

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

THE NITROGEN COMPOUNDS IN PETROLEUM DISTILLATES.  
III. THE STRUCTURE OF A HYDROAROMATIC BASE OF  
THE FORMULA  $C_{16}H_{25}N^1$

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### Introduction

Recently there was published from the Texas Laboratory a paper entitled "An Investigation of the Bases in the Kerosene Distillate of California Petroleum."<sup>4</sup>

This work has been continued in an attempt to establish the structural formula of a *hydroaromatic* base of the formula,  $C_{16}H_{25}N$ , and the reader is referred to the paper cited for detailed information on the procedure followed in its isolation.<sup>5</sup> It is obvious that the structural problems involved here are comparable to those in alkaloidal chemistry; as a matter of fact, were it of plant occurrence, the  $C_{16}H_{25}N$  compound would undoubtedly be termed an alkaloid. Since hydroaromatic bases, in contrast to those of aromatic types, predominate in petroleum distillates,<sup>6</sup> it might seem appropriate to give the hydroaromatic types the class name, "*Petroleum Alkaloids*."<sup>7</sup> While it is true that the so-called petroleum bases,

<sup>1</sup> 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 cooperation of the Central Petroleum Committee of the National Research Council.

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<sup>4</sup> Poth, Schulze, King, Thompson, Slagle, Floyd and Bailey, *THIS JOURNAL*, **52**, 1239 (1930).

<sup>5</sup> Our supply of crude kerosene bases was extracted from 150 barrels of the residue obtained at the Oleum Plant of the Union Oil Company of California in refining their crude kerosene stock with liquid sulfur dioxide. In the paper cited, p. 1242, this material is referred to as "probably the largest amount of so-called petroleum bases ever assembled for investigation."

Mr. H. K. Ihrig of Pittsburgh, Penna., recently informed one of the authors that during 1926-1927, in an investigation financed by the Associated Oil Company, he isolated 1100 gallons of base from 10,000 barrels of Edeleanu extract. U. S. patents, 1,671,721 (5/29/28), and 1,686,136 (10/2/28), assigned "one-half to S. E. Campbell of Associated, California, and one-half to Associated Oil Company, of San Francisco," were an outgrowth of this work.

<sup>6</sup> On the suspected presence of hydroaromatic bases in coal-tar distillates, cf. J. von Braun, *Ann.*, 478, 182 (1930); Decker and Dunant, *Ber.*, **42**, 1178 (1903).

<sup>7</sup> Prof. Austin M. Patterson, to whom the authors are indebted for valuable suggestions in connection with problems of nomenclature presented in this paper, writes:

unlike the most important plant alkaloids, are oxygen-free, there are also oxygen-free plant alkaloids, such as coniine and nicotine. Furthermore, it may be expected that further study of the bases in petroleum distillates will reveal hydroaromatic types containing the *pyrrole* nucleus and a closer analogy be thus established. Whether any of the basic substances formed in the distillation of petroleum will ever attain a pharmacological importance at all comparable to that of plant alkaloids presents a question that cannot be answered at this time.<sup>8</sup>

Developments in connection with A. P. I. Project 20, as well as investigations elsewhere, indicate conclusively that hydroaromatic bases in great numbers and of various types, along with aromatic bases,<sup>9</sup> exist in all unrefined, California, petroleum distillates. The procedure being employed in the Texas Laboratory for the isolation of so-called petroleum bases, and for the perfection of which Research Fellow, E. J. Poth, deserves a large share of credit, involves the successive employment of: (1) dilute sulfuric acid extraction; (2) exhaustive fractional distillation; (3) resolution with buffered acid solutions; and (4) recrystallization of appropriate salts. In this way both types of bases, in contrast to the non-reactive, associated hydrocarbons, can be isolated free of admixtures.

