

DERIVATIVES OF NAPHTHAQUINOLINES AND NAPHTHAISOQUINOLINES.¹

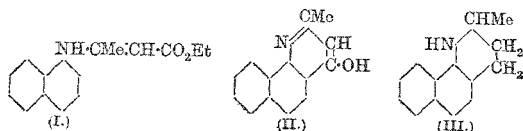
*By Charles Stanley Gibson, Kalvoji Venkatakrishna Hariharan,
Kottiasath Narayana Menon, and John Lionel Simonsen.*

In continuation of the work (Gibson and Simonsen, J., 1915, 107, 1148) which began with the stereochemical investigation of *dl*-tetrahydro- β -naphthaquinoline (*dl*-3-methyl-1:2:3:4-tetrahydro- β -naphthaquinoline) it has been necessary to study some derivatives of the naphthaquinolines in greater detail than was at first anticipated. Whilst the condensation of β -naphthylamine and paraldehyde (Doebner and von Miller, *Ber.*, 1884, 17, 1711) offers no difficulties, we have not been able to isolate the α -naphthaquinoline—2-methyl- α -naphthaquinoline—by condensing α -naphthylamine with paraldehyde as described by the above authors; in numerous experiments, apart from unchanged material, we obtained only amorphous, brown solids. It would appear, therefore, that these authors worked under conditions which we have been unable to reproduce.

In order to obtain *dl*-tetrahydro- α -naphthaquinoline [*dl*-2-methyl-1:2:3:4-tetrahydro- α -naphthaquinoline] we studied the method first adopted by Knorr (*Ber.*, 1884, 17, 543) and subsequently investigated in greater detail by Conrad and Limpach (*Ber.*, 1888, 21, 531). The latter authors state that when α -naphthylamine and ethyl acetoacetate are heated together for a long period on the water-bath ethyl β -1-naphthylaminocrotonate (I), is produced. Under these conditions we were able to isolate only acetoaceto- α -naphthalide (V), even when a considerable excess of ethyl acetoacetate was employed. In the presence of a small quantity of diethylamine, however, α -naphthylamine and ethyl acetoacetate readily condensed to give the desired compound (I). This compound was not obtained crystalline, but when the oil was heated to 240° it was converted into 4-hydroxy-2-methyl- α -naphthaquinoline (II). By the action of phosphorus pentachloride the corresponding 4-chloro-2-methyl- α -naphthaquinoline was easily obtained and this was reduced with sodium and ethyl alcohol

¹ Reprinted from the *Journal of the Chemical Society*, 1926, 2247. The name naphthaquinoline is in established use and hence also the name naphthaisoquinoline has been adopted in the present communication. It should be pointed out, however, that the names benzoquinoline and benzoisoquinoline would be preferable, as being in accordance with the system on which the majority of composite names of ring systems is devised; but no alteration is suggested, as the introduction of fresh synonyms is undesirable.

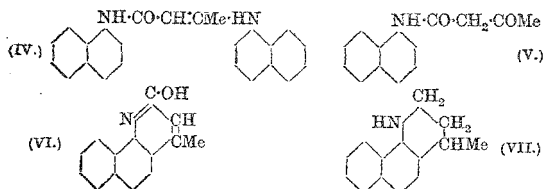
to the desired compound, dl-2-methyl-1 : 2 : 3 : 4-tetrahydro- α -naphthaquinoline (III). This is the compound that should be obtained by the



reduction of the base which Doebner and von Miller describe as having been prepared by the condensation of α -naphthylamine and paraldehyde. The compound is an oil which was readily characterised by the preparation of a number of derivatives.

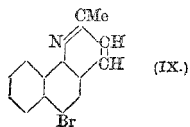
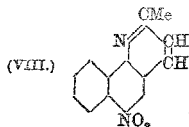
Under the conditions described by Knorr (*loc. cit.*) α -naphthylamine and ethyl acetoacetate alone yield only a small quantity of β -1-naphthylaminocrotono-1-naphthylamide (IV), the chief product of the reaction being a colourless, non-basic, high-melting substance *A* (p. 185). Under the conditions described later, the amount of (IV) obtained is much more satisfactory. This compound exists in two interconvertible forms (see the experimental section), but it has not been determined whether this is a simple case of dimorphism or whether the two forms represent the possible *cis*- and *trans*-modifications.

