A Useful 12-I-5 Triacetoxyperiodinane (the Dess-Martin Periodinane) for the Selective Oxidation of Primary or Secondary Alcohols and a Variety of Related 12-I-5 Species[1a]

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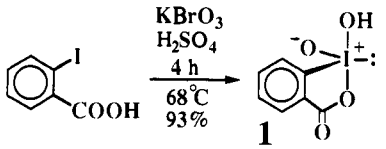
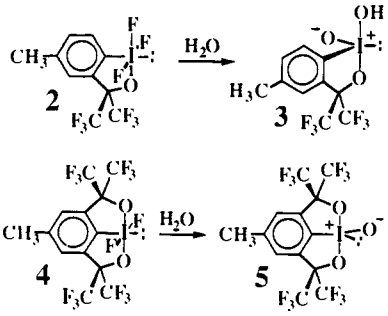
Abstract: The stable 10-I-4 species 1-hydroxy-1,3-dihydro-3,3-bis(trifluoromethyl)-1,2-benziodoxole 1-oxide ((fluoroalkoxy)iodinane oxide **7**) is the ring-closed form of *o*-iodoxyhexafluorocumyl alcohol. It is prepared by the oxidation of chloroiodinane **6** with potassium bromate in aqueous sulfuric acid. The X-ray crystal structure of the tetrabutylammonium salt of **7** (10-I-4 anion **10**) showed the unusual feature of an apical, negatively charged oxide ligand. Iodinane oxides **1** and **7** are readily converted to stable 12-I-5 periodinanes by treatment with carboxylic acid anhydrides or sulfur tetrafluoride. Tris(acyloxy)periodinanes **13** and **14** (derived from the ring-closed form of *o*-iodoxybenzoic acid), 1-hydroxy-1,2-benziodoxol-3(1*H*)-one 1-oxide (**1**), and **17** and **18** (derived from **7**) are extraordinarily stable. 1,1,1-Triacetoxy-1,1-dihydro-1,2-benziodoxol-3(1*H*)-one (**13**), the "Dess-Martin Periodinane", is an extremely useful reagent for the conversion of primary and secondary alcohols to aldehydes and ketones at 25 °C. It does not oxidize aldehydes to carboxylic acids under these conditions. It selectively oxidizes alcohols in the presence of furan rings or sulfides and does not react with vinyl ethers. Geraniol is oxidized to geranial by **13** without isomerization to nerol. Benzylic or allylic alcohols are selectively oxidized in the presence of saturated alkanols. The alcohol oxidation mechanism involves intermediates with alkoxy ligands replacing acetoxy ligands at the 12-I-5 iodine. It also oxidizes *N*-benzylbenzamide to benzaldehyde. Four other 12-I-5 species, 1,1,1-tris(trifluoroacetoxy)-1,1-dihydro-1,2-benziodoxol-3(1*H*)-one (**14**), 1,1,1,-trifluoro-1,1-dihydro-1,2-benziodoxol-3(1*H*)-one (**15**), 1,1,1-tris(acetoxy)-1,1,1,3-tetrahydro-3,3-bis(trifluoromethyl)-1,2-benziodoxole (**17**), and 1,1,1-tris(trifluoroacetoxy)-1,1,1,3-tetrahydro-3,3-bis(trifluoromethyl)-1,2-benziodoxole (**18**), also oxidize alcohols to aldehydes and ketones. All of the tris(acyloxy)periodinanes undergo facile ligand exchange with alcohols. The reaction between triacetoxyperiodinane **13** and pinacol gives an isolable, crystalline, spirobicyclic periodinane, **25**. The acetoxy group of periodinane **25** undergoes degenerate ligand exchange with acetic acid rapidly on the NMR time scale.

Introduction

Several iodinane oxides, pseudo-trigonal-bipyramidal (ψ-TBP) 10-I-4 species with an equatorial oxide ligand, have been reported,[2] but until recently little has been done to establish their patterns of reactivity. Although iodinane oxide **1**,[3] 1-hydroxy-1,2-benziodoxol-3(1*H*)-one 1-oxide (cyclized 2-iodoxybenzoic acid), has been known since the last century, its virtual insolubility in common organic solvents has discouraged the study of its chemical properties. Several acyclic iodinane oxides have been reported, including CF_3IOF_2,[4] $(CH_3O)_3IO$,[5] $PhIOF_2$,[6] IOF_3,[7] CH_3OIOF_2,[8] $ArIO(OCOR)_2$,[9] and Ar_2IOX (X = OH,[10a] F,[10b] Cl,[10b] Br,[10a,b] OAc,[10b] $OCOCF_3$,[10b] IO_3[10b]).



Recent research[11,12] showed that pseudooctahedral (ψ-Oc) 12-I-5 periodinanes **2** and **4** are easily hydrolyzed to form iodinane oxides **3**[11] and **5**,[13] stable crystalline solids. Chloroiodinane **6**[14]



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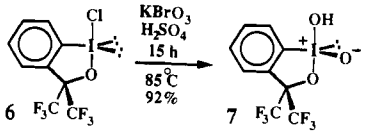
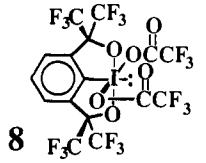
is oxidized to 1-hydroxy-1,3-dihydro-3,3-bis(trifluoromethyl)-1,2-benziodoxole 1-oxide (hydroxyiodinane oxide **7**) by potassium bromate in sulfuric acid, making it easily accessible.



Reported ψ-Oc 12-I-5 periodinanes include IF_5.[15] $IF_{5-n}(OCH_3)n$[16] (n = 1–4), $CF_3IF_{4-n}(OMe)_n$[17] (n = 1–2), $PhIF_4$.[18] $PhI(OCOR_F)_4$[9] (R_F = perfluoroalkyl), $IF_3(OCH_2CH_2O)$.[19a,b] $IF_3(OC(CH_3)_2C(CH_3)_2O)$.[19a,b] and $IF_3(OCH(COOH)CH(COOH)O)$.[19c] With the exception of IF_5, which has been used as an oxidizing agent[20] in organic synthesis, little mention of the chemical reactivity of the other compounds has appeared in the literature. All of these compounds are extremely moisture sensitive and some ($PhIF_4$ and $PhI(OCOR)_4$) are reported to decompose in storage.

Periodinanes **2**,[11] **4**,[12] and **8**[13] are stable enough to allow extensive investigation of their chemical reactivity. Periodinane **2** was found to be an effective reagent for the conversion of primary and secondary alcohols to aldehydes, secondary alcohols to ketones,[11b] and primary amines to imines.[11b] The relative inaccessibility of **2**, however, made it unattractive for use for this purpose. The preparation of stable monocyclic and bicyclic 12-I-5 species from the readily accessible iodinane oxides **1** and **7** and their use as oxidants in organic synthesis is discussed in this paper.



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. Elemental analyses were within 0.4% of theoretical values for the indicated elements unless otherwise noted. The X-ray crystallographic structure determination was carried out by Dr. Scott Wilson of the University of Illinois X-ray Crystallography Laboratory.

1-Hydroxy-1,2-benziodoxol-3(1*H*)-one 1-Oxide (1). Compound **1** was prepared by a variation of the method of Greenbaum.[3b] We found that the yield of **1** was increased by reducing the reaction time, the reaction temperature, the acid concentration, and the amount of $KBrO_3$. Potassium bromate (76.0 g, 0.45 mol) was added over 0.5 h to a vigorously stirred mixture of 2-iodobenzoic acid (85.2 g, 0.34 mol) and 730 mL of 0.73 M H_2SO_4 in a 55 °C bath. The mixture was stirred for 3.6 h at 68 °C and then cooled with an ice bath. Filtration and washing of the solid with 1000 mL of water and 2 × 50 mL of ethanol gave **1** (89.1 g, 0.32 mol, 93%): mp 232–233 °C dec (lit.[3a] mp 233 °C). Anal. ($C_7H_5IO_4$) C, H, I.

CAUTION: Compound **1** was reported to be explosive by Meyer,[3a] and more recently by J. B. Plumb and D. J. Harper, ICI Pharmaceuticals Group, in Chemical and Engineering News[3e] to be explosive similar to trinitrotoluene. The ICI preparation of **1**, found to be explosive, had 43.5% iodine by elemental analysis (calculated 45.32% for **1**) although none of the samples of **1** prepared by our method had any unexpected decrease in the percentage of iodine. They also had some bromine (<1%) in **1** after washing with only water. We washed with water and ethanol to form a nonexplosive sample of **1**. Although we have been unable to induce an explosion of **1** that would break the glass container or an explosion upon hard impact of a steel hammer, we suggest that the synthesis of **1** be handled with care. It is possible that some bromate or other impurity may be included in the samples found to be explosive.[3e]

Tetrabutylammonium 2-Iodoxybenzoate (9). Tetrabutylammonium hydroxide (1.53 mmol, 1 mL of a 1.53 M solution in water) was slowly added to a stirred slurry of **1** (1.2 g, 4.28 mmol) in acetonitrile (60 mL). The resulting mixture was filtered and the solvent removed under vacuum. The remaining solid was dissolved in CH_2Cl_2 and filtered. Removal of the solvent under vacuum gave **9** (0.4 g, 0.77 mmol, 50%): mp 130–133 °C; ^1H NMR (CD_3CN) δ 0.95 (t, 12 H, J_{HH} = 6.9 Hz, CH_3CCCN^+), 1.33 (m, 8 H, CCH_2CCN^+), 1.59 (m, 8 H, $CCCH_2CN^+$), 3.10 (t, 8 H, J_{HH} = 8.6 Hz, $CCCCH_2N^+$), 7.64 (t, 1 H, J_{HH} = 7.3 Hz) and 7.77 (t, 1 H, J_{HH} = 6.4 Hz) (Ar*H* at C-4 and C-5), 8.04 (d, 0.7 H, J_{HH} = 7.3 Hz) and 8.16 (d, 1 H, J_{HH} = 7.6 Hz) (Ar*H* at C-3 and C-6); IR ($CHCl_3$) 1617 cm^{-1}. Anal. ($C_{23}H_{41}IO_4N$) C, H, I, N.

1-Hydroxy-1,3-dihydro-3,3-bis(trifluoromethyl)-1,2-benziodoxole 1-Oxide (7). Potassium bromate (26.0 g, 96 mmol) was added to a vigorously stirred mixture of chloroiodinane **6** (20.5 g, 51 mmol) and 135 mL of 2 M H_2SO_4. After 15 h at 85 °C, cooling in an ice bath and washing the resulting crystals with 3 × 100 mL of H_2O gave **7** (18.8 g, 47 mmol, 92%): mp 203–204 °C dec; ^1H NMR (CD_3CN) δ 7.9–8.1 (m, 3.15 H), 8.61 (d, 0.35 H, J_{HH} = 8.14 Hz), 8.67 (d, 0.5 H, J_{HH} = 7.92 Hz); ^{19}F NMR (CD_3CN) δ −74.41 (q, 3 F, J_{FF} = 8.9 Hz), −74.52 (q, 3 F, J_{FF} = 8.9 Hz), −74.90 (m, 6 F); mass spectrum (field desorption) m/z 804 (M^+ for dimer of **7**), 787 (M^+ for dimer of **7** − OH), 402 (M^+), 385 (M^+ − OH); osmometric M_r (CH_3CN, ~0.1 M) 554. Anal. ($C_9H_5F_6IO_4$) C, H, F, I.

