# CCXXXIX.—*Derivatives of* 7 : 8 : 9 : 10-*Tetrahydro-αβ-naphthacarbazole and of* 8 : 9 : 10 : 11-*Tetrahydro-α′β′-naphthacarbazole.*

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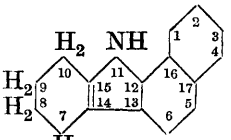
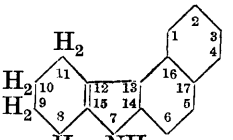
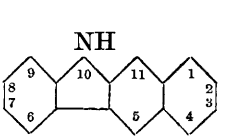
The reactions observed with tetrahydrocarbazole and its 9-acyl derivatives, especially those with nitric acid which involve the addition of OH and $NO_2$ or OH and OH to the double linkage (Perkin and Plant, J., 1921, **119**, 1825; 1923, **123**, 676), made it probable that the investigation of 7 : 8 : 9 : 10-tetrahydro-αβ-naphthacarbazole (I) and 8 : 9 : 10 : 11-tetrahydro-α′β′-naphtha-

carbazole (II) along similar lines would present many interesting points.


(I.)


(II.)


(III.)

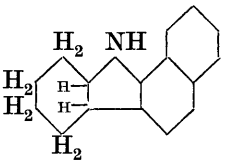
These two compounds (named $\Delta^{1(6)}$-tetrahydrobenzo-α- and -β-naphthindole) have already been prepared by Borsche, Witte, and Bothe (*Annalen*, 1908, **359**, 64) from *cyclo*hexanone-α- and -β-naphthylhydrazone respectively, and these authors have established the constitution of (I) by oxidising it to αβ-naphthacarbazole with lead oxide. There could be no reasonable doubt concerning the structure of (II), but it has now been confirmed by dehydrogenation with sulphur to α′β′-naphthacarbazole, thus disposing of the alternative ββ-naphthacarbazole skeleton (III).

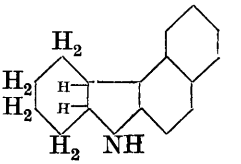
Attempts to acetylate 7 : 8 : 9 : 10-tetrahydro-αβ-naphthacarbazole directly with acetic anhydride failed, but the action of acetyl chloride on magnesium 11-7 : 8 : 9 : 10-tetrahydro-αβ-naphthacarbazyl bromide yielded 11-*acetyl*-7 : 8 : 9 : 10-*tetrahydro*-αβ-*naphthacarbazole*. The 11-*benzoyl* compound was similarly obtained. An investigation of the action of nitric acid on 7 : 8 : 9 : 10-tetrahydro-αβ-naphthacarbazole and its acetyl and benzoyl derivatives has yielded no crystalline substance, with the exception of a *trinitro*-derivative from the benzoyl compound.

The action of hot acetic anhydride on 8 : 9 : 10 : 11-tetrahydro-α′β′-naphthacarbazole in the presence of a few drops of concentrated sulphuric acid gives first 7-*acetyl*-8 : 9 : 10 : 11-*tetrahydro*-α′β′-*naphthacarbazole*, but a *diacetyl* derivative is soon formed in which one of the acetyl groups must be attached to carbon and the other to nitrogen. On boiling with aqueous-alcoholic potassium hydroxide, the acetyl group attached to nitrogen is removed with the production of C-*monoacetyl*-8 : 9 : 10 : 11-*tetrahydro*-α′β′-*naphthacarbazole*, the nature of which is confirmed by the fact that it gives an *oxime*. The point of attachment of the *C*-acetyl group has not been determined. 7-*Acetyl*- and 7-*benzoyl*-8 : 9 : 10 : 11-*tetrahydro*-α′β′-*naphthacarbazole* can be most conveniently obtained by means of the Grignard reaction in processes similar to those used for the isomeric derivatives of αβ-naphthacarbazole. From the product of the action of nitric acid in glacial acetic acid solution on each of these acyl derivatives of (II), a *mononitro*-derivative has been isolated, but from none of the acyl derivatives studied in the naphthacarbazole

series have products formed by the addition of OH and $NO_2$ or OH and OH to the double linkage been isolated. It is not possible to state definitely that such reactions do not occur, since in many experiments a considerable portion of the product could not be crystallised nor its nature determined.

