

expected on the basis of (V) for lycorine, dihydrolycorine anhydromethine (II), but an isomer *which contains a vinyl group*. If, however, the double bond is in the 4 : 5-position (as VI), then the Emde reduction would proceed initially by the attack of two electrons followed by addition of a proton to the mesomeric anion with the resultant allylic shift to produce a vinyl group and a tertiary amine (scheme A).

The final Emde product is probably (VII) for which the ultra-violet absorption spectrum (λ_{max} , 297 m μ , $\log \epsilon$ 3.86; Kondo and Katsura, *loc. cit.*) is in good agreement. The Hofmann degradation is pictured as starting by elimination of a proton from the carbon atom δ to the quaternary nitrogen atom (scheme B), followed by elimination of two molecules of water to give lycorine anhydromethine (I). Further work to substantiate the proposed formula (VI) for lycorine is in progress.

Added in Proof.—Through the kindness of Dr. S. Uyeo, Osaka, Japan, we have shown that our synthetic 1-ethyl-9 : 10-dihydro-10-methyl-6 : 7-methylenedioxyphenanthridine is identical with authentic dihydrolycorine anhydromethine in melting point, mixed melting point, and infra-red spectrum.

EXPERIMENTAL

o-Ethylformanilide.—*o*-Ethylaniline (35 g.) and formic acid (13.2 g.) were heated on a water-bath for 30 min., after which the temperature was raised slowly to 240° to allow water and excess of formic acid to distill off. After cooling, ether (50 c.c.) was added to the mixture and pure *o*-ethylformanilide (28 g.), m. p. 70°, crystallized. For analysis it was recrystallized from ether and dried *in vacuo* at room temperature for 48 hr. (Found: C, 72.4; H, 7.4; N, 9.0. C₉H₁₁ON requires C, 72.5; H, 7.4; N, 9.4%).

o-Ethyl-*N*-methylaniline.—*o*-Ethylformanilide (25 g.) in ether (500 c.c.) was added dropwise to ether (1 l.) containing lithium aluminium hydride (10 g.) and then heated for 15 hr. under reflux. Water was carefully added and after the vigorous reaction had subsided the ethereal solution was separated and the aqueous residue extracted three times with ether. The combined ethereal extracts were dried (Na₂SO₄) and concentrated to dryness, to yield the crude base which after distillation afforded pure *o*-ethyl-*N*-methylaniline (21.8 g.), b. p. 95—97°/11 mm. It gave a *picrate*, m. p. 136—138°, from methanol (Found, in a sample dried *in vacuo* at 45° for 48 hr.: C, 49.6; H, 4.4; N, 15.3. C₁₅H₁₆O₇N₄ requires C, 49.5; H, 4.4; N, 15.4%).

o'-Ethyl-*N*-methyl-4 : 5-methylenedioxy-2-nitrobenzanilide (III).—4 : 5-Methylenedioxy-2-nitrobenzoyl chloride (from 10 g. of acid) was added slowly to a stirred solution of *o*-ethyl-*N*-methylaniline (7 g.) and pyridine (15 c.c.) in ether (500 c.c.). After 48 hr. the mixture was washed with 5% potassium carbonate solution (500 c.c.), then twice with water. The aqueous washings were extracted with ether, and the combined dried ethereal extracts were concentrated to dryness *in vacuo* to give a viscous brown oil (14.4 g.) which was taken up in chloroform and filtered through activated alumina (500 g.). Concentration of the chloroform eluate afforded the crude crystalline *o*-ethyl-*N*-methyl-4 : 5-methylenedioxy-2-nitrobenzanilide (14 g.), m. p. 106° constant after one crystallization from ether (Found, in a sample dried *in vacuo* at 65° for 48 hr.: C, 62.1; H, 5.0; N, 8.5. C₁₇H₁₆O₅N₂ requires C, 62.2; H, 4.9; N, 8.5%).

2-Amino-*o*'-ethyl-*N*-methyl-4 : 5-methylenedioxybenzanilide (IV).—An ethanolic solution of the preceding anilide (10 g.) took up the theoretical volume of hydrogen in 1 hr. in the presence of Raney nickel. The solution was filtered, concentrated to dryness, to yield after one crystallization from ether pure 2-amino-*o*'-ethyl-*N*-methyl-4 : 5-methylenedioxybenzanilide (8.5 g.), m. p. 121° (Found, in a sample dried *in vacuo* at 60° for 48 hr.: C, 68.5; H, 6.1; N, 9.5. C₁₇H₁₈O₃N₂ requires C, 68.4; H, 6.1; N, 9.4%).

1-Ethyl-9 : 10-dihydro-10-methyl-6 : 7-methylenedioxyphenanthridine (II).—Sodium nitrite (0.8 g. in 5 c.c. of water) was added to an ice-cold solution of 2-amino-*o*'-ethyl-*N*-methyl-4 : 5-methylenedioxybenzanilide (2.8 g.) in 5% sulphuric acid (100 c.c.). After 1 hr. the pale yellow solution was heated slowly to 75° and kept thereat for 2 hr. during the slow nitrogen evolution and finally at 100° for 30 min. The mixture was extracted five times with chloroform which was then washed with 10% aqueous sodium hydroxide and water. Evaporation of the dried (Na₂SO₄) chloroform extract gave a dark brown tar (840 mg.) which was chromatographed in ether over activated alumina (2.5 g.). The ether eluate (1300 c.c.) yielded on concentration a pale yellow wax which after sublimation (130—150°/0.1 mm.) yielded crude 1-ethyl-10-methyl-6 : 7-methylenedioxyphenanthridone (255 mg., 10%). The whole of the crude phenanthridone was refluxed for 15 hr. in ether with lithium aluminium hydride (1 g.). Addition of water and extraction with ether afforded a yellow oil (205 mg.) which was converted into a crystalline

picrate (142 mg.), m. p. 175° (decomp.) (from methanol). For analysis the 1-ethyl-9:10-dihydro-10-methyl-6:7-methylenedioxyphenanthridine picrate was dried *in vacuo* at 80° for 48 hr. (Found: C, 55.5; H, 4.2; N, 11.1. $C_{23}H_{20}O_2N_4$ requires C, 55.6; H, 4.1; N, 11.1%).

A chloroform solution of the picrate was filtered through a short column of activated alumina, then concentrated to dryness, to give the base (22 mg.), m. p. 87° constant after one crystallization from ether-light petroleum (b. p. 30–60°) (Found, in a sublimed sample: C, 76.1; H, 6.2. $C_{17}H_{17}O_2N$ requires C, 76.4; H, 6.4%).

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