CCCXXV.—*Derivatives of Tetrahydrocarbazole. Part VII. Reactions of 3-Methyltetrahydrocarbazole, 6-Chlorotetrahydrocarbazole, and their Acyl Derivatives.*

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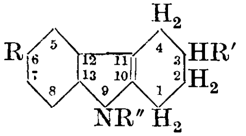
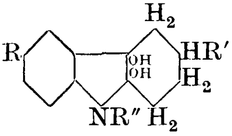
SOME of the most interesting reactions observed with tetrahydrocarbazole (I; R = R′ = R″ = H) are those of its 9-acyl derivatives with nitric acid (Perkin and Plant, J., 1923, **123**, 676). Besides simple nitro-derivatives in all cases, the 9-benzoyl compound forms a product by the addition of OH and NO_2 to the double linkage, and the 9-acetyl, 9-carbethoxy-, and 9-phenylacetyl derivatives add two hydroxyl radicals to this linkage. The reason for this remarkable difference between 9-benzoyltetrahydrocarbazole and the other 9-acyl derivatives investigated has never been explained, although, of course, it may be quite fortuitous. The present work was therefore undertaken with the view of determining (1) how far these additive reactions can be carried out with other tetrahydrocarbazole compounds, and (2) the effect of the nature and position of substituents upon the reactions. The observations of Manjunath and Plant (J., 1926, 2260) with 9-acetyl-6-methyltetrahydrocarbazole indicated that 3-*methyltetrahydrocarbazole* (I; R = R″ = H; R′ = Me), in which the methyl group is in the reduced part of the molecule, and 6-chlorotetrahydrocarbazole (I; R′ = R″ = H; R = Cl), containing a negative atom, would be suitable for investigation. The former has been obtained by Fischer's indole synthesis from 4-*methyl*cyclo*hexanone phenylhydrazone*, and, on nitration in concentrated sulphuric acid solution, it yielded a single product, which was shown to be 6-*nitro*-3-*methyltetrahydrocarbazole* (I; R = NO_2; R′ = Me; R″ = H). In order to identify some of the derivatives obtained in this work, 6-nitro-3-methyltetrahydrocarbazole and 8-*nitro*-3-*methyltetrahydrocarbazole* have been synthesised by eliminating ammonia from 4-*methyl*cyclo*hexanone* p- and o-*nitrophenylhydrazones*, respectively. The isomeric 5(or 7)-*nitro*- and 7(or 5)-*nitro*-3-*methyltetrahydrocarbazoles* were both obtained from 4-*methyl*cyclo*hexanone* m-*nitrophenylhydrazone*. It is not possible to say which of these is really the 5- and which the 7-nitro-derivative, whilst



(I.)



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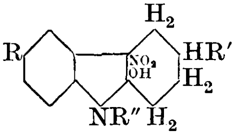

(III.)

