

TRIFLUOROMETHYLPEROXYPHOSPHORYL DIFLUORIDE,  
 $\text{CF}_3\text{OOPOF}_2$ , AND TRIFLUOROMETHOXYPHOSPHORYL DIFLUORIDE,  
 $\text{CF}_3\text{OPOF}_2$

PETER A. BERNSTEIN AND DARRYL D. DESMARTEAU\*

*Department of Chemistry, Northeastern University, Boston, Mass. 02115 (U.S.A.)*

(Received June 24, 1972)

---

SUMMARY

The new compounds  $\text{CF}_3\text{OOPOF}_2$  and  $\text{CF}_3\text{OPOF}_2$  have been prepared by the reaction of trifluoromethyl-hydroperoxide,  $\text{CF}_3\text{OOH}$ , with  $\mu$ -oxo-bis-(phosphoryl difluoride),  $\text{P}_2\text{O}_3\text{F}_4$ , and difluorophosphine- $\mu$ -oxo-phosphoryl difluoride,  $\text{P}_2\text{O}_2\text{F}_4$ . Infrared and NMR spectra, physical properties and some chemical reactions are reported for the compounds.

---

INTRODUCTION

Fluorocarbon derivatives of phosphorus are well known<sup>1-3</sup>. Examples include trivalent phosphorus compounds and 4- and 5-coordinate pentavalent phosphorus derivatives. The majority of these compounds contain the fluorocarbon group bonded directly to phosphorus with a few examples where the fluorocarbon group is attached through nitrogen or sulfur. No examples are known where the fluorocarbon group is attached through oxygen\*\*. This is surprising as a number of organophosphorus derivatives of this type are known<sup>1</sup>.

Fluorinated phosphorus peroxides are virtually unknown and only few compounds containing phosphorus bonded to a peroxide group have been reported<sup>6,7</sup>. Recent work with trifluoromethyl-hydroperoxide<sup>8,9</sup> indicated that this reagent might be used in the synthesis of both trifluoromethylperoxy and trifluoromethoxy derivatives of phosphorus. Initial attempts involving reactions of the hydroperoxide with phosphorus fluorides were unsuccessful. However, attack by

---

\* Department of Chemistry, Kansas State University, Manhattan, Kansas 66502 (U.S.A.).

\*\* After this work was completed, some perfluoroalkoxy fluorophosphoranes were reported<sup>4</sup> as well as several perfluoroaryloxy phosphoranes<sup>5</sup>. However, none of these compounds contain small primary perfluoroalkoxy groups.

trifluoromethyl-hydroperoxide on the phosphorus-oxygen bridge bonds in  $\mu$ -oxo-bis-(phosphoryl difluoride),  $P_2O_3F_4$ , and difluorophosphine- $\mu$ -oxo-phosphoryl difluoride,  $P_2O_2F_4$ , have led to high yields of trifluoromethylperoxyphosphoryl difluoride,  $CF_3OOPOF_2$ , and trifluoromethoxyphosphoryl difluoride,  $CF_3OPOF_2$ .

## EXPERIMENTAL

### General

All manipulations of volatile compounds were carried out in a Pyrex vacuum system equipped with glass-Teflon valves. Connections to the vacuum system were made using ground joints lubricated with Kel-F 90 grease. Pressures were measured with a mercury manometer or a Wallace and Tiernan differential pressure gauge. Molecular weights were determined by vapor-density measurements. Vapor pressures were determined in the usual way<sup>10</sup>.

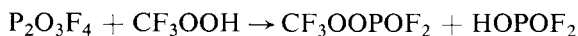
Infrared spectra were recorded on a Beckman IR 10 using a 10 cm cell fitted with silver chloride windows. NMR spectra were taken on a Varian A56-60 spectrometer using trichlorofluoromethane as an internal reference and tetramethylsilane as an external reference.

