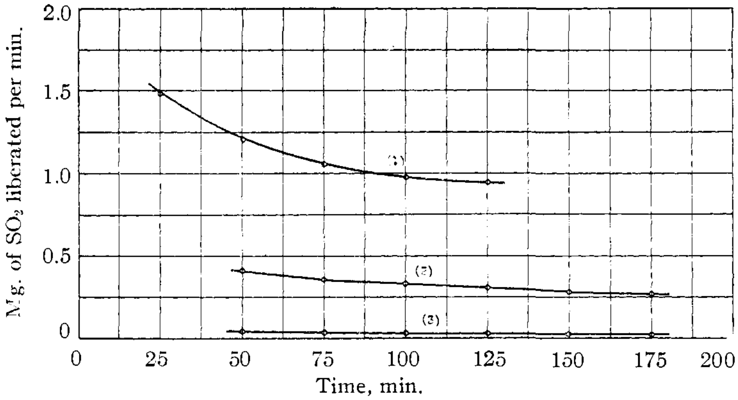

Fig. 4.—Comparison of degassing rates of: (1) non-aromatic fraction, (2) the $C_{16}H_{25}N$ naphthenic base and (3) quinoline acid sulfites.

oxide absorber containing 40% potassium hydroxide. Two absorbers, operating alternately at recorded intervals of time, are connected to the aeration unit through a two-way stopcock so that the rate of degassing can be followed without interruption. The absorbed sulfur dioxide is determined iodometrically. In a series of experiments involving three different bases, the rates of sulfur dioxide evolution from the aeration unit are deduced and plotted against time. At the inflection point of each curve, it is assumed, all of the *excess* sulfur dioxide—*and only the excess*—is removed, leaving behind only base acid sulfite. By shifting the time abscissa of the curve for each base so that the inflection points coincide, a composite set of curves follows whereby a comparison of the degassing rates is presented. Figure 3 shows the degassing rate of the $C_{16}H_{25}N$ naphthenic base. Figure 4 derived from Fig. 3, along with similar curves for quinoline and a complex non-aromatic fraction (b. p. 270–280°), denotes the comparative degassing rates of their acid sulfites.

Summary

Experience has demonstrated that, by following the old beaten track in processing coal tar bases, which are essentially of aromatic character, not much progress can be expected in isolation of the components of the far more complex straight-run petroleum base fractions.

In the present investigation, a new cyclic process of resolution is described which employs the reversible reaction

Sulfiting Degassing

$$(A)\ \text{Base} + SO_2 + H_2O \rightleftarrows (B)\ \text{Base}\cdot H_2SO_3$$

In (A), fractional acid extraction and in (B), fractional acid-sulfite dissociation are involved.

It was beyond the scope of the present investigation to effect quantitative separations of the known components of the complex mixture of the bases processed; on the contrary, the aim was to establish Fractional Sulfiting and Fractional Degassing as general procedures which can contribute to an extension of the chemistry of petroleum bases.

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[CONTRIBUTION NO. 133 FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, THE UNIVERSITY OF TEXAS]

The Nitrogen Compounds in Petroleum Distillates. XIII. Isolation of Four Quinoline Homologs and Two Aromatic Bases of Probable Trinuclear Cyclic Structure[1]

BY W. NELSON AXE[2] AND J. R. BAILEY

Introduction

The main objective of this investigation concerned the isolation of aromatics in the 300° range of kero bases. In refining the crude material, the following steps were involved: (1) fractional acid extraction followed by a rough distillation; (2) fractional distillation of the desired cuts from (1) after appropriate recombinations in the order of boiling points and refractive indices; (3) cumulative extraction[3] of fractions from (2) preceded by the usual recombinations; (4) fractional distillation of the aromatic bases which were concentrated as hydrochlorides in the aqueous layer in step 3.

Attempts to isolate individual components in fractions from step 4 around the 295° boiling range were rewarded by the recovery of two products in poor yield of the composition $C_{13}H_{15}N$ (I) and $C_{14}H_{17}N$ (II) through fractional precipitation and recrystallization of different salts. Further work on these compounds awaits the assembling of sufficient quantities for proof of structure.