Reactions of Iodinane Oxide 7. (a) With HCl. Concentrated HCl (2 mL) was added to a stirred slurry of **7** (1.16 g, 2.9 mmol) in water (20 mL). After stirring for 36 h, the slurry was filtered, washed with water, and dried. This gave chloroiodinane **6** (1.02 g, 2.5 mmol, 87%): mp 163–166 °C (lit. mp 166–168 °C);[14] ^1H NMR and ^{19}F NMR spectra were consistent with published data.[14]

(b) With Benzyl Alcohol. Benzyl alcohol (4.0 mg, 0.037 mmol) was added to a solution of **7** (15 mg, 0.037 mmol) and mesitylene (internal standard, 1.5 mg, 0.012 mmol) in CD_3CN (0.6 mL). The formation of benzaldehyde was detected within 2 min by ^1H NMR spectroscopy. The reaction was almost complete after 25 min. After 2 h, the yield of benzaldehyde was 100%. Iodinane **12** was identified by ^{19}F NMR spectroscopy,[21] a compound with a sharp singlet for its two identical CF_3 groups.

(c) With Pinacol. Pinacol (7 mg, 0.070 mmol) was added to a solution of **7** (7 mg, 0.042 mmol) in CD_3CN (0.4 mL). No reaction was detected by ^1H NMR after 20 min. The solution was then heated at 83 °C for 30 min. The ^1H NMR and ^{19}F NMR spectra of the solution showed that 1 molar equiv of pinacol was oxidized to acetone, with reduction of **7** to **12**.

Tetrabutylammonium 1,3-Dihydro-3,3-bis(trifluoromethyl)-1,2-benziodoxole 1,1-Dioxide (10). Hydroxyiodinane oxide **7** (1.79 g, 4.45 mmol) was added to a solution of n-Bu_4NOH (4.59 mmol) in 80 mL of water. The solution was extracted with 2 × 75 mL of CH_2Cl_2. Removal of the solvent gave a solid, which was recrystallized (CH_2Cl_2–hexane) to give **10** (1.85 g, 2.8 mmol, 63%). Recrystallization from CH_2Cl_2–ether gave colorless cubes: mp 99–100 °C; ^1H NMR ($CDCl_3$) δ 0.95 (t, 12 H, J_{HH} = 7 Hz, CH_3CCCN^+), 1.35 (m, 8 H, CH_2CCN^+), 1.58 (m, 8 H, CH_2CN^+), 2.86 (s, 2 H, H_2O), 3.19 (t, 8 H, J_{HH} = 8 Hz, CH_2N^+), 7.58 (t, 1 H, J_{HH} = 7.05 Hz, H-4), 7.72 (t, 1 H, J_{HH} = 7.4 Hz, H-5), 7.77 (d, 1 H, J_{HH} = 8.3 Hz, H-3), 8.62 (d, 1 H, J_{HH} = 7.8 Hz, H-6); ^{19}F NMR ($CDCl_3$) δ −76.4 (br s); ^{13}C NMR ($CDCl_3$) δ 13.55 (NCCC*C*), 19.60 (NCC*C*), 23.91 (NC*C*), 58.74 (N*C*), 81.41 (m, $C(CF_3)_2$), 124.23 (q, J_{FC} = 290.9 Hz, CF_3), 124.99, 127.76, 120.12, 131.60, 133.88, 144.66 (Ar C-1). Anal. ($C_{25}H_{42}F_6INO_4$) C, H, F, I, N.

Crystal Growth of 10. Crystals of **10** were obtained by slowly cooling a saturated solution of **10** in methylene chloride and ether.

Crystal Data of 10. $C_{25}H_{42}F_6IO_4N$, monoclinic; a = 15.367 (4) Å, b = 17.729 (5) Å, c = 13.249 (3) Å, β = 116.39 (2) Å, V = 3023 (1) Å, Z = 4, ρ_{calcd} = 1.453 g cm^{-3}; μ(Mo K) = 11.10 cm^{-1}, $F(000)$ = 1352.0. Systematic absences for $0k0$, $K - 2n + 1$ and $h0l$, $h + l = 2n + 1$ strongly suggest the space group $P2_1/n$ (C_{2h}^5). A Syntex $P2_1$ diffractometer equipped with a graphite monochromator, λ(Mo K) = 0.710 69 Å was used to obtain the data set and cell parameters. The crystal used for data collection was a colorless prism with dimensions 0.58 × 0.68 × 0.85 mm. The sample was mounted on a glass fiber roughly along the (210) scat-

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tering vector. The octant $\pm hkl$ was collected in the 2θ–θ scan mode for $3.0° < 2\theta < 50.0°$ with a variable scan rate between 2.0 and 29.3 deg min^{-1}. Each peak was scanned from $0.8° = 2\theta$ below the calculated $K\alpha_1$ peak position to 1.0° above the calculated $K\alpha_2$ peak position. The background to scan time ratio was 0.25. Out of a total of 5313 unique reflections, 3540 were considered to be observed at the $3\sigma(I)$ criterion level. The data were corrected for Lorentz and polarization effects. An isotropic correction was applied for crystal decay. The total decline in the standard intensities was 25%.

Solution and Refinement of the Structure of 10. Coordinates for the iodine atom were deduced from a Patterson map. A weighted different Fourier summation revealed positions for 18 non-hydrogen atoms and a second weighted difference map gave positions for all but five of the remaining non-hydrogen atoms. These five atoms were located after subsequent least-squares-difference Fourier calculations. The final difference map had six peaks that were slightly greater than the background. The range of residual intensity was from +1.18 to −0.71 e $Å^{-3}$. These peaks were in the vicinity of the iodine atom, C-26, and the water molecule. In the final cycle of least-squares refinement, C-26 was fixed in a position determined from a difference Fourier map (an isotropic thermal parameter was varied for this atom), coordinates for atom O and C-25 were refined with isotropic thermal parameters, and the remaining non-hydrogen positional parameters were refined with anisotropic thermal coefficients. One isotropic thermal parameter was refined for the hydrogen atoms as a group. Atoms H-1 and H-2 were fixed in positions determined from a difference map and the remaining hydrogen atoms were fixed in idealized positions. These complications are attributed to the rapid decomposition of the sample during data collection. The final agreement factors for 319 variables were $R_1 = 0.069$ and $R_2 = 0.118$ ($R_1 = \sum||F_o| - |F_c||\sum|F_o|$, $R_2 = [\sum w||F_o| - |F_c||^2|\sum w|F_o|^2]^{1/2}$).

The final values of atomic coordinates of **10** are included in the supplementary material. Selected bond lengths and angles are included in Table I.

1,1,1-Triacetoxy-1,1-dihydro-1,2-benziodoxol-3(1*H*)-one (13). Method A. Finely powdered hydroxyiodinane oxide **1** (50.0 g, 0.18 mol) was dissolved by stirring for 20 min at 85 °C in acetic anhydride (172.8 g, 1.69 mol) and acetic acid (139 g, 2.31 mol). (If the sample of **1** is not finely powdered, a longer period of reaction is required. This is probably safer. Continue to heat this mixture until an aliquot is shown by ^1H NMR to be completely tris-acetylated, and then stop the reaction. The temperature, as noted below, can be lower than 85 °C.) The solvent was removed under vacuum at 45 °C, leaving a thick slurry. Filtration in an inert atmosphere and washing the crystals with 3 × 60 mL of anhydrous ether gave **13** (71.0 g, 0.17 mol, 93%): mp 133–134 °C dec; IR (CH_2Cl_2) 1726.9 cm^{-1} (s), 1707.5 cm^{-1} (s); ^1H NMR ($CDCl_3$) δ 2.01 (s, 6 H, $COCH_3$), 2.33 (s, 3 H, $COCH_3$), 7.80 (t, 1 H, J_{HH} = 7.3 and 8.5 Hz) and 8.07 (t, 1 H, J_{HH} = 7.3 and 8.5 Hz) (C-4 and C-5), 8.29 (d, 1 H, J_{HH} = 8.5 Hz) and 8.31 (d, 1 H, J_{HH} = 8.5 Hz) (C-3 and C-6); ^{13}C NMR ($CDCl_3$) δ 20.29 (2 $COCH_3$), 20.43 (1 $COCH_3$), 126.01 (C-2), 126.51, 131.79, 133.81, 135.76, 142.36 (C-1), 166.08 (endocyclic C=O), 173.96 (1 acetate C=O), 175.66 (2 acetate C=O's). Anal. ($C_{13}H_{13}IO_8$) C, H, I.

Hydrolysis converts **13** to iodoxybenzoic acid, **1**, reported[3] to be explosive, so care should be taken to prevent exposure of **13** to atmospheric moisture. Some samples prepared by other groups[3e] were exposed to the atmosphere, providing partial hydrolysis to form the monoacetic iodinane oxide. This could also be explosive with added impurities in **13**. None of our periodinane **13** was explosive upon melting or upon hard impact with a steel hammer.

Method B. In a safer method, a slurry of small crystals of **1** (25.0 g, 0.09 mol) in a mixture of acetic anhydride (92.4 g, 0.9 mol) and acetic acid (92.4 g, 1.5 mol) was stirred for 14.5 h at room temperature and filtered in an inert atmosphere. The reaction should always be tested for tris-acetylation by ^1H NMR and be continued further if not completed. In our experiment, washing the white solid with 3 × 50 mL of anhydrous ether gave **13** (32.2 g, 0.076 mol, 84%). If larger crystals of **1** are used, this reaction is slower. It is therefore helpful to raise the temperature to ca. 80 °C and use ^1H NMR analysis of an aliquot of the product, with removal of the solvent under vacuum, to determine that the formation of triacetate **13** is in high yield. Continue the reaction until **13** is present in high yield. If this does not occur, the precursor **1** is probably not present in high yield.

Reactions of Triacetoxyperiodinane 13. (a) With Ethanol (0.9 Equiv). Evidence for Ethoxyiodinane 20a. Ethanol (1.43 mg, 0.31 mmol) was added to a solution of **13** (14.6 mg, 0.0344 mmol) in $CDCl_3$ (0.6 mL). 1,1-Bis(acetoxy)-1-ethoxy-1,1-dihydro-1,2-benziodoxol-3(1*H*)-one (**20a**) was observed (^1H NMR) within 3 min: δ 1.42 (t, 3 H, J_{HH} = 6.8 Hz, CH_3CH_2OI), 2.03 (s, 6 H, CH_3COOI), 4.68 (q, 2 H, J_{HH} = 6.9 Hz, CH_3CH_2O), 7.85 (t, 1 H, J_{HH} = 7.2 Hz) and 8.03 (t, 1 H, J_{HH} = 7.56 Hz) (ArH at C-4 and C-5), 8.19 (d, 1 H, J_{HH} = 8.0 Hz) and 8.32 (d, 1 H, $J_{HH} \approx$ 7.0 Hz) (ArH at C-3 and C-6).

