

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, $[\text{CF}_2\text{CH}_2\text{OSiMe}_3]_2$ (**1**), and $\text{CF}_2[\text{CF}_2\text{CH}_2\text{OSiMe}_3]_2$ (**2**), and the cyclic siloxanes, $[\text{CF}_2\text{CH}_2\text{O}]_2\text{SiMe}_2$ (**3**), $\text{CF}_2[\text{CF}_2\text{CH}_2\text{O}]_2\text{SiMe}_2$ (**4**) and $[\text{CF}_2\text{CH}_2\text{O}]_2\text{SiPh}_2$ (**5**), are synthesized by reactions of the respective diols with hexamethyl disilazane or by condensation reactions with silyl chlorides in the presence of triethylamine. Reactions of compounds **1–4** with C_6F_6 and $(\text{CNF})_3$ are found to proceed readily in the presence of catalytic amounts of fluoride ion that liberate Me_3SiF , Me_2SiF_2 or Ph_2SiF_2 to form cyclic and acyclic fluorinated ethers $\text{C}_4\text{F}_4\text{COCH}_2(\text{CF}_2)_2\text{CH}_2\text{O}$ (**6**), $\text{C}_6\text{F}_5\text{OCH}_2(\text{CF}_2)_3\text{CH}_2\text{OC}_6\text{F}_5$ (**7**), $\text{C}_6\text{F}_5\text{OCH}_2(\text{CF}_2)_3\text{CH}_2\text{OC}_6\text{F}_5$ (**8**), $\text{C}_3\text{N}_3\text{F}_2\text{OCH}_2(\text{CF}_2)_2\text{CH}_2\text{OC}_3\text{N}_3\text{F}_2$ (**9**) and $\text{C}_3\text{N}_3\text{F}_2\text{OCH}_2(\text{CF}_2)_3\text{CH}_2\text{OC}_3\text{N}_3\text{F}_2$ (**10**). Compound **1** reacts with PhPCl_2 even in the absence of catalyst to form the cyclic phosphite $(\text{CF}_2\text{CH}_2\text{O})_2\text{PPh}$ (**11**).

The new compounds have been characterized by spectral (IR, ^1H and ^{19}F 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 $a = 9.393(3) \text{ \AA}$, $b = 10.588(3) \text{ \AA}$, $c = 11.110(4) \text{ \AA}$, $\beta = 111.42(2)^\circ$, $V = 1028.7(5) \text{ \AA}^3$, $D_{\text{calc}} = 1.990 \text{ mg m}^{-3}$, $Z = 4$ and $R = 0.0351$.

Reactions of $\text{N}_3\text{P}_3\text{F}_6$ 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 $(\text{CF}_2\text{CH}_2\text{O})_2\text{N}_3\text{P}_3\text{F}_4$ (**12**), $\text{CF}_2(\text{CF}_2\text{CH}_2\text{O})_2\text{N}_3\text{P}_3\text{F}_4$ (**13**), $\text{F}_5\text{N}_3\text{P}_3\text{OCH}_2$

$(\text{CF}_2)_2\text{CH}_2\text{ON}_3\text{P}_3\text{F}_5$ (**14**) and $\text{F}_5\text{N}_3\text{P}_3\text{OCH}_2(\text{CF}_2)_3\text{CH}_2\text{ON}_3\text{P}_3\text{F}_5$ (**15**) in good yields. Subsequent reactions of the bridged derivative **14** with $4\text{-FC}_6\text{H}_4\text{OSiMe}_3$, $3\text{-FC}_6\text{H}_4\text{OSiMe}_3$, $\text{CF}_3\text{CH}_2\text{OSiMe}_3$ and **1** give the additional substitution products $(4\text{-FC}_6\text{H}_4\text{O})_5\text{P}_3\text{N}_3\text{OCH}_2\text{CF}_2\text{CH}_2\text{ON}_3\text{P}_3(4\text{-FC}_6\text{H}_4\text{O})_5$ (**16**), $(3\text{-FC}_6\text{H}_4\text{O})_5\text{P}_3\text{N}_3\text{OCH}_2\text{CF}_2\text{CH}_2\text{ON}_3\text{P}_3(3\text{-FC}_6\text{H}_4\text{O})_5$ (**17**) and $(\text{CF}_3\text{CH}_2\text{O})_5\text{P}_3\text{N}_3\text{OCH}_2\text{CF}_2\text{CH}_2\text{ON}_3\text{P}_3(\text{CF}_3\text{CH}_2\text{O})_5$ (**18**), and an incompletely characterized dispiro-bridged moiety, together with facile elimination of Me_3SiF . The reaction of $\text{Me}_3\text{SiO}(\text{CH}_2)_3\text{OSiMe}_3$ with $\text{N}_3\text{P}_3\text{F}_6$ in the presence of CsF gives the monospiro, dangling and bridged derivatives in varying yields depending upon the reaction parameters. Reactions of $\text{N}_3\text{P}_3\text{F}_6$ with excess $\text{CF}_3\text{CH}_2\text{OSiMe}_3$ in the presence of catalytic amounts of CsF or $\text{N}_3\text{P}_3\text{Cl}_6$ with excess KF and $\text{CF}_3\text{CH}_2\text{OSiMe}_3$ in the absence of solvent proceed at 80°C to yield $[\text{CF}_3\text{CH}_2\text{O}]_6\text{N}_3\text{P}_3$ and Me_3SiF .

The X-ray crystal structures of the spiro $[\text{CF}_2\text{CH}_2\text{O}]_2\text{N}_3\text{P}_3\text{F}_4$ (**12**) as well as the bridged $(4\text{-FC}_6\text{H}_4\text{O})_5\text{P}_3\text{N}_3\text{OCH}_2\text{CF}_2\text{CH}_2\text{ON}_3\text{P}_3(4\text{-FC}_6\text{H}_4\text{O})_5$ (**16**) phosphazenes have been determined. Compound **12** crystallizes in the monoclinic system, space group $P2_1/c$ with $a = 14.695(5) \text{ \AA}$, $b = 8.532(2) \text{ \AA}$, $c = 9.600(3) \text{ \AA}$, $\beta = 102.38(2)^\circ$, $V = 1175.6(6) \text{ \AA}^3$, $D_{\text{calc}} = 2.096 \text{ mg m}^{-3}$, $Z = 4$ and $R = 0.0656$. Compound **16** crystallizes in the monoclinic system, space group $P2_1/n$ with $a = 7.738(2) \text{ \AA}$, $b = 46.849(9) \text{ \AA}$, $c = 9.516(2) \text{ \AA}$, $\beta = 108.65(3)^\circ$, $V = 3262.8(13) \text{ \AA}^3$, $D_{\text{calc}} = 1.568 \text{ mg m}^{-3}$, $Z = 2$ 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/ ^{19}F NMR spectroscopy.

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