salt of Reychler's acid is not a substituted sulfonamide (I) and hence, by exclusion, constitute further evidence in favor of the ketimine structure (II).

Experimental

d-**Camphor-10-sulfonyl Chloride.**—The conversion of Reychler's acid to the sulfonyl chloride may be accomplished by means of either phosphorus pentachloride or thionyl chloride. Both reagents were used in order to determine which was the better. Treatment of one mole of *d*-camphor-10-sulfonic acid with one mole of phosphorus pentachloride according to the directions of Reychler[3] gave a 38% yield of the sulfonyl chloride. The thionyl chloride method described by Smiles and Hilditch[6] gave a 98% yield, provided four moles of thionyl chloride is used for each mole of the acid. The recrystallized product melted sharply at 67°, and had a specific rotation[5] of +32.1°.

d-**Camphor-10-sulfonanilide.**—Three-tenths mole of the above sulfonyl chloride and 0.9 mole of aniline were heated on the steam-bath for several hours. The reaction mixture was poured into 1 liter of water, and the product removed by filtration. For purification the anilide was dissolved in ether, extracted several times with 10% hydrochloric acid, and the ether evaporated. The residue was recrystallized repeatedly from alcohol until the melting point became constant at 120.5–121°. The anilide possessed specific rotations[5] of +76° in chloroform, and +29.5° in 95% alcohol. Its solutions did not exhibit mutarotation over a period of three days. It was insoluble in alkalies and could not be titrated to give a neutral equivalent. A sample of the anilide was also prepared by the usual Hinsberg procedure, using *d*-camphor-10-sulfonyl chloride, aniline and 10% sodium hydroxide solution. The anilide precipitated from the alkaline solution. After recrystallization it melted at 120–121°, and was identical with the sample prepared by the first method.

Anal. Calcd. for $C_{16}H_{21}O_3NS$: S, 10.43; N, 4.56. Found: S, 10.38; N, 4.48.

Hydrolysis of *d*-Camphor-10-sulfonanilide.—The sulfonanilide did not undergo hydrolysis on standing in aqueous alcoholic solution. Refluxing the anilide with 25% hydrochloric acid for thirty-six hours, according to the method previously described for benzenesulfonanilides,[7] hydrolyzed it to aniline (77% yield) and *d*-camphor-10-sulfonic acid.

Summary

The anilide of *d*-camphor-10-sulfonic acid has been prepared and found to differ markedly from the dehydration product of the aniline salt of Reychler's acid. This excludes the sulfonanilide from consideration as the dehydration product, and constitutes further proof that the ketimine structure is correct.

---

[6] Smiles and Hilditch, *J. Chem. Soc.*, **90**, 522 (1907).

[7] Schreiber and Shriner, THIS JOURNAL, **56**, 1618 (1934).

URBANA, ILLINOIS RECEIVED NOVEMBER 21, 1935

[CONTRIBUTION FROM THE MORLEY CHEMICAL LABORATORY, WESTERN RESERVE UNIVERSITY]

Fluorination of Sulfuryl Chloride—Sulfuryl Chlorofluoride

BY HAROLD SIMMONS BOOTH AND CARL V. HERRMANN[1]

Of the two possible fluorination products of sulfuryl chloride only one, sulfuryl fluoride, is mentioned in the literature. Moissan and Lebeau[2] prepared sulfuryl fluoride by passing fluorine into sulfur dioxide. Ruff[3] found that sulfuryl fluoride could not be made by distillation of fluorosulfonic acid. Traube[4] was able to prepare the gas by the decomposition of sodium fluorosulfonate according to the reaction $2NaSO_3F \longrightarrow Na_2SO_4 + SO_2F_2$. None of these methods appeared to be of use in the preparation of a possible sulfuryl chlorofluoride.

This Laboratory has prepared a number of inorganic chlorofluorides[5] by a reaction first developed by F. Swarts[6] for the fluorination of organic compounds. The method involves the heating of a non-polar chloride with antimony trifluoride in the presence of an antimony pentahalide as a catalyst. In a preliminary study[7] it was found that the reaction

$$SbF_3 + 3SO_2Cl_2 + (SbCl_5) \longrightarrow SbCl_3 + 3SO_2ClF + (SbCl_5)$$

did not proceed appreciably under reduced pressure, but at atmospheric pressure a small amount of gas was produced which had approximately the anticipated boiling point.

---

[1] Submitted by Carl V. Herrmann to the Graduate School, Western Reserve University, in partial fulfilment of the requirements for the degree of Master of Arts, June, 1934. Reported in the Fluorine Symposium, Cleveland Convention of the American Chemical Society, September 13, 1934.

