In connection with the experiments with hydrosulfite, we have made another observation which shows the reactivity of the chlorophyll compounds as compared with the porphyrins. When the phaeophorbides or chlorin *e* or rhodin *g* in ether solution are shaken with an aqueous solution of sodium acid sulfite, a rapid reaction takes place in which the intensity of the color is much diminished and the shade changes to a reddish-brown, some of the material passing into the aqueous layer. The porphyrins do not show this behavior. We propose to investigate this reaction further.

Summary

1. The action of sodium hydrosulfite in alkaline aqueous solution at 80° on chlorophyll derivatives and porphyrins has been examined. The magnesium-free chlorophyll derivatives are reduced with a change of color; the porphyrins and the magnesium-containing chlorophyll compound isochlorophyllin are not affected. Similar results were obtained with hydrogen and palladium on asbestos suspended in an aqueous alkaline solution at 23°. The amount of hydrogen absorbed was measured in a special micro apparatus. The magnesium-free chlorophyll compounds took up approximately two moles.

2. Catalytic hydrogenation of the porphyrins and the chlorophyll compounds proceeds to leuco compounds in glacial acetic acid. The number of moles of hydrogen absorbed is 3 to 4. On reoxidation with air the porphyrins are regenerated; the chlorophyll compounds yield a mixture of products including some porphyrins.

CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF TEXAS]

AN INVESTIGATION OF THE BASES IN THE KEROSENE DISTILLATE OF CALIFORNIA PETROLEUM[1]

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Introduction

Very little is known regarding the nature of the nitrogen compounds in crude petroleum, and these are at times confused with products in *dis-*

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[1] This paper contains results obtained at the Chemical Laboratory, University of Texas, in an investigation on "The Nitrogen Compounds in Petroleum," listed as Project 20 of American Petroleum Institute Research. Financial assistance in this work has been received from a research fund of the American Petroleum Institute donated by John D. Rockefeller. This fund is being administered by the Institute with the coöperation of the Central Petroleum Committee of the National Research Council.

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tillates that result from decomposition of more complex substances at distillation temperatures.[6] Whereas certain California crude petroleum, that uniformly has a high nitrogen content, yields practically no bases on acid extraction, crude distillates from this source contain bases readily extracted with mineral acids. However, along with bases there are present nitrogen compounds *inert to dilute mineral acids*, for the isolation of which methods have not been developed. In the kerosene distillate produced by the Union Oil Company of California from McKittrick asphalt crude petroleum, with a total nitrogen content of 0.055%, it was found that approximately 55% of the nitrogen compounds could be extracted with dilute sulfuric acid, and in the higher-boiling distillates, with the total nitrogen content greater, the proportion of basic to inert nitrogen compounds decreased with increase of the distillation temperature. The non-basic nitrogen compounds may be of the pyrrole type with the higher members indoles or carbazoles, or there is a further possibility of the occurrence here of heterocyclic compounds containing both nitrogen and sulfur.

The great complexity of the nitrogen compounds in petroleum and its crude distillates, the wide boiling point range of these distillates, all of which contain both basic and non-basic volatile nitrogen compounds, and finally the fact, developed in the present investigation, that exhaustive fractional distillation of California kerosene bases, which have a range of boiling points at atmospheric pressure from 180 to 335°, does not yield any of the components in pure form, make it quite probable that *petroleum offers the greatest wealth of nitrogen compounds of any natural source.*

That a number of substances constitute each of the numerous distillation fractions of kerosene bases is also revealed by the fact that so far in this investigation it has been found that, except as concerns distillation fractions in the 276° zone, picrates do not separate directly in crystalline form. Through the employment of (1) fractional extraction with a buffered acid solution and (2) fractional precipitation of the bases from the resulting acid solution with sodium hydroxide, it is possible, however, to concentrate individual components of the distillation fractions to the point where they form crystalline salts. In this way from 1560 cc. of distillation fractions, boiling at 249–252°, several products have been isolated in apparently pure form[7] and will be investigated later. However, the small, initial yields of these substances indicate quite conclusively that only repeated application of methods (1) and (2) will effect a separation of all the component bases.

It might be contended that failure of fractional distillation to yield

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[6] (a) Day, "Handbook of the Petroleum Industry," p. 529; (b) E. J. Poth, W. D. Armstrong, C. C. Cogburn and J. R. Bailey, *Ind. Eng. Chem.*, **20**, 83 (1928).

