An Organic Tridentate Ligand Stabilizing a 10-I-4 Iodinane Oxide and Related Species[1a,b]

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The tridentate ligand of iodinane **7**, with electronegative apical oxygens joined by five-membered rings to an electropositive equatorial carbon, strongly stabilizes pseudo-trigonal-bipyramidal (Ψ-TBP) 10-I-3 species **7**, as well as 10-I-4 species such as iodinane oxide **5**. Fluorination of **7** forms a pseudooctahedral (Ψ-Oc) 12-I-5 periodinane, **4**, which is easily hydrolyzed to **5**, or reacts with Lewis acids to form 10-I-4 fluoroperiodonium cation **8**. The equatorial I^+-O^- bond of **5** reacts with electrophiles at the oxygen [with trifluoroacetyl triflate (TFAT) to give 10-I-4 (trifluoroacetoxy)periodonium triflate **12**; with triflic acid (TfOH) to form the 10-I-4 hydroxyperiodonium triflate **9**; and with trifluoroacetic anhydride (TFAA) to form the 12-I-5 bis(trifluoroacetoxy)periodinane **11**]. Small amounts of tetrabutylammonium hydroxide give nucleophilic addition to the iodine of **5** to form 12-I-5 intermediates (**18**) leading to rapid inversion of geometry at the 10-I-4 center of the iodinane oxide. Excess KOH cleaves the C–I bond of **5**, forming the reduced arenediol **17**. Diphenyldialkoxysulfurane **14** converts **5** to dialkoxyperiodinane **13**, forming diphenyl sulfoxide. Iodine oxide **5** is a strong oxidizing agent, rapidly oxidizing HCl to Cl_2, or pinacol to acetone. Oxidation of a diaryl sulfide to the sulfoxide and the sulfone occurs unselectively, but slowly, at 160 °C with pure **5**. With a catalytic amount of TFAA, selective oxidation of the diaryl sulfide to the sulfoxide by **5** is rapid at room temperature.

Introduction

The chemistry of organic derivatives of iodine(III) and iodine(V) has been extensively studied. Less is known about the iodine(V) species than the less reactive iodine(III) species. Organoiodine compounds of iodine(VII) have not been reported.

Iodine pentafluoride is the earliest known iodine(V), or 12-I-5 species. At room temperature it is a stable liquid, and it behaves as a fluorinating reagent.[2] It reacts upon contact with water to give iodic acid and hydrogen fluoride.[2,3] Reactions of IF_5 with strong Lewis acids such as SbF_5 or PtF_5 provide periodonium salts ($IF_4^+SbF_6^-$ or $IF_4^+PtF_6^-$).[4] Treatment of IF_5 with the strongly basic alkali-metal fluorides gives $M^+IF_6^-$ salts.[5] Analogues of IF_5, compounds with electronegative ligands other than fluorine, are also known. Trifluorobis(fluorosulfonoxy)periodinane, $IF_3(OSO_2F)_2$, is prepared by the reaction of fluorine, fluorosulfonate anion, and iodine,[6] or by thermal decomposition of $I(OSO_2F)_3$.[7]

Organic analogues of IF_5 have been synthesized by fluorination of alkyl or aryl iodides with fluorine, or with other fluorinating reagents such as ClF, ClF_3, BrF_3, BrF_5, or CF_3OF. Treatment of various perfluoroalkyl or perfluoroaryl iodides with F_2 or ClF_3 gives tetrafluoroperiodinanes, R_FIF_4.[8] Other periodinanes such as $ArI(OCOR)_4$ (R = CF_3, C_3F_7) are made from iodoxybenzene by reaction with appropriate acid anhydrides.[9] Oates and Winfield synthesized[10] a series of compounds of the type $IF_{5-n}(OCH_3)_n$ and $CF_3IF_{4-n}(OCH_3)_n$, where n = 1–4, by treating the fluoroperiodinanes with trimethylsilyl methoxide.

These acyclic periodinanes are reported to be moisture sensitive, reactive toward silicon dioxide,[11] and unstable in storage at room temperature.[12] The series of mono- and bicyclic periodinanes of the type $IF_3[O(CH_2)_xO]$, $IF_3[(OCH_2)_2C(CH_3)_2]$, $IF_2[(OCH_2)_3CCH_3]$, $IF[(OCH_2)_2C(CH_3)_2]_2$, and $IF[O(CH_2)_xO]_2$, where x = 2–4, have been synthesized,[13] but no description of their reactivity patterns was reported.

Another class of iodine(V) species is that of the iodinane oxides. Some examples of acyclic iodinane oxides are IOF_3,[14] CF_3IOF_2,[11] $C_6H_5IOF_2$,[15] CH_3OIOF_2,[13a] $ArIO(OCOR)_2$,[9] $Ar_2IO(OH)$,[16] and $Ar_2IO(X)$[17] (where X = CF_3COO, F, Cl). As in the case with periodinanes, monocyclic iodinane oxides tend to be more stable and less reactive than their acyclic analogues. The cyclic form of *o*-iodoxybenzoic acid **1**[18a–c] and the hydrolysis product of **2**, iodinane oxide **3**,[12b] are stable molecules.

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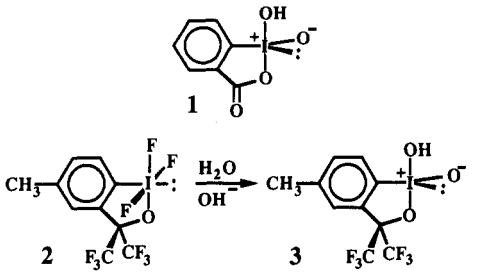
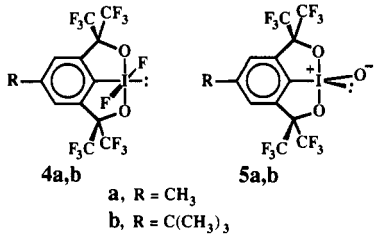


We have reported the synthesis of a very stable 12-I-5 difluoroperiodinane, **4a**.[19] We now report the chemistry of **4** and of its hydrolysis products, 10-I-4 iodinane oxides **5a,b**. Syntheses of various stable 10-I-4 periodonium salts are also discussed. The 10-I-4 iodinane oxides **5a,b** are interesting as oxidizing agents to transfer the oxygen, which will be described, and as oxidizing agents by addition of other groups to the I^+–O^- of **5a,b**. Reaction with trifluoroacetyl anhydride, and other such species, forms the 12-I-5 type of product.



Experimental Section

General Methods. Chemical shifts are reported in parts per million downfield from tetramethylsilane as an internal standard for ^1H NMR spectra and from $CFCl_3$ as an internal standard for ^{19}F NMR spectra.

1,1-Difluoro-10-*tert*-butyl-3,3,7,7-tetrakis(trifluoromethyl)-4,6-benzo-1-ioda-2,8-dioxabicyclo[3.3.0]octane (4b). (a) Reaction with BrF_3. Compound **4b** was synthesized from 1 g (1.7 mmol) of iodo diol **6b** and 0.4 g (2.9 mmol) of BrF_3 by using the same method as in the preparation of **4a**:[19,20] yield 76% (0.8 g, 1.3 mmol): mp 204–205 °C dec; IR (CH_2Cl_2) 3050 (s), 1213 (m), 1086 (m), 1066 (w), 975 (m), 896 (m), 765 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 8.18 (s, 2 Ar H), 1.48 (s, 9, CH_3); ^{19}F NMR ($CDCl_3$) δ −14.64 (m, 2, J = 4.2 Hz, IF), −74.83 [t, (J_{FF} = 4.2 Hz) of d (J_{HF} = 0.8 Hz), 12, CF_3], mass spectrum (10 eV) m/e (relative intensity) 628 (2, M^+), 613 (56, $M^+ - CH_3$), 609 (5, $M^+ - F$), 559 (100, $M^+ - CF_3$), 521 (22, $M^+ - CF_3 - 2F$). Anal. Calcd for $C_{16}H_{11}O_2IF_{14}$: C, 30.59; H, 1.77; I, 20.20; F, 42.34. Found: C, 30.48; H, 1.68; I, 20.09; F, 42.16.

(b) Reaction with F_2. Into a stirred solution of iodo diol **6b** (100 mg, 0.169 mmol) in dry Freon-11 (50 mL) at 0 °C in a Teflon reaction vessel was slowly bubbled 5% fluorine in nitrogen (750 mL, 1.67 mmol) below the solution surface. After the final addition (45 min), the reaction mixture was stirred at 0 °C with a small nitrogen purge for 15 min. The mixture was warmed to room temperature with a constant sweep of N_2. The solvent was evaporated to give the white solid, **4b**, 106 mg (0.169 mmol, 100%).

