CCIX.—*Derivatives of Tetrahydrocarbazole.*

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PLANT.

INTEREST attaches to the reduction products of carbazole and particularly to tetrahydrocarbazole (I), in the first place because it is probable that strychnine is a derivative of the latter substance (compare Perkin and Robinson, T., 1910, **97**, 315), and secondly because tetrahydrocarbazole is structurally somewhat closely related to tetrahydroharmine (II) (T., 1919, **115**, 938).

The reduction of carbazole, $C_{12}H_9N$, was first investigated by Graebe and Glaser (*Annalen*, 1872, **163**, 352), who showed that, when heated with hydriodic acid and phosphorus at 220—240°, it attaches six atoms of hydrogen yielding *carbazoline*, $C_{12}H_{15}N$, which is now known to have the constitution (III).

These investigators also showed that carbazoline hydrochloride is decomposed on distillation into hydrogen, hydrogen chloride, and tetrahydrocarbazole (m. p. 120°):

In 1888, Drechsel (*J. pr. Chem.*, 1888, [ii], **38**, 65) submitted phenol to electrolysis with an alternating current and isolated a substance, $C_6H_{10}O$ (b. p. 153—178°), which he named *hydrophenoketone*. Drechsel combined this substance with phenylhydrazine and treated the product with dilute sulphuric acid, when he obtained a substance, $C_{12}H_{13}N$ (m. p. 108°), which he named *hydrophenanilide*. He recognised the fact that this substance had the same composition as Graebe and Glaser's tetrahydrocarbazole, but concluded that the substances were not identical because of the difference in their melting points.

Baeyer (*Ber.*, 1889, **22**, 2185; *Annalen*, 1894, **278**, 105) was the first to point out that Drechsel's hydrophenoketone is identical with *cyclohexanone* and that hydrophenanilide, in spite of its rather low melting point, is tetrahydrocarbazole. He also pointed out that the conversion of the phenylhydrazone of *cyclohexanone* into tetrahydrocarbazole is an example of the Fischer indole synthesis and that the change is to be represented thus:

It is somewhat remarkable that this interesting substance has been so little investigated; almost all that is known about its derivatives is due to the work of Borsche, Witte, and Bothe (*Annalen*, 1908, **359**, 53). These investigators were unsuccessful in their attempts to nitrate tetrahydrocarbazole (*loc. cit.*, p. 60) and prepared 8-nitro- and 6-nitro-tetrahydrocarbazoles,* m. p. 149° and 174° respectively,

* The scheme of numbering the positions in tetrahydrocarbazole employed in this communication is

from the condensation products of *cyclohexanone* with *o*- and *p*-nitrophenylhydrazine. In the case of the condensation product of *m*-nitrophenylhydrazine with *cyclohexanone* they assume that the nitrotetrahydrocarbazole (m. p. 154°) produced by the action of dilute sulphuric acid is the 7-nitro-derivative, although it might well be the 5-nitro-derivative. This question of constitution is discussed in detail below.

The work described in the present communication may be briefly summarised as follows. We find, in the first place, that the phenylhydrazine of *cyclohexanone* is converted almost quantitatively into tetrahydrocarbazole simply by boiling with glacial acetic acid, and in this and other similar cases the product is much cleaner than that obtained by the usual process, namely, boiling the phenylhydrazones with dilute sulphuric acid. The 9-acetyl derivative of tetrahydrocarbazole (IV, m. p. 78°), is readily obtained either by boiling *cyclohexanone*acetylphenylhydrazone with dilute sulphuric acid,

or directly from tetrahydrocarbazole by boiling with acetic anhydride or with acetyl chloride in the presence of copper powder at the ordinary temperature.

Contrary to the experience of Borsche, Witte, and Bothe (*loc. cit.*, p. 60), we find that it is possible to nitrate tetrahydrocarbazole direct if the solution in sulphuric acid is treated with potassium nitrate at -5° . The sole product is 6-nitrotetrahydrocarbazole melting at 174° , since it is identical with the substance which results from the action of dilute acids on *cyclohexanone-p*-nitrophenylhydrazone. Additional evidence in support of this view of its constitution was obtained in the following way.

