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A NEW REACTIVE MERCURIAL FORMED BY INSERTION OF MERCURY INTO THE O-Cl BOND OF $(CF_3)_3COCl$

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SUMMARY

Elemental mercury inserted into the O-Cl bond of $(CF_3)_3COCl$ to form a stable white solid which when reacted with $CF_3C(O)Br$, CH_3I, $CH_3C(O)Cl$, $(CH_3)_3SiCl$ and $CF_3C(O)SCl$ gave $CF_3C(O)R_f$ ($R_f = (CF_3)_3CO$), CH_3R_f, $CH_3C(O)R_f$, $(CH_3)_3SiR_f$ and the unstable $CF_3C(O)SR_f$. Hydrogen was abstracted from $(CH_3)_3SiH$ to form the silate ester. With $(CF_3)_2C{=}NH$, $(CF_3)_3COH$ was released leaving a solid residue which when treated with Cl_2 gave $(CF_3)_2C{=}NCl$.

INTRODUCTION

It is particularly appropriate that a paper which is dedicated to Professor Emeléus should describe the synthesis and reaction chemistry of a new fluorinated mercurial. In his Cambridge laboratory, the formation of the mercury derivatives, CF_3HgI and $(CF_3)_2Hg$, by photolyzing CF_3I in the presence of mercury and by the action of silver, copper, or cadmium amalgam on trifluoromethylmercuric iodide was the first report of the existence of a perfluoroalkyl organometallic compound [1,2]. Studies were made of the interaction of $(CF_3)_2Hg$ and potassium halides which led to the formation of the complexes $KHg(CF_3)_2X$ and $K_2Hg(CF_3)_2X_2$ [3]. Also, bis(trifluoromethylthio)mercury which has been used widely to introduce the CF_3S- moiety into hundreds of compounds was first

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prepared and used as a synthetic reagent in his laboratory [4-7]. While first prepared by Young et al. [8], Emeléus and Hurst [9] demonstrated later that the fluorination of cyanogen chloride with mercury(II) fluoride was a convenient route to $[(CF_3)_2N]_2Hg$. Mercury(II) fluoride with $(CF_3)_2NN{=}CF_2$ at 140°C formed $[(CF_3)_2NNCF_3]_2Hg$ [10]. Subsequently it was shown that mercury, when shaken with an excess of the stable magenta radical, $(CF_3)_2NO\cdot$, was converted to a very reactive white solid, $[(CF_3)_2NO]_2Hg$ [11]. The reaction chemistries of the mercurials $(R_f)_2N$-Hg-$N(R_f)_2$, R_fS-Hg-$N(R_f)_2$, R-Hg-$N(R_f)_2$ [12] and $(CF_3)_2NO$-Hg-$ON(CF_3)_2$ [12, 13] have been reviewed recently.

Perfluoroalkyl chloroformates and chlorosulfates are the products of the insertion of carbon monoxide and sulfur dioxide into the oxygen-chlorine bond in perfluoroalkyl hypochlorites [14,15]. We now find that mercury also inserts into the O-Cl bond of perfluoro-tert-butyl hypochlorite to give rise to a reactive mercurial which is useful for the introduction of the $(CF_3)_3CO$- group into a variety of compounds.

RESULTS AND DISCUSSION

Mercury and perfluoro-tert-butyl hypochlorite were reacted in a 1:2 molar ratio in the presence of freshly dried Freon 11 (CCl_3F). After shaking for 24 hr, the volatile materials were removed to leave a powdery white solid whose weight indicated that the reaction stoichiometry was 1:1. Continued agitation with more hypochlorite did not alter this ratio. This suggested that the reaction which occurred was

$$(CF_3)_3COCl \;+\; Hg \xrightarrow{CCl_3F} (CF_3)COHgCl$$

Mass spectral data supported this reaction with peaks which were assigned to $ClHgOC(CF_3)_2(CF_2)^+(M^+-F)$, $ClHgOC(CF_2)_3^+$, $ClHgCC(CF_2)_2^+$, $ClHgOC(CF_2)^+$ and $HgCl_2^+$ (base peak). ^{19}F nuclear magnetic resonance spectra showed the presence of a single sharp peak at ϕ75.9. A liquid infrared spectrum which was measured on the mercurial dissolved in dry tetrahydrofuran contained bands at 1289s, 1262vs, 1221vs, 1206s, 1161m, 965s, 930m, 830vs, 720vs, 535w and 380 cm^{-1} w. The infrared spectrum obtained of $HgCl_2$ in tetrahydrofuran did not contain any of the above frequencies. Therefore, the intense peak found in the mass spectrum and assigned to $HgCl_2^+$ must arise from recombination. Further mass spectral studies are underway.

