Synthesis and Reactions of Stable Alkoxyaryltrifluoroperiodinanes.[1] A "Tamed" Analogue of Iodine Pentafluoride for Use in Oxidations of Amines, Alcohols, and Other Species

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Abstract: Stable alkoxyaryltrifluoroperiodinanes **2** and **5** were prepared by oxidation of the respective parent iodo alcohols (**1** and **4**) with excess trifluoromethyl hypofluorite. The stability and low reactivity of **2** and **5** are ascribed to the strong stabilizing influence of the five-membered ring. The reaction of **2** with trimethylsilyl chloride gives the corresponding iodine(III) species, chloroalkoxyaryliodinane **3**, and chlorine. Compound **2** is hydrolyzed with aqueous base to give a species thought to be iodinane oxide **6a**. Periodinane **2** has been demonstrated, by small-scale exploratory reactions, to be a selective reagent for the oxidation of primary and secondary amines or alcohols bearing α hydrogens to the corresponding aldehyde or ketone. In contrast to iodine pentafluoride, **2** does not further oxidize the product aldehydes to acids. *tert*-Butylamine is oxidized by **2** to give 1,1,1',1'-tetramethylazoethane. Phenylmagnesium bromide reacts with **2** to give fluorobenzene. Possible mechanisms for these selective oxidations are discussed. It is suggested that the stabilizing structural features of **2** make it a "tamed" analogue of IF_5.

Introduction

Iodine pentafluoride has been known since 1870[2] and a few organic derivatives, in which one or more of the fluorine ligands has been replaced by a perfluoroalkyl or perfluoroaryl group, have been prepared.[3] In 1972 Oates and Winfield reported[4] a series of derivatives of iodine pentafluoride in which fluorine ligands were replaced by simple alkoxy groups to give species of the type $IF_{5-n}(OCH_3)_n$, $n = 1$-4. These methoxyfluoroperiodinanes were prepared by reaction of IF_5 with methoxymethylsilanes at 20 °C. The periodinanes readily decompose above 20 °C to give iodine(III) or iodine(I) species.

The same workers reported[5] the reaction of CF_3IF_4 with methoxymethylsilanes to yield the alkoxyperiodinanes, $CF_3IF_{4-n}(OCH_3)_n$, $n = 1$-4.

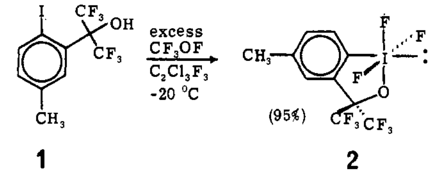
Periodinanes in which a simple alkyl group acts as a carbon ligand are not known. A phenyl ligand is sufficiently stabilizing to allow partial characterization of the highly reactive species, $C_6H_5IF_4$.[6] A related tetraacyloxyperiodinane, $C_6H_5I(OOCR_F)_4$, $R_F = CF_3$, C_3F_7, etc., has recently been reported[7] and found to be relatively stable at room temperature.

None of these periodinanes, with the exception of iodine pentafluoride, has shown any promise as a synthetic reagent. Iodine pentafluoride was shown by Stevens[8] to be useful for the oxidative dehydrogenation of amines to nitriles or azoalkanes and for the oxidative condensation of amides. Olah[9] has shown that selective oxidations of alkyl iodides and of tertiary amines to the corresponding carbonyl compounds may be carried out in inert solvents with IF_5.

The usefulness of IF_5 as an oxidizing agent suggests that more stable organic fluoroperiodinanes may be useful as selective oxidizing agents. The preparation and reactions of stable alkoxyaryltrifluoroperiodinanes are discussed here.

Results

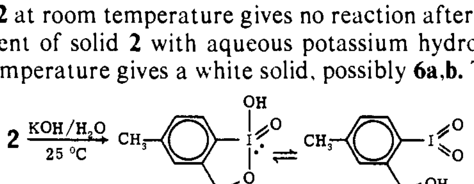
Synthesis. The treatment of a solution of iodo alcohol **1** in Freon-113 (1,1,2-trichlorotrifluoroethane) with excess trifluoromethyl hypofluorite at −20 °C results in the precipitation of **2** as a white, crystalline solid (mp 191–193 °C dec) whose ^{19}F NMR spectrum shows an AB_2 pattern ($J = 116$ Hz) with a doublet at ϕ 13.20 and a triplet at ϕ 41.57. Periodinane **2** is also generated upon reaction of CF_3OF with an iodine(III) species, chloroiodinane **3**.



1 **2**

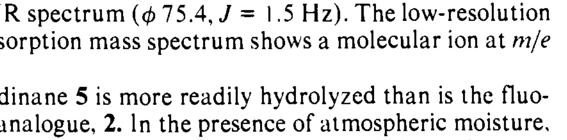
3

The *gem*-dimethyl analogue, **5**, is obtained upon treatment of the parent alcohol, **4**, with excess of the hypofluorite. Periodinane **5** shows an ^{19}F NMR AB_2 pattern with a doublet at ϕ 15.80 and a triplet at ϕ 29.90.



4 **5**

Hydrolysis. Periodinane **2** can be handled in the air and is not readily hydrolyzed. The addition of water to solid periodinane **2** at room temperature gives no reaction after 4 days. Treatment of solid **2** with aqueous potassium hydroxide at room temperature gives a white solid, possibly **6a,b**. The hydrolysis product shows a single, closely spaced doublet in the ^{19}F NMR spectrum (ϕ 75.4, $J = 1.5$ Hz). The low-resolution field-desorption mass spectrum shows a molecular ion at *m/e* 416.



6a **6b**

Periodinane **5** is more readily hydrolyzed than is the fluorinated analogue, **2**. In the presence of atmospheric moisture, **5** is hydrolyzed after 4 h at 25 °C. The hydrolysis product was not isolated nor further studied.

