Tridentate Ligand Useful in Stabilizing Higher Coordination States of Nonmetallic Elements. An Aryldialkoxydifluoroperiodinane

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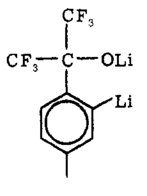
The synthesis of amino diol **2** in several steps from amino alcohol **5** allows the incorporation of the tridentate ligand in a pentacoordinate iodine species. This tridentate ligand provides stability to a hypervalent system due to its various structural features, including the five-membered rings. As a result, difluoroperiodinane **4** is isolated when iodo diol **10** is treated with 2 equiv of bromine trifluoride. This periodinane, which is a strong oxidizing reagent, demonstrated an exceptionally low reactivity. It does, however, rapidly oxidize trimethylchlorosilane or aqueous hydrogen chloride to give chlorine. Oxidation of *p*-chlorophenyl sulfide by **4** gives a mixture of sulfoxide and sulfone upon hydrolysis.

Investigations of the chemistry of the higher valence states of nonmetallic elements with higher coordination numbers, compounds with hypervalent bonds, have been hampered by the instability of many of these species. Work in our laboratory has established that various structural features which can be built into ligands to these nonmetals can provide remarkable stabilizations, allowing the isolation and characterization of hitherto unobserved functional groups. Synthetic procedures have been devised to make many of these species easily accessible. One example uses dilithio derivative **1** which has been very useful[1] in introducing a bidentate ligand which stabilizes higher coordination states of nonmetallic elements.



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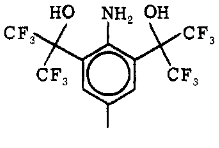
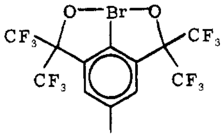


2

We now report the synthesis of **2**, a precursor to compounds in which a tridentate ligand is incorporated to produce extraordinary stabilization of hypervalent species. Examples of new functional groups which are made accessible by the use of this ligand include the previously reported[2] trivalent bromine (10-Br-3) derivative, aryldialkoxybrominane **3**, and the aryldialkoxydifluoroperidodinane (12-I-5 species, **4**) reported here.



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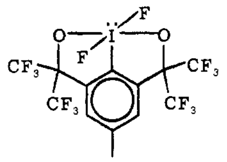

4

Experimental Section

General Methods. Chemical shifts are reported in parts per million downfield from tetramethylsilane as an internal standard for ^1H spectra and from fluorotrichloromethane as an internal standard for ^{19}F spectra.

6-Bromo-4-methyl-2-[1-hydroxy-1-(trifluoromethyl)-2,2,2-trifluoroethyl]aniline (6). To a solution of **5**[3] (106 g, 0.390 mol) containing 0.500 g of iron powder in 1.5 L of CCl_4 was added a solution of Br_2 (60.0 g, 0.390 mol) in 100 mL of CCl_4 dropwise. The precipitated hydrobromide of **6** was collected by filtration, washed with CCl_4, and air-dried. A solution of the salt in 1 L of water was neutralized with 10% aqueous NaOH and extracted with ether. The extract was washed with H_2O and dried (Na_2SO_4), and the solvent was removed to give 129 g (0.370 mol, 94%) of **6**: mp 121-122 °C; IR (Nujol) 3441, 3350 (m, NH_2), 1465 (s), 1370 (m), 1255 (s), 1202 (s), 1150 (s), 1090 (m), 980 (s), 965 (s), 885 (m), 875 (m), 755 (s), 715 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.4 (s, 3, CH_3), 5.0-5.6 (br s, 3, NH_2, OH), 7.3 (br s, 1, Ar H), 7.5 (br s, 1, Ar H); ^{19}F NMR ($CDCl_3$) δ -74.8 (s, CF_3). Anal. ($C_{10}H_8BrF_6NO$) C, H, N.

