Esters could uot be made with chloro- or bromoacetic acids. With phthalic anhydride at 130–140° for one hour the bis-monophthalate, the sodium salt of which gave precipitates with salts of the heavy metals, was formed along with a heavy neutral oil which could not be purified, apparently the neutral ester. This predominates when the reaction temperature is higher, 150–160°, regardless of the proportion of the anhydride.

Other Reactions.—Condensation took place when thiodiglycol was heated with dimethylaniline, raising the temperature gradually from 120 to 160° in eighteen hours with the addition of zinc chloride in portions. The product was a heavy oil boiling at 204–210° (8 mm.), containing sulfur and dissolving in dilute acids.

Mustard gas sulfoxide, $(ClCH_2CH_2)_2SO$, was refluxed with potassium acetate in absolute alcohol and also in acetic acid but no reaction could be detected in either case.

The sulfone, $(ClCH_2CH_2)_2SO_2$, was refluxed with potassium acetate in acetic acid solution; a reaction took place. After filtering off the salt and volatilizing the acetic acid, a reddish viscous liquid remained for which no method of purification could be found. Potassium i-valerate gave a similar product. From the sulfone and sodium benzoate in absolute alcohol the calculated amount of sodium chloride was obtained along with benzoic acid. The benzoate of thiodiglycol has been oxidized to the corresponding sulfoxide and sulfone.[5]

Summary

Thiodiglycol has been purified and its properties determined. Several esters have been made from it and their properties determined.

(5) Fromm and Kohn, *Ber.*, **54**, 321 (1921).

BALTIMORE, MD.   RECEIVED JANUARY 3, 1942

The Nitrogen Compounds in Petroleum Distillates. XXIII. The Structure of a C₁₆H₂₅N Base from California Petroleum[1]

BY BILLIE SHIVE,[2,3] STILES M. ROBERTS,[4] R. I. MAHAN[5] AND J. R. BAILEY[6]

In Edeleanu kerosene extract from California petroleum[7] there occurs in relatively large amounts a C₁₆H₂₅N base which was first isolated by Thompson and Bailey[8] and for which several provisional structures have been proposed.[8,9,10] It has now been shown that the base is 2-(2,2,6-trimethylcyclohexyl)-4,6-dimethylpyridine (I).

I
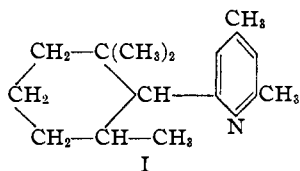
Earlier positive contributions to the structure indicated that the compound contained a pyridine nucleus with two methyl groups and a C₉H₁₇-alicyclic radical as substituents in positions 2, 4

and 6, the exact location of the individual groups being indefinite.

The present investigations deal both with the chemical behavior of the hydrogenated product of the C₁₆H₂₅N base and with the ozonization of the original base. Approximately 48% of the hydrogenation product solidified and melted at 60.5° after purification, while 52% of the product is a liquid, the two compounds evidently being geometrical isomers. Ring cleavage and removal of the nitrogen atom was achieved by the method of von Braun,[11] by which benzoylpiperidine may be converted to pentamethylene dibromide. The steps involved in this degradation are

$$C_{16}H_{25}N \xrightarrow[\text{Raney nickel}]{H_2} C_{16}H_{31}N \xrightarrow[\text{anhydrous pyridine}]{\text{Benzoylation in}}$$

$$C_{16}H_{30}NCO(C_6H_5) \xrightarrow{PBr_5} C_{16}H_{30}NCBr_2(C_6H_5) \xrightarrow[\text{in vacuum}]{\text{Distillation}}$$

$$C_{16}H_{30}Br_2 \text{ (II) and } C_6H_5CN$$

The dibromide (II), obtained by this method, was converted into an olefin, C₁₆H₂₈ (III), by treatment with methyl alcoholic potassium hydroxide. In conformity with formula (I) for the C₁₆H₂₅N base, the structure of (III) should be $C_9H_{17}CH{=}CH{-}CH(CH_3){-}CH{=}CH{-}CH_3$. Complete analysis established the existence of two double bonds and a cyclic structure within

(1) From Ph.D. theses of R. I. Mahan (1938), Stiles M. Roberts (1939), and Billie Shive (1941).

(2) University of Texas Research Institute Research Assistant (1941).

(3) Present address: Chemistry Department, University of Illinois, Urbana, Illinois.

(4) Present address: Research Laboratory, Texas Company, Beacon, N. Y.

(5) Present address: Union Oil Company, Wilmington, California.

