mation or *are at least considerably retarded* after the CH_2Cl group has been "stabilized" by the presence of the two fluorine atoms on the adjacent carbon. The use of mercuric[3] fluoride supplied the needed demonstration. This salt fluorinates C_2H_5Cl easily but affects $CH_2ClCHClF$ very little, and CH_2ClCHF_2 not at all. Similarly, it reacts quantitatively with C_2H_5Br, but not at all with CH_2BrCHF_2; it reacts violently with C_2H_5I but to affect CH_2ICHF_2, it must be heated for a long time at 160°, and yields only some 60% of CH_2FCHF_2. It cannot be held that mercuric fluoride causes fluorination to proceed along different lines, as it reacts with $CHBr_2CHBr_2$ to yield successively $CHBr_2CHBrF \longrightarrow CHBr_2CHF_2$ (where the reaction stops when using SbF_3), then $CHBrFCHF_2 \longrightarrow CHF_2CHF_2$ while its reaction with $CH_2BrCHBr_2$ yields successively $CH_2BrCHBrF$ and CH_2BrCHF_2, where the reaction stops just as it does with antimony fluoride.

The fluorination of CH_3CCl_3 gives successively $CH_3CCl_2F \longrightarrow CH_3CClF_2 \longrightarrow CH_3CF_3$. There is one other example of fluorinating directly to a CF_3 group, and that is $C_6H_5CCl_3 \longrightarrow C_6H_5CF_3$. In both cases, the passage from the $CClF_2$ stage to the CF_3 stage is rapid, an indication that the last chlorine had not been rendered inert by the two fluorine atoms. It should be noted that in both cases there is no halogen atom on the adjacent carbon.

The "stabilization" hypothesis is in good agreement with experimental evidence derived from the interaction of fluorochlorides and zinc in alcohol. From CCl_2FCCl_3, CCl_2FCCl_2F, $CHCl_2CCl_2F$, $CH_2ClCHClF$, $CHCl_2CHClF$ and CH_2ClCCl_2F, it is extremely easy quantitatively to obtain $CClF{=}CCl_2$, $CClF{=}CClF$, $CHCl{=}CClF$, $CH_2{=}CHF$, $CHCl{=}CHF$ and $CH_2{=}CClF$, respectively. It is, however, quite difficult to obtain $CClF{=}CF_2$, $CH_2{=}CHF$, $CHCl{=}CHF$ and $CH_2{=}CF_2$, from CCl_2FCClF_2, CH_2ClCHF_2, $CHCl_2CHF_2$ and $CH_2ClCClF_2$, respectively, and the yields are not good. It is almost impossible to obtain $CF_2{=}CF_2$ from CF_2ClCF_2Cl, and even at 1000 pounds pressure, the yield is only 30–35%.

Summing up the above observations the conclusion is reached that the presence of a lone fluorine atom in an aliphatic molecule produces an unstable compound, which shows a great tendency to liberate hydrogen fluoride. In contradistinction, compounds having a halogen atom on the carbon bearing the fluorine are more stable. The presence of two fluorine atoms on the same carbon is attended with (1) a very great increase of the strength of the carbon–fluorine bonds; (2) a strengthening of the linking of any third halogen atom that may be present on this same carbon; and (3) a great increase of the stability of any halogen atoms present on adjacent carbon atoms.

Summary

A general survey is presented of the effects that the presence of fluorine has on the stability and reactivity of aliphatic compounds.

THE MIDGLEY FOUNDATION
COLUMBUS, OHIO

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(3) See following paper, THIS JOURNAL, 58, 884 (1936).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AT THE OHIO STATE UNIVERSITY]

Mercuric Fluoride, a New Fluorinating Agent

BY ALBERT L. HENNE AND THOMAS MIDGLEY, JR.

Antimony, silver and mercurous fluorides have been the most important fluorinating agents used to replace halogens by fluorine in organic halides. Antimony fluoride is preferred for fluorinating compounds rich in halogen atoms, as for instance, carbon tetrachloride, chloroform or acetylene tetrabromide. It is a convenient reagent to obtain groups such as $—CX_2F$, $—CXF_2$, $—CHXF$ and $—CHF_2$, and, in rare cases, a $—CF_3$ group. Silver and mercurous fluorides have been used with some success on bromides or iodides containing not more than one halogen atom.

