

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

The Nitrogen Compounds in Petroleum Distillates. XXVI. Confirmation of Presence of Bz-tetrahydroquinolines in California Petroleum

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In a continuation of the study of basic nitrogen compounds present in California petroleum, the 230–232° range has been investigated. By combined use of the chloroform extraction method of Bailey,² fractional neutralization in a "spinner" column,³ and fractional distillation a $C_{11}H_{15}N$ base was isolated, n_D^{20} 1.5165, b.p. 234°, picrate m. p. 154°. This base has been isolated previously in this Laboratory by W. W. Crouch⁴ who obtained a small yield of 3,5-dicarboxypyridine by oxidizing it with alkaline permanganate. Since cyclic groups containing less than five carbon atoms are rarely found in naturally occurring compounds, it seemed probable that the base was 3-cyclopentyl-5-methylpyridine. The synthesis, in this investigation, of this base has proved it to be different from the natural base. The method of synthesis was checked by preparation of 3-ethyl-5-methylpyridine. This synthetic base proved to be identical with the $C_8H_{11}N$ base isolated in this Laboratory by J. L. Meadows.⁵

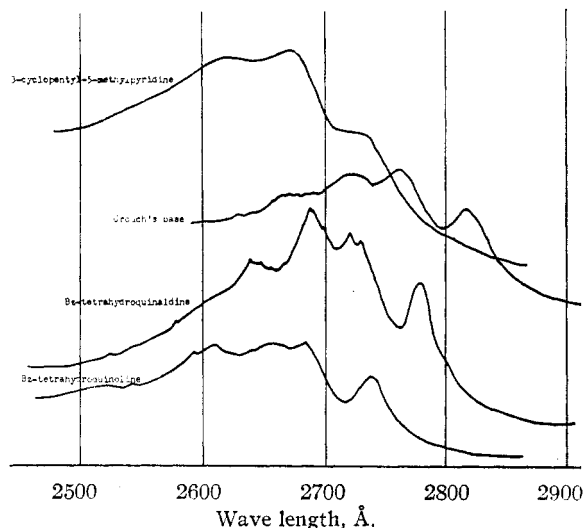


Fig. 1.—Microphotometer tracing of absorption spectra of Bz-tetrahydroquinolines and cyclopentylmethylpyridine.

Since the 3,5-dicarboxypyridine obtained by Crouch may have been formed by decarboxylation of 2,3,5-tricarboxypyridine, the natural base might be an alkylated Bz-tetrahydroquinoline. This hypothesis is supported by the isolation in this Laboratory of Bz-tetrahydroquinoline by

F. M. Garland.⁶ Since synthesis of the theoretically possible $C_{11}H_{15}N$ Bz-tetrahydroquinolines appeared impractical, it was decided to attempt to establish the type structure of the base isolated by Crouch by physical means. To this end the vapor phase ultraviolet absorption spectra of quinoline, quinaldine, the corresponding Py- and Bz-tetrahydro derivatives, Crouch's base and the synthetic 3-cyclopentyl-5-methylpyridine were obtained.

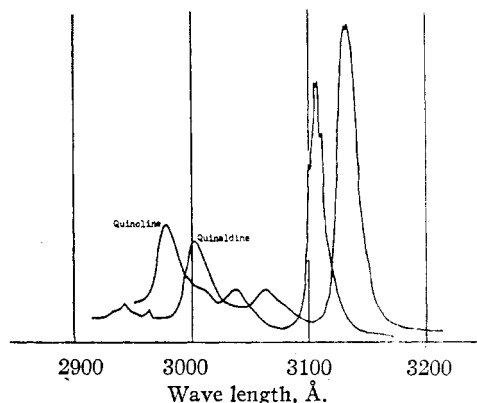


Fig. 2.—Microphotometer tracing of absorption spectra of quinolines.

