of lead sulfate was removed by centrifuging. The dialdehyde formed was determined by titration according to Willstätter and Schudel; 25 cc. of the solution used up 61.0 cc. of 0.1 *N* iodine solution: dialdehyde calculated, 208.8 mg.; found, 211.0 mg.

For the oxidation of the dialdehyde the solution was freed from the excess of sulfuric acid by dropwise addition of barium acetate and diluted to 300 cc. with distilled water; 15 g. of bromine was added and the resulting mixture was placed in a tightly sealed bottle and allowed to stand for two days with occasional shaking. The excess bromine was removed by aeration, the hydrobromic acid formed was removed with silver acetate and the excess silver was precipitated with hydrogen sulfide. The mixture was then evaporated to dryness and the remaining citric acid monomethyl ester was saponified by boiling for half an hour with 60-cc. of 2 *N* sodium hydroxide. An amount of 1 *N* sulfuric acid (120 cc.) equivalent to the sodium hydroxide used was added and the solution evaporated to dryness under reduced pressure. The *citric acid* was separated from the sodium sulfate by extraction of the residue with ethyl acetate; 4.9 g. of crude citric acid was obtained (86% yield). Recrystallization from water yielded pure citric acid (m. p. 151°).

Preparation of *d*-(—)-glyceric acid.[11]—To an aqueous solution of *d*-glyceraldehyde prepared as described on page 2608, Col. 1, from 25 g. of diacetone-*d*-mannitol,[3d] 40 g. of bromine was added and the solution was shaken for two hours. After standing at room temperature for an additional fifteen hours, the excess bromine was removed by aeration and the bromide ions by shaking with silver carbonate or acetate. The silver ions were precipitated by hydrogen sulfide. The solution was then evaporated at 40° (10 mm.) to a dry sirup of constant weight; 15.4 g. (76% of the theoretical) of glyceric acid was obtained.

Preparation of *d*-Glyceric Acid Methyl Ester (Dextrorotatory).—Eleven grams of glyceric acid together with 250 cc. of dry methyl alcohol, containing 1.5% of hydrochloric acid (gas), was refluxed for twenty-four hours. After shaking the liquid for twelve hours with finely powdered silver carbonate, the silver salts were removed by centrifuging. The methyl alcohol was evaporated at reduced pressure and the residue was distilled *in vacuo:* yield, 11.5 g. (92% of the theoretical) of glyceric acid methyl ester; b. p. (8 mm.) 114–116°. Calculated for $C_4H_8O_4$ (120): C, 40.00; H, 6.70. Found: C, 39.96; H, 6.70. *Optical rotation* in homogeneous substance: $\alpha^{26}D$ +5.92 (1-dm. tube, d^{26}_4 1.279, $[\alpha]^{26}D$ +4.7).[12]

Preparation of the Calcium Salt of *d*-Glyceric Acid.—Eight grams of *d*-glyceric acid methyl ester was added to a solution of 2.47 g. of calcium hydroxide in 40 cc. of distilled water. After warming on the water-bath for one hour, the solution was neutralized with a few drops of 5 *N* hydrochloric acid and filtered, while still hot. Warm ethanol was then added until the clear and hot solution became turbid and the mixture was allowed to cool in the refrigerator; 8.0 g. of calcium salt was precipitated after six hours (84% yield). Calcd. for $(C_3H_5O_4)_2Ca\cdot 2H_2O$ (286): Ca, 13.99. Found: Ca, 13.95. *Optical rotation* of the calcium salt containing 2 moles of crystal water, in aqueous solution: 1-dm. tube, c = 5.19, $\alpha^{20}D$ +0.67°, $[\alpha]^{20}D$ +12.9°.[13]

(11) Wohl and Freudenberg, *Ber.*, **56**, 309 (1923).

