(1979).
(8) W. P. Weber and G. W. Gokel, "Phase Transfer Catalysis in Organic Synthesis", Springer-Verlag, Berlin, 1977.
(9) J. M. J. Fréchet and C. Schuerch, *J. Am. Chem. Soc.*, **93**, 492–496 (1971).
(10) J. T. Ayres and C. K. Mann, *J. Polym. Sci., Polym. Lett. Ed.*, **3**, 505–508 (1965).
(11) M. J. Farrall and J. M. J. Fréchet, *J. Am. Chem. Soc.*, **100**, 7998 (1978).
(12) C. Bied-Charreton, J. P. Idoux, and A. Gaudemer, *Nouv. J. Chim.*, **2**, 303–304 (1978).
(13) C. U. Pittman, Jr., and B. Kim, personal communication. The anion of diethyl 2-methylmalonate is generated using an essentially equimolar amount of sodium hydride in ethanol; the final polymer also had approximately 10% ethoxide substitution. If this result is applicable to diethyl malonate with its two acidic protons, this method would be the method of choice for the preparation of this type of functional polymers.

Synthesis and Reaction of Substituted Arylalkoxyiodinanes: Formation of Stable Bromoarylalkoxy and Aryldialkoxy Heterocyclic Derivatives of Tricoordinate Organoiodine(III)

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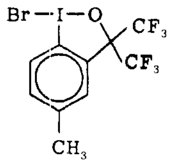
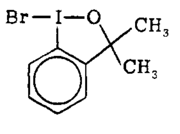
The first stable, crystalline bromoiodinanes, **1a** and **2a**, as well as the first aryldialkoxyiodinanes, have been synthesized from the respective alcohols **4** and **5**. Two chloroiodinanes, **1b** and **2b**, have been prepared by chlorination of the parent alcohols. Bromo- and chloroiodinanes have been shown to be synthetically useful as highly selective, free-radical halogenating agents for benzylic and allylic hydrogens. Reactivity patterns of these species differ sufficiently from those evidenced by other iodine(III) species, to suggest a possible niche for these compounds in synthetic organic chemistry. Treatment of either **1b** or **2b** with potassium hexafluorocumyl oxide (KOR$_F$) gives the respective dialkoxy species **8** or **9**. Degenerate ligand exchange for either **8** or **9** occurs rapidly on the NMR time scale with 0.08–0.10 M KOR$_F$ (T_8 = 56 °C, T_9 = 93 °C), but not with a comparable concentration of R$_F$OH, suggesting an associative exchange mechanism.

Stable bromoiodinanes have never been isolated, although both chloro and fluoro analogues have been known for over 40 years.[1] The preparation of phenyliodine dibromide was reported in 1905,[2] but the compound was not isolated nor characterized, and subsequent attempts at its synthesis in these laboratories have failed. There are no reports of the isolation of inorganic analogues such as IBr_3, although the possible existence of the latter in solution[3] and as a complex with theobromine[4] has been discussed.

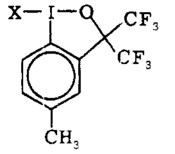
We report here the details of the synthesis of two stable isolable bromoiodinanes, **1a** and **2a**, as well as chloro and fluoro analogues, **1b–c** and **2b**.



1a

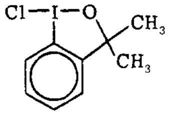


2a



1b, X = Cl

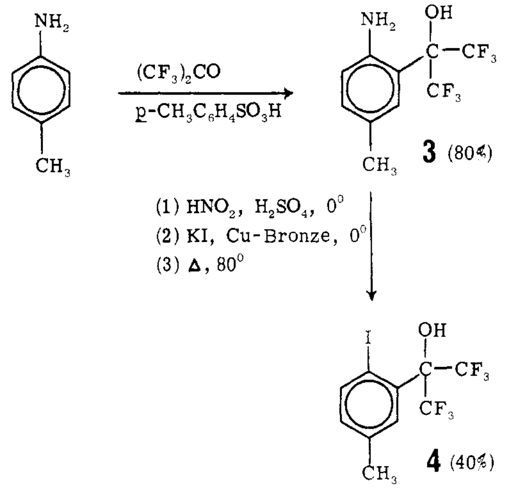
1c, X = F



2b

Our success in isolating the stable bromoiodinanes **1a** and **2a** is attributed to the stabilizing influence of the five-membered ring and, in the case of **1a**, to the highly electronegative trifluoromethyl substituents. The trifluoromethyl-substituted species are markedly more stable than their simple methyl analogues.

Scheme I



Results

The trifluoromethyl-substituted alcohol **4**, the key intermediate in the synthesis of iodinanes **1a–c**, is readily prepared by the method of Scheme I. This utilizes the known[5] reaction of hexafluoroacetone with *p*-toluidine, in the presence of a suitable catalyst, to introduce the perfluoroalkyl groups.

