (0.5 g.) in glacial acetic acid (25 c.c.) and 10% hydrochloric acid solution (10 c.c.) was diazotised with sodium nitrite (0.5 g.) in a few drops of water and glacial acetic acid (10 c.c.). A further 0.5 g. sodium nitrite was added in the solid state.

A clear red solution resulted. On heating, the colour changed to brownish yellow, and a solid separated. When the product was crystallised from aqueous acetic acid a mixture of red and yellow crystals was obtained. The red changed to yellow on heating. Crystallisation from pyridine yielded homogeneous crystals which were red in colour (powdered yellow)., m.p. 229-232°. These lost weight and changed to yellow on heating. (Found , pyridine, 12.24: $C_{19}H_{11}O_2N_5 \cdot C_5H_5N$ requires pyridine, 18.82%. Found N, 15.3, 15.1: $C_{19}H_{11}O_2N_5$ requires 20.52%). 1-(2-nitro-4-carboxyphenyl)-diphenyltriazole, $C_{19}H_{12}O_4N_4$ requires N, 15.5% but requires pyridine, 15.9%. The compound moreover exhibited no acidic properties.

2:2'-Di-(2''-4''-dinitrophenylamino)diphenyl and 2:2'-di-2''-nitro-4''-cyanophenylamino)diphenyl (21) were also found to exist in two crystalline forms, one red and the other yellow, although in these cases it was the yellow form which contained solvent of crystallisation.

PREPARATION OF N-2'-4'-DINITROPHENYLCARBAZOLE AND ITS REDUCTION PRODUCTS.

N-2'-4'-Dinitrophenylcarbazole:- A mixture of carbazole (20 g.), 1-chloro-2-4-dinitrobenzene (52 g.) and anhydrous potassium carbonate (20 g.) was heated in an oil bath at 170-180° for 12 (1) hours with frequent shaking, and was then extracted with acetic acid (charcoal). The product which crystallised therefrom contained carbazole. Crystallisation from xylene, in which the carbazole remained dissolved, gave orange brown crystals (powdered yellow) m.p. 188-190° of N-2'-4'-dinitrophenylcarbazole. (20 g: yield 50%). (Found, C, 64.6; H, 3.3; N, 12.5. $C_{18}H_{11}O_4N_3$ requires C, 64.9; H, 3.3; N, 12.6%).

The substance was sparingly soluble in alcohol, but crystallised from anisole, pyridine, xylene, acetic acid, acetic anhydride and acetone.

The addition of copper bronze has no apparent effect on the condensation.

(1) Heating for 14 hours gave a poorer yield.

N-2'-Nitro-4'-aminophenylcarbazole:- Sodium sulphide (7.5 g.) sulphur (2 g.) and rectified spirits (0.5 c.c.) were heated together, and added to the above nitro compound (9 g.) in methylated spirits (50 c.c.). The solution was boiled for 2 hours, filtered hot and allowed to crystallise. The red solid obtained was converted to the hydrochloride by passing

dry hydrogen chloride into a dry solution of it in benzene. On decomposing the hydrochloride with ammonia a red solid m.p. 135-140° resulted. This solid crystallised from benzene ~~benzene~~ in tiny scarlet needles, which blackened at 140°, and had m.p. 165°. The substance separated from alcohol in long red needles, s.p. 145°, m.p. 164-166°. The preliminary softening seemed to be due to the presence of solvent of crystallisation, since the product lost weight on heating, but concordant analyses results could not be obtained. (6 g.: yield 75%).

N-2'-Nitro-4'-acetaminophenylcarbazole:- N-2'-Nitro-4'-aminophenylcarbazole was boiled with acetic anhydride for a few minutes, and the solution was allowed to cool. The acetyl compound separated, and on recrystallisation from acetic acid gave pale yellow rectangular prisms m.p. 261-263°. (Found: N, 12.05. $C_{20}H_{15}O_3N_3$ requires N, 12.17%).

Action of cuprous cyanide solution on N-2'-nitro-4'-aminophenylcarbazole diazonium sulphate.

