Infrared Absorption Spectra.—The infrared absorption spectra were determined using a Perkin–Elmer model 21 recording infrared double-beam spectrophotometer. Specimens were prepared by melting and pressing the sample between two flat rock salt plates separated near their edges by metal shims approximately 1 mm. thick. The infrared determinations were made by Miss Doris Huck.

Derivatives of the Polyamines

Preparation of Polyamine Salts.[5] A.—These were prepared by the addition of the desired acid to a benzene solution of polyamine followed by removal of the solvent by vacuum distillation. For example, a polyamine of neutral equivalent 526 (27 g.) was treated with 85% lactic acid (5.9 g.) in benzene (100 ml.) to obtain a colorless, water-soluble, resinous lactate (30 g.). The lactate showed a saponification equivalent of 680. Similarly, a polyamine (25 g.) of neutral equivalent 515 was treated with 37% hydrochloric acid (5 ml.) in benzene (200 ml.), and the benzene and water were removed by distillation to obtain a gummy, reddish solid, difficultly soluble in water.

Anal. Calcd. for $(RNH_2)\cdot HCl$, where RNH_2 has neut. equiv., 515; Cl, 6.48. Found: Cl, 6.32.

B.—Salts of the polyamines with long chain acids have been made by metathesis of soluble polyamine salts with appropriate acid salts. For example, aqueous solutions of the acetate of a polyamine of neutral equivalent 523 and of sodium dodecyl sulfate were mixed in equivalent proportions. The poly-(dodecylammonium sulfate) precipitated immediately as an amber, tacky resin, which was dried in vacuum.

Anal. Calcd. for $RNH_2\cdot HSO_4C_{12}H_{25}$, where RNH_2 has a neut. equiv. of 523; S, 4.14. Found: S, 3.25.

Preparation of a Polyquaternary Salt.[6]—A polytertiary amine (made from dimethylamine) of neutral equivalent 327 (34 g.) and benzyl chloride (13.2 g.) were allowed to stand in benzene solution (200 ml.) at room temperature for 24 hours. The benzene was then removed by vacuum distillation to obtain an amber-colored, glassy, water-soluble resin.

Anal. Calcd. for $R(CH_3)_2C_7H_7NCl$, where $RN(CH_3)_2$ has a neut. equiv. of 327; Cl, 7.8. Found: Cl, 6.0.

Preparation of a Polyamine Oxide.—A tertiary polyamine made with dimethylamine and having a neutral equivalent of 327 (25 g.) was treated with 30% hydrogen peroxide (28 ml.) in 3:1 isopropyl alcohol:water (200 ml.) at 70° for seven hours. The resulting solution was evaporated to dryness on the steam-bath to obtain a colorless, tacky resin, which readily oxidized aqueous potassium iodide solutions.

Anal. C, 72.54; H, 12.23; N, 3.63; O (difference), 11.60; neut. equiv., 458.

Preparation of a Polyamide.—A polyprimary amine of neutral equivalent 523 (54 g.) and an equivalent quantity of stearic acid (29 g.) were heated in refluxing xylene (50 ml.) at 165–200°. The water formed was removed by azeotropic distillation and was collected in a conventional liquid separator. When evolution of water was complete (7.5 hours), the xylene was removed by vacuum distillation to obtain a hard wax, insoluble in dilute acid and alkali. The acid number of the product was found to be 0.8, showing that the amidation was essentially complete.

Preparation of a Polyurea.[7]—A solution of potassium cyanate (9.75 g.) in water (40 ml.) was added with stirring to a solution of a polyprimary amine of neutral equivalent 515 (54 g.) in 400 ml. of water containing 7.2 ml. of glacial acetic acid. A gummy mass of the desired polyurea formed during the addition. After about an hour of stirring, the mass hardened and broke into solid, somewhat tacky granules. The polyurea was filtered off by suction and was dried in vacuum over concentrated sulfuric acid.

Anal. Calcd. for $RNHCONH_2$, where RNH_2 has a neut. equiv. of 515; N, 5.02. Found: N, 5.17.

The polyurea was insoluble in water but was soluble in isopropyl alcohol. Addition of a small amount of 37% formaldehyde to an isopropyl alcohol solution of the polyurea caused immediate precipitation of an insoluble, facticelike resin.