### Reagents

Hydrogen sulfide, HCl and  $Cl_2$  were obtained from the Matheson Co.,  $CF_3CO_2H$  from Eastman Kodak and  $CH_3OH$  was of reagent grade. All were used without further purification. Tetrafluoroethylene<sup>11</sup>,  $CF_3OOH$ <sup>8</sup>,  $P_2O_3F_4$ <sup>12</sup>,  $P_2O_2F_4$ <sup>13</sup>,  $CF_3OF$ <sup>14</sup>,  $CF_2(OH)_2$ <sup>15</sup>,  $SF_5OF$ <sup>16</sup> and  $S_2O_6F_2$ <sup>17</sup> were obtained by literature methods.

### Preparation of $CF_3OOPOF_2$ (nc)

In a typical experiment, 2.1 mmole each of  $P_2O_3F_4$  and  $CF_3OOH$  were condensed into a 25 ml Pyrex vessel cooled to  $-196^\circ$ . The mixture was allowed to warm to  $22^\circ$  over a 15 min interval and held at this temperature for an additional 20 min. The products were separated through traps at  $-55$ ,  $-111$  and  $-196^\circ$  after first removing oxygen at  $-196^\circ$ . The  $-55^\circ$  trap contained  $HOPOF_2$ ,  $CF_3OOPOF_2$  was retained at  $-111^\circ$  and the  $-196^\circ$  trap contained  $POF_3$ ,  $COF_2$  and small amounts of  $CF_3OOPOF_2$ . The yield of pure  $CF_3OOPOF_2$  was 87% based on the equation



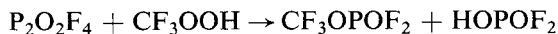
Trifluoromethylperoxyphosphoryl difluoride,  $CF_3COOPOF_2$ , had the following physical and spectroscopic characteristics: b.p.  $15.5^\circ$ ; m.p.  $-88.6^\circ$ ; mol. wt.: calcd., 186.6; found, 185.8;  $\Delta H_{vap} = 7.65$  kcal mole<sup>-1</sup>;  $\Delta S_{vap} = 26.5$  e.u.; IR,  $cm^{-1}$ : 1395 (s),  $\nu(P=O)$ ; 1285 (s), 1245 (vs), 1195 (vs),  $\nu(CF)$ ; 980 (s), 960 (s), 910 (s), 860 (m), 825 (m),  $\nu$ (asym. PF, sym. PF, PO, CO, OO); 675 (w), 595 (w),

495 (vs), 460 (s),  $\delta(\text{PO}_2\text{F}_2, \text{CF}_3\text{OO})$ ; NMR:  $\varphi^*$  88.3 (d, q, PF),  $\varphi^*$  69.8 (d, t, CF),  $J(\text{PF}) = 1109$  Hz,  $J(\text{PCF}) = 1.3$  Hz,  $J(\text{FF}) = 2.6$  Hz. The vapor pressure over the range  $-32.4$  to  $7.4^\circ$  followed the equation

$$\log P(\text{mmHg}) = 8.677 - \frac{1672.8}{T}$$

#### Preparation of CF<sub>3</sub>OPOF<sub>2</sub> (nc)

The following procedure was the most satisfactory one of several that were tried. A 3.64 mmole sample each of P<sub>2</sub>O<sub>2</sub>F<sub>4</sub> and CF<sub>3</sub>OOH were condensed into a 125 ml Pyrex vessel at  $-196^\circ$ . The reaction mixture was allowed to warm slowly to  $22^\circ$  over a 4 h period. The products were immediately separated by pumping through traps held at  $-78$ ,  $-130$  and  $-196^\circ$ . The  $-78^\circ$  trap retained HOPOF<sub>2</sub>, CF<sub>3</sub>OPOF<sub>2</sub> collected at  $-130^\circ$  and COF<sub>2</sub> and POF<sub>3</sub> were found in the  $-196^\circ$  trap. The yield of pure CF<sub>3</sub>OPOF<sub>2</sub> was 65% based on the reaction