(6) The experimental work on which this paper is based was completed before the death of Professor Bailey.

(7) The authors are indebted to the Union Oil Company for donation of large supplies of petroleum bases.
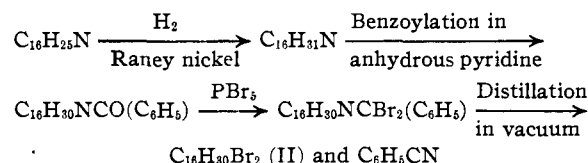
(8) Thompson and Bailey, THIS JOURNAL, **53**, 1002 (1931).

(9) Armendt and Bailey, *ibid.*, **55**, 4145 (1933).

(10) Lackey and Bailey, *ibid.*, **56**, 2741 (1934).

(11) von Braun, *Ber.*, **37**, 3210 (1904); **38**, 2339 (1905).

the molecule. Ozonolysis of this hydrocarbon yielded acetaldehyde and a $C_9H_{17}COOH$ acid. The $C_{16}H_{28}$ unsaturated compound proved to be a mixture presumably of geometrical isomers of which four are possible; however, ozonolysis should yield the same acid—a prediction borne out by data.

The position of the C_9H_{17}-substituent on the pyridine nucleus of the $C_{16}H_{25}N$ base was conclusively established by the unexpected discovery that direct ozonolysis of the base led to the formation of the amide of the $C_{10}H_{18}O_2$ acid which was obtained previously in the degradation of the benzoyl derivative of the hydrogenated base. The isolation of this amide was made possible by its great stability toward hydrolysis. The reactions involved may be depicted as

$$C_9H_{17}CONH_2 + 2CH_3COOH + 2HCOOH$$
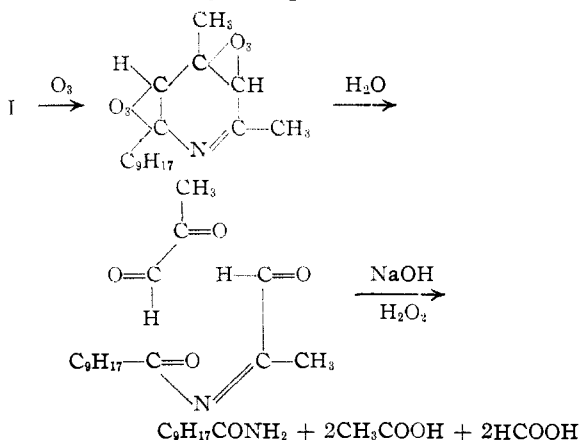
The C_9H_{17}-radical must then be in the alpha position to the nitrogen of the pyridine ring to obtain the amide. Fortunately the $C_{10}H_{18}O_2$ acid, *trans*-2,2,6-trimethylcyclohexanecarboxylic acid, corresponding to this amide had just been studied intensively in connection with the discovery by Shive, Horeczy, Wash and Lochte[12] that this naphthenic acid is present in large amounts in straight run distillate from California petroleum; hence, its identification was easily accomplished. This establishes for the first time a structural correlation of a naphthenic base and a naphthenic acid from petroleum.

The most important of the earlier positive contributions to the structure of the base were: (1) isolation of pyridine-2,4,6-tricarboxylic acid[13] from the oxidation products of the base with di-

lute nitric acid proved alkylation at positions 2, 4 and 6. (2) Formation of a phthalone established the presence of a methyl group at position 2 or 6. (3) Condensation of the base with formaldehyde and nitric acid oxidation of the product yielded a dicarboxylic acid, $C_{14}H_{19}N(COOH)_2$, which was decarboxylated first to $C_{14}H_{20}NCOOH$ and then to $C_{14}H_{21}N$, indicating the presence of two reactive methyl groups. (4) Formation of a dibenzal derivative also indicated the presence of two reactive methyl groups. (5) High pressure hydrogenation in the presence of Raney nickel as a catalyst resulted at 250° in the consumption of six atoms of hydrogen[14] per molecule of the base. Dehydrogenation yielded the original base. The base with one mole of methyl iodide formed a quaternary ammonium salt which was not converted into a methylated free base by sodium hydroxide. The non-reactivity of the base with ammonium iodide and hydriodic acid in an atmosphere of carbon dioxide showed the absence of an N-alkyl group. All of these facts indicated that the base was a substituted pyridine.

One of the confusing facts about the base was its stability toward oxidizing agents. Alkaline permanganate as well as chromic acid have no effect at room temperature. Acid permanganate attacks the base but no product except carbon dioxide could be isolated.

