*Price, As. 12.*] [*Vol. 10A, Part I, pp. 1 to 13.*

# JOURNAL

OF THE

# Indian Institute of Science.

## CONTENTS.

# CONTENTS.

# ABBREVIATIONS OF TITLES.

| *Abbreviation* | *Name of Periodical* |
|---|---|
| Agric. J. of India | Agricultural Journal of India. |
| Amer. J. Sci. and Arts | American Journal of Science and Arts. |
| Annalen | Justus Liebig's Annalen der Chemie. |
| Ann. de la Science Agronomique | Annales de la Science agronomique. |
| Ann. de l'Inst. Pasteur | Annales de l'Institut Pasteur. |
| Arch. Pharm. | Archiv der Pharmazie. |
| Ber. | Berichte der deutschen chemischen Gesellschaft. |
| Biochem. J. | The Biochemical Journal. |
| Bull. Amer. Inst. Mining Eng. | Bulletin of the American Institute of Mining Engineers. |
| Bull. Intr. Ac. Sci. Cracovia | Bulletin international de l'Académie Polonaise des Sciences. |
| Bull. Soc. Chim... | Bulletin de la Société chimique de France. |
| Chem. Ztg. | Chemiker Zeitung. |
| Compt. rend. | Comptes rendus hebdomadaires des Séances de l'Académie des Sciences. |
| Gazzetta | Gazzetta Chimica Italiana. |
| Helv. Chim. Acta | Helvetica Chimica Acta. |
| J. | Journal of the Chemical Society. |
| J. Agric. Sci. | Journal of Agricultural Science. |
| J. Amer. Chem. Soc. | Journal of the American Chemical Society. |
| J. Bact. | Journal of Pathology and Bacteriology. |
| J. Biol. Chem. | Journal of Biological Chemistry. |
| J. Chem. Soc. | Journal of the Chemical Society. |
| J. Chim. physique | Journal de la Chimie physique. |
| J.C.S. | Journal of the Chemical Society. |
| J. Ind. Eng. Chem. | Journal of Industrial and Engineering Chemistry. |
| J. Indian Inst. Sci. | Journal of the Indian Institute of Science. |
| Journ. Chem. Soc. | Journal of the Chemical Society. |
| J. pr. Chem. | Journal für praktische Chemie. |
| J.S.C.I. | Journal of the Society of Chemical Industry. |
| J. Soc. Chem. Ind. | Journal of the Society of Chemical Industry. |
| Landw. Versuch. Stat. | Die landwirthschaftlichen Versuchs Stationen. |
| Monatsh. | Monatshefte für Chemie und verwandte Theile anderer Wissenschaften. |

| | |
|---|---|
| Pharm. Indica ... ... ... | Pharmacographia Indica. |
| Proc. Chem. Soc. ... ... | Proceedings of the Chemical Society. |
| Rec. Trav. Chim. ... ... | Recueil des travaux chimiques des Pays-Bas et de la Belgique. |
| Soil Sci. ... ... ... | Soil Science. |
| Trans. Amer. Inst. Mining Eng. ... | Transactions of the American Institute of Mining Engineers. |
| Z. Anorg. Chem. ... ... | Zeitschrift für anorganische und allgemeine Chemie. |
| Zentr. Bakt. ... ... ... | Centralblatt für Bakteriologie, Parasitenkunde und Infektionskrankheiten. |
| Z. physikal. Chem. ... ... | Zeitschrift für physikalische Chemie, Stöchiometrie und Verwandtschafts-Lehre. |
| Z. physiol. Chem. ... ... | Hoppe-Seyler's Zeitschrift für physiologische Chemie. |

## Author Index.

## Subject Index.

## List of Parts, Volume X (A) of the Journal

OF THE

## Indian Institute of Science, with prices.

*Price, As. 12.*] [*Vol. 10A, Part I, pp. 1 to 13.*

# JOURNAL

OF THE

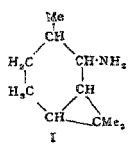
# Indian Institute of Science.