Preparation of a Polythiourea.—A polyprimary amine of neutral equivalent 523 was treated with a slight excess of ammonium thiocyanate as in the previous experiment. The resulting polythiourea was obtained as an amber-colored, tacky resin.

Anal. Calcd. for $RNHCSNH_2$, where RNH_2 has a neut. equiv. of 523; N, 4.81; S, 5.5. Found: N, 4.61; S, 4.57.

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(5) M. E. Cupery, U. S. Patent 2,579,033, December 18, 1951.

(6) D. D. Coffman, U. S. Patent 2,595,225, May 6, 1952.

(7) J. T. Maynard, U. S. Patent 2,595,400, May 6, 1952.

WILMINGTON, DELAWARE

[CONTRIBUTION FROM HERCULES EXPERIMENT STATION, HERCULES POWDER COMPANY]

The Synthesis and Polymerization of Ethylenesulfonic Acid

BY DAVID S. BRESLOW AND GEORGE E. HULSE

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Ethylenesulfonic acid has been prepared by saturating an aqueous solution of sodium ethylenesulfonate with hydrogen chloride, separating precipitated sodium chloride, and distilling the free acid. It polymerizes readily in aqueous solution in the presence of free-radical catalysts or when exposed to ultraviolet light. Both the rate of polymerization and the molecular weights of the polymers are increased with increased monomer concentration. Ethylenesulfonic acid copolymerizes slowly with methyl acrylate and with acrylonitrile.

Only two syntheses of ethylenesulfonic acid, $CH_2{=}CHSO_3H$, are reported in the literature, the classical procedure of heating 1,2-ethanedisulfonyl chloride[1] and, more recently, the dehydration of sodium 2-hydroxyethanesulfonate with polyphosphoric acid.[2] It has now been found that ethylenesulfonic acid can be prepared in good yields from sodium ethylenesulfonate.[3]

The preparation of ethylenesulfonic acid from sodium ethylenesulfonate is based on the low solubility of sodium chloride in concentrated aqueous hydrochloric acid. A solution of sodium ethylenesulfonate was saturated in the cold with hydrogen chloride; sodium chloride was filtered off, and the filtrate was distilled. A 74% yield of crude ethylenesulfonic acid was obtained, redistillation giving a 66% yield of pure acid.

The literature on the polymerization of ethylenesulfonic acid and its derivatives has been summarized recently.[4] Alderman and Hanford[5] reported that ethylenesulfonic acid polymerized in bulk very slowly to a dark-colored, rubbery polymer when

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(1) E. P. Kohler, *Am. Chem. J.* **19**, 728 (1897); **20**, 680 (1898).

(2) J. A. Anthes and J. R. Dudley, U. S. Patent 2,597,696 (1952).

(3) D. S. Breslow, R. R. Hough and J. T. Fairclough, THIS JOURNAL, **76**, 5361 (1954).

(4) C. E. Schildknecht, "Vinyl and Related Polymers," John Wiley and Sons, Inc., New York, N. Y., 1952, pp. 643–648.

(5) V. V. Alderman and W. E. Hanford, U. S. Patent 2,348,705 (1944).

irradiated with ultraviolet light. Jones and Barnes[6] claimed that ethylenesulfonic acid polymerized readily when exposed to ultraviolet light if it was distilled in the complete absence of oxygen.

Ethylenesulfonic acid, as prepared by us, was stable indefinitely at room temperature.[7] However, aqueous solutions of ethylenesulfonic acid have been found to polymerize readily under the influence of ultraviolet light or peroxide. It was necessary for this study to devise a method for separating polyethylenesulfonic acid from ethylenesulfonic acid. This was accomplished by converting both monomer and polymer to their sodium salts and precipitating the polymer by the addition of methanol; the polymer was found to be insoluble in 70% (by weight) aqueous methanol, whereas the monomer was highly soluble. Relative molecular weights in this work were followed by determining the specific viscosity of 1% solutions of polymer in water.

Both the rate of polymerization and the molecular weight of the polymer were highly dependent on the monomer concentration. Thus, under comparable conditions, a 50% solution of ethylenesulfonic acid gave a 37% conversion to polymer with a specific viscosity of 0.483, whereas a 67% solution gave a 62% conversion and a specific viscosity of 0.988. Polymerization could be initiated by hydrogen peroxide, potassium persulfate or ultraviolet light. As is frequently observed in other free-radical polymerizations, lowering the polymerization temperature increased the molecular weight. The highest molecular weight was obtained by irradiating a 75% ethylenesulfonic acid solution at 0°, but even higher molecular weights should be possible by increasing the concentration and lowering the temperature. The sodium salt of this polymer was estimated[8] to have a weight-average molecular weight of about 250,000.