1-Oxo-10-*tert*-butyl-3,3,7,7-tetrakis(trifluoromethyl)-4,6-benzo-1-ioda-2,8-dioxabicyclo[3.3.0]octane (5b). To 2.5 g (4.0 mmol) of difluoroperiodinane **4b** in 50 mL of CH_3CN was added 0.22 g (4.0 mmol) of KOH in 50 mL of H_2O with stirring. The solution turned slightly yellow after 30 min. It was dried ($MgSO_4$), and the solvent was removed. Recrystallization from acetonitrile gave 2.2 g (3.6 mmol, 90%) of white crystalline iodinane oxide **5b**: mp 241–242 °C dec; IR (CH_2Cl_2) 3055 (s), 2987 (m), 1424 (m), 1290 (s), 1270 (s), 1160 (w), 1145 (w), 1084 (s), 974 (s), 896 (s), 864 (w), 840 (w), 750 (s) cm^{-1}; ^1H NMR (CD_3CN) δ 8.15 (s, 2, Ar H), 1.43 (s, 9, CH_3); ^{19}F NMR (CD_3CN) δ −74.3 (q, 6, J = 8.4 Hz, CF_3), −74.85 (q, 6, J = 8.4 Hz, CF_3); mass spectrum (10 eV) m/e (relative intensity) 591 (7, $M^+ - CH_3$), 590 (5, $M^+ - O$), 575 (3, $M^+ - CH_3 - O$), 537 (100, $M^+ - CF_3$), 521 (70, $M^+ - CF_3 - O$). Anal. Calcd for $C_{16}H_{11}O_3IF_{12}$: C, 31.70; H, 1.83; I, 20.94; F, 37.61. Found: C, 31.61; H, 1.97; I, 21.11; F, 37.17.

1-Oxo-10-methyl-3,3,7,7-tetrakis(trifluoromethyl)-4,6-benzo-1-ioda-2,8-dioxabicyclo[3.3.0]octane (5a). A similar procedure was used to synthesize **5a**. From 0.36 g (0.62 mmol) of difluoroperiodinane **4a** was obtained 0.30 g (0.50 mmol, 85%) of **5a**: mp 179–180 °C; ^1H NMR ($CDCl_3$) δ 7.97 (s, 2, Ar H), 2.73 (s, 3, CH_3); ^{19}F NMR ($CDCl_3$) δ −74.05 (q, 6, J = 8.4 Hz, CF_3), −74.6 (q, 6, J = 8.4 Hz, CF_3); mass spectrum (70 eV) m/e (relative intensity) 495 (100, $M^+ - CF_3$), 479 (62, $M^+ - CF_3 - O$), 357 (37, $M^+ - 3CF_3$), 341 (58, $M^+ - 3CF_3 - O$). The isopiestic method used a solution of **5a** (10 mg) in CH_3CN (2.5 mL) and another solution of dibenzothiophene sulfone (10.1 mg, 0.0487 mmol) in CH_3CN (2.4 mL). Each solution was in one of the two isopiestic tubes with both coordinated in a closed vacuum. After 12 h the two solutions were no longer changing their sizes, providing the same concentrations of the two dissolved species in CH_3CN. This made it clear that **5a** in CH_3CN was partly a dimer of **5a**: 747 g mol^{-1} for **5a**, calcd MW 564 for a monomer of **5a**. Anal. Calcd for $C_{13}H_5O_3IF_{12}$: C, 27.68; H, 0.89; I, 22.50; F, 40.42. Found: C, 27.56; H, 1.14; I, 22.64; F, 40.22.

1-{1-Fluoro-10-*tert*-butyl-3,3,7,7-tetrakis(trifluoromethyl)-4,6-benzo-1-ioda-2,8-dioxabicyclo[3.3.0]octyl} Trifluoromethanesulfonate (8). (a) Trifluoroacetyl trifluoromethanesulfonate (triflate) (TFAT)[21] (3 mL, 20 mmol), in the presence of a small amount of triflic acid (TfOH), was added to difluoroperiodinane **4b** (0.24 g, 0.40 mmol). (Without the addition of TfOH the reaction proceeds slowly to give about 20% of **8** after 2 days.) The mixture was stirred for 30 min. Then TFAT and TfOH were removed in vacuum, leaving solid fluoroperiodonium triflate **8** (0.21 g, 0.28 mmol, 72%): mp 183–185 °C dec; ^1H NMR (CD_2Cl_2) δ 8.33 (s, 2, Ar H), 1.49 (s, 9, CH_3); ^{19}F NMR (CD_2Cl_2) δ −27.54 (sep, 1, J = 9.26 Hz, IF), −73.65 (q, 6, J = 9.32 Hz, CF_3), −74.85 [d (J = 9.26 Hz) of q (J = 9.32 Hz), 6, CF_3], −78.3 (s, 3, $CF_3SO_3^-$). Anal. Calcd for $C_{17}H_{11}O_5F_{16}IS$: C, 26.92; H, 1.46; I, 16.72; S, 4.23; F, 40.09. Found: C, 26.81; H, 1.58; I, 16.63; S, 4.29; F, 40.35.

(b) Treatment of difluoroperiodinane **4b** (0.26 g, 0.41 mmol) with TfOH (1.5 mL, 17 mmol) at room temperature instantly gave **8** as indicated by the liberation of HF (gas). The reaction was completed after 30 min. Excess TfOH was removed in vacuum. The ^1H and ^{19}F NMR spectra showed about 80% of **8**.

1-{1-Hydroxy-10-*tert*-butyl-3,3,7,7-tetrakis(trifluoromethyl)-4,6-benzo-1-ioda-2,8-dioxabicyclo[3.3.0]octyl} Trifluoromethanesulfonate (9). Triflic acid (20 μL, 0.2 mmol) was added to a solution of iodinane oxide **5b** (0.15 g, 0.2 mmol) in 3 mL of CH_2Cl_2. The mixture was stirred at room temperature for 2 h. Filtration of the precipitate gave **9** (0.14 g, 0.18 mmol, 92%): mp 185–186 °C dec; ^1H NMR (CD_3CN) δ 13.4 (s, 1, OH), 8.23 (s, 2, Ar H), 1.45 (s, 9, CH_3); ^{19}F NMR (CD_3CN) δ −74.25 (q, 6, J = 8.9 Hz, CF_3), −75.15 (q, 6, J = 8.9 Hz, CF_3), −78.6 (s, 3, $CF_3SO_3^-$). Anal. Calcd for $C_{17}H_{12}O_6IF_{15}S$: C, 27.00; H, 1.60; I, 16.78. Found: C, 26.67; H, 1.91; I, 16.40.

Compound **9** was obtained when a small sample of fluoroperiodonium salt **8** was stored in a glass vial at room temperature over a period of 6 months.

1-Fluoro-1-[2,2,2-trifluoro-1-phenyl-1-(trifluoromethyl)-ethoxy]-10-*tert*-butyl-3,3,7,7-tetrakis(trifluoromethyl)-4,6-benzo-1-ioda-2,8-dioxabicyclo[3.3.0]octane (10). Difluoroperiodinane **4b** (0.32 g, 0.50 mmol) and potassium 1,1,1,3,3,3-hexafluoro-2-phenyl-2-propoxide (R_FOK) (0.29 g, 1.0 mmol) suspended in 7 mL of dry CH_2Cl_2 were stirred for 30 days at room temperature. The ^{19}F NMR spectrum of the mixture showed that **4b** was converted to **10** in quantitative yield. The solvent was removed under vacuum, and the resulting white solid was stirred in 20 mL of dry hexane. The KF and R_FOK were removed by filtration, and the filtrate was concentrated to crystallize **10** (0.30 g, 0.35 mmol, 70%): mp 188–190 °C; ^1H NMR (CD_2Cl_2) δ 8.27 (s, 2, Ar H), 7.38 (m, 1, R_FO), 7.28 (m, 4, R_FO), 1.54 (s, 9, CH_3); ^{19}F NMR (CD_2Cl_2) δ −4.81 (br s, 1, IF), −71.30 (br s, 6, R_FO), −74.02

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(q, J = 9.9 Hz, 6, CF_3), -74.60 [d (J = 9.6 Hz) of q (J = 9.9 Hz), 6, CF_3 syn to IF]; mass spectrum (70 eV) m/e (relative intensity) 837 (1, $M^+ - CH_3$), 783 (6, $M^+ - CF_3$), 609 (100, $M^+ - R_FO$), 521 (40, $M^+ - R_FO - F - CF_3$), 471 (23, $M^+ - R_FO - 2CF_3$). Anal. Calcd for $C_{25}H_{16}O_3IF_{19}$: C, 35.23; H, 1.89. Found: C, 35.19; H, 1.99.