The  $C_{16}H_{25}N$  base shows an unusual stability toward permanganate in both neutral and alkaline solution but is quite readily attacked in acid solution. However, it is very resistant to oxidation with chromic acid in sulfuric acid solution. Heated with fuming sulfuric acid, it is oxidized with a violent evolution of sulfur dioxide just above  $200^{\circ}$ , but the reactions involved have not been studied. After numerous preliminary experiments

"These hydroaromatic bases are like plant alkaloids in structure and the term, alkaloid, has been used for organic bases of non-vegetable origin; still, the tendency in recent times has been to restrict it to plant bases." On prior use of phrase "petroleum alkaloids," cf. A. Weller, *Ber.*, 20, 2098 (1887); F. X. Bandrowski, *Monatsh.*, 8, 224 (1887).

<sup>8</sup> A report on physiological tests, carried out on dogs and guinea pigs with the hydrochloride of the  $C_{16}H_{25}N$  base, by Dr. E. J. Poth of Johns Hopkins University is submitted: "It is of low toxicity. Upon intravenous administration to anesthetized animals, the blood pressure and heart-rate are not altered and there is no action on bronchial musculature. However, there is a low-grade irritant action, from which recovery is slow, on isolated strips of virgin guinea pig's uterus. The substance was not further investigated."

As an indication of the importance petroleum bases may assume, the following communication from Dr. Erich Hesse, Professor of Pharmacology and Experimental Therapy in the University of Breslau, Breslau, Germany, is of interest: "I am anxious to examine the different fractions of your crude bases in their action on tubercular bacilli. Strong evidence warrants the forecast of anti-bacterial, active constituents among the kerosene bases."

<sup>9</sup> King and Bailey obtained 2,3,8-trimethylquinoline from the distillation fraction where the  $C_{16}H_{25}N$  base occurs and proved its structure by synthesis (Ref. 4, p. 1245). Proof is furnished in the same article, p. 1240, for the assumption of a great complexity of kerosene bases.



3,5,7 a-trinitro-4,8-ethenopyrindacine-8-carboxylic acid, (IV) octahydro-7-methyl-7-nitro-1,4-carbonylpyrindine-3-carboxylic acid.

Formula I, which may be considered elucidated in its most important features, reflects an important structural relationship between this hydroaromatic base and the petroleum naphthenes. In view of the wealth of bases in petroleum distillates it is highly probable that the  $C_{16}H_{25}N$  product is the forerunner of a family of compounds of a type that may be termed appropriately "Naphthenic Bases," a study of which may contribute to a solution of the difficult structural problems presented by the naphthenic acids.<sup>12</sup>

It soon became evident in this investigation that the  $C_{16}H_{25}N$  base represents an unusual type of compound. The failure of all hydrogenation and dehydrogenation experiments to effect a chemical change in the substance makes improbable such products as a heptamethyltetrahydroquinoline or a trimethyldecahydroacridine. Further evidence of the improbability of such structural types is also furnished by the great stability of the base toward alkaline permanganate.

Since in numerous instances it has been established conclusively that the so-called naphthenes are alkylated cyclopentanes, and since the chemical behavior of the  $C_{16}H_{25}N$  compound, where its basic properties are not involved, strongly parallels that of methylcyclopentane,<sup>13</sup> a structural interpretation is presented in I that assumes a condensation of two cyclopentane nuclei with a piperidine nucleus. In each of the five-membered rings a tertiary carbon appears in explanation of the fact that, analogous to corresponding naphthenes containing one tertiary carbon and forming mononitro derivatives,<sup>14</sup> our product yields a colorless, alkali-insoluble, dinitro derivative, II. The assumption of a piperidine complex in the molecule is warranted by the formation of product V,  $C_8H_5O_6N$ , in the nitric acid oxidation. The only structure admissible for this substance is that of a pyridine tricarboxylic acid. All six isomers are known and the properties of our product prove it to be pyridine-2,4,5-tricarboxylic acid, *i. e.*, berberonic acid.<sup>15,16</sup> This substance is of very little importance in proof of structure other than to indicate that the nitrogen in the  $C_{15}H_{25}N$

<sup>12</sup> On the cyclopentane structure of naphthenic acids see Zelinsky, *Ber.*, 57, 51, 57 (1924); Bushong and Humphry, "Eighth International Congress of Applied Chemistry," Vol. VI, p. 58; von Braun, *Z. angew. Chem.*, 43, 1051 (1930).

