

[CONTRIBUTION NO. 304 FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF TEXAS]

The Nitrogen Compounds in Petroleum Distillates. XXIV. Isolation and Identification of a $C_{11}H_{17}N$ Base from California Petroleum

BY H. L. LOCHTE, W. W. CROUCH¹ AND E. D. THOMAS

The identification of the $C_{16}H_{25}N$ base isolated by Thompson and Bailey² from the kerosene distillates of California petroleum as 2-(2,2,6-trimethylcyclohexyl)-4,6-dimethylpyridine³ suggests that the so-called "non-aromatic" bases of Perrin and Bailey⁴ might consist of mixtures of highly substituted pyridines. These bases are separated from the other bases present in kerosene distillates by extraction of an aqueous solution of the mixed base hydrochlorides with chloroform, the "non-aromatic" base hydrochlorides being found in the chloroform layer. The mixture of bases remaining in the water layer always has the higher refractive index and density, and a number of these compounds have been identified by Bailey and co-workers as alkylated quinolines.

Besides the $C_{16}H_{25}N$ base, two other bases having physical constants and chemical properties similar to the known alkylated pyridines have been isolated previously from the chloroform-soluble hydrochlorides of petroleum bases. These are a $C_{10}H_{15}N$ base isolated by Roberts⁵ and a $C_{13}H_{21}N$ base isolated by Armendt,⁶ neither of which has been identified.

The bases used in this study were recovered from the hydrochlorides found in the chloroform layer after extraction of an aqueous solution of the hydrochlorides of kerosene bases boiling at 210–213°. After fractional distillation and fractional extraction with hydrochloric acid, the fractions were sufficiently pure to form crystalline picrates from which pure bases were recovered. A $C_{11}H_{17}N$ base was isolated and identified as *dl*-2-*s*-butyl-4,5-dimethylpyridine by the following facts: (1) condensation of the base with benzaldehyde to form a mono-addition compound indicated that one methyl group was in position 2, 4 or 6 on the pyridine ring. (2) Failure of the base to condense with acetic anhydride to form a picolide showed that the reactive methyl group was not in position 2 or 6. (3) Ozonolysis to pro-

duce diacetyl indicated that two methyl groups were present in adjacent positions. (4) Isolation of the amide of *dl*-methylethylacetic acid after ozonolysis showed that a secondary butyl group was at position 2. (5) The structure was confirmed by permanganate oxidation to give pyridine-2,4,5-tricarboxylic acid.

Small quantities of two other bases were isolated by means of crystalline picrates analysis of which corresponded to formulas of $C_{12}H_{19}N$ and $C_{13}H_{21}N$ for the bases. While not obtained in sufficient quantities for identification, the physical characteristics and formulas of the bases suggest that they are probably alkylated pyridines.

Experimental

The material for this investigation consisted of 6.8 liters of bases that had been obtained from kerosene distillates, carefully fractionated and donated to this Laboratory in 1940 by the Union Oil Company of California. The boiling point of the material used ranged from 210–213° and the index of refraction at 20° from 1.4982 to 1.5040. The mixture was acidified with 3750 cc. of concentrated hydrochloric acid in 4 kg. of chipped ice, then divided into six aliquots and extracted by stirring successively with six portions of 1500 cc. of chloroform, the chloroform then being washed with 800-cc. portions of water similar to the multiple-fractional-extraction method described by Morton.⁷ The chloroform was distilled off and the base was recovered by addition of sodium hydroxide solution. In this way there was obtained 2 liters of material with n_D^{20} 1.4922–1.4904. It was combined and distilled at 20 mm. through a 12-ft. packed column with 10:1 reflux ratio; b. p. 99–103° (20 mm.).

Fractional Acid Extraction.—The highest boiling material from the distillation, 190 g. with n_D^{20} 1.4916, was dissolved in 500 cc. of petroleum ether and extracted in thirteen fractions using the apparatus of Fig. 1. A 1.5 *N* solution of hydrochloric acid was introduced into the top flask, extracting the base from the solvent and passing down the spinner⁸ column. At the bottom of the column, 1.5 *N* sodium hydroxide solution was added at one-half the rate of addition of the acid so that one-half of the base was released and carried up the column by the rising stream of petroleum ether, thus furnishing reflux for the descending salt solution. The aqueous extract was taken off in 300-cc. portions from which the base was recovered, volume and refractive indices of the fractions being shown in Table I.