## CONTENTS.

# I. SOME REACTIONS OF CARONE.

*By Kottiazath Narayana Menon and John Lionel Simonsen.*

In a recent communication (*Journ. Chem. Soc.*, 1926, 2049) experiments were described which had as their object the preparation of the secondary alcohol (II) for which the name *carol* is suggested. It was found that when carone was catalytically hydrogenated it behaved like an $\alpha\beta$-unsaturated ketone, fission of the *cyclo*propane ring taking place with formation of monocyclic derivatives. We decided to attempt the preparation of the alcohol by the action of nitrous acid on carylamine (I). *d*-Carylamine was prepared by Baeyer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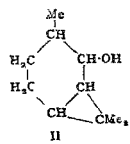
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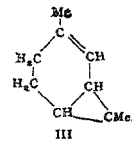
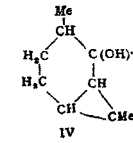

III


IV

(*Ber.*, 1894, **27**, 3485) by the reduction of *d*-caroneoxime with alcohol and sodium, the base, which was not isolated in a pure state, being characterised by the preparation of derivatives. Although the hydrochloride of the base is unstable and passes readily into the monocyclic unsaturated base, vestrylamine, we have found no difficulty in obtaining *d*-carylamine in considerable quantity as a mobile oil b.p. 86–89°/15 mm. When the sulphate is treated with nitrous acid it is readily converted into l-*carol* (II) although the yield is poor. The alcohol is laevorotatory and is undoubtedly bicyclic since it is comparatively stable to an alkaline solution of potassium permanganate and on oxidation with chromic acid yields carone. The alcohol has a remarkably high molecular refraction $[R_L]_D$ 46.78; calc. 46.2) and we cannot offer any explanation of this abnormality.

It was of interest to attempt the elimination of water from carol since if this proceeded normally it should yield $\Delta^4$-carene (III). Owing to the marked instability of the bicyclic structure the reagents available for this reaction were somewhat limited; we have only examined the action of the Grignard reagent on the alcohol and the decomposition of its methyl xanthogenate.

When *l*-carol is treated with a large excess of the Grignard reagent elimination of water takes place but the reaction proceeds

apparently in a complex manner since the hydrocarbon obtained distils over a wide range. A consideration of the physical constants of the oil and an examination of its reaction with bromine lead us to the conclusion that the mixture consists essentially of monocyclic terpenes. On treatment with hydrogen chloride a small quantity of a crystalline hydrochloride was obtained which was identified as terpinene dihydrochloride. The amount of terpinene present in the hydrocarbon mixture cannot however be large since we were unable to prepare the characteristic nitrosate nor could $\alpha\gamma$-dihydroxy-$\alpha$-methyl-$\delta$-*iso*propyladipic acid be separated from the acids formed on oxidation with potassium permanganate. We were not able to identify the other terpenes present, but no evidence could be obtained of the presence of either dipentene or sylvestrene.

When the sodium derivative of *l*-carol is treated with carbon bisulphide followed by methyl iodide, *methyl carylxanthogenate* is obtained as a viscid oil which shows no tendency to crystallise. On distillation at the ordinary pressure the xanthogenate is decomposed with formation of a hydrocarbon which after repeated distillation over sodium boils at 165–170°/685 mm. This hydrocarbon has constants agreeing very closely with those of $\Delta^4$-carene as will be seen from the following comparative table.

| | *d*-$\Delta^4$-*Carene* | *Synthetic Hydrocarbon* |
|---|---|---|
| b.p. | 165·5–167°/707 mm. | 165–170°/685 mm. |
| $d_{30^\circ}^{30^\circ}$ | 0·8552 | 0·8551 |
| $n_D^{30^\circ}$ | 1·474 | 1·473 |
| $[\alpha]_D$ | 62·2° | −5·96° (in acetic acid) |

When available only in small quantity $\Delta^4$-carene is not readily identified, since it does not yield any crystalline derivatives and it can only be characterised by conversion into sylvestrene dihydrochloride or by oxidation to 1 : 1-dimethyl-2-$\gamma$-keto*cyclo*propane-3-carboxylic acid. The quantity (2 g.) of synthetic hydrocarbon was insufficient for oxidation and we therefore treated an acetic acid solution with hydrogen chloride. The resulting product was an oil which, when cooled in a mixture of solid carbon dioxide and acetone crystallised, but melted below −15°. In view of the low rotation of the hydrocarbon the products of the reaction, assuming it to have been $\Delta^4$-carene would consist of carvestrene and dipentene dihydrochlorides, a mixture which would undoubtedly have a very low melting point. We do not therefore consider that the result of this experiment can be regarded as definite evidence that the terpene was not $\Delta^4$-carene. The yield of the hydrocarbon by this method of synthesis is however so extremely poor that we are not at present in a position to repeat its preparation.

