A STUDY

of

THE OXIDATION PRODUCTS OF CARBAZOLE

by

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THESIS

for the degree of

DOCTOR OF PHILOSOPHY

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INTRODUCTION

INTRODUCTION

Much research has been done on carbazole, with a view, chiefly, to obtain its substitution derivatives. Such derivatives having been once obtained from carbazole itself, many of them were subsequently synthesised from diphenyl or diphenylamine compounds, and their respective constitutions thereby arrived at. The reduction products of carbazole have been fairly exhaustively studied and their constitutions similarly obtained after synthesis.

The work described in this thesis, however, touches a side of the chemistry of carbazole which has seldom been investigated by former workers, namely the oxidation of carbazole and its derivatives. The results of past researches in this branch of the subject have generally been somewhat indefinite, if not entirely negative, until the work of Perkin and Tucker in 1921 produced two definite crystalline oxidation products. The first part of the work herein set forth, describes the method by which one of these compounds has been shown to be 9:9'- or N:N'- dicarbazyl. This part of the work forms by itself a complete research, although a direct synthesis of the compound in question has not yet been accomplished. The attempts to effect such a synthesis constitute Part II of this work.

A brief summary of the principal results described in Part I will not be out of place at this point.

(1) 3:6- dibromocarbazole on oxidation is found to give 3:6:3':6'- tetrabromo- N:N'- dicarbazyl.

(2) This is proved by the synthesis of the latter compound through the potassium derivative of the former.

(3) The dicarbazyl A of Perkin and Tucker, on bromination, gives the same compound showing that that dicarbazyl has a N-N structure.

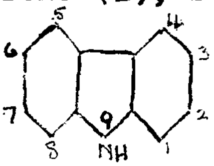
(4) N:N'- dicarbazyl is not capable of conversion into 3:3'- dicarbazyl.

PART I.

N:N'- DICARBAZYL AND SOME HALOGEN DERIVATIVES

PART I.

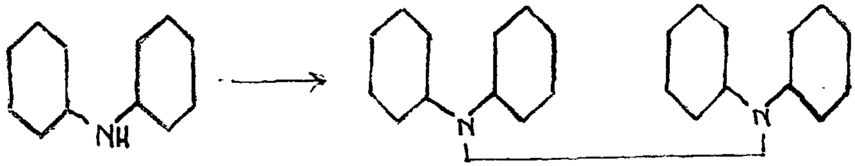
Graebe and Glaser (Ber., 1872, 5, 12) found that chromic acid, in glacial acetic acid solution, reacted very vigorously with carbazole (I), but the product obtained contained chromium.



(I)

Wieland and Gambarjan, (Ber., 1906, 39, 1499.), showed that when diphenylamine (II) is oxidised with lead peroxide in benzene solution, or with potassium permanganate in acetone solution, tetra-phenylhydrazine is formed. (III)

(II)



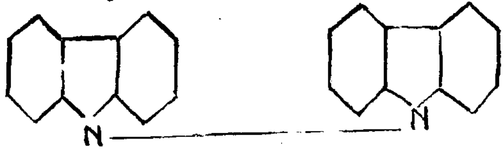
(III)

The above reagents however had no effect on carbazole, no bis-diphenylene hydrazine or (as it may suitably be called), N:N'- dicarbazyl (IV) being formed.

Later Branch and Smith, (J. Amer. Chem. Soc., 1920, 42, 2405.), by oxidising carbazole in dry benzene with silver oxide, obtained two compounds, one of which they claim to be a dicarbazyl or tricarbazyl derivative of N:N'- dicarbazyl. The compound contained a small percentage of silver, but this was regarded as an impurity.

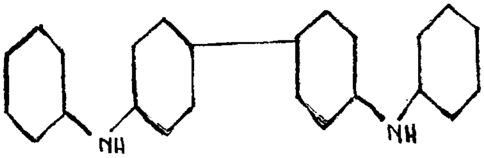
The most definite results in the oxidation of carbazole have been obtained by Perkin and Tucker (J.C.S. 1921, 119· 216). They have shown that when a boiling acetone solution of carbazole was treated with finely divided potassium permanganate a vigorous reaction set in, which resulted in the formation of two well defined crystalline compounds and an amorphous product. The last was the main product of the oxidation and was designated C. The crystalline substances were shown to have the composition and molecular weight of dicarbazyls and were designated Dicarbazyl A and Dicarbazyl B (m.p. 265° C.). No investigations were made into the structure of any of these compounds.

The oxidation of carbazole to a dicarbazyl may take place in a variety of ways. As already stated Wieland failed to imitate his oxidation of diphenylamine when the latter was replaced by carbazole. Such an oxidation of carbazole should be possible however, with the production of N:N'- dicarbazyl (IV)



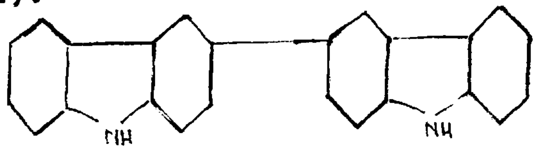
(IV)

Again it was shown by Wieland that if diphenylamine was oxidised in acetic acid solution, with sodium dichromate, in presence of concentrated sulphuric acid, N:N'- diphenylbenzidene (V) results.



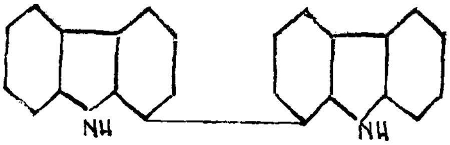
(V)

From analogy with this reaction, it is not unlikely that carbazole might give a similar product - namely 3:3'- dicarbazyl (VI).



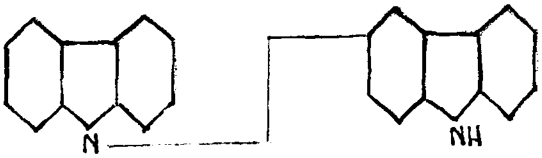
(VI)

particularly as the 3-position in the carbazole nucleus is known to be specially reactive, substitution, for example, nearly always taking place in this position first. The hydrogen in the 1-position is (excluding the hydrogen of the imino group) the next most reactive in the carbazole molecule and it is quite conceivable that oxidation might take place here with the production of a compound of the type (VII).



(VII)

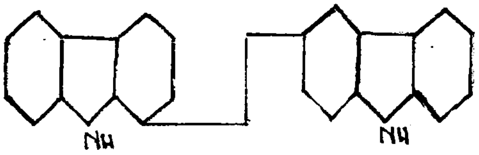
Finally we may have a C:N- dicarbazyl of the type (VIII) which may represent the constitution of one

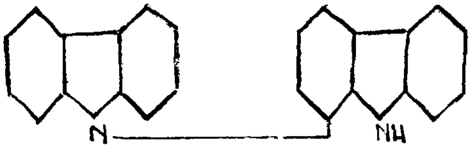


(VIII)

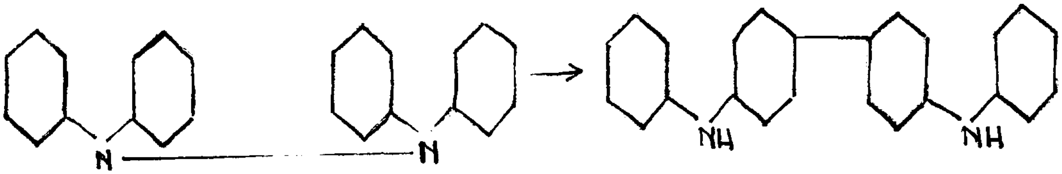
or other of the substances obtained by Perkin and Tucker, although no analogous oxidation product of diphenylamine is known.

Various combinations of these three main types of dicarbazyl may also exist e.g. 3:1- dicarbazyl, or 1:N-dicarbazyl.





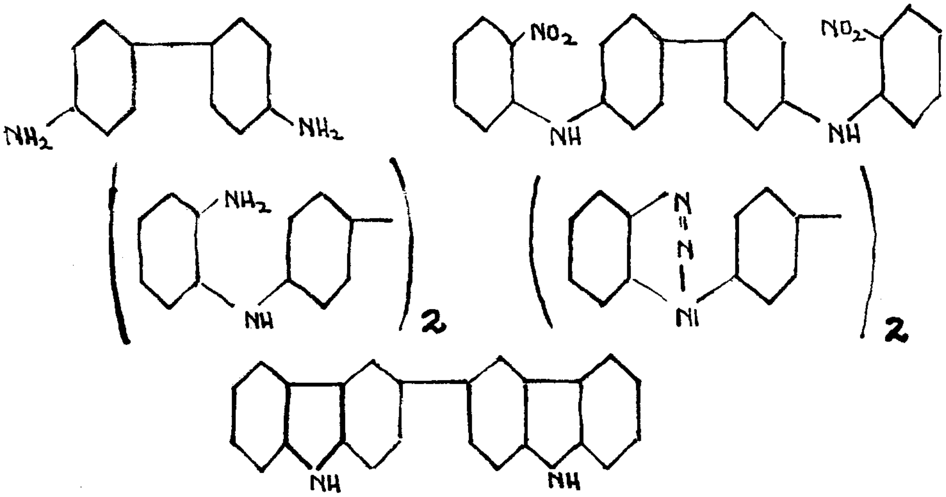
As already stated the 3-position in the carbazole nucleus is the most reactive and not only does substitution almost invariably take place here first, but certain groups wander from the 9-position into the 3- or 1- positions. Thus 9-nitroso-carbazole on treatment with hydrochloric acid in acetic acid solution passes into 3- nitroso-carbazole (H. Schott, Stuttgart, D.R.-P. 134983, Kl. 12p., 7 June 1901.) Similarly carbazole- 9- carboxylic acid gives, under certain conditions, carbazole -1- carboxylic acid (Ciamician and Silber, Gazzetta, 1882, 12, 272). Further, Wieland and Gambarjan, (loc. cit.), and Wieland (Ber., 1913, 46, 3296), have shown that tetraphenylhydrazine, on treatment with concentrated sulphuric acid, undergoes an intramolecular rearrangement, with the formation of N:N'- diphenylbenzidene.



(IV) (V)

From analogy with these reactions, therefore, it is quite probable that the dicarbazyls isolated by Perkin and Tucker are not the first products of the oxidation of carbazole. Thus N:N'- dicarbazyl if formed first, may undergo subsequent change and be converted into 3:3'- or 1:1' dicarbazyl.

A synthesis of 3:3'- dicarbazyl by Tucker, (J.C.S. 1926, <u>129</u>, 3033.), by the following series of reactions,

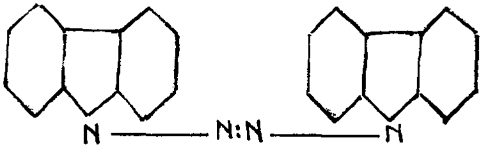


has definitely established the fact, however, that this substance is not one of the products obtained in the oxidation of carbazole with potassium permanganate in acetone.

There is however the possibility that one of these compounds is N:N'- dicarbazyl. Wieland has made several attempts to obtain this substance but without success. As for instance:-

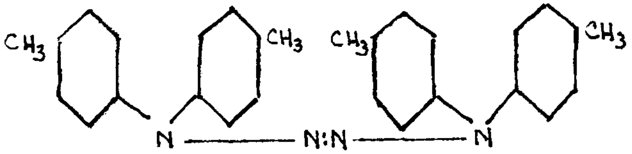
(1) By the oxidation of carbazole with PbO_2 and with $KMnO_4$ (p. 3)

(2) By the action of heat on the substance (IX) (Wieland and Fressel Ann. 1912, 392, 169)



(IX)

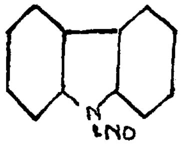
by analogy from similar treatment of tetratolyltetrazene (X).



(X)

(Ber., 1908, 41, 3498) which yields tetratolylhydrazine and N_2 on heating.

(3) By the action of heat on 9- nitroso carbazole (XI)

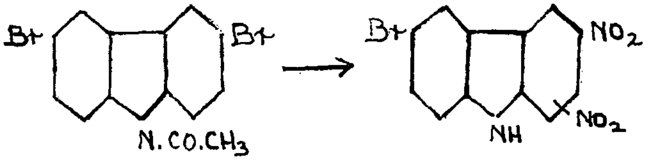


(XI)

(Wieland and Lecher, Ann. 1912, 392, 156), since N-nitrosodiphenylamine can be converted into tetraphenylhydrazine.

