lium temperatures showed a variation of only 0.006%.

No resistance hysteresis was found following the passage of a current.

The increase of resistance in a magnetic field was measured at 4.2 and 1.5°K. It was found to be larger at the lower temperature and proportional to the square of the applied field at both temperatures.

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

The Fluorination of Aliphatic Substances with Mercurous Fluoride

BY ALBERT L. HENNE AND MARY W. RENOLL

Mercurous fluoride, correctly prepared and used,[1–6] is a valuable fluorinating agent but excessive claims and implications have been made for it and it is therefore the purpose of this paper to describe in detail a convenient laboratory preparation of the pure, anhydrous salt, to outline the limitations of its use, and to present a simple method which circumvents some of its defects.

Preparation of Mercurous Fluoride.—Previously described methods of preparation are unreliable, time-consuming and yield products whose analyses (when reported) demonstrate the presence of water and oxides. The use of organic solvents in washing and drying does not make any improvement, and chemical reagents less than "chemically pure" cause unneeded complications.

First mercurous nitrate is prepared by dissolving 40 g. of red mercuric oxide in a mixture of 28 cc. of concentrated nitric acid and 60 cc. of water. This solution is shaken vigorously in a bottle with 40 g. of mercury, until the mercury ceases to dissolve readily, at which point mercurous nitrate starts to crystallize out. A solution of 4 cc. of concentrated nitric acid in 45 cc. of water is then added to redissolve the crystals, and the excess of mercury is decanted. The solution is next poured into a freshly prepared solution of 48 g. of potassium bicarbonate in 200 cc. of water, and the resulting mercurous carbonate is filtered by suction in the presence of a few pieces of solid carbon dioxide, and finally washed thoroughly with 1400 cc. of water saturated with carbon dioxide. All operations should be carried out in diffused light. The moist mercurous carbonate is added immediately, in small portions and with constant stirring, to a mixture of 100 cc. of 48% hydrofluoric acid and 260 cc. of water, in a platinum dish, which is then heated on the water-bath, with gentle stirring, until a dry, sandy powder is obtained. This powder, which is quite friable, is rapidly scraped off the walls, coarsely crushed under the bottom of a platinum crucible, and then heated for an hour on the water-bath. The salt should be removed from the dish and stored immediately in tightly stoppered copper or resin containers. The yield is about 80 g. Analysis indicates 91.28% mercury and 8.86% fluorine. Theory requires 91.35% mercury and 8.65% of fluorine.

Fluorination Procedure.—In addition to the described procedures[1–6] it is possible to operate substantially as described for mercuric fluoride,[7] particularly when the compound to be fluorinated boils at a temperature lower than the threshold at which fluorination proceeds. Fluorination with mercurous fluoride is lively, but never as violent as with mercuric fluoride.

Limitations.—Mercurous fluoride gives generally very good yields of alkyl monofluorides from alkyl monoiodides and good yields from bromides; from polyiodides, it gives very poor yields of polyfluorides; from polybromides, the results were as follows: ethylidene bromide yielded vinyl bromide, and so also did ethylene bromide; 1,1,2-tribromoethane yielded a mixture of $CHFBrCH_2Br$, $CH_2{=}CBr_2$ and $CHBr{=}CHBr$, with the latter two substances far predominant; acetylene tetrabromide gave a very small quantity of $CHBrFCHBr_2$, contaminated by ethylenic and acetylenic decomposition products and their polymers. In general the reaction with polybromides starts between 120 and 140°. Polychlorides, when affected at all, lose hydrochloric acid.

From Mercurous to Mercuric Salt.—A method to circumvent some of the fluorination difficulties is to cause a transformation of the mercurous fluoride into a mercuric salt. The high fluorinating power of mercuric fluoride, even at low temperature, has been described before.[8] This transformation was performed very simply by Swarts,[4] while preparing methyl fluoride, by dissolving one gram atom of iodine in a large amount of methyl iodide and progressively feeding one gram molecule of mercurous fluoride into the solution, presumably causing the formation of one gram molecule of mercuric fluoroiodide; the latter produced a gram molecule of methyl fluoride with an 80% yield.

This method has now been extended to polybromides and polyiodides, and the qualitative results obtained were those which would have prevailed had mercuric fluoride been used; the difference appears only in yields and ease of operation, and consequently the use of an equimolecular mixture of mercurous fluoride and iodine can be regarded as a substitute for the use of mercuric fluoride. Ethyli-

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(1) Swarts, *Bull. acad. roy. Belg.*, [3] **31**, 675–688 (1896).

(2) Swarts, *Bull. soc. chim. Belg.*, **30**, 302 (1921).

(3) Desreux, *ibid.*, **44**, 1 (1935).

(4) Swarts, *ibid.*, **46**, 10–12 (1937).

(5) Ruff and others, *Ber.*, **69B**, 299 (1936).

(6) Van Arkel and Zanetzky, *Rec. trav. chim.*, **56**, 167 (1937).

