CARBAZOLE DERIVATIVES

A Thesis

submitted by

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C O N T E N T S.

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INTRODUCTION

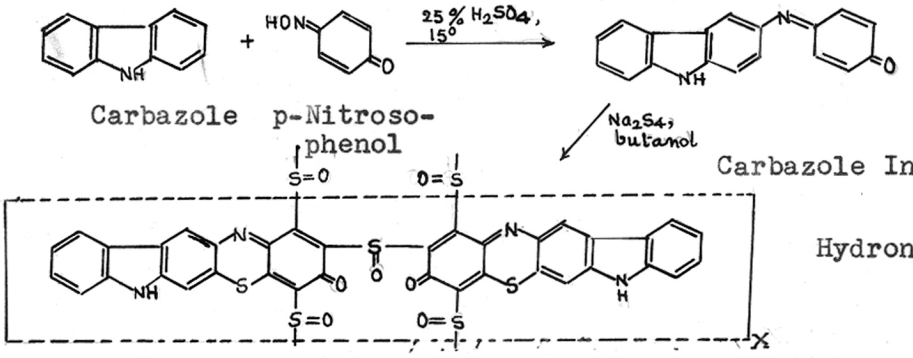
Chemistry of Carbazoles

1. HISTORICAL

Carbazole was discovered by Graebe and Glaser[1] in 1872 as an impurity in crude anthracene obtained from coal tar. Anthracene is the chief constituent of anthracene oil, the final fraction (B.p. 270-346°) obtained in the distillation of coal tar. On cooling anthracene oils which solidifies and sets to a soft crystalline mass, consisting chiefly of a mixture of hydrocarbons. In addition to anthracene and carbazole the anthracene oil fraction also contains substantial quantities of phenanthrene and acenaphthene, fluorene and acridine to a smaller extent. Among the constituents of anthracene oil, anthracene and carbazole are of outstanding importance in the dyestuff industry. In addition to the use of carbazole as an intermediate for dyestuffs, it is also being increasingly used in the manufacture of insecticides, plastics, anaesthetics, etc. , and in recent years technical methods for the synthesis of carbazole, e.g. the Tauber synthesis[2] from o-nitrochlorobenzene and synthesis from 6-xenylamine,[3] have been evolved to meet the increasing demand for it. The percentage of carbazole in crude anthracene may be up to 40 depending upon the sample of coal.

Coke oven tars are refined in India by the following distillers: (1) Bareree Coke Co., Ltd., Kusunda; (2) Shalimar Tar Products (1935) Ltd. (Both situated near Jharia coal fields) ; and (3) Bengal Chemical and Pharmaceutical Works Ltd. (situated in Panihatti near Calcutta). Generally speaking, however, Indian coal tars are comparatively poor in the more important fractions of coal tar.[4] Crude carbazole is present in coal tar to the extent of about 0.05% and the potential production of carbazole from 90,000 tons of crude tar (quantity of tar obtained from Indian coke ovens at present) is therefore 450 tons per annum. Under actual conditions, however, economic recovery of carbazole is not likely to exceed 200 tons annually.

The first important use of carbazole was in the synthesis of the sulfurized vat dye, Hydron Blue, which is obtained by the thionation of carbazole-indophenol, the latter being obtained by the condensation of carbazole and p-nitrosphenol. Even today a major portion of carbazole produced is used in the production of Hydron Blue. The steps in the synthesis of Hydron Blue and the probable constitution[5,6] are as follows:



Carbazole p-Nitroso-phenol

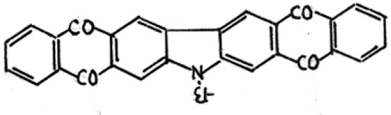
Carbazole Indophenol

Hydron Blue

Condensation of chloranil and 3-amino-N-ethyl-carbazole or similar other compounds of carbazole lead to useful pigments.[7]

Carbazole is also used for the manufacture of 2-hydroxycarbazole, an intermediate in the preparation of Naphtol AS-LB.

Condensation of phthalic anhydride with N-ethyl-carbazole in presence of aluminium chloride followed by the cyclization of the intermediate keto acid by sulphuric acid leads to a yellow vat dye, Hydron Yellow G.[8]



Hydron Yellow G

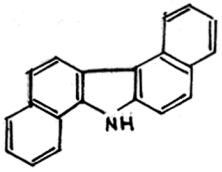
Nitration of carbazole with excess nitric acid gives the tetranitrocarbazole which is used as an insecticide.

One of the most important applications of carbazole is in the manufacture of plastics by the polymerization

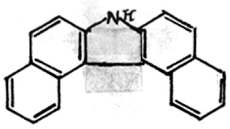
of its N-vinyl derivatives.

The carbazole ring system is also present in many naturally occurring products, in some vat dyes of outstanding fastness, although these products have not been synthesized from carbazole itself. As an example of a naturally occurring carbazole derivative may be mentioned Strychnine and Brucine from which it can be obtained by dry distillation.[9]

It has also been recently found that certain dibenzcarbazoles such as 1:2:5:6-dibenzcarbazole and 3:4:5:6-dibenzcarbazole possess carcinogenicity.[10] Specially important from this point of view is 3:4:5:6-dibenzcarbazole on account of its possible formation from 2-naphthylamine, one of the intermediates believed to be responsible for occupational cancer of the bladder in dyeworks (Rehn 1895) and now known to be able to induce this disease experimentally in dogs (Hueper,Bonser). 3:4:5:6-Dibenzcarbazole has the property of inducing tumours not only locally but in the liver as well.



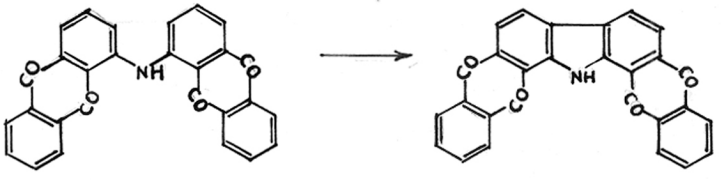
1:2:5:6-Dibenzcarbazole



3:4:5:6-Dibenzcarbazole

The anthrimide carbazoles, a very important branch of anthraquinone vat dyestuffs containing the carbazole

nucleus possess the best average all round fastness. Their chief mode of formation is by ring closure of poly-α-anthrimides with or without substituents, the latter being usually benzoylamino groups. Thus the treatment of 1:1'-dianthrimide with aluminium chloride followed by hypochlorite treatment yields 1:2:7:8-diphthaloylcarbazole, which is marketed under the name Indanthrene Yellow FFRK.



1:1'-Dianthrimide Indanthrene Yellow FFRK

Increase in the number of anthraquinone residues in the anthrimide carbazole leads to vat dyes of increased fastness; and example of a pentaanthrimide carbazole which contains 5-anthraquinone and 4 carbazole residues is Indanthrene Khaki 2G which is one of the most important vat dyes.[11]

The present work was undertaken under the auspices of the Shalimar Tar Products (1935) Ltd., to explore the methods for the utilization of carbazole, which is present in substantial quantities in the crude anthracene obtained in the above Works. Among the derivatives of carbazole which are technically useful is 2-hydroxycarbazole, an intermediate in the

preparation of Naphthol AS-LB, an azoic coupling component which is extensively used for brown shades on cotton. The I.G. method for the preparation of the hydroxycarbazole leaves some doubt as regards its constitution. The constitution of Naphtol AS-LB has likewise not been definitely established. The umambiguous synthesis of 2-hydroxycarbazole through the tetrahydro derivative as also the known 3-hydroxycarbazole were therefore undertaken for the purpose of comparison with the hydroxycarbazole obtained from Naphtol AS-LB by alkaline pressure hydrolysis. The comparison of the hydroxycarbazoles from Naphtol AS-LB and 2-hydroxycarbazole revealed their identity thereby proving the constitution of Naphtol AS-LB as the p-chloroanilide of 2-hydroxycarbazole-3-carboxylic acid. Apart from the above synthesis, attempts for the synthesis by other simpler methods were also undertaken.

A series of aminocarbazoles were prepared and their utility examined as fast colour bases and as intermediates in the synthesis of azoic coupling components by condensation with 2-hydroxy-3-naphthoic acid. It is important to discuss the chemistry of carbazoles and substituted carbazoles before the present work on the above lines is described.

II. ISOLATION FROM COAL TAR

The anthracene oil fraction (B.p. 290-380°) of coal tar serves as the main source of carbazole.

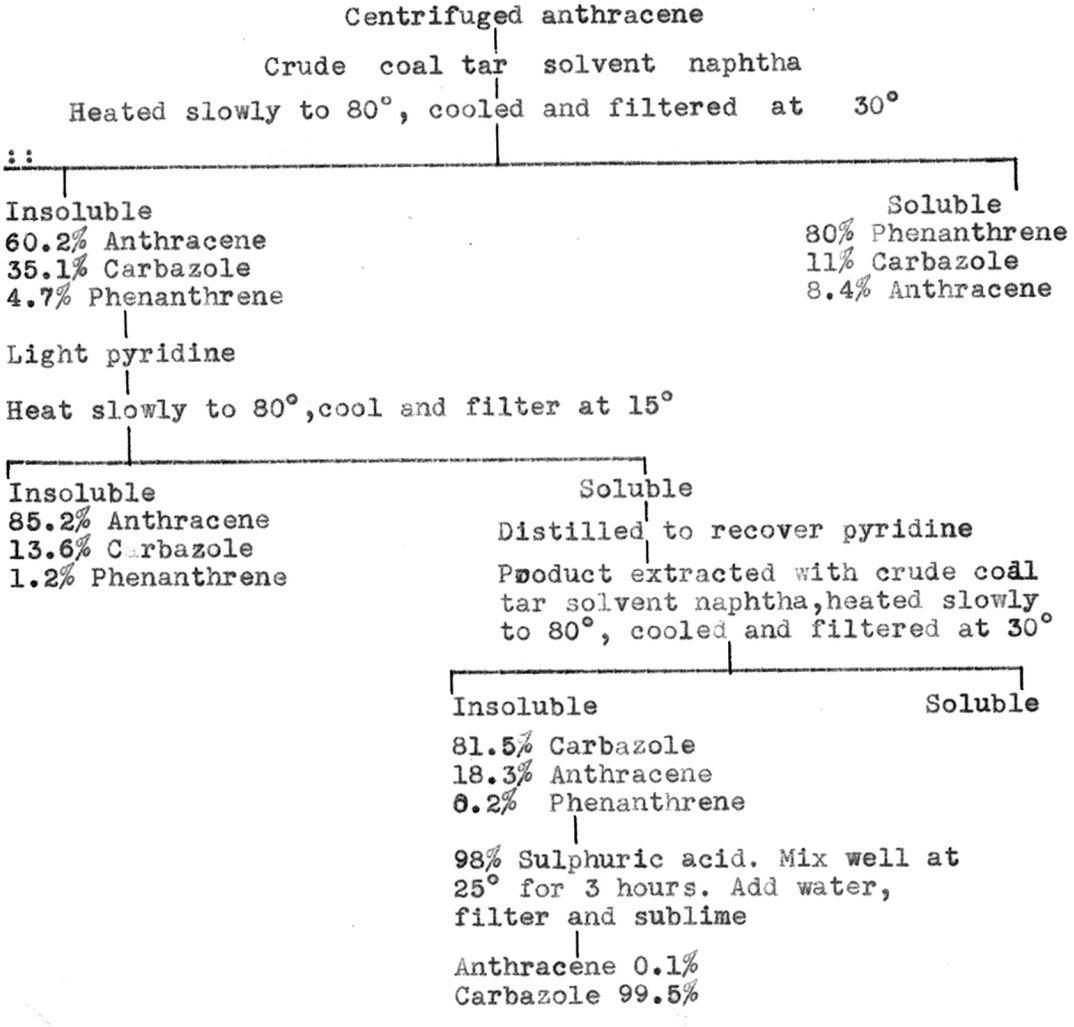
This fraction containing mainly anthracene, carbazole and phenanthrene is cooled and drained from the creosote oil and the anthracene "salts" thus obtained are centrifuged or hot or cold pressed to separate the adhering creosote oil. The crude anthracene thus obtained is generally an olive green solid containing varying amounts of the main constituents, anthracene (15-25%), phenanthrene (50%) and carbazole (20-30%).

Successive washings of the crude anthracene with solvent naphtha and pyridine yield a product which consists mainly of anthracene (about 80%) and carbazole. The older method of removing carbazole was to heat the anthracene-carbazole mixture with potassium hydroxide at about 230°, when potassium carbazole separated as the lower layer.[12] The usual method now employed is to selectively extract the carbazole with pyridine; thus 70% anthracene containing 20-25% carbazole can be raised to 94-95% purity by two extractions with warm pyridine bases (b.p. 130-150°). Carbazole can be recovered from the pyridine washings

and purified by repeated crystallization from solvent naphtha.

It has, however, been found that it is not possible to completely purify anthracene and carbazole by solvent extraction alone and it is necessary to employ chemical methods in the final step. Thus anthracene in carbazole (80%) can be removed as the sulphonic acid by treating with 98% sulphuric acid in the cold and washing with large quantities of water. Carbazole is scarcely affected under these conditions. The anthracene, however, is not recovered when this method is used and consequently a combination of solvent and chemical methods such as treatment of the mixture of anthracene and carbazole with boiling solvent naphtha containing powdered potassium hydroxide may be preferably employed as the anthracene can be recovered from the solvent naphtha extract and carbazole can be obtained from the sandy precipitate of potassium carbazole.

The following table due to Clarke[12] gives an idea of the number of operations involved in the isolation of pure carbazole from crude anthracene.



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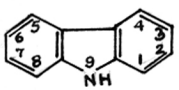
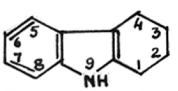
A solvent process for the isolation of pure carbazole from crude anthracene in 74% yield has been described. It consists in distilling the pyridine extract obtained from crude anthracene under reduced pressure and treating the residue with chlorobenzene at 140° under mechanical agitation.

After cooling to 40°, stirring is stopped and carbazole which settles quickly is removed from the supernatant liquid which is decanted off. On repeating the treatment carbazole of 97-98% purity is obtained. Another method for isolating carbazole directly from the coal tar fraction boiling at 320-360° by the intermediate preparation of the picrate has also been described.

III. SYNTHESIS OF CARBAZOLE AND ITS DERIVATIVES.

In carbazole there is a tricyclic ring system obtained by the fusion of two benzene rings symmetrically to a pyrrole ring. There are several syntheses given below which do not leave any doubt about this constitution. Of the various systems of numbering

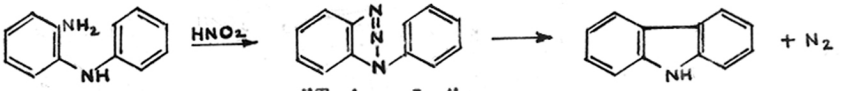
(I)  (II) 

Carbazole Tetrahydrocarbazole

the carbazole and tetrahydrocarbazole found in the literature, the one used in most American and British journals for carbazole (I) and tetrahydrocarbazole (II) has been followed in the present work.

(A) Graebe-Ullmann method : The method of Graebe and Ullmann[14] for the synthesis of carbazole is of wide application and consists in the treatment of o-amino-

diphenylamine with nitrous acid to give 1-phenyl-1:2:3-benzotriazole which when heated loses nitrogen to give



"Triazole" Carbazole

a quantitative yield of carbazole.

Preston, Tucker and Cameron[15] have synthesized nitrocarbazoles (trace), acetylcarbazoles (22%) and cyanocarbazoles (34%) by this method.

(B) Borsche's method : Carbazole can be prepared by the dehydrogenation of tetrahydrocarbazole which is readily synthesized by the Fischer indole synthesis from cyclohexanone phenylhydrazone by treatment with hot dilute sulphuric acid as condensing agent. Borsche[16] who first realized the full scope of the reaction prepared many substituted tetrahydrocarbazoles and carbazoles in this manner. Reagents other than

Tetrahydrocarbazole

sulphuric acid may be used; glacial acetic acid, for example, has been found to give cleaner products.