[7] This phase of the investigation has been developed by E. J. Poth and Ivy Parker.

individual products in pure form is due to the formation of *constant boiling mixtures* with the components differing within wide ranges of boiling points. The present investigation, so far as it has progressed, indicates, however, that fractional distillation yields mixtures of products, which even at atmospheric pressure boil within a range of a few degrees. Since the distillations, to prevent decomposition of the bases, are preferably carried out at low pressures, it is not at all improbable that with the reflux column it is possible to separate the bases in fractions with the components boiling at highly reduced pressure within a range of less than two degrees. In confirmation of this tentative claim it may be cited that in a fraction of bases under investigation there have been isolated in pure form two compounds of the formula, $C_{12}H_{13}N$, boiling at atmospheric pressure (746 mm.) at 280.6 and 278.9°, respectively, and a substance of the formula, $C_{16}H_{25}N$, boiling at 278.2°. What is equally conclusive of the claim advanced is that the residual bases in this fraction, after removal of the three products referred to, boil to the last drop at constant temperature, making impossible the use of fractional distillation in their separation. Furthermore, in the distillation of these residual bases, where several cuts are made, each shows the same refractive index. Undoubtedly several products here remain to be isolated in pure form, and it may be expected that all of them have boiling points in close proximity.

The only investigation of bases from California distillates thus far published was carried out by Mabery and Wesson,[8] and, regarding the source of their material, there occurs the following statement: "They were separated from California distillates by Peckham and Solathé by washing a large quantity of the *distillates* with dilute sulfuric acid and precipitating the bases with alkali."[9] Since no individual base was isolated by Mabery and Wesson, it is not surprising that some of their conclusions as to the structure of these products are disproved by the present investigation in the Texas Laboratory.

More recently from shale oil distillates there have been isolated and identified several alkylated pyridines.[10]

The first year on Project 20 was devoted to an exhaustive survey of the nitrogen content of petroleum from the most important oil fields of this continent and preliminary work in the location of the most available source of petroleum nitrogen compounds in quantity. The results of this phase of the work are embodied in part in a paper, entitled "The Estimation of Nitrogen in Petroleum and Bitumens."[11]

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[8] C. F. Mabery and L. G. Wesson, This Journal, **42**, 1014 (1920).

[9] C. F. Mabery, *J. Soc. Chem. Ind.*, **19**, 505 (1900).

[10] Takashi Eguchi, *Bull. Chem. Soc.* (*Japan*), **2**, 176 (1927); **3**, 227 (1928); *C. A.*, **21**, 3197 (1927); **23**, 391 (1929).

[11] Ref. 6 a, p. 83.

In this investigation it developed, because of the amount of material to be handled, that only through the coöperation of some refinery, working petroleum of high nitrogen content, would it be practicable to assemble material sufficient in amount for an exhaustive investigation of petroleum nitrogen. Furthermore, it was equally evident that the desired coöperation would be extended only on condition that it would involve a minimum of inconvenience in plant operation.

In refining crude distillates either with sulfuric acid or liquid sulfur dioxide, practically all the contained nitrogen is eliminated from the finished products. However, in sulfuric acid refining, even if the nitrogen compounds are not sulfonated, polymerized or changed in other ways, the cost involved in their isolation from the acid extract would be very heavy. On the other hand, in the Edeleanu process the liquid sulfur dioxide apparently exerts merely solvent action, and, after recovery of the sulfur dioxide, the residue contains the nitrogen compounds admixed with a large quantity of hydrocarbon oil. From this residue the bases can be extracted with dilute sulfuric acid and the water-insoluble bases separated from the acid layer with caustic soda. It is probable that extraction with a suitable solvent would yield here at times water-soluble bases.

An arrangement was effected with the Union Oil Company of California whereby 150 barrels of the residue from refining their kerosene distillate with liquid sulfur dioxide were extracted with dilute sulfuric acid, and from this material 50 liters of water-insoluble bases, free of hydrocarbon oil and containing only a trace of sulfur, were obtained.[12]

The following information regarding the potential supply of petroleum nitrogen compounds was furnished by Mr. Haylett: Edeleanu residues represent about 30% by volume of the stock treated. Four companies in California equipped to use the process have a combined daily capacity of about 10,000 barrels of oil. While lubricating, transformer and spray oils are refined by this method, around 80% of the capacity is devoted to kerosene and similar distillates.

The Edeleanu residues do not represent waste products; they are valuable for the production of aromatic oils, employed as special solvents and, on account of their detonation suppressing qualities, are included, as far as boiling points permit, in motor fuels. One company uses Edeleanu residues in the manufacture of insecticides.