Summary

It has been shown that oxidation with lead tetraacetate can be carried out quantitatively in *aqueous* solution and in water-containing solvents. This observation that the reaction does not always require dry organic solvents enlarges the field of its application. Lead tetraacetate yields the same oxidation products in water as in organic solvents, except in rare cases where secondary hydrolytic reactions may occur.

(12) Frankland and Turnbull, *J. Chem. Soc.*, 459 (1914).

(13) E. Fischer and Jacobs, *Ber.*, **40**, 1069 (1907); Wohl and Schellenberg, *ibid.*, **55**, 1404 (1922).

TORONTO, CANADA RECEIVED JULY 5, 1939

[CONTRIBUTION NO. 150 FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, THE UNIVERSITY OF TEXAS]

The Nitrogen Compounds in Petroleum Distillates. XV. Counter-Current Acid Extraction of Kero Bases. Isolation of 2,4-Dimethyl-8-*n*-propylquinoline

BY W. NELSON AXE[1] AND J. R. BAILEY

Introduction

It has been reported previously[2] that a satisfactory separation of 2,3-dimethyl-8-*n*-propyl- and 2,3,4,8-tetramethylquinoline from associated bases in the 300° boiling range of kero bases was accomplished by supplementing the conventional methods of processing petroleum bases with so-called fractional degassing of their acid sulfite solution under aeration.

In Jantzen's monograph,[3] the author reports the isolation of the following products from coal tar bases (b. p. 238–266°), through employment of counter-current extraction: quinoline, each of the seven monomethylquinolines, 2,8-dimethylquinoline,[4] isoquinoline, 1- and 3-methylisoquinoline, 1,3-dimethylisoquinoline, two $C_{10}H_9N$ bases (probably 6-methyl- and 5- or 7-methylisoquino-

(1) Research Department, Phillips Petroleum Company, Bartlesville, Oklahoma.

(2) W. N. Axe and J. R. Bailey, THIS JOURNAL, **60**, 3028 (1938).

(3) Ernst Jantzen, "Das fraktionierte Destillieren und das fraktionierte Verteilen," Verlag Chemie, Berlin, 1932, pp. 117–137.

(4) Isolated from California petroleum by Lake and Bailey, THIS JOURNAL, **55**, 4143 (1933).

line, respectively), and a C_7H_5NS compound (a thioisoquinoline?). Of these sixteen products, relatively few had been encountered by previous investigators in processing coal tar bases.

Lately, through employment of counter-current extraction,[5] 2,4-dimethyl-8-ethylquinoline was obtained from the kero base fraction of b. p. 292–293°.[6]