Trifluoromethoxyphosphoryl difluoride, CF<sub>3</sub>OPOF<sub>2</sub>, had the following physical and spectroscopic characteristics: b.p.  $4.6^\circ$ ; m.p.  $-96.2^\circ$ ; mol. wt.: calcd., 170.6; found, 169.6;  $\Delta H_{\text{vap}} = 6.56$  kcal mole<sup>-1</sup>;  $\Delta S_{\text{vap}} = 23.6$  e.u.; IR, cm<sup>-1</sup>: 1405 (s),  $\nu(\text{P}=\text{O})$ ; 1275 (s), 1255 (vs), 1201 (vs),  $\nu(\text{CF})$ ; 1048 (s),  $\nu(\text{PO})$ ; 978 (s), 903 (s), 800 (m),  $\delta(\text{asym. PF, sym. PF, CO})$ ; 675 (w), 625 (w), 575 (s), 460 (w), 415 (m),  $\delta(\text{PO}_2\text{F}_2, \text{CF}_3\text{O})$ ; NMR:  $\varphi^*$  81.7 (d, q, PF),  $\varphi^*$  54.2 (d, t, CF),  $J(\text{PF}) = 1064$  Hz,  $J(\text{PCF}) = 7.1$  Hz,  $J(\text{FF}) = 3.9$  Hz. The vapor pressure over the range  $-48.5$  to  $-9.8^\circ$  is given by the equation

$$\log P(\text{mmHg}) = 3.302 + \frac{1.99 \times 10^2}{T} - \frac{3.65 \times 10^5}{T^2}$$

#### Reactions of CF<sub>3</sub>OPOF<sub>2</sub>

Several reactions were carried out between CF<sub>3</sub>OPOF<sub>2</sub> and various substrates to see if the peroxide might be a useful synthetic reagent. The reactions were carried out in Pyrex or stainless-steel vessels by condensing in the reactants at  $-196^\circ$  and allowing the reactor to warm to  $24^\circ$ . Products were separated by fractional condensation and identified by IR spectroscopy and vapor-density molecular weight. The amounts of the products formed were not determined and small amounts of other materials may have been present. The reactions are summarized in Table 1.

The reaction products with CH<sub>3</sub>OH were separated through traps at  $-50$ ,  $-111$  and  $-196^\circ$ . The  $-50^\circ$  trap retained a colorless liquid which is believed to be CH<sub>3</sub>OPOF<sub>2</sub>; mol. wt.: calcd., 116.0; found, 119.0; IR, cm<sup>-1</sup>: 2990 (w),  $\nu(\text{CH})$ ; 1370 (s),  $\nu(\text{P}=\text{O})$ ; 1075 (s),  $\nu(\text{PO})$ ; 935 (s), 800 (w); NMR:  $\varphi^*$  82.8 (d, PF),  $\delta$  4.11 (d, CH),  $J(\text{PF}) = 1012$  Hz,  $J(\text{FH}) = 12$  Hz.