[2] H. Moissan and P. Lebeau, *Compt. rend.*, **132**, 374 (1901).

[3] Otto Ruff, *Ber.*, **47**, 656 (1914).

[4] W. Traube, *ibid.*, **46**, 2523 (1913).

[5] Booth and Swinehart, THIS JOURNAL, **54**, 4750, 4751 (1932); **57**, 1333, 1337 (1935); Booth and Bozarth, *ibid.*, **55**, 3890 (1933); Booth and Stillwell, *ibid.*, **56**, 1531 (1934).

[6] F. Swarts, *Bull. soc. chim.*, [4] **35**, 1557 (1924).

[7] We are indebted to Miss Ida Lieb of this Laboratory for this preliminary study.

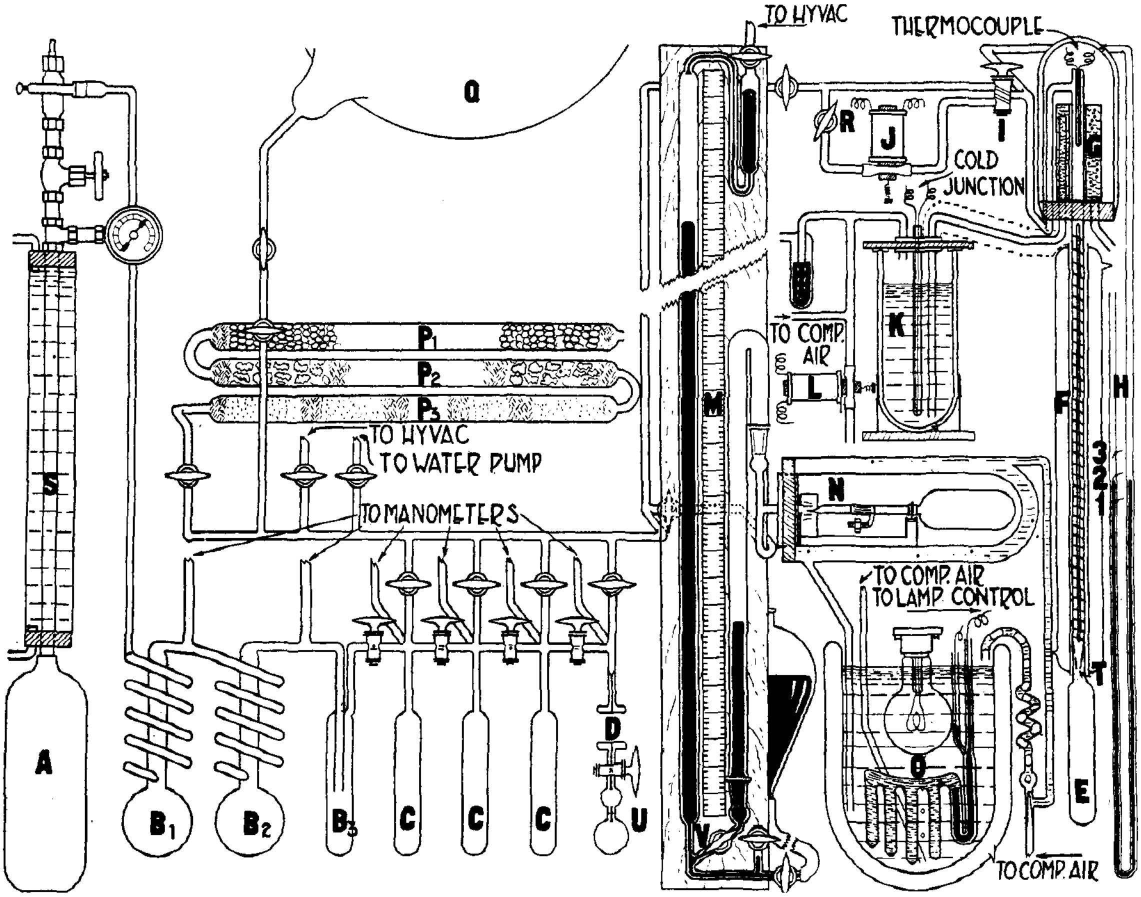

Fig. 1.

