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

The Nitrogen Compounds in Petroleum Distillates. VI. The Occurrence of 2,8-Dimethylquinoline in the Crude Kerosene Distillate of California Petroleum

BY G. R. LAKE AND J. R. BAILEY

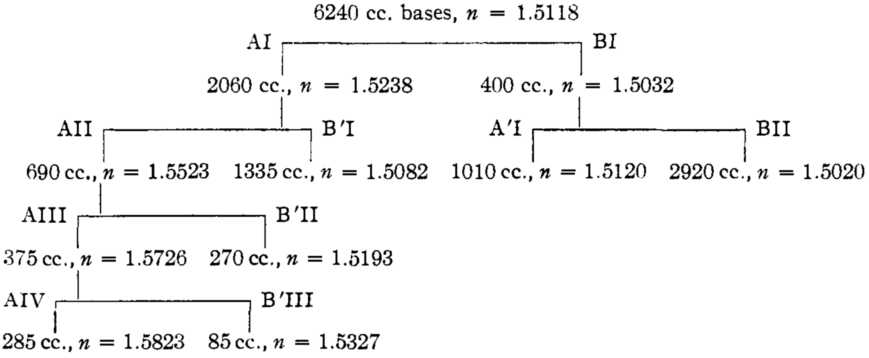
Introduction.—All the quinolines so far encountered among the kero bases are 2, 3, 4 or 8 polymethyl homologs *with one methyl at position 2;* no quinoline substituted at positions 5, 6 or 7 has been identified. Whereas quinaldine is the only coal-tar quinoline yielding a phthalone (Quinoline Yellow), petroleum offers in synthesis of this class of dyes[1] a wealth of intermediates none of which has been obtained from any other natural source.

When the present investigation was begun, two of the three possible dimethylquinolines, with one methyl in position 2 and the other at position 3, 4 or 8, were known to exist among the kero bases,[2] but the 2,8-isomer[3] had not been encountered. Employing cumulative extraction on the 253–256° fractions, we have found 2,8-dimethylquinoline and established its identity with the synthetic base.

Experimental Part

Cumulative Extraction of the 253–256° Fraction of Kero Bases.—A quantity of this fraction was distributed between equal volumes of 1:1 hydrochloric acid and chloroform, and the two solutions were extracted further according to the method described in Paper IV.[4] The results are summarized in the subjoined flow sheet (see paper IV for an explanation of the symbols).

FLOW SHEET



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(1) *Cf.* A. Eibner, *Ber.*, **37**, 3605 (1904).

(2) See Paper V of this series by Biggs and Bailey.

(3) (a) O. Doebner and W. von Miller, *Ber.*, **16**, 2469 (1883); **23**, 2259 (1890); (b) A. Eibner and Frz. Peltzer, *ibid.*, **33**, 3467 (1900); **34**, 2450 (1901); (c) M. Wyler, *ibid.*, **60**, 398 (1927); (d) Max Möller, *Ann.*, **242**, 309 (1887).

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

Final data from processing 6240 cc. of bases into six fractions are

	1	2	3	4	5	6
n_D^{25}	1.5832	1.5327	1.5193	1.5120	1.5082	1.5020
Vol., cc.	285	85	270	1010	1335	2920
Vol., %	4.6	1.4	4.3	17.6	21.4	46.8

Isolation of 2,8-Dimethylquinoline.—The aqueous solution of hydrochlorides marked AIV, representing 285 cc. of bases, *i. e.*, 4.6% of the starting material, was evaporated to a small volume from which on chilling the greater part of the 2,8-dimethylquinoline hydrochloride separated. Smeary admixtures were removed with a small amount of cold acetone, followed by recrystallization of the residue from alcohol. The yield of practically pure hydrochloride was 32 g. (0.4%). In a second extraction of 2250 cc. of bases, carried out more carefully, the yield was increased to 1.8%.

In final purification the hydrochloride was treated with the calculated amount of sodium bisulfate in concentrated aqueous solution and the separated acid sulfate recrystallized from 95% alcohol. Next the picrate, prepared from the acid sulfate in alcoholic solution, was recrystallized from 50% acetic acid and then from water. Finally the base, liberated from the picrate with ammonium hydroxide, was converted to the zinc chloride salt and the latter recrystallized from dilute hydrochloric acid. The base, regained from the zinc chloride salt by dry distillation,[3c] gave the following constants: m. p. 24°;[5] b. p. 252.4° (754 mm.); n_D^{25} 1.5997; mol. wt. (by Rast micro camphor method) calcd. 157, found 159.