it is interesting to note that *cyclo*hexanone *m*-nitrophenylhydrazone yields only one compound, assumed to be 7-nitrotetrahydrocarbazole (Borsche, Witte, and Bothe, *Annalen*, 1908, **359**, 53), under similar conditions. 3-Methyltetrahydrocarbazole has been converted into its 9-*acetyl* derivative with acetic anhydride, but the corresponding 9-*benzoyl* and 9-*carbethoxy*-compounds were made by first obtaining *magnesium* 9-3-*methyltetrahydrocarbazyl iodide* (I; R = H; R′ = Me; R″ = MgI) and subsequently treating this with benzoyl chloride and ethyl chloroformate, respectively. When 9-acetyl-3-methyltetrahydrocarbazole was treated with nitric acid in acetic acid solution, 5(or 7)-*nitro*-9-*acetyl*-3-*methyltetrahydrocarbazole* and 10 : 11-*dihydroxy*-9-*acetyl*-3-*methylhexahydrocarbazole* (II; R = H; R′ = Me; R″ = Ac) were obtained, but the exact nature of the product depended on the conditions used (p. 2458). The position of the nitro-group in the former of these two derivatives was established by hydrolysis to one of the isomeric nitro-compounds obtained synthetically from 4-methyl*cyclo*hexanone *m*-nitrophenylhydrazone. In view of the results obtained with tetrahydrocarbazole itself and the assumptions then made (Perkin and Plant, J., 1921, **119**, 1825), it seems advisable to avoid confusion by regarding this nitro-compound as the 5-nitro-derivative, but to admit the possibility of an alternative structure by adopting the designation "5(or 7)-nitro." The dihydroxy-compound obtained in this reaction was found to lose water on boiling with acetic anhydride, presumably to give 6-*acetyl*-3-*methyl*-ψ-*indoxyl*spirocyclo*pentane*, by a reaction analogous to that observed with the parent substance (Perkin and Plant, *loc. cit.*). 9-Benzoyl-3-methyltetrahydrocarbazole, on treatment with nitric acid in acetic acid solution, yielded a mixture of 11-*nitro*-10-*hydroxy*-9-*benzoyl*-3-*methylhexahydrocarbazole* (III; R = H; R′ = Me; R″ = Bz) and 5(or 7)-*nitro*-9-*benzoyl*-3-*methyltetrahydrocarbazole*, whilst under similar conditions ethyl 3-methyltetrahydrocarbazole-9-carboxylate behaved like the 9-acetyl derivative and gave a mixture of *ethyl* 5(or 7)-*nitro*-3-*methyltetrahydrocarbazole*-9-*carboxylate* and *ethyl* 10 : 11-*dihydroxy*-3-*methylhexahydrocarbazole*-9-*carboxylate* (II; R = H; R′ = Me; R″ = CO_2Et). It is apparent, therefore, that in general the results obtained with 3-methyltetrahydrocarbazole are similar to those in the case of tetrahydrocarbazole itself, but the addition products were not produced quite so readily and were more difficult to isolate.

The three isomeric mononitro-derivatives of 6-chlorotetrahydrocarbazole were obtained synthetically, the 8-*nitro*-compound from cyclo*hexanone* 4-*chloro*-2-*nitrophenylhydrazone*, and a mixture of the 5(or 7)- and 7(or 5)-*nitro*-compounds from cyclo*hexanone* 4-*chloro*-3-*nitrophenylhydrazone*. When 6-chlorotetrahydrocarbazole was nitrated directly in sulphuric acid, 5(or 7)-nitro-6-chlorotetrahydrocarbazole was produced. 6-*Chloro*-9-*acetyltetrahydrocarbazole* was prepared from its parent substance by direct acetylation, but the 9-*benzoyl* and 9-*carbethoxy*-derivatives were obtained by employing Grignard reactions as in the case of the corresponding products from 3-methyltetrahydrocarbazole. When nitric acid acted on this 9-acetyl compound in acetic acid solution, both 6-*chloro*-5(or 7)-*nitro*-9-*acetyltetrahydrocarbazole* and 6-*chloro*-10 : 11-*dihydroxy*-9-*acetylhexahydrocarbazole* (II; $R = Cl$; $R' = H$; $R'' = Ac$) were produced, but the relative amounts could be varied by altering the conditions. From 6-chloro-9-benzoyltetrahydrocarbazole both 6-*chloro*-5(or 7)-*nitro*-9-*benzoyltetrahydrocarbazole* and 6-*chloro*-11-*nitro*-10-*hydroxy*-9-*benzoylhexahydrocarbazole* (III; $R = Cl$; $R' = H$; $R'' = Bz$) were obtained, but in the case of ethyl 6-chlorotetrahydrocarbazole-9-carboxylate unexpected results were observed. *Ethyl* 6-*chloro*-5(or 7)-*nitrotetrahydrocarbazole*-9-*carboxylate* was isolated, but the second product proved to be *ethyl* 6-*chloro*-11-*nitro*-10-*hydroxyhexahydrocarbazole*-9-*carboxylate* (III; $R = Cl$; $R' = H$; $R'' = CO_2Et$), thus providing an example of the addition of OH and NO_2 to the double linkage in a 9-carbethoxy-derivative. When a solution of this addition compound in alcohol was boiled, a product, which appeared on analysis to be *ethyl* 6-*chloro*-10 : 11-*dihydroxyhexahydrocarbazole*-9-*carboxylate* (II; $R = Cl$; $R' = H$; $R'' = CO_2Et$), was obtained, apparently by the replacement of NO_2 by OH. The products resulting from the addition of nitric acid decompose, on melting, with the evolution of oxides of nitrogen. The preparation of these compounds from 6-chlorotetrahydrocarbazole required more vigorous conditions than in the case of tetrahydrocarbazole itself.

