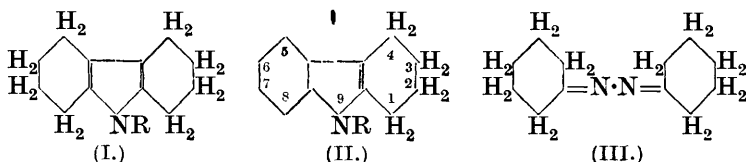


CCVI.—*The Structures of the Octahydrocarbazoles.*

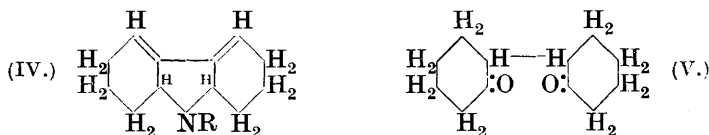
By SYDNEY GLENN PRESTON PLANT.

A FEW years ago, von Braun and Ritter (*Ber.*, 1922, **55**, 3792) claimed to have prepared 9-methyl- and 9-ethyl-1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-octahydrocarbazole (I) by the catalytic hydrogenation under very vigorous conditions of the corresponding alkylcarbazoles, a process which was believed to involve the intermediate formation of the

9-alkyltetrahydrocarbazoles (II). A little later, Perkin and Plant (J., 1924, 125, 1503) claimed to have obtained 1:2:3:4:5:6:7:8-octahydrocarbazole (I; R = H) by the removal of ammonia from



cyclohexylideneazine (III), a reaction which was thought to be analogous to that described by Robinson and Robinson (J., 1918, 113, 639) for the synthesis of tetraphenylpyrrole, but, on alkylation of the product, methyl and ethyl derivatives were isolated which were undoubtedly different from the compounds of the first authors. Furthermore, the two series of octahydro-derivatives each yielded a different series of decahydro-compounds, and it became apparent that these alternative reactions had given rise to isomeric products which differed in the positions of the double linkages. From the methods of preparation employed, Perkin and Plant (see also J., 1925, 127, 1138) assigned the symmetrical structure (I) to their products and suggested alternative constitutions for those of von Braun and Ritter. These views were not accepted by von Braun and his co-workers (*Ber.*, 1925, 58, 389, 2156), who, among other things, submitted 6:9-dimethyl- and 3:9-dimethyl-tetrahydrocarbazole (see formula II) to catalytic hydrogenation, but under vigorous conditions, and obtained the same dimethyloctahydrocarbazole in each case, and suggested the formula (IV) for the compounds of Perkin and Plant.



A consideration of the known facts makes it clear, however, that the evidence is not really conclusive, and it seemed desirable to settle some of the questions involved by the preparation of the 9-alkyl-1:2:3:4:5:6:7:8-octahydrocarbazoles by a procedure which can leave no doubt concerning their constitution. For this purpose the well-known method of synthesising pyrroles by the action of amines on 1:4-diketones was employed. 2:2'-*Diketodicyclohexyl* (V), apparently hitherto unknown, was prepared by hydrolysis of the *ester* obtained from the interaction of 2-bromocyclohexanone with the sodium derivative of ethyl cyclohexanone-2-carboxylate,

and, on treatment with methylamine in glacial acetic acid, it yielded 9-methyl-1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-octahydrocarbazole (I; R = Me). The product melted at 94°, failed to give a picrate or methiodide, and, on reduction with tin and hydrochloric acid, gave an oily decahydro-compound, the picrate of which melted at 165°. The corresponding 9-ethyl derivative (I; R = Et) melted at 42.5° and gave an oily decahydro-compound, the picrate of which melted at 130°. Reference to the properties of the various products previously described makes it quite certain that the claim of von Braun and his co-workers is correct. It is thus apparent that the elimination of ammonia from *cyclohexylideneazine* has not proceeded along the lines expected. It is, however, extremely unlikely that this reaction can lead to other than a symmetrical structure, and, of the possible alternatives, that suggested by von Braun (formula IV) must be considered to be the most probable. No such alternative course is possible during the synthesis of tetraphenylpyrrole from phenyl benzyl ketazine.

The action of 10% potassium hydroxide solution on ethyl 2 : 2'-diketodicyclohexyl-1-carboxylate has been found to give not only 2 : 2'-diketodicyclohexyl; from the alkaline solution, an *acid* was isolated which, on analysis, was found to have the formula $C_{12}H_{20}O_3$. The nature of this product is under investigation.

EXPERIMENTAL.