Compounds (I) and (II) have been reduced to 7 : 8 : 9 : 10 : 14 : 15-*hexahydro-αβ-naphthacarbazole* (IV) and 8 : 9 : 10 : 11 : 12 : 15-*hexahydro-α'β'-naphthacarbazole* (V) respectively. Theoretically

(IV.) 

 (V.)

each of these hexahydro-derivatives should exist in two stereoisomeric forms (*cis-* and *trans-*) analogous to the two forms of hexahydrocarbazole (Gurney, Perkin, and Plant, J., 1927, 2676), but the formation of the *trans*-modification in other than very small quantities in each case is not to be expected on account of the much greater strain in these configurations. Therefore the two hexahydronaphthacarbazoles here described almost certainly have the *cis*-configurations (IV and V). The former can be prepared by the electrolytic reduction of the corresponding tetrahydro-compound, but a similar method for (V) gave a very poor yield, hydriodic acid and phosphorus being used finally for the reduction.

## EXPERIMENTAL.

7 : 8 : 9 : 10-*Tetrahydro-αβ-naphthacarbazole* (I).—α-Naphthylhydrazine hydrochloride, prepared from α-naphthylamine (100 g.) by the method of Fischer (*Annalen*, 1886, **232**, 236), was mixed with alcohol (1000 c.c.) and shaken for a short time at 50—60° with crystallised sodium acetate (80 g.); *cyclo*hexanone (60 c.c.) was then added and, after ½ hour, the solution was diluted with water (2000 c.c.). The hydrazone separated as a sticky mass which was washed with water and warmed with 1100 c.c. of 14% sulphuric acid (by vol.); the compound (I) then separated in good yield. It was recrystallised from glacial acetic acid and obtained in colourless needles, m. p. 139—140° (compare Borsche, Witte, and Bothe, *loc. cit.*). It can also be obtained by boiling the alcoholic mixture of crude α-naphthylhydrazine hydrochloride, sodium acetate, and *cyclo*hexanone. The product soon begins to separate, and can be isolated in a pure condition by adding an equal volume of water and cooling the mixture. Its *picrate* separates from benzene in very dark brown prisms, m. p. 172° (decomp.). All attempts to

nitrate the compound (I) in either acetic acid or sulphuric acid solution failed to yield any crystalline substance.

*Oxidation of 7 : 8 : 9 : 10-Tetrahydro-αβ-naphthacarbazole.*—A mixture of this compound (6·8 g.), sulphur (2 g.), and quinoline (20 c.c.) was boiled for 45 minutes, cooled, and poured into a mixture of ice and dilute hydrochloric acid. The sticky product was washed with dilute hydrochloric acid, dried, mixed with a little iron filings, and distilled. The αβ-naphthacarbazole obtained crystallised from benzene–petroleum in colourless needles, m. p. 225—226°. It dissolved in concentrated sulphuric acid to give a yellow solution, which changed to a dark green on the addition of a drop of concentrated nitric acid. There is no doubt that this product is identical with the αβ-naphthacarbazole previously described (compare, *e.g.*, Japp and Maitland, J., 1903, **83**, 267; Borsche, Witte, and Bothe, *loc. cit.*; Bucherer and Schmidt, *J. pr. Chem.*, 1909, **79**, 384).

*11-Acetyl-7 : 8 : 9 : 10-tetrahydro-αβ-naphthacarbazole.*—Magnesium (4·8 g.) was dissolved in a mixture of ethyl bromide (16 c.c.) and ether (150 c.c.). When a solution of the compound (I) (25 g.) in dry ether was slowly added, a brisk evolution of ethane occurred and a dark oil separated. The mixture was treated gradually with acetyl chloride (15 c.c.), warmed on the water-bath for a few minutes, and then cautiously treated with ice and dilute hydrochloric acid. The whole was extracted with more ether, and the extract was washed with aqueous sodium carbonate and dried over potassium carbonate. After removal of the solvent, the residue was crystallised from glacial acetic acid or methyl alcohol, from which *11-acetyl-7 : 8 : 9 : 10-tetrahydro-αβ-naphthacarbazole* separated in colourless needles, m. p. 125° (Found : N, 5·2. $C_{18}H_{17}ON$ requires N, 5·3%). This acetyl derivative is slightly soluble in cold ether and alcohol, readily soluble in benzene, and practically insoluble in petroleum.

