asymmetric valency hybrid Hb having one cyanometheme in one of the α subunits has a larger cooperativity and a smaller affinity for the first oxygen ligand than the complementary hybrid having one cyanometheme in one of the β subunits.[27] These observations suggest that the binding of the first ligand to the α subunit in Hb may induce less pronounced changes in its quaternary structure and in its metal-His coordination than the binding of the first ligand to the β subunit, in accordance with the present NMR results. Since Adair equilibrium constants for the first and second oxygen molecules are almost unchanged in FeHb,[28] the affinities of the subunits accepting these ligands must also be similar. This implies that the first oxygen molecule binds to one of the α subunits in natural FeHb. A higher affinity for oxygen of the α subunits than that of the β subunits has been observed in FeHb by ^{1}H NMR spectroscopy.[29]

Since the Fe(II)-His bond is the only covalent linkage between the heme and the globin moieties in Hb, roles in controlling ligand affinity and in triggering the allosteric transition have been attributed to the Fe-His bond.[30] Spectroscopic parameters representing the Fe-His bond such as the resonance Raman Fe-His stretching mode at 210-225 cm^{-1}, the hyperfine-shifted ^{1}H NMR signals of the proximal His N_δ H protons, and the EPR characteristics of divalent porphyrin metal ions show significant differences between Hb molecules having a T quaternary structure and those having an R quaternary structure, so that these spectroscopic parameters have often been used as convenient quaternary state indicators. Strictly speaking, however, these spectroscopic parameters represent only the tertiary structural changes near the metal-His bond. The assumed correlation between these spectroscopic parameters and the quaternary structural state may be coincidental, and it must be analyzed with caution, as clearly demonstrated by the present ^{1}H NMR study. On the other hand, some of the ^{1}H NMR signals in the hydrogen-bonded region have been explicitly assigned to specific hydrogen bonds involved in the inter- and intrasubunit interactions that are directly related to the quaternary structure of Hb. However, the assigned T-state and R-state markers in this spectral region represent only a fraction of the total number of hydrogen bonds involved, so that some uncertainty exists as to whether or not the limited number of hydrogen bonds observable by NMR can adequately represent the quaternary structural changes of this macromolecule. Nevertheless, the observed behaviors of the hydrogen-bonded resonances, namely asynchronous decreases in the T-state markers and absence of a concomitant increase in the R-state marker upon ligation of a single CO molecule to the asymmetric Fe-Co hybrid Hbs, have convincingly demonstrated that the synchronized breakage and formation of all of the hydrogen bonds involved in the quaternary structural transition in Hb, which is predicted by the two-state allosteric mechanism, do not always take place.

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A Stable Aryldialkoxybrominane: Synthesis, Structure, and Reactions of an Organo-Nonmetallic 10-Br-3 Species[1a]

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Abstract: The syntheses of 4-methyl-2,6-bis[1-hydroxy-1-(trifluoromethyl)-2,2,2-trifluoroethyl]bromobenzene (**7a**) and its 4-*tert*-butyl analogue **7b** are described. The oxidations of bromo diols **7** with BrF_3 give brominanes **8**, 10-Br-3 species. These first examples of organobromine(III) species are stable at their melting points (153-154 °C for **8a**, 168-170 °C for **8b**). Brominanes are strong oxidizing agents, oxidizing hydrogen bromide to bromine and aromatizing hydroaromatics such as tetralin in a controlled reaction at 130 °C. Synthesis of the iodinane analogous to brominane **8b**, 10-*tert*-butyl-3,3,7,7-tetrakis(trifluoromethyl)-4,6-benzo-1-ioda-2,8-dioxabicyclo[3.3.1]octane (**10b**), is effected by a route similar to that used for the brominane. Complete X-ray crystal structures of **8a** and **10b** are described. Both halogenanes are pseudo-trigonal-bipyramidal (Ψ-TBP) species with bond angles between the two apical halogen-oxygen bonds deviating from the ideal 180° by 12.4° (for the brominane) and 21.8° (for the iodinane). This distortion is in the direction predicted by VSEPR theory with the magnitude of the deviation determined largely by the length of the equatorial carbon-halogen bond. Reactions of the brominane and the iodinane with reducing agents and with nucleophiles are described.

Examples of organic compounds containing tricoordinate iodine, such as iodobenzene dichloride and its analogues, were described as early as 1885. Since then, many organic compounds containing iodine in oxidation states of three and five have been studied.[2] In contrast to the large numbers of iodine compounds known, no tricoordinate organobromine(III) compound had been synthesized prior to the research described in this paper. The few known

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10-Br-3 species, bromine trifluoride and its analogues, all have very electronegative inorganic ligands.

Bromine trifluoride, which is a stable liquid at room temperature, was observed and characterized in the early years of this century.[3] It is a very strong oxidant. It has been reported to react violently with water, oxidizable organic solvents, and metals. In 1960 Roberts and Cady reported[4] the synthesis of $Br(OSO_2F)_3$ from peroxydisulfuryl difluoride and bromine. Schmeisser and Brandle reported the preparation of bromine trinitrate by the reaction of bromine trifluoride with either dinitrogen pentoxide or nitric acid.[5] Recently, $Br(OSeF_5)_3$ was prepared by the reaction of bromine trifluoride and $HOSeF_5$.[6] These compounds are in general very reactive toward organic solvents, in many cases forming mixtures which detonate.

Attempts to oxidize pentafluorobromobenzene with chlorine trifluoride to give derivatives of bromine(III) and bromine(V) gave instead addition to the ring to form cyclohexenes C_6BrClF_8 and C_6BrF_9.[7] The formation of $C_6F_5BrF_4$ (a bromine(V) species) was recently claimed to result from the reaction of pentafluorobromobenzene with elemental fluorine.[8] The evidence for the species claimed was, however, based primarily on mass spectrometry, a technique which would distinguish between the claimed addition of fluorine at bromine and its addition to the aromatic ring only with difficulty.[9] No ^{19}F NMR peaks for the fluorines attached to bromine were observed. A passing reference was made in the paper to $C_6F_5BrF_2$ (a bromine(III) species), but no evidence for its presence was mentioned. Another bromine(V) species, n-$C_3F_7BrF_4$, was claimed to result from the treatment of C_3F_7Br with fluorine at 0 °C.[11] For all of these bromine species the reported method of isolation (gas–liquid chromatography at 80 °C on the oxidizable stationary phase, 30% SE-30 on Chromasorb P) is surprising in view of the expectation that all of the species would be very strong oxidizing and fluorinating reagents.

Chlorine trifluoride, a product of the reaction of chlorine and chlorine monofluoride with elemental fluorine at 200–300 °C,[3f] is a stronger oxidant than bromine trifluoride. It reacts explosively with water and with most organic compounds.[12] An organic analogue of chlorine trifluoride, $C_6F_5ClF_2$, a product of the reaction of pentafluorochlorobenzene with fluorine at 117 °C, has also been claimed.[13] The compound was also purified by gas–liquid chromatographic techniques. As in the case of $C_6F_5BrF_4$, no C–F stretching in the 1000–1400-cm^{-1} range and no C=C stretching frequency were noted in the infrared spectrum of this material. None of the previously claimed derivatives of hypervalent organobromine or organochlorine species have been isolated.

We here report the synthesis, X-ray structure, and reactions of the first well-characterized organobromine(III) species, aryldialkoxybrominane **8a**, a stable 10-Br-3 species. We also report the synthesis and X-ray structure of the analogous iodine(III) compound, **10b**, and unsuccessful attempts to prepare an organochlorine(III) compound.

Experimental Section

General Methods. Chemical shifts are reported in parts per million downfield from tetramethylsilane as an internal standard for ^1H and ^{13}C NMR spectra and from fluorotrichloromethane as internal standard for ^{19}F spectra. Elemental analyses are within 0.4% of theoretical values unless otherwise noted.

Oxidation of Bromo Alcohol 1 with BrF_3. To a solution of bromo alcohol **1**[14] (1.0 g, 2.9 mmol) in 30 mL of $CF_2ClCFCl_2$ at −20 °C was added 0.4 g (2.9 mmol) of BrF_3 in 20 mL of the same solvent under N_2. The solution instantly became brown. Evaporation of the solvent by a constant sweep of N_2 provided an oil, whose ^1H and ^{19}F NMR spectra indicated the major product to be fluorinated bromo alcohol **3**. A prominent $-CH_2F$ absorption was found at 5–6 ppm with J_{HF} = 48 Hz. No brominane **2** was observed.

1,4-Dihydro-8-bromo-6-*tert*-butyl-2,2-dimethyl-4,4-bis(trifluoromethyl)-2*H*-[3,1]benzoxazine (4b). Compound **4b** was synthesized from 259 g (0.75 mol) of 6-bromo-4-*tert*-butyl-2-[1-hydroxy-1-(trifluoromethyl)-2,2,2-trifluoroethyl]aniline[15] by using the same method as in the preparation of **4a**:[16] yield 88%; bp 96–99 °C (1.5 mmHg); ^1H NMR ($CDCl_3$) δ 7.59 (d, 1, J = 2 Hz, Ar H), 7.49 (s, 1, Ar H), 4.52 (br s, 1, N*H*), 1.53 (s, G, CH_3), 1.3 (s, 9, $C(CH_3)_3$); ^{19}F NMR ($CDCl_3$) δ −74.8 (s, CF_3). Anal. ($C_{16}H_{18}ONF_6Br$) C, H, N.