Experimental

The material for this investigation was obtained from 18.5 liters of kerosene bases boiling between 279 and 284° with $n^{23}D$ values ranging from 1.5271 to 1.5303. These bases were converted to the hydrochlorides and then extracted with chloroform according to the method of Bailey and Perrin.[15] The hydrochlorides isolated from the chloroform layer were then recrystallized from acetone, and the base liberated from the purified hydrochloride. The base was then further purified through multiple fractional acid extraction,[16] the end fractions not corresponding in physical constants to those of the base being discarded. These operations yielded 1706 cc. of material, which was further purified through recrystallization of the free base from petroleum ether and of the nitrate of the base from water. The base finally obtained had the physical constants: b. p. 279–281° (747 mm.); m. p. 24.5°; $n^{25}D$ 1.5086; $n^{20}D$ 1.5106; picrate, m. p. 164°.

Hydrogenation of the $C_{16}H_{25}N$ Base.—Hydrogenation of the base to the corresponding piperidine was effected by means of hydrogen under 2000–6000 lb./sq. in. pressure

(12) Shive, Horeczy, Wash and Lochte, THIS JOURNAL, 64, 385 (1942).

(13) Thompson and Bailey originally reported this product as berberonic acid, pyridine-2,4,5-tricarboxylic acid, but a sample of the compound proved to be the 2,4,6-tricarboxylic acid as sublimation of the tricarboxylic acid yielded isonicotinic acid.

(14) We are indebted to Professor Homer Adkins, University of Wisconsin, for carrying out the initial hydrogenation of the base and reporting the hydrogen consumption.

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

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

at 250° in the presence of Raney nickel catalyst. On standing, the reduction mixture deposited crystals of the solid isomer, which after recrystallization from methanol melted sharply at 60.5°. A further crop of crystals was obtained upon standing for several days at −10° so that the total yield of solid product reached approximately 48% of the hydrogenated material.

Benzoylation of the $C_{16}H_{30}NH$ Base.—A slight excess of freshly distilled benzoyl chloride was allowed to drop into a stirred mixture of the hydrogenated base and three times the amount of *anhydrous* pyridine required to salify the hydrochloric acid liberated, at such a rate that the temperature remained between 27 and 30°. Then, while stirring was continued, the mass was heated on the steam cone for eight hours. The resulting reddish-brown mass was poured while still hot onto fifteen times its weight of cracked ice. Concentrated hydrochloric acid was then added until just acid to congo red. The heavy dark oil that remained was taken up in ether, dried and fractionated under reduced pressure. The benzoyl derivative formed a very viscous glassy sirup which may be obtained crystalline upon long standing or on recrystallization from 70% ethyl alcohol or from ethyl acetate as long hexagonal prisms terminated with hexagonal pyramids, m. p. 120.5°; b. p. 208–212° (3 mm.); yield, 92.5%.

Anal. Calcd. for $C_{23}H_{35}ON$: C, 80.88; H, 10.33. Found: C, 80.84; H, 10.35.

Action of Phosphorus Pentabromide on Benzoyl Derivative of the $C_{16}H_{30}NH$ Base.—To the light yellow colored solution produced by adding one mole of phosphorus tribromide to one mole of benzoyl derivative, one mole of anhydrous bromine was added with shaking and cooling. The reaction mixture was gradually heated until the rapid evolution of gas ceased, and finally heated to 140° for one-half hour. Next, the mixture was distilled under 10 mm. pressure until a dark yellow solid began to collect in the receiver. The distillate, which consisted of phosphorus oxychloride, benzonitrile and the dibromide, was poured onto ice in order to destroy the phosphorus oxychloride. The residual oily layer was heated under reflux with a large excess of 40% hydrobromic acid to hydrolyze the nitrile. Without purification, the ether-soluble material, after being washed with sodium carbonate solution, was refluxed for twenty-four hours with a large excess of methyl alcoholic potassium hydroxide. After removal of the alcohol followed by addition of water there remained an oil which, after distillation, corresponded to the formula $C_{16}H_{28}$, b. p. 109–115° (6 mm.); 260–267° (746 mm.).

Anal. Calcd. for $C_{16}H_{28}$: C, 87.19; H, 12.81. Found: C, 86.92; H, 12.69. *Titration.* Subs., 84.9 mg.; 14.12 cc. of 0.1062 N bromide–bromate solution. Calcd. for $C_{16}H_{28}$ with two double bonds: 14.50 cc.; for $C_{16}H_{28}$ with three double bonds: 21.75 cc.

