straight line was obtained when rotation was plotted against concentration of starch. When the starch concentration was held constant and the concentration of stannic chloride was varied, a curve was obtained when the rotation was plotted against the concentration of stannic chloride. Since the behavior of all of the starches tested was practically identical, the results of the experiments with each starch could be reduced to a comparable basis by expressing the rotations in terms of the original rotation prior to the addition of stannic chloride. This has been done and the values plotted in Fig. 1. The curve was calculated from the equation

$$(0.9 + \text{g. SnCl}_4\cdot5\text{H}_2\text{O})(\%\ \text{change in rotation}) = 17\ (\text{g. SnCl}_4\cdot5\text{H}_2\text{O})$$

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L-Talitol

BY F. L. HUMOLLER,[1] M. L. WOLFROM,[2] B. W. LEW[3] AND R. MAX GOEPP, JR.[4]

All of the isomeric hexitols have been reported in crystalline form except L-talitol. The synthesis of crystalline β-L-altrose from L-ribose by Austin and Humoller[5] makes this very rare sugar available for the synthesis of its reduction product L-talitol. This step has now been accomplished and L-talitol has been obtained in crystalline form, with melting point 87–88° and rotation $[\alpha]^{20}\text{D}$ −2.9° (water) in agreement with those (m. p. 86°, $[\alpha]^{18}\text{D}$ +3.0° in water) recorded by Bertrand and Bruneau[6] for crystalline D-talitol, which had been reported previously as a sirup by Fischer.[7]

Fischer[7] had also subjected dulcitol to oxidation with lead peroxide and hydrochloric acid followed by reduction with sodium amalgam. After separation of a considerable amount of dulcitol, Fischer obtained a crystalline tribenzylidene derivative which yielded a crystalline product of melting point 66–67° after hydrolysis of the benzylidene groups. Fischer considered that this substance was D,L-talitol. An authentic sample of D,L-talitol has now been prepared in crystalline form from its pure components and found to melt at 95–96°. Thus the original product of Fischer must have been either an impure preparation or a lower-melting polymorph.

Experimental

L-Talitol.—A solution of 400 mg. of crystalline β-L-altrose in 30 cc. of water containing a suspension of 150 mg. of a nickel catalyst supported on kieselguhr was treated for twelve hours at 100° with hydrogen under a pressure of 2000 lb. per sq. in. (133 atm.). The cooled reaction mixture (non-reducing toward Fehling solution) was filtered and concentrated to a sirup under reduced pressure; yield 320 mg. Pure material was obtained on crystallization from absolute ethanol, from which L-talitol separated in spherical clusters of colorless, well-defined needles; yield 280 mg., m. p. 87–88°, $[\alpha]^{20}\text{D}$ −2.9° (*c* 5, H_2O, 2-dm. tube), taste sweet.

Anal. Calcd. for $C_6H_{14}O_6$: C, 39.55; H, 7.75. Found: C, 39.59; H, 8.06.

D,L-Talitol.—An accurately weighed amount of 6.1 mg. of pure D-talitol[8] was mixed with a like amount of pure L-talitol and the mixture was recrystallized from 95% ethanol, from which D,L-talitol crystallized in clusters of colorless prisms; yield 11.1 mg., m. p. 95–96°.

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(2) The Ohio State University.

(3) Atlas Powder Company Research Associate of The Ohio State University Research Foundation.

(4) Director of Organic Research, Atlas Powder Company, Wilmington, Delaware.

(5) W. C. Austin and F. L. Humoller, THIS JOURNAL, **56**, 1153 (1934).

(6) G. Bertrand and P. Bruneau, *Bull. soc. chim.*, [4] **3**, 495 (1908).

(7) E. Fischer, *Ber.*, **27**, 1524 (1894).

(8) We are indebted to Professor C. S. Hudson of the National Institute of Health, U. S. Public Health Service, Bethesda, Maryland, for a sample of pure D-talitol.

Studies in the Terpene Series. III.[1] Hydrogen Transfer Reaction During the Dehydration of Terpenic Alcohols

BY V. N. IPATIEFF AND HERMAN PINES

It has been reported[2] that terpenic alcohols undergo dehydration by means of dilute aqueous magnesium chloride solution to form terpenic hydrocarbons; the structure of some of the terpenic hydrocarbons obtained was determined. In view of the recent observation made by the authors and R. C. Olberg[1] that limonene in the presence of halogen-containing catalysts undergoes hydrogen disproportionation resulting in the formation of *p*-cymene, it was decided to reinvestigate some of the higher boiling hydrocarbons resulting from the treatment of terpineol and 1,8-*p*-menthanediol. The experiments were made by treating one mole of the alcohols with 0.03 mole of magnesium chloride dissolved in 5.5 moles of water. The mixture was heated in an autoclave of 850 cc. capacity at 250° for three hours. It was found that the higher boiling fractions of the reaction product contained a large proportion of *p*-cymene. The yield of *p*-cymene produced amounted to about 18–20 mole per cent. based on the alcohols charged.

The presence of *p*-cymene in the mixture of hydrocarbons was demonstrated by means of selective hydrogenation. It was found that only olefinic hydrocarbons underwent hydrogenation when an equimolal mixture of limonene, dihydrolimonene and *p*-cymene, diluted with an equal volume of *n*-pentane, was subjected to treatment with hydrogen under a pressure of 80 atm. at 45° and in the presence of nickel–kieselguhr catalyst, *p*-cymene remains unchanged. The amount of *p*-cymene obtained from the hydrogen transfer reaction was determined by: (1) ultraviolet absorption, (2) extraction of the *p*-cymene, after selective

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(1) For paper II of this series, see V. N. Ipatieff, H. Pines and R. C. Olberg, THIS JOURNAL, **67**, 694 (1945).

(2) V. N. Ipatieff and H. Pines, *ibid.*, **66**, 1120 (1944).

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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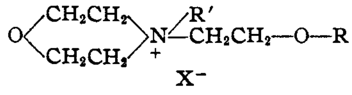
Invert Soaps. Quaternary Salts of Long Chain Morpholine Ethers

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).