1,4-Dihydro-8-(1-hydroxy-1-(trifluoromethyl)-2,2,2-trifluoroethyl)-6-*tert*-butyl-2,2-dimethyl-4,4-bis(trifluoromethyl)-2*H*-[3,1]benzoxazine (5b). Alcohol **5b** was prepared in the same manner as its methyl analogue **5a**.[16] The only change in the procedure was a solvent change; a mixture of ether and tetrahydrofuran (2:1) was employed instead of pure ether. From 52.5 g (0.12 mmol) of **4b**, 28 g (0.05 mmol, 44%) of 5b was obtained: mp 110–111 °C; IR ($CHCl_3$) 3300 (w), 3020 (m), 2970 (w), 1520 (w), 1480 (w), 1465 (w), 1417 (w), 1390 (w), 1370 (w), 1260 (s), 1200 (s), 1150 (m), 1130 (w), 1100 (m), 1070 (m), 975 (w), 960 (m), 893 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.8 (s, 1, Ar H), 7.75 (s, 1, Ar H), 3.5 (br s, 2, N*H* and O*H*), 1.55 (s, 6, $C(CH_3)_2$), 1.35 (s, 9, $C(CH_3)_3$); ^{19}F NMR ($CDCl_3$) δ −75.15 (s, 6, CF_3), −75.8 (s, 6, CF_3), mass spectrum (70 eV), m/e (relative intensity) 521 (7, $M^{\cdot+}$), 506 (100, $M^{\cdot+} - CH_3$), 452 (5, $M^{\cdot+} - CF_3$). Anal. ($C_{19}H_{19}O_2NF_{12}$) C, H, N, F.

4-*tert*-Butyl-2,6-bis[1-hydroxy-1-(trifluoromethyl)-2,2,2-trifluoroethyl]aniline (6b). Amino diol **6b** was synthesized in the same manner as its methyl analogue, **6a**.[16] From 30 g (58 mmol) of **5b**, 22 g (46 mmol) of **6b** was obtained: mp 183–185 °C; ^1H NMR ($CDCl_3$) δ 7.7 (s, 2, Ar H), 5.5–6.1 (br s, 4, NH_2 and O*H*), 1.33 (s, 9, CH_3); ^{19}F NMR ($CDCl_3$) δ −74.8 (s, CF_3); mass spectrum (70 eV), m/e (relative intensity) 481 (19, $M^{\cdot+}$), 466 (100, $M^{\cdot+} - CH_3$). Anal. ($C_{16}H_{15}O_2NF_{12}$) C, H, N, F.

4-Methyl-2,6-bis[1-hydroxy-1-(trifluoromethyl)-2,2,2-trifluoroethyl]bromobenzene (7a). To a solution of amino diol **6a** (2.0 g, 4.6 mmol) in 60 mL of acetic acid, 6 mL of 48% aqueous HBr, 1 mL of concentrated H_2SO_4, and sodium nitrite (0.6 g, 8.6 mmol) were added in small portions at 10 °C with stirring. The mixture was stirred for 1.5 h, and then 10 mg of copper powder was added. The reaction mixture became dark brown and bubbled. It was heated to 100 °C for 1.5 h and then poured into 200 g of cracked ice. The precipitate was filtered and washed (H_2O) to give white powdery **7a** (1.5 g, 3.0 mmol, 65%): mp 85–87 °C; ^1H NMR ($CDCl_3$) δ 7.6 (s, 2, Ar H), 5 (s, 2, O*H*), 2.4 (s, 3, CH_3); ^{19}F NMR ($CDCl_3$) δ −72.8 (s, CF_3); ^{13}C NMR ($CDCl_3$, ^1H decoupled) δ 21.3 (s, *C*H_3), 81.6 (septet, $^2J_{CF}$ = 30 Hz, *C*$(CF_3)_2$), 122.8 (q, J_{CF} = 289 Hz, *C*F_3), 130.9 (s, aromatic C-2), 133.4 (s, aromatic, C-3), 137.7 (s, aromatic C-4), 117.5 (s, aromatic C-1); mass spectrum (70 eV), m/e (relative intensity) 504, 502 (99, $M^{\cdot+}$), 435, 433 (63, $M^{\cdot+} - CF_3$), 416, 414 (67, $M^{\cdot+} - CF_3$–F). Anal. ($C_{13}H_7O_2BrF_{12}$) C, H, Br, F.

4-*tert*-Butyl-2,6-bis[1-hydroxy-1-(trifluoromethyl)-2,2,2-trifluoroethyl]bromobenzene (7b). Compound **7b** was prepared by the same procedure as was used for **7a**. From 4.5 g (9.4 mmol) of **6b**, 4.8 g (8.8 mmol, 94%) of **7b** was obtained after recrystallization from pentane: mp 106–108 °C; IR (CCl_4) 3580 (m, OH), 3470 (m), 2970 (m), 1550 (w), 1368 (w), 1260 (s), 1230 (s), 1210 (s), 1185 (m), 1150 (m), 1125 (m), 995 (m), 965 (m), 895 (w) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.85 (s, 2, Ar H), 4.4–4.6 (br s, 2, OH), 1.3 (s, 9, CH); ^{19}F NMR ($CDCl_3$) δ −73.13 (s, CF_3); ^{13}C NMR ($CDCl_3$ and CD_3CN, ^1H decoupled) δ 30.8 (s, C-$(CH_3)_3$), 35.1 (s, *C*$(CH_3)_3$), 81.9 (septet, $^2J_{CF}$ = 30 Hz, *C*$(CF_3)_2$, 116.9 (s, C–Br), 123.2 (q, J_{CF} = 289 Hz, C-7), 130.1 (s, aromatic C-3), 132.9 (s, aromatic C-2), 152.2 (s, aromatic C-4); mass spectrum (70 eV), m/e (relative intensity) 544, 546, (13, $M^{\cdot+}$), 529, 531 (100, $M^{\cdot+} - CH_3$).

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Anal. ($C_{16}H_{13}O_2BrF_{12}$) C, H, Br, F.

10-Methyl-3,3,7,7-tetrakis(trifluoromethyl)-4,5,6-benzo-1-broma-2,8-dioxabicyclo[3.3.1]octane (8a). To a stirred solution of bromo diol **7a** (3.4 g, 6.7 mmol) in freshly distilled CCl_2FCF_2Cl (50 mL) in a Teflon container at −20 °C under N_2, a solution of BrF_3 (0.80 g, 5.8 mmol) in 20 mL of CCl_2FCF_2Cl was transferred from another Teflon container under a positive pressure of N_2.[16] The brown color of bromine was observed instantaneously. The mixture was warmed to room temperature and stirred for 12 h with a constant sweep of N_2. When the solvent was evaporated, 3.2 g (6.3 mmol, 94%) of **8a** was collected: mp 153–154 °C; IR ($CHCl_3$) 1239 (m), 1084 (s), 1040 (m), 945 (m), 855 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.65 (s, 3, CH_3), 7.7 (s, 2, Ar H); ^{19}F NMR ($CDCl_3$) δ −75.8 (s, CF_3); mass spectrum (10 eV) *m/e* (relative intensity) 502, 500 (2, $M^{\cdot+}$), 433, 431 (100, $M^{\cdot+} - CF_3$), 295, 293 (7.0, $M^{\cdot+} - 3CF_3$). Anal. ($C_{13}H_5O_2BrF_{12}$) C, H, Br, F.

10-*tert*-Butyl-3,3,7,7-tetrakis(trifluoromethyl)-4,5,6-benzo-1-broma-2,8-dioxabicyclo[3.3.1]octane (8b). The same procedure was used to convert 7.0 g (12.8 mmol) of **7b** to 6.5 g (12.2 mmol, 94%) of **8b**: mp 168–170 °C; IR ($CHCl_3$) 3020 (m), 2980 (w), 1520 (w), 1480 (w), 1420 (w), 1295 (m), 1270 (m), 1225 (m), 1210 (s), 1157 (w), 1145 (w), 1094 (m), 1080 (m), 970 (m), 930 (w) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.45 (s, 9, CH_3), 7.95 (s, 2, Ar H); ^{19}F NMR ($CDCl_3$) δ −75.8 (s, CF_3); mass spectrum (10 eV), *m/e* (relative intensity) 544, 542 (4, $M^{\cdot+}$), 529, 527 (5, $M^{\cdot+} - CH_3$), 475, 473 (100, $M^{\cdot+} - CF_3$), 377, 335 ($M^{\cdot+} - 3CF_3$). Anal. ($C_{16}H_{11}O_2BrF_{12}$) C, H, Br.

4-*tert*-Butyl-2,6-bis[1-hydroxy-1-(trifluoromethyl)-2,2,2-trifluoroethyl]iodobenzene (9b). The same procedure used in the synthesis of **9a**[16] converted 5.5 g (11.4 mmol) of **6b** into 4.1 g (6.9 mmol, 60%) of **9b**: mp 106–107 °C; IR ($CHCl_3$) 3560 (w), 3400 (m), 3160 (w), 3020 (w), 2970 (w), 1603, (w), 1425 (w), 1340 (w), 1230 (s), 1150 (m), 1125 (m), 1060 (w), 1040 (w), 1000 (m), 963 (m), 933 (w), 895 (w) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.8 (s, 2, ArH), 4.7 (s, 2, O*H*), 1.33 (s, 9, CH); ^{19}F NMR ($CDCl_3$) δ −74.8 (s, CF_3); ^{13}C NMR ($CDCl_3$, ^1H decoupled) δ 31.0 (s, C-8), 34.9 (s, C-5), 81.3 (s, $^2J_{CF}$ = 30 Hz, C-6), 84.9 (s, C-1), 130. 4, (s, C-3), 133.2 (s, C-2), 151.1 (s, C-4); mass spectrum (10 eV), *m/e* (relative intensity) 592 (95, $M^{\cdot+}$, 577 (100, $M^{\cdot+} - CH_3$). Anal. ($C_{16}H_{13}O_2IF_{12}$) C, H, I, F.

