Some Gas-Phase Reactions of Fluoroallyl Halides[1a]

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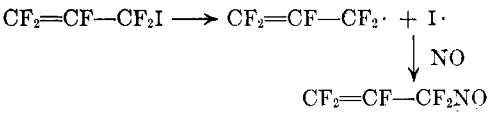
Miller and his coworkers[2–4] have prepared several highly fluorinated allyl halides and described reactions of these compounds with halide ion. Perfluoroallyl iodide[2b] (I) was prepared by halogen exchange of perfluoroallyl chloride with sodium iodide in acetone solution. The iodine atom in this compound was very reactive and was readily replaced by either bromine or chlorine using the free halogen in the dark at room temperature. Zinc dust in methanol caused replacement of the iodine with hydrogen, and coupling to decafluoro-1,5-hexadiene was effected using zinc dust in anhydrous dioxane.

The high reactivity of the iodine in I suggested that this and similar compounds might be used in the synthesis of polyfluoronitroso compounds. The only olefinic nitroso compound of this type which had been reported was trifluoronitrosoethylene.[5] This compound has been synthesized by the photochemical reaction of trifluoroiodoethylene with nitric oxide in the presence of mercury.

We, therefore, synthesized two polyfluoroallyl iodides in order to convert them into the polyfluoroallyl nitroso compounds. I was prepared by pyrolysing chlorotrifluoroethylene to perfluoroallyl chloride[6] and converting this to the iodide using sodium iodide in acetone.[1] The corresponding 2*H*-tetrafluoroallyl iodide (II) had not been prepared previously. The synthesis was accomplished by preparing 2*H*-tetrafluoroallyl bromide (III) by the dehydrobromination of 1,3-dibromo-1,1,3,3-tetrafluoropropane (IV) which was obtained from the benzoyl peroxide initiated addition of dibromodifluoromethane to 1,1-difluoroethylene.[7] III was converted into II by treatment with sodium iodide in acetone.

A photochemical reaction was carried out in sunlight between I and nitric oxide in the presence of mercury, using a technique described by Barr and Haszeldine.[8] The reaction product was worked up by introduction of oxygen, which converted unchanged nitric oxide into nitrogen dioxide; the latter was removed by reaction with mercury to form mercurous nitrate.[9]

Hexafluoropropene (V) (20%), 3-nitrosopentafluoropropene (34%) (VI), and perfluoroacryloyl fluoride (27.5%) (VII) were obtained. Formation of VI was obviously *via* a simple free radical reaction.



$$\begin{tikzcd}
\mathrm{CF_2{=}CF{-}CF_2I} \arrow[r] & \mathrm{CF_2{=}CF{-}CF_2\cdot + I\cdot} \arrow[d, "\mathrm{NO}"] \\
 & \mathrm{CF_2{=}CF{-}CF_2NO}
\end{tikzcd}$$

VI was relatively stable in sunlight for the length of time the reaction mixture was irradiated. It was, therefore, unlikely that V or VII resulted from its decomposition. The formation of V and VII was attributed to the presence of mercurous nitrate in the reaction mixture and is discussed later in the article.

The photochemical reaction between II and nitric oxide gave 1,1,3,3-tetrafluoro-3-nitrosopropene (VIII) (24.5%). 2*H*-pentafluoropropene (IX) (38%) and β,β-difluoroacryloyl fluoride (X) (32%) also were formed by reaction between II and mercurous nitrate formed *in situ* during the purification process.

Both VI and VIII had a deep blue color characteristic of monomeric nitroso compounds. VIII was relatively unstable; a sample left in the dark at 25° lost all its blue color after approximately fifteen hours. VI was a little more stable and had to be left for eighty-four hours before all the blue material had decomposed. The mixture of products from the decomposition of either VI or VIII was quite complex. In both cases, there was some solid, high boiling oil and volatile material consisting of several components.

Attention was next turned to the novel reaction between mercurous nitrate and either I or II to form the unsaturated acyl fluorides and fluoropropenes. In most cases, the mercurous nitrate was formed *in situ* from mercury and nitrogen dioxide in the presence of excess oxygen. It was shown in a separate experiment that oxygen itself did not react with I. This made it safe to carry out the reactions with mercurous nitrate in the presence of oxygen, which ensured that all oxides of nitrogen were removed during the reaction, thus giving a cleaner reaction product. The results of these reactions with mercurous nitrate are summarized in Table I.

