

[CONTRIBUTION FROM THE UNIVERSITY OF MANCHESTER.]

**THE PREPARATION OF PYRIDINE AND OF CERTAIN OF ITS
HOMOLOGS IN A STATE OF PURITY.**

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The preparation of highly purified pyridine has not yet been described, while in the case of its homologs widely discordant results are recorded for the physical properties. It was therefore considered of interest to undertake the preparation of the bases in a pure form.

Pyridine.

Crude coal tar bases vary greatly both in the nature and in the proportion of the bases which they contain. The nature of the bases depends on whether they are derived from light or middle oil. The following results were obtained with bases derived from a light oil.

The crude bases were dehydrated with solid sodium hydroxide. From 2 liters 800 cc. of a pyridine fraction, b. p. 113° to 117° , and 200 cc. of a 2-methylpyridine fraction, b. p. 127° to 130° , were obtained after six successive fractional distillations through a glass fractionating column 110 cm. long and 2 cm. in diameter (Col. A).

Pure pyridine was obtained by converting the former fraction into the pure compound $2C_5H_5N \cdot ZnCl_2$. For this purpose, 845 g. of zinc chloride is dissolved in a mixture of 690 cc. of water, 345 cc. of conc. hydrochloric acid (sp. gr. 1.18) and 690 cc. of absolute alcohol. One liter of the pyridine fraction is added to this mixture.

A crystalline precipitate is obtained which is separated from the mother liquor and recrystallized twice from absolute alcohol. To liberate the base, a concentrated aqueous solution of 26.7 g. of sodium hydroxide is added to 100 g. of the dry recrystallized compound. The base with dissolved water is separated from the precipitate by filtration and is dried over solid sodium hydroxide. This sample of pyridine, on distillation in a dry apparatus, distills completely at 115.3° , measured on the international hydrogen scale, under 760 mm. of mercury. The mass of 1 cc. of pyridine at 25° (d_{4}^{25}) is 0.9776 g. All weighings were corrected for air displacement. Previous determinations of the boiling point are as follows.

Innes,¹ 115.2° to 115.5° ; Constam and White,² 115.2° ; Zawidzki,³ 115.1° to 115.3° ; Hartley, Thomas and Applebey,⁴ 115.3° to 115.4° . The density (d_{4}^{25}) is variously given, as 0.97721 (Hartley, Thomas and Applebey), 0.97795 (Zawidzki), 0.97832 (Dunstan, Thole and Hunt).⁵

¹ Innes, *J. Chem. Soc.*, **79**, 261 (1901).

² Constam and White, *Am. Chem. J.*, **29**, 1 (1903).

³ Zawidzki, *Chem. Ztg.*, **30**, 299 (1906).

⁴ Hartley, Thomas and Applebey, *J. Chem. Soc.*, **93**, 538 (1908).

⁵ Dunstan, Thole and Hunt, *ibid.*, **91**, 1738 (1907).

2-Methylpyridine.

Pure 2-methylpyridine can be prepared by a method analogous to the preceding, if the fraction distilled from crude bases between 127° and 130° is employed. The resulting product, in a dry apparatus, distils completely at 128° to 9°, measured on the international hydrogen scale, under 760 mm. of mercury. The mass of 1 cc. at 25° (d_{4}^{25}) is 0.9404 g. when all weighings are corrected for air displacement.

Thorpe⁶ gives b. p. 133.5°; d_{4}^{25} 0.9384, d_{4}^{15} 0.9616; Ladenburg and Lange⁷ give b. p. 129°, d_{4}^{15} 0.9652; Constam and White⁸ give b. p. 128.8, d_{4}^{15} 0.9497; Garrett and Smythe⁹ give b. p. 129.4°.

3-Methylpyridine.

(A) Two liters of crude bases derived from a light oil was dehydrated with solid sodium hydroxide and the dry oil was fractionally distilled twelve times successively through a Young's⁹ 8-chamber evaporator fractionating column, 110 cm. long and 3 cm. in diameter. Fractions were collected at every degree from 120° to 150°. The fraction 143° to 144° (227 cc.) was converted into the zinc chloride compound, $2C_6H_7N \cdot ZnCl_2$, by dissolving it in 1135 cc. of water and adding the solution to a conc. aqueous solution of 243 g. of zinc chloride clarified by treatment with hydrochloric acid. The precipitate was separated from the mother liquor, dried, and weighed. The 360 g. obtained was dissolved in 1400 cc. of boiling absolute alcohol. When the solution was cooled to room temperature, the zinc chloride compound crystallized. It was recrystallized from alcohol, until its melting point, determined in a sealed tube, was unaltered by further crystallization. Four crystallizations sufficed, and the melting point was 115°. The 93 g. of the zinc chloride compound of 3-methylpyridine obtained, was decomposed by treatment with a concentrated aqueous solution of 24 g. of sodium hydroxide. The base containing dissolved water, separated by filtration, was dried over solid sodium hydroxide. When placed in a dry apparatus, it distilled completely at 143.8°, measured on the international hydrogen scale, under 760 mm. pressure. The mass of 1 cc. at 25° is 0.9515 g. All weighings were corrected for air displacement.

