ium nitrate was added and the solution gently refluxed. The color of the solution changed quickly from pale yellow to orange, at the end of one minute. The solution was refluxed thirty minutes longer and diluted with cold water. The red precipitate was collected and recrystallized from 80% acetic acid; yield, 0.35 g. of isatin, melting at 199°. A mixed melting point with pure synthetic isatin[7] showed no depression.

TABLE I

Substance	Used, g.	Product	M. p., °C.	Yield, g.
Benzoin	2.12	Benzil	95–96	2.04
Anisoin[8]	1.2	Anisil	132–133	0.8
p-Toluoin	1.9	*p*-Tolil	102	.9
Furoin	1.1	Furil	160	.5
Dioxindole[6]	0.5	Isatin	199	.35

I am deeply indebted to Prof. David Davidson, of Brooklyn College, for his interest and suggestions and to Dr. M. Jacobi, Director of Laboratories, Beth-El Hospital.

[7] "Organic Syntheses," Coll. Vol. I, p. 321.

[8] Bosler, *Ber.*, **14**, 423 (1881).

CHEMICAL LABORATORIES
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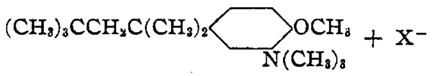
RECEIVED MARCH 14, 1940

Invert Soaps. Quaternary Ammonium Salts of Derivatives of Long Chain Phenols

BY JOSEPH B. NIEDERL AND MARTIN I. DEXTER[1]

Some of the previously reported "invert soaps" involve long chain ethers of *o*-, *m*- and *p*-aminophenol.[2] It has now been found that invert soaps can also be obtained by using short chain ethers of the long chain substituted phenols as follows: $\alpha,\alpha,\gamma,\gamma$-tetrametho-butylphenol ("diisobutylphenol"), prepared by condensing diisobutylene with phenol,[3] was methylated and the resulting methyl ether (I) was subsequently nitrated to yield the mono nitro derivative of *p*-($\alpha,\alpha,\gamma,\gamma$-tetrametho)-butyl-anisole (II). This compound in turn was reduced to the respective amine (III), which was then converted into the tertiary dimethylamine (IV), from which, then, water soluble "invert soaps" were prepared by converting this tertiary amine into the respective ammonium salts, the 2-trimethylammonium-4-($\alpha,\alpha,\gamma,\gamma$-tetrametho)-butylphenol methyl ether iodide (V) and methosulfate (VI), using methyl iodide and dimethyl sulfate, respectively.

The structure of these salts is



$$(CH_3)_3CCH_2C(CH_3)_2C_6H_3(OCH_3)\,N(CH_3)_3 + X^-$$

$(X = I;\ CH_3OSO_2O-)$

Experimental

Nitration.—Fifty grams of the methyl ether (I) was dissolved in 300 cc. of a mixture of equal parts of acetic acid and acetic acid anhydride. The mixture was then placed in an ice-bath, and 50 cc. of concentrated nitric acid (sp. gr. 1.42) was then added cautiously in small amounts, while the reaction mixture was kept at a temperature not exceeding 10°. After the completion of the addition, the reaction mixture was allowed to come to room temperature gradually and to stand for thirty minutes; 500 cc. of water was added to hydrolyze the acetic anhydride and the nitrated ether (II) precipitated at the same time. It was crystallized from methyl alcohol, in large, yellow plates, possessing a faint floral odor.

The same product may also be obtained by nitrating first the phenol and methylating the mononitrodiisobutylphenol afterward.

Reduction.—Thirteen grams of the above nitro compound (II) was dissolved in 50 cc. of ethyl alcohol. To this solution were added 15 g. of tin and 27 cc. of hydrochloric acid over a period of two hours. During this period the mixture was refluxed. Complete reduction was indicated when all color had disappeared, and when a small sample withdrawn from the reaction mixture dissolved completely in water. The mixture was then cooled, and 50% sodium hydroxide solution was added until the precipitated tin hydroxide had dissolved. From this the amine (III) was extracted with ether, and the ether extract dried over anhydrous sodium sulfate. The ether was then distilled off and the amino compound redistilled *in vacuo* under reduced pressure.

