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Direct Synthesis of Fluorinated Peroxides. 7. Perfluoro-*tert*-butyl Fluoroformyl Peroxide[1]

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The synthesis and properties of the new peroxides $(CF_3)_3COOC(O)F$, $(CF_3)_3COOC(O)OCF_3$, $(CF_3)_3COOH$, $(CF_3)_3COOCF_2OF$, $(CF_3)_3COOCF_2OCl$, and $(CF_3)_3COOCl$ are described. The fluoroformyl peroxide, $(CF_3)_3COOC(O)F$, is prepared from $(CF_3)_3COOSO_2F$ by a novel nucleophilic substitution reaction and it is the precursor to the other compounds.

The perfluoro-*tert*-butoxy group has a high electronegativity as shown by the properties of the alcohol[3] and the existence of stable halogen derivatives $(CF_3)_3COX$ (X = Cl, F).[4,5] Two peroxides containing this group are well characterized, $(CF_3)_3COOC(CF_3)_3$[6] and $(CF_3)_3COOSO_2F$,[7] and it was of interest to synthesize other peroxygen derivatives in order to ascertain if this electronegative group was capable of stabilizing certain unusual structures containing oxygen–oxygen bonds.

In previous work by us, comparisons of peroxygen derivatives containing CF_3O and SF_5O groups had demonstrated greater thermal stability for the trifluoromethyl derivatives in all cases, although it was possible to obtain analogous compounds with each, i.e., R_fO_2X (X = H, Cl, F), $R_fO_3R_f$, and R_fO_2R where R = a variety of halogenated and nonhalogenated organic and inorganic radicals. With the $(CF_3)_3CO$ group, we hoped to obtain compounds with thermal stabilities equal to or exceeding those of the trifluoromethyl compounds.

In order to prepare a variety of perfluoro-*tert*-butyl peroxygen derivatives, we believed that the hydroperoxide, $(CF_3)_3COOH$, would be the key reagent just as CF_3OOH and SF_5OOH had been for compounds containing these groups. The only practical route to these hydroperoxides is via the hydrolysis of the fluoroformyl peroxides, $R_fOOC(O)F$. In this paper we describe the synthesis and properties of $(CF_3)_3COOC(O)F$ and its conversion to certain other new peroxygen compounds.

Experimental Section

General. Volatile compounds were handled in a glass and stainless steel vacuum system equipped with glass–Teflon or stainless steel valves. Pressures were measured with a Wallace and Tiernan differential pressures gauge, Series 1500. All reactions were carried out in 75-mL 304 stainless steel reactors or glass bulbs fitted with glass–Teflon valves. Separation of volatile products was by trap to trap distillation and GLC using columns packed with 40% Halocarbon 11-21 polymer oil on Chromosorb P.

Infrared spectra were recorded on Perkin-Elmer Model 180 and 337 spectrometers using 10-cm gas cells fitted with AgCl windows. Raman spectra were recorded on a Spex 14018 monochrometer employing photon counting detection. Excitation was by the 514.5-nm line of an argon laser. NMR spectra were recorded on a Varian XL-100-15 spectrometer using 15 mol % solutions in $CFCl_3$.

Reagents. $(CF_3)_3COOSO_2F$ was obtained by the literature method.[7] Carbonyl fluoride was prepared by reacting $COCl_2$ with NaF in CH_3CN at 40 °C. Chlorine monofluoride was prepared by heating equimolar amounts of Cl_2 and F_2 at 250 °C in a Monel bomb. Fluorine was obtained from Air Products and passed through a NaF scrubber before use. Potassium fluoride and CsF were activated by placing the solids in a metal reactor containing several stainless steel balls. They were pumped under dynamic vacuum for 12 h (CsF, 22 °C; KF, 80 °C) and then treated with 2 atm of F_2 for several hours. The vessels were violently agitated in a paint shaker several times with the F_2. All other reagents were obtained from commercial sources and used without further purification.

