melting point determination with an authentic sample of 2,3,4-trimethylquinoline-8-carboxylic acid[8] 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.

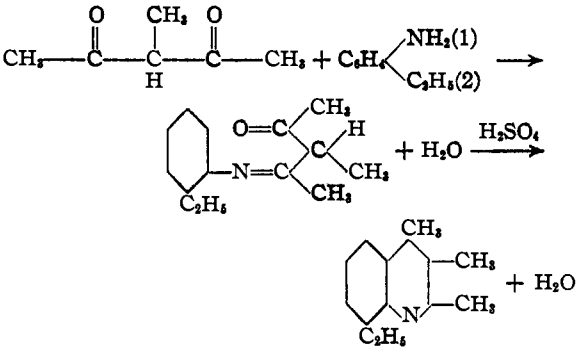
Acid Sulfate.—On addition of concentrated sulfuric acid to an alcohol or acetone solution of the free base, the acid sulfate precipitates and recrystallizes from water in microscopic fan-like needles melting without decomposition at 245–246°.

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, methylacetylacetone[8] is condensed in two steps[9] with *o*-aminoethylbenzene.[10] A mixed melt of the 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 Axe[6] 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.

(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).

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.

AUSTIN, TEXAS RECEIVED MAY 19, 1939

[CONTRIBUTION NO. 162 FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, THE UNIVERSITY OF TEXAS]

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 increased 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-tetramethylquinoline[1] 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).

nature of the propyl group it was necessary to supplement degradation by synthesis. Accordingly, in anticipation of an *n*- and not an isopropyl, a Combes synthesis[3] with the intermediates methylacetylacetone and *o*-*n*-propylaniline was carried out. The product obtained proved identical with the kero base.

The subjoined diagram shows an interesting relationship between eleven of the twelve quinoline homologs so far isolated from California petroleum. The base not included is 2,8-dimethylquinoline. A futile search was made for 2,3,4-trimethylquinoline.[4,5] With this exception, the recent discovery of 2,3,4-trimethyl-8-ethylquinoline and 2,3,4-trimethyl-8-*n*-propylquinoline completes the series.

DIAGRAM I

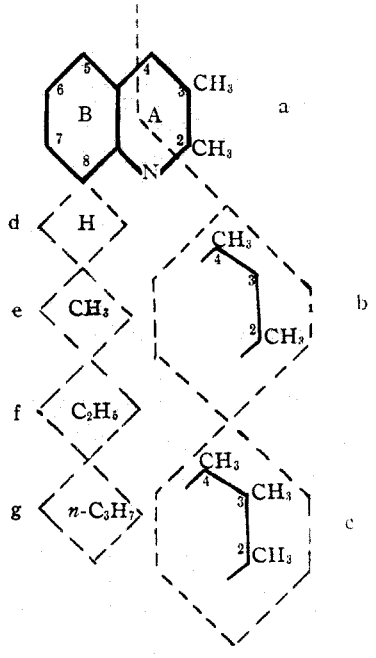
TWELVE QUINOLINE HOMOLOGS OCCURRING IN STRAIGHT-RUN DISTILLATES OF CALIFORNIA PETROLEUM

A and B refer to the Py- and Bz-nuclei, respectively. Aa, Ab and Ac show variation in methylation in the Py-nucleus.

Bd, Be, Bf and Bg show the substituent, if any, at position 8.

2,3,4-Trimethylquinoline (AcBd) has not been found.

2,8-Dimethylquinoline, a known kero base, is omitted.



Experimental

Our limited supply of pyrolyzed transformer oil bases (600 cc.) was carried through cumulative extraction,[6] followed by exhaustive fractional distillation. Fractions over a boiling range of 240–360° were obtained. Several multiple acid extractions[7] of each fraction yielded on picration small quantities of several known bases previously isolated in this Laboratory. After recombinations in the order of *n*-values of the extraction fractions in the 340° range, cumulative extraction and counter current extraction yielded in the first fraction (Table I) only 100 mg. of 2,3,4-trimethyl-8-*n*-propylquinoline.

