Anal. Calcd. for $C_7H_3Cl_2F_5$: C, 33.16; H, 1.19; F, 37.55. Found: C, 33.09; H, 1.39; F, 37.87.

An infrared spectrum showed strong bands at 4.94 and 6.14 (C=C) and 7.15 to 8.85 μ (C–F).

The third component was not identified.

A similar experiment carried out at 150° for 12 hr. gave very little reaction of III with chlorotrifluoroethylene.

Reaction of III with Hydrogen Fluoride.—III (15.0 g., 0.11 mole) and anhydrous hydrogen fluoride (4.4 g., 0.22 mole) were stirred in a nitrogen atmosphere at −22° for 1 hr. and then kept at 25° for 12 hr. The reaction mixture was then poured onto ice (75 g.), washed with three 10-ml. portions of water, and dried over calcium chloride. Analytical v.p.c. showed that only unchanged III was present.

The same quantities of reactants were sealed in a 335-ml. stainless steel autoclave and heated to 85° for 20 hr. The product was worked up as before to give a black liquid (14.0 g.). This was shown by analytical v.p.c. to consist of at least fourteen components. Some free carbon was deposited on the sides of the autoclave during the reaction.

Acknowledgment.—We are grateful to the U. S. Army Natick Laboratories, Natick, Massachussetts, for financial support of this project. Dr. Malcolm Henry acted as the project officer. We wish to thank Dr. W. S. Brey and Dr. Kermit Ramey for the n.m.r. analyses; their results will be reported in detail elsewhere.
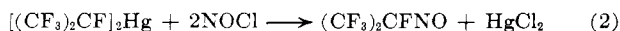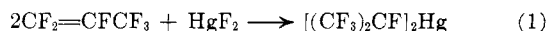

Fluoroolefins. XI. The Conversion of Fluoroolefins to Fluoroalkyl Nitroso Compounds *via* Alkylmercury Compounds

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Fluoroalkyl nitroso compounds have been prepared by the reaction of perfluoroalkyl iodides with nitric oxide,[1] by the addition of nitrosyl chloride to a fluoroolefin,[2] or more recently by the thermal decomposition of perfluoroacyl nitrites.[3] We now wish to report that fluoroalkyl nitroso compounds can be made from the reaction of fluoroalkylmercury compounds with nitrosyl chloride. Since the fluoroalkylmercury compounds are made by adding mercuric fluoride across the double bond of the olefin, the over-all reaction involves the addition of nitrosyl chloride to a fluoroolefin in a two-step operation.

$$2CF_2=CFCF_3 + HgF_2 \longrightarrow [(CF_3)_2CF]_2Hg \quad (1)$$

$$[(CF_3)_2CF]_2Hg + 2NOCl \longrightarrow (CF_3)_2CFNO + HgCl_2 \quad (2)$$

The addition of mercuric fluoride to a series of fluoroolefins was carried out by Krespan's method[4] in which hydrogen fluoride was used as the solvent instead of arsenic trifluoride. Since the completion of our work, Miller[5] has described the addition of mercuric fluoride to $CF_2=CHCF_3$ and $CF_2=CFCF_3$ in the

presence of hydrogen fluoride, while Aldrich[6] has described similar reactions with 1,1-dichlorodifluoroethene and a series of longer chain polyfluoroolefins containing the —C=CF₂ group.

It appears that the addition of mercuric fluoride to fluoroolefins is limited to those containing a difluoromethylene group, *i.e.*, terminal olefins, since neither hexafluorocyclobutene nor 2,3-dichloro-1,1,1,4,4,4-hexafluoro-2-butene formed an adduct.

The reaction of $(CF_3CFCl)_2Hg$ and nitric oxide was attempted in the gas phase under the influence of ultraviolet radiation. However, the formation of the blue nitroso compound occurred so slowly that this method was judged unsatisfactory. The reaction of nitrosyl chloride with certain fluoroalkylmercury compounds did take place at a reasonable rate in dimethylformamide (DMF) and $CF_3CFClNO$, $(CF_3)_2CFNO$, and CF_3CCl_2NO were prepared from the corresponding fluoroalkylmercury. This type reaction was first used by Baeyer[8] in preparing nitrosobenzene from diphenylmercury and nitrosyl chloride.

The reaction was carried out at room temperature with DMF. Although the reaction seemed to proceed at a comparable rate in dimethyl sulfoxide, the yield of nitroso compound was considerably lower. In the dimethyl ether of diethylene glycol (diglyme) the reaction was much too slow to be useful while in acetone and in benzene the desired reaction did not take place. It is not practical to increase the temperature of the reaction appreciably since nitroso compounds disproportionate rapidly at elevated temperatures.[9]

The great increase in reaction rate with increase in dielectric constant of the solvent seems to indicate that the formation of a charged species is a factor in the over-all rate.

Qualitatively, the order of reactivity of the alkylmercury compounds with nitrosyl chloride is $(CF_3CFCl)_2Hg > [(CF_3)_2CF]_2Hg > (CF_3CCl_2)_2Hg > (CF_3CHF)_2Hg >> (CF_3CFBr)_2Hg$ and $(CF_3CH_2)_2Hg$. No nitroso compound was obtained from the last two mercury derivatives.