Even if the intramolecular changes suggested on p. 6 did not take place, the very fact that the 9-, the 3-, and the 1- positions of each carbazole nucleus are all free and unsubstituted, and all (especially the 9- and 3- positions) susceptible to oxidation, renders the probability of the formation of complex oxidation products very likely. Any method of oxidation, therefore, which will tend to reduce this complexity, will perhaps produce some clue as to the constitution of one or more of the products, and may render the course of the reaction more intelligible. Should, for example, the 3- and 6- positions in the carbazole molecule, be occupied by atoms or groups other than hydrogen, any migration of N- groups to these positions is most unlikely, if not impossible. (It is known, nevertheless, that 9- acetyl 3:6- dibromocarbazole (XII) on nitration gives 3-nitro-6- bromo-nitro carbazole (XIII) (Mazzara and Leonardi, Gazz., 1895, 25, 397).

(XII)



(XIII)

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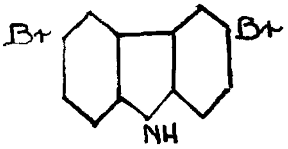
The action of the HNO_3 here may be (1) hydrolysis (2) N- substitution giving a $N\text{-}NO_2$ with subsequent migration to 3- position of the $-NO_2$ group (3) further direct substitution. Such a replacement of halogen by say, a carbazyl group, attached to the nitrogen is, however, very improbable.) It was therefore thought suitable to attempt to oxidise derivatives of carbazole in which the 3- and 6-positions were occupied, in the hope that, not only would migration be prevented, but that oxidation might be confined to imino group.

The first compound to be thus examined was 3:6- dibromocarbazole (XIV).



(XIV)

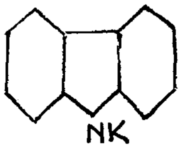
The method of oxidation was the same as that used by

Perkin and Tucker. It was found, that when a solution of 3:6- dibromo carbazole in pure acetone was boiled with an excess of finely divided potassium permanganate, a crystalline compound could be isolated, which showed all the characteristic properties of the dicarbazyls obtained by the above workers. An analysis and a molecular weight determination showed the substance to have the composition $C_{24}H_{12}Br_4N_2$. This corresponds to a tetrabromodicarbazyl. If, as was quite probable, this compound had the structure of a derivative of N:N'- dicarbazyl, it would be expected to reduce, with comparative ease, to the original 3:6- dibromocarbazole. Wieland and his collaborators have shown that tetra-aryl hydrazines reduce easily to the diaryl amines, but the application of his methods to the compound in question, failed to bring about reduction (See Appendix I). Such resistance to reduction called, therefore, for more drastic treatment. The tetrabromodicarbazyl was accordingly treated under pressure with concentrated hydriodic acid. The sole product of this reaction was carbazole, the bromine atoms having been removed. This fact alone is no proof of the existence of a N-N linkage in the compound. A C-C bond would certainly not be broken by hydriodic acid; but again there is the possibility of the formation (during oxidation) of a C-N- dicarbazyl (VIII, p. 5). Such a compound might break down under such violent treatment.

It was not found possible to methylate, acetylate or form a nitroso compound of the tetrabromodicarbazyl, however, all of which reactions would be possible, were there an imino-hydrogen atom in the molecule; and in further, though less definite support of an N-N structure, it was found that, if the imino hydrogen atom of 3:6- dibromocarbazole were substituted by an alkyl group - in this case $.CH_3$- the alkylated body was not capable of oxidation by the methods employed for 3:6- dibromocarbazole itself.

It was decided that any proof of an N-N' constitution in this tetrabromodicarbazyl, must come through a synthesis of the compound in question, and experiments were instigated to this end.

After several unfruitful attempts at such a synthesis, success was attained as follows: (see also Appendix II, p. 48). It is known that carbazole on fusion with solid caustic potash, forms a potassium compound (XV).

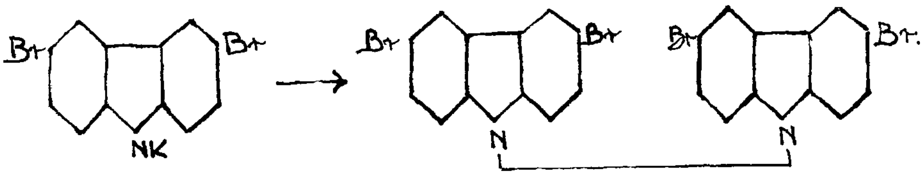


(XV)

The presence of halogen atoms in the carbazole nucleus ought to render the molecule, as a whole, somewhat more acid in character, and it might therefore be expected that a halogen-carbazole would form a metallic derivative more easily than carbazole itself, and further any such metallic derivative on treatment with iodine should form a N:N'-

dicarbazyl derivative with elimination of potassium iodide. 3:6- Dibromo-N-potassium-carbazole (XVI) could not be obtained by fusing potash with 3:6- dibromocarbazole, but was easily and cleanly obtained by treating the dibromo compound with finely divided potassium.

(XVI)



(XVII)

This derivative (XVI) was treated with iodine (without isolation) and 3:6:3':6'- tetrabromo- N:N'- dicarbazyl (XVII) was obtained. This was found to be identical in all respects with the oxidation product of 3:6- dibromocarbazole.

The oxidation of the 3:6- dibromocarbazole, therefore, takes place entirely at the nitrogen atom.

Following on this, the first recorded, synthesis of a derivative of N:N'- dicarbazyl, attempts were made to isolate the unsubstituted hydrazine. As already mentioned (p. 4) Perkin and Tucker obtained three compounds from the oxidation of carbazole and it seemed highly probable that one of these might be N:N'- dicarbazyl, but from the extremely limited knowledge of the compounds in question, it was not possible to decide whether A, B, or C had this structure. Reduction of all three seemed to be the most suitable method of approaching the problem. Accordingly, each was treated with concentrated hydriodic acid under pressure, with the following results.

Dicarbazyl A, (m.p. 220°) gave carbazole and no other products.

Dicarbazyl B, (m.p. 265°) gave a product which has not yet been identified.

Amorphous Substance C, (m.p. 175°) gave a mixture of carbazole and a small amount of a high melting substance.*

Since N:N'- dicarbazyl, on reduction, would be expected to give nothing but carbazole, it seemed very probable that if any of the above three compounds was N:N'- dicarbazyl, dicarbazyl A was that one. This substance was therefore brominated with the amount of bromine theoretically required to give a tetrabromoderivative, when it yielded a compound which was, in every way, identical with (a) the oxidation product of 3:6- dibromocarbazole and (b) the synthetic 3:6:3':6'- tetrabromo- N:N'- dicarbazyl.

From this and from the other experiments described it is therefore logical to conclude that the dicarbazyl A (m.p. 220°) of Perkin and Tucker is N:N'- dicarbazyl.

In confirmation and extension of the above results, the whole series of reactions was repeated using 3:6- di-iodocarbazole instead of 3:6- dibromocarbazole. The di-iodo derivative on oxidation gave a tetra-iodo-decarbazyl; while on treatment with potassium, followed by iodine, the

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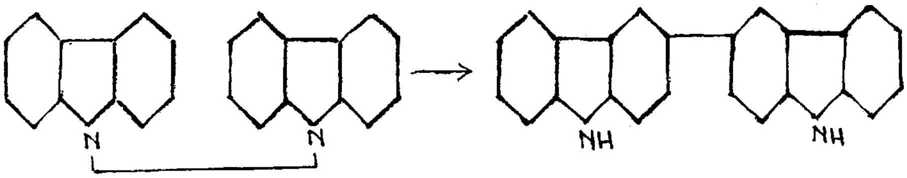
*See Appendix IV, p. 61 for further investigation of C.

same compound was obtained; and on iodination of dicarbazyl A (by two different methods) exactly the same substance was produced. Several small differences were noted in the "iodo" series which are dealt with in the experimental section.

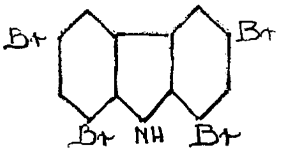
In view of the very close similarity in structure between N:N'- dicarbazyl and tetraphenylhydrazine, it was considered of interest to compare their chemical properties. The most outstanding feature of the latter compound is the comparative ease with which it can be converted into NN'-diphenylbenzidene (p. 6). It therefore seemed highly probable that N:N'- dicarbazyl should be convertible into 3:3'- dicarbazyl.



All attempts to bring about such a change, however, have met with failure. NN'- diphenylbenzidene is likewise obtained by the acid oxidation of diphenylamine (Wieland, Ber., 1913, 46, 3296.) and it has recently been found by Maitland and Tucker (private communication), that a similar acid oxidation of carbazole results in the formation of 3:3'- dicarbazyl. The mechanism of the oxidation of diphenylamine to diphenylbenzidene is a controversial question. Marqueyrol and Muraour (Bull. Soc. Chim., 1914, 15, 191.) support the view that an intermediate ·N: derivative of diphenylamine is first formed, while Wieland holds that the benzene nucleus is at once attacked by the oxidising agent. The work of Maitland and Tucker substantiates Wieland's theory, (since they find that the sulphuric acid present in the oxidation of carbazole protects the -NH- group), and definitely disproves the results of Marqueyrol and Muraour. The negative results indicated above, support Maitland and Tucker's contention in that they eliminate the possibility of N:N'- dicarbazyl being an intermediate product in the oxidation of carbazole to 3:3'- dicarbazyl.

The results obtained by Maitland and Tucker, prompted an investigation into the acid oxidation of 3:6- dibromocarbazole. It was thought that since a derivative of 3:3'-dicarbazyl was incapable of formation, a 1:1'- dicarbazyl derivative might result. When 3:6- dibromocarbazole was oxidised in acetic acid solution (in presence of sulphuric acid) with sodium dichromate a high melting amorphous product was obtained. This may be a 1:1'- dicarbazyl derivative but it has not been found possible to identify it. In the absence of the sulphuric acid, as above, 3:6:3':6'-tetrabromo -N:N'- dicarbazyl was formed. Here, again, the protecting action of the sulphuric acid seems to make itself evident preventing as it does in the first of these oxidations the formation of an N:N'- derivative.

A fact of some interest arose out of attempts to oxidise 1:3:6:8- tetrabromocarbazole (XVIII). It was with a view to obtaining 1:3:6:8:1':3':6':8'- octabromo -9:9-dicarbazyl that the tetrabromocarbazole was treated with, first, potassium permanganate in acetone, and secondly, with sodium dichromate in acetic acid. In the former experiment no oxidation took place, while in the latter, only a very small yield of some high melting bromine derivative was obtained. This resistance to oxidation can be explained on the assumption that the 1- and 8- bromine atoms exercise some steric effect on the imine group.



(XVIII)

This idea is substantiated by the fact that it was not found possible to obtain an acetyl derivative, or a nitroso derivative of 1:3:6:8- tetrabromcarbazole by any of the ordinary methods. Furthermore it is exceedingly difficult to introduce more bromine atoms into 3:6:3':6'- tetrabromo N:N'- dicarbazyl, so that octabromo -N:N'- dicarbazyl would appear to be very difficult of formation. The action of finely divided metal on the tetrabromo compound, followed by treatment with iodine was tried, and here again the yield was exceedingly small, but the substances obtained by oxidation of tetrabromocarbazole and by this last method appeared to be the same.

EXPERIMENTAL

3:6- Dibromocarbazole.

Some difficulty was encountered in obtaining this substance in quantity.

1. The Method of List (Verd. a. Rh. D.R.P. 275833, Kl. 12 p., 14 August 1912):

(a) Carbazole (1.7 gms.), glacial acetic acid (18 ccs.) and acetic anhydride (7.5 gms.) were boiled under a reflux condenser till solution had taken place. Bromine (1.1 ccs) dissolved in glacial acetic acid (10 ccs.) was then added, drop by drop, to the boiling mixture. When all the bromine had been added, the contents of the flask were allowed to cool. A pale yellow flocculent substance was precipitated. This was removed by filtration. The filtrate on further standing deposited a second crop of the same substance. The residual filtrate on pouring into water produced a thick tar. The yellow compound melted 142-146° C.

