

A Direct Synthesis of Fluorocarbon Peroxides. The Addition of Bistrifluoromethyl Trioxide to Chlorotrifluoroethylene

By FREDERICK A. HOHORST and DARRYL D. DESMARTEAU*

(Department of Chemistry, Kansas State University, Manhattan, Kansas 66506)

Summary The addition of bistrifluoromethyl trioxide to chlorotrifluoroethylene at 70° produces the peroxides $\text{CF}_3\cdot\text{O}\cdot\text{O}\cdot\text{CF}_2\cdot\text{CFCl}\cdot\text{O}\cdot\text{CF}_3$ and $\text{CF}_3\cdot\text{O}\cdot\text{CF}_2\cdot\text{CFCl}\cdot\text{O}\cdot\text{O}\cdot\text{CF}_3$.

THE number of known fluorocarbon peroxides is small; nearly all examples have been obtained by the coupling of two oxyradicals. Recently, trifluoromethyl hydroperoxide has been used in the synthesis of both organic and inorganic trifluoromethylperoxy-derivatives¹⁻⁴ and bis-(trifluoromethyl) trioxide has been used in the preparation of several inorganic peroxides.⁵ However, no general method for the synthesis of bis(perfluoroalkyl) peroxides has been reported.

We have found that bistrifluoromethyl trioxide adds readily to chlorotrifluoroethylene to give a 20% yield of the

new peroxide $\text{CF}_3\cdot\text{O}\cdot\text{O}\cdot\text{F}_2\cdot\text{CFCl}\cdot\text{O}\cdot\text{CF}_3$ (I) and $\text{CF}_3\cdot\text{O}\cdot\text{CF}_2\cdot\text{CFCl}\cdot\text{O}\cdot\text{O}\cdot\text{CF}_3$ (II). In a typical reaction, $\text{C}_2\text{F}_3\text{Cl}$ (4.2 mmol) and $\text{CF}_3\cdot\text{O}\cdot\text{O}\cdot\text{O}\cdot\text{CF}_3$ (6.7 mmol) were heated to 70° for 1 h in 500 ml Pyrex bulb. G.l.c. of the products gave O_2 , $\text{FCIC}\cdot\text{CF}_2\cdot\text{O}$, $\text{CF}_3\cdot\text{O}\cdot\text{O}\cdot\text{CF}_3$, $\text{CF}_3\cdot\text{O}\cdot\text{O}\cdot\text{O}\cdot\text{CF}_3$, the peroxides (I) and (II), and small amounts of higher molecular weight products. The peroxides (I) and (II) were not separated from each other but ¹⁹F n.m.r. showed the isomer ratio to be 1:6. The new peroxides are colourless liquids (b.p. 20.8° at 190 mmHg) which are stable to at least 100° in glass. They are non-explosive, insensitive to atmospheric moisture, and readily handled in both glass and metal equipment.

The presence of both trifluoromethoxy- and trifluoromethylperoxy-groups in (I) and (II) was confirmed by ¹⁹F

n.m.r. (ϕ^* ca. 56 and 69 for can be assigned to $\text{CF}_3\cdot\text{O}$ and $\text{CF}_3\cdot\text{O}\cdot\text{O}$, respectively^{6,7}). The spectrum of each isomer was assigned as follows with the aid of homonuclear spin decoupling:† $\text{C}(\text{F}^{\text{A}})_3\cdot\text{O}\cdot\text{C}(\text{F}^{\text{B}})_2\cdot\text{C}(\text{F}^{\text{C}})\text{Cl}\cdot\text{O}\cdot\text{C}(\text{F}^{\text{D}})_3$ ϕ^* 69.0 (F^A, t), 94.3 (F^B, dq), 77.3 (F^C, tq), and 55.6 (F^D, dt) (J_{AB} 4.5, J_{BC} 4.0 and 5.0, J_{CD} 10.1, J_{BD} 0.6 Hz); $\text{C}(\text{F}^{\text{A}})_3\cdot\text{O}\cdot\text{C}(\text{F}^{\text{B}})_2\cdot\text{C}(\text{F}^{\text{C}})\text{Cl}\cdot\text{O}\cdot\text{O}\cdot\text{C}(\text{F}^{\text{D}})_3$ 56.4 (F^A, td), 84.6 (F^B, dq), 83.1 (F^C, tq), and 68.4 (F^D, d) (J_{AB} 9.1, J_{BC} 4.3 and 4.8, J_{CD} 5.1, J_{AC} 0.6 Hz). Additional support for the identification of (I) and (II) came from i.r. and molecular weight data (found 302.0; calc. 302.5).

The addition of bistrifluoromethyl trioxide to olefins is apparently a general reaction. Work in progress indicates

that it occurs readily with both cyclic and acyclic alkenes and perfluoroalkenes. It probably proceeds by a free-radical mechanism; it is necessary to heat the reactants to ca. 70° for initiation. At this temperature the trioxide also undergoes decomposition to oxygen and bistrifluoromethyl peroxide, which probably involves the formation of the radicals $\text{CF}_3\text{OO}\cdot$ and $\text{CF}_3\text{O}\cdot$.

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† In each isomer the two atoms F^B are non-equivalent owing to the presence of the chiral centre. The observed spectra constitute an ABX system with Δ 8.7 and 4.4 Hz for (I) and (II), respectively. There are two J_{BC} values for each isomer as indicated, but only one value for each of the other couplings. The coupling constant between the nonequivalent atoms F^B could not be determined.

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