It has been found recently by Rogers and Corson[17] that 1:2:3:4-tetrahydrocarbazole and some of its derivatives can be prepared in one step without isolation of the intermediate phenylhydrazone. An organic acid such as formic, acetic or propionic can be used as a solvent and condensing agent or the reaction can also

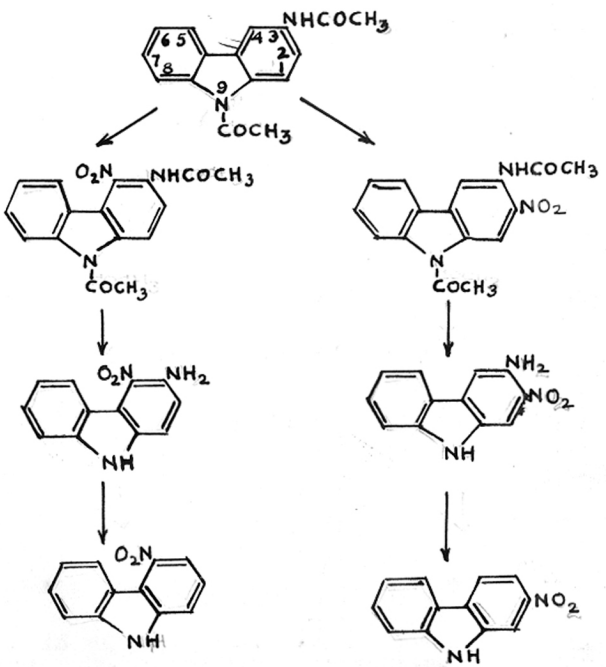
be carried out in aqueous or aqueous alcoholic solution in the presence of hydrochloric, phosphoric or sulphuric acids.

The value of the Borsche synthesis depends on a suitable means of dehydrogenation of tetrahydrocarbazoles to carbazoles. Many reagents such as lead oxide,[16] mercurous acetate[18] and palladous chloride[19] have been employed for effecting dehydrogenation, but the yields of carbazole derivatives are small in most cases. The recent method due to Barclay and Campbell[20] in which chloranil is used for effecting dehydrogenation gives good yields of the dehydrogenated derivatives.

Borsche's synthesis of carbazole, like that of Graebe and Ullmann, proves the constitution of carbazole as 2:3:4:5-dibenzpyrrole. The o- and p-substituted phenylhydrazines yield 6- and 8-substituted tetrahydrocarbazoles, but when a m-substituted phenylhydrazine is employed, a mixture of 5- and 7-substituted tetrahydrocarbazole is obtained which is difficult to purify. Separation of such a mixture can, however, be effected by chromatographic adsorption in certain cases.

(C) Synthesis of substituted carbazoles: Carbazole behaves as a derivative of diphenylamine in its substi-

tution reactions, the o- and p- positions to the nitrogen atom (1 and 3 positions) being first substituted. The reactive positions are therefore the 1,3, 6 and 8 positions. The 3-position is the most reactive and 3-substituted derivatives are readily obtained as the first step in substitution reactions followed by substitution in the 6, 1 and 8 positions. The introduction of a substituent in the m-position to the nitrogen atom can only be effected indirectly. Thus 2- and 4-nitrocarbazoles are prepared according to the following scheme :



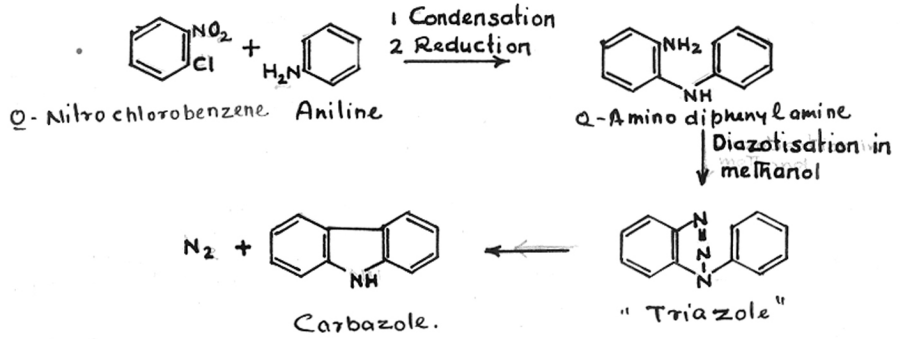
Synthesis of other substituted carbazoles will be discussed later.

(D) Miscellaneous methods : Several methods have been suggested for the synthesis of carbazole and its derivatives, but only a few of them have preparative value.

Mention may be made of the following reactions by which carbazole is obtained : (1) From diphenylamine by passage through an incandescent tube, or in the presence of a platinum catalyst at 300°. (2) From phenothiazine by heating with copper powder. (3) From 2-aminobiphenyl by distillation over lime. (4) From 2:2'-diaminodiphenyl by heating with acids and (5) From derivatives of 2:2'-diaminodiphenyl by tetrazotisation and treatment with copper.

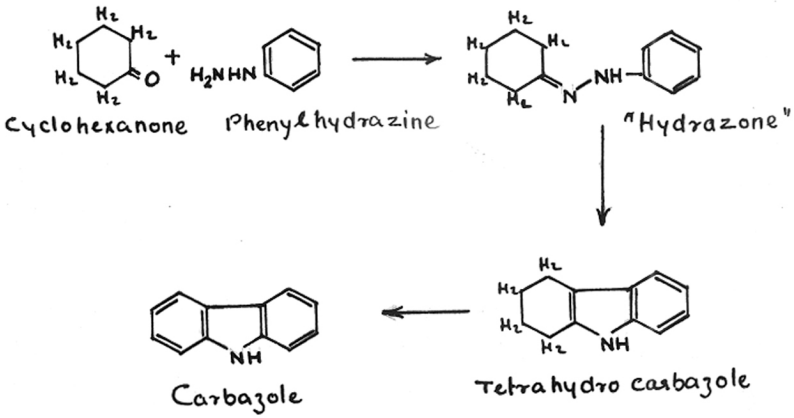
I.G.[2] attempts during the war to manufacture carbazole synthetically in view of the restricted supplies of anthracene oil, which was needed for carbon black, have been described recently. These may be briefly summarized as follows :

(1) The work undertaken at Hochst on the synthesis of carbazole was carried out along the following lines :-

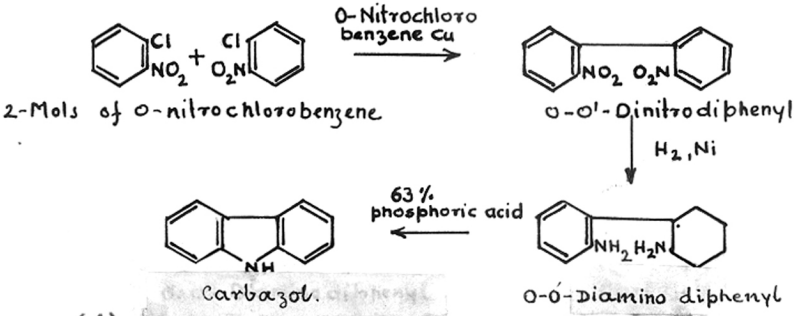


Orthonitrochlorobenzene was condensed with aniline to yield o-aminodiphenylamine. This was diazotized in methanol solution to the triazole which on heating to 350° yielded carbazole, nitrogen being evolved.

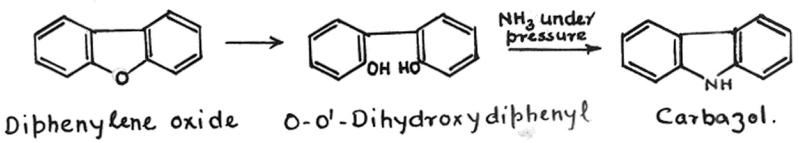
(2) A synthesis developed by Bucherer involved the reaction of cyclohexanone with phenylhydrazine to form hydrazone, which on heating with boiling 20% sulfuric acid yielded tetrahydrocarbazole. The latter compound was heated in naphthalene solution in the presence of nickel to 150° to yield carbazole.



(3) The Tauber synthesis consisted first in the reaction of two moles of o-nitrochlorobenzene in the presence of metallic copper powder to yield o:o'-dinitrobisphenyl. This was reduced with nickel in alcohol solution to the corresponding diamine. The diamine on heating with 63% phosphoric acid gave a practically quantitative yield of carbazole.

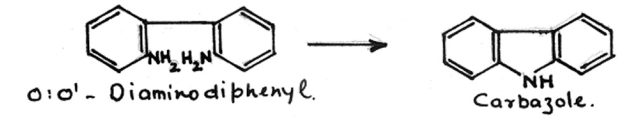


(4) Diphenylene oxide was available in Germany as a ~~by~~ by-product from coal tar distillation. Reaction with molten caustic soda yielded o-o'-dihydroxybiphenyl which on treating with ammonia under pressure at 180° yielded carbazole but the yield even under optimum conditions was 25%.



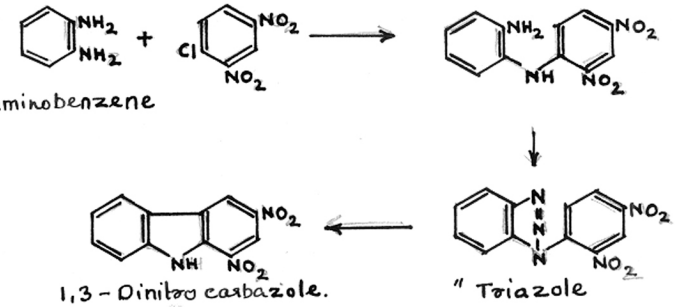
(5) o:o'-Diaminodiphenyl resulted in about 15% yield as a by-product in the manufacture of benzidine. Heating ~~mit~~ this with lime yielded 2-aminocarbazole. However, this compound could not be converted readily

to carbazole nor to carbazole derivatives suitable for dyestuff or insecticidal uses.



o:o'- Diaminodiphenyl. Carbazole.

(6) 1:3-Dinitrocarbazole was prepared in good yields from o-diaminobenzene. However, nitration to the desired tetranitrocarbazole was not practicable. Mononitrocarbazole could be synthesized fairly readily but it too proved to be undesirable as such or for nitration to the tetra-compound.



o-Diaminobenzene

1,3-Dinitro carbazole. " Triazole

The conclusion of the I.G. was that the best method for the preparation of synthetic carbazole was that based on the Tauber synthesis, but production by this method was however ~~not~~ not possible during the war due to an extreme shortage both of copper and phosphoric acid.

The method of Morgan and Walls[3] for the production of of carbazole by pyrolysis of o-xenylamine at 500-600° in the presence of vanadium pentoxide or other oxidation catalysts, has found industrial application since diphenyl from the pyrolysis of benzene has become readily available,

and o-xenylamine can be prepared in good yield from diphenyl. o-Xenylamine is fed at a measured rate into a vertical tubular furnace containing the catalyst, the furnace being uniformly heated throughout its length. Various catalytic materials are employed, and in general oxidation catalysts are found to become efficacious, giving higher yields of carbazole than the alkaline catalysts.

A method, which holds promise of technical exploitation, consists in the condensation of aromatic amines and 2-chloro-cyclohexanone to give good yields of tetrahydrocarbazole.[21]

IV. PROPERTIES OF CARBAZOLE

(a) Physical : Carbazole is a white substance crystallizing in lustrous flakes from hot alcohol, glacial acetic acid, benzene or toluene. The isolation of pure carbazole from crude anthracene is difficult and various melting points are quoted in the literature for carbazole, e.g. Tucker,[22] 245° ; Aristov,[23] 246° ; and Kirby,[24] 247°. Pure synthetic carbazole is fairly fluorescent and melts at 245° but most technical samples melt at about 235°.

(b) Chemical : Carbazole is a stable compound and is unchanged by distillation over glowing zinc dust. It dissolves unchanged in cold concentrated sulphuric acid and is reprecipitated on dilution with water.

Commercial carbazole gives a yellow solution in cold sulphuric acid but pure carbazole gives a colourless solution.

Of the many colour tests that are used for the detection of carbazole, one of the most characteristic is the bluish-green colour which is obtained when a trace of carbazole is dissolved in cold concentrated sulfuric acid and a drop of nitric acid added. Also a pine splint soaked in alcoholic hydrogen chloride develops a red colour when treated with vapours from an alcoholic solution of carbazole indicating that carbazole is a derivative of Indole.

Carbazole does not exhibit basic properties and is on the contrary a weak acid forming potassium salts with potassium hydroxide. It gives molecular complexes with picric acid and trinitrobenzene, which melt at 185° and 166° respectively.

As indicated above the 3- and 6-positions and to a lesser extent the 1- and 8-positions are the reactive positions involved in the direct substitution of carbazole.

This is clearly demonstrated by nitration which gives 75% of 3-nitro and 4 per cent of 1-nitro carbazole and by exhaustive nitration which yields 1:3:6:8-tetranitrocarbazole.

Direct substitution is generally employed for the preparation of 3-substituted carbazoles. The 1-isomers which are also formed to a small extent are generally separated only with difficulty. Morgan and Mitchell,[25] for example, separated 1- and 3-nitrocarbazoles by making use of their different basicities, but Preston, Tucker and Cameron[15] obtained most satisfactory results by chromotographic analysis. 1-Substituted carbazoles have to be prepared by indirect methods.

Tucker and coworkers,[15] for example, nitrated -- carbazole-3:6-dicarboxylic acid to give 1-nitrocarbazole-3:6-dicarboxylic acid, and then decarboxylated the acid to 1-nitrocarbazole.

Nitrous acid converts carbazole to N-nitrosocarbazole, which is rearranged by mineral acids to 3-nitrosocarbazole; the latter on reduction gives 3-aminocarbazole.

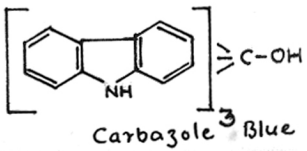
When heated with potassium hydroxide carbazole forms a potassium compound $(C_6H_4)_2NK$, which gives with methyl iodide 9-methylcarbazole, m.p. 87°, which is converted to phenanthridine by passing through an

incandescent tube.[26] This conversion is analogous to the conversion of pyrole to pyridine, and of indole to quinoline.

With methyl magnesium iodide, carbazole reacts like pyrole and indole, giving carbazole magnesium ø iodie, $(C_6H_4)_2$ NMgI, and methane.

Concentrated nitric acid or better ethyl nitrate and concentrated sulphuric acid yield nitrocarbazoles. 3-Nitrocarbazole, m.p. 214°, is obtained from carbazole by the action of nitrous anhydride (N_2O_3), the N-nitroso compound being an intermediate in the reaction; the nitro carbazole gives 3-aminocarbazole on reduction. Because of their sensitivity to light, the diazo compounds, of the latter are used in the production of photographic copies.[27] 1:3:6:8-Tetranitrocarbazole, m.p. 289°, is obtained from carbazole with ethyl nitrate and concentrated sulphuric acid.[28]

Fusion of carbazole with oxalic acid produces tricarbazolemethanol or carbazole blue.[29]

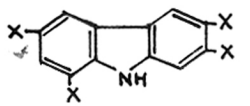


Carbazole Blue

On halogenation, as usual, the 3, and 3:6-positions are preferentially attacked. Sulfonation likewise leads

to the 3, 3:6 and the 1:3:6:8- substituted sulfonic acids of carbazole. Thus sulfonation under vacuum at 100° with molal quantity of sulphuric acid or sulfonation with molal quantities of chlorosulfonic acid or fuming sulphuric acid at low temperatures gives carbazole-3-sulphonic acid.[30] On further sulphonation, 3:6-disulphonic acid and the 1:3:6:8-tetrasulphonic acid are formed.

When carbazole is sulphonated under conditions where the water formed in the tetra sulphonation is removed immediately chemically by the use of fuming sulphuric acid or with other reagents such as phosphorous pentoxide which are capable of removing the water, the unusually orientated 2:3:6:8-tetrasulphonic acid is claimed to have been formed:[31]



X= SO_3H

A large number of metallized derivatives of carbazole and its derivatives especially the lithium and mercuric derivatives have been prepared by Gilman and his coworkers[32] who have converted these subsequently to the corresponding acids by treatment with solid carbondioxide. The position of the lithium group was established by comparison of the carboxylic acids derived from them with acids of known structure.