1,4-Dihydro-8-bromo-6-methyl-2,2-dimethyl-4,4-bis(trifluoromethyl)-2*H*-[3,1]benzoxazine (7). Amino alcohol **6** (138 g, 0.390 mol) in 500 mL of benzene was boiled with 150 mL of acetone and 15 mL of glacial acetic acid; water was collected with a Dean-Stark trap. After 32 h, the solvent was removed under vacuum. The remaining solid was washed with hexane to give white powdery **7**: 138 g (0.350 mol, 90%); mp 78-79 °C; ^1H NMR ($CDCl_3$) δ 1.6 (s, 6, $C(CH_3)_2$), 2.2 (s, 3, Ar CH_3), 4.6 (br s, 1, NH), 7.3 (br s, 1, Ar H), 7.4 (br s, 1, Ar H); ^{19}F NMR ($CDCl_3$) δ -74.9 (s, CF_3). Anal. ($C_{13}H_{12}BrF_6NO$) C, H, N.

1,4-Dihydro-8-[1-hydroxy-1-(trifluoromethyl)-2,2,2-trifluoroethyl]-6-methyl-2,2-dimethyl-4,4-bis(trifluoromethyl)-2*H*-[3,1]benzoxazine (9). To a solution of bromobenzoxazine **7** (59 g, 0.15 mol) in 300 mL of ether at -78 °C was added 128 mL (0.31 mol, 2.4 M in hexane) of *n*-butyllithium dropwise over 30 min. The mixture was transferred into a flask containing 18 mL (0.15 mol) of hexafluoroacetone in 400 mL of ether at -78 °C, stirred for 15 min, and then quenched with 50 mL of saturated aqueous NH_4Cl solution. The solution was extracted with ether at room temperature. The extract was dried ($MgSO_4$) and the solvent removed to give a dark oil, which upon being cooled in pentane to -10 °C gave transparent crystals of **9**: 29 g (0.060 mol, 40%); mp 84-85 °C; ^1H NMR ($CDCl_3$) δ 1.6 (s, 6, $C(CH_3)_2$), 2.5 (s, 3, CH_3), 3.6 (br s, 1, NH), 7.6 (br s, 2, Ar H); ^{19}F NMR ($CDCl_3$) δ -75.2 (s, 6, CF_3), -75.8 (s, 6, CF_3); mass spectrum (70 eV), *m/e* (relative intensity) 479 (7.1, $M^{+\cdot}$), 464 (100, $M^{+\cdot} - CH_3$), 410 (9, $M^{+\cdot} - CF_3$). Anal. ($C_{16}H_{13}O_2NF_{12}$) C, H, N, F.

4-Methyl-2,6-bis[1-hydroxy-1-(trifluoromethyl)-2,2,2-trifluoroethyl]aniline (2). A solution of **9** (15.0 g, 31.3 mmol) in 100 mL of glacial acetic acid, 25 mL of water, and 20 mL of concentrated sulfuric acid was boiled for 24 h. The hot mixture was poured into 300 g of cracked ice, filtered, and washed with water to give white powder of **2**: 12.5 g (28.5 mmol, 91%); mp 175-177 °C; ^1H NMR ($CDCl_3$) δ 2.4 (s, 3, CH_3), 5.2-5.75 (br s, OH and NH_2), 7.45 (s, 2, Ar H); ^{19}F NMR ($CDCl_3$) δ -74.9 (s, CF_3); mass spectrum (70 eV), *m/e* (relative intensity) 439 (81, $M^{+\cdot} - CF_3$), 352 (29, $M^{+\cdot} - CF_3 - H_2O$). Anal. ($C_{13}H_9O_2NF_{12}$) C, H, N.

4-Methyl-2,6-bis[1-hydroxy-1-(trifluoromethyl)-2,2,2-trifluoroethyl]iodobenzene (10). To a mixture of amino diol **2**

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(1) Perozzi, E. F.; Michalak, R. S.; Figuly, G. D.; Stevenson, W. H., III; Dess, D. B.; Ross, M. R.; Martin, J. C. *J. Org. Chem.* **1981**, *46*, 1049.