Since hexahydrocarbazole has been shown to exist in two stereoisomeric modifications (Gurney, Perkin, and Plant, J., 1927, 2676), it follows that theoretically four modifications of 3-methylhexahydrocarbazole might appear during the reduction of 3-methyltetrahydrocarbazole. Two of these would result from the *cis*-addition of hydrogen at the double linkage and would be less strained than the other two, which would result from the *trans*-addition of hydrogen. From the results obtained in the reduction of tetrahydrocarbazole, it might be expected that the former two would be formed in relatively great amounts, but that only very small quantities of the latter two would be present in the reduction product. This point has been investigated, but only one product (presumably one of the *cis*-modifications) resulted on electrolytic reduction. This, which melts at 58·5°, has been called 3-*methylhexahydrocarbazole* (A). When, however, 3-methyltetrahydrocarbazole was reduced with tin and hydrochloric acid in aqueous alcohol, a small quantity of a second form, 3-*methylhexahydrocarbazole* (B), m. p. 128°, was isolated in addition to the modification (A), which formed the main product. It is hardly possible, on account of the small yield of 3-methylhexahydrocarbazole (B), to say whether this is the second *cis*-modification or one of the two *trans*-forms. It is theoretically possible for all the products formed by addition of OH and NO_2, or OH and OH, at the double linkage in tetrahydrocarbazole to exist in more than one stereoisomeric modification, but so far in no case has more than a single form been isolated.

EXPERIMENTAL.

3-*Methyltetrahydrocarbazole and its Nitro-derivatives*.—The crude, solid 4-*methyl*cyclo*hexanone phenylhydrazone* (7 g.), obtained by mixing equal weights of 4-methyl*cyclo*hexanone and phenylhydrazine, was warmed with aqueous sulphuric acid (120 c.c. of 17%) for 15 minutes on the water-bath, with shaking. 3-*Methyltetrahydrocarbazole* was isolated from alcohol in colourless, rhombic prisms, m. p. 109—110° (Found: N, 7·5. $C_{13}H_{15}N$ requires N, 7·6%).

From a solution of *p*-nitrophenylhydrazine (1·7 g.) and 4-methyl*cyclo*hexanone (1·2 g.) in hot alcohol, 4-*methyl*cyclo*hexanone* p-*nitrophenylhydrazone* separated, on cooling, in yellow needles, m. p. 128·5°, and, after treatment with boiling 25% sulphuric acid for a few minutes, it yielded 6-*nitro*-3-*methyltetrahydrocarbazole*, which crystallised from alcohol (charcoal) in brown prisms, m. p. 165—166° (Found: N, 12·2. $C_{13}H_{14}O_2N_2$ requires N, 12·2%). By a similar process, 4-*methyl*cyclo*hexanone* o-*nitrophenylhydrazone* was obtained in crimson prisms, m. p. 59°, and converted into 8-*nitro*-3-*methyltetrahydrocarbazole*, which separated from alcohol in bright red needles, m. p. 188° (Found: N, 12·1%). 4-*Methyl*cyclo*hexanone* m-*nitrophenylhydrazone*, from alcohol in orange-red prisms, m. p. 80—81°, yielded a mixture with boiling 27% sulphuric acid. The filtered solution of the crude product (6 g.) in hot alcohol deposited, on cooling and leaving for 24 hours, 5(or 7)-*nitro*-3-*methyltetrahydrocarbazole* in yellow needles, m. p. 188° (Found: N, 12·0%), whilst, on concentration of the mother-liquor, a further quantity, contaminated with a little of the isomeride, was obtained. The crude 7(or 5)-*nitro*-3-*methyltetrahydrocarbazole* was then isolated by adding water to the mother-liquor, and purified by crystallisation from chloroform, separating in orange-red plates, m. p. 175° (Found: N, 12·2%). These two nitro-compounds were formed in approximately equal amounts.