(b) The above experiment was repeated, the bromine being added to the cold solution and the flask well shaken after each addition of bromine. Some unchanged carbazole was removed from the solution and the latter then allowed to stand. The same yellow substance as before, this time m.p. 140-145° C. was deposited. About 1 gm. of the substance was obtained in both experiments.

The substance was exceedingly sparingly soluble in cold alcohol, and somewhat more soluble in hot. It was extracted six times, with about 25 ccs. of boiling alcohol. This solvent removed the yellow colour and left a small amount, (about .2 gms.), of small white needles, m.p. 187°-189° C. This on hydrolysis with alcoholic KOH produced a compound m.p. 211-212° which was identical with a specimen of pure 3:6- dibromocarbazole, a mixed m.p. of the two showing no lowering. The compound m.p. 187-189° C., will therefore be N-Acetyl -3:6- dibromocarbazole which has m.p. 189°-190° C. when pure.

(c) The experiment was carried out in the absence of acetic anhydride. Carbazole (1.7 gms.) was dissolved in glacial acetic acid (20 ccs.) and to the boiling solution two molecules of bromine were added and the solution was allowed to stand overnight. The yellow substance was again obtained as a deposit. The filtrate from the yellow body was poured into water. A whitish green ppt. was obtained which on recrystallisation from alcohol melted 121°-125° C. This was possibly 3- bromo -N- acetylcarbazole (m.p. 128° C.)

2. Bromination of N-Acetylcarbazole (Mazzara and Leonardi, Gazz. 25, (2) 397).

No experimental details are given in this paper of Mazzara and Leonardi, so the following procedure was adopted.

(a) N-acetyl carbazole (Graebe and Glaser, Ann. 1872, 163, 350; Boesken, R. 31, 350) (1 gm.) was dissolved in chloroform (5 ccs.) and to the boiling solution, bromine (2 gms.) in chloroform (3 ccs.), was added drop by drop. HBr was copiously evolved. On cooling the reaction mixture a solid separated out. (Occasionally this precipitation did not occur in which cases the chloroform was evaporated; a tar was left which on treatment with alcohol became solid). This substance having been removed, was washed with cold alcohol and subsequently crystallised from (a) absolute alcohol and (b) benzene. Yellow needles were thus obtained of m.p. 140-144° C. (b) The same substance was obtained when twice the theoretical amount of bromine was used. Prolonged boiling of the brominated solution and bromination in the cold produced the same result.

For the bromination of N- Acetylcarbazole in carbon-disulphide solution see Appendix III p. 55.

The yellow substance obtained in the above experiments was found to be identical with that previously obtained in the direct bromination of carbazole. It crystallises quite well from alcohol and benzene but always melts over a range of temperature. Various experiments have been performed on it, such as hydrolysis, acetylation, further bromination etc., etc., but no definite results have been obtained. It is being further investigated.

3. Bromination of N- Benzoylcarbazole (Mazzara and Leonardi, Gazz. 22, 1892, 569).

A slightly modified method from the original was found better than the latter, in giving a larger yield.

N- Benzoylcarbazole (Stevens and Tucker, J.C.S. 1923 123, 2146 and Tucker J.C.S. 1926, 129, 546, footnote) (10 gms.) was dissolved in cold glacial acetic acid (140 ccs.) To this was added, fairly rapidly, a solution of bromine (6 ccs.) in glacial acetic acid (10 ccs.) The product almost immediately crystallised out as long needles. The mixture was then allowed to stand for 3 or 4 hours with occasional stirring. It was found that no heat of any kind need be applied at any time during the reaction; in fact, such application spoiled the preparation in a great many cases. The solid product was filtered free from the acetic acid mother liquors, washed once with a few ccs. of dilute alcohol and then crystallised twice from acetic acid and finally once from benzene when the m.p. was 213-214° C. Found Br, 37.8% 3:6- dibromo -N- Benzoylcarbazole ($C_{19}H_{11}Br_2NO$) requires Br, 38.2%.

The hydrolysis of this benzoyl derivative was easily accomplished by boiling 2 gms. of it with a few ccs. of alcoholic potash for $\frac{1}{4}$ hour, pouring the solution into water, filtering off the white precipitate and crystallising twice from absolute alcohol. Short white needles were thus obtained m.p. 211-213° C. A mixed melting point with a specimen of pure 3:6- dibromocarbazole showed no lowering.

4. Direct Bromination of Carbazole in Carbon Disulphide Solution.*

Carbazole (50 gms.) was dissolved in boiling carbon disulphide (600 ccs.). A solution of bromine (34 ccs.) in carbon disulphide (130 ccs.) was added cautiously through a condenser to the boiling solution,HBr was copiously evolved from the vigorously reacting substances. When nearly all the bromine was added a solid separated, rendering the mobile solution thick and pasty. The bromine solution was now added cc. by cc. till the consistency of the mass was visibly thinner. The product was then removed and washed twice (in the filter funnel) with cold carbon disulphide. Two crystallisations from alcohol converted the slightly purple, crude product into small pure white needles m.p. 211-213° C. The substance was identical with the dibromocarbazole obtained from N- benzoylcarbazole. Yield 60% of theory.

In preparing dibromocarbazole by this method, it was

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*See Appendix II. page 41, note.

found that when working with smaller quantities of carbazole, the above proportions of bromine and solvent did not give a proportionately good yield. This was most noticeable. The following quantities were found to be most suitable for smaller amounts of carbazole:-

Carbazole in CS_2		Bromine in CS_2	
2 gms.	40 ccs.	2.6ccs.	11 ccs.
4 "	70 "	3 "	12 "
8 "	125 "	6.2 "	25 "
10 "	150 "	8.5 "	32 "
20 "	250 "	14 "	50 "
50 "	600 "	34 "	130 "

This method of preparation was, latterly, the only one used.

Purification of Acetone for Use in Oxidations.

About two litres of ordinary acetone were boiled with 40-50 gms. of finely powdered potassium permanganate for 1-1½ hours. The acetone was then removed by distillation, the fraction 50°-58° being collected. This fraction was redistilled twice through a long column, the fraction 55°-57° being kept for use. In some experiments with tetraphenylhydrazine (p. 76) the acetone used was purified by distillation of the compound of sodium iodide and acetone.

Oxidation of 3:6- Dibromocarbazole.

1. With Potassium Permanganate in Acetone:

3:6- dibromocarbazole (5 gms.) was dissolved in pure acetone (40 ccs.), and to the solution was added 7 grams of finely powdered potassium permanganate. The whole was then boiled for $3\frac{1}{2}$ to 4 hours under a reflux condenser. The mixture was poured into water and the products thus precipitated. Sulphur dioxide was passed through the suspension till all the manganous precipitate had dissolved. The remaining solid substance was a light reddish-brown colour. It was removed from the water by filtration and extracted three times with boiling absolute alcohol (10 ccs.) which process obviously dissolved a part of the solid and left a brownish-white residue. This residue was crystallised twice from benzene thus giving small white cubes, m.p. 249-250° C. Yield 50-60% of pure material. (Found Br, 49.2%; M, (cryoscopic in C_6H_6), 630. 3:6:3':6'- tetrabromo -N:N'- dicarbazyl, $C_{24}H_{12}N_2Br_4$, requires Br, 49.4%; M, 648.) The substance is obviously therefore a tetrabromodicarbazyl. It is practically insoluble in alcohol; fairly soluble in acetone or glacial acetic acid, crystallising from the latter in beautiful shining plates; very soluble in benzene and its homologues.

The alcohol extracts obtained as above were concentrated to about $\frac{1}{2}$ bulk, when a small amount (negligible) of the tetrabromodicarbazyl was obtained. The remainder, on further concentration, deposited unchanged 3:6- dibromocarbazole. This was carefully purified by crystallisation from alcohol and the mother liquors examined for traces of any other oxidation product. None could be found.

The compound was first obtained by simply filtering the original oxidation mixture, when it was deposited from the filtrate in white plates, very pure but in poor yield.

2. With Sodium dichromate in Acetic Acid:

3:6- dibromocarbazole (2 gms.) was dissolved in glacial acetic acid (40 ccs.). Sodium dichromate (0.4 gms.) dissolved in about ½ cc. of water was added. A green colour at once developed, showing oxidation, to be taking place. The solution was boiled for ¼ hour, and then poured into cold water and the precipitate removed by filtration. The solid was thoroughly extracted with boiling alcohol (three times with 20 ccs.) and the insoluble residue then crystallised twice from benzene, when small white cubes exactly similar in appearance to those obtained in the permanganate oxidation, were obtained. The melting point of these was 250° C. and a mixed m.p. with the tetrabromodicarbazyl obtained in the last experiment, showed no lowering. The yield was about 40-50% of the pure material. The alcohol extracts were found to contain only unchanged 3:6- dibromocarbazole, only one product of oxidation having been formed.

3. With Sodium Dichromate in Acetic Acid in Presence

of Sulphuric Acid:

(Cf. Wieland, Ber., 1913, 46, 3296)

Dibromocarbazole (2 gms.) was dissolved in 100 ccs. of cold glacial acetic acid. Concentrated sulphuric acid (2.5 ccs.) was added. A slight green colour developed on the addition of the acid. The solution was kept cold by standing in cold water, and sodium dichromate (.5 gms.) dissolved in the minimum quantity of water was added. The solution at once became a dark greenish-brown in colour. It was allowed to stand for half an hour and was then poured into water. The brown solid so produced was filtered off and dried, when a pale brown amorphous powder was obtained. This did not respond to any of the tests for chromium. M.p. over 300° C. (indefinite).

Reduction of Tetrabromodicarbazyl with Hydriodic Acid.

Tetrabromodicarbazyl (.5 gms.) and concentrated hydriodic acid (3 ccs.) were sealed in a thick-walled tube which was maintained at a temperature of 150° C. in a Gattermann furnace for five hours. The contents of the tube were then washed out into water, and sulphur dioxide passed through the suspension to remove the free iodine. The solid was removed, ground to a powder, and rewashed with SO_2 water. It was then extracted with boiling alcohol.

The alcohol extract thus obtained was boiled with animal charcoal, filtered and the filtrate poured into water. The precipitate was collected and dried, and subsequently crystallised twice from benzene, from which solvent it deposited white plates M.p. 235-239° C., with sublimation. A mixed m.p. with pure carbazole melted 235-240° C. The substance is therefore carbazole. This was verified by brominating a small quantity of the compound in carbon disulphide, when 3:6- dibromocarbazole was produced.

That part of the crude reduction product which was insoluble in alcohol (about .03 gm.) was dissolved in a small quantity of benzene and acetone was added to this solution till preciptation took place. There was thus obtained a fine white micro-crystalline powder, m.p. 249-250°. A mixed m.p. of this with a specimen of pure tetrabromodicarbazyl showed no lowering.

Attempts to Acetylate Tetrabromodicarbazyl.

(1) Boiling with acetyl chloride.

(2) do. acetic anhydride.

(3) do. do. and a trace of concentrated sulphuric acid, produced no acetyl derivative.

Attempts to nitrosate Tetrabromodicarbazyl.

A small quantity of the tetrabromodicarbazyl was dissolved in the minimum quantity of glacial acetic acid and treated with (a) sodium nitrite (b) amyl nitrite but in both cases all the starting material was recovered unchanged.

N- methyl -3:6- dibromocarbazole.

3:6- dibromocarbazole (3.25 gms.) was dissolved in acetone (20 ccs.). To this was added solid sodium hydroxide (0.8 gm.) and dimethyl sulphate (0.95 ccs.), the latter being added in three portions. The reaction mixture was boiled on the water bath for fifteen minutes and then poured into water. The solid product was filtered off dissolved in the minimum quantity of hot alcohol, and the solvent was then evaporated till crystallisation commenced. The substance so obtained was recrystallised in the same manner, when it was isolated as long white needles m.p. 159-161° C. Found Br, 47.0%, $C_{13}H_{9}NBr_{2}$ requires Br, 47.2%.

Oxidation of N- methyl -3:6- dibromocarbazole.

Attempts were made to oxidise N- methyl - 3:6- dibromocarbazole with potassium permanganate in acetone, under conditions exactly similar to the methods used for the unalkylated dibromocarbazole. The starting material was recovered unchanged in every case. No investigations have as yet been made into the oxidation of N-methyl-3:6- dibromocarbazole in acetic acid with sodium dichromate.

