Reactions.—Iodine was liberated when the peroxide was brought into contact with KI solution.

Registry No.—Fluorocarbonyl trifluoromethyl peroxide, 16118-40-4.

Acknowledgment.—This work was performed in part under contract with the Office of Naval Research. The nmr spectrum was acquired by B. J. Nist.

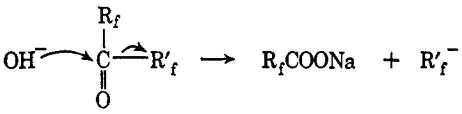
Metal Derivatives of Fluorinated *gem*-Diols

Julianne H. Prager and Paul H. Ogden

Contribution No. 471 from the Central Research Laboratories,
Minnesota Mining and Manufacturing Company,
St. Paul, Minnesota 55101

Received November 15, 1967

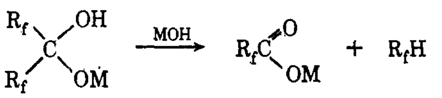
Although the strongly acidic properties of fluorinated *gem*-diols are well known and pK_a values for the first ionization of these compounds have been recorded,[1] their salts have not previously been described. Hexafluoroacetone and chloropentafluoroacetone have been reported to react with excess metal hydroxide to produce the metal trifluoroacetate without haloform formation.[2] Other ketones such as perfluoro-4-heptanone and nitropentafluoroacetone, however, have been shown to form the corresponding haloform with excess base,[3] presumably by a displacement reaction, *i.e.*



$$\mathrm{OH^-} \curvearrowright \overset{R_f}{\underset{\underset{O}{\|}}{C}}\!\!-\!R'_f \longrightarrow R_fCOONa + R'^{-}_f$$

We have examined the reaction of aqueous solutions of several fluorinated ketones with metal hydroxides and find that addition of 1 equiv of base produces salts which are stable and detectable in solution.

Some of these can be isolated, but in most cases such attempts bring about decomposition. In the presence of *excess* base all of these salts decompose, more or less easily, to the related carboxylate and in most cases a haloform. Thus, hexafluoroacetone produces



duces fluoroform in 60% yield upon treatment with excess base, and perfluoro-4-heptanone is converted almost quantitatively into 1-hydroperfluoropropane. Chlorodifluoromethane was obtained only in about 5–10% yield, however, from chloropentafluoroacetone.

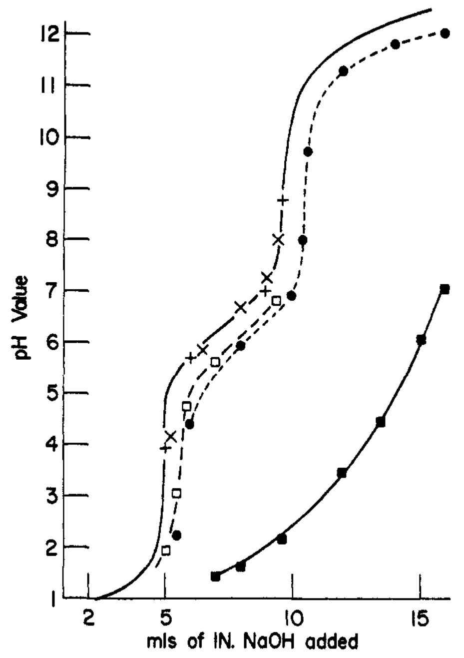


Figure 1.—+, titration of $(CF_3)_2C{=}O$ with sodium hydroxide; ×, titration of $(CF_2Cl)_2C{=}O$ with sodium hydroxide; ●, back-titration of solution + with perchloric acid; ■, back-titration of solution × with perchloric acid; □, back-titration of × from pH 7.0.