(2) Nguyen, T. T.; Martin, J. C. *J. Am. Chem. Soc.* **1980**, *102*, 7382.

(3) Gilbert, E. E.; Jones, E. S.; Sibilia, J. P. *J. Org. Chem.* **1965**, *30*, 1001.

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(1.0 g, 2.3 mmol) in 70 mL of glacial acetic acid and 20 mL of concentrated sulfuric acid at 10 °C was added sodium nitrite (0.20 g, 2.9 mmol). After 2 h, 0.20 g of urea was added, and the mixture was stirred for 15 min. Excess potassium iodide (0.5 g, 3.0 mmol) and then 10 mg of copper powder was added, and the solution was heated to 100 °C for 3 h. Saturated aqueous $NaHSO_3$ was added until the mixture became clear yellow. The solution was poured into cracked ice (300 g), filtered, and washed (H_2O) to give a white powder, **10**: 0.90 g (1.6 mmol, 72%); mp 115–116 °C; ^1H NMR ($CDCl_3$) δ 2.5 (s, 3, CH_3), 4.8 (s, 2, OH), 7.5 (s, 2, Ar H); ^{19}F NMR ($CDCl_3$) δ −72.8 (s, CF_3); mass spectrum (70 eV), *m/e* (relative intensity) 550 (100, $M^{+\cdot}$), 481 (6.2, $M^{+\cdot} - CF_2$), 463 (78, $M^{+\cdot} - CF_3 - H_2O$). Anal. ($C_{13}H_7O_2IF_{12}$) C, H, I, F.

10-Methyl-3,3,7,7-tetrakis(trifluoromethyl)-4,6-benzo-1-ioda-2,8-dioxabicyclo[3.3.1]octane (12). To a solution of iodo diol **10** (0.23 g, 0.40 mmol) in 5 mL of chloroform was added *tert*-butyl hypochlorite (50 mL, 0.40 mmol). After 10 min the solvent was removed to give a white powder, which was purified by chromatography on neutral alumina (ether) to give pure **12**: 0.16 g (0.30 mmol, 70%); mp 195–200 °C; ^1H NMR ($CDCl_3$) δ 2.7 (s, 3, CH_3), 7.7 (s, 2, Ar H); ^{19}F NMR ($CDCl_3$) δ −75.8 (s, CF_3); mass spectrum (70 eV), *m/e* (relative intensity) 548 (7.9, $M^{+\cdot}$), 5.29 (6.2, $M^{+\cdot} - F$), 479 (100, $M^{+\cdot} - CF_3$), 410 (12, $M^{+\cdot} - 2CF_3$), 341 (80, $M^{+\cdot} - 3CF$). Anal. ($C_{13}H_5O_2IF_{12}$) C, H, I, F.

1,1-Difluoro-10-methyl-3,3,7,7-tetrakis(trifluoromethyl)-4,6-benzo-1-ioda-2,8-dioxabicyclo[3.3.1]octane (4). To a solution of iodo diol **10** (2.0 g, 3.6 mmol) in 100 mL of CCl_2FCClF_2 at −20 °C in a Teflon container was added bromine trifluoride (0.80 g, 5.9 mmol) in 20 mL of CCl_2FCClF_2 one portion under N_2. After 12 h, the solvent was evaporated, leaving a white powder which was sublimed [90 °C (5 torr)] to give crystalline **4**: 1.7 g (2.9 mmol, 80%); mp 205–210 °C (sublimes); ^1H NMR (CD_3CN) δ 2.7 (s, 3, CH_3), 8.1 (s, 2, Ar H); ^{19}F NMR (CD_3CN) δ −17.7 (br m, 2, IF), −74.25 (t, 12, CF_3, J = 4.5 Hz); mass spectrum (field desorption), *m/e* 586 ($M^{+\cdot}$); mass spectrum (70 eV), *m/e* (relative intensity) 567 (14.9, $M^{+\cdot} - F$), 517 (100, $M^{+\cdot} - CF_3$). Anal. ($C_{13}H_5O_2IF_{14}$) C, H, I, F.