The present paper deals with a new base of the formula, $C_{12}H_{13}N$ (A),

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[12] Acknowledgment is due Mr. R. E. Haylett, Technical Assistant, Dr. Carl Iddings, Plant Chemist, and Mr. T. F. Ott, Lubricating Technologist of the Union Oil Company, and also Research Fellow W. M. Slagle, for services rendered in preparing what is probably the largest amount of so-called petroleum bases ever assembled for investigation.

with its structure established as 2,3,8-trimethylquinoline. It occurs to the extent of about 18% in the fraction of kerosene bases boiling at atmospheric pressure around 276–277°. Only negligible amounts are present outside the range 274–280°. From the same fractions there have been isolated in pure form a second $C_{12}H_{13}N$ (B) base and a third base of the formula, $C_{16}H_{25}N$ (C). In addition, there occur in the same temperature zone several other bases for the isolation of which methods are now being successfully developed. Since only the investigation of 2,3,8-trimethylquinoline has been concluded, the other products will be reported on later.

With Base A assumed to be an alkylated quinoline, the structure was correctly deduced from its behavior toward (1) methyl iodide and (2) formaldehyde. Since it does not react at water-bath temperature with methyl iodide to form a quaternary ammonium salt, steric hindrance, due to substituents at positions 2 and 8, was inferred.[13]

With the known 2,4,8-trimethylquinoline[14] excluded, methyls at 2 and 3 were indicated by condensation of the base with *two* and not *three* moles of formaldehyde.[15]

Methyls in positions 2 and 3 were confirmed by the formation of a dimethylquinolinic acid in chromic acid oxidation of the $C_{12}H_{13}N$ base, in that this carboxylic acid on distillation with soda lime gave a product of the formula, $C_{11}H_{11}N$, identified as 2,3-dimethylquinoline.[16] Oxidation of the *formaldehyde* compound of the $C_{12}H_{13}N$ base also gave a dimethylquinolinic acid, converted by soda lime distillation to a new base, $C_{11}H_{11}N$, the structure of which as 3,8-dimethylquinoline was proved by its synthesis from *o*-toluidine, methylal and propionic aldehyde.[17]

Finally, through the Doebner–Miller synthesis,[18] 2,3,8-trimethylquinoline was prepared by the action of hydrochloric acid on a mixture of *o*-toluidine and tiglic aldehyde, and its identity with the kerosene base confirmed.

Since among the kerosene bases there are undoubtedly many components which are hydrides of alkylated quinolines or other heterocyclic complexes with the possibility of asymmetric carbon atoms present, it is of interest to note that an examination of all the different distillation fractions failed to reveal in any case optical activity. This applies also to the $C_{16}H_{25}N$ base, obtained in large amount from fractions in the 276° zone; this prod-

[13] *Cf.* J. v. Braun, W. Gmelin and A. Petzold, *Ber.*, **57**, 389 (1924).

[14] S. Yamaguchi, *J. Pharm. Soc.* (*Japan*), **503**, 23–33 (1924); *C. A.*, **18**, 1666 (1924).

[15] For literature references see Meyer and Jacobson's "Lehrbuch der Organischen Chemie," Vol. II, Part 3, p. 933.

[16] G. Rohde, *Ber.*, **20**, 1911 (1887).

[17] Acknowledgment is due G. R. Lake of the Texas Laboratory for this synthesis. *Cf.* Carl Beyer, *J. prakt. Chem.*, **33**, 419 (1886); W. v. Miller and Fr. Kinkelin, *Ber.*, **20**, 1916 (1887).

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

uct is undoubtedly hydro-aromatic with the possibility of one or more asymmetric carbon atoms in the molecule.