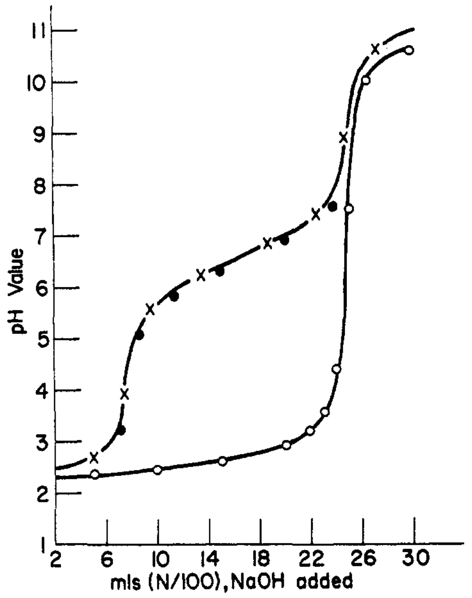


Figure 2.—×, titration of $(C_3F_7)_2C{=}O$ with sodium hydroxide; O, back-titration of × with perchloric acid; ●, back-titration of × from pH 8.0.

The basic hydrolysis of the metal salts of fluorinated *gem*-diols presumably occurs as in Scheme I. The low yield of chlorodifluoromethane from the hydrolysis of chloropentafluoroacetone is believed to result from the reduced stability of the chlorodifluoromethyl anion, which rapidly eliminates chloride ion. The resulting difluorocarbene yields carbon dioxide, and not a haloform, upon hydrolysis. The reactivity of the chlorodifluoromethyl anion was noted by Hine[4] during the hydrolysis of chlorodifluoromethane. The rapid rate at which CHF_2Cl reacted indicated that the half-life of CF_2Cl^- is very short (or possibly that difluorocarbene is eliminated by a concerted reaction).

---

[1] W. J. Middleton and R. V. Lindsey, Jr., *J. Amer. Chem. Soc.*, **86**, 4948 (1964).

[2] Allied Chemical Co., Product Data Sheet PD 56FK-663, 1962.

[3] (a) I. L. Knunyants, *et al., Zh. Vses. Khim. Obshchest.*, **7**, 709 (1962); (b) R. N. Haszeldine, *J. Chem. Soc.*, 1748 (1953).

[4] J. Hine and P. B. Langford, *J. Amer. Chem. Soc.*, **79**, 5497 (1957).

SCHEME I

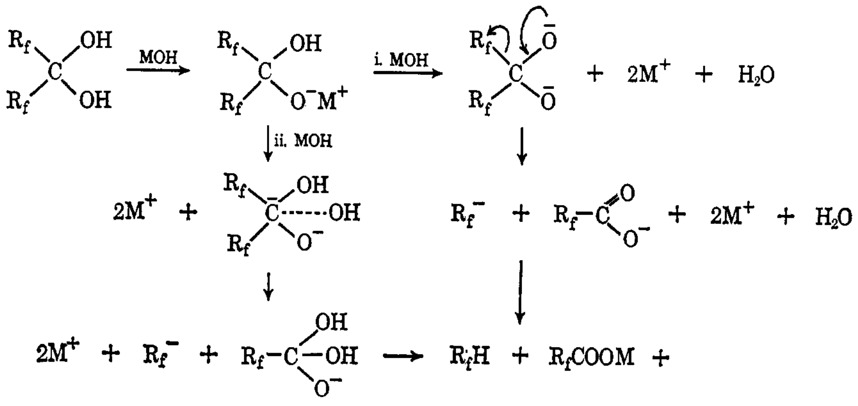
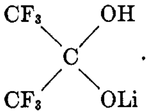
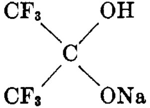
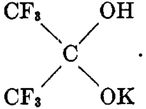
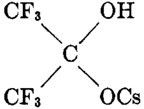
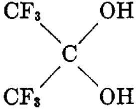


