Tetrahedron, 1966, Vol. 22, pp. 1747 to 1754. Pergamon Press Ltd. Printed in Northern Ireland

# ARSENIC TRIFLUORIDE, AS A FLUORINATING AGENT—I*

## FLUORINATION OF SATURATED HALOALKANES

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(*Received 9 August* 1965; *in revised form 22 December* 1965)

**Abstract**—The reactions of a number of saturated aliphatic halogen compounds have been studied with arsenic trifluoride using various catalysts. The fluorination can be done in laboratory glassware with a minimum of etching. The advantages of $AsF_3$ are its liquid state and its ready miscibility with many organic liquids, allowing a wide range of reaction conditions.

At atmospheric pressure one or two fluorine atoms could be introduced selectively into a $CCl_3$ group of polyhaloalkanes. Reaction of mono- and dichloroalkanes resulted in tar formation. The degree of fluorination of selected halogenated groups was established and the influences of various reaction conditions (time, temperature, catalyst and concentration) were determined.

## INTRODUCTION

A NUMBER of fluorinating agents have been described in the chemical literature. For laboratory organic chemists, however, each has some limitations. The high reactivity of elemental fluorine, etching of laboratory glassware by hydrogen fluoride or the high pressures required with sulfur tetrafluoride might discourage chemists from work in fluorine chemistry.

The most frequently used laboratory fluorinating agent is $SbF_3$, which is used with small amounts of a pentavalent antimony halide as catalyst. The reaction was discovered by Swartz[1] in 1895 and its use in halogen exchange reactions has expanded rapidly,[2] since glass equipment can be used with a minimum of etching. It is useful especially in the fluorination of highly halogenated compounds. The main disadvantages are its insolubility in most organic compounds, resulting in heterogeneous reactions, and the fact that a minimum 100–120° reaction temperature is required.

The nearest neighbor of antimony in the periodic system is arsenic. In contrast to $SbF_3$, however, arsenic trifluoride has not been used often in the laboratory. The first published report of its use as a fluorinating agent was made in 1875, in which it was shown that $PF_3$ could be prepared from $PBr_3$.[3] Meslans[4] described its first application in organic chemistry seventeen years later in the preparation of acetylfluoride from acetylchloride. Since then only a few scattered reports of arsenic trifluoride as a

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* A general description of this work was presented at the *XIXth International Congress of Pure and Applied Chemistry* London (1963).

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[1] F. Swartz, *Bull. Acad. Roy. Belg.* (3) **24**, 474 (1892).

[2] Because of the large amount of work, it is impossible to give detailed refs. The reader is directed to such Monographs as A. M. Lovelace, D. A. Rausch and W. Postelnek, *Aliphatic Fluorine Compounds* ACS Monograph No. 138. Reinhold, New York (1958) and M. Hudlicky, *Chemistry of Organic Fluorine Compounds*. MacMillan New York (1962).

[3] I. R. McIvor, Ref. R. Gerstl, *Ber. Dtsch. Chem. Ges.* **8**, 1466 (1875).

[4] M. Meslans, *C. R. Acad. Sci. Paris* **114**, 1020 (1982).

fluorinating agent for organic compounds have appeared in the literature. These are generally special applications, such as the preparation of $CF_2Cl_2$ and $CF_3Cl$ from phosgene at high temperature and pressure;[5] the preparation of $CF_4$ and $C_2F_4$ from carbon at 1100° or in an electric arc,[6] or the preparation of fluorophosphoranes from chlorophosphines.[7]