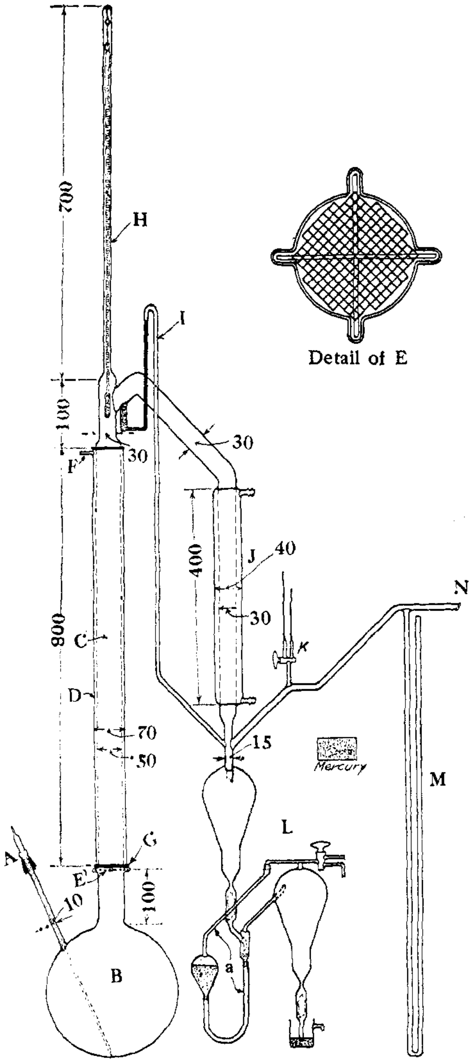

Fig. 1.—Vacuum distillation apparatus (pyrex glass, dimensions in millimeters). A, Ground-glass seal; B, 5-liter flask; C, still column (chain filling); D, column jacket; E, support for chain in column; F, air inlet to jacket; G, transite support for jacket; H, thermometer tube; I, capillary manometer; J, condenser; K, capillary leaks; L, receiver; M, manometer; N, lead to vacuum pump; 'a,' rubber tubing.

Experimental Part

Fractional Distillation of the Kerosene Bases.—The apparatus employed in fractional distillation of the 50 liters of crude bases can be understood by reference to the accompanying figure.[19]

Through the use of mercury check-valves in the vacuum distillation receiver, stopcocks are entirely eliminated in the distillation train and contamination of the distillate with tap grease is obviated. The use of capillary leaks for pressure control proved more satisfactory than the expensive electrical devices usually employed in this connection.

In the largest type of apparatus used, B is a 5-liter flask sealed to C, a jacketed reflux column, which is packed with No. 18, double jack iron chain.[20] Provision is made for heating the reflux column by resistance wire circularly wound around the jacket, D. The support, E, at the

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[19] This apparatus was patterned after one in use at the Bureau of Standards by E. W. Washburn and J. H. Brunn in connection with Project No. 6. Acknowledgment is hereby given for a blue print of their apparatus. Acknowledgment is also due Research Fellow E. J. Poth for construction and. operation of the stills in use as well as for innovations in the Washburn–Brunn apparatus, consisting of the manometer, I, capillary leaks, K, and receiver, L ["A Receiver for Vacuum Distillation," by Edgar Poth, *Ind. Eng. Chem.* (*Analytical Ed.*), 1, 111 (1929)], shown in accompanying figure.

[20] This chain is manufactured by the Corbin Screw Corporation, New Britain, Conn.

lower end of C contains four protrusions, into which lead heavy iron wires supporting a wire gauze on which rests the coiled chain. The ground-glass seal, A, serves for charging or cleaning B and is extended in the form of a bubble tube of the ordinary type used in vacuum distillation to obviate bumping. Three-way stopcock K affords an air intake through capillaries which were regulated so as to provide in the system pressures of either 4 or 11 mm. The lower pressure was used with high-boiling residues to obviate as far as possible decomposition of the bases.

The rate of distillation was kept as near one drop a second as possible, this being regulated, where necessary, either by forcing cold air into F or heating D through the resistance coil. All the material at hand was carried through six fractionations and, in the temperature zones where the largest amount of material was available, eight fractionations were made. After it became evident that fractional distillation alone would not lead to a separation of any of the bases in pure form, this procedure was supplemented by isolation of the bases through appropriate salts.

Isolation and Synthesis of 2,3,8-Trimethylquinoline[21]

A very satisfactory method is to isolate this $C_{12}H_{13}N$ base in the form of the picrate, admixed with the picrate of base $C_{16}H_{25}N$, by the addition of successive portions of 20 g. of picric acid in 50 cc. of 50% acetic acid to 100 cc. of a distillation fraction in 350 cc. of 50% acetic acid. The picrate of the latter base, in contrast to that of the former, is readily soluble in both benzene and alcohol, and, therefore, a mixture of these salts is easily separated.

A second method of isolation of 2,3,8-trimethylquinoline is offered through its acid sulfate. Preliminary tests indicate the amount of 50% sulfuric acid to be used as well as the concentration of this base in different fractions. Through the sulfate test fractions boiling from 274 to 280° (748 mm.), inclusive, were found to contain 2,3,8-trimethyl quinoline with the maximum amount of around 20% in the 276–277° fraction. Since the sulfate of base $C_{16}H_{25}N$ is very soluble, it is not precipitated but can be subsequently separated as picrate. However, admixed with this sulfate there occurs in small amount the sulfate of a second $C_{12}H_{13}N$ base, as yet unidentified. This latter base is an odorless solid, melting at 43° and boiling at 278.9° (748 mm.). It reacts with formaldehyde and with methyl iodide forms the corresponding quaternary ammonium salt at water-bath temperature.