The method of Kötze (*Annalen*, 1908, **358**, 195) for the preparation of 2-bromocyclohexanone requires considerable time, and bromination is liable to cease at the temperature used. The following procedure is more convenient when considerable quantities are required, although the yield is somewhat diminished. A mixture of cyclohexanone (60 g.), water (40 c.c.), and precipitated chalk (30 g.) was stirred continuously, and bromine (32 c.c.) was added at such a rate that the temperature remained at 50°. The product was extracted with ether, the solution dried over sodium sulphate, the solvent removed under reduced pressure, and the residual liquid distilled, 2-bromocyclohexanone (40 g.) being collected at 95—115°/22 mm.

2 : 2'-Diketodicyclohexyl.—A suspension of sodium (5.2 g., previously pulverised under boiling toluene) in dry ether (200 c.c.) was treated with ethyl cyclohexanone-2-carboxylate (40 g., prepared as described by Kötze and Michels, *Annalen*, 1906, **350**, 210; 1908, **358**, 198); the formation of the sodium derivative of the latter substance proceeded steadily and was complete after 3 hours. After the addition of 2-bromocyclohexanone (40 g.), the mixture was boiled under reflux for 5 hours and then shaken with water.

The ethereal solution was dried over sodium sulphate, the solvent removed, and the residual liquid submitted to distillation; after a fraction had been collected at 100—120°/20 mm., ethyl 2 : 2'-diketodicyclohexyl-1-carboxylate was obtained at 190—210°/20 mm. as a pale yellow oil. This ester was treated with boiling aqueous potassium hydroxide (200 c.c. of 10%) for 5 hours, the oily product extracted with ether, and the ethereal solution dried over sodium sulphate. After the removal of the ether, the residue was distilled, 2 : 2'-diketodicyclohexyl being collected as a colourless liquid, b. p. 174—177°/25 mm. It rapidly solidified, and, on crystallisation from light petroleum, was obtained in colourless plates, m. p. 70—71° (Found : C, 74.2; H, 9.3. $C_{12}H_{18}O_2$ requires C, 74.2; H, 9.3%).

The alkaline solution from the hydrolysis of the ester was acidified with hydrochloric acid, and an oily product was extracted with ether. After this solution had been dried with sodium sulphate and the solvent removed, the residual liquid was distilled. The main quantity boiled at 203—206°/13 mm., and solidified on cooling; after crystallisation from light petroleum (charcoal), an acid was obtained in long colourless needles, m. p. 41° (Found : C, 68.0; H, 9.5. $C_{12}H_{20}O_3$ requires C, 67.9; H, 9.4%). This acid was readily soluble in aqueous sodium carbonate and was reprecipitated on the addition of hydrochloric acid.

9-Methyl-1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-octahydrocarbazole. — The diketone (1 g.) was treated with acetic acid (10 c.c.) in which methylamine (1.6 g.) had been dissolved, and the whole was boiled under reflux for 2 hours. The solution rapidly became deep green, but the colour changed to brown after 15 minutes. After the mixture had been made alkaline with aqueous sodium hydroxide, the product was obtained as a solid, and, on crystallisation from methyl alcohol, it was isolated in colourless plates, m. p. 94° (Found : C, 82.6; H, 10.1. Calc. : C, 82.5; H, 10.1%). It was readily soluble in 20% hydrochloric acid, from which it was reprecipitated on the addition of sodium hydroxide. An attempt to prepare a picrate from cold toluene solution was unsuccessful, the liquid rapidly becoming dark green and depositing a sticky green product, on keeping; furthermore, no methiodide could be obtained (compare von Braun and Ritter, *loc. cit.*).

When 9-methyl-1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-octahydrocarbazole was reduced by the action of tin and boiling 20% hydrochloric acid for several hours, an oily hydrochloride separated. The mixture was made alkaline with potassium hydroxide and extracted with ether; from the extract, dried over potassium carbonate, a colourless oil was obtained which, when treated with picric acid in hot alcohol, yielded a picrate in yellow prisms, m. p. 165°. A mixture of this

picrate with that (m. p. 162—163°) of the methyldecahydrocarbazole described by Perkin and Plant (*loc. cit.*) melted at 133—135°.

9-*Ethyl-1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-octahydrocarbazole*.—Prepared by a process analogous to that used for the corresponding methyl derivative, this product separated first as an oil, which was then extracted with ether and subsequently distilled under reduced pressure. After crystallisation from methyl alcohol, it was finally isolated in colourless plates, m. p. 42·5° (Found : C, 83·1; H, 10·5. Calc. : C, 82·8; H, 10·3%). When reduced in the same way as the methyl compound, it yielded an oily base, the picrate of which crystallised from alcohol and melted at 130°.

THE DYSON PERRINS LABORATORY,
OXFORD.

[Received, June 11th, 1930.]