Previous determinations of the boiling point are as follows: Schwarz,¹⁰ 143.5°; Constam and White,² 143.4°; Flaschner,¹¹ 143.9°; Constam and White give d_{4}^{15} 0.96134 for 3-methylpyridine.

The base obtained in this manner was found to be completely miscible with water between 15° and 100°. It was identified as 3-methylpyridine by oxidation to the

⁶ Thorpe, *J. Chem. Soc.*, **37**, 222 (1880).

⁷ Ladenburg and Lange, *Ann.*, **247**, 6 (1888).

⁸ Garrett and Smythe, *J. Chem. Soc.*, **81**, 452 (1902).

⁹ "Fractional Distillation," The Macmillan Company, **1903**.

¹⁰ Schwartz, *Ber.*, **24**, 1676 (1891).

¹¹ Flaschner, *J. Chem. Soc.*, **95**, 668 (1909).

carboxylic acid, pyridine-3-carboxylic acid, which without further purification melted sharply at 228° in a sealed tube. Since the acid gave no red coloration with ferrous sulfate solution, complete absence of any 2-6 dimethylpyridine in the sample of 3-methylpyridine may be assumed.

The oxidation was carried out in the following manner. Four g. of the base was dissolved in 400 cc. of water and 13.6 g. of potassium permanganate added. The mixture was heated on the steam-bath and a continuous stream of carbon dioxide was passed through it during the period of oxidation. The passage of carbon dioxide improves the yield of the carboxylic acid, presumably because the free potassium hydroxide formed during oxidation in the absence of carbon dioxide, decomposes the acid with formation of pyridine.

After 6 hours, the hot liquid was filtered. The precipitate of manganese dioxide was boiled with water and the solution filtered. The combined filtrates were concentrated to small volume, neutralized with sulfuric acid, cooled and treated with silver nitrate. The solid silver salt of pyridine-3-carboxylic acid was collected on a filter and washed with distilled water; then it was suspended in distilled water and a stream of hydrogen sulfide was passed through the liquid. After the liquid had been boiled, the precipitate of silver sulfide was removed and the filtrate was evaporated to dryness. A white residue of the carboxylic acid was obtained; m. p. 228° .

(B) 3-Methylpyridine can also be obtained from crude pyridine bases of middle oil. The crude bases were dried over solid sodium hydroxide and 3 liters of the dry oil was 5 times successively fractionally distilled through Column A; fractions were collected every degree from 139° to 170° . The fractions from 139° to 143° , total volume 200 cc., were combined and converted into the zinc chloride compound by the method described under (A). An oil separated which would not crystallize even on standing for 24 hours. This oil was collected, dissolved in 800 cc. of boiling alcohol and concentrated to half the volume. Crystallization could be brought about only by cooling the solution to -15° . (The further treatment of the mother liquor is described under the preparation of 2,6-dimethylpyridine.) The crystals were redissolved in 250 cc. of boiling alcohol and the solution was cooled again to -15° . The crystals which then separated were dissolved once more in 250 cc. of boiling alcohol. When this solution cooled to room temperature, crystallization occurred. Two recrystallizations from 250 cc. of alcohol sufficed to give a product, m. p. 115° , whose melting point was unaltered on recrystallization.

The base obtained from these crystals was identical in all respects with the 3-methylpyridine described under (A).

We find that 3-methylpyridine is completely miscible in all proportions with water between 15 and 100° ; therefore our results conflict with those of Flaschner¹¹ who states that 3-methylpyridine is only partially miscible with water. There is no doubt that Flaschner was dealing with a mixture containing 2,6-dimethylpyridine, which we find to be partially miscible with water, and that he did not obtain pure 3-methylpyridine. In contrast to our procedure, Flaschner did not identify any of the materials

he dealt with. Therefore we can state positively that his results for 3-methylpyridine are incorrect.

It is difficult to see how Flaschner could have obtained 4-methylpyridine by crystallization of the zinc chloride compound, since Constam and White² state that 4-methylpyridine is a very weak base. Both Constam and White, and Meisenheimer¹² had to resort to crystallization of the mercuric chloride compound for the preparation of this base. In addition, we have failed entirely to repeat Flaschner's preparation of 4-methylpyridine, the product which we obtained proving to be 3-methylpyridine.