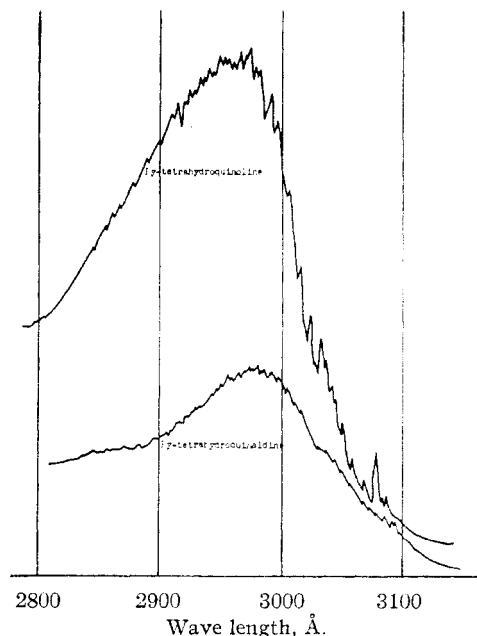


Fig. 3.—Microphotometer tracing of absorption spectra of Py-tetrahydroquinolines.

(1) General Aniline Fellow, 1944–1946.

(2) Perrin and Bailey, *THIS JOURNAL*, **64**, 2753 (1942).

(3) Ney and Lochte, *Ind. Eng. Chem.*, **33**, 825 (1941).

(4) W. W. Crouch, Ph. D. Dissertation, University of Texas, 1942.

(5) J. L. Meadows, Ph. D. Dissertation, University of Texas, 1937.

(6) F. M. Garland, Ph. D. Dissertation, University of Texas, 1939.

The absorption curve of the natural base (Fig. 1) indicates that it is probably an alkylated Bz-tetrahydroquinoline. Figures 2 and 3 are included for comparison of type of absorption curves and wave length at which peaks occur. Inasmuch as the spectra were not observed at equivalent vapor pressures, the absolute intensities of absorption are not significant.

Experimental

Methyl- β -bromoisobutyrate (I).—One hundred grams of methyl methacrylate⁷ was placed in a three-necked flask fitted with a gas inlet dipping below the surface, a high speed stirrer directly beneath the inlet, and a reflux condenser through which was hung a thermometer with its bulb beneath the surface. The flask was cooled in an ice-salt-bath to -10° and dry hydrogen bromide, generated by dropping bromine into a slurry of red phosphorus, was passed in slowly, so as to keep the temperature below -5° , until 81 g. had been absorbed. The flask was then stoppered tightly, covered with chipped ice, and left in the ice-box overnight. The reaction mixture was washed with water, 10% sodium bicarbonate solution, and twice more with water. It was dried and distilled at 22 mm., the main portion distilling between $75-76^{\circ}$. The yield was 151 g. (83.5%); n_D^{20} 1.4550; d_4^{20} 1.4277; MR, found 34.39; calcd. 34.69.

Diethyl Cyclopentylmalonate (II).—Clean sodium (12.7 g.) was dissolved in anhydrous ethanol and 96.0 g. (0.60 mole) of malonic ester was added dropwise with stirring. The mixture was cooled to room temperature and 82.0 g. (0.55 mole) of cyclopentyl bromide was added with stirring over a three-hour period. The mixture was then refluxed on a steam cone for sixteen hours, poured into a large amount of cracked ice, neutralized with dilute hydrochloric acid and extracted with ether. The extract was washed with 10% sodium carbonate and dried over anhydrous magnesium sulfate. The ether was removed by evaporation and the residue distilled *in vacuo*. The main portion of the distillate, 89.5 g., distilled from $100-104^{\circ}$ at 1-2 mm., n_D^{20} 1.4448,^{8,9}

Diethyl β -Carbomethoxypropylmalonate (III).—Clean sodium (11.5 g.) was dissolved in ethanol and 80.0 g. (0.50 mole) of malonic ester was added dropwise at room temperature. At 50° there was added 90.5 g. (0.50 mole) of I, and the mixture stirred overnight. The mixture was poured into water, extracted with ether, and the ether extract washed with dilute hydrochloric acid and water, dried and distilled. The yield was 69.0 g. (53%), boiling from $120-127^{\circ}$ at 1-2 mm.; n_D^{20} 1.4328; d_4^{20} 1.0769; MR, found 62.79; calcd. 62.43; sapon. equiv., found 86.3; calcd. 86.7.

Diethyl β -Carbomethoxypropylcyclopentylmalonate (IV).—(A) In 100 cc. of dry xylene was dissolved 45.6 g. (0.20 mole) of II, and 4.6 g. (0.20 mole) of sodium was added slowly with stirring and refluxing. To this mixture was added 36.2 g. (0.20 mole) of I and the resulting solution was refluxed forty minutes, after which time it was neutral to phenolphthalein. The mixture was diluted with water, acidified and the xylene layer separated, washed, dried over magnesium sulfate, and distilled. The yield was 19.20 g. (41%, based on the recovered II), distilling from $158-168^{\circ}$ at 4-5 mm.; n_D^{20} 1.4564; d_4^{20} 1.0702; MR, found 83.68; calcd. 83.33.

