hydroxide and 30 cc. of ethyl alcohol was carried through the same process as described above for the 7-nitro isomer. The orange red crude product, crystallized from dilute ethyl alcohol, yielded red needles, insoluble in aqueous caustic alkali and melting at 171°. Mixed with a sample of authentic disulfide,[2] the melting point was unchanged.

6-Methoxy-5-nitrobenzothiazole.—To a cold solution of 69 g. of 2-nitro-4-aminoanisole (m. p. 57–57.5°) in 420 g. of glacial acetic acid, there was added 350 g. of well cooled sulfur monochloride, and the mixture was heated at 75° for about five hours, with constant stirring. The crude product amounted to 105 g.

Of this crude 1-chloro-5-nitro-6-methoxyisobenzo-1,2,3-dithiazole, 100 g. was stirred into 2–3 liters of cold water. There resulted a yellow flocculent precipitate, presumably the corresponding hydroxy dithiazole. After allowing the mixture to stand overnight, to complete this primary hydrolysis, an excess of aqueous sodium hydroxide was poured in and the color of the solution changed to a blood-red. To the filtered solution, there was added 200 cc. of mixed formic–acetic anhydride and the reaction mixture was stirred vigorously for about ten minutes. The gummy precipitate was removed and crystallized from alcohol in the presence of Norit; yield, 11 g. Recrystallized from alcohol, it gave long fine pale yellow needles, m. p. 184–184.5°.

Anal. Calcd. for $C_8H_6O_3N_2S$: C, 45.7; H, 2.9. Found: C, 46.0; H, 2.9.

Since this compound is quite different from the 4- and 7-nitro isomers in melting point and other respects, it must be the other possible *bz*-nitro derivative, *viz.*, the 5-nitro derivative.

Summary

1. 6-Alkoxy-7-nitrobenzothiazoles, in the presence of various alcohols and small amounts of dilute caustic alkali, exchange their alkyls for the radicals of the alcohols used.

2. The melting points of the thiazyl ethers so produced sink with increasing molecular weight of the alcohol radical thus introduced, and the normal melts higher than the isopropyl ether.

3. A nitro group in position 7 on the 6-alkoxybenzothiazole nucleus appears to labilize the alkoxy group and stabilize the thiazole nucleus toward alkali. When the nitro group, however, is in position 4, the reverse is true; the alkoxy group remains intact and the thiazole ring is broken open, with formation of the corresponding *o*-aminothiophenol, or its disulfide.

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[CONTRIBUTION FROM THE HAYDEN MEMORIAL LABORATORIES, NORTHEASTERN UNIVERSITY]

The Preparation of Some Alkane-α,ω-disulfonic Acids

BY SAVERIO ZUFFANTI AND RUDOLPH HENDRICKSON

Introduction

The method used for the preparation of monosulfonic acids of the alkane series,[1] must be modified slightly due to the decreased solubility of the disulfonic acids in the ether used as a suspension medium for the sodium salts.

Gilbert C. Stone[2] has outlined a satisfactory method of preparing the sodium salts of the α,ω-disulfonic acids of the alkane series. This method was used for the preparation of the sodium salts of α,ω-disulfoethane, -propane, -butane, -pentane, -hexane, and -decane.

Experimental

Preparation of the Anhydrous α,ω-Decamethylene-disulfonic Acid.—55.9 grams of the purified and dried sodium salt was suspended in 400 cc. of absolute methanol. Dry hydrogen chloride gas was introduced to decompose the sodium salt. The suspended salt changes in appearance from glossy flakes to a granular residue of sodium chloride that tends to settle quickly, thus affording a means of following the decomposition which, in this case, seemed to be complete in eighteen hours. The residue was filtered off into a sintered glass funnel and the weight of the dried residue indicated that the decomposition was not quantitative. The filtrate was allowed to evaporate (at room temperature) in a vacuum desiccator, leaving a clear oily liquid that was soluble in water but insoluble in ether. This material failed to crystallize while kept under vacuum in the desiccator over a period of two weeks. Accidentally breaking the vacuum too quickly caused the liquid to be splashed onto the walls of the desiccator with immediate crystallization taking place. It was subsequently discovered that if a stream of dry air is allowed to spread the oily liquid into a thin layer it shortly crystallizes to a pasty solid. Washing with ether leaves a white crystalline solid on the sintered glass funnel, yield 46.3 g. The yields varied between 80 and 95% except for the α,ω-hexamethylene-disulfonic acid where the yield was but 68%.