10-*tert*-Butyl-3,3,6,6-tetrakis(trifluoromethyl)-4,5,6-benzo-1-ioda-2,8-dioxabicyclo[3.3.1]octane (10b). Iodinane **10b** was prepared by the same procedure used for **10a**.[16] From 0.20 g (0.34 mmol) of **9b**, 0.14 g (0.23 mmol, 71%) of **10b** was obtained: mp 240–242 °C; IR ($CHCl_3$) 3020 (m, CH), 1600 (w), 1295 (m), 1270 (m), 1230 (m), 1212 (m), 1204 (m), 1084 (m), 970 (m) cm^{-1}; ^1H NMR ($CDCl_9$) δ 8 (s, 2, Ar H), 1.45 (s, 9, CH_3); ^{19}F NMR ($CDCl_3$) δ −75.8 (s, CF_3); mass spectrum (10 eV), *m/e* (relative intensity) 590 (6, $M^{\cdot+}$), 575 (6, $M^{\cdot+} - CH_3$), 521 (100, $M^{\cdot+} - CF_3$). Anal. ($C_{16}IH_{11}O_2IF_{12}$) C, H, I, F.

4-*tert*-Butyl-2,6-bis[1-hydroxy-10-(trifluoromethyl)-2,2,2-trifluoroethyl]chlorobenzene (11b). To 5.0 g (10.4 mmol) of amino diol **6b** in 200 mL of acetic acid, 40 mL of concentrated HCl, 10 mL of concentrated H_2SO_4, and 10 mL of H_2O was added 2.0 g (29 mmol) of sodium nitrite at room temperature in small portions. The mixture was stirred for 2 h, and then 10 mg of copper was added. The reaction mixture was heated at 100 °C for 10 h and then poured into 800 g of cracked ice. Filtration of the precipitate and recrystallization from hexane gave 3.5 g (7.0 mmol, 61%) of **11b**: mp 74–75 °C; ^1H NMR ($CDCl_3$) δ 7.91 (br s, 2, Ar H), 4.82 (br s, 2, O*H*), 1.32 (s, 9, CH_3); ^{19}F NMR ($CDCl_3$) δ −73.53 (s, CF_3); mass spectrum (70 eV), *m/e* (relative intensity) 500 (9, $M^{\cdot+}$), 485 (100, $M^{\cdot+} - CH_3$). Anal. ($C_{16}H_{13}O_2F_{12}Cl$) C, H, Cl, F.

Attempt To Oxidize 11b with BrF_3. To 0.5 g (1 mmol) of **11b** in 50 mL of CF_2ClCCl_2F at −20 °C, 0.1 g (1 mmol) of BrF_3 in 10 mL of CF_2ClCCl_2F was added. The reaction mixture became brown. The reaction mixture was warmed to room temperature. The solvent was evporated to give an oil whose ^{19}F NMR spectrum showed multiplets in the region −70 to −80 ppm. Addition of sodium bromide produced no change in the NMR spectrum or the color of the solution. No evidence of a chlorinane was found. An attempt to oxidize the monolithiated salt of **11b** with CF_3OF gave a similar result.

Attempt To Oxidize the Dipotassium Salt of 11b with BrF_3. To 0.82 g (1.6 mmol) of **11b** in 50 mL of tetrahydrofuran (THF) was added 0.12 g (3.0 mmol) of potassium hydride in small portions. The reaction mixture became yellow and then orange after 2 h of stirring at room temperature. It was then filtered to remove excess KH. The solvent was removed under vacuum to give a bright orange solid, which was then dissolved in 100 mL of CF_2ClCCl_2F. Bromine trifluoride (0.22 g, 1.6 mmol) in 20 mL of CF_2ClCCl_2F was added to this solution. The orange color was replaced by the color of bromine. A solid obtained upon removal of solvent gave ^1H NMR absorptions for chloro diol **11b** plus several multiplets in the regions 1.5–2.5 and 4–5 ppm and gave a broad ^{19}F NMR singlet at −73.5 ppm, the same place as the CF_3 absorption of **11b**.

Reaction of 8b with C_6F_5Li. To 0.11 mL (1.0 mmol) of pentafluorobenzene in 30 mL of THF at −78 °C, 0.48 mL (1.0 mmol) of 2.18 M *n*-BuLi in hexane was added. The mixture was stirred at −78 °C for 1 h, and then 0.55 g (1.0 mmol) of **8b** in 2 mL of THF was added. The slightly brownish solution became colorless. After 0.5 h the solution was warmed to room temperature, quenched with aqueous NH_4Cl, and extracted with 25 mL of ether. The ether layer was dried ($MgSO_4$) and evaporated under vacuum to give an oil. The NMR spectrum of this oil showed ca. 80% of **12**. Crystallization from pentane gave 0.3 g (43%) of **12**: mp 114–115 °C; ^1H NMR ($CDCl_3$) δ 7.9 (s, 1, Ar H), 7.77 (s, 1, Ar H), 6.0 (s, 1, O*H*), 1.35 (s, 9, CH_3); ^{19}F NMR ($CDCl_3$) δ −68.05 (t, 6, J = 2.8 Hz, $-C(CF_3)_2OC_6F_5$), −71.7 (s, 6, CF_3), −149.7 (br d, 2, J = 22.4 Hz, *o*-Ar*F*), −160 (t, 1, J = 20 Hz, *p*-Ar*F*), −163 (dd, 2, J_{AM} = 20.5 Hz, J_{AX} = 22.4 Hz, *m*-Ar*F*); mass spectrum (10 eV), *m/e* (relative intensity) 710, 712, (4.6, $M^{\cdot+}$), 527, 529 (100, $M^{\cdot+} - OC_6F_5$). Anal. ($C_{22}H_{12}O_2BrF_{17}$) C, H, Br, F.

Reactions of Brominane 8a. (a) Reaction with 9,10-Dihydroanthracene. A mixture of **8a** (20 mg, 0.04 mmol) and 9,10-dihydroanthracene (7.0 mg, 0.04 mmol) was heated at 130 °C for 1 min. The mixture melted and then resolidified. The NMR spectrum of this mixture showed that **8a** was reduced to **7a** and 9,10-dihydroanthracene was converted to anthracene in quantitative yield.

(b) Reaction with Tetralin. A mixture of **8a** (40 mg, 0.08 mmol) and tetralin (5.7 mL, 0.04 mmol) was heated at 130 °C for 12 h. The products were identified by NMR. The yield of naphthalene was shown, by integration of peak areas, to be about 50%. The other product was bromo diol 7a.

(c) Reaction with Thiophenol. Treatment of **8a** (30 mg, 0.06 mmol) with thiophenol (12 mL, 0.12 mmol) in 0.5 mL of $CDCl_3$ at room temperature instantly gave 100% of diphenyl disulfide and bromo diol **7a**. The products were identified by NMR spectroscopic comparison with authentic samples.

(d) Reaction with Aniline. A mixture of **8a** (30 mg, 0.06 mmol) and aniline (5.5 mL, 0.06 mmol) was heated to 80 °C for 5 h. All **8a** was converted into bromo diol **7a**. The ^1H NMR spectrum showed azobenzene (50%) and unidentified products. The identity of the azobenzene was confirmed by TLC (silica gel/ether).

(e) Reaction with NaI. To a solution of **8a** (30 mg, 0.06 mmol) in 0.5 mL of THF, an excess of NaI was added. The solution turned dark brown. The reaction was completed after 24 h when all of the **8a** was reduced to the sodium salt of bromo diol **7a**. The presence of iodine was confirmed by the starch–iodide paper test.

(f) Reaction with HX (X = I, Br). Aqueous HX was added to a solution of **8a** in THF. The reaction was complete after 48 h. The presence of bromo diol **7a** with confirmed by NMR spectroscopy, and X_2 was identified by the starch–iodide paper test. Brominane **8a** also reduces *n*-Bu_4NBr in the same manner.

(g) Reaction with Potassium Hydroxide. To 60 mg (0.12 mmol) of **8b** in a NMR sample tube, 8.0 mg (0.14 mmol) of potassium hydroxide and 0.5 mL of ethanol were added. The tube was degassed, sealed, and heated at 65 °C for 2.5 h. The NMR spectrum of the mixture showed 90% of the brominane was reduced. There was no NMR evidence for an aldehydic proton. The mixture was acidified with 6 M H_2SO_4 to give a precipitate whose ^1H and ^{19}F NMR spectra showed a mixture of brominane (10%) and bromo diol (90%). Parallel results were obtained when the reaction was performed in methanol or *tert*-butyl alcohol.

(h) Reaction with $K^{18}OH$ and *tert*-Butyl Alcohol. To a solid mixture of brominane **8b** (1.1 g, 2.0 mmol) and $K^{18}OH$ (0.23 g, 4.0 mmol), *tert*-butyl alcohol (50 mL) was added by distillation. The mixture was heated at 65 °C for 6 h, until the evolution of a gas subsided. The gas sample was collected and analyzed by mass spectrometry. The gas gave ions at *m/e* 56 and 41 for isobutylene and ions at 28 and 32 for N_2 and O_2 with a ratio N_2/O_2 = 2/1. No recognizable amount of mass 36 (for $^{18}O_2$) was detected.

Reaction of 10b with Phenyllithium. To a solution of **10b** (0.59 g, 1.0 mmol) in 10 mL of ether at −78 °C, 0.5 mL (1.0 mmol) of 2 M phenyllithium in benzene/ether was added dropwise. The clear solution became citrus yellow. It was stirred for 1 h and then warmed to room temperature, during which time the solution became brown. The reaction mixture was quenched with aqueous NH_4Cl and extracted with 30 mL of ether. The ether layer was dried ($MgSO_4$) and evaporated under vacuum to give a semisolid mixture. Addition of pentane to this mixture gave solid starting material **10b** (0.42 g, 0.07 mmol, 70%). Recrystallization of the resulting oil gave 90 mg (0.02 mmol, 20%) of **13**: 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 (s, CF_3); mass spectrum (10 eV), *m/e* (relative intensity) 466 (12.5, $M^{\cdot+}$), 451 (100, $M^{\cdot+} - CH_3$), 446 (9, $M^{\cdot+}$ − HF). Anal. ($C_{16}H_{14}O_2F_{12}$) C, H.