(b) With Ethanol (1.5 Equiv). Ethanol (3.12 mg, 0.0605 mmol) was added to a solution of **13** (17.3 mg, 0.041 mmol) in $CDCl_3$ (0.6 mL) at −14 °C. Ethoxyperiodinane **20a** and 1,1-diethoxy-1-acetoxy-1,1-dihydro-1,2-benziodoxol-3(1*H*)-one (**22**) were identified by ^1H NMR spectroscopy (−7 °C): δ 1.25 (t, 3 H, J_{HH} = 7 Hz, CH_3CH_2OI on **22**), 1.40 (t, 3 H, J_{HH} = 7.1 Hz, CH_3CH_2OI on **20a**), 1.46 (t, 3 H, J_{HH} = 7 Hz, CH_3CH_2OI on **21**), 1.94 (br s, 3 H, CH_3COOI on **22**), 2.03 (s, 6 H, CH_3COOI on **20a**), 4.00 (m, 1 H), 4.11 (m, 1 H), 4.44 (m, 1 H) and 4.54 (m, 1 H) (diasterotopic methylene protons on **22**), 4.67 (q, 2 H, J_{HH} = 7.1 Hz, CH_3CH_2OI on **20a**).

(c) With Ethanol in the Presence of Triethylamine. Triethylamine (6.9 mg, 0.068 mmol) was added to a solution of **13** (29 mg, 0.068 mmol) and mesitylene (internal standard, 2.7 mg, 0.033 mmol) in $CDCl_3$ (0.6 mL). Within 2 min of the addition of triethylamine, ethanol (3.1 mg, 0.068 mmol) was added. After 30 min, **20a** (86%) was detected by ^1H NMR spectroscopy. No acetaldehyde was detected. After 5 h only a trace of acetaldehyde (<5%) was detected. Acetic acid (4.1 mg, 0.068 mmol) was added to the solution and 60% acetaldehyde was present after 70 min.

(d) With 2,3-Butanediol. 2,3-Butanediol (3.8 mg, 0.042 mmol) was added to a solution of **13** (17.7 mg, 0.042 mmol) and mesitylene (internal standard, 3.4 mg, 0.028 mmol) in $CDCl_3$ (0.5 mL). Acetaldehyde was detected within minutes by ^1H NMR spectroscopy and was present in 68% yield after 18 h at 25 °C.

(e) With Oxalic Acid. Excess oxalic acid was added to a solution of **13** in $CDCl_3$. Evolution of gas from the solution was noted for several minutes. By ^1H NMR spectroscopy, only acetic acid and iodinane **21** were shown to be present in solution.

(f) With *N*-Benzylbenzamide. A solution of *N*-benzylbenzamide (0.91 g, 4.32 mmol) and **13** (2.04 g, 4.80 mmol) in CD_3CN (30 mL) was heated at 83 °C for 100 min. Water (4 mL) was added and the solution was boiled for 20 min, giving a copious precipitate. The mixture was poured into 40 mL of 1 N aqueous NaOH and 100 mL of ether and stirred until the solid dissolved. The ether layer was extracted with 2 × 40 mL of water and the ether was removed under vacuum. Treatment of the remaining oil with an excess of (2,4-dinitrophenyl)hydrazine gave the 2,4-DNPH derivative of benzaldehyde (1.24 g, 2.51 mmol, 58%): mp 233–235 °C (lit.[22] mp 234–236 °C).

(g) Examples of the General Procedures for the Oxidation of Alcohols by 13. Method A. A solution of geraniol (2.67 g, 17.3 mmol) in CH_2Cl_2 (14 mL) was added to a stirred solution of **13** (8.40 g, 19.8 mmol) in CH_2Cl_2 (52 mL) over 2 min. The solution came to a spontaneous boil for about 5 min. After 19 min the homogeneous solution was diluted with 100 mL of ether and poured into 100 mL of saturated aqueous $NaHCO_3$ containing 25 g of $Na_2S_2O_3$. The mixture was stirred for 5 min. After 100 mL of ether was added, and the layers were separated. The ether layer was extracted with 100 mL of saturated aqueous $NaHCO_3$ and 100 mL of water and dried ($MgSO_4$). Removal of the ether under vacuum followed by Kugelrohr distillation (85 °C, 1.0 mm) gave pure geranial (2.22 g, 14.6 mmol, 84%), which was identified by its ^1H NMR spectrum.[23]

Method B. A solution of cyclooctanol (0.9 g, 7.0 mmol) in CH_2Cl_2 (10 mL) was added to a stirred solution of **13** (3.5 g, 8.3 mmol) in CH_2Cl_2 (30 mL). After 2.1 h the solution was poured into a separatory funnel containing 70 mL of 1 N NaOH and 150 mL of ether. The layers were separated, and the ether layer was extracted with 2 × 50 mL of water. The ether layer was dried ($MgSO_4$) and the ether removed under vacuum. Kugelrohr distillation of the remaining oil gave cyclooctanone (0.76 g, 6.02 mmol, 86%): mp 34–37 °C (lit.[24] mp 43 °C).

1,1-Diacetoxy-1-(1,1-dimethylethoxy)-1,1-dihydro-1,2-benziodoxol-3-(1*H*)-one (20b). *tert*-Butyl alcohol (2.3 mg, 0.031 mmol) was added to a solution of **13** (13.2 mg, 0.031 mmol) in $CDCl_3$ (0.5 mL) to give **20b**: ^1H NMR δ 1.60 (s, 9 H, $(CH_3)_3CI$), 2.00 (s, 6 H, CH_3COOI), 7.83 (t, 1.2 H, J_{HH} = 8 Hz) and 8.02 (t, 1.0 H, J_{HH} = 8 Hz) (ArH at C-4 and C-5), 8.18 (d, 0.7 H, J_{HH} = 8 Hz) and 8.31 (d, 1.2 H, J_{HH} = 8 Hz) (ArH at C-3 and C-6).

Reaction between 20b and Ethanol. Ethanol (2.03 mg, 0.044 mmol) was added to a solution of **20b** (0.049 mmol) and mesitylene (internal standard) (1.77 mg, 0.044 mmol) in $CDCl_3$ (0.5 mL). The ethanol was oxidized to acetaldehyde (0.044 mmol, 100%) within 8 min at 25 °C (^1H NMR).

1,1,1-Tris(trifluoroacetoxy)-1,1-dihydro-1,2-benziodoxol-3(1*H*)-one

(22) *Handbook of Tables for the Organic Compound Identification*; Rappoport, Z., Ed.; CRC Press: Boca Raton, FL, 1980; p 147.
(23) Ohtsura, M.; Tersoka, M.; Tori, K.; Takeda, K. *J. Chem. Soc. B* **1967**, 1033.
(24) Corson, B. B.; Ipatieff, V. N. *J. Am. Chem. Soc.* **1939**, *61*, 1056. Baker, G. P.; Mann, F. G.; Sheppard, N.; Tetlow, A. J. *J. Chem. Soc.* **1965**, 3721.

(14). Trifluoroacetic anhydride (5.3 g, 25 mmol) was added to a stirred mixture of iodinane oxide **1** (0.54 g, 1.93 mmol) and acetonitrile (15 mL). The solution became homogeneous after 30 min. After 10 min the solvent was removed under vacuum to give **14** (0.93 g, 1.59 mmol, 83%): mp 100–105 °C dec; ^{1}H NMR (CD_3CN) δ 8.31 (m, 1 H), 8.39 (m, 2 H), 852 (m, ArH at C-6); ^{19}F NMR (CD_3CN) −74.03 (br s). Anal. ($C_{13}H_4F_9IO_8$) C, H, I (calcd 21.65%, found 22.11%).

Reaction of Periodinane 14 with 2-Propanol. 2-Propanol (4.4 mg, 0.073 mmol) was added to a solution of **14** (57.0 mg, 0.097 mmol) in CD_3CN. After 19 h, ^{1}H NMR spectroscopy showed only 10% oxidation to acetone. When excess 2-propanol (2 equiv) was added to a solution of **14** in CD_3CN, acetone was detected (^{1}H NMR) in 100% yield, based on the amount of **14**, within 10 min.

1,1,1-Trifluoro-1,1-dihydro-1,2-benziodoxol-3(1*H*)-one (15). A stainless steel bomb containing a slurry of **1** (1.0 g, 3.57 mmol) in $CHCl_3$ (5 mL) was cooled to −78 °C and SF_4 (5.0 g, 46 mmol) was condensed into it. The mixture was stirred for 5 h at 20 °C. The solvent was removed under vacuum, leaving behind white platelets of trifluoroperiodinane **15** (0.98 g, 3.22 mmol, 90%): mp 165–168 °C dec; IR (CH_2Cl_2) 1752.9 cm^{-1} (s); ^{1}H NMR (CD_2Cl_2) δ 7.96–8.10 (m, 1 H, ArH), 8.11–8.36 (m, 3 H, ArH); ^{19}F NMR (CD_2Cl_2) δ −34.32 (t, 1 F, J_{FF} = 139.3 Hz), −24.20 (d, 2 F, J_{FF} = 140.6 Hz). Anal. ($C_7H_4F_3IO_2$) C, H, F, I.

Reaction of 15 with 2-Propanol. 2-Propanol (4.2 mg, 0.063 mmol) was added to a solution of **15** (21 mg, 0.070 mmol) in CD_2Cl_2 (0.6 mL): ^{1}H NMR (after 15 min) 1.20 (d, J_{HH} = 6 Hz, $(CH_3)_2CHOH$, 76%), 1.53 (d, J_{HH} = 6 Hz, $(CH_3)_2CHOIF_2$, 16%), 2.13 (s, $CH_3)_2C{=}O$, 8%). After 5 h, mesitylene (internal standard) (2.5 mg, 0.021 mmol) was added: ^{1}H NMR δ 2.13 (s, $(CH_3)_2C{=}O$, 89%).

1-Acetoxy-1,3-dihydro-3,3-bis(trifluoromethyl)-1,2-benziodoxole 1-Oxide (16). After 2 h, the solvent was removed from a solution of **7** (1.0 g, 2.49 mmol) in acetic anhydride (6 mL). Washing the resulting solid with anhydrous ether in an inert atmosphere gave **16** (0.37 g, 0.83 mmol, 33%): mp 193–194 °C dec; ^{1}H NMR (CD_3CN) δ 2.18 (s, 3 H, $OCOCH_3$), 7.83 (m, 3 H, Ar*H* at C-3, C-4, and C-5), 8.43 (m, 1 H, Ar*H* at C-6); ^{19}F NMR (CD_3CN) δ −74.25 (q, 3 F, J_{FF} = 9 Hz), −73.70 (q, 3 F, J_{FF} = 9 Hz). Anal. ($C_{11}H_7F_6IO_4$) C, H.