The reaction of $(CF_3CHF)_2Hg$ with nitrosyl chloride did not give the expected nitroso compound nor the oxime that might be derived from it. Instead, 1-chloro-1-nitrosotetrafluoroethane, 1,1-dichlorotetrafluoroethane, and 1-chloro-1,3,3,3-tetrafluoroethane were obtained.

$$(CF_3CHF)_2Hg \xrightarrow{\text{NOCl}} CF_3CFClNO + CF_3CFCl_2 + CF_3CHFCl$$

Similar results were obtained in another investigation when nitrosyl chloride was added to trifluoroethylene.

$$CF_2=CFH + NOCl \longrightarrow CF_2ClCFClNO$$
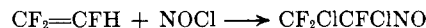
It seems unlikely that the hydrogen atoms of such dissimilar compounds as $(CF_3CHF)_2Hg$ and $CF_2=CFH$ would be replaced by chlorine and the resulting mercury compound and olefin then undergo the cleavage reactions to give $CF_3CFClNO$ and $CF_2ClCFClNO$.

(1) R. N. Haszeldine, *J. Chem. Soc.*, 2075 (1953).

(2) J. D. Park, A. P. Stefani, and J. R. Lacher, *J. Org. Chem.*, **26**, 4017 (1961).

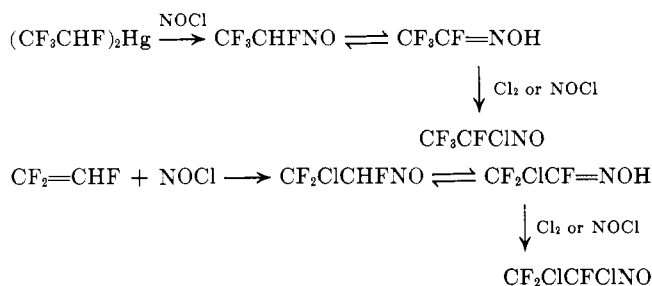(3) J. D. Park, R. W. Rosser, and J. R. Lacher, *ibid.*, **27**, 1462 (1962).

(4) C. G. Krespan, *ibid.*, **25**, 105 (1960).

(5) W. T. Miller, Jr., M. B. Friedman, J. H. Fried, and H. F. Koch, *J. Am. Chem. Soc.*, **83**, 4105 (1961).

(6) P. E. Aldrich, E. G. Howard, W. J. Linn, W. J. Middleton, and W. H. Sharkey, *J. Org. Chem.*, **28**, 184 (1963).

(7) The reaction of mercuric fluoride and bromotrifluoroethylene in hydrogen fluoride gave a 63% yield of bis(1-bromo-1,2,2,2-tetrafluoroethyl)mercury, m.p. 53–56°. *Anal.* Calcd. for $C_4Br_2F_8Hg$: Br, 28.51. Found: Br, 28.23.

(8) A. Baeyer, *Ber.*, **7**, 1638 (1874).

(9) D. E. O'Connor and P. Tarrant, *J. Org. Chem.*, **29**, 1793 (1964).

A more probable course would involve the replacement of hydrogen in the corresponding oximes and could arise as follows.

$$(CF_3CHF)_2Hg \xrightarrow{NOCl} CF_3CHFNO \rightleftharpoons CF_3CF{=}NOH$$

$$\downarrow Cl_2 \text{ or } NOCl$$

$$CF_3CFClNO$$

$$CF_2{=}CHF + NOCl \longrightarrow CF_2ClCHFNO \rightleftharpoons CF_2ClCF{=}NOH$$

$$\downarrow Cl_2 \text{ or } NOCl$$

$$CF_2ClCFClNO$$

In every reaction of a fluoroalkylmercury compound with nitrosyl chloride that took place, except with bisheptafluoroisopropylmercury, some of the corresponding dichlorofluoroalkane was obtained. These

$$(CF_3CFCl)_2Hg \xrightarrow{NOCl} CF_3CFCl_2 \ (5\%)$$

$$(CF_3CCl_2)_2Hg \xrightarrow{NOCl} CF_3CCl_3 \ (37\%)$$
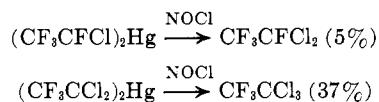
compounds could arise either from the displacement of mercury by chlorine or from the decomposition of the resulting α-chloronitroso compound by a free-radical process.[9] Since the last step of the reaction is es-

$$CF_3CCl_2NO \longrightarrow CF_3CCl_2 \cdot \xrightarrow[\text{NOCl}]{Cl_2 \text{ or}} CF_3CCl_3$$
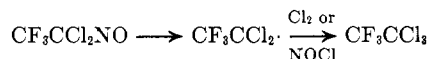
sentially irreversible, the extent to which the more highly chlorinated product is formed depends on the stability of the free radical. These are $CF_3CCl_2 \cdot > CF_3CFCl \cdot > (CF_3)_2CF \cdot$. Since the bisheptafluoroisopropylmercury gave no chloride in the presence of nitrosyl chloride and the other compounds gave polychlorides in amounts proportional to the radical stabilities, the radical process probably operates in this reaction.