The nitro-derivative, on reduction, yields 6-aminotetrahydrocarbazole, which melts at 152° and yields an acetyl derivative melting at 208° , and these substances have been synthesised by the following steps. *p*-Acetylaminophenylhydrazine,

prepared from *p*-aminoacetanilide by diazotisation and reduction, condenses readily with *cyclohexanone*, yielding *cyclohexanone-p*-acetylaminophenylhydrazone (m. p. 166°), and this substance, when digested with glacial acetic acid, is converted into 6-acetylaminotetrahydrocarbazole (m. p. 208°), which was found to be identical

with the derivative of this composition obtained from the product of the nitration of tetrahydrocarbazole. On hydrolysis, it yielded 6-aminotetrahydrocarbazole melting at 152°.

Unexpected results were obtained in a series of experiments on the nitration of 9-acetyltetrahydrocarbazole (IV) in acetic acid solution. The product of nitration is a single *acetylnitrotetrahydrocarbazole* which melts at 174° and, on hydrolysis, yields a new *nitrotetrahydrocarbazole* melting at 172°. It was at first thought that the latter was identical with the 6-nitro-derivative (m. p. 174°), but this was shown not to be the case, (i) by a mixed melting point determination, and (ii) by preparing the *acetyl* derivative of 6-nitrotetrahydrocarbazole, which was found to melt at 244° instead of 174°.

It is certainly remarkable that the action of nitric acid on the acetyl derivative should lead to the introduction of the nitro-group into a different position from that which it takes up when tetrahydrocarbazole itself is nitrated. With regard to the constitution of the acetyl derivative of the new nitrotetrahydrocarbazole, two formulæ only are possible for reasons given below, namely, V and VI.

The question has an important bearing on the difficult problem of the nature of the nitrotetrahydrocarbazole which is formed from *cyclohexanone-m-nitrophenylhydrazine* by the action of dilute acids. We have repeated the experiments of Borsche, Witte, and Bothe (*loc. cit.*, p. 68) and have satisfied ourselves that the action of dilute sulphuric acid on this *m-nitrophenylhydrazine* leads to the formation of a single nitrotetrahydrocarbazole (m. p. 154°) and not to a mixture of isomerides. The above-named investigators assign the 7-nitro-structure to this substance, and we are inclined to agree with their view that it is 7-nitrotetrahydrocarbazole.

It is, of course, conceivable that the *m-nitrophenylhydrazine* might yield 5-nitrotetrahydrocarbazole, but this, in our view, is probably the constitution of the isomeride which results from the nitration of 9-acetyltetrahydrocarbazole. Unfortunately, the experimental data available at the present time are not sufficient to allow of a decision as to the actual formula either of the product of the nitration of 9-acetyltetrahydrocarbazole or of the nitro-derivative formed from *cyclohexanone-m-nitrophenylhydrazine* by the action of dilute sulphuric acid.

After the unexpected results which have been obtained in the nitration of 9-acetyltetrahydrocarbazole, it was thought that it would be interesting to investigate the nitration of a derivative of tetrahydrocarbazole containing a different radicle attached to the nitrogen atom, and for this purpose, 9-methyltetrahydrocarbazole (VII) was selected.

This substance, which appears to be new, was obtained by combining *as*-phenylmethylhydrazine, $C_6H_5 \cdot NMe \cdot NH_2$, with cyclohexanone and then digesting the resulting cyclohexanonephenylmethylhydrazone with dilute sulphuric acid. 9-Methyltetrahydrocarbazole melts at 50° and, on nitration, readily yields 6-nitro-9-methyltetrahydrocarbazole (VIII, m. p. 192°). That the nitro-group in this substance occupies the 6-position was proved in the following way. On reduction, it yields 6-amino-9-methyltetrahydrocarbazole (m. p. 105°), the acetyl derivative of which melts at 238° . In order to synthesise this substance, *p*-aminomethylaniline was acetylated and the *p*-acetylaminomethylaniline converted into *p*-acetylaminonitrosomethylaniline, $CH_3 \cdot CO \cdot NH \cdot C_6H_4 \cdot NMe \cdot NO$, by means of nitrous acid. This, on reduction with zinc dust and acetic acid, yielded *p*-acetylaminophenylmethylhydrazine, $CH_3 \cdot CO \cdot NH \cdot C_6H_4 \cdot NMe \cdot NH_2$, which combined readily with cyclohexanone.

