hydrogenation, with sulfuric acid containing 15% sulfur trioxide, (3) specific dispersion of the selectively hydrogenated product.

Menthol and dicyclic terpenic alcohols such as borneol and isoborneol did not undergo hydrogen transfer reaction during dehydration treatment in the presence of magnesium chloride solution.

Limonene, however, on treatment under similar conditions but at 300° with magnesium chloride solution, yielded likewise about 20% of *p*-cymene.

In view of the ease with which hydrogen transfer occurs by treating cyclic diols, terpenic alcohols and limonene with halogen containing catalysts, many of the experiments cited in the literature dealing with similar types of reactions should be reinvestigated.

THE IPATIEFF HIGH PRESSURE AND
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The Preparation of Monomeric Acrylic Acid

BY FRANK J. KASZUBA

Despite the large number of methods[1] reported in the literature for the preparation of monomeric acrylic acid, none gives the details for the direct hydrolysis of acrylonitrile. Ellis[2] simply makes a statement of fact but lists neither a reference nor the procedure. Hence, when a need for the acid occurred in our laboratory, the following method was developed.

A five-liter flask is charged with 1 kg. of well-chilled acrylonitrile, 6 g. of hydroquinone, 14 g. of powdered copper and, finally, an ice-cold mixture of 1012 ml. concd. sulfuric acid and 648 g. of ice. The flask is then equipped with a wide-mouth reflux condenser,[3] surmounted by a conventional condenser, and heat is applied by means of a steam-bath. During the first hour the reaction becomes exothermic and it is advisable to interrupt the external heating until the vigorous ebullition subsides.

After forty-eight hours, the solution is cooled and, when the crystallization of the ammonium bisulfate is complete, the mixture is filtered with suction.[4] The crude acrylic acid is then subjected to a "flash" distillation; that is, a dropping funnel which serves as a reservoir is fitted to an ordinary 500-ml. round-bottom boiling flask the neck of which is loosely packed with fine copper wire to inhibit the polymerization of the hot acid vapors; the rest of the apparatus consists of a long (50-cm.) West condenser and a receiver (packed in an ice-salt mixture). The distilling flask is heated to 250° by means of a paraffin-bath contained in a deep 1-liter copper beaker and the apparatus is evacuated (*ca.* 10 mm.). The crude acid is then allowed to flow into the flask at a rate adequate to maintain a steady distillation.[5] A kilo of a clear, colorless distillate is obtained which is free of sulfur and nitrogen.

Anal. Titration: 86.3%, purified by freezing once (after the fashion of acetic acid), 96.1%; molecular weight: calcd. 72.0; found (for the 96% material): 70.1.

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[1] Twenty-eight references listed in "Beilstein" and *Chemical Abstracts*.

[2] C. Ellis, "Chemistry of Synthetic Resins," Reinhold Publishing Corp., New York, N. Y., 1935, p. 1070.

[3] About 1 inch inside diameter.

[4] Maximum recovery of crude acid is obtained by pressing the crystals.

[5] The distilling flask should be replaced as residue accumulates.

ANSCO DIVISION
GENERAL ANILINE & FILM CORP.
BINGHAMTON, N. Y.

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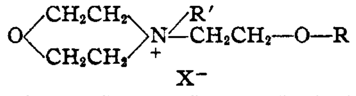
Invert Soaps. Quaternary Salts of Long Chain Morpholine Ethers

BY J. B. NIEDERL, M. WOLF[1] AND E. SLOBODIANSKY[2]

As part of a general study of invert soaps in the morpholine series,[3] it was decided to prepare the quaternary salts of several long chain ethers containing a morpholine ring. For this purpose, the previously unreported long chain ethers of N-ethylol-morpholine were selected for study. N-Ethylol-morpholine was converted into its dodecyl, tetradecyl, and hexadecyl ethers by treatment with sodium and the respective halides. The ethers thus obtained were then converted into representative tertiary amine salts. Reaction of the ethers with methyl iodide, benzyl chloride, and benzyl bromide, gave the corresponding quaternary morpholinium salts. The latter proved to be soluble in warm water, and possessed the structures indicated below.



(R $= C_{12}H_{25}^-, C_{14}H_{29}^-, C_{16}H_{33}^-$)
(R′ $= CH_3^-, C_6H_5CH_2^-$)
($X^- = Cl^-, Br^-, I^-$)

Procedure

Four-tenths mole of N-ethylol-morpholine was heated to 110°, and this temperature maintained throughout the reaction. Four-tenths mole of sodium and 0.4 mole of the respective halide (lauryl, myristyl, or cetyl) were then added slowly and alternately over a period of one hour. A copious precipitate of sodium halide formed. After an additional hour of reaction, the mixture was cooled, extracted with ether, and filtered. The filtrate was fractionated *in vacuo* (2 mm.), and the β-4-morpholyl ethyl ether, which constituted the highest boiling fraction (above 200°), was collected.

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[1] M. Wolf: now of United States Army; Master of Science thesis, New York University, May, 1944.

[2] E. Slobodiansky: Master of Science thesis, New York University, April, 1945.

[3] J. B. Niederl and co-workers: THIS JOURNAL, **63**, 1476 (1941); **66**, 840, 1601 (1944).

The corresponding methiodide was prepared by adding 2 g. of methyl iodide to 1 g. of the amine ether, and allowing the mixture to stand for forty-eight hours. The benzyl chloride and the benzyl bromide were obtained by heating 1 g. of the amine ether with 2 g. of the benzyl halide for eight hours. The salts were recrystallized from ethyl acetate.