(B) To a solution of 1.15 g. (0.05 mole) of sodium in absolute alcohol was added 11.4 g. (0.05 mole) of II, and the mixture stirred until the sodio compound precipitated. To this was added 5.0 g. (0.05 mole) of methyl methacrylate and the mixture refluxed forty hours, cooled, and poured into a cold solution of dilute acetic acid. The oily layer was extracted with ether, dried over magnesium

sulfate, and distilled *in vacuo*. The tricarboxy ester obtained amounted to 6.5 g. (40%). It was identical with that obtained in (A).

(C) The sodio derivative of III was prepared from 65.0 g. (0.25 mole) of III, and 38.0 g. (0.255 mole) of cyclopentyl bromide was added with stirring at 50° . The mixture was refluxed for ten hours, worked up as before, and distilled in a twenty-eight inch spinner column at 3-4 mm. About 30 g. of III was recovered, and 14.6 g. of IV was obtained, n_D^{20} 1.4568.

α -Carboxy- α' -cyclopentyl- α' -methylglutaric Acid (V).—A solution of 14.6 g. of IV was refluxed for eight hours with an excess of 15% alcoholic potassium hydroxide. Upon acidification with hydrochloric acid an insoluble oil formed which crystallized rapidly when cooled and stirred. It was filtered, dissolved in sodium carbonate, extracted with ether and precipitated with hydrochloric acid. The white crystalline material obtained (10.9 g.) melted at 161° with decomposition.

α -Cyclopentyl- α' -methylglutaric Acid (VI).—The tricarboxy acid V was heated at 180° on an oil-bath for thirty minutes, after which no more carbon dioxide was evolved. The oil remaining was dissolved in Skellysolve C and placed in the ice box. In a few hours, 6.5 g. (77.5%) of white crystals precipitated, m. p. $149-150^{\circ}$; neut. equiv., found 110; calcd. 107.1.

Anal. Calcd. for $C_{11}H_{18}O_4$: C, 61.66; H, 7.02. Found: C, 61.45; H, 7.10.

Upon evaporating liquors from crystallization of the glutaric acid, there was obtained 1.0 g. of a second acid, m. p. $118-119^{\circ}$; neut. equiv., found 106.8; calcd. 107.1.

Anal. Calcd. for $C_{11}H_{18}O_4$: C, 61.66; H, 7.02. Found: C, 61.50; H, 7.04.

This low melting form was found in considerably larger quantities when the acid was prepared from the ester obtained by the Michael reaction between methyl methacrylate and II.

α -Cyclopentyl- α' -methylglutarimide (VII).—A solution of 2.8 g. of the high melting form of VI in acetyl chloride was refluxed for two hours. The excess acetyl chloride was evaporated, and the oily anhydride was distilled from $160-170^{\circ}$ at 3 mm., n_D^{20} 1.4855. The anhydride was dissolved in ether and liquid ammonia added slowly with shaking. The excess ammonia was evaporated, and the residue was warmed on a steam cone and stored in a vacuum desiccator over concentrated sulfuric acid for twenty-four hours. Recrystallization from acetone gave 2.0 g. of pure imide melting sharply at 160° .

Anal. Calcd. for $C_{11}H_{17}O_2N$: N, 7.17. Found: N, 7.18.

When this procedure was repeated using the low melting form of the acid, the same imide was obtained.

2,6-Dichloro-3-cyclopentyl-5-methylpyridine (VIII).—A mixture of 0.2 g. (0.001 mole) of VII and 0.65 g. (0.003 mole) of phosphorus pentachloride was warmed slowly to 50° , at which temperature a vigorous evolution of hydrogen chloride was observed. After no more gas was evolved, the temperature was increased slowly to 100° and maintained for thirty minutes. The resulting oil was poured into a watch glass and left under a hood one day. Sticky brown crystals formed and were recrystallized from hot alcohol-water, yielding 0.2 g. of white crystals, m. p. 54° .

Anal. Calcd. for $C_{11}H_{13}NCl_2$: N, 6.08. Found: N, 6.14.