TABLE I

REACTION OF FLUOROALLYL HALIDES WITH MERCUROUS NITRATE (X = F, H)

Compound	Conversion, %	Yield of $CF_2=CX-CF_3$, %	Yield of $CF_2=CXCOF$, %
$CF_2=CF-CF_2I$[a,c]	100	13.5	80
$CF_2=CFCF_2I$[b]	75	13	70.5
$CF_2=CH-CF_2I$[a,c]	100	19	76
$CF_2=CH-CF_2Cl$[a]	90	2	93
$CF_2=CF-CF_2Cl$[a]	0		
$CF_2=CF-CF_3$[a]	0		

[a] Reactions carried out with mercurous nitrate formed *in situ* from mercury and nitrogen dioxide. [b] Reaction carried out with commercial mercurous nitrate. [c] A trace of nitroso compound, $CF_2=CX-CF_2NO$, was also formed.

Table I indicates clearly that reaction of the fluoroallyl halide with mercurous nitrate depends on the reactivity of the halogen used. Obviously the chlorine in $CF_2=CF-CF_2Cl$ is less reactive than the iodine in $CF_2=CF-CF_2I$, and it is, therefore, not surprising that the latter reacts with mercurous nitrate to form an acryloyl fluoride whereas the former does not react. We were surprised to find, however, that the other allyl chloride ($CF_2=CH-CF_2Cl$) reacted readily under the same conditions to form the acryloyl fluoride. The

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(1) (a) Halogen, in the sense used in this paper, does not include fluorine; (b) presented at the Annual Southeastern Regional Meeting of the American Chemical Society, Gatlinburg, Tenn., November 1–3, 1962.

(2) (a) W. T. Miller and A. H. Fainberg, *J. Am. Chem. Soc.*, **79**, 4164 (1957); (b) A. H. Fainberg and W. T. Miller, *ibid.*, **79**, 4170 (1957).

(3) J. H. Fried and W. T. Miller, *ibid.*, **81**, 2078 (1959).

(4) W. T. Miller, J. H. Fried, and H. Goldwhite, *ibid.*, **82**, 3091 (1960).

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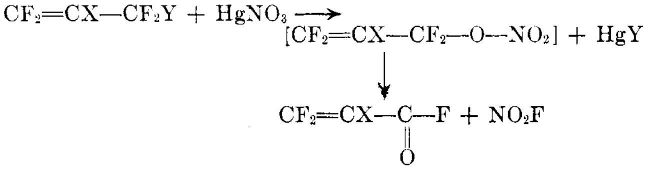
reason for the lack of reactivity of $CF_2{=}CF{-}CF_2Cl$ compared to that of $CF_2{=}CH{-}CF_2Cl$ must be due to the presence of a fluorine atom on the β-carbon atom. This fluorine atom can exhibit the well known mesomeric effect and back donate nonbonding π-electrons to the olefinic double bond. This would withdraw electron density from the chlorine and make loss of chloride ion as mercury chloride more difficult than in $CF_2{=}CH{-}CF_2Cl$.

The formation of acryloyl fluoride from the reactions of these allyl halides with mercurous nitrate could be by initial formation of mercury halide and an allyl nitrate. It seems reasonable to suppose that the latter could lose nitryl fluoride to form the acyl fluoride. This course of events could also explain the formation of the fluoropropene ($CF_2{=}CX{-}CF_3$) since nitryl fluoride has been reported[10] to be very reactive and a powerful fluorinating agent. It would then either react with allyl halide to form a fluoropropene, or possibly convert some mercurous nitrate to mercurous or mercuric fluoride which could then fluorinate the allyl halide.



$$\begin{array}{rl} CF_2{=}CX{-}CF_2Y + HgNO_3 \longrightarrow & \\ & [CF_2{=}CX{-}CF_2{-}O{-}NO_2] + HgY \\ & \qquad\qquad\downarrow \\ & CF_2{=}CX{-}\underset{\underset{O}{\|}}{C}{-}F + NO_2F \end{array}$$

$$CF_2{=}CX{-}CF_2Y + \underset{(\text{or } HgF_2)}{NO_2F} \longrightarrow CF_2{=}CX{-}CF_3$$

