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Directed Dilithiation of Hexafluorocumyl Alcohol—Formation of a Reagent for the Facile Introduction of a Stabilizing Bidentate Ligand in Compounds of Hypervalent Sulfur (10-S-4), Phosphorus (10-P-5), Silicon (10-Si-5), and Iodine (10-I-3)[1]

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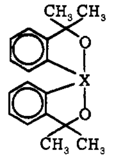
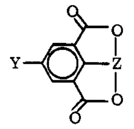
The reaction of 1,1,1,3,3,3-hexafluoro-2-phenyl-2-propanol (R_FOH) with either *sec*-butyllithium or *n*-butyllithium/*N,N,N',N'*-tetramethylethylenediamine (TMEDA) provides **3**, a reagent for the facile introduction of a bidentate ligand which is particularly effective in stabilizing the higher coordination states of nonmetallic elements. This reagent is used to prepare a series of spiro compounds in which two of these ligands are attached to hypervalent silicon (anionic 10-Si-5 species **6a–d**, **13**), phosphorus (10-P-5 phosphoranoxide salt **8**), sulfur (the very unreactive sulfurane, 10-S-4 species **9**), or iodine (10-I-3 species **15**). Reaction of **3** with $SiCl_4$ gives the expected spirosilane, **12**, an 8-Si-4 species which reacts with a variety of nucleophiles to give pentacoordinate silicon (10-Si-5) species. For example, reaction of **12** with phenyllithium gives **6a**. The much weaker nucleophile 4-(dimethylamino)pyridine gives a stable complex which involves nitrogen attack at silicon. Reaction of **3** with elemental sulfur gives disulfide diol **7a**. Reaction with either 1,2-dibromoethane or elemental bromine gives bromo alcohol **11a**, while I_2 reacts with **3** to give iodo alcohol **11b**.

Introduction

Recent success in the isolation of novel anionic hypervalent phosphorus 10-P-4 species, phosphoranides[2] (**1c**), and the 10-P-5 phosphoranoxides[3] (**1d**), isoelectronic with the analogous stable 10-S-4 sulfuranes[4] (**1a**) and 10-S-5 sulfurane oxides[4] (**1b**), has underscored the postulate that one can, at least qualitatively, assess the probability that a hypervalent species will be stable enough to isolate by extrapolation from a knowledge of stabilities of analogous derivatives of atoms from adjacent columns of the periodic table. Closely analogous (essentially isoelectronic) derivatives of electrically neutral 10-S-4 sulfur[4] (**1a**) and 10-Se-4 selenium[5] (**1e**) and anionic 10-P-4 phosphorus[3] (**1c**), of neutral 10-S-5 sulfur[4] (**1b**) and anionic 10-S-5 phosphorous(V)[2] (**1d**), and of neutral 10-I-3 iodine[6] (**2a**) and anionic 10-S-3 sulfur[7] (**2b**) have been studied with results supporting this postulate. In order to further study the stabilities of systems analogous to those in **1**, a better synthetic method was sought which would give improved yields of these hypervalent molecules as well as shorter synthetic routes.



1a X = S
b X = SO
c X = P^-
d X = PO^-
e X = Se



2a Z = I, Y = H
b Z = S^-, Y = t-butyl

Results and Discussion

The bidentate ligand introduced by dilithio derivative **3** is extraordinarily well suited for the synthesis of stable hypervalent species. The greater effective electronegativity

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[1] (a) Species prepared in this paper will be designated *N*-X-*L* species where *N* is the number of formally valence-shell electrons about atom X, involved in bonding *L* ligands to X. (b) For a preliminary communication of this article see: Perozzi, E. F.; Martin, J. C. *J. Am. Chem. Soc.* **1979**, *101*, 1591.

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[3] Granoth, I.; Martin, J. C. *J. Am. Chem. Soc.* **1979**, *101*, 4618.

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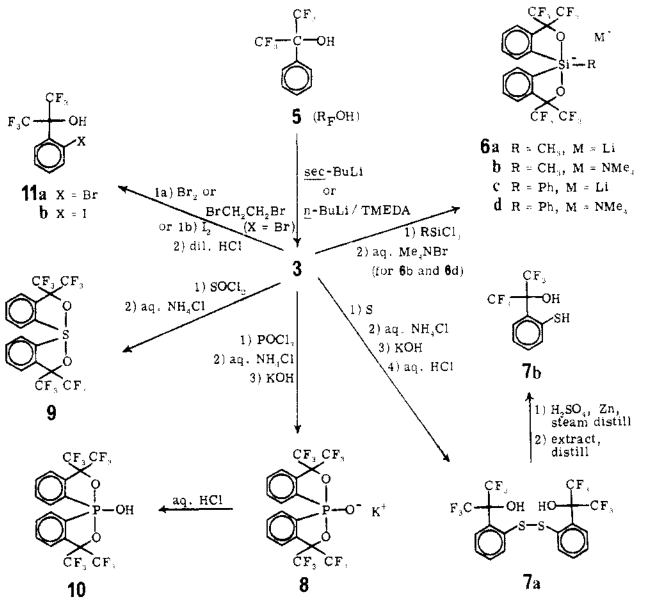
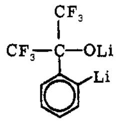
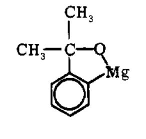
Scheme I