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Table I. Comparison of Selected Amine Oxidations by **2** and IF_5

amine	**2**	IF_5
$C_6H_5CH_2NH_2$	C_6H_5CHO (40%)[a]	C_6H_5CN (90%)[b]
$CH_3(CH_2)_5NH_2$	$CH_3(CH_2)_4CHO$ (36%)[a]	$CH_3(CH_2)_4CN$ (51%)[b]
$(C_6H_5CH_2)_2NH$	C_6H_5CHO (61%)[c]	C_6H_5CHO (40%)[b]
$C_6H_5N(CH_3)_2$	no reaction[a]	C_6H_5CHO (30%)[d]
$(CH_3)_3CNH_2$	$(CH_3)_3CN{=}NC(CH_3)_3$ (42%)[a]	$(CH_3)_3CN{=}NC(CH_3)_3$ (48%)[b]

[a] No optimization of yields was attempted (determined by ^1H NMR spectroscopy); reaction for 15 min, a time which was later shown to be too brief. [b] Reference 8b. [c] Reaction for 12 h; no unreacted amine present. [d] Reference 9.

Reactions. Periodinane **2** disappears slowly (4 days) in acetonitrile-d_3, as evidenced by ^{19}F NMR spectroscopy. A freshly prepared solution of **2** in acetonitrile rapidly etches glass in the presence of air. No reaction products from **2** in solution have been identified.

The addition of 3 or more equiv of trimethylsilyl chloride to a carbon tetrachloride solution of **2** at 35 °C forms the chloroiodinane **3**, trimethylsilyl fluoride, and chlorine. The latter was identified by collection of a very volatile yellow material capable of oxidizing iodide ion to free iodine. The analogous reaction of **2** with methoxytrimethylsilane gives several unidentified products but not the desired tetraalkoxyperiodinane.

The irradiation of **2** in the presence of toluene or anisole, either with or without added azobisisobutyronitrile, with a 275-W GE sunlamp at 50 °C gives no reaction.

Periodinane **2** reacts rapidly with phenylmagnesium bromide, in ether, to give 90% of fluorobenzene, as determined by ^{19}F NMR spectroscopy.

$$\mathbf{2} + PhMgBr \xrightarrow{\text{ether}} PhF$$

The reaction of periodinane **2** with primary and secondary amines bearing α hydrogen atoms gives the corresponding carbonyl compounds upon hydrolysis. The carbonyl compounds were obtained in good to excellent yields even though reaction conditions (15 min at 25 °C) were not optimized (Table I). *tert*-Butylamine gives, upon reaction with **2** and subsequent hydrolysis, 42% of azoisobutane. Periodinane **2** does not react with tertiary amines under conditions in which rapid oxidation of primary or secondary amines occurs.

$$RCH_2NH_2 \xrightarrow{\mathbf{2}} \xrightarrow{H_2O} RCHO$$

$$R_2CHNH_2 \rightarrow \rightarrow R_2CO$$

$$(RCH_2)_2NH \rightarrow \rightarrow 2RCHO$$

$$(CH_3)_3CNH_2 \rightarrow \rightarrow (CH_3)_3CN{=}NC(CH_3)_3$$

Primary and secondary alcohols react with **2** to give the corresponding aldehydes and ketones (Table II). Reaction conditions for these oxidations were found to be near optimal at 25 °C and 10-12 h.

Table II. Oxidation of Alcohols by **2**, **5**, and IF_5

alcohol	**2**[a]	**5**[b]	IF_5
$C_6H_5CH_2OH$	C_6H_5CHO (86%)	C_6H_5CHO (26%)	
p-$CH_3C_6H_4CH_2OH$	p-$CH_3C_6H_4CHO$ (56%)		p-$CH_3C_6H_4CHO$ (39%)[c]
$(CH_3)_2CHOH$	$(CH_3)_2CO$ (86%)	$(CH_3)_2CO$ (46%)	

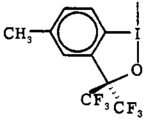
[a] Optimum reaction conditions, 12 h, yields determined by ^1H NMR spectroscopy. [b] Conditions not optimized. [c] Reference 9.

Table III. Competitive Oxidations of Selected Substrates by **2**[a]

substrate	k_{rel}
$C_6H_5CH_2NH_2/C_6H_5CH(CH_3)NH_2$	3.11
$CH_3CH_2CH_2OH/(CH_3)_2CHOH$	8.40
$C_6H_5CH_2NH_2/((CH_3)_2CH)_2NH$	14.8
$C_6H_5CH_2NH_2/C_6H_5CH_2OH$	18.5

[a] Excess of substrates, 2 h reaction time, product ratios determined by ^1H NMR spectroscopy.

In no case has any further oxidation by **2** of the product aldehydes to carboxylic acids been observed. Samples of aldehydes were treated with excess periodinane **2** but gave no reaction after 2 days. In all oxidation reactions the reduction product from periodinane **2** is the iodine(III) species, fluoroiodinane **7**.



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Competitive oxidations by **2** of primary and secondary amines, primary and secondary alcohols, primary amine and primary alcohol, and primary amines with primary and secondary alkyl groups were studied (Table III). No competitive studies utilizing periodinane **5** were done.

On short-term storage (7 days) at room temperature or longer storage (2-3 weeks) at −20 °C, **5** slowly decomposes, with an accompanying loss of its oxidative power. No decomposition products have been identified. Periodinane **5** does not oxidize benzylamine or isopropylamine to the corresponding carbonyl compound under controlled conditions analogous to those used with **2**. A tarry, intractable precipitate is produced in these reactions. Compound **5** does, however, oxidize alcohols to the corresponding carbonyl compounds in good yield (Table II).