Experimental[10]

Reactions of Alkylmercury Compounds with Nitrosyl Chloride. —The general procedure used in preparing the nitroso compounds is as follows. Dimethylformamide and the mercury alkyl were added to a 250-ml., three-necked flask, fitted with a magnetic stirrer, a gas inlet tube, and a take-off leading to a Dry Ice–acetone-cooled condenser. Nitrosyl chloride was bubbled into the solution until it was dark red. The reaction proceeded very

TABLE I

PRODUCTS FROM THE REACTION OF FLUOROALKYLMERCURY
COMPOUNDS WITH NITROSYL CHLORIDE

Mercury compound formula	Mole	Products, %	
$(CF_3CFCl)_2Hg$	0.095	$CF_3CFClNO,^a$ 79	$CF_3CFCl_2,^b$ 5
$[(CF_3)_2CF]_2Hg$	0.037	$(CF_3)_2CFNO,$ 64	
$(CF_3CHF)_2Hg$	0.057	$CF_3CFClNO,^c$ 14	$CF_3CFCl_2^b$
			CF_3CHFCl^d
$(CF_3CCl_2)_2Hg$	0.10	$CF_3CCl_2NO,^e$ 28	$CF_3CCl_3,^b$ 14

^{a} The n.m.r. F^{19} spectrum confirmed the structure $CF_3CFClNO$ which had a b.p. of $-5°$ determined isoteniscopically. *Anal.* Calcd. for C_2ONClF_4: N, 8.46; Cl, 21.43; mol. wt., 165.5. Found: N, 7.65; Cl, 20.63; mol. wt., 165. ^{b} Identified by comparison of its infrared spectrum with an authentic sample and by its n.m.r. spectrum. ^{c} The boiling point of this material is $-5°$ and its infrared spectrum was found to be identical with that of an authentic sample of $CF_3CFClNO$. ^{d} Identified by its n.m.r. and infrared spectra. ^{e} B.p. $36°$, determined isoteniscopically. *Anal.* Calcd. for $C_2ONCl_2F_3$: Cl, 38.96. Found: Cl, 38.60.

(10) Analyses were by Galbraith Laboratories, Knoxville, Tenn.

slowly, normally requiring from 3 to 4 days. More nitrosyl chloride was added from time to time when the color of the solution had changed from dark red to green. Most of the nitroso compound passed into the Dry Ice trap as it was formed. The flask was swept with nitrogen at the end of the reaction. The product was washed twice with sodium bicarbonate to remove oxides of nitrogen and was then purified by passing it through a preparative scale vapor phase chromatographic column. The 2.5 cm. × 250 cm. column was packed with Celite with dinonyl phthalate used as the liquid phase and was operated at room temperature. This operation was necessary because the boiling point of the major impurity is very nearly the same as that of the nitroso compound. The results are shown in Table I.


1-Deoxy-1-(methylnitrosamino)pentitols[1]

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The synthesis of 1,4-dideoxy-1,4-bis(methylnitrosamino)erythritol and the corresponding 1,6-disubstituted mannitol has recently been reported.[3a] Interest in this type of compound is due to the postulate[3b] that alkyl N-nitroso compounds are metabolized to diazoalkanes which can alkylate essential cell constituents and result in an altered metabolic pattern.

The isolation of a small proportion of 1-deoxy-1-(methylnitrosamino)-D-xylitol during the synthesis of the 1,4-anhydrides of D-iditol and D-gulitol[4] led to the present study. The synthesis of the anhydrides involved nitrous acid deamination of the 1-amino-1-deoxyalditols derived from the condensation of nitromethane[5] with D-xylose. The nitrosamine (I) is the

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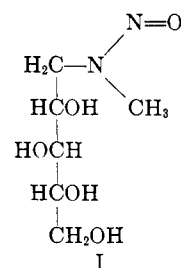
product expected from the treatment of a methylglycamine (1-deoxy-1-methylaminoalditol) with nitrous acid[6] and the methylglycamine could have arisen from the condensation of nitromethane, or a reduction product thereof, with D-xylose so as to have resulted in the

(1) Supported by a grant from the Atlas Chemical Industries, Wilmington, Del.

(2) Department of Biochemistry, State University of Iowa, Iowa City, Iowa.

(3) (a) F. Berger, S. S. Brown, C. L. Leese, G. M. Timmis, and R. Wade, *J. Chem. Soc.*, 846 (1963); (b) D. F. Heath, *Nature*, **192**, 170 (1961).

(4) R. Barker, *J. Org. Chem.*, **29**, 869 (1964).

(5) J. C. Sowden and H. O. L. Fischer, *J. Am. Chem. Soc.*, **69**, 1963 (1947).

(6) A. I. Vogel, "Practical Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1957, p. 426.