of the apical oxygen in the fluoroalkoxy ligand and the electropositive character of the carbon ligand equatorial to the central atom enhance the difference in electronegativity between the central atom and apical ligand which strengthens the hypervalent bond.[8] The ligand is also thought to provide stabilization by the five-membered-ring effect[9] and the *gem*-dialkyl (Thorpe–Ingold) effect[10] favoring the ring-closed hypervalent species.



3



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Earlier success in our laboratory[11] in the preparation of cyclic sulfuranes by the reactions of dimetalated species **4** led us to explore[1] the directed ortho lithiation of hexafluorocumyl alcohol (R_FOH), **5**, as a more direct route to **3** than had been available. Independently Seebach[12] has demonstrated that other benzyl alcohols can be directly dilithiated in this manner.

Although the reaction of **5** with *sec*-butyllithium provides a relatively facile route to **3**,[1] it can be prepared at lower cost and with better reproducibility by the reaction of R_FOH in tetrahydrofuran (THF) with 2.2 equiv of a hexane solution of *n*-butyllithium and *N*,*N*,*N'*,*N'*-tetramethylethylenediamine (TMEDA) at room temperature. Reaction of **3** with CH_3SiCl_3, $C_6H_5SiCl_3$, $POCl_3$, or $SOCl_2$ at 0 °C in THF gives the hypervalent species **6a**, **6c**, **8**, and **9**, respectively (Scheme I).

Varying amounts of TMEDA were used in the lithiation. Over the range of TMEDA/BuLi ratios from 0.1 to 1.0, little difference was seen in the degree of ortho lithiation which was reflected in the level of incorporation of ring deuterium upon quenching with D_2O. The reaction media containing the smaller proportions of TMEDA provided more easily purified products in the subsequent reactions with electrophiles other than water. A TMEDA/*n*-BuLi ratio of 0.1 was therefore used in most of our reactions.

The isolation of siliconates[13] **6a** and **6c** (10-Si-5 species) provides an opportunity for the comparison of such group IVa species with analogous group Va (10-P-5) or VIa (10-S-5) species with identical bidentate ligands. Several other pentacoordinate silicon species have been described including, for example, complexes of fluoride ion,[14] amines,[15] pyridine,[16] and bipyridyl.[17] The bicyclic silatranes[18] (bicyclic intramolecular amine adducts), tetraoxyspirosiliconates,[19] and pentaoxysiliconates[20] are also examples.[21]

High-melting **6a** (71.3% isolated yield) and **6c** (79.9% yield) were isolated by crystallization from the oil initially obtained in these reactions. Recrystallization failed to remove traces of LiCl (determined by analysis for ionic chloride). Precipitation of the tetramethylammonium salts **6b** or **6d** from an aqueous solution of **6a** or **6c** upon addition of tetramethylammonium bromide gave analytically pure materials, however. Notable among the lines of evidence for these structures is the low-field chemical shift seen for protons ortho to silicon (δ 8.05–8.25), a spectral feature which has been shown to be characteristic of such protons in many sulfuranes,[22] iodinanes,[23] and phosphoranes,[2,3] a consequence of the close proximity of these protons to the dipolar apical X–O bonds.[24]

The reaction of **3** with $SiCl_4$ gives silane **12** isolated (42%) by recrystallization from hexane and sublimation. Silane **12** shows a remarkable level of electrophilicity, reacting with the nucleophiles phenyllithium (to give **6c**, 22.4%) and 4-(dimethylamino)pyridine (to give **13**, 47.2%). The reaction of **12** with phenyllithium to give **6c** provides additional evidence for the structure of siliconate **6c**.

Sulfurane **9** was prepared in highest yield (62% based on unrecovered R_FOH) by the reaction of **3** with an excess of $SOCl_2$ at 0 °C. The requirement of an excess of $SOCl_2$