Preparation of $(CF_3)_3COOC(O)F$. In a typical reaction, 2 mmol of $(CF_3)_3COOSO_2F$ and 10 mmol of COF_2 were condensed into a metal reactor containing ~20 g of activated KF. The reactor was held at ~23 °C for 1 day, and the contents were then fractionated through traps at −30, −78, and −196 °C. The −30 °C trap contained a colorless liquid, identified as $(CF_3)_3COOC(O)OCF_3$ (see below). The −78 °C trap contained a mixture of $(CF_3)_3COOSO_2F$, $(CF_3)_3COC(O)F$, and $(CF)_3COOC(O)F$,[9] which was separated by GLC. The −196 °C trap contained COF_2, SO_2F_2, and small amounts of $(CF_3)_2CO$ and CF_3OSO_2F. Yields of $(CF_3)_3COOC(O)F$ were highly variable and the average yield was ~30%. $(CF_3)_3COOC(O)F$: mol wt 296.0, calcd 298.0; bp 60.9 °C; $\log P(\mathrm{mm}) = 8.2655 - (1798.9/T)$; $\Delta H_v = 8.23$ kcal/mol; $\Delta S_v = 24.6$ eu; IR 1915 (s), 1310–1260 (vs), 1185 (s), 1105 (s), 1015 (s), 980 (s), 890 (w), 770 (m), 735 (m), 614 (m), 532 (m), 498 (m) cm^{-1}; ^{19}F NMR $\phi^*((CF_3)_3C)$ 70.0, $\phi^*(C(O)F)$ 30.9, $J_{FF} \simeq 0.5$ Hz.

Preparation of $(CF_3)_3COOC(O)OCF_3$. Using a procedure similar to that for $(CF_3)_3COOC(O)F$, 2 mmol of $(CF_3)_3COOSO_2F$ and 10 mmol of COF_2 were added to a metal reactor containing activated KF. After 50 h at 23 °C, the contents were separated through −30, −75, and −196 °C traps. The −196 °C trap contained SO_2F_2 and small amounts of $(CF_3)_2CO$ and CF_3OSO_2F. The excess COF_2 was absorbed by the KF, as proven by subsequent fluorination to yield the expected amount of CF_3OF. The −78 °C trap contained a small amount of $(CF_3)_3COOC(O)F$ and $(CF_3)_3COC(O)F$ and the −30 °C trap an ~90% yield of $(CF_3)_3COOC(O)OCF_3$. The yield of the latter varies depending on the activity of the KF. If the KF will absorb considerable amounts of COF_2, the yield is high. $(CF_3)_3COOC(O)OCF_3$: mp ca. −30 °C; mol wt 362, calcd 364.0; IR 1880 (m), 1865 (w), 1310–1260 (vs), 1230 (w), 1190 (w), 1165 (s), 1138 (w), 1110 (sh), 1100 (s), 1053 (w), 1010 (s), 985 (s), 959 (m), 880 (w), 850 (w), 728 (m, complex), 590 (w), 578 (w), 537 (w); ^{19}F NMR $\phi^*((CF_3)_3C)$ 70.19, $\phi^*(CF_3)$ 70.24, $J_{F-F} \simeq 0$ Hz.

Preparation of $(CF_3)_3COOH$. A typical reaction was carried out by condensing 1.0 mmol of $(CF_3)_3COOC(O)F$ into a 1-L glass reactor containing ~10 mmol of H_2O. The temperature was held at 0 °C for 1 day and the contents were separated by pumping through traps at −40, −78, and −196 °C. The −40 °C trap contained H_2O and other products, the −78 °C trap contained a mixture of $(CF_3)_3COH$ and $(CF_3)_3COOH$ and the −196 °C trap contained CO_2. The hydroperoxide was purified by GLC giving a yield of ~80%.