Crystal Data for 8a. $C_{13}H_5O_2BrF_{12}$, monoclinic, a = 6.966 (1) Å, b = 16.958 (4) Å, c = 14.584 (3) Å, β 98.92 (2)°, V = 1701.9 (6) Å^3,

Table I. Positional Parameters for Brominane **8a** (Estimated Standard Deviations in Parentheses)

atom	x	y	z
Br	0.09307 (6)	0.38210 (2)	0.49238 (3)
F1	−0.4230 (5)	0.3941 (2)	0.4552 (2)
F2	−0.5578 (5)	0.4066 (2)	0.3135 (3)
F3	−0.4612 (4)	0.5092 (2)	0.3941 (2)
F4	−0.2180 (6)	0.5506 (2)	0.2732 (2)
F5	−0.0222 (7)	0.4637 (2)	0.2388 (3)
F6	−0.3248 (7)	0.4516 (2)	0.1901 (2)
F7	0.3421 (6)	0.1120 (2)	0.4299 (3)
F8	0.5203 (5)	0.1780 (3)	0.5336 (3)
F9	0.4287 (6)	0.2272 (3)	0.4003 (3)
F10	0.2389 (6)	0.1538 (3)	0.6414 (3)
F11	0.0538 (7)	0.0963 (2)	0.5316 (3)
F12	−0.0423 (6)	0.2003 (3)	0.5929 (3)
O1	−0.0864 (5)	0.4596 (2)	0.4208 (2)
O2	0.2491 (5)	0.2899 (2)	0.5408 (2)
C2	−0.2167 (6)	0.4266 (2)	0.3495 (3)
C3	−0.1697 (6)	0.3392 (2)	0.3370 (2)
C4	−0.2570 (6)	0.2862 (2)	0.2714 (3)
C5	−0.2005 (7)	0.2069 (2)	0.2758 (3)
C6	−0.0552 (7)	0.1815 (2)	0.3461 (3)
C7	0.0345 (6)	0.2341 (2)	0.4122 (3)
C8	−0.0264 (6)	0.3107 (2)	0.4031 (2)
C9	−0.4177 (7)	0.4339 (3)	0.3771 (3)
C10	−0.1946 (9)	0.4733 (3)	0.2614 (3)
C11	0.1922 (6)	0.2196 (2)	0.4952 (3)
C12	0.3726 (7)	0.1832 (3)	0.4654 (4)
C13	0.1111 (9)	0.1660 (3)	0.5658 (3)
C14	−0.298 (1)	0.1493 (4)	0.2051 (5)
H1	−0.30 (1)	0.102 (4)	0.226 (5)
H2	−0.27 (1)	0.164 (5)	0.148 (7)
H3	−0.42 (1)	0.168 (4)	0.193 (5)
H4	−0.346 (6)	0.302 (2)	0.219 (3)
H5	−0.010 (6)	0.130 (2)	0.349 (3)

$F(000) = 968.00$, μ(Cu Kα) = 46.29 cm^{-1}. Conditions limiting possible reflections ($h0l$, $l = 2n$; $0k0$, $k = 2n$) established the space group as $P2_1/c$ (C_{2h}^5). The calculated density for $Z = 4$ was 1.955 g cm^{-3}. A Syntex $P2_1$ diffractometer equipped with a graphite monochromator, λ(Cu Kα) = 1.541 78 Å, was used to obtain the data set and cell parameters for a transparent crystal of dimensions 0.35 × 0.43 × 0.73 mm. The quadrant $h,k \pm l$ was collected in the 2θ–θ scan mode for $3.0° \leq 2\theta \leq 130.0°$ with a variable scan rate between 2 and 29.3 deg min^{-1}. The scan range was from 1.0° in 2θ below the calculated Kα_1 peak position to 1.1° above the calculated Kα_2. The background time to scan time ratio was 0.25. Out of 2775 reflections processed (nonunique data treated, standards removed), 2441 were considered to be observed at the 3σ criterion level. The data were corrected for Lorentz and polarization effects and anomalous dispersion and empirically corrected for absorption and extinction; the isotropic extinction coefficient was refined to a value of 1.71 (8) × 10^{-6}.

Solution and Refinement of the Structure of 8a. The solution and refinement were straightforward. The position of the bromine atom was deduced from a Patterson map, and subsequent difference Fourier synthesis revealed positions for all remaining atoms including the hydrogens. Full-matrix least-squares refinement of all positional parameters with isotropic thermal parameters for hydrogen atoms and anisotropic thermal coefficients for non-hydrogen atoms led to final agreement factors of $R = 0.0446$ and $R_w = 0.0562$. The range of residual electron density in the final difference Fourier synthesis was balanced with the highest positive peaks in the vicinity of the bromine; this final map was otherwise featureless. The positional parameters are shown in Table I. The thermal parameters, observed and calculated structure factors, and a complete list of bond lengths and angles are available in supplemental material.

Crystal Data for 10b. $C_{16}H_{11}O_2IF_{12}$, monoclinic, $a = 17.520$ (5) Å, $b = 12.498$ (4) Å, $c = 9.091$ (3) Å, $\beta = 91.79$ (2)°, $V = 1990$ (1) Å^3, $F(000) = 1136.0$, μ(Mo kα) = 17.08 cm^{-1}. Conditions limiting possible reflections ($h0l$, $h + l = 2n$; $0k0$, $k = 2n$), established the space group as $P2_1/n$ (C_{2h}^5). The calculated density for $Z = 4$ was 1.970 g cm^{-3}. A Syntex $P2_1$ diffractometer equipped with a graphite monochromator, λ(Mo Kα) = 0.710 69 Å, was used to obtain the data set and cell parameters for a transparent crystal of dimensions 0.20 × 0.23 × 0.40 mm. The quadrant $\pm hkl$ was collected in the 2θ–θ scan mode for $3.0° < 2\theta < 55.0°$ with a variable scan rate from 2.0 to 29.3 deg min^{-1}. The scan range was 0.8° in 2θ below the calculated Kα_1 peak to 0.9° above the calculated Kα_2 peak. The ratio of background time to scan time was 0.25. Out of 4589 intensities processed (excluding standards and nonunique data), 3050 were considered to be observed at the 3σ criterion level. The data were corrected for Lorentz and polarization effects and anomalous dispersion and were numerically corrected for adsorption.

Table II. Positional Parameters for Iodinane **10b** (Estimated Standard Deviations in Parentheses)

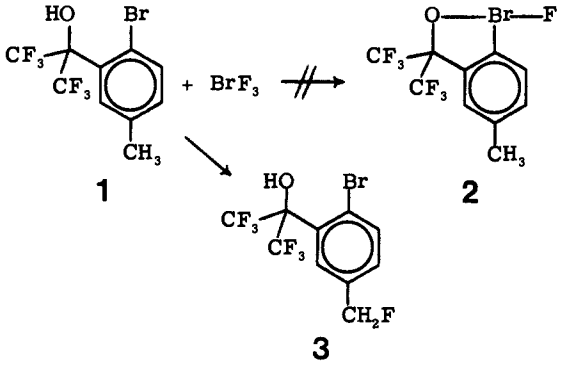
atom	x	y	z
I	0.10833 (2)	0.47455 (3)	0.39739 (3)
F1	−0.0147 (3)	0.2031 (3)	0.3987 (5)
F2	−0.0962 (3)	0.1984 (3)	0.2210 (5)
F3	−0.1208 (2)	0.2867 (3)	0.4152 (4)
F4	−0.1450 (2)	0.4554 (3)	0.2326 (4)
F5	−0.0497 (2)	0.5147 (3)	0.1202 (5)
F6	−0.1054 (2)	0.3737 (4)	0.0431 (4)
F7	0.3306 (2)	0.4148 (3)	0.0388 (4)
F8	0.3481 (2)	0.5350 (3)	0.2041 (5)
F9	0.2505 (2)	0.5406 (3)	0.0574 (5)
F10	0.3573 (2)	0.3657 (3)	0.3936 (4)
F11	0.3219 (2)	0.2487 (3)	0.2342 (4)
F12	0.2541 (2)	0.2757 (4)	0.4215 (4)
O1	−0.0071 (2)	0.4256 (3)	0.3807 (4)
O2	0.2232 (2)	0.4818 (3)	0.3481 (4)
C2	−0.0271 (2)	0.3611 (4)	0.2610 (5)
C3	0.0427 (2)	0.3285 (4)	0.1729 (5)
C4	0.0451 (3)	0.2627 (4)	0.0511 (5)
C5	0.1132 (3)	0.2418 (4)	−0.0187 (5)
C6	0.1804 (3)	0.2876 (4)	0.0389 (5)
C7	0.1800 (2)	0.3549 (4)	0.1620 (5)
C8	0.1101 (3)	0.2725 (4)	0.2208 (5)
C9	−0.0646 (3)	0.2610 (5)	0.3250 (6)
C10	−0.0829 (3)	0.4252 (5)	0.1623 (6)
C11	0.2475 (3)	0.4097 (4)	0.2423 (5)
C12	0.2951 (3)	0.4754 (5)	0.1352 (7)
C13	0.2961 (3)	0.3250 (5)	0.3224 (6)
C14	0.1144 (3)	0.1728 (4)	−0.1595 (6)
C15	0.1842 (8)	0.0951 (13)	−0.1531 (16)
C16	0.1307 (9)	0.2506 (12)	−0.2938 (16)
C17	0.0406 (8)	0.1187 (13)	−0.2010 (16)
C15A	0.0591 (11)	0.0719 (17)	−0.1329 (22)
C16A	0.1927 (11)	0.1524 (17)	−0.2053 (21)
C17A	0.0761 (12)	0.2354 (16)	−0.2833 (21)
C15B	0.1705 (15)	0.2327 (22)	−0.2769 (28)
C16B	0.0403 (15)	0.1774 (24)	−0.2450 (28)
C17B	0.1547 (15)	0.0714 (23)	−0.1246 (29)
H4	0.0045 (27)	0.2302 (42)	0.0213 (53)
H6	0.2244 (32)	0.2766 (46)	−0.0114 (60)

