Experimental

Fractions 3 and 4 previously obtained (ref. 4, Table I) were combined and fractionated into 12 cuts of 12 ml. each. Their boiling points at 2 mm. increased regularly from 145.0 to 155.5°, and the refractive indices $n^{16}D$ of the first and last samples were 1.5845 and 1.5890, respectively. Those of the other fractions varied irregularly within the narrow limits of 1.5870 and 1.5879, respectively.

2,3,4-Trimethyl-8-*i*-propylquinoline.—On cooling to −10° a solution of fractions 5 to 9, inclusive, in six volumes of methanol, 3 g. of this base separated. It was recrystallized from the same solvent in small needles of m. p. 106–107° and b. p. 327° (750 mm.).

Anal. Calcd. for $C_{15}H_{19}N$: C, 84.45; H, 8.98; N, 6.57. Found: C, 84.31; H, 9.00; N, 6.49.

2,3,4-Trimethylquinoline-8-carboxylic Acid.—The base (0.5 g.) in dilute sulfuric acid was oxidized with the calculated quantity of potassium dichromate in 6 *N* sulfuric acid to 2,3,4-trimethylquinoline-8-carboxylic acid, which was identified by the usual comparison with an authentic sample.[6]

Picrate.—This salt was prepared in the usual way and recrystallized from alcohol in yellow needles melting at 165–166°. In comparison with picrates of other petroleum quinolines, it is more readily soluble in organic solvents.

Anal. Calcd. for $C_{21}H_{22}O_7N_4$: C, 57.07; H, 5.01. Found: C, 57.05; H, 5.03.

Nitrate.—The calculated amount of concentrated nitric acid added to an acetone–ether solution of the base precipitated the nitrate which was recrystallized from water in long needles melting with decomposition at 143–144°.

Anal. Calcd. for $C_{15}H_{19}N \cdot HNO_3$: C, 65.18; H, 7.23; NO_3, 22.44. Found: C, 65.05; H, 7.41; NO_3, 22.54.

Acid Sulfate.—The salt was formed on addition of the calculated volume of concd. sulfuric acid to the base in acetone, and crystallizes from absolute alcohol in irregular platelets melting at 204–205° undecomposed.

Anal. Calcd. for $C_{15}H_{19}N \cdot H_2SO_4$: SO_4, 30.86. Found: SO_4, 30.71.

Synthesis of 2,3,4-Trimethyl-8-*i*-propylquinoline.—Cumene was nitrated at 0° with a mixture of concd. nitric and sulfuric acids to *o*- and *p*-nitrocumene, which were segregated by fractional distillation. A quantitative reduction of the *o*-isomer to *o*-cumidine in one-half hour was effected through hydrogenation over Raney nickel catalyst at 70° and 2600 lb. pressure. The quinoline base was synthesized by condensation of methylacetylacetone and *o*-cumidine.[7] Here is involved elimination of two molecules of water in a double phase reaction. As concerns the present preparation, it was found advantageous in the initial condensation to reflux the intermediates only a few minutes rather than to follow the standard procedure of prolonged heating at steam-bath temperature. A mixed melt of the synthetic and petroleum base showed no depression.

Summary

The isolation of 2,3,4-trimethyl-8-*i*-propylquinoline from California petroleum is reported. Its structure was established through chromic acid oxidation to the known 2,3,4-trimethylquinoline-8-carboxylic acid and was confirmed by synthesis from methylacetylacetone and *o*-cumidine.

AUSTIN, TEXAS RECEIVED JANUARY 20, 1941

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF TEXAS]

The Nitrogen Compounds in Petroleum Distillates. XXII. Isolation and Synthesis of 2,3-Dimethyl-4,8-diethylquinoline (I) and 2,3-Dimethyl-4-ethyl-8-*n*-propylquinoline (II)

BY LESLIE M. SCHENCK AND J. R. BAILEY

Introduction

For isolation of base I, highly processed fractions of aromatic kero bases in the 320–330° range were employed.[1] Initially, the bases were precipitated in acetone–ether solution as nitrates which were converted to picrates. Purification was effected by recrystallization of the picrates in alcohol, followed by conversion to acid sulfates, then back to picrates, the procedure being repeated until the preparation had a constant melting point.