Discussion

Structure and Stability of Periodinanes. The exceptionally low reactivity of periodinanes **2** and **5**, in comparison to their acyclic analogues, suggests the importance for pentacoordinate iodine(V) species of the stabilizing five-membered ring effect, for which evidence has been adduced in the chemistry of pentacoordinate phosphorus(V),[10] tetracoordinate sulfur(IV),[11] hexacoordinate sulfur(VI),[12] and tricoordinate iodine(III).[13]

In addition to the effect of the ring, the periodinanes are expected to be further stabilized by the presence of the *gem*-dialkyl substituents (Thorpe-Ingold effect).[14] This stabilization, expected for both **2** and **5**, is further enhanced in **2** by the increased electronegativity of the apical ligands accompanying replacement of the methyl groups in **5** by trifluoromethyl groups in **2**. The composite operation of these three effects in **2** leads to a highly stable, crystalline compound which is stable indefinitely at room temperature and is unreactive toward atmospheric moisture. This is in sharp contrast to the analogous phenyltetrafluoroperiodinane,[6] which decomposes rapidly on contact with water and is unstable to storage for more than a few hours at temperatures of 20 °C or above.

The "octahedral" structure postulated for **2** (counting the electron pair as the sixth ligand) is assigned primarily on the basis of the ^{19}F NMR spectrum by comparison to the spectra of other periodinanes and to the known structure for iodine pentafluoride.[15] The ^{19}F NMR doublet at ϕ 13.20 (J = 116 Hz) is assigned to the two identical fluorines and the triplet at

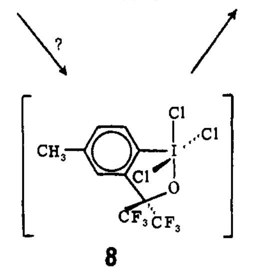
ϕ 41.57 (J = 116 Hz) is assigned to the unique fluorine. These assignments are parallel to those made by Oates and Winfield[5] for the series of compounds $CF_3IF_{4-n}(OCH_3)_n$, n = 1-4. For n = 1, a doublet at ϕ 10.0 (J = 113 Hz) and a triplet at ϕ 46.5 (J = 113 Hz) were observed in the ^{19}F NMR spectrum.

Although other structures for **2** are consistent with the available spectral data (for example, one which places the alkoxy ligand opposite the electron pair), the structure illustrated is preferred on the basis of the structures reported for several phosphorus analogues.[16]

Similar arguments on the basis of spectral data are applicable to the structure of periodinane **5**.

Ligand Exchange Reactions. Because IF_5 has been shown to react with various silyl derivatives[4] (such as $(CH_3)_3SiOCH_3$, $(CH_3)_3SiCl$, etc.), it is not unexpected that periodinane **2** reacts similarly.

Treatment of iodine pentafluoride with $(CH_3)_3SiCl$ yields trimethylsilyl fluoride and a yellow solid presumed to be iodine trichloride.[4] The reaction of **2** with trimethylsilyl chloride at room temperature gives a chloroalkoxyiodinane, **3**, perhaps via trichloroperiodinane **8**. Decomposition of this species into a chloroiodinane (**3**) and chlorine is likely to be rapid. The presence of chlorine was confirmed by the trapping of a volatile yellow liquid at −78 °C which was capable of oxidizing iodide anion to free iodine. An aryldichloroiodinane would be expected to react similarly with iodide ion but would not be volatile.



$$\mathbf{2} + (CH_3)_3SiCl \xrightarrow[35\ °C]{CCl_4} \mathbf{3} + (CH_3)_3SiF + Cl_2$$

8

The success of this ligand exchange reaction, even though accompanied by reduction, suggested that analogous reactions utilizing alkoxysilanes would make a variety of substituted periodinanes accessible. Reactions of iodine pentafluoride with methoxysilanes yield alkoxyfluoroperiodinanes.[4] The reaction of **2** with $(CH_3)_3SiOCH_3$ gives unidentifiable products. It was initially assumed that the stability characteristic of **2** would also be imparted to the alkoxy product, allowing its possible isolation. Further work is required to test this assumption.

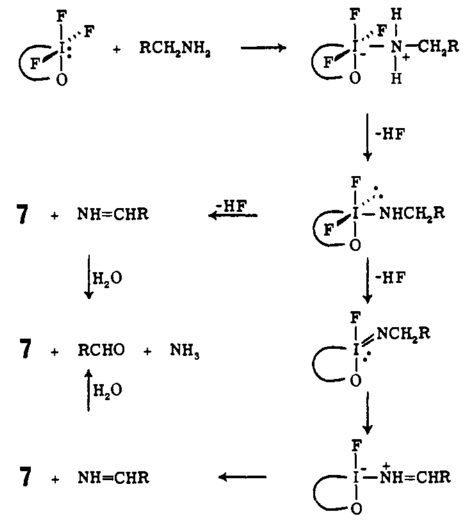
Oxidations via Periodinanes. The work of Stevens[8] with iodine pentafluoride demonstrated that primary amines bearing α hydrogens could be oxidatively dehydrogenated to the corresponding nitrile. Where α hydrogens were lacking in the amine, as in *tert*-butylamine, oxidation with IF_5 gave azoalkanes as the product.[8] Certain selected secondary and tertiary amines with α hydrogens gave primarily the corresponding carbonyl compounds. Olah[9] later demonstrated that iodine pentafluoride reacts rapidly with amines, alcohols, and alkyl iodides bearing α hydrogens to give the corresponding carbonyl compounds. Iodine pentafluoride will also oxidize the product aldehydes to the corresponding carboxylic acids.[9]

$$IF_5 + RCH_2NH_2 \xrightarrow{pyr/CH_2Cl_2} RC{\equiv}N$$

$$IF_5 + (CH_3)_3CNH_2 \rightarrow (CH_3)_3CN{=}NC(CH_3)_3$$

Treatment of primary or secondary amines which contain α hydrogens by periodinane **2** gives, on aqueous workup, high yields of the corresponding aldehyde or ketone (Table I). Although all the reaction conditions were not optimized, periodinane **2** generally gives yields comparable to or better than those from iodine pentafluoride. In the case of dibenzylamine, the reaction with **2** was carried out to its highest conversion, as indicated by the lack of unreacted starting amine in the final reaction mixture.

