[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF STEVENS INSTITUTE OF TECHNOLOGY]

ALIPHATIC SULFINIC ACIDS.[1] II. PREPARATION OF ALIPHATIC SULFONES. III. PREPARATION OF ALIPHATIC *alpha*-DISULFONES

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II. SULFONES

The sodium salts of aliphatic and aromatic sulfinic acids react with alkyl halides to form sulfones (1–4). Only a few aliphatic sufones have heretofore been made this way. The reaction has now been used to prepare symmetrical aliphatic sulfones, RSO_2R, in which R stands for the straight chain radicals with an even number of carbon atoms, from hexyl to myristyl.

Magnesium alkane 1-sulfinate was converted to the sodium salt and the latter heated in propyl alcohol with the corresponding alkyl bromide. The resulting sulfone was purified by recrystallization.

III. DISULFONES

In Part I of this series (1) it was found that although magnesium aliphatic 1-sulfinates could be titrated in neutral or alkaline solution with aqueous permanganate they could not be accurately titrated in acid, only 80–90% of the theoretical values being obtained. It was suspected that part of the discrepancy was due to oxidation of some of the material to a disulfone rather than to a sulfonate. This side reaction has now been proved in the case of oxidation with acid permanganate.

By this method and modifications of it and by oxidation of the free sulfinic acids aliphatic *alpha*-disulfones, RSO_2SO_2R, have been made, in which R stands for the straight chain radicals with an even number of carbon atoms, from butyl to cetyl and for the normal five and seven carbon radicals. The only other aliphatic *alpha*-disulfone known was obtained by the oxidation of camphor β-sulfinic acid (5).

The present work and Part I (1) show that the disulfones can be made only in acid solution, not in neutral or alkaline permanganate.

Attempts were made, but without success, to prepare butyl disulfone by the following methods: (a) Reaction of silver butane 1-sulfinate with iodine. (b) Reaction of butane 1-sulfonyl chloride with finely divided sodium, potassium, silver, iron, or mercury. (c) Reaction of butane 1-sulfonyl chloride with sodium or silver butane 1-sulfinate. (d) Oxidation of butyl disulfide by potassium permanganate in acetic acid, by 30% hydrogen peroxide, and by benzoyl peroxide.

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[1] Taken in part from the M.S. theses of L. S. Karger, J. D. Haygood, Jr., and Julius Shrensel.

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The conditions of oxidation and formation of by-products are being investigated further. The chemical properties of the disulfones are being studied.

TABLE I

ALKYL SULFONES RSO_2R

NO. OF CARBON ATOMS IN R	SULFUR		M.P., °C. (CORR.)
	Calc'd	Found[a]	
6	13.68	13.70	72.6-73.0
8	11.04	11.03	76.0-76.8[b]
10	9.25	9.26	85.8-86.6
12	7.96	8.05	91.3-92.4
14	6.99	6.92	98.7-99.5

[a] Analyses by R. H. Seavy, Stevens Institute. [b] Octyl sulfone, m.p. 76°, has been made by oxidation of the sulfide, Fenton and Ingold, *J. Chem. Soc.*, 3127 (1928).

TABLE II

ALKYL *alpha*-DISULFONES $RSO_2 \cdot SO_2R$

NO. OF CARBON ATOMS IN R	% YIELD, (BASED ON RSO_2H)	SULFUR		M.P., °C. (CORR.)
		Calc'd	Found[a]	
4	6.3	26.46	26.46	58.8- 59.6
5[b]	4.4	23.71	24.09	76.2- 77.1
6	15.4	21.49	21.92	74.1- 74.9
7[b]	16.0	19.64	19.59	91.5- 92.5
8	13.4	18.08	18.08	89.2- 89.8
10	16.1	15.61	15.62	96.0- 96.6
12	13.0	13.74	14.11	101.7-102.5
14	>12.	12.26	12.33	105.3-106.2
16	8.3	11.08	11.05	108.2-109.0

[a] Analyses, except of C_4 and C_5 compounds, by R. H. Seavy, Stevens Institute. [b] Made by A. W. Casey, General Foods Corporation, Hoboken, N. J.

EXPERIMENTAL

The *magnesium 1-sulfinate dihydrates* were made as described previously (1).

II. Sulfones. Powdered magnesium sulfinate dihydrate was shaken with dilute sulfuric acid and ether. The solid dissolved and the aqueous layer was extracted several times more with ether. The ether extract, containing the free sulfinic acid, was shaken with dry sodium carbonate and after standing two hours (without filtering) the ether was boiled off. The solid residue, sodium sulfinate and excess sodium carbonate, was extracted with hot propyl alcohol. The alcohol extract was filtered, mixed with an excess of the alkyl bromide corresponding to the sulfinic acid, and refluxed overnight or up to 28 hours. The mixture was poured into water and the insoluble crude sulfone was filtered off, washed, and recrystallized. The yields ranged from 27-42%. Alcohol or alcohol-benzene was used for purification except for myristyl sulfone which was very difficult to purify and was repeatedly recrystallized from isobutyl alcohol, methylene chloride, and ligroin.