Three specific properties of II contributed to a segregation from admixtures: (1) in contrast to I it separated as acid sulfite[2] in the form of an oil when base fractions suspended over sodium sulfite, chloride or nitrate brine were salified with sulfurous acid; (2) from acetone–ether solution of the base, liberated by degassing the acid sulfite,[3] concentrated nitric acid precipitated the

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(1) This material was furnished the Texas Laboratory by the Union Oil Company of California; Schenck and Bailey, THIS JOURNAL, **61**, 2613 (1939).

(2) Through employment of so-called sulfiting over sodium chloride brine, C. O. Edens and J. R. Bailey in unpublished research discovered that a series of 2,3-dimethyl-8-alkylquinolines, in contrast to 2,4-dimethyl-8-alkyl analogs, are precipitated as base hydrochlorides. Where nitrate brine was used, only base-acid sulfites separated.

(3) *Cf.* Stiles M. Roberts and J. R. Bailey, THIS JOURNAL, **60**, 3025 (1938).

crystalline nitrate; (3) finally the nitrate was recrystallized to purity from water.

In partial proof of structure of I and II, chromic acid oxidation in each case yielded the same $C_{13}H_{14}NCOOH$ acid, thus revealing the origin of the carboxyl to be an ethyl and propyl, respectively. Quinoline rather than isoquinoline structure appeared probable because the latter type of compound from petroleum has not been reported. The ease of chromic acid oxidation of the bases indicated an alkyl on the *Bz*-nucleus and, since no petroleum quinoline homolog with a substituent at position 5, 6 or 7 has been encountered in this Laboratory, alkylation at position 8 was inferred.

Confirmation of a methyl at position 2 followed from precipitation of a red sodium salt on addition of sodium alcoholate to an alcoholic solution of the phthalones.

Among the ozonolysis products of the ozonide of II, *n*-butyric acid[4] was isolated, thus revealing *n*-propyl rather than *i*-propyl as a substituent.

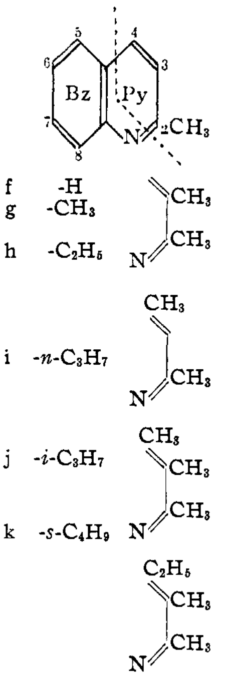
Based on the correctness of the above structural forecasts, and the absence of a propyl on the *Py*-nucleus, two of the remaining carbon atoms not accounted for had to be in the form of an ethyl at position 3 or 4; *i. e.*, each base contains a 2,3-dimethyl-4-ethyl or a 2,4-dimethyl-3-ethyl nucleus. On a chance assumption of an ethyl at position 4, syntheses were carried out by a modification of the Beyer synthesis of 2,4-dimethylquinoline[5] and products were obtained identical with the new petroleum bases. The intermediates used were diethyl ketone and paraldehyde, along with *o*-aminoethylbenzene for I and *o*-amino-*n*-propylbenzene for II.

When it is considered that the available supply of base I was 1.5 g. and of base II 11 g., the attainable refinement in this field of petroleum research is, to say the least, exceptional.

Until recently no quinoline homolog had been isolated from petroleum with alkylation of the *Py*-nucleus higher than methyl. With the discovery of 2,3,8-trimethyl-4-ethylquinoline[6] the initial representative of a new series of bases was contributed. In this paper, the series is extended to include bases I and II. The present status of petroleum quinoline bases is clarified in the subjoined Structural Digram I.[7]

DIAGRAM 1.—THE QUINOLINE HOMOLOGS ISOLATED FROM PETROLEUM DISTILLATES

The bases thus far isolated include quinoline and the following homologs:



A	Af	quinaldine
	Ag	2,8-dimethylquinoline
	Ah	2-methyl-8-ethylquinoline
B	Bf	2,3-dimethylquinoline
	Bg	2,3,8-trimethylquinoline
	Bh	2,3-dimethyl-8-ethyl
	Bi	2,3-dimethyl-8-*n*-propyl
C	Cf	2,4-dimethylquinoline
	Cg	2,4,8-trimethylquinoline
	Ch	2,4-dimethyl-8-ethyl
	Ci	2,4-dimethyl-8-*n*-propyl
	Ck	2,4-dimethyl-8-*s*-butyl
D	Dg	2,3,4,8-tetramethylquinoline
	Dh	2,3,4-trimethyl-8-ethyl
	Di	2,3,4-trimethyl-8-*n*-propyl
	Dj	2,3,4-trimethyl-8-*i*-propyl
E	Eg	2,3,8-trimethyl-4-ethyl
	Eh	2,3-dimethyl-4,8-diethyl
	Ei	2,3-dimethyl-4-ethyl-8-*n*-propyl