Synthesis of 3:6:3':6'- tetrabromo- N:N'- dicarbazyl by the Action of Potassium and Iodine on 3:6- dibromocarbazole.

To finely divided metallic potassium (0.5 gm.) in pure, dry benzene was added 3:6- dibromocarbazole (1 gm.). The mixture was boiled for 1 hour. A yellow powder separated in the course of this time. It was probably the potassium derivative of 3:6- dibromocarbazole (XVI). It was not isolated, but after cooling, iodine (0.6 gm.) in dry benzene (10 ccs.) was added with constant shaking. After allowing to stand for half an hour the mixture was filtered through a fluted filter paper, and the residue on the paper well washed with benzene containing a little iodine. The main filtrate, combined with the washings, was then evaporated almost to dryness, when alcohol was added. A solid was immediately precipitated, which was filtered off and extracted three times with boiling alcohol. The portion which remained undissolved was crystallised from (a) a mixture of benzene and alcohol and then (b) glacial acetic acid. The substance was obtained from the latter solvent in small, white plates m.p. 249-250° C. Yield 20% of theoretical. A mixed melting point of this substance and that obtained by the oxidation of 3:6- dibromocarbazole showed no lowering. The substances also, crystallised in the same forms from the same solvents, and had the same solubilities. No substance except the unchanged starting material was found in the alcohol extracts.

3:6- Di-iodocarbazole:

This compound was prepared by the method of Tucker (J.C.S. 1926, 129, 546) Purification of the crude product was effected, however, by a simple method which obviated the necessity of acetylating and subsequently hydrolysing the pure acetyl derivative, as described in the above paper. 3:6- di-iodocarbazole (crude) (1 gm.) was dissolved in 20-30 ccs. of pure acetone and this solution boiled with powdered potassium permanganate (0.1-0.2 gm.) for 20 minutes. The reaction mixture was then poured into water, sulphur dioxide was passed through the suspension till the manganous precipitate had dissolved and the white solid was then removed and purified further by crystallisation from alcohol (once) when 3:6- di-iodocarbazole m.p. 204-206° C. was obtained. The m.p. of the crude material may be raised as much as 15 degrees by this method.

Oxidation of 3:6- di-iodocarbazole.

1. With potassium permanganate in acetone:

Di-iodocarbazole (2 gms.) was dissolved in a mixture of pure acetone (20 ccs.), and benzene (6 ccs.). A large excess (2-3 gms.) of finely divided potassium permanganate was added in four portions while the mixture was boiled.

Boiling was continued for 2 hours. The manganous residues were removed by filtration, extracted with benzene and the extracts added to the main filtrate, the whole of which was then evaporated to dryness. The residue thus obtained was washed with a few ccs. of warm acetone to remove any unchanged starting material. It was next mixed with enough acetone to give a thin paste, which was boiled and benzene added till all had dissolved. On allowing to stand small white crystals grew out of the solution. The first crop of these was the purest, and on recrystallising in the above manner gave white cubes m.p. 269-270°. The second and third crops were further purified by washing with cold acetone, and crystallising as before. (Found I, 60.9%; M (cryoscopic in benzene), 824. 3:6:3':6' tetraiododicarbazyl $C_{24}H_{12}N_2I_4$ requires I, 60.8% M, 834.) Yield, 20-25% of the theoretical. All the unchanged 3:6- di-iodocarbazole was recovered from the acetone washings. The tetraiododicarbazyl is very similar to the tetrabromo-compound, the solubility in all solvents being markedly less however.

The use of the mixed solvent in the above oxidation was found to materially increase the yield of the tetraiododicarbazyl. If no benzene were present the yield was never greater than 15% of the theoretical. A similar case has been noted by Branch and Smith (J.A.C.S. 1920, 42, 2405). These workers, when oxidising carbazole with silver oxide in benzene obtained two compounds, one soluble, and the other insoluble in ether. If the oxidation was performed in ether however the ether-soluble compound predominated.

2. With Sodium dichromate in glacial acetic acid:

3:6- di-iodocarbazole (1 gm.) was dissolved in glacial acetic acid (80 ccs.), and sodium dichromate (0.5 gm.), dissolved in the minimum quantity of water, was added. The solution, which became slightly green, was boiled for half an hour, during which time a solid separated. This was removed and was extracted several times with boiling alcohol. The alcohol insoluble portion was crystallised from a benzene-acetone mixture and finally (twice) from benzene alone. The m.p. of the pure product was 269-270° C. and a mixed m.p. with the compound obtained in the previous experiment showed no lowering. No oxidations have been performed in presence of sulphuric acid.

Synthesis of 3:6:3':6'- tetra-iodo- N:N'- dicarbazyl.

3:6- di-iodocarbazole (1 gm.) was added to molecular potassium (0.3 gm.) in pure dry benzene (20 ccs.). The whole was boiled for $1\frac{1}{2}$ hours. After cooling, a solution of iodine (0.5 gm.) in dry benzene (10 ccs.) was added with shaking. The mixture was allowed to stand for half an hour and was then filtered through a fluted paper, the residue on the paper being well washed with benzene containing a little iodine. The combined filtrate and washings were then evaporated to dryness. The solid residue was extracted three times with 5 ccs. of boiling alcohol and the insoluble residue crystallised twice from a benzene-acetone mixture. Small white crystals were thus obtained of m.p. 269-270°. A mixed melting point of this compound with a specimen of the pure product obtained in the oxidation of di-iodocarbazole, showed no lowering.

Reduction of the Dicarbazyls A and B and of the Amorphous Product C (Perkin and Tucker, J. 1921, 119, 216).

I. Dicarbazyl A:-

Dicarbazyl A m.p. 220° C. (.5 gm.) was heated in a sealed tube with concentrated hydriodic acid (3 ccs.) at 150° C. for 15 hours. The contents of the tube were then washed out into water, and the suspension treated with sulphur dioxide to remove free iodine. The solid substance, having been removed by filtration, was extracted with boiling alcohol (10 ccs.) to remove any unchanged starting material, in which solvent it should be insoluble. The whole of the product went into solution. The alcohol solution was then concentrated till short yellowish needles crystallised out. After one recrystallisation from benzene these had m.p. 235-238° C. and sublimed readily. The substance was identified with carbazole by means of a mixed m.p.

No other substance could be isolated from any of the mother liquors. .45 gms. of carbazole were recovered from the reaction mixture.

2. Dicarbazyl B:-

Dicarbazyl B, m.p. 265° C., (0.17 gm.) was heated for 5 hours, at 150° C., with concentrated hydriodic acid under pressure. The contents of the tube were then treated in a manner exactly similar to that described in the reduction of dicarbazyl A. The whole of the products in this experiment were soluble in alcohol and consisted of a white non-crystallisable substance of m.p. 100-110°. The reduction was repeated, heating for fifteen hours as in the case of dicarbazyl A, and the above result was again obtained. The product m.p. 100-110° has not yet been identified, but is being further investigated.

3. Amorphous Substance C:-

The substance C, m.p. 175° C., (0.5 gm.) was treated with concentrated hydriodic acid under pressure for 20 hours at 150° C. The products of reduction were isolated as in the case of the reduction of dicarbazyl A. A portion of these products was found to be insoluble in alcohol. After repeated extractions with this solvent, the insoluble portion melted 245°-260°. It was then dissolved in benzene and the solution boiled with animal charcoal for ¼ hour. The charcoal having been removed by filtration, the liquid was poured into a slight excess of boiling alcohol. The precipitate thus formed was redissolved and treated again as above with charcoal and alcohol. The benzene solution exhibited a strong green fluorescence. The above purification was repeated some five or six times, when there was obtained a very small amount of a cream coloured amorphous substance of m.p. 300°-310°. No solvent could be found from which it would crystallise. It is being further investigated.

The major portion of the reduction products of the substance C, were soluble in alcohol however. The alcoholic solution, on evaporation, deposited small plates, which on recrystallisation from benzene (using animal charcoal) melted 235-238° C., and were found by means of a mixed m.p. to be carbazole.

See also, Appendix IV p. 61.

Bromination of Dicarbazyl A.

It was found essential, in both the bromination, and iodination of dicarbazyl A, to use only the purest dicarbazyl. Even an amount of impurity causing a depression of 2 or 3 degrees in the melting point of the dicarbazyl (217° instead of 220°) renders the product of halogenation practically impossible to purify.

Pure dicarbazyl A (0.5 gm.) was dissolved in the minimum quantity of boiling glacial acetic acid. To the hot solution was added 3.5 ccs. of a solution of bromine in glacial acetic acid (1 cc. Br in 9 ccs. of acetic acid). The solution became turbid and was heated on the water bath for about half an hour, at the end of which time small white glistening plates had separated in fair quantity. After cooling the mixture, these were removed and washed once or twice with boiling alcohol, and finally crystallised twice from benzene, when small hard cubes m.p. 248-250° were obtained. A mixed m.p. of these, with a specimen of pure synthetic 3:6:3':6'- tetrabromo- N:N'- dicarbazyl, established the identity of the two substances.

Iodination of Dicarbazyl A.

1. Pure dicarbazyl A (0.5 gm.) and finely divided iodine (0.75 gm.) were dissolved in boiling glacial acetic acid (35 ccs.). To the boiling solution was added, drop by drop, a solution of concentrated nitric acid in acetic acid (2.5 ccs. in 10 ccs.) till the iodine colour of the solution was discharged. The iodinated product was precipitated during this addition. After cooling the mixture, the solid was removed and washed, first with sulphurous acid, secondly with boiling water, and lastly with boiling alcohol. It was finally crystallised from benzene, when white cubes

slightly tinged with yellow and of m.p. 269-270° were obtained. A mixed m.p. of this substance with a specimen of pure 3:6:3':6'- tetraiodo -N:N'- dicarbazyl showed no lowering, thus proving their identity. The slight yellow colour, which no amount of animal charcoal would remove, was probably due to slight nitration, the amount of which, does not affect the m.p. of the substance. It was noted that the second crop of crystals obtained from the final benzene solution, was almost entirely free from the yellow tinge and melted 269-270°.

2. Pure dicarbazyl A (0.23 gm.) was dissolved in the minimum amount of hot glacial acetic acid. Finely powdered potassium iodide (0.36 gm.) was added and the mixture boiled. To the boiling solution potassium iodate (0.5 gm.) was added and the whole was then boiled till the iodine colour was discharged. The tetra iodinated product separated from the solution during the course of the heating. After completion of the iodination, the reaction mixture was poured into water and a solution of sulphur dioxide added to remove the last traces of iodine. The solid was then isolated by filtration, thoroughly washed with boiling water, and then boiling alcohol, and finally crystallised twice from benzene. White cubes m.p. 270° were thus obtained which were shown to be identical with synthetic 3:6:3':6'- tetraiodo- N:N'- dicarbazyl by the usual method. These halogenation

experiments, as stated, clearly indicate that dicarbazyl A may be represented by formula (IV) as N:N' or 9:9'- dicarbazyl.

Attempts to convert N:N'- Dicarbazyl into 3:3'- Dicarbazyl.

Attempt 1. Pure N:N'- dicarbazyl (0.1 gm.) was mixed with cold concentrated sulphuric acid (2 ccs.) and allowed to stand for 24 hours. An emerald green colour developed. The mixture was then poured into water and the solid thereafter isolated. The whole of the starting material was recovered unchanged. The absence of any 3:3'- dicarbazyl was clearly shown also, by the fact the whole of the acid treated product was soluble in a small amount of benzene, in which the 3:3'- dicarbazyl is practically insoluble.

Attempt 2. N:N'- dicarbazyl (0.2 gm.) was heated with concentrated sulphuric acid (4 ccs.). The dicarbazyl dissolved with the formation of an intense green colour. On cooling the solution, and pouring into a large excess of water no solid was precipitated. Sulphonation had probably taken place.

Attempt 3. N:N- dicarbazyl (0.25 gm.) was dissolved in the minimum amount of cold glacial acetic acid. The solution was kept cold and concentrated sulphuric acid (2.5 ccs.) was added. A bluish-green colour slowly developed. After allowing to stand for 3 or 4 hours the whole was poured into water. The precipitate was isolated and found to consist entirely of unchanged starting material, .24 gm. of which was recovered. The conditions in this experiment are essentially the same as those used in the acid oxidation of carbazole (without the oxidising agent), which is known to yield 3:3'- dicarbazyl.