Reactions of Periodinane 4. (a) With Trimethylchlorosilane. To 200 mg (0.34 mmol) of **4** in 3 mL of Freon-113 and 1 mL of CCl_4 was added 0.17 mL (1.4 mmol) of trimethylchlorosilane with stirring under a nitrogen atmosphere. After 15 min, the solvent was swept into a cold trap (−180 °C) by N_2. A solid condensed in the cold trap. When this solid melted, it gave a yellowish solution. This solution turned purple when aqueous KI was added. The proton NMR spectrum of this solution indicated the presence of trimethylfluorosilane. The ^1H and ^{19}F NMR spectra of the solid left in the reaction flask are identical with those of **12**.

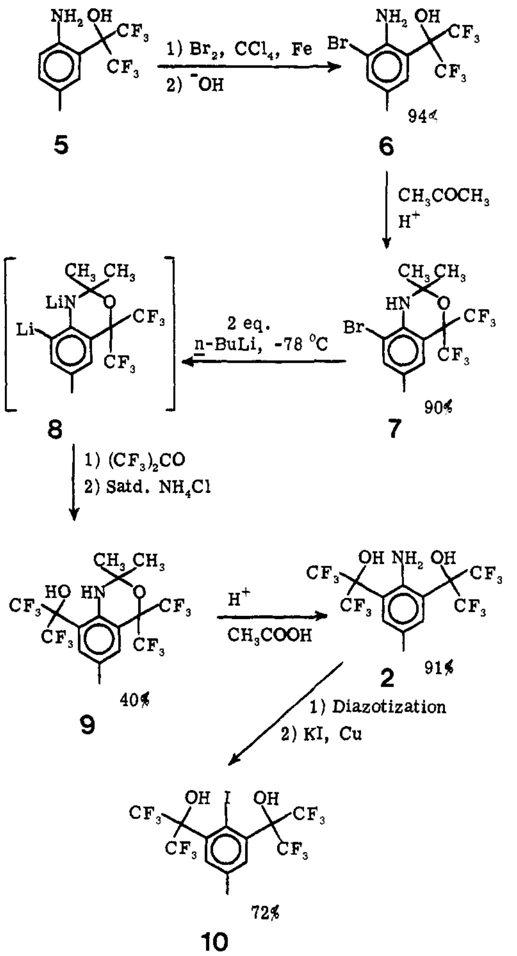
(b) With Aqueous HCl. To a solution of **4** (20 mg) in acetonitrile in an NMR sample tube was added a drop of 3 M aqueous HCl. The reaction mixture turned slightly yellow. After 5 min, ^1H and ^{19}F NMR spectra of the reaction mixture showed that all the **4** was reduced to iodinane **12**. This solution oxidized aqueous KI to I_2, suggesting the presence of Cl_2 since iodinane **12** does not oxidize iodide to iodine.

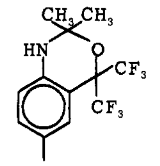
(c) With *p*-Chlorophenyl Sulfide. A mixture of **4** (41 mg, 70 mmol) and *p*-chlorophenyl sulfide (17 mg, 67 mmol) in acetonitrile was allowed to stand at room temperature. No reaction was detected by NMR spectroscopy after 2 days. But when a solid mixture of **4** (40 mg, 69 mmol) and the sulfide (18 mg, 67 mmol) in an NMR sample tube was heated at 135 °C for 30 min, it turned slightly red. Proton and fluorine NMR spectra which were taken in acetonitrile-d_6/D_2O showed a mixture of sulfoxide, sulfone, and iodinane **12**. Integration of the ^1H NMR spectrum gave 53% of sulfoxide, 21% of sulfone, 26% of sulfide, and 100% of iodinane.