Since the results reported above were disappointing, resort was had to degassing of acid sul-

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[1] Presented before the Petroleum Division of the American Chemical Society, Dallas, Texas, April 19, 1938.

[2] From a dissertation presented by W. N. Axe 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.

[3] Perrin and Bailey, THIS JOURNAL, **55**, 4136 (1933).

fites. In the initial experiment on acid sulfites of aromatic fractions from cumulative extraction, the evolution of sulfur dioxide ceased abruptly when 90% of the original bases had layered out. An explanation of this observation was furnished by the discovery that, on prolonged degassing at different temperature levels, acid sulfites of aromatic bases may undergo oxidation to acid sulfates, provided aeration is employed to facilitate the removal of sulfur dioxide.[4]

From the base fractions obtained in the degassing experiment, a product of the composition $C_{14}H_{17}N$ (III) was isolated through its characteristic nitrate. The residual base fraction, obtained by sodium hydroxide precipitation of the acid sulfate solution, yielded a $C_{13}H_{15}N$ base (IV). This latter base was separated from the mixture as the characteristic acid sulfate. These bases are isomers of (II) and (I), respectively.

The structures of (III) and (IV) have been established conclusively through both degradation and synthesis. In accordance with the general observation that, in chromic acid oxidation of quinoline homologs, the stability of alkyls is in the progressive order of their positions of substitution from 1 to 8, inclusive,[5] the monocarboxylic acids from oxidation of (III) and (IV) proved to be 2,3-dimethylquinoline-8-carboxylic acid (V) and 2,3,-4-trimethylquinoline-8-carboxylic acid (VI), respectively.

Acid (V) proved identical with 2,3-dimethylquinoline-8-carboxylic acid, previously obtained in chromic acid oxidation of 2,3,8-trimethylquinoline[6] and 2,3-dimethyl-8-ethylquinoline.[7] Since this acid contains two carbons less than does base (III), it follows that the latter is a 2,3-dimethyl-8-propylquinoline. Accordingly, resort was had to synthesis to determine whether an *n*- or isopropyl was involved. The *n*-propyl isomer was prepared by a modification of Rhode's[8] synthesis of 2,3-dimethylquinoline through the action of concentrated hydrochloric acid on a mixture of *o*-amino-*n*-propylbenzene and tiglic aldehyde. The 2,3-dimethyl-8-*n*-propylquinoline, so obtained, proved identical with the kero base (III).

Decarboxylation of acid VI gave 2,3,4-trimethylquinoline, a base known to synthesis.[9] The position of the carboxyl at 8 was inferred from the fact that, among the six previously isolated quinoline homologs, none is substituted at positions 5, 6 or 7. The bases referred to include: 2,3-, 2,4-[10] and 2,8-dimethylquinoline,[11] 2,3,8-[6] and 2,4,8-trimethylquinoline,[3] 2,3-dimethyl-8-ethylquinoline.[7] The usual comparison of (IV) with a synthetic sample of 2,3,4,8-tetramethylquinoline[12] revealed the identity of the kero base.

Two transformer-oil bases of the composition $C_{15}H_{13}N$ and $C_{16}H_{15}N$ have been isolated. Obviously, they do not belong to the quinoline series, since the rather closely cut fraction of bases from which they were isolated possessed a refractive index of 1.6570 at 25°, indicating the presence of polynuclear types of a higher order. Furthermore, the empirical formulas correspond to a dimethyl and a trimethyl homolog of acridine or one of the three types of naphthoquinolines of the general formula $C_nH_{2n-17}N$, as compared with $C_nH_{2n-11}N$ for the quinoline series. Experimental evidence indicates that these provisionally assumed trinuclear types first occur in the 320° range of straight-run petroleum base fractions. Since acridine and its homologs have very high boiling points, it may be inferred that they are not represented, if at all, much below the 345° range.