The synthesis of the mercurial could be carried out with equal ease in CCl_3F, CH_2Cl_2 or $\emptyset CH_3$. Unlike bis(trifluoromethyl)mercury and bis(trifluoromethylthio)mercury, but similar to $[(CF_3)_2NO]_2Hg$ and $[(CF_3)_2N]_2Hg$, the white solid is extremely sensitive to moisture, hydrolyzing instantaneously to form yellow mercury(II) oxide and perfluoro-tert-butyl alcohol. Like the fluoroalkylaminomercury compounds, it is soluble in freshly dried tetrahydrofuran but not in CCl_3F. It is stable at 25°C in Pyrex glass under vacuum for extended periods.

In its reactions with compounds which contain labile halogens, the products seemed to form in reasonable yield with or without solvent. One exception which might be cited was the case with CNCl where, in the absence of a solvent, the gaseous reactant was taken up by the solid mercurial and the product, $(CF_3)_3COCN$, was released only upon the addition of some other reactive material or by carrying out the reaction in toluene.

With CF_3SCl, the ester of trifluoromethanesulfenic acid, perfluoro-tert-butyl trifluoromethanesulfenate $[CF_3SOC(CF_3)_3]$, was formed in about 90% yield. There is apparently only one other totally fluorinated ester of this type, $(CF_3)_2CFSOCF(CF_3)_2$, which was obtained when $[(CF_3)_2CF]_2SF_2$ was heated with B_2O_3 at 150°C [16]. Others, such as $CFCl_2SOCF_3$ [17] and those obtainable from R_fSCl with ROH (R = alkyl, fluoroalkyl) [18,19] or $Hg(SCF_3)_2$ with ROCl ($R = CH_3$, C_2H_5) [20], are in the literature. To our surprise, we were not successful in preparing this ester either from a neat mixture of CF_3SCl with $(CF_3)_3COH$ or with $(C_2H_5)_3N$ added. However, with the mercurial the ester formation proceeded smoothly.

A quantitative yield of $CF_3C(O)OC(CF_3)_3$ was produced when $CF_3C(O)Br$ was reacted with an excess of the mercurial. It was identified by comparison of infrared and mass spectral data with those given in the literature [21]. Perfluoro-tert-butyl trifluoroacetate resulted also from the decomposition of $CF_3C(O)SOC(CF_3)_3$ which was formed when $CF_3C(O)SCl$ was added to the mercurial. Elemental sulfur was the other product. Although there are examples of compounds, $R_fC(O)SR$ [22,23], formed by the addition of $R_fC(O)SH$ to olefins, there seem to be no reports of other thioperoxides of this type. Analogous peroxides are well known and are stable [24].

In none of the reactions did chlorine-halogen exchange between $ClHgOC(CF_3)_3$ and reactant occur. With CH_3I, red HgI_2 formed on contact and after a few hours the colorless methyl ester could be distilled off in 73% yield. Similarly with $(CH_3)_3SiCl$ and $CH_3C(O)Cl$ the metathetical reactions occurred neat and the volatile products, $(CH_3)_3SiOC(CF_3)_3$ (70%) and $CH_3C(O)OC(CF_3)_3$ (∿100%), were purified by gas chromatography. These stable colorless compounds are relatively volatile liquids, e.g., $(CH_3)_3SiOC(CF_3)_3$ has a vapor pressure of 112 Torr at 28.8°C. One of the preparations of $CH_3C(O)OC(CF_3)_3$ was carried out using an excess of $CH_3C(O)Cl$ with a carefully weighed amount of the mercurial. All of the $(CF_3)_3CO$- contained by the mercurial was exchanged to form $CH_3C(O)OC(CF_3)_3$.

It is particularly interesting to note that the mercurial will abstract hydrogen atoms from $(CH_3)_3SiH$ to form the same ester, $(CH_3)_3SiO$-$C(CF_3)_3$ although in somewhat lower yield. An equimolar quantity of $(CF_3)_3COH$ and, also, elemental mercury were formed. This behavior is similar to that reported for $[(CF_3)_2NO]_2Hg$ [25] with compounds which contained Si-H, Ge-H, N-H, As-H, C-H or Sb-H bonds. After hexafluoroisopropylidenimine, $(CF_3)_2C{=}NH$, was allowed to contact an excess of the mercurial at 0°C for 12 hr, it was completely replaced by approximately an equivalent amount of $(CF_3)_3COH$ as the only volatile material in the reaction flask. When an excess of chlorine gas was added to the solid residue, a 94% yield of $(CF_3)_2C{=}NCl$ was obtained. This would support the formation of another solid mercurial which contained $-Hg-N{=}C(CF_3)_2$.