Results

Synthesis. Amino diol **2** was synthesized as shown in Scheme I. The synthesis of **5** has been reported.[3] Using the method developed by Cope,[4] we prepared **7** in 90% yield. Reaction of **7** with 2 equiv of *n*-butyllithium gives dilithio derivative **8**. Quenching with D_2O at −78 °C gives introduction of 95% deuterium into the position ortho to the nitrogen. When the reaction is carried out at temperatures considerably higher than −78 °C (−20 or 0 °C) the only observed product is undeuterated **11** after quenching with D_2O. At room temperature no evidence for deuterium incorporation is detected. Formation of **11** is thought to arise from the dehydrobromination of *n*-butyl bromide by lithio derivative **8**.

Scheme I





11

$$8 + n\text{-butyl bromide} \rightarrow 11 + n\text{-butene} + \text{LiBr}$$

Dilithio derivative **8** is quite stable in ether or in tetrahydrofuran at −78 °C. Reaction in tetrahydrofuran gives a larger amount of **11**, suggesting that **8** reacts with tetrahydrofuran. Addition of the solution of hexafluoroacetone to **8**, rather than the prescribed inverse order of addition, gives back **7** and a lesser amount of **9**. This observation is rationalized by invoking a rapid-exchange process between **8** and *n*-butyl bromide to give a small equilibrium concentration of *n*-butyllithium and aryl bromide. If hexafluoroacetone reacts with *n*-butyllithium sufficiently rapidly, slow addition of the ketone to the equilibrating mixture of lithium reagents could favor the undesired reaction with *n*-butyllithium. When an excess of hexafluoroacetone is used, unidentified products are

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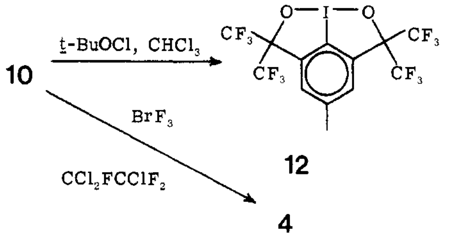
[4] Holly, F. W.; Cope, A. C. *J. Am. Chem. Soc.* **1944**, *66*, 1875.

observed by ^{19}F NMR spectroscopy. Hydrolysis of **9** in acetic acid/sulfuric acid gives **2**. Attempts to hydrolyze **9** with acetic acid/hydrochloric acid or 10% potassium hydroxide/methanol were not successful.

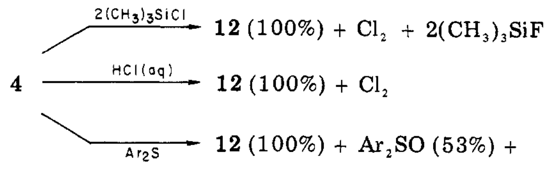
Oxidation of **10** with *tert*-butyl hypochlorite gives stable iodinane **12**. Treatment of **10** with 2 equiv of bromine trifluoride gives aryldialkoxydifluoroperiodinane **4**.



Crystalline periodinane **4** melts with sublimation at 205–210 °C. It is unreactive toward atmospheric moisture. A solution of **4** in acetonitrile–water showed no significant change in its ^{19}F NMR spectrum after 1 week. The difluoroperiodinane in acetonitrile does not react with glass or silica gel at room temperature over 2 days. it remains unchanged for at least 1 month when it is kept at room temperature in a Teflon container.

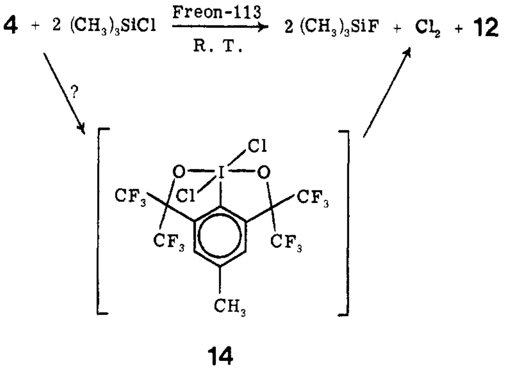
Reactions of 4. Periodinane **4** is a strong oxidizing reagent. Its reactions with trimethylchlorosilane, aqueous hydrogen chloride, and *p*-chlorophenyl sulfide are shown in Scheme II.