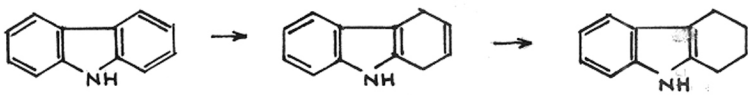
On progressive reduction of carbazole, 1:4-dihydrocarbazole (?), 1:2:3:4-tetrahydrocarbazole and hexahydro-

carbazole are obtained. While carbazole itself is catalytically hydrogenated with difficulty, the N-alkylcarbazoles are readily hydrogenated. Like the hydrogenated pyrroles and indoles, the hydrogenated carbazoles which are discussed in detail later are strong bases.

Carbazole may be oxidized by sodium dichromate in a mixture of sulphuric and acetic acids or potassium permanganate in acetone. With the latter reagent, Perkin and Tucker[33] isolated three products: (A) m.p. 220°; (B) m.p. 265°; and (C)(amorphous) m.p. about 175°; (A) and (B) were shown to be dicarbazyls. Product A was shown by Tucker and McLintock[34] to be 9:9'-dicarbazyl. The constitution of the dicarbazyl (B) has not been proved as yet. It differed from synthetic 3:3'-, 1:1'-dicarbazyls prepared by Tucker[35] and it is not unlikely that it is either the 1:3'- or the 1:9'-dicarbzyls.

V. REDUCTION OF CARBAZOLE

By analogy with naphthalene it might be expected that

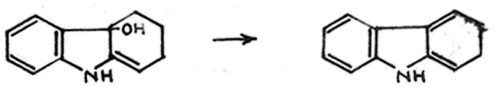


Carbazole 1:4-Dihydrocarbazole 1:2:3:4-Tetrahydrocarbazole.

hydrogenation of carbazole would yield first 1:4-dihydro- and then 1:2:3:4-tetrahydrocarbazole.

Schmidt and Schall[36] did claim to have prepared the dihydro compound by reduction of carbazole with sodium and

boiling amyl alcohol, but a critical examination of the resulting so-called 1:4-dihydrocarbazole by Barclay, Campbell and Gow[37] proved it to be a mixture containing at least 50% of carbazole. Of the five possible dihydrocarbazoles, 2:3-dihydrocarbazole prepared by Plant and Tomlinson[38] by the dehydration of 11-hydroxy-2:3:4:11-



11-Hydroxy-2:3:4:11-tetrahydrocarbazole 2:3-Dihydrocarbazole.

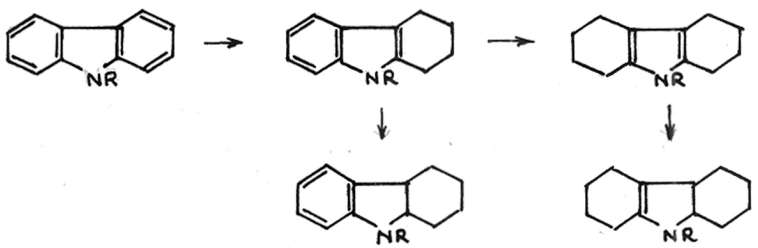
~~hexahydroca~~ tetrahydrocarbazole, is the only known example.

The tetrahydrocarbazole, m.p. 116°, prepared either by reduction of carbazole with sodium and alcohol[39] or more conveniently from cyclohexanone phenylhydrazone by the Borsche method,[16] is unambiguously constituted as 1:2:3:4-tetrahydrocarbazole. Shah, Tilak and Venkataraman[40] have isolated tetrahydrocarbazole from the reduction products obtained from carbazole by treatment with freshly prepared Raney nickel.[41] It has been stated that tetrahydrocarbazole decomposes on standing in air, but this holds only for the impure substance. When crystallized from light petroleum (100-120°), it separates as a colourless, stable substance, m.p. 116°.

1:2:3:4:10:11-Hexahydrocarbazole is obtained by reducing carbazole with hydriodic acid and phosphorous at 130°,[41] but it is more conveniently prepared either by the reduction of tetrahydrocarbazole with tin and

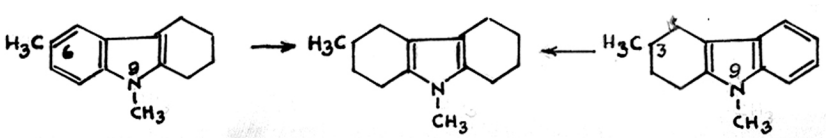
hydrochloric acid[16] or in quantitative yield by electrolytic reduction.[42]

Reduction of N-methyl or N-ethyl carbazole under more vigorous conditions such as treatment with hydrogen at 210° and 25 atm. pressure in the presence of a nickel catalyst, gives a mixture of tetra- and octahydrocarbazoles, along with the unchanged material.[43] The double

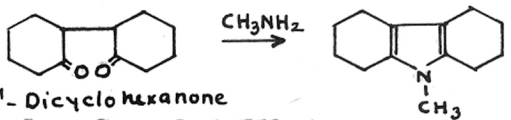


bonds ~~in~~ of the pyrrole ring in both the product remain in tact under the above conditions, but they may be attacked by tin and hydrochloric acid to give hexahydro- and a decahydrocarbazole, respectively. The decahydrocarbazole is extremely resistant to further reduction.

The position of the double bonds in the octahydrocarbazole was demonstrated in two ways by Von Braun and ~~Sh~~hornig[44] who obtained the same octahydrocarbazole by the reduction of both 6:9-dimethyl- and 3:9-dimethyl-1:2:3:4-tetrahydrocarbazoles. This result is consistent only with a pyrrole structure of the octahydrocarbazole as formulated below :



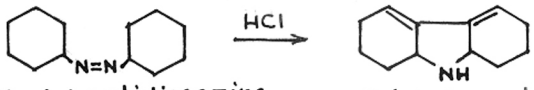
The correctness of Von Braun's conclusions was confirmed by Plant's synthesis from 2:2'-dicyclohexanone and methylamine - an extension of the well known synthesis



2:2'- Dicyclohexanone N-Methyloctahydro carbazole

of pyrroles from 1:4-diketones.

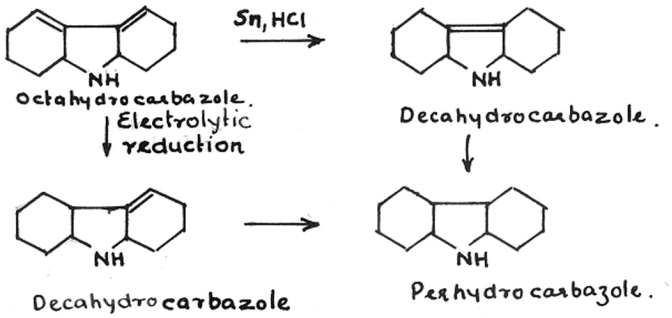
Perkin and Plant[46] prepared a second octahydrocarbazole by treating cyclohexylidine azine with hydrochloric acid.



Cyclohexylidineazine. Octahydro carbazole.

It is highly probable that the substance has the above structure, first suggested by Von Braun and Schornig,[44] but it has not been proved as yet. The same compound was also obtained by Benary[47] by treatment of the azine with chloroacetylchloride at room temperature, followed by hydrolysis.

More highly reduced carbazoles have also been prepared. Perkin and Plant[46] have obtained a decahydrocarbazole by reduction of the above octahydrocarbazoles with tin and hydrochloric acid and dodecahydrocarbazole (perhydrocarbazole) by electrolytic reduction. The decahydrocarbazole was stable to electrolytic reduction and could not therefore be an intermediate in the reduction to perhydrocarbazole. The latter substance is probably formed as shown below :



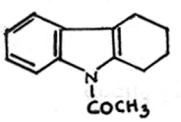
By hydrogenation of carbazole with copper chromite and Raney nickel catalyst under pressure, Adkins and Coonvadt[48] obtained 1:2:3:4-tetrahydrocarbazole, cis-1:2:3:4:10:11-hexahydrocarbazole, and dodecahydrocarbazole according to the catalyst and the conditions -- employed.

(A) Properties of Tetrahydrocarbazole : Tetrahydrocarbazole behaves like an alkalylated indole and is much more basic than carbazole. This is the basis for an elegant method for the separation of a mixture of carbazole, tetrahydrocarbazole and other reduced carbazoles.[48] On treatment of the mixture with concentrated hydrochloric acid, carbazole remains insoluble while the reduced carbazoles go into solution. Tetrahydrocarbazole can be separated from the extract by graded dilution with water; the mixture of the higher hydrogenated derivatives being finally obtained by neutralization of the diluted acid solution with ammonia.

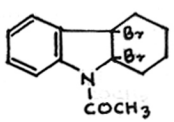
Of the different reduced carbazoles, tetrahydrocarbazole is the most important. Nitration of tetrahydrocarbazole or its N-methyl derivative with concentrated nitric and sulphuric acids at -5°, gives 6-nitro-1:2:3:4-tetrahydrocarbazole or its N-methyl derivative; while nitration of the N-acetyl or N-benzoyl derivatives give the 7-nitro-N-acetyl or 7-nitro-N-benzoyl derivative.

The fact that substitution takes place in the 7-position in tetrahydrocarbazole when the imino nitrogen has been substituted by an acyl group provides a route for the preparation of m-substituted carbazole derivatives which are difficult to prepare by direct substitution. Dehydrogenation of the substituted tetrahydrocarbazole with chloranil gives a nearly quantitative yield of the corresponding substituted carbazole.

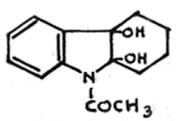
Bromination of N-substituted tetrahydrocarbazoles[49] leads to the formation of unstable 10:11-dibromoderivatives of the same, which react instantaneously with water to give the corresponding dihydroxy compounds or their anhydro derivatives. Thus, N-acetyltetrahydrocarbazole yields N-acetyl-10:11-dihydroxyhexahydrocarbazole.



N-Acetyl tetrahydro carbazole

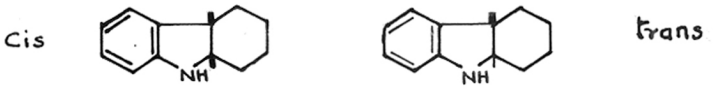


N-Acetyl-10:11-di
- bromohexahydro-
- carbazole.



N-Acetyl-10:11-
- dihydroxy-
- hexahydro carbazole.

(B) Properties of 1:2:3:4:10:11-hexahydrocarbazole. - Hexahydrocarbazole exists in cis- and trans- forms.



The atomic model for the cis- form shows that it is less strained than the trans- form and should consequently be more stable. In comformity with this expectation, Gurney, Perkin and Plant[50] have found that the hydrogenation of tetrahydrocarbazole gave the cis- form in greater yield than the trans- form which amounted only to 1 to 2 per cent of the reaction product.

VI. SIMPLE DERIVATIVES OF CARBAZOLE.

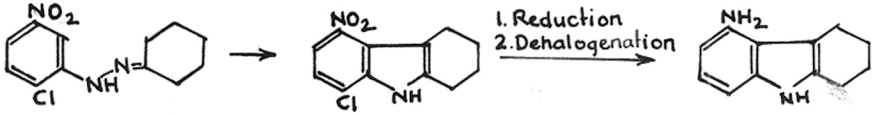
(A) Nitro carbazoles. - 3-Nitrocarbazole, m.p. 214°, is the most accessible of the nitrocarbazoles and is best prepared by modifications of the method of Ruff and Stein[51] i.e. by the action of nitric acid on N-nitrosocarbazole. While Ruff and Stein removed the nitroso group by boiling with amyl alcohol it has now been found that the nitroso group is subsequently best removed by heating with alkali, glacial acetic acid or urea.[52]

Another mononitro carbazole, m.p. 187°, first isolated by Votocek in 1896,[53] was shown by Lindemann[54] to be 1-nitrocarbazole as it gave on reduction an amino carbazole which was identical with 1-aminocarbazole prepared unambiguously by the Graebe-Ullmann method. The nitro

compound, m.p. 164°, obtained by Ziersch[55] which was mistaken for 1-nitrocarbazole for a long time was shown by Morgan and Michell[25] to be an equimolecular mixture of 1- and 3-nitrocarbazoles.

1-Nitrocarbazole may be prepared by the decarboxylation of 1-nitrocarbazole-3:6-dicarboxylic acid[25] or by the desulphonation of 1-nitrocarbazole-3:6:8-trisulphonic acid.

Borsche, Witt and Bothe[16] claimed to have obtained a single compound by the ring closure of cyclohexanone-m-nitrophenylhydrazone, but Plant showed that their product was a mixture of 5-nitro- and 7-nitrotetrahydrocarbazoles, although a pure sample of the 5-isomer was not isolated. The constitution of these compounds was proved by reduction to the corresponding amines and by comparison of their properties with an authentic sample of 5-nitro-tetrahydrocarbazole prepared from cyclohexanone-2'-chloro-5'-nitrophenylhydrazone according to the following scheme :



Barclay and Campbell[20] isolated pure 5- and 7-nitro-tetrahydrocarbazoles by chromatographic separation of the mixture of nitrocarbazoles obtained from cyclohexanone-m-nitrophenylhydrazone. The tetrahydro derivatives were subsequently dehydrogenated by chloranil to give

the 2- and 4-nitrocarbazoles respectively.

(B) Aminocarbazoles. - The accessibility of the aminocarbazoles depends on the ease of preparation of the nitro derivatives from which they are obtained by reduction. Thus, 3-aminocarbazole is obtained by reduction of the easily synthesized nitrocarbazole.

Lindemann and Werther[54] prepared 1-aminocarbazole in low yields by the reduction of 1-nitrocarbazole. Better results were obtained by starting with 1-phenyl-5-carboxy-7-aminobenzotriazole,[55] but this method is also unsuitable for preparative work.

A substance claimed to be 2-aminocarbazole, m.p.238°, was prepared by Blank[56] by the pyrolysis of "diphenylin" (a compound which was probably 2:4'-diaminodiphenyl) but in view of the uncertain nature of the starting material, lack of experimental details and also in view of the fact that the final product was not analysed, the identity of Blank's compound with 2-aminocarbazole cannot be regarded as established. The ambiguous nature of the synthesis of a product claimed to be 2-aminocarbazole prepared by the I.G. from m-aminodiphenylamine has been mentioned earlier. 2-Aminocarbazole, m.p. 236°, has now been synthesized unambiguously by the Raney nickel reduction of authentic 2-nitrocarbazole.

(C) Halogeno carbazoles. - Halogenation of carbazole like nitration yields the 3-substituted derivatives in the first step followed by substitution in the 3:6-positions, The dihalogenation takes place so readily that the dihalogeno derivatives are the most accessible halogen derivatives of carbazole. Unlike 3-nitrocarbazole, 3-halogenocarbazoles cannot be obtained in a pure condition by direct halogenation. Attempts to replace the amino group in 3-aminocarbazoles by the Sandmeyer reaction under the usual experimental conditions lead to the unreactive carbazole-3-diazonium hydroxide; Morgan and Read's discovery[57] that carbazole-3-diazonium chloride, which was prepared by them in a crystalline condition under closely defined experimental conditions is therefore important and the diazonium chloride was subsequently used by Tucker[58], e.g. by treating carbazole-3-diazonium chloride in methyl acetate solution with copper bronze powder, he obtained pure 3-chlorocarbazole in good yield.

All the monochlorocarbazoles have been prepared. Moggridge and Plant[59] obtained 5- and 7-chlorotetrahydrocarbazoles from cyclohexanone-m-chlorophenylhydrazone and prepared 2- and 4-chlorocarbazoles by dehydrogenation with sulphur in quinoline. Barclay and Campbell[20] obtained all the monochloro- and monobromocarbazoles by

chloranil dehydrogenation of the corresponding halogeno-tetrahydrocarbazoles.

