135. *Dehydrogenation of Tetrahydrocarbazoles by Chloranil.*

By (Miss) Bessie M. Barclay and Neil Campbell.

Chloranil has been shown to be an excellent dehydrogenating agent for the preparation of carbazoles from tetrahydrocarbazoles. Twenty carbazoles have been obtained in this way, the yields in most cases lying between 75 and 95%. Mixtures of tetrahydrocarbazoles obtained from *cyclo*hexanone-*m*-phenylhydrazones may be separated by chromatographic adsorption on alumina.

The dehydrogenation of the readily obtained substituted 1 : 2 : 3 : 4-tetrahydrocarbazoles forms one of the best methods for the preparation of substituted carbazoles (Borsche, Witte, and Bothe, *Annalen*, 1908, **359**, 49). The reagents employed for this purpose have proved successful only in a few cases : yields are generally poor and in some cases substituents are removed during the process. For example, 6- and 8-chlorotetrahydrocarbazoles when passed over heated lead oxide gave carbazole (*idem*, *ibid.*), and the same result was obtained when 7-chloro- and 8-carboxy-tetrahydrocarbazole were oxidised by palladised charcoal in a stream of hydrogen (Plant and Moggridge, J., 1937, 1125). Dehydrogenation with sulphur and quinoline has been proved to be of service (Perkin and Plant, J., 1923, **123**, 676), but the yields are low (15—30%) and in some cases, such as that of 6-nitrotetrahydrocarbazole, intractable tars are obtained. The need of a dehydrogenating agent free from such disadvantages is obvious (cf. *idem*, J., 1921, **119**, 1825). It is now shown that chloranil in boiling xylene is a most satisfactory dehydrogenating agent, high yields of clean products being obtained (see table). The claims of Arnold and his co-workers (*J. Amer. Chem. Soc.*, 1939, **61**, 1407; 1940, **62**, 983), who used this method to prepare aromatic hydrocarbons, are thus confirmed. It is also clear that dehydrogenation alone occurs, sensitive groups such as the nitro- and carboxy-groups remaining intact. The method can be used for both large- and small-scale preparations, its only disadvantage being the rather long time (24 hours in some cases) required for complete dehydrogenation.

Summary of Results.

Original carbazole.	Product carbazole.	Time of heating (hrs.).	Yield, %.	Original carbazole.	Product carbazole.	Time of heating (hrs.).	Yield, %.
Tetrahydro-	Unsub.	24	95	5-Chlorotetrahydro-	4-Chloro-	23	50
Hexahydro-	,,	1	70	5 : 8-*Dichlorotetrahydro-*	1 : 4-*Dichloro-*	11	75
Dihydro-	,,	24	85	8-Bromotetrahydro-	1-*Bromo-*	21	90
8-Nitrotetrahydro-	1-Nitro-	6½	50	7-Bromotetrahydro-	2-*Bromo-*	24	85
7-Nitrotetrahydro-	2-*Nitro-*	18	70	6-Bromotetrahydro-	3-Bromo-	18	70
7-Nitrohexahydro-	2-Nitro-	19	75	5-*Bromotetrahydro-*	4-*Bromo-*	24	55
6-Nitrotetrahydro-	3-Nitro-	24	85	8-Carboxytetrahydro- (ethyl ester)	1-Carboxy- (ethyl ester)	24	75
5-*Nitrotetrahydro-*	4-*Nitro-*	24	65	6-Carboxytetrahydro- (ethyl ester)	3-Carboxy- (ethyl ester)	18	75
8-*Methyltetrahydro-*	1-Methyl-	18	70	6-Carboxytetrahydro-	3-Carboxy-	24	—
2-Methyltetrahydro-	2-Methyl-	18	75	6-Ethoxytetrahydro-	3-Ethoxy-	1	90
6-Methyltetrahydro-	3-Methyl-	18	50	9-Phenyltetrahydro-	9-Phenyl-	24	95
8-Chlorotetrahydro-	1-Chloro-	24	90				
7-Chlorotetrahydro-	2-Chloro-	23	80				
6-Chlorotetrahydro-	3-Chloro-	24	50				

Schmidt and Sigwart (*Ber.*, 1913, **46**, 1491) noted that dihydrocarbazole was partly oxidised by benzoquinone to carbazole, and that 9-methylhexahydrocarbazole reduced benzoquinone to quinol but did not investigate the matter further. We have found that benzoquinone did not oxidise tetrahydrocarbazole to any extent, but a considerable amount of tar was obtained.

