

promote a reaction of the halogens with such reagents as thiourea, potassium thiocyanate, or amines.

The 1-phenyl-3-methyl- and 3-*n*-butylbarbituric acids, their 5,5-dibromo, and their 5-anilinomethylene derivatives have been prepared.

A convenient procedure has been developed which gives satisfactory yields of both mono and di nitrogen substituted barbituric acids from the substituted urea and malonic acid in acetic anhydride solution.

COLUMBIA, Mo.

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[CONTRIBUTION NO. 159 FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, THE UNIVERSITY OF TEXAS]

The Nitrogen Compounds in Petroleum Distillates. XIV. Isolation of 2,4-Dimethyl-8-ethylquinoline from the Kerosene Distillate of California Petroleum¹

BY W. NELSON AXE²

Introduction

The positions of alkylation of kero quinolines thus far isolated in the Texas Laboratory are 2, 3, 4 and 8 with a methyl invariably at position 2. Substitution at positions 5, 6 or 7 has not been observed, whereas we now have examples of two bases with an ethyl at 8 and two with an *n*-propyl at 8. In this paper is reported the discovery of 2,4-dimethyl-8-ethylquinoline, along with proof of its structure through degradation and synthesis.

Since completion of the research reported in this paper, another base of the composition, C₁₄H₁₇N³ has been identified through degradation and synthesis as 2,4-dimethyl-8-*n*-propylquinoline.

It is of interest to note that alkylation higher than methyl has not been encountered in the pyridine nucleus of any of the following ten kero quinolines isolated in the Texas Laboratory: 2,3-,⁴ 2,4-⁴ and 2,8-dimethylquinoline⁵; 2,3,8-⁶, and 2,4,8-trimethylquinoline⁷; 2,3,4,8-tetramethylquinoline³; 2,3-dimethyl-8-ethyl-⁸ and 2,4-dimethyl-8-ethylquinoline; 2,3-dimethyl-8-*n*-propylquinoline³ and 2,4-dimethyl-8-*n*-propylquinoline.

Kero quinoline homologs alkylated at positions 2, 3 and 8 occur in relatively large quantities, whereas homologs alkylated at positions 2, 4 and 8 have been encountered only in small amounts;

(1) Acknowledgment is due Professor J. R. Bailey for the cooperation extended in supplying the fractions of bases used in this work. The original crude bases were furnished by the Union Oil Company of California.

(2) Research Department, Phillips Petroleum Company, Bartlesville, Okla.

(3) Axe and Bailey, *THIS JOURNAL*, **60**, 3028 (1938).

(4) Biggs and Bailey, *ibid.*, **55**, 4141 (1933).

(5) Lake and Bailey, *ibid.*, **55**, 4143 (1933).

(6) King and Bailey, *ibid.*, **52**, 1239 (1930).

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

(8) Key and Bailey, *ibid.*, **60**, 763 (1938).

as an example, only 4 g. of 2,4-dimethyl-8-ethylquinoline was available for characterization and proof of structure.

Experimental

The crude kero bases, as received from the Union Oil Company, were refined through the following procedures: I, fractional acid extraction; II, fractional distillation under atmospheric and under reduced pressure; III, cumulative extraction.⁷

At the end of each step recombinations of fractions in the order of boiling points and refractive indices were made and the new fractions were employed in the next step.

Since the objective in this investigation was the isolation and identification of *aromatic* bases associated with 2,3-dimethyl-8-ethylquinoline (b. p. 284.6°), the *non-aromatics*, which in step III were segregated as hydrochlorides in the *chloroform* layer, were not investigated.

Isolation of 2,4-Dimethyl-8-ethylquinoline.—The separate fractions of *aromatic* bases present in step III as hydrochlorides in the *aqueous* layer were liberated and, after exhaustive distillation, cuts within the boiling range of 290–291° were combined and processed for 2,3-dimethyl-8-ethylquinoline previously isolated by Key and Bailey.⁸ This base is conveniently removed as the acid sulfate by the addition of concd. sulfuric acid to an alcohol-acetone solution of the base mixture. The yield from the purified acid sulfate amounted to 18.5% of the original aromatic fraction.

