797. *The Pyrolysis of Some Complex Urethanes.*

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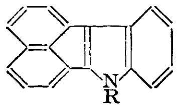
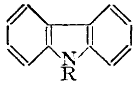
The products formed when the *N*-methoxycarbonyl and *N*-ethoxycarbonyl derivatives of carbazole, tetrahydrocarbazole, hexahydrocarbazole, and 1-naphthylamine are boiled under reflux at atmospheric pressure have been investigated. In the case of methyl carbazole-9-carboxylate the effect of the addition of various substances has been studied.

DUTHIE and PLANT (*J.*, 1952, 1899) found that when methyl acenaphthyleno(7′ : 8′-2 : 3)indole-1-carboxylate (I; R = CO_2Me) was heated for a few minutes at 300° it was largely decomposed to give, besides carbon dioxide, a substantial amount of 1-methylacenaphthyleno(7′ : 8′-2 : 3)indole (I; R = Me) and a little acenaphthyleno(7′ : 8′-2 : 3)-indole (I; R = H). The latter substance was formed almost quantitatively in the presence of an excess of 2-naphthylamine. This interesting pyrolytic process has now been explored with a number of other urethanes. When the closely related, but more readily accessible, methyl carbazole-9-carboxylate (II; R = CO_2Me) was refluxed at atmospheric pressure, it decomposed nearly quantitatively during 2 hr. into carbon dioxide and 9-methylcarbazole. In the presence of an excess of 1-naphthylamine, carbazole was obtained in excellent yield, but it was not possible to determine the fate of the methyl group. Refluxing with 2-naphthol again yielded carbazole, and some, but probably not all, of the methyl appeared as methyl 2-naphthyl ether. One of the mechanisms which may be adduced for the reaction can be represented as :


(I)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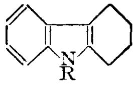
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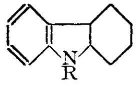
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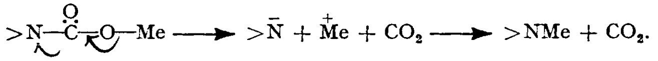

$$>\text{N}-\overset{\text{O}}{\text{C}}-\text{O}-\text{Me} \longrightarrow >\overset{-}{\text{N}} + \overset{+}{\text{Me}} + \text{CO}_2 \longrightarrow >\text{NMe} + \text{CO}_2.$$

With this in mind it seemed possible that the carbazolyl and methyl groups might add under these conditions to 1-naphthonitrile, which has a conveniently high boiling point, with the formation of an amidine, a reaction which would be somewhat reminiscent of that observed by Dyson and Hammick (*J.*, 1937, 1724) in the formation of alcohols by the decarboxylation of quinaldinic and related acids in the presence of some aldehydes and ketones. In fact, this reaction could not be effected, and the nitrile acted to some extent like the substances mentioned above, for both carbazole and 9-methylcarbazole were obtained from the product. A very substantial amount of carbazole was formed when the pyrolysis was carried out in the presence of 7 : 8-benzoquinoline (b. p. 338°), a convenient tertiary base of pyridine type, but with 1-nitronaphthalene the product was black and resinous, probably through the oxidising action of the nitro-compound at the high temperature involved.

Pyrolysis of methyl tetrahydrocarbazole-9-carboxylate (III; $R = CO_2Me$) proceeded rather differently. A considerable quantity of tetrahydrocarbazole was isolated from the product, but there was also much resin. With methyl hexahydrocarbazole-9-carboxylate (IV; $R = CO_2Me$) the pattern was more complex : carbon dioxide and methanol were evolved, and hexahydrocarbazole, 9-methylhexahydrocarbazole, and a resinous, non-basic fraction were formed.

Ethyl carbazole-9-carboxylate (II; $R = CO_2Et$) and ethyl tetrahydrocarbazole-9-carboxylate (III; $R = CO_2Et$) gave carbon dioxide, ethylene, and, almost quantitatively, carbazole and tetrahydrocarbazole respectively under similar conditions; but the process was again more complex when applied to ethyl hexahydrocarbazole-9-carboxylate (IV; $R = CO_2Et$), which gave carbon dioxide, ethylene, a little ethanol, hexahydrocarbazole, 9-ethylhexahydrocarbazole, and a non-basic resin.

All the above urethanes are derived from substances containing the secondary >NH group, and it seemed of interest to examine similar compounds from a primary amine. Methyl 1-naphthylcarbamate, $C_{10}H_7{\cdot}NH{\cdot}CO_2Me$, when refluxed for 3½ hr., gave a large proportion of methanol, but carbon dioxide was evolved and *NN'*-di-1-naphthylurea was isolated from the complex residue. No ethylene was detected when ethyl 1-naphthylcarbamate was pyrolysed under similar conditions, but the products were analogous to those obtained from the methyl ester. It seems probable that here a substantial amount of the urethane undergoes dissociation into the corresponding alcohol and *iso*cyanate, but the latter is involved in further complex changes. Such a simple dissociation is, of course, not possible in urethanes derived from secondary bases.