The cyclohexanone-*p*-acetylaminophenylmethylhydrazone was then boiled with glacial acetic acid, when it yielded 6-acetyl-amino-9-methyltetrahydrocarbazole, which melted at 238° and proved to be identical with the substance of this composition obtained from the direct nitration of 9-methyltetrahydrocarbazole in the way described above.

During the course of these experiments, we were anxious to ascertain whether the presence of substituents in the 2- and 5-positions in phenylhydrazine would, by steric hindrance, prevent the Fischer indole synthesis from taking place, and we selected for experiment, 2-chloro-5-nitrophenylhydrazine (IX).

This substance, which does not appear to have been described, was made as follows. *o*-Chloroaniline, on nitration in concentrated sulphuric acid solution, yields 2-chloro-5-nitroaniline which, when diazotised and reduced with stannous chloride, is converted into 2-chloro-5-nitrophenylhydrazine (m. p. 160°). This combines readily with cyclohexanone, and the resulting cyclohexanone-2-chloro-5-nitrophenylhydrazone (m. p. 78°) reacts readily with hot dilute sulphuric acid, yielding 8-chloro-5-nitrotetrahydrocarbazole (X), which crystallises in orange prisms melting at 214°. This rather unexpected result shows that the occupation of the 2- and 5-positions in phenylhydrazine does not inhibit tetrahydrocarbazole formation.

The new carbazole derivatives which have been synthesised during the course of this investigation from cyclohexanone are in all cases derivatives of tetrahydrocarbazole, and it seemed desirable to endeavour to discover some process of oxidation which would remove the additional hydrogen atoms and yield the corresponding derivatives of carbazole. The information thus obtained would also be valuable in deciding the constitution of some nitro- and other derivatives of carbazole as to which there is still some doubt.

Borsche, Witte, and Bothe (*Annalen*, 1908, **359**, 75) heated tetrahydrocarbazole and several of its methyl derivatives with lead oxide at a high temperature and obtained small yields of carbazole and the corresponding methyl derivatives, but such a process is obviously inapplicable to the nitro- or halogeno-derivatives of tetrahydrocarbazole. During the investigation of harmine and harmaline, Perkin and Robinson (T., 1919, **115**, 961) showed that tetrahydroharmine, $C_{13}H_{16}ON_2$, is converted into harmaline, $C_{13}H_{14}ON_2$, when it is oxidised with permanganate. We were unsuccessful when we attempted to obtain dihydrocarbazole or carbazole from tetrahydrocarbazole by a similar process. An oxidising agent which has proved valuable in cases of this kind is mercuric acetate, thus, for example, tetrahydroepiberberine is readily oxidised to epiberberine by this reagent with the loss of four atoms of hydrogen (Perkin, T., 1918, **113**, 515). On investigating the behaviour of tetrahydrocarbazole and 9-methyltetrahydrocarbazole towards mercuric acetate, we find that oxidation takes place readily with the formation of carbazole and 9-methylcarbazole, although the yields at present are not good. There are indications that this process may also be successfully applied in the case of halogeno- and nitro-derivatives of tetrahydrocarbazole, and this point is being investigated.

EXPERIMENTAL.

Tetrahydrocarbazole, $C_{12}H_{13}N$ (I).

In preparing this substance, Borsche (*Annalen*, 1908, **359**, 60) combines *cyclohexanone* with phenylhydrazine and boils the resulting hydrazone with dilute sulphuric acid, but the product obtained in this way is always impure and pink-coloured. We find that a purer product is obtained direct when the hydrazone is boiled for a few minutes with five times its weight of glacial acetic acid, from which it separates, on cooling, as a mass of crystals melting at 119° , whereas Borsche gives 116° as the melting point.

