order as the intrinsic viscosities. After lengthy sedimentation, however, the differences in heterogeneity assert themselves and the order of the curves becomes the same as that of the dilute solutions.

Acknowledgment.—The authors are greatly indebted to E. I. du Pont de Nemours and Company for permission to use the oil-turbine ultracentrifuge. They also wish to express their appreciation of the help given to them during the investigation by Dr. J. B. Nichols of the du Pont Experimental Station.

Summary

1. The sedimentation constants of four different brands of commercial gelatin in 0.4% solution at *p*H 7.5, measured at approximately 34°, vary between 2.60 and 3.30, compared with 3.43, the value found by Krishnamurti and Svedberg at 20° for a gelatin solution of the same concentration and *p*H, and 3.55, the constant for egg albumin, a normal globular protein of molecular weight 43,000.
2. The sedimentation constants in the dilute solutions were found to increase regularly with the intrinsic viscosities.
3. The sedimentation constants for the 2% solutions were found to be from 29 to 52% (average 41%) higher than for the dilute solutions; from the available data it is impossible to decide whether the increase is due to aggregation, or whether it is only apparent, the result of an over-correction for viscosity.
4. All the solutions were found to be heterogeneous, to various degrees, with respect to particle size.

PHILADELPHIA, PENNA. RECEIVED JANUARY 12, 1938

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF TEXAS]

Nitrogen Compounds in Petroleum Distillates. XI. Isolation of 2,3-Dimethyl-8-ethylquinoline from the Kerosene Distillate of California Petroleum[1]

BY C. L. KEY AND J. R. BAILEY

Introduction

The crude bases, used in this investigation and referred to as "kero" bases, were furnished by the Union Oil Company of California from the residual sulfur dioxide extract, obtained in refining kerosene by the Edeleanu process. Previously, the following polymethylated quinolines had been obtained from the same source: 2,3-, 2,4-[2] and 2,8-dimethylquinoline[3] along with 2,3,8-[4] and 2,4,8-trimethylquinoline.[5]

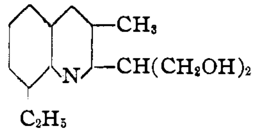
Whereas the coal-tar bases, quinoline, quinaldine, lepidine, and isoquinoline do not occur, so far as is known, in *straight run* petroleum distillates, the first two substances have been separated from *cracked* gasoline.[6]

All of the above kero quinolines are methylated at 2, the other positions of substitution being 3, 4 and 8. With the exception of the 2,3,8-homolog, they were known to synthesis, prior to being obtained from petroleum. Recently, 2,3,8-trimethylquinoline, together with quinoline, isoquinoline and lepidine, was encountered among the complex mixture of bases formed in pyrolysis of cottonseed meal.[7]

It is worthy of note that quinaldine is the only coal-tar base which yields a quinphthalone (Quinoline Yellow), whereas all of the six known kero quinolines condense readily with phthalic anhydride in the formation of quinphthalones of the same shade of color as Quinoline Yellow.

2,3-Dimethyl-8-ethylquinoline represents the only ethyl homolog so far encountered. The structure assigned was deduced from its oxidation to 2,3-dimethylquinoline-8-carboxylic acid and was confirmed by synthesis.

Through condensation with formaldehyde, it was converted to 3-methyl-8-ethyl-2-dimethylolmethylquinoline



---

[1] From a dissertation presented by C. L. Key to the Faculty of the Graduate School of the University of Texas in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Biggs and Bailey, THIS JOURNAL, **55**, 4141 (1933).

[3] Lake and Bailey, *ibid.*, **55**, 4143 (1933).

[4] King and Bailey, *ibid.*, **52**, 1239 (1930).

[5] Perrin and Bailey, *ibid.*, **55**, 4136 (1933).

[6] Bratton and Bailey, *ibid.*, **59**, 175 (1937).

[7] Parker and Bailey, *ibid.*, **58**, 1102 (1936).

which through nitric acid oxidation, followed by decarboxylation of the resulting acid, yielded 3-methyl-8-ethylquinoline.

A characteristic and distinctive salt of the kero base is the nitrate, through which the base can be readily separated and purified.

Experimental Part

2,3-Dimethyl-8-ethylquinoline.—Initially, the crude kero bases were processed by five distillations at 5 to 7 mm. pressure through a reflux column and, then, in order to segregate aromatic and non-aromatic components, the 285° fraction was dissolved in dilute hydrochloric acid and carried through exhaustive cumulative extraction[5] with chloroform. In this way, the aromatic base hydrochlorides were concentrated in the aqueous layer. Picrates, prepared from the regained bases, were recrystallized from glacial acetic acid. In final purification of the dimethylethylquinoline, it was liberated from the picrate and dissolved in a slight excess of nitric acid, with constant stirring for thirty minutes at the temperature of a salt–ice bath. The nitrate, which separated in good yield, was recrystallized from water. The regained and distilled base, after being dried over solid potassium hydroxide, had the following physical constants: m. p. 36.5°; b. p. 284.6° (755 mm.); d^{20}_4 1.017; n^{20}_D 1.5940. From petroleum ether, the base crystallizes in large hexagonal plates. Characteristic of this quinoline is the non-formation of a quaternary salt with methyl iodide at water-bath temperature.