The crotonyl derivative was readily converted into acetoaceto- α -naphthalide (V) by hydrolysis with dilute hydrochloric acid, but the



conversion of this product into 2-hydroxy-4-methyl- α -naphthaquinoline (VI) by means of concentrated hydrochloric acid presented great difficulties on account of hydrolysis and the production of α -naphthylamine. Sufficient of the hydroxy-base was obtained, however, for the preparation of the corresponding *chloro*-compound and the reduction of the latter to dl-4-methyl-1 : 2 : 3 : 4-tetrahydro- α -naphthaquinoline (VII). This base does not give a crystalline *benzoyl* derivative, but it is readily characterised by its crystalline *picrate*.

During the course of this work very marked differences in the behaviour of α - and β -naphthylamines towards paraldehyde and ethyl acetoacetate were repeatedly noticed, and similar difficulties in obtaining derivatives of α -naphthaquinoline from α -naphthylamine were encountered by John and his collaborators (*J. pr. Chem.*, 1925, III, 65 *et seq.*). Experiments to throw light on this problem have shown that, unlike α -naphthylamine itself, 4-nitro- α -naphthylamine and 4-bromo- α -naphthylamine both condense readily with paraldehyde,

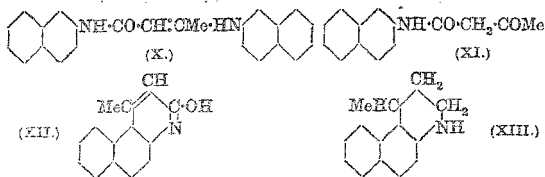


yielding 6-nitro-2-methyl- α -naphthaquinoline (VIII) and 6-bromo-2-methyl- α -naphthaquinoline (IX) respectively. Mr. Unni Nair and one of us (J. L. S.) have also recently found that 4-aminoaceneaphthene condenses readily with paraldehyde, and thus we have definite evidence that substitution in the 4-position in α -naphthylamine seems to be a determining factor in making α -naphthylamine behave more nearly like β -naphthylamine.

By condensing β -naphthylamine and ethyl acetoacetate under the conditions described later (p. 187; compare Knorr, *loc. cit.*, and Conrad and Limpach, *loc. cit.*), β -2-naphthylaminocrotono-2-naphthylamine (X) was readily obtained. From this compound, by hydrolysis with dilute hydrochloric acid, acetoaceto- β -naphthalide (XI) was prepared, and this, when heated with concentrated hydrochloric acid, was converted into 3-hydroxy-1-methyl- β -naphthaquinoline (XII). By reactions which have already been indicated, the corresponding 3-chloro-1-methyl- β -naphthaquinoline and dl-1-methyl-1:2:3:4-tetrahydro- β -naphthaquinoline (XIII) were obtained. This externally compensated base, like the analogous one prepared from α -naphthylamine, is a viscous oil which crystallises in liquid air. Its benzoyl derivative could not be obtained crystalline, but the crystalline *picrate* serves for its easy characterisation.

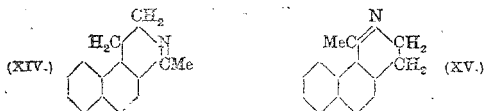
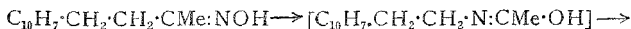
Under suitable conditions, the reaction between β -naphthylamine and ethyl acetoacetate goes differently from that described above and a colourless non-basic, high-melting substance, *B* (p. 188), is formed. This is isomeric with substance *A* (p. 185), with which it has been carefully compared. The substances *A* and *B* are undoubtedly the ureas, $\text{CO}(\text{NH}\cdot\text{C}_{10}\text{H}_7)_2$, of α - and β -naphthylamine respectively and their formation is explicable by the mechanism suggested by Hurst

and Thorpe (J., 1915, 107, 934; compare Ewins and King, J., 1913, 103, 104; Young and Clark, J., 1897, 71, 1200).



The possible occurrence in nature of naphthaisoquinoline derivatives made it desirable to attempt the preparation of compounds having this ring structure, no representatives of which seem to have been described. Our work is based on that of Kaufmann and Radosevic (*Ber.*, 1916, 49, 675), who treated the oximes of substituted γ -ketobutylbenzenes with phosphorus pentoxide and obtained methylidihydroisoquinoline derivatives.