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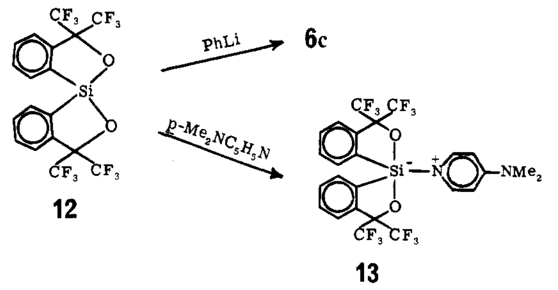
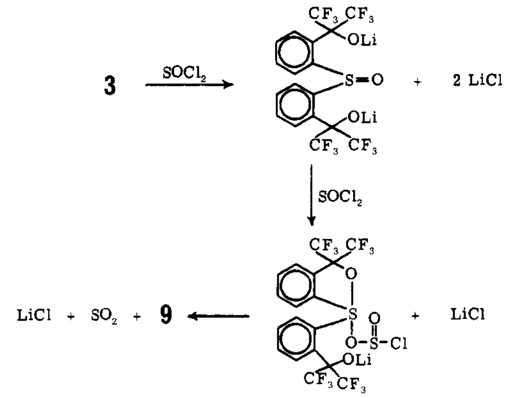


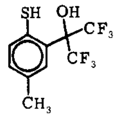
suggests the operation of a mechanism similar to that pictured.



The reactions of 3 with SO_2 or SCl_2 give less efficient production of sulfurane 9 (8% and 16% conversion, respectively).

Phosphoranoxide 8 was obtained in 19.1% conversion. Phosphoranoxide 8 was converted to hydroxyphosphorane 10 upon acidification with hydrochloric acid.

Lithium reagent 3 also reacts with elemental sulfur, albeit in low (~24%) isolated yield, to give disulfide diol 7a. This can be reduced to thiol 7b, an analogue of a thiol 14, which has been found to be very useful as an intermediate in the synthesis of trialkoxysulfuranes.[20] Bromo alcohol derivative 11a was also obtained in low (20%) conversion upon reaction of 3 with either $BrCH_2CH_2Br$ or Br_2. The reasons for the low yields obtained for 7 and 11a were not ascertained although in both cases the regeneration of R_FOH was the principal competing process. Iodo alcohol 11b was obtained in a much higher yield (42%, isolated) from the reaction of 3 and I_2. Alcohol 11b was purified, according to the literature precedent,[23b] by conversion to the easily recrystallized chloroiodinane 15. Reconversion to 11b by reduction with hydrogen sulfide is followed by distillation to give pure 11b.



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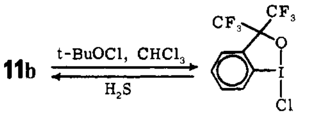

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Lithium reagent 3 is demonstrated to be a reagent for the facile introduction of an important new bidentate ligand to a variety of central elements in compounds in which these elements are covalently bonded in higher coordination states. Our observations of enhanced stability of these products lead us to explore the utility of this ligand in making hypervalent derivatives of other nonmetallic elements available for direct study.

Experimental Section

General Procedures. Chemical shifts were determined on $CDCl_3$ solutions unless otherwise noted and are reported as parts per million downfield from tetramethylsilane internal standard (for ^1H), from fluorotrichloromethane internal standard (for ^{19}F), or from external standard 85% H_3PO_4 (for ^{31}P).

Solvents and Reagents. Thionyl chloride was purified according to the procedure given by Vogel.[25] Tetrachlorosilane and methyltrichlorosilane were purified by distillation. Commercially available phenyltrichlorosilane and phosphorus oxytrichloride were used without further purification. THF was dried by distillation from sodium wire–benzophenone. The preparation of R_FOH (5) followed published procedures.[26]

Preparation of Lithium Reagent 3. Lithium 1,1,1,3,3,3-Hexafluoro-2-(2-lithiophenyl)-2-propoxide. Method A. To a solution of 3 mL of R_FOH (4.38 g, 18 mmol) in 5 mL of dry THF at 0 °C under N_2 was added *sec*-butyllithium solution (28.8 mL of a 1.31 M solution in cyclohexane, 2.1 equiv). The resulting solution was stirred at room temperature for 12–14 h. Quenching a 2-mL aliquot with D_2O and comparison of the ^1H NMR spectrum of the aqueous phase with that of R_FOK[27] showed 70% conversion to 3.

Method B. To a stirred solution of *n*-butyllithium (20.0 mL of a 2.2 M hexane solution, 44 mmol) was added TMEDA (0.46 g, 4 mmol, ~10 mol %). This mixture was allowed to stir at 25 °C for 15–20 min until it became cloudy. The mixture was then cooled to 0 °C and R_FOH (4.88 g, 20 mmol), dissolved in 3 mL of THF, was then slowly added dropwise to the mixture. After 30 min, the ice bath was removed and the mixture was allowed to stir for an additional 18–24 h. Quenching a 0.5-mL aliquot with D_2O and comparison of the ^1H NMR spectrum of the aqueous phase with that of R_FOK showed 98% conversion to 3.

In a series of experiments, it was found that the time required to form 3 is greatly affected by the amount of TMEDA present. When 100 mol % (based on *n*-butyllithium) TMEDA is present at 0 °C, reaction is essentially instantaneous; with 50 mol %, reaction occurs within 5 h; with 10 mol %, at least 18 h is required; with 1 mol %, at least 24 h is required for complete reaction.