Mĕtayer (*Bull. Soc. chim.*, 1951, 802) found that some urethanes of the type $R{\cdot}NH{\cdot}CO_2Et$, on distillation at atmospheric pressure with or without the addition of Raney nickel, give ethanol and the corresponding *iso*cyanate, while urethanes of the type $RR'N{\cdot}CO_2Et$ are more stable and distil unchanged. The observations now described are not in conflict with those of Mĕtayer. It follows that many urethanes of fairly high boiling point distil essentially unchanged, but gradually decompose when boiled under reflux for some time.

EXPERIMENTAL

Methyl Carbazole-9-*carboxylate*.—Carbazole (3 g.) in hot acetone (45 c.c.) was added to potassium hydroxide (5·1 g.) in water (2·55 c.c.) and treated gradually, with vigorous shaking, with methyl chloroformate (8·7 g.). After dilution with water, the precipitated *methyl carbazole*-9-*carboxylate* separated from ethanol in colourless needles (2·1 g.), m. p. 77° (Found: C, 74·8; H, 4·6. $C_{14}H_{11}O_2N$ requires C, 74·7; H, 4·9%).

When this urethane (3 g.) was refluxed (b. p. 325°) in a long-necked distilling flask and the issuing gas passed through a water-cooled trap, no liquid was collected, but carbon dioxide was detected with lime-water. After 2 hr., the residue was submitted to fractional steam-distillation, and all the solid fractions were found to melt at, or near, 86°. The united material (2·3 g.) gave 9-methylcarbazole, colourless needles, m. p. 87—88° (from ethanol), not depressed by admixture with an authentic sample.

After a mixture of the urethane (0·5 g.) and 1-naphthylamine (3·5 g.) had been similarly refluxed for 1 hr., the cold product was powdered and extracted with very dilute hydrochloric acid until the solution no longer gave a precipitate with ammonia. The filtered solution of the residue in hot acetone was diluted with water, and the solid crystallised from acetone, from which carbazole (94%) separated in colourless plates, m. p. 240° (identified by mixed m. p.).

A mixture of the urethane (3 g.) and 2-naphthol (30 g.) was refluxed until evolution of carbon dioxide ceased (1¾ hr.) and the residue well shaken with aqueous sodium hydroxide (300 c.c. of 10%) and ether. When the material recovered from the ethereal layer was steam-distilled, the more volatile methyl 2-naphthyl ether (0·6 g.) was removed from carbazole (2·1 g.), both substances being identified by mixed m. p.

After a mixture of the urethane (2 g.) and 1-naphthonitrile (10 g.) had been refluxed for 3 hr., it deposited crystals of carbazole (0·3 g.) on cooling. These were filtered off, and the unchanged nitrile removed by distillation under reduced pressure. When the pasty residue was treated with methanol, a solid (0·48 g.), m. p. 82—84°, was obtained, and this gave almost colourless needles, m. p. 85° (from methanol), identified (mixed m. p.) as 9-methylcarbazole.

A mixture of the urethane (1 g.) and 7 : 8-benzoquinoline (10 g.) was refluxed for 1 hr. and all basic material extracted with dilute hydrochloric acid. The residue, m. p. 230°, was crystallised from acetone and shown to be carbazole (0·6 g.) by mixed m. p.

Methyl Tetrahydrocarbazole-9-*carboxylate*.—To avoid the presence of unchanged tetrahydrocarbazole in the product, not more than 80% of the theoretical amount of this substance must be used in the preparation of the urethane. Tetrahydrocarbazole (4·55 g.) was gradually added to ethylmagnesium iodide, prepared from magnesium (0·8 g.), ethyl iodide (5·3 g.), and ether (100 c.c.), and the whole warmed for a few minutes. After the gradual addition of methyl chloroformate (3·5 g.) in ether (15 c.c.), the mixture was left for 1 hr. and then treated with dilute hydrochloric acid. When the dried ethereal layer was fractionated, *methyl tetrahydrocarbazole*-9-*carboxylate* was collected at 210°/12 mm. as an almost colourless oil (2 g.) which solidified (m. p. 35°) (Found: C, 73·3; H, 6·5. $C_{14}H_{15}O_2N$ requires C, 73·4; H, 6·5%). All the samples of this urethane were analysed before pyrolysis to ensure the absence of significant amounts of tetrahydrocarbazole (Calc. for $C_{12}H_{13}N$: C, 84·2; H, 7·6%).