(1) Research Assistant, University Research Institute Project No. 49.

(2) Thompson and Bailey, *THIS JOURNAL*, **53**, 1002 (1931).

(3) Shive, Roberts, Mahan and Bailey, *ibid.*, **64**, 909 (1942).

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

(5) Roberts, Ph.D. Thesis, The University of Texas, 1939.

(6) Armendt, Ph.D. Thesis, The University of Texas, 1932.

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

(8) Schutze and Lochte, *Ind. Eng. Chem., Anal. Ed.*, **10**, 675 (1938).

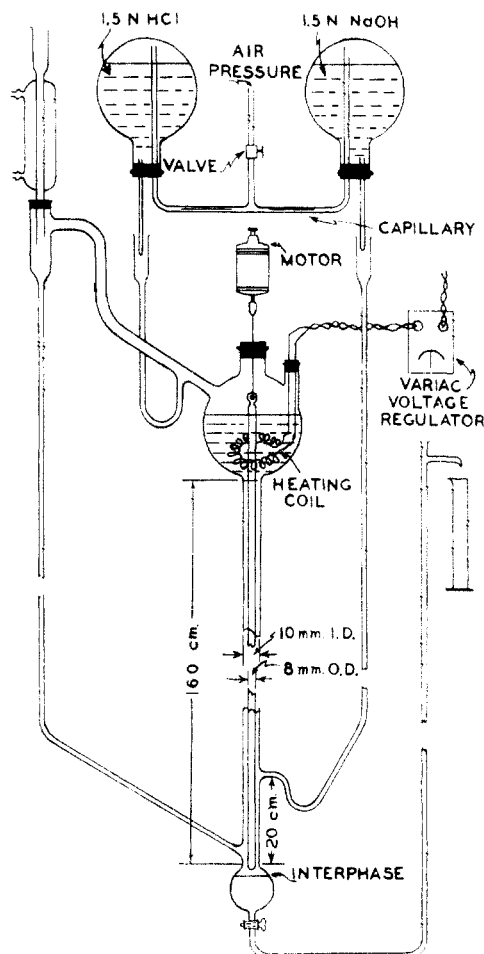


Fig. 1.

Isolation of the $C_{11}H_{17}N$ Base.—To one-gram samples of these fractions dissolved in sulfurous acid solution, 1.5 g. of picric acid in saturated aqueous solution was added. Oily picrates formed but after several days in the icebox the picrate of fraction 6 crystallized. It was recrystallized from ethyl alcohol and dilute acetic acid to a constant melting point of 127–128°.

Anal. Calcd. for $C_{17}H_{26}O_7N_4$: C, 52.04; H, 5.14; N, 14.28. Found: C, 52.12; H, 4.99; N, 14.13.

By seeding the other fractions with the pure picrate,

TABLE I

Fraction no.	Volume, cc.	n_{20}^D
1	8	1.4943
2	12	1.4921
3	12	1.4921
4	13	1.4931
5	10	1.4938
6	14	1.4938
7	14	1.4936
8	13	1.4925
9	13	1.4907
10	15	1.4901
11	14	1.4880
12 (Residue)	33	1.4871

crystals were obtained from fractions 4–8. They were recrystallized until pure and warmed with excess concentrated ammonium hydroxide to give the free base which was separated, washed, dried over solid sodium hydroxide and distilled; b. p. 214° (752 mm.); d_4^{20} 0.8991; n_{20}^D 1.4947.

Anal. Calcd. for $C_{11}H_{17}N$: C, 80.92; H, 10.50; N, 8.58. Found: C, 80.89; H, 10.44; N, 8.47.

From fractions 5 and 6, 40% by weight of the mixture was recovered as pure base. More of the base was obtained by processing in a similar way petroleum bases from the same source boiling at 214–215.5°.

Condensation of the $C_{11}H_{17}N$ Base with Benzaldehyde.