$(X = H;\ Y = I, Cl)$
$(X = F;\ Y = I)$

Andreades[11] has reported a similar dissociation of a perfluoroalkyl nitrite to an acyl fluoride and nitrosyl fluoride.

$$\begin{array}{lcl} C_2F_5NO & \longrightarrow & C_2F_5ONO + \text{other products} \\ & & \qquad \downarrow\uparrow \\ & & CF_3COF + NOF \end{array}$$

The table shows that the ratio of olefin ($CF_2{=}CX{-}CF_3$) to acryloyl fluoride ($CF_2{=}CX{-}COF$) was higher for reaction of an iodide than for a chloride. These data fit our reaction scheme since the more reactive iodide would be fluorinated with nitryl fluoride more readily than the chloride, thus giving a higher yield of the fluoropropene ($CF_2{=}CX{-}CF_3$).

Experimental

Analyses were performed by Galbraith Laboratories, Knoxville, Tenn., and by Schwarzkopf Laboratories, Woodside, N. Y.

1,1,3,3-Tetrafluoro-3-iodopropene.—1,1,3,3-Tetrafluoro-3-bromopropene was prepared as described by Tarrant, Lovelace, and Lilyquist.[7]

1,1,3,3-Tetrafluoro-3-bromopropene (63.5 g., 0.33 mole) and sodium iodide 70 g., 0.466 mole) reacted in acetone (160 ml.) solution for 16 days at room temperature. Solvent was removed by adding water (1000 ml.), separating the two layers, and washing the organic layer with dilute sodium bisulfite (three 25-ml. portions). This organic material was dried over phosphoric anhydride and distilled in a nitrogen atmosphere through a 24-plate spinning band column to give 1.6 g. of recovered 1,1,3,3-tetrafluoro-3-bromopropene, boiling range 34–36°, and 50.6 g. of 1,1,3,3-tetrafluoro-3-iodopropene (64%), boiling range 61–62°, $n^{20}D$ 1.4046.

Anal. Calcd. for C_3HF_4I: C, 15.01; H, 0.42; F, 31.47. Found: C, 15.09; H, 0.60; F, 31.76.

An infrared spectrum showed C=C stretching frequency at 5.73 (m) μ and bands at 7.39 (s), 7.98 (m), 8.30 (m), 9.30 (s), 10.25 (s) and 12.35 (m) μ.

3-Nitroso-1,1,3,3-tetrafluoropropene.—A 2-l. Pyrex flask containing mercury (70 ml.) was evacuated and charged with 3-iodo-1,1,3,3-tetrafluoropropene (4.8 g., 0.02 mole), nitric oxide (1.2 g., 0.04 mole), and mechanically shaken in bright sunshine for 105 min. Oxygen (1.28 g., 0.04 mole) was slowly introduced, and the flask shaken for an additional 30 min. Volatile material was isolated by slowly pumping through two traps cooled in liquid nitrogen. This mixture was separated by large scale v.p.c. (dinonyl phthalate, 25°) into the following three components.

2*H*-Pentafluoropropene, 1.0 g. (38%); an infrared spectrum was identical with that of an authentic sample.

3-Nitroso-1,1,3,3-tetrafluoropropene, 0.7 g. (24.5%).

Anal. Calcd. for C_3HF_4NO: mol. wt., 143. Found: mol. wt., 142.

An infrared spectrum showed C=C and NO stretching absorptions at 5.71 (vs) and 6.29 (m), and bands at 7.30 (s), 7.9 (m), 8.1 (m), 8.9 (ms), 9.7 (w), and 10.5 (m) μ.

β,β-Difluoroacryloyl fluoride, 0.7 g. (32%), b.p. 45.0°.

Anal. Calcd. for C_3HF_3O: C, 32.73; F, 51.83; H, 0.91; mol. wt., 110. Found: C, 32.55; F, 51.60; H, 0.81; mol. wt., 109.