Anal. Calcd. for $C_{13}H_{15}N$: C, 84.32; H, 8.10; N, 7.57; mol. wt., 185. Found: C, 83.94; H, 7.89; N, 7.54; mol. wt., subs. 15.50 mg., camphor 155.55 mg., d*t* 21°, mol. wt., 189.

Picrate.—This salt, which is difficultly soluble in the common solvents, crystallizes from glacial acetic acid in slender yellow needles melting with decomposition at 220°.

Anal. Calcd. for $C_{19}H_{18}O_7N_4$: C, 55.07; H, 4.35; N, 13.53. Found: C, 55.19; H, 4.34; N, 13.46.

Nitrate.—This salt crystallizes from alcohol or water in fine needles melting at 166° and decomposing just above this temperature.

Anal. Calcd. for $C_{13}H_{16}O_3N_2$: C, 62.90; H, 6.45; N, 11.29. Found: C, 63.19; H, 6.39; N, 11.30.

Hydrochloride.—On dissolving the base in a slight excess of concentrated hydrochloric acid, the hydrochloride separates and can be recrystallized from alcohol or water in long slender needles melting at 212–214° with decomposition.

Anal. Calcd. for $C_{13}H_{15}N \cdot HCl$: C, 70.40; H, 7.22; N, 6.32; Cl, 16.02. Found: C, 70.43; H, 7.24; N, 6.33; Cl, 16.06.

Acid Sulfate.—This salt, prepared by adding a slight excess of concentrated sulfuric acid to an acetone solution of the base, crystallizes from alcohol in fine needles melting at 239–240° undecomposed.

Anal. Calcd. for $C_{13}H_{15}N \cdot H_2SO_4$: N, 4.95. Found: N, 4.98.

Mercuric Chloride Salt.—Mercuric chloride added to the base in equimolar amounts in dilute hydrochloric acid solution precipitates the double salt. It crystallizes from water in large needles and from alcohol in microscopic needles melting at 212–214° undecomposed.

Anal. Calcd. for $C_{13}H_{15}N \cdot HCl \cdot HgCl_2$: N, 2.84. Found: N, 2.88.

Chromate.—On addition of potassium chromate to the hydrochloride in weak acid solution, the chromate separates in a gelatinous form which on standing becomes crystalline. It crystallizes from 50% glacial acetic acid in microscopic rhombic prisms which decompose around 100°.

Anal. Calcd. for $C_{13}H_{15}N \cdot H_2CrO_4$: N, 4.62. Found: N, 4.61.

2,3-Dimethylquinoline-8-carboxylic Acid.—A mixture of 3 g. of base, 6 g. of chromic anhydride and 78 cc. of 1:5 sulfuric acid is refluxed for sixty hours. The solution, after neutralization with ammonium hydroxide to incipient precipitation of chromic hydroxide, is extracted with chloroform in a yield of about 19%. For purification, the reaction product is decolorized in aqueous solution with filt-char, followed by recrystallization from alcohol and water in long needles melting at 202°. A mixed melting point with an authentic sample of 2,3-dimethylquinoline-8-carboxylic acid[4] (p. 1249) showed no depression.

Anal. Calcd. for $C_{12}H_{11}O_2N$: C, 71.64; H, 5.47; N, 6.97. Found: C, 71.64; H, 5.46; N, 6.87.

2,3-Dimethylquinoline.—The above acid was decarboxylated by distillation with soda-lime and the resulting base was dissolved in ether and precipitated with an alcoholic solution of picric acid. The picrate recrystallizes from glacial acetic acid in microscopic hexagonal prisms melting at 231°. This product, mixed with an authentic sample of 2,3-dimethylquinoline picrate, showed no depression in melting point.

3-Methyl-8-ethyl-2-dimethylolmethylquinoline.—In conformity with the procedure of Koenigs and Stockhausen,[8] 5 g. of the dimethylethylquinoline and 25 ml. of formalin in a sealed tube are heated on a steam cone for forty-five hours. The reaction mixture, processed in the usual way, yields the dimethylol compound which, after recrystallization from chloroform and ethyl acetate, melts at 94–95°.

Anal. Calcd. for $C_{15}H_{19}O_2N$: C, 73.47; H, 7.75; N, 5.71. Found: C, 73.31; H, 7.69; N, 5.91.

Picrate.—This salt precipitates on the addition of an alcoholic solution of picric acid to the dimethylol base in ether and can be recrystallized from water or alcohol in long slender needles melting at 165.5°.

Anal. Calcd. for $C_{21}H_{22}O_9N_4$: C, 53.16; H, 4.64; N, 11.81. Found: C, 53.47; H, 4.80; N, 11.88.

3-Methyl-8-ethylquinoline.—The dimethylol compound (5 g.) in 250 ml. of 1:1 nitric acid is boiled for six hours. On evaporation of the solution, a practically quantitative yield of 3-methyl-8-ethylquinoline-2-carboxylic acid melting at 84–85° results. Since a well-known procedure is involved here for conversion of a methyl at position 2 to carboxyl in quinoline homologs, this product was not analyzed. After decarboxylation at a temperature of

---

(8) W. Koenigs and F. Stockhausen, *Ber.*, **34**, 4331 (1901).

