

121. Long-chain Alkylpyridines and their Derivatives. New Examples of Liquid Crystals.

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The methods which serve for the production of simple homologues of pyridine are inapplicable to long-chain compounds; the latter can be prepared by Tschitschibabin's method (condensation of 2-picoline with an alkyl chloride in presence of sodamide), provided that the reaction is carried out at 100°.

The products are wax-like solids, soluble in strong acids, to form salts which lather freely in aqueous solution. The hydrochlorides melt to form birefringent, anisotropic, viscous masses, which, at higher temperatures, pass abruptly into isotropic, mobile liquids. The corresponding 1-alkylpyridinium salts behave similarly.

The following are described: 1-n-dodecylpyridinium chloride, bromide and iodide; 1-n-tetradecylpyridinium chloride and iodide; 1-cetylpyridinium chloride and iodide; 1-n-octadecylpyridinium chloride and iodide; 2-n-tridecyl-, 2-n-pentadecyl-, 2-n-heptadecyl-, and 2-n-nonadecyl-pyridine, and the hydrochlorides, picrates, and picrolonates of these bases.

PRIOR to the publication by Tschitschibabin (*Bull. Soc. chim.*, 1936, **3**, 1607) of the method which he justly claims must take first place among reactions for the preparation of 2- and 4-alkylpyridines, the authors had tried in vain to prepare long-chain 2-alkyl derivatives of pyridine which were required for another investigation. Dodecylpyridinium chloride decomposed at 200°, in the presence of copper, forming dodecylene and pyridinium chloride; attempted condensation of dodecyl alcohol with pyridine in presence of zinc chloride gave a similar result; and tridecaldehyde yielded no condensation product with 2-picoline.

Tschitschibabin obtained good yields of bases such as 2-n-amylypyridine by condensing simple chlorides with 2-picoline in presence of sodamide at room temperature; bromides and iodides gave much lower yields owing to quaternary salt formation. The authors have repeated some of Tschitschibabin's work with these simple halides and find that his claims are fully justified.

Extension of the method to long-chain halides, however, gave negligible yields in 72 hours, and the reaction was incomplete after 12 weeks. Yields of 47—70% of the theoretical were obtained by conducting the reaction at 100° during 24 hours; quaternary chloride formation at this temperature is negligible.

The long-chain 2-alkylpyridines are feeble bases whose salts with strong acids resemble soaps in lathering freely in aqueous solution, and acting as emulsifying agents. The hydrochlorides melt to form viscous liquids which, under the microscope, between crossed nicols, exhibit birefringence and anisotropic colours. At higher temperatures they pass abruptly into mobile isotropic liquids. This property is not shown by the free bases, or by their picrates or picrolonates.

Tschitschibabin obtained, as by-products, compounds formed by the condensation of two mols. of alkyl chloride with one of 2-picoline. No such compounds were obtained in the present investigation owing, no doubt, to the low reactivity of long-chain chlorides.

The long-chain 1-alkylpyridinium salts are readily soluble in water, the solutions foam readily, form more stable emulsions with oils than either soaps or sodium alkyl sulphates containing the same number of carbon atoms in the open chain, and impart a greasy appearance to the surface of glass. These salts also form liquid crystals.

EXPERIMENTAL.

Quaternary Salts.—Alkyl chlorides were heated with pyridine for 8 hours at 150°, the bromides required 1 hour at 150°, and the iodides 3 hours at 100°. Dodecyl chloride, heated with pyridine at 100° for 24 hours, gave a product containing only 1.7% of the theoretical amount of ionisable chlorine. The iodides were also prepared by treating the chlorides with potassium iodide in concentrated aqueous solution. The salts were crystallised by solution in the minimum quantity

of dry alcohol, dilution with dry ether, and cooling (to 0° for the dodecyl compounds). The solubility in water and in alcohol diminishes with increase in length of the hydrocarbon chain, but that in benzene increases. The two m. p.'s are recorded as I and II. 1-Dodecylpyridinium chloride, m. p. I, 71°, II, 145° (Found: Cl, 12.2. $C_{17}H_{30}NCl$ requires Cl, 12.5%), bromide, m. p. I, 89—90°, II, 125° (Found: Br, 24.1. $C_{17}H_{30}NBr$ requires Br, 24.4%), iodide, m. p. I, 88—89°, II, 93° (Found: I, 33.6. $C_{17}H_{30}NI$ requires I, 33.9%). 1-Tetradecylpyridinium chloride, m. p. I, 77°, II, 205° (Found: Cl, 11.0. $C_{19}H_{34}NCl$ requires Cl, 11.4%), iodide, m. p. I, 94°, II, 155° (Found: I, 31.2. $C_{19}H_{34}NI$ requires I, 31.5%). 1-Cetylpyridinium chloride, m. p. I, 83°, II, 217° (Found: Cl, 10.3. $C_{21}H_{38}NCl$ requires Cl, 10.5%), iodide, m. p. I, 98°, II, 205° (Found: I, 29.4. $C_{21}H_{38}NI$ requires I, 29.5%); Macovski (*Bull. Soc. chim.*, 1936, 3, 498) gives m. p. 110° for the chloride, and 101° for the iodide. 1-Octadecylpyridinium chloride, m. p. I, 89°, II, 220° (Found: Cl, 9.4. $C_{23}H_{42}NCl$ requires Cl, 9.7%), iodide, m. p. I, 103°, II, 221° (Found: I, 27.5. $C_{23}H_{42}NI$ requires I, 27.7%).

