

Summary

This paper deals with the isolation through counter-current hydrochloric acid extraction of a new kero base, 2,4-dimethyl-8-*n*-propylquinoline, the structure of which was established by chromic acid oxidation to a $C_{17}H_{16}NCOOH$ acid, pre-

viously obtained in the Texas Laboratory by a similar oxidation of the kero base, 2,4,8-trimethylquinoline. This orientation was confirmed by synthesis, in which acetylacetone and *o*-*n*-propylaniline were the intermediates.

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The Nitrogen Compounds in Petroleum Distillates. XVI. Use of Multiple Acid Extraction in Isolation of 2,3,4-Trimethyl-8-ethylquinoline

BY RICHARD A. GLENN AND J. R. BAILEY

Introduction

In a systematic investigation in the Texas Laboratory of kero quinoline homologs from crude bases furnished by the Union Oil Company of California, the 310° fraction was processed through cumulative extraction¹ in order to segregate the aromatic components in satisfactory concentration. In further refining, the latter material in the 305–315° range was processed through multiple acid-extraction.²

This method of separation yielded a $C_{14}H_{17}N$ base which degradation and synthesis revealed as 2,3,4-trimethyl-8-ethylquinoline. In chromic acid oxidation a $C_{12}H_{12}NCOOH$ acid was obtained which proved the replacement of an *ethyl* by *carboxyl*. The 8-position of the ethyl follows from the fact that the acid was identical with one previously obtained by chromic acid oxidation of 2,3,4,8-tetramethylquinoline.³ Its structure was confirmed by synthesis from methylacetylacetone and *o*-aminoethylbenzene.⁴

Experimental

In carrying out multiple acid-extraction with 4000 cc. of aromatic bases in the 305–315° range, the procedure charted by Morton⁵ was followed. By this method the bases were resolved into ten fractions of varying volume. Next, separate fractions were carried through one fractional distillation. The physical constants, including boiling point, density and refractivity, of each of the 95 distillation cuts were determined for comparative purposes.

In the present work only fractions IX 14, IX 15, X 12 and X 13, in the 314–319° range, were of interest, because

lower boiling fractions had been investigated previously. From all of this material on picration in alcohol, crystalline salts, free of smears, separated. However, in further purification, the four fractions were combined and carried through counter current extraction using the equipment described in the preceding paper by Axe and Bailey.⁶

TABLE I

COUNTER CURRENT EXTRACTION DATA

| Cut | Volume, cc. | n_D^{25} | d_4^{25} |
|-----|-------------|------------|------------|
| 1 | 22 | 1.5841 | 1.0174 |
| 2 | 36 | 1.5878 | 1.0237 |
| 3 | 21 | 1.5888 | 1.0277 |
| 4 | 30 | 1.5920 | 1.0386 |

Isolation of 2,3,4-Trimethyl-8-ethylquinoline.—From Fractions 1, 2 and 3, this base⁷ was separated as the picrate which after four recrystallizations from 60% acetic acid was obtained in lemon-colored, long rectangular microscopic plates, melting at 216° without decomposition. This salt is readily soluble in glacial acetic acid but only sparingly soluble in other common solvents.

Anal. Calcd. for $C_{20}H_{20}O_7N_4$: C, 56.07; H, 4.71; N, 13.08. Found: C, 56.00; H, 4.51; N, 13.11.

Free Base.—The base was liberated from the picrate and recrystallized from methyl alcohol in ill-defined microscopic plates. The following constants were determined: m. p. 52.5–53.0°; b. p. 320°; n_D^{25} 1.5798. Methyl alcohol has proved a selective solvent in recrystallization of 2,3,4-trimethyl kero quinolines alkylated at position 8.³

Anal. Calcd. for $C_{14}H_{17}N$: C, 84.42; H, 8.54; N, 7.03. Found: C, 84.23; H, 8.29; N, 7.19.

2,3,4-Trimethylquinoline-8-carboxylic Acid.—To a boiling solution of 1 g. of the base in 6 *N* sulfuric acid, a mixture of 2.5 g. of potassium dichromate, 3.8 g. of sulfuric acid and 4.2 g. of water is added slowly. The reaction is complete in twelve hours. The solution is cooled, made alkaline with ammonium hydroxide, acidified with acetic acid and extracted with chloroform. The acid crystallizes from alcohol in needles melting at 233.5–234.0°. A mixed

(1) Perrin and Bailey, *THIS JOURNAL*, **55**, 4186 (1933).

(2) Ernst Jantzen, "Das fraktionierte Destillieren und das fraktionierte Verteilen," Verlag Chemie, Berlin, 1932, pp. 117–137.

(3) Axe and Bailey, *THIS JOURNAL*, **60**, 3031 (1938).

(4) Combes, *Bull. soc. chim.*, [2] **49**, 91 (1838).

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

(6) Axe and Bailey, *THIS JOURNAL*, **61**, 2609 (1939).

(7) None of the base was found in Fraction 4, but here 24 g. of the crude picrate of 2,3,4,8-tetramethylquinoline was encountered (Axe and Bailey, reference 3).

melting point determination with an authentic sample of 2,3,4-trimethylquinoline-8-carboxylic acid⁸ showed no depression.