<sup>13</sup> Wischin, "Die Naphthene," 1901, p. 20, states: "permanganate in neutral as well as in alkaline solution reacts very slightly on naphthenes; only after prolonged action at 40° can a weak oxidizing effect be observed." The extraordinary stability of methylcyclopentane against dehydrogenation was established by Zelinsky, *Ber.*, 45, 678 (1912).

<sup>14</sup> Markownikoff and Konovalow, *ibid.*, 28, 1234 (1895); Kijner, *J. prakt. Chem.*, 56, 364 (1897); Markownikoff, *Ann.*, 307, 335 (1899).

<sup>15</sup> H. Weidel, *Ber.*, 12, 410 (1879).

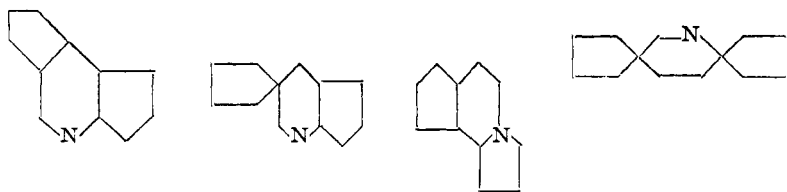
<sup>16</sup> Mumm and Hüneke, *ibid.*, 51, 162 (1918).

base is in a six-membered ring. It cannot be employed in proof of how the methyl cyclopentane rings are condensed with the six-membered ring, because the higher pyridine-polycarboxylic acids readily split out carbon dioxide at temperatures lower than that at which this pyridine acid was formed. The location of a methyl at the  $\gamma$ -position in the piperidine ring harmonizes with our failure to isolate a *trimethyl-trinitro* derivative among the nitric acid reaction products corresponding to the *dinitro* compound, II.

The only unsaturated group assumed in the structurally symmetrical formula assigned the naphthenic base is the etheno bridging between the nitrogen and the  $\gamma$ -carbon in the piperidine ring. The fact that this part of the molecule is attacked readily by neither oxidizing nor reducing agents may be plausibly accounted for by steric hindrance. Not until one of the cyclopentane nuclei is disrupted, does the  $-\text{CH}=\text{CH}-$  grouping disappear, as in the  $\text{C}_{11}\text{H}_{14}\text{O}_5\text{N}_2$  oxidation product, IV, where there is assumed a carbonyl bridging, due to an inner amide formation between a  $\gamma$ -carboxyl and the imino group of the piperidine complex. Failure to obtain a nitroso derivative eliminates the isomeric anhydride that would result from dehydration between two carboxyl groups.

Intermediary between products II and IV is the trinitrocarboxylic acid, III, where the presence of three *tertiary* nitro groups was confirmed by titration; this revealed a monobasic acid, whereas, if there were present in addition to the carboxyl a *secondary* nitro group, the substance would be a dibasic acid.

Despite the satisfactory interpretation of the reactions of the  $\text{C}_{16}\text{H}_{26}\text{N}$  base furnished by the structure assigned, there are a number of trinuclear cyclic arrangements other than that proposed in I which remain to be eliminated. As examples of other possible condensations of one six- and two five-membered rings there may be considered



It is obvious that, in the absence of a synthesis of the naphthenic base, absolute proof of structure here presents a very difficult problem in orientation.

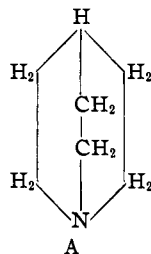
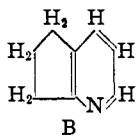
Even granted that the position of contact of the two methylcyclopentane rings with the piperidine ring is as shown in Formula I, the location of methyls at positions 3 and 5, respectively, involves an arbitrary assumption.