1,1-Bis(trifluoroacetoxy)-10-*tert*-butyl-3,3,7,7-tetrakis(trifluoromethyl)-4,6-benzo-1-ioda-2,8-dioxabicyclo[3.3.0]octane (11). Trifluoroacetic anhydride (TFAA) (3.0 mL, 21 mmol) was added by distillation to 0.27 g (0.45 mmol) of iodinane oxide **5b**. After 2 h the solvent was removed to give 0.31 g (0.38 mmol, 85%) of bis(trifluoroacetoxy)periodinane **11**: mp 165–168 °C dec; ^1H NMR (CD_3CN) δ 8.25 (s, 2, Ar H), 1.45 (s, 9, CH_3); ^{19}F NMR (CD_3CN) δ -74.03 (s, 12, CF_3), -74.4 (s, 6, $^-OCOCF_3$). Anal. Calcd for $C_{20}H_{11}O_6IF_{18}$: C, 29.43; H, 1.36. Found: C, 29.61; H, 1.28.

1-{1-(Trifluoroacetoxy)-10-*tert*-butyl-3,3,7,7-tetrakis(trifluoromethyl)-4,6-benzo-1-ioda-2,8-dioxabicyclo[3.3.0]octyl} Trifluoromethanesulfonate (12). To 0.63 g (1.0 mmol) of iodinane oxide **5b** was added TFAT (4.0 mL, 26 mmol) by distillation. The slurry was stirred for 3 h, and then the excess TFAT was removed under vacuum. Solid **12** was obtained after washing with 10 mL of pentane (0.81 g, 0.95 mmol, 95%): mp 161–162 °C; ^1H NMR (CD_3CN) δ 8.4 (s, 2, Ar H), 1.45 (s, 9, CH_3); ^{19}F NMR (CD_3CN) δ -73.25 (q, 6, J = 9 Hz, CF_3), -73.8 (m, 3, J = 1 Hz, $^-OCOCF_3$), -74.3 (q, 6, J = 9 Hz, CF_3), -77.9 (s, 3, $CF_3SO_3^-$). Anal. Calcd for $C_{19}H_{11}O_7IF_{18}S$: C, 26.78; H, 1.30; I, 14.89; S, 3.77; F, 40.13. Found: C, 26.95; H, 1.36; I, 14.49; S, 3.93; F, 40.53.

1,1-Bis[1-phenyl-1-(trifluoromethyl)-2,2,2-trifluoroethoxy]-10-*tert*-butyl-3,3,7,7-tetrakis(trifluoromethyl)-4,6-benzo-1-ioda-2,8-dioxabicyclo[3.3.0]octane (13). A suspension of iodinane oxide **5b** (1.5 g, 2.47 mmol) and bis[2,2,2-trifluoro-1-phenyl-1-(trifluoromethyl)ethoxy]diphenylsulfurane (**14**) (1.7 g, 2.52 mmol) in 30 mL of dry CH_2Cl_2 was mixed at room temperature for 15 min. The solvent was removed under vacuum, and the resulting white solid was recrystallized from a mixture of ethyl ether and hexane (1:2) to give white crystalline **13** (2.4 g, 2.23 mmol, 90%): mp 209–210 °C; ^1H NMR (CD_2Cl_2) δ 8.33 (s, 2, Ar H), 7.37 (m, 2, R_FO), 7.26 (m, 8, R_FO), 1.55 (s, 9, CH_3); ^{19}F NMR (CD_2Cl_2) δ -71.09 (br s, 12, R_FO), -73.47 (br s, 12, CF_3 groups of tridentate ligand); mass spectrum (70 eV) m/e (relative intensity) 833 (43, $M^+ - R_FO$), 521 (100, $M^+ - R_FO - CF_3$). Anal. ($C_{34}H_{21}O_4IF_{24}$): C, 37.94; H, 1.97. Found: C, 37.96; H, 2.13.

1-{1-[2,2,2-Trifluoro-1-phenyl-1-(trifluoromethyl)ethoxy]-10-*tert*-butyl-3,3,7,7-tetrakis(trifluoromethyl)-4,6-benzo-1-ioda-2,8-dioxabicyclo[3.3.0]octyl} Trifluoromethanesulfonate (15). To 0.18 g (0.16 mmol) of dialkoxyperiodinane **13** was added triflic anhydride (4 mL, 23 mmol) by distillation. The mixture was stirred at room temperature for 10 h, and then excess anhydride was removed under vacuum. The remaining solid was washed with hexane to give **15** (0.10 g, 0.10 mmol, 63%): mp 162–165 °C dec; ^1H NMR (CD_2Cl_2) δ 8.40 (s, 2, Ar H), 7.51 (m, 1, R_FO), 7.43 (m, 4, R_FO), 1.53 (s, 9, CH_3); ^{19}F NMR (CD_2Cl_2) δ -70.50 (br s, 6, R_FO), -73.17 (q, 6, J = 9.6 Hz, CF_3), -73.83 (br q, 6, J = 9.6 Hz, CF_3), -78.77 (s, 3, $CF_3SO_3^-$). Anal. Calcd for $C_{26}H_{16}O_6IF_{21}S$: C, 31.79; H, 1.64. Found: C, 31.58; H, 1.68.

Reaction of Difluoroperiodinane 4b with Triflic Anhydride (Tf_2O). In an NMR tube Tf_2O (0.1 mL, 0.58 mmol) was added by distillation to 30 mg (0.048 mmol) of **4b**. $CDCl_3$ (0.5 mL) was added by distillation, and the NMR tube was sealed. After 2 days of reaction at room temperature, 30% of fluoroperiodonium triflate **8** was identified by ^1H and ^{19}F NMR.

Reaction of Unsymmetrical Alkoxyfluoroperiodinane 10 with Triflic Anhydride (Tf_2O). To a solution of **10** (30 mg, 0.035 mmol) in 0.5 mL of dry $CDCl_3$ was added Tf_2O (0.05 mL, 0.29 mmol) by distillation. After 2 days of reaction at 25 °C, the ^1H and ^{19}F NMR spectra showed that the reaction mixture contained unsymmetrical periodinane **10** (30%), alkoxyperiodonium triflate **15** (35%), and difluoroperiodinane **4b** (35%).

Reactions of Dialkoxyperiodinane 13. (a) Reaction with Trifluoroacetyl Triflate (TFAT). To 50 mg (0.046 mmol) of **13** in an NMR sample tube were added TFAT (0.10 mL, 0.65 mmol) and $CDCl_3$ (0.5 mL) by distillation, and the sample tube was sealed. After 5 h at room temperature, 38% of alkoxyperiodonium triflate **15** was formed. Products were analyzed by ^1H and ^{19}F NMR spectroscopy and identified by comparison with authentic samples.

(b) Reaction with Trifluoroacetic Anhydride (TFAA). To 20 mg (0.018 mmol) of **13** was added TFAA (1 mL, 7 mmol) by distillation. After 4 h of reaction at room temperature, solvent was removed. ^1H and ^{19}F NMR spectra of the product showed a mixture of dialkoxyperiodinane **13** (24%), bis(trifloroacetoxy)periodinane **11** (51%), and another product (25%), which was not isolated but identified as the unsymmetrical alkoxy(trifluoroacetoxy)periodinane **16**: ^1H NMR ($CDCl_3$) δ 8.27 (s, 2, Ar H), 7.45 (m, 2, R_FO), 7.30 (m, 3, R_FO), 1.54 (s, 9, CH_3); ^{19}F NMR ($CDCl_3$) δ -71.33 (br s, 6, R_FO), -74.02 (m, 6, CF_3), -74.17 (m, 6, CF_3), -75.25 (s, 3, $^-OCOCF_3$).