Anal. Calcd. for $C_{13}H_{13}O_2N$: C, 72.04; H, 6.11; N, 6.51. Found: C, 72.03; H, 5.87; N, 6.72.

Phthalone.—Molar amounts of phthalic anhydride and base are heated together for four hours at 190°. The melt is recrystallized from 70% acetic acid in yellow microscopic plates melting at 253°.

Anal. Calcd. for $C_{22}H_{19}O_2N$: C, 80.24; H, 5.77; N, 4.26. Found: C, 80.01; H, 5.48; N, 4.31.

Nitrate.—Concentrated nitric acid added to an alcohol or ether solution of the base precipitates the nitrate which recrystallizes from alcohol in tetragonal truncated pyramids, melting with decomposition at 159.5–160.0°.

Anal. Calcd. for $C_{14}H_{17}N \cdot HNO_3$: C, 64.10; H, 6.91; N, 10.69. Found: C, 64.33; H, 6.96; N, 10.51.

Acid Sulfate.—On addition of concentrated sulfuric acid to an alcohol or acetone solution of the free base, the acid sulfate precipitates and recrystallizes from water in microscopic fan-like needles melting without decomposition at 245–246°.

Anal. Calcd. for $C_{14}H_{17}N \cdot H_2SO_4$: SO_4 , 32.32. Found: SO_4 , 32.26.

Hydrochloride.—This salt is prepared by passing hydrogen chloride into an ether solution of the base. It crystallizes difficultly from acetone in fan-like microscopic needles, melting without decomposition at 203–204°.

Anal. Calcd. for $C_{14}H_{17}N \cdot HCl$: Cl, 15.05. Found: Cl, 15.25.

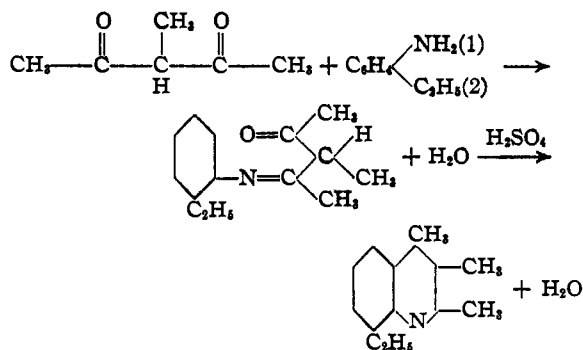
Synthesis of 2,3,4-Trimethyl-8-ethylquinoline.—As outlined below, methylacetylacetone⁸ is condensed in two steps⁹ with *o*-aminoethylbenzene.¹⁰ A mixed melt of the

(8) Auwers and Jacobsen, *Ann.*, **426**, 227 (1922).

(9) Von Braun, Gmelin and Petzold, *Ber.*, **57**, 387 (1924).

(10) Axe, *THIS JOURNAL*, **61**, 1017 (1939).

purified synthetic base and the kero base gave no depression.



It is of interest to note that the spread in refractive index and in density obtained by multiple acid extraction compares favorably with that obtained by Axe⁶ in counter-current extraction of a lower boiling base fraction. However, it may be emphasized that multiple acid extraction, unlike counter-current extraction, admits of a minimum of supervision and the processing of large quantities of bases in one operation.

Summary

This paper deals with multiple acid extraction in the isolation of a new $C_{14}H_{17}N$ kero base, 2,3,4-trimethyl-8-ethylquinoline. Its structure has been established by chromic acid oxidation to a $C_{12}H_{12}NCOOH$ acid, identical with the acid Axe and Bailey reported from a similar oxidation of 2,3,4,8-tetramethylquinoline. This structure was confirmed through synthesis of the base from methylacetylacetone and *o*-ethylaniline.

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The Nitrogen Compounds in Petroleum Distillates. XVII. The Use of Multiple Acid Extraction in Isolation of 2,3,4-Trimethyl-8-*n*-propylquinoline

BY LESLIE M. SCHENCK AND J. R. BAILEY

Introduction

In multiple extraction of a pyrolysis distillate from transformer oil bases, furnished by the Union Oil Company of California, a new $C_{15}H_{19}N$ base, b. p. 330°, was isolated in the form of the picrate. To determine whether a *pyrolysis* or a *preformed* product was involved, a search was made for this particular base among the *aromatic* kero bases in the 320–330° range. Multiple extraction was also employed here, and the $C_{15}H_{19}N$ base was encountered in greatly in-

creased yield, due probably to its presence in very small amount in high-boiling transformer oil bases.

The $C_{15}H_{19}N$ compound on chromic acid oxidation was converted to a $C_{12}H_{12}NCOOH$ acid which proved identical with the oxidation product of both 2,3,4,8-tetramethylquinoline¹ and 2,3,4-trimethyl-8-ethylquinoline.² In this way orientation of the base as a 2,3,4-trimethyl-8-propylquinoline was established. In determining the

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

(2) See preceding paper by Glenn and Bailey, *THIS JOURNAL*, **61**, 2612 (1939).