Most of the carbazoles listed in the table have been previously prepared, but, with the preparation of 1-, 2-, and 4-bromo- and 2- and 4-nitro-carbazoles for the first time, all the isomeric monobromo- and mononitrocarbazoles are now known.

The apparently homogeneous compound, m. p. 154° (Borsche's compound), obtained when Fischer's indole synthesis is applied to *cyclo*hexanone-*m*-nitrophenylhydrazone (Borsche, Witte, and Bothe, *loc. cit.*; Perkin and Plant, *loc. cit.*), was shown by Plant (J., 1936, 899) to be a mixture of 5- and 7-nitrotetrahydrocarbazoles, though the 5-isomer was not isolated. We have found that the mixture can be separated into its isomers by chromatographic adsorption of a benzene solution on alumina, 5-nitrotetrahydrocarbazole, m. p. 155—156°, being obtained along with the known 7-isomer. Our results indicate that Borsche's compound is composed of equal weights of the two isomers, in contrast to Plant's conclusion (*loc. cit.*) that the ratio of 5- to 7-isomer was approximately 2 : 1. In support of our conclusion, we found that hot alcoholic solutions containing equal weights of the isomers on cooling deposit Borsche's compound almost quantitatively. In view of its homogeneous appearance under the microscope and its sharp m. p., which is not altered by crystallisation from various solvents, we regard Borsche's compound as an equimolecular compound of the two constituents.

Separation of the isomers gave two compounds, m. p. 171—172° and 155—156°. The former must be 7-nitrotetrahydrocarbazole (Plant, *loc. cit.*), and the latter consequently is the 5-isomer. Dehydrogenation of the isomers resulted in the preparation of 2- and 4-nitrocarbazoles, the former being identical with the dehydrogenation product of 7-nitrohexahydrocarbazole (Gurney, Perkin, and Plant, J., 1927, 1320; Plant, *loc. cit.*). It is noteworthy that, whereas hexahydrocarbazole is dehydrogenated completely in one hour, 7-nitrohexahydrocarbazole requires 19 hours.

Theoretically, 3-methyl*cyclo*hexanonephenylhydrazone can undergo cyclisation to give two isomeric methyltetrahydrocarbazoles, but the only product we were able to isolate was 2-methyltetrahydrocarbazole, which on dehydrogenation yielded 2-methylcarbazole. This confirms the orientation of the former compound (Borsche, Witte, and Bothe, *loc. cit.*).

It was shown by Plant and Wilson (J., 1939, 237) that *cyclo*hexanone-*m*-bromophenylhydrazone underwent ring closure to give a mixture of 5- and 7-bromotetrahydrocarbazoles, only the latter being isolated as a crystalline compound. We have obtained the former in crystalline form though analysis indicated that it was not quite pure. Pure 2- and 4-bromocarbazoles, however, were easily obtained by dehydrogenation. The structures of these compounds follow from those of 5- and 7-bromotetrahydrocarbazoles which were determined by Plant and Wilson (*loc. cit.*).

Tetrahydrocarbazolecarboxylic acids are dehydrogenated by chloranil to the corresponding carbazole acids in good yield; it is preferable, however, to use methyl or ethyl esters, as they are readily separated from the tetrachloroquinol formed during the reaction.