The considerable quantities of α - and β -naphthaldehydes required were conveniently prepared by Sonn and Müller's method (*Ber.*, 1919, 52, 1927). α - And β -naphthaldehydes condensed readily with acetone to give 1- and 2- γ -ketobutenylnaphthalenes, $\text{C}_{10}\text{H}_7\cdot\text{CH}:\text{CH}\cdot\text{COMe}$, respectively, from which the corresponding γ -ketobutenylnaphthalenes, $\text{C}_{10}\text{H}_7\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{COMe}$, were obtained by catalytic reduction. These were converted into the corresponding oximes, and, although the preparation from these of the dihydrobases was attended by the formation of much resinous by-product, sufficient 4-methyl-1:2-dihydro- β -naphthaisoquinoline (XIV) (from α -naphthaldehyde) and 1-methyl-3:4-dihydro- α -naphthaisoquinoline (XV) (from β -naphthaldehyde) were obtained in the crystalline condition for identification. The following scheme represents the formation of these compounds.



The stereochemical investigation of the externally compensated bases now described is in progress.

EXPERIMENTAL.

Condensation of α -Naphthylamine and Ethyl Acetoacetate.—A mixture of ethyl acetoacetate (13 g.) and α -naphthylamine (14.3 g.) containing 2 drops of 33% diethylamine solution became cloudy in a few hours and the calculated quantity of water had separated in 3 days. The thick, red oil was extracted with ether, the solution dried, and the ether distilled. The residual oil, when heated at 240° , was converted into a crystalline solid, which was ground with alcohol and crystallised from amyl alcohol or nitrobenzene. As stated by Conrad and Limpach, the 4-hydroxy-2-methyl- α -naphthaquinoline (II) did not melt below 300° (Found: N, 7.1. Calc.: N, 6.7%).

4-Chloro-2-methyl- α -naphthaquinoline.—A mixture of 4-hydroxy-2-methyl- α -naphthaquinoline (10 g.), tetrachloroethane (20 c.c.) and phosphorus pentachloride (10 g.) was heated at 130 – 140° for 2 hours and finally at 160 – 170° for 1 hour; evolution of hydrogen chloride had then ceased. The clear, deep brown solution, which deposited crystals on cooling, was poured on to ice; the greater part of the chloro-derivative separated in the form of the sparingly soluble hydrochloride. A solution of this in hot water was filtered from a little tar and basified, the chloro-derivative separating as a colourless, crystalline solid. A further quantity was obtained from the tetrachloroethane solution by removal of the solvent with steam and basification of the filtered acid solution. *4-Chloro-2-methyl- α -naphthaquinoline* crystallised from alcohol, in which it was somewhat sparingly soluble, in long needles, m. p. 92 – 93° (Found: N, 6.6. $C_{14}H_{10}NCl$ requires N, 6.2%). The *picrate*, prepared from equivalent quantities of the base and picric acid in alcoholic solution, separated in yellow prisms, m. p. 196 – 197° , which could not be recrystallised owing to their sparing solubility.

dl-2-Methyl-1:2:3:4-tetrahydro- α -naphthaquinoline (III).—To a solution of 4-chloro-2-methyl- α -naphthaquinoline (20 g.) in boiling alcohol (900 c.c.), sodium (60 g.) was added as rapidly as possible. When all the sodium had dissolved, the alcohol was removed in steam, the residual oil extracted with ether, and the ether dried and evaporated. On distillation under diminished pressure, the base was obtained as a pale yellow, somewhat mobile, uncrystallisable oil, b. p. 202 – $203^{\circ}/20$ mm. In solution it showed a marked blue fluorescence (Found: C, 85.0; H, 8.0. $C_{14}H_{13}N$ requires C, 85.3; H, 7.6%). The *benzoyl* derivative crystallised from methyl alcohol, in which it was readily soluble, in clusters of colourless needles, m. p. 102 – 103° (Found: N, 4.7. $C_{21}H_{19}ON$ requires N, 4.6%). The *hydrochloride* crystallised from hot dilute hydrochloric acid, in which it was somewhat sparingly soluble, in glistening prisms, decomp. 252 – 253° (Found: Cl, 15.2. $C_{14}H_{13}N, HCl$ requires Cl, 15.2%). The

sulphate crystallised from dilute sulphuric acid in iridescent prisms, decomp. $211-212^{\circ}$ (Found: S, 10.6. $C_{14}H_{15}N, H_2SO_4$ requires S, 10.9%). The *chloroplatmate* was a very sparingly soluble, brown powder, decomp. $207-208^{\circ}$. The *picrate* crystallised from dilute alcohol in fine, yellow needles, m. p. $88-89^{\circ}$. These evidently contained solvent of crystallisation, for, after being dried in a vacuum over calcium chloride prior to analysis, they melted at $153-154^{\circ}$ and decomposed at a slightly higher temperature (Found: N, 13.4. $C_{20}H_{18}O_7N_4$ requires N, 13.1%).