Properties of sulfones. These compounds are soluble in hot, but insoluble in cold alcohols from which they separate as fine colorless needles; soluble in warm, but insoluble in cold benzene from which they separate as white powders; soluble in hot, insoluble in cold ligroin and ether; moderately soluble in chloroform and methylene chloride at room temperature; insoluble in water.

III. Disulfones. Although the disulfones may be made by oxidation of the magnesium sulfinate suspended in dilute acid the results are better if the sulfinic acid is separated and oxidized. Two disulfones, the butyl and cetyl, were made by the former method and all of them by the latter. The yields reported in Table II are based on the weight of sulfinic acid oxidized by the second method.

Oxidation of magnesium butane 1-sulfinate. The magnesium butane 1-sulfinate dihydrate (90 g.) was suspended in 500 ml. of 2 *N* sulfuric acid at room temperature and powdered potassium permanganate was slowly added with stirring. The mixture became brown after the addition of 25.5 grams (theory requires 18.8 g. for conversion to disulfone only; 37.6 g. for conversion to sulfonic acid only). It was decolorized with a little sodium bisulfite. Suspended solids were filtered off and extracted with ether. On evaporation of the ether, the residue melted at 51° and weighed 4.3 g., yield 6.0%; the average of two runs was 5.6%. One recrystallization from hot concentrated nitric acid gave m.p. 58–59°; however, butyl alcohol is the most convenient solvent for purification; molecular weight by freezing-point depression of benzene, 232, 234; calculated, 242.

When the magnesium sulfinate was suspended in glacial acetic acid, cooled in ice-water, and oxidized with powdered potassium permanganate the yield of disulfone was 6.2%.

A trace of disulfone resulted when magnesium sulfinate was suspended in acetone and a little phosphoric acid and oxidized with permanganate. No disulfone was obtained with sodium dichromate as the oxidizing agent; a green precipitate, probably chromic sulfonate and phosphate, formed in large amount.

Oxidation of magnesium hexadecane 1-sulfinate. Just 9.9 g. of powdered sulfinate was added slowly to 100 ml. of 6 *N* sulfuric acid kept red by running in aqueous potassium permanganate solution (4 g. of solid in 100 ml. water). After a small excess of permanganate had been added the mixture was decolorized with peroxide and filtered. The dried residue on extraction with hot carbon tetrachloride gave a 2.1% yield of cetyl disulfone and a small amount of another organic compound which is being investigated.

Oxidation of sulfinic acids. The following is typical of the general procedure. Magnesium decane 1-sulfinate dihydrate was extracted with water and organic solvents to remove impurities, air-dried, and powdered. Then 6 g. of sulfinate was shaken with sulfuric acid (20 ml. of concentrated acid added to 100 ml. of water) and 50 ml. of ether. The sulfinate slowly dissolved and the aqueous layer was repeatedly extracted with ether. The ether extract (171 ml.) was dried with sodium sulfate, filtered, and the ether removed under a vacuum; to avoid decomposition of the sulfinic acid (6) the ether was warmed only slightly. The residue, 5.06 g. of decane 1-sulfinic acid, was dissolved in 70 ml. of glacial acetic acid and oxidized at room temperature by adding, with vigorous stirring, a solution of potassium permanganate (about 4 g. of solid in 100 ml. of water). As the permanganate was run in a white suspension formed. After 42 ml. had been added (calc'd about 37 ml.) a brown color appeared; further addition deepened the color. The mixture was diluted with water, decolorized with a few drops of peroxide, and filtered. The residue on the filter was air-dried and extracted with chloroform; the chloroform gave 0.82 g. of disulfone (16.1% yield) and a little by-product.

Modifications of procedure. Methylene chloride can well be used instead of ether for the extraction of free sulfinic acid. Sulfinic acid dissolved in acetic acid may be oxidized by adding powdered permanganate slowly. The acids of twelve or more carbon atoms form insoluble manganese sulfonates.

A very poor yield resulted on oxidation of butane sulfinic acid in acetone with powdered permanganate with or without added phosphoric acid. Hydrogen peroxide and potassium persulfate with acetic acid were ineffective as oxidizing agents.

Properties of disulfones. The disulfones form colorless plates. The lower ones may be recrystallized from hexane or ligroin but for the higher members methylene chloride is the best solvent. They are soluble in hot, insoluble in cold ligroin or hexane; sparingly soluble in ether, ethyl alcohol, and isobutyl alcohol; insoluble in water; the lower members are readily soluble, the higher ones slightly so, in methylene chloride, chloroform, and benzene at room temperature.

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REFERENCES

(1) ALLEN, *J. Org. Chem.*, **7**, 23 (1942).
(2) OTTO, *J. prakt. Chem.*, (2) **36**, 436 (1887); *Ber.*, **13**, 1272 (1880).
(3) WHITNER AND REID, *J. Am. Chem. Soc.*, **43**, 638 (1921).
(4) MICHAEL AND PALMER, *Am. Chem. J.*, **6**, 253 (1885).
(5) SMILES AND HILDITCH, *J. Chem. Soc.*, **91**, 519 (1907).
(6) MARVEL AND JOHNSON, *J. Org. Chem.*, **13**, 822 (1948).