In an attempt to isolate the residual bases from the distillation fractions, in which the three components referred to above occur, experiments are under way in which fractional extraction with buffered solutions is employed. That this procedure will prove effective is indicated by the recovery of considerable amounts of the $C_{16}H_{25}N$ base that escaped isolation in the original picrate precipitation. The control conveniently employed in this process is the determination of refractive indices.

The following refractive indices, n_D^{60}, are of interest: (A) 2,3,8-trimethylquinoline, 1.5828; (B) $C_{12}H_{13}N$ base of unknown structure, 1.5828; (C) $C_{16}H_{25}N$ base, 1.4958; (D) composite refractive index of bases in the 276° zone, 1.5119; (E) composite refractive index of residual bases after withdrawal of A, B and C, 1.5008. The low refractive index of B is in line with the fact that this product is undoubtedly hydroaromatic, and the composite refractive index of the residual bases, lying only slightly above that of C, indicates these in the main to be hydroaromatic.

Preparation of 2,3,8-Trimethylquinoline from its Picrate and Sulfate.—When either the picrate or sulfate is heated with ammonium hydroxide, the base separates as an oil which later solidifies. This is taken up with ether, the ethereal layer washed with water and the ether allowed to evaporate. Recrystallized from 50% alcohol, the

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[21] By W. A. King and J. R. Bailey.

new product separates in lustrous, rectangular plates without end faces, melts sharply at 55–56° and boils with partial decomposition at 280° (747 mm.). Characteristic of this substance is its faint fecal odor. It is readily soluble in the common organic solvents, very difficultly soluble in water even at boiling temperature and volatile with steam.

Anal. Calcd. for $C_{12}H_{13}N$: C, 84.21; H, 7.60; N, 8.19. Found: C, 84.25; 7.59; N, 8.11.

Synthesis of 2,3,8-Trimethylquinoline.—Through the use of *o*-toluidine and tiglic aldehyde in the process employed by G. Rohde for the synthesis of 2,3-dimethylquinoline,[16] 2,3,8-trimethylquinoline was obtained in a yield of about 10%. The synthetic product, as well as numerous derivatives, was compared with the $C_{12}H_{13}N$ kerosene base and corresponding derivatives, with the result that identity of the products was confirmed in each case.

Anal. Calcd. for $C_{12}H_{13}N$: N, 8.19. Found: N, 8.07.

Sulfate, $C_{12}H_{13}N \cdot H_2SO_4$.—After the base, dissolved in a little more than the calculated amount of 50% sulfuric acid, separates as sulfate, the salt is filtered, washed with alcohol and recrystallized from 95% alcohol in prisms with dome-shaped end faces. The sulfate can also be prepared directly from fractions containing appreciable amounts of 2,3,8-trimethylquinoline. It decomposes around 275°.

Anal. Calcd. for $C_{12}H_{16}O_4NS$: C, 53.53; H, 5.58; N, 5.20; S, 11.89. Found: C, 53.13; H, 5.87; N, 5.52; S, 11.90.

Hydrochloride, $C_{12}H_{13}N \cdot HCl$.—This salt is prepared by dissolving the base in 18% hydrochloric acid, from which it separates on cooling. Recrystallized from either water or alcohol, it is obtained in long, slender needles, which on heating blacken around 230° and at 260° completely decomposes without leaving a residue.

Anal. Calcd. for $C_{12}H_{14}HCl$: N, 6.75; Cl, 17.11. Found: N, 6.53; Cl, 17.03.

Nitrate, $C_{12}H_{13}N \cdot HNO_3$.—The base is dissolved in a slight excess of concentrated nitric acid diluted to twice the original volume, then alcohol added, and the salt precipitated with ether. On recrystallization from 95% alcohol, the nitrate separates in radiating clusters of fine needles, melting at 160.5° with gas evolution.

Anal. Calcd. for $C_{12}H_{14}O_3N_2$: N, 11.96. Found: N, 12.24.

Picrate, $C_{12}H_{13}N \cdot C_6H_3O_7N_3$.—Because of its difficult solubility in all the common solvents, this salt, like the sulfate, can be employed in estimating the amount of 2,3,8-trimethylquinoline in different fractions of the kerosene bases. Dissolved in hot glacial acetic acid, it separates on cooling in arborescent, canary-yellow crystals, which blacken and decompose with gas evolution at 242–245°. On heating in ammonium hydroxide solution, the base is liberated.

Anal. Calcd. for $C_{18}H_{16}O_7N_4$: C, 54.00; H, 4.00; N, 14.00. Found: C, 54.20; H, 4.24; N, 13.96.