Hexahydrocarbazole was dehydrogenated by chloranil much more quickly than tetrahydrocarbazole—a somewhat unexpected result, for it is known that other forms of dehydrogenation, such as that with selenium, are not effective with fully reduced rings. Another unexpected result was the time required to dehydrogenate dihydrocarbazole (24 hours) in view of the ease with which it is oxidised by benzoquinone and other agents (Schmidt and Schall, *Ber.*, 1907, **40**, 3225; Schmidt and Sigwart, *loc. cit.*). The structure of this compound, however, has not been unequivocally determined and we are at present engaged upon this.

Experimental.

Unless otherwise stated, the preparation, purification, and properties of compounds are those given in the literature. The purity of compounds was checked by the sharpness of their m. p.'s on a Fuchs micro-m. p. apparatus (*Mikrochim. Acta*, 1937, **2**, 317); sublimation was also detected by means of this apparatus. Analyses were done by Drs. Weiler and Strauss, Oxford, and Mr. Macdonald, Heriot-Watt College, Edinburgh. Some of the picrates and phenylhydrazones decomposed in air and in consequence gave unsatisfactory analyses.

In all the chromatographic adsorption experiments, aluminium oxide (Brockmann) was used as adsorbent, benzene as solvent, and benzene (3 parts)–light petroleum (b. p. 100—120°, 1 part) as developer.

Except 3-ethoxy- and 1-nitro-carbazole, all the carbazoles give a strong greenish-blue colour with sulphuric acid and a drop of nitric acid.

Substituted Phenylhydrazines.—Many methods for the preparation of the required substituted phenylhydrazines were unsatisfactory. Reduction of the diazotised toluidines with sodium bisulphite gave excellent yields of the tolylhydrazines, but was valueless for the preparation of the halogenophenylhydrazines. The method finally adopted was the stannous chloride reduction of diazonium salts in a large excess of concentrated hydrochloric acid (see Bülow, *Ber.*, 1918, **51**, 404). Yields of pure phenylhydrazines: *o*-bromo-, 80; *p*-bromo-, 80; *m*-bromo-, 75; *o*-chloro-, 90; *m*-chloro-, 90; *o*-carboxy-, 60; *p*-carboxy-phenylhydrazine, 50%.

The phenylhydrazines were immediately converted into the corresponding hydrazones, as some of them decomposed on standing; some, however, *e.g.*, 2 : 5-dichlorophenylhydrazine, are stable provided they are not purified by crystallisation.

Considerable difficulty was encountered in the preparation of *p*-ethoxyphenylhydrazine. Hoshino and Takiuri's method (*Bull. Chem. Soc. Japan*, 1936, **11**, 218) gave very unsatisfactory results. The method finally adopted was the following, care being taken to avoid the excess of nitrous acid used by the Japanese workers. *p*-Phenetidine (17 g.) in dilute hydrochloric acid (200 c.c.) was added with stirring to cooled concentrated hydrochloric acid (320 c.c.). The resulting suspension was cooled to − 3° and diazotised with a solution of sodium nitrite (20 g. in 90 c.c. of solution)

until a definite positive starch–iodide test was obtained 5 minutes after the last drop of nitrite solution had been added (43 c.c. of solution : slight excess). The solution was cooled to — 5°, and a solution of stannous chloride (64 g. " A.R." in 80 c.c. of concentrated hydrochloric acid) run in with stirring so that the temperature never rose above + 3°. The mixture was then shaken thoroughly and kept for 3 hours in an ice mixture. The precipitate was filtered off, washed with saturated sodium chloride solution, then shaken with 300 c.c. of 2N-sodium hydroxide, extracted with ether, and the extract dried (sodium sulphate). On evaporation, plates were obtained (15 g.; 85%).

Phenylhydrazones.—Most of the phenylhydrazones were prepared by gently heating equimolecular mixtures of the phenylhydrazines and ketones either alone or in alcohol, but the hydrazino-benzoic acids gave the best results when shaken with a hot aqueous suspension of the ketone. cyclo*Hexanone*-2 : 5-*dichlorophenylhydrazone*, colourless prisms (methyl alcohol), m. p. 65° (Found : N, 10·9. $C_{12}H_{14}N_2Cl_2$ requires N, 10·9%).