β -1-Naphthylaminocrotono-1-naphthylamide (IV).—A mixture of α -naphthylamine (2 mols.) and ethyl acetoacetate (1 mol.) was heated on the water-bath for 24 hours and then at $150-170^{\circ}$ for 4 hours. The semi-solid red condensation product was extracted with boiling 88 per cent. alcohol; a considerable quantity of the crystalline solid *A* remained undissolved. The filtrate, when kept in the ice chest, slowly deposited *β -1-naphthylaminocrotono-1-naphthylamide*, and a further quantity was obtained by removing the alcohol and grinding the residue with benzene or light petroleum. The substance usually separated from the alcoholic solution as a fine, crystalline powder, m. p. $135-145^{\circ}$, but occasionally it was deposited in well-formed needles, m. p. $145-147^{\circ}$. It was apparently dimorphous and the crystalline form and m. p. varied according to the solvent used for crystallisation. When crystallised from absolute alcohol, the compound separated in well-formed, prismatic needles, m. p. $167-168^{\circ}$, and this m. p. was unaltered by recrystallisation from this solvent. From benzene, the compound was deposited in fine, silky needles which softened at 135° and melted at $144-145^{\circ}$. Crystallisation of the substance of higher m. p. from benzene yielded the form, m. p. $144-145^{\circ}$, which could be reconverted into the form of higher m. p. by crystallisation from alcohol. The lower-melting form was also converted into the higher-melting form by heating it above its melting point, since, after solidification in the m. p. tube, the m. p. was $167-168^{\circ}$. Both forms had the same composition (Found: (1) C, 81.8; H, 5.6. (2) C, 81.3; H, 6.0. $C_{24}H_{20}ON_2$ requires C, 81.8; H, 5.7 per cent.).

Acetoaceto- α -naphthalide (V) was obtained in a quantitative yield when the preceding compound was digested on the water-bath with 4 per cent. hydrochloric acid for $\frac{1}{2}$ hour. It crystallised from benzene in needles, m. p. 107° (Found: N, 6.2. $C_{14}H_{13}O_2N$ requires N, 6.2 per cent.).

The finely divided naphthalide, after remaining in contact with concentrated hydrochloric acid for some weeks, was converted into 2-hydroxy-4-methyl- α -naphthaquinoline (VI), which crystallised from alcohol in needles having the m. p. recorded by Knorr.

2-Chloro-4-methyl- α -naphthaquinoline was obtained when the hydroxyquinoline was heated at 130—140° with the required amount of phosphorus pentachloride for 2 hours. The product, after treatment with dilute alkali, was dissolved in cold concentrated hydrochloric acid, filtered from a little resin, and precipitated by addition of water. It crystallised from alcohol in prisms, m. p. 134—135° (Found: Cl, 15.3. $C_{14}H_{10}NCl$ requires Cl, 15.6 per cent.).

dl-4-Methyl-1 : 2 : 3 : 4-tetrahydro- α -naphthaquinoline (VII), prepared by reducing the preceding chloro-compound under the conditions employed in the reduction of 4-chloro-2-methyl- α -naphthaquinoline (see p. 183), was obtained as a viscous, pale yellow, uncrystallisable oil, b. p. 186—188°/10 mm. (Found: C, 85.0; H, 7.8. $C_{14}H_{15}N$ requires C, 85.3; H, 7.6 per cent.).

It showed a bluish-green fluorescence in benzene or alcohol and the solution darkened rapidly on exposure to the air. The sulphate and hydrochloride were somewhat readily soluble in water, the hydrobromide more sparingly soluble. The *picrate* crystallised from much alcohol in pale yellow prisms, decomp. 205—206° (Found: N, 13.6. $C_{20}H_{18}O_7N_4$ requires N, 13.1 per cent.).