A solution of 3-methyltetrahydrocarbazole (10·6 g.) in concentrated sulphuric acid (70 c.c.) was kept at − 10° and treated gradually with pulverised potassium nitrate (5·9 g.), with continuous stirring. After being poured on ice and collected as quickly as possible, the product, when dried in a desiccator, melted at 159°. It separated from alcohol in brown prisms, m. p. 165—166°, and was shown to be 6-nitro-3-methyltetrahydrocarbazole by a mixed m. p. determination. No other substance could be isolated from the reaction mixture.

Action of Nitric Acid on 9-Acetyl-3-methyltetrahydrocarbazole.—When a solution of 3-methyltetrahydrocarbazole in 2½ times its weight of acetic anhydride was boiled under reflux for 3 hours and cooled, 9-*acetyl*-3-*methyltetrahydrocarbazole* separated, and was obtained from glacial acetic acid in colourless needles, m. p. 108·5° (Found : N, 6·1. $C_{15}H_{17}ON$ requires N, 6·2%). When a solution of the acetyl derivative (3·6 g.) in glacial acetic acid (50 c.c.) was treated with nitric acid (1·8 g., *d* 1·42, dissolved in a little acetic acid) at room temperature, 5(or 7)-*nitro*-9-*acetyl*-3-*methyltetrahydrocarbazole* separated during 24 hours in clusters of yellow needles, m. p. 134° (after recrystallisation from alcohol) (Found : N, 10·3. $C_{15}H_{16}O_3N_2$ requires N, 10·3%). A mixture of this nitro-compound (1·5 g.), sodium hydroxide (9 g.), alcohol (60 c.c.), and water (60 c.c.) was boiled for some time and then diluted with water. When the product was crystallised from alcohol, 5(or 7)-nitro-3-methyltetrahydrocarbazole separated in orange prisms, m. p. 187°. It was shown by a mixed m. p. determination to be identical with one of the products obtained from 4-methyl*cyclo*hexanone *m*-nitrophenylhydrazone. The m. p. of the mixture with 8-nitro-3-methyltetrahydrocarbazole was much lower.

When 9-acetyl-3-methyltetrahydrocarbazole (18 g.) in acetic acid (66 c.c.) was treated at 50° with nitric acid (9·2 g.; *d* 1·42) in acetic acid (10 c.c.), 5(or 7)-nitro-9-acetyl-3-methyltetrahydrocarbazole (3 g.) again separated over-night, but after pouring the mother-liquor into water, adding aqueous sodium hydroxide until nearly neutral, and stirring, a product was obtained which could be easily collected and after being dried in a desiccator yielded 10 : 11-*dihydroxy*-9-*acetyl*-3-*methylhexahydrocarbazole* on crystallisation from benzene. After recrystallisation from alcohol, it was obtained in almost colourless plates, m. p. 189—190° (Found : N, 5·4. $C_{15}H_{19}O_3N$ requires N, 5·4%). When a solution of this dihydroxy-compound (2·5 g.) in acetic anhydride (40 c.c.) was boiled under reflux for 2 hours, cooled, and shaken with water, the product, after crystallisation from alcohol, yielded 6-*acetyl*-3-*methyl*-ψ-*indoxyl*spirocyclo*pentane* in colourless plates, m. p. 93·5° (Found : N, 5·8. $C_{15}H_{17}O_2N$ requires N, 5·8%). 3-*Methyl*-ψ-*indoxyl*spirocyclo*pentane*, obtained from its acetyl derivative by hot aqueous-alcoholic potassium hydroxide and subsequent addition of water, separated from alcohol in colourless prisms, m. p. 114·5°.

Action of Nitric Acid on 9-*Benzoyl*-3-*methyltetrahydrocarbazole.*—3-Methyltetrahydrocarbazole (14·7 g.) was added in portions to a solution of magnesium (1·9 g.) in ethyl iodide (12·8 g.) and dry ether (180 c.c.), and, after the evolution of ethane had ceased, benzoyl chloride (11·4 g.) was gradually introduced with shaking. After some time, ice and dilute hydrochloric acid were added, the ethereal solution was dried with calcium chloride, the ether removed, and the residual red oil distilled under reduced pressure. The distillate, collected at 255—265°/11 mm., was crystallised from alcohol, from which 9-*benzoyl*-3-*methyltetrahydrocarbazole* separated in colourless prisms, m. p. 99° (Found : N, 4·9. $C_{20}H_{19}ON$ requires N, 4·8%).