In certain cases detailed later, it proved desirable to use inverse addition of 3. In order to affect a homogeneous solution of 3 needed to facilitate its dropwise addition, we used a volume of THF four times that prescribed above.

Tetramethylammonium Bis[α,α-bis(trifluoromethyl)-benzenemethanolato(2–)-C^2,O]methylsilicate(1–) (6b). Methyltrichlorosilane (5.23 g, 35 mmol) was added dropwise under N_2 to lithium reagent 3 (70 mmol, method B) at 0 °C. After being stirred for 1 h at 25 °C the mixture was quenched with 20 mL of water, dissolved in ether, extracted with 0.2 M HCl and water, and dried ($MgSO_4$). The solvent was removed under vacuum to give crude 6a (13.33 g, 25 mmol, 71.3%). A suspension of the crude product (3.8 g, 7 mmol) in 20 mL of hot water was filtered to give a clear filtrate and a quantity of filter cake. Tetramethylammonium bromide (3.0 g, 19 mmol) was added to the filtrate to give a mixture which was stirred at 0 °C for 1 h and filtered to give 6b (0.60 g, 1.0 mmol, 14.1%). Additional 6b was obtained from the crude 6a filter cake. Adding tetramethylammonium bromide (3.0 g, 19 mmol) to a suspension of the filter cake in water and stirring for 12 h gave 6b (2.46 g, 4.1 mmol, 57.5%): mp 267–269 °C, resolidifies and does not melt <350 °C; ^1H NMR (Me_2SO-d_6) δ 8.05 (m, 2.0, Ar H ortho to Si), 7.32 (m, 6.1, remaining Ar H), 3.11 (s, 12.0, $^+N(CH_3)_4$), 0.12 (s, 2.9, $SiCH_3$); ^{19}F NMR (Me_2SO-d_6) δ -73.9, -74.2 (2 q, J_{FF} = 7.8 Hz); FD mass spectrum, *m/e* (relative intensity) 675 (1.0, anion + 2 cations), 601 (1.0, M^+ containing both anion and cation), 600 (1.0, M^+ containing both anion and cation - H), 527 (6.2, anion - $2e^-$), 512 (100.0, anion - $2e^-$ - CH_3). Anal. ($C_{23}H_{23}F_{12}NO_2Si$) C, H, F, N.

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Tetramethylammonium Bis[*α*,*α*-bis(trifluoromethyl)-benzenemethanolato(2−)-*C*^{2},*O*]phenylsilicate (6d). Phenyltrichlorosilane (10.6 g, 50.4 mmol) in 20 mL of THF was added dropwise under a N_2 atmosphere to lithium reagent **3** (100.8 mmol), method B) at 0 °C. After being stirred for 3.5 h at 25 °C the mixture was dissolved in ether, extracted with 0.5 N HCl and water, and dried ($MgSO_4$). The solvent was removed under vacuum to give crude **6c** (24 g, 40.3 mmol, 79.9%). A mixture of **6c** (10 g, 16.8 mmol) in 200 mL of hot water was filtered and tetramethylammonium bromide (8.5 g, 55 mmol) was added. The mixture was stirred for 2 h, cooled to 0 °C, and filtered to give **6d** (5.7 g, 8.6 mmol, 51.2%): mp 325.5–328.0 °C, resolidifies and does not melt <350 °C; ^{1}H NMR (Me_2SO-d_6) δ 8.27 (m, 2.0, H ortho to Si on spirobicyclic rings), 7.80 (m, 2.0, H ortho to Si on nonspirobicyclic rings), 7.34 (m, 6.3, remaining H on spirobicyclic rings), 6.98 (m, 2.9, remaining H on nonspirobicyclic ring), 3.11 (s, 12.4, $^+N(CH_3)_4$); ^{19}F NMR (Me_2SO-d_6) δ −73.0, −74.4 (A_3B_3, J_{FF} = 9.02 Hz); FD mass spectrum, *m*/*e* (relative intensity) 737 (5.1, anion + 2 cations), 589 (100.0, anion − 2e$^-$), 588 (13.8, anion − 2e$^-$ − H), 512 (9.48, anion − 2e$^-$ − C_6H_5). Anal. ($C_{28}H_{25}F_{12}NO_2Si$) C, H, F, N.