N-2'-Nitro-4'-aminophenylcarbazole (2 g.) was heated with sulphuric acid (5 c.c. concentrated acid in 25 c.c. water), and the product was cooled in ice. Sodium nitrite solution (0.6 g. in water) was added gradually, and the dark red solution thus obtained was poured into cuprous cyanide solution (4 g. KCN, 4 g. $CuSO_4$), the addition being made at 70°. A brown solid separated and was removed by filtration

after the solution had been boiled. The solid was extracted with glacial acetic acid, and a red solution, which turned yellow on boiling, was obtained. After treatment with charcoal, a yellow solid was precipitated from the solution by the addition of water. This substance m.p. 50-70° turned red on warming with sodium hydroxide, thus indicating that a nitrophenolic and not a nitrocyano compound had been formed.

Action of boiling alcohol on N-2'-nitro-4'-amino-phenylcarbazole diazonium sulphate.

The N-2'-Nitro-4'-aminophenylcarbazole was diazotised as before and the diazonium solution was poured into alcohol (50 c.c.), and heated on the waterbath until effervescence ceased. The product was filtered hot to remove the small quantity of tar which had been formed. A yellow solid crystallised from the filtrate. Repeated crystallisation from alcohol yielded long yellow needles m.p. 151-153°. These showed no depression of m.p. on admixture with N-2'-nitrophenylcarbazole.

N-2'-4'-Diaminophenylcarbazole:- N-2'-4'-Dinitrophenylcarbazole (2 g.) was boiled with stannous chloride (20 g.) and glacial acetic acid saturated with dry hydrogen chloride (100 c.c.) until only a faint yellow colour persisted. The solution was poured into a concentrated solution of sodium hydroxide, and the solid formed was

separated by filtration. The product dissolved readily in cold benzene and the solution was dried and concentrated. The amine was precipitated by adding ligroin, and crystallised from aqueous alcohol in tufts of colourless needles m.p. 128-130°. (1 g.: yield 63%). (Found, N, 15.0. $C_{18}H_{15}N_3$ requires N, 15.3%).

CONDENSATION OF CARBAZOLE WITH BENZOYL CHLORIDE.

Carbazole (5 g.), anhydrous potassium carbonate (5 g.), and benzoyl chloride (10 g.) were heated together in an air bath at 140-160° for 1 hour. The solid mass, which had a greenish colour, was washed with water to remove the inorganic matter and the excess benzoyl chloride. The residue was crystallised from alcohol, m.p. 98° (5 g.: yield 60%). Concentration of the alcohol residues yielded carbazole.

The Photographs.

The model represents a 4'- (or 3-) substituted 8:9-phenylenecarbazole molecule. The hydrogen atoms of the benzene rings have been omitted for simplicity.

1 and 2, 3 and 4, are stereoscopic photographs.

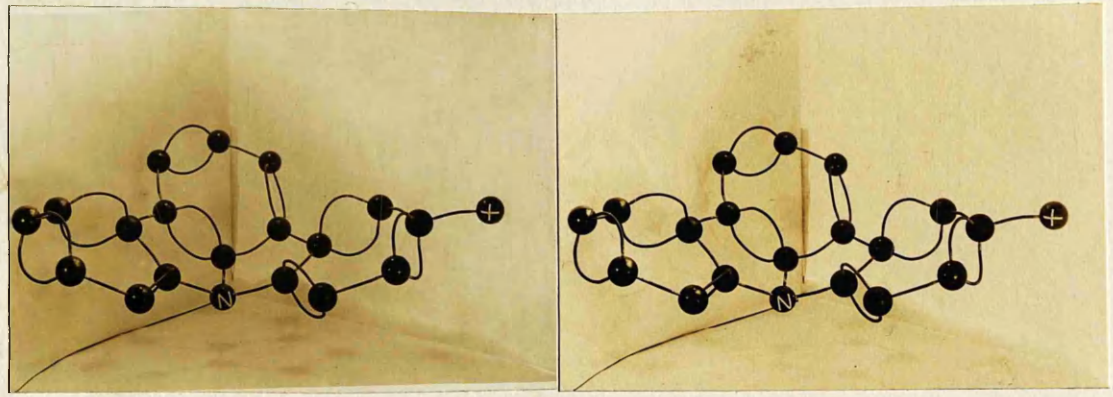
In these the inclination of the rings is exaggerated.