The following characteristic salts of 2,3,8-trimethylquinoline, which were prepared but not analyzed, can be obtained from a hydrochloric acid solution of the base: gold chloride gives a salt of a yellow color, resembling the picrate and recrystallizing from water in long, slender rods; platinum chloride forms a granular, light orange-colored salt, difficultly soluble in water and alcohol; potassium dichromate gives an orange-yellow salt, best recrystallized from water in a fine, granular condition; potassium ferrocyanide precipitates the difficultly soluble hydroferrocyanide, of a light cream color, which in boiling water decomposes with evolution of prussic acid; zinc chloride gives a salt, recrystallizing from alcohol in long, slender prisms; the mercuric chloride salt is readily soluble in hot water and hot alcohol and separates from either solvent in long, slender rods; the stannous chloride salt has solubilities similar to the mercuric chloride salt and is best recrystallized from glacial acetic acid in the form of rods.

Action of Benzaldehyde on 2,3,8-Trimethylquinoline.—The base (1 g.), benzaldehyde (1.5 g.) and zinc chloride (0.08 g.) are heated in a sealed tube at 130° for four hours, at the end of which time the contents of the tube solidify on cooling. This material is treated with ether and dilute sulfuric acid, producing separation of a deep yellow product which, when purified by recrystallization from alcohol, is obtained in sheaves of slender prisms. This substance is difficultly soluble in the common solvents other than alcohol and, on heating, begins to sinter around 198°, decomposing completely at 205°. The analysis indicates a dibenzal compound of trimethylquinoline, differing markedly in physical properties from the corresponding dibenzal-2,4,6-trimethylquinoline.[22]

Anal. Calcd. for $C_{26}H_{21}N$: N, 4.03. Found: N, 4.30.

3,8-Dimethyl-2-styrylquinoline.—The dibenzal compound described above, on dissolving in hot glacial acetic acid and precipitating with water, is changed to a light cream-colored substance, crystallizing from alcohol in sheaves of short, fine needles melting undecomposed at 120°. This product, unlike the dibenzal compound, is readily soluble in cold ether and benzene and resembles in its properties the monobenzal compound of 2,4,6-trimethylquinoline.

Anal. Calcd. for $C_{19}H_{17}N$: N, 5.41. Found: N, 5.36.

3,8-Dimethyl-2-dimethylolmethylquinoline.—In conformity with the procedure of Koenigs and Stockhausen,[23] 1 g. of the trimethylquinoline is heated with 5 cc. of 40% formaldehyde in a sealed tube for seven hours, whereby complete solution of the original base is effected. Upon dilution of the mixture to twice its volume, the reaction product separates as an oil, which is ethered out. The ether solution is then transferred to an evaporating dish, and after removal of the ether the residue is made to crystallize by protracted digestion with water on a boiling water-bath.

Another satisfactory method of isolation of the formaldehyde compound is precipitation as picrate by the addition of one mole of picric acid in hot alcohol to its ethereal solution. The picrate is decomposed with ammonium hydroxide and the base extracted with ether. For purification the product is recrystallized from ether or acetic ether in long, slender prisms with well-defined end faces. It is readily soluble in alcohol, difficultly soluble in water, melts at 111.5° and boils at 170–172° (3 mm.).

Anal. Calcd. for $C_{14}H_{17}O_2N$: C, 72.73; H, 7.36; N, 6.06. Found: C, 72.79; H, 7.45; N, 6.13.

Picrate of 3,8-Dimethyl-2-dimethylolmethylquinoline.—This characteristic salt is readily soluble in alcohol and more difficultly soluble in acetic ether and water, crystallizing from all these solvents in rods of a light orange color. It melts at 180°, apparently undecomposed.

Anal. Calcd. for $C_{20}H_{20}O_9N_4$: C, 52.17; H, 4.35; N, 12.17. Found: C, 52.17; H, 4.39; N, 12.20.

3,8-Dimethylquinoline-2-carboxylic Acid.—To 10 g. of the formaldehyde compound in 200 cc. of acetone and 10 cc. of glacial acetic acid is added in small portions with cooling 41.3 g. of finely ground potassium permanganate. The sludge containing the potassium salt of the oxidation product is filtered off, the cake extracted with hot water and the dimethylquinolinic acid precipitated with hydrochloric acid. For purification it is dissolved in ammonium hydroxide, decolorized with filt-char, and precipitated with hydrochloric acid. Finally the product is dissolved in boiling glacial

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[22] Fischer, Müller and Merkel, *J. prakt. Chem.*, **100**, 100 (1919).