1-Acetoxy-1,2-benziodoxol-3(1*H*)-one 1-Oxide (19). *tert*-Butyl alcohol (0.18 g, 2.48 mmol) was slowly added to a stirred solution of **13** (1.00 g, 2.36 mmol) in CH_3CN (15 mL). The solution was concentrated to ca. 3 mL under vacuum, ether was added, and the solution was cooled to −4 °C. The resulting solid was washed with anhydrous ether to give pure **19** (0.27 g, 0.84 mmol, 36%): mp 115–120 °C dec; ^{1}H NMR ($CDCl_3$) δ 2.21 (s, 3 H, CH_3COOI), 7.85 (m, 2 H, ArH at C-4 and C-5), 8.08 (d, 1 H, J_{HH} = 8 Hz) and 8.25 (d, 1 H, J_{HH} = 8 Hz) (ArH at C-3 and C-6). Anal. ($C_9H_7I_5O$) C, H.

1,1,1-Triacetoxy-1,1,1,3-tetrahydro-3,3-bis(trifluoromethyl)-1,2-benziodoxole (17). After a solution of iodinane oxide **7** (5.0 g, 12.4 mmol) in acetic anhydride (40 mL) was heated at 110 °C for 6.5 h, the solvent was removed under vacuum and the resulting solid was washed with ether in an inert atmosphere to give **17** (4.4 g, 9.0 mmol, 73%): mp 173–175 °C dec; IR (CH_2Cl_2) 1706.8 cm^{-1} (s); ^{1}H NMR ($CDCl_3$) δ 1.97 (s, 6 H, CH_3COOI), 2.31 (s, 3 H, unique CH_3COOI), 7.85–8.05 (m, 3 H, ArH at C-3, C-4, and C-5), 8.45 (d, 1 H, J_{HH} = 7.2 Hz, ArH at C-6); ^{19}F NMR (CH_3CN) δ −74.50 (s); ^{13}C NMR ($CDCl_3$) δ 20.25 (CH_3COOI), 20.65 (unique CH_3COOI), 84.25 (m, $C(CF_3)_2$), 122.54 (q, J_{FC} = 289.6 Hz, CF_3), 127.54, 127.79, 128.75, 133.16, 133.23, 139.66 (C-1), 174.01 (s, unique CH_3CO), 175.02 (s, CH_3CO). Anal. ($C_{15}H_{13}F_6IO_7$) C, H, F, I.

1,1,1-Tris(trifluoroacetoxy)-1,1,1,3-tetrahydro-3,3-bis(trifluoromethyl)-1,2-benziodoxole (18). Trifluoroacetic anhydride (1.04 g, 4.96 mmol) was added to a stirred slurry of iodinane oxide **7** (0.5 g, 1.24 mmol) in $CHCl_3$ (15 mL). The solution became homogeneous after 10 min. After 10 more min the solvent was removed under vacuum to give **18** (0.84 g, 1.19 mmol, 96%): mp 99–100 °C dec; IR (CH_2Cl_2) 1758.5 cm^{-1} (s); ^{1}H NMR ($CDCl_3$) δ 7.92–8.30 (m, 3 H, ArH at C-3, C-4, and C-5), 8.5 (m, ArH at C-6); ^{19}F NMR (22 °C) (CD_2Cl_2) δ −73.97 (s, 9 F, $OCOCF_3$), −74.74 (s, 6 F, $C(CF_3)_3$); ^{19}F NMR (−45 °C) −73.54 (s, 3 F, unique $OCOCF_3$), −73.63 (s, 6 F, $COCF_3$), −74.68 (s, 6 F, $C(CF_3)_2$). Anal. ($C_{15}H_4F_{15}IO_7$) C, H, I.

Reactions of (Trifluoromethyl)periodinane 18. (a) With Ethanol. Ethanol (1.6 mg, 0.035 mmol) was added to a solution of **18** (25 mg, 0.035 mmol) in CD_3CN (0.5 mL): ^{1}H NMR (after 30 min) δ 1.25 (t, 3 H, J_{HH} = 6 Hz, CH_3CH_2OI), 4.60 (q, 2 H, J_{HH} = 6 Hz, CH_3CH_2OI). No change was detected after 56 h.

(b) With Excess Ethanol. Ethanol (2.0 mg, 0.044 mmol) was added to a solution of **18** (16 mg, 0.022 mmol) to give 0.022 mmol (100%) of acetaldehyde within 20 min (^{1}H NMR).

Pinacolate Complex 25. A solution of pinacol (0.41 g, 3.44 mmol) in CH_3CN (5 mL) was slowly added to a stirred slurry of triacetoxyperiodinane **13** (1.4 g, 3.44 mmol) in CH_3CN (15 mL). The solvent was removed from the resulting solution under vacuum and the solid residue was recrystallized from CH_3CN (5 mL) and ether (40 mL) at 0 °C to give **25** (0.88 g, 2.01 mmol, 60%): mp 127–128 °C dec; IR (CH_2Cl_2) 1689.6 cm^{-1} (s); ^{1}H NMR ($CDCl_3$) δ 0.84 (s, 3 H, equatorial $CCCH_3$ cis to Ph), 1.19 (s, 3 H, $CCCH_3$), 1.34 (s, 3 H, $CCCH_3$), 1.46 (s, 3 H, $CCCH_3$), 1.89 (s, 3 H, $OCOCH_3$), 7.85 (t, 1 H, J_{HH} = 7.13 Hz, ArH at C-5), 7.95 (t, 1 H, J_{HH} = 7.26 Hz, ArH at C-4), 8.19 (d, 1 H, J_{HH} = 8.24 Hz, ArH at C-3), 8.28 (d, 1 H, J_{HH} = 7.45 Hz, ArH at C-6); ^{13}C NMR ($CDCl_3$) δ 20.83 ($COCH_3$), 24.45 (pinacol CH_3), 24.85 (pinacol CH_3), 25.16 (pinacol CH_3), 83.41 $(CH_3)_2C$), 83.86 $(CH_3)_2C$), 125.65, 129.41 (C-2), 130.89, 133.82, 134.0, 147.83 (C-1), 165.72 (endocyclic $C{=}O$), 181.39 ($C{=}O$). Anal. ($C_{15}H_{19}IO_6$) C, H, I.

Reactions of Pinacolate Complex 25. (a) Degenerate Ligand Exchange between 25 and Acetic Acid. Acetic acid (2.80 mg, 0.0467 mmol) was added to a solution of **25** (19.7 mg, 0.0467 mmol) in $CDCl_3$ (0.5 mL): ^{1}H NMR (25 °C) δ 1.97 (br s, 6 H); ^{1}H NMR (15 °C) δ 1.99 (br s, 6 H); ^{1}H NMR (10 °C) δ 1.92 (br s, 3 H, CH_3COOI), 2.05 (br s, 3 H, CH_3COOH); ^{1}H NMR (−45 °C) δ 1.93 (s, 3 H, CH_3COOI), 2.16 (s, 3 H, CH_3COOH).

(b) With Trifluoroacetic Acid. Trifluoroacetic acid (6.1 mg, 0.0535 mmol) was added to a solution of pinacol complex **25** (22.6 mg, 0.0535 mmol) in $CDCl_3$ (0.5 mL): ^{1}H NMR δ 1.00 (s, 3 H, equatorial $CCCH_3$ cis to Ph), 1.23 (s, 3 H), 1.73 (s, 3 H) and 1.83 (s, 3 H) (3 pinacolate CH_3), 2.1 (s, 3 H, CH_3COOH), 7.73–8.03 (m, 4 H, ArH).

(c) With Benzyl Alcohol. Benzyl alcohol (5.73 mg, 0.053 mmol) was added to a solution of **25** (22.5 mg, 0.053 mmol) and mesitylene (internal standard) (2.12 mg, 0.0177 mmol) in $CDCl_3$ (0.5 mL). No detectible (^{1}H NMR) reaction had occurred after 15 min. After 2.25 h, benzaldehyde (12%), acetone (17%), and iodinane **28** (17%) were detected. After 26 h, benzaldehyde (32%), acetone (23%), and **28** (21%) were detected.

Kinetic Studies. All reactions were carried out in $CDCl_3$ and the concentration of **13** was approximately 0.07 M in each reaction. Mesitylene was used as an internal standard and was present at one-third of the concentration of **13**. Proton NMR spectroscopy was used to monitor the reactions. Reactions using excess ethanol were carried out at 3.5 °C. The concentration of excess ethanol ranged from 0.006 to 0.031 M.

The reactions between ethanol and excess **13** in the presence of pyridine (ca. 0.1 M), between ethanol and excess **13** in the presence of acetic acid (ca. 0.07 M), and between ethanol and excess **13** were qualitatively monitored by ^{1}H NMR spectroscopy at 35 °C by observing the disappearance of starting materials and the appearance of products. All three reactions proceeded at approximately the same rate.

Reaction between Acetoxyiodinane 21 and Ethanol. Ethanol (3.8 mg, 0.0082 mmol) was added to a solution of **21** (22.6 mg, 0.0082 mmol) in $CDCl_3$.[1] ^{1}H NMR spectroscopy showed no changes after 1 h. After 24 h, 50% of **21** was converted to **23**.[24c] No further change was observed after 72 h.

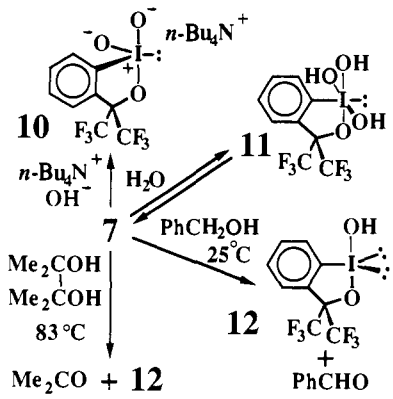
Results

Synthesis of Iodinane Oxides. Greenbaum[3] reported that treatment of 2-iodobenzoic acid with potassium bromate in 2 M sulfuric acid for 6 h at 85 °C gave the iodoxy analogue **1** in about 75% yield. By reducing the amount of oxidizing agent used, the acid concentration, the reaction temperature, and the reaction time, we find that the yield of **1** can be increased to 93%. Chloroiodinane **6**, with an apical alkoxide with two α,α-trifluoromethyl groups, is oxidized to **7** by using the same method, but longer times and higher temperatures are required. Both iodinane oxides **1** and **7** are stable indefinitely at room temperature. While **1** is reported to decompose explosively at 233 °C,[3] **7** decomposes at 204 °C without exploding. No explosion was observed by us for either **1** or **7** at higher temperatures or upon striking a sample with a hammer.