## RESULTS AND DISCUSSION

Arsenic trifluoride is a heavy liquid, boiling at 58°. It is miscible with many organic solvents and has moderate solubility in haloalkanes. It can be prepared from $As_2O_3$ and HF,[8] $CaF_2$–$H_2SO_4$[9] or $FSO_3H$.[10] The last two methods can be performed in common glass equipment with surprisingly little etching, if a small (2–3%) excess of $As_2O_3$ is used. The preparation from $As_2O_3$ and $FSO_3H$

$$2As_2O_3 + 6FSO_3H \rightarrow 2AsF_3 + 3H_2SO_4 + SO_3 + As_2O(SO_4)_2$$

was modified according to the following reaction equation, to utilize all the arsenic values

$$As_2O_3 + 6FSO_3H + 3H_2O{\cdot}H_2SO_4 \rightarrow 2AsF_3 + 6H_2SO_4$$

The conversion of $AsCl_3$ to $AsF_3$ by anhydrous HF was also achieved at slightly above room temperature. Its preparation from $As_2O_3$ and $SiF_4$ at higher temperature was reported earlier.[11]

The fluorination of various halogenated methanes, ethanes, propanes and cyclobutane was investigated in solution. Because of the limited solubility of $AsF_3$ in haloalkanes, the reaction mixture was heterogeneous at the beginning, but the inorganic layer slowly disappeared as the reaction proceeded. This was caused by the formation of $AsCl_3$, which is miscible with most of the haloalkanes. Table 1 lists those compounds, the fluorination of which was investigated in solution at atmospheric pressure under gentle reflux. In all reactions $SbCl_5$ was used as a catalyst. Based on these results the following generalizations can be made.

Compounds containing monochloro substitution (primary, secondary and tertiary) gave only tar or dehydrohalogenated if possible, probably promoted by the strong Lewis acid properties of the antimony pentachloride catalyst. When more than one chlorine atom was present on the same carbon atom, such as in the case of $—CHCl_2$ or $>CCl_2$ groups, less, if any, decomposition was observed, but fluorination occurred only in poor yield. The $—CCl_3$ group is the easiest to fluorinate. Depending on the starting material, total as well as partial fluorination could be accomplished. The reactivity of these groups in this fluorination can be written in the following order:

$$CCl_3 > CCl_2 > CHCl_2 \gg\ >CHCl > CH_2Cl$$

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[5] E. L. Muetterties, U.S. Patent 2,757,214 (1956); *Chem. Abstr.* **51**, 2016 (1957).

[6] M. W. Farlow, and E. L. Meutterties, U. S. Patent 2,709,186 (1955); *Chem. Abstr.* **50**, 6499 (1956).

[7] R. Schmutzler, *Inorg. Chem.* **3**, 410 (1964).

[8] G. Breuer, *Handbuch der Präparativen Anorgansichen Chemie* Vol. I; p. 189. Ferdinand Enke Verlag, Stuttgart (1960).

[9] J. C. Bailar, Jr, *Inorganic Synthesis* Vol. IV; p. 150. McGraw-Hill (1953).

[10] A. Engelbrecht, A. Aignesberger and E. Hayek, *Mh. Chem.* **86**, 470 (1953).

[11] K. O. Christe and A. E. Pavlath, *J. Chem. Soc.* 827 (1965).

