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Polyfluoroalkoxy and aryloxy cyclic phosphazenes: an alternative synthetic route to substitution reactions using siloxanes in the presence of fluoride ion catalysts

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The stability and strength of silicon-oxygen bonds $(\sim 106 \text{ kcal mol}^{-1})$ are well known in organic as well as inorganic synthetic chemistry and these properties are used fully in the versatile practical applications of siloxanes. The acyclic disiloxanes, [CF₂CH₂OSiMe₃]₂ (1), and $CF_2[CF_2CH_2OSiMe_3]_2$ (2), and the cyclic siloxanes, [CF₂CH₂O]₂SiMe₂ (3), CF₂[CF₂CH₂O]₂SiMe₂ (4) and $[CF_2CH_2O]_2SiPh_2$ (5), are synthesized by reactions of the respective diols with hexamethyl disilazane or by condensation reactions with silvl chlorides in the presence of triethylamine. Reactions of compounds 1-4 with C_6F_6 and $(CNF)_3$ are found to proceed readily in the presence of catalytic amounts of fluoride ion that liberate Me₃SiF, Me₂SiF₂ or Ph₂SiF₂ to form cyclic and acyclic fluorinated ethers $C_4F_4CQCH_2(CF_2)_2CH_2O$ (6), $C_6F_5OCH_2(CF_2)_3CH_2OC_6F_5$ (7), $C_6F_5OCH_2(CF_2)_3$ $CH_2OC_6F_5$ (8), $C_3N_3F_2OCH_2(CF_2)_2CH_2OC_3N_3F_2$ (9) and C₃N₃F₂OCH₂(CF₂)₃CH₂OC₃N₃F₂ (10). Compound 1 reacts with PhPCl₂ even in the absence of catalyst to form the cyclic phosphite $(CF_2CH_2O)_2PPh$ (11).

The new compounds have been characterized by spectral (IR, ¹H and ¹⁹F NMR, MS) and analytical methods, while the X-ray crystal structure of the bicyclic ether **6** has been determined. Compound **6** crystallizes in the monoclinic system, space group $P2_1/n$ with a = 9.393(3) Å, b = 10.588(3) Å, c = 11.110(4) Å, $\beta = 111.42(2)^\circ$, V = 1028.7(5) Å³, $D_{calc} = 1.990$ mg m⁻³, Z = 4 and R = 0.0351.

Reactions of $N_3P_3F_6$ with 1 and 2 in the presence of CsF as a catalyst were found to proceed readily under mild conditions to yield the monospiro and bridged fluorophosphazene derivatives (CF₂CH₂O)₂N₃ P₃F₄ (12), CF₂(CF₂CH₂O)₂N₃P₃F₄ (13), F₅N₃P₃OCH₂) CF_2 ₂ $CH_2ON_3P_3F_5$ (14) and $F_5N_3P_3OCH_2(CF_2)_3CH_2$ $ON_3P_3F_5$ (15) in good yields. Subsequent reactions of the bridged derivative 14 with 4-FC₆H₄OSiMe₃, 3-FC₆H₄OSiMe₃, CF₃CH₂OSiMe₃ and 1 give the additional substitution products (4-FC₆H₄O)₅P₃N₃OCH₂CF₂ $CF_2CH_2ON_3P_3(4-FC_6H_4O)_5$ (16), $(3-FC_6H_4O)_5P_3N_3O$ $CH_2CF_2CF_2CH_2ON_3P_3(3-FC_6H_4O)_5$ (17)and (CF₃CH₂O)₅P₃N₃OCH₂CF₂CF₂CH₂ON₃P₃(CF₃CH₂O)₅ (18), and an incompletely characterized dispiro-bridged moiety, together with facile elimination of Me₃SiF. The reaction of Me₃SiO(CH₂)₃OSiMe₃ with N₃P₃F₆ in the presence of CsF gives the monospiro, dangling and bridged derivatives in varying yields depending upon the reaction parameters. Reactions of N₃P₃F₆ with excess $CF_3CH_2OSiMe_3$ in the presence of catalytic amounts of CsF or N₃P₃Cl₆ with excess KF and CF₃CH₂OSiMe₃ in the absence of solvent proceed at 80 °C to yield [CF₃CH₂O]₆N₃P₃ and Me₃SiF.

The X-ray crystal structures of the spiro $[CF_2CH_2O]_2N_3P_3F_4$ (12) as well as the bridged (4-FC₆H₄O)₅P₃N₃OCH₂CF₂CF₂CH₂ON₃P₃(4-FC₆H₄O)₅ (16) phosphazenes have been determined. Compound 12 crystallizes in the monoclinic system, space group $P2_1/c$ with a = 14.695(5) Å, b = 8.532(2) Å, c = 9.600(3)Å, $\beta = 102.38(2)^\circ$, V = 1175.6(6) Å³, $D_{calc} = 2.096$ mg m⁻³, Z=4 and R=0.0656. Compound 16 crystallizes in the monoclinic system, space group $P2_1/n$ with a = 7.738(2)Å, b = 46.849(9) Å, c = 9.516(2) Å, $\beta = 108.65(3)^\circ$, V = 3262.8(13) Å³, $D_{calc} = 1.568$ mg m⁻³, Z = 2 and R = 0.740. The bridged phosphazene derivatives 14 and 15 were found to undergo a facile transformation to the spiro phosphazenes 12 and 13, respectively, on heating at 82 °C in the presence of CsF in THF. This transformation was monitored by variable temperature/ time ¹⁹F NMR spectroscopy.

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