Reaction of Iodinane Oxide 5b. (a) Reaction with 1 Equiv of Bis(4-chlorophenyl) Sulfide. A mixture of **5b** (31 mg, 0.05 mmol) and bis(4-chlorophenyl) sulfide (12 mg, 0.05 mmol) was heated in a sealed NMR tube without solvent for 24 h at 130 °C. The ^1H and ^{19}F NMR spectra of this mixture showed the presence of bis(4-chlorophenyl) sulfide (31%), bis(4-chlorophenyl) sulfoxide (46%), bis(4-chlorophenyl) sulfone (23%), and iodinane **7b** (100%), upon the basis of a comparison with the spectra of authentic samples.

(b) Reaction with 0.5 Equiv of Bis(4-chlorophenyl) Sulfide. A mixture of **5b** (55 mg, 0.09 mmol) and bis(4-chlorophenyl) sulfide (10 mg, 0.04 mmol) was heated without solvent at 160 °C for 1.5 h. The ^1H and ^{19}F NMR spectra of this mixture showed bis(4-chlorophenyl) sulfoxide (11%), bis(4-chlorophenyl) sulfone (88%), and iodinane **7b** (100%). The composition of the product mixture was confirmed by comparison of its NMR spectra with those of authentic samples.

(c) Reaction with Bis(4-chlorophenyl) Sulfide and TFAA. To a solution of iodinane oxide **5b** (40 mg, 0.06 mmol) in 0.5 mL of CD_3CN at room temperature was added bis(4-chlorophenyl) sulfide (16 mg, 0.06 mmol). No reaction was detected by NMR spectroscopy. To this solution was added 7.0 mL (50 mmol) of TFAA. The ^1H and ^{19}F NMR spectra of the mixture immediately showed the presence of bis(4-chlorophenyl) sulfoxide (28%), iodinane **7b** (30%), and bis(trifluoroacetoxy)periodinane **11** (70%).

(d) Reaction with Hydrogen Chloride. To a solution of **5b** (20 mg, 0.03 mmol) in 0.5 mL of CD_2Cl_2 were added two drops of 6 M aqueous HCl. The ^1H and ^{19}F NMR spectra of the resulting yellow solution indicated that all of the **5b** was reduced to iodinane **7b**. The solution, containing chlorine, gave a positive test with starch–iodide paper. Iodinane **7b** does not oxidize iodide to iodine.

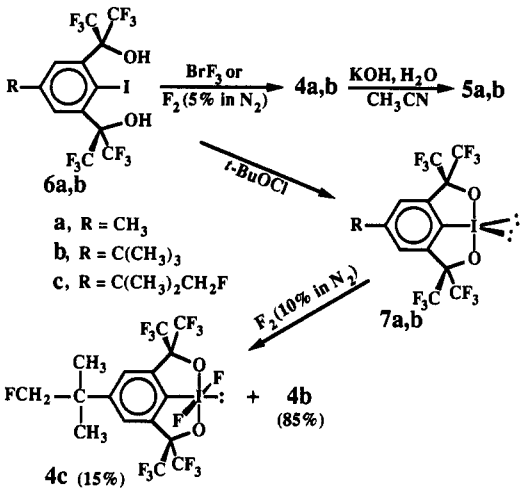
(e) Reaction with Pinacol. Pinacol (6.0 mg, 0.05 mmol) was added to a solution of **5b** (30 mg, 0.05 mmol) in 0.5 mL of CD_2Cl_2. No reaction was detected by NMR spectroscopy. A solution of **5b** (35 mg, 0.055 mmol) and 7.0 mg (0.055 mmol) of pinacol in 0.5 mL of *o*-dichlorobenzene was heated at 125 °C for 24 h. The ^1H and ^{19}F NMR spectra of this mixture showed all pinacol to have been converted to acetone, with reduction of **5b** to **7b**.

(f) Reaction with Excess Potassium Hydroxide. To a solution of **5b** (65 mg, 0.11 mmol) in 3 mL of acetonitrile was added a solution of KOH (96 mg, 1.7 mmol) in 0.3 mL of water. The mixture was stirred for 10 h, and then it was acidified with 3 M H_2SO_4. Water was added, and the reaction mixture was extracted with ether. The ether layer was dried ($MgSO_4$) and evaporated under vacuum to give reduced diol **17** (40 mg, 0.09 mmol, 78%): mp 67–68 °C; ^1H NMR ($CDCl_3$) δ 8.02 (s, 1, Ar H), 7.95 (s, 2, Ar H), 1.47 (s, 9, CH_3): ^{19}F NMR ($CDCl_3$) δ -76.0 (s, 12, CF_3). The water layer gave a positive test with starch–iodide paper.

(g) Variable-Temperature Studies of the Treatment of 5b with Tetra-*n*-butylammonium Hydroxide. The ^{19}F NMR spectra of a solution of **5b** (20 mg, 0.034 mmol) and tetra-*n*-butylammonium hydroxide (1.2 mg, 4.6 μmol) in 1 mL of $CD_3CN/CFCl_3$ were recorded at various temperatures. The chemical shifts for the CF_3 groups coalesced at -74.55 ppm at 27 °C. Upon cooling, the signals gave two quartets (J = 7 Hz) and then merged back to a broad singlet at temperatures lower than -15 °C: 35 °C (s, -74.55), 27 °C (s, -74.55), 9 °C (q, -74.48, -74.62), 3 °C (q, -74.50, -74.60), 0 °C (q, -74.49, -74.59), -4 °C (s, -74.55), -15 °C (br s, -74.55), -45 °C (br s, -74.55).

Attempted Synthesis of 13. To 13 mg (0.02 mmol) of **5b** and P_2O_5 (10 mg, 0.07 mmol) in an NMR sample tube was added 10 mg (0.04 mmol) of R_FOH in 0.5 mL of toluene. The sample was sealed, and it was heated at 100 °C for 6 h. The NMR spectrum of the mixture showed that iodinane oxide **5b** was partially re-

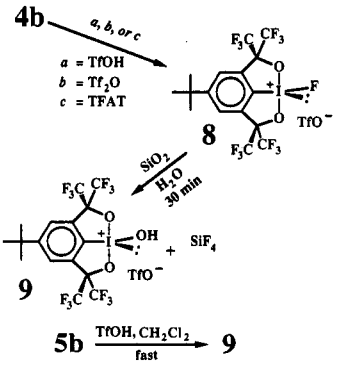
Scheme I



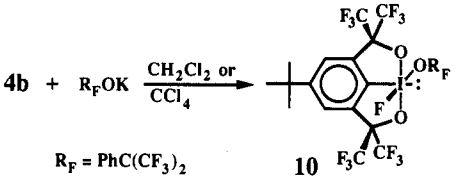
duced (ca. 20%) to iodinane **7b**, and no dialkoxyperiodinane **13** was observed.

Results

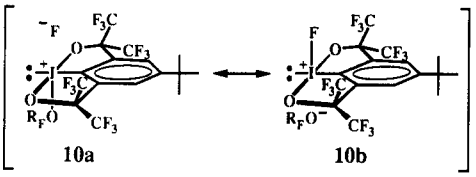
Synthesis. Syntheses of iodo diols **6a,b**, 10-I-3 iodinanes **7a,b** and difluoroperiodinane **4a** have been reported by us in earlier papers.[19,20] Iodinane oxides **5a** and **5b** were synthesized as shown in Scheme I. Fluorination of iodo diol **6b** with bromine trifluoride gave a yield of 76% of periodinane **4b**, whereas fluorination with a large excess of fluorine (5% in N_2) at 0 °C gave a quantitative yield. When iodinane **7b** was treated with a higher concentration of fluorine (10% in N_2) at low temperature, some radical fluorination (ca. 15%) of the *tert*-butyl group of **4b** also occurred by F_2 forming **4c** in an inert solvent. Difluoroperiodinane **4b** reacts with strong Lewis acids such as antimony pentafluoride or sulfur trioxide to give fluoroperiodonium salts. It reacts rapidly with triflic acid (TfOH) and more slowly with triflic anhydride (Tf_2O) or the mixed anhydride trifluoroacetyl triflate (TFAT)[21] to give the 10-I-4 fluoroperiodonium triflate **8**. The iodinane oxide **5b** also provides **9** rapidly with triflic acid.