Preparation of Sulfuryl Chlorofluoride

Generating Apparatus.—Since the preliminary study indicated that pressure would increase the yields, the gas was generated in an apparatus (Fig. 1) which could withstand high pressures and yet be amenable to rather close control. A small compressed gas cylinder (A) of about 1000-cc. capacity which served as a reaction vessel was fitted with a water-jacketed iron pipe (S) to act as a reflux condenser and a pressure gage reading to 100 pounds per square inch surmounted by a needle valve to permit the gaseous products of the reaction to be bled off slowly. The valve which had been in the cylinder was connected above the needle valve. A standard threaded yoke[8] connected this valve to the glass system. To control the reaction temperature a low melting lead alloy bath heated by a Fisher burner surrounded (A). The products of reaction were bled off through three traps (B) surrounded by freezing mixtures: ice in case of B_1 to catch any SO_2Cl_2; acetone–carbon dioxide snow mixture around B_2 to retain the high boiling gases; and liquid nitrogen around B_3 to retain the low boiling gases. The three ampoules (C) served for preliminary fractional distillations and also to store the liquefied gases. Gases were stored in three glass balloons (Q).

Purification Apparatus.—The sulfuryl chlorofluoride was isolated and purified by fractional distillation, in a column by the technique described by Booth and Bozarth.[9] The change from one gas phase to another was observed by the gas density balance (N) and by means of the thermocouples in the column head (G), so that a new ampoule (C) could be connected to collect the next fraction by condensation with liquid nitrogen. The cold junction of the thermocouple was immersed in the liquid nitrogen in (K). Only one junction was necessary with this arrangement since comparatively large potentials were produced by the temperature difference between the liquid nitrogen and the still head. As is customary in this Laboratory the apparatus was repeatedly rinsed with dry carbon dioxide-free air obtained by passing it through three tubes containing potassium hydroxide (P_1), barium oxide (P_2)[10] and phosphorus pentoxide (P_3).

Fluorination of Sulfuryl Chloride.—The sulfuryl chlorofluoride was generated by the reaction:

$$SbF_3 + 3SO_2Cl_2 + (SbCl_5) \longrightarrow SbCl_3 + 3SO_2ClF + (SbCl_5)$$

With a charge of 220 cc. (365 g.) of sulfuryl chloride, 187 g. finely powdered antimony trifluoride, and 40 cc. of antimony pentafluoride as a catalyst in the generator (A), the following results were obtained:

---

[8] H. S. Booth, *J. Chem. Ed.*, **7**, 1249 (1930).

[9] To be published shortly in the *Analytical Edition of Industrial and Engineering Chemistry*.

[10] Booth and McIntyre, *Ind. Eng. Chem., Anal. Ed.*, **2**, 12 (1930).

1. With a temperature of about 100° around the generator (A) and with the water jacket (S) cold, a maximum pressure of 16 pounds per square inch was obtained, but upon any attempt to bleed off the gas the pressure immediately fell, indicating very little reaction. After a two-hour run only a fraction of a cc. of liquefied product was obtained.

2. At a temperature of about 175° the pressure went as high as 40 pounds per square inch before it seemed to stop. A gas, mainly sulfuryl chlorofluoride, could be bled off continuously at a very slow rate at about 20 pounds per square inch pressure. A two-hour run produced about 8 cc. of liquefied product.

3. With a temperature of 300° a pressure of over 100 pounds per square inch was easily attained in the generator. Gases were drawn off at about 90 pounds. In two hours about 80 cc. of liquid product was obtained. Approximately 10 cc. of this were low boiling gases, about 60 cc., sulfuryl chlorofluoride, and 10 cc. sulfuryl chloride. Bleeding off at a lower pressure caused the sulfuryl chloride to pass as a liquid into trap B_1. All the sulfuryl chloride was not used because the experiment was stopped when sufficient product had been obtained. Obviously, high temperature and pressure are necessary to get an appreciable rate of reaction. Most of the product was sulfuryl chlorofluoride although some low boiling gases were also formed at the same time. It is possible that at high enough temperatures sulfuryl fluoride would be formed also.

Purification

The products of the reaction were separated roughly in the fractionating column. The rate of distillation was controlled so as to produce about 4 cc. of distillate per hour. The composition of the distillate was checked by means of the density balance and by the distilling temperature.

Sixty cubic centimeters of crude product gave about 5 cc. of hydrogen chloride, about 0.5 cc. of another gas (which could not be identified exactly, but judging from the boiling point was sulfur dioxide) about 50 cc. of sulfuryl chlorofluoride and about 5 cc. of sulfuryl chloride. There was no evidence of any sulfuryl fluoride. The portion corresponding to sulfuryl chlorofluoride was refractionated very slowly in the column (about 1 cc. of distillate per hour) to get sharp separation from any impurities. The first and last fractions were discarded; the middle portion was taken for analysis and study.