Substituted Tetrahydrocarbazoles.—Cyclisation of the phenylhydrazones generally occurred readily on heating with ten times their weight of dilute sulphuric acid (1 : 9 by vol.), but purer products were obtained when the heating was omitted and the mixture merely shaken. On the other hand, *cyclo*hexanone-*o*-tolylhydrazone and -2 : 5-dichlorophenylhydrazone required 6 and 4½ hours' refluxing, respectively. The product obtained from treatment of the nitrophenylhydrazones often contained unchanged hydrazone, and if so it was ground to a fine powder and again treated with dilute sulphuric acid. *cyclo*Hexanone-2 : 4-dinitrophenylhydrazone could not be made to undergo ring closure. 6-Ethoxytetrahydrocarbazole was obtained as an oil by mixing *p*-ethoxyphenylhydrazine (15 g.) with *cyclo*hexanone (9·7 g.) and subsequent treatment with dilute sulphuric acid. The oil was dissolved in methyl alcohol, an equal volume of boiling water added, and the mixture allowed to cool. Crystals were then separated from the semi-solid mass, which on repeated treatment with methyl alcohol and boiling water gave more clean crystals. In all, 6 g. of 6-ethoxytetrahydrocarbazole were collected and crystallised from methyl alcohol in clean needle-prisms, m. p. 102—104° (lit. 105—106°).

5 : 8-*Dichlorotetrahydrocarbazole* was obtained with some difficulty in poor yield by the standard method and also by heating *cyclo*hexanone-2 : 5-dichlorophenylhydrazone with a mixture of equal weights of concentrated hydrochloric acid and alcohol; colourless square plates, m. p. 91—93°, by repeated precipitation of alcoholic solutions with water (Found : N, 5·9; Cl, 28·9. $C_{12}H_{11}NCl_2$ requires N, 5·8; Cl, 29·5%). 6-*Bromotetrahydrocarbazole picrate*, orange-red elongated prisms, m. p. 135°, decomposes in air (Found : N, 12·3. $C_{18}H_{15}O_7N_4Br$ requires N, 11·7%).

Chloranil Dehydrogenations.—1—2 G. of the substituted tetrahydrocarbazole, chloranil (exactly 2 mols.), and the minimum volume of boiling, sulphur-free xylene required to form a clear solution were refluxed until a few drops of the solution gave no red colour when heated with sodium hydroxide (1—24 hours, see table). The solution was then cooled, separated from tetrachloroquinol, diluted with ether, shaken first with sodium hydroxide and then with water, and finally dried (sodium sulphate). On evaporation of the solvents, the impure crystalline compound separated and was purified by crystallisation from methyl alcohol, benzene, or xylene; when this method failed, purification was effected by chromatographic adsorption. The resulting carbazoles were identified by their m. p.'s, mixed m. p.'s with authentic samples, picrates, coloration tests where possible, and in some cases by analysis.

Small quantities of yellow compounds which gave the characteristic " carbazole test " with sulphuric and nitric acids were isolated. They had high m. p.'s and might be dicarbazyls, but were not further investigated.

Nitrocarbazoles.—1-Nitrocarbazole, yellow-brown needles (alcohol), m. p. 185—187° (lit., 187°), sublimes in yellow prisms. 3-Nitrocarbazole, yellow crystals (xylene), m. p. 203—206° (lit. 213°). 7-Nitrohexahydrocarbazole on dehydrogenation gave 2-nitrocarbazole, which crystallised from benzene (twice) in yellow elongated prisms, m. p. 164—166°, undepressed in admixture with substance prepared as below.

