

Preliminary Note

The reversible difluorocarbene elimination from hexafluoropropylene epoxide

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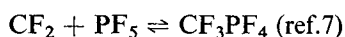
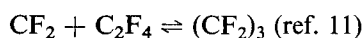
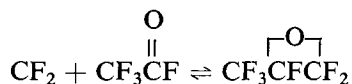
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The pyrolysis of hexafluoropropylene epoxide is one of the more convenient and synthetically useful methods of generating difluorocarbene^{1,2}. In the absence of basic or acid catalysts which cause rearrangements, the half-life of hexafluoropropylene epoxide is *ca.* 6 h at 165°. At this temperature, trifluoroacetyl fluoride and difluorocarbene are formed virtually exclusively. The alternative cleavage to (trifluoromethyl)fluorocarbene and carbonyl fluoride amounts to less than 0.01%. A similar preference for expulsion of difluorocarbene rather than (trifluoromethyl)fluorocarbene from octafluoromethylcyclopropane has been noted³, and difluorocarbene forms in preference to chlorofluoro- and dichloro-carbene on pyrolysis of cyclopropanes⁴.

We find that the fragmentation of hexafluoropropylene epoxide is reversible: the epoxide can be formed by adding difluorocarbene to trifluoroacetyl fluoride.

(CF₃)₃PF₂⁵ (4 mmol) and 6 mmol CF₃C(O)F were heated together at 130° for 3 h in an 80 ml Pyrex glass tube to give 1.5 mmol of hexafluoropropylene epoxide isolated by fractionation and characterized by IR and NMR^{6,7} spectroscopic comparisons with known material. Except for a frequently quoted peak near 1555 cm⁻¹, the IR spectrum has not been published. We find absorptions (in cm⁻¹) at 1613 (w), 1555 (m), 1527 (w), 1375 (m), 1277 (vs), 1235 (s), 1166 (s), 1128 (m), 1024 (vs), 726 (m), 720 (m) and 714 (m).

Thermal elimination of CF₂ from a wide variety of its adducts occurs quite generally and smoothly. Contributing factors are the high stability of singlet CF₂⁸ and the opportunity for lone-pair assisted non-linear cheletropic departure of the carbene^{9,10}.



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This effect is presumably responsible for the lack of success in preparing difluoroketene by attempted addition of CF_2 to CO or by more classical methods^{13,14}. Difluoroketene decomposes to CF_2 and CO at modest temperature¹⁴. In contrast, we have found that the known bis-trifluoromethylketene¹⁵ is formed quantitatively on pyrolyzing bis-trifluoromethyl diazirine in carbon monoxide at 180°.

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