Attempt 4. N:N'- dicarbazyl (0.2 gm.) was dissolved in boiling glacial acetic acid (9 ccs.). To the hot solution was added 1.5 ccs. of concentrated sulphuric acid. A green colour developed, along with very slight turbidity. After heating on the water bath for twenty minutes the solution was poured into water. No precipitate was produced, sulphonation, again, probably having taken place.

Attempt 5. A small amount of N:N'- dicarbazyl was heated with acetic anhydride (in the presence of a trace of conc. sulphuric acid) in a sealed tube at 180° for about 1 hour. Much charring occurred. A very small quantity of a low melting, alcohol soluble, product was obtained but could not be crystallised. It may possibly be N- Acetylcarbazole.

Attempt 6. To a small quantity of N:N'- dicarbazyl dissolved in the minimum of acetic acid was added a few ccs. of fuming hydrochloric acid and the mixture was heated under pressure. The whole of the starting material was recovered unchanged.

Oxidation of 1:3:6:8- Tetrabromocarbazole.

1:3:6:8- Tetrabromocarbazole (Votocek, Ch. Z. Rep. 1896, 20, 190) (1 g.), was dissolved in glacial acetic acid (60 cc.) and sodium dichromate (0.75 g.) was added, and the mixture boiled for 1 hour, after which it was poured into excess of water. The precipitate so formed was separated, and extracted with hot acetone. A brown powder remained undissolved, m.p. about 275°. After many recrystallisations from benzene, it melted above 300°. It contained bromine, but a sufficient quantity for analysis, was never obtained.

Tetrabromocarbazole dissolved in acetone and boiled for several hours with potassium permanganate showed no trace of having been oxidised. Tetrabromocarbazole when boiled with acetic anhydride and a trace of concentrated sulphuric acid, did not form an acetyl derivative; and when treated with nitrous acid, or amyl nitrite in acetic acid, no nitroso derivate could be isolated.

Action of Finely divided Metal and Iodine on 1:3:6:8- Tetrabromocarbazole.

Tetrabromocarbazole (2 g.) was added to a fairly large excess of finely divided potassium in dry benzene (60 c.c.) and the mixture boiled for about 2 hours. Excess of iodine dissolved in benzene was then added, and after warming gently for $\frac{1}{4}$ hour the mixture was filtered. The filtrate was evaporated to dryness and the residue extracted with boiling alcohol. The alcohol insoluble substance melted 250-260° C. Two crystallisations from benzene raised the m.p. to over 300° C. The yield of the pure product was exceedingly small. A mixed m.p. with the compound obtained by the oxidation of tetrabromocarbazole showed no lowering, but owing to the very high temperature the m.ps. were not considered to be accurate. The solubilities and crystalline forms of the two products were similar and it is quite probable that the compounds are identical.

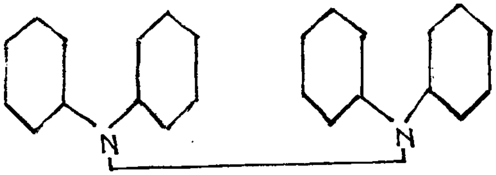
* * *

APPENDIX I.

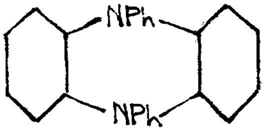
ATTEMPTS TO REDUCE DICARBAZYL DERIVATIVES

APPENDIX I.

It was stated on p. 10 that 3:6:3':6'- tetrabromo- N:N' -dicarbazyl was very resistant to reduction. Wieland and his collaborators have shown that tetra-aryl hydrazines of the type,



are easily reduced by the ordinary methods, and also that certain reagents bring about a dissociation of the molecule, the diarylamine being amongst the products of dissociation. Thus tetraphenylhydrazine, (above formula) by boiling in toluene, decomposes giving diphenylamine, 5:10- diphenyldihydrophenazine,



and o-anilino-triphenylamine. N:N'- dicarbazyl and its derivatives being essentially hydrazines, it was expected that they would reduce easily and might show some tendency to dissociate. A fairly exhaustive series of experiments was therefore performed, to obtain some idea of the stability of these compounds. No reduction could be brought about with the usual reagents however, many of which had been shown to act on tetraphenyl-hydrazine, and no dissociation could be detected when the compounds were acted upon by various reagents, which are known to cause dissociation to similarly constituted bodies.

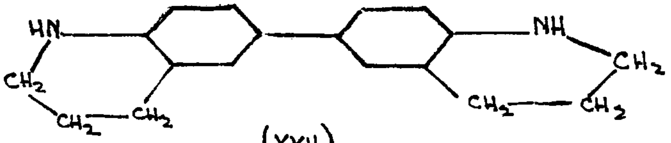
EXPERIMENTAL

Attempts to reduce 3:6:3':6'- Tetrabromo -N:N'- dicarbazyl.

1. Wieland and Gambarjan (Ber., 1906, 39, 1499) showed that tetraphenylhydrazine is reduced, with zinc dust and glacial acetic acid, to diphenylamine.

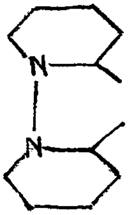
3:6:3':6'- Tetrabromo- N:N'- dicarbazyl (0.5 g.) was therefore dissolved in boiling glacial acetic acid (10 c.c.) and to the solution zinc dust (2 g.) was gradually added, and boiling continued for 20 minutes. The solution (freed from zinc) was then poured into a concentrated solution of ammonia (sp. gr. .880) and the precipitate thus obtained extracted with alcohol. The alcohol insoluble residue was found to be unchanged starting material (.47 g.) m.p. 247-249° C. The alcohol extract did not deposit any substance on evaporation. No reduction had taken place.

2. Wieland and Haas (Ber., 1922, 55 (B), 1804) have found that by the action of hydrochloric-acetic acid and zinc dust, the bishydrazine of quinobenzidene is reduced to quinobenzidene (XXII).



(XXII)

Such a bishydrazine (which would contain the structure)



closely resembles a dicarbazyl derivative.

3:6:3':6'- Tetrabromo- N:N'- dicarbazyl (.5 g.) was dissolved in hot glacial acetic acid (10 c.c.) and to the solution concentrated hydrochloric acid (2 c.c.) was added. Zinc dust was used as in experiment 1, and the product isolated in the same way, but here again no trace of reduction could be observed.

3. With sodium and alcohol:- 3:6:3':6'- tetrabromo- N:N'- dicarbazyl (0.5 g.) was dissolved in dry benzene (10 c.c.) and alcohol was added till the solution became turbid. Small pieces of metallic sodium were then dropped in to the solution, these being pressed against the bottom of the flask. When about 1-2 g. of sodium had been added, the solution was evaporated to dryness and the residue digested with water to remove sodium ethylate. The residue was extracted with alcohol. The alcohol insoluble residue was identified as unchanged starting material m.p. (after one crystallisation) 249-250°. The alcohol extract contained no substances. No reduction had taken place.

4. Tetrabromodicarbazyl (0.5 g.) was suspended in 8-10 c.c. of boiling amyl alcohol and sodium was added, as

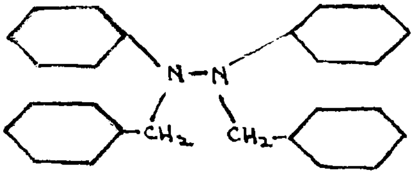
above, to the boiling solution. The alcohol was removed by steam distillation, the residue extracted with alcohol, and treated as in Nos. 1, 2 and 3 with the same results.

5. Tetrabromo-dicarbazyl (0.5 g.) was suspended in absolute alcohol (5 c.c.) and concentrated hydrochloric acid (5 c.c.). Granulated tin (5 g.) was added and the whole boiled for 1 hour. The solid obtained by pouring the above solution into water, was extracted with benzene, which extract, after purification and concentration, deposited unchanged starting material. No alcohol soluble reduction product could be obtained from the benzene mother liquors.

N.B. All the above experiments were repeated using N:N- dicarbazyl in place of the halogen derivative, but no reduction could be effected.

Attempts to Dissociate 3:6:3':6'- Tetrabromo- N:N'- dicarbazyl.

1. Franzen and Zimmerman (Ber., 1906, 39, 2566) have shown that diphenyldibenzylhydrazine (XIX)



(XIX)

is dissociated by treatment with 2N- sulphuric acid.

3:6:3':6'- Tetrabromo- N:N'- dicarbazyl (0.2 g.) was boiled for half an hour with (approx.) 2N- sulphuric acid.

A green colour developed, which vanished on pouring into water, a white solid remaining. This on separation and treatment in the usual way proved to be unchanged starting material.

2\. The tetrabromodicarbazyl (0.3 g.) was heated with concentrated sulphuric acid (2 c.c.), till the mixture was a very dark green colour. The product was isolated by pouring into water and working up in the usual way with alcohol. No alcohol soluble compounds were found, the whole of the starting material being recovered unchanged.

3\. Tetrabromdicarbazyl was dissolved in glacial acetic acid and the solution treated with concentrated sulphuric acid in the cold, and also at the boil. Pouring into water precipitated the product which was examined as before and with the same results.

4\. Wieland (Ann., 1911, <u>381</u>, 200 and 1912, <u>392</u>, 156) found that tetraphenylhydrazine decomposes rapidly in boiling xylene or after some months in chloroform or benzene, in the dark, at ordinary temperature to give diphenylamine and 5:10- diphenyldihydrophenazine.

Tetrabromo- N:N'- dicarbazyl (0.5 g.) was boiled in dry xylene (5 c.c.) for periods varying from $\frac{1}{2}$ to 8 hours. The xylene was removed in a current of air. The residue was dissolved in benzene and alcohol added to the solution. The whole of the starting material was precipitated unchanged.

5. Wieland (Ann., 1911, 381, 200) has caused dissociation of tetraphenylhydrazine by passing nitric oxide into a toluene solution of the hydrazine at 90°-95°, diphenylnitrosamine being quantitatively formed. A small amount of 3:6:3':6'- tetrabromo- N:N'- dicarbazyl was therefore dissolved in toluene at 95° C. and nitric oxide was bubbled through the solution for 1 hour. The mixture was then treated as in Expt. No. 5 with the same results, no N-nitroso- 3:6- dibromocarbazole or 3:6- dibromocarbazole being detected.

N.B. Here again, these experiments were repeated using the unhalogenated N:N'- dicarbazyl, but no dissociation took place.

The reduction of 3:6:3':6'- tetrabrom- N:N'- dicarbazyl with hydriodic acid has already been described on p. 25.

APPENDIX II.

ATTEMPTS TO SYNTHESISE HALOGEN DERIVATIVES OF N:N'- DICARBAZYL

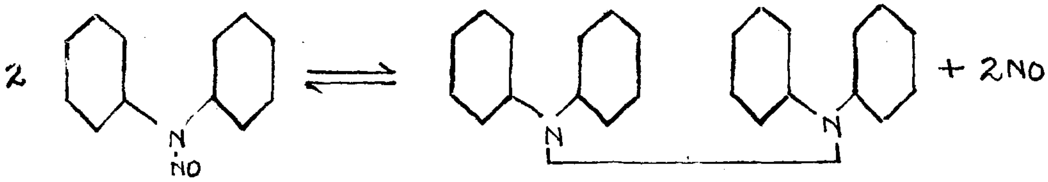
and

SOME CARBAZOLE COMPOUNDS

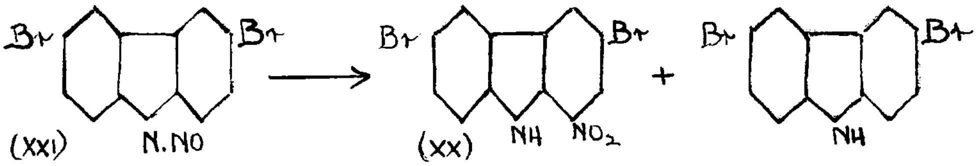
APPENDIX II.

The synthesis of 3:6:3':6- tetrabromo- N:N'- dicarbazyl described on p.28 was worked out only after several other methods had been tried and had failed.

