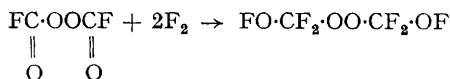


The Formation of Bis(difluorofluoroxymethyl) Peroxide

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RECENTLY, the preparations of compounds containing more than one fluoroxyl group have been reported.^{1a,1b,1c,2} We now report the synthesis of a new bis(fluoroxy)-derivative which also contains a peroxide linkage, bis(difluorofluoroxymethyl) peroxide, $\text{FO}\cdot\text{CF}_2\cdot\text{OO}\cdot\text{CF}_2\cdot\text{OF}$. The compound is prepared by the catalytic fluorination of the corresponding acyl fluoride, bis(fluorocarbonyl) peroxide:³



In a typical experiment, equimolar quantities of bis(fluorocarbonyl) peroxide and fluorine were allowed to react at -95° for 5 hr. in the presence of an excess of KF in a prefluorinated stainless steel cylinder. The volatile contents of the cylinder were then fractionated through cold traps on a vacuum apparatus. A trap set at -126° retained fairly high purity $\text{FO}\cdot\text{CF}_2\cdot\text{OO}\cdot\text{CF}_2\cdot\text{OF}$ (yield 95%). Further purification of the fluoroxyl compound was accomplished by passing it through a 15 ft. perfluorotri-*t*-butylamine on Chromosorb P column at -30° .

The $\text{FO}\cdot\text{CF}_2\cdot\text{OO}\cdot\text{CF}_2\cdot\text{OF}$ thus obtained is colourless (Found: C, 11.40, F, 56.0. Calc. for $\text{C}_2\text{F}_6\text{O}_4$: C, 11.88; F, 56.43%; *M* (vapour density), 202.9 Calc. 202.0). The infrared spectrum shows bands at 1258vs, 1193vs, and 1143vs cm^{-1} in the C-F stretching region and at 939m and 869w cm^{-1} which are both in the O-F⁴ and C-O⁵ stretching regions. The ¹⁹F n.m.r. spectrum is diagnostic and consists of a triplet centred at $\phi -158.6$ and a doublet at $\phi 80.9$ relative to CCl_3F which was used as an internal standard. The splitting of each resonance is 36 c./sec. The area ratio of the lower field to the higher field resonance is 1.0:1.8. According to this data, the O-F fluorine nuclear absorptions are assigned to the low-field multiplet⁴ while the doublet is assigned to the CF_2 group fluorines. Furthermore, the chemical shift and splitting values are very close to those reported for $\text{CF}_2(\text{OF})_2$.¹ Consequently, both the chemical and physical data are in good accord with the suggested structure, $\text{FO}\cdot\text{CF}_2\cdot\text{OO}\cdot\text{CF}_2\cdot\text{OF}$.

CAUTION! Explosions have been encountered when working with bis(difluorofluoroxymethyl) peroxide. Workers should therefore be properly shielded.

(Received, June 5th, 1967; Com. 563.)

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