Scheme I



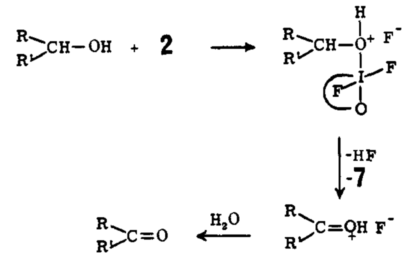
Both periodinane **2** and iodine pentafluoride react with *tert*-butylamine (no α hydrogens) to give azoisobutane. Yields from the two reactions are comparable (**2**, 42%; IF_5, 48%), even without any optimization of reaction conditions for **2**. This suggests a possible synthetic use for **2** in this alternative to other syntheses of azoalkanes.[17]

Compound **2** does not react with tertiary amines, unlike iodine pentafluoride which rapidly oxidizes tertiary amines at room temperature to give a mixture of carbonyl compounds.[9] This more selective oxidizing agent, in contrast to iodine pentafluoride,[9] is found not to oxidize aldehydes nor cleave methyl or benzyl ethers. Thus, periodinane **2** is a much more selective reagent than IF_5 for the oxidation of amines or alcohols in the presence of other sensitive functional groups. The increased selectivity of **2** relative to IF_5 may be attributed, in part, to the increased stability (lower reactivity) of **2** and to the larger steric bulk of **2** relative to that of iodine pentafluoride.

Further evidence of the selectivity of **2** is indicated by the competitive oxidations illustrated in Table III. Periodinane **2** reacts much more rapidly with the more nucleophilic nitrogen centers of amines than with alcohols and also reacts more rapidly with the less sterically hindered primary amines than with secondary amines. A similar selectivity is observed for the primary and secondary alcohols and for primary amines with primary and secondary alkyl substituents. These selectivity data also suggest that periodinane **2** is a highly selective, potentially useful synthetic reagent for the oxidation of amines and alcohols.

Stevens[8] suggested that amine oxidations proceed through iminium ion intermediates. Olah[9] suggested similar species as intermediates in the oxidations of tertiary amines and analogous oxonium intermediates for alcohol oxidations.

Several routes are possible for the reaction of periodinane **2** with amines (Scheme I, the curved lines joining O to I schematically represent the five-membered ring of **2**). All of the reaction pathways of Scheme I provide fluoroiodinane **7** and, upon hydrolysis, the carbonyl compound. Since fluoroiodinane **7** is observed in the spectrum of the hydrolysis product (^{19}F NMR spectrum, singlet at ϕ 161.3), this product alone does not aid in distinguishing among the several possible routes. Nor does the fact that a white, crystalline solid, presumed to be an amine–periodinane adduct, can be isolated from the reaction of benzylamine with **2** prior to hydrolysis, Scheme II

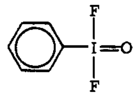


since the solid remains unidentified owing to its thermal instability, water sensitivity, and lack of solubility in common NMR solvents. The white solid etches glass in the solid state and in suspension, suggesting the loss of hydrogen fluoride from the compound.

An oxonium ion intermediate has been suggested[9] for the reaction of iodine pentafluoride with alcohols and ethers, and a similar intermediate may be involved in the oxidation of alcohols with **2.** Scheme II suggests a possible, generalized sequence leading to the observed products.

The lower stability (higher reactivity) of *gem*-dimethylperiodinane **5** is evidenced, in part, by its rapid decomposition on short-term storage at room temperature. It is further manifest in the reactions of **5** with amines in comparison to **2.** Although both periodinanes react with amines, only **2** does so in a controlled fashion to give carbonyl compounds. Periodinane **5** reacts to give only tarry decomposition products on workup.

Hydrolysis. An organic acyclic iodinane oxide, **9,** was first reported[18] in 1901 but the compound was not adequately characterized and no further work on **9** has been reported. More recently[19] a relatively stable alkyl iodinane oxide, **10,** has been synthesized and fully characterized. Both species are derivatives of the tetracoordinate iodine(V) species IF_3O,[20] in which one equatorial fluorine has been replaced by an alkyl or aryl ligand.



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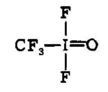

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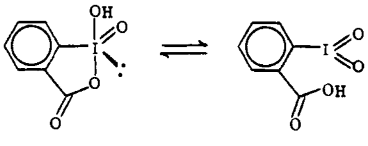
A species which is more closely related to **6a,b** is *o*-iodoxybenzoic acid (**11a,b**), which was reported by Hartmann and Meyer.[21] Although the acid was fully characterized and a wide variety of its reactions were studied, no conclusions as to the position of iodinane oxide–iodoxy acid equilibrium were reached. A similar question concerning this type of equilibrium is applicable to the system **6a** ⇌ **6b.**

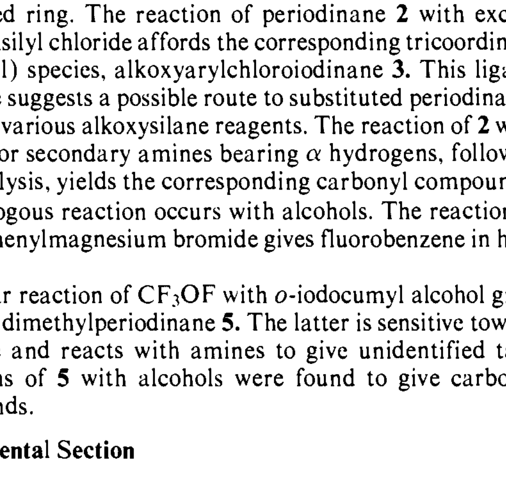


11a **11b**

The reaction of periodinane **2** with aqueous potassium hydroxide results in a white, crystalline solid, mp 215–217 °C, presumed to be one, or both, of structures **6.** The ^{19}F NMR spectrum shows only a single, closely spaced doublet ($J = 1.5$ Hz), which is consistent neither with the hydroxyiodinane oxide, **6a,** which is expected to show two fluorine quartets of equal area, nor with the acyclic iodoxy alcohol, which is expected to show a fluorine singlet, without any long-range coupling to the aromatic ring protons. It is possible that a rapid equilibrium between **6a** and **6b,** or a mixture of internally hydrogen-bonded species, could account for the observed spectrum.