One of the first of these unsuccessful attempts was based on the fact, that N- nitrosodiphenylamine on heating evolves NO quantitatively and forms tetraphenylhydrazine (the reaction being reversible. See p. 8) (Wieland, and Lecher, Ann., 1912, 392, 156)



The analogous reaction with N- nitrosocarbazole - to give N:N'- dicarbazyl - does not take place however, 3- nitrocarbazole and carbazole being produced. (Wieland and Lecher loc. cit.) Should the 3- and 6- positions in the carbazole nucleus be occupied, as in 3:6- dibromo- N- nitrosocarbazole, however, migration of the nitroso group to these positions becomes, if not impossible, improbable. It was found, however, that on heating N- nitroso- 3:6- dibromocarbazole (XXI) in toluene in an atmosphere of CO_2 that 1- Nitro- 3:6- dibromo carbazole (XX) was formed in small quantity and 3:6- dibromocarbazole in correspondingly greater yield. The yield of the 1- nitro- 3:6- dibromocarbazole was immensely increased by heating the nitroso compound in acetic acid and only this reaction is worthy of experimental description. The reaction may be represented:-



Attempts were also made to obtain 3:6:3':6'- tetrabromo-N:N'- dicarbazyl by the method of Chattaway and Ingle (J.C.S., 1895, 67, 1090), using sodium ethylate to form the sodium derivative of 3:6- dibromocarbazole, and subsequently treat this with iodine. This was not successful.

Metallic sodium (finely divided) would not form a compound with 3:6- dibromocarbazole.

EXPERIMENTAL

(Note:- The difficulties encountered in obtaining 3:6-dibromocarbazole, in reasonably large quantities, have been indicated in the main part of this thesis. Carbon disulphide was first used as the solvent, when an attempt was made to obtain an additive compound of carbazole with bromine. It was then found that this furnished by far the best method of preparing 3:6- dibromocarbazole. Shortly after this discovery, Lindemann, (Ber., 1925, 58, 2371), in a paper on derivatives of 1- amino-carbazole, published a method of preparation of 3:6- dibromocarbazole almost identical with the one described here on p. 21. Lindemann also described, for the first time, N- nitroso- 3:6- dibromocarbazole, N-methyl- 3:6- dibromocarbazole, 1- nitro- 3:6- dibromocarbazole and 1- amino- 3:6- dibromocarbazole. All these compounds had been independently prepared by the present author several months before Lindemann's paper appeared. The methods described herein, are therefore, entirely original. The only part of Lindemann's work of which the author has made use, is his statement that the nitration product of 3:6-dibromocarbazole is the 1- nitro- derivative, a fact which the author had not settled, when the work in question was published.)

N- Nitroso- 3:6- dibromocarbazole.

Pure 3:6- dibromocarbazole (8 g.) was suspended in cold glacial acetic acid (350 ccs.). To this was added, during the course of half an hour finely powdered sodium nitrite (6-7 g.), the whole being vigorously stirred and kept cold by standing the vessel in water. A pale yellow flocculent precipitate was thrown down. This was removed, washed well with cold water and finally digested for a few minutes with boiling absolute alcohol (250 ccs.) in which the final product is practically insoluble. The alcohol-insoluble substance after some six crystallisations from benzene gave long yellow needles of N- nitroso- 3:6- dibromocarbazole m.p. 188-190° (decomp.) (Found Br, 45.1%; $C_{12}H_6N_2OBr_2$ requires Br, 45.2%).

Action of Heat on N- Nitroso- 3:6- dibromocarbazole.

N- nitroso- 3:6- dibromocarbazole when heated alone, above its melting point gives off nitrous fumes, a substance of high m.p. being left. When heated in xylene solution, nitrous fumes are again given off, and the pale yellow solution becomes orange yellow. 1- nitro- 3:6- dibromocarbazole may be isolated by evaporating the solution to small bulk. No dicarbazyl derivative is formed.

Action of Glacial Acetic Acid on N- Nitroso- 3:6- dibromocarbazole.

N- nitroso- 3:6- dibromocarbazole (5 g.) was dissolved in boiling glacial acetic acid (120 c.c.) and the solution kept at the boiling point till nitrous fumes ceased to be evolved (about $\frac{3}{4}$ hour) The pale yellow solution had by this time changed to a deep orange yellow. On allowing to cool, round clusters of orange coloured needles were deposited. These were removed and crystallised several times from glacial acetic acid when long bright yellow needles were obtained m.p. 259° C. A mixed m.p. of these with a specimen of 1- Nitro- 3:6- dibromocarbazole obtained by the nitration of 3:6- dibromocarbazole (List, Verd. a. Rh. D.R.P. 275833) showed no lowering. Yield, 2 gm. The acetic acid mother liquors from the above reaction were concentrated to about $\frac{1}{4}$ of their original bulk, when hard, pale yellow prisms were obtained, which were further purified several times by crystallisation from alcohol (animal charcoal). Pure white needles m.p. 210-212° C. were thus obtained which were identified as 3:6- dibromocarbazole, not only by a mixed m.p. but by the formation of N- acetyl- 3:6- dibromocarbazole. No other substances could be isolated from the reaction mixture.

1- Amino- 3:6- dibromocarbazole.

1- nitro- 3:6- dibromocarbazole (10 g.) was dissolved in absolute alcohol (60 c.c.) and sodium sulphide (15 g.), dissolved in water, (30 c.c.) was added, and the whole then boiled under reflux on the water bath for 3 hours. At the end of this time the yellowish brown solution was poured into excess of water and the resulting suspension heated to coagulate the precipitate which was then removed (6.5 g.) and recrystallised several times from 90% alcohol, when very small, white plates m.p. 189-191° C. were obtained. Found Br, 46.8%, $C_{12}H_8N_2Br_2$, requires Br, 47.05%. Acetyl derivative was obtained by allowing the amine to stand in the cold for a few hours with acetic anhydride.

Other Attempts to Synthesise 3:6:3':6'- Tetrabromo- N:N'- dicarbazyl.

1. By the action of NaOEt and Iodine on 3:6- dibromocarbazole: (a) 3:6- dibromocarbazole was dissolved in dry ether, and to this solution, sodium ethylate (in alcohol) was added. After allowing to stand for several hours, a solution of iodine in ether was added. The ether was then evaporated off, but the residue contained no trace of a dicarbazyl derivative.

(b) The above experiment was repeated, using solid, dry sodium ethylate. The same result was obtained.

(c) Pyridene was used as a solvent, and solid sodium ethylate was added but the results were again negative. Similarly using anisole both in the cold and at 100° no synthesis could be accomplished.

2. Dibromocarbazole dissolved in benzene was treated

with finely divided sodium. No metallic derivative appeared to be formed but the reaction mixture was, nevertheless, treated with iodine. No dicarbazyl derivative could be isolated however. The same results were obtained in solvents of higher boiling point.

Synthesis could only be accomplished as described on p. 28.

* * *

APPENDIX III.

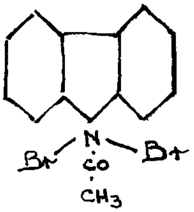
AN ADDITION COMPOUND OF N-ACETYL-CARBAZOLE WITH BROMINE

APPENDIX III

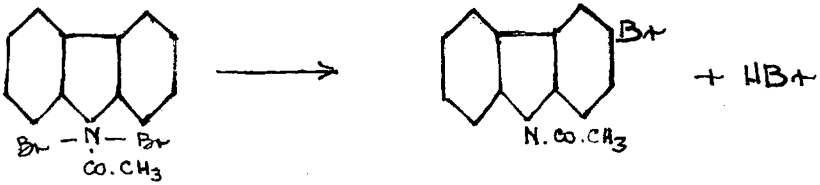
An Additive Bromine Compound.

While attempting to obtain 3:6- dibromocarbazole by the bromination of N- Acetylcarbazole in carbon disulphide solution an interesting fact was noticed. As soon as the bromine was added to the solution a flocculent precipitate formed. On continued boiling of the solution however this substance went into solution and it was only after boiling for the specified time that the 3: bromo- N- Acetyl- carbazole could be isolated. It would seem that this first flocculent precipitate was an additive compound of bromine with N- Acetylcarbazole.

N- Acetylcarbazole (1 gm.) was dissolved in carbon disulphide (5 ccs.) and a solution of bromine (.8 gms.) in carbon disulphide (5 ccs.) was added with shaking. All the solutions were kept at the freezing point (0° C.) On the addition of bromine the yellow solid separated. After a few minutes this solid was removed by filtration and washed thoroughly with ice-cold carbon disulphide several times. It was then immediately transferred to a portion of porous plate and a melting point taken within $\frac{1}{4}$ minute. M.P. - 88°-95° C. On leaving the compound (which was pale yellow) to stand in the air, it very rapidly became a deep red colour and bromine was evolved. The substance decomposed even in the dark. The residue left, after the evolution of bromine, was sticky. It was well washed with ice-cold CS_2 and was found to consist of N- Acetylcarbazole. There is no doubt from these observations that N- Acetylcarbazole forms an unstable additive compound with bromine. A suggested formula is



On further boiling in CS_2 this may pass to N- Acetyl -3-bromocarbazole with evolution of HBr



It is noteworthy that no HBr is evolved on or before the production of this compound but only on boiling the suspension in CS_2, and with the quantities of materials used N- acetyl-3-bromocarbazole is formed in good yield after such boiling.

Attempts were made to obtain a similar compound from N- benzoylcarbazole and from carbazole itself but without success. Such attempts were made exactly on the lines of the above experiment. No solid product was formed, and HBr was evolved immediately the bromine solution was added to the solution of the other reagent.

In the case of carbazole 3:6- dibromocarbazole was obtained, while N- benzoylcarbazole gave a small amount of 3- bromo- N- benzoylcarbazole.

When N- acetyl-3-nitrocarbazole was used no reaction at all took place.

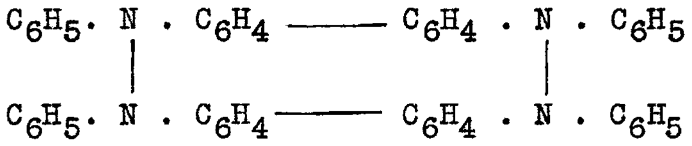
APPENDIX IV.

PRELIMINARY INVESTIGATION OF AMORPHOUS SUBSTANCE C

APPENDIX IV.

The results obtained in the reduction of the amorphous product C (p. 33) (Perkin and Tucker, loc. cit.) prompted a further investigation of this compound, which forms 75% of the products of oxidation of carbazole in acetone with potassium permanganate.

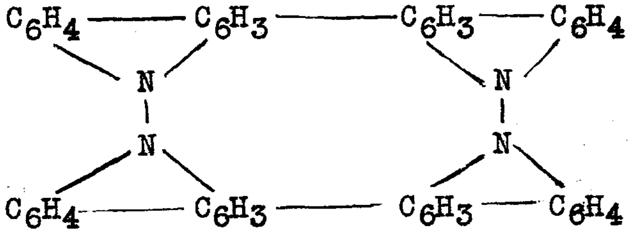
It has been shown (Wieland, Ber., 1922, 25, 1804) that NN'- diphenylbenzidene (V) is oxidised by potassium permanganate in acetone, or by silver oxide in presence of pyridine, to bisdiphenyldibiphenylenehydrazine (XXVI).



$$\begin{array}{ccccccc} C_6H_5 . & N & . C_6H_4 & \text{———} & C_6H_4 . & N & . C_6H_5 \\ & | & & & & | & \\ C_6H_5 . & N & . C_6H_4 & \text{———} & C_6H_4 . & N & . C_6H_5 \end{array}$$

(XXVI)

which is an amorphous substance. 3:3'- Dicarbazyl (VI) might be expected to undergo a similar oxidation with the formation of the compound (XXVII).



(XXVII)

Tucker (J.C.S., 1926, 129, 3033) showed that 3:3'- dicarbazyl was oxidised by potassium permanganate in acetone, to an amorphous substance, probably (XXVII), but the latter was not identical with C.

As already indicated C, on reduction, gave carbazole and a high melting substance. This latter does not appear to be 3:3'- dicarbazyl nor a hydrogenated derivative of it. The reduction would seem to point to some form of N-N linking; yet it was shown that N:N'- dicarbazyl could not be further oxidised. No acetyl, methyl or nitroso compounds of the substance C could be obtained which would indicate the absence of an imino group. It has not been found possible to obtain any crystalline derivatives of C.