2-*n*-Tridecylpyridine.—2-Picoline (23.0 g.; 1.0 mol.) and finely divided sodamide (10 g.; 1.0 mol.) were stirred mechanically in a flask with a mercury seal; the mixture became yellow, then deep red. *n*-Dodecyl chloride (34.0 g.; 0.6 mol.) was added slowly, and the mixture maintained at 100° for 24 hours, with frequent stirring. Isolation of the product presented difficulty at first. 2*N*-Hydrochloric acid extracted very little of the new base, and more concentrated acid produced a semi-solid, soap-like mass, which included unchanged dodecyl chloride. Precipitation as the perchlorate was fairly satisfactory, but yielded a slimy mass which was difficult to manipulate. The following method was adopted finally; the crude product, after decomposition of unchanged sodamide with water, and removal of 2-picoline in steam, was extracted with petroleum (b. p. 60—80°; 300 c.c.). The extract was dried over sodium sulphate, and the hydrochloride precipitated with dry hydrogen chloride, washed with petroleum, and decomposed with hot 10% sodium hydroxide solution. On distillation, 95% of the total yield had b. p. 335—336° and solidified to a wax-like solid (39 g.). Purified *via* the picrate, the base had m. p. 19°, b. p. 199°/10 mm. (Found: C, 82.6; H, 11.9; N, 5.4. $C_{18}H_{31}N$ requires C, 82.8; H, 11.9; N, 5.4%). The hydrochloride had m. p. I, 52°, II, 109° (Found: Cl, 11.8. $C_{18}H_{31}N.HCl$ requires Cl, 11.9%). The picrate, precipitated from alcohol-acetone and recrystallised from ethyl acetate, had m. p. 78° (Found: C, 58.8; H, 7.0. $C_{18}H_{31}N.C_6H_5O_7N_3$ requires C, 58.8; H, 6.9%), and the picrolonate, from alcohol, had m. p. 85° (Found: C, 63.9; H, 7.7. $C_{18}H_{31}N.C_{10}H_8O_5N_4$ requires C, 64.0; H, 7.4%). The other bases and their salts were prepared and purified by similar methods.

2-Picoline (45 g.), sodamide (20 g.), and *n*-tetradecyl chloride (78 g.) gave 2-*n*-pentadecylpyridine (43 g.), m. p. 29°, b. p. 215°/10 mm. (Found: C, 83.1; H, 12.0; N, 4.8. $C_{20}H_{35}N$ requires C, 83.1; H, 12.1; N, 4.8%); hydrochloride, m. p. I, 59°, II, 118° (Found: Cl, 10.7. $C_{20}H_{35}N.HCl$ requires Cl, 10.9%); picrate, m. p. 85° (Found: C, 60.7; H, 7.5. $C_{20}H_{35}N.C_6H_5O_7N_3$ requires C, 60.2; H, 7.3%); picrolonate, m. p. 92° (Found: C, 64.9; H, 7.6. $C_{20}H_{35}N.C_{10}H_8O_5N_4$ requires C, 65.1; H, 7.8%).

2-Picoline (46 g.), sodamide (20 g.), and *n*-hexadecyl chloride (75 g.) gave 2-*n*-heptadecylpyridine (48 g.), m. p. 37°, b. p. 231°/10 mm. (Found: C, 83.1; H, 12.3; N, 4.5. $C_{22}H_{39}N$ requires C, 83.3; H, 12.3; N, 4.4%); hydrochloride, m. p. I, 65°, II, 125° (Found: Cl, 9.9. $C_{22}H_{39}N.HCl$ requires Cl, 10.0%); picrate, m. p. 85—86° (Found: C, 61.7; H, 7.9. $C_{22}H_{39}N.C_6H_5O_7N_3$ requires C, 61.5; H, 7.7%); picrolonate, m. p. 95.5° (Found: C, 66.0; H, 8.2. $C_{22}H_{39}N.C_{10}H_8O_5N_4$ requires C, 66.1; H, 8.1%).

2-Picoline (46 g.), sodamide (20 g.), and *n*-octadecyl chloride (96 g.) gave 2-*n*-nonadecylpyridine (40 g.), m. p. 46°, b. p. 247—248°/10 mm. (Found: C, 83.2; H, 12.3; N, 4.3. $C_{24}H_{43}N$ requires C, 83.5; H, 12.5; N, 4.1%); hydrochloride, m. p. I, 73°, II, 134° (Found: Cl, 9.2. $C_{24}H_{43}N.HCl$ requires Cl, 9.3%); picrate, m. p. 93—94° (Found: C, 62.8; H, 7.7. $C_{24}H_{43}N.C_6H_5O_7N_3$ requires C, 62.7; H, 8.0%); picrolonate, m. p. 99—100° (Found: C, 67.0; H, 8.4. $C_{24}H_{43}N.C_{10}H_8O_5N_4$ requires C, 67.0; H, 8.4%).

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