

[CONTRIBUTION No. 207 FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF TEXAS]

The Nitrogen Compounds in Petroleum Distillates. XX. Isolation of 2-Methyl-8-ethylquinoline from California Petroleum and Proof of Structure through Degradation and Synthesis

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Introduction

Two new $C_{12}H_{13}N$ components have been isolated from the 258–264° fraction of aromatic bases obtained in processing through fractional distillation, cumulative extraction,¹ and multiple acid extraction² the crude base mixture in the Edeleanu extract of California petroleum.³

One of the products is 2-methyl-8-ethylquinoline with its structure established through degradation and synthesis.⁴ A methyl at position 2 follows from an alcoholic solution of the phthalone of the base precipitating on addition of sodium alcoholate as a red sodium salt.⁵

The base was oxidized to 8-ethylquinoline-2-aldehyde with selenium dioxide.⁶ In conversion of this aldehyde to the corresponding acid using silver oxide⁷ and hydrogen peroxide, yields of 8 and 90%, respectively, were obtained. However, apart from yields, the latter procedure is preferable. The acid *on simple fusion* was decarboxylated to form 8-ethylquinoline—proof that a carboxyl in α -position to nitrogen was involved.

Final proof of structure of the $C_{12}H_{13}N$ base (I) and the $C_{11}H_{11}N$ base (II) from degradation of I, follows from their unexpected behavior on oxidation with potassium dichromate in sulfuric acid solution. With I, *instead of a carboxylic acid, a ketone was formed*, even when sufficient dichromate to convert an ethyl to carboxyl was used. In similar oxidation, II yielded a mixture of 8-quinolyl methyl ketone⁸ (III) and quinoline-8-carboxylic acid⁹ (IV). Although ketone III was resistant to chromate oxidation it was readily oxidized to the known 2-methylquinoline-8-carboxylic acid¹⁰ with sodium hypobromite.¹¹

(1) Perrin and Bailey, *THIS JOURNAL*, **55**, 4136 (1933).

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

(3) Our material was furnished by the Union Oil Company of California.

(4) The structure of the other base has been only partially determined.

(5) A. Eibner, *Ber.*, **37**, 3605 (1904).

(6) Cf. Burger and Modlin, *THIS JOURNAL*, **62**, 1081 (1940).

(7) Cf. Reference 6 and Besthorn and Geisselbrecht, *Ber.*, **53**, 1031 (1920).

(8) Howitz and Koepke, *Ann.*, **396**, 48 (1913).

(9) Koenigs and Mengel, *Ber.*, **37**, 1327 (1904).

(10) Doebner and Miller, *ibid.*, **17**, 939 (1884).

(11) Cf. Nenitzescu and Ionescu, *Ann.*, **491**, 207 (1931).

Final confirmation of structures of bases I and II was effected by their preparation through a Doebner–Miller synthesis and a Skraup synthesis, respectively.

Experimental

Processing 6315 ml. of bases in the 258–264° boiling range through cumulative extraction yielded 632 ml. of aromatic components with n_D^{20} 1.5575, which was divided into eight fractions (E_1 to E_8 , inclusive) by multiple acid extraction using five portions of acid.

Fraction E_1 , representing the weakest bases, was distilled at atmospheric pressure using a 2.0×90.5 cm., carding-teeth packed, total-reflux, column-heated distillation unit provided with partial take-off.

TABLE I

DISTILLATION DATA ON FRACTION E_1			
Distillation fraction	Temp. range, °C.	Volume, ml.	Refractive index at 25°C.
A	259–265	38	1.5542
B	265–267	39	1.5598
C	267–269	32	1.5650

Isolation of Two $C_{12}H_{13}N$ Bases as Picrates.—Fractions E_1B and E_1C were picrated separately in alcohol. The crude picrates which precipitated from the solutions were filtered off, leached with boiling alcohol and the undissolved material was removed at steam-bath temperature. The two insoluble portions of picrates, totaling 35 g., were combined and a sample, after recrystallization from dilute acetic acid, showed no depression in a mixed melt with *synthetic* 2-methyl-8-ethylquinoline picrate described below. From the above alcoholic filtrates, 30 g. of crude picrate of another $C_{12}H_{13}N$ base crystallized upon standing.

Picrate of the $C_{12}H_{13}N$ Base of Undetermined Structure.—Recrystallized several times from alcohol in fine crystals, this picrate melts at 153.0–153.5°.