The *picrate* separates, when a hot alcoholic solution of tetrahydrocarbazole is mixed with alcoholic picric acid, in dark red crystals melting at 147° , and recrystallisation from alcohol does not alter this melting point. Padoa and Chiaves (*Atti R. Accad. Lincei*, 1907, [v], **16**, 765) give the melting point of a specimen of the *picrate* prepared from tetrahydrocarbazole obtained by the reduction of carbazole as 133° , but most probably their tetrahydrocarbazole contained some unchanged carbazole.

9-Acetyltetrahydrocarbazole (IV).—The *cyclohexanoneacetylphenylhydrazone* used in the preparation of this substance was obtained by heating *cyclohexanonephenylhydrazone* with an equal weight of freshly-distilled acetic anhydride on the steam-bath for two hours and then distilling under reduced pressure, when the acetyl derivative passed over at $210\text{--}220^{\circ}/14$ mm. as a viscous liquid which did not crystallise (Found: $N = 12.1$. $C_{14}H_{18}ON_2$ requires $N = 12.2$ per cent.).

When this acetyl-hydrazone was heated with dilute sulphuric acid (20 per cent.) for a few minutes, an oil resulted which solidified on cooling. This product was recrystallised from alcohol, from which it separated in thick prisms melting at 77° , and this proved to be pure *9-acetyltetrahydrocarbazole*. In this particular case it was found rather unexpectedly that the closing of the indole ring, by boiling with acetic acid, occurred with some difficulty, and even after boiling for an hour some acetyl-hydrazone remained unchanged. The same acetyl derivative was obtained by the direct acetylation of tetrahydrocarbazole under the following conditions: Tetrahydrocarbazole (30 grams) was mixed with glacial acetic acid (150 c.c.) and acetyl chloride (50 c.c.), and after adding a little copper powder, the whole was allowed to remain for fourteen days in a flask fitted with a calcium chloride tube. The product was decomposed by ice and water, the sticky, dark green solid extracted with chloroform, the extract dried over calcium chloride, the chloroform removed, and the residue distilled under reduced pressure,

when an almost colourless distillate was obtained which solidified on cooling. This separated from alcohol in colourless crystals melting at 77° , and proved to be identical with the 9-acetyltetrahydrocarbazole obtained from the acetyl-hydrazone as explained above (Found : $N = 6.5$. $C_{14}H_{15}ON$ requires $N = 6.6$ per cent.).

This acetyl derivative may also be obtained by boiling tetrahydrocarbazole with three times its weight of acetic anhydride for six hours and then distilling the product. Several attempts were made to prepare 9-benzoyltetrahydrocarbazole from tetrahydrocarbazole by the action of benzoyl chloride under varying conditions, but the product was always resinous and could not be purified. Similar results were obtained when benzoic anhydride was used. If the solution of tetrahydrocarbazole in glacial acetic acid is boiled with benzoyl chloride in the presence of a little copper powder, and the product distilled, a solid is obtained which after crystallisation melts at 77° and consists of 9-acetyltetrahydrocarbazole.

The Nitration of Tetrahydrocarbazole.

6-Nitro- and 6-Amino-tetrahydrocarbazole.

It is explained in the introduction (p. 1827) that the nitration of tetrahydrocarbazole may be directly accomplished at low temperatures, and the following conditions have been found to work well :

Tetrahydrocarbazole (10 grams), dissolved in concentrated sulphuric acid (70 c.c.), is cooled to -5° and then the theoretical quantity (5.9 grams) of powdered potassium nitrate added in small quantities at a time, the solution being continuously stirred and kept below -3° . The product is poured on to ice, the crude, yellow nitro-compound collected, washed thoroughly with water, and dried over sulphuric acid. It is then recrystallised from alcohol, from which it separates in small, thick prisms melting at 174° , and careful comparison showed that this substance is identical with the nitro-tetrahydrocarbazole obtained by Borsche (*Annalen*, 1908, **359**, 67) from *cyclohexanone-p*-nitrophenylhydrazone by warming with sulphuric acid.

The 9-Acetyl Derivative.—This substance, which was required for comparison with the acetyl derivative obtained by nitrating acetyl-tetrahydrocarbazole (compare p. 1828), was prepared in the following manner. 6-Nitrotetrahydrocarbazole (5 grams) was boiled with acetic anhydride (50 c.c.) for two hours, when, on cooling, yellow needles separated, which were recrystallised from glacial acetic acid (Found : $N = 10.8$. $C_{14}H_{14}O_3N_2$ requires $N = 10.8$ per cent.).