TABLE I

BASE FRACTIONS FROM COUNTER CURRENT EXTRACTION

Fraction	$n^{25}D$	Vol., cc.
1	1.6143	4
2	1.6195	5
3	1.6154	8

Since the meager amount of the new base obtained above was insufficient for even a complete analysis, 13.5 liters of kero bases with $n^{20}D$ 1.5698 and b. p. 320–330° were cumulatively extracted and an aromatic fraction, 3.7 liters with $n^{20}D$ 1.5841, was obtained. Below are tabulated the results obtained in processing this material through multiple acid extraction.

TABLE II

FRACTIONAL ACID EXTRACTION

Fraction	B. p., °C.	Volume, cc.	$n^{20}D$
1	317	705	1.5760
2	319	715	1.5794
3	322	713	1.5829
4	323	711	1.5853
5	323	740	1.5890

Picrates were prepared in alcohol from 100 cc. of no. 5. Three 80-g. batches of crystalline salts were obtained. For purification, the picrates were converted to nitrates and acid sulfates with recrystallization at each stage, followed by reconversion to picrates. Since only 2,3,4-trimethyl-8-ethylquinoline[2] was encountered, the search for the 8-propyl homolog was shifted to Fraction 3, Table II. This material was further processed through a second multiple extraction, the tabulated results being given in Table III.

TABLE III

SECOND MULTIPLE EXTRACTION

Fraction	B. p., °C.	Volume	$n^{20}D$
1	325	62	1.5755
2	322	65	1.5749
3	315	60	1.5784
4	316	68	1.5798
5	326	62	1.5807
6	323	66	1.5807
7	317	63	1.5818
8	318	68	1.5805
9	320	61	1.5835
10	320	70	1.5810

2,3,4-Trimethyl-8-*n*-propylquinoline Nitrate.—Fractions 5 and 6 were combined and dissolved in five volumes of 1:10 acetone–ether mixture. On addition of concen-

(3) Combes, *Bull. soc. chim.*, [2] **49**, 91 (1888).
(4) Combes, *Compt. rend.*, **106**, 143 (1888).
(5) Braun, Gmelin and Petzold, *Ber.*, **57**, 387 (1924).
(6) Perrin and Bailey, THIS JOURNAL, **55**, 4136 (1933).
(7) *Cf.* Morton, "Laboratory Technique in Organic Chemistry," McGraw-Hill Book Co., Inc., New York, 1938, p. 200.

trated nitric acid in slight excess, 28 g. of nitrate separated from which the base was liberated and converted to the picrate. The picrate after digestion with benzene was changed through the liberated base to the nitrate, a *selective* salt for this base. The nitrate crystallizes from acetone–ether in long slender needles melting with decomposition at 160.1°.

Anal. Calcd. for $C_{15}H_{19}N \cdot HNO_3$: C, 65.18; H, 7.23. Found: C, 64.99; H, 7.32.

Base.—This odorless base crystallizes from methyl alcohol in fine radiating needles and has the following constants: m. p. 69–70°; b. p. 330°; $n^{70}D$ 1.5618; $n^{44}D$ 1.5731.

Anal. Calcd. for $C_{15}H_{19}N$: C, 84.45; H, 8.98; N, 6.57. Found: C, 84.62; H, 9.12; N, 6.41.

Picrate.—This salt which, with the exception of glacial acetic acid, is difficultly soluble in ordinary solvents, crystallizes from 50% acetic acid in long lemon colored hexagonal needles melting undecomposed at 211–211.5°.

Anal. Calcd. for $C_{21}H_{22}O_7N_4$: C, 57.07; H, 5.01; N, 12.66. Found: C, 56.85; H, 5.08; N, 12.45.

Acid Sulfate.—On the addition of the calculated amount of concentrated sulfuric acid to the base in acetone, this salt precipitates. It crystallizes from *t*-butyl alcohol in small irregular platelets melting without decomposition at 230.5–231°.

