and the hydrogen uptake measured in an appropriate apparatus.[5] The data, reduced to a common basis, are given in Table I.

TABLE I

HYDROGENATION OF SPHINGOSINE SULFATES

Substance	Hydrogen absorbed in t minutes[a] $t =$ 15	30	45	75	105	135	165	255	315	375
α-Sulfate(α$_2$)	56	81	89	94	95	95				
β-Sulfate (β$_2$)	8	22	28	41	53	62	67	80	87	90

[a] Expressed as per cent. of the theoretical quantity required for the conversion of sphingosine sulfate into dihydrosphingosine sulfate.

Examination with Ultraviolet Light.[4]—Specimens of all of the α- and β-sphingosine sulfates described above were examined with a Hanovia "Luxor Scientific" lamp. All of the β-sphingosine sulfate preparations exhibited a weak violet fluorescence which was less intense than that shown by quinine sulfate under comparable conditions. In the case of α-sphingosine sulfate the color of the fluorescence, but not the intensity, varied with the age of the sample. With freshly prepared α-sulfate the color was a blue-white but with the older, cream-colored samples the color lost its bluish character and appeared as white or ivory. The intensity of the fluorescence was very much greater than that exhibited by quinine sulfate.

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(5) A. N. Prater and A. J. Haagen-Smit, *Ind. Eng. Chem., Anal. Ed.*, **12**, 705 (1940).

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The Preparation of Trichloromethanesulfonyl Chloride

BY MILTON S. SCHECHTER AND H. L. HALLER

A recent article by Pelikh[1] describes the use of trichloromethanesulfonyl chloride, Cl_3CSO_2Cl, for the control of the sugar-beet weevil and gives a method for its preparation. In response to a request for some of the material by one of the entomologists of this Bureau, attempts were made to obtain the Russian journal. These having been unsuccessful, some of the compound was prepared by the method described by Rathke.[2] In this procedure trichloromethanesulfenyl chloride (perchloromethyl mercaptan), Cl_3CSCl, is oxidized at room temperature with nitric acid (sp. gr. 1.2). The reactants are immiscible so that the reaction is very slow; after two to three weeks a low yield of the acid chloride was obtained.

It has now been found that the oxidation proceeds smoothly and rapidly in acetic acid. The trichloromethanesulfonyl chloride is obtained in a yield of about 50%.

According to Richter-Anschütz[3] the compound possesses a penetrating camphoraceous odor, and Pelikh[1] states that it has a beet-like smell. The pure product obtained by us had a penetrating odor and was a lachrymator. The use of calcium trichloromethanesulfonate[4] as specified by Pelikh may circumvent the lachrymatory effect.

The trichloromethanesulfenyl chloride can be prepared readily from carbon disulfide and chlorine, with iodine as a catalyst, by the procedure of Helfrich and Reid[5] or that described in "Organic Syntheses.[6] It has now been found that this reaction also can be carried out conveniently by shaking the carbon disulfide plus iodine in an apparatus such as the Burgess-Parr shaker used in catalytic hydrogenation, while passing chlorine into the bottle under slight pressure at such a rate that the temperature of the solution does not exceed 30°. The reaction is completed when the absorption of chlorine practically ceases. The volume of solution should approximately be doubled. Over-chlorination decreases the yield owing to the formation of carbon tetrachloride. Allowing the solution to stand for a day or two increases the yield.[5] The reaction product is then subjected to fractional distillation under reduced pressure. The fraction boiling at 65-68°, $p = 50$ mm., was collected and used for the subsequent oxidation experiments.

The oxidation procedure given below was chosen as the best after a number of experiments had been tried in which the concentrations of trichloromethanesulfenyl chloride, acetic acid, and nitric acid were varied.

Ten grams of trichloromethanesulfenyl chloride dissolved in 30 cc. of glacial acetic acid is refluxed gently, and 15 cc. of concentrated nitric acid is added drop by drop over a period of ten to fifteen minutes. The reaction is exothermic and brown fumes are evolved. The amount of heat supplied may have to be decreased. After all the nitric acid has been added, the solution is refluxed for twenty minutes longer, cooled and diluted with several volumes of water. The separated trichloromethanesulfonyl chloride is filtered, washed well with water, and dried. Such a preparation is fairly pure, but if necessary it may be recrystallized by dissolving in warm ethanol and diluting with water. It may also be purified by sublimation or steam distillation. The melting point is 140-140.5°

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(1) N. D. Pelikh, *Sakhar* (U. S. S. R.), No. 6, 40 (1937). *Khim. Referat. Zhur.*, **1**, No. 8-9, 45 (1938). Through *C. A.*, **33**, 7031 (1939).

(2) B. Rathke, *Ber.*, **3**, 858 (1870); *Ann.*, **167**, 195 (1873).

(3) Richter-Anschütz, "Chemie der Kohlenstoffverbindungen," Ed. 12, Vol. I, p. 541, 1928.