Anal. Calcd. for $C_{13}H_{16}O_7N_4$: C, 54.00; H, 4.00; N, 14.00. Found: C, 53.61; H, 4.17; N, 14.12.

2-Methyl-8-ethylquinoline Picrate.—Recrystallized several times from dilute acetic acid in platelets, this picrate melts at 169°.

Anal. Calcd. for $C_{13}H_{16}O_7N_4$: C, 54.00; H, 4.00; N, 14.00. Found: C, 53.98; H, 3.93; N, 14.20.

Free Base.—Liberated from the picrate with ammonium hydroxide, the ether extracted base was distilled and the following constants determined: b. p. 263.0–263.5° (755 mm.), n_D^{20} 1.5870, d_4^{20} 1.0175.

Anal. Calcd. for $C_{12}H_{13}N$: C, 84.21; H, 7.60; N, 8.19. Found: C, 83.90; H, 7.50; N, 8.34.

Phthalone.—A molar mixture of base and phthalic anhydride was heated for four hours at 190°. The melt

recrystallized from alcohol yielded the phthalone melting at 246°. Addition of sodium ethylate to the phthalone in alcohol precipitates its red sodium salt.

Anal. Calcd. for $C_{20}H_{16}O_2N$: C, 79.73; H, 4.98; N, 4.65. Found: C, 79.72; H, 4.93; N, 4.80.

Nitrate.—Concentrated nitric acid added to the base in 1:1 alcohol-ether precipitated the nitrate which, recrystallized from alcohol, melts at 143° with decomposition.

Anal. Calcd. for $C_{12}H_{13}N \cdot HNO_3$: C, 61.54; H, 5.98; N, 11.97. Found: C, 61.69; H, 5.94; N, 12.11.

8-Ethylquinoline-2-aldehyde.¹²—The base, 3 g., and 2.1 g. of selenium dioxide in 60 ml. of alcohol were heated under reflux on the steam cone overnight, and filtered hot to remove the precipitated selenium. The solvent was distilled off and the residue, dissolved in 50 ml. of benzene, was agitated with an equal volume of saturated aqueous sodium bisulfite. After ten hours the filtered-off addition product was agitated with dilute caustic and the solution extracted with ether. Evaporation of the solvent yielded 3 g. of aldehyde (90% of theoretical).

Semicarbazone.—From molar quantities of aldehyde, semicarbazide hydrochloride and sodium acetate in aqueous solution, the precipitation of the semicarbazone was completed in fifteen minutes. Purified from dilute alcohol in the form of needles, it melts at 189–190°.

Anal. Calcd. for $C_{13}H_{14}ON_4$: C, 64.46; H, 5.79; N, 23.13. Found: C, 64.42; H, 5.84; N, 23.21.

8-Ethylquinoline-2-carboxylic Acid.—8-Ethylquinoline-2-aldehyde (3 g.) in 60 ml. of alcohol was oxidized with the calculated amount of freshly precipitated silver oxide according to the procedure of Burger and Modlin.⁶ Only 0.3 g. of acid, or an 8% yield, was obtained. Recrystallized from methanol it melts at 121°.

Anal. Calcd. for $C_{12}H_{11}O_2N$: C, 71.64; H, 5.47; N, 7.04. Found: C, 71.72; H, 5.74; N, 7.24.

In a second experiment 0.5 g. of the aldehyde in 40 ml. of acetone was refluxed for one hour with 3 ml. of 30% hydrogen peroxide. Evaporation of the solvent yielded a thick sirup which was taken up in chloroform and extracted with caustic. Acidification of the aqueous layer followed by chloroform extraction and evaporation of the solvent yielded 0.5 g. of 8-ethylquinoline-2-carboxylic acid (90% yield).

Decarboxylation of 8-Ethylquinoline-2-carboxylic Acid.—On fusion, the acid evolved carbon dioxide and, from the melt in alcohol, 0.7 g. of 8-ethylquinoline picrate (60% yield) was prepared. Recrystallized from alcohol in needles, it showed no depression in a mixed melt with synthetic 8-ethylquinoline picrate melting at 146°.