The new compounds have been characterized in the usual manner with infrared, mass and ^{19}F and ^{1}H NMR spectral and elemental analyses data. When the mass spectra were measured at 17 eV with a reduced inlet temperature (<50°C), molecular ions were usually obtained.

EXPERIMENTAL

Materials

The compounds used in this work were obtained from commercial sources --- $(CF_3)_3COH$, $(CH_3)_3SiCl$, $(CH_3)_3SiH$ and $CF_3C(O)SH$ (PCR); and CH_3I and $CH_3C(O)Cl$ (J. T. Baker) or via literature methods --- CF_3SCl [26], $(CF_3)_2C{=}NH$ [27], $(CF_3)_3COCl$ [14] and $CF_3C(O)SCl$ [22].

General Procedures

A conventional Pyrex glass vacuum apparatus equipped with a Heise-Bourdon tube gauge was employed for manipulation and quantitative measurement of gases and volatile liquids. PVT techniques were used to determine quantities of reactants and products. Fractional condensation aided in the separation and purification of reaction products. In some cases gas chromatography was necessary for final purification. Columns were constructed of 0.25 in. copper or aluminum tubing packed with 20% Kel-F oil (3M Co.) or FS-1265 (Varian) on Chromosorb P and SE 30 (Loenco) on Chromosorb W. A Perkin-Elmer 457 infrared spectrometer was used to record infrared spectra with the samples contained in a 10 cm cell equipped with KBr windows. ^{19}F NMR spectra and ^{1}H NMR spectra were obtained at 94.1 and 100 or 60 Mc on a Varian HA-100 or Varian 360 spectrometer. Freon 11 (CCl_3F) and tetramethylsilane were used as internal references, respectively. Chloroform was used in cases where the resonance band of the compound of interest overlapped with $(CH_3)_4Si$. Mass spectra were obtained with a Hitachi Perkin-Elmer RMU-6E mass spectrometer which was operating at 15 or 17 eV. Elemental analyses were performed with a Perkin-Elmer 240 Elemental Analyzer by Mr. David Harsch.

Preparation of the Mercury Salt

In a typical reaction, mercury, say 1.3 mmol, was placed into a well-dried 25 ml Pyrex reaction vessel. The vessel was reweighed to determine the exact weight of mercury taken. Then a twofold molar excess of perfluoro-tert-butyl hypochlorite and 2 mmol of dry CCl_3F were condensed into the vessel at -196°C. Either dry CH_2Cl_2 or $C_6H_5CH_3$ could be used also. The mixture was allowed to warm slowly to 25°C over a period of several hours. It was agitated on a mechanical shaker for $\sim$24 hr. At the end of this time, all volatile materials were removed under vacuum and the white solid was subjected to dynamic vacuum for 0.5 hr. A white, powdery mercurial remained.

In a quantitative preparation, 0.1944 g mercury (0.97 mmol) was reacted with 2 mmol $(CF_3)_3COCl$ in the presence of 2 mmol CCl_3F. The white solid which remained after all volatile materials had been removed weighed 0.4229 g. For a reaction ratio of 1:1, the solid should have weighed 0.4565 g. No further gain in weight was noted when more $(CF_3)_3COCl$ was added and allowed to contact the solid for additional time.

The solid is insoluble in CCl_3F but is soluble in tetrahydrofuran and is readily hydrolyzed by water to $(CF_3)_3COH$ and yellow HgO. Its

^{19}F NMR spectrum contained a sharp singlet at ϕ75.9. In a melting point tube, decomposition to a yellow solid occurred at 125°C.

Reactions of the Mercury Salt

(a) With CH_3I

Typically, 1 mmol of CH_3I was condensed into a 25 ml Pyrex reaction vessel which contained an excess of the mercury salt. After standing at 0°C for 24 hr, the volatile materials were separated by using fractional condensation. The ether, $(CF_3)_3COCH_3$, was isolated in 73% yield. In the NMR spectra a fluorine resonance at ϕ71.0 (q, J = 1 Hz) and a proton resonance at δ3.82 (multiplet) were found. The infrared spectrum contained bands at 2980w, 2865vw, 1470w, 1320w, 1250vs,br, 1245w, 1180w, 1155s, 1000s, 970s, 730s, 540w and 490 cm^{-1} vw. A molecular ion and other appropriate fragments were observed in the mass spectrum.

Anal. Calc'd for $(CF_3)_3COCH_3$: C, 24.02, H, 1.21; Found: C, 23.75, H, 1.25.