It was mentioned above that on reduction carone behaved like an $\alpha\beta$-unsaturated ketone, and it appeared to us of interest to examine its reactions with hydrogen cyanide and ethyl sodiocyanoacetate. With hydrogen cyanide carone behaves like a saturated ketone yielding the corresponding *cyanhydrin* (IV). Attempts to hydrolyse this to the hydroxy-acid by means of alkali were unsuccessful, hydrogen cyanide being eliminated with regeneration of the ketone. This result was not unexpected in view of the previous work of Lapworth (*Journ. Chem. Soc.*, 1910, **97**, 12) and Auwers and Kroll-pfeiler (*Ber.*, 1915, **48**, 1389). With ethyl sodiocyanacetate carone shows no tendency to react although the experiment was made under various conditions.

## EXPERIMENTAL.

### d-*Carylamine.*

*d*-Carylamine was prepared by the reduction of caroneoxime as described by Baeyer (*loc. cit.*). It was a colourless mobile oil possessing a somewhat characteristic basic smell; b.p. 86–89°/15 mm., in 2·8 per cent. alcoholic solution $[\alpha]_D^{24°}$ 72·3° (Found: N, 9·5; $C_{10}H_{19}N$ requires N, 9·2 per cent.).

### l-*Carol.*

To sulphuric acid (32·2 cc.; 9·62 per cent.) which was well cooled in a freezing mixture and mechanically stirred, *d*-carylamine (5 g.) was slowly added, care being taken that the temperature did not rise above 0°. When the addition was complete a solution of barium nitrite (7·5 g.) was added, the temperature being maintained between 5° and 10°. A brisk evolution of nitrogen was observed and the stirring was continued until this ceased (about 8 hours). When the reaction was complete the solution was basified and distilled in steam, the aqueous distillate saturated with ammonium sulphate and repeatedly extracted with ether. The combined ethereal extract was washed with dilute sulphuric acid (10 per cent.) to remove any unchanged base, then with dilute sodium carbonate solution, dried and evaporated. The oil which remained (30 per cent.) had b.p. 141–142°/100 mm. *l*-Carol is a colourless oil with a pleasant smell reminiscent of linalol; in alkaline solution it only very slowly decolorises a solution of potassium permanganate. The following constants were observed:—$d_{30°}^{30°}$ 0·9181, $n_d^{30°}$ 1·472; $[\alpha]_D^{26°}$ −42·92°; $[R_L]_D$ 46·78 (Found: C, 77·8; H, 11·9; $C_{10}H_{18}O$ requires C, 77·9; H, 11·7 per cent.).

When the alcohol was dissolved in acetic acid and the solution treated with the calculated quantity of chromic acid, it was slowly oxidised to carone which was identified by the preparation of the semicarbazone.

*Action of magnesium methyl iodide on* l-*Carol.*

*l*-Carol (50 g.) dissolved in twice its volume of ether was added gradually to a well-cooled solution of the Grignard reagent prepared from 30 grams of magnesium. The reaction was vigorous, and after three days at the room-temperature ice was added and sufficient hydrochloric acid to decompose the magnesium salts. On removal of the solvent an oil remained which on distillation was separated into two main fractions (i) b.p. 172–174°/683 mm.; $d_{30^\circ}^{30^\circ}$ 0·8392; $n_d^{30^\circ}$ 1·4678, $[\alpha]_D^{26^\circ}$–46·52°, $[R_L]_D$ 45·07; (ii) b.p. 180–190°/683 mm.: $d_{30^\circ}^{30^\circ}$ 0·8624, $n_D^{30^\circ}$ 1·4745, $[\alpha]_D^{26^\circ}$–58·48°, $[R_L]_D$ 44·42. Titration with bromine indicated that both fractions consisted essentially of monocyclic hydrocarbons containing two ethylene linkages. On treatment with hydrogen chloride in acetic acid solution an oil was obtained which on cooling in ice deposited a small quantity of a crystalline solid, m.p. 51–52°. This was identified as terpinene dihydrochloride by the method of mixed melting point. The yield of dihydrochloride was small and the oil did not yield terpinene nitrosite, whilst the product of oxidation with an alkaline solution of potassium permanganate was a viscid oil which could not be induced to crystallise.

l-*Methyl carylxanthogenate.*

*l*-Carol (22 g.) was added to finely divided sodium (5 g.) suspended in toluene (75 g.) and the mixture heated to boiling for 20 hours. The toluene solution of the sodium derivative was decanted from unchanged sodium and after the addition of ether (100 cc.) the well-cooled mixture was gradually treated with carbon bisulphide (25 g.). To the xanthogenate prepared in this manner methyl iodide (20 g.) was added and the conversion into the methyl ester completed by digestion on the water bath for one hour. The reaction product was poured into water, the toluene-ether separated and the solvents removed under diminished pressure. l-*Methyl carylxanthogenate* was a viscid yellow oil which did not crystallise. On distillation at the ordinary pressure an oil was obtained containing considerable quantities of sulphur compounds. It was purified by repeated distillation over sodium when it had b.p. 165–170°/685 mm. and the constants given on p. 2 (Yield 3 g.) When dissolved in acetic anhydride and treated with a drop of sulphuric acid a purple colour developed which on keeping gradually changed to red. The action of hydrogen chloride has already been discussed.