TABLE 1. FLUORINATION IN BATCH REACTION AT 58°, 2 HR

| Reactant | $AsF_3$ mol/mol of reactant | $SbCl_5$ (ml) | Yield (%) | Product |
|---|---|---|---|---|
| $CH_2Cl_2$ | 1·0 | 3·0 | — | [a] |
| $CHCl_3$ | 1·2 | 2·5 | 22 | $CHFCl_2$ |
|  | 1·2 | 4·0 | 35 | $CHFCl_2$ |
| $CCl_4$ | 1·0 | 3·0 | 70 | $CCl_3F$ (64%), $CCl_2F_2$ (36%) |
| $CHBr_3$ | 1·0 | 3·0 | — | dec[b] |
| $CH_3I$, $CH_2I_2$, $CHI_3$ | 1·0 | 3·0 | — | dec[b] |
| $CHCl_2$—$CH_2Cl$ | 1·0 | 3·0 | 1·2 | $CHClF$—$CH_2Cl$ |
| $CHCl_2$—$CHCl_2$ | 1·33 | 2·0 | 9·9 | $CHClF$—$CHCl_2$ |
| $CCl_3$—$CH_2Cl$ | 0·66 | 2·0 | 88 | $CCl_2F$—$CH_2Cl$ |
|  | 2·0 | 8·0 | 75 | $CClF_2$—$CH_2Cl$ |
| $CCl_3$—$CH_3$ |  | see Table 3 |  |  |
| $CCl_3$—$CHCl_2$ |  | see Fig. 1 |  |  |
| $CCl_3$—$CCl_3$ | 2·0 | 6·0 | 35 | $CCl_2F$—$CCl_3$ |
|  |  |  | 5 | $CCl_2F$—$CCl_2F$ |
| $CFCl_2$—$CHCl_2$ | 2·0 | 8·0 | 20 | $CF_2Cl$—$CHCl_2$ |
| $CF_2Cl$—$CH_2Cl$ | 1·0 | 3·0 | — | [a] |
| $CF_2Cl$—$CH_3$ | [c] |  | 85 | $CF_3$—$CH_3$ |
| $CH_3$—$CH_2Br$ | 0·6 | 2·0 | 4 | $CH_2$=$CH_2$ |
| $CF_2Br$—$CH_2Br$ | 1·0 | 3·0[d] | 45 | $CF_3$—$CH_2Br$ |
| $CCl_2Br$—$CH_2Br$ | 2·0 | 12·0 | 84 | $CCl_2$=$CHBr$ |
| n- and i-$C_3H_7Cl$ | 0·6 | 2·0 | 5 | $CH_3$—$CH$=$CH_2$ |
| $CCl_3$—$CH_2$—$CH_3$ | 1·5 | 6·0 | 2·5 | $CCl_2F$—$CH_2$—$CH_3$ |
| $CCl_3$—$CHCl$—$CH_3$ | 1·5 | 6·0 | 5·2 | $CCl_2F$—$CHCl$—$CH_3$[e] |
| $CCl_3$—$CCl_2$—$CHCl_2$ | 2·8 | 8·0 | 92 | $CCl_2F$—$CCl_2$—$CHCl_2$ |
| $CCl_3$—$CHCl$—$CCl_3$ |  | see Fig. 3, Table 4 |  |  |
| $CCl_3$—$CCl_2$—$CCl_3$ | 2·4 | 8·0 | 22 | $C_3Cl_6F_2$[f] |
| $CF_2$—$CCl_2$<br>\|   \|<br>$CF_2$—$CCl_2$ | 1·2 | 4·0 | 32 | $CF_2$—$CFCl$<br>\|   \|<br>$CF_2$—$CCl_2$ |
| $(CH_3)_3CCl$ | 0·6 | 2·0 | 12 | $(CH_3)_2C$=$CH_2$ |
| $CH_3$—$CH_2$—$CHCl$—$CH_3$ | 0·6 | 2·0 | 6 | $CH_3$—$CH$=$CH$—$CH_3$ |

[a] Starting material was recovered with no sign of dec.

[b] No fluorinated product could be detected. Most of the starting material decomposed. No attempts were made to identifiy the dec products.

[c] This run was made in a continuous reactor described in the experimental.

[d] During the reaction 0·05 mole $Cl_2$ was passed into the mixture in slow continuous flow. Without $Cl_2$, no fluorination was observed.

[e] The same reaction in an autoclave at 220° gave mostly $CClF_2$—$CCl_2$—$CHCl_2$ with $C_3HCl_4F_3$ and $C_3HCl_3F_4$ isomers, which were not separated and identified.

[f] No $C_3Cl_8$ was recovered. Mostly $C_2Cl_4$, $CCl_4$ and $CCl_3F$ were obtained. The $C_3Cl_6F_2$ was a mixture of isomers, the composition of which could not be determined.