Polyethylenesulfonic acid can be prepared from the sodium salt by saturating an aqueous solution with hydrogen chloride, the removal of sodium being almost quantitative. The free acid forms a brittle, highly hygroscopic film.

The ready polymerization of ethylenesulfonic acid is rather surprising, since ethylenesulfonate esters polymerize by themselves only very slowly.[4,5] There appears to be little, if any, resonance stabilization of the radical $-CH_2\dot{C}HSO_2-$ in either methyl sulfones[9] or in sulfonate esters.[10] Ethylenesulfonic acid undoubtedly polymerizes as the anion,[11] and it has been suggested that there is increased resonance stabilization in the anion.[10] A more important factor would seem to be that the negative charge on the anion increases the electron density of the double bond, counterbalancing to a certain extent the low electron density of the double bond in vinyl sulfones and in sulfonate esters. The increase in the rate of polymerization of ethylenesulfonic acid with increased concentration is probably also best explained on the basis of electrostatic effects. In dilute solution ethylenesulfonate ions repel each other, thus making polymerization difficult. In more concentrated solutions, however, the negative charges are partially neutralized by ion-pair formation, and thus the approach of two ethylenesulfonate ions is facilitated.

Ethylenesulfonic acid has been copolymerized with methyl acrylate and with acrylonitrile, but all attempts to prepare copolymers with styrene, α-methylstyrene or vinyl acetate have been unsuccessful. The copolymerization of ethylenesulfonic acid and methyl acrylate or acrylonitrile by using ultraviolet light as initiator was very slow, both in bulk and in a concentrated solution. With equimolar quantities of ethylenesulfonic acid and methyl acrylate, a copolymer was obtained containing 15% ethylenesulfonic acid. A copolymer containing 9% ethylenesulfonic acid was soluble in dilute alkali and precipitated on acidification. With acrylonitrile the yield of copolymer was very low in either dioxane or dimethylformamide. With equimolar quantities of the two monomers the copolymer contained about 20% ethylenesulfonic acid. Rather surprisingly, the copolymer was highly swollen by water but the gel coagulated on the addition of dilute sodium hydroxide.

Experimental[12]

Preparation of Ethylenesulfonic Acid from Sodium Ethylenesulfonate.—Fourteen hundred grams of a 30% solution of sodium ethylenesulfonate in water was chilled in an ice-bath and saturated with dry hydrogen chloride. Precipitated sodium chloride was filtered off and the filtrate was evaporated to dryness on a steam-bath *in vacuo*. To remove the last traces of hydrogen chloride, two 100-ml. portions of water were added to the residue and distilled *in vacuo*. The residue was then distilled, 257 g. (74% of theory) of crude ethylenesulfonic acid being collected up to 150° at 5 mm. On redistillation the pressure rose from 1 mm. at 25° to 4 mm. at 125° and then dropped, 230 g. (66%) of ethylenesulfonic acid being collected at 127–132° at 1–1.4 mm., $n^{20}\text{D}$ 1.4514 (b.p. 125° at 1 mm., $n^{20}\text{D}$ 1.4493).[4]

Anal. Calcd. for $C_2H_4O_3S$: neut. equiv., 108.1; H_2 absorption, 1.86. Found: neut. equiv., 108.9; H_2 absorption, 1.83, 1.84; SO_2, 0.009. 0.015.

Effect of Concentration on Polymerization of Ethylenesulfonic Acid.—To 10 g. of ethylenesulfonic acid dissolved in 10 ml. of water was added 1 ml. of a 1% potassium persulfate solution. The solution was placed in a glass ampoule, which was evacuated and sealed. Heating at 55° overnight yielded a colorless, slightly viscous solution, which was made neutral to phenolphthalein with 40% sodium hydroxide solution. Addition of 150 ml. of methanol precipitated a gummy solid, which was purified by twice dissolving it in 40 ml. of water and precipitating with 120 ml. of methanol. The polymer was slurried with methanol, which converted it into a granular, white solid, which was filtered and dried *in vacuo* at 60°; 4.4 g., a conversion of 37%, was obtained. A 1% solution in water had a specific viscosity of 0.483.