d-*Caronecyanhydrin.*

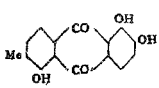
To a freshly prepared solution of hydrogen cyanide (2 g.) in alcohol (20 cc.) *d*-carone (10 g.) in alcohol (10 cc.) was added. After remaining overnight an aqueous solution of potassium cyanide (4 g. in 10 cc.) was added and the mixture digested on the water bath for three hours. The oil which separated on addition of water was extracted with ether, the ethereal extract washed with dilute alkali and the solvent removed. The crude cyanhydrin still contained much unchanged ketone and the treatment with hydrogen cyanide was repeated when the nearly pure *cyanhydrin* was ultimately obtained as a viscid oil (Found : N, 7·1 ; $C_{11}H_{17}ON$ requires N, 7·8 per cent.). When the cyanhydrin was digested with an aqueous solution of potassium hydroxide, ammonia was evolved and *d*-carone regenerated, the yield being quantitative.

# II. A SYNTHESIS OF MORINDONE.

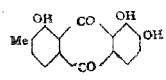
*By Ramkanta Bhattacharya and John Lionel Simonsen.*

The mordant dyestuff, morindone, occurs in the root bark of *Morinda citrifolia* and *M. umbellata* mainly as the glucoside morindin. It was first isolated by Anderson (*Annalen*, 1849, **71**, 216) and was subsequently investigated by Thorpe and Greenall (*Journ. Chem. Soc.*, 1887, **51**, 52), Thorpe and Smith (*Ibid.*, 1888, **53**, 171) Perkin and Hummel (*Ibid.*, 1894, **65**, 851) and by Oesterle and Tisza (*Arch. Pharm.*, 1907, **245**, 534). As the result of these investigations it was established that morindone was a trihydroxy-6-methyl-anthraquinone, the position of the three hydroxy-groups remaining undetermined although from the general properties of the substance there appeared to be little doubt that two of the hydroxy-groups were in the 1 : 2–position.

An analytical investigation led one of us to suggest (*Journ. Chem. Soc.*, 1918, **113**, 768) that morindone was either hydroxymethylanthrarufin (I) or hydroxymethylchrysazin (II), the former being preferred, since in its colour reactions, morindone more closely resembles hydroxyanthrarufin than hydroxychrysazin.




I

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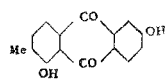


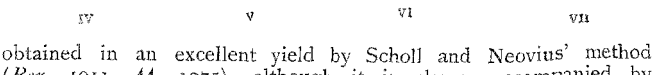

III

It is well known (*cf.* Liebermann, *Ber.*, 1876, **11**, 1617; *D.R.P.*, 195028, 196980) that 2-hydroxyanthraquinones on fusion with alkali, either alone or in the presence of oxidising agents, readily yield dihydroxyanthraquinones the second hydroxy-group entering the 1-position, a reaction which is analogous to the conversion of resorcinol into phloroglucinol by fusion with sodium hydroxide. Simonsen and Rau (*Journ. Chem. Soc.*, 1921, **118**, 1340) therefore synthesised 2 : 5-dihydroxy-6-methylanthraquinone (1 : 6-dihydroxy-2-methylanthraquinone, III) since on fusion with alkali this should yield the trihydroxy-methylanthraquinone (I). Unfortunately the yield of 2 : 5-dimethoxy-6-methylanthraquinone from 2 : 4'-dimethoxy-3-methylbenzophenone-6-carboxylic acid (IV) was so poor that systematic experiments on its oxidation were not possible.

Additional evidence of the correctness of the suggested formula for morindone was furnished by the synthesis of 1 : 2 : 8-trimethoxy-7-methylanthraquinone (*Journ. Chem. Soc.*, 1924, **125**, 721) which was found not to be identical with morindone trimethyl ether. In 1925 Adams and Jacobson (*Journ. Am. Chem. Soc.*, 1925, **47**, 283) devised an ingenious synthesis of 1 : 2 : 5-trihydroxy-6-methylanthraquinone (I) and showed this to be identical in all respects with morindone.