Solution and Refinement of the Structure of 10b. Coordinates for the iodine atom were deduced from a Patterson map. A weighted-difference Fourier synthesis revealed positions for all but three of the non-hydrogen atoms (the methyl carbon atoms for the *tert*-butyl group). Subsequent least-squares–difference Fourier calculations gave positions for nine disordered carbon atoms in groups of three with roughly tetrahedral geometry about atom C14 and two aromatic hydrogen atoms. The relative occupancy factors for the three groups of disordered carbon atoms were determined by assigning all nine carbon atoms a fixed isotropic thermal coefficient, estimated from a Wilson plot, while refining the occupancy factors and positions. The resulting occupancy factors (normalized) were 0.44, 0.32, and 0.24 for the major group (C15, C16, C17), group A (C15A, etc.), and group B, respectively. In the final cycle of the least-squares refinement all atomic positional parameters were varied, and the ordered non-hydrogen atoms were refined with anisotropic thermal coefficients. The aromatic hydrogen atoms were refined with isotropic thermal coefficients, and the disordered carbon atoms, now with fixed occupancy factors, were refined with a single isotropic group thermal parameter. Contributions from the aliphatic hydrogen atoms were not included in the structure factor calculations. Successful convergence of the least-squares refinement was indicated by the maximum change/error in the final cycle, 0.08. The final difference Fourier map had no peak with a density greater than 0.75 e Å^{-3}, and all the peaks above the background were within 1 Å of the iodine or one of the disordered carbon atoms. The map was otherwise featureless. The final agreement factors R and R_w were 0.033 and 0.045, respectively. The positional parameters are shown in Table II. The thermal parameters, observed and calculated structure factors, and a complete list of bond lengths and angles are available in supplemental material.

Results

Synthesis. We were unsuccessful in several preliminary attempts to synthesize the first organic 10-Br-3 species by employing bi-

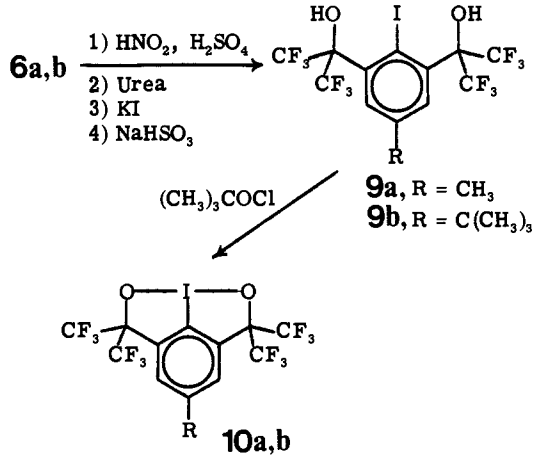
dentate ligands to stabilize the hypervalent Ψ-TBP brominanes. For example, reaction of bromo alcohol **1** with BrF_3 gave no fluorobrominane **2**, but instead gave benzylic fluoride **3**.



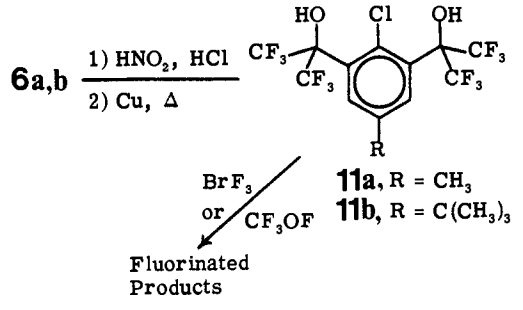
Brominane **8a** and its analogue **8b** were synthesized as shown in Scheme I. The synthesis of amino diol **6a**, a key intermediate for introducing the tridentate ligand, has been reported. The *tert*-butyl-substituted species **4b**, **5b**, and **6b** have been prepared in the same manner as their methyl analogues.

Reactions with BrF_3 were carried out at low temperature in an inert solvent, since it is reported to react violently with hydrocarbons.[3] When excess bromine trifluoride is used (more than $^2/_3$ molar equiv), fluorination of the alkyl substituents occurs. Brominanes **8a** and **8b** are stable for an indefinite period at room temperature. They can be sublimed or passed through a neutral alumina column (ether/pentane) without decomposition. The compounds are inert toward aqueous base, aqueous hydrogen chloride, and trifluoromethanesulfonic acid at room temperature.

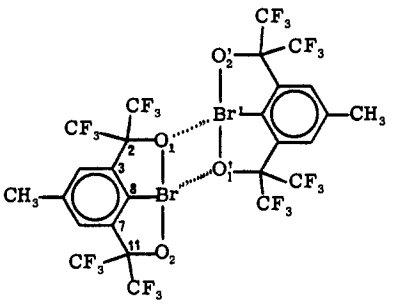
Compounds **9a** and **10a** were reported in an earlier paper.[16] Iodinane **10b** was synthesized by the same method used for **10a**.



Analogoues of **7** and **9**, chloro diols **11a** and **11b**, were prepared by a similar method from amino diol **6**. Attempts to oxidize these diols or their potassium salts with BrF_3 or CF_3OF gave unidentified fluorinated products. For compound **11a**, the major product seems



to be a benzyl fluoride, since the ^1H NMR spectrum shows a peak at 5.26 ppm with J_{HF} = 48 Hz. In the oxidation of **11b**, multiplets were observed in ^1H NMR spectra and many broad multiplets were found in ^{19}F NMR from −70 to −80 ppm.



distances (Å)		angles (deg)	
O_1–Br	1.995 (3)	O_1–Br–O_2	167.6 (1)
O_2–Br	1.971 (3)	O_1–Br–C_8	83.5 (1)
C_8–Br	1.875 (4)	O_1–Br–O_1'	65.03 (10)
O_1'–Br	2.971 (3)	O_2–Br–C_8	84.1 (1)
C_8–C_3	1.365 (5)	Br–O_1–Br′	115.0 (1)
C_3–C_2	1.534 (5)	Br–O_1–C_2	114.2 (2)
O_1–C_2	1.388 (5)	Br–O_2–C_{11}	114.1 (3)
C_{11}–C_7	1.524 (6)	Br–C_8–C_3	117.3 (3)
C_7–C_8	1.367 (5)	Br–C_8–C_7	116.7 (3)
		C_8–C_7–C_{11}	113.8 (3)
		C_8–C_3–C_2	113.9 (3)
		C_3–C_2–O_1	110.6 (3)
		C_7–C_{11}–O_2	111.0 (3)

Figure 1. Brominane **8a** and its interaction with a neighboring molecule.

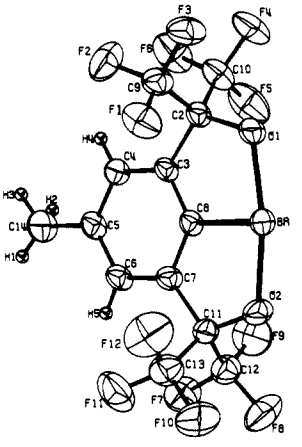


Figure 2. X-ray crystallographic structure of brominane **8a**.

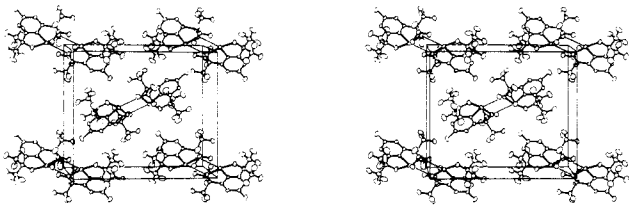
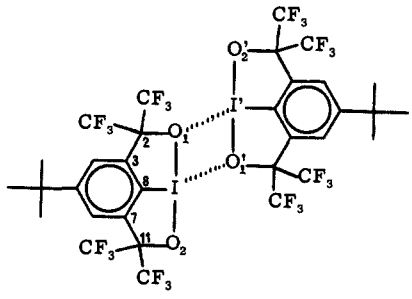


Figure 3. Stereoscopic view of the crystal packing of **8a**.

X-ray Structures. The crystal structure of **8a** reveals a somewhat distorted Ψ-TBP geometry around the central bromine atom. The two lone pairs of electrons are considered to occupy equatorial ligand sites. The molecule is coplanar, except for a small deviation from the plane (of the aromatic ring) by two atoms: C_2 (torsion angle Br–C_8–C_3–C_2 = 2.6°) and O_2 (torsion angle C_8–C_7–C_{11}–O_2 = 3.9°). Figure 1 summarizes the basic geometry of brominane **8a**, selected bond lengths and bond angles, and intermolecular distances. Views of a single molecule and the packing in one unit cell are depicted in Figure 2 and Figure 3.

Iodinane **10b** shows similar structural features as brominane **8a**. The molecule is not exactly coplanar. The phenyl ring is slightly bent (torsion angles C_3–C_8–C_7–C_6 = 1.8°, C_7–C_6–C_5–C_4 = −1.7°). The five-membered rings are also slightly distorted from planarity (O_1–I–C_8–C_3 = 3.1°, I–O_1–C_2–C_3 = 6.2°, O_2–I–C_8–C_7 = 2.3°). Figure 4 summarizes the structure of **10b**, selected bond lengths and bond angles, and intramolecular distances and angles.



Distances (Å)		Angles	
$I-O_1$	2.113 (3)	O_1-I-O_2	158.2 (1)
$I-O_2$	2.077 (3)	O_1-I-C_6	78.6 (2)
$I-C_6$	2.052 (4)	O_2-I-C_6	79.6 (2)
$I-O_1'$	3.000 (3)	C_6-I-O_1'	144.0 (1)
O_1-C_2	1.390 (6)	O_1-I-O_1'	65.4 (1)
C_2-C_3	1.537 (6)	O_1-I-O_2'	136.4 (1)
C_3-C_8	1.362 (6)	$I-O_1-I'$	114.6 (1)
C_6-C_7	1.368 (6)	$I-O_1-C_2$	116.2 (3)
C_7-C_{11}	1.533 (6)	$I-O_2-C_{11}$	116.1 (3)
$C_{11}-O_2$	1.395 (6)	$O_1-C_2-C_3$	112.1 (3)
		$C_2-C_3-C_6$	115.0 (4)
		C_3-C_6-I	117.8 (3)
		C_7-C_6-I	116.2 (3)
		$C_6-C_7-C_{11}$	115.4 (4)
		$C_7-C_{11}-O_2$	111.7 (4)

Figure 4. Iodinane **10b** and its interaction with a neighboring molecule.

