methyl-, dimethyl-, trimethyl-, and tetramethylpyridines with their intensity becoming weaker in that order. These studies were made in order to utilize the data for analyses of pyridines in coal tar bases.

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36. **Nobuo Ikekawa:** Studies on the Coal Tar Bases. V1). Pyridine Bases from Low-Temperature Coking Tar (1).

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Some time ago, the author took part in a study2), in collaboration with others, on the constituent of a fraction below 150° of pyridine bases contained in the coal tar of low-temperature coking. The present paper discusses the pyridine bases contained in the fraction of b.p. 150∼190° from the same tar.

There are some references to the pyridine bases in the fraction of b.p. 150∼190° from coal tar bases3), California cracked gasoline4), and shale tar5). In these studies, the bases were isolated as picrates or mercuric chloride double salts from which the bases were isolated and oxidized to pyridine-carboxylic acids to determine their structures. In a majority of cases, the melting points of picrates were compared with those described in literature.

In the present series of experiments, all the methyl derivatives of pyridine, except 3,4,5-trimethylpyridine, were synthesized6) for comparison, and direct comparisons were made by the mixed fusion of picrates or other salts. This seemed to offer a more conclusive evidence and also need only a small amount of material.

Separation of bases from the light oil of low-temperature coking tar with sulfuric acid yields about 0.2% of bases, which are acetylated to remove primary and secondary amines. This

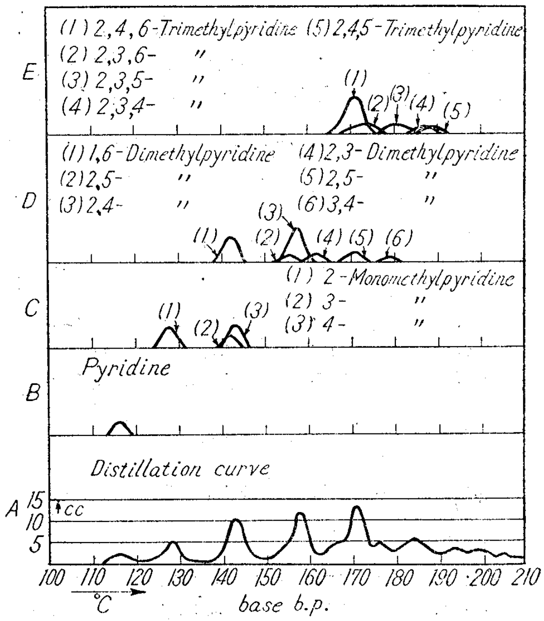

Fig. 1 Distribution of Pyridines in Fraction of 110∼190° in Low-Temperature Coking Tar

Abscissa: Distillation temperature

Ordinate: Unit showing quantitative relationship: No. of cc. in A, amount of base calculated from the amount of picrate in B, C, D, and E. Total amount of each pyridine compound is indicated by the area bound within the curve.

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affords tertiary amines in approximately 70% yield and these amines are fractionally distilled to every 10° by the Fenske packing still. Every fraction thereby obtained is again fractionally distilled every 1°. The distillation curves are shown in Fig. 1.

Each fraction divided by 1° is derived to the picrate and the recrystallized sample is submitted to analyses and mixed fusion with synthetic specimen to determine the structure of the base. Part of the samples was also compared by infrared absorption spectrum[1].

Composite ratio of the pyridines in each fraction was approximately found by the determination of weight of picrates. The pyridines isolated from the fraction of b.p. 150∼190° were: 2,5-, 2,4-, 2,3-, 3,5-, and 3,4-lutidine, and 2,4,6-, 2,3,6-, 2,3,5-, 2,3,4-, and 2,4,5-collidine. The melting points, properties, and analytical values of the picrates of these bases are given in Table I, and their distribution in each fraction is shown in Fig. 1. The pyridines (pyridine, α-, β-, and γ-picoline, and 2,6-lutidine) in the fraction below b.p. 150° are given from the previous paper[2].

As can be seen from Fig. 1, bases from the low-temperature coking tar contain comparatively larger amount of polymethyl derivatives than the bases of high-temperature coal tar. Especially large were the contents of 2,6- and 2,4-lutidine, and 2,4,6-collidine.

TABLE I Pyridines found in the b.p. 150∼190° Fraction of Low-Temperature Coking Tar Bases

Lutidine	b.p. °C	Fraction temp. °C	Picrate			Analyses found		
			m.p. °C	Crystal form[a]	Solty. MeOH	C%	H%	N%
2,5-	157	155∼158	166∼167	prisms or needles	Easily sol.	46.1	3.5	16.2[b]
2,4-	157	155∼160	181∼182	Long needles	Easily sol.			16.5
2,3-	163	157∼164	186∼187	Long needles or cubic	Spar. sol.	46.3	3.4	16.4
3,5-	171	165∼173	240	Long needles or plates	Spar. sol.	46.1	3.8	16.7
3,4-	179	176∼182	159∼160	Plates or prisms	Easily sol.	46.0	3.2	16.3
Collidine								
2,4,6-	170	165∼175	155	Needles	Easily sol.			15.4[c]
2,3,6-	173	168∼177	144∼145	Plates (brown)	Easily sol.	47.5	3.2	15.4
2,3,5-	184	180∼186	181	Long needles	Spar. sol.			16.3
2,3,4-	187	186∼193	163∼164	Needles	Comp. sol.			16.2
2,4,5-	188	186∼193	159∼160	Plates	Easily sol.	48.3	4.2	16.0

[a] All colored yellow.
[b] Calcd. for $C_7H_9N \cdot C_6H_3O_7N_3$ (Lutidine picrate): C, 46.4; H, 3.6; N, 16.7.
[c] Calcd. for $C_8H_{11}N \cdot C_9H_3O_7N_3$ (Collidine picrate): C, 48.0; H, 4.0; N, 16.0.