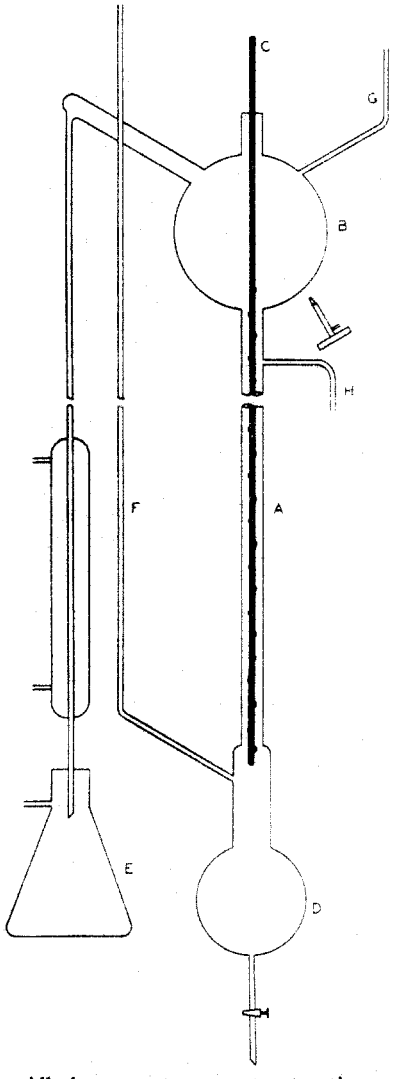

Fig. 1.—All-glass countercurrent extraction equipment. A, extraction column, height 125 cm., internal diameter 1.1 cm.; B, boiler from which solvent is distilled progressively into E; C, stirrer with nodes—above B is a bell-cup type mercury seal; F, inlet tube for bases in petroleum ether solution into B; G, inlet tube for dilute hydrochloric acid into B; H, outlet tube for withdrawal of base fraction in petroleum ether at the end of each extraction; D, reservoir for base-hydrochloride solution which is run off as desired.

(5) The column used was designed by Schutze, Quebedeaux and Lochte, *Ind. Eng. Chem., Anal. Ed.*, **10**, 676 (1938), Fig. 3.

(6) W. N. Axe, THIS JOURNAL, **61**, 1017 (1939).

We find in separation of mixtures of aromatic petroleum bases that fractional degassing of their acid sulfites, because of the simplicity in operation, can be employed to advantage frequently in their partial separation, preliminary to the use of exhaustive counter-current extraction.

This paper deals with the isolation of a $C_{14}H_{17}N$ base[2] by the extraction method and its identification as 2,4-dimethyl-8-*n*-propylquinoline through degradation and synthesis. The formation of 2,4-dimethylquinoline-8-carboxylic acid in chromic acid oxidation was confirmed by the usual comparison with an authentic sample of this preparation.[6] This showed the original base to be an 8-*n*- or isopropyl homolog of 2,4-dimethylquinoline. The *n*-propyl derivative was synthesized from acetyl acetone and *o*-amino-*n*-propylbenzene[2] and was proved to be the $C_{14}H_{17}N$ kero base.

Experimental

The preliminary work carried out for assembling the 292–293° fraction of aromatic base, known to contain the $C_{14}H_{17}N$ quinoline homolog, has been published previously.[2]

Prior to counter-current extractions, the base mixture was processed through acid sulfites to yield 10% of 2,3-dimethyl-8-ethylquinoline.[7]

Figure 1 shows the construction of the unit employed in counter-current extraction. The bases are dissolved in petroleum ether in the volume ratio of 1:2. Enough 2 *N* hydrochloric acid is used for the partial neutralization of the bases and the acid is diluted to a volume equal to that of the petroleum ether solution of bases. The final concentration of the acid in all extractions was close to 1.5 *N*. The bases are fed in at the bottom of the column through F and the acid above the column through G, an approximately equal flow-rate of the two solutions being maintained through stopcock control of the proportioning ratio. The maximum throughput without reducing contact efficiency is around 80 cc. of bases per hour. Thorough interdispersion of the acid and base solutions is accomplished by operating the stirrer at the maximum speed allowable without producing emulsions. At the end of the extraction, the petroleum ether solution containing Base Fraction I is run off through H. From their hydrochlorides collected in D, the bases are recovered and carried through a second partial extraction to yield Base Fraction II. Table 1 summarizes the final results from a repetition of the above procedure so as to obtain a total of seven fractions.

To effect separation of the component bases, the separate fractions were processed as follows: (1) picration was carried out in hot acetone; (2) the acetone-insoluble picrates were recrystallized from glacial acetic acid; (3) the acetone-soluble picrates were recrystallized from alcohol, followed by liberation of the bases from the alcohol-insoluble salts; (4) the bases obtained from the

(7) C. L. Key and J. R. Bailey, *ibid.*, **60**, 763 (1938).