Experimental

The Union Oil Company of California in processing 3000 barrels of kerosene Edeleanu extract obtained 3 barrels of bases. A supply of this crude material was partially refined in the Texas Laboratory by fractional acid extraction, followed by fractional distillation at reduced pressure.

The separate fractions, totalling 38.7 liters, which were obtained from the second distillation through recombinations in the order of boiling points and refractivities, were carried through cumulative extraction. Only the bases present as hydrochlorides in the water layer from this form of solvent extraction, and representing a relatively high concentration of aromatics, were used in this investigation. The so-called non-aromatic hydrochlorides which are segregated, in large part, in the chloroform layer have been reserved for future study. The yield of aromatic bases in this process is approximately 28% by volume. When it is considered that the average n^{25}D value of the non-aromatics is not much above 1.5, while that of quinoline homologs approaches 1.6, the data in Table I emphasize the efficiency of this process.

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(4) An experimental confirmation that the temperature of dissociation of base acid-sulfites rises progressively with their ionization constants has been established. When partial sulfite–sulfate conversion takes place, as in the present case, the bases of highest ionization constants are the ones involved. Proof of these conclusions will appear in a subsequent publication.

(5) Miller, *Ber.*, **23**, 2252 (1890).

(6) King and Bailey, THIS JOURNAL, **52**, 1239 (1930).

(7) Key and Bailey, *ibid.*, **60**, 763 (1938).

(8) Rhode, *Ber.*, **20**, 1911 (1887).

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

(10) Biggs and Bailey, THIS JOURNAL, **55**, 4141 (1933).

(11) Lake and Bailey, *ibid.*, **55**, 4143 (1933).

(12) This compound was synthesized by C. L. Key in anticipation of its discovery among the kero bases.

TABLE I

CUMULATIVE EXTRACTION OF KERO BASES

Fraction	B. p., °C.	A n^{25}D (Mixed type)	B n^{25}D (Aromatics)	B Vol., cc. (Aromatics)
1	292	1.5449	1.5850	850
2	293	1.5483	1.5842	980
3	294	1.5488	1.5845	635
4	296	1.5494	1.5830	520
5	292	1.5510	1.5848	560
6[a]	297	1.5502	1.5850	1400
7[a]	296	1.5522		
8	303	1.5520	1.5832	900
9	301	1.5534	1.5832	850
10	307	1.5544	1.5832	760
11	300	1.5544	1.5850	650
12	304	1.5554	1.5855	780
13	303	1.5559	1.5848	1100
14	310	1.5559	1.5847	800

[a] Fractions 6 and 7 were combined prior to extraction.

Distillation data obtained on each of the fractions 1B to 7B, inclusive, showed a negligible variation in physical constants, indicating fractional distillation of the remaining fractions to be superfluous. In processing these fractions, bases (I) and (II) referred to in the introduction were isolated.

The individual fractions 8, 9, 10 and 11(B) dissolved in sulfurous acid were fractionally degassed through aeration. This procedure led to the isolation, in a favorable yield, of 2,3-dimethyl-8-*n*-propylquinoline (III) and 2,3,4,8-tetramethylquinoline (IV), neither of which was separated in applying the conventional methods hitherto employed in resolution of mixtures of bases. Table II is submitted as an example of the results obtained.

TABLE II

FRACTIONAL DEGASSING OF SULFITE SOLUTION OF FRACTION 9B (TABLE I)

Vol. 850 cc. (n^{25}D 1.5832)

Fraction	Temp., °C.	Fraction time, hrs.	Total time, hrs.	Vol., cc.	n^{25}D
1	10	6.5	6.5	135	1.5754
2	20	2.0	8.5	95	1.5754
3	20	2.0	10.5	82	1.5778
4	25	2.0	12.5	90	1.5808
5	25	18.0	30.5	160	1.5838
6	90	2.0	32.5	94	1.5889
7	90	2.0	34.5	Trace	...
8 Residue	..	..	..	164	1.5916

Fractions 1 through 7 comprise free bases which separated as a result of the dissociation of acid sulfites. The residual fraction, 8, did not degas due to oxidation of the original acid sulfites to acid sulfates.