The field-desorption mass spectrum (low resolution) of the hydrolysis product shows a peak at *m/e* 416, which is consistent with **6** (molecular weight of 416). The elemental composition of a peak at *m/e* 384 has been determined by high-resolution mass spectrometry to correspond to $C_{10}H_7F_6IO$, the ion which would be produced upon loss of two oxygen atoms from the parent ion. Although such fragmentations have not been reported for iodoxybenzene derivatives, they are consistent with such fragmentations (losses of O and O_2) observed for inorganic iodinane oxides such as IF_3O and IF_3O_2.[22] Other fragmentations which involve losses of CF_3 groups have also been identified. Further work is necessary to confirm the structure of the hydrolysis product.

Attempted Synthesis of an Acyloxyperiodinane. Although periodinane **2** is a potentially useful oxidizing agent, difficulties in its synthesis render it somewhat less accessible than might be desirable. With this problem in mind, the synthesis of an acyloxyperiodinane from readily available starting materials was attempted. The reaction of chloroacyloxyperiodinane **12** with excess trifluoromethyl hypofluorite gave a sample whose ^{19}F NMR spectrum was consistent with periodinane **13.** The spectrum showed a distinct AB_2 pattern ($J = 118$ Hz) with a doublet centered at ϕ 26.7 and a triplet at ϕ 36.5. All attempts to repeat this reaction in order to isolate **13** have failed.



12 **13**

Summary

Alkoxyaryltrifluoroperiodinane **2**, the first example of a stable pentacoordinate organoiodine species containing a simple aryl ligand and an alkoxy ligand bonded to iodine(V), has been prepared in 95% yield by treatment of 1-(2-iodo-5-methylphenyl)-1-trifluoromethyl-2,2,2-trifluoroethanol (**2**) with excess trifluoromethyl hypofluorite. The solid periodinane **2** is stable indefinitely at room temperature and unreactive toward atmospheric moisture. Its stability and low reactivity are ascribed to the strong stabilizing influence of the five-membered ring. The reaction of periodinane **2** with excess trimethylsilyl chloride affords the corresponding tricoordinate iodine(III) species, alkoxyarylchloroiodinane **3.** This ligand exchange suggests a possible route to substituted periodinanes by use of various alkoxysilane reagents. The reaction of **2** with primary or secondary amines bearing α hydrogens, followed by hydrolysis, yields the corresponding carbonyl compounds. An analogous reaction occurs with alcohols. The reaction of **2** with phenylmagnesium bromide gives fluorobenzene in high yield.

Similar reaction of CF_3OF with *o*-iodocumyl alcohol gives the *gem*-dimethylperiodinane **5.** The latter is sensitive toward moisture and reacts with amines to give unidentified tars. Reactions of **5** with alcohols were found to give carbonyl compounds.

Experimental Section

General. Chemical shifts for ^1H NMR are in parts per million (ppm, δ scale) downfield from tetramethylsilane (internal standard); for ^{19}F NMR, in parts per million upfield from $CFCl_3$ (ϕ scale). Elemental analyses are within 0.4% of theoretical values. Melting points are uncorrected.

Iodo alcohols **1** and **4** were prepared as previously described[23] and recrystallized prior to use. Chloroiodinanes **3** and **12** as well as fluoroiodinane **7** were prepared as described previously.[23] Freon-113 was distilled from P_2O_5 prior to use.

Trifluoromethyl hypofluorite (PCR, Inc.) is a toxic material whose powerful oxidizing properties cause it to present a possible *explosion hazard when dissolved in oxidizable solvents. Suitable precautions should be employed when it is used.*

1,1,1-Trifluoro-3,3-bis(trifluoromethyl)-5-methyl-3*H*-1,2-benziodoxole (2). A. A suspension of iodo alcohol **1** (0.2 g, 0.52 mmol) in 10 mL of Freon-113 was treated with excess CF_3OF at −20 °C. A white precipitate of **2** was collected by filtration, washed with pentane, and dried (0.2 g, 0.45 mol, 95%): mp 191-193 °C, dec; IR (KBr) 1635 (s), 1538 (s), 1298 (m), 1271 (s), 1241 (s), 1175 (s), 1156 (s), 1128 (s), 971 (s), 820 (m), 753 (m), 736 cm^{-1} (m); ^1H NMR (CD_3CN) δ 2.56 (s, 3, CH_3), 7.73 (s, 1, H ortho to $C(CF_3)_2$), 7.89 (d, 1, H para to $C(CF_3)_2$, $J = 8$ Hz), 8.29 (d, 1, H ortho to I, $J = 8$ Hz); ^{19}F NMR (CD_3CN) ϕ 13.20 (d, 2, equatorial F, $J = 116$ Hz), 41.57 (t, 1, apical F, $J = 116$ Hz), 74.30 (br t, 6, CF_3, $J = 8$ Hz); UV (pentane) λ_{max} 200 (ϵ 6740), 230 (3512); mass spectrum (field desorption (FD), high resolution) *m/e* (calculated value, assignment) 439.9313 (439.9319, $M^{+\cdot}$), 420.9333 (420.9335, M − F), 370.9377 (370.9367, M − CF_3), 332.9411 (332.9399, M − 2F, CF_3). Anal. ($C_{10}H_6F_9IO$) C, H, I.