The X-ray structure[25] of **1** showed it to be polymerically associated along the equatorial I–O bond axis, with hydrogen bonds to the carbonyl oxygens stabilizing the polymeric structure. It is essentially a five-coordinate polymeric iodine species in the solid state, accounting for its virtual insolubility in common organic solvents. In contrast, **7** is moderately soluble in acetone or acetonitrile. The ^{19}F NMR spectrum of **7** in acetonitrile shows two quartets and a multiplet (relative areas 1:1:2) for the dimer, instead of the two quartets expected for the monomer.[26] The field

(25) Gougoutas, J. Z. *Cryst. Struct. Commun.* **1981**, *10*, 489.

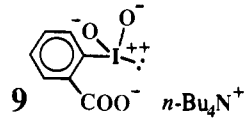
Scheme I



desorption mass spectrum of **7** suggests that it is associated in the solid state. The peak at m/z 402 corresponds to the molecular ion of **7** and a peak at 804 corresponds to the molecular ion of a dimer[26] of **7**.

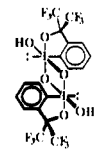
Both **1** and **7** are acidic. The pK_a of **7** is 3.8 and that of water-insoluble **1** is less than 4, as evidenced by its solubility in aqueous pyridine. Both are soluble in dilute aqueous sodium hydroxide, although **1** undergoes appreciable decomposition within 1 h in the presence of hydroxide. Other iodoxyarenes disproportionate[10b,b] in the presence of hydroxide to form diarylhydroxyiodinane oxides. Products resulting from the base-catalyzed decomposition of **1** have not yet been identified because of their insolubility. The anion of **7** reacts much less rapidly with hydroxide.

The conjugate base of **1** is soluble as the tetrabutylammonium salt **9**. Its ^1H NMR spectrum shows a doublet at 8.16 ppm and the infrared spectrum ($CHCl_3$) shows a strong band at 1617 cm^{-1}, consistent with anion **9** having the structure shown,[27] with small bonding interaction between the carboxylate group and the iodine. The conjugate base of **7** is isolable as the hydrated tetrabutylammonium salt **10**. The bonding of the alkoxide oxygen to the iodine of **10**, evidenced by NMR spectroscopy,[27] is confirmed by X-ray crystallography.



Reactions of Bis(trifluoromethyl) Iodinane Oxide 7. While solid **7** is not hygroscopic, it undergoes rapid ligand exchange with water in solution in acetonitrile, possibly via the symmetrical hydrate **11** (Scheme I). When water is added to a solution of **7** in acetonitrile, the multiplets in the ^{19}F NMR spectrum disappear and a singlet appears. A solution of **7** rapidly oxidizes benzyl alcohol to benzaldehyde at 25 °C. Under the same conditions, ethanol is oxidized to acetaldehyde but more slowly. Pinacol is oxidatively cleaved to acetone after 30 min by a solution of **7** in acetonitrile at 83 °C, but with no observable reaction during the same time period at 25 °C. Reduction of **7** to (fluoroalkoxy)-hydroxyiodinane **12** occurs in these reactions, but no NMR evidence for intermediates is detected.

(26) A possible structure for the dimer is shown. The cis aryl isomer may also be present.



(27) (a) Dess, D. B.; Martin, J. C. Submitted for publication. (b) Granoth, I.; Martin, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 2711.

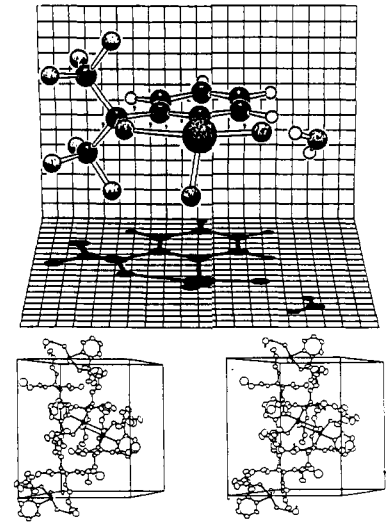


Figure 1. KANVAS plot and ORTEP crystal packing diagram of **10**.

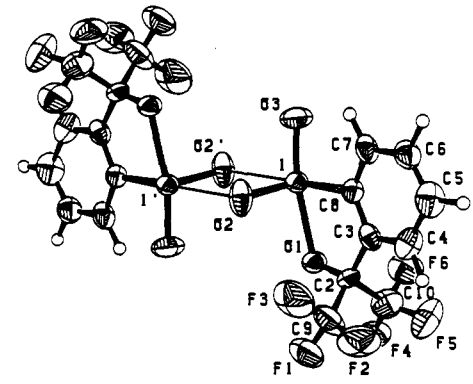


Figure 2. ORTEP drawing of **10**.

Table I. Selected Bond Lengths and Angles for Iodinane Oxide **10**[a]

bond	length, Å	bond angle	value, deg
I–O(1)	2.296 (7)	O(1)–I–O(2)	86.9 (4)
I–O(2)	1.794 (8)	O(3)–I–O(1)	165.3 (4)
I–O(3)	1.776 (9)	O(3)–I–O(2)	101.0 (5)
I–O(2′)	3.063 (9)	I–C(8)–C(7)	113.7 (8)
I–C(8)	2.14 (1)	O(3)–I–C(8)	91.9 (4)
C(8)–C(3)	1.36 (2)	C(2)–O(1)–I	117.3 (6)
C(3)–C(2)	1.54 (2)	O(1)–C(2)–C(3)	112.6 (9)
C(2)–O(1)	1.33 (1)	C(3)–C(8)–I	118.8 (8)
C(2)–C(9)	1.55 (2)	O(1)–C(2)–C(9)	109 (1)
C(2)–C(10)	1.53 (2)	O(1)–C(2)–C(10)	108 (1)
C(8)–C(7)	1.34 (2)	C(3)–C(2)–C(9)	111 (1)
		C(3)–C(2)–C(10)	111.1 (10)
		C(9)–C(2)–C(10)	105 (1)
		O(2)–I–C(8)	105.2 (4)
		O(1)–I–C(8)	74.0 (3)

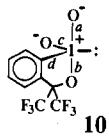
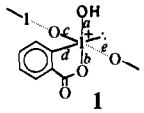
[a] Standard deviations in parentheses.

X-ray Structure of Anion 9. Figure 1 shows the KANVAS[28] plot and the ORTEP[29] crystal-packing diagram of **10**. Figure 2 shows the ORTEP[29] drawing of the anion of **10**. Selected bond lengths and angles for **10** are listed in Table I. Comparisons of bond lengths and angles for **10**, **1**,[25] and IF_3O[7b] are listed in Table II.

(28) Using the coordinates from the X-ray crystallographic analysis, the KANVAS program plots a shaded ball and stick model, perpendicular back and shadow planes, and a shadow projection. The spacing between the grid lines represents 0.5 Å. In the above plots the light source is normal to the plane of the phenyl ring. This program is based on the program SCHAKAL of E. Keller (Kristallographischer Institut der Universität Freiburg, FRG), which was modified by A. J. Arduengo, III (Du Pont Central Research and Development, Experimental Station, Wilmington, DE) to produce the back and shadowed planes.

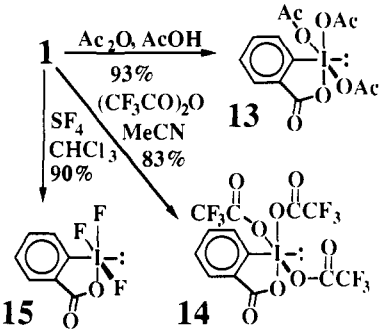
(29) Johnson, C. K. *ORTEP II: A thermal ellipsoid plot program*; ORNL, Oak Ridge National Laboratory: Oak Ridge, TN, 1971.

Table II. Bond Lengths and Angles in 10-I-4 Iodinane Oxides[a,b,c]

	bond	distance, Å	angle, deg
 **10**	a	1.776 (9)	ab 165.3 (4)
	b	2.296 (7)	ad 91.9 (4)
	c	1.794 (8)	ac 101.0 (5)
	d	2.140 (10)	dc 105.2 (4)
 **1**	a	1.895 (3)	ab 162.6 (1)
	b	2.324 (3)	ad 89.0 (2)
	c	1.784 (3)	ac 98.2 (2)
	d	2.107 (4)	dc 101.6 (2)
	e	2.71	db 75.6 (1)
	a	1.83	ab 168
	b	1.90	ad 90
	c	1.74	ac 95
	d	1.82	dc 98
			db 82

[a] Estimated standard deviations in parentheses. [b] The X-ray structure data of the central compound is from ref 25. [c] That of IF_3O is from ref 7b.

Scheme II



The distance between the apical single oxygen, O(3), in Figure 1 and the oxygen of the water molecule in the crystal lattice of **10** is 2.67 Å. The distance between the nearest proton of the water molecule and the oxygen of **10**, O(3), is 2.0 Å in the X-ray structure, suggesting that the hydrogen bonding[30] between the water molecule and the anion is weak.

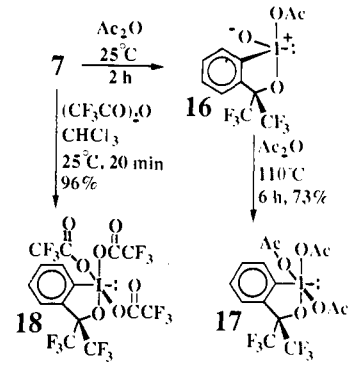
The geometry about the iodine atom is roughly ψ-TBP. The O(3)–I–O(1) bond deviates from linearity by 14.7°, essentially bending away from each single iodine lone pair of electrons. Most of the deviation from ψ-TBP geometry may be attributed to compression of angle db (Table II) resulting from inclusion of the long C(8)–I and O(1)–I bonds into the five-membered ring. The X-ray structure[25] of **1** shows a similar deformation.

Although **10** is an anion, it crystallizes as a dimer with a 3.06-Å intermolecular distance between O(2) and I′, which is much longer than the sum of the covalent radii (2.0 Å)[31a] but less than the sum of the van der Waals radii (3.30 Å).[31b] It is, however, longer than the intermolecular iodine–oxygen distances in the crystal lattice of the polymer of neutral **1**, with intermolecular I–O bond e (Table II) having a length of 2.71 Å.[25]

Syntheses of 12-I-5 Species from 10-I-4 Iodinane Oxides. Iodinane oxides **1** and **7** are readily converted to stable 12-I-5 periodinanes by treatment with carboxylic acid anhydrides or sulfur tetrafluoride (Scheme II). The rapid reaction of **1** with acetic anhydride at 85 °C gives a high yield of triacetoxyperiodinane **13**.[32]

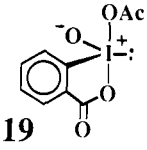
Analogue **7** reacts rapidly with acetic anhydride to give monoacetate **16** (Scheme III), and at higher temperature, 110 °C, forms triacetate **17** in 6 h. Both **1** and **7** react rapidly at 25 °C

Scheme III



with dilute solutions of the more electrophilic trifluoroacetic anhydride to form tris(trifluoroacetates) **14** and **18**, and **1** reacts with sulfur tetrafluoride to give high yields of trifluoroperiodinane **15**.