Ozonolysis of the $C_{16}H_{28}$ Hydrocarbon.—A stream of ozonized oxygen was passed through a 20% solution of the hydrocarbon in anhydrous carbon tetrachloride, which was cooled to −10° as long as ozone was absorbed. The diozonide separated as a white wax-like solid but went back into solution when the solvent was allowed to warm to room temperature. The hydrolysis of the diozonide was effected by adding ice, followed by heating under reflux for four hours. Steam distillation was employed to re-

move the carbon tetrachloride and volatile ozonolysis products. The aqueous portion of the distillate, treated with dimethylamine and sodium nitroprusside, yielded an intense indigo coloration which is a specific test for acetaldehyde.[17] To the residue a strong solution of sodium hydroxide was added, and the reaction mixture was heated under reflux for several hours. Acidification, followed by extraction with ether, yielded an acid of the composition $C_{10}H_{18}O_2$, which was purified by sublimation under reduced pressure. On recrystallization from dilute acetic acid, the colorless and beautifully crystalline rectangular plates melted at 82–83°; yield, 29%.

Anal. Calcd. for $C_{10}H_{18}O_2$: C, 70.54; H, 10.65. Found: C, 70.53; H, 10.51.

The silver salt, prepared by adding silver nitrate to a dilute aqueous solution of the ammonium salt, was obtained as a fine white powder. It was purified by washing with water followed with acetone.

Micro Anal. Calcd. for $C_{10}H_{17}O_2Ag$: Ag, 38.93. Found: Ag, 38.94.

Degradation of the $C_{10}H_{18}O_2$ Acid.—The degradation of the $C_{10}H_{18}O_2$ acid to the $C_9H_{17}NH_2$ amine was carried out according to the method of K. F. Schmidt.[18] A slight excess of hydrazoic acid dissolved in chloroform was added to the acid dissolved in twice its volume of concentrated sulfuric acid at such a rate that a moderate evolution of nitrogen was observed. The temperature was kept between 35 and 40° until all the hydrazoic acid had been added and was then raised to 100° for a few minutes. The resulting solution was poured onto finely divided ice and the amine then liberated by addition of sodium hydroxide. The yield varied from 85 to 90%, b. p. 184–185° (747 mm.); d^{20}_4 0.8596; $n^{20}D$ 1.4596.

The picrate was prepared for the purpose of analysis by adding a saturated aqueous solution of picric acid to the base dissolved in sulfurous acid. It precipitated immediately and on recrystallization from dilute alcohol appeared as microscopic needles melting at 226–227°.

Anal. Calcd. for $C_{15}H_{22}O_7N_4$: C, 48.65; H, 5.99. Found: C, 48.78; H, 5.98.

Ozonolysis of the $C_{16}H_{25}N$ Base.—After investigation of several solvents for the ozonization and many methods of hydrolysis of the ozonide, the following procedure was found most feasible. A stream of ozonized oxygen was passed into a 20% solution of 5 g. of the base in carbon tetrachloride at room temperature for twenty-four hours. During the first part of the reaction, an oil separated. It dissolved on warming the solution.

Without removal of the solvent, hydrolysis of the ozonide was effected in 20% sodium hydroxide containing 5% hydrogen peroxide, the volume of this solution being proportioned so as to furnish four moles of sodium hydroxide per mole of the organic base. The function of the peroxide was to oxidize the aldehydes formed, thus inhibiting their polymerization in the caustic solution. *Since none of the amide or the corresponding acid is formed by hydrolysis of the ozonide in neutral or acid solution,* the function of the sodium hydroxide was to hydrolyze the —CO—N=C-(CH₃)— complex. After standing for thirty minutes, the

(17) Power and Chesnut, This Journal, **42**, 1509 (1920).
(18) Oesterlin, *Angew. Chem.*, **45**, 536 (1932).

mixture was refluxed one hour, cooled to 0°, and allowed to stand one hour. Separating in large cubical crystals, the amide—after filtering off and recrystallizing from petroleum ether—melted at 190–191° undecomposed; yield, 23% of theoretical.

Anal. Calcd. for $C_{10}H_{19}ON$: C, 70.96; H, 11.31. Found: C, 71.17; H, 11.10.

The carbon tetrachloride layer from the filtrate was dried over sodium sulfate and re-ozonized as above to give an additional 23% of the amide; total yield, 46% of the theoretical. The carbon tetrachloride layer from this first treatment was extracted with dilute hydrochloric acid to obtain 15% of the unchanged base. After evaporation of the solvent, there remained a small amount of neutral residue which gave qualitative reactions of an alcohol but was not further investigated.