When two or more kinds of groups are present in the same molecule, fluorination will take place at the most reactive site. Other groups show no sign of fluorination before the more reactive group is completely fluorinated. When two of the same types of groups are available for fluorination in the same compound, the reaction proceeds in parallel on both groups. The presence of fluorine decreases the reactivity of the group, but is still more reactive than the next group in the above order. Compounds containing bromide or iodine atoms, however, can result in decomposition during

TABLE 2. FLUORINATION OF $CCl_4$ USING DIFFERENT CATALYSTS
(1·0 mole $AsF_3$, 0·02 mole catalyst, 58°, 2 hr)

| Catalyst | Conversion (%) | Product |
|---|---|---|
| — | — | |
| $SbCl_5$ | 75 | $CFCl_3$ (64%), $CF_2Cl_2$ (36%) |
| $NbCl_5$ | 75 | $CFCl_3$ |
| $TaCl_5$ | 52 | $CFCl_3$ |
| $AsCl_4^+AsF_6$[b] | 41 | $CFCl_3$ (85%), $CF_2Cl_2$ (15%) |

[a] Without any catalyst no fluorination was observed after 24 hr.

[b] This catalyst was prepared in situ according to Kolditz's method[12] by bubbling the necessary amount of $Cl_2$ into the $AsF_3$. A small amount of water was added to catalyze the formation of $AsCl_4^+AsF_6^-$ as described in the lit.[13]

fluorination. While $CF_2Br—CH_2Br$ gave $CF_3—CH_2Br$ readily, the reaction of $CCl_2Br—CH_2Br$ with $AsF_3$ resulted in the formation of $CCl_2{=}CHBr$ through dehydrobromination. In the case of $CH_3I$, $CH_2I_2$ and $CHI_3$, slow decomposition was observed without fluorination.

In Meslans' experiment, $AsF_3$ was used without any catalyst for the fluorination of acetyl chloride. In Table 1, however, all compounds required a catalyst; otherwise no fluorination was observed. The best results were obtained using pentavalent antimony halides such as $SbCl_5$ or $SbF_5$, but other pentavalent halides from the fifth column of the periodic system also catalyzed fluorination, although these were less effective. The quantity of the catalyst varied between 2–5 mole percent calculated on the amount of $AsF_3$. Just as in the Swartz reaction, here also the addition of small amounts of $Cl_2$ activated $AsF_3$ towards fluorination.[12] Because of their weaker Lewis acid character, these catalysts can be useful, where $SbCl_5$ might cause dehydrohalogenation during the fluorination. Table 2 gives a comparison of the catalytic effects of these other halides on the fluorination of $CCl_4$.

The mechanism of this reaction is not clear at this time. Evaporation of solutions of the various catalysts in arsenic trifluoride left solid residues containing arsenic values in addition to the catalysts. The structure of the solids was not determined, but a strong interaction between $AsF_3$ and the catalyst is indicated. The fluorination

TABLE 3. FLUORINATION OF $CCl_3—CH_3$ IN BATCH[a] REACTION AT 45°
(5·0 ml $SbCl_5$, 2 hr)

| Ratio | | Products | | |
|---|---|---|---|---|
| $AsF_3$–$C_2H_3Cl_3$ | Conversion (%) | $CF_3CH_3$ | $CF_2Cl—CH_3$ | $CFCl_2—CH_3$ |
| 1·5 | 52 | 16 | 62 | 22 |
| 1·8 | 58 | 27 | 58 | 15 |
| 2·5 | 65 | 40 | 48 | 12 |
| 3·0 | 68 | 54 | 38 | 8 |

[a] For continuous reaction see experimental.

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[12] The reaction between $AsF_3$ and $Cl_2$ was reported by Kolditz to give $AsCl_4^+AsF_6^-$, the ionic dimer of $AsF_3Cl_2$. However, he described it as a non-reactive compound with respect to $PCl_3$ and $CCl_4$. L. Kolditz, *Z. Anorg. Chem.* **280**, 313 (1955).

[13] H. M. Dess, R. W. Parry and G. L. Vidale, *J. Amer. Chem. Soc.* **78**, 5730 (1956).

probably occurs through these species regenerated by arsenic trifluoride. Further studies are very much needed on the mechanism of the fluorine-chlorine exchange reactions. Arsenic trifluoride would seem to be a good medium for these investigations, since the reaction could be carried out in homogeneous solution, in glassware at atmospheric pressure.