Potassium 3,3,3′,3′-Tetrakis(trifluoromethyl)-1,1′-spiro[1*H*,3*H*-2,1-benzoxaphosphole]-1-oxide (8). A solution of lithium reagent **3** (18 mmol, method A) was cooled to 0 °C and a solution of 0.84 mL of $POCl_3$ in 5 mL of dry THF was added dropwise with stirring over a 15-min period under a N_2 atmosphere. After warming to room temperature, the mixture was stirred for 6 h and then was quenched with 20 mL of a saturated NH_4Cl solution. Addition of 70 mL of $CHCl_3$ was followed by separation of the organic phase, this being repeated once more. The combined organic phase was dried (Na_2SO_4) and solvent was removed to leave an oil. This was treated with pentane to give a solid (1.02 g) which was removed by filtration. This material is a mixture of several compounds as determined by ^{31}P NMR [(THF) +26.5, −5.0, −6.1, −7.8, −12.8, −17.6, −20.5, and −28.1 ppm from external standard H_3PO_4]. Treatment of the pentane filtrate with 10 mL of a 10% aqueous KOH solution resulted in a precipitate which was filtered, washed with four 10-mL portions of water, and dried to give 0.710 g (13.8%) of white solid **8**, mp 285–295 °C. Recrystallization of a sample from either–petroleum ether gave analytically pure material, mp 285 °C, which sublimes, then solidifies, and remelts at 302–305 °C. Acidification of the KOH solution gave 1.20 g of recovered R_FOH, providing a yield of 19.1% of **8** based on unrecovered R_FOH: ^{1}H NMR (Me_2SO-d_6) δ 8.41 (m, 2.1, H ortho to P), 7.50 (m, 6.0, remaining Ar H); ^{19}F NMR (Me_2SO-d_6) δ −73.6 (s); ^{19}F NMR (THF-d_8) δ −74.3 and −75.2 (2 q, J_{FF} = 8.5 Hz); ^{31}P NMR (THF) −16.1 ppm; mass spectrum (70 eV), *m*/*e* (relative intensity) 532 (3.67, M$^+$ + H − K), 463 (59.04, M$^+$ + H − CF_3 − K), 393 (11.7), 346 (7.85), 74 (100.00); IR (Nujol) 3540 cm^{-1} (m), 2940 (s), 2885 (s, sh), 1215 (s), 1195 (s). Anal. ($C_{18}H_8F_{12}KO_3P$) C, H, P, K.

3,3,3′,3′-Tetrakis(trifluoromethyl)-1,1′-spiro[3*H*-2,1-benzoxathiole] (9). A solution (1400 mL) of lithium reagent **3** (0.77 mol), prepared according to method B, was added at 0 °C under N_2 over a 3-h period to 250 mL (3.43 mol) of $SOCl_2$. The gases evolved from the solution decolorized a solution of malachite green, indicating the presence of SO_2. The solution was stirred for 14 h and 250 mL of saturated aqueous NH_4Cl was added at 0 °C. The resulting suspension was filtered and the solids were washed with CH_2Cl_2. The filtrate was concentrated and the crude sulfurane was collected and recrystallized from CH_2Cl_2 to give 65 g of white, crystalline sulfurane **9** (0.13 mol, 62% based on unrecovered R_FOH), mp 161–162 °C. Distillation of the mother liquor gave R_FOH (103 g, 0.42 mol): IR ($CHCl_3$) 3039 cm^{-1} (m), 1471 (m), 1453 (m), 1302 (s), 1275 (s), 1227 (s), 1171 (m), 1119 (s), 969 (s), 788 (s, br), 708 (s); ^{1}H NMR δ 8.34 (m, 2.0, H ortho to S), 7.72, (m, 6.0, remaining Ar H); ^{19}F NMR δ −73.5 and −76.7 (A_3B_3, J = 8.7 H_3); mass spectrum (70 eV), *m*/*e* (relative intensity) 516 (4.28, M$^+$), 497 (4.63, M$^+$ − F), 447 (100, M$^+$ − CF_3). Anal. ($C_{18}H_8F_{12}O_2S$) C, H, S, F.

Attempts to prepare **9** by the reaction of **3** with SO_2 or with SCl_2 under conditions analogous to those used above led to low yields of **9** as evidenced by ^{19}F NMR (8% and 16%, respectively). These were not further pursued.

3,3,3′,3′-Tetrakis(trifluoromethyl)-1,1′-spiro[1*H*,3*H*-2,1-benzoxaphosphole]-1-hydroxide (10). Potassium phosphoranoxide **8** (0.233 g, 0.409 mmol) was partially dissolved in 10 mL of $CHCl_3$ and extracted with 10 mL of 1 N aqueous HCl. The $CHCl_3$ layer was separated and the aqueous phase reextracted with $CHCl_3$. The organic phase was dried ($MgSO_4$) and solvent was removed to give 0.198 mg of cream white crystalline solid **10** (91.2%), mp 124.5–126.5 °C. A sample purified by sublimation [70 °C (0.05 torr)] gave analytically pure material: mp 126.0–127.5 °C; ^{1}H NMR δ 8.32 (m, 2.1, Ar H ortho to P), 7.73 (m, 6.0, remaining Ar H), 3.73 (br s, 0.9, OH, disappears with D_2O shake); ^{19}F NMR δ −74.8 and −75.5 (A_3B_3, J_{FF} - 9 Hz); ^{31}P NMR (THF) −17.6 ppm; mass spectrum (70 eV), *m*/*e* (relative intensity) 532 (14.03, M$^+$), 463 (100.00, M$^+$ − CF_3), 393 (9.61), 346 (4.58), 226 (18.81), 197 (7.50), 137 (8.64). Anal. ($C_{18}H_8F_{12}O_3P$) C, H, P.