Isolation of 2,3-Dimethyl-8-*n*-propylquinoline as the Nitrate.—To the cooled solution of each of the first seven fractions (Table II) dissolved in an equal volume of 1:1 ether–alcohol, nitric acid was added in slight excess (deduced from an assumed average base mol. wt. of 198). The precipitated nitrates after recrystallization gave the following yields: 22 g. (1), 16.5 g. (2), 8.5 g. (3) and 2.5 g. (4). Fractions 5, 6 and 7 gave negative results. This total yield of 49.5 g. came from fraction 9B (Table I). In processing fractions 8, 10 and 11(B) in a similar way, the amount of pure nitrate was increased to 112 g. This selective salt for the isolation of the dimethylpropylquinoline crystallizes from water containing a very small amount of nitric acid in slender rods melting at 169° with decomposition.

Anal. Calcd. for $C_{14}H_{17}N \cdot HNO_3$: C, 64.10; H, 6.91; N, 10.67. Found: C, 64.33; H, 6.93; N, 10.50.

Free Base.—The following constants were determined for the base prepared in the usual way from the pure nitrate or picrate: m. p. 14.5–15.5°; b. p. 299.5°; d^{20}_4 0.9996; n^{25}D 1.5778. It is insoluble in water and readily soluble in the common organic solvents. It is practically odorless.

Anal. Calcd. for $C_{14}H_{17}N$: C, 84.42; H, 8.54; N, 7.03. Found: C, 84.22; H, 8.58; N, 7.07.

Picrate.—This salt, which is difficultly soluble in the common solvents, crystallizes from glacial acetic acid in long lemon colored rectangular prisms which melt undecomposed at 198–199°.

Anal. Calcd. for $C_{20}H_{20}N_4O_7$: C, 56.07; H, 4.71; N, 13.08. Found: C, 55.83; H, 4.63; N, 13.14.

Acid Sulfate.—On addition of concentrated sulfuric acid to an alcohol–ether solution of the base, this salt precipitates and can be recrystallized from *t*-butyl alcohol in small rectangular prisms melting at 212–212.5°. It is readily soluble in water and ethyl alcohol.

Anal. Calcd. for $C_{14}H_{17}N \cdot H_2SO_4$: C, 56.56; H, 6.39; N, 4.71. Found: C, 56.20; H, 6.42; N, 4.97.

Hydrochloride.—This salt, prepared by passing hydrogen chloride into an ether solution of the base, crystallizes from acetone containing a trace of alcohol in microscopic rhombic prisms which, after drying in a vacuum desiccator, melt at 161–162°. It is readily soluble in water and alcohol.

Anal. Calcd. for $C_{14}H_{17}N \cdot HCl$: C, 71.31; H, 7.67; N, 5.93. Found: C, 71.32; H, 7.91; N, 6.19.

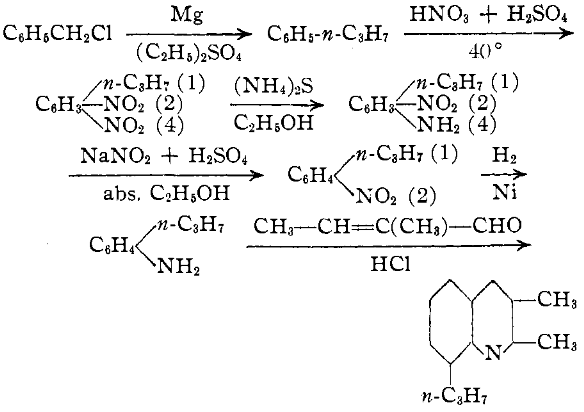
Zinc Chloride Salt.—For precipitation of this salt, an aqueous solution of zinc chloride is added to a molar amount of the base in dilute hydrochloric acid. Recrystallization from an alcohol–acetone mixture yields ill-defined microscopic crystals melting at 193–194°.

Anal. Calcd. for $C_{14}H_{17}N \cdot HCl \cdot ZnCl_2$: C, 45.19; H, 4.87; N, 3.91. Found: C, 45.09; H, 5.10; N, 3.89.