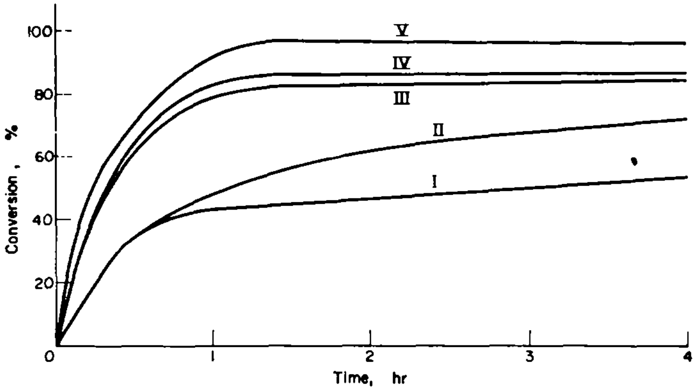

FIG. 1. $3CCl_3\text{—}CHCl_2 + AsF_3 \xrightarrow{Sb^{V+}} 3CCl_2F\text{—}CHCl_2 + AsCl_3$

I 5% excess of $AsF_3$, 60°, 2·5 mol% of $SbCl_5$
II 100% excess of $AsF_3$, 20°, 5·0 mol% of $SbCl_5$
III 5% excess of $AsF_3$, 60°, 5·0 mol% of $SbCl_5$
IV 50% excess of $AsF_3$, 60°, 5·0 mol% of $SbCl_5$
V 100% excess of $AsF_3$, 60°, 5·0 mol% of $SbCl_5$

The fluorination of haloalkanes with $AsF_3$ seems to proceed rapidly in most cases, if the reaction is possible at all. Figure 1 shows that fluorination within a certain period reaches a level beyond which the reaction will not go even with a longer reaction time. This level is dependent on the amount of $AsF_3$ and catalyst in the starting reaction mixture. Additional amounts of $AsF_3$ and catalyst, after it had reached the level, did not increase the conversion. After the reaction starts the mixture slowly becomes colored. Probably tar formation inhibits further reaction. This assumption is supported by the fluorination of methylchloroform, where for the maximum yield and conversion special reaction conditions had to be used to assure contact between the fresh $AsF_3$-$SbCl_5$ mixture and $CH_3\text{—}CCl_3$. Similarly, better results were obtained if $SbCl_5$ was added slowly to the $CH_3CCl_3$-$AsF_3$ mixture. When one of the milder catalysts was used, less color formation and better yields were obtained, but the conversion was lower.

The number of fluorine atoms introduced into a molecule depend on the positions of the halogen atoms to be replaced and the amount of $AsF_3$ used. The relative ease of replacement of chlorine in different groups was discussed before. The fluorination of $CCl_3CHCl_2$ gave 78% conversion to $CCl_2FCHCl_2$ using stoichiometric amounts of $AsF_3$. A second fluorine could be introduced on the same carbon atom, but even the use of six times the stoichiometric amount of $AsF_3$ gave only a 40% conversion to $CF_2Cl\text{—}CHCl_2$ (Fig. 2). The fluorination of $CH_3CCl_3$ gave mostly $CF_2Cl\text{—}CH_3$ and $CF_3\text{—}CH_3$, while $CCl_3\text{—}CH_2Cl$ gave only the monofluoro derivative $CFCl_2\text{—}CH_2Cl$. Table 3 shows the composition of the fluorinated product obtained from $CCl_3CH_3$.