A mixture of 5- and 7-nitrotetrahydrocarbazoles, obtained from *cyclo*hexanone-*m*-nitrophenylhydrazone, had m. p. 154—155° (Borsche's compound). It was invariably obtained in compact red or orange-red prisms from various solvents. In this way it differs from one of its components, 5-nitrotetrahydrocarbazole, m. p. 155—156° (see below), which crystallises from methyl alcohol in compact prisms, but from aqueous methyl alcohol in elongated prisms. The two compounds when mixed show a m. p. depression. When 4 mg. of each of 5- and 7-nitrotetrahydrocarbazoles were dissolved in the minimum volume of boiling alcohol, and the solution cooled, 6 mg. of compact red prisms separated, m. p. 154—155°, giving no depression when mixed with Borsche's compound.

Borsche's compound (3·2 g.) was resolved into its components by chromatography in benzene solution (300 c.c.) through a column, 30" × ½". Two distinct bands resulted, the upper layer orange-red, and the lower bright orange-yellow. The lower layer was completely washed through the column, and partial evaporation of the solvent gave 5-*nitrotetrahydrocarbazole* in orange-red, elongated prisms (1·40 g.), m. p. 155—156° (Found : C, 66·3; H, 5·75; N, 13·4. $C_{12}H_{12}O_2N_2$ requires C, 66·6; H, 5·6; N, 13·2%). Dehydrogenation gave 4-*nitrocarbazole*, orange prisms (benzene, charcoal), m. p. 179—180° (sublimes) (Found : C, 67·4; H, 3·71; N, 12·9. $C_{12}H_8O_2N_2$ requires C, 67·9; H, 3·8; N, 13·1%). The upper layer was extracted repeatedly with hot alcohol, the solution evaporated to 50 c.c., and 50 c.c. of hot water added. Orange, elongated prisms (1·40 g.) of 7-nitrotetrahydrocarbazole, m. p. 171—172°, separated on cooling. The compound, which can be crystallised from benzene, was oxidised to 2-*nitrocarbazole*, m. p. 165—166°, yellow plates (benzene, charcoal) (Found : C, 67·0; H, 3·79; N, 13·1%). A mixed m. p. with 7-nitrotetrahydrocarbazole showed a depression of 20°.

In a second experiment Borsche's compound (2·31 g.) was dehydrogenated for 25 hours. A product, m. p. 132—133° (60% yield), was obtained, 1·14 g. of which were dissolved in benzene (100 c.c.) and chromatographed (column 15" × ½") Two coloured bands resulted, the orange-yellow lower band being washed through the column. The compound obtained by evaporation of the solvent and recrystallisation from benzene was 4-nitrocarbazole (0·33 g.), m. p. and mixed m. p. with above sample 182—183° (Found : C, 67·4; H, 4·13%). The upper deep-orange layer was repeatedly extracted with methyl alcohol which, on evaporation to 50 c.c. and addition of boiling water (50 c.c.), gave 0·49 g. of crude 2-nitrocarbazole, m. p. 165—166° after recrystallisation from benzene : no m. p. depression when mixed with the dehydrogenation product of 7-nitrotetrahydrocarbazole. From the middle region in the column 0·21 g. of a mixture, m. p. 150—170°, was obtained, giving a total of 1·03 g. (90% recovery).

The four nitrocarbazoles give a bright red colour with methyl-alcoholic potassium hydroxide. With concentrated sulphuric acid 1-nitrocarbazole gives a bluish-black colour, and 3-nitrocarbazole a brilliant red.

Methylcarbazoles.—cyclo*Hexanone-o-tolylhydrazone*, crystallised from methyl alcohol, had m. p. 61—62° (Found : N, 10·0. $C_{13}H_{18}N_2$ requires N, 13·8%); it decomposes rapidly at room temperature. Proof of its constitution is afforded by its conversion into 8-*methyl*-1 : 2 : 3 : 4-*tetrahydrocarbazole*, colourless plates, m. p. 97—98° (Found : N, 7·3. $C_{13}H_{15}N$ requires N, 7·6%); *picrate*, chocolate-brown needles (after two crystallisations from methyl alcohol), m. p. 131—133° (Found : N, 15·1. $C_{19}H_{18}O_7N_4$ requires N, 13·5%), decomposing on standing. 1-Methylcarbazole formed colourless plates, m. p. 110—114° (lit., 120°), from light petroleum (b. p. 80—100°); picrate, m. p. 143° (lit. 143·5°).