Experimental

Fractions 2, 3 and 4[8] were combined and salified in acetone–ether solution with nitric acid (sp. gr. 1.42). The precipitated nitrates were converted in alcohol directly to picrates, from which the bases were liberated and precipitated in acetone with the calculated amount of sulfuric acid (sp. gr. 1.84) as acid sulfates, an exchange in the last two types of salts being repeated, along with recrystallization of all picrate portions, until a pure product in the form of yellow plates melting at 174–175° was obtained.

Anal. Calcd. for $C_{21}H_{22}O_7N_4$: C, 57.01; H, 5.01; N, 12.66. Found: C, 56.77; H, 5.00; N, 12.71.

2,3-Dimethyl-4,8-diethylquinoline.—On the base, liberated from the picrate by the usual procedure and the resultant odorless oil dried over sodium hydroxide pellets, the following constants were determined: b. p. 319° (752 mm.), n^{20}_{D} 1.5871, d^{25}_{4} 1.008.

Anal. Calcd. for $C_{15}H_{19}N$: C, 84.45; H, 8.98. Found: C, 84.31; H, 8.92.

Acid Sulfate.—This salt was precipitated with a molar amount of concentrated sulfuric acid from an acetone solution of the base. It crystallized in small needles from absolute alcohol melting undecomposed at 170–171°.

Anal. Calcd. for $C_{15}H_{19}N \cdot H_2SO_4$; SO_4, 30.86. Found: SO_4, 30.91.

2,3-Dimethyl-4-ethylquinoline-8-carboxylic Acid.—Potassium dichromate (12 g.) in 6 *N* sulfuric acid was added dropwise to the base (0.5 g.) in 20 ml. of 12 *N* sulfuric acid heated under reflux. The carboxylic acid from chloroform

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[4] *Cf.* Schenck and Bailey, THIS JOURNAL, **62**, 1967 (1940).

[5] C. Beyer, *J. prakt. Chem.* (2) **33**, 393 (1886).

[6] R. A. Glenn and J. R. Bailey, THIS JOURNAL, **63**, 637 (1941).

[7] For the original diagram, see Schenck and Bailey, *ibid.*, **61**, 2614 (1939). Quinoline and quinaldine were isolated by C. A. Walker and J. R. Bailey, unpublished research, The University of Texas.

[8] The condensed data pertaining to these fractions are enumerated by Schenck and Bailey, THIS JOURNAL, **63**, 1364 (1941).

extraction recrystallized from alcohol in long needles melting undecomposed at 177–178°. A mixed melting point determination of this acid and an authentic sample[6] showed no depression.

Anal. Calcd. for $C_{14}H_{15}O_2N$: C, 73.36; H, 6.55; N, 6.11. Found: C, 73.06; H, 6.50; N, 5.95.

Synthesis of 2,3-Dimethyl-4,8-diethylquinoline.—In accordance with a simplified Beyer procedure for the preparation of 2,4-dimethylquinoline,[5] a mixture of 24.6 cc. of diethyl ketone and 9 cc. of paraldehyde was saturated with dry hydrogen chloride at 0° and, after standing eight hours, was poured into 12.11 g. of *o*-aminoethylbenzene dissolved in 20.4 cc. of concentrated hydrochloric acid and heated on the steam-cone for two hours. The reaction mixture was then diluted with water, non-basic admixtures were extracted with ether and the quinoline base was freed with an over-all yield of 25% from the aqueous layer with caustic. Its picrate, which was prepared in dilute sulfurous acid, on purification showed no depression in a mixed melt with a picrate sample of the petroleum base.

Where the yield of this base is of primary importance, no doubt the lengthy procedure of Beyer may be preferable.