TABLE I  
REACTION OF  $\text{CF}_3\text{OOPOF}_2$

Reactant, mmole <sup>a</sup>	Time, 24 <sup>o</sup>	Products
$\text{H}_2\text{O}^b$ , 0.22	4 h <sup>c</sup>	$\text{HOPOF}_2$ , $(\text{HO})_2\text{POF}$ , $\text{SiF}_4$ , $\text{CF}_3\text{OOH}$
$\text{H}_2\text{S}^d$ , 0.23	1 d	$\text{HOPOF}_2$ , $\text{POF}_3$ , S, $\text{O}_2$ , $\text{COF}_2$ , $\text{CF}_3\text{OOH}$
$\text{HCl}^d$ , 0.25	14 d	$\text{POF}_3$ , $\text{Cl}_2$ , $\text{O}_2$ , HCl, $\text{COF}_2$ , $\text{CF}_3\text{OOH}$
$\text{CF}_3\text{CO}_2\text{H}^d$ , 0.21	1 d	$\text{CF}_3\text{CO}_2\text{H}$ , $\text{CF}_3\text{OOPOF}_2$
$\text{CH}_3\text{OH}^b$ , 1.22	4 h <sup>c</sup>	$\text{CH}_3\text{OPOF}_2$ , $\text{CF}_3\text{OOH}$ , $\text{SiF}_4$ , other <sup>f</sup>
$\text{C}_2\text{F}_4^b$ , 1.0	3 d	$\text{CF}_3\text{OOPOF}_2$ , $\text{C}_2\text{F}_4$
$\text{CF}_3\text{OOPOF}_2^c$ , 0.75	1 h	$\text{POF}_3$ , $\text{PF}_5$ , $\text{P}_2\text{O}_5\text{F}_4$ , $\text{COF}_2$ , $\text{CF}_3\text{OOCF}_3$ , $\text{CF}_3\text{OOOCF}_3$ , $\text{O}_2$
$\text{CF}_3\text{OF}$ , 0.50	1 d	$\text{POF}_3$ , $\text{COF}_2$ , $\text{CF}_3\text{OOOCF}_3$ , $\text{CF}_3\text{OOCF}_3$ , $\text{O}_2$
$\text{CF}_2(\text{OF})_2^d$ , 0.25	4 h	$\text{POF}_3$ , $\text{COF}_2$ , $\text{CF}_2(\text{OF})_2$ , $\text{O}_2$
$\text{SF}_5\text{OF}^d$ , 0.25	2 d	$\text{POF}_3$ , $\text{COF}_2$ , $\text{SF}_5\text{OF}$ , $\text{O}_2$
$\text{S}_2\text{O}_6\text{F}_2^b$ , 0.25	1 d	$\text{POF}_3$ , $\text{COF}_2$ , $\text{S}_2\text{O}_6\text{F}_2$ , $\text{O}_2$

<sup>a</sup> An equimolar amount of  $\text{CF}_3\text{OOPOF}_2$  was used in each case.

<sup>b</sup> 100 ml Pyrex vessel.

<sup>c</sup>  $-196$  to  $22^\circ$ .

<sup>d</sup> 15 ml Pyrex vessel.

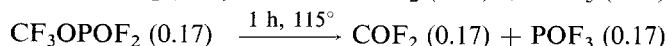
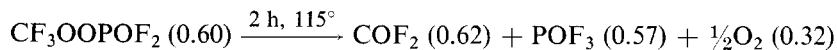
<sup>e</sup> Photolyzed with 2.5 W 2537 Å UV in 500 ml vessel.

<sup>f</sup> Non-volatile liquid at  $22^\circ$ .

## RESULTS AND DISCUSSION

The new compounds  $\text{CF}_3\text{OOPOF}_2$  and  $\text{CF}_3\text{OPOF}_2$  have been obtained in high yield by reactions of  $\text{P}_2\text{O}_3\text{F}_4$  and  $\text{P}_2\text{O}_2\text{F}_4$  with  $\text{CF}_3\text{OOH}$ . Both of these compounds are novel in that  $\text{CF}_3\text{OOPOF}_2$  is the first fluorinated peroxide of phosphorus to be isolated and characterized and  $\text{CF}_3\text{OPOF}_2$  is the only reported trifluoromethoxy derivative of phosphorus. The reaction to form  $\text{CF}_3\text{OPOF}_2$  probably occurs *via* the intermediate formation of the peroxide  $\text{CF}_3\text{OOPF}_2$ , which immediately undergoes rearrangement forming the observed product.

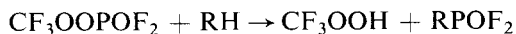
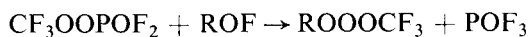
The new compounds were observed to decompose slowly at  $22^\circ$  in both Pyrex or stainless-steel containers. The rate of decomposition increased with increasing pressure and was considerably faster if a liquid phase was present at  $22^\circ$ . Under all conditions,  $\text{CF}_3\text{OPOF}_2$  decomposed somewhat faster than  $\text{CF}_3\text{OOPOF}_2$ . At an initial pressure of 50 mmHg in a 100 ml Pyrex vessel,  $\text{CF}_3\text{OOPOF}_2$  required 57 days for complete decomposition. In a 10 ml vessel, a 1 mmole sample, which was partially liquid at  $22^\circ$ , required only 9 days for complete decomposition. Both compounds were rapidly decomposed at elevated temperatures forming the same products observed at  $22^\circ$  (mmole)