Anal. Calcd. for $C_2H_3O_3SNa$: S, 24.6. Found: S, 23.5, 23.2.

The above experiment was repeated using 10 g. of ethyl-

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[6] G. D. Jones and C. E. Barnes, U. S. Patent 2,515,714 (1950).

[7] It is quite possible that the free acid is stabilized by traces of sulfur dioxide found in the product distilled under ordinary conditions and that, in the absence of sulfur dioxide, ethylenesulfonic acid polymerizes readily, as described by Jones and Barnes.[6]

[8] This was done by comparing specific viscosities with weight-average molecular weights as determined by light scattering. We are indebted to Dr. Paul Doty of Harvard University for the latter measurements.

[9] C. C. Price and J. Zomlefer, THIS JOURNAL, **72**, 14 (1950).

[10] C. G. Overberger, D. E. Baldwin and H. P. Gregor, *ibid.*, **72**, 4864 (1950).

[11] Sodium ethylenesulfonate has been reported[10] to polymerize readily in aqueous solution, although no details were given. This has been confirmed; our results will be reported in a subsequent communication.

[12] Analyses were carried out by the Analytical Division of Hercules Experiment Station.

enesulfonic acid, 4 ml. of water and 1 ml. of 1% potassium persulfate solution. After polymerization, 15.08 ml. of 6.07 *N* sodium hydroxide was required for neutralization, the calculated quantity being 15.25 ml. The yield of polymer was 7.5 g., a conversion of 62%, with a specific viscosity of 0.988.

Effect of Conditions on Polymerization of Ethylenesulfonic Acid.—Experiments were run and the polymers were isolated as described above. A 50% ethylenesulfonic acid solution with 0.1% hydrogen peroxide as catalyst gave a 44% conversion to polymer in 16 hours at 55°, the specific viscosity of a 1% solution in water being 0.466.

A 50% ethylenesulfonic acid solution with 0.1% potassium persulfate gave a 22% conversion to polymer in 15 hours at room temperature, the specific viscosity being 1.162.

A 75% ethylenesulfonic acid solution irradiated with an ultraviolet lamp gave a 73% conversion to polymer in 16 hours at 0°, the specific viscosity being 5.613. This polymer was estimated to have a weight-average molecular weight of about 250,000.

Polyethylenesulfonic Acid.—A solution of 156 g. of sodium polyethylenesulfonate (having a specific viscosity of 0.675 in a 1% aqueous solution) in 400 ml. of water was chilled in ice and saturated with hydrogen chloride. The precipitate of sodium chloride was filtered off and was washed with 50 ml. of cold, concentrated hydrochloric acid. The combined filtrates were evaporated to dryness on a steam-bath *in vacuo.* Water was added and distilled off until the distillate gave a negative test for chloride ion, the final distillation not being carried to completion. The resulting reddish-brown, viscous solution contained 46.3% polymer, and sodium analysis indicated that the conversion to free acid was 98% complete. Evaporation of a portion of this solution on a glass plate yielded a brittle, very hygroscopic film of polyethylenesulfonic acid.

Copolymerization of Methyl Acrylate and Ethylenesulfonic Acid.—A solution of 1 g. (0.0093 mole) of ethylenesulfonic acid in 3 g. (0.035 mole) of methyl acrylate was irradiated *in vacuo* with a Hanovia EH-4 lamp for 48 hours. The resulting hard, dark brown copolymer was dissolved in 300 ml. of 1% sodium hydroxide and the clear, tan, viscous solution obtained was added to 800 ml. of methanol. The white, rubbery copolymer was purified by solution in water and precipitation with methanol. A hard, white solid (1.7 g.) was obtained after drying *in vacuo* at 80°. It contained 2.9% sulfur, equivalent to 11.8% sodium ethylenesulfonate.

Repetition of the experiment with 4 ml. of dioxane as solvent yielded 2.3 g. of rubbery polymer, isolated by solution in dioxane and precipitation with isopropyl alcohol. The copolymer contained 2.5% sulfur, equivalent to 8.5% ethylenesulfonic acid. It was soluble in aqueous alkali but precipitated on acidification. With equimolar quantities of ethylenesulfonic acid and methyl acrylate and dioxane as a solvent, a copolymer was obtained containing 4.1% sulfur, equivalent to 14.8% ethylenesulfonic acid.

