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.

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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.

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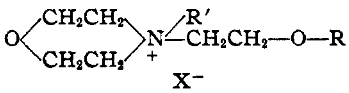
Invert Soaps. Quaternary Salts of Long Chain Morpholine Ethers

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).