Scheme II^a



^{a} Ar = *p*-chlorophenyl.

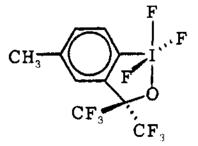
Scheme III



14

Discussion

Stability and Structure of Periodinane 4. Various pentacoordinate iodine(V) species are known. Iodine pentafluoride was reported in 1870.[5] Oates and Winfield prepared[6] a series of the types $IF_{5-n}(OCH_3)_n$ and $CF_3IF_{4-n}(OCH_3)_n$, where n = 1–4. Yagupolskii and coworkers reported[7] the synthesis of $C_6H_5IF_4$ and its derivatives $C_6H_5I(OOCR_F)_4$ (R_F = CF_3, C_3F_7). These acyclic periodinanes are moisture sensitive and decompose upon storage. Some are not stable above 20 °C. Recently we have reported[8] a "tamed" periodinane, **13**, which has shown an exceptionally low reactivity in comparison to acyclic fluoroperiodinanes.



13

A solution of **13** in acetonitrile rapidly etches glass in the presence of air and decomposes completely after 4 days. Solid **13** is unreactive toward atmospheric moisture and is stable indefinitely at room temperature. Periodinane **4** is comparably stable as a solid. It is also stable for extended periods in acetonitrile solution in marked contrast to **13**. It is sublimable at 90 °C (5 torr), and it melts without decomposition.

The lower reactivity of **4** relative to other periodinanes, even the monocyclic **13**, suggests the importance of the stabilizing effect of the two five-membered rings, linking apical with equatorial positions of **4**. The five-membered-ring effect has been observed as a stabilizing structural factor in the chemistry of phosphoranes,[9] sulfuranes,[10] persulfuranes,[11] brominane,[2] siliconates,[10d] and pentacoordinate carbon.[12] In addition to the two five-membered rings, the tridentate ligand of **4** has *gem*-trifluoromethyl groups which stabilize the hypervalent bond through the *gem*-dialkyl effect.[13] The trifluoromethyl groups also increase the effective electronegativity of the oxygen-centered apical ligands. These highly electronegative apical ligands and the electropositive carbon atom of the equatorial ligand stabilize the charge distribution which is developed in the hypervalent bond, positive charge on the central atom and negative charge on the apical ligands.[14]

The structure of **4** is assigned primarily from the NMR spectra. The ^1H NMR spectrum shows a singlet for the two aromatic protons, so there must be a plane of symmetry bisecting the phenyl ring through the carbon–iodine bond. The ^{19}F NMR triplet at −74.25 ppm (J = 4.5 Hz) is consistent with the absorption of CF_3 groups which are coupled to two equivalent fluorine atoms. The fluorines attached to iodine are coupled to CF_3 fluorine atoms (there are cis and trans couplings) and are observed as a broad multiplet at −17.7 ppm.[15]

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(5) Gore, G. *Proc. R. Soc. London* **1870**, *19*, 235.

(6) (a) Oates, G.; Winfield, J. M. *Inorg. Nucl. Chem. Lett.* **1972**, *8*, 1093. (b) Oates, G.; Winfield, J. M. *J. Chem. Soc., Dalton Trans.* **1974**, 119.

(7) (a) Yagupolskii, L. M.; Maletina, I. I.; Kondratenko, N. V.; Orda, V. V. *Synthesis* **1977**, 574. (b) Yagupolskii, I. M.; Lyalin, V. V.; Orda, V. V.; Alekseeva, L. A. *Zh. Obshch. Khim.* **1968**, *38*, 2813.

(8) (a) Amey, R. L.; Martin, J. C. *J. Am. Chem. Soc.* **1978**, *100*, 300. (b) Amey, R. L.; Martin, J. C. *Ibid.* **1979**, *101*, 5294.