In the fluorination of $CCl_3\text{—}CHCl\text{—}CCl_3$ relatively more $AsF_3$ had to be used to

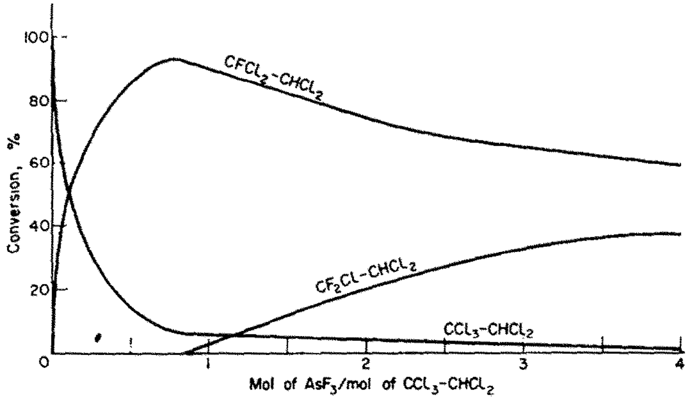

FIG. 2. Fluorination of $CCl_3$—$CHCl_2$.

introduce 1, 2, 3 and 4 fluorine atoms into two equivalent trichloromethyl groups.[14] Figure 3 gives the conversion *vs.* amount of $AsF_3$, while Table 4 gives the isomer ratio. The fluorination of the isomeric heptachloropropane, gave only $CCl_2F$—$CCl_2$—$CCl_2H$ even with a large excess of $AsF_3$.

Fluorination in solution at atmospheric pressure is limited by the 58° b.p. of $AsF_3$. This is a disadvantage compared to $SbF_3$. In some reactions $SbF_3$ gives better yields, but they are carried out generally at higher temperature. For example, $CHCl_2$—$CHCl_2$ gave $CHClF$—$CHCl_2$ in a yield of only 9·9% using $AsF_3$, while at 130° 83% was obtained with $SbF_3$.[15] Unfortunately, there are not enough data available on the fluorination with $SbF_3$ at lower temperature for comparison. A few runs were made

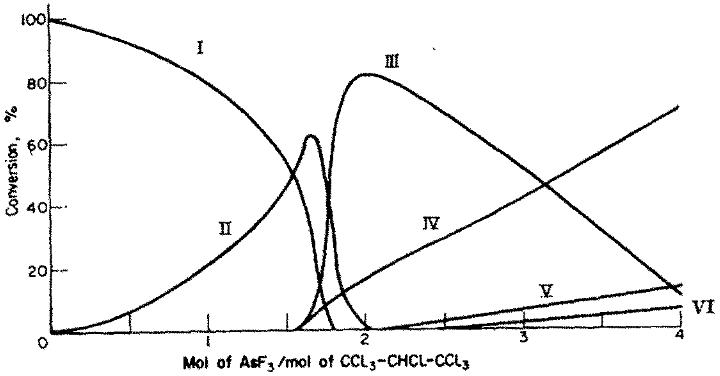

FIG. 3. Fluorination of $CCl_3$—$CHCl$—$CCl_3$.
I $C_3HCl_7$
II $C_3HCl_6F$
III $C_3HCl_5F_2$
IV $C_3HCl_4F_3$
V $CF_3$—$CCl$=$CCl_2$
VI $C_3HCl_3F_4$

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[14] The formation of $CF_3$—$CCl$=$CCl_2$ was observed as a by-product. Through dehydrohalogenation $CCl_3$—$CCl$=$CCl_2$ formed which can be rapidly fluorinated with $AsF_3$. This is part of a separate work, which is to be published next in the series.

[15] S. Kolesnikov and M. G. Avetyan, *Izvest. Akad. Nauk. S.S.S.R., Atdel. Khim. Nauk.* 331 (1959); *Chem. Abstr.* **53**, 19942 (1959).

with $AsF_3$–$SbCl_5$ at higher temperature in an autoclave under autogeneous pressure using $CCl_3$—$CCl_2$—$CCl_2H$ as starting material. Mono-, di-, tri- and tetrafluoro derivatives were obtained with some decomposition, while at 58° only $C_3FCl_6H$ formed.