Tucker[22] has prepared iodocarbazoles by the action of potassium iodide and potassium iodate on carbazole in glacial acetic acid, the main product of the reaction being 3-iodocarbazole, which was identical with a specimen prepared from 3-aminocarbazole by the Sandmeyer reaction. Tucker also isolated a diiodo compound which was constituted as 3:6-diiodo carbazole. Although the positions of the iodine atoms in the latter have not been proved, it is reasonable to assume that substitution takes place in the 3:6-position by analogy with other disubstitution reaction; for example, Gilmann and Kirby[32] have obtained 3:6-diiodo-N-ethylcarbazole by iodination from N-ethylcarbazole.

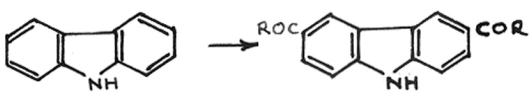
(D) Hydroxycarbazoles. - Of the four possible monohydroxycarbazoles, only 3-hydroxycarbazole, m.p. 261°, has been fully described in literature. It has been prepared in low yield (10%) by Ruff and Stein[51] by heating carbazole-3-diazonium chloride. The alkaline pressure hydrolysis[60] of the halogenocarbazoles has also been found to yield the 3-hydroxy derivative in 33% yield from 3-chlorocarbazole.

A patent claim has been made for the synthesis of 1-hydroxycarbazole, by the desulphonation of the potassium salt of a hydroxycarbazoledisulphonic acid with 5% sulphuric acid for five hours in an autoclave at 180°; the hydroxycarbazole crystallizes in white plates, m.p. 163°.[61]

2-Hydroxycarbazole, (m.p. 276°), which crystallizes in leaflets with a silvery luster from alcohol is soluble in most organic solvents and is a useful intermediate in the preparation of Naphtol AS-LB, which is widely used for producing fast brown shades on cotton. While it is claimed that it is prepared from 2-aminocarbazole by diazotisation followed by boiling the reaction mixture in water, the source of 2-aminocarbazole is not mentioned.[62] It is also claimed that it can be obtained by alkaline pressure hydrolysis of the corresponding halogenocarbazoles.[60] The I.G. method of preparation[63] consists in sulphonating carbazole to 2:3:6:8-tetrasulphonic acid, followed by partial hydrolysis to 2-hydroxycarbazole-3:6-8-trisulphonic acid; the latter on desulphonation gives 2-hydroxycarbazole. The orientation of the hydroxycarbazoles and the interim sulphonic acids has not been proved. 2-Hydroxycarbazole has now been prepared by an unambiguous synthesis.

(E) Carbazyl ketones. - The acyl carbazoles, prepared by the Friedel-Craft's reaction have been extensively studied by Plant and his coworkers. The course of the acylation depends on several factors.

Reaction of carbazole with even limited quantities of acid chlorides in the presence of aluminium chloride in carbon disulphide solution yields mainly 3:6-disubstituted products, the monosubstituted derivatives being obtained only in small quantities; 3:6-dibenzoyl[64] and diacetyl derivatives[65] are prepared in this manner. The structure of



these compounds were determined by comparison with samples synthesized by unambiguous methods.

3-Benzoyl and 3-acetylcarbazoles were obtained by "baking" N-benzoyl or N-acetylcarbazoles with aluminium chloride at 120°. The constitution of the 3-acetyl derivative was proved by reduction to 3-ethylcarbazole, whose structure was determined by synthesis. Plant[64] and Meitzner,[66] however, found that baking does not always proceed smoothly and that the best results are obtained when nitrobenzene is used as a solvent for the reaction with aluminium chloride.

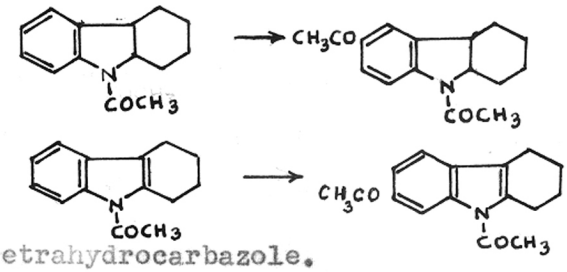
9-Alkylcarbazoles react with acid chlorides and aluminium chloride in the same way as carbazole;

9-methylcarbazole, for example, giving with acetyl bromide and aluminium chloride 3:6-diacetyl-9-methylcarbazole. 9-Acylcarbazoles on the other hand give 2:9-derivatives; thus, Plant and Williams[72] found that 9-acetylcarbazole gave 2:9-diacetylcarbazole. Results with 9-benzylcarbazole have not been consistent. Plant and Tomlinson[65] found that it yielded with benzoyl chloride and alumium chloride 3:6-dibenzoylcarbazole, but later Plant, Williams and Rogers[64] were unable to repeat this result and obtained instead 2:9-dibenzoylcarbazole; these discordant observations have yet to be explained. The reactivity of the two positions in the above experiments was also shown by Ruberg and Small,[66] who obtained 2-chloroacetyl-9-acetylcarbazole from 9-acetylcarbazole and chloroacetylchloride.

Hydrolysis of the 2:9-derivatives gives 2-acetyl- and 2-benzoylcarbazoles. 2-Benzoylcarbazole, m.p. 163°, prepared in this manner by Plant, Rogers and Williams,[64] was different from the substance,[67] m.p.350°, which was previously regarded as having this structure.

Another factor which affects the course of acylation of the carbazole nucleus by the Friedel-Craft reaction is the degree of reduction of carbazole. Mitchell and Plant obtained 6:9-diacetylhexahydrocarbazole from 9-acetylhexahydrocarbazole, but Plant and Rogers found

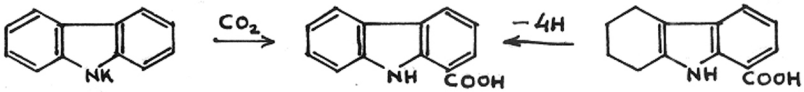
the product from 9-acetyltetrahydrocarbazole to be 7:9-



diacetyltetrahydrocarbazole.

(F) Carbazolecarboxylic acids. - The carbazolecarboxylic acids are not readily prepared in large quantities, but 1-, 2- and 3-carbazolecarboxylic acids have been prepared and characterized.

Ciamiacian and Silber[70] obtained a monocarboxylic acid, m.p. 271-272°, by passing carbondioxide into potassium carbazole, followed by treatment with dilute sulphuric acid. This acid was shown by Briscoe & Plant[67] to be identical with carbazole-1-carboxylic acid, obtained by



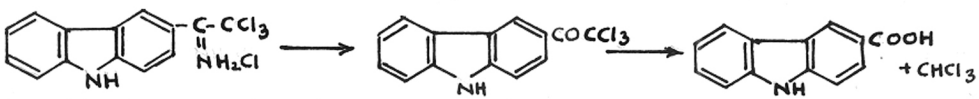
the dehydrogenation of 1:2:3:4-tetrahydrocarbazole-8-carboxylic acid.

Gilman and Kirby[32] found that interaction of carbazole and N-butyllithium followed by carbonation gave carbazol-1-carboxylic acid in low yield. Better results were obtained with N-methylcarbazole, the resulting 9-ethylcarbazole-1-carboxylic acid being identical with that obtained by treating carbazole-1-carboxylic acid with diethyl sulphate.

and potassium hydroxide.

Carbazole-2-carboxylic acid was prepared by Borsche and Fiese[71] by fusing 2-acetylcarbazole with potassium hydroxide; by Moggridge and Plant[59] by dehydrogenation of 1:2:3:4-tetrahydrocarbazole-7-carboxylic acid with palladized charcoal; and also from 2-benzoylcarbazole by fusion with potassium hydroxide.

Carbazole-3-carboxylic acid has been prepared by similar methods, viz., fusion of 3-acetylcarbazole with potassium hydroxide[72] dehydrogenation of the methyl ester of the corresponding tetrahydrocarbazolecarboxylic acid;[59] and the mercuration of N-ethylcarbazole and suitable treatment of the product, when the N-ethylderivative of carbazole-3-carboxylic acid was obtained.[32] It is of interest that whereas metallization of N-ethylcarbazole with lithium gives the 1-lithium compound, mercuration occurs in the 3-position. More recently Dunlop and Tucker[58] have prepared the acid by the Houben-Fischer method. Action of trichloroacetonitrile on carbazole in chlorobenzene solution in presence of aluminium chloride and dry hydrogen chloride gave 3-trichloroacetylcarbazole, which on alkaline hydrolysis yielded carbazole-3-carboxylic acid.



Carbazole-4-carboxylic acid has not yet been prepared, since efforts to dehydrogenate 1:2:3:4-tetrahydrocarbazole-5-carboxylic acid were unsuccessful.[59]

A carbazoledicarboxylic acid is stated in the patent literature[73] to have been prepared by the action of carbondioxide on potassium carbazole, but no proof of structure is given. Mitchell and Plant[68] were the first to prepare carbazole-3:6-dicarboxylic acid and prove its structure by shewing it to be identical with the product of fusion of ~~3:6-dicarbx~~ 3:6-dibenzoylcarbazole with potassium hydroxide. It has also been prepared by the Houben-Fischer method.[58]

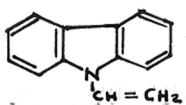
(G) N-substituted carbazoles. - N-alkyl, -acyl, or -aryl derivatives have been obtained by the action of the appropriate reagents on (1) carbazole, (2) potassium carbazole and (3) carbazole magnesium iodide. Carbazole gives the N-potassium derivative when fused with potassium hydroxide and reacts with methyl magnesium iodide to give the compound $C_{12}H_8NMgI$. N-alkylcarbazoles result on treatment of the N-potassium derivative with alkyl halides, preferably iodides under mild conditions. N-Acetylcarbazoles may be obtained from the potassium or magnesium derivative by treatment with acyl halides. N-Acetylcarbazole can also be prepared in good yield by the action of acetic anhydride containing a trace of sulphuric acid on carbazole.

Carbazole yields N-nitrosocarbazole, m.p. 82°, on treatment with potassium nitrite and acetic acid.

None of the methods mentioned above are satisfactory

for preparative work and hence the method developed by Tucker and Stevens[74] which gives nearly quantitative yields of the N-substituted derivatives is particularly important. It consists in the treatment of carbazole in acetone or alcohol solution with the required alkylating or acylating agent at room temperature in the presence of sodium or potassium hydroxide. Tucker and Stevens found that with greater acidity of the imino hydrogen, the reaction was more successful. The process, however, is not infalliable and is unsuccessful in a few cases. Tucker found that vigorous shaking must be avoided in preparation of N-benzoylcarbazole, and Ruberg and Small[66] were able to methylate 2-chloroacetylcarbazole only to a small extent. It may be noted that the N-benzoyl compound is obtained in 60% yield by heating carbazole with anhydrous potassium carbonate and benzoyl chloride in the presence of copper bronze.

N-Vinylcarbazole,[75] which is prepared in a number



N-Vinyl-carbazole

of ways such as the interaction of carbazole and acetylene with an alkali catalyst under pressure and at moderate temperature yields a transparent thermoplastic polymer with valuable electrical properties and a

high softening temperature (250°). The latter plastic is sold under the name "Luvican".

VII. METHODS OF ESTIMATION OF CARBAZOLE

In addition to the analysis of carbazole and its derivatives by estimation of elementary nitrogen by Dumas' and Kjeldahl's methods, a few other methods are also available.

A suitable method [76] for the routine determination of carbazole in semirefined and refined technical anthracenes containing 1-6% of carbazole depends on the formation of a blue condensation product on reacting carbazole with salicylaldehyde at or near room temperature in the presence of glacial acetic acid and sulphuric acid. A blank with carbazole free anthracene and salicylaldehyde under parallel conditions is red. The method may be extended to samples which contain up to 24% of carbazole by quantitative dilution of the test sample to about 6% with purified anthracene.

In another method [77] the carbazole is separated as N-nitrosocarbazole. It is then decomposed by boiling with ferrous sulphate solution and the nitric oxide produced is measured. Phenanthrene, anthracene and acridine do not interfere with the

estimation.

For the qualitative testing of the purity of carbazole, the determination of the melting point, solubility in chlorobenzene and the percentage of chlorobenzene insoluble substances are carried out. The anthracene content in carbazole can be estimated either gravimetrically or by measuring the strength of its fluorescence. The latter property can be considerably intensified if the fluorescence of the carbazole is removed chemically by converting it into the non-fluorescent N-nitroso derivative.

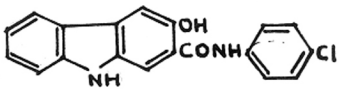
Carbazole can also be determined quantitatively according to Kraemer and Spilker, by either of the two following methods: (1) The basic impurities are removed by extraction of the sample with warm dilute sulphuric acid and the percentage of nitrogen in the treated product is determined by Kjeldahl's or by Dumas' method. From this, the amount of carbazole is calculated. (2) Carbazole is converted into potassium carbazole by the action of potassium hydroxide on carbazole at 220-240° in a steel crucible. The impurities present in carbazole are driven off at a temperature not exceeding 240°. Potassium carbazole so obtained is then hydrolyzed, carbazole washed and dried. From this, the purity is calculated Thede two methods however do not give very reliable results.

PART I

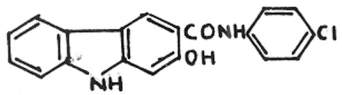
I. CONSTITUTION OF NAPHTOL AS-LB (BRENTHOL BT).

Naphtol AS-LB (Brenthol BT) is an azoic coupling component derived from carbazole which is used extensively for the production of fast brown shades on cotton.

There is conflicting data regarding its constitution. While Mehta and Desai [78] consider it to be the /p-chloroanilide of 3-hydroxycarbazole-2-carboxylic



(I) [79]



[80] (II)

acid (I), Lapworth and Dieserens state that it is the p-chloroanilide of 2-hydroxycarbazole-3-carboxylic acid (II).

A B.I.O.S. Report [63] gives details of the manufacture of the product claimed to be 2-hydroxycarbazole-3-carboxylic acid but the constitution of this acid has not been definitely established. The present work was undertaken with a view to establish the constitution of Naphtol AS-LB and it has now been shown that Naphtol AS-LB is correctly represented by II.

3-Hydroxycarbazole, m.p. 259°, was prepared from 3-chlorocarbazole by alkaline pressure hydrolysis in an autoclave in the presence of copper-bronze as catalyst. Since the orientation of the chlorine

atom in the latter compound has been definitely established by Ullmann,[81] the hydroxycarbazole obtained from it is, therefore, 3-hydroxycarbazole. Alkaline pressure hydrolysis of Naphtol AS-LB results not only in the hydrolysis of the anilide group, but also in the decarboxylation of the resulting hydroxycarboxylic acid, the parent hydroxycarbazole, m.p. 269° and p-chloroaniline being isolated as the final products of hydrolysis. The melting point of 3-hydroxycarbazole was depressed by admixture of the hydroxycarbazole from Naphtol AS-LB. The latter hydroxy derivative cannot therefore be 3-hydroxycarbazole. The nature of Naphtol AS-LB as an o-hydroxycarbaxyanilide functioning as an azoic coupling component rules out the 1- and 4- positions in the carbazole nucleus for the hydroxyl groups. The hydroxycarbazole obtained from Naphtol AS-LB must therefore be 2-hydroxycarbazole.

The non-identity of the two hydroxycarbazoles was further confirmed by comparison of their absorption spectra and the comparison of their respective acetates and 3:5-dinitrobenzoates. The absorption spectra of the two hydroxycarbazoles showed marked divergence and the corresponding derivatives of the two compounds were also not identical.