6-Nitro-9-acetyltetrahydrocarbazole melts at 244° and is readily hydrolysed to 6-nitrotetrahydrocarbazole when it is digested with a solution of sodium hydroxide in 50 per cent. aqueous alcohol.

6-Aminotetrahydrocarbazole.—In order to prepare this substance, the nitro-derivative (4 grams) was added to a mixture of iron filings (10 grams), water (100 c.c.), and hydrochloric acid (3 c.c.) and the whole heated on the steam-bath for an hour with frequent shaking. The product was cooled, made alkaline with sodium hydroxide, and the solid collected and extracted several times with boiling water, when, on cooling, the amino-derivative separated in crystals, the yield being about 40 per cent. of the theoretical.

6-Aminotetrahydrocarbazole separates from alcohol or toluene in colourless plates and melts at 152° (Found: N = 15.1. $C_{12}H_{14}N_2$ requires N = 15.0 per cent.). The picrate was prepared by mixing the hot alcoholic solution of the amino-derivative (1 gram) with picric acid (1.2 grams), when, on cooling, bright red needles separated which, after recrystallisation from alcohol, melted at 214° with decomposition.

6-Acetylaminotetrahydrocarbazole was prepared by mixing the amino-derivative in hot benzene with a slight excess of acetic anhydride. The crystalline mass was collected and recrystallised from dilute acetic acid, from which it separated in thick, colourless prisms melting at 208°.

6-Benzoylaminotetrahydrocarbazole was precipitated when the amino-derivative, dissolved in hot benzene, was mixed with benzoyl chloride, and separated from alcohol in clusters of short prisms melting at 207° (Found: N = 9.6. $C_{19}H_{18}ON_2$ requires N = 9.7 per cent.).

Synthesis of 6-Acetylaminotetrahydrocarbazole.—For the purpose of this synthesis, *p*-acetylaminophenylhydrazine hydrochloride was prepared from *p*-aminoacetanilide by reduction with stannous chloride in the usual manner (Riedel, D.R.-P. 80843) and was employed as such because the free base is difficult to obtain pure and rapidly decomposes on standing in the air. Sodium (5 grams) dissolved in alcohol (80 c.c.) was mixed with cyclohexanone (6.5 grams) and the hydrazine hydrochloride from 10 grams of *p*-aminoacetanilide added, when there was considerable rise of temperature. The whole was warmed on the steam-bath for a few minutes, mixed with water, the precipitate collected and recrystallised from alcohol, from which it separated in needles melting at 165–166°, and this substance, which decomposed gradually on keeping, is cyclohexanone-*p*-acetylaminophenylhydrazone (Found: N = 17.1. $C_{14}H_{19}ON_3$ requires N = 17.1 per cent.). When an attempt was made to convert this substance into the corresponding indole

derivative by the action of sulphuric or hydrochloric acid, simultaneous elimination of the acetyl group took place.

It was, however, found that glacial acetic acid leads directly and easily to 6-acetylaminotetrahydrocarbazole. The hydrazone was simply heated with glacial acetic acid almost to the boiling point, the flame was then removed, when the formation of the indole ring took place so energetically that the acid boiled for some time. On the addition of a little water, 6-acetylaminotetrahydrocarbazole separated from the dilute acetic acid in short, colourless prisms melting at 208° (Found : N = 12.5. $C_{14}H_{16}ON_2$ requires N = 12.3 per cent.). The free amino-derivative was obtained by boiling the acetyl derivative with concentrated hydrochloric acid for ten minutes, during which time the hydrochloride separated as a gelatinous precipitate. The whole was mixed with ice, made alkaline with ammonia, and the amino-derivative collected, washed, dried, and recrystallised from alcohol, from which it separated in small plates melting at 152° . A careful comparison showed that this base (and its acetyl derivative) is identical with 6-aminotetrahydrocarbazole (and its acetyl derivative) prepared from 6-nitrotetrahydrocarbazole by reduction in the manner described above.