For characterization of the base the phthalone, as well as the following new salts, was prepared.

Acid Sulfate.—The calculated amount of sodium acid sulfate is added to a concentrated solution of the hydrochloride in water and the filtered sulfate crystallized from absolute alcohol in radiating clusters of needles melting at 187°.

Perchlorate, $C_{11}H_{11}N \cdot HClO_4$.—This salt, prepared by adding an aqueous solution of sodium perchlorate to the hydrochloride in water, crystallizes from water in slender rods and from alcohol in fine needle clusters melting at 189°. It is insoluble in the other common solvents with the exception of glacial acetic acid. Owing to its explosive nature concordant results were not obtained in the analysis.

Mercuric Chloride Salt.—Prepared in the usual way in dilute hydrochloric acid, this salt crystallizes from glacial acetic or hydrochloric acid in hair-like needles melting at 211°. Its solubilities are similar to those of the perchlorate.

Phthalone.—The base is heated with the calculated amount of phthalic anhydride for two hours at 200° and the melt crystallized from chloroform, glacial acetic acid or nitrobenzene in long slender rods melting with decomposition at 283°. It is only sparingly soluble in the other common solvents.

ANALYSES ON THE BASE AND DERIVATIVES

	Carbon, %		Hydrogen, %		Nitrogen, %		Chlorine, %	
	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
Base, $C_{11}H_{11}N$	84.08	83.78	7.01	7.13	8.92	9.06		
Phthalone, $C_{19}H_{13}O_3N$	79.41	79.20	4.56	4.73	4.88	5.16		
$C_{11}H_{11}N \cdot H_2SO_4$					5.49	5.72		
$(C_{11}H_{11}N \cdot HCl)HgCl_2$					3.01	3.16	22.87	23.05

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(5) Wyler reports a melting point of 27°.

Summary

This paper reports the isolation of 2,8-dimethylquinoline from the kerosene distillate of California petroleum.

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The Nitrogen Compounds in Petroleum Distillates. VII. New Reactions of the Naphthenic Base, $C_{16}H_{25}N$.[1] A New Naphthenic Base, $C_{13}H_{21}N$

BY B. F. ARMENDT AND J. R. BAILEY

Introduction.—Unrefined California petroleum distillates yield, along with aromatic bases, in preponderant amount a host of non-aromatic bases.[2] Since these non-aromatics represent, not only new substances, but also new structural types, their investigation may be considered of unusual scientific interest. In this connection, it may be mentioned, work is in progress to obtain experimental evidence of a possible structural relationship between the non-aromatic bases and petroleum hydrocarbons.

Because both the isolation and proof of structure of the low-boiling non-aromatic bases might be expected to present the least experimental difficulty, an investigation of fractions within the boiling point range of 215–216° was undertaken. Three barrels of kero bases originally available gave only 708 cc. of this material and from this 20 g. (0.004% of the three barrels) of a base of the formula $C_{13}H_{21}N$ was obtained. Research on this product has been limited to a comparison of its general behavior with that of the $C_{16}H_{25}N$ base.

All attempts to hydrogenate both the $C_{13}H_{21}N$ and the $C_{16}H_{25}N$ base ended in failure. They also resist dehydrogenation, a stability hardly to be expected of true *hydroaromatic* bases, and prolonged heating with alkaline permanganate has no oxidizing effect. The $C_{16}H_{25}N$ compound reacts readily with methyl iodide, but the methiodide of the $C_{13}H_{21}N$ compound is not formed under similar conditions. Attempts to employ the Hofmann reaction in degradation of the $C_{16}H_{25}N$ base were unsuccessful, probably due to rearrangement of the quaternary base to a pseudo form.

From the many theoretical possibilities, there has been selected provisionally formula I, for the $C_{13}H_{21}N$ base and the original structural interpretation of the $C_{16}H_{25}N$ base has been changed to II.

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(1) W. C. Thompson and J. R. Bailey, THIS JOURNAL, **53**, 1002 (1931).

(2) Shale and bones on distillation yield exclusively aromatic bases and the same applies to coal with one exception [Decker and Dunant report the isolation of dihydroacridine from a coal tar distillate, *Ber.*, **42**, 1178 (1909)].