B. Chloroiodinane **3** (0.2 g, 0.48 mmol) was suspended in 25 mL of Freon-113 and treated with excess trifluoromethyl hypofluorite at 20 °C. Completion of the reaction was marked by decolorization of the initially yellow suspension. The beige solid, **2**, was washed with pentane and dried (0.17 g, 0.41 mol, 85%), mp 190-192 °C dec.

1,1,1-Trifluoro-3,3-dimethyl-3*H*-1,2-benziodoxole (5). A solution of 0.03 g (0.1 mmol) of iodo alcohol **4** in 0.5 mL of CCl_4 and 0.1 mL of CH_2Cl_2 was treated with excess CF_3OF. The initially yellow solution completely decolorized upon completion of reaction. Removal of the solvent in vacuo gave a white powder, **5** (0.03 g, 0.09 mmol, 87%): mp 123-124 °C; IR (KBr) 3000 (m), 1650 (m), 1460 (m), 1385 (m), 1270 (s), 1175 (s), 1095 (s), 960 (m), 879 (m), 775 (s), 570 cm^{-1} (s); ^1H NMR (CCl_4/CD_2Cl_2) δ 1.70 (s, 6, CH_3), 7.40-7.60 (m, 1, H ortho to $C(CH_3)_2$), 7.65-7.80 (m, 2, H para to I, H para to $C(CH_3)_2$), 8.20-8.41 (m, 1, H ortho to I); ^{19}F NMR (CCl_4/CD_2Cl_2) ϕ 15.80 (d, 2, equatorial F, $J = 110$ Hz), 29.90 (t, 1, apical F, $J = 110$ Hz); mass spectrum (10 eV) *m/e* (rel intensity) 303 (94.8, M − CH_3), 280 (87.8, M − 2F), 265 (100, M − CH_3, 2F), 262 (24.7), 231 (23.7), 123 (22.7), 119 (26.5), 43 (25). Anal. ($C_9H_{10}F_3IO$) C, H, I.

Attempted Synthesis of 13. A suspension of **12** (0.05 g, 0.18 mmol) in 0.5 mL of $CHCl_3$ was treated with excess CF_3OF at 25 °C. At the end of 20 min a portion of the suspended solid had dissolved and spectra were taken. ^1H NMR spectrum shows a complex multiplet, δ 7.6-8.1; ^{19}F NMR ($CDCl_3$) ϕ 26.7 (d, 2, equatorial F, $J = 118$ Hz), 36.5 (t, 1, apical F, $J = 118$ Hz). Several attempts to repeat this reaction in order to isolate **13** failed.

Oxidations of Amines. General. A suspension of 0.01 g (0.02 mmol) of **2** in 0.5 mL of CCl_4 was treated with 3.0 mg (0.03 mmol) of benzylamine. The NMR sample was allowed to stand for 2 h, quenched with water, and mixed with 2.0 mg (7.0×10^{-6} mol) of triphenylmethane (internal standard). Areas of the aldehyde proton and the methine proton were integrated at least six times. Comparison of the areas allowed calculation of the relative yield of product (47% in this case). Yields are accurate to within ±3%.

Alcohol oxidations by **2** and by **5** were performed in a similar fashion.

Competitive Reactions. All of the amines and alcohols, which are commercially available, were used without further purification. Periodinane **2** was prepared as above and used without further purification. NMR sample tubes were filled with appropriate amounts of **2**, mixed substrates, and either CCl_4 or Freon-113 (solvent). Periodinane **2** was used in a concentration such that the products formed did not exceed 5% of total substrates initially present. Samples were allowed to stand for 1-2 h and were then treated with water to quench the reaction. The relative reactivities of the substrates toward oxidation by **2** were calculated using the integrated rate equation (1) for the analysis.

$$k_{rel} = \frac{\log\left[\frac{A - X}{A}\right]}{\log\left[\frac{B - Y}{B}\right]} \qquad (1)$$

Relative concentrations of products and of remaining amines or alcohols were determined by integration of the areas of the ^1H NMR signals. At least six integrals were run on every sample and results are precise to within ±3%.

Reactions of Periodinane 2. Reaction with Silanes. A solution of 50.0 mg (0.11 mmol) of **2** in 0.5 mL of CD_3CN was treated with excess trimethylsilyl chloride. The initially colorless solution became brilliant yellow upon addition of the $(CH_3)_3SiCl$. The ^{19}F NMR spectrum showed a decet at ϕ 154.9 consistent with trimethylsilyl fluoride (lit.[24] ϕ 157.4). The presence of chloroiodinane **3** was confirmed by comparison of the ^1H NMR spectrum of the reaction mixture with that of an authentic sample.[23] A yellow, volatile material was collected from the sample by bulb-to-bulb distillation and collection at −78 °C. The material oxidizes aqueous KI solution to give the characteristic dark brown color of iodine. The yellow material is presumed to be chlorine.

Reaction with KOH. A suspension of periodinane **2** (0.35 g, 0.8 mmol) in 10 mL of CD_2Cl_2 was mixed with 0.13 g (2.4 mmol) of powdered KOH in 1.0 mL of water. The sample, after being stirred for 5 h at 25 °C, was neutralized with dilute aqueous HCl and extracted with ether. The extract, dried over Na_2SO_4, was stripped of solvent to give a white powder (**6**): mp 215-217 °C; ^1H NMR ($CDCl_3$) δ 2.56 (s, 3, CH_3), 7.50-7.78 (m, 3, ArH); ^{19}F NMR ($CDCl_3$) ϕ 76.10 (d, CF_3, $J = 1.8$ Hz); mass spectrum (FD) *m/e* (rel intensity) 416 (3.7, $M^{+\cdot}$), 384 (100, M − 2O), 347 (34.3, M − CF_3), 315 (48.9 *m/e* 384 − CF_3), 245 (46.7), 217 (10.9).