The residual bases from the above 290–291° fraction (460 cc., *d*₄²⁰ 1.0074, *n*_D²⁰ 1.5846) were processed through counter-current extraction using Schutze's⁹ modification of the Jantzen¹⁰ column.

The 460 cc. of the bases was mixed with petroleum ether to a volume of 1380 cc.; 2 *N* hydrochloric acid in an amount sufficient to neutralize 330 cc. of the bases (calculation based on mol. wt., 185) was diluted likewise to 1380 cc. The acid was fed in at the top of the column at the same rate as the base solution entered the bottom, intimate contact of the acid and bases being attained with a

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

(10) Jantzen, "Das fraktionierte Destillieren und das fraktionierte Verteilen," Verlag Chemie, Berlin, 1932, pp. 108–116.

rotary stirrer. At the end of the experiment, the supernatant petroleum ether contained unneutralized bases (Fraction A).

The bases, liberated from the aqueous layer with sodium hydroxide, were used in a second extraction, the amount of acid being regulated to again leave unsalified 130 cc. of bases (Fraction B). A third extraction left 100 cc. of free bases (Fraction C), in petroleum ether and 100 cc. (Fraction D) as hydrochlorides in the aqueous layer. In Table I the fractions are listed in progressive order of ionization constants.

TABLE I

EXTRACTION OF BASES IN THE 290-291° RANGE			
Fraction	Vol., cc.	n_D^{20}	d_4^{20}
A	130	1.5766	1.0031
B	130	1.5808	1.0128
C	100	1.5862	1.0203
D	100	1.5898	1.0293

The general procedure followed in processing the extraction fractions involved the following steps: (1) conversion of the bases in acetone solution to picrates; (2) recrystallization of picrates, insoluble in hot acetone, from glacial acetic acid; (3) recovery of bases from *acetone-soluble* picrates after one recrystallization from alcohol; (4) conversion of the bases from step 3 to zinc chloride salts, with subsequent recrystallization from a dilute zinc chloride-hydrochloric acid solution.

Application of step 2 to fractions A, B and C, Table I, yielded 16, 12 and 6%, respectively, of 2,3-dimethyl-8-ethylquinoline.

Step 4 applied to fractions A and B furnished a small quantity of the zinc chloride salt of 2,4-dimethyl-8-*n*-propylquinoline. No pure base was obtained from fraction D.

The same procedure used on fraction C gave a different zinc chloride salt which after a fifth recrystallization melted undecomposed at 261-262°. This salt crystallizes in double pyramids of the orthorhombic system. The base (2,4-dimethyl-8-ethylquinoline) liberated with ammonium hydroxide from this salt has the following physical constants: b. p. 288° (747 mm.); n_D^{20} 1.5846; d_4^{20} 1.017. The picrate of this base is conveniently recrystallized from alcohol or 50% acetic acid in triclinic plates melting at 165-166°.

Anal. of zinc chloride salt. Calcd. for $(C_{13}H_{16}N \cdot HCl)_2 \cdot ZnCl_2$: C, 53.86; H, 5.56; Cl, 24.46. Found: C, 53.67; H, 5.51; Cl, 24.30.

Anal. of base. Calcd. for $C_{13}H_{16}N$: C, 84.32; H, 8.10. Found: C, 84.43; H, 8.16.

Anal. of picrate. Calcd. for $C_{13}H_{16}N_4O_7$: C, 55.07; H, 4.38. Found: C, 55.11; H, 4.37.

Preparation of 2,4-Dimethylquinoline-8-carboxylic Acid.—To a boiling solution of 1.75 g. of base in 6 *N* sulfuric acid, there is added, slowly, a mixture of 3.8 g. of potassium dichromate, 5 g. of sulfuric acid and 6 g. of water. The reaction is complete in less than one hour. Ammonium hydroxide is then added to incipient precipitation of chromium hydroxide and the organic acid is extracted with chloroform. The acid was recrystallized from alcohol with a yield of 0.35 g. in the form of orthorhombic double pyramids melting with decomposition at 241-242°.