Isolation of 2,3-Dimethyl-4-ethyl-8-*n*-propylquinoline (Base II).—A 130-ml. portion of fraction 2, Table II,[1] was agitated for one hour with an equal volume of saturated sodium nitrate brine in an ice-bath, sulfur dioxide being led in continuously to ensure complete salification of the bases. The acid-sulfite oily layer was separated and dissolved in a liter of acetone. After twelve hours, the precipitated solid base acid-sulfite was removed and dissolved in water. On heating the solution, the salt dissociated with evolution of sulfur dioxide and the water insoluble base. The latter was dissolved in an acetone–ether mixture, and salified with a slight excess of nitric acid (sp. gr. 1.42). The precipitated nitrate crystallized from water in long needles, melting with violent decomposition at 161°. The base was liberated with caustic, ether extracted, and dried over pellets of sodium hydroxide. After evaporation of the solvent, the following constants were determined on the residual odorless base: b. p. 327° (752 mm.), n^{20}_D 1.5751, d^{25}_4 1.003.

Anal. Calcd. for $C_{16}H_{21}N$: C, 84.72; H, 9.32; N, 6.17. Found: C, 84.84; H, 9.30; N, 6.07.

Acid Sulfate.—Addition of the calculated amount of concentrated sulfuric acid to an acetone–ether solution of the base precipitates this salt as a viscous oil which crystallized from acetone in platelets melting undecomposed at 163–164°.

Anal. Calcd. for $C_{16}H_{21}N \cdot H_2SO_4$: C, 59.02; H, 7.13; N, 4.31. Found: C, 58.78; H, 7.22; N, 4.60.

2,3-Dimethyl-4-ethylquinoline-8-carboxylic Acid.—The base (2 g.) was oxidized in a manner analogous to that employed on 2,3-dimethyl-4,8-diethylquinoline. The acid proved identical with the one from oxidation of base I.

Ozonization of 2,3-Dimethyl-4-ethyl-8-*n*-propylquinoline.—Ozonolysis of the ozonide[4] from 1 g. of base yielded a mixture of aliphatic acids from which *n*-butyric acid was isolated and identified through the anilide, thus establishing the presence of a *n*-propyl substituent in the original compound.

Synthesis of 2,3-Dimethyl-4-ethyl-8-*n*-propylquinoline.—With the exception of a substitution of *o*-amino-*n*-propylbenzene as the primary amine, the procedure was the same as that followed in the synthesis of base I. A mixed melt of picrate samples of the synthetic and petroleum bases showed no depression.

Summary

The isolation of a new quinoline homolog, 2,3-dimethyl-4,8-diethylquinoline, from petroleum is reported. The use of sulfur dioxide in segregation of a second new nitrogen base, 2,3-dimethyl-4-ethyl-8-*n*-propylquinoline, is also described. The structure of these hitherto unknown petroleum bases has been established through degradation and confirmed by synthesis.

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[CONTRIBUTION FROM THE HALL LABORATORY OF CHEMISTRY, WESLEYAN UNIVERSITY]

Hexabenzylethane

BY G. ALBERT HILL, W. C. NELSON, R. L. DUNNELL AND L. S. MOODY

In 1909 Schmerda[1] reported the preparation of hexabenzylethane. The same substance was obtained by Trotman,[2] who accepted Schmerda's conclusions regarding its structure. By investigations in this Laboratory[3] the compound was shown to be tribenzylmethane.

The present study was undertaken to prepare the long-sought hydrocarbon, 2,2,3,3-tetrabenzyl-1,6-diphenylbutane, hexabenzylethane. For this purpose tribenzylmethyl bromide[4] was treated in dry ether, and in dry benzene, with sodium, with mercury, and with zinc. The substance most readily obtained, sometimes in yields of 90%, was 2-benzyl-1,3-diphenylpropene, m. p. 33.8°. It was identified by forming the dibromo derivative, 2-benzyl-1,2-dibromo-1,3-diphenylpropane,[5] melting at 127–128°.

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(1) Schmerda, *Monatsh.*, **30**, 387 (1909).

(2) Trotman, *J. Chem. Soc.*, **127**, 88 (1925).

(3) Hill, Little, Wray and Trimbey, THIS JOURNAL, **56**, 911 (1934).

(4) A comprehensive study of the tribenzylmethyl halides is now in progress in this Laboratory.

(5) Orechov and Grinberg, *J. Russ. Phys.-Chem. Soc.*, **48**, 1713 (1916); *J. Chem. Soc.*, **112**, 450 (1917).