Preparation of the N-Alkyl-*p*-bromobenzenesulfon-*p*-anisidides.—The preparation of the N-butyl derivative is described below. The other derivatives listed in Table I were all prepared in a similar manner, and recrystallized twice or thrice to constant melting point.

TABLE I

N-ALKYL SUBSTITUTED *p*-BROMOBENZENESULFON-*p*-ANISIDIDES

The writer is indebted to Mr. William Saschek for the microanalytical work.

Substituent	M. p., °C., (uncorr.)	Formula	Bromine, % Calcd.	Bromine, % Found
CH_3	96–97	$C_{14}H_{14}O_3NSBr$	22.47	22.40
C_2H_5	113.5	$C_{15}H_{16}O_3NSBr$	21.62	21.50
n-C_3H_7	75	$C_{16}H_{18}O_3NSBr$	20.83	20.99
i-C_3H_7	107	$C_{16}H_{18}O_3NSBr$	20.83	20.98
n-C_4H_9	74.5	$C_{17}H_{20}O_3NSBr$	20.10	20.35
i-C_4H_9	78–79	$C_{17}H_{20}O_3NSBr$	20.10	20.17
n-C_5H_{11}	88.5	$C_{18}H_{22}O_3NSBr$	19.41	19.25
i-C_5H_{11}	52.5	$C_{18}H_{22}O_3NSBr$	19.41	19.20
n-C_7H_{15}	56	$C_{20}H_{26}O_3NSBr$	18.18	17.96
$CH_2{=}CHCH_2$—	82	$C_{16}H_{16}O_3NSBr$	20.94	20.96
$C_6H_5CH_2$—	167.5	$C_{20}H_{18}O_3NSBr$	18.51	18.55
$HOCH_2CH_2$—	92–93	$C_{15}H_{16}O_4NSBr$	20.72	20.55
$CH_3CHOHCH_2$—	92	$C_{16}H_{18}O_4NSBr$	20.00	20.12

To a solution of 1 g. of *p*-bromobenzenesulfon-*p*-anisidide in 5 cc. of 5% potassium hydroxide and 5 cc. of alcohol, there was added 0.2 cc. of butyl bromide. The mixture was heated under reflux on the steam-bath for one hour. Then 5 cc. of water was added and the mixture chilled. The alkali-insoluble product was washed with 5 cc. of 5% potassium hydroxide and then with water, and recrystallized from 10 cc. of 75% alcohol. There was obtained 0.43 g. of the product melting at 74.5°. Recrystallization did not raise the melting point.

Summary

p-Bromobenzenesulfon-*p*-anisidide reacts in alkaline solution with alkyl halides to give N-alkyl substituted *p*-bromobenzenesulfon-*p*-anisidides which are useful for purposes of identification.

NEW YORK CITY RECEIVED OCTOBER 4, 1934

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF TEXAS]

The Nitrogen Compounds in Petroleum Distillates. VIII. Degradation of the Naphthenic Base $C_{16}H_{25}N$ to the Lower Homolog, $C_{14}H_{21}N$*

BY R. W. LACKEY AND J. R. BAILEY

Introduction

In an investigation of nitrogen bases from the crude kerosene distillate of California petroleum[1] the unexpected discovery was made that the completely saturated non-aromatic kero base, $C_{16}H_{25}N$,[2] like quinolines methylated at position 2, condenses with phthalic anhydride in phthalone formation.[3]

In the present paper it is shown that, although formaldehyde does not condense with this naphthenic base as readily as with quinaldine,[4] the reaction proceeds smoothly around 200° and the resultant product yields in nitric acid oxidation a dicarboxylic acid, $C_{14}H_{19}N(COOH)_2$, from which was prepared a monocarboxylic acid, $C_{14}H_{20}N$-COOH, and an oxygen-free base, $C_{14}H_{21}N$.

An important consideration is the resistance of the 14-carbon base to hydrogenation, from which behavior it follows that it, like the parent 16-carbon compound, is *completely saturated*. An unsaturated molecule would have resulted had either of the carboxyls in the dicarboxylic acid come from cleavage and subsequent oxidation of a methylene or ethylene bridge. From these considerations, the existence of at least two methyls in the $C_{16}H_{25}N$ base is established.