2,3-Dimethylquinoline-8-carboxylic Acid.—To a boiling solution of 5 g. of the base in 6 *N* sulfuric acid, is added, slowly, 15 g. of potassium dichromate in 23 g. of concentrated sulfuric acid diluted with 25 cc. of water. The reaction is complete in one hour. After neutralization of the sulfuric acid, the solution is extracted with chloroform. The crude product crystallizes from alcohol in needles melting at 201–202°: yield 1.75 g. or 27%. A mixture of this acid with an authentic sample of 2,3-dimethylquinoline-8-carboxylic acid showed no depression in melting point, thus confirming a propyl at position 8 of the original base. Decarboxylation of the acid through soda-lime distillation yielded the kero base 2,3-dimethylquinoline.

Anal. Calcd. for $C_{12}H_{11}O_2N$: C, 71.64; H, 5.47. Found: C, 71.43; H, 5.53.

Synthesis of 2,3-Dimethyl-8-*n*-propylquinoline.—In this synthesis the following series of reactions was involved



The *n*-propylbenzene was prepared according to the procedure of Gilman and Catlin.[13] The method described by Brady and Cunningham[14] was followed in the conversion of the hydrocarbon to *o*-nitro-*n*-propylbenzene. Reduction of the nitro compound to the corresponding amine was carried out in a high-pressure hydrogenator using a Raney nickel catalyst. Equimolecular proportions of *o*-amino-*n*-propylbenzene and tiglic aldehyde were heated with an excess of concentrated hydrochloric acid in accordance with Rhode's synthesis of 2,3-dimethylquinoline.[8]

Isolation of 2,3,4,8-Tetramethylquinoline through the Acid Sulfate.—The residual bases in Fraction 8 (Table II) were dissolved in a 1:1 alcohol–acetone solution. On the addition of concentrated sulfuric acid, a sticky mass separated which on recrystallization from water yielded a colorless crystalline product. From this salt was recovered 13 g. of pure base. The total over-all yield increased to 20.5 g. or approximately 4.5%, after fractions 8, 10 and 11 (Table I) had been processed as outlined for fraction 9 (Table II).

The acid sulfate crystallizes from alcohol in hexagonal prisms melting with decomposition at 298°.

Anal. Calcd. for $C_{13}H_{15}N \cdot H_2SO_4$: C, 55.10; H, 6.04; N, 4.94. Found: C, 54.88; H, 6.07; N, 4.87.

Free Base.—This base crystallizes from methyl alcohol in translucent, long, slender, rectangular prisms melting at 77–78°.

Anal. Calcd. for $C_{13}H_{15}N$: C, 84.32; H, 8.10; N, 7.56. Found: C, 84.41; H, 8.23; N, 7.55.

Picrate.—This salt crystallizes from glacial acetic acid in characteristic small, rectangular plates melting with decomposition at 240°. It is very difficultly soluble in other common solvents.

Anal. Calcd. for $C_{19}H_{18}N_4O_7$: C, 55.07; H, 4.35; N, 13.53. Found: C, 55.26; H, 4.48; N, 13.58.

Hydrochloride.—On addition of concentrated hydrochloric acid to an acetone solution of the base, the hydrochloride is precipitated. The salt crystallizes from an acetone–alcohol solution in ill-defined microscopic crystals melting with decomposition at 252–253°.

Anal. Calcd. for $C_{13}H_{15}N \cdot HCl$: C, 70.42; H, 7.27; N, 6.32. Found: C, 70.51; H, 7.46; N, 6.56.

Nitrate.—Concentrated nitric acid and a well-cooled alcoholic solution of the base yields a crystalline nitrate which after recrystallization from alcohol melts at 184.5° with decomposition.

Anal. Calcd. for $C_{13}H_{15}N \cdot HNO_3$: C, 62.89; H, 6.49; N, 11.29. Found: C, 63.10; H, 6.40; N, 11.30.