TABLE I

EXTRACTION OF AROMATIC BASES IN THE 292–293° RANGE

Fraction	Vol., cc.	$n^{25}D$	d^{20}_4	Bases isolated	Yield, %
1	76	1.5760	1.0035	2,3-Me_2-8-*n*-PrQ[a]	21
2	40	1.5770	1.0039	2,3-Me_2-8-*n*-PrQ	22
3	70	1.5774	1.0057	2,3-Me_2-8-*n*-PrQ	14
				2,4-Me_2-8-*n*-PrQ	5
4	80	1.5820	1.0166	2,3-Me_2-8-EtQ	11
				2,4-Me_2-8-*n*-PrQ	8
5	50	1.5848	1.0203	2,3-Me_2-8-EtQ	3
6	47	1.5886	1.0246	None	
7	70	1.5920	1.0309	None	

[a] In this paper, the abbreviations Me_2, Et, Pr and Q denote dimethyl, ethyl, propyl and quinoline, respectively. In this and subsequent tables, *yield* applies to the volume of base in each fraction.

picrates in (3) were dissolved in dilute hydrochloric acid and converted to zinc chloride salts, with subsequent recrystallization from a dilute zinc chloride–hydrochloric acid solution. Step 2 in several fractions yielded 2,3-dimethyl-8-ethyl- and 2,3-dimethyl-8-*n*-propylquinoline. 2,4-Dimethyl-8-*n*-propylquinoline was encountered in Step 4 in processing fractions 3 and 4.

Characterization and Proof of Structure of the $C_{14}H_{17}N$ Base as 2,4-Dimethyl-8-*n*-propylquinoline

Zinc Chloride Salt.—This salt crystallizes in lustrous oblique parallelograms melting at 225–226°.

Anal. Calcd. for $(C_{14}H_{17}N\cdot HCl)_2\cdot ZnCl_2$: C, 55.33; H, 5.96; Cl, 23.34. Found: C, 55.14; H, 6.08; Cl, 23.12.

Free Base.—Prepared from the zinc chloride salt, the base is a colorless, viscous liquid with the following constants: b. p. 298° (747 mm.); $n^{25}D$ 1.5748; d^{20}_4 0.9992.

Anal. Calcd. for $C_{14}H_{17}N$: C, 84.42; H, 8.54. Found: C, 84.71; H, 8.56.

Phthalone.—On heating the base and phthalic anhydride at 200° for four hours, an orange yellow phthalone is formed which, after recrystallization from alcohol, melts at 198–199°.

Anal. Calcd. for $C_{22}H_{19}O_2N$: C, 80.21; H, 5.81. Found: C, 80.15; H, 5.90.

2,4-Dimethylquinoline-8-carboxylic Acid.—To a boiling solution of 5 g. of base in 6 *N* sulfuric acid is added slowly 15 g. of potassium dichromate in 12 cc. of concentrated sulfuric acid diluted with 25 cc. of water. The oxidation is complete in one hour and the carboxylic acid melting at 241–242° can be isolated in a yield of 45%.[2] This product, like an authentic sample of 2,4-dimethylquinoline-8-carboxylic acid, crystallizes from alcohol in long, slender needles melting at 241–242°. A mixed melting point of the two preparations showed no depression. This degradation product established a 2,4-dimethyl-8-*n*- or isopropyl structure for the original base.

Anal. Calcd. for $C_{12}H_{11}O_2N$: C, 71.64; H, 5.47. Found: C, 71.38; H, 5.44.

2,4-Dimethylquinoline.—Soda-lime distillation of the above carboxylic acid gives a liquid base, the picrate of which crystallizes from alcohol in long needles, melting at 194°. This salt was recognized as the suspected 2,4-dimethylquinoline picrate by the exceptional property of a rapid color change from bright yellow to brown on exposure to sunlight. Further confirmation of structure was obtained by the usual mixed melting point method.

Anal. of picrate. Calcd. for $C_{17}H_{14}O_7N_4$: C, 52.85; H, 3.64. Found: C, 52.92; H, 3.75.

Synthesis of 2,4-Dimethyl-8-*n*-propylquinoline.—Synthesis of the base from ortho-*n*-propylaniline[2] and acetylacetone[3] was confirmed by the same melting point for the individual and mixed picrates of the synthetic base and the kero base.