Scheme I

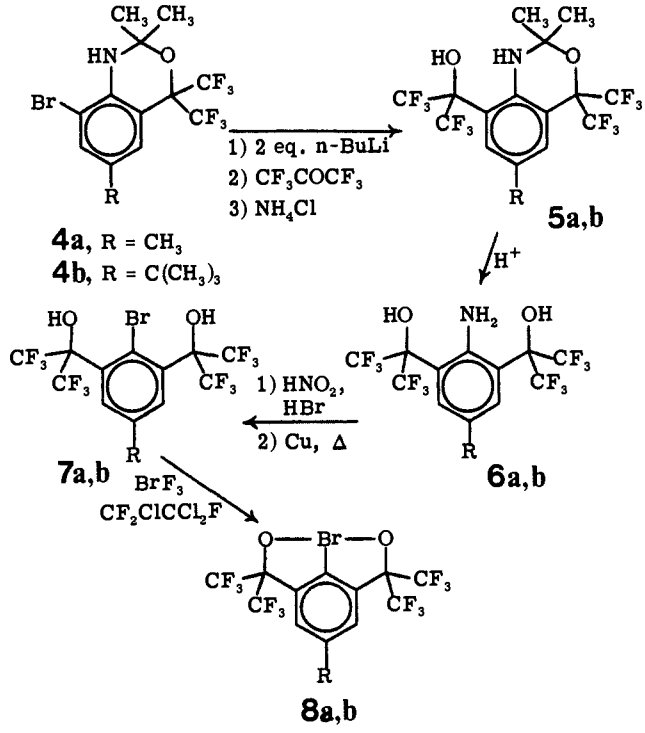


Figure 5 and Figure 6 show the view of the single molecule and the packing in one unit cell.

The greater deviation from the ideal TBP value of 180° for the O–I–O angle (158.2°) than for the O–Br–O angle (167.6°) is an expected result of the greater length of the C–I bond (2.052 Å) compared to the C–Br bond (1.875 Å).

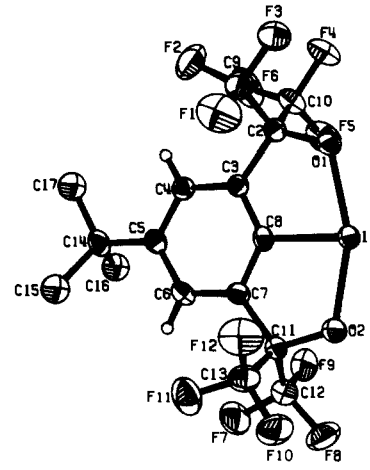


Figure 5. X-ray crystallographic structure of iodinane **10b**.

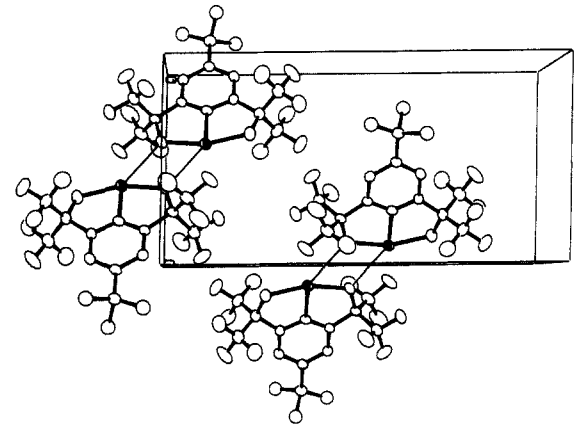


Figure 6. Unit cell view of the crystal packing of **10b**.

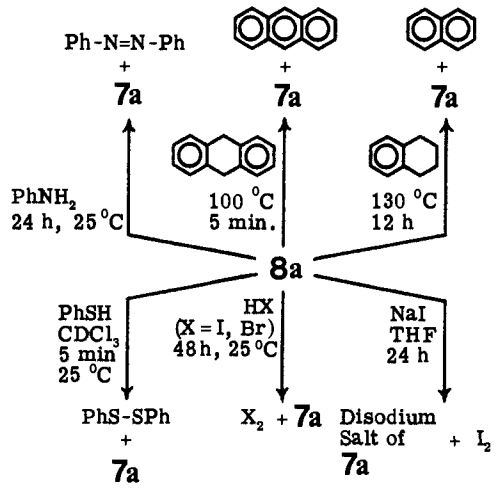
Both the brominane and iodinane exhibit some degree of intermolecular interaction. The crystal structures of these molecules show dimerization. The distance between the halogen atom of one molecule and its nearest oxygen atom of the neighbor compound (O···Br = 2.97 Å, O···I = 3.00 Å) is well within the sum of van der Waals radii (3.35 and 3.55 Å).[18] The molecular weight of brominane **8b** in acetonitrile was found to be 551 g mol^{-1}, within experimental error of the calculated value for the monomer (543 g mol^{-1}). The low-temperature (−75 °C) ^{19}F NMR spectrum of iodinane **10b** did not show any change in the absorption for the CF_3 groups. The intermolecular bonding is therefore probably very weak. Such interactions in the crystal lattice are well-known in iodinane chemistry. The crystal structure of $C_6H_5ICl_2$[19] indicates an intermolecular distance of 3.40 Å between the iodine and the nearest neighboring chlorine atom.

As expected, the O–X bonds in our 10-X-3 species are longer than the sum of their covalent radii. The O–Br bonds (1.99 and 1.97 Å) are slightly longer than the sum of the covalent radii (1.81 Å).[18] In close parallel to this, the I–O bonds in iodinane **10b** (2.11 and 2.08 Å) are also longer than the sum of the covalent radii (2.06 Å).[18] The two O–X bonds in each halogenane are unequal in length. This difference is an expected result of the intermolecular interaction in the crystal lattice. The oxygen engaged in intermolecular interaction with the Lewis acidic bromine (or iodine) of an adjacent molecule is less strongly bonded to the halogen(III) atom in the same molecule.

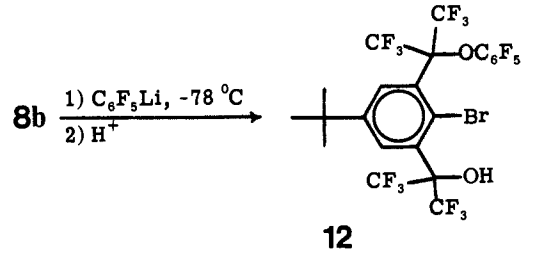
Reactions. Our brominanes are strong oxidizing agents. Reactions of **8a** with iodide ion, bromide ion, thiophenol, aniline, 9,10-dihydroanthracene, and tetralin, all oxidations with **8a** being reduced to **7a**, are shown in Scheme II.

(18) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, New York, 1960.
(19) Archer, E. M.; van Schalkwyk, T. G. D. *Acta Crystallogr.* **1953**, *6*, 88.

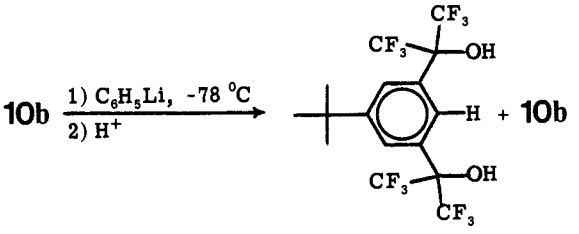
Scheme II



Brominanes **8a** and **8b** also react as electrophiles. At room temperature, **8b** gives no reaction with $K^{18}OH$; however at higher temperature in *tert*-butyl alcohol, it is reduced to **7b**. Two gaseous



12



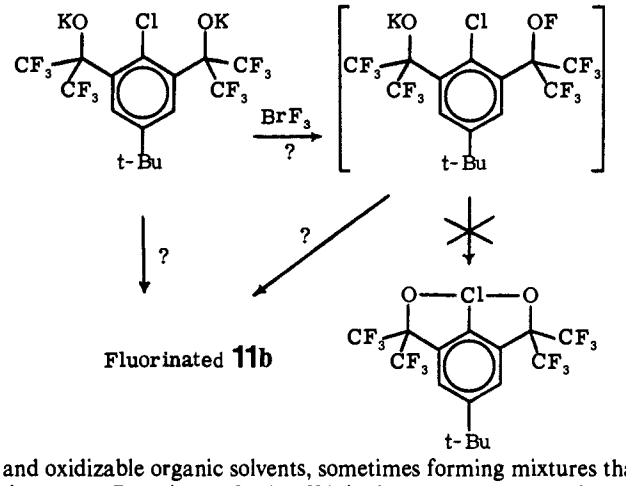
13

products were identified as $^{16}O_2$ and isobutylene. No $^{18}O_2$ or $^{18}O^{16}O$ was detected. Treatment of brominane **8b** with (pentafluorophenyl)lithium provides pentafluorophenyl ether **12**. Treatment of iodinane **10b** with (pentafluorophenyl)lithium or phenyllithium gives starting material, iodinane **10b**, and the reduced diol **13**, upon quenching with ammonium chloride. Low-temperature ^{19}F NMR spectra of the solution of **10b** with phenyllithium gave a broad absorption at −75.3 ppm at −30 °C.

