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

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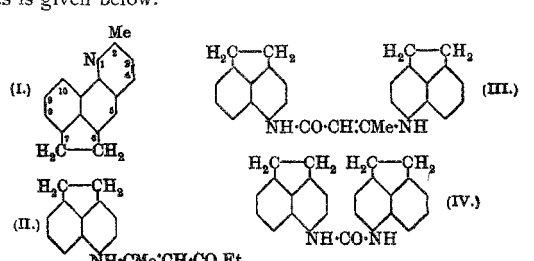
During an investigation of derivatives of naphthaquinoline (*Journ. Chem. Soc.*, 1926, 2247) it was observed that, while α-naphthylamine itself could not be condensed with paraldehyde, its derivatives substituted in the 4-position readily underwent this reaction. In order to ascertain whether 4-substitution 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.