Table III. It has been shown[2] that 2- and 4-chloro-, 4-bromo- and 3-nitrobenzalchlorimines, compounds that have relatively high decomposition temperatures, are changed only slightly at 30° within a few hours, whereas the 2- and 4-methoxy and 3,4-methylenedioxy derivatives, which have somewhat lower decomposition temperatures, are decomposed almost completely at 30° during the same time. Moreover, cinnamalchlorimine, which has the lowest decomposition temperature of any of the compounds listed in Table III, decomposes vigorously within thirty minutes when allowed to stand at room temperatures. *o*-Nitrobenzalchlorimine, however, seems to be exceptional in that decomposition temperatures have been found ranging from 180–200°; also, at 30°, it decomposes much more rapidly than its isomers.

The writers wish to express their indebtedness to Dr. L. A. Bigelow and Dr. P. M. Gross, whose valuable suggestions have contributed to the progress of the work.

Summary

1. Eleven new ald-chlorimines have been synthesized.

2. The products formed by the instantaneous decomposition of certain ald-chlorimines have been determined. In general, 90% of a chlorimine decomposed to form primary products, nitrile and hydrogen chloride, and only about 5% to form the secondary products, imine hydrochloride and free chlorine.

3. The temperatures of instantaneous decomposition of 22 ald-chlorimines have been measured. They are reproducible to within ±5° and range from 120 to 215°.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF WASHINGTON]

The Preparation of Sodium Alkyl Sulfonates

BY R. M. REED WITH H. V. TARTAR

A method for the preparation of high molecular weight alkyl sulfonic acids has been described recently by Noller and Gordon.[1] They prepared the corresponding alkyl mercaptans and then oxidized the lead mercaptides to sulfonates with 50% nitric acid. Collins, Hilditch, Marsh and McLeod[2] later described a similar method in which alkyl mercaptans or disulfides were oxidized to the corresponding sulfonic acids by powdered potassium permanganate in acetone or acetic acid solution. These methods were both modifications of those of Reychler[3] and Norris.[4]

Norris reported that many unsuccessful attempts were made to prepare cetyl sulfonic acid from cetyl iodide by using sulfite or bisulfite with solvents such as water, methyl alcohol, ethyl alcohol, acetone and ether. Collins and his co-workers verified this report of Norris as follows: "We confirmed the statement of Norris that the alkyl iodides do not yield the sulfonic acid salts when heated with ammonium sulfite under pressure."

The reaction referred to by these workers

$$RI + (NH_4)_2SO_3 = RSO_3NH_4 + NH_4I$$

is known as the Strecker reaction, and was reported as early as 1868 by Strecker[5] and various other workers. It has been applied successfully to the preparation of sulfonates from such substances as methyl and ethyl iodides, chloroform, ethylene bromide, chlorinated quinones, benzyl chloride and many others, but until very recently had never been used with alkyl halides of high molecular weight (such as octyl or cetyl iodides). It was known, however, that any of the halides could be used in the reaction, and that sodium, potassium and ammonium sulfites were all effective in the sulfonation.

Although Collins and his co-workers were unsuccessful in applying the Strecker reaction to the preparation of alkyl sulfonic acids of high molecular weight, its successful use in such cases had been reported in the patent literature some time previously.[6] These references describe the preparation of such typical high molecular weight

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(1) Noller and Gordon, THIS JOURNAL, **55**, 1090 (1933).

(2) Collins, Hilditch, Marsh and McLeod, *J. Soc. Chem. Ind.*, **52**, 272T (1933).

(3) Reychler, *Bull. soc. chim. Belg.*, **27**, 110, 217, 300 (1913).

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

(5) Strecker, *Ann.*, **148**, 90 (1868).

(6) (a) French Patent 711,210, *C. A.* **26**, 1732 (1932); (b) French Patent 716,715, *ibid.*, **26**, 2288 (1932); (c) British Patent 360,539, *ibid.*, **27**, 575 (1933); (d) British Patent 369,301, *ibid.*, **27**, 2661 (1933).

sulfonic acids (as the sodium salts) as lauryl, cetyl and octadecyl. The essential procedure consists in heating the alkyl halide with an excess of aqueous sodium sulfite solution in an autoclave at about 200° for several hours. The reaction proceeds smoothly and the yields are good (60–70%).

Following the general procedure outlined in these references, sodium octyl, decyl, myristyl, cetyl and octadecyl sulfonates were prepared from the corresponding bromides, and sodium lauryl sulfonate was prepared from lauryl chloride.

