peared and the product was precipitated by the addition of water. There was obtained a quantitative yield of compound melting at 188–192°. Two crystallizations from ethanol gave a product melting at 199–200° and a recrystallization from methanol gave a final melting point of 200–201°. A mixed melting point with the tetrabromodihydroxybiphenyl (m. p., 200–201°) prepared directly from 2,2′-dihydroxybiphenyl, according to the directions of Diels and Bibergeil,[1] showed no depression. Accordingly, two of the bromine atoms in the 200–201° melting tetrabromo compound are in the 5,5′-positions. The remaining two bromine atoms are shown, in a subsequent experiment, to be in the 3,3′-positions.

Under corresponding conditions, 5,5′-dibromo-2,2′-dimethoxybiphenyl was not brominated. The starting material was recovered unchanged after being allowed to stand with the calculated quantity of bromine in acetic acid for thirty-six hours and being heated at 80° for two hours.

3,3′,5,5′ - Tetrabromo - 2,2′ - dimethoxybiphenyl.—The tetrabromo-2,2′-dihydroxybiphenyl, prepared according to the directions of Diels and Bibergeil,[1] melting at 200–201°, was quantitatively methylated by treatment with methyl sulfate and alkali to yield a product which melted at 84–85° after crystallization from ethanol. Recrystallization from methanol raised the melting point to 86–87°.

Anal. Calcd. for $C_{14}H_{10}O_2Br_4$: methoxyl, 11.7. Found: methoxyl, 11.5.

Tetrabromo-2,2′-dimethoxybiphenyl with Phenyllithium.—To 0.012 mole of phenyllithium in 50 cc. of ether was added with stirring 3.18 g. (0.006 mole) of the tetrabromo-2,2′-dimethoxybiphenyl. The bromo compound went into solution and a few seconds later a white precipitate began to appear. This precipitate became very thick so an additional 50 cc. of ether was added. After one hour of stirring the mixture was carbonated by pouring it upon crushed solid carbon dioxide and there was obtained 1.7 g. (72.6%) of crude acid which melted at 220–230°. Four recrystallizations from glacial acetic acid gave 0.3 g. (12.8%) of white crystalline **2,2′-dimethoxy-5,5′-dibromo-3,3′-biphenyldicarboxylic acid** which sintered at 265° and melted at 274–275° with decomposition.

Anal. Calcd. for $C_{16}H_{12}O_6Br_2$: methoxyl, 13.48. Found: methoxyl, 13.58.

Fifty milligrams of the bromo-acid was dehalogenated by shaking for one hour with one-half gram of palladium–calcium carbonate catalyst in 15 cc. of ethanol under 3 atmospheres of hydrogen. There was obtained 25 mg. of acid melting at 203–206°. Recrystallization from dilute ethanol raised the melting point to 207° and a mixed melting point with authentic 2,2′-dimethoxy-3,3′-biphenyldicarboxylic acid (m. p. 208–209°) showed no depression. Accordingly, the remaining two bromine atoms in the tetrabromo compound are in the 3,3′-positions.

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Summary

Halogen–metal and hydrogen-metal interconversion reactions by organolithium compounds have been used to establish the structures of some derivatives of 2,2′-dihydroxybiphenyl. These biphenyl compounds were examined incidental to studies on the preparation of difficultly accessible dibenzofurans from derivatives of 2,2′-dihydroxybiphenyl by ring closure reactions.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, THE UNIVERSITY OF TEXAS]

Nitrogen Compounds in Petroleum Distillates. XVIII. Isolation, Ozonization and Synthesis of 2,4-Dimethyl-8-*s*-butylquinoline

BY LESLIE M. SCHENCK AND J. R. BAILEY

Introduction

2,3,4-Trimethyl-8-ethylquinoline and 2,3,4-trimethyl-8-*n*-propylquinoline have been isolated from the 320–330° kero base fraction[1] by the employment of cumulative extraction[2] and multiple acid extraction[3] in their segregation.

In order to compare the efficiency of multiple acid extraction and counter-current extraction the authors have reworked the residual material from which the above bases were separated. The original base fractions are listed in Tables II and III of a previous paper.[1] The residual bases were processed through cumulative extraction, followed by counter-current extraction. The column used is a semi-automatic modification of the original designed by Schutze, Quebedeaux and Lochte.[4] The efficiency of the modified column is more than fifteen theoretical plates in separation of acetic acid from water with methyl isobutyl ketone the solvent medium, when plotted according to the method described by Varteressian and Fenske.[5]

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(1) This material was furnished the Texas Laboratory by the Union Oil Company of California. Schenck and Bailey, THIS JOURNAL, **61**, 2613 (1939).

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

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

(4) Schutze, Quebedeaux and Lochte, *Ind. Eng. Chem., Anal. Ed.*, **10**, 676 (1938).

(5) Varteressian and Fenske, *Ind. Eng. Chem.*, **28**, 1353 (1936). The efficiency of the column was tested by Ney; unpublished observation by William O. Ney, Jr., Texas Laboratory.