The substance *A* produced in the condensation of α -naphthylamine and ethyl acetoacetate (see p. 184) became the main product if the preliminary heating on the water-bath was omitted. It was very sparingly soluble in all the ordinary solvents and had no basic properties. It crystallised from much acetic acid or from nitrobenzene in fine needles, decomp. 280°. When distilled with zinc dust, or heated with hydrochloric acid or alcoholic potassium hydroxide in a sealed tube at 150°, it gave α -naphthylamine only, and oxidation with potassium permanganate in acid solution produced phthalic acid (Found: C, 81.05, 80.9; H, 5.1, 5.15; N, 9.0, 8.9. Calc. for $C_{21}H_{16}ON_2$: C, 80.8; H, 5.2; N, 9.0 per cent.). It was proved to be the urea of α -naphthylamine by comparison with an authentic specimen.

Condensation of 4-Nitro- α -naphthylamine and Paraldehyde.—A mixture of 4-nitro- α -naphthylamine (20 g.), concentrated hydrochloric acid (40 g.), and paraldehyde (30 g.) was heated at 110—115° for 4 hours with constant agitation. The cooled reaction mixture was poured into water, the solid collected and repeatedly triturated with concentrated hydrochloric acid. The filtered solution was diluted with water until no further precipitate formed, and after remaining over-night the yellow solid, which was not investigated, was removed and the acid solution basified. The dark brown solid thus precipitated was dried (5 g.) and repeatedly extracted with boiling light petroleum (b. p. 60—80°), which left undissolved a considerable quantity of carbonaceous matter. The petroleum solution slowly deposited a

greenish-yellow, crystalline solid which, after recrystallisation from alcohol with the aid of animal charcoal, was obtained in soft, yellow needles, m. p. 141—142° (Found: N, 11·8. $C_{14}H_{10}O_2N_2$ requires N, 11·8 per cent.).

6-Nitro-2-methyl- α -naphthaquinoline (VIII) is very soluble in all the ordinary organic solvents except alcohol and light petroleum. The sulphate and hydrochloride are readily soluble in water; the nitrate, which crystallises in needles, is less soluble. The *chloroplatinate* is very sparingly soluble in water, crystallising in glistening, golden prisms, decomp. 229—230° [Found: Pt, 22·5. $(C_{14}H_{10}O_2N_2)_2, H_2PtCl_6$ requires Pt, 22·0 per cent.].

Condensation of 4-Bromo- α -naphthylamine and Paraldehyde.—A mixture of 4-bromo- α -naphthylamine hydrochloride (10 g.), paraldehyde (15 g.) and hydrochloric acid (20 g.) was heated at 110° for 4 hours. The cooled reaction mixture was mixed with alkali, and the deep brown solid which separated was collected. This was dissolved in hydrochloric acid, the non-basic impurities were separated by filtration, the solution was boiled with animal charcoal, and the mixture of bases reprecipitated with alkali. The crude bases were collected, dissolved in dilute sulphuric acid, treated with an excess of sodium nitrite solution to remove any primary and secondary bases, and the filtered solution basified. The crystalline base (2 g.) was purified by solution in light petroleum and finally recrystallised from methyl alcohol, from which it separated in colourless, felted needles, m. p. 99—100° (Found: N, 5·1; Br, 29·4. $C_{14}H_{10}NBr$ requires N, 5·1; Br, 29·4 per cent.).

6-Bromo-2-methyl- α -naphthaquinoline (IX) is readily soluble in benzene, ethyl acetate, or light petroleum, and more sparingly soluble in ethyl or methyl alcohol. It is insoluble in water. The hydrochloride separated from concentrated hydrochloric acid in needles which were readily soluble in water. The hydrobromide was somewhat more sparingly soluble and crystallised in prismatic needles. The *chloroplatinate* was a microcrystalline, brown powder, very sparingly soluble in water or dilute hydrochloric acid; it decomposed at 238° (Found: Pt, 20·2. $(C_{14}H_{10}NBr)_2, H_2PtCl_6$ requires Pt, 20·4 per cent.). The *picrate* separated from alcohol, in which it was very sparingly soluble, in glistening, yellow prisms, m. p. 185—186°, and slowly decomposed above this temperature (Found: N, 11·6. $C_{20}H_{15}O_7N_4Br$ requires N, 11·2 per cent.).