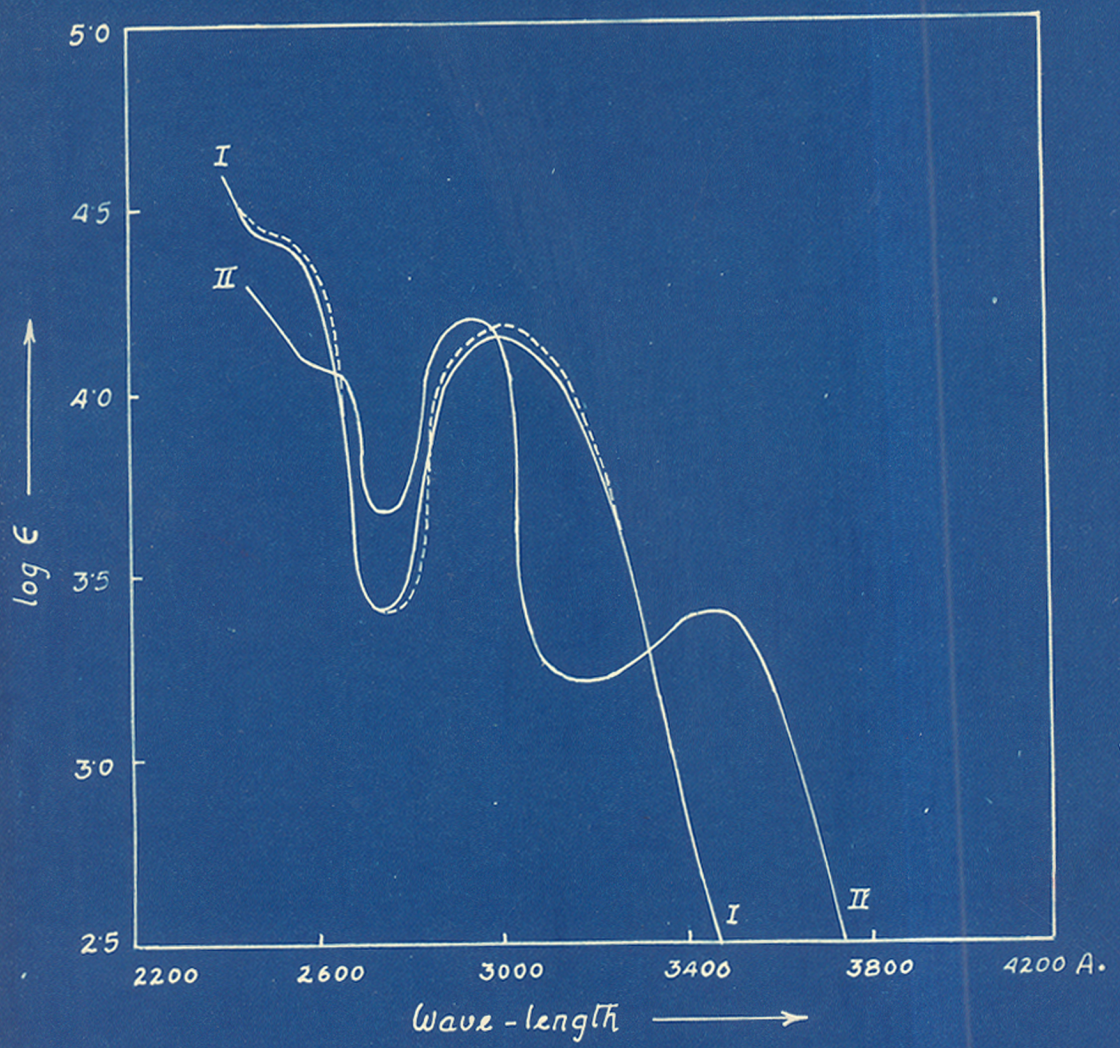


Fig. 1. Absorption spectra of

(i) Hydroxycarbazole from Naphtol AS-LB (I; —);

(ii) Synthetic 2-hydroxycarbazole (I; ----);

(iii) Synthetic 3-hydroxycarbazole (II; —);

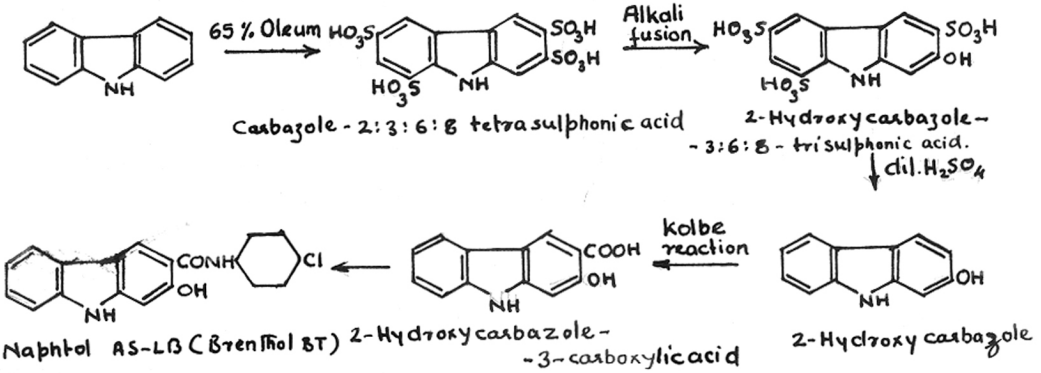
(Solvent – alcohol)

Since the Kolbe reaction is employed in the preparation of the hydroxycarbazolecarboxylic acid, it is obvious that the hydroxyl and the carboxylamide groups are in the ortho positions in Naphtol AS-LB. This is further confirmed by the fact that the hydroxycarbazole carboxylic acid which is obtained from the Naphtol in small quantity by alkaline hydrolysis of Naphtol AS-LB at atmospheric pressure for 120 hours gives a deep green coloration in alcoholic solution with ferric chloride, characteristic of o-hydroxycarboxylic acids. Naphtol AS-LB is therefore the p-chloroanilide of 2-hydroxycarbazole-3-carboxylic acid.

II. SYNTHESIS OF 2-HYDROXYCARBAZOLE.

2-Hydroxycarbazole, the intermediate necessary for the preparation of 2-hydroxycarbazole-3-carboxylic acid which is subsequently used for the synthesis of Naphtol AS-LB is prepared by the I.G. by tetrasulphonation of carbazole to the 2:3:6:8-sulphonic acid, followed by partial hydrolysis to the 2-hydroxycarbazole-3:6:8-trisulphonic acid and desulphonation of the latter to give 2-hydroxycarbazole. The I.G. synthesis[63] of Naphtol AS-LB is outlined in Chart 1.

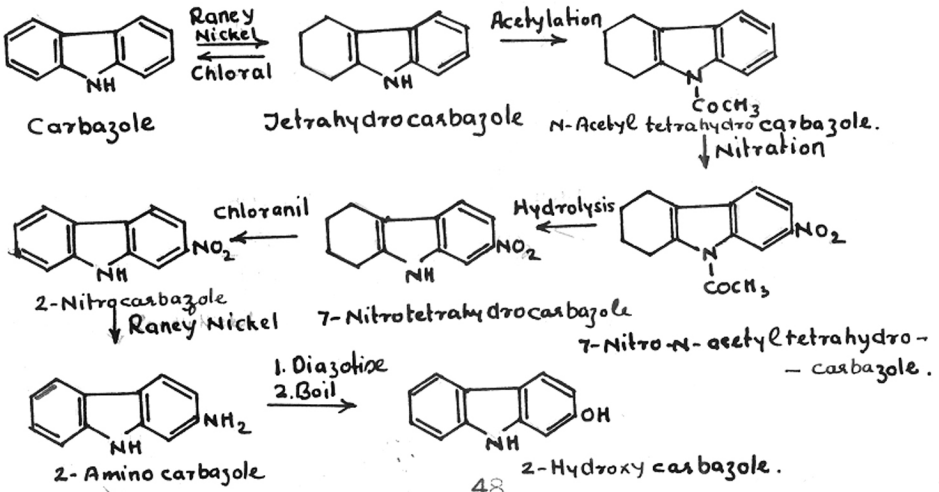
Chart 1.



The constitution of hydroxycarbazoles and the interim sulphonic acids has not been definitely established and attempts were, therefore, made to prepare 2-hydroxycarbazole unambiguously and if possible by a technically feasible process.

The favoured positions in the carbazole molecule which are substituted in reactions such as nitration and halogenation are the 3, 3:6 and the 1:3:6:8-positions(mentioned in decreasing order of reactivity). Tetrahydrocarbazole likewise gives the 6-nitro derivative by nitration, but substitution in the desired 7-position takes place on nitration of the N-acetyl derivative, and advantage was taken of this fact to prepare 2-hydroxycarbazole by the following series of reactions.(Chart 2):

Chart 2.



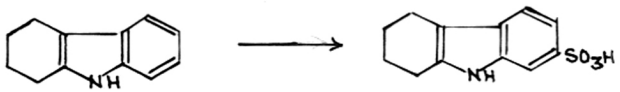
While Adkins and Coonvadt[48] have found that the hydrogenation of carbazole to tetrahydrocarbazole and higher hydrogenated derivatives take place only under high pressure, it has now been found that the reduction of carbazole to tetrahydrocarbazole can be effected under milder conditions, such as treatment with Raney nickel (10 parts) in 90% yield on the basis of the carbazole reduced, although 50% of the original carbazole was recovered unconverted. The nitration of N-acetyltetrahydrocarbazole gave N-acetyl-7-nitrotetrahydrocarbazole (III)[82] which on hydrolysis yielded 7-nitrotetrahydrocarbazole (IV). The orientation of the nitro groups in the latter compound has been unambiguously established by Plant[83] and Barclay and Campbell[20] obtained the same compound by

chromatographic separation of the mixture of 5- and 7-nitrotetrahydrocarbazoles obtained by the cyclization of cyclohexanone-m-nitrophenylhydrazone. 7-Nitrotetrahydrocarbazole was dehydrogenated to 2-nitrocarbazole (V) according to Barclay and Campbell by heating with chloranil in xylene solution. The conversion of 2:2'-diaminodiphenyl to 2-aminocarbazole has been claimed by Blank[56] and also by I.G.[2] A patent claim for the synthesis of 2-hydroxycarbazole from 2-aminocarbazole has been made, but the source of the latter compound has not been mentioned.[62] An authentic sample of 2-aminocarbazole has now been prepared by reducing with Raney nickel in alcohol medium with hydrogen under pressure (42 lbs. per sq. inch) and the amino group has been replaced by hydroxyl by diazotisation and boiling to form 2-hydroxycarbazole.

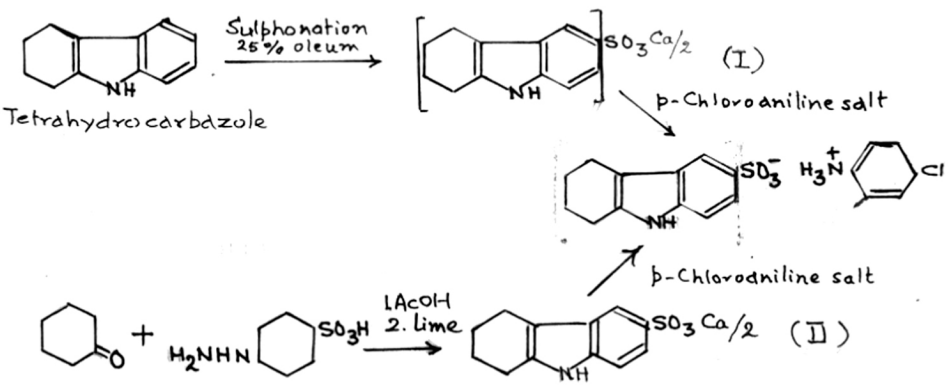
III. SULPHONATION OF TETRAHYDROCARBAZOLE

Another possible route to 2-hydroxycarbazole is through the tetrahydrocarbazole-7-sulphonic acid, which may result if the sulphonation is carried out with fuming sulphuric acid by analogy to the m-sulphonation of o-toluidine or its N-alkyl derivatives by means of fuming sulphuric acid,[84] tetrahydrocarbazole being regarded as an analogue of N-alkyl-o-toluidine.

This is due to the fact that while the free amino group has an o- and p- orienting influence on the freshly entering group in the case of aromatic compounds, the sulphate of the same free amino group which would be formed with oleum would be meta-orienting in respect to the newly entering substituent. The



tetrahydrocarbazole-7-sulphonic acid mentioned above has not been described in literature. Tetrahydrocarbazole was sulphonated with 25% oleum and the monosulphonic acid obtained was isolated as the calcium salt. The calsium salt on boiling with an aqueous solution of p-chloraniline and excess of hydrochloric acid gave the p-chloroaniline salt, m.p. 230°, of the tetrahydrocarbazole sulphonic acid. The latter salt can be diazotized and coupled with secondary coupling components and its titre with alkali and sulphur content corresponded to the p-chloroaniline



salt of tetrahydrocarbazole monsulphonic acid.

With a view to determine the orientation of the tetrahydrocarbazole-monosulphonic acid (I) obtained above, experiments were then undertaken to synthesize authentic samples of the hitherto unknown 1:2:3:4-tetrahydrocarbazole-6- and 7-sulphonic acids for comparison. 1:2:3:4-Tetrahydrocarbazole-6-sulphonic acid (decomp. 285°) (II) was obtained in an unambiguous manner in one step by boiling cyclohexanone with phenylhydrazone-p-sulphonic acid in dilute acetic acid according to Rogers and Corson. The m.p. 230° of the p-chloroaniline salt of authentic tetrahydrocarbazole-6-sulphonic acid described above was not depressed by admixture with the p-chloroaniline salt of the sulphonic acid (I) prepared by direct sulphonation of tetrahydrocarbazole. The sulphonic acid obtained by direct sulphonation of tetrahydrocarbazole is therefore 1:2:3:4-tetrahydrocarbazole-6-sulphonic acid.

The sulphonation of tetrahydrocarbazole with 80% oleum at 10° also gave the 6-sulphonic acid, which was isolated as the calcium salt and characterized by the preparation of the p-chloroaniline salt which was found to be identical with the authentic salt from synthetic tetrahydrocarbazole-6-sulphonic acid.

An attempt at obtaining tetrahydrocarbazole-7-sulphonic acid which would be probably obtained as a mixture with the 5-acid by the condensation of phenylhydrazine-m-sulphanic acid with cyclohexanone in acetic acid solution failed, the phenylhydrazine-m-sulphonic acid being recovered unconverted. It was also found that as against the nitration of N-acetylcarbazole which gives the 7-nitro derivative, sulphonation of this compound gave the 6-sulphonic acid which was characterized as above.

IV. CHLORINATION OF TETRAHYDROCARBAZOLE

Chlorination of tetrahydrocarbazole and acetyltetrahydrocarbazole was undertaken in an attempt to synthesize 2-hydroxycarbazole. Tetrahydrocarbazole was unaffected when treated with gaseous chlorine in acetic acid at room temperature for 2 hours. When the chlorination of tetrahydrocarbazole was attempted in boiling chloroform solution with sulphuryl chloride as the chlorinating agent, a dark colored product was obtained from which the alcohol soluble portion was extracted sinee all theknown monochloro -tetrahydrocarbazoles obtained synthetically by the Borsche reaction are soluble in alcohol. The alcohol insoluble product gave a test for chlorine, was amorphous and melted 280° and could not be identified. Chlorination of tetrahydrocarbazole in acetic acid solution with gaseous chlorine on boiling water bath gave a precipitate melting 290°. Dilution of acetic acid solution gave --

another chlorinated product, m.p. 180°(decomp.). It was not crystallizable and has not been identified so far.

Chlorination of acetyltetrahydrocarbazole was attempted in boiling carbontetrachloride solution with sulphonyl chloride as the chlorinating agent. The viscous product obtained gave a white solid after hydrolysis with alcoholic alkali. The hydrolyzed product, m.p. 215°, was also noncrystallizable and has not been characterized as ǽ yet.

EXPERIMENTAL

1. Pressure hydrolysis of Naphtol AS-LB:

Naphtol AS-LB (20 g.) was hydrolyzed according to Mehta by heating with caustic potash (50% by weight, 100 g.) in an autoclave at 200° for 12 hours. The crude hydroxycarbazole (9.29 g.) melted at 240-250°. After recrystallization from solvent naphtha and dilute alcohol (plates), m.p. 270° (Formula: $C_{12}H_9NO$ requires N, 7.65%. Found: N, 7.6%).