The acyloxy analogue of **16**, acetoxyiodinane oxide **19**, is not available by any direct method. Triacetoxyperiodinane **13** is observed in the presence of unreacted **1** when only 1 equiv of acetic anhydride is used.


19

Periodinanes **13**, **14**, **15**, **17**, and **18** are stable indefinitely when protected from atmospheric moisture. Tris(trifluoroacetoxy)periodinanes **14** and **18** are extremely reactive toward atmospheric moisture. Triacetoxyperiodinanes **13** and **17** and trifluoroperiodinane **15** are less reactive and may be exposed to the atmosphere for short periods of time without loss by hydrolysis. Triacetoxyperiodinanes **13** and **17** decompose when exposed to light for long periods of time (several weeks) and should therefore be stored in amber vials.

Triacetoxyperiodinanes **13** and **17** are the first examples of stable isolable acetoxyperiodinanes. The stabilities of tris(trifluoroacetoxy)periodinanes **14** and **18** contrast sharply with the stabilities of the acyclic tetrakis(perfluoroacyloxy)periodinanes, which decompose upon storage.[9] The stability of trifluoroperiodinane **15** parallels the stability of cyclic fluoroperiodinanes **2** and **4** and contrasts sharply with the instability of $PhIF_4$.[18]

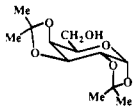
The ^1H NMR spectra of triacetoxyperiodinanes **13** and **17** show two singlets (1:2) for the two types of acetate methyl groups. The ^{19}F NMR spectrum of trifluoroperiodinane **15** shows a doublet and triplet (J_{FF} = 140 Hz). These features of the spectra are consistent with the structures shown, or with structures in which the unique exocyclic ligand is opposite the aryl ligand. The low-field chemical shifts (8.3–8.5 ppm) of the protons on the bidentate ligand ortho to the iodine provides good evidence for the pictured structures.[14,27b]

The ^{19}F NMR spectra of tris(trifluoroacetoxy)periodinones **14** and **18** show a singlet for the trifluoroacetoxy groups at 25 °C. At −45 °C, the ^{19}F NMR spectrum of **18** shows two singlets for the two types of trifluoroacetoxy groups. The exchange process observed at 25 °C may be due to the presence of a small amount of trifluoroacetic acid. The trifluoroacetoxy groups of **18** undergo rapid exchange with trifluoroacetic acid on the NMR time scale at 25 °C.

Oxidation of Alcohols by the Dess–Martin Triacetoxyperiodinane 13. The data of Table III shows that triacetoxyperiodinane **13** oxidizes benzylic and allylic alcohols more rapidly than it does saturated alkanols. When less than 1 molar equiv of benzyl alcohol, furfuryl alcohol, *p*-nitrobenzyl alcohol, or geraniol is added to a solution of **13** in chloroform-*d*, the corresponding aldehyde is formed quantitatively in less than 20 min at 38 °C, while primary alkanols show less than 20% reaction in this time. A competitive oxidation using 1 equiv of triacetoxy-

(30) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*; 4th ed.; John Wiley and Sons, 1980; p 221.
(31) (a) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: New York, 1960; p 224. (b) *Ibid.*, p 260.
(32) Dess, D. B.; Martin, J. C. *J. Org. Chem.* **1983**, *48*, 4155.

Table III. Oxidations of Alcohols to Aldehydes or Ketones with **13**

alcohol	yield of aldehyde or ketone: isolated %	yield of aldehyde or ketone: NMR, %	time, h (eqiv of **13**)
cyclooctanol	86		2.1 (1.15)
3,4,5-trimethoxybenzyl alcohol	94		0.3 (1.1)
2,5-dimethoxybenzyl alcohol	94		1.0 (1.1)
fenchyl alcohol[a]	70		1 (1.3)
cholesterol	53		6 (1.1)
	58	100	12 (1.2)
2-(phenylthio)ethanol	76	100	1 (1.1)
geraniol	84	100	0.25 (1.1)
geraniol[b]	80	100	0.25 (1.1)
furfurol		95	0.33 (1.1)
α-methylcyclopropanemethanol		100	0.33 (1.1)
4-nitrobenzyl alcohol		100	0.33 (1.1)
2-pyridylcarbinol		100	0.1 (1.1)

[a] The reaction mixture was approximately 0.03 M in trifluoroacetic acid. [b] The reaction mixture was approximately 0.65 M in pyridine.

Table IV. Pseudo-First-Order Rate Constants Observed for the Decomposition of **20a** in the Presence of Excess Ethanol at 3.5 °C

([EtOH] − [**13**]) × 10^3	k_{obsd} (s^{-1}) × 10^3
5.80	0.324
14.2	0.486
30.3	0.820

periodinane **13** with 1.05 equiv each of ethanol and benzyl alcohol gives 22% of acetaldehyde and 78% benzaldehyde (k_{benzyl}/k_{ethyl} = 5.9).[33] In similar competitive oxidations, triacetoxyperiodinane **13** shows no selectivity between 2-propanol and ethanol nor between the two hydroxyl groups in 2-ethyl-1,3-hexanediol ($k_{primary}/k_{secondary}$ = 1).

If less than one molar equivalent of ethanol is added to a solution of triacetoxyperiodinane **13** in chloroform-*d*, a compound is formed whose ^{1}H NMR spectrum is consistent with ethoxyperiodinane **20a**. The methylene quartet appears at 4.68 ppm. The quartet for the methylene group of uncomplexed ethanol, at 3.68 ppm, is not seen. Ethoxyperiodinane **20a** is stable at −20 °C, but at 25 °C gives acetaldehyde, acetic acid, and iodinane **21** over a period of 2.0 h (Scheme IV). The decomposition of ethoxyperiodinane **20a** follows first-order kinetics (k_1 = 2.47 × 10^{-4} s^{-1}). The rate of the decomposition is unaffected by added pyridine or acetic acid. It is, however, strongly retarded in the presence of triethylamine.

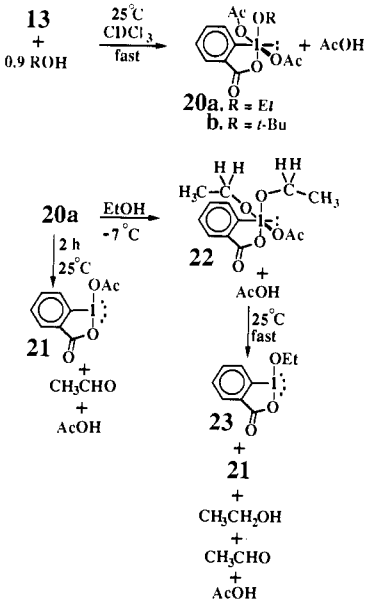
When excess ethanol is added to a solution of triacetoxyperiodinane **13**, the oxidation reaction proceeds much more rapidly. Addition of 5% excess ethanol to a solution of **13** at 25 °C causes the oxidation reaction to go to completion in less than 20 min; addition of 50% excess causes the oxidation reaction to go to completion almost instantly.

The decomposition of ethoxyperiodinane **20a** in the presence of excess ethanol at 3.5 °C follows pseudo-first-order kinetics through the first two half-lives of the reaction. The reaction was followed at different concentrations of added excess ethanol (Table IV) and the rate was found to be linearly dependent on the concentration of added ethanol (in excess of 1 equiv). The linear plot of the data of Table IV shows an intercept of 2.03 × 10^{-4} s^{-1}, the rate constant, k_1, for the decomposition of **20a** in the absence of excess ethanol. The linear measure in pseudo-first-order rate constant, k_{obsd}, shows with

$$k_{obsd} = k_1 + k_2[\mathrm{EtOH}]$$

(33) The relative reactivities of the substrates toward oxidation by **13** were calculated from the integrated rate equation (A_0 and B_0 are the initial concentrations and A and B are the final concentrations of the reactants): k_{rel} = [log (A/A_0)]/[log (B/B_0)].

Scheme IV



k_2 = 0.020 s^{-1} M^{-1}. The increase in rate dependence on [EtOH] is explained by the observation of the reaction of ethanol with ethoxyperiodinane **20a** at −7 °C to give a compound whose ^{1}H NMR spectrum shows four multiplets of equal areas at 4.00, 4.11, 4.44, and 4.54 ppm, consistent with the structure of diethoxyperiodinane **22** with its four nonequivalent methylene protons. Diethoxyperiodinane **22** is fairly stable at this temperature, but decomposes rapidly above 0 °C to give iodinanes **21** and **23** with the expected amounts of acetaldehyde and ethanol. The rapid decomposition of **22** explains the increase in the rate of oxidation of ethanol by **13** in the presence of excess ethanol.

Alcohols lacking α-hydrogens form stable products by ligand exchange with periodinane **13**. The addition of 1 equiv of *tert*-butyl alcohol to a solution of **13** gives a compound whose ^{1}H NMR spectrum is consistent with *tert*-butoxyperiodinane **20b**. Its reactivity toward primary alcohols is analogous to that of **20a**. It oxidizes ethanol to acetaldehyde very rapidly at 25 °C. Attempts to isolate **20b** resulted in the isolation of acetoxyiodinane oxide **19**. It is possible that this resulted from dehydration of the alcohol.

$$\mathbf{20b} \rightarrow \mathbf{19} + \mathrm{AcOH} + \mathrm{H_2C{=}CMe_2}$$

Reactions of Triacetoxyperiodinane 13 with Other Functional Groups. Periodinane **13** (as well as **14**, **15**, **17**, and **18**) reacts with primary amines in acetonitrile-d_3 or chloroform-*d* to give insoluble products that are difficult to analyze. No evidence for the oxidation of secondary or primary amines to imines or iminium salts was observed.

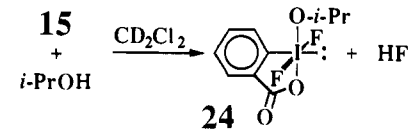
Treatment of *N*-benzylbenzamide with a solution of periodinane **13** in acetonitrile at 83 °C for 90 min followed by hydrolysis gives benzaldehyde. Attempts to oxidize *N*-(phenylethyl)acetamide, 2-pyrrolidinone, and *N*-cyclohexylbenzamide to aldehydes or ketones failed. At room temperature, triacetoxyperiodinane **13** reacts slowly enough with secondary amides to make it possible to oxidize alcohols in the presence of this functional group.

Although it is possible to oxidize an alcohol selectively in the presence of a sulfide functional group, periodinane **13** does react with sulfides over a period of several hours at 25 °C to give complex unidentified products and acetoxyiodinane **21**. Periodinane **13** does not react with olefins, such as cyclohexene, nor with electron-rich vinyl ethers under the conditions used for the oxidation of alcohols.