Two grams of the base, 4 g. of benzaldehyde and 0.5 g. of zinc chloride were heated for twenty-four hours at 200° in a sealed tube. The dark, viscous product was shaken with 2 N hydrochloric acid but only a few drops of base was recovered from the water layer. The residue was washed twice with ether to remove benzaldehyde, made alkaline with sodium hydroxide solution, separated, dissolved in alcohol and added to two grams of picric acid in alcohol. Three grams of the picrate of the benzal derivative was obtained which was recrystallized to a constant melting point of 143°.

Anal. Calcd. for $C_{24}H_{24}O_7N_4$: C, 59.99; H, 5.03. Found: C, 59.98; H, 5.05.

Attempted Condensation of the $C_{11}H_{17}N$ Base with Acetic Anhydride.

Following the procedure employed by Scholtz⁹ for the condensation of acetic anhydride with 2-methyl- and 2,4-dimethylpyridine, 1.7 g. of the natural base was heated with 10 g. of acetic anhydride for eight hours at 210° in a sealed tube. The dark, resinous product was heated with water, alcohol and chloroform in an attempt to obtain a crystalline picolide. No such compound was obtained by cooling or evaporating the solvents.

Ozonolysis of the $C_{11}H_{17}N$ Base.—Through 4 g. of the $C_{11}H_{17}N$ base dissolved in 20 cc. of carbon tetrachloride and cooled to 0° there was passed a stream of 10% ozone at a rate of 1200 cc. per hour for four hours. Five grams of 30% sodium hydroxide solution was added and the mixture shaken vigorously for ten minutes, during which white crystals separated. They were filtered off, the carbon tetrachloride layer was dried, and the ozonolysis repeated. In this way, 250 mg. of amide was obtained melting, after recrystallization from benzene-petroleum ether, at 112°. A mixed melting point showed it to be the amide of *dl*-methylethylacetic acid.

Anal. Calcd. for C_5H_9ON : N, 13.85. Found: N, 13.71.

The ozonolysis was repeated, the ozonide was decomposed by adding water and stirring, and *p*-nitrophenylhydrazine hydrochloride solution was added to the product. The mixture was warmed and the dark red crystals of the *p*-nitrophenylosazone of diacetyl separated. It was recrystallized from nitrobenzene and melted with decomposition at 332°. The melting point and mixed melting point of this derivative of synthetic diacetyl showed the two compounds to be identical.

Permanganate Oxidation of the $C_{11}H_{17}N$ Base.—Ten grams of the base was added to two liters of 2% potassium

(9) Scholtz, *Ber.*, **45**, 734 (1912).

permanganate solution and the mixture was stirred on a steam-bath with reflux. After twelve hours the solution was decolorized and 40 g. more of potassium permanganate was added in concentrated solution. After twelve hours the addition was repeated, after which the solution was not completely decolorized by heating for four days. The excess permanganate was reduced with formaldehyde, the solution was filtered, concentrated to 200 cc. and neutralized with dilute nitric acid. Silver nitrate solution was added and the flocculent precipitate of silver salt was filtered, washed, dissolved in ammonium hydroxide and reprecipitated in three fractions by the slow addition of 1 *N* nitric acid. The second fraction was suspended in water and hydrogen sulfide passed into the mixture. The silver sulfide was removed and the solution evaporated to leave white crystals of pyridine-2,4,5-tricarboxylic acid, melting with decomposition at 242–243°. It was recrystallized from dilute hydrochloric acid from which it precipitated slowly. The air-dried sample was heated one hour at 120° to remove water of crystallization.¹⁰

Anal. Calcd. water of crystallization for $C_8H_5O_6N \cdot H_2O$: H_2O , 7.86. Found: H_2O , 7.90.

The anhydrous acid was analyzed for nitrogen.

Anal. Calcd. for $C_8H_5O_6N$: N, 6.63. Found: N, 6.69.

The acid was readily soluble in water and gave a dark red color with ferrous sulfate solution. It was heated to 170° without appreciable carbon dioxide evolution, a reaction that is reported¹¹ to be rapid above 140° for pyridine-2,3,6-tricarboxylic acid. It was apparently unaffected by boiling for two hours with acetic anhydride, giving none of the chloroform-soluble cinchomeronic anhydride which is formed¹² by this treatment of pyridine-2,3,4-tricarboxylic acid.