It is now found that mercuric fluoride can be substituted for silver or mercurous fluorides in every case where these salts have or could have been used; the yields are considerably increased, most reactions take place swiftly at room temperature, and side reactions are minimized, or absent. Moreover, mercuric fluoride can be used in many cases where antimony fluoride has been used heretofore, more specifically with polybromides or polyiodides; most polychlorides are so little affected that they can be used as solvents for the fluorination of a bromide or an iodide. Mercuric fluoride is superior to antimony fluoride for treating compounds which contain an appreciable number of hydrogen atoms: in such cases, antimony fluoride causes an important splitting of hydracids with consequent formation of ethylenic derivatives and frequently complete destruction of the organic molecule.

It has been shown before,[1] and it is now confirmed, that pure mercuric fluoride cannot be prepared by treating an oxide or salt of mercury with concentrated aqueous hydrofluoric acid. Moreover, it is found that the reaction between an anhydrous mercuric salt, such as the chloride, bromide, acetate or cyanide and anhydrous hydrogen fluoride is not a suitable method of preparation, even though some mercuric fluoride is formed. It is also found that the action of fluorine on mercurous fluoride is quite incomplete at temperatures lower than 200°; above 200°, this reaction becomes efficient but is quite impractical on a laboratory scale. Similarly, the action of fluorine on mercuric oxide or oxyfluoride is inefficient at low temperatures and impractical at high temperatures.

The method adopted consists in treating finely ground mercuric chloride with fluorine in a revolving copper reaction chamber, at room temperature. The average yield is about 75% and it can be increased by mechanical improvements: fluorine is quantitatively absorbed at the beginning of the reaction, and only in the last quarter of the reaction does any come through with the evolved chlorine. The formation of a considerable amount of bromine or iodine fluoride makes the use of mercuric bromide or mercuric iodide less desirable, though both salts yield pure mercuric fluoride.

Mercuric fluoride is a white, fluffy powder, extremely sensitive to moisture. Exposure to air causes a yellowish discoloration of the surface at once; this becomes progressively orange, pink and red, due to the formation of a coat of mercuric oxide. In the presence of a limited amount of water, the salt stays white, as the water is used to form white $HgF_2 \cdot 2H_2O$. If the salt is to be used for the fluorination of organic compounds, it must be kept rigorously dry, which is done by keeping it in a tightly stoppered copper container.

The reaction between mercuric fluoride and a substance such as ethyl or amyl bromide may be performed in glass, since fluorination occurs as soon as the mercuric fluoride comes in contact with the organic halide, and there is, consequently, little chance of its reacting with the glass. The reaction with a substance such as ethyl iodide or iodoform must be performed in a solvent as it is so rapid that an explosion may occur without this precaution; chloroform is a convenient solvent, but methylene chloride is preferred on account of its low boiling point. Benzene or other hydrocarbons may be used, but have shown no particular advantage. It is imperative not to use an alcohol, an ester or an ether as a solvent since the presence of these substances prevents fluorination. This adverse action remains unexplained; mercuric fluoride reacts quite visibly with alcohols and evolves a small quantity of the corresponding alkyl fluoride, but the mercuric fluoride becomes intensely yellow and the reaction quickly stops. With dry ethyl ether, there is no visible reaction, and the salt becomes only slightly yellowish; after recovery from the ether, the fluorine content of the salt is very slightly decreased. Whether ether attaches itself to the fluoride and thereby inhibits fluorination is not known.

When mercuric fluoride is to be used at temperatures up to 160°, a copper reaction container is quite satisfactory; at 180° corrosion of the copper takes place. Nickel equipment used from 160 to 240° did not show any damage. Soft solder can never be used, and silver solder stands up well at low temperatures only. Brazing or welding is satisfactory.

Mercuric fluoride has been allowed to react with a variety of compounds, and widely different results have been obtained depending on the type of reactant tried and the type of fluoride to be derived from the reaction. Some organic fluorides are decidedly unstable, as shown in the preceding paper,[2] and the failure to obtain them efficiently is frequently due to their instability rather than to the inability of generating them by means of mercuric fluoride on the appropriate reactant.

An aliphatic monobromide or monoiodide treated with mercuric fluoride gives the corresponding fluoride, and the reaction is almost quantitative for the lower members of the series; the yields become smaller as the length of the chain in-

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(1) Ruff and Bahlau, *Ber.*, **51**, 1752 (1918).

(2) THIS JOURNAL, **58**, 882 (1936).

creases, due to decomposition of the organic fluoride to hydrogen fluoride and the corresponding ethylenic hydrocarbon; this decomposition is so marked, with some ramified and secondary or tertiary compounds, that hardly any organic fluoride can be detected. Aliphatic monochlorides react considerably less than the bromides, but the trends of the reaction are substantially the same.