2,6-Dimethylpyridine.

When the alcoholic mother liquor from the first crystallization of the zinc chloride compound of 3-methylpyridine (Section B under "3-Methylpyridine") stood for several days, it separated into two layers. The lower sirupy layer contained the whole of the zinc chloride compound and was separated (224 g.). Fifty g. of sodium hydroxide was added in the form of a concentrated aqueous solution and the regenerated base dried over sodium hydroxide. The 107 cc. of base obtained was mixed with 107 cc. of conc. hydrochloric acid (sp. gr. 1.18) and then added to a solution of 542 g. of mercuric chloride dissolved in 2 liters of boiling alcohol. The compound, $C_7H_9N.HCl.2HgCl_2$, which separated when the solution was cooled to 15° was recrystallized five times from 1400 cc. of boiling alcohol. The product obtained melted at 131° in a sealed tube, and its melting point was unaltered by further crystallization. Yield, 147 g. This was decomposed with a concentrated aqueous solution of 50 g. of sodium hydroxide. The base containing dissolved water separated by filtration from the precipitated mercuric oxide was dried over solid sodium hydroxide and distilled in a dry apparatus. Thus only 13 g. of pure base was obtained and in consequence an accurate reading of the boiling point was not possible; that observed was about 137.5°. The mass of 1 cc. of 2,6-dimethylpyridine at 25° is 0.9200 g. The base was not completely miscible with water at 90°. It was identified as 2,6-dimethylpyridine by oxidation to pyridine-2,6-dicarboxylic acid, which melted sharply at 228° in a sealed tube. In an open tube the acid melted with decomposition. An aqueous solution of the acid, on addition of ferrous sulfate solution, gave a red color, followed by precipitation of a grayish precipitate, presumably an iron salt of the acid. The red coloration indicates the presence of a methyl group in Position 2 in the original base.

2,4-Dimethylpyridine.

The material used for the preparation of this base was the fractions distilled between 155° and 156°, and between 156° and 157°, obtained in the

¹² Meisenheimer, *Ann.*, **420**, 197 (1920).

fractionation described under "3-Methylpyridine," Section B. The total volume, 200 cc., was converted into the compound $C_7H_9N.HCl.2HgCl_2$ by mixing it with 187 cc. of conc. hydrochloric acid and adding the mixture to a solution of 950 g. of mercuric chloride in 3600 cc. of boiling absolute alcohol. The compound which separated as the solution cooled to 15° was recrystallized four times from 1 liter of boiling alcohol. The melting point of the product was 128° , which remained unaltered by further crystallization. The yield was 80 g.

The base was regenerated by treatment with a concentrated solution of 19 g. of sodium hydroxide. The base containing dissolved water was separated from the precipitate by filtration and was dried over solid sodium hydroxide. Through a dry apparatus the base distilled completely at 157.1° under 760 mm. pressure. The mass of 1 cc. at 25° is 0.9273 g. With water it gives a minimum critical solution temperature of 22.5° . The base was identified as 2,4-dimethylpyridine by oxidation to pyridine-2,4-dicarboxylic acid by the method described in the case of 3-methylpyridine, using double the proportion of potassium permanganate. The product melted sharply at 241° ; vigorous evolution of carbon dioxide commenced at once, indicating a dicarboxylic acid. An aqueous solution of the acid gave a deep red coloration with ferrous sulfate solution, which indicates a methyl group in Position 2 in the original base.

Summary.

Pure samples of pyridine and certain of its homologs have been prepared. Boiling points and densities have been determined and found to be as follows: pyridine, b. p. 115.3° , d_4^{25} 0.9776; 2-methylpyridine, b. p. $128-9^\circ$, d_4^{25} 0.9404; 3-methylpyridine, b. p. 143.8° , d_4^{25} 0.9515; 2,6-dimethylpyridine, b. p. about 137.5° , d_4^{25} 0.9200; 2,4-dimethylpyridine, b. p. 157.1° , d_4^{25} 0.9273.

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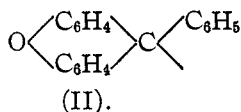
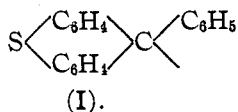
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PHENYL-THIO-XANTHYL.

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The free radical, phenyl-thio-xanthyl (I), differs structurally from phenyl-xanthyl (II) only in the substitution of a sulfur for an oxygen



atom. The difference in the degree of dissociation of the dimolecular forms of these two radicals, as reported in the literature, is therefore