TABLE I

4-[β-OXY-ETHYL]-MORPHOLINE

Compound	Formula	M. p., °C. (uncor.)	Analyses, % N Calcd.	Analyses, % N Found
	O-Dodecyl-			
Hydrochloride	$C_{18}H_{38}O_2NCl$	97	4.17	3.99
Hydrobromide	$C_{18}H_{38}O_2NBr$	105	3.69	3.53
Oxalate	$C_{20}H_{39}O_6N$	108	3.29	3.39
Picrate	$C_{24}H_{40}O_9N_4$	62	10.60	10.53
Methiodide	$C_{19}H_{40}O_2NI$	56	3.17	3.10
Benzyl chloride	$C_{25}H_{44}O_2NCl$	96	3.29	3.51
Benzyl bromide	$C_{25}H_{44}O_2NBr$	105	2.98	2.98
	O-Tetradecyl-			
Hydrochloride	$C_{20}H_{42}O_2NCl$	112	3.85	3.85
Hydrobromide	$C_{20}H_{42}O_2NBr$	115	3.43	3.55
Oxalate	$C_{22}H_{43}O_6N$	109	3.35	3.52
Picrate	$C_{26}H_{44}O_9N_4$	80	10.07	9.96
Methiodide	$C_{21}H_{44}O_2NI$	73	2.98	3.20
	O-Hexadecyl-			
Hydrochloride	$C_{22}H_{46}O_2NCl$	105	3.59	3.37
Hydrobromide	$C_{22}H_{46}O_2NBr$	112	3.22	3.17
Oxalate	$C_{24}H_{47}O_6N$	112	3.16	3.21
Picrate	$C_{28}H_{48}O_9N_4$	78	9.62	9.48
Methiodide	$C_{23}H_{48}O_2NI$	80	2.83	2.83

DEPARTMENT OF CHEMISTRY
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The Aqueous Solubility of Hydrated Chromic Nitrate at 25°

BY NORMAN O. SMITH

In connection with the recrystallization of chromic nitrate the author was surprised to discover that there is no information in the literature as to the solubility of this common salt. The following solubility determination was therefore carried out.

Samples of J. T. Baker Analyzed chromic nitrate nonahydrate were rocked in a 15-ml. glass-stoppered tube in a thermostat at 25 ± 0.03° for several days. Equilibrium was approached from both under- and over-saturation and concentrations were measured by means of chromium analyses. Chromium was determined by oxidation to chromate with sodium peroxide followed by the iodometric determination of the chromate. The resulting values of the solubility were

	Wt., % $Cr(NO_3)_3$
From undersaturation	44.95
From oversaturation	44.71
	Av. 44.83

The solid phase was removed by filtration, centrifuged, air-dried for ten minutes and then analyzed. It was found to contain 59.33% $Cr(NO_3)_3$. Calculated for $Cr(NO_3)_3 \cdot 9H_2O$: 59.48% $Cr(NO_3)_3$. The solid phase is therefore the nonahydrate.

Apparently hydrolysis is not sufficient to produce any solid basic compound. Furthermore, the ready attainment of equilibrium distinguishes the behavior of the nitrate from that of several other chromic compounds.[1,2,3]

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(1) Olie, *Z. anorg. Chem.*, **51**, 29 (1906).

(2) Montemartini and Vernazza, *L'Industria chimica*, **8**, 445 (1933).

(3) Hill, Smith and Ricci, THIS JOURNAL, **62**, 858 (1940).

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On Phosphorescence Vibration Spectra of Polyatomic Molecules

BY O. REDLICH AND E. K. HOLT

A few more details can be read from the phosphorescence vibration spectra recently published and interpreted by Lewis and Kasha[1] on the basis of the principle of Franck and Condon.

(1) For a complete interpretation, the analysis of the vibration spectra and the knowledge of the parameters of the phosphorescent state is required. If x denotes a $(3n - 6)$-dimensional vector representing the elongations in internal geometric coördinates, and $q = Ax$ is the vector of the normal coördinates, then the vector $p = Bx$ representing the distortion of the phosphorescent molecule determines, according to the Franck–Condon principle, the amplitudes $q_v = AB^{-1}p$ of the vibrations excited in the transition to the ground state. The quantum number v of the k^{th} vibration is given by $2v + 1 = 3(q^k_v/q^k_1)^2$ where q^k_1 denotes the amplitude of the first quantum state. This somewhat crude application of the Franck–Condon principle should furnish a fair approximation if, as in the measurements of Lewis and Kasha, only the zero-point vibration of the phosphorescent molecule is excited.

The distortion p can be represented as a vector in the space spanned by the amplitudes q^k_1. If p has a lower symmetry than q_1, the vector p lies in the subspace spanned by those amplitudes which are symmetric with respect to the phosphorescent molecule. Only the corresponding vibrations are excited. Provided the symmetry of p is not higher than that of q_1, the totally symmetric vibrations are always permitted. If p has no symmetry element, all vibrations are permitted. The interpretation of the phosphorescent molecule as a biradical suggests the assumption that a center of symmetry, if present in the ground state, is maintained in the phosphorescent state.

(2) For a crude analysis of the spectrum of benzene, approximate normal coördinates are derived from the assumptions that the vibrations are carried out either by the rigid CH groups or by the hydrogens against the carbons, and that they are either stretching or bending vibrations. The

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(1) G. N. Lewis and M. Kasha, THIS JOURNAL, **66**, 2100 (1944).