Reactions of Periodinanes 14, 15, 17, and 18. Fluoroalkoxytris(trifluoroacetoxy)periodinane **18** reacts with less than 1 equiv of ethanol to give an ethoxyperiodinane that is more stable toward decomposition to acetaldehyde and iodinane than ethoxyperiodinane **20a**. The ^{1}H NMR spectrum of this compound shows a quartet at 4.60 ppm and a triplet at 1.25 ppm for the ethoxy

group. No uncomplexed ethanol is observed. After 56 h no acetaldehyde is observed by ^1H NMR spectroscopy. The ^{19}F NMR spectra of the reaction mixture is too complex to analyze. If a second equivalent of ethanol is added to this solution, it is instantly oxidized to acetaldehyde. Tris(trifluoroacetoxy)periodinane **14** reacts with alcohols in a manner similar to that of **18**.

Trifluoroperiodinane **15** oxidizes alcohols to aldehydes and ketones, but unlike the other periodinanes, it does not undergo complete ligand exchange with alcohols. When 2-propanol is added to a solution of **15** in methylene-d_2 chloride, only a small amount of alkoxyperiodinane **24** (16%) is observed by ^1H NMR spectroscopy after 15 min. (Fluoroalkoxy)triacetoxyperiodinane **17** reacts with alcohols in a manner very similar to that of tetrakis(acyloxy)periodinane **13**.



Acetoxyiodinane Oxides. Acetoxyiodinane oxides **16** and **19** react rapidly with atmospheric moisture and must be handled in an inert atmosphere. If less than 1 equiv of ethanol is added to a solution of either acetoxyiodinane oxide in acetonitrile-d_3, it is oxidized to acetaldehyde almost instantly.

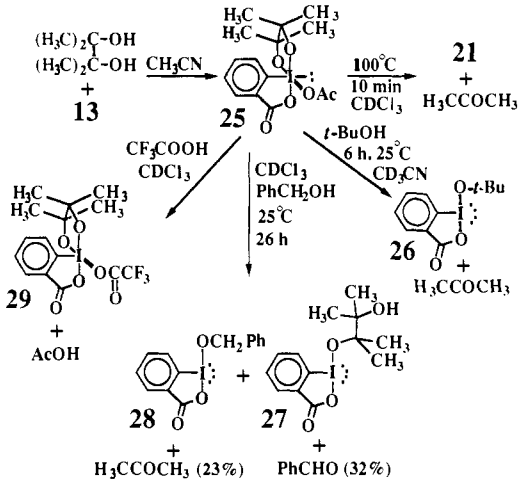
Synthesis of New Periodinanes by Ligand-Exchange Reactions with Triacetoxyperiodinane 13. A solution of periodinane **13** and acetonitrile reacts rapidly with 1 equiv of pinacol to give pinacolate complex **25**[34] (Scheme V). This compound is stable indefinitely at 25 °C when protected from atmospheric moisture. It decomposes rapidly in solution in chloroform above 65 °C to give acetone and acetoxyperiodinane **21**. Pinacolate complex **25** and the iodine pentafluoride–diol reaction products are iodine(V) analogues to the cyclic intermediates proposed for the oxidation of glycols by periodate.[35]

Pinacolate compiex **25** is much less reactive toward alcohols than periodinanes **13**, **14**, **15**, **16**, and **17**. When 1 equiv of *tert*-butyl alcohol is added to a solution of **25** in acetonitrile-d_3, no change is observed (^1H NMR) after 15 min. Acetone is observed after 6 h. The coproduct may be *tert*-butoxyiodinane **26**. Acetoxyiodinane **21** is not observed in the reaction mixture. Benzyl alcohol reacts with **25** to give benzaldehyde and iodinane **27** as well as acetone and (benzyloxy)iodinane **28**. No direct evidence for the presence of a trialkoxyperiodinane is observed by ^1H NMR spectroscopy during the course of either reaction. Similar results are obtained from the reaction between ethanol and pinacol complex **25**.

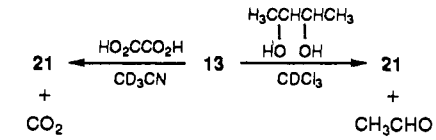
The acetoxy group of the pinacol complex (**25**) undergoes degenerate ligand exchange with a dilute solution of acetic acid (ca. 0.09 M) in chloroform-*d* or acetonitrile-d_3 on the ^1H NMR time scale at 25 °C. The coalescence temperature for this process is 13 °C ($\Delta G^*_{13\,°C}$ = 13 kcal/mol).[36] Under the same conditions, the acetoxy groups of triacetoxyperiodinanes **13** and **17** and alkoxyperiodinanes **20a,b** do not undergo degenerate ligand exchange with acetic acid on the ^1H NMR time scale. Even at 65 °C, there was no evidence for ligand exchange between triacetoxyperiodinane **13** and acetic acid (ca. 0.1 M) by ^1H NMR spectroscopy. When 1 equiv of trifluoroacetic acid was added to a solution of pinacol complex **25**, trifluoroacetoxyperiodinane **29** was evidenced by ^1H NMR spectroscopy, but was not isolated.

The reaction between triacetoxyperiodinane **13** and other potential bidentate ligands that were studied failed to produce stable periodinanes. For example, 12-I-5 triacetoxyperiodinane **13** reacts with 2,3-butanediol to give acetaldehyde and 10-I-4 acetoxyiodinane **21** during 1 h. It reacts with oxalic acid to give carbon dioxide and **21** over several hours. Proton NMR spectroscopy

Scheme V



shows that **13** and 2,3-butanediol initially form a dialkoxyperiodinane, analogous to pinacolate complex **25**, which decomposes to give analogous products. No intermediates are observed by ^1H NMR spectroscopy in the reaction between **13** and oxalic acid.



Discussion

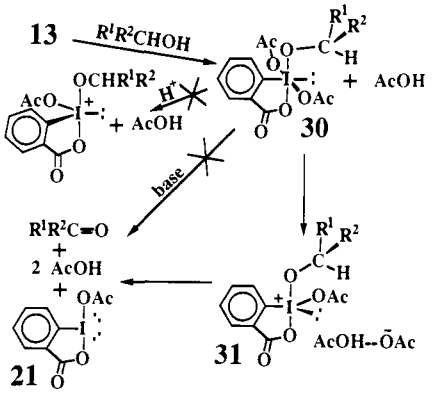
Synthetically Useful Oxidation of Alcohols by Triacetoxyperiodinane 12. Triacetoxyperiodinane **13**, which has been called[37] the "Dess–Martin Periodinane", is a practical reagent for the facile and efficient oxidation of primary alcohols to aldehydes and secondary alcohols to ketones. The reaction proceeds under mildly acidic or neutral conditions and no further oxidation of aldehydes to carboxylic acids has been observed. The reaction avoids some of the difficulties encountered in using other methods for the oxidation of alcohols, such as long reaction times, the need to use a large excess of the oxidizing agent, or difficult experimental procedures.

With few exceptions, the oxidation of saturated alcohols with excess **13** goes to completion within 2 h at 25 °C. Oxidation of allylic and benzylic alcohols occurs within 30 min. The reaction rate is markedly increased by the addition of more than 1 equiv of an alcohol,[38] including the unoxidizable *tert*-butyl alcohol. With more than 1 equiv of alcohol, some of the periodinanes have two alkoxide ligands as in **22**. Quantitative conversion of the alcohol to the aldehyde or ketone is accomplished by using only a 5–10% excess of **13**.

The experimental procedure for oxidation by triacetoxyperiodinane **13** is very simple. Preparation for reaction simply involves dissolving **13** in the appropriate anhydrous solvent (chloroform, methylene chloride, acetonitrile, etc.) and adding the substrate. Two workup procedures are available for separating the aldehyde or ketone product from the reaction mixture: (a) the reaction mixture is diluted with ether and extracted with dilute aqueous sodium hydroxide, which hydrolyzes acetoxyperiodinane **21** to 2-iodosobenzoate, or (b) if the substrate is base-sensitive, the reaction mixture is extracted with aqueous sodium bicarbonate and sodium thiosulfate, which reduces acetoxyiodinane **21** to the even more water-soluble 2-iodobenzoate. Either procedure removes all iodine-containing species from the reaction mixture as well

(34) Other cyclic acyloxyalkoxytrifluoroperiodinanes have been observed by ^{19}F NMR spectroscopy. See: Kokunov, Y. V.; Sharkov, S. A.; Buslaev, Y. A. *Koord. Khim.* **1982**, *8*, 55.
(35) Buist, G. J.; Burton, C. A.; Miles, J. H. *J. Chem. Soc.* **1959**, 743.
(36) Gutowsky, H. S.; Holm, C. H. *J. Chem. Phys.* **1956**, *25*, 1228.
(37) Triacetoxyperiodinane **13** was earlier marketed as the Dess-Martin Periodinane by Aldrich Chemical Co., but it is not now available.
(38) The alkoxyperiodinanes produced when more than 1 molar equiv of alcohol is used are not readily reduced by thiosulfate and use of the reductive workup procedure.

Scheme VI



as the other product, acetic acid. By performing the reaction in a pyridine buffer and using the thiosulfate workup procedure, it is possible to maintain near-neutral conditions throughout the entire oxidation and isolation sequence.

Triacetoxyperiodinane **13** selectively oxidizes alcohols in the presence of non-hydroxylic functional groups such as sulfides, enol ethers, furans, and secondary amides. The ligand exchange reaction between **13** and alcohols is rapid and for primary alcohols essentially quantitative, while the introduction of ligands to iodine by reactions with substrates lacking a hydroxyl group is unfavored.

As an oxidizing agent, triacetoxyperiodinane **13** is in several ways preferable to chromium(VI) reagents[3]19 and reagents derived from dimethyl sulfoxide,[40] which were earlier the most commonly used reagents for the oxidation of alcohols to aldehydes or ketones. Some chromium(VI) reagents[39b,h] require long reaction times (6–12 h) and it is often necessary to use a severalfold excess of these reagents[39b,f-h] to obtain a high yield of oxidized product. Workup procedures for chromium(VI) oxidations are more complicated than those for triacetoxyperiodinane **13** oxidations. All chromium(VI) reagents produce solid chromium-containing byproducts, which cannot be removed by extraction, necessitating time-consuming filtration or chromatographic procedures. Some chromium(VI) reagents produce reaction mixtures that are difficult to work up.[39c,f,g] Many chromium(VI) reagents are not compatible for alcohol oxidations in the presence of sulfides, enol ethers, furans, or other easily oxidized non-hydroxylic functional groups. All chromium-containing reagents are, of course, possibly toxic and carcinogenic, making them difficult to use in the preparation of pharmaceuticals.

The Swern[40a] dimethyl sulfoxide reagents are selective and workup procedures are simple, but these reagents must be prepared immediately prior to use by cautious addition of dimethyl sulfoxide to a solution of oxalyl chloride or trifluoroacetic anhydride in methylene chloride at −60 °C. The Moffat[40d] oxidation can be carried out at room temperature, but removal of unreacted dicyclohexylcarbodiimide and *N,N'*-dicyclohexylurea from the product mixture is often difficult.

