Journal of Fluorine Chemistry, 12 (1978) 315–320

Received: May 9, 1978

DIRECT SYNTHESIS OF FLUORINATED PEROXIDES. 9. SOME REACTIONS OF PERFLUOROTERTIARYBUTYL HYDROPEROXIDE.[1]

SIN-LING YU and DARRYL D. DESMARTEAU[2]

Department of Chemistry, Kansas State University, Manhattan, Kansas
66506, USA.

SUMMARY

The reaction of $(CF_3)_3COOH$ with perfluoroacyl fluorides in the presence of NaF results in the formation of new peroxy esters of the type, $(CF_3)_3COOC(O)R_f$. Addition of the hydroperoxide to CF_3NCF_2 yields the unstable amine $(CF_3)_3COOCF_2N(H)CF_3$. These reactions of $(CF_3)_3COOH$ are compared with analogous reactions of CF_3OOH and SF_5OOH.

INTRODUCTION

The recent synthesis of $(CF_3)_3COOH$[3] represents the third example of a fluorinated hydroperoxide. The other two examples, CF_3OOH[4] and SF_5OOH[5], have been useful reagents for the synthesis of many CF_3OO- and SF_5OO- derivatives and $(CF_3)_3COOH$ should be equally useful. Unfortunately, whereas CF_3OOH and SF_5OOH are readily obtained in multigram quantities, the preparation of $(CF_3)_3COOH$ is rather difficult. In spite of this limitation, we have investigated several reactions of $(CF_3)_3COOH$ which illustrate its utility in the direct synthesis of fluorinated peroxides.

Reactions with acid fluorides and CF_3NCF_2 proceed in good yield, quite analogous to the reactions of CF_3OOH and SF_5OOH with the same substrates. Three new peroxides are described and these are compared to the related CF_3OO- and SF_5OO-compounds.

EXPERIMENTAL

All volatile compounds were manipulated in a glass or stainless steel vacuum system. The glass system employed glass-Teflon valves throughout and connections were made via ground joints lubricated with Halocarbon grease. The metal system employed Teflon-packed valves and connections were by compression fittings using Teflon ferrules. Pressures were measured with a precision Wallace and Tiernan differential pressure gauge, series 1500.

Ir spectra were obtained on Perkin-Elmer model 337 and 180 spectrometers using 10 cm glass cells fitted with AgCl windows. Nmr spectra were recorded on a Varian XL-100-15 spectrometer using ∿ 10 mol% solutions in $CFCl_3$.

Reagents

The compounds $CF_3C(O)F$ and $C_2F_5C(O)F$ were obtained from PCR Inc. Carbonyl fluoride was prepared by the fluorination of $COCl_2$ with NaF in CH_3CN at 22° and $(CF_3)_3COOH$[3] and CF_3NCF_2[6] were prepared by literature methods.

Preparation of $CF_3C(O)OOC(CF_3)_3$ and $C_2F_5C(O)OOC(CF_3)_3$.

In a typical reaction, 1.0 mmol of $(CF_3)_3COOH$ and 3.0 mmol of R_f-C(O)F were condensed into a 100 ml glass reactor containing 10 g of dry NaF. The mixture allowed to warm slowly from -196 to 22° over a 2 hr interval. The products were collected by vacuum distallation through a trap at -60°.

$CF_3C(O)OOC(CF_3)_3$: yield 90%; mp-45°; mol wt 344.0, calcd 348.0; ir 1836(s), 1355(m), 1295-1255(vs), 1160(s), 1110(s), 1010(s), 957(s), 880(w), 835(m), 770(w), 730(s), 675(w), 600(w), 572(w), 535(w) cm^{-1}; nmr $CF_3^{A}C(O)OOC(CF_3^{B})_3$ ϕ_A^* 70.0, S; ϕ_B^* 69.8,S; $J_{AB} \simeq$ 0Hz.

$C_2F_5C(O)OOC(CF_3)_3$: yield 70%; mp-30°; mol wt 401.0, calcd 398.0; ir 1848(s), 1300-1250(vs), 1230(m), 1190(m), 1105(s), 1016(m), 1000(s), 975(s), 880(w), 843(w), 770(m), 730(s), 640(w), 570(w), 536(m), 485(w) cm^{-1}; nmr $CF_3{}^ACF_2{}^BC(O)OOC(CF_3{}^C)_3$ ϕ_A^* 83.8, m; ϕ_B^* 120.0, q; ϕ_C^* 69.7, q; J_{AB} = 8.3, $J_{AC} \simeq$ 1.0, $J_{BC} \simeq$ 0 Hz.