Condensation of β -Naphthylamine and Ethyl Acetoacetate.—3-Hydroxy-1-methyl- β -naphthaquinoline (XII) was most conveniently prepared by the following modification of Knorr's method (*loc. cit.*). A mixture of β -naphthylamine (2 mols.) and ethyl acetoacetate (1 mol.)

was heated on the water-bath for 12 hours and at 150—180° for 3 hours. The crystalline magma thus produced was cooled, crushed, and after removal of a little adherent oil, was well washed with hot alcohol. The crude β -2-naphthylaminocrotono-2-naphthylamide (X) was dissolved in much boiling xylene and filtered from a small quantity of sparingly soluble residue, *B* (see below) (yield 71 per cent.). The properties of the recrystallised substance agreed in all respects with Knorr's description. Acetoaceto- β -naphthalide (XI) was prepared from it by Knorr's method; the solution, however, was not boiled, the hydrolysis taking place readily on the water-bath. The naphthalide separated, on cooling, as a curious, gelatinous solid which could not be filtered and was therefore isolated by extraction with ethyl acetate, in which it was very readily soluble (yield 94 per cent.).

3-Hydroxy-1-methyl- β -naphthaquinoline was obtained when the naphthalide was heated on the water-bath with concentrated hydrochloric acid. If the solution was boiled as recommended by Knorr, a considerable quantity of β -naphthylamine was formed simultaneously.

When distilled with zinc dust, the hydroxy-compound gave a poor yield of 1-methyl- β -naphthaquinoline, m.p. 91—92°, the *picrate* of which, after crystallisation from much alcohol, melted at 230—231° with previous softening (Found: N, 12.5. $C_{20}H_{14}O_7N_3$ requires N, 13.3 per cent.).

3-Chloro-1-methyl- β -naphthaquinoline.—A mixture of 3-hydroxy-1-methyl- β -naphthaquinoline (5 g.), tetrachloroethane (10 c.c.), and phosphorus pentachloride (5.5 g.) was heated at 170—180° for 3 to 4 hours. The solvent and the phosphorus oxychloride were then removed under diminished pressure, and the residual solid, after trituration with dilute alkali, was crystallised from alcohol; the *chloro*-compound was thus obtained in colourless needles, m.p. 153—154° (yield 95 per cent.) (Found: Cl, 15.6. $C_{14}H_{10}NCl$ requires Cl, 15.6 per cent.).

dl-1-Methyl-1 : 2 : 3 : 4-tetrahydro- β -naphthaquinoline (XIII) was obtained when 3-chloro-1-methyl- β -naphthaquinoline was reduced under conditions similar to those employed for the preparation of *dl*-2-methyl-1 : 2 : 3 : 4-tetrahydro- α -naphthaquinoline (p. 183). The greater part of the base distilled at 188—195°/10 mm., but was contaminated with a considerable quantity of resinous impurity which was only removed with difficulty by fractional distillation. The base was therefore converted into the *picrate*, which crystallised from alcohol in pale yellow needles; these decomposed at 162°, and at 167—168° when rapidly heated (Found: C, 56.2; H, 4.4; N, 13.1. $C_{20}H_{18}O_7N_4$ requires C, 56.3; H, 4.2; N, 13.1 per cent.). During the purification of the *picrate* a very small amount of a very sparingly soluble *picrate*

was separated which crystallised from a large volume of alcohol in glistening, yellow leaflets, m.p. 201—202°. This picrate had the same composition as the picrate, m.p. 162° (Found; C, 56.1; H, 4.2 per cent.), but it was not obtained in sufficient quantity for investigation.

dl-1-Methyl-1 : 2 : 3 : 4-tetrahydro- β -naphthaquinoline regenerated from the picrate was a thick, yellow oil, b. p. 187—190°/10 mm., which darkened rapidly on exposure to air (Found; C, 84.8; H, 7.6. C₁₄H₁₅N requires C, 85.3; H, 7.6 per cent.). It showed a blue fluorescence in benzene solution. It did not solidify in a freezing mixture, but at the temperature of liquid air it set to a crystalline mass of long needles which melted at room temperature. The hydrochloride was readily soluble in water; the sulphate, which crystallised in needles, was not so soluble.

The sparingly soluble substance *B*, obtained during the condensation of β -naphthylamine and ethyl acetoacetate was formed in much larger quantity if the preliminary heating on the water-bath was omitted. This substance (compare substance *A*, p. 185) was insoluble in all the ordinary organic solvents, but crystallised from nitrobenzene in large, colourless needles sintering at 288° and decomposing at 293—294° (Found; C, 80.8, 80.8; H, 5.1, 5.1; N, 8.9, 8.95 per cent. Calc. for C₂₁H₁₅ON₂: C, 80.8; H, 5.2; N, 9.0 per cent.). It was shown to be the urea of β -naphthylamine by comparison with an authentic specimen.