$(CF_3)_3COOH$: mol wt 256.0, calcd 252.0; mp −35 to −37 °C; bp 72 °C; $\log P(\mathrm{mm}) = 8.423 - (1.914/T)$; $\Delta H_v = 8.76$ kcal/mol; $\Delta S_v = 25.36$ eu; IR 3580 (m), 1379 (m), 1310–1250 (vs), 1182 (m), 1110 (s), 1010 (s), 988 (s), 880 (w), 765 (w), 730 (Q, s), 542 (w), 495 (w) cm^{-1}; Raman (l) 1300 (w, br), 1120 (w, br), 1044 (w, p), 1031 (m, p), 885 (m, p) 865 (w), 775 (vs, p), 752 (m, p), 740 (w), 648 (w, p), 576 (w, dp), 546 (m, dp), 507 (w, p), 374 (m, p), 320 (s, p), 244 (w, p), 155 (w, br), 125 (w, p) cm^{-1}; NMR $\phi^*((CF_3)_3C)$ 70.7, δ 3.6, $J_{F-H} \simeq 0$ Hz.

Preparation of $(CF_3)_3COOCF_2OF$. $(CF_3)_3COOC(O)F$ (1.0 mmol) was condensed into a metal reactor containing ~10 g of dry powdered CsF. F_2 (2 mmol) was added and the vessel was held at −78 °C for 15 h. The excess fluorine was then removed at −196 °C and the product was collected at −111 °C. Essentially complete conversion was observed. $(CF_3)_3COOCF_2OF$: mol wt 326.0, calcd 328.0; bp 74 °C; $\log P(\mathrm{mm})\ 11.120 - (3990.5/T) + (392860/T^2)$; $\Delta H_v = 7.8$ kcal/mol; $\Delta S_v = 22.7$ eu; IR 1315–1260 (vs), 1240 (m), 1201 (s), 1178 (s), 1110 (vs), 1018 (s), 984 (s) 944 (w), 890 (w), 775 (w), 732 (m), 654 (w), 539 (w), 507 (w) cm^{-1}; NMR $(CF_3)_3{}^{A}COOCF_2{}^{B}OF^{C}$, ϕ_A^* 69.95, ϕ_B^* 59.82, ϕ_C^* −157.5, $J_{AB} = 1.5$, $J_{BC} = 34.5$, $J_{AC} \simeq 0$ Hz.

Preparation of $(CF_3)_3COOCl$. In a typical reaction, 1.2 mmol of $(CF_3)_3COOC(O)F$ and 1.3 mmol of ClF were condensed into a metal reactor containing 15 g of CsF. The vessel was maintained at −65

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°C for 2 days. The contents were then pumped through traps at −60, −78, and −196 °C as the vessel warmed from −65 °C. All connections were as short as possible. The −60 °C trap contained a small amount of $(CF_3)_3COOCF_2OCl$ (see Discussion), the −78 °C trap contained $(CF_3)_3COOCl$, and the −196 °C trap contained COF_2 and a small amount of CF_3Cl. The amount of COF_2 corresponded to 1.2 mmol and agrees with the calculated amount for the reaction

$$(CF_3)_3COOC(O)F + ClF \xrightarrow{CsF} (CF_3)_3COOCl + COF_2$$

$$CF_2(OF)_2 + CsOCF_3 + COF_2 \rightarrow CF_3OF + CsF + CF_3OOC(O)F$$

The instability of $(CF_3)_3COOCl$ prevented complete characterization. Decomposition to CF_3Cl, $(CF_3)_2CO$, and O_2 was rapid at 22 °C. The relative amounts of the decomposition products were in the ratio 1:1:0.5, respectively. By transferring a sample through a short connection an NMR sample was prepared and run at −65 °C. The major component was a singlet at ϕ^* 69.57.

