Isolation of 2, 3-Cyclopenteno-5-methylpyridine from Coal Tar Bases

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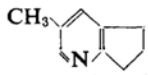
It was previously reported that 3, 4, 5-collidine and 2, 3-cyclopenteno-6-methylpyridine were isolated from the tertiary amine fraction boiling about 210°C in coal tar bases and their chemical structure were confirmed[1]. On further investigation, a $C_9H_{11}N$ base was isolated by solvent extraction and picrate formation from bases boiling about 220°C. This was identified as 2, 3-cyclopenteno-5-methylpyridine, comparing the physical properties of the isolated base and its derivatives with those of the synthesized base[2].



2, 3-Cyclopenteno-5-methylpyridine

The presence of this base in coal tar and petroleum distillates has not hitherto been reported. In Table I is shown the comparison of the isolated base with the synthesized compound.

Experimental

Original Material. — The material used in the present investigation is a coal tar base fraction called "toluidine-xylidine fraction" (TX_n) furnished by Yawata Chemical Industry Co., Kyushu, Japan. The boiling point range of the material is shown in Table II. This sample contains 10% of neutral oil and 34% of primary amines determined as xylidines by diazotization-titration, therefore the content of the tertiary amines which constitute the rest of the sample is approximately 56%.

Separation of the Tertiary Amines.—A mixture of 6 kg. TX_n and 1350 cc. of concentrated sulfuric acid was steam-distilled and neutral oil and a small amount of tar acids were respectively removed as a distillate. By addition of sodium hydroxide to the residual acidic solution, 4.84 kg. of the base was recovered. Then, 2.9 kg. of acetic anhydride was added and refluxed to remove the primary amines. The reaction mixture was distilled through a 30 cm. column and the distillate up to 250°C was collected and made alkaline with sodium hydroxide and steam-distilled. The disillate, after being dried over solid sodium hydroxide, was distilled in vacuo through a fractionating column[1] with a reflux ratio of 20 : 1 and divided into the fractions shown in Table III.

In the fractions Nos. 5 and 6, which were to be examined, the primary amines were still present to a minor extent and the acetylation procedure was repeated.

TABLE I. 2,3-CYCLOPENTENO-5-METHYLPYRIDINE

Property	The isolated base	The synthesized base	
		By the author	Literature[2]
M. p.*, °C	38.5～ 41	38.7～ 41	39～ 41
B. p.*, °C	225 (756 mmHg)	225 (756 mmHg)	222 (752 mmHg)
M. p. of picrate, °C	205.2～206.2	204.8～205.8	204～206
D. p. of picrolonate, °C	211.5～212.5	211.5～212.5	210～212
Elementary analysis			(calcd.)
C, %	80.75	81.12	81.16
H, %	8.39	8.44	8.33
N, %	10.41	10.31	10.52
Neutralization equivalents	134	—	133.2

* M. p. and b. p. (micro method) are corrected values.

TABLE II

Distillate Vol. %	First drop	5	10	50	90	95	Dry point
B. p., °C	200.5	204.0	206.0	210.0	222.5	225.0	228.0

1) S. Jifuku, S. Nakayama, H. Suzumura and M. Uemura, *Coal Tar (Tokyo)*, **10**, 126 (1958).

2) H. L. Lochte and A. G. Pittman, *J. Am. Chem. Soc.*, **82**, 469 (1960).

TABLE III. FRACTIONATION OF THE TERTIARY AMINES

No. of fraction	B. p. (30 mmHg) °C	Distillate g.	n_D^{25}	B. p. (micro) °C	Xylidine %
1	FD~102	277.7	1.5160		
2	102~106	112.9	1.5207		
3	106~111	163.7	1.5348		
4	111~114	65.5	1.5319	213.1	12.1
5	114~117	135.3	1.5309	223.6	7.3
6	117~121	64.7	1.5387	227.6	3.6
7	121~125	109.1	1.5720	231.0	
8	125~	1941.0			
	Total	2869.9			

The properties of the fraction, after this treatment, are shown in Table IV.