As a comparative study of the effectiveness of countercurrent extraction and degassing of acid sulfites in separation of 2,3-dimethyl-8-*n*-propylquinoline and 2,3,4,8-tetramethylquinoline,[9] the data in Tables II and III are submitted.

TABLE II

EXTRACTION OF AROMATIC BASES IN THE 303° RANGE

Fraction	Vol., cc.	$n^{25}D$	d^{20}_4	Bases isolated	Yield, %
1	28	1.5720	0.9955	2,3-Me_2-8-*n*-PrQ	4.5
2	62	1.5748	0.9988	2,3-Me_2-8-*n*-PrQ	11.5
3	60	1.5760	1.0017	2,3-Me_2-8-*n*-PrQ	17.5
4	32	1.5760	1.0080	2,3-Me_2-8-*n*-PrQ	23.0
5	75	1.5774	1.0024	2,3-Me_2-8-*n*-PrQ	14.0
6	66	1.5792	1.0057	2,3-Me_2-8-*n*-PrQ	1.2
7	72	1.5810	1.0088	None	
8	62	1.5828	1.0137	None	
9[a]	35	1.5834	1.0147		
10[a]	67	1.5872	1.0211		
11[a]	63	1.5896	1.0245		
12[a]	35	1.5916	1.0280		
13	62	1.5935	1.0328	None	
14	72	1.5960	1.0398	2,3,4,8-Me_4Q	29.0

[a] No attempt was made to isolate bases from these fractions.

TABLE III

EFFECT OF METHOD OF SEPARATION ON YIELDS OF PURE BASES

Extraction type	Charge B. p., °C.	$n^{25}D$	$C_{14}H_{17}N$, %	$C_{13}H_{15}N$, %
Fractional degassing	300	1.5850	1.8	0.8
Counter-current extraction	303	1.5855	4.7	2.5

In Table IV are results obtained in the separation of four well-known kero quinoline homologs through countercurrent extraction of an aromatic base fraction in the 280–283° range.

TABLE IV

EXTRACTION OF AROMATIC BASES IN THE 280–283° RANGE

Fraction	Vol., cc.	$n^{25}D$	d^{20}_4	Bases isolated	Yield, %
1	55	1.5724	1.0095	2,3-Me_2Q	33
2	35	1.5706	1.0083	2,3-Me_2-8-EtQ	20
3	55	1.5766	1.0069	2,3,8-Me_3Q	26
4	65	1.5840	1.0301	2,3,8-Me_3Q	25

(8) *Cf.* Königs and Mengel, *Ber.*, **37**, 1325, 1333 (1904).

(9) *Cf.* ref. 2 for the discovery of these quinoline homologs through employment of the degassing procedure.

Summary

This paper deals with the isolation through counter-current hydrochloric acid extraction of a new kero base, 2,4-dimethyl-8-*n*-propylquinoline, the structure of which was established by chromic acid oxidation to a $C_{11}H_{10}NCOOH$ acid, previously obtained in the Texas Laboratory by a similar oxidation of the kero base, 2,4,8-trimethylquinoline. This orientation was confirmed by synthesis, in which acetylacetone and *o*-*n*-propylaniline were the intermediates.

AUSTIN, TEXAS RECEIVED MAY 19, 1939

[CONTRIBUTION NO. 161 FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, THE UNIVERSITY OF TEXAS]

The Nitrogen Compounds in Petroleum Distillates. XVI. Use of Multiple Acid Extraction in Isolation of 2,3,4-Trimethyl-8-ethylquinoline

BY RICHARD A. GLENN AND J. R. BAILEY

Introduction

In a systematic investigation in the Texas Laboratory of kero quinoline homologs from crude bases furnished by the Union Oil Company of California, the 310° fraction was processed through cumulative extraction[1] in order to segregate the aromatic components in satisfactory concentration. In further refining, the latter material in the 305–315° range was processed through multiple acid-extraction.[2]