When a solution of 9-benzoyl-3-methyltetrahydrocarbazole (2·6 g.) in glacial acetic acid (47 c.c.) was treated with nitric acid (0·9 g., *d* 1·42) at 30° and then left for 24 hours, 11-*nitro*-10-*hydroxy*-9-*benzoyl*-3-*methylhexahydrocarbazole* separated in pale yellow prisms, m. p. 123° (decomp., with evolution of oxides of nitrogen). It separated from benzene–petroleum in small prisms, m. p. 123—124° (decomp.) (Found : N, 7·6. $C_{20}H_{20}O_4N_2$ requires N, 7·9%). When the solid precipitated by pouring the acetic acid mother-liquor into water was crystallised from methyl alcohol, 5(or 7)-*nitro*-9-*benzoyl*-3-*methyltetrahydrocarbazole* separated in yellow needles, m. p. 142·5° (Found : N, 8·4. $C_{20}H_{18}O_3N_2$ requires N, 8·4%). This compound, which formed by far the greater part of the product, was hydrolysed by aqueous-alcoholic sodium hydroxide to 5(or 7)-nitro-3-methyltetrahydrocarbazole, m. p. 186°, the identity of which was established by a mixed m. p. determination with the synthetical product.

Action of Nitric Acid on Ethyl 3-*Methyltetrahydrocarbazole*-9-*carboxylate.*—*Ethyl* 3-*methyltetrahydrocarbazole*-9-*carboxylate* was prepared by the Grignard reaction, similar to that used for the 9-benzoyl derivative, ethyl chloroformate being used. It was unnecessary here to distil the crude product, and the ester separated from alcohol in colourless prisms, m. p. 66—67° (Found : N, 5·7. $C_{16}H_{19}O_2N$ requires N, 5·5%). A solution of the ester (9·2 g.) in glacial acetic acid (16 c.c.) at 25° was treated with nitric acid (3·6 g., *d* 1·42), dissolved in acetic acid (4 c.c.), the temperature not being allowed to rise above 50°. After a short time, the yellow needles, m. p. 101°, which separated, were collected and recrystallised from alcohol, from which *ethyl* 5(or 7)-*nitro*-3-*methyltetrahydrocarbazole*-9-*carboxylate* was isolated in yellow prisms, m. p. 104° (Found : N, 9·2. $C_{16}H_{18}O_4N_2$ requires N, 9·3%). When treated with boiling aqueous-alcoholic sodium hydroxide, this product yielded 5(or 7)-nitro-3-methyltetrahydrocarbazole, m. p. 187° (mixed m. p. 187°). The acetic acid mother-liquor deposited, on being kept for 24 hours, a further quantity, m. p. 100°, of this nitro-derivative. When the filtrate was subsequently concentrated by keeping in a vacuum desiccator over solid sodium hydroxide for several days a second product, m. p. 121—129°, separated, and, after recrystallising this from alcohol, *ethyl* 10 : 11-*dihydroxy*-3-*methylhexahydrocarbazole*-9-*carboxylate* was obtained in clusters of small, colourless prisms, m. p. 135° (Found : N, 4·7. $C_{16}H_{21}O_4N$ requires N, 4·8%).

Reduction of 3-*Methyltetrahydrocarbazole.*—A mixture of 3-methyltetrahydrocarbazole (10 g.), alcohol (20 c.c.), concentrated hydrochloric acid (20 c.c.), and granulated tin (20 g.) was boiled under reflux for 5 hours, filtered, as much alcohol as possible was distilled off, and the residue was made alkaline with sodium hydroxide (20 g. in concentrated aqueous solution). The solid product was collected on asbestos and extracted with ether, the filtrate being also extracted with ether. The solid then remaining was ground with aqueous sodium hydroxide and again extracted with ether. The united ethereal solutions were dried with potassium carbonate, and the oily residue remaining after removal of the solvent was crystallised from alcohol, 3-*methylhexahydrocarbazole* (A) separating in colourless prisms, m. p. 58·5° (Found : C, 83·6; H, 9·1; N, 7·4. $C_{13}H_{17}N$ requires C, 83·4; H, 9·1; N, 7·5%). On concentrating the alcoholic mother-liquor, further quantities of 3-methylhexahydrocarbazole (A) were obtained, but ultimately a product, melting at 50—90°, began to separate. At this point the whole was dissolved in 60% sulphuric acid and then diluted with water to precipitate the very small quantity of non-basic, unreduced 3-methyltetrahydrocarbazole which was present. After filtration and basification by addition of concentrated aqueous ammonia, the resulting solid was recrystallised from alcohol, and 3-*methylhexahydrocarbazole* (B) separated in colourless needles, m. p. 128° (Found : C, 83·8; H, 9·4. $C_{13}H_{17}N$ requires C, 83·4; H, 9·1%).