Fluoroperiodonium triflate **8** was isolated as a crystalline solid, while other fluoroperiodonium salts, the hexafluoroantimonate and the fluorosulfonate, were observed by NMR only. The ^{19}F NMR spectrum of compound **8** in methylene dichloride shows a quartet (6F), a doublet of quartets (6F), and a singlet (3F) all in the region where CF_3 groups are expected. Therefore the quartet (J = 9.3 Hz) is assigned to the CF_3 groups anti to the fluorine ligand, and the doublet (J = 9.2 Hz) of quartets (J = 9.3 Hz) is assigned to the CF_3 groups syn to the fluorine ligand. The CF_3 groups of **8**, cis to the equatorial F, provide short distances between the fluorines. This is thought to give direct ^{19}F NMR interaction of these fluorines, rather than interaction through the five bonds connecting the two types of fluorine. The septet (J = 9.2 Hz) for the fluorine ligand attached to iodine is observed at −27.54 ppm. The ^{19}F chemical shift of the singlet assigned to the triflate CF_3 group of **8** was found in the range (ca. −78 ppm) typical for triflate salts.[21,22] It is therefore unlikely that the signal at −78.3 ppm is due to a covalently bonded TfO group in a covalent periodinane. We therefore conclude that the peak is best assigned to the triflate salt, **8**. Fluoroperiodonium triflate **8** upon storage for 6 months in a glass vial at room temperature reacts to give hydroxyperiodonium triflate **9**. Difluoroperiodinane **4b** reacts slowly with the potassium salt of hexafluorocumyl alcohol (R_FOK) to give the unsymmetrical fluoroalkoxyperiodinane **10**.



Periodinane **10** shows in its ^{19}F NMR spectrum a singlet for the R_FO ligand and two multiplets for the nonequivalent CF_3 groups. A singlet at −4.8 ppm ($W_{1/2}$ = 42 Hz) for the fluorine ligand attached to iodine is broadened by coupling to the two cis trifluoromethyl fluorines. Periodinane **10** is much more rapidly hydrolyzed than is the symmetrical difluoroperiodinane **4**, as expected in view of the unsymmetrical F–I–O three-center four-electron bond. The three-center bond of **10** may be represented by resonance structures **10a** and **10b**, with **10a** contributing more to the structure than **10b** as a result of the inductive electron withdrawal of the fluorine ligand.[23] The polarization of the hypervalent bond could well provide increased reactivity of unsymmetrical periodinane **10**. Compound **10** is much more reactive toward water than the symmetrical analogues **4b** and **13**.

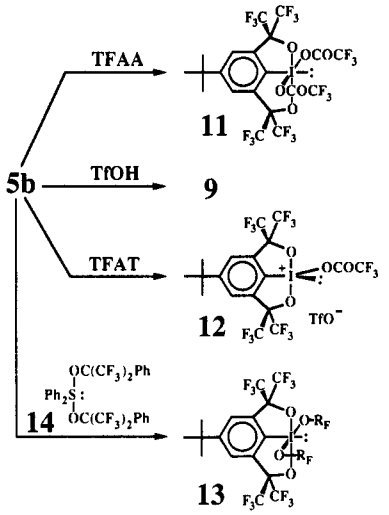


The products of hydrolysis of difluoroperiodinanes **4a,b** 10-I-4 iodinane oxides **5a,b**, are stable as solids up to their melting points. They are not moisture sensitive and can be safely stored at room temperature for an indefinite period. They do not detonate when struck by a hammer on concrete. Iodinane oxide **5b** does not react with acetic anhydride (80 °C, 6 h), but when it is treated with trifluoroacetic anhydride at room temperature, bis(trifluoroacetoxy)periodinane **11** is formed. Similar reactions of iodinane oxide **5b** with TfOH and TFAT provide periodonium triflates **9** and **12**, respectively. Iodinane oxide **5b** reacts within seconds with sulfurane **14** to give dialkoxyperiodinane **13**. Periodinane **13** can be stored at room temperature for an indefinite period of time. It partially (34%) decomposes after heating at 215 °C for 1 h to give

(21) Taylor, S. L.; Forbus, T. R., Jr.; Martin, J. C. *Org. Synth.* **1985**, *64*, 217. Forbus, T. R., Jr.; Taylor, S. L.; Martin, J. C. *J. Org. Chem.* **1987**, *52*, 4156.

(22) (a) Beyl, V.; Niederprum, H.; Voss, P. *Justus Liebigs Ann. Chem.* **1970**, *731*, 58. (b) Grakauskas, V. *J. Inorg. Nucl. Chem.* **1973**, *35*, 3034. (c) Peringer, P. *J. Inorg. Nucl. Chem.* **1980**, *42*, 1501.

(23) Adzima, L. J.; Duesler, E. N.; Martin, J. C. *J. Org. Chem.* **1977**, *42*, 4001.



iodinane **7b** (27%) and iodinane oxide **5b** (7%). Other products of decomposition of dialkoxyperiodinane **13** were not identified. The product formed simultaneously with **7b** might be the dialkyl peroxide R_FOOR_F. A similar ligand–ligand coupling reaction was seen by Arduengo and Burgess[24] in a 10-S-3 species with two R_FO ligands attached to sulfur.

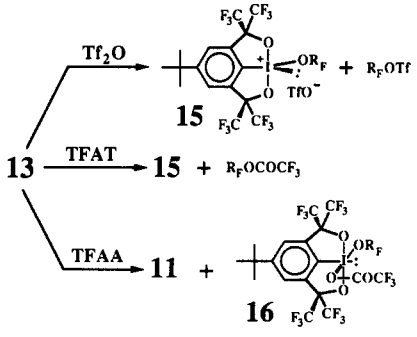
$$13 \xrightarrow{\Delta} 7b + R_FOOR_F$$

Other unsuccessful attempts made to synthesize **13** are listed below:

$$5b + 2R_FOH \xrightarrow[100\ °C,\ 6\ h]{P_2O_5} \text{no reaction}$$

$$7b + 2R_FOH \xrightarrow[rt]{Cl_2,\ CCl_4} \text{alkyl chlorinated } 7b$$

Reactions of 5b, 10, and 13. Dialkoxyperiodinane **13** reacts with trifluoroacetic anhydride to form the analogous bis(trifluoroacetate) **11** (51%), as evidenced by ^1H and ^{19}F NMR spectroscopy, as well as the unsymmetrical alkoxy(trifluoroacetoxy)periodinane **16** (25%). Optimization of yields was not attempted. Treatment of dialkoxyperiodinane **13** excess TFAT or Tf_2O forms the 10-I-4 alkoxyperiodonium triflate, **15**. Compound **15** shows in its ^{19}F NMR spectrum a broad singlet for the R_FO ligand, a singlet for the triflate CF_3 group, and two multiplets. The quartet (J = 9.6 Hz) at −73.17 ppm is assigned to the CF_3 groups anti to the R_FO ligand, and the broadened quartet at −73.83 ppm is assigned to the CF_3 groups syn to the fluoroalkoxy ligand, with F–F coupling. Alkoxyperiodonium triflate **15** is extremely moisture sensitive.

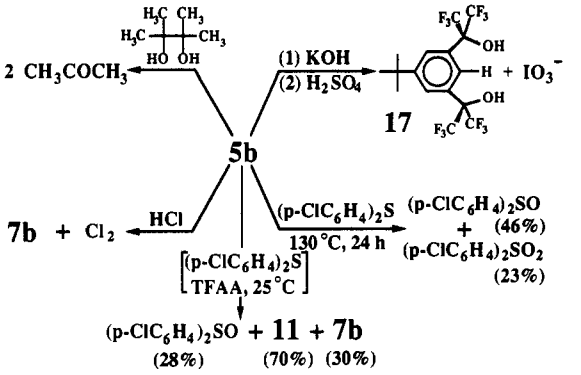


Unsymmetrical alkoxyfluoroperiodinane **10** in 2 days of reaction with Tf_2O forms alkoxyperiodonium triflate **15** (35%) and difluoroperiodinane **4b** (35%) as evidenced by ^1H and ^{19}F NMR. The formation of **4b** probably results from the transfer of a fluoride anion from **10** to the iodine of periodonium triflate **8** formed in the early stage of the reaction of **10** with Tf_2O.

$$10 \xrightarrow{Tf_2O} 8 + TfOR_F \xrightarrow{10} 4b + 15$$

Iodinane oxides are strong oxidants. They oxidize hydrogen chloride, pinacol, bis(4-chlorophenyl) sulfide, and bis(4-chlorophenyl) sulfoxide to give chlorine, acetone, diaryl sulfoxide, and diaryl sulfone, respectively. The oxidation of bis(4-chlorophenyl) sulfide does not occur significantly at room temperature. When a small amount of trifluoroacetic anhydride is added to the reaction mixture, however, the sulfoxide is formed instantaneously at room temperature. Iodinane oxide **5b** is not seen to react with potassium fluoride. No changes in ^{19}F NMR were observed after 16 h of treatment at 60 °C. Iodinane oxides react with excess potassium hydroxide to give the reduced diol **17**, upon workup with aqueous acid. The other product is presumed to be potassium iodate, since the aqueous layer oxidizes iodide to iodine. Some reactions of iodinane oxide **5b** are shown in Scheme II.