This method of preparing sodium alkyl sulfonates appears much simpler than that involving the oxidation of alkyl mercaptans, as the preparation of the mercaptans from the alkyl halides is eliminated, and the final purification of the sulfonates seems much less troublesome than in the other case.

Experimental Part

Preparation of Alcohols and Alkyl Bromides.—The alcohols used in the following experiments were obtained by repeated fractional distillation of lorol (commercial mixed primary alcohols obtained by the high pressure reduction of palm kernel or coconut oils). The bromides were prepared by the method of Kamm and Marvel[7] in yields of 70% or better except in the case of octadecyl bromide in which considerable charring occurred and the yield dropped to about 40%. Table I gives the boiling points of the alcohols and bromides which were used.

TABLE I

BOILING POINTS OF ALCOHOLS AND ALKYL BROMIDES

Alkyl radical	B. p. of alcohol, °C. 10 mm. press.	B. p. of bromide, °C. 10 mm. press.
n-Octyl	89–90	77
n-Decyl	106–119	110–111
Lauryl	135–137	139
Myristyl	159–161	164
Cetyl	179–181	188
n-Octadecyl	202	190–191 (5 mm.)

Lauryl chloride was also prepared, and had a boiling point of 125–126° at 10 mm. pressure.

Preparation of Sodium Alkyl Sulfonates.—One mol of alkyl bromide, 1.15 mols of anhydrous sodium sulfite and 750 cc. of water were placed in an autoclave (capacity about 1100 cc.) and heated for about nine hours at 180–200°. The autoclave was fitted with a rocking attachment to provide stirring. After the reaction mixture had cooled, it was removed from the autoclave and evaporated to dryness on a steam-bath. It was then pulverized in a mortar and extracted with petroleum ether to remove organic impurities, the sodium alkyl sulfonates being insoluble in petroleum ether. Usually about 10–15% of the alcohol corresponding to the bromide used was recovered in this extraction. This presumably was formed by hydrolysis of the alkyl bromide in the hot aqueous solution of sodium sulfite.

Following the petroleum ether extraction, the crude sodium alkyl sulfonate was dissolved in hot ethyl alcohol (denatured formula No. 30) and filtered through a hot funnel to remove inorganic impurities. The alcoholic solution was cooled overnight in a refrigerator, whereupon the sodium alkyl sulfonate crystallized out in lustrous white plates. These were filtered on a Buchner funnel and dried in an oven at 105° for about two hours. A second crystallization from alcohol ordinarily was sufficient to complete the purification of the sodium alkyl sulfonate. The yields of purified sodium alkyl sulfonate obtained averaged about 70%.

The sulfur content of the purified samples was determined by the method of Pollock and Partansky,[8] which was found to give excellent results. As a further check on their purity, the sodium content of the samples was determined by careful ashing in a platinum crucible in the presence of excess sulfuric acid. These analyses are given in Table II.

TABLE II

ANALYSES OF SODIUM ALKYL SULFONATES

Substance	Sulfur, % Calcd.	Sulfur, % Found	Sodium, % Calcd.	Sodium, % Found
Sodium *n*-octyl sulfonate	14.8	14.9	10.6	10.6
Sodium *n*-decyl sulfonate	13.1	13.2	9.4	9.3
Sodium lauryl sulfonate	11.8	11.7	8.4	8.4
Sodium myristyl sulfonate	10.7	10.7	7.7	7.6
Sodium cetyl sulfonate	9.8	9.8	7.0	6.9
Sodium *n*-octadecyl sulfonate	9.0	9.0	6.4	6.4

None of the samples gave any evidence of decomposition on being dried at 105°. The sodium octyl and decyl sulfonates were somewhat hygroscopic, but none of the other sulfonates showed this behavior. All of them, including the sodium octyl sulfonate, which has not been prepared before, dissolved readily in hot water, producing typically soap-like solutions.

Acknowledgment.—Grateful acknowledgment is made to the Procter and Gamble Company for providing the equipment and materials used in the preparation of these sodium alkyl sulfonates, and also for the helpful advice given by members of the chemical staff during the course of this work.

Summary

The use of the Strecker reaction as a very suitable method for the preparation of high molecular weight sodium alkyl sulfonates has been emphasized. The procedure followed in preparing a number of these compounds has been described, and analyses have been given to show the high purity of the products obtained by this method.

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[7] Kamm and Marvel, "Organic Syntheses," Coll. Vol. I, 1932, p. 23.

[8] Pollock and Partansky, *Ind. Eng. Chem., Anal. Ed.*, **6**, 330 (1934).