From the above discussion it is obvious, and likewise not surprising, that the experimental evidence so far obtained does not offer conclusive

proof of the structure of the naphthenic base; still the formulas, tentatively assigned to the different products concerned, should contribute to a clearer conception of their interrelationship.

It is interesting to note that the structure assigned the  $C_{16}H_{25}N$  base is related to quinuclidine, *i. e.*, 1,4-ethanopiperidine, A, assumed by Koenigs<sup>17</sup> as one of the parent cyclic nuclei in quinine. Quinuclidine,<sup>18</sup> as well as its alkyl derivatives, is readily synthesized and, like our  $C_{16}H_{25}N$  base, piperidine derivatives of this type possess an unusual stability.

Quite recently there has been isolated from Fushun shale oil a base of the formula,  $C_8H_9N$ ,<sup>19</sup> that is undoubtedly 5,6-dihydropyridine, B.<sup>19a</sup> This formula not only harmonizes with the pyridacine structure assigned the  $C_{16}H_{25}N$  base but makes it highly probable, even if 5,6-dihydropyridine itself is not present among the numerous kerosene bases, that compounds of the pyridine type occur here.



### Experimental Part

The Naphthenic Base,  $C_{16}H_{25}N$ .—After several crystallizations of the picrate from 95% alcohol, the salt is decomposed with ammonium hydroxide, ammonium picrate washed out of the supernatant oil with water and the base dried at 100° in a current of air. In final purification it can be distilled undecomposed at 10–15 mm. pressure.

The following physical constants were determined: b. p. at 746 mm. 278.2°;  $d_4^{20}$  0.9391;  $n_D^{20}$  1.5129. It is a colorless, odorless, optically inactive oil, only slightly soluble in water and readily soluble in the common organic solvents. With the common alkaloidal reagents it forms difficultly soluble salts.

*Anal.* Calcd. for  $C_{16}H_{25}N$ : C, 83.12; H, 10.82; N, 6.06. Found: C, 83.25, 83.30; H, 10.78, 10.81; N, 5.95, 6.12. *Mol. wt. Subs.*, 0.1694 g.; benzene, 21.915 g.;  $\Delta t$ , 0.183°. Calcd. for  $C_{16}H_{25}N$ : mol. wt., 231. Found: mol. wt., 211.

### Salts of the Naphthenic Base

Picrate.—This salt separates from a hot, alcoholic solution of the base and picric acid in slender, yellow prisms melting at 151°. It is readily soluble in hot alcohol, glacial acetic acid, benzene, acetone and ethyl acetate and only slightly soluble in water, ether and petroleum ether.

<sup>17</sup> Koenigs, *Ber.*, 37, 3244 (1904).

<sup>18</sup> Löffler and Stietzel, *ibid.*, 42, 124 (1909).

<sup>19</sup> Eguchi, *Bull. Chem. Soc. Japan*, 3, 239 (1928); *Chem. Zentr.*, 100, 331 (1929).

<sup>19a</sup> Since this paper was submitted to the Journal, one of the authors, W. C. Thompson, has confirmed the structure of the Eguchi base by its synthesis through condensation of hydroxymethylene-cyclopentanone [Wallach, *Ann.*, 329, 114 (1903)] with cyanoacetamide to 2-hydroxy-3-cyano-5,6-dihydropyridine [*cf.* Sen-Gupta, *J. Chem. Soc.*, 107, 1347 (1915)], followed by the series of reactions developed by J. von Braun [*Ann.*, 478, 191 (1930)], in the conversion of 2-hydroxy-3-cyano-5,6,7,8-tetrahydroquinoline to 5,6,7,8-tetrahydroquinoline. The results of this investigation will be published in the near future.

*Anal.* Calcd. for  $C_{22}H_{28}O_7N_4$ : C, 57.39; H, 6.11; N, 12.17. Found: C, 57.00; H, 6.36; N, 12.46.