The <sup>19</sup>F NMR spectra provide unequivocal identification of both compounds. The chemical shift of the CF<sub>3</sub>O and CF<sub>3</sub>OO groups are analogous to those in other compounds containing these groups and the expected spin coupling is observed<sup>18,19</sup>. Two overlapping triplets are observed for the CF<sub>3</sub> groups in each compound giving rise to a five-line multiplet with CF<sub>3</sub>OOPOF<sub>2</sub> and a six-line pattern with CF<sub>3</sub>OPOF<sub>2</sub>. The IR spectra of the compounds provide further positive identification and the expected number of fundamental stretching frequencies are observed. Only ν(P=O) and ν(CF) can be positively assigned, and tentative assignments are given in the experimental section.

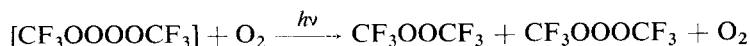
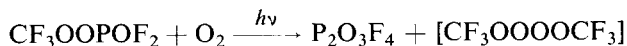
The ν(P=O) stretches at 1405 and 1395 cm<sup>-1</sup> for CF<sub>3</sub>OPOF<sub>2</sub> and CF<sub>3</sub>OOPOF<sub>2</sub>, respectively, indicate a high group electronegativity for both CF<sub>3</sub>O and CF<sub>3</sub>OO. Comparison with the halogens as a plot of 1/3(Σ electronegativities) versus ν(P=O) gives values of 3.9 for CF<sub>3</sub>O and 3.8 for CF<sub>3</sub>OO<sup>20</sup>. The values obtained in this comparison agree well with those predicted by the method of plotting the electronegativity versus the average of the ν(S=O) symmetric and asymmetric stretching frequencies in FSO<sub>2</sub>X<sup>21,22</sup>, where the compounds CF<sub>3</sub>OSO<sub>2</sub>F and CF<sub>3</sub>OOSO<sub>2</sub>F<sup>23</sup> are compared with fluorosulfonyl halides.

Trifluoromethylperoxyphosphoryl difluoride was viewed as a possible reagent for the synthesis of compounds containing the POF<sub>2</sub> and CF<sub>3</sub>OO groups. Several reactions were carried out but only two were successful. As shown in Table 1, either the reactions did not go under the conditions employed or the reaction served to promote the decomposition of CF<sub>3</sub>OOPOF<sub>2</sub>. It was hoped that the reactions would proceed according to the equations



The reaction with CF<sub>3</sub>OF is noteworthy in that some CF<sub>3</sub>OOOCF<sub>3</sub> was observed. With CH<sub>3</sub>OH, the new compound CH<sub>3</sub>OPOF<sub>2</sub> was obtained in low yields. The low yield can probably be attributed to competing reactions of CH<sub>3</sub>OH and possibly CF<sub>3</sub>OOH with PF bonds forming HF and additional CH<sub>3</sub>O and CF<sub>3</sub>OO bonds to phosphorus.

The photolysis of CF<sub>3</sub>OOPOF<sub>2</sub> gives rise to products which are similar to those observed when OPF<sub>2</sub>Br is photolyzed with oxygen forming P<sub>2</sub>O<sub>3</sub>F<sub>4</sub> and Br<sub>2</sub><sup>12</sup>. Taking into account the fact that CF<sub>3</sub>OOPOF<sub>2</sub> can decompose to COF<sub>2</sub>, POF<sub>3</sub> and O<sub>2</sub> and that CF<sub>3</sub>OOOOCF<sub>3</sub> would be unstable under these conditions, unlike Br<sub>2</sub>, the following scheme is reasonable to explain the observed products.