As is well known, 2,6-lutidine is isolated from the fraction of b.p. 140∼145° as a urea adduct and purified as the hydrochloride. 2,4-Lutidine can be isolated in a pure state by the distillation of its N-oxide. The fraction of b.p. 155∼162° contains 2,4-, 2,3-, and 2,5-lutidine. Derivation to their N-oxides with hydrogen peroxide and glacial acetic acid[2] and fractional distillation give 2,3- and 2,5-lutidine in a low-temperature distillate, and 2,4-lutidine in a high-temperature distillate. 2,4-Lutidine is obtained from the fraction of b.p. 155∼162° in approximately 40% yield.

2,4,6-Collidine is obtained in ca. 35% yield from the fraction of b.p. 168∼172°, and is isolated in pure enough form by the recrystallization of its picrate.

The author expresses his deep gratitude to Prof. E. Ochiai and Prof. K. Tsuda for their unfailing guidance and kind advices throughout the course of this work.

Experimental

Crude Material—Two hundred kg. of light oil obtained from the low-temperature coking tar, manufactured by the Daiichi Kagaku Plant at Wakamatsu, Kyushu, was treated with 20% H_2SO_4.

from which 400 g. of base was obtained. Removal of the neutral portion by acetylation with acetic anhydride gave 250 g. of tertiary amines.

Distillation—Fenske packing still with the column of 100 cm. in length, and 1.7 cm. in inside diameter was used, in the column of which 1.5 mm. dia. single turn nichrome helices was paked. Number of theoretical plates was 35. After fractionally distilling every 10° with this still, each fraction was further fractionated every 1°.

Isolation as a picrate—0.5 g. of each fraction obtained by every 1° fractionation was dissolved in 4 cc. of alcohol, and saturated alcoholic solution of one-half the theoretical amount of picric acid was added. After allowing the mixture to stand overnight, the crystals of picrate (A) thereby obtained was collected by filtration. The same amount of picric acid as previously was added to the filtrate, allowed to stand overnight, and the picrate crystals (B) were collected by filtration. Evaporation of the filtrate afforded further amounts of picrate crystals (C). Crystals (A), (B), and (C) were each recrystallized from methanol. This general procedure was used to separate various pyridines by utilizing the difference of their solubility in methanol. Usually, each fraction yielded 2∼3 kinds of picrates.

Isolation of 2,4-lutidine—This base is contained in approximately 70% yield in the fraction of b.p. 155∼162°. Recrystallization of its picrate failed to effect purification and, therefore, following procedure was taken. To a solution of 8 g. of the base dissolved in 30 cc. of glacial acetic acid, 15 cc. of 35% hydrogen peroxide was added in several portions. The mixture was warmed at 80° for 12 hours, glacial acetic acid removed by low-pressure distillation, and the residue was extracted with chloroform after alkalization with sodium carbonate. The base thereby obtained was submitted to a low-pressure distillation from which following fractions were obtained: (A) 0.9 g. of b.p$_4$ 80∼100°; (B) 1.3 g. of b.p$_4$ 100∼112°; (C) 1.5 g. of b.p$_4$ 112∼115°; and (D) 2.3 g. of b.p$_4$ 115∼116°.

Each of these fractions was dissolved in 10 volumes of chloroform, and three volumes of phosphorus trichloride was added during 4 hours, while chilling the mixture at 0° to 5°. After allowing the mixture to stand for 3 hours, it was poured into ice-water, alkalized with sodium carbonate, and the base thereby liberated was extracted with ether.

The base obtained from each of the above fractions was derived to a picrate and afforded 2,3-lutidine from (A), 2,3- and 2,5-lutidine from (B), and 2,4-lutidine from (C) and (D). By this procedure, 60% of the estimated amount of 2,4-lutidine can be collected.

Isolation of 2,4,6-collidine—This base is contained in approximately 70% yield in the fraction of b.p. 168∼172°. Derivation of this fraction to picrates and recrystallization from methanol afforded the picrate of 3,5-lutidine which was sparingly soluble in hot methanol. Cooling of its filtrate separated the picrate of 2,4,6-collidine in a few hours. This filtrate, when left to stand overnight, yielded the picrates of 2,4,6- and 2,3,6-collidine.

Addition of one-half the theoretical amount of picric acid dissolved in alcohol to the alcoholic solution of the fraction of b.p. 168∼172° gave crystals of 2,4,6-collidine picrate.

This picrate method affords approximately 50% of the estimated amount of 2,4,6-collidine.

Summary

Pyridines contained in the fraction of b.p. 150∼190° from the low-temperature coking tar bases were examined. This fraction was found to contain all the lutidine isomers except 2,6-lutidine, and all the collidine isomers except 3,4,5-collidine. Identification of these pyridines was made by direct comparison with the synthetic specimens.

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