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A New Preparation for Trifluoromethyl Fluoroformyl Peroxide and Bis(trifluoromethyl) Trioxide[1]

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The metal fluoride catalyzed oxidation of fluoro ketones and thionyl tetrafluoride with elemental fluorine was first described by Ruff and coworkers.[2,3] The reaction was shown to be quite general and to produce compounds containing the fluoroxy (–OF) grouping. It is now the most widely used synthetic method for obtaining these interesting materials.

We have recently demonstrated that oxidants other than fluorine could be successfully used in similar metal fluoride catalyzed reactions and that the products derived from these were often quite unusual. For example, the reaction of carbonyl fluoride with oxygen difluoride gives bis(trifluoromethyl) trioxide[4] while oxidation of fluoro ketones with chlorine monofluoride produces fluoroalkyl hypochlorites.[5-8]

We have now shown that bis(fluoroxy)difluoromethane, $F_2C(OF)_2$, can also be utilized successfully to oxidize carbonyl fluoride. The products in this case are trifluoromethyl fluoroformyl peroxide and bis(trifluoromethyl) trioxide. The availability of the starting materials and the ease with which the reaction can be carried out make it a useful alternative to the previously described synthetic methods for $CF_3OOC(O)F$.[9-11]

Experimental Section

Carbonyl fluoride was prepared by heating phosgene with excess sodium fluoride in a stainless steel bomb at 250° for 16 hr.

Bis(fluoroxy)difluoromethane was prepared by the catalytic fluorination of carbon dioxide as has been previously described.[12-14] Cesium fluoride, obtained from the American Potash and Chemical Co., was dried at 150° *in vacuo* and finely ground before use. It was transferred to the reaction cylinder in a dry-box atmosphere.

Preparation of $CF_3OOC(O)F$.[1]—Standard vacuum techniques were used to condense carbonyl fluoride (10 mmol) and bis(fluoroxy)difluoromethane (5 mmol) into a 30-ml stainless steel cylinder containing cesium fluoride. The mixture was allowed to warm to room temperature and remain at that temperature for 3 hr. After that time, the product mixture was fractionated between traps set at -130 and $-196°$. Essentially pure $CF_3OOC(O)F$ ($\sim$1 mmol; 20% according to eq 2, Discussion) was retained in the $-130°$ trap and CF_3OF ($\sim$4 mmol) was retained in the $-196°$ trap. In addition, a small amount of elemental oxygen was produced along with some of the nonvolatile $CsOCF_3$.

It was later found that the yield could be improved by interrupting the reaction at $\sim$1.5-hr intervals, fractionating to recover $CF_3OOC(O)F$, and then returning the reaction mixture to the reaction cylinder. Three or four repetitions of this procedure led to 40% yields of $CF_3OOC(O)F$ (eq 2, Discussion).

Preparation of CF_3OOOCF_3.—A reaction mixture exactly analogous to the one described above was prepared. It was, however, allowed to react for 24 hr without interruption. After this time, fractionation of the product yielded CF_3OOOCF_3, but no $CF_3OOC(O)F$, in the $-130°$ trap. As before, the principal product was CF_3OF, retained in the $-196°$ trap. Yields of the trioxide were variable, ranging from 2 to 20%. The trioxide was identified by comparing its infrared spectrum with that of an authentic sample of CF_3OOOCF_3.[4]

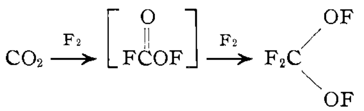
Attempted Preparation of $C_2F_5OOC(O)F$.—A reaction similar to the one first described above was carried out except that $CF_3C(O)F$ was substituted for F_2CO. The material retained in the $-130°$ trap consisted of very small amounts of two unidentified compounds both containing the carbonyl functional group (infrared absorptions at 5.2 and 5.4 μ, respectively). Repeated attempts were made to separate these in sufficient quantity for identification, but vacuum-line fractionation, codistillation, and chromatography were all unsuccessful.