This reaction scheme implies that  $\text{CF}_3\text{OOPOF}_2$  does not form  $\text{CF}_3\text{O}\cdot$  radicals directly. Photolysis of  $\text{CF}_3\text{OOOCF}_3$  forms  $\text{CF}_3\text{OOFCF}_3$  and  $\text{O}_2^{24}$  and other sources of  $\text{CF}_3\text{O}\cdot$  radicals such as  $\text{CF}_3\text{OF}$  and  $\text{CF}_3\text{OOCF}_3$  do not yield  $\text{CF}_3\text{OOOCF}_3$  when photolyzed in the presence of  $\text{O}_2$ . On the other hand, compounds which are possible sources of  $\text{CF}_3\text{OO}\cdot$  radicals, such as  $\text{CF}_3\text{OOF}$ , do yield  $\text{CF}_3\text{OOOCF}_3$  on photolysis in the presence of  $\text{O}_2^{25}$ .

#### ACKNOWLEDGMENT

This work was supported in part by the National Science Foundation, Grant No. GP-23098, and the Petroleum Research Fund of the American Chemical Society, Grant No. 4653-AC3.

The authors thank D. T. Dix and the Dow Chemical Co. for the use of the NMR spectrometer.

#### REFERENCES

- 1 R. SCHMUTZLER, *Adv. Fluorine Chem.*, **5** (1965) 31.
- 2 R. E. BANKS, *Fluorocarbons and their Derivatives*, Oldbourne Press, London, 1964, p. 82-126.
- 3 A. B. BURG, *Accounts Chem. Res.*, **2** (1969) 353.
- 4 D. E. YOUNG AND W. B. FOX, *Inorg. Nuclear Chem. Letters*, **7** (1971) 1033.
- 5 S. C. PEAKE, M. FILD, M. J. C. HEWSON AND R. SCHMUTZLER, *Inorg. Chem.*, **10** (1971) 2723.
- 6 G. SOSNOVSKY AND J. H. BROWN, *Chem. Rev.*, **66** (1966) 529.
- 7 V. E. FLUCK AND W. STECK, *Z. Anorg. Allgem. Chem.*, **388** (1972) 53.
- 8 P. A. BERNSTEIN, F. A. HOHORST AND D. D. DESMARTEAU, *J. Amer. Chem. Soc.*, **93** (1971) 3882.
- 9 D. D. DESMARTEAU, *Inorg. Chem.*, **11** (1972) 193.
- 10 K. B. KELLOGG AND G. H. CADY, *J. Amer. Chem. Soc.*, **70** (1948) 3986.
- 11 E. E. LEWIS AND M. A. NAYLOR, *J. Amer. Chem. Soc.*, **69** (1947) 1968.
- 12 P. A. BERNSTEIN, F. A. HOHORST, M. EISENBERG AND D. D. DESMARTEAU, *Inorg. Chem.*, **10** (1971) 1549.
- 13 D. D. DESMARTEAU, *J. Amer. Chem. Soc.*, **91** (1969) 6211.
- 14 J. K. RUFF, A. R. PITOCHELLI AND M. LUSTIG, *J. Amer. Chem. Soc.*, **89** (1967) 2841.
- 15 F. A. HOHORST AND J. M. SHREEVE, *J. Amer. Chem. Soc.*, **89** (1967) 1809.
- 16 J. K. RUFF, *Inorg. Synth.*, **XI** (1968) 131.
- 17 F. B. DUDLEY AND G. H. CADY, *J. Amer. Chem. Soc.*, **89** (1957) 513.
- 18 D. D. DESMARTEAU, *Inorg. Chem.*, **9** (1970) 2179.
- 19 P. G. THOMPSON, *J. Amer. Chem. Soc.*, **89** (1967) 4316.
- 20 V. A. MÜLLER, E. NIECKE AND O. GLEMSER, *Z. Anorg. Allgem. Chem.*, **350** (1967) 246.
- 21 W. B. FOX AND G. FRANZ, *Inorg. Chem.*, **5** (1966) 946.
- 22 E. A. ROBINSON, *Canad. J. Chem.*, **39** (1961) 247.
- 23 W. P. VAN METER AND G. H. CADY, *J. Amer. Chem. Soc.*, **82** (1960) 6005.
- 24 L. R. ANDERSON, D. E. GOULD, W. B. FOX, F. A. HOHORST AND D. D. DESMARTEAU, to be submitted for publication.
- 25 D. D. DESMARTEAU, unpublished results.