Isolation of a $C_{12}H_{19}N$ Base.—An intermediate fraction of bases from the distillation described above, 80 g. with

(10) Weidel, *Ber.*, **12**, 410 (1879).

(11) Weiss, *ibid.*, **19**, 1310 (1886).

(12) Kirpal, *Monatsh.*, **26**, 53 (1905).

n_D^{20} 1.4904 and b. p. 101° (20 mm.), was extracted from 500 cc. of petroleum ether in seven fractions using the apparatus of Fig. 1. Fraction 6 was converted to the picrate as described above, giving a crude picrate which was recrystallized repeatedly from dilute ethanol and dilute acetic acid to a constant melting point of 174°.

Anal. Calcd. for $C_{18}H_{22}O_7N_4$: C, 53.20; H, 5.46. Found: C, 53.20; H, 5.51.

One-half gram of the picrate was heated with concentrated ammonium hydroxide to liberate the base which was extracted in ether, dried and distilled in a semi-micro distillation apparatus. A middle fraction gave the following constants: b. p. 214° (754 mm.); n_D^{20} 1.4832.

Anal. Calcd. for $C_{12}H_{19}N$: N, 7.90. Found: N, 7.79.

Isolation of a $C_{13}H_{21}N$ Base.—Fraction 7 of the extraction series described above from which the $C_{12}H_{19}N$ base was obtained was converted to the picrate and recrystallized repeatedly to give yellow needles having a constant melting point of 121°.

Anal. Calcd. for $C_{19}H_{24}O_7N_4$: C, 54.28; H, 5.75; N, 13.33. Found: C, 53.87; H, 5.74; N, 13.52.

Summary

1. A sample of California petroleum bases boiling at 210–213° has been fractionated by efficient methods of extraction and distillation to yield products of sufficient purity that crystalline picrates of three new bases were obtained.

2. By a process of degradation a $C_{11}H_{17}N$ base has been identified as *dl*-2-*s*-butyl-4,5-dimethylpyridine.

3. Two other bases having molecular formulas of $C_{12}H_{19}N$ and $C_{13}H_{21}N$ were isolated in quantities too small for identification. It is believed that they are also alkylated pyridines.

AUSTIN, TEXAS

RECEIVED JULY 31, 1942

[CONTRIBUTION FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 909]

Stereoisomeric Diphenyloctatetraenes

By L. ZECHMEISTER AND A. L. LERSEN

While some earlier authors¹ have denied the existence of *cis*–*trans* isomers in the case of an extended conjugated double bond system, Kuhn² correctly summarized the situation in 1933 by the following statement: “. . . according to the available evidence a strong accumulation of double bonds does not exclude the occurrence of *cis*–*trans* isomerism. That the higher diphenylpolyenes are known only in one spatial form is due to the in-

(1) G. Wittig and W. Wiemer, *Ann.*, **483**, 144 (1930).

(2) R. Kuhn, in Freudenberg's "Stereochemie," F. Deuticke, Vienna, 1933, p. 915.

adequacy of the preparative methods.” In the series mentioned, $C_6H_5(CH=CH)_n C_6H_5$, so far as we know, stereoisomeric forms have been obtained³ only in the case $n < 3$. According to X-ray studies by Hengstenberg and Kuhn⁴ the prepa-

(3) F. Straus, *Ann.*, **342**, 190 (1905). An alleged white modification of diphenyl-octatetraene (H. Stobbe, *Ber.*, **42**, 567 (1909)) was later identified as stilbene by R. Kuhn and A. Winterstein (footnote 5). Accordingly, text and formulas on pp. 179–180 of the following book should be corrected: G. Egloff, G. Hulla and V. I. Komarewsky, "Isomerization of Pure Hydrocarbons," Reinhold Publishing Corp., New York, N. Y., 1942.

(4) J. Hengstenberg and R. Kuhn, *Z. Krystall. Miner.*, **75**, 301 (1930).