1-Methyl-3 : 4-dihydro- α -naphthaisoquinoline (XV).—For the preparation of β -naphthaldehyde, a mixture of β -naphthanilide¹ (8 g.), tetrachloroethane (25 c.c.), and phosphorus pentachloride (7 g.) was heated at 140—150° until evolution of hydrogen chloride ceased (1 hour). The phosphorus oxychloride and a part of the solvent were removed under diminished pressure; on cooling, the iminochloride separated as a yellow, crystalline solid. This was redissolved in tetrachloroethane, and the solution gradually added to an ethereal solution of stannous chloride saturated with hydrogen chloride (ether, 250 c.c.; stannous chloride, 30 g.). A somewhat vigorous reaction took place and the stannichloride of the Schiff's base separated as a yellow, gelatinous solid. After some hours, the ether was decanted from the salt, dilute hydrochloric acid (50 c.c.) added, and the aldehyde distilled in steam (yield 80—90 per cent.).

2- γ -Ketobutenylnaphthalene.—A mixture of the aldehyde (1 part), acetone (6 parts), water (30 parts), and 20 per cent. sodium hydroxide

¹ This substance crystallised from alcohol, in which it was somewhat sparingly soluble, in colourless prisms, m. p. 171° (Found; N, 5.8. C₁₇H₁₃ON requires N, 5.7 per cent.).

solution (0.2 part) was agitated, and occasionally warmed on the water-bath, for 2 or 3 days. The aldehyde gradually liquefied and remained as a semi-solid oil until the condensation was nearly complete; the butenyl derivative then separated as a crystalline solid. When the reaction was complete, the solid was collected and dissolved in benzene, a small quantity of *di-β-naphthylvinyl ketone* (see below) remaining undissolved. The benzene solution was dried and evaporated.

2-γ-Ketobutenyl-naphthalene separated from methyl alcohol in nodules of yellow needles, m. p. 102°, after sintering at 95–96°. It was readily soluble in the ordinary organic solvents, but very sparingly soluble in water (Found: C, 85.5; H, 6.3. $C_{14}H_{12}O$ requires C, 85.7; H, 6.2 per cent.).

Di-β-naphthylvinyl ketone, $CO(CH:CH \cdot C_{10}H_7)_2$, which was only formed in traces when the condensation of β -naphthaldehyde and acetone was carried out under the above-mentioned conditions, formed the main product of the reaction when a solution of the aldehyde in acetone was treated with a drop of a sodium methoxide solution. It was very sparingly soluble in most of the ordinary organic solvents, but crystallised from hot toluene in fine, sulphur-yellow needles, m. p. 241° (Found: C, 89.5; H, 5.6. $C_{28}H_{18}O$ requires C, 89.8; H, 5.4 per cent.).

2-γ-Oximinobutenyl-naphthalene, prepared by treating the corresponding ketone with hydroxylamine hydrochloride and sodium acetate in absolute-alcoholic solution, crystallised from methyl alcohol in glistening plates, m. p. 158–160°. Indications of the presence of an isomeride in the mother-liquor were obtained, but this was not isolated in a pure state (Found: C, 79.7; H, 6.6. $C_{14}H_{13}ON$ requires C, 79.6; H, 6.2 per cent.).

2-γ-Ketobutyl-naphthalene was readily obtained in a quantitative yield when the unsaturated ketone, suspended in acetic acid, was reduced, in the presence of colloidal platinum, by hydrogen under a pressure of 2 atmospheres. It was a somewhat viscous, colourless oil, b. p. 180–182°/8 mm. In alcoholic solution it gave no colour with ferric chloride (Found: C, 84.6; H, 7.3. $C_{14}H_{14}O$ requires C, 84.8; H, 7.1 per cent.). The *oxime* crystallised from methyl alcohol in long, glistening needles, m. p. 129° (Found: N, 6.8. $C_{14}H_{15}ON$ requires N, 6.6 per cent.). The *semicarbazone* separated from methyl alcohol in small prisms, m. p. 161–162° (Found: N, 16.6. $C_{15}H_{17}ON_3$ requires N, 16.5 per cent.).