Isolation of the $C_{10}H_{18}O_2$ Acid.—The sodium hydroxide layer from the ozonization of the base was acidified with dilute sulfuric acid and extracted with ether. The residual oil, after removal of the ether, was refluxed six hours with 2% methyl alcoholic hydrogen chloride. Following removal of alcohol, the residue was dissolved in ether and extracted with 10% sodium carbonate solution. Acidification of the alkaline solution gave an oil which was extracted with ether, dried over sodium sulfate and fractionated through a semi-micro column. All fractions solidified upon standing, and after recrystallization from dilute acetic acid, the product melted at 82–83° and by mixed melting point determination was shown to be identical with the $C_{10}H_{18}O_2$ acid obtained by degrading the benzoyl derivative of the $C_{16}H_{31}N$ base.

Hydrolysis of the $C_{10}H_{19}ON$ Amide.—A 20% solution of sodium hydroxide failed to completely hydrolyze the amide in a sealed tube at 140° for twelve hours. Refluxing with concentrated hydrochloric acid or dilute nitric acid gave an acid which was identical with that obtained from the ozonolysis products.

Degradation of the $C_{10}H_{19}ON$ Amide.—Six grams of the amide obtained by ozonolysis of the base was treated at 0°

with an equal molecular quantity of bromine dissolved also at 0° in six times the molecular quantity of 10% potassium hydroxide. The mixture was stirred vigorously one hour, then gradually heated to 70° and maintained with stirring at this temperature one hour. Steam distillation of the mixture, extraction of the distillate with ether, drying over potassium hydroxide pellets and fractionation gave a $C_9H_{17}NH_2$ amine identical in physical properties with that obtained by the action of hydrazoic acid upon the naphthenic acid. The mixed melting point of the picrates of the amines obtained by both methods showed no depression.

Proof of the Identity of the Naphthenic Acid (*trans*-2,2,6-Trimethylcyclohexanecarboxylic Acid) from Petroleum and the $C_{10}H_{18}O_2$ Acid from Degradation of the $C_{16}H_{25}N$ Base.—A mixture of the naphthenic acid isolated from California petroleum by Shive, Horeczy, Wash and Lochte[12] and shown to be *trans*-2,2,6-trimethylcyclohexanecarboxylic acid, and the acid obtained by degradation of the naphthenic base gave no depression in melting point, 82–83°. The amide of the isolated acid prepared through the acid chloride did not depress the melting point, 190–191°, of the amide obtained by ozonolysis of the $C_{16}H_{25}N$ base.

Likewise the picrates (m. p. 226–227°) of the $C_9H_{17}NH_2$ amines obtained from the two sources by degradation of the acids with hydrazoic acid showed no depression in a mixed melting point determination.

Summary

1. The structure of the $C_{16}H_{25}N$ base isolated from California petroleum by Thompson and Bailey[8] has been shown to be 2-(2,2,6-trimethylcyclohexyl)-4,6-dimethylpyridine.

2. A structural correlation of a naphthenic acid and a naphthenic base from petroleum has been established for the first time.

The Preparation of Alpha and Beta Indanol and Some of Their Derivatives from Indene[1,2]

BY WILLET F. WHITMORE AND ARTHUR I. GEBHART

α-Indanol was first prepared by Wislicenus and König[3] and later by Weisgerber[4] in 50% yields by hydrolysis of chloroindane with aqueous potassium carbonate. It seemed likely that this alcohol might be obtained in better yield by the dehalo-

genation of indenebromohydrin by catalytic reduction with Raney nickel in the presence of potassium hydroxide. The bromohydrin, prepared by the method of Read and Hurst,[5] reduced rapidly to β-indanol instead of the anticipated α-indanol. Attempts to reduce indenebromohydrin in the presence of magnesium hydroxide, silver oxide or pyridine failed. Apparently potassium hydroxide reacted with the bromohydrin to produce indene oxide (indene epoxide) which

(1) An abstract of a dissertation presented in 1941 to the Faculty of the Graduate School of the Polytechnic Institute of Brooklyn by Arthur I. Gebhart in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) The authors wish to thank the United Gas Improvement Company of Philadelphia who generously supplied the indene used in this study.

(3) Wislicenus and König, *Ann.*, **275**, 349 (1893).

(4) Weisgerber, *Ber.*, **44**, 1445 (1911).

(5) Read and Hurst, *J. Chem. Soc.*, **121**, 2552 (1922).