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
of New York University
Washington Square College
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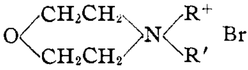
Invert Soaps. Quaternary Morpholonium Salts[1]

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.



(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).

For analysis by the present procedure a substance must have a hydroxyl group on the carbon atom adjacent to the primary carbinol group, and must yield no product precipitating with the dimedon reagent except formaldehyde. (The latter point may be checked conveniently by the sharp and characteristic melting point of the formaldehyde–dimedon compound.) Unsatisfactory for one or both of the above reasons are monoacetone glucose and α-methyl glucoside. The low value obtained with fructose (86% theory) remains to be explained.

TABLE I

FORMALDEHYDE FROM CARBOHYDRATES BY OXIDATION WITH PERIODATE

Substance	Mg. taken	Mg. ppt.	M. p. ppt., °C.	% theor. CH_2O
d-Glucose	18.0	29.6	189–90	101.3
		29.3	....	100.0
		29.0	....	99.3
		29.4	....	100.6
d-Galactose	18.0	28.8	189–90	98.8
		29.1	....	99.7
d-Xylose	15.0	28.8	188–90	98.8
		29.1	....	99.7
Mannitol	9.1	29.5	189–90	101.0
		29.5	....	101.0
2,3-Dimethyl glucose	20.8	29.2	189–90	100.0
		28.6		98.0
2,3,4,6-Tetramethylglucose	23.6	0.0	....	...
		0.0	....	...
Fructose	9.0	25.1	189–90	86.0
		25.1	....	86.0
Monoacetone glucose	22.0	30.2	187–90	(103.3)
		33.6	....	(115.0)
α-Methyl glucoside	19.4	1.9	200–210	...
		2.7	....	...

Reagents and Procedure

Periodic acid solution, approximately 0.3 molar, is prepared by dissolving 7.0 g. of $HIO_4 \cdot 2H_2O$ in water and making up to a volume of 100 cc. After standing overnight the solution is decanted from a small yellow precipitate.

Sodium arsenite solution, 1.2 *N*, is prepared by dissolving 20.4 g. of pure Na_2HAsO_3 in water and making up to 100 cc. This solution should completely reduce an equal volume of the periodic acid reagent in the presence of 0.1–0.2 *N* hydrochloric acid.

The dimedon solution contained 80 mg. of 5,5-dimethyldihydroresorcinol per cc. of 95% alcohol. We used *N* sodium bicarbonate solution, *M* sodium acetate solution and *N* hydrochloric acid solution.

The following directions provide sufficient reagent to oxidize 0.1 mmole (18 mg.) of hexose and to precipitate 0.1 mmole (3 mg.) of formaldehyde. The substance to be analyzed may be dissolved in water or dilute acid, but not more than 0.6 mequiv. of free acid or buffer should be introduced with the sample. The sample dissolved in 2.0 cc. of solution is placed in a test-tube and treated with 2.0 cc. of *N* sodium bicarbonate and 2.0 cc. of periodic acid reagent. The solutions are mixed and allowed to stand at room temperature for one hour (with glucose the reaction is nearly complete in ten minutes). Then are added in turn with thorough mixing 3.0 cc. of *N* hydrochloric acid and 2.0 cc. of sodium arsenite solution. When the precipitate and yellow color have completely disappeared 2.0 cc. of sodium acetate solution and 1 cc. of dimedon reagent are added. The test-tube is then placed in a boiling water-bath for ten minutes, after which it is allowed to stand at room temperature for at least one hour (or it may stand at room temperature overnight without heating). The precipitate is then filtered on a weighed sintered glass filter stick, washed thoroughly with water, and dried in a current of dry air at 85–95° for twenty minutes. (If this temperature is exceeded there will be loss due to sublimation.) The crystalline precipitate should melt sharply at 189–190° cor. The weight of formaldehyde is equal to 0.10274 times the weight of the precipitate.[4,5]

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(4) D. Vorländer, *Z. anal. Chem.*, **77**, 241 (1929).

(5) M. V. Ionescu and C. Bodea, *Bull. Soc. Chim.*, [4] **47**, 1408 (1930).

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Chemiluminescence of Luminol Catalyzed by Iron Complex Salts of Chlorophyll Derivatives

BY ERICH SCHNEIDER

Cook[1] demonstrated that the chemiluminescence of luminol (3-aminophthalhydrazide) which takes place when the peroxide of luminol formed during oxidation is decomposed,[2] occurs with iron phthalocyanines as catalysts as well as with catalysts like hemin, hemoglobin, and catalases (iron porphyrin complex salts) as reported by earlier investigators. Other metal phthalocyanines have a weaker or no catalytic action upon the reaction.

I wish to report that iron chlorophyll derivatives have the same catalytic effect, and have tested a number of these and related compounds as to their ability to catalyze the chemiluminescence of luminol. Iron chlorin e_6, iron pheophorbide a and iron bacteriochlorin e_6 showed strong luminescence; copper chlorin e_6, copper deuteroporphyrin and sulfonated copper phthalocyanine a weak luminescence; chlorophyllin a still weaker or no luminescence; pheophorbide, chlorin e_6, deuteroporphyrin and coproporphyrin showed no luminescence.

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(1) A. H. Cook, *J. Chem. Soc.*, 1845 (1938).

(2) H. D. K. Drew and R. F. Garwood, *ibid.*, 791 (1938).