Discussion

Syntheses. The syntheses of **4a** and iodine compounds **9a** and **10a** have been discussed elsewhere.[16] While the oxidations of iodo diols **9** to **10** are effected by bromine–pyridine or *tert*-butyl hypochlorite, bromo diols **7a,b** or their dipotassium salts do not give brominanes **8a,b** upon treatment with *tert*-butyl hypochlorite or chlorine gas. With BrF_3 as an oxidizing reagent, however, brominanes are formed in high yield. Attempts to oxidize chloro diol **11b** or its dipotassium salt with BrF_3 gave no evidence for a chlorinane; however various unidentified fluorinated products were obtained. In the oxidation of the dipotassium salt of **11b**, the *tert*-butyl group was attacked. Several multiplets were observed in the ^1H NMR spectrum in the region from 1.5 to 2.5 ppm, and broad absorption for hydroxy proton was observed from 5 to 6 ppm. If the hypofluorite is formed, as pictured, it reacts with the more easily oxidized organic portion of the molecule rather than the more difficulty oxidized chlorine. No evidence for the chlorinane was seen in any spectra.

Stability and Structure. Bromine trifluoride and other inorganic analogues of brominanes **8a** and **8b** are very reactive toward water



and oxidizable organic solvents, sometimes forming mixtures that detonate. Brominane **8a** (or **8b**) is, by contrast, not moisture-sensitive, nor does it react with common organic solvents at room temperature. The contrast between **8a** and its acyclic inorganic analogues emphasizes the importance of the incorporation of the bromine(III) atom of **8a** in a molecule whose ligands stabilize its pseudo-trigonal-bipyramidal (Ψ-TBP) geometry. The stabilizing structural features of the tridentate ligand of **8a** and of related bidentate ligands have been well-documented in the chemistry of Ψ-TBP sulfuranes, phosphoranes, iodinanes, siliconates, telluranes, and carbon.[20] While we were unable to synthesize monocyclic brominane **2** by using the bidentate ligand which has shown to be useful in stabilizing other hypervalent species,[20f] the tridentate ligand stabilizes it enough to make its isolation very easy. Monocyclic brominane **2** might have been formed in the reaction of **1** with BrF_3; if so, it is too reactive to make its isolation possible under the conditions used for the reaction. The fluoride ligand of **2** is expected to ionize much more readily than the alkoxy ligand that forms the ring in the case of **8**. The stabilizing effect of such chelation is also well-known in transition-metal chemistry.[21]

The ^{19}F NMR chemical shifts of the CF_3 peaks of both brominanes, **8a** and **8b**, and iodinane **10b** are identical (−75.8 ppm). They are found 3 ppm upfield from those of the corresponding alcohols (−72.8 ppm), while the aromatic proton peaks are found downfield of those for the alcohols. These observations can be reconciled with the electron distribution expected for species with hypervalent bonds. There is an increase of electron density at the oxygen atoms of the apical ligand, while the equatorial ligand, the aromatic ring, inductively donates electrons to the positive-charged central halogen atom.

Reactions. In general, higher valent halogen compounds behave as strong oxidizing reagents and electrophiles. Brominanes **8a,b** are not as reactive as their acyclic analogues, but they are still strong oxidizing agents. The dehydrogenation of 9,10-dihydroanthracene and tetralin is compatible to that with other dehydrogenating reagents such as Pt, S, Se, or SeO_2.[22] A radical-chain route for dehydrogenation is an attractive possibility, but we failed to obtain any evidence that brominane **8a** can act as a radical initiator in the copolymerization of styrene and methyl methacrylate at 55 °C.

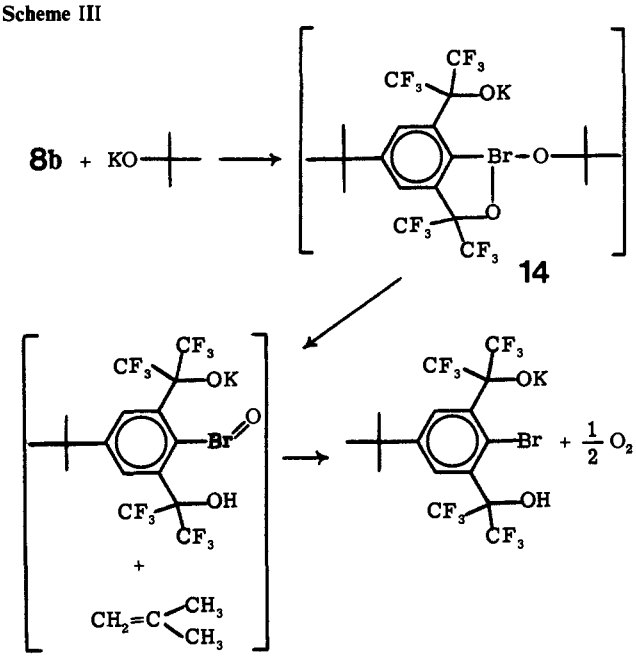
Attempts to hydrolyze the brominane with potassium hydroxide have not provided any direct evidence for a bromoso compound.

(20) (a) The stabilizing structural features (the five-membered rings, the *gem*-dialkyl groups, the electronegative apical ligands, the electropositive carbon equatorial ligand, and the ring fusion of the six-membered ring to the two five-membered rings) are discussed in the following references. (b) Perozzi, E. F.; Martin, J. C. *J. Am. Chem. Soc.* **1972**, *96*, 5519. (c) Martin, J. C.; Perozzi, E. F. *Ibid.* **1974**, *96*, 3155. (d) Westheimer, F. H. *Acc. Chem. Res.* **1968**, *1*, 70. (e) Granoth, I.; Martin, J. C. *J. Am. Chem. Soc.* **1979**, *101*, 4618. (f) 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. (g) Forbus, R. T.; Martin, J. C. *J. Am. Chem. Soc.* **1979**, *101*, 5057. (h) Lam, W. Y.; Martin, J. C. *Ibid.* **1977**, *99*, 1659. (i) Lam, W. Y.; Martin, J. C. *Ibid.* **1981**, *103*, 120.

(21) Lustig, M.; Cady, G. H. *Inorg. Chem.* **1962**, *1*, 714.

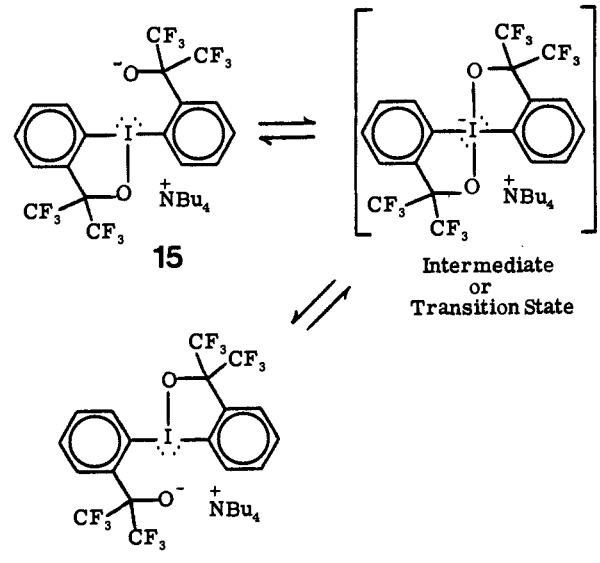
(22) March, J. *Advanced Organic Chemistry*, 2nd ed.; McGraw-Hill: New York, 1977; p 1078.

Scheme III



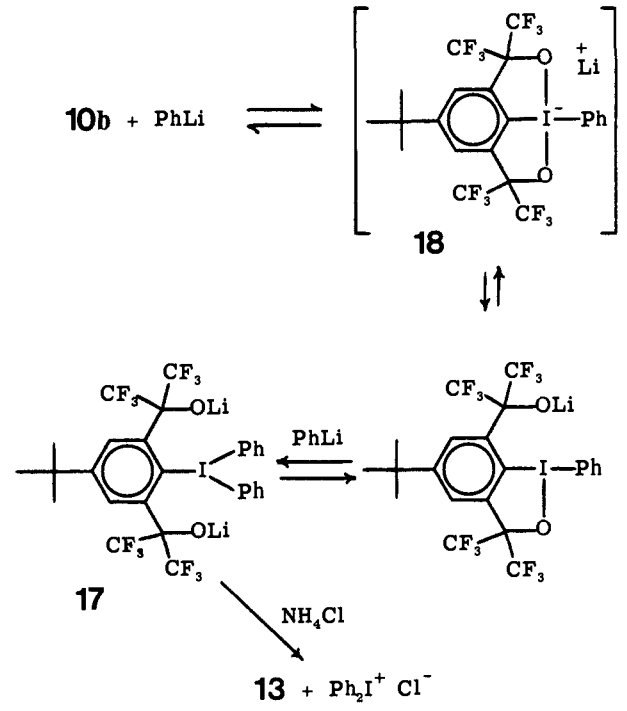
Brominane **8b** does not react with hydroxide at room temperature, but at higher temperature, the compound is reduced to the 8-Br-1 bromide. Gas evolution is observed when a sample is heated with potassium hydroxide in *tert*-butyl alcohol. When the reaction is done with ^{18}O-labeled KOH, $^{32}O_2$ and isobutylene are detected by mass spectrometry. A base-catalyzed reaction of *tert*-butyl alcohol with the brominane could give an intermediate, brominane **14**. A subsequent elimination reaction, parallel to the thoroughly studied reaction between a dialkoxysulfurane and *tert*-butyl alcohol,[23] would give isobutylene and a bromosobenzene derivative, which could react with itself to give O_2 and the reduced product (Scheme III).