*11-Benzoyl-7 : 8 : 9 : 10-tetrahydro-αβ-naphthacarbazole* was prepared similarly, benzoyl chloride being used in place of acetyl chloride. The crude product was a dark yellow syrup, which crystallised on treatment with glacial acetic acid, and after recrystallisation from petroleum (b. p. 100—120°) *11-benzoyl-7 : 8 : 9 : 10-tetrahydro-αβ-naphthacarbazole* separated in short, yellow needles, m. p. 146—147° (Found : N, 4·3. $C_{23}H_{19}ON$ requires N, 4·3%).

When a solution of the benzoyl derivative (1 g.) in glacial acetic acid (10 c.c.) at 95° was treated with nitric acid (5 c.c. of *d* 1·4), left at 100° for ½ hour, and then kept over-night, *trinitro-11-benzoyl-7 : 8 : 9 : 10-tetrahydro-αβ-naphthacarbazole* separated; after recrystallisation from acetone, it was obtained in yellow needles, m. p. 255° (decomp.) (Found : C, 60·8; H, 3·3; N, 12·2. $C_{23}H_{16}O_7N_4$

requires C, 60·0; H, 3·5; N, 12·2%). Attempts to control this reaction in order to isolate simpler products yielded no crystalline material.

7 : 8 : 9 : 10 : 14 : 15-*Hexahydro*-αβ-*naphthacarbazole*.—A solution of the compound (I) (10 g.) in a mixture of sulphuric acid (100 c.c. of *d* 1·5) and alcohol (100 c.c.) at 80° was submitted to electrolytic reduction during 20 hours, lead electrodes and a current of 5 amps. (0·03 amp. per sq. cm. of cathode) being used. The mixture was diluted with water (300 c.c.), filtered, and made alkaline with concentrated aqueous ammonia. Ether extracted an oil which solidified when left in contact with petroleum. On recrystallisation from a small quantity of methyl alcohol, 7 : 8 : 9 : 10 : 14 : 15-*hexahydro*-αβ-*naphthacarbazole* was obtained in colourless needles, m. p. 88° (Found: C, 86·2; H, 7·7. $C_{16}H_{17}N$ requires C, 86·1; H, 7·6%). The base soon develops a mauve colour on exposure to the air, is readily soluble in ether with a blue fluorescence, and gives with mineral acids salts which are only slightly soluble in water.

A solution of the base (2·2 g.) in glacial acetic acid (7 c.c.), after being treated with concentrated nitric acid (2 c.c., previously treated with urea nitrate) dissolved in acetic acid (3 c.c.), was diluted with water (10 c.c), and made alkaline with ammonia. Ether extracted a syrup which was crystallised from alcohol, *dinitro*-7 : 8 : 9 : 10 : 14 : 15-*hexahydro*-αβ-*naphthacarbazole* separating in small, yellow needles, m. p. 139—140° (Found: N, 13·6. $C_{16}H_{15}O_4N_3$ requires N, 13·4%).

11-*Acetyl*-7 : 8 : 9 : 10 : 14 : 15-*hexahydro*-αβ-*naphthacarbazole*.—A mixture of 7 : 8 : 9 : 10 : 14 : 15-hexahydro-αβ-naphthacarbazole (2 g.) and acetic anhydride (10 c.c.) was boiled for 5 minutes, allowed to cool, diluted with water, and left over-night. The product crystallised from a small quantity of petroleum (b. p. 80—100°) in long, colourless needles, m. p. 132° (Found: N, 5·3. $C_{18}H_{19}ON$ requires N, 5·3%).

11-*Benzoyl*-7 : 8 : 9 : 10 : 14 : 15-*hexahydro*-αβ-*naphthacarbazole*.—The base (5 g.) was shaken with aqueous sodium hydroxide and benzoyl chloride (6 g.). The product separated as a crystalline mass and after recrystallisation from methyl alcohol was obtained in colourless needles, m. p. 148—149° (Found: N, 4·3. $C_{23}H_{21}ON$ requires N, 4·3%).

8 : 9 : 10 : 11-*Tetrahydro*-α′β′-*naphthacarbazole* (II).—This substance was obtained by a process similar to that described for compound (I) but using β-naphthylhydrazine hydrochloride. It separated from glacial acetic acid in colourless prisms, m. p. 137° (Found: C, 86·9; H, 7·0. Calc.: C, 86·9; H, 6·8%). Borsche, Witte, and Bothe (*loc. cit.*) give the m. p. 152°. When equal

quantities of the compound (II) and picric acid were mixed in hot alcohol, the solution filtered and allowed to cool, the *picrate* separated in black needles, m. p. 194° (decomp.). Attempts to nitrate the compound (II) yielded nothing crystalline.