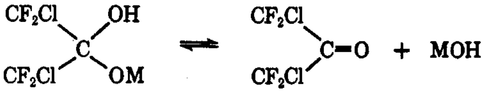
TABLE I: PHYSICAL PROPERTIES OF THE ALKALI METAL SALTS OF $(CF_3)_2C(OH)_2$

Salt		F^{19} nmr	Infrared,[a] µ	Calcd, %			Found, %			Registry no.
				C	H	F	C	H	F	
	$\cdot 1.5H_2O$	82.5	2.73 (s), 2.96 (mb), 8.22, 9.46 10.46, 13.84	16.4	1.8	52.2	16.8	1.7	52.4	16031-69-9
	$\cdot 1H_2O$	83.4	2.6–4.5 (b), 8.35, 9.45, 10.48, 13.82, 14.34	16.1	1.4	51.0	16.6	1.1	50.7	15982-38-4
	$\cdot 1H_2O$	82.5	2.74 (s), 2.91 (s), 2.7–4.5 (b), 8.22, 9.38, 10.40, 13.93	15.0	1.3	47.5	15.5	1.3	48.7	15982-39-5
		81.5	2.7–4.5 (b), 8.35, 9.45, 10.48, 13.89	11.2	0.3	35.4	11.8	1.0	35.7	15982-40-8
		82.3	2.7–4.5 (b), 8.20, 8.55, 9.30, 10.55, 13.90							677-71-4

[a] s = sharp, mb = medium broad, b = broad.

Scheme I implies a dependence of the rate of formation of haloform upon the rate of decomposition of the metal derivative, $(R_f)_2C(OH)OM$, by either route i or ii. Potentiometric titration of aqueous solutions of several fluorinated *gem*-diols with base indicates that there is, indeed, a considerable difference in the stability of these salts. Figures 1 and 2 show the titrations of $(CF_3)_2C(OH)_2$, $(CF_2Cl)_2C(OH)_2$, and $(C_3F_7)_2C(OH)_2$ with aqueous solutions of sodium hydroxide. It can be seen that the salt of hexafluoro-2,2-propanediol is relatively stable, since it is possible to recover the *gem*-diol upon acidification of a solution of high pH. This stability is further evidenced by the isolation of $(CF_3)_2C(OH)ONa$ upon evaporation of its aqueous solution. On the other hand, 1,3-dichlorotetrafluoro-2,2-propanediol and perfluoro-4,4-heptanediol could not be recovered from their highly basic solutions. Evaporation of solutions of these salts (pH 8.0) produced only the corresponding carboxylate.

These latter two metal derivatives, which are clearly present in aqueous solution but decompose upon evaporation of the solvent, probably exist in equilibrium with the corresponding ketone, *i.e.*



Evaporation of a solution of pH 8.0 causes removal of ketone from the system as ketone hydrate, as well as water. This results in a shift in the equilibrium with a corresponding increase in the concentration of metal hydroxide. Decomposition of the salt of the *gem*-diol can then occur *via* the mechanism previously suggested.

The lithium, sodium, potassium, and cesium salts of hexafluoro-2,2-propanediol were prepared by addition of 1 mol of base to the *gem*-diol with subsequent evaporation. They were characterized by their infrared and F^{19} nmr spectra and elemental analyses (Table I). All of these salts are extremely soluble in water and, with the exception of cesium, they contain water of crystallization which was not removed fully even after they had been kept for several days under vacuum. It is interesting to note that the amount of water of crystallization (lithium, 1.5 H_2O; sodium, 1.0; potassium, 1.0; cesium, 0) is in accord with Fajan's rule. These salts are also soluble in certain organic solvents, including acetone, methanol, and diethyl ether.

Thermogravimetric analysis[5] indicates that these salts are thermally unstable, $(CF_3)_2C(OH)ONa$ decomposing at about 100° to produce fluoroform, hexa-

---

[5] For further details, see G. C. Nicholson and P. H. Ogden, *J. Inorg. Nucl. Chem.*, in press.

fluoroacetone, hexafluoro-2,2-propanediol, and the metal trifluoroacetate. Such decomposition products give some support for the previously described mechanism of reaction of fluorinated ketone hydrates with alkali. Thermal decomposition probably involves initial elimination of 1 mol of base from the salt, with subsequent attack of this base on residual salt to form the observed products.

