

The solution of the above reaction products was concentrated to a sirup, thinned with absolute alcohol and ether, and yielded 7 g. of crystalline *l*-arabinose. This sugar was recrystallized to 5.5 g. of pure *l*-arabinose, with m. p. 159–160° and  $[\alpha]_D^{20-25} +104.6^\circ$ , in water. The solution containing the remaining larger portion of the reaction products was again concentrated to a sirup, from which no more *l*-arabinose could be crystallized. After three weeks crystal nuclei appeared spontaneously in this sirup. These were stirred into the sirup after the addition of absolute alcohol. Refrigeration overnight resulted in the formation of 15 g. of crystalline *l*-ribose, with m. p. 81–84° and  $[\alpha]_D^{20-25} +23.85^\circ$  (seventeen hours after solution in water). One recrystallization from absolute alcohol has raised its melting point to 85–87°. From the mother liquors an additional 13 g. of *l*-ribose has been secured by direct crystallization, and 8.7 g. more by way of the *p*-bromophenylhydrazone in the method of van Ekenstein and Blanksma [*Chem. Weekblad*, **22**, 373 (1909)]. The purified *p*-bromophenylhydrazone of *l*-ribose melted at 171–172°, while the value given by Levene and Jacobs [*Ber.*, **42**, 2474 (1909)] for the same derivative of *d*-ribose was 170°.

The synthesis of both *d*- and *l*-ribose may now be accomplished by the above reactions more quickly and cheaply than by preparations from any other sources. Our studies, which were supported in part by a Grant-in-aid from the National Research Council, will be more fully described in a future publication.

From the *l*-ribose which has thus been formed we shall undertake the preparation, by the cyanhydrin reaction, of the remaining unknown aldohexoses, *l*-allose and *l*-altrose.

DEPARTMENT OF PHYSIOLOGICAL CHEMISTRY  
LOYOLA UNIVERSITY SCHOOL OF MEDICINE  
CHICAGO, ILLINOIS

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W. C. AUSTIN  
FRED L. HUMOLLER

## THE FLUOROCHLORIDES OF SILICON

Sir:

Since 1915 this Laboratory has been engaged in the investigation of the fluorides, especially in Groups III and IV of the periodic table.<sup>1</sup> Unaware of any other investigators working on the problem, we have continued the studies begun in this Laboratory some time ago on the fluorination of

<sup>1</sup> Germann and Booth, *J. Phys. Chem.*, **21**, 92 (1917); Germann and Cleaveland, *Science*, [2] **53**, 582 (1921); Germann and Torrey, *ibid.*, **54**, 16 (1921); Germann and Booth, *J. Phys. Chem.*, **30**, 369 (1926); Booth and Starrs, *ibid.*, **35**, 3553 (1931); Booth and Carter, *ibid.*, **36**, 1359 (1932); Booth, Mong and Burchfield, *Ind. Eng. Chem.*, **24**, 328 (1932); Booth and Bixby, *ibid.*, **24**, 637 (1932); Booth, Swinehart and Morris, *THIS JOURNAL*, **54**, 2561 (1932).

halides and have prepared the compounds  $\text{SiFCl}_3$ ,  $\text{SiF}_2\text{Cl}_2$ ,  $\text{SiF}_3\text{Cl}$  by the direct method of the reaction of antimony trifluoride on silicon tetrachloride in the presence of either antimony pentachloride, chlorine or similar catalyst, obtaining large quantities of these products very readily along with lesser amounts of silicon tetrafluoride.

Recently in an excellent paper Schumb and Gamble<sup>2</sup> have obtained the last three of these compounds, that is,  $\text{SiF}_2\text{Cl}_2$ ,  $\text{SiF}_3\text{Cl}$  and  $\text{SiF}_4$  by the indirect method of the more difficult explosive reaction of chlorine on  $\text{Si}_2\text{F}_6$  at elevated temperatures. However, our method permits ready control of the product obtained, that is, the fluorination can be made progressive by condensing the higher boiling compounds, for instance the  $\text{SiFCl}_3$ , and letting them run back into the generator. By this reaction we have prepared over 200 liters of  $\text{SiFCl}_3$ , 100 liters of  $\text{SiF}_2\text{Cl}_2$  and 75 liters of  $\text{SiF}_3\text{Cl}$ . As would be expected, much larger quantities of the least fluorinated compound were obtained. The boiling points of  $\text{SiF}_2\text{Cl}_2$  and  $\text{SiF}_3\text{Cl}$  observed by us agree closely with the values obtained by Schumb and Gamble.

They found a very small amount of a higher boiling material of which they say, "Because of the difficulty of purifying the small quantity of this higher boiling residue, its composition was not definitely established but it is probable that a little of the third fluorochloride,  $\text{SiFCl}_3$ , was contained therein." We have definitely prepared and purified large quantities of  $\text{SiFCl}_3$ , boiling point  $12.2^\circ$ , and established its composition.

The critical constants of these three gases have also been determined

For  $\text{SiFCl}_3$ ,  $T_c = 165.17 \pm 0.05^\circ$  and  $P_c = 34.34$  atm.

For  $\text{SiF}_2\text{Cl}_2$ ,  $T_c = 95.75 \pm 0.05^\circ$  and  $P_c = 34.57$  atm.

For  $\text{SiF}_3\text{Cl}$ ,  $T_c = 34.50 \pm 0.10^\circ$  and  $P_c = 34.42$  atm.

All these gases are completely hydrolyzed by water, yielding hydrated silica, fluosilicic and hydrochloric acids. We have found them somewhat nauseating and very irritating when inhaled. The complete data and physical and chemical properties will be reported in a subsequent article.

<sup>2</sup> Schumb and Gamble, THIS JOURNAL, 54, 3943 (1932).

MORLEY CHEMICAL LABORATORY  
WESTERN RESERVE UNIVERSITY  
CLEVELAND, OHIO

HAROLD SIMMONS BOOTH  
CARL F. SWINEHART

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## A NEW GENERAL METHOD FOR FLUORINATION OF INORGANIC HALIDES

Sir:

The fluorination of silicon chloride by antimony trifluoride with a catalyst to yield fluorochlorides and fluorides as described in the previous