TABLE IV

No. of fraction	4'	5'	6'
n_D^{25}	1.5277	1.5281	1.5345
Yield, g.	50	117	49

Isolation of 2, 3-Cyclopenteno-5-methylpyridine. —As the chromatographic separation using a column of cupric chloride-aluminum oxide and also the urea adduct method were ineffective, the separation by solvent extraction was carried out. As the solutes, the fractions Nos. 5' and 6' of Table IV were used. A countercurrent extraction apparatus of semiautomatic type equipped with one hundred distribution tubes was employed. The volume of each tube was 20 cc. Ligroin was introduced into the apparatus as the light phase and the acidic sodium phosphate buffer solution (pH 4.78) as the heavy phase. By a single withdrawal procedure, the ligroin layers were transferred successively, giving a series of fractions, and from those fractions the bases were collected as the picrates. Results of the extractions using Nos. 5' and 6' as the solutes are shown in Table V.

The melting points shown in the table were determined on the picrates once recrystallized from ethanol. From Table V, it was observed that the new component was, next to quinoline, not easily soluble in the buffer solution; the base had a relatively large distribution coefficient.

In order to obtain a large amount of the base to work with, the extraction whose scheme is shown in Table VI was carried out using a 300 cc. separating funnel. Twenty-five grams of the fraction No. 6' was diluted with ligroin to 100 cc., to which 100 cc. of the buffer solution was added, shaken for 3 min., then allowed to settle. The heavy phase

TABLE V. COUNTERCURRENT EXTRACTION

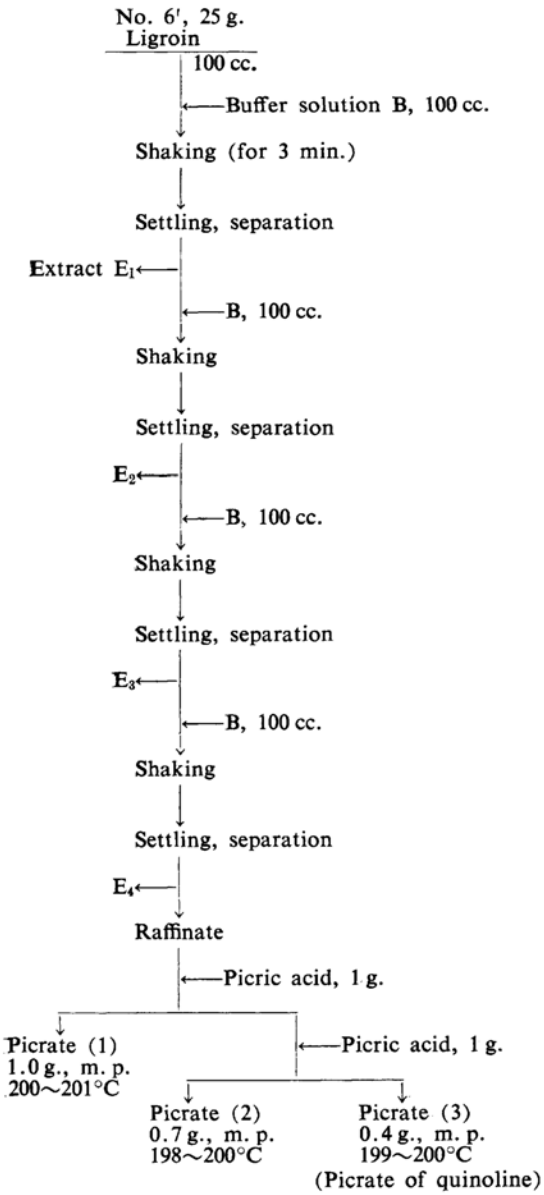
Light phase No.	No. 5' (0.6 g.) M. p. of picrate °C	No. 5' (0.6 g.) Yield and appearance	No. 6' (1.0 g.) M. p. of picrate °C	No. 6' (1.0 g.) Yield and appearance
1	187~189	Yellow needles	197 ~199	Orange yellow plates, 0.2 g.
2	160~167		198 ~200	
3	164~178		199 ~200	
4	189~194	Pale yellow needles	185 ~192	Yellow needles, 0.1 g.
5	191~194		168 ~171	
6	195~198		175 ~181	
7	192~198		193 ~196	
8	192~196		197 ~199	
9	191~195		199.5~200.5	
10	189~192		199 ~200	
11			199 ~200	
12			199.5~200	
13			198.5~199.5	
14			198 ~199	
15			197 ~198	
16			197 ~198	