2. 3-Chlorocarbazole :

Carbazole (20 g.) was suspended in chloroform (250 g.) and to the refluxing solution sulphuryl chloride (20 g.) diluted with an equal equivalent amount of chloroform was added drop by drop. It was then refluxed for six hours. The solvent was then distilled off and the residue thrice crystallized from benzene (norit). Colourless plates, m.p. 198-199°(Yield, 20%).

3. Pressure hydrolysis of 3-chlorocarbazole :

3-Chlorocarbazole (30 g.), copper bronze powder (3 g.) and 10% alkali (250 c.c.) in the proportion 2½ moles of alkali: 1 mol. of 3-chlorocarbazole were well mixed in a rotating, horizontal autoclave and the hydrolysis carried out at 350° for 10 hours. After cooling to room temperature, the sludge of

copper powder and chlorocarbazole was filtered and the filtrate acidified. The hydroxycarbazole (9.5 g.) was repeatedly crystallized from solvent naphtha and dilute alcohol and 3-hydroxycarbazole (2 g.) were obtained, m.p. 259°. (Found: N, 7.4. $C_{12}H_9NO$ requires N, 7.65%).

Mixed melting point of 3-hydroxycarbazole and hydroxycarbazole from Naphtol AS-LB : 242°.

4. Preparation of monoacetyl derivatives of hydroxycarbazoles :

Hydroxycarbazole (0.2 g.) was dissolved in 0.5 cc. of 5% alkali and a suitable amount of crushed ice added followed by acetic anhydride (0.2 g.).The mixture was shaken vigorously and after a few minutes the acetyl derivative separated in a practically pure condition. The solid was filtered off and crystallized from dilute alcohol in the form of needles, m.p. of monoacetyl derivative of 3-hydroxycarbazole 184-186° (Found: N, 6.3. $C_{14}H_{11}O_2N$ requires N, 6.2%).

Melting point of monoacetyl derivative of hydroxycarbazole from Naphtol AS-LB, 182-184° (Found: N,6.2. $C_{14}H_{11}O_2N$ requires N, 6.2%).

Mixed m.p. of the two acetyl derivatives: 148-152°.

5. 3:5-Dinitrobenzoates of the hydroxycarbazoles :

Hydroxycarbazole (0.2 g.) and 3:5-dinitrobenzoyl-chloride (0.4 g.) were added to pure pyridine (10 cc.) and the mixture heated on the waterbath for 3 hours. After cooling the liquid was poured into ice-cold dilute sulphuric acid (40 c.c. 5%) and the crude product separated as a solid. It was filtered and washed with water until the washings were free from acid. The solid was ground in a mortar with dilute sodium hydroxide (40 c.c. 2%), filtered, washed with water and crystallized from o-dichlorobenzene in the form of yellow needles (0.2 g.), m.p. of 3:5-dinitro-benzoate of 3-hydroxycarbazole 280°(Found: N, 11.2. $C_{19}H_{11}N_3O_6$ requires N, 11.5%). M.p. of 3:5-dinitro-benzoate of hydroxycarbazole from Naphtol AS-LB, 314° (Found: N, 11.1. $C_{19}H_{11}N_3O_6$requires N, 11.5%).

Mixed m.p. of the two: 262°.

6. Preparation of hydroxycarboxylic acid from Naphtol AS-LB :

Naphtol AS-LB (20 g.) was refluxed with potassium hydroxide (30 g.), and alcohol (100 c.c.) for 120 hours. The alcohol was distilled and the product remaining steam-distilled to remove parachloraniline. The unconverted Naphtol (14.1 g.) was precipitated by

passing carbondioxide (a crystallized portion of the same had a m.p. of 260°). The filtrate was acidified with hydrochloric acid and the precipitate obtained (0.1 g.) was crystallized from dilute alcohol, m.p. 270°, gives a deep coloration in alcohol with ferric chloride.

7. Preparation of tetrahydrocarbazole :

Carbazole (4 g.), Raney nickel (80 g.) (for preparation refer to Organic Synthesis, Vol.21, p.15) and alcohol (250 c.c.) refluxed for 6 hours with vigorous stirring. The major portion of alcohol was distilled and the product separated extracted with ether and their solution evaporated. The product was dissolved in 33% hydrochloric acid and the carbazole (unconverted)(0.3 g.) was filtered off. The hydrochloric acid solution of the reduced carbazoles was diluted to 20% hydrochloric acid content by dilution with water when the tetrahydrocarbazole separated which was filtered off (1.6 g., m.p. 110°; m.p. of pure tetrahydrocarbazole after crystallization from dilute alcohol: 112°; m.p. of picrate: 140°), Neutralizing the acid solution with ammonia the octa and dodecahydrocarbazoles separated (yield, 0.2 g.).

Acetylation and nitration of N-acetyltetrahydrocarbazole and subsequent hydrolysis were done according

to the method of Perkin and Plant.

8. Preparation of N-acetyltetrahydrocarbazole :

Tetrahydrocarbazole (10 g.) and acetic anhydride (30 g.) refluxed for 6 hours. The product so obtained was poured on broken ice. The semisolid separated was extracted with chloroform, dried with anhydrous calcium chloride and chloroform removed by distillation on waterbath. N-Acetyltetrahydrocarbazole was vacuum distilled at 150-160° under 0.5 to 0.6 mm. reduced pressure. The low melting solid so obtained was crystallized from alcohol. Yield of crystallized product 4.8 g., m.p. 77°.

9. Nitration of N-acetyltetrahydrocarbazole :

N-acetyltetrahydrocarbazole (3.8 g.) and glacial acetic acid (66.5 c.c.) and then nitric acid (2.3 cc. 1.4 d.) diluted with a little glacial acetic acid gradually added at room temperature. The mixture was allowed to remain overnight, when long/ pale yellow prisms separated which were collected and recrystallized from glacial acetic acid. Yield of Nitro compound 2 g., m.p. 164°.

10. Hydrolysis of the acetyl group :

7-Nitro-N-acetyltetrahydrocarbazole (2 g.) and 5% alcoholic alkali (alcohol: water - 50:50)(20 cc.) were heated to boiling point and then diluted with 50 c.c. of water. Yield of 7-nitrocarbazole after crystallization from chloroform, 1.2 g., m.p. 170°.

11. Dehydration with chloranil :

7-Nitrotetrahydrocarbazole (2.4 g.) and sulphur-free xylene (50 c.c.) plus chloranil (5.6 g.) (1 mole of nitrotetrahydrocarbazole: 2 moles of chloranil) heated at reflux for ⁄ 18 hours, cooled and filtered, diluted with 50 c.c. of ether, washed with alkali, and finally with water to free from alkali, dried (anhydrous sodium surphate) and evaporated to dryness. Substance obtained was crystallized from benzene. Wt. of nitrocarbazole obtained, 1.3 g., m.p. 260°.

12. Reduction of 2-nitro to 2-aminocarbazole :

2-Nitrocarbazole (1.3 g.) plus alcohol (100 cc.) and active Raney nickel (2 g. in 20 cc.) shaken in the hydrogenation apparatus for 6 hours in presence of hydrogen under pressure (45 lbs. per sq.inch),the Raney nickel filtered and solution concentrated, crystallized from dilute alcohol in plates, yield 0.3 g., m.p. 235°. (Found: N, 15.1. $C_{12}H_{10}N_2$ requires N, 15.3%0.

13. Preparation of 2-hydroxycarbazole from 2-amino-carbazole.

2-Aminocarbazole (0.2 g.) plus hydrochloric acid (2½ moles, 0.3 c.c.) and water (20 c.c.) heated to boiling when 2-aminocarbazole hydrochloride completely dissolved. This was cooled to 0° and diazotized with sodium nitrite (0.08gin 2 c.c. of water). The diazo solution stirred for half an hour and then concentrated sulphuric acid (2 c.c.) added, warmed on the waterbath and then heated directly under reflux for 1 hour until no coupling takes place, with -naphtol solution, cooled and filtered. The black substance obtained crystallized twice from dilute alcohol in plates, m.p. 266°; mixed m.p. with a sample of hydroxycarbazole from Naphtol AS-LB (m.p. 270°)=268° (Found: [illegible], 15.1. $C_{12}H_9NO$ requires [illegible]).

14. Sulphonation of tetrahydrocarbazole : Tetrahydrocarbazole (5 g.) was added under stirring to oleum 25% (d: 1.966)(10 cc.) at 30°. Reaction product was heated at 60-70° for 7 hours until the product became alkali soluble. Then it was poured into 200 cc. ice-cold water when a blue solution was obtained. This was neutralized with fresh lime and at the point of neutralization a sharp colour change from blue to

red took place. The precipitate formed was filtere and washed with 150 cc. boiling water. The filtrate was norited and concentrated to 50 cc. - precipitate of calcium sulphate separated (gave no test for nitrogen), filtered. The filtrate was concentrated to dryness and the calcium salt obtained was deep brown in colour. Weight of calcium salt obtained, 5.5 g.

15. Preparation of p-chloroaniline salt :

Calcium salt of the above sulphonic acid (0.75 g.) was mixed with p-chloroaniline (0.75 g.) (1½ moles on the basis of the monosulphonic acid) and hydrochloric acid (0.3 c.c.) in water (50 c.c.) and refluxed for half an hour. Norited, filtered and cooled. Long plates of the p-chloroaniline salt were obtained, m.p. 230° (Yield 1 g.).

The molecular weight of the above salt as calculated by its titre against alkali agrees with that of the p-chloroaniline salt of tetrahydrocarbazol-monosulphonic acid (Found: S, 8.19. $C_{18}H_{17}N_2O_2SCl$ requires S, 8.88%).

16. Preparation of tetrahydrocarbazol-6-sulphonic acid (Synthetic method) :

Phenylhydrazine-p-sulphonic acid (10 g.) was suspended in acetic acid (100 c.c.) and water (10 cc.

Cyclohexanone (6 c.c.) (Phenylhydrazine-p-sulphonic acid and cyclohexanone taken in molal proportions) was added during one hour with reflux. Homogenous solution was observed after one hour. After six hours reflux and stirring, the solution was cooled, concentrated to small volume, and filtered. Solid separated crystallized from a small quantity of water when irregular plates of sulphonic acid were obtained. Weight of the compound 6 g., m.p. 285°(decomp.). (Found: S, 12.34. $C_{12}H_{13}NO_3S$ requires S, 12.75%).

17. Preparation of p-chloroaniline salt of the above sulphonic acid :

Tetrahydrocarbazole-6-sulphonic acid (0.5 g.) and p-chloroaniline (0.3 g.) were added to hydrochloric acid (3 c.c.) and water (100 c.c.). The solution was refluxed for half an hour,(norit) and cooled. p-Chloroaniline salt which separated was filtered, m.p. 232°.

Molecular weight of the above p-chloroaniline salt of the tetrahydrocarbazole-6-sulphonic acid as found from its titre against standard alkali agrees with the one obtained by theoretical calculation. (Found: S, 8.724. $C_{18}H_{17}N_2O_2SCl$ requires S, 8.88%).

Mixed m.p. of the p-chloroaniline salts of the two sulphonic acids - one obtained by direct sulphonation and other by synthesis - 230°(undepressed by admixture).

18. Sulphonation of tetrahydrocarbazole with 80% oleum:

Tetrahydrocarbazole (5 g.) was added in small portions to 70-80% oleum (d: 1.923) during one hour at 10°. The resulting product was stirred for half an hour at room temperature and then poured into 200 g. of broken ice. The resulting solution was filtered and neutralized with fresh lime. The pale ~~bax~~ blue solution becomes brown at the point of neutralization. This was filtered and the calcium salt -- extracted from the precipitate with 200 cc. of hot water and the solution of calcium salt was boiled down to dryness.

19. Preparation of p-chloroaniline salt of the above acid:

Calcium salt of the above acid (0.2 g.) was added to hydrochloric acid (2 c.c.) and water (10 cc.) p-Chloroaniline (0.2 g.) was added to the above solution. The solution was refluxed for 1 hour (norit), filtered and cooled. The p-chloroaniline salt (plates) obtained was filtered, m.p. 225° (undepressed by admixture with the p-chloroaniline salt of the sulphonic acid obtained by direct sulphonation of ~~mk~~ tetrahydrocarbazole with 25% oleum).

20. Preparation of tetrahydrocarbazole-7-sulphonic acid:

(a) Phenylhydrazine-m-sulphonic acid (6 g.) was added to hydrochloric acid (10 c.c.) and water (50 cc.). Cyclohexanone (5 c.c.) was added during one hour with stirring under reflux. For 6 hours, the reflux was continued, then cooled and concentrated. While solid separated filtered. Weight, 6 g. The titre of this was found to be the same as for phenylhydrazine-m-sulphonic acid. Hence no formation of tetrahydrocarbazole-7-sulphonic acid took place.

(b) The same experiment as above was repeated with 21. (50 cc.) acetic acid as solvent instead of water (50 cc.)(No hydrochloric acid). It was found again in this case that there was no conversion to tetrahydrocarbazole-7-sulphonic acid.

PART II

1. USE OF AMINOCARBAZOLES AS FAST BASES.

Any primary aromatic amine which is capable of diazotization and coupling and is free from sulphonic and other solubilizing groups, may, in principle, be used for azoic dyeing; but shade requirements, fastness and other considerations, such as the ability to couple smoothly with "Naphthols" on the fiber uder normal conditions have restricted the number of technically used amines to about fifty. The amines recommended for azoic dyeing are marketed as Fast Bases (I.G.) or as bases with a prefix indicated the trade name for an azoic coupling component. They vary in complexity from o- and m-chloroaniline (yellow and orange base G) to o-anisidine-4-sulphodiethylamide (Red I.T.R.), -aminoanthraquinone (Red AL), 4-amino-4'-methoxydiphenylamine (Variamine Blue B), 4-benzamido-2:5-diethoxyaniline (Blue BB) and 4-o-ethoxybenzeneazo-1-naphthylamine (Black LB).

The utility of the following aminocarbazoles for use as Fast bases was examined in the course of the present work: (1) 3-Aminocarbazole, (2) 2-Aminocarbazole, (3) Mixture of 3-amino and 1-aminocarbazoles, (4) 3-Chloro-6-aminocarbazoles, (5) 3:6-Diaminocarbazole, (6) 3-Amino-N-ethylcarbazole, (7) 3-Amino-N-methylcarbazole,

(8) 3-Amino-N-p-toluenesulphonylcarbazole, (9) 3-Amino-N-acetylcarbazole, (10) 3-Amino-N-benzoylcarbazole, and (11) 3-Amino-6-benzamidocarbazole. 2-Aminocarbazole was prepared by reduction of 2-nitrocarbazole which was obtained synthetically as described above. 3-Aminocarbazole was prepared by reduction of 3-nitrocarbazole which was obtained by nitration of N-nitrosocarbazole. The latter was easily synthesized from carbazole by the action of sodium nitrite and acetic acid. 3-Nitro-N-methyl, 3-nitro-N-ethyl, 3-nitro-N-acetyl, 3-nitro-N-benzoyl, and 3-nitro-N-p-toluenesulphonylcarbazoles were prepared by the action of the required alkylating or acylating agents on 3-nitrocarbazole in acetone solution in presence of sodium hydroxide. Most of the amino compounds were obtained by Raney nickel reduction of the corresponding nitro compounds.

3:6-Diaminocarbazole was prepared by the reduction of 3:6-dinitrocarbazole with sodium sulphide, the latter compound being obtained by direct nitration of carbazole in acetic acid with two moles. of nitric acid. 3-Chloro-6-aminocarbazole was prepared from 3-chloro-6-nitrocarbazole by Raney nickel reduction, the nitro chlorocarbazole being prepared from carbazole in two stages by chlorination to 3-chlorocarbazole by means of sulphuryl chloride in chloroform

solution, followed by nitration in acetic acid solution.