Preparation of $CF_3N(H)CF_2OOC(CF_3)_3$

The reaction of $(CF_3)_3COOH$ (1.0 mmol) and CF_3NCF_2 (3.0 mmol) was carried out in a 6ml Kel-F reactor. After condensing in the reactants at -196°, the mixture was allowed to stand at 22° for ∿ 2 hours with occasional recooling to -196°, followed by fast warming to 22°. The volatile products were vacuum distilled through traps at -78 and -196°. The product, which slowly decomposes at 22°, was contained in the -78° trap. The -196° trap contained unreacted CF_3NCF_2, CF_3NCO and other unidentified products.

$CF_3N(H)CF_2OOC(CF_3)_3$: yield ∿ 30%; ir 3450(m), 1490(m), 1300-1260 (vs), 1190(s), 1110(vs), 1015(s), 1005(s), 945(w), 860(w), 770(w), 735 (m), 535(w) cm^{-1}; nmr $CF_3{}^AN(H)CF_2{}^BOOC(CF_3{}^C)_3$ ϕ_A^* 80.2, t-d; ϕ_B^* 68.3, m-br; ϕ_C^* 69.2, m; δ(NH)5.0, br; J_{AB} = 8.3, J_{A-H} = 4.0, $J_{B-H} \simeq$ 4.0, J_{BC} < 1.0 Hz.

RESULTS AND DISCUSSION

Reaction of $(CF_3)_3COOH$ with Acyl Fluorides

The reactions of $(CF_3)_3COOH$ with acid fluorides in the presence of NaF produce the corresponding peroxy esters in high yield.

$$(CF_3)_3COOH + R_fC(O)F + NaF \rightarrow (CF_3)_3COOC(O)R_f + NaF{\cdot}HF$$

$$(R_f = CF_3,\ C_2F_5)$$

While only two examples have been studied, these reactions are analogous to the more extensively investigated reactions of CF_3OOH[4] and SF_5OOH[7], and indicate the utility of $(CF_3)_3COOH$ in the direct synthesis of fluorinated peroxides. The new peroxy esters are thermally stable at 22° and characterization by ir, nmr and mol wt was straight forward. Detailed thermal decomposition studies on the new compounds have not been made, but the apparent order of stability for the three classes of fluorinated peroxy esters now available is $CF_3OOC(O)R$ > $SF_5OOC(O)R$ >

$(CF_3)_3COOC(O)R$. If R is a perfluoroalkyl group, the tendency of these compounds towards explosive decomposition is remarkably low. Routine handling of < 1 g quantities of these perfluoro compounds for several years has not resulted in a single explosion.

Reaction of $(CF_3)_3COOH$ with CF_3NCF_2

The reaction of $(CF_3)_3COOH$ with CF_3NCF_2 proceeds in rather low yield compared to the reactions of CF_3OOH and SF_5OOH.[8]

$$(CF_3)_3COOH + CF_3NCF_2 \rightarrow (CF_3)_3COOCF_2N(H)CF_3 \quad (30\%)$$

The resulting amine is unstable at 22°, in contrast to $CF_3OOCF_2N(H)CF_3$ and $SF_5OOCF_2N(H)CF_3$, and was characterized only by ir and nmr. The ir spectrum shows characteristic $(CF_3)_3CO$- frequencies[9] along with $\nu(NH)$ and $\delta(NH)$ at 3450 and 1490 cm^{-1} respectively. The ^{19}F nmr is consistent with that observed for $CF_3OOCF_2N(H)CF_3$ and $SF_5OOCF_2N(H)CF_3$,[8] although the resolution of the CF_2 group is lower.