Anal. Calcd. for $C_{12}H_{11}O_2N$: C, 71.64; H, 5.47. Found: C, 71.78; H, 5.53.

The same acid was obtained in chromate oxidation of 2,4,8-trimethylquinoline as confirmed by each preparation, as well as a mixture of both having the same melting point of 241-242°.

Separation of Ortho and Para Aminoethylbenzenes.—In connection with the synthesis of 2,4-dimethyl-8-ethylquinoline considerable difficulty was experienced in preparing *o*-aminoethylbenzene free from the *para* isomer. The usual method of separation involves the troublesome recrystallization of acetyl derivatives.¹¹ Another method¹² employs the sulfate for isolation of the *para* isomer, but no mention is made of the *ortho* isomer.

In this work, it was found that 80 g. of fractionated aminoethylbenzene could be made to yield 60 g. of relatively pure *o*-ethylaniline by the following procedure. The base mixture is dissolved in an equal volume of 1:1 alcohol-ether solution and an equimolecular quantity of concd. sulfuric acid is added with cooling. On addition of water to turbidity, a crystalline precipitate forms after vigorous stirring. The refractive index of the base obtained from the crystalline salt (n_D^{20} 1.5536) and that from the filtrate (n_D^{20} 1.5580) compare favorably with Schreiner's¹³ values for *p*-ethylaniline (n_D^{20} 1.5529) and *o*-ethylaniline (n_D^{20} 1.5584), respectively.

Both these *ortho* and *para* isomers, when used in synthesis of quinoline homologs, yielded different bases with acetylacetone. On the other hand, fractions of *o*-ethylaniline which were processed merely by careful fractionation of the mixture of nitro isomers as well as their reduction products, yielded nothing but 2,4-dimethyl-6-ethylquinoline on reaction with acetylacetone. Thus it is quite clear that this condensation will take place preferably with *p*-aminoethylbenzene, if present in appreciable quantity.

Synthesis of 2,4-Dimethyl-8-ethylquinoline.—Following the procedure of Königs and Mengel¹⁴ for the production of 2,4-methylated quinolines, equimolecular proportions of acetylacetone and *o*-ethylaniline were heated for one-half hour at 100°. Ring closure of the initial condensation product was effected by addition to concd. sulfuric acid, followed by a few minutes of heating on a steam-bath. Purification of the base was carried out through its picrate, m. p. 165-166°. A mixture of this picrate with that of the *kero* quinoline melted without depression.

Anal. Calcd. for $C_{19}H_{17}N_4O_7$: C, 55.07; H, 4.38. Found: C, 54.89; H, 4.34.

Summary

1. The isolation, from a complex mixture of petroleum bases, of the hitherto unknown compound, 2,4-dimethyl-8-ethylquinoline, is described.

2. The structure of the petroleum quinoline is established by oxidation to a known acid and by synthesis of the base.

(11) Paucksch, *Ber.*, **17**, 2801 (1884).

(12) Willgerodt and Bergdolt, *Ann.*, **156**, 208 (1903).

(13) Schreiner, *J. prakt. Chem.*, [2] **81**, 559 (1910).

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

3. A rapid method for the separation of benzene is proposed. the ortho and para isomers of aminoethyl-

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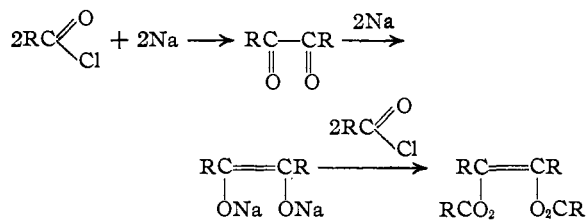
[CONTRIBUTION FROM THE RESEARCH LABORATORY OF ARMOUR AND COMPANY]

Action of Sodium upon High Molecular Weight Fatty Acid Chlorides

BY A. W. RALSTON AND W. M. SELBY

Previous work upon the action of sodium with acid chlorides has been confined to chlorides of aromatic and low molecular weight aliphatic acids. Recently Pearl, Evans and Dehn¹ have shown that sodium reacts with benzoyl chloride in anhydrous ether to give ethyl benzoate, and that potassium reacts with benzoyl chloride in anhydrous xylene to give benzoic anhydride. Münchmeyer,² Klinger and Schmitz,³ and Basse and Klinger⁴ obtained the dibutyrate of 4-octene-4,5-diol by the action of sodium upon butyryl chloride in anhydrous ether. In view of the decrease in chemical activity with increase in molecular weight, the action of the high molecular weight fatty acid chlorides with sodium in ether is of interest.