**Acid Sulfate.**—The calculated amount of concentrated sulfuric acid is added to the base in glacial acetic acid and the salt precipitated with ether. It crystallizes from acetone in square, colorless plates melting at  $196^\circ$  and is readily soluble in water and alcohol.

*Anal.* Calcd. for  $C_{16}H_{25}N \cdot H_2SO_4$ : S, 9.72. Found: S, 9.69.

**Hydrochloride.**—A hydrochloric acid solution of the base is evaporated to dryness, the residue dissolved in hot acetone and the salt precipitated with ether. It is readily soluble in water and alcohol and crystallizes from acetone in prisms melting at  $251^\circ$ .

*Anal.* Calcd. for  $C_{16}H_{25}N \cdot HCl$ : N, 5.23. Found: N, 5.14, 5.38.

**Nitrate.**—Very characteristic of the base is its behavior toward nitric acid. When it is introduced into an excess of not too dilute nitric acid, two layers are formed. On cooling and vigorous stirring of the upper layer, the nitrate separates with one molecule of water in crystals of octahedral appearance. A convenient method of preparation is to suspend the base in twice its weight of water, add the calculated amount of nitric acid of sp. gr. 1.30, heat until all the oil has disappeared and chill with stirring. It melts at  $79^\circ$ , at  $110^\circ$  is dehydrated and then has a melting point of  $141^\circ$ . Its solubility in water is 1:20 at  $30^\circ$ . The nitrate is readily soluble in alcohol, glacial acetic acid and acetone. Samples with and without water of crystallization were analyzed.

*Anal.* Calcd. for  $C_{16}H_{25}N \cdot HNO_3 \cdot H_2O$ : N, 8.97. Found: N, 8.82. Calcd. for  $C_{16}H_{25}N \cdot HNO_3$ : N, 9.52. Found: N, 9.57.

The chloroplatinate, prepared in dilute hydrochloric acid and then recrystallized from the same medium, is obtained in slender rods decomposing at  $240^\circ$ .

*Anal.* Calcd. for  $(C_{16}H_{25}N)_2 \cdot H_2PtCl_6$ : Pt, 22.35. Found: Pt, 22.29.

The zinc chloride salt, prepared by the addition of a solution of zinc chloride to the base in hydrochloric acid, crystallizes from water in rosetts of short, pointed prisms melting at  $171^\circ$ . It is readily soluble in alcohol, hot water and hot glacial acetic acid.

*Anal.* Calcd. for  $C_{16}H_{25}N \cdot ZnCl_2$ : N, 3.81. Found: N, 4.12.

The mercuric chloride salt, prepared similarly to the zinc chloride salt, is obtained as an oil which on stirring solidifies. It crystallizes from alcohol in clusters of slender rods melting at  $157.5^\circ$ . It is very difficultly soluble in water and quite soluble in hot alcohol and hot glacial acetic acid.

*Anal.* Calcd. for  $C_{16}H_{25}N \cdot HgCl_2$ : N, 2.78. Found: N, 2.86.

The methiodide, prepared in quantitative yield by heating the base with an excess of methyl iodide at  $100^\circ$  in a sealed tube for twenty-four hours, is obtained in the form of slender, colorless prisms by crystallization from alcohol, then from water. It begins to soften around  $250^\circ$  and finally decomposes without melting.

*Anal.* Calcd. for  $C_{17}H_{28}NI$ : N, 3.75. Found: N, 3.99.

**Proof of the Absence of an N-Alkyl Group in the Naphthenic Base.**—In accordance with the procedure of Herzig and Meyer,<sup>20</sup> 1 g. of base, 5 g. of ammonium iodide and 12 cc. of hydriodic acid, sp. gr. 1.70, were heated slowly in a current of carbon dioxide up to  $300^\circ$  and this temperature was maintained for two hours longer. No alkyl iodide was formed and the unchanged base after recovery in the usual way was identified by conversion to the picrate. The hydrochloride of the base heated in a current of hydrogen chloride, in accordance with the method of Ladenburg,<sup>21</sup> also gave a negative result.