The hydrochloride of the amine (IIIa) was prepared by passing dry hydrogen chloride gas through a solution of the amine in petroleum ether. The benzoate (IIIb) was prepared by employing the usual Schotten–Baumann procedure, using 0.5 cc. of the amine, 2 cc. of benzoyl chloride, and 5 cc. of 20% sodium hydroxide solution.

Methylation.—Eight grams of the above primary amine (III), and 8.5 g. of the dimethyl sulfate contained in a stoppered Erlenmeyer flask, were heated in a steam-bath for two hours. The reaction mixture was then cooled and treated with 50 cc. of 2 *N* sodium hydroxide solution.

The mixture was then extracted with ether and the ether dried over sodium sulfate. The ether was then distilled off and the tertiary amine (IV) redistilled at reduced pressure.

Methiodide.—Two cc. of the above tertiary amine (IV) was dissolved in 20 cc. of methyl iodide and, after a short period of warming, the excess methyl iodide was distilled off. The residue (V) was recrystallized from ethyl acetate. The compound is soluble in water.

Methosulfate.—To 5.3 g. of the tertiary amine (IV) were added 2.6 g. of freshly distilled dimethyl sulfate and 4 cc. of dry benzene. The mixture was refluxed at 120° for two hours. After this time, the benzene was distilled off at reduced pressure. The residue was then dissolved in 20 cc. of methanol, treated with a little barium carbonate, and with charcoal. It was filtered and the .methyl alcohol

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[1] Abstracted from the thesis presented by M. I. Dexter to the Graduate School of New York University in partial fulfillment of the requirements for the degree of Master of Science, May, 1941.

[2] R. Kuhn and D. Jerchel, *Ber.*, **73**, 1100 (1940).

[3] J. B. Niederl, *Ind. Eng. Chem.*, **30**, 1269 (1938).

TABLE I

	Compounds	Formulas	M. p., °C. (uncor.)	B. p., °C. (uncor.)	Analyses, % N Calcd.	Found
I	4-($\alpha,\alpha,\gamma,\gamma$-Tetrametho)-butylphenol-methyl ether[3]	$CH_3OC_6H_4C_8H_{17}$	46	272 (760 mm.)		
II	2-Nitro-	$C_{15}H_{23}NO_3$	58	151 (3 mm.)	5.28	5.12
III	2-Amino-	$C_{15}H_{25}NO$		160 (8 mm.)	5.94	5.86
	(a) Hydrochloride	$C_{15}H_{26}NOCl$	75–77		5.49	5.36
	(b) Benzoyl deriv.	$C_{22}H_{29}NO_2$	111		4.13	4.03
IV	2-Dimethylamino-	$C_{17}H_{29}NO$		163–165 (8 mm.)	5.32	5.21
V	Methiodide	$C_{18}H_{32}NOI$	172		3.46	3.61
VI	Methosulfate	$C_{19}H_{34}NSO_5$	154		3.61	3.57

distilled off under reduced pressure. The residue, the methosulfate (VI), was recrystallized from ethyl acetate. The methosulfate dissolves in water instantaneously.

CONTRIBUTION FROM THE CHEMICAL LABORATORIES
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NEW YORK, N. Y.
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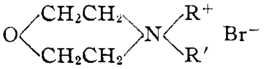
Invert Soaps. Quaternary Morpholonium Salts[1]

BY MARTIN E. MCGREAL AND JOSEPH B. NIEDERL

Since none of the previously reported[2] "invert soaps" contain a mixed heterocyclic radical it was thought desirable to prepare and study invert soaps containing a sulfur–nitrogen (long chain ethers of thiazoline phenols),[3] or an oxygen–nitrogen heterocyclic ring. For the latter purpose N-tertiary morpholines were chosen as starting materials. N-Ethyl- and N-ethylol-morpholine were converted into N-long chain substituted quaternary morpholonium salts upon treatment with lauryl, myristyl and cetyl bromide, respectively. All the resulting quaternary ammonium salts, which possess the structure as given below, proved to be soluble in water.