An infrared spectrum showed C=C and C=O stretching frequencies at 5.43 (vs) and 5.81 (vs) and bands at 7.26 (s), 7.85 (m), 8.2 (ms), 9.15 (s), and 10.2 (s).

The nuclear magnetic resonance spectral data[12] on the last two compounds were in agreement with the formulations $CF_2{=}CH{-}CF_2NO$ and $CF_2{=}CH{-}COF$, respectively.

3-Nitrosopentafluoropropene.—Perfluoroallyl iodide was prepared from perfluoroallyl chloride as described by Miller and Fainberg.[1] Perfluoroallyl chloride was prepared by the pyrolysis of chlorotrifluoroethylene as described by Miller.[6]

Perfluoroallyl iodide (5.16 g., 0.02 mole) reacted with nitric oxide (1.2 g., 0.04 mole) and mercury in bright sunshine for 6 hr.

Separation of the products gave perfluoropropene, 0.6 g. (20%), identified by its infrared spectrum and 3-nitrosoperfluoropropene, 1.1 g. (34%).

Anal. Calcd. for C_3F_5NO: C, 22.39; N, 8.70; F, 59.00; mol. wt., 161. Found: C, 22.66; N, 8.60; F, 58.68; mol. wt., 161.

An infrared spectrum showed C=C and NO stretching absorptions at 5.61 (vs) and 6.29 (s) μ, and bands at 7.30 (vs), 7.58 (vs), 8.40 (vs), 9.18 (vs), 10.5 (w), 11.1 (w), and 13.9 (w).

Perfluoroacryloyl fluoride, 0.7 g. (27.5%), b.p. 25.5°.

Anal. Calcd for C_3F_4O: C, 28.13; F, 59.37; mol. wt., 128. Found: C, 28.35: F, 59.12; mol. wt., 128.

An infrared spectrum showed C=C and C=O stretching absorptions at 5.40 (vs) and 5.72 (vs) and bands at 7.3 (s), 7.55 (s), 8.41 (s), 8.50 (sh), 9.50 (ms), and 9.59 (doublet), 9.75 (s) and 9.80 μ (doublet); nuclear magnetic resonance data[13] confirmed the formula $CF_2{=}CF{-}COF$ for this compound.

Reaction of Perfluoroallyl Iodide with Mercurous Nitrate.—A 2-l. flask containing mercurous nitrate (75 g., 0.286 mole) was evacuated and charged with perfluoroallyl iodide (5.16 g., 0.02 mole) and mechanically shaken in the dark for 2 hr. Some brown vapor, obviously nitrogen dioxide, was formed during reaction but only in small amount. Volatile material was isolated by vacuum transfer and separated into 0.29 g. of hexafluoropropene (13%), 1.35 g. of perfluoroacryloyl fluoride (70.5%), and 1.29 g. of recovered perfluoroallyl iodide. The previously white mercurous nitrate turned red during reaction, but the red coating was soluble in acetone. This indicated that it was mercuric iodide.

Reactions between Allyl Halides, Mercury, and Mercurous Nitrate.—Mercurous nitrate was prepared *in situ* from mercury and nitrogen dioxide and oxygen.

Allyl halide (0.02 mole), nitrogen dioxide (1.38 g., 0.03 mole), oxygen (0.96 g., 0.03 mole), and mercury (70 ml.) were shaken together in the dark for 1 hr. in a 2-l. flask. All brown vapor had disappeared after this time, and volatile material was isolated under vacuum and separated into its various components by large scale v.p.c.

The results of these reactions are summarized in Table I.

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Reaction of Perfluoroallyl Iodide with Oxygen.—Perfluoroallyl iodide (5.16 g., 0.02 mole), oxygen (0.64 g., 0.02 mole), nitrogen (0.84 g., 0.03 mole), and mercury (70 ml.) were shaken together in the dark for 1 hr. in a 2-l. flask. The only organic material isolated was 4.7 g. of unchanged perfluoroallyl iodide (91% recovery).