Crude picrates from Nos. 5—9 were combined and after recrystallization from ethanol, 0.1 g. of picrate was obtained, m. p. 201~202°C.

Base from Nos. 1, 2 and 3 were identified as quinoline by their picrates and tartrates.

was drawn off and the new buffer solution was added; the extraction was repeated three more times in the same manner as described above. After the bulk of the solvent was removed by distillation, the raffinate was purified as a picrate. Recrystallization from ethanol yielded 1.7 g. of picrate, which melted at about 200°C. This picrate, when admixed with the picrate of quinoline, m. p. 198~200°C (uncorr.), showed a large melting point depression amounting to 20°C, hence it is obviously different from that of quinoline.

TABLE VI. EXTRACTION USING A SEPARATING FUNNEL



From 20 g. of fraction No. 5' by the same procedure, 0.9 g. of picrate, m. p. 196~198°C (uncorr.), was obtained. The picrate, recrystallized from ethanol melted at 201~202°C (uncorr.). This purified picrate was decomposed by addition of sodium hydroxide and the regenerated base was recovered by steam distillation followed by extraction with ether. The ether extract of the distillate was concentrated to give colorless plates, m. p. 38.5~41°C.

Properties, Derivative and Absorption Spectra of the Isolated Base.—*Neutralization Equivalents.*—The base (0.073 g.) was titrated by 0.1 N hydrochloric acid (F 0.999) using bromophenol blue as an indicator and measuring the pH of the solution. For the neutralization of the base, 5.45 cc. of 0.1 N hydrochloric acid was required.

Found: 134. Calcd. for $C_9H_{11}N$; 133.

The Picrate.—Several recrystallizations from ethanol yielded yellow needles, m. p. 205.2~206.2°C.

Found: N, 15.16. Calcd. for $C_{15}H_{14}N_4O_7$: N, 15.47%.

The Picrolonate.—It was prepared from equimolar quantities of picrolonic acid and the base in ethanol. Recrystallization from ethanol yielded yellow needles which decomposed at 211.5~212.5°C.

The Ultraviolet Absorption Spectrum.—The spectrum in cyclohexane is shown in Fig. 1.

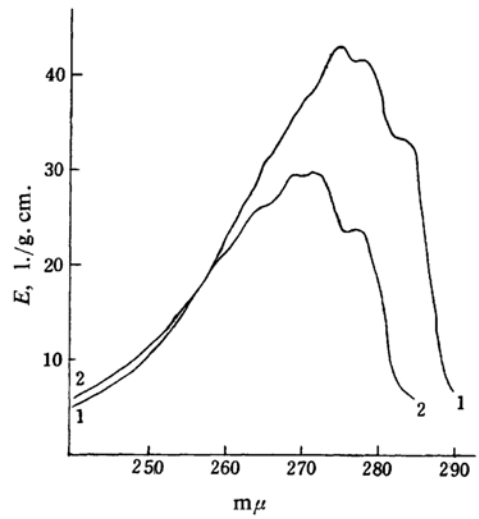


Fig. 1.
1, 2,3-Cyclopenteno-5-methylpyridine
2, 2,3,5-collidine

The ultraviolet spectrum of 2,3-cyclopenteno-5-methylpyridine (λ_{max} 276 mμ) has the same similarity to that of 2,3,5-collidine (λ_{max} 271 mμ) as the spectrum of 2,3-cyclopenteno-6-methylpyridine (λ_{max} 275 mμ) has to that of 2,3,6-collidine (λ_{max} 270 mμ)[1,2].