Scheme II

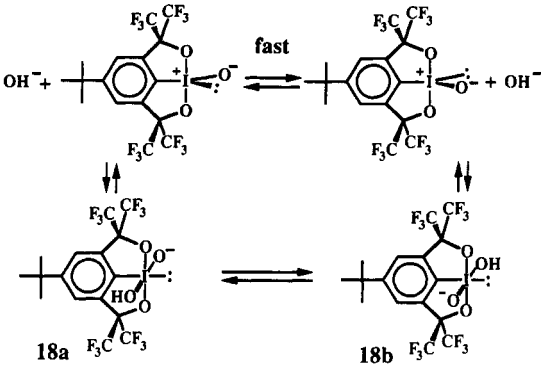


Iodinane oxide **5** exhibits two sets of quartets in its ^{19}F NMR spectrum at temperatures from −50 to 50 °C. Upon addition of small amounts of hydroxide to the solution of **5b** in acetonitrile, an exchange process occurs. The two sets of quartets coalesce near room temperature, probably resulting from an exchange process, in which hydroxide ion adds to the iodine atom to form an intermediate such as **18** which serves to invert the configuration of iodine. The two quartets also merge to a broad singlet at temperatures below −10 °C. This probably arises from the temperature dependence of the chemical shifts of the two CF_3 groups. As the temperature decreases, they move closer to one another with concomitant loss of fine structure. At still lower temperatures, as the chemical shifts become identical and then diverge again, other processes, such as perhaps intermolecular association, are slowed, resulting in a broadening of the signal.

Discussion

Ligand Stabilization of Iodinane Oxides (5). Although examples of iodinane oxides are known,[9,11,13-17] their chemistry has been relatively unexplored, partly because most known iodinane oxides are not stable at room temperature. They readily hydrolyze upon exposure to moisture. The monocyclic compounds are more stable than the acyclic ones. One example is the cyclic form of 2-iodoxybenzoic acid, compound **1**. Its synthesis was reported in 1893.[18a] Based on the infrared spectrum of 2-iodoxybenzoic acid (**1**), the cyclic structure, proposed in

(24) Private communication from A. J. Arduengo, III, and E. M. Burgess.

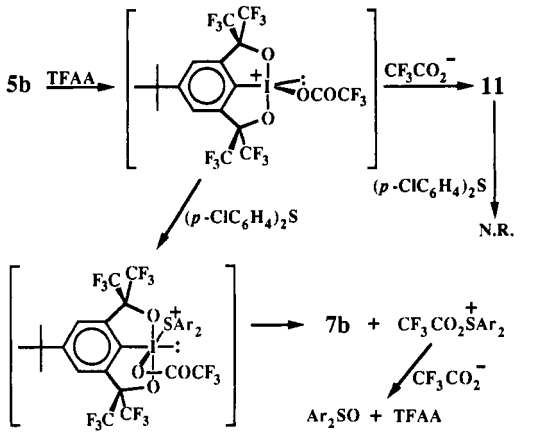


1960,[18b] was confirmed by X-ray crystallography in 1981.[18c] Compound 1 has a polymeric structure with strong intermolecular interactions of iodine and oxygen atoms making the iodine pseudooctahedral (Ψ-Oc) in geometry. The bicyclic iodinane oxides reported here, compounds **5a,b** are hydrolysis products of difluoroperiodinanes **4a,b**. Either acid or base catalyzes the hydrolyses.

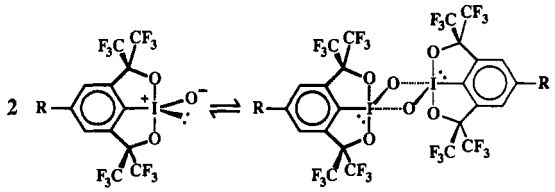
The enhanced stability of **5a,b** is attributed to the structure of the tridentate ligand. The linear three-center four-electron bond centered at the iodine provides increased negative charge at the apical oxygen centers and increased positive charge at the iodine, as is characteristic of hypervalent[25] species. The two adjacent CF_3 groups stabilize the negative charge on the apical oxygens, and the more electropositive carbon attached to the iodine stabilizes the more positive charge at the center of the three-center bond. The two five-membered rings linking the apical and equatorial sites also provide marked stabilization[26] of the hypervalent species, as a reflection of the ideal (ca. 90°) bond angle between an apical bond and an equatorial bond.

The structure of **5** is strongly supported by its NMR spectra. The ^{19}F NMR spectrum shows two quartets for the CF_3 groups, indicating that the two geminal CF_3 groups are not equivalent. The ^1H NMR spectrum gives a singlet for the aromatic protons, consistent with the plane of symmetry bisecting the phenyl ring through the carbon–iodine bond. The mass spectrum of **5** (**a** or **b**) shows no molecular ion of the dimeric species. A molecular weight determination of **5a** in acetonitrile (~0.1 M) gives a mass of 747 g mol^{-1}, which is higher than the calculated molecular weight of the monomer (564 g mol^{-1}). This is done by having two solutions in CH_3CN, one for **5a** and one for any other stable dissolved compound that is not distilled. When the two solutions are connected together in a closed vacuum, the two solutions will move CH_3CN to prepare both with identical concentrations within a few hours. The measured concentration of **5a** in CH_3CN, when there is no further change in concentration, shows that the dissolved material is 32.4% of the dimer of **5a**, with 67.6% of the monomer. This observation is attributed to the pictured dimerization process, one of the type commonly observed for iodine compounds of higher oxidation states, such as

Scheme III



I_2O_5.[27] The X-ray crystal structure[18c] of 1 provided evidence for a related intermolecular interaction leading to polymeric species.



Reactions of Iodinane Oxides. The iodine(V) species of this paper, which we draw as 10-I-4 iodinane oxides **5a,b** with a single bond joining iodine and the equatorial oxygen, undergo several reactions analogous to those of the iodine(VII) species, periodate ion. The periodate anion was used by Leonard and Johnson[28] to oxidize diphenyl sulfide selectively, first to sulfoxide and then to sulfone, at 0 °C. Iodinane oxide **5b**, with a lower iodine oxidation state, oxidizes bis(4-chlorophenyl) sulfide considerably less selectively at the required temperature of ~130 °C to a mixture of sulfoxide (46%) and sulfone (23%). The lowered selectivity of the iodinane oxide may result from the higher reaction temperatures required for this oxidation. The ability of **5b** to rapidly oxidize chloride ion to chlorine in acid suggests that its unreactivity in nonacidic media is attributable to kinetic rather than thermodynamic factors. When a small amount of trifluoroacetic anhydride is added to a mixture of iodinane oxide **5b** and bis(4-chlorophenyl) sulfide, at 25 °C, the oxidation of the sulfide occurs very rapidly, giving three products: the sulfoxide, the iodinane, and bis(trifluoroacetoxy)periodinane 11. We suggest that the catalytic effect of added anhydride results from the formation of a reactive intermediate periodonium ion, which then either oxidizes the sulfide, regenerating the trifluoroacetic anhydride, or combines with the trifluoroacetic anion to form bis(trifluoroacetoxy)periodinane 11. Periodinane 11 was found to be unreactive, in accord with the mechanistic pathway for this reaction depicted in Scheme III. Further support for this mechanistic hypothesis was provided by the observation that periodonium ion 12 reacts with bis(4-chlorophenyl) sulfide, to give the sulfoxide very rapidly.

The use of periodate ion to cleave glycols[29] has been shown[30] to involve a cyclic periodate ester as an interme-

(25) A simple approximate molecular orbital description of the three-center four-electron bond, in species defined as "hypervalent" (Musher, J. I. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 54), makes it clear how the typical charge distribution can be expected. The central fluorine in the trifluoride anion is found to be positively charged, although a part of an anion (Cahill, P. A.; Dykstra, C. E.; Martin, J. C. *J. Am. Chem. Soc.* **1985**, *107*, 6359–6362).