Polybromides and iodides have offered the most interesting results and led to the production of several new polyfluorides. These new compounds are described in the two papers following the present one, while the methods used to obtain better yields of the compounds already known are given in the experimental part. Ethylene bromide gives an excellent yield of CH_2BrCH_2F, but only 10% of the unstable ethylene fluoride; butadiene and butyl fluoride are formed as by-products in almost 10 and 30% yields, respectively. Ethylidene bromide gives a small yield of CH_3CHFBr and an excellent yield of ethylidene fluoride, CH_3CHF_2, as the fluorination proceeds rapidly to completion. Symmetrical tribromoethane gives easily $CH_2BrCHFBr$ or CH_2BrCHF_2, depending on the proportion of the reactants, and in each case the yield is about 80%; it is, however, impossible to fluorinate directly to CH_2FCHF_2, because the high temperature and pressure required cause decomposition of the intermediate mono- or di-fluoride; nevertheless, this trifluoride is conveniently obtained by first transforming CH_2BrCHF_2 into CH_2ICHF_2 by means of calcium iodide (60% yield): the latter undergoes fluorination with mercuric fluoride in the manner reported above. Bromoform and iodoform give good yields of fluoroform, together with the intermediate bromofluoro- or iodofluoro-methane compounds expected. Acetylene tetrabromide gives quantitatively $CHBr_2CHBrF$ or $CHBr_2CHF_2$; at high pressure and temperature, a small amount (10%) of $CHBrFCHF_2$ and 40–50% of acetylene tetrafluoride CHF_2CHF_2 are obtained.

Polychlorides give disappointing results, as illustrated by the reaction with $CH_2ClCHCl_2$. From this derivative, about 45% of $CH_2ClCHClF$ and hardly 10% of CH_2ClCHF_2 are formed.

Acyl chlorides give the corresponding acyl fluoride, in good yield.

Phenyl chloride, bromide, iodide, hexachlorobenzene and benzene hexachloride do not react with mercuric fluoride; alcohols, glycols, ethers, esters, acids, anhydrides or acetone react little, and the reaction stops promptly. Cyclohexyl bromide, *o*-dibromocyclohexane, β-dichloroethyl ether and dichlorodioxane react in the expected fashion but the resulting fluorides liberate hydrofluoric acid and yield the corresponding ethylenic hydrocarbon almost quantitatively.

Experimental Data

Mercuric Fluoride.—Fluorine (obtained from a generator similar to that described by Dennis and co-workers[3]) is led through flexible copper tubing into a horizontal cylindrical reaction container; this container, which is made entirely of copper and revolves around its axis at about twenty revolutions per minute, holds finely ground mercuric chloride and a few pieces of copper to prevent the formation of crusts. The long fluorine inlet (through the left bearing) extends clear to the right face of the container, and the short outlet for the chlorine is through the left bearing, adjacent to the inlet. The progress of the operation is followed by taking a sample of the salt, dissolving in nitric acid and testing qualitatively for chlorine. When this test becomes negative, the mercuric fluoride is removed and stored in a tightly stoppered copper container. Its analysis indicates 84.03% Hg and 15.93% F, compared with 84.07 and 15.93, calculated.

Ethyl Fluoride.—The apparatus consists of a copper reaction vessel equipped with a copper reflux condenser kept at 0° and an inlet for the mercuric fluoride. Ethyl bromide is placed in the vessel; mercuric fluoride is fed slowly through a wide piece of rubber hose pinched by two screw clamps about 5 cm. apart. During the addition of the salt, the reaction vessel is kept in an ice-bath. Ethyl fluoride is generated as soon as the reagents come in contact; it passes through the reflux condenser and is conveniently collected in a receiver cooled with solid carbon dioxide, while ethyl bromide is returned by the condenser to the reaction chamber. The mercuric fluoride is added at a rate that maintains a steady distillation of the ethyl fluoride. The reaction is quantitative, and the salt left in the vessel is pure mercuric bromide.

Aliphatic Monofluoride.—The preparation is similar to that of ethyl fluoride, except that for higher homologs heating on a water-bath is recommended after the mercuric fluoride has been fed into the bromide. Should one operate on an aliphatic iodide instead of bromide, it is recommended that the iodide be dissolved in three volumes of chloroform, or better, methylene chloride. The reaction yields are higher than 80%, usually in the vicinity of 90%. All the fluorine available in mercuric fluoride is used, and pure mercuric bromide is left as the residue. The yield deficiency is due to a partial decomposition of the organic fluoride into hydrogen fluoride and the corresponding ethylenic hydrocarbon.