Properties of $CF_3OOC(O)F$.—Trifluoromethyl fluoroformyl peroxide was identified by infrared[10] and nmr spectroscopy[10] as well as elemental analysis. *Anal.* Calcd for $CF_3OOC(O)F$: C, 16.20; F, 51.3. Found: C, 16.15; F, 51.62. The nuclear magnetic resonance spectrum showed absorptions at $+73.3$ and $+36.2$ ppm relative to $CFCl_3$. The resolution was insufficient to detect spin–spin coupling. An extrapolated boiling point of about $-10°$ was determined from vapor pressure measurements. This is within the range originally predicted by Cady.[10]

Trifluoromethyl fluoroformyl peroxide is somewhat less stable than bis(trifluoromethyl) trioxide; a sample of the former stored at $-20°$ for 5 months was found to be totally decomposed with the formation of large amounts of CO_2 and CF_3OF, whereas CF_3OOOCF_3 stored under the same conditions for the same time was unchanged.

Discussion

The oxidative fluorination of substances by $CF_2(OF)_2$, with reduction of the latter to $FC(O)OF$, was initially viewed as an attractive approach to the synthesis of $FC(O)OF$, an interesting but almost inaccessible intermediate.[4] Fluoroformyl hypofluorite is believed to be a precursor to $CF_2(OF)_2$ in the catalytic fluorination of CO_2[13]



$$CO_2 \xrightarrow{F_2} \left[FC(=O)OF\right] \xrightarrow{F_2} F_2C(OF)_2 \qquad (1)$$

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[1] During the latter stages of this work we learned that Professor D. DesMarteau had made similar studies and obtained the same principal products. He was, however, successful in isolating and identifying $CF_3OOOCF_2OOCF_3$ as well. His results are reported in *Inorg. Chem.*, **9**, 2179 (1970).

[2] J. K. Ruff, A. R. Pitochelli, and M. Lustig, *J. Amer. Chem. Soc.*, **88**, 4531 (1966).

[3] J. K. Ruff and M. Lustig, *Inorg. Chem.*, **3**, 1422 (1964).

[4] L. R. Anderson and W. B. Fox, *J. Amer. Chem. Soc.*, **89**, 4313 (1967).

[5] D. E. Gould, L. R. Anderson, D. E. Young, and W. B. Fox, *Chem. Commun.*, 1564 (1968).

[6] D. E. Gould, L. R. Anderson, D. E. Young, and W. B. Fox, *J. Amer. Chem. Soc.*, **91**, 1310 (1969).

[7] C. J. Schack and W. Maya, *ibid.*, **91**, 2902 (1969).

[8] C. J. Schack, R. D. Wilson, J. S. Muirhead, and S. N. Cohz, *ibid.*, **91**, 2907 (1969).

[9] R. L. Cauble and G. H. Cady, *ibid.*, **89**, 5161 (1967).

[10] R. L. Cauble and G. H. Cady, *J. Org. Chem.*, **33**, 2099 (1968).

[11] R. L. Talbott, *ibid.*, **33**, 2095 (1968).

[12] F. A. Hohorst and J. M. Shreeve, *J. Amer. Chem. Soc.*, **89**, 1809 (1967).

[13] R. L. Cauble and G. H. Cady, *ibid.*, **89**, 1962 (1967).

[14] P. G. Thompson, *ibid.*, **89**, 1811 (1967).

but has never been isolated from this system, despite considerable effort by investigators.[9] Presumably this is because FC(O)OF is fluorinated much more rapidly than the CO_2, so that reaction leads invariably to $CF_2(OF)_2$ only.

It was therefore of some interest to try to obtain the interesting material FC(O)OF through the stepwise defluorination of $F_2C(OF)_2$. The earlier observation[15] that SF_5OF reacted with COF_2 over a metal fluoride catalyst to produce not the expected SF_5OOCF_3, but rather SOF_4 and CF_3OF, indicated that metal fluoride catalyzed defluorination of fluoroxy compounds was possible.

However, instead of the desired simple defluorination of $F_2C(OF)_2$ to FC(O)OF, the reaction observed in the present study was more complex and can probably be represented by the idealized equation

$$F_2C(OF)_2 + 2F_2CO \longrightarrow CF_3OF + CF_3OOC(O)F \qquad (2)$$

Secondary and/or competing reactions also occur and lead to certain other products, notably CF_3OOOCF_3 and elemental oxygen.