Results and Discussion

Preparation of $(CF_3)_3COOC(O)F$. The syntheses of $CF_3OOC(O)F$[10] and $SF_5OOC(O)F$[11] are easily carried out by quite different methods as shown in the following idealized equations.

$$2SF_5OCl + FC(O)OOC(O)F \xrightarrow{h\nu} 2SF_5OOC(O)F + Cl_2$$

In order to prepare $(CF_3)_3COOC(O)F$, a photochemical reaction between $(CF_3)_3COCl$ and $FC(O)OOC(O)F$ seemed the logical choice. However, after considerable effort, no trace of the desired compound was found by this procedure. It appeared either that the compound was unstable or that a nonphotochemical method of synthesis was needed. A good possibility for the latter appeared to be the nucleophilic attack by fluorine on sulfur in $(CF_3)_3COOSO_2F$ to give the peroxy anion $(CF_3)_3COO^-$ and SO_2F_2. This anion could then react with COF_2 to give the desired compound. There was some evidence in the literature to suggest that generation of a peroxy anion by this method was plausible.[12]

Cesium fluoride was tried first as the fluoride source, but its activity was sufficient to attack both $(CF_3)_3COOSO_2F$ and the desired compound so that only traces of the latter were obtained. A change to KF finally proved successful. We propose the following scheme for the preparation of $(CF_3)_3COOC(O)F$, although we have no direct proof that the peroxy anion, $(CF_3)_3COO^-$, is actually formed in the reaction.

$$(CF_3)_3COOSO_2F + KF \rightarrow (CF_3)_3COOK + SO_2F_2$$
$$(CF_3)_3COOK + COF_2 \rightarrow KF + (CF_3)_3COOC(O)F$$

This reaction would be ideal except for four side reactions that are always present.

$$KOOC(CF_3)_3 \rightarrow KOC(CF_3)_3 + {}^1/_2O_2$$
$$KOC(CF_3)_3 + COF_2 \rightarrow KF + (CF_3)_3COC(O)F$$
$$KF + COF_2 \rightarrow KOCF_3$$
$$KOCF_3 + (CF_3)_3COOC(O)F \rightarrow KF + (CF_3)_3COOC(O)OCF_3$$

The last two reactions are strongly dependent on the activity of the KF. If it is too active, the peroxy carbonate is the major product. On the other hand, if its activity is too low, attack on $(CF_3)_3COOSO_2F$ is slow and conversion to either $(CF_3)_3COOC(O)F$ or $(CF_3)_3COOC(O)OCF_3$ is low. Sodium fluoride is inactive and RbF is too active. In short we found no satisfactory way to avoid the side reaction except that by chance the KF activity was occassionally just right to give $(CF_3)_3COOC(O)F$ as the main product.

The new peroxyfluoroformate is only the third example of this type of compound and it is stable at 22 °C as are $CF_3OOC(O)F$[10] and $SF_5OOC(O)F$.[13] Unfortunately, it is far more difficult to obtain in appreciable quantities.

Reactions of $(CF_3)_3COOC(O)F$. In order to compare the three known compounds of this type, reactions with H_2O, F_2, and ClF were carried out. These reactions had previously given high yields of R_fOOH,[14,15] R_fOOCF_2OF,[8,15] and R_fOOCl[11,17] with the trifluoromethyl and pentafluorosulfur derivatives, and it was hoped that similar results would be found for the perfluoro-*tert*-butyl derivative. With H_2O and F_2, the results were identical. With ClF a more complex but interesting reaction was observed.

Hydrolysis of $(CF_3)_3COOC(O)F$ is best carried out in the gas phase at 0 °C.

$$(CF_3)_3COOC(O)F + H_2O \xrightarrow{0\,°C} (CF_3)_3COOH + CO_2 + HF$$

The HF is consumed by the glass container and up to 80% yields of the hydroperoxide are obtained. The main difficulty with this reaction was the formation of $(CF_3)_3COH$ along with the peroxide. They can only be separated by GLC and this proved tedious. The alcohol may be formed by loss of oxygen, although it is possible that it comes from a reaction of the hydroperoxide with H_2O to form H_2O_2 and alcohol. The corresponding hydroxy compounds are not observed with $CF_3OOC(O)F$ and $SF_5OOC(O)F$ if they are in fact formed, because both CF_3OH[18] and SF_5OH[19] are very unstable at 22 °C. Like SF_5OOH and CF_3OOH, $(CF_3)_3COOH$ is a stable, water-like liquid at 22 °C. The pK_a of the compound was not determined, but it is believed to be as acidic as CF_3OOH.[15]