Analysis and molecular weight determination of the amorphous substance C, indicate the presence of three carbazole nuclei and of the absence of oxygen.

The results so far obtained do not justify the assignation of any constitutional formula to the compound in question.

The substance C obtained by Perkin and Tucker does not appear to be identical with any of the compounds B, E or A obtained by Branch and Smith (J. Amer. C.S., 1920, 42, 2405.) and Branch and Hall (J. Amer. C.S., 1924, 46, 438.) It is certainly not A, since the latter is soluble in alcohol. Branch and Hall (loc. cit.) have shown that their compound E contains 2.4% of oxygen, whereas the analysis of C indicates that no oxygen is present in this substance. Finally, the high melting point of B (Branch and Smith, loc. cit.) - 283-287° (292-296° corr.) precludes the possibility of this substance being identical with the amorphous substance C under discussion.

EXPERIMENTAL

Analysis of Amorphous Substance C.

C,	86.8	86.8
H,	5.1	5.1
N,	8.1	8.0

$C_{36}H_{23}N_3$ requires C, 86.9; H, 4.5; N, 8.4

Molecular Weight.

Rast's Method: 429, 459.

Cryoscopic Method (in benzene): 500, 543, 546, 558,

Mean = 544.

$C_{36}H_{23}N_3$ requires M = 497.

Distillation of Amorphous Substance.

1. About half a gram of the amorphous substance was strongly heated in a small test-tube. A white crystalline substance collected in the cool part of the tube. This melted 235°-238° and the m.p. was not lowered on admixture of the substance with carbazole.

2. The amorphous substance (2 g.) was heated in a wide mouthed tube in a paraffin bath at 300° C. for several hours. The carbazole was periodically removed from the cooler part of the tube. Finally, when no more carbazole was formed, the tube was cooled and the residue removed. This, when powdered, was a brown non-crystalline substance, m.p. 270°-280° C. It could not be crystallised from any of

many solvents tried. It was purified as follows: After dissolving in benzene, the solution was boiled with animal charcoal for ½ hr., and then filtered into boiling alcohol, when a whitish precipitate was obtained. This was collected, dissolved in benzene and treated as above. After four repetitions of this process there was obtained, in very small quantity, a cream coloured, amorphous powder of m.p. 326° C. Found: C, 86.1, 86.2; H, 49.9, 4.95; N, 8.0, 8.2.

The substance closely resembles in appearance and in solubilities, the high melting product obtained on reduction of C (p. 33). It is not 3:3'- dicarbazyl, being very soluble in benzene, in which 3:3'- dicarbazyl is insoluble. The benzene solution shows a green fluorescence. A small amount of the compound was boiled for half an hour with excess of acetic anhydride containing a trace of concentrated sulphuric acid. A very dark, purplish amorphous powder was obtained, which could not be crystallised. M.p. over 300° C.

Acetylation and Methylation.

(a) The amorphous substance C was boiled for varying periods of time, up to 8 hours with acetic anhydride containing a trace of sulphuric acid. The whole of the starting material was returned unchanged in every case.

(b) The amorphous substance C (0.5 g.) was dissolved in acetone (15 c.c.). Sodium hydroxide and a large excess of dimethylsulphate were then added and the whole boiled for 2 hours. From the reaction mixture only the unchanged starting material could be isolated.

Bromination.

The amorphous substance C (0.5 g.) was dissolved in carbon disulphide (2 c.c.). Bromine (1 g.) in carbon disulphide was added and the solution boiled. HBr was evolved. On evaporating the solvent an amorphous residue was obtained which shrank at 240° and did not melt by 290° C.

Attempted Oxidation of N:N'- Dicarbazyl.

N:N'- dicarbazyl (0.25 g.) was dissolved in acetone (15 c.c.) and boiled with potassium permanganate (2 g.) for 3 hours. The product was isolated by pouring into sulphurous acid. The starting material (0.24 g.) was recovered unchanged.

* * *

PART II.

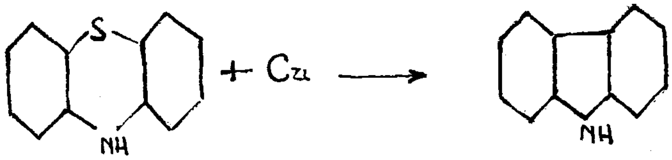
UNSUCCESSFUL ATTEMPTS TO SYNTHESISE N:N'- DICARBAZYL

PART II.

Following the identification of N:N'- dicarbazyl, and the study of its properties in the light of its newly found constitution, it was thought that this research could be brought to a fitting close by a direct synthesis of the dicarbazyl in question, by some method other than the oxidation of carbazole; or failing this to obtain an oxidation of carbazole in which N:N'- dicarbazyl would be the main, if not the sole product. Many such methods were tried but none, so far, have been successful. Many of the attempts may seem to offer little hope of attaining the desired result but these were tried after the failure attendant upon the more simple and obvious methods.

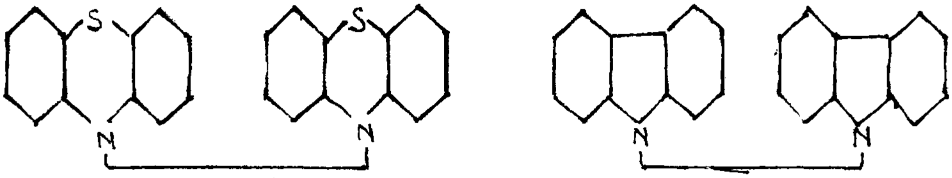
A method which suggested an immediate and neat solution to the problem, was based on the fact that thiodiphenylamine (XXIII) when heated under certain conditions with copper powder, yields carbazole.

(xxiii)



(Goske, Ber., 1887, 20, 233.   )

Now Pesci (Gazz. Chem. Ital. 1916, 46 (i), 103) has shown that thiodiphenylamine on oxidation with yellow mercuric oxide gives a compound which he claims to be dithiotetraphenylhydrazine (XXIV). There seemed no reason, therefore, why this compound on treatment with copper powder, should not be converted into N:N'- dicarbazyl thus:-

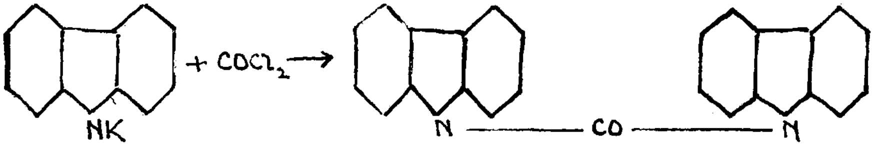


(XXIV)

Such a reaction could not be brought about however, mainly owing to the fact that di-o-thiotetraphenylhydrazine decomposes without melting and hence could not be obtained in the liquid state.

It seemed possible to get N:N'- dicarbazyl from the halogen derivatives described in Part I. Unfortunately the bromine and iodine atoms in these compounds appear to be very firmly attached to the nucleus, and all attempts to eliminate them have met with failure.

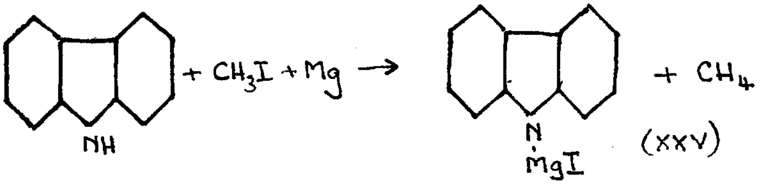
The success which attended the synthesis of 3:6:3':6'-tetrabromo- N:N'- dicarbazyl (p. 28) naturally suggested this method of obtaining the unsubstituted dicarbazyl. The reaction of Chattaway and Ingle (J.C.S., 1895, 1090) (see also p. 53) was tried, and failed. The action of halogens (particularly iodine) on N-potassium carbazole (obtained by fusion of carbazole with KOH) was then investigated. N-Potassium carbazole is known to react with acid chlorides, e.g.



(Copizarow, J.C.S. 1918, 113, 816.)

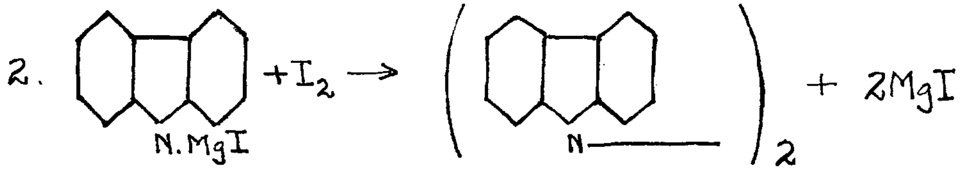
and, theoretically, with iodine it should give N:N'- dicarbazyl. Treatment of the K-carbazole, in the usual solvents, with iodine produced no results and even in a high boiling solvent such as tetralin, (tetrahydronaphthalene) no dicarbazyl was formed. The action of finely divided metal on carbazole, followed by treatment with iodine was then tried. No dicarbazyl could be isolated however. The fact that a synthesis of a dicarbazyl derivative could be accomplished by this method when using 3:6- dibromocarbazole, might be explained on the assumption that the halogen atoms in the latter compound render the whole molecule somewhat more negative in character, thereby making the formation of a metallic derivative easier.

A somewhat similar synthesis to the above was next attempted. Carbazole on treatment (in dry ethereal solution) with magnesium and methyl iodide forms carbazole-magnesium iodide (XXV), thus.



(Oddo, Gazz, Chem. Ital., 1911, 41, 235; 1914, 44, 482).

It seemed highly probable that this compound (XXV), on treatment with iodine, should decompose as below giving the required dicarbazyl and magnesium iodide.

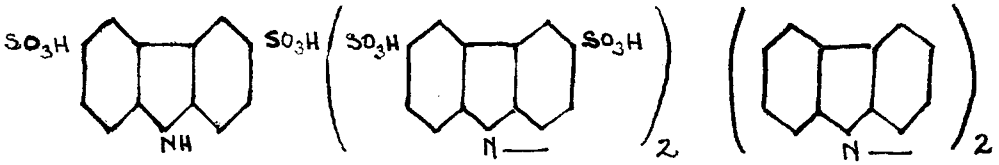


Such a reaction could not be induced to take place however. Carbazole magnesium iodide was also treated with anhydrous cupric sulphate (cf. Krizewsky and Turner J.C.S. 1919, <u>115</u>, 559, who showed that the following reaction took place.

$$2CuSO_4 + 2C_6H_5MgI \qquad Cu_2I_2 + 2MgSO_4 + C_6H_5.C_6H_5)$$

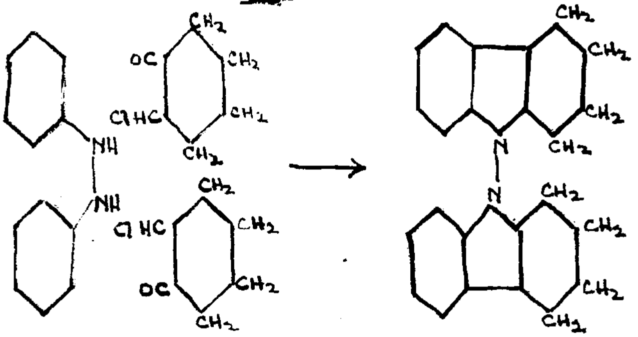
No dicarbazyl was obtained however.

Attempts were next made to oxidise carbazole -3:6- disulphonic acid, and subsequently to remove the sulphonic acid groups, according to the following scheme:



The difficulty of isolating the sulphonic acids made it very uncertain whether any dicarbazyltetrasulphonic acid had been obtained, but no synthesis could be accomplished in any case.

It has been shown that 1:2 halogen cyclohexanones can be condensed with primary and secondary aromatic amines, with at least one ortho position free, to give tetrahydrocarbazole and its derivatives. (D.R.-P. 374098/1923). It seemed not altogether improbable therefore, that hydrazobenzene might be induced to condense with O-chlorocyclohexanone, to give octahydro- N:N'- dicarbazyl (XXVIII) which could be oxidised (with sulphur in quinolene) to N:N'- dicarbazyl, thus:



(XXVIII)

The condensation could not be brought about.

Finally attempts were made to eliminate the four ortho hydrogen atoms in tetraphenylhydrazine, in order to form a pyrole ring. This too proved unsuccessful.

Methods of synthesis involving an oxidation of carbazole, only at the imino group were also unsuccessful.

