Bis(perfluoro-t-butyl) Peroxide

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Summary The oxidation of perfluoro-t-butyl alcohol with chlorine trifluoride produces bis(perfluoro-t-butyl) peroxide.

OUR recent studies of the oxidation of perfluoroalkoxide salts[1,2] and alcohols[3] with chlorine monofluoride have led to the isolation and identification of a large number of polyfluoroalkyl hypochlorites. Extension of these oxidation studies to the reaction of perfluoro-t-butyl alcohol with chlorine trifluoride has provided a surprising and unique synthesis of the previously unknown[4] bis(perfluoro-t-butyl) peroxide, $(CF_3)_3CO{\cdot}OC(CF_3)_3$.

$$2(CF_3)_3COH + ClF_3 \rightarrow (CF_3)_3CO{\cdot}OC(CF_3)_3 + 2HF + ClF$$

This peroxide is the totally fluorinated analogue of $Me_3CO{\cdot}OCMe_3$.

The new peroxide is prepared (standard vacuum techniques; nickel-Monel system) by condensing stoicheiometric amounts of chlorine trifluoride and perfluoro-t-butyl alcohol together into a stainless steel or Kel-F reaction vessel at −196° and allowing the mixture to warm slowly to room temperature. Fractionation of the resulting mixture through traps set at −23 and −196° leads to isolation of the pure peroxide in the former. Yields ranged from 50—70% based upon the amount of $(CF_3)_3COH$ introduced.

Bis(perfluoro-t-butyl) peroxide is a colourless liquid boiling with slight decomposition at 99°. It was identified by correct elemental analysis, ^{19}F n.m.r. (a single resonance at $\delta = +70{\cdot}0$ p.p.m. relative to internal $CFCl_3$), and mass spectrometry (a parent ion peak at $m/e = 470$ with a cracking pattern consistent with the peroxide structure).

The i.r. spectrum has strong absorptions at 1290, 1110, 1008, and 988 cm^{-1} which are typical of the $(CF_3)_3CO$ group.[3]

The reaction appears to be general for the conversion of highly fluorinated tertiary alcohols into peroxides, as we have also shown that $CF_3{\cdot}CF_2{\cdot}C(CF_3)_2OH$ can readily be converted into the peroxide by a similar process. This new peroxide was also identified by elemental analysis, ^{19}F n.m.r., mass, and i.r. spectra.

The new peroxides are non-explosive, stable at room temperature for indefinite periods, unaffected by atmospheric moisture, and may easily be handled in glass equipment.

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[1] D. E. Gould, L. R. Anderson, D. E. Young, and W. B. Fox, *Chem. Comm.*, 1968, 1564.
[2] D. E. Gould, L. R. Anderson, D. E. Young, and W. B. Fox, *J. Amer. Chem. Soc.*, 1969, **91**, 1310.
[3] D. E. Young, L. R. Anderson, D. E. Gould, and W. B. Fox, in the press.
[4] Bis(perfluoro-t-butyl) peroxide has never been isolated or positively identified but has been suggested as a possible intermediate: J. H. Prager and P. G. Thompson, *J. Amer. Chem. Soc.*, 1965, **87**, 230.