The hydrolysis of $(CF_3)_3COOC(O)OCF_3$ was also carried out as a possible alternate route to $(CF_3)_3COOH$, since the peroxycarbonate is more easily prepared than $(CF_3)_3COOC(O)F$. Unfortunately the rate of hydrolysis was too slow to be of use. If the hydrolysis of compounds of the $R_fOOC(O)X$ type proceed by the addition of H_2O to form a *gem*-diol, followed by an elimination reaction, the formation of HF in the case of $R_fOOC(O)F$ is clearly the driving force for these reactions.[8]

$$R_fOOC(O)X + H_2O = R_fOOC(OH)_2X$$
$$R_fOOC(OH)_2X \rightarrow R_fOOH + CO_2 + HX$$

The reaction of $(CF_3)_3COOC(O)F$ with F_2 in the presence of CsF is identical for all three fluoroformyl peroxides.

$$(CF_3)_3COOC(O)F + F_2 \xrightarrow{CsF,\ -78\,°C} (CF_3)_3COOCF_2OF$$

The new peroxy-OF derivative is one of ten known compounds of this type and underwent no decomposition in glass after several hours at 35 °C.[20]

The reaction of $R_fOOC(O)F$ with ClF in the presence of CsF is an effective preparative route to R_fOOCl. In previous work with $R_f = CF_3$ and SF_5, we suggested that reaction occurred by the addition of ClF across the carbonyl group, followed by elimination of COF_2.

$$R_fOOC(O)F + ClF \xrightarrow{CsF,\ -78\,°C} R_fOOCF_2OCl$$
$$R_fOOCF_2OCl \rightarrow R_fOOCl + COF_2$$

In the previous work, we could not obtain any evidence for the intermediate hypochlorite. However, with $(CF_3)_3COOC(O)F$, we believe the unstable intermediate hypochlorite is observed. If the reaction is carried out at −78 °C, an unstable yellow liquid, thought to be $(CF_3)_3COOCF_2OCl$, can be trapped at −65 °C. On warming, this material decomposes cleanly to COF_2, O_2, CF_3Cl, and $(CF_3)_2CO$. If the reaction is carried out at −60 to −65 °C, a different compound, believed to be $(CF_3)_3COOCl$ is formed along with an equal amount of COF_2. While both materials are too unstable to be well characterized, we believe these results are explicable in the following way.

$$(CF_3)_3COOC(O)F + ClF \xrightarrow{CsF,\ -78\ ^\circ C} (CF_3)_3COOCF_2OCl$$

$$(CF_3)_3COOCF_2OCl \xrightarrow{-65\ ^\circ C} (CF_3)_3COOCl + COF_2$$

$$(CF_3)_3COOCl \xrightarrow{22\ ^\circ C} CF_3Cl + (CF_3)_2CO + {}^1/_2O_2$$

$$(CF_3)_3COOCF_2OCl \xrightarrow{22\ ^\circ C} CF_3Cl + COF_2 + (CF_3)_2O + {}^1/_2O_2$$

This supports our earlier contention that the reactions of $R_fOOC(O)F$ with F_2 and ClF in the presence of CsF are identical, but the OF derivatives are stable. However, it was most disappointing to find the thermal stability of $(CF_3)_3COOCl$ so low. Both CF_3OOCl and SF_5OOCl are unstable at 22 °C, but they can be prepared and isolated pure in reasonable quantities. Both are very useful reagents for the direct synthesis of fluorinated peroxides.[17]