9-Methyltetrahydrocarbazole (VII) and its 6-Nitro- (VIII) and 6-Amino-derivatives.

9-Methyltetrahydrocarbazole, which does not appear to have been described, may be obtained from *cyclohexanone* and *as-phenylmethylhydrazine* in the following manner: The phenylmethylhydrazine (5 grams) is mixed with *cyclohexanone* (4.1 grams), when there is a considerable rise of temperature and the mixture becomes cloudy owing to the separation of water.

After heating on the steam-bath for a few minutes, the hydrazone is converted into the carbazole by boiling with sulphuric acid (20 c.c.) and water (90 c.c.), when an oil separates which crystallises on cooling, and on recrystallisation from alcohol 9-methyltetrahydrocarbazole separates in colourless needles. Alternatively, the hydrazone is boiled with glacial acetic acid for a few minutes, when, on diluting with water, the carbazole separates as an oil which soon solidifies and is again crystallised from alcohol (Found : N = 7.5. $C_{13}H_{15}N$ requires N = 7.6 per cent.).

9-Methyltetrahydrocarbazole melts at 50° and yields a picrate which separates from alcohol in dark red needles melting at 116° .

6-Nitro-9-methyltetrahydrocarbazole was obtained in almost quantitative yield by the method used in the case of the preparation of 6-nitrotetrahydrocarbazole, and the crude product was crystallised

from glacial acetic acid, from which it separated in long, yellow prisms melting at 192° (Found: N = 12.2. $C_{13}H_{14}O_2N_2$ requires N = 12.2 per cent.).

6-Amino-9-methyltetrahydrocarbazole was prepared by reducing the nitro-derivative with iron and a little hydrochloric acid (compare p. 1829), and the product was extracted with boiling water, when, on cooling, the amino-derivative separated in colourless prisms melting at 105° .

The picrate crystallises from hot alcohol in orange needles and melts at 212° (Found: N = 16.1. $C_{13}H_{16}N_2 \cdot C_6H_2(OH)(NO_2)_3$ requires N = 16.3 per cent.).

6-Acetylamino-9-methyltetrahydrocarbazole is readily obtained by adding acetic anhydride to the solution of the amino-compound in benzene and is purified by crystallisation from acetic acid, from which it separates in colourless needles melting at 238° (Found: N = 11.6. $C_{15}H_{18}ON_2$ requires N = 11.6 per cent.).

Synthesis of 6-Acetylamino-9-methyltetrahydrocarbazole.—For the purpose of this synthesis, *p*-aminomethylaniline, $NH_2 \cdot C_6H_4 \cdot NHMe$, was prepared by the reduction of *p*-nitrosomethylaniline with sodium sulphide. This was dissolved in benzene and treated with the theoretical amount of acetic anhydride, when there was considerable rise of temperature and *p*-acetylaminomethylaniline separated as an oil. This was extracted and separated from the benzene by the calculated quantity of dilute hydrochloric acid, the solution was cooled below 0° , and the required amount of sodium nitrite, dissolved in a little water, added gradually with continuous stirring. The *p*-acetylaminonitrosomethylaniline, $CH_3 \cdot CO \cdot NH \cdot C_6H_4 \cdot NMe \cdot NO$, which separated in rather poor yield as a yellow, crystalline mass, was collected, washed with water, and recrystallised from alcohol, from which it separated in almost colourless plates and melted at 146° (Found: N = 21.7. $C_9H_{11}O_2N_3$ requires N = 21.8 per cent.). This acetyl derivative (4 grams) was made into a paste with glacial acetic acid (6 grams) and gradually added to water (21 c.c.) and zinc dust (12 grams of 90 per cent.) with continuous stirring, when there was some rise of temperature, which, however, was kept below 25° .

After remaining over-night, the product was rendered alkaline by the addition of sodium hydroxide, extracted with much ether, the ethereal solution dried over potassium carbonate, and evaporated, when *p*-acetylaminophenylmethylhydrazine,

remained as a dark oil.