[23] Wilhelm Koenigs and Ferdinand Stockhausen, *Ber.*, **34**, 4331 (1901).

acetic acid, water added to turbidity and the solution treated with filt-char. From alcohol the acid separates in long, slender prisms and from water in fine needles, melting with decomposition at 157.5°. Boiled in water with calcium carbonate, it forms a readily soluble salt which gives gelatinous precipitates with soluble salts of silver, copper and lead. Permanganate oxidation gives a 50% yield of the dimethylquinolinic acid. After several failures to employ nitric acid successfully in oxidation of the formaldehyde compound, the following conditions were found to give a 95% yield of crude dimethylquinolinic acid: one g. of the formaldehyde compound is warmed with a mixture of 25 cc. of concentrated nitric acid and 25 cc. of water until the copious evolution of nitrous fumes ceases, and then the mixture is heated to boiling for four hours. The nitric acid is neutralized with sodium hydroxide to the point where a precipitate begins to form, when, on addition of several grams of sodium acetate, the dimethylquinolinic acid separates. A small amount remaining in solution can be extracted with chloroform.

Anal. Calcd. for $C_{12}H_{11}O_2N$: N, 6.97. Found: N, 7.01.

3,8-Dimethyl-2-hydroxyethylquinoline.—In the oxidation of the formaldehyde compound in acetone without the presence of acetic acid only a 17% yield of the dimethylquinolinic acid was obtained. Considerable amounts of the by-products of the oxidation remained in the acetone. On distillation the acetone residue yielded at first an oil and then a solid base. Of these two products only the latter was investigated. It was purified by crystallization from petroleum ether, followed by a second distillation. The product is readily soluble in the common organic solvents, crystallizes from petroleum ether in an arborescent, granular form and melts at 99°. This product is of interest, because it indicates that in one stage of the oxidation one mole of formaldehyde is eliminated and the $—CH(CH_2OH)_2$ complex converted to $—CH_2CH_2OH$. It gives a beautifully crystallizing picrate which separates from alcohol in long, slender prisms, melting with decomposition at 162°.

Anal. Calcd. for $C_{13}H_{15}ON$: N, 6.97. Found: N, 6.91.

Anal. of picrate. Calcd. for $C_{19}H_{18}O_8N_4$: N, 13.02. Found: N, 13.26.

3,8-Dimethylquinoline from 3,8-Dimethylquinoline-2-carboxylic Acid.—The dimethylquinolinic acid on distillation with four times its weight of soda lime is converted to a new base of the formula $C_{11}H_{11}N$, the structure of which was established as 3,8-dimethylquinoline by synthesis. It has a faint quinoline odor and possesses the following physical constants: b. p. (751 mm.) 269°; d_{20}^{20} 1.051; n_D^{20} 1.6063.

Anal. Calcd. for $C_{11}H_{11}N$: N, 8.92. Found: N, 9.16.

Synthesis of 3,8-Dimethylquinoline.—A moderate stream of dry hydrogen chloride gas is led into a mixture of propionic aldehyde (30 g.) and methylal (39.3 g.) for five minutes. On addition of this mixture to *o*-toluidine (42 g.) and concentrated hydrochloric acid (72 g.), the reaction begins and is completed by gently boiling the solution for three hours. The reaction mixture is then added to an equal volume of water and, after filtration, treated with a slight excess of sodium nitrite. The filtered solution is finally concentrated to a small volume, the bases liberated with sodium hydroxide and, after extraction with ether, the mixture fractionated in a vacuum. Further purification of the dimethylquinoline, obtained in a yield of about 7%, is effected through the picrate. On crystallization by-product picrates first separate and are discarded. For comparison the following salts were made of both the synthetic base and the base prepared from 2,3,8-trimethylquinoline in the series of reactions described above. The sample of synthesized base analyzed had a refractive index, n_D^{20} 1.6069.

Anal. Calcd. for $C_{11}H_{11}N$: N, 8.92. Found: N, 8.98.

Picrate.—This salt is readily soluble in glacial acetic acid and difficultly soluble in alcohol and water. It crystallizes from acetic acid in thin prismatic plates and from water in needles which under the microscope appear as long slender prisms. It melts at 207° with decomposition.

Anal. Calcd. for $C_{17}H_{14}O_7N_4$: N, 14.51. Found: N, 14.73.

Picrolonate.—This salt crystallizes from alcohol in a form similar to the picrate and melts with decomposition at 199°.

Anal. Calcd. for $C_{21}H_{19}O_5N_5$: N, 16.63. Found: N, 16.79.

1,2,3-Trimethylquinolinium Iodide.—Methyl iodide reacts with 3,8-dimethylquinoline in a sealed tube at water-bath temperature, giving a product that crystallizes from alcohol in long, thin, slender prisms melting at 197°.

Anal. Calcd. for $C_{12}H_{14}NI$: N, 4.68. Found: N, 4.71.