6-Methyl-1 : 2 : 3 : 4-tetrahydrocarbazole was obtained in 50% yield when *cyclo*hexanone was shaken with *p*-tolylhydrazine hydrochloride and sodium acetate, there being presumably sufficient free acid to convert the intermediate tolylhydrazone into the tetrahydrocarbazole; m. p. 141—142° (Found : N, 7·75%). 3-Methylcarbazole, m. p. 199—202° (lit. 203°); picrate, red needles, m. p. 179—181° (lit. 180°).

3-Methyl*cyclo*hexanonephenylhydrazone (27 g.) was converted in the usual manner into a yellow oil which distilled at 180—200°/20 mm., forming a solid which crystallised from alcohol in white crystals (6 g.), m. p. 94° (lit. 98—100°). This was shown to be 2-methyl-1 : 2 : 3 : 4-tetrahydrocarbazole, since on dehydrogenation a good yield of 2-methylcarbazole, m. p. 259° (lit. 259°), was obtained (Found : C, 85·8; H, 5·8. Calc. for $C_{13}H_{11}N$: C, 86·2; H, 6·1%); picrate, bright orange-red, elongated prisms, m. p. 166° (lit. 167°). No 4-methyltetrahydrocarbazole was detected.

Bromocarbazoles.—3-Bromocarbazole, m. p. 201—202° (lit. 201°). 1-*Bromocarbazole*, from the semi-solid mass obtained by treatment of *cyclo*hexanone-*o*-bromophenylhydrazone and assumed to be 8-bromotetrahydrocarbazole, was purified by chromatographic adsorption and trituration with light petroleum; m. p. 111—112° (Found : Br, 32·2. $C_{12}H_8NBr$ requires Br, 32·5%).

The mixture of 5- and 7-bromotetrahydrocarbazoles, obtained by the method of Plant and Wilson (J., 1939, 237), was crystallised from alcohol, and the precipitate of the 7-isomer removed. The filtrate was evaporated to remove alcohol completely, and the resulting oil (2·8 g.) dissolved in benzene and chromatographed (18″ × ¾″ column). The eluate was collected in 50-c.c. fractions, and from the first three, plates separated which after one crystallisation from alcohol melted at 171—172° (lit. 183°) and were found to be impure 7-bromotetrahydrocarbazole. The 5-isomer is more strongly adsorbed on alumina and from the next three fractions nodules of crystals separated on partial evaporation. 5-*Bromotetrahydrocarbazole* was crystallised several times from alcohol (hexagonal prisms or plates) and once from benzene; m. p. 131—132° (Found : Br, 29·2. $C_{12}H_{12}NBr$ requires Br, 32·0%). On dehydrogenation 4-bromocarbazole was obtained (see below).