TABLE 4. STRUCTURE AND ISOMER DISTRIBUTION IN FLUORINATED $CCl_3CHClCCl_3$

| Formula | Structure | Distribution |
|---|---|---|
| $C_3HCl_6F$ | $CCl_2F$—CHCl—$CCl_3$ | 100% |
| $C_3HCl_5F_2$ | $CCl_2F$—CHCl—$CCl_2F$ | 65% |
| | $CClF_2$—CHCl—$CCl_3$ | 35% |
| $C_3HCl_4F_3$ | $CClF_2$—CHCl—$CCl_2F$ | 100% |
| $C_3HCl_3F_4$ | $CF_2Cl$—CHCl—$CF_2Cl$ | 72% |
| | $CF_3$—CHCl—$CCl_2F$ | 28% |

The use of $AsF_3$ was also studied in the vapor phase at 100–270°. No catalyst was used. The fluorination of $CCl_4$ and $CHCl_3$ was observed under these conditions but yields and conversions were less than in solution at lower temperatures in the presence of a catalyst (Table 5).

TABLE 5. VAPOR PHASE FLUORINATION WITHOUT CATALYST

| Compound | Temp. | Conversion % | Product |
|---|---|---|---|
| $CCl_4$ | 100° | — | — |
| | 180° | 2 | $CFCl_3$ |
| | 240° | 8 | $CFCl_3$ |
| | 270° | 20 | $CFCl_3$ |
| $CHCl_3$ | 200° | — | — |
| | 270° | 5 | $CHFCl_2$ |

## EXPERIMENTAL

All halogenated hydrocarbons were commercially available products except $CCl_2Br$—$CH_2Br$ and $CF_2Br$—$CH_2Br$, which were prepared from the corresponding olefins by addition of $Br_2$.

$AsF_3$, which is also available commercially from Ozark-Mahoning Company (310 W. 6th St., Tulsa, Oklahoma), was prepared in large quantities from $As_2O_3$, $CaF_2$ and cc $H_2SO_4$ according to the method described in the literature.[9] Commercial acid grade fluorspar was used. In order to prevent the etching of the glass apparatus, 2–3% of excess $As_2O_3$ was used. The yield based on $As_2O_3$ was over 92% after a single plate fractionation. The thermodynamic properties of $AsF_3$ were determined and found to be in good agreement with values reported by Russell.[16] The b.p. of $AsF_3$ is given erroneously in many places as 63°. The correct value is 58°.

*Caution.* In $AsF_3$ it is the F, which is the more toxic and not the As. A dose of $AsF_3$ which contains lethal amount of F has only 12–15% of the lethal dose for As. The toxicity of $AsF_3$, therefore, is similar to that of other inorganic fluorinating agents. It can easily hydrolyze; therefore, it is a vesicant just as HF and $SbF_3$. Care has to be taken to avoid breathing and contact with skin. During our research with $AsF_3$ the As level was checked regularly in each person involved in intensive work. In a period of 2 years, no health hazard was detected.

### *Arsenic trifluoride from* $As_2O_3$ *and* $FSO_3H$

A mixture of $As_2O_3$ (49·5 g; 0·25 mole) and $FSO_3H$ (150 g) was heated to 120° under stirring, and $H_2SO_4 \cdot H_2O$ (93 g; 0·8 mole) was added dropwise to the mixture in 30 min. $AsF_3$ started to distill almost immediately. The reaction mixture was heated for 1 hr after the addition, and the product was redistilled, yield 55·5 g $AsF_3$ (83·2%).

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[16] H. Russell, Jr. R. E. Rundle and D. M. Yost, *J. Amer. Chem. Soc.* **63**, 2826 (1941).

*Arsenic trifluoride from* $AsCl_3$ *and* HF

Arsenic trichloride (181·5 g; 1 mole) and anhydrous HF (200 g; 10 moles) were placed in a stainless steel vessel (vol 1 l.), equipped with reflux condenser and press. gauge. The vessel was heated in 2 hr to 90°, where it was kept for 4 hr. The press. was not allowed to go over 150 psi, using a relief valve at the top of the reflux condenser. After cooling it to room temp the reaction mixture was fractionated from the vessel. After redistillation in glass equipment from 25 ml of cc $H_2SO_4$ (25 ml) $AsF_3$ (94 g) was obtained (71·2%). The unreacted $AsCl_3$ was recovered almost quantitatively.