Reaction with Phenylmagnesium Bromide. A suspension of **2** (16.0 mg, 0.037 mmol) in 0.5 mL of Freon-113 was treated with 6.6 mg (0.037 mmol) of phenylmagnesium bromide (2.8 M in ether). A clear solution formed upon addition of water, the ^{19}F NMR of which showed a multiplet at ϕ 112.7 characteristic of fluorobenzene (lit.[24] ϕ 113.1). The yield was 90% based on integration relative to 1,1,1-trifluoroethanol as internal standard.

Reaction with Aldehydes. A suspension of 16.1 mg (0.037 mmol) of periodinane **2** in 0.5 mL of CCl_4 was treated with excess of benzaldehyde. After the sample was allowed to stand at 25 °C overnight, it was quenched with water and the ^1H NMR spectrum was taken. No oxidation of the aldehyde to benzoic acid was observed nor were any other changes in the starting materials observed.

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References and Notes

(1) Organic derivatives of iodine(V) are termed periodinanes; see R. L. Amey and J. C. Martin, *J. Am. Chem. Soc.*, **100**, 300 (1978).

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

(3) (a) C. S. Rondestvedt, Jr., *J. Am. Chem. Soc.*, **91**, 3054 (1969); (b) O. R. Chambers, G. Oates, and J. M. Winfield, *J. Chem. Soc., Chem. Commun.*, 839 (1972); (c) J. A. Berry, G. Oates, and J. M. Winfield, *J. Chem. Soc., Dalton Trans.*, 509 (1974).

(4) (a) G. Oates and J. M. Winfield, *Inorg. Nucl. Chem. Lett.*, **8**, 1093 (1972); (b) G. Oates, J. M. Winfield, and O. R. Chambers, *J. Chem. Soc., Dalton Trans.*, 1380 (1974).

(5) G. Oates and J. M. Winfield, *J. Chem. Soc., Dalton Trans.*, 119 (1974).

(6) L. M. Yagupolskii, V. V. Lyalin, V. V. Orda, and L. A. Alekseeva, *Zh. Obshch. Khim.*, **38**, 2813 (1968).

(7) L. M. Yagupolskii, I. I. Maletina, N. V. Kondratenko, and V. V. Orda, *Synthesis*, 574 (1977).

(8) (a) T. E. Stevens, *Tetrahedron Lett.*, 16 (1959); (b) *J. Org. Chem.*, **26**, 2531, 3451 (1961); (c) *ibid.*, **31**, 2025 (1966).

(9) G A. Olah and J. Welch, *Synthesis*, 419 (1977).

(10) (a) J. Kumamoto, J. R. Cox, Jr., and F. H. Westheimer, *J. Am. Chem. Soc.*, **78**, 4858 (1956); (b) F. H. Westheimer, *Acc. Chem. Res.*, **1**, 70 (1968); (c) R. F. Hudson and C. Brown, *ibid.*, **5**, 204 (1972); (d) S. J. Benkovic in "Comprehensive Chemical Kinetics", Vol. 10, C. H. Bamford and C. F. H. Tipper, Eds., American Elsevier, New York, 1972, pp 1-56.

(11) (a) E. F. Perozzi and J. C. Martin, *J. Am. Chem. Soc.*, **94**, 5519 (1972); (b) L. J. Kaplan and J. C. Martin, *ibid.*, **95**, 793 (1973); (c) J. C. Martin and E. F. Perozzi, *ibid.*, **96**, 3155 (1974).

(12) (a) D. B. Denney, D. Z. Denney, and Y. F. Hsu, *J. Am. Chem. Soc.*, **95**, 8191 (1973); (b) W. Y. Lam and J. C. Martin, *ibid.*, **99**, 1659 (1977).

(13) For a qualitative comparison of iodinane reactivities, compare the following: (a) C. Willgerodt, *J. Prakt. Chem.*, **33**, 154 (1886); (b) G. P. Baker, F. G. Mann, N. Sheppard, and A J. Tetlow, *J. Chem. Soc.*, 3721 (1965); (c) W. C. Agosta, *Tetrahedron Lett.*, 2681 (1965).

(14) See: E. L. Eliel, "Stereochemistry of Carbon Compounds", McGraw-Hill, New York, 1962, p 196 ff.

(15) (a) H. S. Gutowsky and C. J. Hoffman, *J. Chem. Phys.*, **19**, 1259 (1951); (b) R. C. Lord, M. A. Lynch, Jr., W C. Schumb, and E. J. Slowinski, Jr., *J. Am. Chem. Soc.*, 72, 522 (1950).

(16) For example, hexacoordinate phosphorus ions such as $R_2PF_4^-$ and $RHPF_4^-$ have been shown to exist with the more apicophilic ligands disposed trans to each other. See: (a) E. O. Bishop, P. R. Carey, J. F. Nixon, and J. R. Swain, *J. Chem. Soc. A*, 1074 (1970); (b) R. G. Cavell and J. F. Nixon, *Proc. Chem. Soc., London*, 229 (1964); (c) J. Jander, D. Börner, and U. Engelhardt, *Justus Liebigs Ann. Chem.*, **726**, 19 (1969).