<sup>20</sup> Herzig and Meyer, *Monatsh.*, 15, 613 (1894).

<sup>21</sup> See Cohen, "Organic Chemistry for Advanced Students," Vol. III, p. 353.

Finally the base was heated with benzoic acid at 250–280° for twelve hours,<sup>22</sup> in the hope of obtaining the benzoyl derivative of a secondary amine and the alcohol corresponding to the alkyl that might be joined to nitrogen. Here again only unchanged base was recovered.

**Dehydrogenation Experiments.**—One-half gram of base, 2.5 g. of mercuric acetate and 2.5 cc. of 50% acetic acid were heated in a sealed tube at 150° for twelve hours.<sup>23</sup>

There was no separation of mercury and the original base was recovered in the usual way. The method of Kann and Tafel,<sup>24</sup> where distillation with admixed silver sulfate and kieselguhr is employed, gave back the base unchanged. The dehydrogenation method of Borsche,<sup>25</sup> employing pumice stone impregnated with lead dioxide, also failed to alter the base. Finally it was found that the base mixed with zinc dust could be distilled out unchanged.<sup>26</sup>

**Action of Bromine on the C<sub>16</sub>H<sub>25</sub>N Base.**—With an excess of bromine in chloroform solution 1,2,3,4-tetrahydroquinoline is readily converted to tribromoquinoline.<sup>27</sup> When to the naphthenic base in chloroform an excess of bromine is added, there remains after evaporation of the solvent a red, oily residue. This represents a loose bromine addition product, since from its alcoholic solution the characteristic picrate of the original base separates on addition of picric acid. On treatment of the base with bromine water the color of the solution disappears and there is formed a viscous, red-brown gum, insoluble in water and dilute acids and soluble in glacial acetic acid. Caustic soda reconverts this product to the original base.

Since the aromatic base, 2,3,8-trimethylquinoline, accompanies the hydroaromatic base in the 276° fraction of the kerosene bases, their difference in behavior toward bromine is of especial interest. The addition of bromine to a chloroform solution of the aromatic base is followed by an immediate separation of a reaction product crystallizing in light yellow needles. This, however, is a loose bromine addition product since caustic soda solution removes the bromine and restores the original base.

**Oxidation with Permanganate.**—The naphthenic base in permanganate solution was boiled over a period of one hundred and fifty hours, when the greater part of the base was ethered out unchanged. The remaining solution was then decolorized with sulfur dioxide, filtered, acidified with nitric acid, and, in order to remove free nitric acid, evaporated to dryness. The residue dissolved in water gave with a silver nitrate solution a precipitate that proved to be silver oxalate.

**Hydrogenation Experiments.**—With sodium and absolute alcohol pyridine is reduced to piperidine,<sup>28</sup> and 5,6,7,8-tetrahydroquinolines to decahydroquinolines.<sup>29</sup> This procedure proved ineffective with the naphthenic base, as did the employment of sodium and amyl alcohol. Without avail reduction with tin and hydrochloric acid was attempted in accordance with the method employed in the conversion of 5,6,8-trimethylquinoline to the corresponding Py-tetrahydroquinoline.<sup>30</sup> Although 1,2,3,4-tetrahydroquinoline is reduced to decahydroquinoline with hydriodic acid and red phosphorus,<sup>31</sup> this form of reduction gave with the naphthenic base likewise a negative result.

<sup>22</sup> Cf. von Braun and Weissbach, *Ber.*, **63**, 489 (1930).

<sup>23</sup> Cf. Tafel, *ibid.*, **25**, 1619 (1892).

<sup>24</sup> Kann and Tafel, *ibid.*, **27**, 826 (1894).

<sup>25</sup> Borsche, *Ann.*, **359**, 49 (1908).

<sup>26</sup> Cf. Ferratini, *Ber.*, **26**, 1812 (1893).

<sup>27</sup> Hoffmann, Leo and Koenigs, *ibid.*, **16**, 727 (1883).