Bis[2-[1-(trifluoromethyl)-1-hydroxy-2,2,2-trifluoroethyl]phenyl] Disulfide (7a). A solution of lithium reagent **3** (18 mmol, method A) at 0 °C was added dropwise with stirring to a mixture of 1.12 g (35 mmol, excess) of powdered sulfur in 10 mL of dry THF at 0 °C under N_2. The mixture was stirred at 25 °C for 48 h and then quenched with 20 mL of a saturated aqueous NH_4Cl solution. After addition of 70 mL of $CHCl_3$, the organic phase was separated and the aqueous phase was reextracted with 70 mL of $CHCl_3$. Removal of the solvent left an oil to which was added 30 mL of ether followed by two 20-mL portions of 10% aqueous KOH. The organic phase was dried (Na_2SO_4) and evaporated to leave 0.325 g of an oil which was not further purified. Acidification of the KOH layer with 1 N HCl gave a brown-black oil which crystallized. Chromatography of this material on alumina (1 × 4 in. column) using pentane gave a straw colored solution which gave 1.18 g of **7** (23.7%), mp 127–137 °C. Recrystallization of a sample from ether–pentane gave analytically pure material: mp 138–139 °C; ^{1}H NMR δ 7.47–7.83 (m, 4.0, Ar H at 3 and 6 positions), 7.13–7.47 (m, 4.0, Ar H at 4 and 5 positions), 4.76 (s, 2.0, disappears with D_2O shake, OH); ^{19}F NMR δ −74.33 (s); mass spectrum (10 eV), *m*/*e* (relative intensity) 550 (20.43, M$^+$), 276 (94.51, M$^+$/2 + H), 274 (70.73, M$^+$/2 − H), 258 (19.14, M$^+$/2 − HO), 207 (53.45, M$^+$/2 − CF_3 + H), 205 (100.00, M$^+$/2 − HCF_3), 137 (21.31, M$^+$/2 − 2 CF_3); IR ($CHCl_3$) 3570 cm^{-1} (br, w), 3370 (br, w), 2940 (br, w), 2860 (br, w), 2262 (w), 1264 (s), 1235 (s), 1217 (s). Anal. ($C_{18}H_{10}F_{12}O_2S_2$) C, H, S, F.

2-[1-(Trifluoromethyl)-1-hydroxy-2,2,2-trifluoroethyl]-phenylthiol (7b). To 10.0 g (18.18 mmol) of **7a** was added 10.0 g of zinc dust (275 mmol) and 250 mL of 30% aqueous H_2SO_4. Steam distillation under N_2, with concurrent CH_2Cl_2 extraction of the distillate, provided 9.85 g (98%) of a light yellow oil. Vacuum distillation gave pure thiol **7b**: 9.23 g (92.3%); bp 60–62 °C (6.0 mm); ^{1}H NMR (220 MHz) δ 3.75 (br s, 1, SH, disappears with D_2O shake), 5.95 (br s, 1, OH, disappears with D_2O shake), 7.237–7.369 (m, 2), 7.400–7.528 (m, 1), 7.588–7.707 (m, 1, H ortho to fluoroalkoxy); ^{19}F NMR δ −74.87 (s); mass spectrum (10 eV), *m*/*e* (relative intensity) 276 (100.0, M$^+$), 258 (16.68, M$^+$ − H_2O), 207 (41.18, M$^+$ − CF_3), 137 (11.69, M$^+$ − CF_3 − HCF_3). Anal. ($C_9H_6F_6OS$) C, H, S.

2-(2-Bromophenyl)-1,1,1,3,3,3-hexafluoro-2-propanol (11a). To 1,2-dibromoethane (24.0 g, 0.128 mol) in 50 mL of THF at 25 °C was added dropwise lithium reagent **3** (0.063 mol, method A). The reaction mixture was stirred for 1 h and boiled for 44 h. The mixture was then hydrolyzed with 5% HCl. Ether was added and the organic layer was separated, washed with water, and dried with $MgSO_4$–K_2CO_3. All volatiles were removed to leave a golden residue. A 15% conversion to the bromo alcohol **11** was seen by ^{19}F NMR. The residue was vacuum distilled to give the crude bromo alcohol (0.53 g, 2.6%) as light yellow-green waxy crystals. Column chromatography on silica gel with CH_2Cl_2 as eluant gave pure **11** as colorless needles: bp 72 °C (0.3 torr); mp 42–43 °C; ^{1}H NMR δ 5.18 (br s, 1, OH), 7.22 (m, 2), 7.67 (m, 2); ^{19}F NMR δ −74.1 (br s, CF_3); mass spectrum (10 eV), *m*/*e* (relative intensity) 322 (51.8, M$^+$), 253 (97.73, M$^+$ − CF_3), 183 (45.14, M$^+$ − CF_3 − HCF_3). Anal. ($C_9H_5BrF_6O$) C, H.