Synthesis of 8-Ethylquinoline.—The reagents employed in this synthesis corresponded to the molar proportions used by Cohn¹³ in the preparation of quinoline. To a mixture of 14 g. of ferrous sulfate, 49.5 g. of *o*-aminoethylbenzene, and 29.5 g. of nitrobenzene was added a cooled solution of 25 g. of boric acid in 152 g. of glycerol. Finally, 130 g. of concentrated sulfuric acid was added slowly with agitation and then a simmering temperature was maintained for twenty-four hours under reflux. After

dilution and steam distillation to remove any nitrobenzene, the solution was basified and again steam distilled. From the ether extract of the distillate, the contained bases were withdrawn with dilute hydrochloric acid and diazotized at 0° to remove any primary amines. After neutralization with caustic, followed by ether extraction and evaporation of the solvent, the residue contained 8-ethylquinoline admixed with a small amount of quinoline. Separation of the two bases was effected by precipitation of the 8-ethylquinoline as the nitrate by addition of concentrated nitric acid to their alcohol-ether solution (yield of crude nitrate, 22.5 g. or 50%). This salt recrystallized from alcohol-ether in platelets, melts at 146° with decomposition.

Anal. Calcd. for $C_{11}H_{11}N \cdot HNO_3$: C, 60.00; H, 5.46; N, 12.72. Found: C, 59.97; H, 5.46; N, 12.65.

8-Ethylquinoline Picrate.—Addition of an alcoholic solution of picric acid to the base in alcohol precipitates the picrate which recrystallized from dilute acetic acid melts at 146°.

Anal. Calcd. for $C_{17}H_{14}O_7N_4$: C, 52.85; H, 3.63; N, 14.51. Found: C, 52.78; H, 3.62; N, 14.59.

8-Ethylquinoline.—The following constants were determined on the free base obtained from the nitrate by treatment with ammonium hydroxide followed by ether extraction: b. p. 256°, n_D^{25} 1.6020, d_4^{20} 1.0499.

Anal. Calcd. for $C_{11}H_{11}N$: C, 84.08; H, 7.01; N, 8.92. Found: C, 83.83; H, 7.09; N, 9.07.

Synthesis of 2-Methyl-8-ethylquinoline.¹⁴—To a cold solution of 39 g. (0.32 mole) of *o*-aminoethylbenzene in 120 ml. of concentrated hydrochloric acid was added slowly 35 g. (0.8 mole) of acetaldehyde with stirring. After thirty minutes, 24 g. of freshly fused zinc chloride was added and the reaction mixture was heated on the steam cone for twenty-four hours. The solution was made basic and steam distilled. The distillate was extracted with ether. After evaporation of the solvent, 28 g. of picrate (22% yield) precipitated from an alcoholic solution of the residue on addition of an alcoholic solution of picric acid. After recrystallization from dilute acetic acid this preparation melts at 169° and a mixed melt with the picrate of the petroleum base showed no depression.

2-Methyl-8-acetylquinoline or 2-Methyl-8-quinolyl Methyl Ketone.—To a boiling solution of 1 g. of 2-methyl-8-ethylquinoline in 40 ml. of 6 *N* sulfuric acid was added eight 5-cc. portions of 2.3 g. of potassium dichromate in 40 ml. of 6 *N* sulfuric acid, time being allowed after each addition for complete reduction of the oxidant. Finally, the mixture was made alkaline with ammonium hydroxide and then reacidified with acetic acid. In three extractions with 15 ml. portions of chloroform, 0.5 g. (46% yield) of 2-methyl-8-quinolyl methyl ketone was obtained.

Picrate of 2-Methyl-8-quinolyl Methyl Ketone.—The picrate was precipitated by addition of alcoholic picric acid to the ketone in alcohol. Recrystallized from 40% acetic acid in fine needles, it melts at 182° with decomposition.

Anal. Calcd. for $C_{13}H_{14}O_8N_4$: C, 52.17; H, 3.38; N, 13.53. Found: C, 52.01; H, 3.43; N, 13.66.

(12) Cf. Reference 6 and Henze, *Ber.*, **67**, 750 (1934); Kwartler and Geisselbrecht, *ibid.*, **53**, 1017 (1920).

(13) Cf. E. W. Cohn, *THIS JOURNAL*, **52**, 3685 (1930).

(14) Cf. Mills, Harris and Lambourne, *J. Chem. Soc.*, **119**, 1294 (1921).

Semicarbazone of 2-Methyl-8-quinolyl Methyl Ketone.—This salt, prepared by treating the ketone with molar amounts of semicarbazide hydrochloride and sodium acetate in a small volume of water, melts at 209° after recrystallization from dilute alcohol.

Anal. Calcd. for $C_{13}H_{14}ON_4$: C, 64.46; H, 5.79; N, 23.13. Found: C, 64.38; H, 5.86; N, 22.92.

