

JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

VOLUME 63

MARCH 5, 1941

NUMBER 3

[CONTRIBUTION No. 206 FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF TEXAS]

The Nitrogen Compounds in Petroleum Distillates. XIX. The Isolation from California Petroleum and Synthesis of 2,3,8-Trimethyl-4-ethylquinoline

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Introduction

The isolation of 2,3,4-trimethyl-8-ethylquinoline from the 310° fraction of bases obtained from the Edeleanu extract of California petroleum¹ has been previously reported.² For that work the crude bases were processed through cumulative extraction,³ followed by multiple acid extraction⁴ and fractional distillation. From the resulting 95 fractions, five of b. p. 314–319° and n_D^{25} 1.5872–1.5911 were used.

In the present investigation seven fractions of b. p. 308–313° and n_D^{25} 1.5894–1.5905 were combined and processed further through counter current extraction⁵ to obtain four fractions listed in Table I. This material contained, in addition to 2,3,4-trimethyl-8-ethylquinoline and 2,3,4,8-tetramethylquinoline,⁶ a new C₁₄H₁₇N base (A) which proved to be 2,3,8-trimethyl-4-ethylquinoline.

In chromic acid oxidation of A an unknown C₁₃H₁₄NCOOH acid resulted which on soda-lime distillation was decarboxylated to an unknown C₁₃H₁₅N base (B), *i. e.*, the next lower homolog of A. Since no keroquinolines have been encountered with alkylation of the Bz-nucleus at a position other than 8 and since chromic acid oxidation

converts alkyls at position 8 to carboxyl, it appeared highly probable that base A is either 2,3,8-trimethyl-4-ethylquinoline or 2,4,8-trimethyl-3-ethylquinoline and that base B is either 2,4-dimethyl-3-ethylquinoline or 2,3-dimethyl-4-ethylquinoline. The two bases with ethyl at position 4 were synthesized and the 13-carbon base was found identical with B and the 14-carbon base identical with A.

Up to the isolation of this new C₁₄H₁₇N base, all of the known petroleum quinolines contained only methyls on the Py-nucleus.

Experimental

Counter Current Extraction of Base Fractions.—A 165-ml. fraction of aromatic bases in the 308–313° range, which had been previously processed through cumulative extraction, multiple acid extraction and fractional distillation, was carried through counter current extraction. The usual Jantzen procedure was followed in that fractional extraction in ascending order of base pH values was effected by employing at each step an amount of hydro-

TABLE I
COUNTER CURRENT EXTRACTION DATA

Cut no.	Volume, ml.	n_D^{25}	d_{20}^{25}	Base isolated	Picrate, g.
1	64	1.5893	1.021	2,3,8-Mes-4-Et-Q (A)	9
				2,3,4-Mes-8-Et-Q (B)	48
2	35	1.5921	1.023	2,3,8-Mes-4-Et-Q (A)	10
				2,3,4-Mes-8-Et-Q (B)	25
3	38	1.5948	1.031	2,3,4-Mes-8-Et-Q (B)	56
				2,3,4,8-Mes-Q (C)	0.8
4*	22	1.5960	1.038	2,3,4,8-Mes-Q (C)	26

* Partially crystallized on standing.

(1) This material was furnished by the Union Oil Company of California.

(2) Glenn and Bailey, *THIS JOURNAL*, **61**, 2612 (1939).

(3) Perrin and Bailey, *ibid.*, **55**, 4136 (1933).

(4) Morton, "Laboratory Technique in Organic Chemistry," McGraw-Hill Book Company, Inc., New York, N. Y., 1938, p. 200.

(5) Ernst Jantzen, "Das fraktionierte Destillieren und das fraktionierte Verteilen," Verlag Chemie, Berlin, 1932, pp. 108–116.

(6) Axe and Bailey, *THIS JOURNAL*, **60**, 3028 (1938).

chloric acid sufficient for complete neutralization of all but any desired amount of the total bases. The extractions were carried out in descending order and the base fractions were assembled in ascending order of their pH values.⁷ Data on the five fractions are given in Table I.

Processing of Extraction Fractions for Contained Bases.—An alcoholic solution of picric acid precipitated from an alcoholic solution of fractions 1 and 2, 65 g. and 42 g., respectively, of picrates which on recrystallization from glacial acetic acid yielded 48 g. and 25 g., respectively, of the crude picrate of B. Addition of ether to each mother liquor separated 9 and 10 g., respectively, of the crude picrate of A.

Through the above procedure, fraction 3 yielded 56 g. of the picrate of C from which a small admixture of the picrate of B was leached out with boiling alcohol.

After removal of 5 g. of C which had crystallized out in fraction 4, 10 g. of the acid sulfate of C was precipitated by addition of concentrated sulfuric acid to an alcoholic solution of the filtrate.

2,3,8-Trimethyl-4-ethylquinoline Picrate.—This salt was purified by four recrystallizations from alcohol in rectangular needles melting at 178°.

Anal. Calcd. for $C_{20}H_{20}O_7N_4$: C, 56.07; H, 4.71; N, 13.08. Found: C, 56.00; H, 4.55; N, 13.33.