When the reaction is done with addition of Br_2 to lithium reagent **3** prepared by method B a 20% conversion to **11** is seen by ^{19}F NMR after stirring at 0 °C for 30 min.

2-(2-Iodophenyl)-1,1,1,3,3,3-hexafluoro-2-propanol (11b). To lithium reagent **3** (472 mmol, method B) was added, in portions under nitrogen at 0 °C, solid I_2 (126.9 g, 500 mmol). The reaction mixture was stirred for 12 h at 25 °C and then hydrolyzed with saturated aqueous NH_4Cl. The aqueous layer was extracted with ether (4 × 250 mL). The extracts were washed with 10% aqueous $Na_2S_2O_3$ and dried ($MgSO_4$). Removal of solvent left a dark brown oil (113.5 g, 65%). To the crude oil in CCl_4 at 0 °C was added *tert*-butyl hypochlorite (500 mmol, 54.35 g, 54.1 mL). The resulting yellow precipitate was recrystallized from $CHCl_3$ to give 105.5 g (260.8 mmol, 85%) of chloroiodinane **15**: mp 166–168 °C; ^1H NMR ($CDCl_3$–Et_2O) δ 7.63–7.88 (m, 3), 8.09 (d, 1, H ortho to I); ^{19}F NMR ($CDCl_3$–Et_2O) δ −76.2 (s). Into a solution of 105.5 g of **15** in 500 mL of $CHCl_3$ was bubbled H_2S for 1 h. The product, an orange oil, was distilled (75–78 °C, 0.28 torr) to give iodo alcohol **11b** as a clear oil which crystallized as the dihydrate (81.1 g, 199.8 mmol, 76.6%, overall from **3**, 42.3%): mp 30–32 °C; ^1H NMR δ 7.07 (t of d, 1, J = 7.8, 1.2 Hz, H para to fluoroalkyl), 7.40 (t of d, 1, J = 7.8, 1.8 Hz, H para to I), 7.60 (d, 1, J = 8.4 Hz, H ortho to fluoroalkyl), 8.10 (dd, 1, J = 7.8, 1.2 Hz, H ortho to I); ^{19}F NMR δ −74.05 (s); mass spectrum (70 eV), *m/e* (relative intensity) 370 (100.0, M^+), 301 (73.6, $M^+ - CF_3$), 231 (62.3, $M^+ - CF_3 - HCF_3$), 204 (12.4, $M^+ - HI - F_2$), 145 (25.7), 123 (12.6), 105 (40.97), 77 (22.2), 76 (14.5), 69 (10.1, CF_3), 50 (10.45, CF_2). Anal. ($C_9H_5F_6OI{\cdot}2H_2O$) C, H, I.

3,3,3′,3′-Tetrakis(trifluoromethyl)-1,1′(3*H*,3′*H*)-spirobi[2,1-benzoxasilole] (12). A solution of lithium reagent **3** (0.745 mol, method B) was added over 45 min at −78 °C to stirred silicon tetrachloride (74.0 g, 0.436 mol) under N_2. The mixture was stirred at 25 °C for 12 h. After being quenched with water (50 mL) the mixture was dissolved in ether and extracted with 0.5 M HCl (4 × 300 mL) and water (300 mL). The ether phase was dried ($MgSO_4$) and filtered, and the solvent removed under vacuum. The residue was crystallized from hexane to give an off-white solid (119 g, 0.232 mol, 62.4%). Recrystallization of a portion of the crude product (54.6 g, 0.107 mol) from hexane followed by sublimation gave **12** (36.7 g, 0.0716 mol, 67.0%): mp 131.8–132.2 °C; ^1H NMR δ 7.9–7.55 (m); ^{19}F NMR δ −76.35 and −76.8 (A_3B_3, J_{FF} = 7.8 Hz); mass spectrum (70 eV), *m/e* (relative intensity) 512 (55.56, M^+), 443 (100.00, $M^+ - CF_3$), 239 (78.71). Anal. ($C_{18}H_8F_{12}O_2Si$) C, H, F.