Except for 3:6-diaminocarbazole, all the aminocarbazoles were readily diazotizable and coupled readily with Naphthols. Cotton yarn impregnated with Naphtols AS, AS-SW, and AS-TR was treated with diazotized aminocarbazoles and the resulting shades and their fastness to chlorine and light are described in the following Table I :-

Table I

Name of the Base	Naphtol	Shade	Fastness	
			Chlorine	Light
1) 3-Aminocarbazole.	AS	Bluish-violet	1-2	2-3
	AS-TR	Bluish with deeper violet tinge	1-2	2-3
	AS-SW	Bluish-Black	1-2	2-3
2) Mixed Aminocarbazoles	AS	Bluish-violet	1-2	2-3
	AS-TR	"	1-2	2-3
	AS-SW	B "	1-2	2-3
3) 3:6-Diaminocarbazole	AS	Violet-black	1-2	2-3
	AS-TR	Bluish-black	1-2	2-3
	AS-SW	Deep black	1-2	2-3

Name of the Base	Naphtol	Shade	Fastness	
			Chlorine	Light
4) 3-Chloro-6-aminocarbazole.	AS	Pale purple	1-2	2-3
	AS-TR	Reddish blue	1-2	2-3
	AS-SW	Reddish blue	1-2	2-3
5) 3-Amino-6-benzamidocarbazole.	AS-TR	Bluish-violet	1-2	2-3
6) 3-Amino-N-ethylcarbazole	AS	Light bluish violet	1-2	2-3
	AS-TR	Deep bluish violet	1-2	2-3
	AS-SW			
7) 3-Amino-N-methylcarbazole	AS	Dull violet	2	3
	AS-TR	Light violet black	2	3
	AS-SW	Violet black	5	4-5
8) 3-Amino-N-p-toluenesulphonylcarbazole	AS	Dull pink	3-4	3
	AS-TR	Dark red	4	3-4
	AS-SW	Red	4	4-5
9) 3-Amino-N-acetylcarbazole	AS	Brick red	2	2
	AS-TR	Garnet	2	2-3
	AS-SW	Bordeaux	3	3-4
10) 3-Amino-N-benzoylcarbazole	AS	Dull pink	2-3	2
	AS-TR	Garnet	3	2-3
	AS-SW	Bordeaux	4	3-4

Name of the Base	Naphtol	Shade	Fastness	
			Chlorine	Light
11) 2-Aminocarbazole	AS	Pale-violet	3	4
	AS-TR	Violet	4	4
	AS-SW	Bluish violet	4-5	5

3-Aminocarbazole, mixed aminocarbazoles, 3:6-diaminocarbazole, 3-chloro-6-aminocarbazole, 3-amino-6-benzamidocarbazole, 3-amino-N-ethylcarbazole and 3-amino-N-methylcarbazole gave bluish-violet shades of xxxx mixed violet shades revealing thereby that the introduction of a chlorine atom in the carbazole nucleus or alkylating the nitrogen atom had no effect on the shade obtained by coupling with Naphtols. 2-Aminocarbazole with Naphtol AS-TR gave a pure violet shade, while coupling with Naphtol AS and AS-SW gave pale violet and brown violet shades respectively. Thus, the alteration in the position of the amino group from 2- to 3- position in the carbazole nucleus has a deepening effect on the shade of the dyeing obtained. N-Acylation of the 3-aminocarbazole gave fast bases which gave red-bordeaux shades on diazotization and coupling with naphtholated yarn.

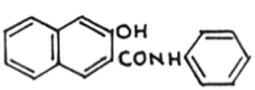
The chlorine fastness of the azoic dyeings were generally poor. Introduction of a chlorine atom in the

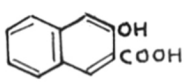
carbazole nucleus or alkylation of the imino nitrogen did not improve the fastness properties of the azoic dyeings from the parent 3-aminocarbazole. N-Acylation, however, effected a minor improvement in the fastness properties of 3-aminocarbazole.

The light fastness of the aminocarbazoles was also generally poor and here again the introduction of chlorine in the carbazole nucleus or alkylation of the imino nitrogen did not improve the fastness properties of the azoic dyeings from 3-aminocarbazole. Introduction of acyl groups on the imino nitrogen also gave fast bases which gave shades with improved fastness to light.

2. USE OF AMINOCARBAZOLES FOR THE PREPARATION OF AZOIC COUPLING COMPONENTS OF THE TYPE OF NAPHTOL AS.

By the commercial name "Naphtols" is understood such compounds which are analogous to Naphtol AS (I), the anilide of 2-hydroxy-3-naphthoic acid (II) or to acetoacet-

(I) 



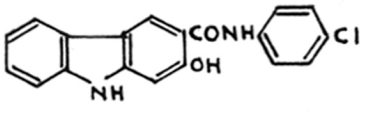
(II)

anilides such as Naphtol AS-G. Naphtol AS discovered by Griesheim Electron (later part of the I.G.) in 1911 is used as a dye component. On impregnation with an alkaline solution of Naphtol AS and developing with a solution of diazo salt, cotton is dyed bright shades which

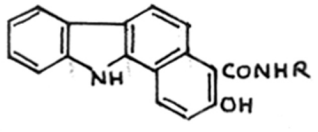
are due to the formation of azo dyes on the fibre. The colors so obtained belong to the class of "azoic" colours to distinguish them from the soluble azo dyes. Arylides of other hydroxycarboxylic acids are also used. The azoics constitute about a fifth of the dyes in commercial use and are invaluable for deep and brilliant shades of scarlets, reds, maroons and chocolates. The azoic coupling components are sold under the names Naphtols (I.G.), Brenthols (I.C.I.) and Ciba Naphtols (Ciba).

The Naphtol AS series now comprises two types of coupling components: (1) for all shades other than yellow, arylamides of o-hydroxycarboxylic acids in which the second position adjacent to the hydroxyl is free for coupling with diazo salts, and (2) for yellow shades, acylacetic arylamides, in which the reactive methylene group is responsible for the coupling power. Naphtols of the first type are prepared mainly from 2-hydroxy-3-naphthoic acid (II), the variations being in the arylamine half. These arylides of hydroxynaphthoic acid are mainly used for the production of scarlet, red, violet and blue shades, specially reds.

The carbazole nucleus has been used for preparing commercially valuable naphthols which give distinctive shades on cotton. Thus, Naphtol AS-LB which gives brown shades on cotton is obtained from 2-hydroxycarbazole-3-carboxylic acid and has been described earlier. Naphtols AS-SR and AS-SG which are obtained by condensing 2-hydroxy-1-2'-benzocarbazole-3-carboxylic acid with 5-methoxy-o-toluidine and p-anisidine respectively are used for producing black shades on cotton.

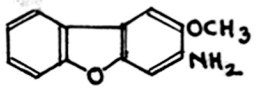


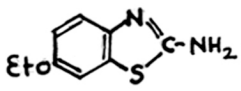
Naphtol AS-LB



Naphtol AS-SR. R = 5 Methoxy-o-toluidine
Naphtol AS-SG. R = p-Anisidine

Azoic coupling components from aminocarbazoles and o-hydroxyarylcarboxylic acids, e.g. 2-hydroxy-3-naphthoic acid, do not, however, appear to have been described. Such naphtols may possess high substantivity to cotton in view of the fast arylides of 2-hydroxy-3-naphthoic acid with heterocylcic amines, e.g. 2-aminopyridine, p-aminodimethylaniline, 3-methoxy-2-amino-

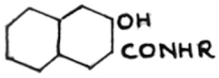
(I) 



(II)

(I)
dibenzfuran, possess high substantivity.[85] Acetoacetarylides from 2-amino-6-methoxybenzthiazole (II), Naphtol AS-L_4G like wise possesses high substantivity.

With a view therefore to synthesize highly substantive naphthols, the aminocarbazoles prepared in the course of the present work were condensed with 2-hydroxy-3-naphthoic acid leading to the following azoic coupling components :



I. R : 3-Aminocarbazole

II. R : 3-Amino-N-methylcarbazole

III. R : 3-Amino-N-ethylcarbazole

IV. R : 3-Amino-N-acetylcarbazole

V. R : 3-Amino-N-benzoylcarbazole

VI. R : 3-Chloro-6-aminocarbazole

VII. R : 3:6-Diaminocarbazole

VIII. R : 3-Amino-N-p-toluenesulphonylcarbazole.

IX R : 2-Aminocarbazole.

Cotton yarn impregnated with the naphthols described above was treated with a solution of stabilized diazo salts Scalret 2G and Blue 2B and the fastness properties of the shades so obtained were examined. (Table II).

Table II.

2-Hydroxy-3-naphthoic arylides with amino-carbazoles.

Amine from which the naphthol is prepared and the naphthol	Fast Bases used for coupling	Shade obtained	Fastness	
			Chlorine	light
1. 3-Aminocarbazole (I)	Scarlet 2G	Dull red	4	4-5
	Blue 2B	Blue	2	4-5
2. 3-Amino-N-methyl-carbazole (II)	Scarlet 2G	Brown Red	3-4	6-7
	Blue 2B	Reddish blue	4-5	6
3. 3-Amino-N-ethyl-carbazole (III)	Scarlet 2G	Brownish-red	3-4	5-6
	Blue 2B	Reddish-blue	4-5	6
4. 3-Amino-N-acetyl-carbazole (IV)	Scarlet 2G	Brownish-red	3-4	6
	Blue 2B	Reddish-blue	4-5	5-6
5. 3-Amino-N-benzoyl-carbazole (V)	Scarlet 2G	Brownish-red	5	6
	Blue 2B	Reddish-blue	5	6
6. 3-Chloro-6-amino-carbazole (VI)	Scarlet 2G	Scarlet-red	3-7	6-7
	Blue 2B	Blue	4	6
7. 3:6-Diaminocarbazole (VII)	Scarlet 2G	Dull red	2-3	6-7
	Blue 2B	Reddish-blue	4	6
8. 3-Amino-N-p-toluene-sulphonylcarbazole (VIII)	Scarlet 2G	Scarlet	2	4
	Blue 2B	Pink	2	3-4
9. 2-Aminocarbazole (IX)	Scarlet 2G	Bright-red scarlet	4-5	6-7
	Blue 2B	Blue	5	5-6

As it is obvious from the above table, the effect of introdcing chlorine in the carbazole nucleus or of alkylating or acylating the imino nitrogen atom has very

little effect on the shade obtained with the diazo salts. The same holds good with respect to the change in the position of the amino group. While most of the shades have good light fastness (6-7) and a moderate chlorine fastness, none of them except the dyeings with the Naphtols (VI) and (IX) from 3-chloro-6-aminocarbazole and 2-aminocarbazole respectively had bright shades. These naphthols (VI) and (IX) gave bright red scarlet shades with Scarlet 2G and bright blue shades with Blue 2B. Unlike the distinctive brown shades -- obtainable with arylides from o-hydroxycarbazolecarboxylic acids, such as Naphthols AS-LB and AS-SR, the azoic dyeings from the Naphthols (I) to (IX) from aminocarbazoles do not possess distinctive shades which were found to be roughly analogous to the shades from the related 2-hydroxy-3-naphthoicarylide, Naphtol AS.

EXPERIMENTAL.

1. 3-Nitrocarbazole: -

To a suspension of carbazole (200 g.), chlorobenzene (1200 g.) and sodium nitrite (120 g.) at 60°, glacial acetic acid (100 g.) was added. It was kept at 60° for 5 hours, then cooled to 28° and at 28-30° nitric acid (65%)(444 g.) was added in two hours. Cooling was necessary. Then it was stirred at 28-30° for 4 hours. It was neutralized with sodium hydroxide (40° Be, 120 g.) and water (150 g.). Then a solution of urea (100 g.) added in water (150 g.). It was heated to 80-85°; at 60-65° nitrogen evolved. At this point, the temperature was raised very carefully. It was held at 80-85° for 3 hours. It was cooled, filtered off at the pump and washed with warm water. Reddish brown crystals. Weight of 3-nitrocarbazole obtained, 205 g. m.p. 195-200°. Percentage yield, 80.

2. 3-Aminocarbazole :

Alcohol (170 g.) and 3-Nitrocarbazole (35 g.) were agitated and then a filtered solution of sodium acid sulphide (NaSH)(60 g.)(61-63% NaSH). It was heated to boiling point in 1 hour, boiled for 6 hours, cooled in 1 hour to 40° and filtered. The cake was washed with alcohol,(20 g.) and three times with a solution

of hydrosulphite (0.05 g.) in alcohol (30 g.) and then with water (100 g.). The cake agitated with water in a vessel at room temperature, washed neutral and dried at 60-70°. Grey powder. Yield, 20 g. Percentage yield, 66.6.

3. 3-Nitro-N-methylcarbazole :

3-Nitrocarbazole (5 g.) dissolved in 66% aqueous potassium hydroxide solution (5 c.c.) and acetone (50 c.c.) by warming and methyl sulphate (5 c.c.) added. The mixture well shaken for a few seconds until the deep red colour of potassium-nitrocarbazole has been replaced by yellow. Warm water (25 cc.) was added to the semi solid product which was then put aside to crystallize and the 3-nitro-N-methylcarbazole isolated and pumped by crystallization from slightly dilute acetic acid . Yield, ∅ 4.5 g., m.p. 169-171°.

4. 3-Amino-N-methylcarbazole :

3-Nitro-N-methylcarbazole (4 g.), stannous chloride (6 g.), hydrochloric acid (20 c.c.) and 5 c.c. of acetic acid heated to boiling for 5 hours, cooled and filtered. The precipitate of 3-amino-N-methylcarbazole stannichloride filtered and then suspended in 50 cc. of alcohol and made alkaline with sodium hydroxide (5 g.) and the precipitate filtered, washed free from alkali and crystallized from dilute alcohol.

Yield, 2 g., m.p. 174°.

5. 3-Nitro-N-ethylcarbazole :

Experiment carried out as in the method for 3-nitro-N-methylcarbazole using an equivalent quantity of ethyl sulphate. Yield from 3-nitrocarbazole (4 g.), 4 g. of crystallized nitro product from alcohol (in yellow needles), m.p. 126-128°.

6. 3-Amino-N-ethyl carbazole :

Experiment carried out as under 3-Nitro-N-ethyl-carbazole. Yield from nitrocarbazole (4 g.), 2 g. of crystallized amino compound from alcohol, m.p. 110°.

7. 3-Nitro-N-acetylcarbazole :

3-Nitrocarbazole (2 g.) was dissolved in acetone (30 cc.) and 66% aqueous potassium hydroxide solution (3 cc.) by warming. Acetyl chloride (4 cc.) was added to the cold solution and the mixture shaken until the violent reaction has had subsided. The product was then poured into water and filtered. In order to remove traces of unaltered 3-nitrocarbazole, the solid was boiled with acetone (10 cc.) for a few seconds, a little dilute sodium hydroxide solution added and the mixture at once filtered. The almost white product was crystallized from acetic acid. The yield was nearly theoretical.

8. 3-Amino-N-acetylcarbazole :

3-Nitro-N-acetylcarbazole (2 g.), alcohol (100cc), & Raney nickel suspended in alcohol (1 g. in 100 c.c.) shaken in the hydrogenator with hydrogen under pressure of 45 lbs. per sq. inch. for 6 hours, and then the Raney nickel filtered. The solution of this amine in alcohol concentrated and the amine crystallized from dilute alcohol. Yield 1 g., m.p. 80° (Found: N, 11.7. $C_{14}H_{12}N_2O$ requires N, 12.5%).

9. 3-Nitro-N-benzoylcarbazole :

3-Nitrocarbazole (5 g.), was added to 60% aqueous potassium hydroxide solution (1 cc.) and acetone (25 cc.). Benzoyl chloride (5 cc.) were added slowly and on shaking the red colour was discharged and a yellow solid separated. The mixture was poured into water, the product filtered and recrystallized from glacial acetic acid. Yield, 4 g., m.p. 181-183°.

10. 3-Amino-N-benzoylcarbazole :

3-Nitro-N-benzoylcarbazole (2 g.) was added to alcohol (100 c.c.) and Raney nickel suspended in alcohol (1 g. in 10 cc.). The whole was shaken in the hydrogenator with hydrogen under pressure of 45 lbs. per sq.inch for 6 hours and then the Raney nickel filtered. The solution of the amine in alcohol concentrated and the amine was crystallized from

dilute alcohol. Yield, 1 g., m.p. 245-250° (Found: N, 9.9. $C_{19}H_{14}N_2O$ requires N, 9.7%).