*Oxidation of* 8 : 9 : 10 : 11-*Tetrahydro-α′β′-naphthacarbazole.*—This was carried out as described on p. 1843. The semi-solid distillate was dissolved in toluene and the solution was dried over calcium chloride, filtered, and treated with a toluene solution of picric acid. The crimson picrate, m. p. 165—168°, which separated was decomposed by grinding with dilute aqueous sodium hydroxide, and the product was dried and recrystallised from benzene–petroleum; α′β′-naphthacarbazole then separated in colourless plates, m. p. 134—135° (Found: C, 88·7; H, 5·1. Calc.: C, 88·5; H, 5·1%). The mixture with compound (II) melted completely below 110°. α′β′-Naphthacarbazole, prepared in this way, dissolved in concentrated sulphuric acid to give a yellowish-brown solution which turned yellowish-green on addition of a drop of concentrated nitric acid (compare Ullmann, *Annalen*, 1904, **332**, 102), and gave a picrate which separated from toluene in crimson plates, m. p. 175° (compare Japp and Maitland, *loc. cit.*). There can be no doubt, therefore, that this product is identical with the α′β′-naphthacarbazole previously described. The isomeric ββ′-naphthacarbazole melts at 330° (Graebe and Knecht, *Annalen*, 1880, **202**, 1).

*Acetyl Derivatives of* 8 : 9 : 10 : 11-*Tetrahydro-α′β′-naphthacarbazole.*—Boiling acetic anhydride alone has no action on the compound (II). When, however, the substance (10 g.) was boiled for 45 minutes with acetic anhydride (60 c.c.) containing a few drops of concentrated sulphuric acid, a dark green solid separated. After recrystallisation from glacial acetic acid containing some charcoal, a C-*acetyl*-7-*acetyl*-8 : 9 : 10 : 11-*tetrahydro*-α′β′-*naphthacarbazole* separated in greenish-yellow prisms, m. p. 185° (Found: C, 78·8; H, 6·2; N, 4·7. $C_{20}H_{19}O_2N$ requires C, 78·7; H, 6·2; N, 4·6%). This diacetyl derivative (4 g.) was heated on the water-bath for ½ hour with potassium hydroxide (8 g.) dissolved in aqueous alcohol, the alcohol distilled off, and the residue treated with water; C-*acetyl*-8 : 9 : 10 : 11-*tetrahydro-α′β′-naphthacarbazole* then remained and after crystallisation from alcohol was obtained in yellow plates, m. p. 213° (Found: N, 5·2. $C_{18}H_{17}ON$ requires N, 5·3%). This regenerated the diacetyl compound (m. p. 185°) when treated with acetic anhydride and a drop of concentrated sulphuric acid on the water-bath, and when boiled for an hour with an excess of hydroxylamine hydrochloride and sodium acetate in alcohol, yielded an *oxime* which crystallised from aqueous alcohol in pale yellow plates, m. p. 213—216° (Found: N, 10·2. $C_{18}H_{18}ON_2$ requires N, 10·1%).

When the compound (II) was warmed on the water-bath with acetic anhydride containing a few drops of concentrated sulphuric acid for 5 minutes only and the mixture cooled and diluted with water, the product, after crystallisation from alcohol and then from glacial acetic acid, yielded 7-*acetyl*-8 : 9 : 10 : 11-*tetrahydro*-α′β′-*naphthacarbazole* in colourless plates, m. p. 162° (Found : N, 5·2. $C_{18}H_{17}ON$ requires N, 5·3%). Owing to the readiness with which the diacetyl derivative (m. p. 185°) is produced, it is, however, difficult to prepare 7-acetyl-8 : 9 : 10 : 11-tetrahyro-α′β′-naphthacarbazole in any quantity by this method, and a much more satisfactory process is to use the Grignard reagent as described above for the preparation of 11-acetyl-7 : 8 : 9 : 10-tetrahydro-αβ-naphthacarbazole. In this case the product was practically insoluble in either the ether or the aqueous layer, and was collected by filtration and recrystallised from glacial acetic acid. 7-Acetyl-8 : 9 : 10 : 11-tetrahydro-α′β′-naphthacarbazole was hydrolysed to the compound (II) on boiling its alcoholic solution with potassium hydroxide for ½ hour, the product being obtained on diluting the solution with water.