The Infrared Absorption Spectrum.—The spectrum in carbon disulfide is shown in Fig. 2.

Characteristic absorption bands at 13.7 μ and 14.1 μ are similar to those of 2,3,5-collidine. This similarity may well be explained by the relationship between absorption bands and the position of substituents of alkyl pyridines[3].

3) H. Shindo and N. Ikekawa, *Pharm. Bull.* (*Tokyo*), **4**, 192 (1956).

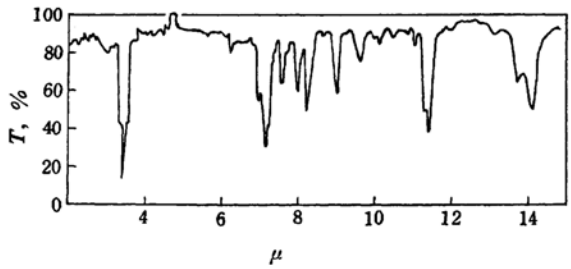


Fig. 2.

In Fig. 3 are shown the specific absorption bands appearing in the fingerprint region of cyclopenteno-pyridine, 2,3-dimethylpyridine, 2,3-cyclopenteno-6-methylpyridine and 2,3,6-collidine.

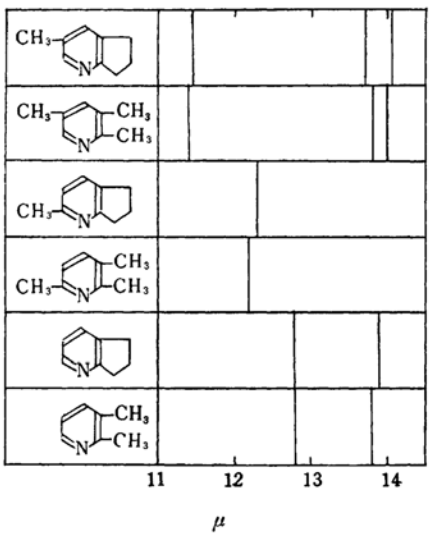
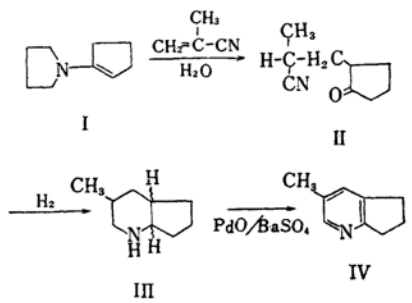


Fig. 3.

The Synthesis of 2,3-Cyclopenteno-5-methylpyridine.—In order to compare the isolated base from coal tar with the authentic sample of the base, a synthesis was carried out in the manner similar to that described by Lochte et al.[2]. The procedure is schematically shown below.



Cyclopentano-pyrrolidine Enamine (I).—A solution of 10 g. of cyclopentanone and 26 g. of pyrrolidine in 140 cc. of dry benzene was refluxed for 6 hr. in a flask fitted with an azeotropic water separator. The benzene and the excess of pyrrolidine were distilled off leaving a viscous liquid, 15.8 g., which was used without further purification in the subsequent reaciton.

2-(2-Methyl-2-cyanoethyl)-cyclopentanone (II).—Methacrylonitrile* (9.5 g.) was added to a solution of the enamine I in 100 cc. of dimethylformamide. The resulting solution was refluxed for 31 hr. in a flask fitted with a tower of calcium chloride. The bulk of the solvent was then removed by distillation and to the residue were added 57 cc. of water and 4 cc. of glacial acetic acid. This solution was refluxed for 2 hr. 40 min., cooled and extracted four times with benzene. The combined benzene extracts were washed three times with 10% hydrochloric acid, twice with 10% potassium carbonate solution, and once with water and dried over sodium sulfate. After removal of the benzene, the residue was distilled in vacuo giving 4.6 g. of a liquid boiling at 125~126°C (5 mmHg), n_D^{25} 1.4580 and 1.1 g., n_D^{25} 1.4709 (reported $n_D^{25.5}$ 1.4624). The semicarbazone prepared from the two fractions melted at 195.4°C and 189~190°C respectively (reported 195°C).