During the course of their experiments Simonsen and Rau obtained some evidence of the conversion of 2 : 5-dihydroxy-6-methylanthraquinone into morindone and it appeared to be not without interest to repeat and extend their experiments since it has been shown by Bistrzycki and his collaborators in a series of papers (*c. f. Helv. Chim. Acta*, 1923, **6**, 750) that an excellent yield of anthraquinone derivatives can usually be obtained if, instead of the benzophenone-carboxylic acid, the diphenylmethanecarboxylic acid is treated with sulphuric acid and the resulting anthrone subsequently oxidised to the corresponding anthraquinone.

The reduction of 2 : 4'-dimethoxy-3-methylbenzophenone-6-carboxylic acid (IV) to *2 : 4'-dimethoxy-3-methyldiphenylmethane-6-carboxylic acid* (V) offered some difficulty, but this acid was ultimately




IV V VI VII

obtained in an excellent yield by Scholl and Neovius' method (*Ber.*, 1911, **44**, 1075), although it is always accompanied by *2 : 4'-dimethoxy-3-methylphenylphthalide* (VI). When 2 : 4'-dimethoxy-3-methyldiphenylmethane-6-carboxylic acid is treated at the ordinary temperature with sulphuric acid it passes readily into *2 : 5-dimethoxy-6-methyl-9-anthrone* (VII), which on oxidation yields the dimethyl ether of 2 : 5-dihydroxy-6-methylanthraquinone (III). The dimethylation of the ether was most readily effected by somewhat prolonged digestion with aluminium chloride and the yield did not exceed 50 per cent. When the dihydroxyanthraquinone was fused with potassium hydroxide in presence of sodium arsenate at a temperature not exceeding 260°, the melt gradually changed from red to violet owing to formation of the trihydroxyanthraquinone. The oxidation was never complete, and if the temperature was allowed to rise above 260° profound decomposition took place and the melt became colourless. The mixture of hydroxyanthraquinones obtained on acidification of the melt was digested with barium hydroxide solution,

when the sparingly soluble barium salt of 1 : 2 : 5-trihydroxy-6-methylanthraquinone separated. The hydroxyanthraquinone from this barium salt was further purified by conversion into its acetyl derivative which, after repeated crystallisation from acetic acid, melted at 249° and was identical in all respects with the triacetyl derivative of morindone. On hydrolysis 1 : 2 : 5-trihydroxy-6-methylanthraquinone, m.p. 275°, was obtained and had all the properties of natural morindone.

## EXPERIMENTAL.

*2 : 4'-Dimethoxy-3-methyldiphenylmethane-6-carboxylic acid* (V).

2 : 4'-Dimethoxy-3-methylbenzophenone-6-carboxylic acid (15 g.) was dissolved in sodium hydroxide solution (2 N; 475 cc.), an ammoniacal solution of copper sulphate (40 cc. from 2 N ammonia and 2 N copper sulphate) with zinc dust (25 g.) being added. The mixture was boiled under reflux for 140–150 hours, small additional quantities of sodium hydroxide solution and zinc dust being added every 12 hours. The hot reaction mixture was filtered, the residue washed with hot dilute ammonia and the filtrate acidified, when a pasty mass separated which rapidly solidified. The solid was dissolved in ether, the ethereal extract repeatedly washed with sodium bicarbonate solution, dried and evaporated. The viscid oil which remained slowly crystallised on keeping, more rapidly on inoculation, and was recrystallised from methyl alcohol, separating in glistening cubes m.p. 78–79°. *2 : 4'-Dimethoxy-3-methylphenylphthalide* was found to be readily soluble in the usual organic solvents; in cold alkalies it was insoluble but dissolved slowly on boiling (Found: C, 71·6; H, 5·7; $C_{17}H_{16}O_4$ requires C, 71·8; H, 5·6 per cent.).

The sodium bicarbonate solution (see above) on acidification deposited *2 : 4'-dimethoxy-3-methyldiphenylmethane-6-carboxylic acid*. The acid, which was readily soluble in the ordinary organic solvents and very sparingly so in water, was best purified by crystallisation from methyl alcohol from which it separated in glistening leaflets, m.p. 103–104° (Found: C., 71·3; H, 6·2; M, 284·6; $C_{17}H_{18}O_4$ requires C, 71·3; H, 6·3 per cent.; M, 286).

*2 : 5-Dimethoxy-6-methyl-9-anthrone* (VII).

