dimethyl sulfate in alcohol, in which the salt is only moderately soluble.

Anal. Calcd. for $C_{21}H_{29}O_7NS$: S, 7.29. Found: S, 7.28.

Methylmorphenol by Decomposition of β-Methylmorphimethine Methohydroxide.—Sixty-six grams of β-methylmorphimethine methomethyl sulfate was saponified by refluxing with 130 cc. of 20% sulfuric acid for one and a half hours. The solution was diluted and the sulfate ion was precipitated with approximately 120 g. of barium hydroxide (slight excess). The filtrate from the barium sulfate was evaporated under diminished pressure (15–20 mm.) and the residue dried at 100–105° for four hours at 15 mm. When treated with 150 cc. of water, the mass became warm, amine escaped, and the methylmorphenol separated as an oil. This was taken up in ether, washed with dilute hydrochloric acid and with sodium bicarbonate. The residue crystallized when methyl alcohol was added: yield, 21 g. or 65% of the theoretical.

Methylmorphenol by Decomposition of the Methyl Sulfates.—The degradation was carried out in a 2-liter 3-necked flask fitted with a mercury-sealed stirrer, a thermometer, and a delivery tube through which the gases passed into dilute hydrochloric acid. Twenty-eight grams of sodium was added slowly with stirring to 800–850 cc. of cyclohexanol at 110°. The temperature must be raised to 140° to keep the sodium cyclohexanolate from separating, but should be maintained at 120° during the addition of the salt. When the sodium was dissolved, 220 g. of the β-methylmorphimethine methomethyl sulfate (or 250 g. of the α-salt) was added in portions over a period of thirty minutes. Stirring was then continued for fifteen minutes.

The cyclohexanol was distilled off with steam and the residue extracted with ether. The extraction was hindered by the formation of emulsions. The ether extract was washed with dilute hydrochloric acid and sodium bicarbonate. After evaporation of the ether, the methylmorphenol remained as an oil, which was crystallized by addition of 100 cc. of methyl alcohol. The product was purified by crystallization from methyl alcohol or distillation at 1 mm.

The average yield from twenty runs with β-methomethyl sulfate was 65–70% of pure material (m. p. 64–65°). The mother liquors were treated with picric acid, and yielded a crude picrate which gave after decomposition a mixture of about 50% methylmorphenol and a white crystalline compound, m. p. 116–116.5° (nitrogen-free), which has not yet been investigated.

Because of the difficulty in obtaining crystalline α-methylmorphimethine methomethyl sulfate, most of the degradations were carried out with the β-compound. Later we obtained a crystalline α-salt (with acetone) which could be degraded in yields of 60–65%. The conversion of α- into β-methylmorphimethine is thus rendered unnecessary.

Morphenol.—A mixture of 25 g. of methylmorphenol, 50 cc. of 48% hydrobromic acid and 175 cc. of acetic acid was heated under reflux in a sand-bath. A homogeneous solution was obtained after a few minutes of refluxing. After eight hours, the mass was poured into 600 cc. of water. The morphenol, which is thus precipitated in almost quantitative yield, melted at 140–143°, after one recrystallization from benzene at 145°.

Summary

A method for the large-scale preparation of methylmorphenol (3-methoxy-4,5-phenanthrylene oxide) from β- (and α-) methylmorphimethine by a modified Hofmann degradation is described.

UNIVERSITY, VIRGINIA RECEIVED SEPTEMBER 29, 1934

[CONTRIBUTION FROM THE DEPARTMENT OF BIOLOGICAL CHEMISTRY, COLUMBIA UNIVERSITY]

Identification of Alkyl Halides: N-Alkyl-*p*-bromobenzenesulfon-*p*-anisidides

BY H. B. GILLESPIE

The reaction between alkyl halides and a selected arylsulfonanilide should yield derivatives whose melting points would be useful constants to aid in the identification of the halides. In order to obtain solid products *p*-bromobenzenesulfon-*p*-anisidide[1] was selected as the reagent for study. This amide dissolves readily in 5% potassium hydroxide and the alcoholic solution of the potassium salts reacts smoothly with alkyl halides to yield the corresponding N-alkyl derivatives. The procedure is simpler than are those which have been used to give alkyl phthalimides.[2]

(1) Marvel and Smith, THIS JOURNAL, **45**, 2696 (1923).

(2) Sah and Ma, *Ber.*, **65**, 1630 (1932); Allen and Nichols, THIS JOURNAL, **56**, 1409 (1934).

Experimental Part

***p*-Bromobenzenesulfon-*p*-anisidide.**—To a solution of 14.8 g. (0.12 mole) of *p*-anisidine and 7.9 g. (0.1 mole) of pyridine in 150 cc. of ether, there was added at room temperature with mechanical stirring during the course of one hour a solution of 25.6 g. (0.1 mole) of *p*-bromobenzenesulfonchloride in 150 cc. of ether. When the addition was complete, the reaction mixture was heated on the steam-bath under reflux for thirty minutes. After distilling the ether, the red colored residue was washed with dilute hydrochloric acid (1:1), then with water and filtered on a Büchner funnel. After two recrystallizations from 150 cc. of alcohol, 23.7 g. (69.3%) of *p*-bromobenzenesulfon-*p*-anisidide, melting at 142° (uncorr.), was obtained.

Small amounts of this compound can be prepared as described by Marvel and Smith.[1]

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

Substituent	M. p., °C., (uncorr.)	Formula	Bromine, % Calcd.	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.

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

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.

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[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]

* 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.* Elbner, *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*.