Oxalate.—The base with oxalic acid in absolute alcohol separates the oxalate in long slender prisms melting at 128°.

Anal. Calcd. for $C_{13}H_{13}O_4N$: N, 5.66. Found: N, 5.43.

2,3-Dimethylquinoline-8-carboxylic Acid.—2,3,8-Trimethylquinoline (11.5 g.) is boiled for thirty hours with 23 g. of chromic anhydride in 100 cc. of 1:5 sulfuric acid. The dimethylquinolinic acid in a yield of about 16% can be extracted with chloroform, after the oxidation mixture is neutralized with ammonium hydroxide to the point where chromic hydroxide begins to precipitate. With this oxidation product removed, a considerable amount of unchanged trimethylquinoline can be regained by addition of ammonium hydroxide in excess. The dimethylquinolinic acid is purified by recrystallization from alcohol and finally from water with the addition of filt-char. It separates from benzene, acetic ether, alcohol and water in long needles, melting apparently undecomposed at 202°.

Anal. Calcd. for $C_{12}H_{11}O_2N$: N, 6.97. Found: N, 7.05.

2,3-Dimethylquinoline.—Soda lime distillation converts the acid just described to a base of the formula $C_{11}H_{11}N$, from which, after distillation, a small amount of liquid impurity can be absorbed on porous plate. Only a few of the known dimethylquinolines are solids at room temperature, and of these the 2,3-dimethyl isomer has the highest melting point, 67.5–69°. The identity of our product with 2,3-dimethylquinoline, synthesized from *o*-aminobenzaldehyde and methyl ethyl ketone, was established in the usual way, and further confirmed by a comparison of the picrate made from the two samples of base.[24]

Anal. of base. Calcd. for $C_{11}H_{11}N$: N, 8.92. Found: N, 8.99.
Anal. of picrate. Calcd. for $C_{17}H_{14}O_7N_4$: N, 14.51. Found: N, 14.62.

Summary

1. The preparation of 50 liters of bases from 150 barrels of residues obtained in refining California crude kerosene distillate is described.

2. A figure of the distillation apparatus employed in rectifying the bases is given.

3. The separation of the bases into approximately fifty fractions, with a boiling-point range of 180 to 335°, by repeated fractional distillation at reduced pressures is outlined.

4. The different methods being employed in isolation of the component bases in the distillation fractions in the 276° zone (atmospheric pressure) are discussed.

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[24] J. Eliasberg and P. Friedländer, *Ber.*, **25**, 1754 (1892).

5. The structure of a base occurring in California kerosene stock as 2,3,8-trimethylquinoline is established, and its synthesis effected.

6. The preparation of 3,8-dimethyl- from 2,3,8-trimethylquinoline through a series of reactions, with the structure of the 3,8-dimethylquinoline confirmed by synthesis, is described.

7. This investigation reveals in Edeleanu residues from refining California crude petroleum distillate a vast wealth of nitrogen bases, probably in the main hydro-aromatic and in *greater amount* volatile, non-basic nitrogen compounds. For the separation of the latter methods remain to be developed. Although there is a practically inexhaustible potential supply of material for research in this field, anything like an intensive investigation of petroleum nitrogen will involve a great amount of labor and expense.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

THE PREPARATION OF SEMICARBAZIDE

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Semicarbazide in the form of its compounds has been used extensively in various organic reactions, but no simple method for the preparation of the free base has, as yet, been reported in the literature. The action of liquid ammonia upon certain hydrazine[1] and hydroxylamine[2] salts, in particular the sulfates, has afforded a convenient and expeditious means for the preparation of these bases, suggesting that this reaction might also be applied to semicarbazide. It was found that semicarbazide sulfate would react with liquid ammonia to give the free base in excellent yields. This method is both rapid and convenient and one which is highly desirable in view of the fact that semicarbazide undergoes decomposition rapidly and must, therefore, be prepared fresh. The reaction proceeds in accordance with the equation

$$NH_2CON_2H_3 \cdot H_2SO_4 + 2NH_3 = NH_2CON_2H_3 + (NH_4)_2SO_4$$

The ammonium sulfate settles out as an insoluble precipitate from which the liquid ammonia solution of semicarbazide may readily be decanted. The ammonia may be removed by evaporation and the semicarbazide purified by recrystallization from absolute ethanol.

An alternative method employed by the author for preparing the free base involves the action of barium hydroxide upon the sulfate. An excess of barium hydroxide must be avoided since alkalies induce hydrolysis of semicarbazide. After removal of the precipitated barium sulfate, the

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[1] Browne and Welsh, THIS JOURNAL, 33, 1728 (1911).

[2] Browne and Audrieth, unpublished investigations.