2 : 4'-Dimethoxy-3-methyldiphenylmethane-6-carboxylic acid (5 g.) was mixed with sulphuric acid (*d.* 1·84; 50 cc.) and the brown solution allowed to stand at room-temperature for ten minutes. The reaction mixture was poured on ice, the solid which separated collected,

triturated with dilute sodium carbonate solution to remove unchanged acid and recrystallised from acetic acid. The anthrone separated in faintly yellow needles, m.p. 111–112° (Yield 4 g. Found: C, 75·9; H, 6·2; $C_{17}H_{16}O_3$ requires C, 76·1; H, 6·0 per cent.).

*2 : 5-Dimethoxy-6-methylanthraquinone.*—The anthrone (1 mol.) having been dissolved in acetic acid, chromic acid (2 mols.) was gradually added, the oxidation being completed by digestion on the water bath. The anthraquinone was precipitated by water and recrystallised from either acetic acid or benzene, yellow needles, m.p. 192°[1] (Found: C, 72·9; H, 5·1; calc. C, 72·3; H, 5·0 per cent.).

*2 : 5-Dihydroxy-6-methylanthraquinone.*—The dimethyl ether (5 g.) was mixed with finely powdered aluminium chloride (10 g.), heated to 200° during one hour and maintained at this temperature for 30 minutes. A further quantity of aluminium chloride (5 g.) was added and the heating continued for another 15 minutes. The cooled reaction mixture was treated with ice and hydrochloric acid and the hydroxyanthraquinone collected. It was purified by solution in alkali and crystallisation from acetic acid, m.p. 280–281°.

*1 : 2 : 5-Trihydroxy-6-methylanthraquinone.*

2 : 5-Dihydroxy-6-methylanthraquinone (1 g.) was dissolved in potassium hydroxide solution (10 cc. of 50 per cent.) and the mixture heated in a nickel crucible with gradual addition of sodium arsenate (1 to 2 g.) at 220–230° (bath-temperature) for 1·5 hours. The red melt gradually became bluish violet owing to the conversion of the di- into trihydroxyanthraquinone. After dilution with water (100 cc.) the solution was boiled for 30 minutes and acidified. The mixture of hydroxyanthraquinones which separated was digested with an excess of barium hydroxide solution, when a sparingly soluble violet barium salt was precipitated. This was collected, decomposed with hydrochloric acid and the somewhat impure 1 : 2 : 5-trihydroxy-6-methylanthraquinone acetylated. The triacetyl derivative crystallised from acetic acid in needles, m.p. 249° uncorr. and this m.p. was unaltered on admixture with a specimen of triacetylmorindone. On hydrolysing the acetyl derivative, 1 : 2 : 5-trihydroxy-6-methylanthraquinone was obtained and crystallised from toluene in orange red needles m.p. 275° uncorr. It had all the properties of morindone and did not depress the m.p. of this substance (Found: C, 66·8; H, 3·8; calc. C, 66·6; H, 3·7 per cent.).

[1] The m.p. 182° given in the previous communication (*loc. cit.*, p. 1347) is a clerical error.

# III. DERIVATIVES OF ACENAPHTHPYRIDINE. PART I.[1]

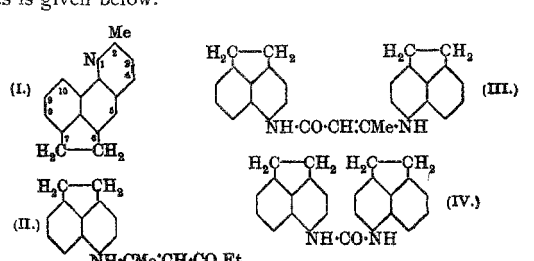
*By Srikumaran Unni Nair and John Lionel Simonsen.*

During an investigation of derivatives of naphthaquinoline (*Journ. Chem. Soc.*, 1926, 2247) it was observed that, while α-naphthylamine itself could not be condensed with paraldehyde, its derivatives substituted in the 4-position readily underwent this reaction. In order to ascertain whether 4-substitution was the determining factor, we decided to examine the condensation of 5-aminoacenaphthene with paraldehyde, since this base may be regarded as a derivative of α-naphthylamine in which the 4-position is substituted.

Cyclic nitrogen derivatives containing the acenaphthene nucleus have been little investigated and it was only when this work was nearing completion that a paper appeared (Stewart, J., 1925, **127**, 1331), in which an account was given of the preparation of acenaphthpyridine.[2]

When digested with hydrochloric acid, 5-aminoacenaphthene and paraldehyde readily condense with formation of *2-methylacenaphthpyridine* (I), thus confirming the suggestion that substitution in position 4 is the deciding factor in this reaction. On reduction with sodium and alcohol, 2-methylacenaphthpyridine is converted into the corresponding *tetrahydro-base*, but the yield is poor owing to the simultaneous production of more highly reduced bases. No better results were obtained by using other reducing agents.