The $C_{16}H_{25}N$ compound parallels 2,4-dimethylquinoline[5] in its behavior toward formaldehyde and subsequent oxidation of the product formed to a dicarboxylic acid, with the analogy further extended in the ready elimination of one carboxyl from this acid at a temperature just above its melting point.

The abnormal aromatic character of the saturated naphthenic base[6] suggests *the same relative positions of two methyls to nitrogen as exists in 2,4-dimethylquinoline;* so, in order to show such an analogy, the following revised formula with methyls in alpha and gamma positions to nitrogen is proposed[7]

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* An abstract of the dissertation submitted by R. W. Lackey to the faculty of the University of Texas in partial fulfilment of the requirements for the degree of Doctor of Philosophy, June, 1934.

(1) Poth, Schulze, King, Thompson, Slagle, Floyd and Bailey, THIS JOURNAL, **52**, 1239 (1930).

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

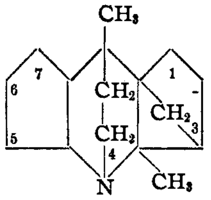
(3) Armendt and Bailey, *ibid.*, **55**, 4145 (1933).

(4) Koenigs, *Ber.*, **32**, 223 (1899).

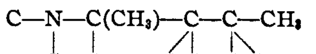
(5) Koenigs and Mengel, *ibid.*, **37**, 1322 (1904).

(6) *Cf.* Eibner, *ibid.*, **37**, 3605 (1904); König, *J. prakt. Chem.*, **73**, 102 (1906); Doja, *Chem. Reviews*, **11**, 278 (1932).

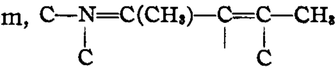
(7) From this formula is derived the name, decahydro-3a,8-dimethyl-4,8-ethano-1a-3-methanopyrindacine. Should *two methano* bridges be established, then it would be necessary to increase the *methyl* side chains from *2 to 3.*



If this interpretation be correct, then it appears that the neo-carbon system



$$\mathrm{C{-}\underset{C}{\underset{|}{N}}{-}\underset{C}{\underset{|}{C}}(CH_3){-}\underset{C\;C}{C}{-}\underset{C\;C}{C}{-}CH_3}$$

induces the same reactivity in its two methyls as is common to the methyls in the conjugate double bond system,  $\mathrm{C{-}\underset{C}{\underset{|}{N}}{=}C(CH_3){-}\underset{|}{C}{=}\underset{C}{\underset{|}{C}}{-}CH_3}$.

Experimental Part

Melting Point of the $C_{16}H_{25}N$ Base.—Although the high molecular weight of this substance would indicate a melting point above room temperature, previous attempts to effect crystallization in an ice–salt bath were unsuccessful. In an ether–solid carbon dioxide mixture (−77°), it congeals to a glass-like solid which liquefies readily on removal from the bath. However, if kept at this low temperature for twelve hours, it assumes a crystalline structure and melts at 23–24.3°. At a temperature below its melting point, the liquid base crystallizes readily when seeded.

Bromination of the $C_{16}H_{25}N$ Base to $C_{16}H_{24}NBr$.[8]—When to 3 cc. of the base is added drop-wise 2 cc. of bromine, a vigorous reaction ensues with the evolution of considerable heat and the formation of a tough red gum which on standing slowly evolves hydrogen bromide and changes to a heavy red liquid containing some excess bromine. This product, agitated at 90° with 10% sodium hydroxide, becomes colorless and, when dried and distilled under reduced pressure, solidifies to a white crystalline solid with the following physical constants: m. p. 55.7; n^{60}_{D} 1.5268; n^{20}_{D} (subcooled liquid). 1.5431. The substance does not distil undecomposed at atmospheric pressure.

The brominated base does not undergo the Fittig reaction, is unaffected by heating with metallic sodium at 250°, cannot be made into a Grignard reagent, and is unchanged by prolonged refluxing with alcoholic or aqueous potassium hydroxide. Failure to oxidize the brominated base with nitric acid or with potassium permanganate in acetone solution indicates that the introduction of bromine does not render the compound more susceptible to oxidation. Efforts to replace the halogen by heating with silver acetate in glacial acetic acid were ineffective. The compound is unaffected by prolonged heating at 250° with sodium methylate, as well as by treatment with moist silver oxide or alcoholic silver nitrate.