A major interest in the preparation of $(CF_3)_3COOCF_2N(H)CF_3$ was to dehydrofluorinate the compound with NaF. With $CF_3OOCF_2N(H)CF_3$ and SF_5OOCF_2-$N(H)CF_3$, the reaction results in the formation of the novel cyclic compound, $CF_3\overline{NCF_2O}$.[8]

$$CF_3N(H)CF_2OOCF_3 + NaF \rightarrow COF_2 + NaF{\cdot}HF + CF_3\overline{NCF_2O}$$

$$CF_3N(H)CF_2OOSF_5 + NaF \rightarrow SOF_4 + NaF{\cdot}HF + CF_3\overline{NCF_2O}$$

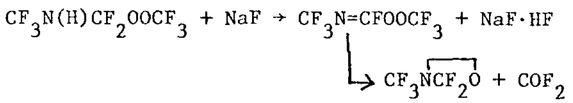
By analogy, it was hoped that the following reaction would occur with $(CF_3)_3COOCF_2N(H)CF_3$.

$$CF_3N(H)CF_2OOC(CF_3)_3 + NaF \rightarrow (CF_3)_2CO + NaF{\cdot}HF + CF_3\overline{NCF(CF_3)O}$$

The main products of the reaction were not $(CF_3)_2CO$ and the oxazirane, but rather $(CF_3)_3COH$ and CF_3NCO. Previously, two possible mechanisms for the reaction of $CF_3OOCF_2N(H)CF_3$ with NaF were suggested.[8]

$$\begin{aligned} CF_3N(H)CF_2OOCF_3 + 2NaF \rightarrow\ & NaN(CF_3)CF_2OOCF_3 + NaF{\cdot}HF \\ & \hookrightarrow NaOCF_3 + CF_3\overline{NCF_2O} \end{aligned}$$

$$NaOCF_3 \rightarrow NaF + COF_2$$

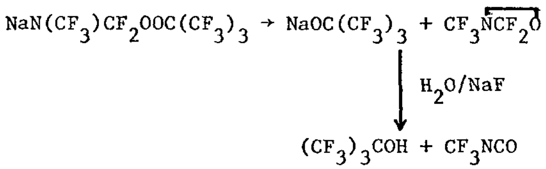


$$CF_3N(H)CF_2OOCF_3 + NaF \rightarrow CF_3N{=}CFOOCF_3 + NaF\cdot HF$$

$$\hookrightarrow CF_3\overline{NCF_2O} + COF_2$$

It would appear based on these results, that the first mechanism is most reasonable. If small amounts of H_2O were present in $CF_3N(H)CF_2OOC(CF_3)_3$ or the NaF, the observed products are consistent with the following reaction sequence.

$$CF_3N(H)CF_2OOC(CF_3)_3 + 2NaF \rightarrow NaN(CF_3)CF_2OOC(CF_3)_3 + NaF\cdot HF$$



$$NaN(CF_3)CF_2OOC(CF_3)_3 \rightarrow NaOC(CF_3)_3 + CF_3\overline{NCF_2O}$$

$$\downarrow H_2O/NaF$$

$$(CF_3)_3COH + CF_3NCO$$

In support of this proposed sequence, subsequent work with $CF_3\overline{NCF_2O}$ shows that it can be readily converted to CF_3NCO by H_2O[10], and $NaOC(CF_3)_3$ will react with H_2O to form $(CF_3)_3COH$.

ACKNOWLEDGEMENT

The financial support of the National Science Foundation and the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

REFERENCES

1 Part 8. S.-L. Yu and D. D. DesMarteau, Inorg. Chem., 17, 0000 (1978).

2 Alfred P. Sloan Fellow, 1975-77.

3 S.-L. Yu and D. D. DesMarteau, Inorg. Chem., 17, 304 (1978).

4 P. A. Bernstein, F. A. Hohorst and D. D. DesMarteau, J. Am. Chem. Soc., 93, 3882 (1971).

5 D. D. DesMarteau, J. Am. Chem. Soc., 94, 8933 (1972). D. D. DesMarteau and R. M. Hammaker, Israel J. Chem., 17, 000 (1978).

6 D. A. Barr and R. N. Haszeldine, J. Chem. Soc., 1881 (1955).

7 M. J. Hopkinson and D. D. DesMarteau, J. Fluorine Chem., 7, 501 (1976).

8 E. R. Falardeau and D. D. DesMarteau, J. Am. Chem. Soc., 98, 3529 (1976).

9 N. Walker and D. D. DesMarteau, J. Fluorine Chem., 5, 127 (1975).

10 A. Sekiya and D. D. DesMarteau, to be published.