(17) (a) J. W. Timberlake and J. C. Stowell in "The Chemistry of the Hydrazo, Azo and Azoxy Groups", S. Patai, Ed., Wiley-Interscience, New York, 1975, pp 69–108; (b) J. W. Timberlake, M. L. Hodges, and K. Betterton, *Synthesis*, 632 (1972).
(18) R. F. Weinland and W. Stille, *Chem. Ber.*, **34**, 2631 (1901).
(19) D. Naumann, L. Deneken, and E. Renk, *J. Fluorine Chem.*, **5**, 509 (1975).
(20) (a) E. E. Aynsley, R. Nichols, and P. L. Robinson, *J. Chem. Soc.*, 623 (1953); (b) J. W. Viers and H. W. Baird, *Chem. Commun.*, 1093 (1967); (c) A. J. Edwards and P. Taylor, *J. Fluorine Chem.*, **4**, 173 (1974).
(21) C. Hartmann and V. Meyer, *Chem. Ber.*, **26**, 1727 (1893).
(22) See, for example, A. Engelbrecht, P. Peterfy, and E. Schandara, *Z. Anorg. Allg. Chem.*, **384**, 202 (1971).
(23) R. L. Amey and J. C. Martin, *J. Org. Chem.*, **44**, 1779 (1979).
(24) C. H. Dungan and J. H. van Wazer, "Compilation of Reported F^{19} NMR Chemical Shifts", Wiley-Interscience, New York, 1970.

Hydrogen Transfer Reactions of Arenes in Molten Antimony Trichloride

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Abstract: The reactions of polycyclic aromatic hydrocarbons in molten antimony trichloride at temperatures from 80 to 175 °C have been studied by in situ ^{1}H NMR and quench and separation techniques. Decomposition takes place by a complex series of hydrogen redistribution reactions whose net effect is a disproportionation of a type not previously known to occur. The reaction of anthracene (I) was studied in detail. Some of the anthracene molecules lose aryl-bound hydrogen and are condensed into larger molecules with aryl-aryl bonds such as the asymmetric bianthracenes (IV, V, and VI) and anthraaceanthrylenes (VII and VIII). The hydrogen released by these reactions is quantitatively captured by other anthracene molecules to form hydroaromatic molecules such as the 9,10-dihydro- and 1,2,3,4-tetrahydroanthracenes (II and III). The catalytic role of the solvent's Lewis acidity was demonstrated by the fact that the addition of a few mol % of a strong chloride donor reduced the reaction rates by a large factor. The reaction behavior of a group of related arenes (naphthalene, phenanthrene, chrysene, pyrene, perylene, and naphthacene) of widely varying basicity and oxidizability was also surveyed.

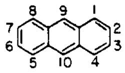
Introduction

We have briefly reported[1] that anthracene (I) dissolved in high-purity molten antimony trichloride under an inert atmosphere undergoes spontaneous hydrogen transfer reactions at temperatures as low as 100 °C with I serving as an efficient hydrogen acceptor for its own Scholl condensation reactions.[2] It has long been known that strong Lewis acids, such as molten aluminum trichloride, catalyze dehydrogenation–condensation reactions of aromatic compounds (Scholl reactions), but the fate of the hydrogen thus released had not been demonstrated. In the absence of added oxidizing agents, it has generally been assumed that hydrogen is evolved as a gas. Thus, our results are novel in two important respects: first, they demonstrate that the substrate aromatic can serve as an efficient hydrogen acceptor for its own Scholl reactions; and second, they demonstrate that Scholl reactions can be catalyzed by a mild Lewis acid, antimony trichloride. A full account of this aspect of Friedel–Crafts chemistry is reported in this article. The reaction behavior of a group of related arenes with widely varying basicity and oxidizability is also described. Most prior research on the behavior of polycyclic aromatics in liquid antimony trichloride was done at 74–99 °C[3] where we found that anthracene disproportionates quite slowly. Some research at higher temperatures[4] encountered reactions of an undetermined nature.

Results and Discussion

Solutions of anthracene in $SbCl_3$ prepared by melting together the high-purity components at 80 °C under an inert argon atmosphere were initially yellow. After about 2 h at this temperature, the solutions took on a greenish tinge. This very slow color change was greatly accelerated by increasing temperature such that at 125 °C the solutions were a very dark green almost immediately. Except for the first few minutes at 125 °C, the 100-MHz ^{1}H NMR spectrum of the melt was dominated by a pattern fully consistent in position and fine structure with that of molecular anthracene in nonreactive solvents ($CDCl_3$). The appropriateness of antimony trichloride as an NMR solvent was demonstrated by the observation of the spectrum of the triphenylmethyl cation comparable to that reported in FSO_3H.[5] The bands in the anthracene spectrum were initially broadened with the bands of $H_{9,10}$ being the broadest and those for $H_{2,3,6,7}$ being narrowest at any given instant. Since this order also corresponds to the relative magnitude of the hyperfine coupling constants in the anthracene radical cation, the broadening was attributed to exchange with traces of radical cation.[6] However, the spectrum rapidly sharpened as the radical cations decayed or as the unpaired electron was transferred to products of greater oxidizability. The presence and decay of these radical cations were confirmed by ESR at 80 °C where the decay rate was much slower. Both the color change and spectral sharpening were irreversible since they persisted when the solution was cycled between 125 and 80 °C.

Coincident with the sharpening of the anthracene spectrum, the lines for 9,10-dihydroanthracene (II) were observed and grew with time at the expense of those of anthracene. The methylene singlet at $\delta = 3.99$ ppm (referenced to $Me_4Si = 0$) and ten resolvable lines of the AA′BB′ pattern centered at $\delta = 7.33$ ppm for II were completely distinguishable from the anthracene spectrum in which no lines were further upfield than $\delta = 7.5$ ppm. After about an hour at 125 °C, bands at $\delta = 1.85$ ppm and 2.93 ppm attributable to the methylene groups in 1,2,3,4-tetrahydroanthracene (III) appeared and also continued to grow with time. Hydrogenated products II and III



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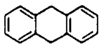
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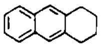
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