Zinc Chloride Salt.—The base in alcohol is treated with a molar proportion of hydrochloric acid and one-half mole of zinc chloride. The precipitated salt crystallizes from 95% alcohol in hexagonal prisms with dome-shaped end faces melting at 266–267°.

Anal. Calcd. for $(C_{13}H_{15}N \cdot HCl)_2 \cdot ZnCl_2$: C, 53.86; H, 5.56. Found: C, 53.89; H, 5.38.

Phthalone.—Molar amounts of the base and phthalic anhydride are heated for four hours at 200°, the melt is dissolved in glacial acetic acid and the phthalone is precipitated by dilution of the solution with water. Microscopic plates melting at 264° are obtained on recrystallization from alcohol.

Anal. Calcd. for $C_{21}H_{17}O_2N$: C, 79.97; H, 5.43; N, 4.43. Found: C, 79.81; H, 5.43; N, 4.40.

Chromic Acid Oxidation of the Base.—This experiment was carried out under conditions similar to those described for the oxidation of 2,3-dimethyl-8-*n*-propylquinoline. Here 5 g. of base, 8.5 g. of potassium dichromate and 12 g. of concentrated sulfuric acid diluted with 15 cc. of water were used. Four hours were required for the reaction; yield 0.8 g. of acid. After recrystallization from alcohol, the acid melted at 233.5–234°.

Anal. Calcd. for $C_{13}H_{13}O_2N$: C, 72.04; H, 6.11. Found: C, 72.35; H, 6.10.

Decarboxylation of the $C_{13}H_{13}O_2N$ Acid.—An intimate mixture of acid and soda-lime in the proportion of 1:4 was heated well above 360°. The base, extracted from the fusion residue with ether, formed a picrate melting at 220°. Comparison of this picrate with an authentic sample of 2,3,4-trimethylquinoline revealed an identity.

Synthesis of 2,3,4,8-Tetramethylquinoline.[12]—Synthesis of this base was effected by the Combes method.[15] Methylacetylacetone (0.7 mole) was condensed with *o*-toluidine (0.6 mole) in the presence of hydrochloric acid at water-bath temperature for eight hours. The base, isolated in the usual way, had the following physical constants after recrystallization from petroleum ether: m. p. 77–78°, b. p. 298–300°. The picrate melted at 240° and the acid sulfate melted with decomposition at 298°. Melting points of mixtures of the synthetic and kero base, as well as mixtures of the respective picrates, showed no depression, thus affording conclusive proof of structure.

Isolation of a $C_{15}H_{18}N$ Transformer-Oil Base.—To 54 g. of a fraction of bases (b. p. 340°, n^{25}_D 1.6570)[16] in an equal volume of glacial acetic acid, was added a hot acetic acid solution of 55 g. of picric acid. The reaction mixture was kept at ice-box temperature for twelve hours. The smeary picrates which separated were crystallized from

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[13] Gilman and Catlin, "Organic Syntheses," John Wiley and Sons, New York, Coll. Vol. I, 1932, p. 458.

[14] Brady and Cunningham, *J. Chem. Soc.*, 121 (1934).

[15] Combes, *Bull. soc. chim.*, [2] **49**, 91 (1888).

[16] For an investigation of the next higher boiling fraction (n^{25}_D 1.6605) see Axe, Henson and Schuhardt, *Ind. Eng. Chem.*, **29**, 503 (1937).

glacial acetic acid: yield 40 g., m. p. 178–183°. Two recrystallizations left 15 g. of picrates (m. p. 201–203°). Next, the crude viscous bases (n^{25}D 1.6096) liberated from the picrates were dissolved in a 1:1 alcohol–ether solution and a slight excess of concentrated sulfuric acid was added. The resulting acid sulfates after three recrystallizations from alcohol melted at 265–267° with decomposition. A base melting at 82–82.5° was liberated from the acid sulfate which after two recrystallizations from petroleum ether melted at 83.5–84°; yield of pure base, 0.7 g. The pure picrate of the base melted at 228.5–229.5°. From another fraction boiling at 340° (n^{25}D 1.6504), an additional quantity of the base was recovered, bringing the total yield up to 1.9 g.