Lauroyl, myristoyl, palmitoyl and stearoyl chlorides react smoothly at the boiling point of ether to give the corresponding diesters of the unsaturated diols in substantial yields. The failure to form ethyl esters of the corresponding acids, which would require scission of the ether, is noteworthy. Using stearoyl chloride and sodium as an example, the formation of the diesters of the diols can be explained as follows



Experimental

Preparation of the Acid Chlorides.—Stearic acid (586 g., 2 moles), m. p. 67–70°, was placed in a three-necked flask fitted with a dropping funnel, reflux condenser, mechanical stirrer and thermometer. Thionyl chloride (285.5 g., 2.4 moles) was then added over a period of two and one-half hours and the mixture heated at 75° for two hours. The temperature was then increased to 90°

and the heating continued for an additional two hours. The excess thionyl chloride was then removed under a vacuum and the product fractionally distilled. An 81% yield of stearoyl chloride boiling at 200–215° at 13–15 mm. was obtained.

The acid chlorides of lauric, myristic and palmitic acids were prepared in a similar manner. Approximately 80% yields were obtained with the following boiling ranges: lauroyl chloride, 146–150° at 16–17 mm.; myristoyl chloride, 175–176° at 16–17 mm.; and palmitoyl chloride, 191–194° at 14–15 mm.

Preparation of the Dilaurate of 12-Tetracosene-12,13-diol.—Sodium (27.5 g., 1.2 moles) was pressed as wire into a two-liter three-necked flask containing 1 liter of sodium dried ether. The flask was fitted with a reflux condenser, stirrer, thermometer and dropping funnel. Lauroyl chloride (218 g., 1 mole) dissolved in 200 cc. of dry ether was then added over a period of four hours. Stirring was not started until the addition of the lauroyl chloride was completed. The mixture was then refluxed and stirred for ten hours.

The sodium chloride and unreacted sodium were filtered from the ether solution and the filter washed with ether. The ether was then removed by distillation. After four crystallizations from a 3:1 acetone–benzene solution the product melted at 39–41° and weighed 110 g. (60% yield). It was then further crystallized to a constant melting point of 42–43°.

Anal. Calcd. for C₄₈H₉₂O₄: C, 78.63; H, 12.64; iodine no., 34.7; sap. no., 153. Found: C, 78.87; H, 12.63; iodine no., 35.9; sap. no., 158.

Saponification of the diester was accomplished by refluxing with 0.5 N alcoholic potassium hydroxide for one hour. The product was separated into an alkali soluble and insoluble portion. The alkali insoluble product was crystallized six times from alcohol to a constant melting point of 62–63.5°. This product showed no depression in melting point when mixed with a sample of lauroin prepared from methyl laurate and sodium.⁵

The alkali soluble portion was acidified with hydrochloric acid and the product crystallized from acetone. It melted at 44–45° and showed no melting point depression with known lauric acid. The 2-alkylbenzimidazole⁶ melted at 107–107.5° and was not depressed in melting point when mixed with known 2-undecylbenzimidazole.

Preparation of the Dimyristate of 14-Octacosene-14,15-diol.—Sodium wire (13.8 g., 0.6 mole) in 500 cc. of dry ether was treated over a period of two and one-half hours

(1) Pearl, Evans and Dehn, *THIS JOURNAL*, **60**, 2478 (1938).(2) Münchmeyer, *Ber.*, **19**, 1846 (1886).(3) Klinger and Schmitz, *ibid.*, **24**, 1271 (1891).(4) Basse and Klinger, *ibid.*, **31**, 1217 (1898).(5) Hansley, *THIS JOURNAL*, **57**, 2303 (1935).(6) Pool, Harwood and Ralston, *ibid.*, **59**, 178 (1937).