180°, the resulting base is purified through recrystallization of its picrate (A) from benzene and glacial acetic acid. The assigned structure, 3-methyl-8-ethylquinoline, was confirmed by synthesis.[9]

Synthesis of 3-Methyl-8-ethylquinoline.—Dry hydrogen chloride is introduced at a moderate rate into a mixture of propionic aldehyde (5 g.) and methylal (6 g.) for five minutes. On the addition of *o*-ethylaniline (1.8 g.) in concentrated hydrochloric acid (5 g.), a reaction begins and is completed by boiling the solution for three hours. An equal volume of water is added, the filtered solution is treated with a slight excess of sodium nitrite, and, after concentration to a small volume, the bases are liberated with sodium hydroxide and extracted with ether. Final purification of the methylethylquinoline, after fractional distillation at diminished pressure, is effected through the picrate (B). The identity of salts A and B was confirmed by a mixed melting point determination. The new base which was obtained in a yield of 8% has the following physical constants: b. p. 263° with partial decomposition (at 746 mm.); n^{25}_{D} 1.5946.

Anal. Calcd. for $C_{18}H_{16}O_7N_4$: C, 54.00; H, 4.00; N, 14.00. *Picrate A.* Found: C, 53.84; H, 4.07; N, 14.02. *Picrate B.* Found: C, 54.01; H, 4.00; N, 14.03.

Synthesis of 2,3-Dimethyl-8-ethylquinoline.—Final confirmation of the structure of the original kero base was effected through its synthesis[10] which can be carried out as follows: a mixture of concentrated hydrochloric acid (4 moles), tiglic aldehyde (1 mole) and *o*-ethylaniline hydrochloride (4 moles) is heated for four hours on a water-bath and then steam distilled. The solution, after liberation of the bases with sodium hydroxide, is again steam distilled and the distillate, acidified with hydrochloric acid, is treated at room temperature with sodium nitrite. Following the removal of the supernatant oil by ether extraction, the solution is boiled, filtered, made alkaline with sodium hydroxide, steam distilled and again extracted with ether. The base, regained from the solvent, gave a picrate which, mixed with the kero base picrate, produced no depression of the melting point (220°).

Anal. Calcd. for $C_{19}H_{18}O_7N_4$: C, 55.07; H, 4.35; N, 13.53. Found: C, 55.19; H, 4.27; N, 13.46.

Summary

The isolation of 2,3-dimethyl-8-ethylquinoline (I) from the complex mixture of bases obtained from the kerosene distillate of California asphalt-base petroleum is described. The structure assigned this product has been confirmed by synthesis.

2,3-Dimethylquinoline (II) and 3-methyl-8-ethylquinoline (III) were obtained by indirect dealkylation of base I at positions 8 and 2, respectively. Base II is one of five kero quinolines which were isolated in the Texas Laboratory prior to the present investigation. The structure of base III, a new quinoline homolog, was established by synthesis.

AUSTIN, TEXAS RECEIVED NOVEMBER 26, 1937

---

[9] *Cf.* Carl Beyer, *J. prakt. Chem.*, **33**, 419 (1886); von Miller and Kinkelin, *Ber.*, **20**, 1916 (1887).

[10] *Cf.* Doebner and von Miller, *ibid.*, **16**, 2464 (1883).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE WASHINGTON SQUARE COLLEGE, NEW YORK UNIVERSITY]

Change in the Optical Rotation of Gluconpremise

BY PHILIPPOS E. PAPADAKIS AND HAROLD JEROME COHEN

Geza Zemplén[1] prepared gluconpremise, m. p. 145° and $[\alpha]^{21}_{\mathrm{D}}$ +8.8, by hydrolyzing pentaacetyl gluconpremise. He found that by recrystallizing the product from absolute alcohol he could get gluconpremise melting at 115–120°. A. Wohl and O. Wollenberg[2] prepared gluconpremise from glucose and hydroxylamine acetate. The product was washed with different mixtures of acetic acid and acetone and further with acetone and finally with absolute ether. Wohl and Wollenberg did not give the specific rotation of their product. They repeated Zemplén's work and state: "Remarkably also a melting point of 145° and a melting point of the recrystallized substance of 115–120° is reported. By the reported procedure of recrystallization from absolute alcohol as well as by the wash procedure, as was described above, a melting point of 146–148° is found and the substance gives no depression with that produced in the above described manner."

As far as we are aware no further investigation has been made to find out whether Zemplén's observations were correct. As the problem seemed interesting, it was thought advisable to prepare gluconpremise by the Wohl and Wollenberg method and then recrystallize it from absolute ethyl alcohol to find out whether gluconpremise, m. p. 115–120°, could be obtained. If the observations of Zemplén are correct, then both the high and the low melting point glucononi-

---

[1] G. Zemplén, *Ber.*, **60**, 171 (1927).

[2] A. Wohl and O. Wollenberg, *Ann.*, **500**, 281 (1932).