3 and 4 show an "end-on" view of the molecule.

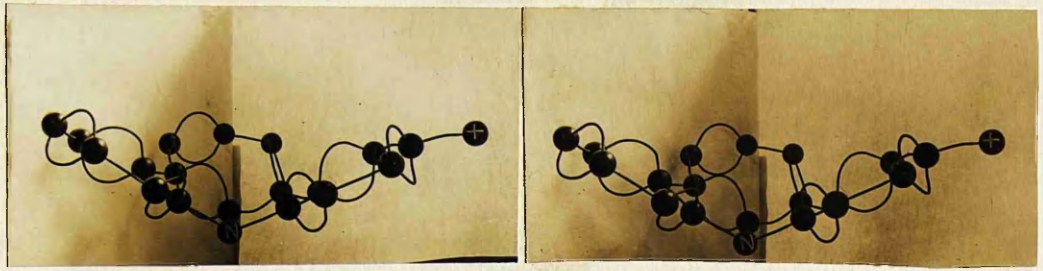
5 and 6 show the object and its mirror image, which are not superimposable.

7 represents the model in elevation.

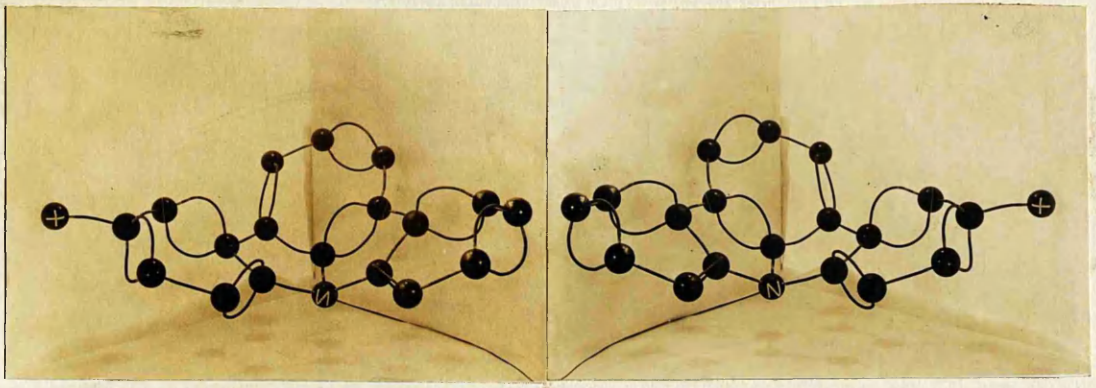
8 shows the probable strained configuration of the five membered rings in one plane.



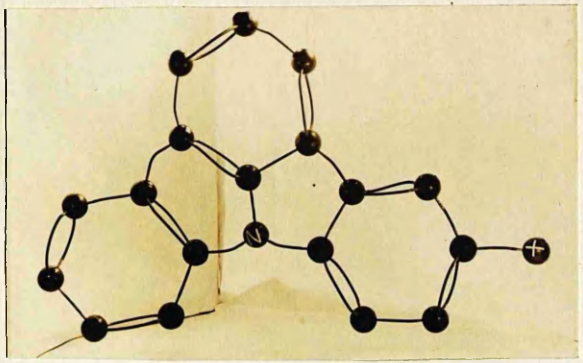
PHOTOGRAPHS. 1 AND 2.



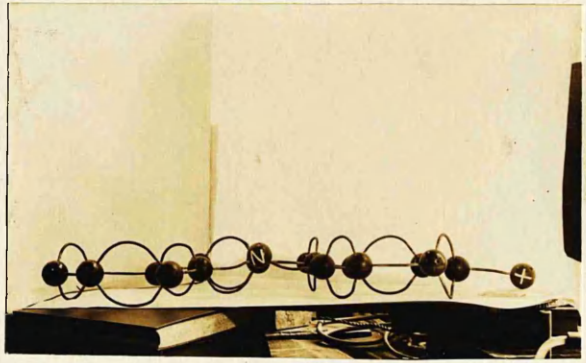
PHOTOGRAPHS 3 AND 4.



PHOTOGRAPHS 5 AND 6.



PHOTOGRAPH 7.



PHOTOGRAPH 8.