This oil was now added to excess of cyclohexanone, and the resulting hydrazone boiled with glacial acetic acid (10 grams),

when the formation of the indole ring proceeded smoothly, and, on the addition of water, 6-acetylamino-9-methyltetrahydrocarbazole was precipitated. After crystallisation from acetic acid, this melted at 238° (Found : N = 11·5. $C_{15}H_{18}ON_2$ requires N = 11·6 per cent.) and was shown to be identical with the substance of this composition obtained from the product of the nitration of 9-methyltetrahydrocarbazole (p. 1835) by careful comparison and by the fact that the mixture of the two preparations melted at 238°.

5(?) - Nitrotetrahydrocarbazole.

Although tetrahydrocarbazole and 9-methyltetrahydrocarbazole, on nitration under the conditions given on pp. 1832 and 1834, give almost quantitative yields of the corresponding nitro-derivatives in which the nitro-group occupies the 6-position, 9-acetyltetrahydrocarbazole behaves quite differently. When nitration was attempted in sulphuric acid solution with potassium nitrate, an unsatisfactory product was obtained, from which nothing definite could be isolated by recrystallisation from the usual solvents.

It was, however, ultimately discovered that nitration may be satisfactorily carried out in glacial acetic acid solution under the following conditions. 9-Acetyltetrahydrocarbazole (3·6 grams) was dissolved in glacial acetic acid (50 c.c.) and then nitric acid (1·7 grams of *d* 1·4) diluted with a little glacial acetic acid gradually added at room temperature. The mixture was allowed to remain over-night, when long, pale yellow prisms separated which were collected and recrystallised from glacial acetic acid (Found : N = 10·7. $C_{14}H_{14}O_3N_2$ requires N = 10·8 per cent.).

5-Nitro-9-acetyltetrahydrocarbazole melts at 174° and is readily hydrolysed when it is warmed with a solution of sodium hydroxide in 50 per cent. aqueous alcohol. On the addition of water, a yellow, crystalline substance separates which may be crystallised either from alcohol or chloroform, from which it separates in long prisms (Found : C = 66·6; H = 5·6; N = 12·9. $C_{12}H_{12}O_2N_2$ requires C = 66·6; H = 5·5; N = 13·0 per cent.).

5-Nitrotetrahydrocarbazole melts at 172°, or at about the same temperature as the 6-nitro-derivative, and as it was at first thought that these two substances might be identical, a mixed melting-point determination was made, when the mixture began to melt at 125° and was completely melted at 151°.

7(?) - Nitrotetrahydrocarbazole and 8-Chloro-5-nitrotetrahydrocarbazole.
(X).

It has already been pointed out (p. 1828) that the action of *m*-nitrophenylhydrazine on cyclohexanone might theoretically lead

to the formation of 7-nitro- or 5-nitro-tetrahydrocarbazole or a mixture of both, and the following experiment was made with the object of ascertaining whether the product is actually a single substance or a mixture of isomerides. *cyclo*Hexanone-*m*-nitrophenylhydrazone (5.4 grams) was mixed with sulphuric acid (10 c.c.) and water (50 c.c.), in which it dissolved, but, on boiling, a brick-red, crystalline precipitate separated which was collected, washed with water, and dried. The yield of this substance was 82 per cent. of that theoretically possible, the loss being due to the hydrolysis of a little of the hydrazone into *m*-nitrophenylhydrazine and *cyclo*-hexanone. In this condition, the substance melted at 154°, and this was not altered by recrystallisation from methyl alcohol, from which the substance separated in clusters of prisms and was obviously homogeneous. Although carefully searched for, no trace of any isomeride of this 7-nitrotetrahydrocarbazole could be detected.

8-Chloro-5-nitrotetrahydrocarbazole (compare p. 1829).—The preparation of this interesting substance was carried out under the following conditions. 2-Chloro-5-nitroaniline was prepared from *o*-chloroaniline by nitration in concentrated sulphuric acid solution, under the conditions recommended by Chattaway, Orton, and Evans (*Ber.*, 1900, **33**, 3062). This substance (6 grams) was added to concentrated hydrochloric acid (50 c.c.) and diazotised below 0° by the addition of sodium nitrite (2.5 grams) dissolved in a little water. A solution of stannous chloride (15.5 grams) in concentrated hydrochloric acid (20 c.c.) was then added, and the precipitate collected, washed with a little water, dissolved in much hot water, and the tin removed by means of hydrogen sulphide. The free 2-chloro-5-nitrophenylhydrazine was obtained from the filtrate by the addition of sodium acetate and was recrystallised from alcohol, from which it separated in long, orange needles melting at 160° (Found: N = 22.5. $C_6H_6O_2N_3Cl$ requires N = 22.4 per cent.).