The condensation of 5-aminoacenaphthene with ethyl acetoacetate proceeds like that of α-and β-naphthylamines. A description of the products is given below.




[1] Reprinted from the Journal of the Chemical Society, 1926, 3140.

[2] The name acenaphthpyridine appears to us to be preferable to that of α-acenaphthaquinoline, since the latter name should really be given to a substance containing both the acenaphthene and the quinoline ring.

## EXPERIMENTAL.

*Condensation of 5-Aminoacenaphthene and Paraldehyde. 2-Methylacenaphthpyridine* (I).—A mixture of 5-aminoacenaphthene (10 g.), hydrochloric acid (*d* 1·19; 20 g.), and paraldehyde (15 g.) developed an intense red colour at 50°, a vigorous reaction took place at 70°, and after 15 minutes the condensation was completed by heating at 110° for 5 hours. An excess of alkali was added, the semi-solid, viscid brown oil that separated was dissolved in dilute sulphuric acid and treated with a slight excess of sodium nitrite solution to remove the secondary base which had been formed, and the filtered solution was made alkaline with ammonia. The base (6 g.) obtained was crystallised from dilute alcohol. *2-Methylacenaphthpyridine* separated from alcohol in irregular, colourless prisms, m.p. 131°, which became brown somewhat rapidly on exposure to air. It was readily soluble in the ordinary organic solvents except light petroleum (Found: C, 87·6; H, 6·1; N, 6·7. $C_{16}H_{13}N$ requires C, 87·7; H, 5·9; N, 6·4 per cent.).

The *hydrochloride* and *hydrobromide* were somewhat sparingly soluble in water and crystallised in needles. The *picrate* separated from alcohol in glistening, yellow prisms, decomp. 225–226° (Found: N, 12·9. $C_{22}H_{16}O_6N_4$ requires N, 13·0 per cent.). The *chloroplatinate*, which was insoluble in water and alcohol, was deposited on the addition of platinic chloride to a solution of the hydrochloride as a brown, crystalline powder, decomp. 251–252° (Found: Pt, 23·1. $C_{32}H_{28}N_2Cl_6Pt$ requires Pt, 23·0 per cent.).

*2-Methyl-1 : 2 : 3 : 4-tetrahydroacenaphthpyridine.*—A solution of 2-methylacenaphthpyridine (10 g.) in boiling alcohol (600 c.c.) was treated with sodium (40 g.), the alcohol then removed in steam, and the *tetrahydro-base* separated by ether. It distilled at 215–217°/14 mm.; the distillate, which slowly crystallised, separated from alcohol in glistening prisms, m.p. 88–89° (Found: C, 85·9; H, 7·9; N, 6·5. $C_{16}H_{17}N$ requires C, 86·1; H, 7·6; N, 6·3 per cent.). The base, which was readily soluble in all the ordinary organic media except alcohol, gave strongly fluorescent solutions which darkened rapidly on exposure to the air. The yield of tetrahydro-base was very poor, a considerable quantity of liquid bases of lower boiling point being formed simultaneously. When other reducing agents such as sodium amalgam, tin and hydrochloric acid, and amalgamated zinc and hydrochloric acid were used, the original base was recovered unchanged.

The *hydrochloride* separated from dilute alcohol in ill-defined crystals, decomp. 260–261° (Found: Cl, 13·8. $C_{16}H_{17}N,HCl$ requires

Cl, 13·7 per cent.). The *benzoyl* derivative crystallised from alcohol in rectangular plates, m.p. 187–188° (Found: C, 84·1; H, 6·8. $C_{23}H_{21}ON$ requires C, 84·4; H, 6·4 per cent.).

*Condensation of 5-Aminoacenaphthene and Ethyl Acetoacetate.*—(i) *Ethyl β-5-acenaphthylaminocrotonate* (II). To a mixture of 5-aminoacenaphthene (9 g.), ethyl acetoacetate (7 g.)., and sufficient alcohol to give a clear solution, piperidine (2 drops) was added. After 12 hours, the crystalline solid was collected; it recrystallised from alcohol in plates, m.p. 83–84°. The *ester* was readily soluble in the ordinary organic solvents (Found: C, 76·9; H, 6·9; N, 5.3. $C_{18}H_{19}O_2N$ requires C, 76·9; H, 6·8; N, 5·0 per cent.).