Since our initial report[32] of the use of **13** as an oxidizing agent, a large number of chemists have found the "Dess–Martin Periodinane" to be a uniquely efficient oxidizing agent for a variety of substrates. We mention 74 papers[41] that describe useful oxidations by **13**. Several applications find **13** to be the only oxidizing agent capable of effecting the desired oxidation. Its selectivity

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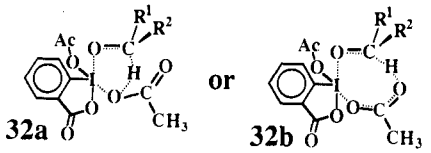
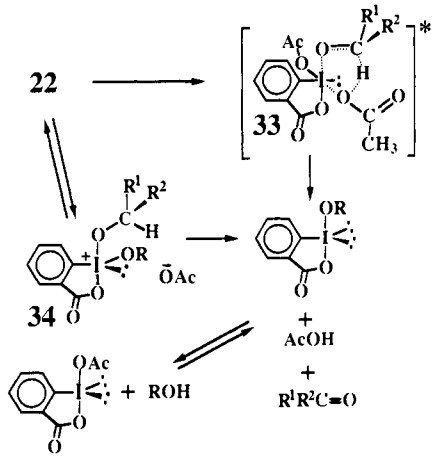
has been found to be very useful in alcohol oxidations in the presence of polypeptides.

Mechanism for the Oxidation of Alcohols by the Dess-Martin Periodinane 13. Triacetoxyperiodinane **13** reacts very rapidly with less than 1 equiv of a primary or secondary alcohol to give an alkoxydiacetoxyperiodinane, **30**. The 12-I-5 alkoxyperiodinanes decompose relatively slowly under these conditions to form aldehydes or ketones and 10-I-3 acetoxyiodinane **21**. The rate of disappearance of alkoxyperiodinane **30** is not noticeably affected by the addition of pyridine or acetic acid. The decomposition reaction of **30** is much faster for benzylic or allylic alcohols than for saturated alkoxy groups. The fact that added pyridine or triethylamine does not increase the rate of the decomposition of **30** (Scheme VI) renders unlikely mechanisms in which deprotonation at the α-carbon of the alkoxy group is the rate-limiting step. Since the acid does not affect the rate (Scheme VI), the fact that alkoxyperiodinanes with benzylic or allylic alkoxy groups decompose much more rapidly than saturated alkoxyperiodinanes provides evidence against mechanisms in which the rate-limiting step is the ionization of **30** to **31**, because allylic and benzylic alkoxy substituents are more electron-withdrawing than saturated alkoxy substituents. The oxidation of the allylic or benzylic group in **31** is in fact faster by removal of an α-proton by the acetate than the same oxidation of the saturated alkoxides. The fact that the intermediate alkoxyperiodinane in the oxidation of cholesterol decomposes more slowly than alkoxyperiodinanes with less bulky saturated alkoxy groups indicates that the rate of the reaction might be affected by steric factors. It is possible that the reaction may proceed by **31**, but perhaps the steric factors are more important for a transfer of the α-proton of the alkoxide ligand to one of the acetate ligands, as shown in transition state **32**.

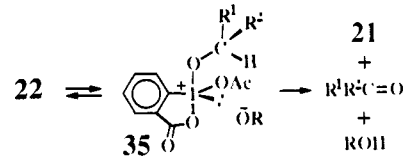


It is interesting that the reaction is much faster when more than 1 equiv of alcohol is added to form **22** or a related species. Al-

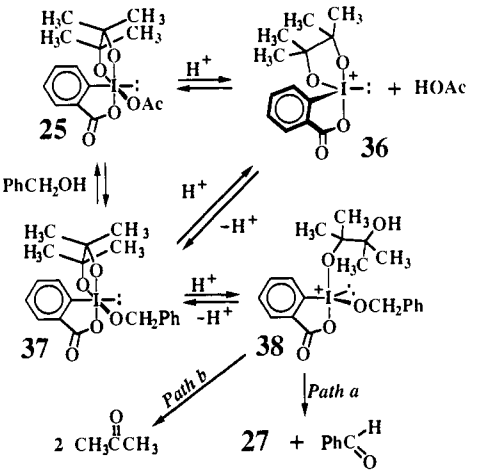


though an alkoxide anion is a stronger base than the acetate anion, **22** has an ethoxide ligand and an acetate ligand trans to each other in the O–I–O three-center four-electron (3c,4e) bond. This puts more negative charge on the acetate than on the alkoxide ligand as is known for all hypervalent species. It is possible that the acetate ligand, which is more negative, could react more rapidly intramolecularly via **33** or by more rapidly ionizing the acetate anion to form **34**.

Although the ionization of the alkoxide anion of **22** is much



Scheme VII

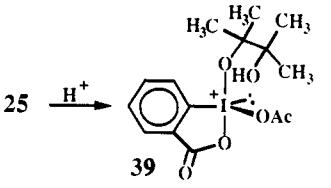


weaker than the ionization of the acetate anion, it is true that the alkoxide anion in **35** is much more basic and the iodine has more plus charge. It is possible that **35** could be faster in removing the α-proton, although **34** is much more available than **35**.

Further work will have to be done to establish the mechanism of the Dess-Martin Periodinane as an oxidizing agent.

Reactions of Pinacolate Complex 25. Pinacolate complex **25** undergoes rapid degenerate ligand exchange with acetic acid on the ^{1}H NMR time scale ($\Delta G^*_{13\,°C}$ = 13 kcal/mol), probably by ionization of the bicyclic periodinane to give the bicyclic periodonium ion,[27] **33** (Scheme VII). This dissociative mechanism is consistent with the observation that the more electrophilic triacetoxyperiodinanes, **13** or **17**, do not undergo degenerate ligand exchange with acetic acid. Periodonium ions formed from periodinanes **13** and **17** would have strongly electron withdrawing acetoxy ligands in the equatorial positions and would be less stable than those such as **36** or **38**, which have less strongly electron withdrawing alkoxy equatorial ligands.

The reactions between pinacol complex **25** and alcohols are also explained by a dissociative mechanism. Compound **25** (Scheme VII) reacts with alcohols to form trialkoxyperiodinane **37**, which ionizes to form either **36** or **38**. Bicyclic periodonium ion **36** does not appear to lead to oxidative cleavage of the pinacolate ligand since the addition of trifluoroacetic acid to a solution of compound **25** did not give any acetone. Ion **38** decomposes by either path a or b to give the observed products. The reaction between pinacol complex **25** and *tert*-butyl alcohol leads to an intermediate analogous to periodonium ion **38**, which has no α-protons on the apical alkoxy group. The cleavage reaction of path b is therefore the only mode of decomposition observed. The fact that *tert*-butyl alcohol catalyzes the cleavage reaction of **25**, which acetic and trifluoroacetic acids do not, shows that periodonium ion **39** with its equatorial acetoxy group is not as easily formed as periodonium ions **36** or **38**.

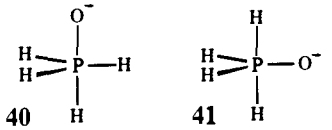


Structural Data for the Iodinane with Two Anionic Oxide Ligands (10). The X-ray structure of **10** shows the exocyclic apical I–O bond (1.779 Å) to be shorter than the apical I–O bond of symmetrical iodinanes (2.0–2.2 Å).[42] The endocyclic apical I–O bond is longer (2.296 Å). The three-center O–I–O bond is distorted by stretching the I–O bond to the more electronegative fluoroalkoxy oxygen, while compressing the I–O bond to the more

(42) For a summary of hypervalent 10-I-3 X-ray structures, see ref 2.

electropositive anionic oxide ligand.[43]

The ring closure of **10** to form the long endocyclic I–O bond is favored by $\Delta G > 9.2$ kcal/mol,[27] so even though the apical anionic oxide ligand is a very unfavorable apical ligand, the σ delocalization of an electron pair of the negatively charged fluoroalkoxide is somewhat favorable. Calculations[44] on TBP 10-P-5 phosphorane oxide anions **40** and **41** showed the isomer



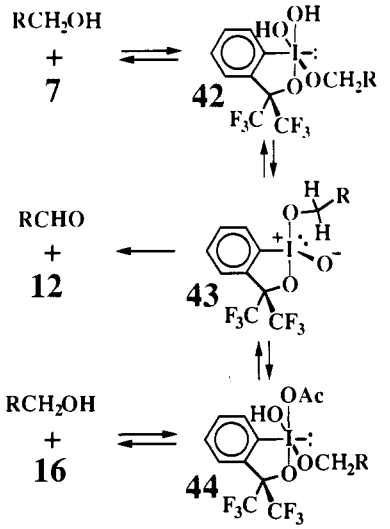
40 **41**

with an apical oxide ligand (**40**) to be 15.5 kcal/mol less stable than isomer **41** with an equatorial oxide ligand. The accompanying paper[27] provides a discussion of the factors to be considered in a ring closure providing an apical oxide ligand.

Oxidation of Alcohols by Iodinane Oxides. The bis(trifluoromethyl)-substituted iodinane oxide **7** rapidly oxidizes primary alcohols to aldehydes in acetonitrile at 25 °C. In contrast, the carbonyl-substituted **1** is so unreactive that it can be purified by washing with ethanol. Its unreactivity may be due to its insolubility.

A possible mechanism[45] for the oxidation of alcohols by **7** is shown in Scheme VIII. Although no evidence is obtained for any intermediates when the reaction is monitored by ^{1}H NMR spectroscopy, periodinane **42** is a close analogue of trihydroxyperiodinane **11**, which is evidenced by ^{1}H NMR spectroscopy. (Fluoroalkoxy)acetoxyiodinane oxide **16** oxidizes primary alcohols to aldehydes much more rapidly than does **7**. It is expected that acetoxyperiodinane **16** would be more reactive than **7** since the acetoxy group is more electron-withdrawing than the hydroxyl group of **7**. The formation of alkoxyiodinane oxide **43** by loss of acetic acid from periodinane **44** should be a more facile process

Scheme VIII



than the formation of **43** from periodinane **42**, since acetic acid is a better leaving group than water.

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Supplementary Material Available: A listing of final coordinates of the atoms of **10**, thermal parameters, and bond lengths and angles (9 pages); tables of observed and calculated structure factors (15 pages). Ordering information is given on any current masthead page.

(43) Similar distortions are seen for 12-S-6 and 10-S-4 species: Lam, W. Y.; Duesler, E. N.; Martin, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 120. Adzima, L. J.; Duesler, E. N.; Martin, J. C. *J. Org. Chem.* **1977**, *42*, 4001.

(44) Deakyne, C. A.; Allen, L. C. *J. Am. Chem. Soc.* **1976**, *98*, 4076.

(45) The mode of decomposition proposed for the alkoxyiodinane oxide **47** is similar to that proposed for the ylide intermediate in the decomposition of dimethylsulfonium ions in the Moffat oxidation with dimethyl sulfoxide. See: Johnson, C. R.; Phillips, W. G. *J. Org. Chem.* **1967**, *32*, 1926.