<sup>28</sup> Ladenburg, *Ann.*, **247**, 43 (1888).

<sup>29</sup> von Braun, Petzold and Seeman, *Ber.*, **55**, 3782 (1922).

<sup>30</sup> Wikander, *ibid.*, **33**, 646 (1900).

<sup>31</sup> Bamberger and Williamson, *ibid.*, **27**, 1485 (1894).



**Action of Nitric Acid on the Naphthenic Base.**—One gram of base is heated in a sealed tube with 10 cc. of nitric acid, sp. gr. 1.260, slowly over a two hour period up to 170° and this temperature then maintained for three hours. The pressure generated makes it inadvisable to employ larger amounts of material. Although the yields were unfavorable, four reaction products in apparently pure form were isolated. These substances of the composition,  $C_{16}H_{20}O_4N_8$ ,  $C_{16}H_{20}O_8N_4$ ,  $C_{11}H_{14}O_6N_2$  and  $C_9H_8O_6N$ , are referred to in the introduction as products, II, III, IV and V, respectively.

For isolation of the nitric acid reaction products, the material from 24 g. of base is combined and concentrated by vacuum distillation to a gummy consistency. In order to remove traces of nitric acid, the residue is taken up in water and the distillation repeated. On addition of 150 cc. of water, product III in poor yield remains undissolved as a smear. The decanted solution is made alkaline to methyl orange with  $N/3$  barium hydroxide and filtered from the barium salt of product V. On further addition of barium hydroxide to the phenolphthalein end-point, product II separates and is ethered out. With all basic material removed the barium in the form of hydroxide and nitrate is exactly precipitated as sulfate, the barium sulfate filtered off and the solution evaporated to dryness. The residue is next taken up in a little alcohol and ether added as long as it causes precipitation. From the gummy material obtained in this way, and dissolved in a small volume of hot acetone, there separates after several days' standing in the ice-box product IV in crystalline form. Methods of isolating the residual products in the acetone solution have not been worked out, and no attempt was made to identify among the oxidation products volatile, fatty acids.

Product II for purification is converted to its picrate and the latter recrystallized from alcohol in diamond-shaped plates melting at 231°. The picrate is then treated with ammonium hydroxide and the liberated base recrystallized from alcohol in the form of colorless, slender rods melting at 116.5° and distilling even at low pressures with partial decomposition. It is readily soluble in organic solvents and insoluble in water.

*Anal.* Calcd. for  $C_{16}H_{20}O_4N_8$ : C, 59.81; H, 7.16; N, 13.09. Found: C, 59.89; H, 7.43; N, 12.80. *Mol. wt.* Subs., 10.8 mg.; camphor, 89.7 mg.;  $\Delta t$ , 15. Calcd. for  $C_{16}H_{20}O_4N_8$ : mol. wt., 321. Found: mol. wt., 320.

Product III on crystallization from alcohol is obtained in the form of yellow, rhombic plates melting with decomposition at 347°. Although insoluble in water it, unlike product I, is alkali soluble.

*Anal.* Calcd. for  $C_{16}H_{20}O_8N_4$ : C, 48.48; H, 5.05; N, 14.14. Found: C, 47.90; H, 4.92; N, 14.47. *Mol. wt.* Subs., 8.8215 mg.; camphor, 92.7 mg.;  $\Delta t$ , 11. Calcd. for  $C_{16}H_{20}O_8N_4$ : mol. wt., 396. Found: mol. wt., 348. *Titration.* Subs., 8.882 mg.: 0.89 cc. of 0.0258 *N* NaOH. Calcd. for  $C_{16}H_{20}O_8N_4$  as monobasic acid: 0.87 cc.

Product IV on crystallization from alcohol separates in the form of colorless prisms melting with decomposition at 189–190°. It is readily soluble in water or hot alcohol and only slightly soluble in ether. In contrast to the parent naphthenic base, it is readily oxidized with alkaline permanganate. It does not give colorations with either ferrous sulfate or ferric chloride. Attempts to prepare a nitroso derivative were unsuccessful.