Hexahydro-2,3-cyclopenteno-5-methylpyridine (III).—Raney nickel** was added to a solution of II in absolute ethanol. This mixture was hydrogenated at an initial H_2 pressure of 34 kg./cm² and 120°C in a 100 cc. autoclave equipped with an elecromagnetic stirring device. The Raney nickel was filtered off and the solvent was removed by distillation in vacuo. The residual liquid was distilled in a Claisen flask yielding a corless liquid, b. p. 85°C (21 mmHg).

The experimental results are shown in Table VII.

2,3-Cyclopenteno-5-methylpyridine (IV).—In the present experiment, III was dehydrogenated in the liquid phase with palladium oxide/barium sulfate in place of palladium-carbon described in the literature cited. A mixture of equal amounts by weight of the base and the catalyst (palladium oxide/barium sulfate) was placed in a flask and refluxed in a nitrogen stream in an oil bath. The cooled mixture was extracted with ether and the ether extract was concentrated to give the crude base.

The experimental result was shown in Table VIII.

The pure base was obtained by the decomposition of the recrystallized picrate as described above.

Preparation of Palladium Oxide/Barium Sulfate[5].—Palladium chloride (0.3 g.) was dissolved in a mixture of 15 cc. of 2 N sulfuric acid and 120 cc.

* Preparation of methacrylonitrile—commercial methacrylamide (17.0 g.) and 20 g. of P_2O_5 were thoroughly mixed and heated in a flask over free flame. The distillate, after treatment with a small amount of K_2CO_3, was distilled to give a fraction, 8 g., boiling at 89~89.5°C, n_D^{22} 1.4001 (reported[4] n_D^{20} 1.4007).

4) Rohm and Haas, G. m. b. H., U. S. Pat. 2210320 (1940).

** Raney nickel—one gram of commercial alloy (Ni: Al=50:50) was gradually added with stirring to 10 cc. of 20% sodium hydroxide solution in a beaker placed in a water bath maintained at 50°C, over a period of about 50 min. After the addition was complete, the resulting Raney nickel was washed with water to the neutral pH, then with 95% ethanol and finally with absolute ethanol.

5) R. Kuhn and H. J. Haas, *Angew. Chem.*, 67, 785 (1955).

Table VII. Hydrogenation

Sample g.	Conditions				Product		
	H_0 kg./cm²	ΔP kg./cm²	Temp. °C	Period	Wt. g.	n_D^{25}	Yield %
2.9	33.8	10.8	108～120	4 hr. 35 min.	3.75	1.4820	63
3.4	34.1	15.7	108～118	5 hr. 30 min.			

Table VIII. Dehydrogenation

Hexahydrobase(III) g.	$PdO/BaSO_4$ g.	Conditions		Product	
		Temp., °C	Period	Yield, g.	M. p., °C
0.37	0.37	180	6 hr.	0.35	below 20
0.52	0.52	200～210	8 hr. 15 min.	0.35	35～37

of water which was kept at 80°C. After the solution was allowed to settle for 20 min., it was poured with vigorous stirring into 165 cc. of 0.2 N barium hydroxide yielding a precipitate. It was filtered off by suction, washed with 240 cc. of water and dried in vacuo. Pale brown powder was obtained; 3.7 g.

Derivatives of the Synthesized Base. — *The Picrate.* — Yellow needles, m. p. 204.8～205.8°C. From 900 mg. of the picrate, 250 mg. of the base, m. p. 38.7～41°C was regenerated by addition of sodium hydroxide followed by steamdistillation.

The Picrolonate.—It was prepared in the same manner as described in the case of the isolated base. Recrystallization from ethanol yielded yellow needles which decomposed at 211.5～212.5°C.

Confirmation. — The isolated 2,3-cyclopenteno-5-methylpyridine, the picrate and the picrolonate when admixed with the corresponding synthesized sample gave no melting point depression. The infrared absorption spectrum of the isolated base and that of the synthesized base were superimposable.

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