A solution of 3-methyltetrahydrocarbazole (10 g.) in 60% sulphuric acid (250 c.c.) was submitted to electrolytic reduction in the cathode compartment of an electrolytic cell, lead electrodes and a current of 5·5 amps. (0·03 amp. per sq. cm. of cathode) for 16 hours at room temperature being used, but, on dilution with water, unchanged 3-methyltetrahydrocarbazole was recovered. The reduction was subsequently repeated, the cell being immersed in boiling water; the solution was then diluted with its own volume of water, filtered, and made alkaline with ammonia. The product was taken up in ether, and, after crystallisation from petroleum, 3-methylhexahydrocarbazole (A) was obtained in colourless plates, m. p. 57—58°, its identity with the substance previously described being established by a mixed m. p. determination. The presence of a second stereoisomeride in this product was not observed.

When 3-methylhexahydrocarbazole (A) was shaken with an equal weight of benzoyl chloride in the presence of dilute aqueous sodium hydroxide, and the product was crystallised from alcohol, 9-*benzoyl*-3-*methylhexahydrocarbazole* (A) was obtained in colourless needles, m. p. 81·5° (Found : N, 4·8. $C_{20}H_{21}ON$ requires N, 4·8%). 9-*Acetyl*-3-*methylhexahydrocarbazole* (A) was isolated by boiling a solution of the base in acetic anhydride for 20 minutes and subsequently shaking with dilute aqueous sodium carbonate, and was obtained from alcohol in colourless, rhombic prisms, m. p. 101°. The *picrate* of 3-methylhexahydrocarbazole (A) separated from toluene in yellow prisms, m. p. 115—116°.

Nitro-derivatives of 6-*Chlorotetrahydrocarbazole*.—6-Chlorotetrahydrocarbazole, prepared as described by Borsche, Witte, and Bothe (*loc. cit.*), was obtained from alcohol in colourless prisms, m. p. 144°. A solution of this chloro-compound (2 g.) in concentrated sulphuric acid (13 c.c.) was treated gradually at − 10° with powdered potassium nitrate (1·15 g.), with continuous stirring, and the whole was then poured on ice. When the product was crystallised from alcohol and then ethyl acetate, 6-*chloro*-5(or 7)-*nitrotetrahydrocarbazole* separated in yellow plates, m. p. 183·5° (Found : N, 11·2. $C_{12}H_{11}O_2N_2Cl$ requires N, 11·2%). A mixed m. p. determination showed this product to be identical with the 6-chloro-5(or 7)-nitrotetrahydrocarbazole described below.