11. 3-Chloro-6-nitrocarbazole :

3-Chlorocarbazole (3.5 g.) was added slowly to a mixture of nitric acid (32.3%)(3.5 cc.) and water (18 cc.) with stirring, the temperature was taken to 80° in the course of 3 hours, and heated for 4 hours at 80-85° and the reaction product was crystallized from xylene. Yield, 2 g. M.p. 226-227°.

12. 3-Chloro-6-aminocarbazole :

3-Chloro-6-nitrocarbazole (2 g.) was added to alcohol (100 c.c.) and Raney nickel suspended in absolute alcohol (1 g. in 10 cc.). The whole was shaken in the hydrogenator apparatus for 6 hours with hydrogen under pressure of 45 lbs. per sq.inch. The solution of the amine was filtered, the alcohol solution concentrated and the amine crystallized from dilute alcohol. Yield, 1.1 g., m.p. 215°. (Found: N, 12.4. $C_{12}H_9N_2Cl$ requires N, 13.0%).

13. 3:6-Dinitrocarbazole :

Carbazole (25 g.) was dissolved in glacial acetic acid (125 cc.) and was heated to 80°. Nitric acid (34 cc., density 1.36) was slowly added. After the addition of nitric acid, the temperature was raised to

100° and was stirred for 1 hour. It was then filtered and crystallized from nitrobenzene. Long yellow plates melting over 320°. Yield 60%.

14. 3:6-Diaminocarbazole :

A mixture of 3:6-dinitrocarbazole (20 g.) and sodium sulphide (40 g.) was dissolved in water (220 cc.) and was introduced in an autoclave and heated to 120-130° for 4 hours. The product was then removed, filtered, washed free from alkali and dried. It was then crystallized from nitrobenzene in plates, m.p. 293-295°, yield 90%.

15. 3-Nitro-N-p-toluenesulphonylcarbazole :

A mixture of 3-Nitrocarbazole (2 g.), toluene-p-sulphonyl chloride (2 g.) and potassium hydroxide powder (1 g.) in acetone (20 cc.) was shaken for ten minutes on the boiling bath and then poured into water. The precipitate obtained crystallized from glacial acetic acid in yellow needles. Recrystallization from glycol methyl ether gave colourless crystals. 3-Nitro-N-p-toluenesulphonylcarbazole (2.3 g.), m.p. 208-211°.

16. 3-Amino-N-p-toluenesulphonylcarbazole :

3-Nitro-N-p-toluenesulphonylcarbazole (2 g.) was dissolved in alcohol (100 cc.) and Raney nickel in absolute alcohol (1 g. in 10 cc.) added. The whole was shaken for six hours with hydrogen under pressure of 42 lbs. per sq. inch. The solution of the amine was filtered from Raney nickel and concentrated. The amine was crystallized from dilute alcohol. Yield, 1 g., m.p. 140° (Found: N, 8.0. $C_{19}H_{16}N_2O_2S$ requires N, 8.3%).

17. 2-Aminocarbazole : Preparation mentioned in Part I :

18. Preparation of new "Naphthols" :

Anhydrous 2-hydroxy-3-naphthoic acid (2 g.), thionyl chloride (2 cc.) and petroleum ether dry (20 cc.) refluxed for 3 hours until clear solution was obtained. The petroleum ether was removed by vacuum. The acid chloride solid was mixed with the amine (2 to 2.3 g. depending upon the molecular weight of the amine) and pyridine dry (30 cc.) and refluxed for 6 hours. It was then poured in broken ice and hydrochloric acid (40 cc., 33%). The solid separated was filtered and the filtered cake was agitated with sodium bicarbonate solution (10%) and filtered. The solid thus obtained was again dissolved in 50 cc. alcoholic alkali (10%)(norit) and

filtered. Carbondioxide was passed through the filtrate until the precipitation of "Naphthol" was complete. (In the case of 3:6-diaminocarbazole, half the weight of the amine mentioned above was taken for condensation). The "Naphthols" so obtained had the following melting points :-

Naphtol from:

1) 3-Aminocarbazole : m.p. 290°
(Found: N, 7.2. $C_{23}H_{15}N_2O_2$ requires N, 7.95%).

2) 3-Amino-N-methylcarbazole : m.p. 181°
(Found: N, 7.40. $C_{24}H_{17}N_2O_2$ requires N, 7.67%).

3) 3-Amino-N-ethylcarbazole: m.p. 200°C
(Found: N, 7.4. $C_{25}H_{20}N_2O_2$ requires N, 7.37%).

4) 3-Amino-N-acetylcarbazole: m.p. 295°
(Found: N, 7.6. $C_{25}H_{18}N_2O_3$ requires N, 7.3%).

5) 3-Amino-N-benzoylcarbazole: m.p. 280°
(Found: N, 6.3. $C_{30}H_{21}N_2O_3$ requires N, 6.1%).

6) 3:6-Diaminocarbazole: m.p. above 290°
(Found: N, 7.6. $C_{34}H_{27}N_3O_4$ requires N, 7.76%).

7) 3-Chloro-6-aminocarbazole: m.p. 273°
(Found: N, 7.0. $C_{23}H_{14}N_2O_2Cl$ requires N, 7.26%).

8) 3-Amino-N-p-toluenesulphonylcarbazole: m.p. 273-274°
(Found: N, 5.3. $C_{30}H_{22}N_2O_4$ requires N, 5.5%).

9) 2-Aminocarbazole: M.p. 315°
(Found: N, 8.1. $C_{23}H_{15}N_2O_2$ requires N, 7.95%).

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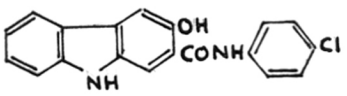
SUMMARY.

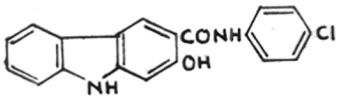
SUMMARY OF WORK.

(1) Constitution of Naphtol AS-LB :

A carbazole derivative used extensively for brown shades in commerce is Naphtol AS-LB. There is conflicting data regarding its constitution. Mehta and Desai consider it to be the p-chloroanilide of 3-hydroxycarbazole-2-carboxylic acid (I). On the other hand, Lapworth and Dieserens state that it is the p-chloranilide of 2-hydroxycarbazole-3-carboxylic acid (II).



(I)



(II)

A B.I.O.S. report gives details of a method of manufacture of 2-hydroxycarbazole-2-carboxylic acid, but the constitution of this acid is not definitely established. It has now been shown that Naphtol AS-LB is correctly represented by (II).

3-Hydroxycarbazole, m.p. 259°, was prepared from 3-chlorocarbazole by alkaline pressure hydrolysis in an autoclave in the presence of copper bronze as catalyst. Since the orientation of the chlorine atom in the latter compound has been established by Ullmann, the hydroxycarbazole obtained from it is therefore 3-hydroxycarbazole. Alkaline pressure hydrolysis of Naphtol AS-LB

results not only in the hydrolysis of the anilide groups, but also in the decarboxylation of the resulting hydroxylic acid, the parent hydroxycarbazole, m.p. 269°, being isolated as the only product of hydrolysis. The m.p. of 3-hydroxycarbazole was depressed by admixture of the hydroxycarbazole from Naphtol AS-LB. The latter is therefore 2-hydroxycarbazole. The nature of Naphtol AS-LB as an o-hydroxycarboxyanilide functioning as an azoic coupling component rules out the 1- and 4- positions in the carbazole nucleus for the hydroxyl group.

The non-identity of the two hydroxycarbazoles was further compared by comparison of their absorption spectra and the comparison of their respective acetates and 3:5-dinitrobenzoates. The absorption spectra of the two hydroxycarbazoles showed marked divergence, and the corresponding derivatives of the two compounds were also not identical.

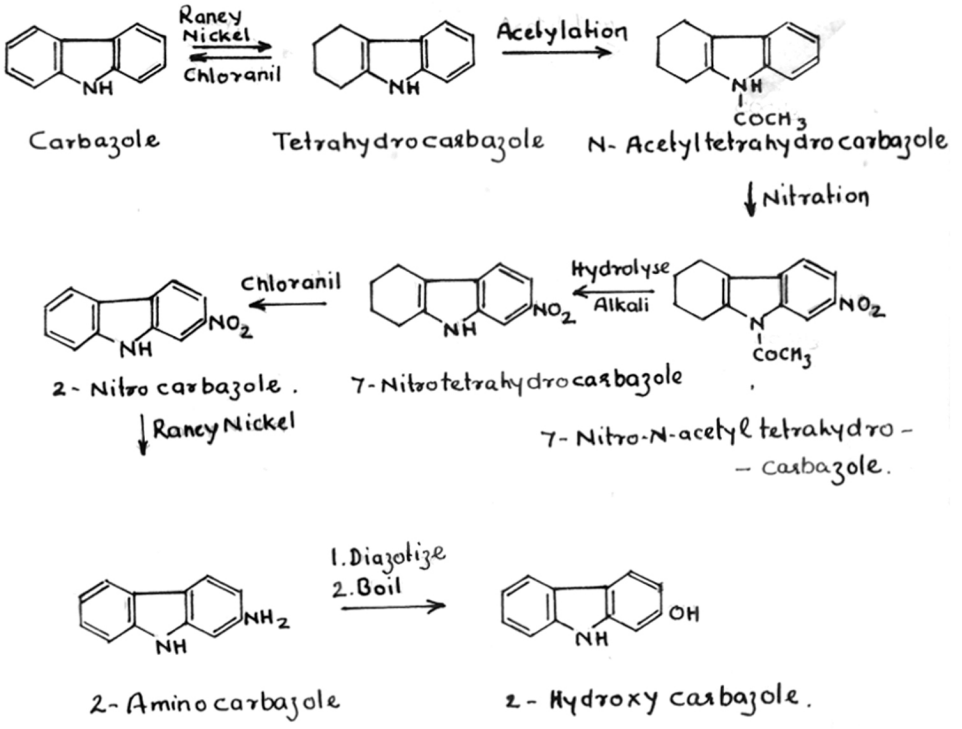
Since the Kolbe reaction is employed in the preparation of the hydroxycarbazole-carboxylic acid it is obvious that the hydroxy and the carboxylamide groups are in the o-position in Naphtol AS-LB. This is further confirmed by the fact that the hydroxycarbazole carboxylic acid which is obtained from the naphthol in very small quantity by alkaline hydrolysis of Naphtol AS-LB at atmospheric pressure for a long time gives a

deep green colouration in alcoholic solution with ferric chloride. Naphtol AS-LB is therefore the p-chloroanilide of 2-hydroxycarbazole-3-carboxylic acid.

(2) New methods for the preparation of 2-hydroxycarbazoles:

2-Hydroxycarbazole, the intermediate necessary for the preparation of Naphtol AS-LB, is prepared by the I.G. by tetrasulphonation of carbazole to the 2:3:6:8-tetrasulphonic acid, followed by partial hydrolysis to the 2-hydroxy-3:6:8-trisulphonic acid and desulphonation of the latter to give 2-hydroxycarbazole. Other routes to 2-hydroxycarbazole have now been investigated.

The favoured positions in the carbazole molecule in which substitution takes place in reactions such as nitration and halogenation are the 3, 3:6-, and 1:3:6:8-positions. Tetrahydrocarbazole likewise gives the 6-nitro derivative by nitration, but substitution in the desired 7-position takes place on nitration of the N-acetyl derivative, and advantage was taken of this fact to prepare 2-hydroxycarbazole by the following series of reactions :



Although the hydrogenation of carbazole to tetrahydrocarbazole under pressure with hydrogen using Raney nickel and copper chromite as catalysts has been done previously by Adkins and Coonradt it was found in our laboratory that the reduction of carbazole under milder conditions at atmospheric pressure in alcoholic solution with 10 times the weight of Raney nickel gave a 90% yield of tetrahydrocarbazole. The nitration of

N-acetyltetrahydrocarbazole gives N-acetyl-7-nitrotetrahydrocarbazole (III), which on hydrolysis gives 7-nitrotetrahydrocarbazole (IV). Plant has definitely established the orientation of the nitro group in the above compound, and Barclay and Campbell obtained the same compound by chromatographic separation of the mixture of 5- and 7-nitrotetrahydrocarbazole obtained by the cyclisation of the m-nitrophenylhydrazole of cyclohexanone. 7-Nitrotetrahydrocarbazole was dehydrogenated to 2-nitrocarbazole (V) according to Barclay and Campbell reduced to 2-aminocarbazole (VI) and the amino group replaced by hydroxyl by diazotization and boiling to form 2-hydroxycarbazole. The overall yield of 2-hydroxycarbazole is small.

3. Sulphonation of tetrahydrocarbazole :

Another possible route to 2-hydroxycarbazole is through the tetrahydrocarbazole-7-sulphuric acid. The latter compound has not been described in the literature and a monosulphonic acid, isolated as the calcium salt, was obtained, by direct sulphonation of tetrahydrocarbazole. The latter by boiling with an aqueous solution of p-chloroaniline and excess hydrochloric acid gave the p-chloroaniline salt, m.p. 230°. It could be diazotized and coupled, and its titre with caustic soda solution and the sulphur content corresponded to the --

p-chloroaniline salt of the monosulphonic acid.

Tetrahydrocarbazole-6-sulphonic acid (decomp.285°) was obtained in an unambiguous manner by boiling cyclohexanone with phenylhydrazine-p-sulphonic acid in acetic acid. The m.p. 230° of the p-chloroaniline salt of tetrahydrocarbazole-6-sulphonic acid was not depressed by admixture with the p-chloroaniline salt of the sulphonic acid prepared by direct sulphonation of tetrahydrocarbazole, so that it is clear that tetrahydrocarbazole sulphonates in the 6-position.

4. Chlorination of tetrahydrocarbazole :

The direct chlorination of tetrahydrocarbazole was attempted in acetic acid solution and sulphuric acid solution with gaseous chloride and in chloroform solution with sulphuryl chloride in an attempt to get 7-chlorotetrahydrocarbazole, which would give on dehydrogenation and alkaline hydrolysis under pressure 2-hydroxycarbazole. However, none of the known chlorotetrahydrocarbazoles obtained by synthetic methods from cyclohexanone and substituted phenylhydrazines could be isolated from the reaction products.

5. Aminocarbazoles as "Fast Bases" :

The following amines from carbazole have been tried as "Fast Bases" in azoic dyeing; those marked with an asterick are new compounds :

(1) 3-Aminocarbazole (m.p. 260°)

(2) 3-Amino-N-methylcarbazole (m.p. 170°)

(3) 3-Amino-N-ethylcarbazole (m.p. 110°)

*(4) 3-Amino-N-benzoylcarbazole (m.p. 245-250°)

*(5) 3-Amino-N-acetylcarbazole (m.p. 80°)

*(6) 3-Amino-N-p-toluenesulphonylcarbazole (m.p.140°)

*(7) 3-Chloro-6-aminocarbazole (m.p. 130°)

(8) 3:6-Diaminocarbazole (m.p. 293-95°)

(9) Mixed aminocarbazole.

*(10) 2-Aminocarbazole (m.p. 235°)

The general method was the reduction of the corresponding nitro compounds with hydrogen in the presence of Raney nickel under pressure. None of the shades obtained by coupling Naphtols AS, AS-TR and AS-SW with the diazonium salts of the above amines, were attractive or novel, and the fastness properties were poor.

6. Preparation of new "Naphtols" :

The utility of the aminocarbazoles mentioned above as intermediates in the synthesis of azoic coupling components was examined. The amines were condensed with the acid chloride of 2-hydroxy-3-naphthoic acid. The new "Naphthols" were coupled on the fiber with diazotized 2:5-dichloroaniline (Scarlet 2G) and 4-benzamido-2:5-diethoxyaniline (Blue 2B), and the shades examined.

While many of them had a light fastness of 6, none of them except the "Naphtol" from 3-chloro-6-aminocarbazole gave bright shades. The latter Naphtol gave a scarlet shade with Scarlet 2G and a bright blue shade with Blue 2B with chlorine fastness of 3-4 and light fastness of 6-7.

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