Anal. Calcd. for $C_{15}H_{19}N \cdot H_2SO_4$: SO_4, 30.86. Found: SO_4, 30.91.

Hydrochloride.—This hygroscopic salt separates on passing dry hydrogen chloride into an ether solution of the base. No solvent was found for its recrystallization. It forms small lustrous ill-defined crystals melting undecomposed at 221–222°.

Anal. Calcd. for $C_{15}H_{19}N \cdot HCl$: Cl, 14.23. Found: Cl, 14.59.

2,3,4-Trimethylquinoline-8-carboxylic Acid.—The base (0.44 g.) is dissolved in a sufficient amount of 12 *N* sulfuric acid to redissolve the initially precipitated acid sulfate and to the boiling solution 2.25 g. of potassium dichromate in 3 g. of concentrated sulfuric acid and 15 cc. of water is added dropwise over a period of forty minutes. The reaction mixture is made alkaline with ammonium hydroxide and then acidified with acetic acid. The chloroform extracted acid crystallizes from ethyl alcohol in long slender needles melting sharply and undecomposed at 234°; yield 0.090 g. A mixed melt of this product with an authentic sample of 2,3,4-trimethylquinoline-8-carboxylic acid[1] showed no depression.

Anal. Calcd. for $C_{13}H_{13}O_2N$: C, 72.53; H, 6.07; N 6.51. Found: C, 72.23; H, 5.89; N, 6.48.

Synthesis of the Base.—In preparation of the intermediate, *o*-*n*-propylaniline from *n*-propylbenzene,[8] the procedure of Axe and Bailey[1] was followed. Molecular amounts of this base and methylacetylacetone are condensed in two steps,[5] with a yield of about 90%. The usual melting point comparison of the kero and synthetic bases established their identity.

Summary

This paper deals with multiple acid extraction in the isolation of a new $C_{15}H_{19}N$ kero base, 2,3,4-trimethyl-8-*n*-propylquinoline. Its structure has been established by chromic acid oxidation to a $C_{12}H_{12}NCOOH$ acid identical with the acid obtained by Axe and Bailey through a similar oxidation of 2,3,4,8-tetramethylquinoline. This structure was confirmed through synthesis of the base from methylacetylacetone and *o*-*n*-propylaniline.

(8) *Cf.* Cohen, "Practical Organic Chemistry," The Macmillan Co., London, 1928, p. 155.

AUSTIN, TEXAS RECEIVED MAY 19, 1939

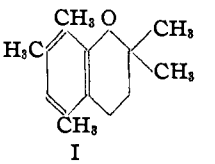
[JOINT CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA AND THE RESEARCH LABORATORIES OF MERCK & CO., INC.]

The Chemistry of Vitamin E. XVIII. Condensation of Phenols and Hydroquinones with Allylic Alcohols, Allylic Halides, and Conjugated Dienes[1]

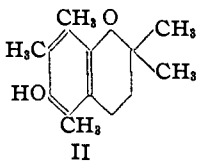
BY LEE IRVIN SMITH, HERBERT E. UNGNADE, J. R. STEVENS AND C. C. CHRISTMAN

In a previous paper[2] it was shown that isoprene could be condensed with 2,3,5-trimethylphenol to give the chroman I, and with trimethylhydroquinone to give the analogous chroman II. The same chroman, II, was obtained by condensing trimethylhydroquinone with γ,γ-dimethylallyl bromide.[3]

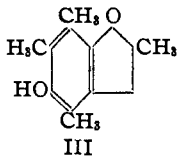
Several years ago Claisen[4] reported that allylic



I



II



III

carbinols as well as appropriate diols which gave dienes when catalytically dehydrated, would con-

(1) Paper XVII, THIS JOURNAL, **61**, 2424 (1939). Presented at the 98th meeting of The American Chemical Society, Boston, Mass., September, 1939.

(2) Paper VI on Vitamin E, *J. Org. Chem.*, **4**, 309 (1939).

(3) Paper V on Vitamin E, *ibid.*, **4**, 305 (1939).

(4) German Patent 394,797 (1924).