General Properties. All the new compounds except $(CF_3)_3COOCl$ and $(CF_3)_3COOCF_2OCl$ have been characterized by IR and NMR and physical properties. Each exhibits IR and NMR spectra consistent with the presence of a $(CF_3)_3CO-$ group[7,9] and different from those of the related nonperoxides, where known [$(CF_3)_3COH$,[22] $(CF_3)_3COC(O)F$,[7] and $(CF_3)_3COCl$[5]]. The peroxide link in $(CF_3)_3COOH$ is supported by its Raman band at 885 cm^{-1},[23] which is absent in the corresponding alcohol run under identical conditions. The molecular weights of all compounds were close to the expected values.

Except for $(CF_3)_3COOCl$ and $(CF_3)_3COOCF_3OCl$ as discussed above, all the compounds are stable colorless liquids at 22 °C. However, the presence of the peroxide linkage provides a relatively low energy path for decomposition. As has been observed previously for $(CF_3)_3CO$ derivatives containing a weak bond, a major decomposition product is hexafluoroacetone. Considering the clean thermal decomposition of $(CF_3)_3COX$ (X = Cl, F) to CF_3X and $(CF_3)_2CO$, the peroxides decompose in a predictable way.

$$(CF_3)_3COOC(O)F \xrightarrow{80\ ^\circ C} (CF_3)_2CO + CF_3OC(O)F$$

$$(CF_3)_3COOC(O)OCF_3 \xrightarrow{80\ ^\circ C} (CF_3)_2CO + CO_2 + CF_3OCF_3$$

$$(CF_3)_3COOH \xrightarrow{120\ ^\circ C} COF_2 + HF + (CF_3)_2CO$$

$$(CF_3)_3COOCl \xrightarrow{22\ ^\circ C} CF_3Cl + (CF_3)_2CO + {}^1/_2O_2$$

The effect of a peroxide or OX bond on thermal stability is illustrated by the fact that $(CF_3)_3COC(O)CF_3$ does not decompose readily even at 500 °C. While the latter is expected to be more stable, it is formally the dimer of hexafluoroacetone.

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Registry No. $(CF_3)_3COOC(O)F$, 64957-47-7; $(CF_3)_3COOC(O)OCF_3$, 64957-48-8; $(CF_3)_3COOH$, 64957-49-9; $(CF_3)_3COOCF_2OF$, 64957-50-2; $(CF_3)_3COOCl$, 64957-51-3; $(CF_3)_3COOSO_2F$, 55064-77-2; COF_2, 353-50-4; F_2, 7782-41-4; ClF, 7790-89-8.

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Electrochemical Preparation of Anhydrous Halides of Transition Metals (Mn–Zn)

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Elemental manganese, iron, cobalt, nickel, copper, and zinc can be oxidized electrochemically at room temperature with halogen (Cl_2, Br_2, I_2) dissolved in an organic solvent mixture. The final products are the anhydrous metal halides, which are important starting materials for synthetic work. In most cases the halides are recovered as solvates of CH_3OH or CH_3CN, which can be removed by heating in vacuo. Adducts of the halides can be prepared in situ in the electrochemical cell or preferably by subsequent reaction. The mechanism of the electrochemical oxidation processes is discussed.

Introduction

Anhydrous halides of metals are important starting materials in many synthetic routes to inorganic and organometallic compounds, but the preparation of the halides themselves is not always a simple problem. Many hydrated halides decompose rather than dehydrate on heating, and the removal of water from such salts requires treatment with thionyl chloride or a similar reagent, although the product may even then be unsatisfactory for some purposes.[1] The alternative routes involve high-temperature reactions between metal and halogen, metal oxide and hydrogen halide, etc. We return to this point later but note here that such procedures have obvious disadvantages.

The present paper is one of a series reporting the preparation of metal halides, anionic halide complexes, and organometallic compounds by electrochemical oxidation of a metal in the

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