7-Acetyl-8 : 9 : 10 : 11-tetrahydro-α′β′-naphthacarbazole (5 g.), dissolved in glacial acetic acid (50 c.c.) at 95°, was treated gradually with nitric acid (2 c.c. of *d* 1·4) in a little acetic acid. Almost immediately a yellow product (2·5 g.), melting indefinitely at about 190°, separated. It was collected after a few hours and crystallised from toluene and then from *cyclo*hexanone. After further recrystallisation from *cyclo*hexanone a *mononitro*-7-*acetyl*-8 : 9 : 10 : 11-*tetrahydro*-α′β′-*naphthacarbazole* was obtained in bright yellow needles, m. p. 222° (Found : N, 9·0. $C_{18}H_{16}O_3N_2$ requires N, 9·1%). It was evident that this is not the only product of this reaction, but efforts to isolate any other substance in a pure condition have so far been unsuccessful.

7-*Benzoyl*-8 : 9 : 10 : 11-*tetrahydro*-α′β′-*naphthacarbazole*.—This derivative was obtained by a process similar to that described for the corresponding 11-benzoyl-7 : 8 : 9 : 10-tetrahydro-αβ-naphthacarbazole. After crystallisation from glacial acetic acid, it separated in clusters of yellowish prisms, m. p. 139° (Found : N, 4·3. $C_{23}H_{19}ON$ requires N, 4·3%).

7-Benzoyl-8 : 9 : 10 : 11-tetrahydro-α′β′-naphthacarbazole (2 g.) was dissolved in glacial acetic acid (40 c.c.) at 80° and treated with nitric acid (1·5 c.c. of *d* 1·5) in a little glacial acetic acid. The mixture was cooled and kept for some days and the product was then collected and crystallised from acetone, from which *mononitro*-7-*benzoyl*-8 : 9 : 10 : 11-*tetrahydro*-α′β′-*naphthacarbazole* separated in yellow needles, m. p. 208—209° (Found : C, 74·8 ; H, 5·1. $C_{23}H_{18}O_3N_2$ requires C, 74·6 ; H, 4·9%).

8 : 9 : 10 : 11 : 12 : 15-*Hexahydro*-α′β′-*naphthacarbazole*.—A mixture of the compound (II) (10 g.), red phosphorus (7 g.), and hydriodic acid (70 c.c. of *d* 1·9) was boiled for 18 hours, cooled, made alkaline with aqueous sodium hydroxide, and extracted with ether. The extract was washed with water and dried over potassium carbonate and then dry hydrogen chloride was passed into it. 8 : 9 : 10 : 11 : 12 : 15-*Hexahydro*-α′β′-*naphthacarbazole hydrochloride* separated; after recrystallisation from hot water, it was obtained in small, buff-coloured prisms, m. p. 265° with sublimation (Found : C, 73·7; H, 7·0. $C_{16}H_{17}N,HCl$ requires C, 73·9; H, 6·9%). The base, liberated by treating the hydrochloride with aqueous sodium hydroxide and isolated by means of ether, was obtained only as a syrup, b. p. 198—202°/10 mm.

7-*Acetyl*-8 : 9 : 10 : 11 : 12 : 15-*hexahydro*-α′β′-*naphthacarbazole* was obtained by boiling the base with acetic anhydride for 5 minutes and then diluting the solution with water. It separated from dilute alcohol in colourless plates, m. p. 120° (Found : N, 5·2. $C_{18}H_{19}ON$ requires N, 5·3%).

7-*Benzoyl*-8 : 9 : 10 : 11 : 12 : 15-*hexahydro*-α′β′-*naphthacarbazole*.—A mixture of the base (2 g.) and benzoic anhydride (2·4 g.) was heated at 150°, cooled, dissolved in chloroform, washed with aqueous sodium carbonate, and dried over potassium carbonate; the solvent was then removed and on crystallisation from petroleum (b. p. 60—80°) the product was obtained in colourless prisms, m. p. 131° (Found : N, 4·3. $C_{23}H_{21}ON$ requires N, 4·3%).

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