[CONTRIBUTION FROM THE DEPARTMENT OF BIOLOGICAL CHEMISTRY, COLUMBIA UNIVERSITY]

Alkane-α,ω-disulfonates

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In order to study the effect of increasing the distance between two strongly polar groups in a molecule, the straight chain, saturated α,ω-disulfonic acids seemed ideal. However, only the first members of this series had been made, and it was necessary to develop syntheses of those of higher molecular weight. The literature[1] reports that some of these have been made by the action of fuming sulfuric acid on the corresponding hydrocarbon, but this method leaves doubt as to the exact location of the sulfonic acid groups. In the studies to be made it was necessary to be certain that the polar groups be on the terminal carbons; other methods were therefore sought. It was found that the Strecker reaction[2] could be applied to the synthesis of these compounds.

$$Br(CH_2)_nBr + 2Na_2SO_3 \longrightarrow NaO_3S(CH_2)_nSO_3Na + 2NaBr$$

It has been reported[3,4,5] that difficulty was encountered in the preparation of alkyl sulfonic acids of higher molecular weight by this reaction without the use of autoclaves and high temperatures. All of the Strecker reactions described in this paper were performed at 100°. The dibromides of lower molecular weight reacted stoichiometrically in twenty-four hours. As the weight increased, the reaction time increased. The decamethylene dibromide required seven days for complete reaction with the sodium sulfite.

Experimental Part

Preparation of α,ω-Dibromoparaffins

Tetramethylene Dibromide.—One mole (296 g.) of finely divided dibenzoylputrescine, prepared by the method of v. Braun and Pinkernelle,[6] 2.2 moles (947 g.) of phosphorus pentabromide and 750 cc. of carbon tetrachloride were refluxed for five days. The resulting homogeneous brown liquid was distilled, the pressure being reduced progressively to 25 mm., and the temperature held below 110°. The distillate was poured on ice and stirred for several hours to hydrolyze the phosphorus oxybromide. The heavy, oily liquid, separated from the aqueous layer and diluted with twice its volume of ethylene chloride, was extracted repeatedly with concentrated sulfuric acid until free of benzonitrile. After a thorough washing with aqueous sodium carbonate[7] and water, the liquid was dried over calcium chloride and vacuum distilled. The fraction distilling at 77–78° at 10 mm. amounted to 105 g. or 49% of the theoretical quantity.

Pentamethylene Dibromide.—This was prepared according to the directions in "Organic Syntheses."[8]

Hexamethylene Dibromide.—Hexamethylene glycol was prepared from ethyl adipate according to the method of Manske.[9] The alkaline reduction mixture was extracted continually for five days with ether. The ethereal solution was then extracted three times with water, the water removed by distillation and the resulting solid distilled *in vacuo;* b. p. 146–147° at 16 mm.; m. p. 56°; yield 65%. 236 grams (2 moles) of the glycol was refluxed for six hours with 835 g. (5 moles) of 48% hydrobromic acid and 650 g. of concentrated sulfuric acid. The resulting dibromide was distilled in a current of steam, washed, dried and vacuum distilled; yield, 363 g. or 75% of the theoretical; b. p. 127–129° at 21 mm., which is in agreement with other observers.[10]

Decamethylene Dibromide.—This substance was made from decamethylene glycol, obtained by the reduction[9] of ethyl sebacate. The procedure followed was essentially the same as that for making the hexamethylene dibromide. It distilled at 161–162° (10 mm.); yield, 80% of the theoretical; f. p. 25–26°; $n^{25}\mathrm{D}$ (supercooled) 1.4927. Molecular refractivity: calcd., 63.91; found, 63.84.

Anal. Calcd. for $C_{10}H_{20}Br_2$: C, 40.00; H, 6.72; Br, 53.28. Found: C, 40.14; H, 6.60; Br, 53.08.

Preparation of Sodium α,ω-Alkanedisulfonates

One mole of the dibromide was added slowly to a hot saturated aqueous solution of 2.5 moles of sodium sulfite. The mixture was heated on a steam plate with stirring until the reaction was complete. This was determined by titration of an aliquot portion with *N*/2 silver nitrate solution after slight acidification with acetic acid, and boiling to remove sulfur dioxide. Sodium chromate was the indicator. Complete conversion took place in from twelve hours to seven days, depending on the molecular weight of the dibromide.

In the case of the ethylene and decamethylene dibromides the corresponding sodium disulfonates crystallized from the reaction mixture and were purified by repeated recrystallizations.

Purification of the other salts involved ridding the solution of the extraneous ions present.