3-Cyclopentyl-5-methylpyridine (IX).—To a solution of 50 mg. of palladium chloride in 3.0 cc. of 2.5 normal hydrochloric acid was added 500 mg. of animal charcoal, previously activated by heating at 150° for eight hours in a slow stream of methane. This mixture was shaken thoroughly and then reduced with hydrogen. To this catalyst was added a solution of 333 mg. of VIII in 10.0 cc. of methanol. Reduction at one atmosphere was complete after eleven hours. This mixture was filtered, the catalyst washed with a few cc. of methanol, and the filtrate evaporated. The crystalline material remaining was dissolved in a small amount of water and neutralized with

(7) Sample kindly furnished by E. I. du Pont de Nemours & Co., Inc.

(8) Verwey, *Ber.*, **29**, 1996 (1896).

(9) B. P. Truitt, Ph. D. Dissertation, University of Texas, 1944.

10% sodium hydroxide. The base was extracted with ether and added to a saturated alcoholic solution of picric acid. The picrate formed immediately, m. p. 173° after recrystallization.

Anal. Calcd. for $C_{17}H_{13}N_4O_7$: C, 52.30; H, 4.61; N, 14.37. Found: C, 52.45; H, 4.75; N, 14.38.

The base obtained by treatment of the picrate with concentrated ammonia amounted to 75% of the theoretical amount, based on the weight of VIII used.

During this investigation it was noted that, while Adams catalyst alone had no effect on VIII, a trace of it added to the palladium chloride during the preparation of the catalyst enabled the hydrogenation to be completed in a matter of minutes instead of hours. In subsequent work using 2,3,6-trichloropyridine¹⁰ this observation has been confirmed, although the effect is not so noticeable since the simple palladium-charcoal catalyst is quite active in the reduction of this compound. Since this effect is similar to that found in the case of the Skita catalyst,¹¹ it was not considered worth while to carry the investigation further, though such a catalyst does not seem to have been reported previously for this type of reduction.

Diethyl β -Carbomethoxypropylethylmalonate (X).—To a solution of 1.15 g. of sodium in ethanol was added 13.0 g. of III. The solution was refluxed and stirred while 8.1 g. of ethyl bromide was added dropwise. After refluxing for three hours, the mixture was poured into ice water and extracted with ether. The ether layer was washed with dilute hydrochloric acid and water and dried over anhydrous magnesium sulfate. Distillation *in vacuo* gave 9.9 g. (68.7%) of material boiling from 142–147° at 6 mm.; n_D^{20} 1.4370; d_4^{20} 1.0578; MR, found 74.90; calcd. 75.20.

α -Ethyl- α' -methylglutarimide (XI).—A solution of 9.9 g. of X was refluxed four hours with an excess of 50% alcoholic potassium hydroxide, the alcohol evaporated, and the residue treated with dilute hydrochloric acid. The resulting oil did not solidify, so the solution was evaporated to dryness on a steam cone. Evolution of carbon dioxide was noted as the material approached dryness. The residue was dried in a vacuum desiccator and then decarboxylated by heating to 150°. The material remaining was distilled *in vacuo* and recrystallized from Skellysolve C, m. p. 177–180°. The acid was refluxed with acetyl chloride thirty minutes, the excess acetyl chloride evaporated, and liquid ammonia added to the residue and shaken vigorously. The ammonia was allowed to evaporate, and the residue was recrystallized from alcohol-water. The yield was 4.2 g. of XI, m. p. 118°.

Anal. Calcd. for $C_8H_{13}NO_2$: N, 8.53. Found: N, 8.70.

3-Ethyl-5-methylpyridine (XII).—A mixture of 1.51 g. of XI and 0.42 g. of phosphorus pentachloride was warmed to 100°. The yellow oil obtained could not be crystallized. It was easily steam distillable and had the sweet odor characteristic of the chloropyridines previously prepared. Reduction of 0.5 g. of this liquid with a palladium-platinum charcoal catalyst gave a base, b. p. 190°. The picrate of this base, m. p. 195°, gave no depression when mixed with a sample of the picrate of the natural base isolated by Meadows.

Py-tetrahydroquinoline.—Twenty-four grams of freshly distilled quinoline was hydrogenated with Raney nickel at 200° and 1700 lb. pressure for two hours. The material distilled at 246–248° (750 mm.), n_D^{20} 1.5950.

