Perfluorophenyl–Silicon Compounds

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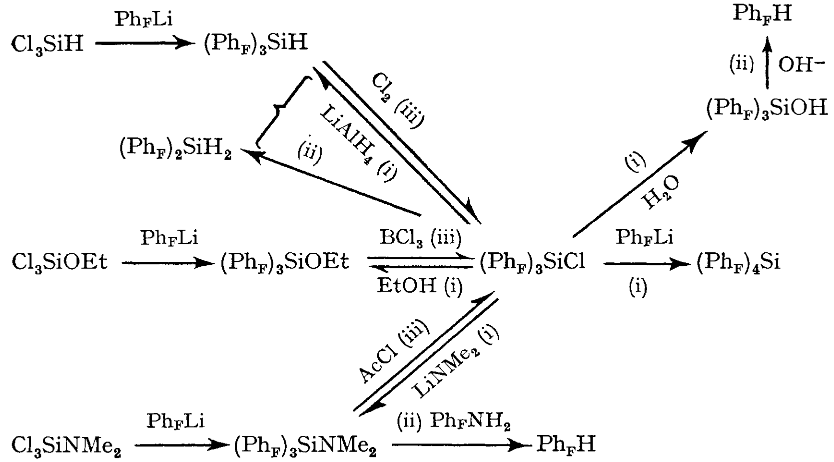
DESPITE the current activity in perfluorophenyl-metal chemistry,[1] few such compounds of silicon are known.[2–5] A difficulty is the choice of suitable starting materials. For example, silicon tetrahalides and either Ph_FMgBr or Ph_FLi ($Ph_F = C_6F_5$) invariably afford $(Ph_F)_4Si$, even with a large excess of SiX_4.[2]

We now report the use of H, OEt, or NMe_2 as protecting groups, which are conveniently replaced by the reactive Cl, on treatment with chlorine, boron trichloride, or acetyl chloride, respectively. Further illustration is provided by the following interconversion scheme in the $(Ph_F)_3SiX$ series. Routes are therefore available to a wide variety of compounds, including the following new species (all characterised by analyses, molecular weights, i.r., u.v., n.m.r., and mass spectra): $(Ph_F)_3SiX$ [b.p. (°/mm.) and m.p. in parentheses]: X = H (110/0·01, 133°), Cl (100/0·01, 83—86°), NMe_2 (120/0·01, 124—130°), Me (119/0·01, 83—85°), OEt (120/0·01, 130—132°); $(Ph_F)_2SiX_2$: X = H (92/2), Cl (78—80/0·01), $CH_2{:}CHCH_2$ (82/0·01); $(Ph_F)_2SiXY$: X,Y = Cl,OEt (74—76/0·01); H,Et (70—74/0·01); H,Pr^i (85/0·01); Ph_FSiX_2Y: X,Y = H,Ph (84/1); Et,H (68—70/10); Pr^i,H (58—60/1·4); Cl,Ph (72—80/0·01, 48—50°); $Ph_FSi(Ph_{Cl})$-MeH (140/0·01, 95—96°).



The reactions of perfluorophenylsilicon compounds may be classified (see scheme) as (i) nucleophilic substitution at Si, (ii) nucleophilic substitution at Si with Ph_F–Si cleavage, and (iii) electrophilic substitution at a site adjacent to silicon. The effect of Ph_F substituents is to increase the rates of (i) and (ii), but to decrease (iii). As further exemplification, Si–Ph bonds are not normally cleaved by $LiAlH_4$, while rates of conversion of silane to chlorosilane decrease in the series $Ph_FSiH_3 > (Ph_F)_2SiH_2 > (Ph_F)_3SiH$. It is interesting that the $(Ph_F)_nSiH_{(4-n)}$–Cl_2 ($n = 1$, 2, or 3) reactions are free radical and light-catalysed; whereas, on the basis *inter alia* of retention of configuration at asymmetric silicon, such processes for other silanes have been assumed to proceed through a polar transition state.[6] In a fourth type of reaction (acid-catalysed Si–aryl cleavage), the effect of nuclear fluorine substituents is to decrease the rate.[3] These data all show that, as regards reactivity, the dominant electronic effect of Ph_F is its electronegativity.

N.m.r. and i.r. data indicate that the Ph_F group when attached to Si (a) can donate π-electron density, (b) is somewhat less electronegative than Br, and (c) may sterically interfere with further Ph_F substituents on Si (as shown[7] by decreasing resolution of the *m*-F resonance). Conclusion (a) is based on (i) an essentially linear plot of $J_{2,4}$ versus δ_4 ($J_{2,4}$ is the *o*-F/*p*-F coupling constant and δ_4 is the *p*-F chemical shift),[8] and (ii) δ_3–δ_4 values.[9]

A plot of τ_{SiH} versus ν(Si–H) is essentially linear; each of these parameters may reflect electronegativity changes at silicon. The Si–H stretching frequency has been used[10] to derive a quantity $E(X)$ related to Gordy electronegativity, whence, in X_3SiH, $E(Cl) > E(Br) \geqslant, E(Ph_F) > E(I)$. From $J_{^{29}Si-^{1}H}$,[11] the electronegativity lies below I.

An unusual feature concerns ν(Si–H) and the solid–melt transition. In $(Ph_F)_3SiH$, ν(Si-H) is at 2296 cm.$^{-1}$ in the solid, 2230 cm.$^{-1}$ in the melt, and 2226 cm.$^{-1}$ in dilute solution in CCl_4; these shifts are reproduced in the deuteride. In other silanes [except $(Ph_F)_2SiH_2$] there are negligible shifts with phase change. A further unexpected, but possibly related, phenomenon, is that in $(Ph_F)_3SiH$ and $(Ph_F)_2SiH_2$, the band due to Si–H stretching is sharpest in the solid.

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