Since the metal salts are unstable in the presence of base, not surprisingly we were unable to prepare dimetal salts.[5a] Evaporation of a solution containing 1 equiv of *gem*-diol and 2 equiv of metal hydroxide yielded metal trifluoroacetate.

Experimental Section

Measurements of pH were made with a Beckman Model G pH meter using a Coleman Instrument 0-11 glass electrode. Infrared spectra were measured on a Perkin-Elmer Model 21 double beam instrument using a 2.5-cm gas cell fitted with NaCl windows or as Nujol mulls. Nuclear magnetic resonance spectra were measured on a Varian V-4502 instrument operating at 40.0 Mc, utilizing acetone as the solvent and an internal reference of trichlorofluoromethane for the determination of chemical shifts. The values reported are phi (ϕ^*) values[6] at a dilution of 10–25%.

Preparation of Metal Salts of Hexafluoro-2,2-propanediol.—A stirred aqueous solution of hexafluoro-2,2-propanediol was carefully titrated with aqueous normal metal hydroxide solution until the pH value reached 8.0. The solution was then evaporated to dryness at room temperature in a stream of air over a period of several days, and finally dried in a vacuum desiccator. The white solid residue was identified as the metal salt of hexafluoro-2,2-propanediol by its infrared and F^{19} nmr spectra together with elemental analyses. These data are summarized in Table I. The ^{19}F nmr spectrum shows a single peak at about ϕ^* 83 corresponding to the CF_3 group, and the infrared spectrum shows broad absorptions at 2.7–4.5 μ, corresponding to OH stretching, and a strong absorption at about 9.5 μ, corresponding to OH bending. In all cases, characteristic absorptions were also present at approximately 8.3, 9.3, 10.4, and 13.9 μ. Strong evidence for the presence of water of crystallization was also observed in the spectra of the lithium, sodium, and potassium salts.

Basic Hydrolysis of Fluorinated *gem*-Diols.—The *gem*-diols, (a) hexafluoro-2,2-propanediol, (b) chloropentafluoro-2,2-propanediol, and (c) perfluoro-4,4-heptanediol, were hydrolyzed by heating with excess 1 *N* sodium hydroxide solution in a conventional hydrolysis bulb. The volatile components were transferred into a vacuum system and distilled through a −78° slush bath. The low-boiling materials were identified by their infrared spectra as (a) fluoroform (60% conversion of $(CF_3)_2C{=}O$), (b) chlorodifluoromethane (5–10% conversion of $CF_3(CF_2Cl)C{=}O$) and carbon dioxide, and (c) 1-hydroperfluoropropane (90% conversion of $(C_3F_7)_2C{=}O$).

Thermal Decomposition of the Sodium Salt of Hexafluoro-2,2-propanediol.—The sodium salt of hexafluoro-2,2-propanediol (2.0 g) was heated under vacuum at 100° for 8 hr and the volatile products (1.2 g) were trapped at −196°. The volatile products were subsequently identified as a mixture of fluoroform, hexafluoroacetone, and hexafluoro-2,2-propanediol by their infrared spectra.

The solid residue (0.7 g) was shown by its infrared spectrum and X-ray powder photograph to contain sodium trifluoroacetate and some sodium fluoride. Although no evidence of sodium hydroxide was detected by this method, this material was probably present in an amorphous state. Pyrolysis of the residue at 270° under vacuum for 1 hr produced further volatile material which was identified by its infrared spectrum as a mixture of carbon dioxide and perfluoroacetyl fluoride. These are typical pyrolysis products from sodium trifluoroacetate.[7] The solid residue was shown by its X-ray powder photograph to be predominantly sodium fluoride.