(b) With CF_3SCl

Onto an excess of the mercury salt was condensed 1 mmol of CF_3SCl. After reaction at 0°C for 24 hr, and separation of the volatile mixture by fractional condensation, $(CF_3)_3COSCF_3$ was obtained in 90% yield. In the ^{19}F NMR spectrum resonances were found at ϕ53.8 (CF_3S) and ϕ71.0 [$(CF_3)_3C$]. The infrared spectrum had absorption bands as follows: 1285vs,br, 1190vs, 1132s, 1093vs, 1002s, 987s, 813w, 768w, and 735 cm^{-1} m. The mass spectrum contained a molecular ion.

Anal. Calc'd for $(CF_3)_3COSCF_3$: C, 17.87; Found: C, 17.06.

(c) With $CF_3C(O)Br$

A quantitative yield of $(CF_3)_3COC(O)CF_3$ was obtained when 0.3 mmol of $CF_3C(O)Br$ was allowed to remain in contact with excess of the mercurial for 12 hr. It was purified by fractional condensation and identified from its infrared, mass and NMR spectra [21]. The frequency assigned to the carbonyl stretching mode (1876 cm^{-1}) is higher than that reported previously.

(d) With $CF_3C(O)SCl$

When 0.5 mmol $CF_3C(O)SCl$ was condensed onto an excess of mercury salt and allowed to react for 24 hr, a volatile liquid which condensed in a trap at -40°C was formed. Although mass spectra evidence and infrared data (1776s, 1293vs,br, 1201s, 1101s, 1057m, 1003s, 985s, 942s, 825m, 807m and 740 cm^{-1} s) were obtained, the compound was too unstable with respect to elemental sulfur and $(CF_3)_3COC(O)CF_3$ at 25°C to be analyzed

$$CF_3C(O)SOC(CF_3)_3 \longrightarrow CF_3C(O)OC(CF_3)_3 + \underline{S}$$

(e) With $(CH_3)_3SiCl$

A small excess of $(CH_3)_3SiCl$ was added to 2.1 mmol of the mercurial at -196°C in a Pyrex vessel. After warming to room temperature, $(CF_3)_3COSi(CH_3)_3$ was purified by fractional condensation and gas chromatography (70% yield). A vapor pressure of 112 Torr was observed at 28.8°C. The ^{19}F NMR spectrum contains a resonance band at $\phi 74.2$ which is a multiplet with the pattern expected for a dectet (J = 0.2 Hz). The ^1H NMR band is at $\delta 0.28$. The infrared spectrum is as follows: 2974m, 2913w, 1344m, 1275vs,br, 1216vs, 1191s, 980vs, 880vs, 856s, 764m and 732 cm^{-1} s. The mass spectrum supported the proposed structure although no molecular ion was observed.

Anal. Calc'd for $(CF_3)_3COSi(CH_3)_3$: C, 27.28, H, 2.94; Found: C, 27.51, H, 2.94.

(f) With $(CH_3)_3SiH$

When 0.5 mmol of $(CH_3)_3SiH$ was condensed onto an excess of the mercurial and allowed to remain at 25°C for 12 hr, $(CF_3)_3COSi(CH_3)_3$ (14% yield) and an equivalent amount of $(CF_3)_3COH$ were isolated.

(g) With $CH_3C(O)Cl$

Typically, a slight excess of $CH_3C(O)Cl$ was condensed onto 1.8 mmol of the mercury salt at -196°C. After reaction at 0°C for 12 hr, and separation by fractional condensation and gas chromatography, a quantitative yield of $(CF_3)_3COC(O)CH_3$ (with respect to the amount of mercurial available) was obtained. The vapor pressure of the liquid was 77 Torr at 32.4°C. NMR spectral analysis showed a singlet for fluorine at $\phi 70.1$ and for hydrogen at $\delta 2.28$. The infrared spectrum consisted of bands at 1838vs, 1380m, 1280vs,br, 1179s, 1125vs, 1020s, 990vs, 861w, 737 cm^{-1} s. A molecular ion was observed in the mass spectrum.

Anal. Calc'd for $(CF_3)_3COC(O)CH_3$: C, 25.92, H, 1.09; Found: C, 26.09, H, 1.32.

(h) With $(CF_3)_2C{=}NH$

When 1 mmol of $(CF_3)_2C{=}NH$ was reacted with excess mercurial for 12 hr, the volatile material was 0.7 mmol of $(CF_3)_3COH$. Excess chlorine was added to the solid residue. After several hours, the volatile material was subjected to fractional condensation and $(CF_3)_2C{=}NCl$ (94% yield) and a trace of $(CF_3)_3COH$ were found.

(i) With $(CH_3)_2NH$

When 1 mmol of $(CH_3)_2NH$ was condensed onto an excess of the mercury salt, the pressure dropped to zero. Elemental chlorine, when added, was recovered unchanged.

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