*4-Hydroxy-2-methylacenaphthpyridine*, obtained in a quantitative yield when ethyl β-5-acenaphthylaminocrotonate was heated to 220°, crystallised from acetic acid in thin, glistening plates, m.p. above 330°. It was insoluble in all the ordinary solvents except acetic acid and nitrobenzene, showed very feeble basic properties, and gave no colour with ferric chloride (Found: C, 81·5; H, 5·6; N, 6·0. $C_{16}H_{13}ON$ requires C, 81·7; H, 5·5; N, 6·0 per cent.).

(ii) *β-5-Acenaphthylaminocroton-5-acenaphthylamide* (III).—A mixture of 5-aminoacenaphthene (23 g.) and ethyl acetoacetate (18 g.) was heated on the water-bath for 8 hours, a further equal quantity of ethyl acetoacetate then added, and the heating continued for 5 hours at 170°. The cooled solid residue was powdered, thoroughly washed with alcohol, and crystallised from toluene, which left undissolved a small quantity of a substance (*A*).

*β-5-Acenaphthylaminocroton-5-acenaphthylamide* crystallised in rosettes of needles, m.p. 189–190°. It was insoluble in water, somewhat readily soluble in acetic acid, ethyl acetate, acetone, or pyridine; and more sparingly soluble in benzene or chloroform (Found: C, 83·2, H, 6·2; N, 7·1. $C_{28}H_{24}ON_2$ requires C, 83·2; H, 5·9; N, 6·9 per cent.).

*5-Acetoacetamidoacenaphthene.*—The crotonamide (III) (20 g.) was mixed with hydrochloric acid (320 c.c. of 4 per cent.) and heated on the water-bath for 15 minutes. The solid product, after being washed with boiling water to remove 5-aminoacenaphthene hydrochloride, crystallised from dilute alcohol in fine needles, m.p. 142–143° (Found: C, 76·0; H, 6·2; N, 5·9. $C_{16}H_{15}O_2N$ requires C, 75·9; H, 5·9; N, 5·5 per cent.).

*2-Hydroxy-4-methylacenaphthpyridine.*—A mixture of 5-acetoacetamidoacenaphthene (11 g.) and concentrated hydrochloric acid (10 c.c.)

was heated on the water-bath for 10 minutes; the solid that separated on pouring the product into water was repeatedly extracted with boiling water to remove 5-aminoacenaphthene hydrochloride formed by hydrolysis. The *hydroxy-base* crystallised from nitrobenzene in glistening prisms, m.p. above 350°. It was extremely sparingly soluble in the ordinary solvents and gave no colour with ferric chloride (Found: C, 82·0; H, 5·8; N, 6·3. $C_{16}H_{13}ON$ requires C, 81·7; H, 5·5; N, 6·0 per cent.). A solution in hot hydrochloric acid, on cooling, deposited a sparingly soluble *hydrochloride* which was readily dissociated by water.

2-*Chloro*-4-*methylacenaphthpyridine*.—A suspension of the hydroxy-base (0·6 g.) and phosphorus pentachloride (1 g.) in phosphorus oxychloride (10 c.c.) was heated at 107° for 3 hours. After addition of ice, the *chloro*-compound was collected; it crystallised from alcohol in needles, m.p. 200–201°. It was readily soluble in benzene, chloroform, or acetic acid, somewhat sparingly soluble in alcohol, and insoluble in light petroleum (Found: N, 5·6; Cl, 14·0. $C_{16}H_{12}NCl$ requires N, 5·5; Cl, 14·0 per cent.).

4-*Methyl*-1 : 2 : 3 : 4-*tetrahydroacenaphthpyridine* was obtained by reducing the above chloro-derivative with sodium and alcohol. After purification through the sparingly soluble *hydrobromide*, it crystallised from alcohol in fine needles, m.p. 87–88° (Found: C, 85·9; H, 7·8. $C_{16}H_{17}N$ requires C, 86·1; H. 7·6 per cent.).

s-*Di*-5-*acenaphthylcarbamide* (IV).—The substance (*A*) (see p. 12) which was insoluble in toluene crystallised from much nitrobenzene in prismatic needles, m.p. 318°. It was identified as the substituted carbamide by direct comparison with a specimen prepared by heating a mixture of urea and 5-aminoacenaphthene at 200° for 2 hours (Found: C, 82·5, 82·1[1]; H, 5·6, 5·5[1]; N, 8·4. $C_{25}H_{20}ON_2$ requires C, 82·4; H, 5·5; N, 7·7 per cent.).

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[1] Specimen prepared from urea.