be the same or different, alkyl, aryl, cyclic, and so forth. This process has a broad application, since, for a given disulfonate, a large number of secondary amines may be chosen. Moreover, the availability of the glycol disulfonates is being greatly increased by the ever-increasing number of glycols which are appearing on the market.

Table I lists the amines synthesized by this method and Table II contains the glycol disulfonates which were prepared as intermediates.

Experimental

General Procedure for the Preparation of Glycol Disulfonates.—The anhydrous glycol (1 mole) is dissolved in 3 to 5 volumes of anhydrous pyridine and the appropriate sulfonyl chloride (2 moles) is added to this well-stirred solution. The temperature is maintained between 5 and 15°. After the reaction is completed, the reaction mixture is stirred into three times its volume of finely crushed ice. The crystalline product which separates is washed with ice-water and then dried. It is purified by recrystallization from ethanol.

General Procedure for the Preparation of N,N,N',N'-Tetrasubstituted Diamines.—A glycol disulfonate is refluxed with 20 equivalents of anhydrous secondary amine under anhydrous conditions, with stirring, for approximately 20 hours. The secondary amine is fractionally distilled, after which an excess of 40% sodium hydroxide solution is added. The oil layer is separated and the water layer extracted with ether. The oil and ether extracts are combined and dried over anhydrous potassium carbonate. After distillation of the ether, the residual oil is fractionated under reduced pressure through a glass-packed column using a variable take-off stillhead.

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On the Preparation of Xanthurenic Acid

BY ALEXANDER D. MEBANE AND WILLIAM OROSHNIK

Xanthurenic acid was first synthesized by Musajo and Minchilli,[1] who reported a melting point of 283–285° (dec.) "with fast heating." Subsequent preparations[2,3,4] have resulted in melting points varying from 250°[3] (in spite of correct elementary analyses) to as high as 289°.[4] When the synthesis was carried out in this Laboratory, a product of m.p. 255° was obtained, although all intermediates had been carefully purified. The explanation was found to lie in incomplete ether-fission under the conditions specified by Musajo and Minchilli; more exhaustive treatment with hydriodic acid raised the melting point to 294°. A subsequent examination of two of the above-mentioned preparations showed the 250° specimen[3] to contain 8.3% of methoxyl, corresponding to 58 mole per cent. of the 8-methyl ether; the 289° specimen,[4] on the other hand, proved to contain only 3.3 mole per cent. of the methyl ether.

Reprecipitation of methoxyl-free material was ineffective in freeing it of inorganic contaminants. None of the common organic solvents permitted recrystallization, but dilute hydrochloric acid proved to be quite satisfactory, giving a chloride-free crystalline product decomposing at 297°.

A simplified version of the Musajo–Minchilli synthesis which embodies these improvements is described below.[5]

Experimental

Commercial sodium salt of oxalacetic ester (49 g.) was shaken with 300 ml. of ether and 400 ml. of ice-cold 5% sulfuric acid until all had dissolved, and the aqueous layer was reextracted with ether. The combined extracts, after drying over anhydrous $MgSO_4$, were concentrated at 20 mm. The residue (38 g., 0.2 *M*) was heated in a boiling water-bath with 25 g. (0.2 *M*) of *o*-anisidine for 90 minutes, after which the water that had separated was evaporated at 20 mm.

The resulting orange sirup was stirred with 1 liter of mineral oil while heating to 240° in an electric mantle. After five minutes at 240–250°, the flask was cooled with an air blast. When the temperature had fallen to 60°, the solution was decanted from precipitated tar, diluted with 2 liters of petroleum ether, and stored for several days in the refrigerator. Tan-colored crystals of crude ethyl xanthurenate 8-methyl ether (23 g.) were obtained. Recrystallization of this material (from toluene, with ligroin) was undesirable for practical purposes, since the best crops were the later and smaller ones (colorless needles, m.p. 100–101°).

The crude ether-ester was dissolved in 350 ml. of 57% hydriodic acid (freshly distilled from hypophosphorous acid; b.p. 126–128°), and the liquid was distilled slowly at atmospheric pressure under an 8″ Vigreux column until the still-head temperature had reached 110° (3 hours). The HI was then distilled off to near-dryness at 20 mm. and the residue taken up in water, made alkaline with bicarbonate, filtered, and acidified to *p*H 3 with dilute HCl in the presence of a little bisulfite. After chilling, the xanthurenic acid was filtered off with water washes and sucked as dry as possible: sulfur-yellow, non-crystalline.

The damp filter cake was dissolved, by boiling, in a mixture of 400 ml. of concd. HCl and 500 ml. of distilled water, and filtered hot with a little Norit and SuperCel, washing with 70 ml. of the hot solvent. To the filtrate was added 2400 ml. of boiling-hot distilled water, and the solution was allowed to stand overnight. Filtration, with water and then acetone washes, furnished 14.5 g. (35% based on *o*-anisidine) of crystalline xanthurenic acid; small, imperfectly-rhombic ochre-yellow flakes.

Anal. Calcd. for $C_{10}H_7NO_4$: C, 58.54; H, 3.44; N, 6.83. Found: C, 58.59, 58.34; H, 3.52, 3.67; N, 6.61, 6.66; methoxyl, none; ash, none; Cl^-, none; Fe, none.

The melting point is quite sensitive to the rate of heating. If the temperature was brought rapidly to 270° and thereafter raised 5° per minute, decomposition occurred at 297°.

At *p*H 6.95, the ultraviolet absorption spectrum of xanthurenic acid in water shows two smooth peaks: $\lambda_{max.}$ 243 mμ, ϵ 30,000; $\lambda_{max.}$ 342 mμ, ϵ 6,500.

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(1) L. Musajo and M. Minchilli, *Ber.*, **74B**, 1842 (1941).

(2) E. C. Miller and C. A. Baumann, *J. Biol. Chem.*, **157**, 554 (1945); **159**, 174 (1945).

(3) C. C. Porter, I. Clark and R. H. Silber, *ibid.*, **167**, 575 (1947). A sample of this material was kindly made available to us by Dr. Silber.

(4) F. Rosen, J. W. Huff and W. A. Perlzweig, *J. Nutrition*, **33**, 561 (1947). The melting point was not reported in the original publication.

(5) A paper by A. Furst and C. J. Olsen (*J. Org. Chem.*, **16**, 412 (1951)), which appeared after this note had been submitted, describes more extensive improvements in this preparation. The melting point of 284° for crystalline material reported by Furst and Olsen is presumably due to a difference in heating rate.

The Activity Coefficients of the Alkaline Earth and Magnesium Perchlorates from Freezing Point Data

BY DAN E. NICHOLSON[1] AND W. A. FELSING

In a previous article,[2] experimental data were presented in which the freezing points for aqueous solutions of barium, strontium, calcium and magnesium perchlorates had been used to calculate the

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(1) Materials Chemistry Division, Oak Ridge National Laboratory.

(2) D. E. Nicholson with W. A. Felsing, THIS JOURNAL, **72**, 4469 (1950).