Reactions of Silane 12. (a) With Phenyllithium. To silane **12** (1.036 g, 2.02 mmol) in 5 mL of THF under N_2 was added phenyllithium (1.01 mL of a 2.0 M solution in 70:30 benzene–ether, 2.02 mmol). The mixture was stirred for 1 h, warmed to 25 °C, extracted with water, and dried ($MgSO_4$), and the solvent removed under vacuum to give off-white solid (1.1 g, 1.85 mmol, 91.3%). Recrystallization of 245 mg of product from pentane–chloroform–ether gave white needles (0.060 g, 0.101 mmol, 24.5%): ^1H NMR (acetone-d_6) shows the four aromatic peaks characteristic of **6d** with minor peaks for ether and THF; ^{19}F NMR (acetone-d_6) δ −73.4 and −74.7 (A_3B_3, $J_{FF} \simeq$ 8 Hz). Tetramethylammonium bromide (0.178 g, 1.16 mmol) was added to a solution of crude product (0.23 g, 0.386 mmol) in 15 mL of water to give a white precipitate (0.18 g, 0.302 mmol, 70.3%): ^1H NMR (acetone-d_6) shows the four aromatic peaks characteristic of **6d** and that due to tetramethylammonium cation; minor impurity peaks occur at δ 8.1 and 2.8; ^{19}F NMR (acetone-d_6) δ −73.3 and −74.6 (A_3B_3, J_{FF} = 9.3 Hz) for silicate **6d** (combined integration = 58.9% with a multiplet hidden superposed on the peak at −74.6 (41.1%)).

(b) With 4-(Dimethylamino)pyridine. To silane **12** (0.0529 g, 0.103 mmol) in 1.5 mL of $CHCl_3$ was added 4-(dimethylamino)pyridine (0.0139 g, 0.114 mmol). After 90 min of stirring a precipitate was removed by filtration, washed ($CHCl_3$), and dried to give 0.0309 g of silicate **13** (47.2%), mp 192–195 °C. A sample was purified by sublimation [140 °C (0.05 torr)]: mp 203–206 °C; ^1H NMR (THF-d_8) δ 7.98 (m, 4.0, H ortho to Si on spirobicyclic rings and on pyridine ring), 7.36 and 7.14 (m, 5.9, remaining H on spirobicyclic rings), 6.74 (d, 2.0, remaining H on pyridine ring), 3.08 (s, 5.9, $N(CH_3)_2$); ^{19}F NMR (THF-d_8) δ −72.9 and −74.3 (A_3B_3, J_{FF} = 8.5 Hz); FD mass spectrum (3.0 kV), *m/e* (relative intensity) 635 (1.97, $M^+ + 1$) 513 (100.00, $M^+ + 1 - NC_5H_4N(CH_3)_2$), 123 (99.9, $^+NC_5H_4N(CH_3)_2 + H$), 122 (96.1, $^+NC_5H_4N(CH_3)_2$). Anal. Calcd for $C_{25}H_{18}F_{12}N_2O_2Si$: C, 47.32; H, 2.86; N, 4.42. Found: C, 46.83; H, 3.05; N, 4.20.

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Registry No. 3, 70091-67-7; **5**, 718-64-9; **6a**, 70083-64-6; **6b**, 70083-66-8; **6c**, 70083-67-9; **6d**, 70083-69-1; **7a**, 76215-46-8; **7b**, 64343-89-1; **8**, 76248-61-8; **9**, 70091-68-8; **10**, 76248-62-9; **11a**, 28180-48-5; **11b**, 76215-47-9; **12**, 70091-69-9; **13**, 76233-03-9; **15**, 76215-48-0; $PhSiCl_3$, 98-13-5; $POCl_3$, 10025-87-3; $SOCl_2$, 7719-09-7; S, 7704-34-9; $BrCH_2CA_2Br$, 106-93-4; $SiCl_4$, 10026-04-7; PhLi, 591-51-5; *p*-$Me_2NC_5H_5N$, 1122-58-3; Br_2, 7726-95-6; I_2, 7553-56-2; CH_3SiCl_3, 75-79-6.

Free-Radical and Anion Intermediates in the Reactions of 5-Halo-2-norbornenes and 3-Halonortricyclenes with (Trimethyltin)sodium

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The reaction of (trimethyltin)sodium with *exo*-5-chloro- and 5-bromo-2-norbornenes, *endo*-5-bromo-2-norbornene, and 3-bromo- and 3-iodonortricyclene in tetrahydrofuran has been examined. Use of dicyclohexylphosphine as a trap for intermediate radicals by hydrogen atom transfer showed that the bromides and chloride reacted predominantly by way of free-radical intermediates and by geminate reactions. The geminate products showed complete equilibration of the intermediate radicals. 3-Iodonorbornene reacted predominantly by an anionic intermediate mechanism as shown by trapping of the anions with *tert*-butylamine.

The reactions of group 4 organometallic anionoids with organic halides are frequently useful in synthesis. They also display characteristics which suggest interesting mechanistic diversity. Yet they have received relatively little attention and are not well understood. Thus one has little basis upon which to select reaction parameters which will lead to satisfactory yields in synthetic applications. These observations, along with interesting observations on the stereochemistry as a function of solvent,[1-3] have led us into a systematic study of the mechanism of organotin alkalis with organic halides. Among the general mechanisms which have been suggested are direct processes involving S_N2 displacement on carbon[2-6] or four-center al-

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