In a second experiment *cyclo*hexanone-*m*-bromophenylhydrazone (24 g.) was cyclised by gently warming it in a mixture of water (170 c.c.), alcohol (100 c.c.), and concentrated sulphuric acid (30 c.c.) until a clear solution resulted; 5·5 g. of crystalline 7-bromotetrahydrocarbazole, m. p. 150° (decomp.), were obtained, as shown by m. p. 178° after chromatographic adsorption and crystallisation from methanol–ethanol. The filtrate on treatment with a little water yielded first some of the 7-isomer (1 g.) and then an oil, which was dissolved in ether, washed with water, and dried (sodium sulphate). On evaporation, an oil (8·5 g.) separated, 2·88 g. of which were dehydrogenated and two-thirds of the xylene evaporated; 0·24 g. of 2-bromocarbazole was obtained, m. p. and mixed m. p. 247—248° (mixed m. p. depression with carbazole). The xylene filtrate was then evaporated to dryness, and the residue (2·10 g.) dissolved in benzene (25 c.c.) and chromatographed (column, 18″ × ¾″). Eight 30-c.c. fractions, each giving the carbazole colour test, were collected and evaporated. The first three fractions afforded small amounts of a high-melting, yellow product, and fractions 5—8 gave 1·17 g. of 4-*bromocarbazole*, which was purified by several recrystallisations from aqueous methyl alcohol; m. p. 104—105° (Found : Br, 33·2%). This is much more soluble in glacial acetic acid than is the 2-isomer. The original oil is clearly a mixture, with the 5-bromo-compound predominating.

2-*Bromocarbazole*, from 7-bromotetrahydrocarbazole, was obtained in colourless plates from glacial acetic acid, m. p. 250—251° (Found : Br, 32·4%).

Chlorocarbazoles.—3-Chlorocarbazole, glistening flakes (acetic acid), m. p. 199—200° (lit. 201·5°). 1-Chlorocarbazole, colourless plates from methyl alcohol or benzene, m. p. 109—110° (lit. 125°) (Found : Cl, 13·4. Calc. for $C_{12}H_8NCl$: Cl, 14·0%). 1 : 4-*Dichlorocarbazole*, purified by chromatographic adsorption and crystallisation from xylene; plates, m. p. 84—85° (Found : Cl, 29·3. $C_{12}H_7NCl_2$ requires Cl, 30·05%).

5- and 7-Chlorotetrahydrocarbazoles were obtained in the same way as the corresponding bromo-compounds (above). The former tetrahydrocarbazole could not be made to crystallise, but on dehydrogenation it yielded crystalline 4-chlorocarbazole, the m. p. of which, and also of the 2-chlorocarbazole (obtained by dehydrogenation of 7-chlorotetrahydrocarbazole), agree with those given by Moggridge and Plant (J., 1937, 1128).

Carbazole-carboxylic Acids.—Ethyl carbazole-3-carboxylate, needle prisms (benzene and light petroleum), m. p. 156—157° (lit. 165°), was hydrolysed to the acid, colourless plates (glacial acetic acid), m. p. 272—274° (lit. 276—278°). This acid was also obtained by dehydrogenation of tetrahydrocarbazole-6-carboxylic acid. *Ethyl carbazole-1-carboxylate*, m. p. 106—107° (Found : C, 74·8; H, 5·3. $C_{15}H_{13}O_2N$ requires C, 75·3; H, 5·5%), was hydrolysed to the acid, colourless prisms (glacial acetic acid, charcoal), m. p. 271—273° (lit. 270—271°), which sublimed in colourless needles.

3-Ethoxycarbazole (0·43 g.), m. p. 85—95°, was obtained with some difficulty from the tetrahydro-compound, and purified by chromatographic adsorption (column 7½″ × ½″) and then by crystallisation (50% methyl alcohol); m. p. 105—106° (lit. 106—107°) (Found : N, 6·4. Calc. for $C_{14}H_{13}ON$: N, 6·6%).

N-Phenyltetrahydrocarbazole, prepared from nitrosodiphenylamine by the method of Linnell and Perkin (J., 1924, **125**, 2451), was dehydrogenated to *N*-phenylcarbazole, which gave a deep bluish-green colour with sulphuric and nitric acids, perhaps owing to the presence of a trace of diphenylamine.

Thanks are due to the Moray Fund for a grant; to Mrs. Marjory Campbell, Mr. R. Gow, and Miss Ester Caplan for assistance in the experimental work; and to Dr. S. H. Tucker for kindly sending us specimens for mixed m. p. determinations.

THE UNIVERSITY, EDINBURGH. [*Received, April 16th*, 1945.]