Not only was an additional 31 g. of 2,3,4-trimethyl-8-*n*-propylquinoline segregated from the residual bases in the first counter-current fraction, but also a small amount of the picrate of a new $C_{15}H_{19}N$ base (A), an outline of the structural proof of which follows:

(1) Chromic acid oxidation converted (A) to a $C_{12}H_{11}O_2N$ acid, identified as 2,4-dimethylquinoline-8-carboxylic acid.[6] Since this 12-carbon acid contains three carbons less than the original 15-carbon base, the location of a butyl at position 8 follows.

(2) Ozonization of (A), followed by ozonolysis under reflux in dilute hydrogen peroxide solution, yielded 2-methylbutanoic acid, identified as the anilide. The refinement attainable with ozonization is attested by the fact that only 1.5 g. of Base A was originally available. Analysis of the base and chromic acid oxidation required about 0.5 g., and less than 1 g. was used for ozonization.

(3) Synthesis of the base was effected by the Combes method[7] with the intermediates acetylacetone and *o*-amino-*s*-butylbenzene.[8] The synthetic 2,4-dimethyl-8-*s*-butylquinoline proved identical with the petroleum product.

Here ozonization of this particular quinoline homolog to 2-methylbutanoic acid directed us in preferential selection for the above synthesis of *o*-amino-*s*-butylbenzene from the four isomeric homologs. It appears probable that the formation of 2-methylbutanoic acid from ozonization of any *s*-butylquinoline homolog under the above experimental conditions would result, regardless of the location of the butyl; at any rate, we synthesized 2,4-dimethyl-6-*s*-butylquinoline, and degraded it in this way to 2-methylbutanoic acid.

The broader generalization may be established that *any alkyl on a quinoline nucleus passes on ozonization of the base, followed by ozonolysis coupled with oxidation, to an acid with one more carbon than the alkyl, and whose carboxyl originates from the nuclear carbon to which the alkyl is attached.* In agreement with this postulate, we identified among the ozonization products of the kero base, 2,3,4-trimethyl-8-*n*-propylquinoline,[1] formic acid, acetic acid, *n*-butyric acid, oxalic acid, ammonia and carbon dioxide.

Experimental

The residual bases referred to above were combined after removal of 2,3,4-trimethyl-8-ethylquinoline and 2,3,4-trimethyl-8-*n*-propylquinoline as nitrates and acid sulfates, respectively, and then 1000 ml. was carried through cumulative extraction, 460 ml. of aromatics with n^{20}_D 1.5845 being concentrated in the aqueous phase. This material was further separated through counter-current extraction into the fractions listed in Table I.

TABLE I

Fraction	Volume, ml.	n^{20}_D
1	52	1.5790
2	76	1.5819
3	75	1.5860
4	81	1.5861
5	72	1.5930
6	72	1.5971

Isolation of 2,4-Dimethyl-8-*s*-butylquinoline.—Fraction 1 was picrated in alcohol, and the filtered picrate recrystallized to constant melting point, yielding 31 g. of 2,3,4-trimethyl-8-*n*-propylquinoline. The resultant smear from evaporation of the solvent was repeatedly leached out with boiling 50% ethyl alcohol.

From the cooled extract, what proved to be a high concentration of the picrate of 2,4-dimethyl-8-*s*-butylquinoline separated and was purified by recrystallization from methyl alcohol as slender yellow needles to a constant melting point of 148–150° without decomposition.

Anal. Calcd. for $C_{21}H_{22}O_7N_4$: C, 57.01; H, 5.01; N, 12.66. Found: C, 56.80; H, 5.13; N, 12.51.

The base, 1.5 g., after liberation from the picrate with concentrated ammonium hydroxide, was extracted with ether, and after drying the solution with stick potassium hydroxide, the solvent was removed in an evacuated desiccator. It is an odorless, water insoluble oil having the following constants: b. p. 310°, n^{20}_D 1.5669, d^{20}_4 0.9824.

Anal. Calcd. for $C_{15}H_{19}N$: C, 84.45; H, 8.98; N, 6.57. Found: C, 84.41; H, 9.01; N, 6.63.

2,4-Dimethylquinoline-8-carboxylic Acid.—To a boiling solution of 0.38 g. of the base in dilute sulfuric acid was slowly added a concentrated solution of potassium dichromate in sulfuric acid to the end-point of oxidation. In chloroform extraction a crystalline acid was obtained in 90% yield. After two crystallizations from ethyl alcohol, it melted at 240–241°. A mixed melting point of this acid with an authentic sample of 2,4-dimethylquinoline-8-carboxylic acid[6] showed no depression.

Anal. Calcd. for $C_{12}H_{11}O_2N$: C, 71.64; H, 5.47; N, 6.96. Found: C, 71.51; H, 5.60; N, 7.14.

Degradation of the Base to Obtain 2-Methylbutanoic Acid.—One gram of the butyl base in 20 ml. of carbon tetrachloride was suspended in an ice-bath and ozonized for fifteen hours. The separated solid ozonide was then hydrolyzed by the addition of 10 ml. of dilute hydrogen peroxide, first for six hours at room temperature, then for one hour on the steam-bath. The carbon tetrachloride phase was extracted twice with dilute caustic, the aqueous extract saturated with sodium chloride, then acidified with dilute sulfuric acid and repeatedly extracted with ether. The ether extract yielded a drop of oil with a typical fatty acid odor. After drying in a desiccator, the acid was con-

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[6] W. N. Axe, THIS JOURNAL, **61**, 1018 (1939).