(26) (a) Astrologes, G. W.; Martin, J. C. *J. Am. Chem. Soc.* **1977**, *99*, 4390. (b) Ross, M. R. Ph.D. Thesis, University of Illinois, Urbana, IL, 1981. (c) Ross, M. R.; Martin, J. C. In *Chemical Approaches to Understanding Enzyme Catalysis: Biomimetic Chemistry and Transition-State Ananogs*; Green, B. S., Ashani, Y., Chipman, D., Eds.; Elsevier: Amsterdam, 1981; pp 155–167.

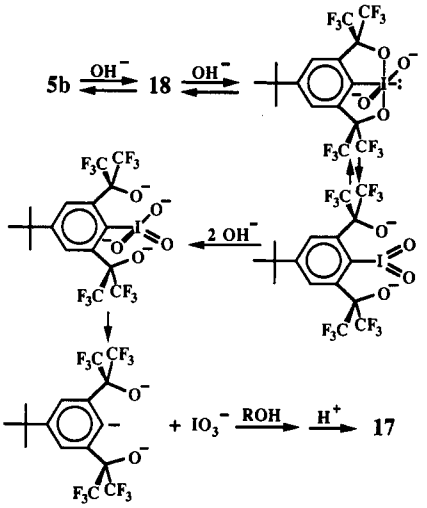
(27) Selte, K.; Kjekshus, A. *Acta Chem. Scand.* **1970**, *24*, 1912.

(28) Leonard, N. J.; Johnson, C. R. *J. Org. Chem.* **1962**, *27*, 282.

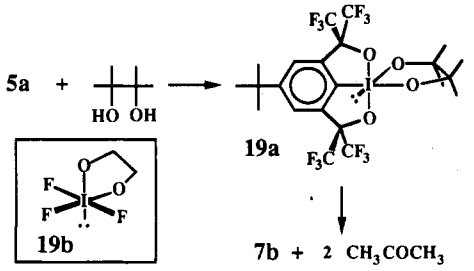
(29) Geissman, T. A. *Org. React. (N.Y.)* **1944**, *2*, 94 and references cited therein.

(30) Buist, G. J.; Burton, C. A.; Miles, J. H. *J. Chem. Soc.* **1959**, 743.

Scheme IV



diate. While iodinane oxides **5a,b** do not oxidatively cleave pinacol at room temperature, at temperatures as high as 130 °C, **5** cleaves pinacol to give acetone in high yield. The intermediacy of cyclic periodinane **19a** is probable. Analogous cyclic periodinanes, such as **19b** with ethylene glycol as a ligand, have been reported.[13]

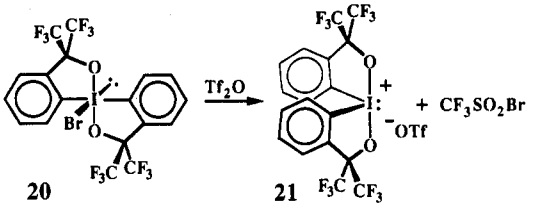


Iodoxybenzene reacts with potassium hydroxide to give benzene and potassium iodate.[16a] In a similar reaction, iodinane oxide **5b** reacts with potassium hydroxide at room temperature to give the reduced product, diol **17**. The other product is presumed to be potassium iodate, since the colorless aqueous layer gives a positive test with starch–iodide paper. This reaction may proceed through successive additions of hydroxide ion to the iodine atom to give a species whose accumulation of negative charge promotes cleavage of the carbon–iodine bond, as shown in Scheme IV.

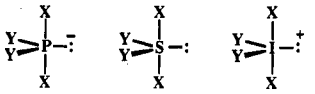
Periodonium Ions (10-I-4 Species). Periodonium ions can be viewed either as a product of the oxidation of an iodinane (10-I-3 species) by transfer of a cation from an oxidizing reagent or as a result of the heterolytic bond cleavage of an anionic ligand of an electrically neutral periodinane (12-I-5 species).

Only a few periodonium ions have been reported. The acyclic periodonium salt from the reaction of IF_5 and SbF_5[4] is very reactive, oxidizing even solvents such as carbon tetrachloride. Its X-ray structure shows a distorted Ψ-TBP geometry about iodine.[31] Another periodonium salt, $C_6F_5IF_3^+SbF_6^-$, was observed by ^{19}F NMR spectroscopy in SO_2Cl_2 solutions of $C_6F_5IF_4$ with SbF_5 at temperatures below −10 °C.[32] This acyclic periodonium salt decomposes rapidly at higher temperatures.

Periodonium salt **21** is prepared from its precursor bromoperiodinane **20** (or a stereoisomer of **20**) by reaction with triflic anhydride.[33] In marked contrast to the known acyclic periodonium ions, periodonium salt **21** demonstrates a very unusual stability. It is a crystalline solid (mp 288–291 °C) and is stable toward atmospheric moisture and aqueous acid.



Periodonium ions are isoelectronic with sulfuranes (10-S-4)[34] and phosphoranide anions (10-P-4).[35] Structural features which stabilize one of these are expected to stabilize the other members of this triad of species as well. The stabilization imparted in the molecule **21** is attributed to the incorporation of the bidentate ligand into its structure, a ligand which has been shown to stabilize a variety of Ψ-TBP species.[34,36]



10-P-4 **10-S-4** **10-I-4**

Trifluoroacetic anhydride was reported to react with $CsIF_4$ and IF_3 to replace fluoride ligands with trifluoroacetoxy groups.[37] In light of these reports, we treated difluoroperiodinane **4b** with trifluoroacetyl triflate to obtain fluoroperiodinane salt **8**.

$$\mathbf{4b} \xrightarrow{\text{TFAT}} \mathbf{8} + CF_3COF$$

The ^1H NMR spectrum shows a singlet for the aromatic proton, consistent with the presence of a plane of symmetry bisecting the phenyl ring along the carbon–iodide bond. The geometry of the compound is therefore Ψ-TBP with a fluorine atom as the equatorial ligand. The very apicophilic fluorine atom is constrained by the geometry of this tridentate ligand to occupy an equatorial position in **8**. The electron-withdrawing fluorine substituent renders **8** strongly electrophilic. Even in the crystalline form **8** is very reactive. A simple stored in a glass vial under an inert atmosphere reacted over a period of weeks to form **9**.

The oxygen atoms of iodosobenzene and iodoxybenzene are relatively nucleophilic. Yagupolski and co-workers[9] have reported several reactions of iodoxybenzene with perfluoroalkyl carboxylic acid anhydrides to form tetrakis[(perfluoroacetyl)oxy]periodinanes. Iodosobenzene diacetate is reported by Koser and Wettach[38] to react with *p*-toluenesulfonic acid to give phenylhydroxyiodonium tosylate **22**. This reaction may go through an iodosobenzene intermediate.

Treatment of iodinane oxide **5b** with trifluoroacetic anhydride gives bis(trifluoroacetoxy)periodinane **11**. The

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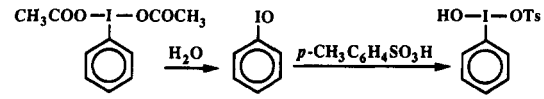

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oxygen of the iodinane oxide is appreciably nucleophilic. It is not, however, sufficiently nucleophilic to react with acetic anhydride. Addition of trifluoromethanesulfonic acid to iodinane oxide **5b** gives the directly observable, isolable hydroxyperiodonium triflate **9**, the first reported periodonium ion with a hydroxy group as a ligand. Similarly, treatment of **5b** with trifluoroacetyl triflate affords triflate salt **12**.

The stability of the 10-I-4 and 12-I-5 species reported here is the consequence of the stabilization provided by the tridentate ligand. The degree of stability of periodonium salts **8**, **9**, **12**, and **15** can be ranked somewhere between the degrees of stability of the salts of the acyclic tetrafluoroperiodonium ion, IF_4^+, and spirobicyclic periodonium ion **21**. One of the main contributors to the stability of these 10-I-4 species is the bridging of apical and equatorial sites by the five-membered rings. It is estimated[26] that ca. 10 kcal/mol of stabilization is gained for each five-membered ring joining an apical to an equatorial site in a TBP species.