BIBLIOGRAPHY.

The following abbreviations are used below:

Ann.	Liebig's Annalen der Chemie.
Ber.	Berichte der Deutschen Chemischen Gesellschaft.
C.	Zentralblatt.
G.	Gazzetta Chimica Italiana.
Helv. Chim. Acta.	Helvetica Chimiqua Acta.
J.A.C.S.	Journal of the American Chemical Society.
J.C.S.	Journal of the Chemical Society.
J. pr. Chemie.	Journal für Praktische Chemie.
Org. Syn.	Organic Syntheses.
Rec. trav. chim.	Recueil des travaux chimiques des Pays-Bas.

---

1. Mills and Bain, J.C.S. 1910, 1866.
2. Mills and Bain, J.C.S. 1914, 64.
3. Mills and Schindler, J.C.S. 1923, 312.
4. Mills and Saunders, J.C.S. 1931, 537.
5. Meisenheimer, Angermann, Finn and Viewig, Ber. 1924, 57, 1744.
6. Meisenheimer, Ber. 1923, 56, 1353.
7. Meisenheimer and Diedrich, Ber. 1924, 57, 1715.
8. Meisenheimer, Ann, 1924, 438, 217.
9. Schreiber and Schriner, J.A.C.S. 1935, 57, 1306, 1445.

10. Mills and Elliott, J.C.S. 1928, 1291.

11. Mills and Breckenridge, J.C.S. 1932, 2209.

12. Bock and Adams. J.A.C.S. 1931, 53, 374.

13. Chang and Adams, J.A.C.S. 1931, 53, 2353.

14. Patterson and Adams, J.A.C.S. 1933, 55, 1069.

15. Meisenheimer, Theilacker and Beiswinger, Ann. 1932, 495, 249.

16. Jackson and Kenner, J.C.S. 1928, 573.

17. Plant and Tomlinson, J.C.S. 1932, 2188.

18. Storrie and Tucker, J.C.S. 1931, 2262.

19. Cook and Hewett, J.C.S. 1934, 375.

20. Luttringhaus and Neresheimer, Ann. 1929, 473, 259.

21. Dunlop, Macrae and Tucker, J.C.S. 1934, 1676.

22. Cassella, C. 1910. II. 700.

23. Guillaume and Marcel de Montmollin, Helv. Chim. Acta. 1923, 6, 94.

24. Eckert, Seidel and Endler, J. pr. Chemie, 1922, 104, 85.

25. Mazzara, Ber. 1891, 24, 278.

26. Tucker and Stevens. J.C.S. 1923, 2146.

27. Rule and Turner, J.C.S. 1935, 317.

28. Brewin and Turner, J.C.S. 1928, 332.

29. Plant and Williams, J.C.S. 1934, 1143.

30. Plant, Rogers and Williams, J.C.S. 1935, 743.

31. Meitzner. J.A.C.S. 1935, 2327.

32. Nelmes and Tucker, J.C.S. 1933, 1525.

33. Org. Syn. 1928, 8, 119.

34. Mattaar, Rec. trav. chim. 1922, 41, 25.

35. Macrae and Tucker, J.C.S. 1933, 1521.

36. Hoffmann, Ann. 1891, 264, 166.

37. Koopal, Rec. trav. chim. 1915, 34, 151.

38. Schmidt and Schultz, Ann. 1881, 207, 334.

39. Zeichmeister and Rom, Ann. 1929, 468, 117.

40. Org. Syn. 1925, 5, 17.

41. Le Fèvre, J.C.S. 1932, 1991.

42. Evans, Morgan and Watson, J.C.S. 1935, 1172.

43. Gattermann, Ber. 1885, 18, 1483.

44. Gattermann and Kaiser, Ber. 1885, 18, 2600.

45. Hey, J.C.S. 1935, 114.

46, Gomberg and Cone, Ber, 1906, 39, 3281.

47. Datta and Chatterjee, J.A.C.S. 1919, 41, 292.

48. Gilman and Kirby, Rec. trav. chim. 1935, 577.

49. Gilman and Brown, J.A.C.S. 1930, 52, 3330.

50. Oddo, G. 41, I, 264.

51. Böeseken, Rec. trav. chim. 1912, 31, 364.