Free Base.—The base was liberated from the picrate with ammonium hydroxide followed by extraction with ether. After removal of the solvent, the base was distilled and dried over solid sodium hydroxide. The following constants were determined: b. p. 310–311° (748 mm.); n_D^{25} 1.5918; d_4^{20} 1.0242.

Anal. Calcd. for $C_{14}H_{17}N$: C, 84.42; H, 8.54; N, 7.03. Found: C, 84.26; H, 8.57; N, 7.28.

Nitrate.—Concentrated nitric acid added to a solution of the base in alcohol-acetone-ether mixture precipitated the nitrate, which was recrystallized from the same solvent in needles, melting at 161° with decomposition.

Anal. Calcd. for $C_{14}H_{17}N \cdot HNO_3$: C, 64.10; H, 6.91; N, 10.69. Found: C, 64.02; H, 6.98; N, 10.84.

Phthalone.—A molar mixture of phthalic anhydride and base was heated for four hours at 190°. The phthalone purified by recrystallization of the melt from alcohol melts at 158°. Treatment of the phthalone in alcohol with sodium ethylate precipitated the red sodium salt.⁸

Anal. Calcd. for $C_{22}H_{19}O_2N$: C, 80.24; H, 5.77; N, 4.26. Found: C, 80.20; H, 5.74; N, 4.35.

2,3-Dimethyl-4-ethylquinoline-8-carboxylic Acid.—To a boiling solution of 1 g. of base in 6 *N* sulfuric acid, a mixture of 3 g. of potassium dichromate, 4.7 g. of sulfuric acid, and 5 g. of water was added slowly over a period of ninety minutes. The solution was cooled, made alkaline with ammonium hydroxide, acidified with acetic acid and extracted with chloroform. The acid (0.5 g.) from evaporation of the solvent recrystallized from methyl alcohol in needles melting at 178°.

(7) Cf. Axe and Bailey, *THIS JOURNAL*, **61**, 2610 (1939).

(8) Cf. A. Eibner, *Ber.*, **37**, 3605 (1904).

Anal. Calcd. for $C_{14}H_{15}O_2N$: C, 73.35; H, 6.55; N, 6.11. Found: C, 73.35; H, 6.22; N, 6.33.

2,3-Dimethyl-4-ethylquinoline.—The above acid was decarboxylated by distillation with soda-lime. The resulting base was dissolved in aqueous sulfurous acid and precipitated as the picrate with aqueous picric acid. It was recrystallized from dilute acetic acid in fine needles melting at 220–221° with decomposition.

Synthesis of 2,3-Dimethyl-4-ethylquinoline.¹⁰—A mixture of 43 g. (1 mole) of diethyl ketone and 22 g. (1 mole) of paraldehyde, saturated with dry hydrogen chloride at 0°, after standing at room temperature for twenty-four hours, was poured into a cooled solution of 21 g. (0.28 mole) of aniline in 54 g. of concentrated hydrochloric acid. The reaction was then completed by heating for twelve hours at 100°. After liberation of the basic material and dehydration over solid sodium hydroxide, it was heated with an equal volume of acetic anhydride for two hours, and poured into a large volume of water. Following liberation of the bases, diazotization of the admixed aniline was carried out at 0° in dilute hydrochloric acid and, after removal from the ice-salt-bath, the reaction mixture was allowed to stand for three hours. The solution was extracted with ether, then basified, and re-extracted with ether. Evaporation of the solvent layer yielded 4 g. of synthetic base which on purification through distillation had the following constants: b. p. 302° (749 mm.), n_D^{25} 1.5982, d_4^{20} 1.0511.

Addition of alcoholic picric acid to the base in alcohol precipitated the picrate melting at 220–221° after recrystallization from dilute acetic acid. A mixed melt of this preparation with the picrate of the base obtained from decarboxylation of 2,3-dimethyl-4-ethylquinoline-8-carboxylic acid showed no depression.

Anal. Calcd. for $C_{19}H_{19}O_7N_4$: C, 55.07; H, 4.35; N, 13.53. Found: C, 55.24; H, 4.51; N, 13.64.

Synthesis of 2,3,8-Trimethyl-4-ethylquinoline.—Substitution of *o*-toluidine for aniline in the preceding synthesis and employment of the same molar quantities of intermediates yielded 6 g. of crude base. A mixed melt of the picrate with the petroleum base picrate showed no depression.

Summary

This paper deals with the isolation and synthesis of 2,3,8-trimethyl-4-ethylquinoline present in the Edeleanu kerosene extract of California petroleum. It is the first quinoline homolog obtained from this source with an alkyl on the Py-nucleus higher than methyl. The base was degraded to the previously unknown 2,3-dimethyl-4-ethylquinoline, the structure of which was confirmed by synthesis.

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RECEIVED NOVEMBER 25, 1940

(9) Determination of carbon miscarried.

(10) Cf. Mikeska and Adams, *THIS JOURNAL*, **42**, 2392 (1920).