The acids were purified by redissolving them in a minimum of absolute methanol and saturating the solutions with dry hydrogen chloride. This procedure carried the reaction further to completion as evidenced by the precipitation of sodium chloride. After filtration, the acids were recovered as previously indicated and recrystallized several times from absolute methanol. Table I summarizes the data obtained on the purified acids.

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(1) Zuffanti, THIS JOURNAL, **62**, 1044 (1940).

(2) Stone, *ibid.*, **58**, 488 (1936).

TABLE I

	Neutral equiv.		M. p., °C.	B. p., °C.	*m*-Toluidine salts M. p., °C.	%, S	
	Calcd.	Found				Calcd.	Found
$HO_3S(CH_2)_2SO_3H$	95	98	97	...	230	33.68	32.62[a]
$HO_3S(CH_2)_3SO_3H$	102	103	..	157 (1.4 mm.)	222	31.35	30.91
$HO_3S(CH_2)_4SO_3H$	109	111	84	...	214	29.34	28.80
$HO_3S(CH_2)_5SO_3H$	116	120	..	198 (1.7 mm.)	187	27.57	26.62[a]
$HO_3S(CH_2)_6SO_3H$	123	125	78	...	158	26.01	25.61
$HO_3S(CH_2)_{10}SO_3H$	151	152	76	...	178	21.19	20.32

[a] Analysis indicates lack of purity.

Preparation of the *m*-Toluidine Salts.—A half gram of the acid was dissolved in a few cubic centimeters of ethyl alcohol and a slight excess of *m*-toluidine added. If precipitation of the salt occurred, more alcohol was added to redissolve it at this point. Slow addition of ether caused the precipitation of the salts which were then purified several times by repeating the above process of precipitation. In this manner it is possible to obtain the pure salt free of excess *m*-toluidine.

Discussion

The α,ω-disulfonic acids of the alkane series resemble the dicarboxylic acids in respect to melting points. The two, four, six, and ten carbon chain acids are white crystalline solids, while the three and five carbon chain members could not be crystallized but remained as clear slightly-colored liquids. These acids are soluble in water and alcohol but are insoluble in ether, carbon tetrachloride, benzene, and acetone. They are slightly hygroscopic, melt sharply, and then decompose. Distillation can be accomplished only under a pressure of below 2 mm.

Summary

1. The α,ω-disulfonic acids of ethane, propane, butane, pentane, hexane, and decane have been prepared in the anhydrous state.

2. The boiling points, melting points and *m*-toluidine salts have been used to characterize the above acids.

BOSTON, MASSACHUSETTS RECEIVED JUNE 14, 1941

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF EMORY UNIVERSITY]

The Hydration of the Ethylenic Linkage.[1] I. The Equilibrium between Isobutene, *t*-Butyl Alcohol and Water[2]

BY CHARLES W. SMART,[3] HERBERT BURROWS,[3] KATHERINE OWEN AND OSBORNE R. QUAYLE

Very few exact data are available on the equilibria between alcohols, olefins and water. Tertiary alcohols with three identical alkyl groups were chosen to be studied as only one olefin results upon dehydration. Ebertz and Lucas[4] have made the only equilibrium study upon the dehydration of isobutene. Since in their work the equilibrium was approached only from the alcohol side of the reaction and with highly disproportionate concentrations of the components (almost 1000 to 1), the equilibrium was investigated using sealed reaction tubes at 100° and was approached from both sides.

Experimental

Procedure.—The reaction tubes were of soft glass, 1 × 7 cm., and contained approximately 5 ml. of the reaction mixture. Those from the alcohol side were made up from a reaction mixture containing known quantities of water, alcohol, the solvent dioxane and the catalyst mercuric chloride. From the olefin side each constituent was weighed separately into the tube. The gaseous isobutene was condensed into the tube by immersion in an acetone–dry-ice bath. The tubes were sealed immediately after filling. After heating for twenty-one days at 100° each tube was broken under carbon tetrachloride, washed with water and analyzed. The unsaturate was determined by quantitative bromination and the alcohol and water calculated by the change in the amount of unsaturate present.

Preparation of Materials.—(1) Water—distilled three times over potassium permanganate and calcium hydroxide. (2) Dioxane—repeatedly frozen to constant freezing

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(2) Abstracted from material presented by Charles W. Smart to the Graduate Faculty of Emory University in partial fulfillment of the requirements for the degree of Master of Science.

(3) Now, respectively, at the University of Texas, Austin, Texas; and the Georgia School of Technology, Atlanta, Ga.

(4) Ebertz and Lucas, THIS JOURNAL, **56**, 1230 (1934).