

depress the melting point of an authentic sample^a of lomatiol of m. p. 127.7–129°. It dissolved in dilute potassium hydroxide with a deep crimson color, and a drop of a solution of its barium salt, prepared as described by Hooker,^{2b} allowed to evaporate on a microscope slide, exhibited the two characteristic forms and the highly characteristic behavior on rubbing described by him.

Dehydroiso- β -lapachone was prepared from a sample (7.1 mg.) of the synthetic lomatiol described above by the method of Hooker.^{2b} After two crystallizations from dilute alcohol 3 mg. of orange-red needles were obtained which exhibited the following very characteristic melting point behavior. An initial melting point of 110–112° was observed (*cf.* refs. 1 and 2b) but if the capillary was held for some time at about 113° the material resolidified and then remelted at 115.2–116.2°. Likewise, if a freshly melted sample of the needles (m. p. 110–112°) was caused to

solidify by brief removal from the bath it remelted at 115.2–116.2°. A precisely similar behavior was exhibited both by a sample of dehydroiso- β -lapachone prepared from an authentic sample^a of lomatiol and by a mixture of the two. The lower of the two melting points corresponds to the metastable needles observed by Rennie,¹ whereas the higher corresponds to the stable prisms reported by Hooker. We have observed both forms, but have not had a sample composed exclusively of the prismatic form.

Summary

A conversion of lapachol to lomatiol has been accomplished.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF NEW YORK UNIVERSITY]

Symmetrical Morpholinium Alkyl Sulfates

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Studies in the morpholinium type of "Invert Soaps"² have now been extended to those derived from symmetrical dialkyl sulfates and morpholines containing a long chain alkyl substituent on nitrogen.

Experimental

Dialkyl Sulfates.—Dimethyl and diethyl sulfates were commercial products; the others were prepared using the method of Barkenbus and Owen.³

N-Alkyl morpholines were prepared by refluxing equimolar quantities of morpholine and the appropriate alkyl bromide in absolute ethyl alcohol with anhydrous potassium carbonate for six hours. The solvent was distilled off, the residue washed with distilled water and the product distilled under reduced pressure.

Morpholinium sulfates were obtained by mixing equimolecular quantities of the alkyl morpholine and the dialkyl sulfate. With methyl sulfate the reaction was quantitative in the cold; with ethyl sulfate slight heating on a steam-bath was necessary; with *n*-butyl and *n*-hexyl sulfates prolonged heating in sealed ampules on a steam-bath was needed; and with hexadecyl sulfate prolonged refluxing of the reactants in toluene was required. The methyl sulfates were recrystallized from water in form of crystalline hydrates while the others were recrystallized from ethyl acetate.

Physiological.—In the phenol coefficient determinations using the U. S. Bureau of Standards technique toward *S. aureus*, the N-hexadecyl morpholinium series exhibited the maximum activity, reaching phenol coefficients of 500 to 600 depending on the pH of the solutions tested, with hardly any difference in the methyl, ethyl and *n*-butyl or *n*-hexyl sulfate series. Toward *E. typhosa*, the N-tetradecyl compounds showed the higher activity, the phenol coefficients being about 200. Equal activities toward both

Gram-positive as well as Gram-negative microorganisms was reached with the hexyl sulfate compounds.

TABLE I

N-ALKYL MORPHOLINES AND MORPHOLINIUM SULFATES

R	R'	Formula	M. p., °C., (uncor.)	Analyses, % N Calcd. Found	
O(CH ₂ CH ₂) _n NR					
Dodecyl	...	C ₁₈ H ₃₇ NO	15	5.72	5.70
Tetradecyl	...	C ₁₈ H ₃₇ NO	17	5.12	5.15
Hexadecyl	...	C ₂₀ H ₄₁ NO	40	4.65	4.68
Octadecyl	...	C ₂₂ H ₄₅ NO	25	4.25	4.31
[O(CH ₂ CH ₂) _n NRR'] ₂ SO ₄ R'					
Dodecyl	Methyl ^a	C ₁₈ H ₃₇ NSO ₄	47	3.59	3.52
Dodecyl	Ethyl	C ₂₀ H ₄₁ NSO ₄	43	3.53	3.45
Dodecyl	<i>n</i> -Butyl	C ₂₄ H ₄₉ NSO ₄	41	3.03	2.68
Dodecyl	<i>n</i> -Hexyl	C ₂₈ H ₅₇ NSO ₄	160	2.74	2.93
Dodecyl	Hexadecyl	C ₄₈ H ₉₉ NSO ₄	93	2.37	2.31
Tetradecyl	Methyl ^a	C ₂₀ H ₃₉ NSO ₄	57	3.35	3.33
Tetradecyl	Ethyl	C ₂₂ H ₄₃ NSO ₄	50	3.27	3.16
Tetradecyl	<i>n</i> -Butyl	C ₂₆ H ₅₁ NSO ₄	90	2.86	2.52
Tetradecyl	<i>n</i> -Hexyl	C ₃₀ H ₅₉ NSO ₄	187	2.59	2.71
Tetradecyl	Hexadecyl	C ₅₀ H ₁₀₃ NSO ₄	127	2.26	1.88
Hexadecyl	Methyl ^a	C ₂₂ H ₄₃ NSO ₄	68	3.19	3.21
Hexadecyl	Ethyl	C ₂₄ H ₄₇ NSO ₄	64	3.08	3.03
Hexadecyl	<i>n</i> -Butyl	C ₂₈ H ₅₅ NSO ₄	142	2.70	2.77
Hexadecyl	<i>n</i> -Hexyl	C ₃₂ H ₆₃ NSO ₄	173	2.47	2.83
Hexadecyl	Hexadecyl	C ₅₂ H ₁₀₇ NSO ₄	104	2.17	2.14
Octadecyl	Methyl ^a	C ₂₄ H ₄₅ NSO ₄	81	2.96	2.88
Octadecyl	Ethyl	C ₂₆ H ₄₉ NSO ₄	75	2.89	2.81

^a Hydrate.

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Summary

A series of new symmetrical morpholinium alkyl sulfates has been prepared and their phenol coefficients determined.

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(1) Abstracted from the theses of Hugh W. Salzberg and John J. Shatynski presented to the Graduate School of New York University in partial fulfillment of the requirements for the degree of Master of Science, 1946. Presented before the Division of Organic Chemistry at the Atlantic City meeting of the American Chemical Society, April 16, 1947.

(2) J. B. Niederl and co-workers, *THIS JOURNAL*, **63**, 1476 (1941); **66**, 840 (1944); **67**, 1227 (1945).

(3) Barkenbus and Owen, *ibid.*, **56**, 1204 (1934).