No FC(O)OF was found among the reaction products but the compounds that were obtained are best explained by the defluorination of $F_2C(OF)_2$ followed by immediate reaction of the resultant FC(O)OF with F_2CO. The proposed mechanism is

$$F_2C(OF)_2 + F_2CO \xrightarrow{CsF} CF_3OF + FC(O)OF \qquad (3)$$

$$FC(O)OF + F_2CO \xrightarrow{CsF} CF_3OOC(O)F \qquad (4)$$

In support of this the following facts should be noted: (a) CF_3OF and $CF_3OOC(O)F$ are the principal products of the reaction; (b) fluorination of carbonyl fluoride did occur and consequently defluorination of $F_2C(OF)_2$ must also have occurred; (c) no carbon dioxide was found among the reaction products so that the defluorination of $F_2C(OF)_2$ must have proceeded only to an intermediate stage, namely, FC(O)OF; (d) the reaction of FC(O)OF with F_2CO to produce a peroxidic structure has precedent in the preparation of CF_3OOCF_3[16] and CF_3OOOCF_3;[4] formation of the latter materials effectively involves the insertion of F_2CO into an O–F bond. (In the CF_3OOOCF_3 case, as well as in the present preparation of $CF_3OOC(O)F$, this is probably achieved through displacement of the fluorine of the fluoroxy grouping by trifluoromethoxide ion.)

The reaction time was found to be critical. Yields of $CF_3OOC(O)F$ reached a maximum at about 3 hr and declined thereafter. After a 24-hr period, no $CF_3OOC(O)F$ remained but a small amount of CF_3OOOCF_3 was found. Apparently $CF_3OOC(O)F$ reacts further, but the mechanism and whether or not it is the direct precursor of CF_3OOOCF_3 are uncertain.

The obvious extension of this reaction to the oxidation of $CF_3C(O)F$ and $(CF_3)_2CO$ with $F_2C(OF)_2$ was attempted, but the results were inconclusive. In the particular case of the reaction of $CF_3C(O)F$ with $F_2C(OF)_2$ over cesium fluoride, two products were obtained with the requisite carbonyl stretching frequency in the infrared, but we were unable to separate and identify either material to confirm the existence of the desired $C_2F_5OOC(O)F$. Hexafluoroacetone gave an even more complex mixture of products. It seems likely, however, that if the proposed mechanism is correct, then other reactions of FC(O)OF formed *in situ* may be found.

Caution! Although we have experienced no explosions while working with the peroxides and fluoroxy compounds described here, it should be recognized that these are powerful oxidants and that proper shielding should be used at all times while they are being handled.

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[15] L. R. Anderson and W. B. Fox, unpublished results.

[16] R. S. Porter and G. H. Cady, *J. Amer. Chem. Soc.*, **79**, 5628 (1957)

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Studies of Boron–Nitrogen Compounds. X. μ-Dimethylaminomethyldiborane

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Although μ-aminodiborane has been known since 1938[1] and a variety of N-substituted derivatives have been prepared,[2–5] there appear to be no known B-substituted derivatives. In relation to the preparation of selectively substituted borazoles and borazanes it seemed desirable to investigate the preparation of B-substituted μ-aminodiboranes since these materials offer one logical starting point in a systematic synthesis of the cyclic compounds. We report here the first example of a B-substituted μ-aminodiborane, μ-dimethylaminomethyldiborane, which has been prepared from μ-dimethylaminodiborane both by a gas-phase exchange using trimethylboron and by reaction with methyl Grignard reagent in ethereal solution.

Experimental Section

The exchange with trimethylboron was carried out for 0.5 hr at 140° in a sealed 1-l. bulb containing approximately 30 mmol of μ-dimethylaminodiborane and 3–4 mmol of trimethylboron. The product was isolated by vacuum distillation of the reaction mixture through a Dry Ice cooled trap, which retained the product as well as some starting material, followed by final purification of the material held in this trap using a low-temperature fractionation column, Figure 1. About 7 mmol of pure product was finally recovered.

Figure 1 is given as a guide to the type of apparatus which has been employed in numerous studies in this laboratory. Several variations upon it have been made and proved useful for specific separation problems.

The mixture to be separated is introduced at the bottom of the column, prechilled to a temperature below which the most volatile component will distil, and the temperature slowly is raised to collect the fractions as they distil in order of volatility from the

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[1] H. I. Schlesinger, D. M. Ritter, and A. B. Burg, *J. Amer. Chem. Soc.*, **60**, 2297 (1938).

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[3] A. B. Burg and C. D. Good, *J. Inorg. Nucl. Chem.*, **2**, 237 (1956).

[4] A. B. Burg and E. S. Kuljian, *J. Amer. Chem. Soc.*, **72**, 3103 (1950).

[5] A. B. Burg and R. I. Wagner, *ibid.*, **76**, 3307 (1954).