(4) N. D. Pelikh and S. I. Lyukin, Russian patent 52,159, Nov. 1937. Through *C. A.*, **34**, 3008 (1940).

(5) O. B. Helfrich and E. E. Reid, THIS JOURNAL, **43**, 591 (1921).

(6) Henry Gilman, "Organic Syntheses," Coll. Vol. I, p. 493.

(cor.), which is 5° higher than that recorded in the literature. The yield is about 50%. The compound is rather resistant to hydrolysis by water or alkali.

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Ferric Thiocyanate

BY H. I. SCHLESINGER

Recently Bent and French[1] indicated that they were unable to confirm the observation of Schlesinger and VanValkenburgh[2] that aqueous solutions of ferric thiocyanate contain a colored substance which migrates to the anode. Such solutions are complex, and observations of the phenomenon must be made under comparable conditions to be reproducible. Some years ago, M. Møller apparently encountered the same difficulty, but communicated with us before publication of his papers on this subject.[3] We were glad to furnish him the necessary information, and would have been glad to do so in the case of Bent and French. Since the matter has come up again, it seems desirable to publish some details concerning the original and some more recent experiments.

In the earlier work (carried out by Dr. VanValkenburgh at the University of Colorado) gelatin was used to decrease diffusion, and the results were later confirmed (with the aid of Dr. A. B. Burg) with solutions fixed with agar-agar. In most experiments the solutions were acidified. Bent and French state that the use of both gelatin and agar agar is out of the question since the thiocyanate solution was decolorized by these solutions. This difficulty is, however, easily overcome. Apparently the color is destroyed by impurities in gelatin or agar-agar. These impurities are rendered ineffective by addition of just enough ferric thiocyanate to produce a faint color, not deep enough to prevent observation of the migration effects.

To make sure that the gelatin or agar-agar had not been responsible for the migration toward the anode, observed in these experiments, Dr. H. C. Brown and I recently carried out additional ones in which these substances were not used. The electrolytic cell was a U-tube (25 mm. in width) to the bottom of which was sealed a narrower bent tube, fitted with a stopcock and storage bulb, from which ferric thiocyanate solution could be delivered into the U-tube. The latter contained a colorless solution. Slow introduction of the ferric thiocyanate resulted in the establishment of a fairly sharp boundary between the colored and colorless solutions, and diffusion across the boundary was very slow compared to the effects produced by the current (18 v., corresponding to a potential gradient of approximately 0.5 v./cm.). In some of the experiments the platinum electrodes were immersed directly in the colorless solution; in those marked* the electrodes were immersed in small secondary compartments (containing dilute sulfuric acid) which were in turn immersed in the colorless solution. This device, described by MacInnes,[4] not only prevents stirring but also avoids disturbing oxidation of thiocyanate ion to dithiocyanogen. Its use did not, however, materially alter the results. The details of the experiments are summarized in the table.

EXPERIMENTAL DATA

	Colored solution, *N*			Colorless solution, *N*	
Expt.	KCNS	Ferric salt	Acid	KCNS	Acid
1 and 2	4.0	0.1	0.1 H_2SO_4	2.0	0.02 H_2SO
3*	like Expt. 1			like Expt. 1 except*	
4	1.0	0.1	0.1 H_2SO_4	0.5	0.02 H_2SO_4
5*	like Expt. 4			like Expt. 4 except*	
6	4.0	0.1	0.1 H_2SO_4	...	0.3 HNO_3
7	4.0	0.1	0.1 HNO_3	2.0	0.1 HNO_3

The ferric salt was the sulfate in all experiments except the seventh in which the nitrate was used. In Expts. 1, 2, and 3, one colored boundary in ten minutes had advanced from 1.5 to 2.0 mm. toward the positive electrode, and the other boundary had receded from 1.0 to 1.5 mm. from the negative electrode. In Expts. 4 and 5 migration was in the same direction but seemed to be slightly slower. The difference was less than 0.5 mm. and is probably not significant; if real, it might be due to the difference in the character of the voltage distribution in the electrolytic column. The sixth experiment was continued for one hour, during which time one boundary moved nearly 5 mm. toward the anode, while the other remained nearly stationary. That the motion was not more extensive is probably due to the absence of thiocyanate ion in the colorless solutions; before a permanent color could persist, enough excess thi-

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(1) Bent and French, THIS JOURNAL, **63**, 568 (1941).

(2) Schlesinger and VanValkenburgh, *ibid.*, **53**, 1212 (1931).

(3) (a) Thesis, "Studies on Aqueous Solutions of the Iron Thiocyanates," Copenhagen, 1937; (b) *Kem. Maanedsblad*, **18**, 138 (1937); (c) *Chem. Abst.*, **33**, 9179 (1939).

(4) MacInnes, "The Principles of Electrochemistry," Reinhold Publishing Corporation, New York, N. Y., 1939, p. 73.