(9) Granoth, I.; Martin, J. C. *J. Am. Chem. Soc.* **1979**, *101*, 4618, 4623.

(10) (a) Adzima, L. J.; Martin, J. C. *J. Am. Chem. Soc.* **1977**, *99*, 1657. (b) Lau, P. H. W.; Martin, J. C. *Ibid.* **1978**, *100*, 7077. (c) Martin, J. C.; Balthazor, T. M. *Ibid.* **1977**, *99*, 152. (d) Perozzi, E. F.; Martin, J. C. *Ibid.* **1979**, *101*, 1591.

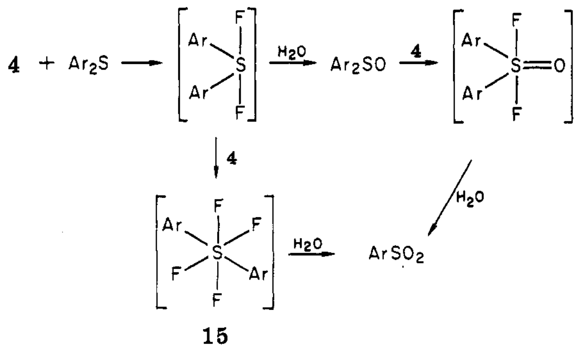
(11) (a) Lam, W. Y.; Martin, J. C. *J. Am. Chem. Soc.* **1977**, *99*, 1659. (b) Lam, W. Y.; Martin, J. C. *Ibid.* **1981**, *103*, 120.

(12) Forbus, R. T.; Martin, J. C. *J. Am. Chem. Soc.* **1979**, *101* 5057.

(13) (a) Beesley, R. M.; Ingold, C. K.; Thorpe, J. F. *J. Chem. Soc.* **1915**, 1080. (b) Ingold, C. K. *Ibid.* **1921**, 305.

(14) (a) Muetterties, E. L.; Schunn, R. A. *Q. Rev., Chem. Soc.* **1966**, *20*, 245. (b) Hoffmann, R.; Howell, J. M.; Muetterties, E. L. *J. Am. Chem. Soc.* **1972**, *94*, 3047.

Scheme IV[a]



[a] Ar = *p*-chlorophenyl.

Reactions. Attempts to replace the fluorine ligands of 13 with chlorine, by treatment with 3 equiv of trimethylchlorosilane, failed to produce an isolable trichloroperiodinane.[8a] Instead, the reduced product, a chloroiodinane, was formed. Since the tridentate ligand stabilizes 4 so effectively, it was thought that the isolation of dichloroperiodinane 14 (Scheme III) might be possible. When 4 is treated with 2 equiv of trimethylchlorosilane at room temperature, however, iodinane 12, trimethylfluorosilane, and chlorine are observed. This reaction may involve the intermediacy of 14 but did not provide direct evidence for the latter's existence in the reaction mixture.

A solution of 4 and *p*-chlorophenyl sulfide in acetonitrile does not react at room temperature. But when a mixture of solid 4 and the sulfide is heated at 135 °C, a mixture of 12, sulfoxide, and sulfone was observed by ^1H and ^{19}F NMR spectroscopy. The presence of the sulfoxide suggests the intermediacy of a difluorosulfurane, which is hydrolyzed to give the sulfoxide. The sulfone could result either from further oxidation of the sulfoxide by 4 or by the formation of a tetrafluoropersulfurane, 15, whcih could be hydrolyzed to sulfone (Scheme IV).