Aliphatic Polyfluorides.—In general mercuric fluoride is added slowly to an organic polybromide kept at 80–90° in a copper vessel equipped with a metallic dephlegmator, and the mixture is then heated. The organic fluoride distils as soon as it is formed, while the unreacted bromide

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[3] THIS JOURNAL, 53, 3263 (1931).

refluxes to the reaction vessel. The heating is to be done in an oil-bath, and should be as high as 160° at the end of the operation to ensure yields better than 80%, usually about 90%. In this manner $CH_2BrCHBrF$ and CH_2BrCHF_2 have been prepared from $CH_2BrCHBr_2$; similarly $CHBr_2CHBr_2$ yields quantitatively $CHBr_2CHFBr$ or $CHBr_2CHF_2$, according to the proportion of the reactants.

Acyl Fluorides.—The mode of operation is similar to that recommended for ethyl fluoride. Mercuric fluoride reacts vigorously with acetyl chloride, and the acetyl fluoride thus formed volatilizes through the reflux condenser. To gage the yields, acetyl fluoride was received in ethanol, with which it reacts at once. The quantity of ethyl acetate recovered corresponded to about a 50% yield of acetyl fluoride; it is felt that this yield could be considerably improved.

Reaction with Ethanol.—A small amount of gas is formed, and the reaction stops promptly. The gas is a mixture of ethylene and ethyl fluoride, the latter in about 2% yield.

Cyclohexyl Derivatives.—Cyclohexyl bromide treated with HgF_2 in a solvent reacts at once, at room temperature. The reaction mass becomes purple, an indication that cyclohexylene is formed. Since it is impractical to separate the cyclohexyl fluoride from the reaction mass, settling is allowed to take place and the mercuric salts are filtered off. The clear filtrate is shaken with water, and examination of the water layer indicates the presence of hydrogen fluoride and cyclohexyl alcohol in quantities corresponding to about 10% yields of cyclohexyl fluoride. The same kind of results have been obtained from ortho- and from para-dibromocyclohexane.

Summary

Mercuric fluoride is proposed as a new fluorinating agent. Its preparation, properties and uses are described.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AT THE OHIO STATE UNIVERSITY]

Fluoro Derivatives of Ethane and Ethylene. IV

BY ALBERT L. HENNE AND MARY W. RENOLL

Preceding papers[1] have described fluoro derivatives of ethane and ethylene containing no hydrogen, one hydrogen and two asymmetrically placed hydrogen atoms. The present paper presents fluoro derivatives containing two asymmetrically placed hydrogen atoms, and places emphasis on the different courses followed by the fluorination, when different fluorinating agents are used.

Swarts[2] has shown that the fluorination of acetylene tetrabromide by means of antimony fluoride yields successively $CHBr_2CHBrF$ and $CHBr_2CHF_2$, where the fluorination stops completely and that acetylene tetrachloride yields $CHCl_2CHClF$ and $CHCl_2CHF_2$, together with a very small amount of $CHClFCHF_2$. Swarts' observations and the physical constants reported by him have been verified, and there is no doubt that his determination of the molecular structure of the difluorides is correct. The only point which was never duplicated was the production of small quantities of $CHClFCHF_2$, and this may be due to the fact that Swarts operated in platinum equipment; it is known that platinum has a catalytic action on fluorination. The experiments carried out in this Laboratory were performed in steel, copper or nickel.

Since the fluorination of acetylene tetrabromide is considerably more rapid than that of acetylene tetrachloride, an effort was made to fluorinate $CHClBrCHClBr$, in the hope that this would yield $CHClFCHClF$, a compound which should undergo further fluorination without great difficulty.[3] However, the usual treatment with antimony fluoride gave rise to the following compounds: $CHCl_2CHClF$, $CHCl_2CHF_2$, $CHCl_2CCl_2F$ and $CHCl_2CClF_2$, which were produced in small quantity, as by-products, and have been previously described, and two new compounds, $CHClBrCHClF$, and $CHClBrCHF_2$. The characteristics of these new compounds were measured and computed as in the preceding papers.[1]

EXPERIMENTAL VALUES

Compound	$CHClBrCHClF$	$CHClBrCHF_2$
B. p., °C.	124.7–125.1	82.3–82.5
At mm.	736	743
d^{20}_4	1.932	1.879
n^{20}_D	1.4776	1.4173
MR_D	28.48	24.04
Cl, %	36.1	19.7
Br, %	40.9	44.6
F, %	9.6	21.0
Mol. wt.	194.2	178.0

Neither substance freezes at solid carbon dioxide temperature. By subtracting from the observed

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[1] THIS JOURNAL, **56**, 1726 (1934); **58**, 402, 404 (1936).

[2] Swarts, *Mem. Acad. Roy. Sci. Belg.*, **61**, 1–94 (1901).

[3] See THIS JOURNAL, **58**, 882 (1936).