*Anal.* Calcd. for  $C_{11}H_{14}O_6N_2$ : C, 51.97; H, 5.51; N, 11.02. Found: C, 52.48; H, 5.43; N, 11.03. *Mol. wt.* Subs., 7.618 mg.; camphor, 92.5 mg.;  $\Delta t$ , 14. Calcd. for  $C_{11}H_{14}O_6N_2$ : mol. wt., 254. Found: mol. wt., 235. *Titration.* Subs., 0.539 mg.: 3.00 cc. of 0.0257 *N* NaOH. Calcd. for  $C_{11}H_{14}O_6N_2$  as dibasic acid: 2.93 cc.

Berberonic Acid, Product V, crystallizes from water with two molecules of water of crystallization in a network of hair-like needles melting with decomposition at 240–241°. It is readily soluble in cold alcohol and possesses a wide difference in solubility in hot and cold water. With ferrous sulfate it gives even at a dilution of 1 part in 2500

parts of water a blood-red coloration. A characteristic property of this acid is the formation of a calcium salt on boiling its aqueous solution with animal charcoal. This salt crystallizes from water in plates with well-defined, diamond-shaped end faces.

*Anal.* Calcd. for  $C_8H_5O_6N$ : C, 45.50; H, 2.37; N, 6.63. Found: C, 45.29; H, 2.56; N, 6.83. *Mol. wt.* Subs., 11.503 mg.; camphor, 118.4 mg.;  $\Delta t$ , 18. Calcd. for  $C_8H_5O_6N$ : mol. wt., 211. Found: mol. wt., 216. *Titration.* Subs., 16.848 mg.: 9.20 cc. of 0.0257 *N* NaOH. Calcd. for  $C_8H_5O_6N$  as tribasic acid: 9.33 cc.

### Summary

1. A hydroaromatic base,  $C_{16}H_{25}N$ , isolated from the crude kerosene distillate as produced at the Oleum Plant of the Union Oil Company of California, is described along with a number of characteristic salts.

2. This base is regarded as 4-methyl-1,4-ethenopiperidine, condensed at 2,3 as well as at 5,6, with methylcyclopentane. In addition to the two cyclopentane nuclei, this structure presents two tetrahydropyridine complexes within the piperidine periphery, so that in all five rings are involved.

3. Corresponding to the structural formula proposed, the  $C_{16}H_{25}N$  compound, apart from possessing the properties of a tertiary amine, behaves similarly to methyl cyclopentane.

4. The term "Naphthenic Bases" is proposed for bases like the  $C_{16}H_{25}N$  compound of the cyclopentane type, in order to emphasize their relationship to the so-called naphthenes.

5. The claim previously advanced that "*petroleum offers the greatest wealth of nitrogen compounds of any natural source*" is strengthened by the results reported in this paper and the isolation, proof of structure and even synthesis of a host of so-called petroleum bases only await a realization of the attractive field of research presented.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE WEST VIRGINIA UNIVERSITY]

## FLUOSILICATES OF ORGANIC BASES. II

BY C. A. JACOBSON<sup>1</sup>

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Continuing the work of Jacobson and Pray,<sup>2</sup> eleven new fluosilicates have been prepared and analyzed.

In general, the preparation of these compounds was similar to that recorded in the first paper. The purest Eastman Kodak Co. bases were

<sup>1</sup> The Author wishes to acknowledge the assistance of the following persons in the completion of the present work: H. McMillen and C. W. Weaver on *o*-tolidine fluosilicate; E. Stutzman on di- $\alpha$ -, and di- $\beta$ -naphthylamine fluosilicate; Christine Arnold on di-diphenylamine and *m*-phenylenediamine fluosilicates; C. G. Rollins on the fluosilicates of ethylaniline, *p*-nitrosodiphenylamine, *p*-aminoazobenzene and *p*-aminobenzoic acid.

<sup>2</sup> Jacobson and Pray, THIS JOURNAL, 50, 3055 (1928).