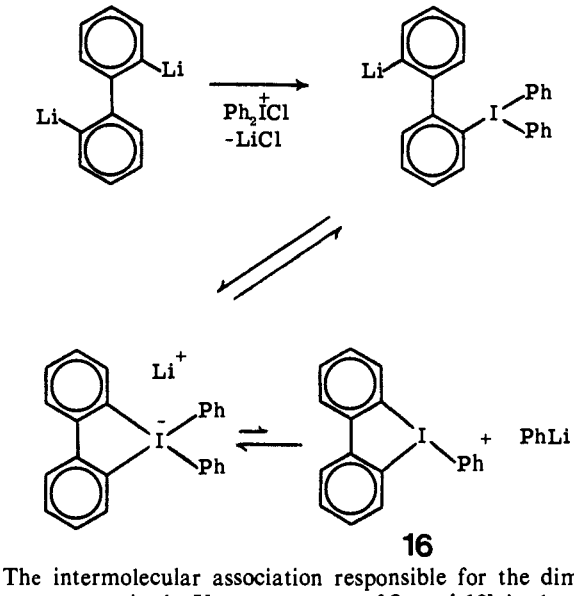
Although several examples of inorganic 12-Br-4 and 12-I-4 species such as $KBrF_4$,[4] $CsI(OCOCF_3)_4$,[24] and $CsIF_4$[25] have been prepared, no organo-nonmetallic analogue has been isolated or observed. There is evidence, however, for rapid exchange of ligands of an organic 10-X-3 species by reaction with nucleophiles. Iodinane **15** shows a rapid exchange of alkoxy ligands with a ΔG^* (−80 °C) of ca. 12 kcal mol^{-1}.[26]



Beringer and Chang proposed a 12-I-4 intermediate (the precursor of **16**) in the reaction of diphenyliodonium chloride with 2,2′-dilithiobiphenyl.[27]

Scheme IV



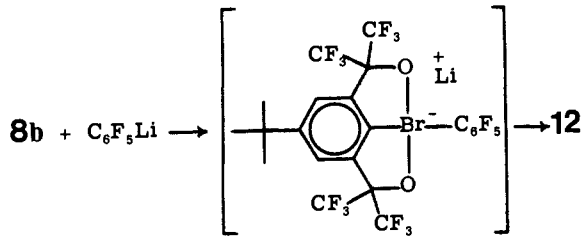


The intermolecular association responsible for the dimeric structures seen in the X-ray structures of **8a** and **10b** is plausibly explained by postulating electrophilic character of the halogen atoms. Treatment of the iodinane with phenyllithium at −78 °C gives a citrus-yellow solution which turns yellow-brown upon warming to room temperature. A color described as citrus yellow was also observed in Beringer's experiment. The ^{19}F NMR spectrum of a mixture of **10b** and phenyllithium in THF at −30 °C shows a broad peak at −75.3 ppm which sharpens slightly when the temperature is raised to 30 °C. At temperatures lower than −30 °C the complex precipitated out of solution. Upon quenching the mixture with aqueous ammonium chloride, we recovered approximately 70% of the iodinane. The remainder of the product which was characterized was the reduced compound **13** (20%). It is possible that reaction with phenyllithium gives iodinane **17**, which undergoes rapid ligand exchange via a 12-I-4 transition state or the metastable intermediate **18**. If the closed form, **18**, were the predominant form present, one would expect a sharper ^{19}F NMR singlet. The reduced product **13** may arise from the pro-

(23) Arhart, R. J.; Martin, J. C. *J. Am. Chem. Soc.* **1971**, *93*, 4327.
(24) Nauman, D.; Schmeisser, M.; Scheele, R. *J. Fluorine Chem.* **1972**, *1*, 321.
(25) Schmeisser, M.; Ludovici, W.; Nauman, D.; Sartori, P.; Scharf, E. *Chem. Ber.* **1968**, *101*, 4214.
(26) Dess, D. B.; Martin, J. C. *J. Am. Chem. Soc.* **1982**, *104*, 902.
(27) Beringer, F. M.; Chang, L. L. *J. Org. Chem.* **1972**, *37*, 1516.

tonolysis of triaryliodinane **17**. Acidification of triaryliodinanes is known to give diaryliodonium ion and benzene.[28] The reaction of iodinane **10b** and phenyllithium is presented in Scheme IV.

Brominane **8b** forms pentafluorophenyl ether **12** upon reaction with (pentafluorophenyl)lithium. It is interesting to speculate that the formation of **12** results from a ligand–ligand coupling reaction of the pictured 12-Br-4 intermediate.



(28) (a) Wittig, G.; Claus, K. *Justus Liebigs Ann. Chem.* **1952**, *578*, 136. (b) Clauss, K. *Chem. Ber.* **1955**, *88*, 268.

Acknowledgment. This research was supported in part by a grant from the National Science Foundation (CHE 81-13142). Mass spectra were obtained by facilities provided under grants from the National Institutes of Health (CA 11388 and GM 16864), and NMR spectra were provided by the University of Illinois Midwest NSF Regional NMR Facility (CHE 79-16100).

Registry No. 1, 71401-76-8; **3**, 101697-22-7; **4b**, 101697-23-8; **5b**, 101697-24-9; **6a**, 76220-90-1; **6b**, 101697-25-0; **7a**, 76220-91-2; **7a**·2Na, 76220-93-4; **7b**, 101697-26-1; **8a**, 76220-92-3; **8b**, 101697-27-2; **9b**, 101697-28-3; **10b**, 101697-29-4; **11b**, 101697-30-7; **12**, 101697-31-8; **13**, 101697-32-9; CF_3COCF_3, 684-16-2; 9,10-dihydroanthracene, 613-31-0; anthracene, 120-12-7; tetralin, 119-64-2; napthalene, 91-20-3; thiophenol, 108-98-5; diphenyl disulfide, 882-33-7; aniline, 62-53-3; azobenzene, 103-33-3; pentafluorobenzene, 363-72-4.

Supplementary Material Available: A listing of thermal parameters, bond lengths and angles, and observed and calculated structure factors for brominane **8a** and iodinane **10b** (30 pages). Ordering information is given on any current masthead page.

Formation of Novel 1,2-Oxathietanes from 2-Chloroethyl Sulfoxide Precursors and Their Reactions in Solution, Including Formal [σ2s + σ2a] Cycloreversions and Rearrangements†

J. William Lown* and R. Rao Koganty

Contribution from the Department of Chemistry, University of Alberta, Edmonton, Alberta T6G 2G2, Canada. *Received July 24, 1985. Revised Manuscript Received January 28, 1986*

Abstract: Spontaneous decomposition of antileukemic 1-[2-[(2-chloroethyl)sulfinyl]ethyl]-3-cyclohexyl-1-nitrosourea and its alkyl-substituted analogues in aqueous buffer (pH 7.0 and 37 °C) affords fragmentation products through the intermediacy of novel 1,2-oxathietanes. This was confirmed by specific deuterium labeling in the formal [σ2s + σ2a] cycloreversion products and by specific $S^{18}O$ labeling which eliminates an alternative pathway via thiirane *S*-oxide. The ^{18}O labeling also demonstrates that alternative ring opening with oxygen transfer occurs with 1,2-oxathietanes unsubstituted at the 4-position to give rearranged aldehyde. 1-[2-[(2-Chloroethyl)sulfinyl]-1,1-dimethylethyl]-3-*tert*-butyl-1-nitrosourea in aqueous buffer (pH 7.0 and 37 °C) affords products corresponding to three distinct pathways involving the formation of both 4,4-dimethyl-1,2-oxathietane and 1,2-oxathietane and the intermediacy of 4,4-dimethyl-1,2,3-oxadiazoline. Minor contribution of products from the parent 1-[2-[(2-chloroethyl)thio]ethyl]-3-alkyl-1-nitrosoureas to the extent of 5–10% occurs via in situ deoxygenation. An alternative and more convenient route to 1,2-oxathietanes was established using diazotization of (2-chloroethyl)alkyl-substituted sulfinylethylamines which provides dilute solutions of 3,3,4,4-tetramethyl-1,2-oxathietane. The latter product, which survives molecular distillation, was characterized by physical data and by the lithium aluminum hydride reduction to 2,3-dimethyl-2-mercapto-3-butanol, isopropyl alcohol, and 2-propanethiol. The thioacetone fragment from the [σ2s + σ2a] cycloreversion of the 1,2-oxathietane is trapped with reactive alkenes to give thietanes and with anthracenes to afford bicyclic thioketone adducts. There was no evidence of concomitant trapping of the acetone fragment nor of detectable chemiluminescence. Preliminary ab initio calculations at the level of SCF 6-21G and 6-31G* are in accord with spontaneous exothermic [σ2s + σ2a] cycloreversion of 1,2-oxathietane to give thioformaldehyde and formaldehyde. The thiocarbonyl fragment is expected to be more readily excited and is therefore more likely to bear the excess energy resulting in the n,π^* state for the thioketone resulting from the spontaneous cycloreversion. Preliminary calculations are in accord with this prediction. Owing to the clean aqueous decomposition of the antileukemic sulfinyl nitrosourea precursor the formation of 1,2-oxathietanes may play a physiological role in the anticancer action of the precursors.

The hitherto unkwown 1,2-oxathietanes are of both practical and theoretical interest. First, there is the analogy with the extensively studied 1,2-dioxetanes, which are of significance in bioluminescent and chemiluminescent reactions.[1] Second, these compounds are of fundamental theoretical interest because of the effects of the sulfur atom on the direction, rates, energetics, and energy distribution in the anticipated pericyclic reactions of the formal [σ2s + σ2a] type.[2] In this regard their relative structural

† Communicated in preliminary form: Lown, J. W.; Koganty, R. R. *J. Am. Chem. Soc.* **1983**, *105*, 126.

(1) (a) Richardson, W. H.; Montgomery, F. C.; Yelvington, M. B.; O'Neal, H. E. *J. Am. Chem. Soc.* **1974**, *96*, 7525. (b) Kopecky, K. R.; Filby, J. E.; Mumford, C.; Lockwood, P. A.; Ding, J.-Y. *Can. J. Chem.* **1975**, *53*, 1103. (c) Turro, N. J.; Lechtken, P. *J. Am. Chem. Soc.* **1972**, *94*, 2886. (d) White, E. H.; Wildes, P. D.; Wiecko, J.; Doshan, H.; Wei, C. C. *J. Am. Chem. Soc.* **1973**, *95*, 7050. (e) Adam, W. In *Chemical and Biological Generation of Electronically Excited States*; Adam, W., Cilento, G., Eds.; Academic: New York, 1982; Chapter 4 and references therein.

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