Slight excess of hot saturated lead acetate solution was added to the reaction mixture. Upon cooling, the lead

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[1] Worstall, *Am. Chem. J.*, **20**, 664 (1898).

[2] Strecker, *Ann.*, **148**, 90 (1868).

[3] Reed and Tartar, THIS JOURNAL, **57**, 570 (1935).

[4] Norris, *J. Chem. Soc.*, **121**, 2161 (1922).

[5] Collins, Hilditch, Marsh and MacLeod, *J. Soc. Chem. Ind.*, **52**, 272T (1933).

[6] Von Braun and Pinkernelle, *Ber.*, **67**, 1058 (1934).

[7] Troublesome emulsions frequently formed during the washing process. When these emulsions could not be broken, it was necessary to resort to a steam distillation.

[8] "Organic Syntheses," Coll. Vol. I, 1932, p. 419.

[9] Manske, *ibid.*, Vol. XIV, 1934, p. 20.

[10] Von Braun and Müller, *Ber.*, **39**, 2020 (1906).

bromide, sulfate and sulfite were filtered off. The addition of silver oxide removed from solution the remaining bromide ion. After filtering off the silver bromide, the solution was made acid to Congo red by the addition of sulfuric acid. The precipitated lead sulfate removed, the solution was taken down almost to dryness by a vacuum distillation, thus ridding it of the acetate ion. Dissolving the solids in a minimum of water and adding ethyl alcohol up to 60% precipitated most of the sodium sulfate. Upon filtering, the addition of the exactly necessary quantity of hot barium hydroxide solution completed the removal of sulfate ion. After evaporating to dryness and redissolving in a minimum of hot water, the addition of ethyl alcohol up to 60% caused the sodium disulfonates to precipitate. The addition of small quantities of ether made the precipitation more complete. The salts were recrystallized in this manner at least four times until free of all traces of extraneous ions; yield, 30–50%; 20–30% can be recovered from mother liquors.

TABLE I

ANALYSIS OF SODIUM ALKANE-α,ω-DISULFONATES

Substance	Carbon, %		Hydrogen, %		Sodium, %	
	Calcd.	Found	Calcd.	Found	Calcd.	Found
$NaO_3S(CH_2)_2SO_3Na$	10.25	10.29	1.72	1.75	19.64	19.60
$NaO_3S(CH_2)_3SO_3Na$	14.51	14.51	2.42	2.44	18.54	18.52
$NaO_3S(CH_2)_4SO_3Na$	18.31	18.58	3.08	3.15	17.54	17.51
$NaO_3S(CH_2)_5SO_3Na$	21.72	21.90	3.65	3.56	16.65	16.62
$NaO_3S(CH_2)_6SO_3Na$	24.81	24.90	4.17	4.16	15.85	16.02
$NaO_3S(CH_2)_{10}SO_3Na$	34.65	34.82	5.82	5.85	13.28	13.15

Titration Curves

A glass electrode, constructed by Mr. F. Rosebury, of these laboratories, was used to measure the e. m. f. of the solutions. The electrode was standardized with 0.1 *N* hydrochloric acid, the *p*H of the acid being taken as 1.08 at 25°.

Since the sodium disulfonates are somewhat hygroscopic, the absorption of moisture being at a maximum with the 4 or 5 carbon compound, they were dried *in vacuo* over phosphorus pentoxide. Quantities were rapidly weighed out and made up to 0.05 molar solutions; 5 ml. of these solutions, diluted to 100 ml. with water, was titrated with 0.1 *N* hydrochloric acid and 0.1 *N* sodium hydroxide from a micro buret.

The titration of the salt with acid and base results in the same curve as would the titration of the free acid. The only difference would be due to a small change in activity coefficient because of the additional ions present. In solutions as dilute as those used and with the precision of the instruments, this error was negligible. A titration of 0.01 *M* sulfuric acid and 0.01 *M* sodium sulfate resulted in identical curves.

The titration curves have not been printed because they were all identical with that of sulfuric acid. The average deviation was ±0.025 *p*H unit; the maximum deviation, ±0.07 *p*H unit.

It can be concluded therefore that the saturated alkane-α,ω-disulfonic acids investigated are at least as strong acids as sulfuric acid. The sodium salts do not hydrolyze to any appreciable extent.

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Summary

The Strecker reaction was employed to prepare a series of saturated alkane sodium disulfonates. The procedure followed in the preparation and purification of these compounds has been described.

Titration curves of these disulfonic acids are identical with that of sulfuric acid and they may be considered at least as strong acids as sulfuric acid.

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