Attempted Preparation of the Salt of Perfluoro-4,4-heptanediol.—An aqueous solution of perfluoro-4,4-heptanediol was carefully titrated with 0.1 *N* sodium hydroxide solution until a pH value of 8.0 was obtained. Subsequent evaporation to dryness in a stream of dry air at room temperature produced a white solid which was shown, by examination of its infrared spectrum, to be mainly sodium heptafluorobutyrate.

Acknowledgment.—The authors are indebted to Dr. J. J. McBrady for interpreting the F^{19} nmr and infrared spectra and to Mr. P. B. Olson for elemental analyses.

[5a] NOTE ADDED IN PROOF.—It has now been found that careful pyrolysis of $(CF_3)_2C(OH)OLi$ does produce $(CF_3)_2C(OLi)_2$.

[6] G. Filipovich and G. V. D. Tiers, *J. Phys. Chem.*, **63**, 761 (1959).

[7] F. Swarts, *Bull. Sci. Acad. Roy. Belg.*, **8**, 343 (1922).

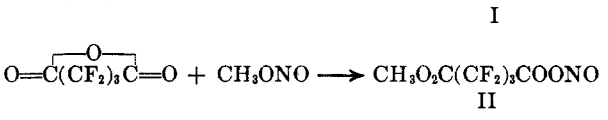
Synthesis of Esters of ω-Nitroso Perfluorinated Carboxylic Acids[1]

EUGENE C. STUMP, WARD H. OLIVER,
AND CALVIN D. PADGETT

Peninsular ChemResearch, Inc., Gainesville, Florida 32601

Received Deecmber 13, 1967

As part of a program to investigate the synthesis and polymerization of functionally substituted, fluorine-containing nitroso compounds, we have found that methyl nitrite will react with both perfluorosuccinic anhydride and perfluoroglutaric anhydride to give the corresponding nitrite esters.



$$O{=}C(CF_2)_2C{=}O\ (\text{ring }{-}O{-}) + CH_3ONO \longrightarrow \underset{\text{I}}{CH_3O_2C(CF_2)_2COONO}$$

$$O{=}C(CF_2)_3C{=}O\ (\text{ring }{-}O{-}) + CH_3ONO \longrightarrow \underset{\text{II}}{CH_3O_2C(CF_2)_3COONO}$$

The reaction was generally carried out by condensing equimolar amounts of the reactants into a sealed glass tube and allowing the tube to warm to room temperature. Larger scale reactions, however, could be run in a three-neck flask at atmospheric pressure by bubbling methyl nitrite into the stirred anhydride and returning unreacted methyl nitrite to the flask by a condenser. The reaction is spontaneous and exothermic, and results in high conversions into the amber, liquid nitrite ester.

The nitrite esters were decarboxylated either by pyrolysis or ultraviolet irradiation to give the corresponding blue, liquid nitroso esters, which could be purified by distillation. Conversions were low

$$CH_3O_2C(CF_2)_2COONO \xrightarrow[\Delta]{\text{uv or}} \underset{\text{III}}{CH_3O_2C(CF_2)_2NO}$$

$$CH_3O_2C(CF_2)_3COONO \xrightarrow[\Delta]{\text{uv or}} \underset{\text{IV}}{CH_3O_2C(CF_2)_3NO}$$

(20–25%) by either method, which may be partially attributed to the formation of nearly equal amounts of a high boiling, colorless by-product. This material was identified as the triester, $[CH_3O_2C(CF_2)_{2,3}]_2NO(CF_2)_{2,3}CO_2CH_3$, (V and VI), which presumably was formed by radical attack on the nitroso ester to give a trisubstituted hydroxylamine.

---

[1] (a) Presented at the 154th meeting of the American Chemical Society, Chicago, Ill., Sept 1967. (b) This work was sponsored by the U. S. Army Natick Laboratories, Natick, Mass., under Contract DA 19-129(AMC)-152 (N) with C. B. Griffis as Project Engineer for the Army.