Catalytic reduction, using the Adams and Voorhees method,[9] was unsuccessful, but surprisingly enough, the halogen is readily reduced away with zinc and acetic acid. The ease with which the original base is regained suggests that at times bromination might be used as a method of resolving mixtures of non-aromatic kero bases.

Failure to brominate the $C_{14}H_{21}N$ base, obtained by elimination of two methyls from the $C_{16}H_{25}N$ compound as described further on, indicates that bromination of the higher homolog replaces a hydrogen of a methyl group.[10]

Anal. Calcd. for $C_{16}H_{24}NBr$: C, 61.91; H, 7.80; N, 4.52; Br, 25.78; mol. wt., 310. Found: C, 62.10; H, 7.73; N, 4.25; Br, 25.79; mol. wt., 319.

Picrate of the Brominated Base.—The product readily forms a picrate which is soluble in acetone and hot glacial acetic acid, more difficultly soluble in hot alcohol, hot benzene, and hot ethyl acetate, and insoluble in water and petroleum ether. It crystallizes from alcohol in beautiful fine yellow prisms, softening slightly at 192°, and melting at 194.2°.

Anal. Calcd. for $C_{22}H_{27}O_7N_4Br$: C, 48.98; H, 5.05; N, 10.39; Br, 14.82. Found: C, 48.91; H, 5.00; N, 10.27; Br, 14.59.

Action of Cyanogen Bromide on the $C_{16}H_{25}N$ Base.—When, in accordance with the general procedure of J. von Braun,[11] a mixture of 2 g. of base and 1.1 g. of cyanogen bromide (20% excess) is warmed at 50°, with shaking, for twenty minutes, a dark red gum results. Unreacted base (about 1 g.) is removed by hydrochloric acid extraction of the reaction product in ether, and unused cyanogen bromide is expelled by evaporation of the ether. The addition product is thus obtained in the form of reddish brown flakes, insoluble in dilute acid and alkali, and melting at 80–100°. All attempts to purify the product further were unsuccessful. The impure substance decomposes when heated to 260° under 4 mm. pressure. The use of benzene as a solvent[12] in the cyanogen bromide reaction resulted in a poorer yield, with no improvement in the purity of the bromocyanamide compound.

The rupture of a 4,8-ethylene bridge from nitrogen should yield bromoethyl joined to carbon at position 8 and replaceable with hydrogen through vinyl and carboxyl. However, the first step here, *i. e.*, elimination of hydrogen bromide, could not be effected. Without a detailed explanation, it may be pointed out that a methylene bridge may be involved in which case normal degradation would be impossible. Therefore, experimental proof of the bridge in the piperidine nucleus could best be carried out on the corresponding 14-carbon base, where structural hindrance would not interfere with hydrogen bromide elimination from the complex $CHCH_2Br$ formed in the cyanogen bromide reaction.

Condensation of the $C_{16}H_{25}N$ Base with Formaldehyde.—In accordance with the general method of Koenigs,[13] if one volume of base and five volumes of 37% formaldehyde in a sealed tube are heated at 190° for eight hours, a heavy oil separates. In further purification, the crude product is dissolved in ether, washed with water to remove formalde-

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[8] *Cf.* Thompson and Bailey, *loc. cit.*, p. 1009.

[9] Adams and Voorhees, *ibid.*, **44**, 1402 (1922).

[10] The CH_2Br complex apparently is attached to a neo-carbon and the non-reactivity of the bromine agrees with the abnormal behavior of neopentyl halides. *Cf.* Whitmore and Fleming, THIS JOURNAL, **55**, 4161 (1933).

[11] J. von Braun, private communication.

[12] Winterfeld and Holschneider, *Ber.*, **64B**, 142 (1931).

[13] Koenigs, *ibid.*, **32**, 224 (1899).

hyde, and extracted with dilute hydrochloric acid. Caustic soda then precipitates a viscous colorless sirup. Since all attempts to crystallize this compound as well as its picrate were unsuccessful, it was oxidized directly with nitric acid.

Oxidation of the Formaldehyde Compound.—After the formaldehyde compound in 40 volumes of 1:1 nitric acid has been boiled for four hours under reflux, the solution is evaporated to remove nitric acid. On repeated dilution and concentration, the oxidation product is obtained as a reddish solid, insoluble in water, soluble in alcohol, ether and acetone, and sparingly soluble in hot benzene or petroleum ether. After two recrystallizations from benzene, a colorless product without definite crystalline form is obtained. It softens at 85° and melts unsharply at approximately 100°. Seven grams of the $C_{16}H_{25}N$ base gave 4.2 g. of the new acid, a yield of 47%.