*cyclo*Hexanone (1.3 grams) and 2-chloro-5-nitrophenylhydrazine (2 grams) were mixed together in boiling alcoholic solution, when, on cooling, *cyclohexanone*-2-chloro-5-nitrophenylhydrazone separated in bright yellow prisms melting at 78° (Found: N = 15.7. $C_{12}H_{14}O_2N_3Cl$ requires N = 15.7 per cent.). The influence on the colour due to the introduction of the chlorine atom is very marked, since *cyclohexanone*-*m*-nitrophenylhydrazone is bright red.

The hydrazone (2 grams) was now heated with sulphuric acid (4 c.c.) and water (20 c.c.), when 8-chloro-5-nitrotetrahydrocarbazole separated as a reddish-brown solid, which was purified by recrystallisation from alcohol, from which it separated in clusters of orange

prisms melting at 214° (Found : N = 11.3. $C_{12}H_{11}O_2N_2Cl$ requires N = 11.2 per cent.).

Oxidation of Tetrahydrocarbazole and of 9-Methyltetrahydrocarbazole.

The interest attaching to the oxidation of hydrocarbazole derivatives is discussed in the introduction (p. 1830), and one of the objects we had in view was the discovery of a process which would be applicable, not only to the hydrocarbazoles themselves, but also to the chloro-, nitro-, and other derivatives. In the first experiments, the oxidation of tetrahydrocarbazole, suspended in dilute sulphuric acid at room temperature, with the theoretical quantity of permanganate was investigated. Oxidation took place very readily with almost immediate disappearance of the pink colour, but no carbazole could be isolated from the product. A similar negative result was obtained when tetrahydrocarbazole, without solution in dilute sulphuric acid, was oxidised with aqueous permanganate at about 80° . Subsequent experiments seemed to indicate that mercuric acetate may prove to be a useful reagent in such oxidations, as the following examples show.

Oxidation of Tetrahydrocarbazole to Carbazole.—This change takes place under the following conditions. Tetrahydrocarbazole (5 grams) is dissolved in glacial acetic acid (25 c.c.) at 85° and the solution added to the theoretical quantity of mercuric oxide (25.5 grams), dissolved in glacial acetic acid (25 c.c.), also at 85° . The mixture is heated on the steam-bath for a few minutes, allowed to cool, the mercurous acetate removed by filtration, and the filtrate diluted with water, when a yellow mercury compound of unknown composition separates. This was collected with the aid of the pump, washed with dilute nitric acid, and dried on porous porcelain. Hydrogen sulphide was now bubbled through this mercury derivative suspended in hot glacial acetic acid (50 per cent.), and the whole filtered hot, when, on dilution with water, the filtrate gave a small quantity of a solid which, after crystallisation from toluene, proved to be *carbazole*, but the yield was small.

Oxidation of 9-Methyltetrahydrocarbazole to 9-Methylcarbazole.

In this experiment, the oxidation with mercuric acetate was carried out under the conditions stated in the case of the oxidation of tetrahydrocarbazole and on diluting the filtrate from the mercurous acetate with water a sticky mass separated. This was extracted with chloroform, the solution dried over calcium chloride, the chloroform removed, and the residue distilled under 23 mm.

pressure, when metallic mercury and a colourless oil collected in the receiver. The oil soon solidified and, after crystallisation from alcohol, melted at 85—86° and proved to be 9-methylcarbazole, as a comparison of the properties and a mixed melting-point determination demonstrated. The yield was better than in the tetrahydrocarbazole experiment, and amounted to at least 20 per cent. of the theoretical.

Lastly, an experiment was made on the action of mercuric acetate on 6-nitrotetrahydrocarbazole, and in this case also mercurous acetate was formed, and water precipitated from the acetic acid filtrate a mercury derivative, the investigation of which is in progress.

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