Copolymerization of Acrylonitrile and Ethylenesulfonic Acid.—The procedure described for methyl acrylate was used; 1.06 g. (0.02 mole) of acrylonitrile and 2.16 g. (0.02 mole) of ethylenesulfonic acid dissolved in 4 ml. of dioxane yielded 0.2 g. of copolymer in 24 hours. The insoluble polymer was filtered and washed thoroughly with methanol. It contained 5.21% sulfur, equivalent to 17.6% ethylenesulfonic acid. The copolymer was highly swollen in water, but the gel was broken by the addition of sodium hydroxide. Substituting dimethylformamide for dioxane and irradiating for four days yielded 0.9 g. of hard, white copolymer after precipitation with methanol. This contained 5.85% sulfur, equivalent to 19.7% ethylenesulfonic acid; the specific viscosity of a 1% solution in dimethylformamide was 5.46.

WILMINGTON, DELAWARE

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF NORTHWESTERN UNIVERSITY]

The Stereochemistry of Several 2,5-Disubstituted Dioxanes

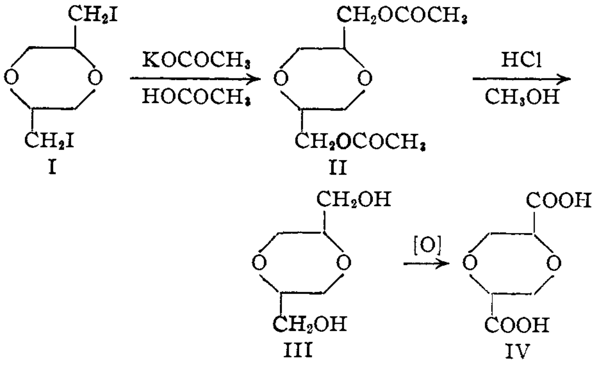
BY ROBERT K. SUMMERBELL AND JAMES R. STEPHENS

RECEIVED JUNE 30, 1954

"Diepiiodohydrin" has previously been shown to be 2,5-bis-(iodomethyl)-*p*-dioxane (I), but the configuration of no 2,5-derivative of dioxane is known. I was converted to the dicarboxylic acid of the same number of carbon atoms which in turn was isomerized by strong alkali to a different acid. The latter was shown to be *cis* by a partial resolution with brucine and by its formation from the hydrolysis of a monomeric anhydride. The *cis*-acid was reduced to the glycol which in turn was converted through the tosylate to *cis*-2,5-bis-(iodomethyl)-*p*-dioxane, a different compound from "diepiiodohydrin." The latter must therefore be *trans.* The *trans*-acid was shown to be the statistically preferred form by partial equilibration with alkali. Also the *trans* forms of the 2,5-series are uniformly higher melting than the corresponding *cis* compounds. Both properties are consistent with the equatorial–polar (axial) concept. A number of venerable glycerol derivatives have been assigned definite structures and configurations.

In a previous paper we have shown[1] the configurations of several key derivatives of 2,6-disubstituted *p*-dioxanes and established that "diepiiodohydrin" (I) is one form of 2,5-bis-(iodomethyl)-*p*-dioxane. This compound then afforded an entry into the study of the stereochemistry of 2,5-disubstituted *p*-dioxanes.

As a step toward the elucidation of the geometry of I, we attempted to convert it to a 2,5-*p*-dioxanedicarboxylic acid of the same configuration. This was accomplished by the following sequence of reactions.



The initial step in this series occasioned some difficulty, a low yield of 2-acetoxymethyl-5-iodomethyl-*p*-dioxane being the only isolated product under the mild conditions first employed. The second iodine atom was replaced readily when the proportion of potassium acetate and time of refluxing were increased, to yield 2,5-bis-(acetoxymethyl)-*p*-dioxane (II). Transesterification occurred readily to give 2,5-bis-(hydroxymethyl)-*p*-dioxane (III). The oxidation of III to a 2,5-*p*-dioxanedicarboxylic acid of m.p. 275°, IV, was accomplished by a variety of reagents. Potassium

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[1] R. K. Summerbell and J. R. Stephens, THIS JOURNAL, **76**, 731 (1954).