The copper and lead salts separate from water as gelatinous precipitates. The calcium salt is water-soluble and crystallizes poorly from alcohol. For purification, the acid is boiled with a water suspension of calcium carbonate, the filtered solution is decolorized with bone black, and the acid is precipitated with hydrochloric acid. Due to its low melting point and the ease of decarboxylation, the acid was dried in a vacuum desiccator at room temperature.

Anal. Calcd. for $C_{16}H_{21}O_4N$: C, 65.95; H, 7.26; N, 4.81. Found: C, 65.38; H, 7.56; N, 4.62.

The Monocarboxylic Acid, $C_{14}H_{20}NCOOH$.—When the dicarboxylic acid is heated in a bath at 235–240° under reduced pressure (30 mm.), a white crystalline product in a yield of 56% sublimes, and there is an appreciable residue from carbonization left behind. The monocarboxylic acid is insoluble in water, sparingly soluble in benzene, and readily soluble in ether, alcohol, acetone and acids or alkalies. On resublimation, the colorless and beautifully crystalline product melts at 218–220°.

Anal. Calcd. for $C_{15}H_{21}O_2N$: C, 72.83; H, 8.56; N, 5.65. Found: C, 72.45; H, 8.52; N, 5.68.

Picrate of the $C_{14}H_{21}N$ Base.—The acid is converted to the sodium salt in the usual way with sodium hydroxide solution, the salt is admixed with 15 parts of soda-lime, and the mixture is distilled under reduced pressure at a temperature well above 360°. The distillate, a dark red oil, is taken up in dilute hydrochloric acid, the solution is washed twice with ether, and then the free base is precipitated with caustic soda in a yield of about 75%. For final purification, it is converted in alcoholic solution to the picrate which is recrystallized from 50% acetic acid with the addition of animal charcoal. It melts at 146.2°, and its solubilities in the common solvents differ very little from those of the $C_{16}H_{25}N$ picrate.

Anal. Calcd. for $C_{20}H_{24}N_4O_7$: C, 55.53; H, 5.59; N, 12.96. Found: C, 55.41; H, 5.79; N, 12.97.

The $C_{14}H_{21}N$ Base.—The base, when freed from its picrate with ammonium hydroxide, dried, and distilled, is a clear oil without odor, insoluble in water, and miscible in all proportions with the common organic solvents. Efforts to obtain it in crystalline form by chilling were unsuccessful. In a mixture of solid carbon dioxide and ether, it congeals to a glass-like solid. The following physical constants were determined: b. p. at 746 mm., 266.4°; *d* 20/4, 0.9588; n^{20}_{D} 1.5158; n^{25}_{D} 1.5132.

Anal. Calcd. for $C_{14}H_{21}N$: C, 82.69; H, 10.41; N, 6.89. Found: C, 82.46; H, 10.52; N, 6.81.

A 0.2-g. sample of the base was shaken with 30 mg. of Adams platinum oxide catalyst and 5 cc. of alcohol under a hydrogen pressure of 8 atmospheres for eight hours at room temperature. The unchanged base was recovered quantitatively.

In an attempt to brominate the 14-carbon base under conditions employed for the 16-carbon base, a perbromide was formed which on caustic treatment gave the original base.

In an experiment, aimed at direct decarboxylation of the dicarboxylic acid through soda-lime distillation, a very unsatisfactory yield of the $C_{14}H_{21}N$ base was obtained.

Summary

The bromination of the $C_{16}H_{25}N$ naphthenic base from the kerosene distillate of California petroleum is described. The unexpected resemblance of this non-aromatic base to 2,4-dimethylquinoline in its reaction with formaldehyde proves the presence of two methyls through oxidation of the addition product to a dicarboxylic acid and subsequent decarboxylation of the latter to a monocarboxylic acid and then to a $C_{14}H_{21}N$ base. From these reactions, the structural possibilities for the 16-carbon base are restricted to trinuclear doubly-bridged ring systems. A provisional formula is advanced in which two methyls occupy the same relative positions to nitrogen as the two methyls in 2,4-dimethylquinoline. In other respects, the structure is little changed from the pyrindacine formula previously proposed.

AUSTIN, TEXAS RECEIVED OCTOBER 9, 1934