Summary

The synthesis of 4-methyl-2,6-bis[1-hydroxy-1-(trifluoromethyl)-2,2,2-trifluoroethyl]aniline (**2**) in several steps from 4-methyl-2-[1-hydroxy-1-(trifluoromethyl)-2,2,2-trifluoroethyl)aniline (**5**) provides a necessary precursor for the incorporation of a stabilizing tridentate ligand in compounds of hypervalent nonmetallic elements. One example of the usefulness of this ligand is the isolation of the exceptionally stable aryldialkoxydifluoroperiodinane 4. It is prepared in quantitative yield by treatment of 4-methyl-2,6-bis[-1-hydroxy-1-(trifluoromethyl)-2,2,2-trifluoroethyl]iodobenzene (**10**) with 2 equiv of bromine trifluoride in Freon 113 at −20 °C. Periodinane 4 is stable for an indefinite period at room temperature and is unreactive toward atmospheric moisture. It is reduced to iodinane 12 by trimethylchlorosilane and by aqueous hydrogen chloride. It oxidizes *p*-chlorophenyl sulfide in the presence of atmospheric moisture to give a mixture of the corresponding sulfoxide and sulfone.

Further studies of the reactions and synthetic utility of periodinane 4 and applications of the tridentate ligand to other nonmetallic elements are currently underway in our laboratory.

Acknowledgment. This research was supported in part by a grant from the National Science Foundation (CHE-7905692). Mass spectra were obtained on instruments provided in part through a grant from the National Institutes of Health.

Registry No. 2, 76220-90-1; **4**, 80360-39-0; **5**, 1992-07-0; **6**, 80360-40-3; **6**·HBr, 80360-41-4; **7**, 76220-89-8; **8**, 80375-25-3; **9**, 80360-42-5; **10**, 80360-43-6; **11**, 80360-44-7; **12**, 80360-45-8; acetone, 67-64-1; hexafluoroacetone, 684-16-2; bromine trifluoride, 7787-71-5; trimethylchlorosilane, 75-77-4; trimethylfluorosilane, 420-56-4; hydrogen chloride, 7647-01-0; *p*-chlorophenyl sulfide, 5181-10-2; *p*-chlorophenyl sulfoxide, 3085-42-5; *p*-chlorophenyl sulfone, 80-07-9.

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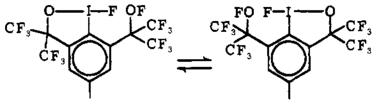
(15) A referee has suggested that the NMR spectrum of 4 is consistent with its being a rapidly equilibrating mixture of equivalent 10-I-2 species as pictured below.



It is true that the expected averaged chemical shift for such an interconverting mixture, the average for the hypofluorite (ca. 140 ppm)[16] and the fluorine of a 10-I-3 fluoroiodinane (ca. −160 ppm),[8] −10 ppm, is very near the value of −17.7 ppm observed for 4. The 338.7-MHz ^{19}F spectrum of 4, taken at −35 °C, shows a relativley sharp peak for the I-F fluorines. Since the expected peak separation for the hydrofluorite and fluoroiodinane ^{19}F peaks would be about 10^5 Hz in the slow-exchange domain, this observation shows that if such a rapid equilibration is occurring it must occur with an improbably low activation barrier, i.e., considerably less than 1 kcal/mol. Since the synthesis of periodinane 13 was effected by the fluorination of the corresponding fluoroiodinane with a hypofluorite, CFOF,[8] one would expect the very similar functional groups in the above-pictured interconverting mixture to react intramolecularly to give 4.

(16) Dungan, C. H.; Van Wazer, J. R. "Compilation of Reported F^{19} NMR Chemical Shifts"; Wiley-Interscience: New York, 1970.

Applications of Artificial Intelligence for Chemical Inference. 40.[1] Computerized Approach to the Verification of Carbon-13 Nuclear Magnetic Resonance Spectral Assignments

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A computerized system for aiding chemists in the assignment of ^{13}C NMR spectra is described. This system checks shift assignments for consistency with known data and for internal consistencies within a set of related compounds. The analysis relies on a data base of substructural environments and correlated chemical shifts. The utility of the system is illustrated through the examination of the assignments of chemical shifts published for germacranolide sesquiterpenes.

Computer programs for the interpretation and prediction of ^{13}C NMR spectra have recently been presented.[2,3] Both programs rely upon the consistency of correlations among chemical shifts and substructural environments.