$$O\left\langle\begin{matrix}CH_2CH_2\\CH_2CH_2\end{matrix}\right\rangle N\left\langle\begin{matrix}R^+\\R'\end{matrix}\right. Br^-$$

(R = $-C_2H_5$; $-CH_2CH_2OH$)
(R′ = $-C_{12}H_{25}$; $-C_{14}H_{29}$; $-C_{16}H_{33}$)

Procedure

A 0.1 mole of N-ethyl or of N-ethylol-morpholine was added to 0.1 mole of the respective halide (lauryl, myristyl or cetyl bromide), dissolved in toluene which equaled one-fourth the volume of the reactants. The solution was gently refluxed for four hours and upon cooling a solid precipitated out. The wax-like precipitate was washed with ether and purified by precipitation with anhydrous ether from a concentrated absolute ethyl alcohol solution.

TABLE I

Morpholonium bromides	Formula	M. p. °C. (uncor.)	Analyses, % Br Calcd.	Found
N-Ethyl-N-lauryl	$C_{18}H_{38}NOBr$	201	21.98	22.30
N-Ethyl-N-myristyl	$C_{20}H_{42}NOBr$	203	20.40	20.80
N-Ethyl-N-cetyl	$C_{22}H_{46}NOBr$	207	19.00	19.20
N-Ethylol-N-lauryl	$C_{18}H_{38}NO_2Br$	92	21.05	20.85
N-Ethylol-N-myristyl	$C_{20}H_{42}NO_2Br$	95	19.60	19.80
N-Ethylol-N-cetyl	$C_{22}H_{46}NO_2Br$	97	18.34	18.45

THE CHEMICAL LABORATORIES OF
ST. JOHN'S UNIVERSITY AND OF
NEW YORK UNIVERSITY
WASHINGTON SQUARE COLLEGE, NEW YORK, N. Y.
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(1) Abstracted from the thesis of M. Buonocore presented to the Graduate School of St. John's University in partial fulfillment of the requirements for the degree of Master of Science, May, 1941.

(2) R. Kuhn and co-workers, *Ber.*, **73**, 1080–1109 (1940).

(3) Wm. F. Hart and J. B. Niederl, THIS JOURNAL, **63**, 945 (1941).

The Estimation of Primary Carbinol Groups in Carbohydrates

BY RICHARD E. REEVES

Fleury and Lange[1] observed that glucose is oxidized by periodic acid to yield five mols of formic acid and one mol or formaldehyde, the latter derived from the terminal or primary carbinol group. Other workers[2,3] have applied this reaction to the quantitative estimation of primary carbinol groups by distilling off and determining the formaldehyde. However, they obtained much less than the theoretical amount of formaldehyde from glucose and their method failed seriously with the methyl glucoses and mannitol.

In the present investigation suitable conditions were found for producing the theoretical amount of formaldehyde from a variety of sugars. Glucose, 2,3-dimethyl glucose and mannitol, which gave, respectively, 91, 30 and 89% of the expected amount of formaldehyde by the earlier procedure, will readily give the theoretical yield by the present method. The primary carbinol groups of certain simple sugars may now be determined almost as conveniently and accurately as the reducing group.

The significant changes in the procedure are (a) the oxidation is carried out in the presence of a slight excess of sodium bicarbonate, instead of in acid medium, and (b) the formaldehyde is precipitated directly from the reaction mixture after reduction of iodate and the excess periodate to iodide.

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(1) P. Fleury and J. Lange, *J. pharm. chim.*, **17**, 1, 409 (1933).

(2) P. Karrer and K. Pfaehler, *Helv. Chim. Acta*, **17**, 766 (1934).

(3) N. Ariyama and T. Kitasato, *J. Biochem.* (*Japan*), **25**, 357 (1937).