Py-tetrahydroquinoline.—Quinaldine was hydrogenated as above and the product distilled from 240–245°. It was purified through its N-benzoyl derivative, m. p. 119–120°. This was hydrolyzed by refluxing with alcoholic hydrochloric acid twenty-four hours. The base was recovered by neutralization and extraction, n_D^{20} 1.5732, picrate m. p. 154°.

Decahydroquinoline (XIII).—Quinoline was reduced at 200° and 2300 lb. pressure with Raney nickel for thirty-six hours. The product distilled at 70–75° (5 mm.). Separation of isomers by the method of Hückel¹² gave approxi-

mately 66% of the *cis* form, m. p. 47°, and 30% of the *trans* form, b. p. 205°.

Decahydroquinoline (XV).—Reduction of quinaldine at 200° and 2300 lb. pressure gave 95% yield of product, b. p. 207°, picrate m. p. 134°, n_D^{20} 1.4828.

Bz-tetrahydroquinoline (XIV).—*cis*-Decahydroquinoline (XIII) was passed over a 30% platinum on asbestos catalyst¹³ at about 5 cc. per hour. The temperature was maintained at about 325°. The product was carefully fractionated *in vacuo* in twenty-eight inch spinner column. The first fraction contained a large amount of *trans*-decahydroquinoline. Fractions having a higher refractive index than that of XIII were combined and poured into a saturated alcoholic solution of picric acid. The picrate which separated was recrystallized from alcohol-water, m. p. 156–157°.

Anal. Calcd. for $C_{15}H_{14}N_2O_7$: C, 49.72; H, 3.89; N, 15.47. Found: C, 49.47; H, 4.13; N, 15.69.

Heating the picrate with concentrated ammonium hydroxide and extraction with benzene yielded the base, b. p. 222°, n_D^{20} 1.5390. The yield was about 10–15% for a single cycle. Recycling the mixture before separating the tetrahydroquinoline resulted in the formation of significant quantities of quinoline. There was a slight amount of cracking under the conditions used, so the catalyst was replaced after every second run.

Bz-tetrahydroquinoline (XVI).—This base was prepared from XV by the procedure outlined for Bz-tetrahydroquinoline, the average yield being slightly higher. The product was purified through its picrate, m. p. 157°, and the base, b. p. 225°, n_D^{20} 1.5325, recovered by heating the picrate with concentrated ammonium hydroxide and extracting with benzene.

Ultraviolet Absorption Spectra.—First order spectra were obtained using a 3-meter, 15,000 lines per inch grating in a modified Eagle mounting. The light source was a 2.5 KVA, water cooled hydrogen discharge tube. The absorption cells were of quartz, with ground glass connections for the sample tube and vacuum pump. Eastman 103-0 film was used with ten minute ultraviolet exposure and a seven second iron arc exposure for reference. Plates were developed five minutes in D-19 high contrast developer. The absorption tube was evacuated to about 2 mm. and the pump shut off. The sample tube, which contained 2–3 drops of sample, was heated with a burner, so that the material distilled into the absorption tube. During exposures, the tube was heated by an electrically wired asbestos jacket. The ends of the tube were warmed occasionally with a burner to prevent fogging. With each compound the temperature was slowly increased until the vapor pressure was high enough to show absorption. The plates were scanned by a Knorr-Alders type, Leeds and Northrup microphotometer which plotted intensity against wave length.

Acknowledgment.—The authors wish to express their appreciation to Dr. F. A. Matsen without whose advice and assistance the work on ultraviolet absorption would have been impossible.

Summary

1. 3-Cyclopentyl-5-methylpyridine has been synthesized and shown to differ from the $C_{11}H_{15}N$ base isolated from petroleum.
2. 3-Ethyl-5-methylpyridine has been synthesized and shown to be identical to the $C_8H_{11}N$ base isolated from petroleum.
3. Ultraviolet absorption studies indicate that the natural $C_{11}H_{15}N$ base is an alkylated Bz-tetrahydroquinoline, thus confirming the presence of this type of base in petroleum.

AUSTIN, TEXAS

RECEIVED SEPTEMBER 23, 1946

(10) Crouch and Lochte, *THIS JOURNAL*, **65**, 270 (1943).

(11) Skita, *Ber.*, **45**, 3588 (1912).

(12) Hückel, *Ann.*, **453**, 172 (1927).

(13) Linstead and Thomas, *J. Chem. Soc.*, 1127 (1940).