Identification of the Sulfuryl Chlorofluoride

By means of the gas density balance the gas was found to have a density of 1.175 g. per liter at 168-mm. pressure and 25.0°, whence a molecular weight of 119.0 (theory for sulfuryl chlorofluoride, 118.5) was calculated.

A preliminary experiment showed that the gas hydrolyzed in water, the reaction probably being, $SO_2ClF + 2H_2O \longrightarrow HF + HCl + H_2SO_4$. Accordingly, absorption of the gas in excess sodium hydroxide solution seemed to be the logical first step in its analysis.

Since the gas was liquid below about 7° it was sampled as a liquid as follows. A small bulb was blown on the end of a glass tube and a flat joint was sealed to the other end. The tube was constricted between the buld and the flat joint.[11] This device was then placed on the apparatus at (D) evacuated and rinsed with dry air several times, and the empty tube weighed. It was replaced on the apparatus and the gas was condensed into it. While the gas was still solid the tube was sealed off at the constriction. When the two pieces had assumed room temperature they were weighed. The difference in weight was corrected for air buoyancy and taken as the weight of the sample. The sealed off bulb was then immersed in liquid nitrogen to solidify the gas, a scratch was made on the stem and the tube was broken at this point. The two pieces were immediately dropped into a liter volumetric flask containing about 200 cc. of $^1/_3$ normal sodium hydroxide solution cooled to about 0°. This was immediately stoppered and as it slowly warmed to room temperature the gas reacted with the alkaline solution. After a thorough shaking, the flask and sample tube were washed out and the total volume was made up to 400 cc. for aliquoting. The volume of the sample tube was ascertained by running water into the two pieces from a buret. This volume was used in correcting the weight of sample for buoyancy of the air.

By titrating the excess alkali the hydrogen equivalents per gram of sample were determined.

Another sample was acidified with nitric acid and the chlorides were precipitated with silver nitrate solution in the usual manner, and collected and weighed in Jena glass crucibles.

Two more samples prepared as described above were acidified with hydrochloric acid and analyzed for sulfates by the usual method of precipitation with barium chloride solution. By using a large volume of acidified solution barium fluoride was prevented from precipitating.

The analyses and molecular weight determination shown in Table I were made on different samples and establish the composition of the gas to be sulfuryl chlorofluoride.

TABLE I

ANALYSIS OF SULFURYL CHLOROFLUORIDE

	Acid equivalents per g.	Cl, %	SO_2, %	Molecular wt.
Observed	0.03387	29.90	54.15	119.0
Observed	.03387	29.81	53.91	119.0
Calcd. for SO_2ClF	.03375	29.92	54.05	118.5

Physical Properties of Sulfuryl Chlorofluoride

Liquid Density.—The liquid density was determined by means of a special pycnometer (U). The gas was condensed in the lower bulb by means of liquid nitrogen after which a bath of melting ice was placed around it. The liquid expanded into the capillary and was allowed to evaporate until the meniscus was level with a mark on the capillary. The stopcock was closed and if after several minutes the meniscus had not moved the tube plus the sample was weighed. The tube was next weighed evacuated. After this the lower bulb was filled with cleaned and dried mercury for calibration. The whole bulb was immersed in boiling water while the upper part was evacuated which served to boil off any gas adsorbed on the sides of the lower bulb. The mercury-filled bulb was then

---

[11] See analytical sample tube shown by Booth and Stillwell, THIS JOURNAL, 56, 1531 (1934).

placed in melting ice and the level adjusted to the mark by drawing off excess mercury through a fine glass tube. When the level was constant the upper bulb was evacuated and the whole weighed. The weight of sulfuryl chlorofluoride had to be corrected for the weight of the vapor in the upper bulb. The volume of this was determined by breaking the tube at the mark, filling the upper bulb with water and allowing this water to run into a partly filled buret. The liquid density of sulfuryl chlorofluoride obtained with two different tubes was 1.623 and 1.622, or an average of 1.623 g. per cubic centimeter at 0°.

Melting Point.—(Triple point.) The melting point of the gas under its own vapor pressure was determined by means of accurately calibrated multiple thermocouples in conjunction with a specially sensitive Leeds and Northrup recording potentiometer. The liquefied gas samples were well stirred by an electromagnetic stirrer during the cooling process. The first formation of crystals was simultaneous with a sharp break in the cooling curve. The melting point of sulfuryl chlorofluoride by several determinations was −124.7 ± 0.1°. J. P. Van der Goot[12] gives the melting point of sulfuryl chloride as −54.1° and Moissan and Lebeau[2] give −120° as the melting point of sulfuryl fluoride. The unsymmetrical structure of sulfuryl chlorofluoride probably accounts for its low melting point.

