PL-2

THE CONVERSION OF PERFLUORO-OLEFINS, PERFLUOROKETONES OR PERFLUOROACIDS INTO PERFLUOROETHERS, PERFLUOROALKYLPEROXIDES OR PERFLUOROCARBONS

R. N. Haszeldine

Great Langdale, Cumbria, U.K.

Part of a study to synthesise via radical reactions perfluoroalkanes containing oxygen is illustrated with the olefin $(CF_3)_2C{:}C(CF_3)_2$. Photochemical oxidation of the olefin with short reaction time gives the ketones $CF_3.CO.CF(CF_3)_2$ (48% yield), $CF_3.O.CF_2.CO.CF_3$, $CF_3.O.CF_2.CO.CF(CF_3)_2$ and $CF_3.CO.CF_3$. The epoxide $(CF_3)_2C\!-\!\!-\!C(CF_3)_2$ (O) is a by-product not an intermediate in these reactions.

Prolonged photochemical oxidation gives perfluorocarbons: $(CF_3)_3CF$, $(CF_3)_2CF.CF(CF_3)_2$, $(CF_3)_3C.CF(CF_3)_2$, $C(CF_3)_4$ plus perfluoroethers: $CF_3.O.C_2F_5$, and $CF_3.O.CF_2.CF(CF_3)_2$ together with smaller quantities of $CF_3.O.CF(CF_3)_2$, $CF_3.O.CF_3$, $CF_3.O.CF_2.C(OCF_3)(CF_3).CF(CF_3)_2$, $(CF_3)_2C(OCF_3)_2$ and $CF_3.C(OCF_3)_3$.

The $CF_3\cdot$ and $CF_3.O\cdot$ radicals are both important intermediates acting (a) via radical addition to >C:C< and to >C:O, and (b) as radical traps; the $CF_3.O\cdot$ radical has additional roles (c) as a source of $F\cdot$, and (d) as a source of $CF_3.O.CF_2\cdot$.

$CF_3.CO.CF_3$ or $CF_3.CO_2H$ can conveniently be converted photochemically (yields > 50%) into $CF_3.O.O.CF_3$ and $CF_3.O.O.O.CF_3$ without use of elemental fluorine, metal fluorides or CF_3OF.

Photochemical reaction of a perfluoroalkyl peroxide $R_F'O.OR_F'$ with an anhydride $(R_FCO)_2O$ gives the perfluoroether R_FOR_F' (> 50%) and R_FF.

Readers are reminded that use of perfluoroalkylperoxides can lead to explosions.