This method of separation yielded a $C_{14}H_{17}N$ base which degradation and synthesis revealed as 2,3,4-trimethyl-8-ethylquinoline. In chromic acid oxidation a $C_{12}H_{12}NCOOH$ acid was obtained which proved the replacement of an *ethyl* by *carboxyl*. The 8-position of the ethyl follows from the fact that the acid was identical with one previously obtained by chromic acid oxidation of 2,3,4,8-tetramethylquinoline.[3] Its structure was confirmed by synthesis from methylacetylacetone and *o*-aminoethylbenzene.[4]

Experimental

In carrying out multiple acid-extraction with 4000 cc. of aromatic bases in the 305–315° range, the procedure charted by Morton[5] was followed. By this method the bases were resolved into ten fractions of varying volume. Next, separate fractions were carried through one fractional distillation. The physical constants, including boiling point, density and refractivity, of each of the 95 distillation cuts were determined for comparative purposes.

In the present work only fractions IX 14, IX 15, X 12 and X 13, in the 314–319° range, were of interest, because lower boiling fractions had been investigated previously. From all of this material on picration in alcohol, crystalline salts, free of smears, separated. However, in further purification, the four fractions were combined and carried through counter current extraction using the equipment described in the preceding paper by Axe and Bailey.[6]

TABLE I

COUNTER CURRENT EXTRACTION DATA

Cut	Volume, cc.	$n^{25}D$	d^{25}_4
1	22	1.5841	1.0174
2	36	1.5878	1.0237
3	21	1.5888	1.0277
4	30	1.5920	1.0386

Isolation of 2,3,4-Trimethyl-8-ethylquinoline.—From Fractions 1, 2 and 3, this base[7] was separated as the picrate which after four recrystallizations from 60% acetic acid was obtained in lemon-colored, long rectangular microscopic plates, melting at 216° without decomposition. This salt is readily soluble in glacial acetic acid but only sparingly soluble in other common solvents.

Anal. Calcd. for $C_{20}H_{20}O_7N_4$: C, 56.07; H, 4.71; N, 13.08. Found: C, 56.00; H, 4.51; N, 13.11.

Free Base.—The base was liberated from the picrate and recrystallized from methyl alcohol in ill-defined microscopic plates. The following constants were determined: m. p. 52.5–53.0°; b. p. 320°; $n^{64}D$ 1.5798. Methyl alcohol has proved a selective solvent in recrystallization of 2,3,4-trimethyl kero quinolines alkylated at position 8.[3]

Anal. Calcd. for $C_{14}H_{17}N$: C, 84.42; H, 8.54; N, 7.03. Found: C, 84.23; H, 8.29; N, 7.19.

2,3,4-Trimethylquinoline-8-carboxylic Acid.—To a boiling solution of 1 g. of the base in 6 *N* sulfuric acid, a mixture of 2.5 g. of potassium dichromate, 3.8 g. of sulfuric acid and 4.2 g. of water is added slowly. The reaction is complete in twelve hours. The solution is cooled, made alkaline with ammonium hydroxide, acidified with acetic acid and extracted with chloroform. The acid crystallizes from alcohol in needles melting at 233.5–234.0°. A mixed

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

(2) Ernst Jantzen, "Das fraktionierte Destillieren und das fraktionierte Verteilen," Verlag Chemie, Berlin, 1932, pp. 117–137.

(3) Axe and Bailey, THIS JOURNAL, **60**, 3031 (1938).

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

(5) Morton, "Laboratory Technique in Organic Chemistry," McGraw-Hill Book Company, Inc., New York, N. Y., 1938, p. 200.

(6) Axe and Bailey, THIS JOURNAL, **61**, 2609 (1939).

(7) None of the base was found in Fraction 4, but here 24 g. of the crude picrate of 2,3,4,8-tetramethylquinoline was encountered (Axe and Bailey, reference 3).