4-Chloro-3-nitroaniline (12·5 g.) was dissolved in a warm mixture of concentrated hydrochloric acid (21 c.c.) and water (20 c.c.), the whole was rapidly cooled in a freezing mixture, and diazotised with aqueous sodium nitrite (6 g.). The filtered liquid was then added gradually during 10 minutes to a well-cooled mixture of saturated aqueous ammonium sulphite (40 c.c.) and concentrated ammonia (8 c.c.), and, after ½ hour, concentrated hydrochloric acid (70 c.c.) was added, the mixture warmed to 30°, and left over-night. The solid product was heated at 80° for a short time with concentrated hydrochloric acid (20 c.c.), and, after cooling and standing, the hydrazine hydrochloride was collected, dissolved in boiling water (200 c.c.), and the filtered solution treated with sodium acetate. After crystallisation from methyl alcohol, 4-*chloro*-3-*nitrophenylhydrazine* separated in orange needles, m. p. 109° (Found : N, 22·1. $C_6H_6O_2N_3Cl$ requires N, 22·4%). cyclo*Hexanone* 4-*chloro*-3-*nitrophenylhydrazone* separated from a hot alcoholic solution of 4-chloro-3-nitrophenylhydrazine (2·5 g.) and *cyclo*hexanone, (1·5 g.), on cooling, in red prisms, m. p. 106—107° (Found : N, 15·7. $C_{12}H_{14}O_2N_3Cl$ requires N, 15·7%). When the mixture obtained by treating this hydrazone (7·5 g.) with boiling aqueous sulphuric acid (170 c.c. of 25%) for 10 minutes was crystallised from methyl alcohol, 6-chloro-5(or 7)-nitrotetrahydrocarbazole separated in brown needles, m. p. 184°, and was found to be identical with the product of the direct nitration of 6-chlorotetrahydrocarbazole. After collecting a further quantity of the same derivative by concentrating the methyl-alcoholic mother-liquor, the remaining filtrate was evaporated to dryness and the residue crystallised from benzene. 6-*Chloro*-7(or 5)-*nitrotetrahydrocarbazole* then separated in orange needles, m. p. 162° (Found: N, 11·1. $C_{12}H_{11}O_2N_2Cl$ requires N, 11·2%). These two isomeric nitro-compounds appeared to be produced in approximately equal amounts.

By a process essentially similar to that described above, 4-chloro-2-nitroaniline was converted into 4-*chloro*-2-*nitrophenylhydrazine*, which was isolated from alcohol in red needles, m. p. 134° (Found: N, 22·0%). cyclo*Hexanone* 4-*chloro*-2-*nitrophenylhydrazone*, which separated from alcohol in red needles, m. p. 101°, was converted into 6-*chloro*-8-*nitrotetrahydrocarbazole* by treating it for 20 minutes with boiling 30% sulphuric acid, the product being obtained from alcohol (charcoal) in orange-red needles, m. p. 213° (Found: N, 11·3%).

Action of Nitric Acid on 6-*Chloro*-9-*acetyltetrahydrocarbazole*.—The acetylation of 6-chlorotetrahydrocarbazole proved to be a slow reaction, but when a solution of the substance in four times its weight of acetic anhydride containing 2 drops of concentrated sulphuric acid was boiled for 24 hours, 6-*chloro*-9-*acetyltetrahydrocarbazole* separated, on cooling, in colourless needles, m. p. 136° (unaltered by recrystallisation from acetic acid) (Found: N, 5·4. $C_{14}H_{14}ONCl$ requires N, 5·6%). Nitric acid (*d* 1·42) did not react with this acetyl derivative in acetic acid until the temperature reached about 80°. A solution of the compound (8·8 g.) in glacial acetic acid (48 c.c.) at 90° was treated with nitric acid (3·5 g., *d* 1·42), in a little acetic acid. A vigorous reaction took place and the solution boiled. During 16 hours a yellow product, m. p. 206—207°, separated, and, on recrystallising this from acetic acid, 6-*chloro*-10 : 11-*dihydroxy*-9-*acetylhexahydrocarbazole* was obtained in colourless prisms, m. p. 222° (Found: N, 4·9. $C_{14}H_{16}O_3NCl$ requires N, 5·0%). If the temperature during this reaction was maintained at 80°, the product, which separated on standing for 24 hours, was clearly a mixture of colourless prisms and yellow needles. After several crystallisations from alcohol, a small quantity of 6-*chloro*-5(or 7)-*nitro*-9-*acetyltetrahydrocarbazole* was isolated in yellow needles, m. p. 184·5—185·5° (Found: N, 9·6. $C_{14}H_{13}O_3N_2Cl$ requires N, 9·6%). This product was much more readily obtained by treating the 9-acetyl compound (0·8 g.) in acetic acid (15 c.c.) at 55° with fuming nitric acid (0·25 g., *d* 1·5), whereupon it crystallised on standing. On hydrolysis, by boiling its solution in aqueous-alcoholic sodium hydroxide, it yielded 6-chloro-5(or 7)-nitrotetrahydrocarbazole, m. p. 184°, identical with one of the products from *cyclo*hexanone 4-chloro-3-nitrophenylhydrazone.