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Ring Conformation in Methyl α- and β-D-Xylothiapyranosides as Demonstrated by Nuclear Magnetic Resonance[1]

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The recent synthesis of sugars in which the ring oxygen is replaced by a sulfur atom[2] makes possible an experimental attack on many interesting questions relative to both chemical and physical–chemical properties of the carbohydrates. However, one question which must be answered before certain other results can be interpreted without ambiguity is that of whether there is a direct effect of this substitution on the ring conformation. The D-xylopyranosides have been shown to exist in the Cl conformation by optical rotatory studies,[3] by stability considerations,[4,5] and by X-ray analysis.[6] It has also been shown in D-xylopyranose tetraacetates that the spin–spin coupling constants observed by n.m.r. are as required for the Cl conformation.[7] The purpose of the present work is to determine if replacement of the ring oxygen by sulfur in D-xylothiapyranose and the methyl D-xylothiapyranosides produces a change in the ring conformation.

The proton magnetic resonance spectra of the various compounds were determined at 60 Mc.p.s. with a Varian A-60 n.m.r. spectrometer using 10–20% by weight solutions of the carbohydrates in deuterium oxide. The assignment of τ values were made by taking the water peak (5.2 τ) as an internal standard. The dihedral angles between the anomeric proton and the proton on the adjacent carbon atom C-2 were calculated from the magnitude of the splitting of the corresponding absorption peak using the modified Karplus equation.[8,9]

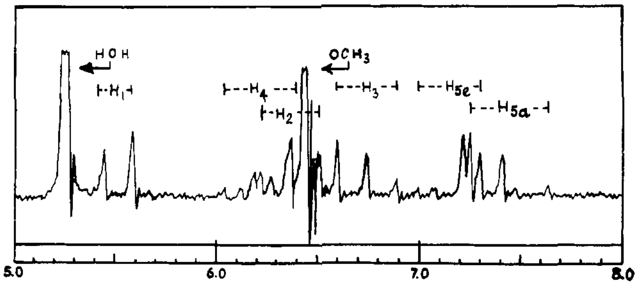

Fig. 1.—N.m.r. spectrum of methyl β-D-xylothiapyranoside in deuterium oxide at 60 Mc., with chemical shifts given in τ values.

It has been shown that the signal due to the anomeric proton of sugars appears at a lower field than that of any of the other carbon-bonded hydrogen atoms.[7,9,10] Further, the signal for an equatorial anomeric proton occurs at a somewhat lower field than for an axial proton. From Table I it is evident that the signal in methyl α-D-xylothiapyranoside appears at a lower field than for the corresponding β-anomer. In all cases the peak corresponding to the anomeric proton is split due to coupling with the proton on C-2. The large values of this coupling constant for methyl β-D-xylopyranoside and methyl β-D-xylothiapyranoside (7.2 and 8.4 c.p.s., respectively) are of the expected order of magnitude for an axial–axial orientation. Similarly the low values for the α-anomers indicate an axial–equatorial situation. The calculated values of the dihedral angles are in reasonable agreement with the expected values for the Cl conformation (60° and 180° for α- and β- anomers, respectively).

Table I

Chemical Shifts and Coupling Constants for Anomeric Protons

	Chemical shifts (τ values)		Coupling constant JH_1H_2, cycles/-sec.	Dihedral angle, deg.
	H_{1e}	H_{1a}		
D-Xylose[a]	4.82	. . .	2.2	60
	. . .	5.45	7.2	148
Methyl β-D-xylopyranoside	. . .	5.62	7.2	148
D-Xylothiapyranose	5.0	. . .	2.5	57
	. . .	5.25	8.2	154
Methyl α-D-xylothiapyranoside	5.35	. . .	2.8	55
Methyl β-D-xylothiapyranoside	. . .	5.52	8.4	156

[a] Data from ref. 9.

The spectra of both D-xylopyranosides and D-xylothiapyranosides show additional fine structure. The spectrum of methyl β-D-xylothiapyranoside is presented in Fig. 1. The splitting pattern in the region 5.8–6.5 τ has been identified as due to the proton at C-2. This indicates that it is coupled to protons at C-1 and C-3 with J values 8.4 and 8.6, respectively. These large values indicate that the C-2 proton is in axial–axial orientation with the protons at C-1 and C-3. The triplet in the region 6.6–6.9 τ is assigned to the C-3 proton. The splitting pattern shows that the C-3 proton is coupled with

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