

NOVEL PHOSPHORUS DERIVATIVES OF PERFLUOROPROPENE

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Perfluoropropene reacts with various phosphorus(III) compounds to furnish phosphoranes, phosphonates, and phosphines, e.g. $R_3P \rightarrow R_3P(F)CF=CFCF_3$ (R=Me, Et) (1a, 1b), $(EtO)_2P(O)SiMe_3 \rightarrow (EtO)_2P(O)CF=CFCF_3$ (2) (+Me₃SiF), $(Me_3SiO)_3P \rightarrow (Me_3SiO)_2P(O)CF=CFCF_3$ (3) (+Me₃SiF), $R_2PH \rightarrow R_2PCF=CFCF_3$ (R=Me, Et) (4a, 4b) (+R₂PH₂F), $tBu_3P \rightarrow tBu_2PCF=CFCF_3$ (tBu₃PHF+Me₂C=CH₂). Monofluorophosphorane 1a is a versatile non-oxidizing fluorinating agent. (CF₃)₂CO adds to give a mono-alkoxy phosphorane which decomposes upon heating to form Me₃PO and a dimer of perfluoropropene. A cycloaddition reaction of 2 and H₂C=C(CH₃)C(CH₃)=CH₂ yields a six-membered ring. The phosphines 4a and 4b are easily oxidized by (CF₃)₂CO, CF₃C(O)F and chlorine. The presence of the Z and E isomers are observed in the 19-F and 31-P NMR spectra. The constitutional isomer of 3, (Me₃SiO)₂P(O)C(=CF₂)CF₃ is found in the reaction of (Me₃SiO)₃P and [(CF₃)₂CS]₂. Methanol adds to this compound forming (Me₃SiO)₂P(O)CH(CF₃)CF₂OMe. Another phosphorus species having the CF₃(CF₂=)C grouping can be obtained from a perfluoropropylidene precursor.