*Flourination with* $AsF_3$

a. *In batch.* The necessary amount of $AsF_3$ was mixed with the catalyst and placed into a 3-neck flask equipped with stirrer, reflux condenser and thermometer. The organic Cl-compound was than added and the mixture was warmed quickly to gentle reflux by a water bath. In general the reflux was continued for 4 hr. The mixture was cooled to room temp and poured into warm (35–45°) dil HCl. The organic layer was washed twice with 1% NaOH aq and water. After drying on $CaCl_2$ the product was analyzed by GLPC to determine its composition. If the conversion was very low, the fluorinated product was separated on a preparative gas chromatograph; otherwise it was fractionated on a Podbielniak spinning band column.

When the products had a b.p. lower than room temp, the reflux condenser was connected to a cold trap kept at −78°. The contents of the cold trap were evaporated through a caustic scrubber and recondensed. The analysis was the same as above.

The results are tabulated in Tables 1 and 2. In the case of $CH_3$—$CCl_3$ the fluorination in batch was carried out in a slightly modified way in order to increase the conversion. The catalyst ($SbCl_5$) was dissolved in an equal volume of $AsF_3$ and added to the stirred mixture of $AsF_3$ and $CH_3$—$CCl_3$ at 45°, dropwise in 2 hr. Results are summarized in Table 3.

All compounds obtained in these reactions were prepared and characterized by others previously. Identification was accomplished by elemental analysis and comparison of IR and NMR spectra to an authenic sample of each compound.

b. *In continuous reactor.* A vertical condenser (20 mm × 120 cm) filled with glass helices was used as the reactor. The temp was maintained at 45° by circulating warm water in the jacket of the condenser. This reactor was used for the fluorination of $CH_3CCl_3$. Both components were added at the top of the reactor and the spent reaction mixture, mostly inorganic, was collected at the bottom. The $CH_3CCl_3$ was introduced at a lower level (approximately 20 cm lower) than the $AsF_3$–$SbCl_5$ mixture in order to achieve maximum fluorination. The partially fluorinated products ($CFCl_2$—$CH_3$ and $CF_2Cl$—$CH_3$) were in the vapor phase at this temp and made counter current contact with the fresh $AsF_3$–$SbCl_5$ mixture. In an average run, $CCl_3$—$CH_3$ (133·5 g; 1 mole) and $AsF_3$ (150 ml; 3 moles) with $SbCl_5$ (10 ml) were introduced in 3 hr. A yield of 65–73% was obtained in 14 separate runs. The product was collected and scrubbed in the same way as described previously. Less than 2% of $CF_2Cl$—$CH_3$ was present. The crude product before scrubbing contained some $SiF_4$, the result of slight etching of the equipment.

The spent reaction mixture was worked up as described under batch reaction, but only unreacted starting material containing 3·5% $CFCl_2$—$CH_3$ was recovered.

Various reaction times were investigated from 40 min to 3 hr. With the shortest reaction time a mixture was obtained (59% $CF_3CH_3$, 41% $CF_2ClCH_3$). In the spent reaction mixture 7·1% $CFCl_2$—$CH_3$ was detected.

The same equipment was used for the fluorination of $CF_2Cl$—$CH_3$. This latter compound was introduced at the bottom of the reactor in counter current (1·0 mole/hr) using the same amount of $AsF_3$–$SbCl_5$, reaction time and procedure described above. An 85% conversion to $CF_3CH_3$ was obtained.

c. *Fluorination in vapor phase.* A vertical quartz tube (20 mm × 60 cm) was filled with quartz granules and a 30 cm section was heated with an electric furnace. $AsF_3$ and the halomethane to be fluorinated were added separately and dropwise from the top of the reactor at equal rates (0·5 mole/hr). The top of the reactor was connected to a cold trap. At the bottom the reaction mixture was collected in a flask cooled with ice. No product was collected in the cold trap. The reaction mixture was worked up as before. Results are shown in Table 5.

*Acknowledgement*—The authors would like to thank Prof. C. Sederholm (University of California, Berkeley) for the measurement and interpretation of the NMR spectra.