Oxidation of 2-Methyl-8-quinolyl Methyl Ketone.¹¹—To a mixture of 0.8 g. of ketone and 42 ml. of 7% caustic at 0° was added slowly 1.1 ml. of bromine with stirring for an hour and a half. The excess sodium hypobromite was destroyed by addition of sulfur dioxide, followed by two extractions with chloroform. Evaporation of the solvent left 2-methylquinoline-8-carboxylic acid in poor yield. After recrystallization from water in fine needles, it showed no depression in a mixed melt with an authentic sample melting at 152–153°.

Anal. Calcd. for $C_{11}H_9O_2N$: N, 7.49. Found: N, 7.62.

Oxidation of 8-Ethylquinoline.—To a boiling solution of the base (1 g.) in 40 ml. of 6 *N* sulfuric acid, the theoretical amount of potassium dichromate for ketone formation was added slowly during one hour. The cooled solution was basified with ammonium hydroxide, acidified with acetic acid and extracted with chloroform. The chloroform layer was extracted twice with 10-ml. portions of 10% sodium hydroxide. Evaporation of the solvent layer

left an oil which readily formed 0.6 g. of *semicarbazone* (40% yield). Recrystallized from dilute alcohol, it melts at 225°.¹⁵

Anal. Calcd. for $C_{12}H_{13}ON_4$: C, 63.16; H, 5.26; N, 24.56. Found: C, 63.43; H, 5.24; N, 24.35.

The aqueous layer was acidified to the phenolphthalein end-point with acetic acid and extracted with two 5-ml. portions of chloroform. Evaporation of the solvent left 0.45 g. (40% yield) of quinoline-8-carboxylic acid⁹ which, recrystallized from methanol, melts at 184°.

Anal. Calcd. for $C_{10}H_7O_2N$: N, 8.09. Found: N, 8.20.

Summary

1. The isolation of two new $C_{12}H_{13}N$ bases from the Edeleanu kerosene extract of California petroleum is reported.

2. The structure of one of the bases has been established as 2-methyl-8-ethylquinoline through degradation and synthesis.

3. The formation of 8-quinolyl methyl ketones in potassium dichromate oxidation of 2-methyl-8-ethyl- and 8-ethylquinoline is described.

(15) Howitz and Koepke (ref. 8) report a melting point of 223° for the semicarbazone of 8-quinolyl methyl ketone.

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A Contribution to Chromic Acid Oxidation of Quinoline Homologs and Oxidation of *Bz*-Ethylquinolines to Quinolyl Methyl Ketones

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Introduction

In the Texas Laboratory, chromic acid in dilute sulfuric acid either as (1) anhydride or (2) dichromate has been employed exclusively as an oxidizing agent for conversion of alkyls at position 8 on the quinoline nucleus to carboxyl. With 2 the reaction proceeds with much greater velocity than with 1. The suggested explanation of this difference is, acid potassium sulfate catalyzes chromic acid oxidation. Comparative data on *step-wise* oxidation of *Bz*-alkylquinolines with anhydride and dichromate are submitted in Tables I and II, respectively.

It has been found that where quinoline-8-carboxylic acids are desired, a decidedly increased yield can be obtained by using a fractional part of the calculated amount of oxidant. The advantage of step-wise oxidation is the maintenance of a favorable equilibrium between the original base and its primary oxidation products in order to

circumvent, as far as possible, excessive degradation of the latter. At the end of the reaction, unchanged base is recovered for recycling.

Certain *Bz*-ethylquinolines are converted to quinolyl methyl ketones; others yield mixtures of ketone and carboxylic acid¹ and a few only carboxylic acids. As concerns a restricted number of bases, the results obtained depend on whether the anhydride or dichromate is used. In dichromate oxidation of 2,3-dimethyl-8-ethyl- and 2,4-dimethyl-8-ethylquinoline, only carboxylic acids are obtained; however, in chromic anhydride oxidation, quinolyl methyl ketones are readily formed. From 8-methyl- and 8-*n*-propylquinolines, only carboxylic acids have been obtained.

Ketone formation from *Bz*-ethylquinolines is analogous to the oxidation of ethylbenzene to acetophenone.² Oxidation of *n*-propylbenzene to

(1) Glenn and Bailey, *THIS JOURNAL*, **63**, 639 (1941).

(2) Friedel and Balsohn, *Bull. soc. chim.*, [2] **32**, 616 (1800).