Vapor Pressure.—The vapor pressure of sulfuryl chlorofluoride was determined by the static method as described in detail by Booth and Swinehart[13] using a platinum resistance thermometer. The purity of the sample was also assured by making check readings of the pressure at a given temperature after some of the sample had been boiled away The results are given in Table II.

TABLE II

VAPOR PRESSURE OF SULFURYL CHLOROFLUORIDE

Temp., °C.	Determined	Calcd. from eq.	Deviation, mm.
−89.30	1.1	1.9	−0.8
−83.22	1.7	3.4	−1.7
−71.81	6.5	8.7	−2.2
−64.34	12.6	15.4	−2.8
−60.73	17.0	20.0	−3.0
−55.14	26.4	29.4	−3.0
−50.21	37.2	40.6	−3.4
−46.05	50.6	52.8	−2.2
−42.22	64.1	66.6	−2.5
−30.85	127.6	127.4	−0.2
−26.74	158.0	158.7	−0.7
−21.79	209.2	205.3	+3.9
−17.50	258.7	253.5	+5.2
−13.49	312.8	307.3	+5.5
−11.29	347.6	340.8	+6.8
− 2.50	515.2	506.3	+8.9
+ 3.81	663.1	662.3	+0.8
+ 6.08	724.6	727.3	−2.7
+ 8.98	809.5	818.0	−8.5

Whence the equation for the vapor pressure is: $\log P = -1385.4\,(1/T) + 7.8241$ (from −80 to +10°).

Boiling Point.—From the vapor pressure equation the boiling point of sulfuryl chlorofluoride was calculated to be +7.1 ± 0.1°. The predicted boiling point of sulfuryl chlorofluoride, assuming that the Swarts rule[6] can be applied to non-carbon, non-polar chlorofluorides, should be halfway between that of sulfuryl fluoride (−52°) and that of sulfuryl chloride (+69.1°), that is 8.5°. The actual boiling point of sulfuryl chlorofluoride, +7.1°, agrees with this fairly well. It is possible that this difference may be due to error in the recorded boiling points of either sulfuryl fluoride or sulfuryl chloride.

Heat of Vaporization.—By means of the Clausius–Clapeyron equation the heat of vaporization of sulfuryl chlorofluoride at its boiling point was found to be 6338 cal. per mole. Troutons' constant calculated from this is 22.6 from which it appears that the liquid is slightly associated.

Surface Tension.—The surface tension of liquid sulfuryl chlorofluoride was measured by the capillary rise method. A thermometer stem calibrated by measuring the capillary rise of pure benzene was placed inside of a tube which contained sulfuryl chlorofluoride liquid under its own vapor pressure so that the liquid–gas interfacial tension was actually measured. The measurements were made with a cathetometer while the liquid was immersed in a bath of melting ice. The surface tension of sulfuryl chlorofluoride at 0° was found to be 17.2 dynes per centimeter. The liquid and gas are both colorless and the solid white and opaque.

Chemical Properties of Sulfuryl Chlorofluoride

No specific investigation of the chemical properties of the gas was made. However, during the course of the study the following observations were recorded.

That the gas hydrolyzes immediately when it comes in contact with water, was indicated by the fact that a sample of gas admitted to water colored by methyl red immediately gave an acid reaction.

Sodium hydroxide solution reacts rapidly with the gas and absorbs it completely.

The gas has a pungent odor similar to sulfuryl chloride, but does not fume in air.

The dry gas does not attack dry glass, mercury, or brass at room temperature.

Summary

Sulfuryl chlorofluoride, a new gas boiling at +7.1 ± 0.1° and melting at −124.7 ± 0.1°, has been prepared by the reaction of antimony trifluoride on sulfuryl chloride in the presence of antimony pentachloride under pressure. Its latent heat of vaporization at the boiling point was found to be 6338 calories. At 0° the liquid has the density of 1.623 g. per cubic centimeter and a surface tension of 17.2 dynes per centimeter.

While the gas does not fume in air it is hydrolyzed by water and is readily absorbed by sodium hydroxide solution. No reaction was observed with dry glass, mercury or brass at room temperatures.

CLEVELAND, OHIO RECEIVED MAY 6, 1935

---

[12] J. P. Van der Goot, *Z. physik. Chem.*, **84**, 419 (1913).

[13] Booth and Swinehart, THIS JOURNAL, **57**, 1333 (1935).