[7] Combes, *Bull. soc. chim.*, [2] **49**, 91 (1888).

[8] Read, Hewitt and Pike, THIS JOURNAL, **54**, 1194 (1932).

verted to its anilide[9] which after two crystallizations from dilute alcohol melted at 109–111°, in agreement with 2-methylbutane anilide.[10] A mixed melt with an authentic sample of this anilide showed no depression, establishing a secondary butyl at position 8.

Synthesis of 2,4-Dimethyl-8-*s*-butylquinoline.—The base was synthesized[11] in 70% yield from equimolar quantities of acetylacetone and *o*-amino-*s*-butylbenzene[8] and corresponded in physical constants to the petroleum base. A mixed melt of the picrates from the two sources showed no depression.

Synthesis of 2,4-Dimethyl-6-*s*-butylquinoline.—This base was synthesized in a manner analogous to that employed in the preparation of 2,4-dimethyl-8-*s*-butylquinoline, from the intermediates acetylacetone and *p*-amino-*s*-butylbenzene.[8] The liquid base has a boiling point of 321° and $n^{25}\text{D}$ 1.5660. The picrate recrystallizes from methyl alcohol in slender yellow needles melting undecomposed at 141–142°.

Anal. Calcd. for $C_{21}H_{22}O_7N_4$: C, 57.01; H, 5.01; N, 12.66. Found: C, 57.20; H, 5.04; N, 12.57.

Upon ozonization of the base, followed by ozonolysis coupled with oxidation, 2-methylbutanoic acid was encountered and identified as its anilide.

Ozonization of 2,3,4-Trimethyl-8-*n*-propylquinoline.[1]—Eight grams of the base in 50 ml. of carbon tetrachloride was ozonized for twenty-four hours in an ice-bath. The solution was then hydrolyzed by six hours of standing and one hour of refluxing with 20 ml. of 3% hydrogen peroxide. The iced solution, made alkaline with potassium carbonate, was aerated for thirty minutes with a stream of purified air, the outlet being led through 50 ml. of standard acid. Upon titration, no decrease in acidity was found. The alkaline solution was next refluxed one hour, being aerated into 50 ml. of standard acid. Back titration showed the consumption of 0.015 mole of acid. Since no ammonia was liberated until the alkaline solution was boiled, the nitrogen was evidently not in the form of an ammonium salt. About 50% of unozonized base (3.9 g.) was recovered by three ether extractions of the caustic solution. The ozonized base represented 0.0192 mole of ammonia, agreeing closely with the amount salified in the dilute standard acid.

Upon acidification of the alkaline hydrolysis solution with dilute sulfuric acid and saturation with sodium chloride, repeated extraction with a large volume of ether was employed to remove acidic components.

After removal of ether, the residual acids were found to reduce immediately ammoniacal silver nitrate solution, indicating the presence of formic acid. Following several days of standing under desiccation, crystalline anhydrous oxalic acid of the melting point 188° began to separate, and was further precipitated by the addition of cold methyl alcohol. It gave all the common tests for this acid.

Upon removal of the methyl alcohol, the residual liquid was fractionated in a micro still, yielding a low boiling formic acid fraction (100–110°) which readily formed a mirror with silver nitrate and reduced mercuric chloride to calomel. A second fraction (110–120°) was recognized as acetic acid by odor and the basic ferric acetate test. The third fraction (150–170°) possessed the odor of rancid butter, and formed an anilide melting at 95–96° after two recrystallizations from dilute ethyl alcohol, corresponding to *n*-butyranilide.[12] A mixed melt with an authentic sample was used to confirm the identification.

During the peroxide hydrolysis, carbon dioxide was liberated in small quantity. This was shown by the gas stream precipitating barium carbonate from a saturated barium hydroxide solution.

Summary

This paper deals with counter-current extraction in the isolation of a new $C_{15}H_{19}N$ kero base, 2,4-dimethyl-8-*s*-butylquinoline. The structure of this compound was established through chromic acid oxidation to the known 2,4-dimethylquinoline-8-carboxylic acid; ozonization, followed by ozonolysis, to yield 2-methylbutanoic acid; and synthesis from the intermediates acetylacetone and *o*-amino-*s*-butylbenzene. Ozonization products of 2,3,4-trimethyl-8-*n*-propylquinoline are described, and the synthesis of 2,4-dimethyl-6-*s*-butylquinoline and its degradation to 2-methylbutanoic acid through ozonization and ozonolysis are reported.

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[9] Shriner and Fuson, "Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1935, p. 144.

[10] *Ibid.*, p. 97. Listed as derivative of ethylmethylacetic acid.

[11] *Cf.* Königs and Mengel, *Ber.*, **37**, 1325, 1333 (1904).

[12] Shriner and Fuson, ref. 9, p. 97.