Anal. of base. Calcd. for $C_{15}H_{13}N$: C, 86.95; H, 6.23; N, 6.76. Found: C, 86.97; H, 6.30; N, 7.00.

Anal. of picrate. Calcd. for $C_{21}H_{16}O_7N_4$: C, 57.79; H, 3.67; N, 12.84. Found: C, 58.10; H, 3.83; N, 12.97.

Isolation of a $C_{16}H_{15}N$ Transformer-Oil Base.—The bases, recovered from the residues after separation of the $C_{15}H_{13}N$ compound, were combined and processed through degassing of their sulfurous acid solution into 8 fractions of bases. To each fraction in alcohol was added a slight excess of concentrated nitric acid. Precipitates in fractions 5, 6, 7 and 8 followed immediately and appeared in very small amount in the first four fractions after seeding and prolonged stirring. The combined nitrates were recrystallized from water containing a trace of nitric acid. The base liberated from the salt melted at 86–87°. The melting point, 228–229°, of the picrate prepared from the base remained unchanged after recrystallization from glacial acetic acid.

The very slight solubility of the nitrate in water at 100°, which is approximately 1 part in 100, offers a selective method for the isolation of this base. This claim is emphasized by the isolation of only 0.6 g. of this substance, or 0.59%, calculated from the quantity of the complex mixture of bases processed.

The slight difference in melting points of this base and the $C_{15}H_{13}N$ compound, as well as the slight difference in melting points of the corresponding picrates, suggested an identity of the two bases. However, the melting point of a mixture of the two picrates showed a depression of 30°. Furthermore, the $C_{15}H_{13}N$ base possesses a pronounced sweet odor, whereas the $C_{16}H_{15}N$ base is odorless.

Anal. of base.[17] Calcd. for $C_{16}H_{15}N$: C, 86.84; H, 6.83; N, 6.32. Found: C, 87.86; H, 6.88; N, 6.60.

Anal. of picrate. Calcd. for $C_{22}H_{18}N_4O_7$: C, 58.66; H, 4.02; N, 12.44. Found: C, 58.62; H, 4.04; N, 12.46.

Summary

Fractional degassing of base acid sulfites as described in the preceding paper by Roberts and Bailey has been employed in isolation, from the 300° range of kero bases, of two quinoline homologs, 2,3-dimethyl-8-*n*-propylquinoline and 2,3,4,-8-tetramethylquinoline. The structures of these products have been established through degradation and synthesis.

Two other bases of undetermined structure of the compositions $C_{13}H_{15}N$ and $C_{14}H_{17}N$ were separated from bases boiling in the neighborhood of 295°.

Two high-boiling bases, $C_{15}H_{13}N$ and $C_{16}H_{15}N$, which are probably of the acridine or naphthoquinoline types, have been isolated from transformer-oil base fractions through employment of selective salts and fractional degassing of base acid sulfites.

[17] The determination of carbon in the free base is obviously in error, but lack of material prevented a duplicate analysis.

AUSTIN, TEXAS RECEIVED JUNE 2, 1938

[CONTRIBUTION NO. 51 FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF UTAH]

A System Correlating Molecular Structure of Organic Compounds with their Boiling Points. I. Aliphatic Boiling Point Numbers

BY CORLISS R. KINNEY

Several systems have been devised for correlating different physical properties of organic compounds with their molecular structure and two are particularly valuable tools in organic chemistry—molecular refraction and the parachor. Unfortunately, however, these methods give no information about certain types of isomerism and the parachor often involves considerable experimental difficulties. Consequently it would be most desirable to have available another method which correlated molecular structure with an easily determined physical property which would be sensitive to types of isomerism not shown by other methods. The boiling temperature of a compound is probably more dependent upon molecular structure, and more easily determined usually, than any other physical property; and yet no attempt has been made to devise a system for correlating the molecular structure of all types of organic compounds with their boiling points. Large numbers of expressions have been devised for correlating the boiling points of members of