(7) Henne, THIS JOURNAL, **59**, 1200 (1937).

(8) Henne and Midgley, *ibid.*, **58**, 884 (1936).

dene bromide yielded ethylidene fluoride, and methylene iodide yielded methylene fluoride, both without stopping at the intermediate stage, CH_3CHFBr and CH_2IF, respectively; $CHBr_2CH_2Br$ yielded CHF_2CH_2Br and $CHFBr$-CH_2Br while acetylene tetrabromide yielded $CHFCHBr_2$ and $CHFBrCHBr_2$, with the difluorides predominant in both cases.

Finally experiments were undertaken to eliminate the use of iodine, which is expensive, cumbersome and causes rearrangements. Mercurous fluoride was treated with chlorine, quantitatively to yield mercuric fluorochloride. The operation is performed as follows.

Preparation of Mercuric Fluorochloride.—Mercurous fluoride is placed in a steel container equipped with a needle valve; this container can be made conveniently of pipe fittings. The container is evacuated, then connected to a chlorine tank; the valve is opened and chlorine admitted at the full pressure of the tank. The reaction is immediate and evolves a great deal of heat. After a few minutes, the chlorine pressure is released, the steel container opened, the mercury salt removed, crushed rapidly in a mortar and placed again in the container for a second chlorine treatment. This second treatment is needed because an appreciable amount of mercuric chloride is formed, which sublimes and builds a protective coat. The mercuric fluorochloride is a pale yellow, light powder, very distinct from the coarser mercurous fluoride. Its mercury content, which theoretically should be 78.65%, is generally found to be approximately 81% after the first chlorine treatment, and about 78.9% after the second treatment.

In its chemical effect, mercuric fluorochloride behaves as a mixture of mercuric fluoride and mercuric chloride. The reactions enumerated for the mixture of mercurous fluoride and iodine are performed with equal ease by this new salt. Some new side reactions are however apparent, as should be expected from the fact that the mixed salt acts like a mixture of salts; this is best illustrated by the fact that the reaction between ethylene dibromide and mercuric fluorochloride gives as main products ethylene fluoride and CH_2-$BrCH_2F$, and as by-product CH_2ClCH_2Br, and consequently the residual mercury salt, after completion of the reaction, is almost pure mercuric bromide instead of mercuric chlorobromide.

Conclusion.—Mercurous fluoride is a good fluorinating agent when it acts on compounds possessing a relatively active bromine or iodine atom. When it is desired to fluorinate a substance with sluggish halogen atoms, the mercurous fluoride should be brought to the mercuric stage, which can be done by combining it with iodine or chlorine. These methods are only substitutes for the use of mercuric fluoride, which remains by far the most powerful and convenient fluorinating agent.

Summary

A preparation of mercurous fluoride is described; its uses and limitations as a fluorinating agent are discussed; its passage to the mercuric stage by means of chlorine or iodine is described. The advantages of a mercuric salt for fluorination purposes are again emphasized.

THE MIDGLEY FOUNDATION
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Sterols. XXIX. Urane Derivatives

BY RUSSELL E. MARKER, OLIVER KAMM, THOMAS S. OAKWOOD, EUGENE L. WITTLE AND ELMER J. LAWSON

The preceding paper[1] in this series described the isolation, from pregnant mares' urine, of two triols. Both compounds form triacetates and these may be hydrolyzed to the original triols, which we designated as pregnanetriol-A and pregnanetriol-B. The latter compound is probably the pregnanetriol isolated by Haslewood, Marrian and Smith.[2]

We are now able to assign a tentative structure (I) to the triol-A. We have evidence that the parent hydrocarbon is an isomer of pregnane, probably differing from the latter only in respect to the configuration at C_9. For this new parent hydrocarbon we propose the name *urane*, thereby indicating its source, from urine. In the case of pregnanediol (II) the hydrogen atom at C_9 is considered to be *trans* to the methyl group at C_{10}, in accordance with the usual conventions regarding the configuration of the steroid nucleus.[3] Isomerism at C_9 has been found to occur in the case of sarmentogenin and digoxigenin[4] (formulas III and IV)

When uranetriol (triol-A) ($C_{21}H_{36}O_3$) is treated with chromic anhydride in acetic acid a derivative, $C_{21}H_{30}O_3$, is formed. This derivative does not form an acetate when heated with acetic anhydride; in fact, the original compound can

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[1] Marker, Kamm, Crooks, Oakwood, Wittle and Lawson, THIS JOURNAL, **60**, 210 (1938).

[2] Haslewood, Marrian and Smith, *Biochem. J.*, **28**, 1316 (1934).

[3] Strain, "The Sterols, Bile Acids, and Related Compounds," Chap. XV, p. 1255, in "Gilman, Treatise on Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1938, Vol. II.

[4] Tschesche and Bohle, *Ber.*, **69**, 2497 (1936).