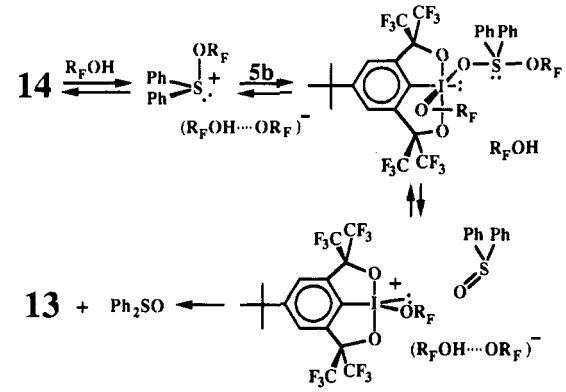
Although both the periodonium ions reported here and spirobicyclic periodonium ion **21** have two five-membered rings in their structures, **21** appears to be more stable. The compounds reported here decompose at their melting points while **21** does not. One reason for the difference between them is the larger number of electron-donating equatorial ligands in **21**, a feature which has been shown[25] to stabilize hypervalent species. In periodonium ion **21**, there are two equatorial carbon ligands, while in the species reported here (**8**, **9**, **12**, and **15**), there is only one equatorial carbon ligand. The other equatorial ligands (F, HO, CF_3COO, or R_FO) are electron withdrawing, which would destabilize the TBP species. The negatively charged oxygen equatorial ligand of iodinane oxide **5** provides some stabilization of the Ψ-TBP species by its electropositive character. It is, however, also a π-donor ligand with an electron pair in a p orbital parallel to the three-center O–I–O bond. This is expected[39] to destabilize **5**, making it less stable than **21**.

Relative Stabilities of 10-I-4 vs 12-I-5 Species in Comparison to 8-S-3 vs 10-S-4 Species. We find that the two bidentate ligands are much more stable with two CF_3 groups adjacent to each apical oxygen, rather than two CH_3 groups. Hypervalent species are much more stable with very electronegative apical ligands and with electropositive central atoms in the 3c–4e bond since the three orbitals, with two having four electrons, make the central atom have more positive charge and the apical ligands have more negative charge. They are therefore stabilized by having CF_3 groups adjacent to the apical oxygens. The phosphoranide (10-P-4) forms coordination to metals at the phosphorus, while those with four identical ligands on phosphorus always tend to have the metal coordinated to both the phosphorus and one of the apical ligands.[35c] They are all more stable with five-membered rings including both one apical and one equatorial ligand center.

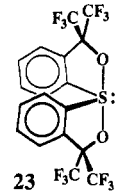
The interesting rapid reaction between 10-S-4 diphenyldialkoxysulfurane **14** and 10-I-4 iodinane oxide **5** results in a disproportionation to form 8-S-3 diphenyl sulfoxide and 12-I-5 periodinane **13** in high yield. The fact that the equilibrium constant strongly favors the Ψ-Oc

(39) Perozzi, E. F.; Martin, J. C. *J. Org. Chem.* **1977**, *42*, 3222.

Scheme V



12-I-5 species relative to the Ψ-TBP 10-I-4 iodinane oxide is, at first glance, surprising. As mentioned earlier, the tridentate ligand was designed for stabilization of TBP or Ψ-TBP hypervalent species. The stabilization of Oc 12-X-6 species by tridentate ligands appears to be most favorable if all three ligand sites are electronegative.[40] In this case the electropositive carbon of the tridentate ligand (12-I-5 species) is trans to the unshared electron pair of **13**. The I–C bond is therefore a standard two-electron two-center bond. The two perpendicular O–I–O three-center four-electron bonds provide positive charge at the iodine center, which is stabilized by the electropositive carbon of the aryl ligand. This tridentate ligand therefore stabilizes this 12-I-5 species at least as much as its stabilization of the 10-I-4 iodinane oxide. The four monodentate ligands of sulfurane **14** provide much less stabilization than the similarly substituted bidentate ligands of **23**. While **14** is rapidly hydrolyzed upon exposure to atmospheric moisture,[41] and rapidly dehydrates tertiary alcohols at −80 °C,[42] the spirosulfurane, **23**, is not hydrolyzed upon boiling with aqueous acid.[34a] The instability of **14** therefore provides a driving force for the reaction, with the stabilization of the 12-I-5 species by its tridentate ligand also helping. The sulfoxide S–O bond strength is also probably greater than that of the equatorial I–O bond of **5**.



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Ligand exchange has been found[41] to be more rapid for sulfurane **14** with the acidic R_FOH than with the nucleophilic R_FOK. This suggests that the mechanism of the reaction of **5** with **14** is as pictured in Scheme V, by reaction of the sulfonium ion at the nucleophilic equatorial oxygen of **5**.

Conclusion

The tridentate ligand incorporated into the species described in this paper provides two electron-withdrawing apical substituents and one electron-donating equatorial substituent to the central iodine. It was originally designed to stabilize hypervalent 10-electron TBP (or Ψ-TBP) species. Because of this molecular design, a variety of

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highly reactive 10-I-4 species have been isolated and characterized. The key precursor for the other 10-I-4 species reported here, iodinane oxide **5b** with a nucleophilic equatorial oxygen atom and an electrophilic iodine center, is also stabilized by the tridentate ligand. Its reaction at oxygen with a variety of electrophiles leads to cationic 10-I-4 species, periodonium ions. The 12-I-5 periodinanes, formed by attack of nucleophiles at the cationic iodine center of 10-I-4 species, have Ψ-Oc geometry about iodine. Because the five ligand sites in this Ψ-Oc geometry include four identical sites incorporated in three-center bonds, plus a two-center bond opposite to the iodine lone pair, the 12-I-5 species also benefit from the difference in electronegativity between the fluoroalkoxy oxygens and the electropositive carbon of the tridentate ligand. The C–I two-center bond therefore provides stabilization by donating electrons to the iodine, which has positive charge because of its central location in two perpendicular three-center bonds. This would not be as likely for species with 12-I-6 Oc geometry in which all six sites are identical. Ionization of 12-I-5 species to give 10-I-4 species was found to be sufficiently facile to provide a wide range of isolable 10-I-4 species of types which have hitherto received little attention. Both the Ψ-Oc 12-I-5 species and the Ψ-TBP 10-I-4 species receive stabilization from the geometric consequences of the two five-membered rings formed by the tridentate ligands of this study. Both types of bicyclic hypervalent iodine species are therefore less reactive, and more easily isolable, than their acyclic or monocyclic analogues which have been studied earlier.

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Registry No. **4a**, 80360-39-0; **4b**, 136213-44-0; **4c**, 136213-45-1; **5a**, 136213-46-2; **5b**, 136213-47-3; **6b**, 101697-28-3; **7b**, 101697-29-4; **8**, 101697-29-4; **9**, 136213-51-9; **10**, 136213-52-0; **11**, 136213-53-1; **12**, 136213-55-3; **13**, 136213-56-4; **14**, 32133-82-7; **15**, 136213-58-6; **16**, 136213-59-7; **17**, 101697-32-9; $PhC(CF_3)_2OK$, 37818-31-8; $(p\text{-}ClC_6H_4)_2S$, 5181-10-2; $(p\text{-}ClC_6H_4)_2SO$, 3085-42-5; $(p\text{-}ClC_6H_4)_2SO_2$, 80-07-9; CH_3COCH_3, 67-64-1; pinacol, 76-09-5.

Preparation of N-Substituted Phthalimides by the Palladium-Catalyzed Carbonylation and Coupling of *o*-Dihalo Aromatics and Primary Amines

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A novel method for the formation of N-substituted phthalimides is described which is based on the palladium-catalyzed carbonylation and coupling of *o*-dihalo aromatics and primary amines. Optimal conditions established for the reaction using *o*-diiodobenzene and aniline were DMAc (0.2 M), 115 °C, 90 psi of CO, 3% $PdCl_2L_2$, and 2.4 equiv of DBU. This process is tolerant of a wide variety of functional groups and gives good yields of the desired products. Variables such as temperature, catalyst type and loading, CO pressure, solvent, and base were examined to optimize this reaction. The reaction of aniline with 1,2-dibromocyclopentene under similar conditions gave a variety of products.

Introduction

In 1974 Heck reported that high yields of amides and esters could be obtained from the treatment of aromatic halides (bromides or iodides) with a catalytic amount of a palladium(0) or palladium(II) species and a primary or secondary amine or alcohol in the presence of carbon monoxide (CO) and a base. These "Heck" reactions have been well documented for not only the formation of amides[1] and esters[2] but also α-keto amides,[3] α-keto esters,[3e,4] α-keto acids,[5] α-hydroxy acids,[6] anhydrides,[7] acid fluorides,[8] acids,[9] lactams,[10] lactones,[11] aldehydes,[12] and ke-

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