EXPERIMENTAL

ATTEMPTS TO OBTAIN N:N'- DICARBAZYL

1. By removal of sulphur from dithiotetraphenylhydrazine.

Dithiotetraphenyl hydrazine (Pesci; Gazz. Chem. Ital. 1916, 46(i), 103) is a greyish white amorphous powder which decomposes without melting at about 270°-280° C. The decomposition point, however is variable. It is soluble in benzene, chloroform, nitro benzene, aniline, methyl iodide, pyridene and cyclohexanone but cannot be crystallised from any of these. On leaving to stand, the surface exposed to the light becomes green, which colour may be easily removed by Pesci's method of treatment with ammonium sulphide. The following attempts were made to eliminate sulphur from this compound, but without success.

(a) The substance (0.5 gm.) was dissolved in boiling nitrobenzene (10 ccs.) and copper powder was added. This mixture was boiled for two hours. It was then filtered. There was no indication that any copper sulphide had been formed. To the filtrate was added an excess of acetone (in which dithiotetraphenylhydrazine is insoluble). A greyish blue compound was precipitated. This was found to be starting material. The nitro benzene-acetone mother liquors were steam distilled, but no solid residue remained.

(b) 1 gm. of the dithiotetraphenylhydrazine was intimately mixed with copper powder in a hard glass tube and the mixture heated over a bare flame for $\frac{1}{4}$ hr. No melting occurred. The resulting brown mass was extracted with (a) benzene (b) chloroform (c) acetone (d) alcohol. The extracts with (a) and (b) when combined and evaporated yielded a minute quantity of what seemed to be starting material. The copper residue was boiled with dilute nitric acid to remove any free copper. A dark brown substance was left which did not melt and on which conc. nitric acid had apparently no action.

(The extracts (c) and (d) above when evaporated gave no solid material).

(c) The hydrazine 1 gm. was heated with copper powder in a sealed tube (cf. Goske, loc. cit.) in an oil bath for 9 hours at 250° C. No pressure was developed in the tube. The "melt" was extracted with (I) acetone which did not dissolve anything (ii) benzene (boiling; 3 times) On adding ether to the benzene extract a whitish substance was precipitated which proved to be starting material.

This method was repeated in a variety of ways but with no success whatever.

(d) The hydrazine (1 gm.) dissolved in boiling xylene was treated with molecular sodium for 10 hours. After removing the free sodium ether was added to the xylene solution.

This caused a precipitate to be thrown down which proved once more to be starting material.

Unless otherwise stated the whole amount of the starting product was recovered unchanged in the above experiments.

(e) Dithiotetraphenylhydrazine (.8 gms.) was strongly in a small hard glass retort. A very small quantity of a yellow crystalline distillate was produced. This smelled strongly of thiodiphenylamine. Much charring occurred. The residue yielded nothing.

(f) 1 gm. of dithiotetraphenylhydrazine was mixed with a large excess of pure zinc dust and the mixture distilled as above. Much less charring occurred and an appreciable quantity of the yellow distillate was formed. The melting point of this (crude substance) was 165° C. After one crystallisation from alcohol however (using charcoal) it melted 176-178° C. and was identified as thiodiphenylamine. No substances could be isolated from the residue.

One of the chief difficulties incurred in the use of dithio tetraphenylhydrazine is the fact that it has no criterion of purity. We have attempted to obtain crystalline derivatives but without success.

2. By Removal of Halogens from Tetrabromo- and Tetraiodo-dicarbazyls.

(a) With Hyrdiodic acid.

The tetrabromodicarbazyl (.5 gm.) if left to stand in the cold with concentrated HI was unaffected. When boiled with the same reagent at ordinary pressure for half an hour it was likewise unchanged.

(b) With sodium in Alcohol.

The tetrabromo (or iodo) derivative was dissolved in excess of benzene and alcohol added. To the solution small pieces of sodium were added on the end of a glass rod. When a large excess of sodium had been added and acted upon the solution was evaporated to dryness. Extracted with boiling water (to remove C_2H_5.ONa), then with alcohol (to remove dibromocarbazole and carbazole). The residue consisted entirely of unchanged product.

(c) Sodium in Amyl Alcohol.

The foregoing experiment was repeated in boiling amyl alcohol in which the tetrahalogen derivatives of N:N'-dicarbazyl are soluble. The alcohol was removed by steam distillation and the solid residue extracted with alcohol. The alcohol insoluble product was entirely composed of the tetrahalogen compound, the whole of which was recovered.

3. Carbazole and finely divided Potassium followed by Treatment with Iodine.

This experiment was performed in benzene and xylene as described on p. 28, but with entirely negative results. Tetralin was then used as a solvent.

Carbazole (1.6 gms.) was boiled in dry tetralin (20 ccs.) with excess of finely divided metallic potassium for 6-7 hours. A solution of iodine (2.5 gms.) in benzene was then added. The excess of potassium and the potassium iodide being removed the filtrate was distilled in steam to remove the solvents. The solid residue, after drying, was thoroughly extracted with boiling alcohol. About .1 gm. of a brown powder remained undissolved. M.p. - over 290° C. It burned away completely and did not contain iodine, soluble in benzene and its homologues, anisole, acetone, carbon disulphide and slightly soluble in glacial acetic acid but could not be crystallised from any of these.

Bromination of the product gave compounds which melted over 290° C.

4. Treatment of Potassium Carbazole with Halogens.

N-Potassium carbazole was prepared as follows:-

Solid, dry potassium hydroxide (25 gms.) was fused in a large nickel crucible which was immersed in an oil bath, the latter being kept at a temperature of 300° C. Carbazole (80 gms.) was added very gradually in small quantities. The molten mass kept well stirred. After all the carbazole was added the melt was stirred at the high temperature for about an hour. It was then allowed to solidify and was powdered. The use of the oil-bath prevents charring, and stirring is made much easier by the use of a thin glass rod than by a sheathed thermometer, as is usually recommended.

(a) Treatment of N- Potassium Carbazole with Iodine.

Freshly prepared potassium carbazole (3 gms.) was suspended in dry benzene (12 ccs.) and iodine (2 gms.) in benzene added. After heating on the water bath for ¼ hour the mixture was filtered and the filtrate evaporated to dryness. The residue was extracted with alcohol. A very small amount of substance - m.p. 240°-255° - remained undissolved. It was soluble in benzene and acetone. To a solution of the substance in a mixture of these two solvents was added a drop or two of alcohol. After two weeks a small amount of a dark brown precipitate had collected. M.p. over 290°.

(b) Higher boiling solvents gave similar results. So carbazole and iodine were heated together, in the solid state, in a sealed tube, at about 150-160° C. for several hours, but no dicarbazyl could be isolated from the reaction mixture.

Attempts were made to obtain <u>pure</u> sodium carbazole by the action of sodamide on carbazole (in solution) but the metallic derivative was not formed.

5. From Carbazole - N- Magnesium Iodide.

(a) Carbazole (2 g.) was converted into carbazole- N-magnesium iodide by the method of Oddo (loc. cit.). To this substance, in ether, (30 ccs.) was added, finely powdered iodine (1.5 g.) After allowing the mixture to stand for some time the ether was allowed to evaporate, and the tarry residue examined. Much carbazole was isolated from it, along with magnesium residues, but no dicarbazyl appeared to have been formed.

(b) Carbazole-magnesium iodide (as above) was suspended in ether. Finely powdered, anhydrous cupric sulphate (2 g.) was added and the whole boiled on the water bath for 6 hours and left to stand overnight. Iodine was liberated during heating. The mixture was poured into ice and water and then extracted with ether. The ether insoluble material was extracted with benzene. The ether extract was evaporated to dryness, the residue freed from iodine and crystallised from benzene, when carbazole was obtained. The benzene extract (above) was concentrated and likewise deposited crystals which were shown to be carbazole.

(c) Similar attempts were made using carbazole-magnesium bromide and anhydrous cupric chloride. (cf. Krizewsky and Turner loc. cit.)

6. From Carbazole- 3:6- disulphonic Acid.

Potassium carbazole -3:6- disulponate (1 g.) was dissolved in water (20 cc.) and oxidised with an excess of potassium permanganate in presence of a few cc. of dilute sulphuric acid. After oxidation appeared to be complete, the whole of the (non-manganous and water soluble) products were (a) heated with HCl (fuming) under pressure or (b) distilled in superheated steam to effect removal of the SO_3H groups. No dicarbazyl could be isolated from any of the reaction mixtures however.

7. From Hydrazobenzene and O-Chlorocyclohexanone.[x]

Attempts were made in several ways to condense these two materials. They were heated together in varying solvents, in various proportions, with different condensing agents, but oxidation of the hydrazobenzene nearly always took place and no dicarbazyl derivative could be obtained.

8. From Tetraphenylhydrazine.

Tetraphenylhydrazine was treated with a large excess of potassium permanganate in boiling acetone for several hours. Only very pure tetraphenylhydrazine, m.p. 147°, could be isolated from the mixture.

9. By Oxidation of Carbazole.

(a) With Ag_2O in Pyridine (Wieland, Ber., 1922, 25, 1804): Carbazole (1.g.) was dissolved in pyridine and silver oxide (1 g.) added. After boiling and filtering, the filtrate was poured into a large excess of hot alcohol. The precipitate was extracted with alcohol. The insoluble

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[x] Bouveault and Cheran, Comp. Ren., 1906, 142, 1086.

residue contained silver which was not removed by treatment with iodine.

(b) With Yellow Mercuric Oxide (Pesci loc. cit.)

Carbazole (1 g.) dissolved in dry xylene (10 c.c.) was treated with yellow HgO for several hours. There was no trace of reduction of the oxide. In other solvents the same result was obtained.

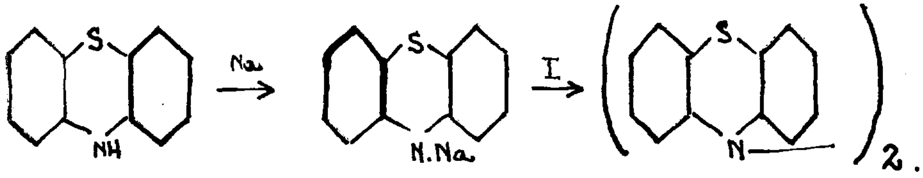
APPENDIX I.

STRUCTURE OF OXIDATION PRODUCT
of
THIO-DIPHENYLAMINE

APPENDIX

The fact that a synthesis of N:N'- dicarbazyl could not be effected through dithiotetraphenylhydrazine, caused some doubt to be thrown on the structure assigned by Pesci to the oxidation product of thiodiphenylamine.

The reaction of Chattaway and Ingle (loc. cit.) was therefore applied to thiodiphenylamine, in the hope that the following series of changes would occur:



The product obtained by such treatment of thiodiphenylamine was very similar to Pesci's substance, but complete identity could not be established owing to the lack of any criterion of purity.

By heating tetraphenylhydrazine with sulphur the former was decomposed, largely to diphenylamine.

ACTION OF SODIUM ETHYLATE AND IODINE ON THIODIPHENYLAMINE.

(1) Thiodiphenylamine (2 gms.) was dissolved in dry ether (40 ccs.). To this was added the paste produced by the action of sodium (.5 gms.) on absolute alcohol (6 ccs.). The mixture turned red and turbid. After leaving to stand overnight a precipitate had formed. To the whole was then added iodine (2.6 gms.) dissolved in ether. A dark green compound was formed. After 2 hours this was filtered off. By suspending in acetone and adding a drop of ammonium sulphide, the green colour was almost entirely removed and the compound was left a yellowish grey amorphous body which decomposed 245-260°. The solubilities were the same as those of Pesci's dithio tetraphenylhydrazine.

(2) Thiodiphenylamine (.5 gms.) was dissolved in the minimum quantity of dry ether. Solid, dry, sodium ethylate was added (.3 gms.) and the mixture heated on the water bath 1 hour and then left for 4-5 hours. The precipitate which had formed was removed and digested with warm alcohol and filtered. The alcohol-insoluble product was dissolved in benzene and a solution of iodine in benzene was added. After leaving for some time the solution was treated with alcohol and a greenish substance was precipitated which was purified as before. The final product was a grey white amorphous powder which decomposed 245-260° C. It was in all respects similar to dithiotetraphenylhydrazine.