1-Methyl 3:4-dihydro-α-naphthaisoquinoline (XV).—A mixture of the oxime (6 g.), toluene (60 c.c.), and phosphorus pentoxide (10 g.)

was boiled with constant agitation for thirty minutes; phosphorus pentoxide (10 g.) was again added and the heating continued for 1 hour. The toluene was decanted from the cooled reaction mixture, and the phosphorus pentoxide dissolved in ice water; a considerable quantity of red tar then separated. The aqueous extract, which had a blue fluorescence, was separated, extracted with ether to remove any neutral products, and basified with potassium hydroxide solution. The thick, colourless oil that separated was extracted with ether, and the ethereal solution dried and evaporated (yield 1.2 g.). The crude oily base was dissolved in alcohol and treated with the calculated quantity of an alcoholic solution of picric acid; the *picrate*, which separated in sparingly soluble, yellow prisms, was recrystallised from acetone; it decomposed at 207—208° (Found: C, 56.8; H, 4.4; N, 13.3. $C_{20}H_{16}O_7N_4$ requires C, 57.9; H, 3.8; N, 13.2 per cent.). The *base* regenerated from the picrate solidified when cooled in a freezing mixture. It had m. p. 36—37°, and this m. p. was unchanged by crystallisation from dilute methyl alcohol, from which the base separated in glistening leaflets, containing apparently a molecule of methyl alcohol of crystallisation (Found: C, 79.8; H, 7.1. $C_{14}H_{13}N \cdot CH_3 \cdot OH$ requires C, 79.3; H, 7.4 per cent.).

4-Methyl-1:2-dihydro-β-naphthaisoquinoline (XIV).—The *α*-naphthaldehyde was prepared from *α-naphthanilide*¹ under exactly similar conditions to those used for the preparation of *β*-naphthaldehyde (yield 75 per cent.).

1-γ-Ketobutenylnaphthalene was prepared in a similar manner to the 2-isomeride (p. 189). It was obtained as a pale yellow, uncrystallisable oil, b. p. 200—201°/10 mm. (Found: C, 85.2; H, 5.9. $C_{14}H_{12}O$ requires C, 85.7; H, 6.2 per cent.).

1-γ-Oximinobutenylnaphthalene crystallised from methyl alcohol in small nodules, m. p. 136—137° (Found: N, 6.6. $C_{14}H_{13}ON$ requires N, 6.6 per cent.).

1-γ-Ketobutylnaphthalene, readily obtained by the reduction of the unsaturated ketone with hydrogen in the presence of colloidal platinum, was a colourless, mobile oil, b. p. 192—195°/17 mm., having a pleasant smell reminiscent of acetophenone (Found: C, 84.8; H, 7.1. $C_{14}H_{14}O$ requires C, 84.8; H, 7.1 per cent.). The *oxime* crystallised from light petroleum (b. p. 60—80°) in long, glistening needles, m. p. 96—97°. It was readily soluble in most of the usual organic solvents (Found: N, 7.0. $C_{14}H_{15}ON$ requires N, 6.6 per cent.).

¹ *α-Naphthanilide* crystallised from alcohol in prisms, m. p. 162—163° (Found: N, 5.8. $C_{17}H_{15}ON$ requires N, 5.7 per cent.).

4-Methyl-1:2-dihydro-β-naphthaisoquinoline was obtained from the oxime by the method employed for the preparation of the isomeride (p. 189). After removal of the ether, the base crystallised immediately in colourless needles which darkened rapidly on exposure to air. It crystallised from dilute acetone in glistening needles, m. p. 101—102° (Found: N, 7·2. $C_{14}H_{13}N$ requires N, 7·2 per cent.). It was very readily soluble in all the ordinary organic solvents, but insoluble in water. In benzene solution it showed a marked blue fluorescence, which was also shown in other solvents but in a less marked degree. The hydrochloride was very readily soluble in water, and the solution gave, on the addition of platinic chloride, a very sparingly soluble chloroplatinate, which separated as a brown, microcrystalline powder. The *picrate* crystallised from a large volume of alcohol or acetone, in both of which solvents it is very sparingly soluble, in fine, sulphur-yellow needles which darkened at 214° and decomposed at 221° (Found: C, 56·8; H, 4·4. $C_{20}H_{16}O_7N_4$ requires C, 56·9; H, 3·8 per cent.).

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Guy's Hospital Medical School,

London, S.E.

Department of Organic Chemistry,

Indian Institute of Science,

Bangalore.

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