

halides and have prepared the compounds SiFCl_3 , SiF_2Cl_2 , SiF_3Cl 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 Gamble² have obtained the last three of these compounds, that is, SiF_2Cl_2 , SiF_3Cl and SiF_4 by the indirect method of the more difficult explosive reaction of chlorine on Si_2F_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 SiFCl_3 , and letting them run back into the generator. By this reaction we have prepared over 200 liters of SiFCl_3 , 100 liters of SiF_2Cl_2 and 75 liters of SiF_3Cl . As would be expected, much larger quantities of the least fluorinated compound were obtained. The boiling points of SiF_2Cl_2 and SiF_3Cl 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, SiFCl_3 , was contained therein." We have definitely prepared and purified large quantities of SiFCl_3 , boiling point 12.2° , and established its composition.

The critical constants of these three gases have also been determined

For SiFCl_3 , $T_c = 165.17 \pm 0.05^\circ$ and $P_c = 34.34$ atm.

For SiF_2Cl_2 , $T_c = 95.75 \pm 0.05^\circ$ and $P_c = 34.57$ atm.

For SiF_3Cl , $T_c = 34.50 \pm 0.10^\circ$ 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.

² Schumb and Gamble, THIS JOURNAL, 54, 3943 (1932).

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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

note appears to be a general reaction which may be expected to proceed whenever both the fluoride and chloride (or bromide or iodide) are non-polar. With a polar fluoride it may proceed providing the mixed fluoro-halide is non-polar and volatile.

It seems further that whenever the heat of this reaction is high, or when the temperature is high, fluorination tends to go to completion but where the heat of reaction is low, or the temperature is kept down, intermediate fluorohalides are obtainable, and fluorination may be made progressive by condensing the least fluorinated compound back into the generator for further reaction. The latter is characteristic of the reaction with halides of Group IV. The reaction of SbF_3 with a catalyst on SiCl_4 is slower than on CCl_4 , on GeCl_4 slower than on SiCl_4 , and slow with SnCl_4 . Since both CCl_4 and SiCl_4 yield fluorochlorides and fluorides, the gases from GeCl_4 and SnCl_4 are probably likewise fluorochlorides and fluorides, especially since the reaction characteristics are precisely the same. Small amounts of gas are evolved with TiCl_4 , but this may be due to impurities. In these cases we have found it advisable to increase the speed of the reaction by warming the reaction flask gently; in others it is necessary to diminish the speed of the reaction by cooling. It is always advisable to use excess of the liquid halide (or an inert solvent) to absorb the heat of reaction, thus controlling its speed.

The reaction with PCl_3 or PBr_3 gives a smooth evolution of gases but the reaction with PCl_5 is violent. When SbF_3 is added to solid PCl_5 , reaction is delayed, begins slowly, gathers speed rapidly, and suddenly clouds of gases evolve, while the reaction mass liquefies. In solvents the violence of this reaction is diminished, and the gases evolved are phosphorus fluorochlorides with some PF_5 and PF_3 .

Non-polar oxychlorides also react with SbF_3 in the presence of a catalyst to yield gases. For instance, SeOCl_2 , SO_2Cl_2 , and even VOCl_3 when gently warmed, evolved gases. POCl_3 evolves gases immediately with SbF_3 without a catalyst.

Even non-polar thiohalides react. For example, PSCl_3 yields gases immediately with SbF_3 without a catalyst. SiHCl_3 yields fluorochlorides with SbF_3 and SbCl_5 , and probably SiBr_4 , Si_2Cl_6 , Si_3Cl_8 , SiSCl_2 , Si_2OCl_2 , BCl_3 , B_2Cl_4 , POCl , SOCl_2 , etc., will react similarly.

This is a simple, general method for preparing fluorohalides, and fluorides, many of which have been difficult to prepare heretofore. As far as we can find this is the first time in the forty years since Swarts [*Acad. Roy. de Belgique*, **24**, 309, 474 (1892)] discovered that SbF_3 and a catalyst would cause partial replacement of a halogen in an aliphatic halide that this reaction has been successfully applied to the preparation of inorganic fluorohalides and fluorides.

Investigations are now in progress in the Laboratory on all the applica-

tions of this reaction to all the non-polar inorganic halides and will be reported as rapidly as possible.

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THE ACTION OF NITROUS ACID ON PHENYL- α -(β -NAPHTHOL)-AMINO-METHANE. A CORRECTION

Sir:

In a recent paper [Ray, THIS JOURNAL, **54**, 295 (1932)] it was reported that phenyl- α -(β -naphthol)-aminomethane on treatment with nitrous acid gave an aliphatic diazo compound. Subsequent work, the details of which are soon to appear, has shown that the reaction is much more complex than was originally supposed. The compound in question is not an aliphatic diazo compound but an N-nitroso derivative of a heterocyclic compound.

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THE ACTION OF SODIUM IN LIQUID AMMONIA ON DERIVATIVES OF OPTICALLY ACTIVE TRIARYLMETHANES

Sir:

In view of a recent publication by Ashley and Shriner [THIS JOURNAL, **54**, 4410 (1932)] on an attempt to prepare an optically active salt of the type $\left[\begin{array}{c} R_2 \\ R_1 : \overset{\ominus}{C} : R_3 \end{array} \right] Na^+$ it seems advisable to place on record certain experiments which have been conducted in this Laboratory, and which were reported to the Society at its meeting in New Orleans, March 28–April 1, 1932.

In recent publications from this Laboratory a method has been described for preparing certain derivatives of optically active triarylmethanes. Investigations of such optically active compounds led us to believe that a study of their behavior toward sodium in liquid ammonia should be of special interest. For this purpose 12-phenyl-12- β -benzoxanthenthio-glycolic acid (I), m. p., 187–188°, has been prepared. The pure *levo* modification of this compound (m. p. 184–185°) prepared by repeated crystallization of its brucine salt gave $[\alpha]_D^{20}$ in acetone -48.5° . This material in liquid ammonia was treated with metallic sodium in the absence of oxygen. The deep orange-brown sodium triarylmethyl so formed was allowed to react with a slight excess