Action of Nitric Acid on 6-*Chloro*-9-*benzoyltetrahydrocarbazole*.—The benzoylation of 6-chlorotetrahydrocarbazole was accomplished as described for the 3-methyl derivative, but it was unnecessary to distil the crude product. After crystallisation from alcohol, 6-*chloro*-9-*benzoyltetrahydrocarbazole* was obtained in colourless needles, m. p. 122—123° (Found : N, 4·4. $C_{19}H_{16}ONCl$ requires N, 4·5%). When a solution of this benzoyl compound (4·1 g.) in glacial acetic acid (20 c.c.) at 80° was treated with nitric acid (1·5 g., *d* 1·42) in a little acetic acid, yellow needles, m. p. 142°, separated gradually during 12 hours. After recrystallisation from alcohol, 6-*chloro*-5(or 7)-*nitro*-9-*benzoyltetrahydrocarbazole* was obtained in yellow needles, m. p. 148° (Found: N, 7·8. $C_{19}H_{15}O_3N_2Cl$ requires N, 7·9%). When this product was hydrolysed by means of aqueous-alcoholic sodium hydroxide, 6-chloro-5(or 7)-nitrotetrahydrocarbazole, m. p. 184°, identical with the synthetical substance, was obtained. The acetic acid mother-liquor, on keeping, deposited first a further quantity of the nitro-compound and then a pale yellow substance, melting at 142° with evolution of oxides of nitrogen. This was clearly different from the first product, since a mixture of the two melted at 130—133°, and the evolution of oxides of nitrogen on melting is characteristic of the nitric acid addition products. The latter substance was more conveniently prepared by treating a solution of the benzoyl compound (1·8 g.) in acetic acid (10 c.c.) with fuming nitric acid (0·6 g., *d* 1·5, in a little acetic acid) at 40—50°. 6-*Chloro*-11-*nitro*-10-*hydroxy*-9-*benzoylhexahydrocarbazole* immediately separated in colourless prisms, m. p. 147° (decomp., with evolution of oxides of nitrogen) (Found : N, 7·3. $C_{19}H_{17}O_4N_2Cl$ requires N, 7·5%).

Action of Nitric Acid on Ethyl 6-*Chlorotetrahydrocarbazole*-9-*carboxylate*.—*Ethyl* 6-*chlorotetrahydrocarbazole*-9-*carboxylate*, prepared by a process similar to that described for the 3-methyl derivative, separated from alcohol in colourless needles, m.p. 111—112° (Found : N, 5·1. $C_{15}H_{16}O_2NCl$ requires N, 5·0%). When the ester (2·0 g.) was treated in glacial acetic acid (6 c.c.) at 60° with nitric acid (0·7 g., *d* 1·42), the product gradually separated as a yellow solid, m. p. 120—125°. After two crystallisations from alcohol, *ethyl* 6-*chloro*-5(or 7)-*nitrotetrahydrocarbazole*-9-*carboxylate* was obtained in yellow needles, m. p. 126° (Found: N, 8·7. $C_{15}H_{15}O_4N_2Cl$ requires N, 8·7%), which, on hydrolysis with aqueous-alcoholic sodium hydroxide, yielded 6-chloro-5(or 7)-nitrotetrahydrocarbazole, m. p. 184°, identical with the synthetical product already described. When ethyl 6-chlorotetrahydrocarbazole-9-carboxylate (2 g.) was treated in acetic acid (12 c.c.) at 40—45° with fuming nitric acid (0·55 g., *d* 1·5), a colourless product immediately separated. This melted at 136—137° with evolution of oxides of nitrogen and was clearly a nitric acid addition product. After crystallisation from ethyl acetate, *ethyl* 6-*chloro*-11-*nitro*-10-*hydroxyhexahydrocarbazole*-9-*carboxylate* was obtained in colourless prisms, m. p. 136—137° (decomp.) (Found: N, 8·1. $C_{15}H_{17}O_5N_2Cl$ requires N, 8·2%). When its solution in alcohol was boiled for an hour, the product, which separated in colourless prisms, m. p. 132°, appeared to be *ethyl* 6-*chloro*-10 : 11-*dihydroxyhexahydrocarbazole*-9-*carboxylate* (Found: C, 58·1; H, 5·8; N, 4·9. $C_{15}H_{18}O_4NCl$ requires C, 57·8; H, 5·8; N, 4·5%).

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