When this urethane (3 g.) was refluxed as described above, no liquid collected in the trap, but carbon dioxide was steadily evolved during 1½ hr. Several solid fractions, all melting in the range 105—112°, were collected on steam-distillation, and these, when united and crystallised from methanol, gave tetrahydrocarbazole (0·9 g.), m. p. 118° (identified by mixed m. p.), but there was a sticky black residue from which nothing pure could be obtained.

Methyl Hexahydrocarbazole-9-*carboxylate*.—Prepared like methyl carbazole-9-carboxylate, and in almost quantitative yield from the common *cis*-hexahydrocarbazole (m. p. 99°), the *urethane* separated from methanol in colourless plates, m. p. 68° (Found: C, 72·8; H, 7·6. $C_{14}H_{17}O_2N$ requires C, 72·7; H, 7·4%).

When this urethane (5 g.) was refluxed as before, carbon dioxide was evolved during 2 hr. and a colourless liquid (about 0·25 g.; b. p. 65°; shown to be methanol by conversion into its 3 : 5-dinitrobenzoate) was collected in the trap. After the residue had been resolved into basic and non-basic fractions by shaking with dilute hydrochloric acid and ether, the acid solution was made alkaline with aqueous sodium hydroxide. The basic product (about 1·6 g.) was collected in ether, dried ($MgSO_4$), recovered by evaporation of the solution, and shaken vigorously with aqueous potassium hydroxide (6 c.c. of 10%) and benzoyl chloride (1·02 g.), added in portions. The product, collected in ether, was extracted with dilute hydrochloric acid, and the ethereal solution, after being dried and evaporated, gave 9-benzoylhexahydrocarbazole

(0·9 g.) which crystallised from ethanol in colourless needles, m. p. 103°, identified by mixed m. p. with an authentic specimen (Gurney and Plant, *J.*, 1927, 1314). The last-named acid solution was made alkaline and the basic product taken up in ether. After this extract had been dried and evaporated, the residue was refluxed for 15 min. with four times its volume of methyl iodide, and the excess of this reagent distilled off. When the solid had been crystallised from ethanol, it melted at 191° (decomp.) and was identified as the methiodide of 9-methylhexahydrocarbazole (0·81 g.) by comparison with an authentic specimen (compare Schmidt and Sigwart, *Ber.*, 1912, **45**, 1784; von Braun and Ritter, *Ber.*, 1922, **55**, 3795). This method of analysis was developed with known mixtures of hexahydrocarbazole and its 9-methyl derivative, and the amounts of the substances obtained above indicated the presence of 1 g. of the former and 0·6 g. of the latter in the pyrolysis product. The ethereal solution of the non-basic portion (2·5 g.) of the pyrolysis product was dried and evaporated, but nothing pure could be obtained from the residue.

Ethyl Carbazole-9-carboxylate.—A method similar to that described above for the corresponding methyl ester was found to be more convenient for the preparation of this urethane, colourless needles, m. p. 75—76° (from ethanol) (Found: C, 75·2; H, 5·3. Calc. for $C_{15}H_{13}O_2N$: C, 75·3; H, 5·4%), than those given in the literature (Oddo, *Gazzetta*, 1911, **41**, 256; U.S.P. 2,089,985, *Chem. Zentr.*, 1938, i, 937).

The urethane (3 g.) was refluxed in a long-necked distillation flask and the gaseous products passed first through a water-cooled trap, then through two bottles containing bromine (a total of 3·9 g.) under water, and finally through lime-water. Nothing collected in the trap, but the lime-water showed a steady evolution of carbon dioxide during 2 hr. The contents of the bottles containing bromine were shaken with aqueous sodium hydroxide and the oily layer (2 g., b. p. 130°) identified as ethylene dibromide by heating it with thiourea in ethanol, conversion into the corresponding *S*-alkyl*iso*thiouronium picrate, m. p. 260° (decomp.), and comparison with an authentic specimen (Brown and Campbell, *J.*, 1937, 1699). When the residue was crystallised from acetone, carbazole, m. p. 235° (identified by mixed m. p.), was obtained in almost quantitative yield.

Ethyl Tetrahydrocarbazole-9-carboxylate.—This substance was prepared by a process similar to that used for methyl carbazole-9-carboxylate and identified (mixed m. p.) with the compound obtained less conveniently by the method of Perkin and Plant (*J.*, 1923, **123**, 676). The urethane (1 g.) was refluxed for 1½ hr. as described for ethyl carbazole-9-carboxylate with very similar results. The residue (0·65 g.) melted at 105—109° (after softening from 70°), and, when crystallised from ethanol, gave tetrahydrocarbazole, m. p. 116° (identified by mixed m. p.).

Ethyl Hexahydrocarbazole-9-carboxylate.—Prepared like the corresponding methyl ester, this *urethane* separated from ethanol in colourless plates, m. p. 42° (Found: N, 5·6. $C_{15}H_{19}O_2N$ requires N, 5·7%).

The substance (5 g.) was refluxed as described for ethyl carbazole-9-carboxylate. Carbon dioxide and ethylene, collected as ethylene dibromide (2·4 g.), were evolved during 2 hr., and ethanol (0·12 g.), identified as its 3 : 5-dinitrobenzoate, condensed in the trap. The residue was resolved into a basic and a non-basic portion and these were examined as described for the pyrolysis of methyl hexahydrocarbazole-9-carboxylate. 9-Benzoylhexahydrocarbazole (1·25 g.) and 9-ethylhexahydrocarbazole methiodide [0·6 g.; m. p. 190° (decomp.)], identical with the substance described below, were obtained. Application of this method of analysis to known mixtures of hexahydrocarbazole and its 9-ethyl derivative showed that these observations corresponded with the presence of 1·3 g. of the former and 0·45 g. of the latter in the pyrolysis product. Nothing pure could be obtained from the non-basic portion (2·5 g.).

9-*Ethylhexahydrocarbazole.*—After a mixture of *N*-ethyl-*N*-phenylhydrazine (60 g.) and *cyclo*hexanone (64 g.) had been warmed on the steam-bath for a few minutes, sulphuric acid (500 c.c. of 10%) was added, and the whole boiled for a short time. When the benzene solution of the oily product was dried and fractionated, 9-ethyltetrahydrocarbazole (50 g.), b. p. 188°/17 mm., was collected as a pale yellow liquid (Found: C, 84·5; H, 8·4. Calc. for $C_{14}H_{17}N$: C, 84·4; H, 8·5%). It has previously been obtained as a product of the catalytic hydrogenation of 9-ethylcarbazole (von Braun and Ritter, *loc. cit.*; Adkins and Coonradt, *J. Amer. Chem. Soc.*, 1941, **63**, 1563) and by the action of ethylaniline on 2-chloro*cyclo*hexanone (D.R.-P., 374,098; *Chem. Zentr.*, 1923, iv, 724). A mixture of this substance (47 g.), ethanol (94 c.c.), concentrated hydrochloric acid (94 c.c.), and granulated tin (94 g.) was refluxed for 3 hr. and then filtered, and the ethanol distilled from the filtrate. After being made alkaline with aqueous sodium hydroxide, the volatile material was removed in steam, and the distillate acidified, and shaken with ether to remove unchanged 9-ethyltetrahydrocarbazole. The aqueous solution was made alkaline, the product extracted with ether, and the extract dried (K_2CO_3) and fractionated. 9-Ethylhexahydrocarbazole was collected as a colourless oil (39 g.), b. p. 146°/10 mm. (294°/753 mm.) (Found : C, 83·7; H, 9·6. Calc. for $C_{14}H_{19}N$: C, 83·6; H, 9·5%). One of the values given by von Braun and Ritter (*loc. cit.*) for the b. p. of this substance (155—157°/8 mm.; 292—293°/749 mm.) is not in good agreement with the above.

After the base had been refluxed for 15 min. with excess of methyl iodide and the volatile material removed, the methiodide was obtained from ethanol in colourless plates, m. p. 190° (decomp.) (fairly rapid heating) (Found : C, 52·9; H, 6·3. Calc. for $C_{15}H_{22}NI$: C, 52·5; H, 6·4%). Much lower values for the m. p. of this methiodide were obtained on slow heating, and von Braun and Ritter (*loc. cit.*) give m. p. 174°.

Pyrolysis of Methyl and Ethyl 1-*Naphthylcarbamate.*—When the former urethane (10 g.) was refluxed as described for methyl carbazole-9-carboxylate, the liquid (1·2 g.) which collected in the trap boiled completely at 66° and was shown to be methanol by conversion into its 3 : 5-dinitrobenzoate. Carbon dioxide was evolved during 3½ hr., and a considerable amount of sublimate appeared in the reaction flask. After the latter had been crystallised from *cyclo*hexanone, it melted at 286° and was shown to be *NN'*-di-1-naphthylurea (0·3 g.) by mixed m. p. with an authentic specimen, but no other pure substance could be isolated from the residue.

The corresponding ethyl ester (10 g.), on pyrolysis under similar conditions, gave no ethylene, but carbon dioxide was evolved during 4 hr., and the whole of the liquid (1·5 g.) which collected in the trap boiled at 78° and was shown to be ethanol by conversion into its 3 : 5-dinitrobenzoate. The only pure substance isolated from the residue was *NN'*-di-1-naphthylurea (0·25 g.), which sublimed as before. With neither urethane was it possible to detect the presence of 1-naphthyl *iso*cyanate by extraction of the reaction mixture with petroleum (b. p. 80—100°).

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