Treatment of **4** with suitable oxidizing agents results in the formation of the stable, crystalline iodinanes **1a–c**. In the

$$\mathbf{4} \xrightarrow{[O]} \mathbf{1a\text{-}c}$$

1a, [O] = (1) KH, (2) Br_2 (90%)
1b, [O] = tert-BuOCl or Cl_2 (96%)
1c, [O] = CF_3OF (95%)

preparation of **1c**, care must be taken to avoid excess trifluoromethyl hypofluorite as further oxidative fluorination of **1c** to the iodine(V), periodinane, species occurs.[6] Compound **1c**

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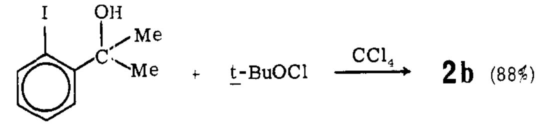
is also prepared directly from chloroiodinane, **1b**, by reaction with a mercuric oxide/aqueous HF slurry.[7]

$$\mathbf{1b} + HgO + HF/H_2O \xrightarrow{CH_2Cl_2} \mathbf{1c}$$

All three of the trifluoromethyl-substituted iodinanes (**1a–c**) are stable, crystalline species, which may be handled in the atmosphere without decomposition. They are thermally stable, even above their melting points, but the bromo- and chloro-substituted species are destroyed upon prolonged irradiation in solution. The products of these decompositions have not been identified.

Alcohol **5**, prepared by the literature method,[8] is not readily purified by chromatography or recrystallization. Treatment of crude **5** with *tert*-butyl hypochlorite produces the pure, crystalline iodinane **2b**. The isolated iodinane is then treated with hydrogen sulfide or other reducing agents to produce the pure alcohol **5**.



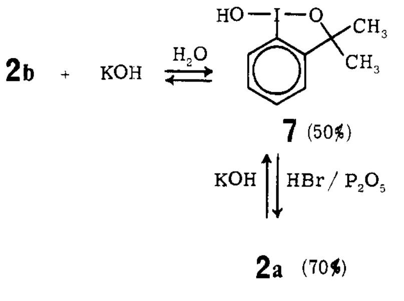
5

Chloroiodinane **2b** is the starting point for the synthesis of other iodinanes in the *gem*-dimethyl series. Unlike the trifluoromethyl species **1b**, which hydrolyzes very slowly to the hydroxyiodinane in the presence of KOH, **2b** reacts rapidly under the same conditions with aqueous potassium hydroxide to produce the hydroxyiodinane **7** (Scheme II). Treatment of a solution of **7** with anhydrous hydrogen bromide in the presence of P_2O_5 gives a solution of a second stable bromoiodinane, **2a**. In contrast to the preparation of bromoiodinane **1a**, the reaction of bromine with the potassium salt of **5** gives not bromoiodinane **2a** but an intractable tarry mass.

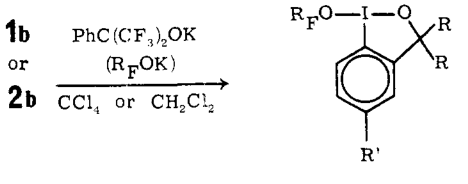
Reaction of either **1b** or **2b** with the potassium salt of hexafluorocumyl alcohol (KOR_F)[9] results in the formation of the respective dialkoxyiodinane **8** or **9** (Scheme III). The dialkoxy compound **9** and the bromo species **2a** react rapidly with water to form hydroxyiodinane **7**. The trifluoromethyl analogues **8** and **1a** show no reaction with water under these conditions.

The (trifluoromethyl)dialkoxyiodinane **8** (0.04 M) undergoes rapid degenerate ligand exchange (NMR time scale, T_c = 56 °C, second-order rate constant = 49 M^{-1} s^{-1})[10] with added R_FOK (0.12 M). No exchange is observed in the presence of a comparable concentration of R_FOH up to 175 °C on the NMR time scale.

Scheme II



Scheme III



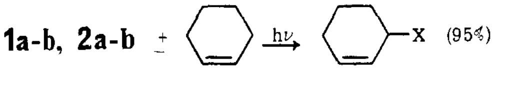
8, R = CF_3, R' = CH_3 (77%)

9, R = CH_3, R' = H (90%)

The iodinane **9** (0.04 M) in the presence of R_FOK (0.10 M) shows coalescence of the ^{19}F NMR singlets at 93 °C. This corresponds to a second-order rate constant for exchange of 61 M^{-1} s^{-1} at 93 °C. Exchange reactions for **9** with the alcohol R_FOH (ca. 0.10 M) are slow on the NMR time scale up to 175 °C.

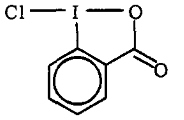
The (trifluoromethyl)iodinanes (**1a,b**) and the *gem*-dimethyl species (**2a,b**) all act as free-radical halogenating agents. Our interest in these compounds lies in their use for selective allylic and benzylic halogenations. The irradiation of **1a,b** or **2a,b** with substituted toluenes in benzene solution gives the benzyl halide in 95% yield (based on iodinane). Irradiation of the haloiodinanes with cyclohexene in carbon tetrachloride gave 95% of 3-halocyclohexene (based on iodinane).

$$\mathbf{1a\text{-}b,\ 2a\text{-}b} + ArCH_3 \xrightarrow{h\nu} ArCH_2X \ (95\%)$$



X = Cl, Br

The known[11] chloroiodinane **10** containing an acyloxy ligand to iodine, when irradiated with toluenes in benzene, gives several unidentified products in addition to benzyl chloride. The details of a mechanistic study of these halogenations are discussed in another publication.[12]



10

Discussion

Cyclic iodinanes containing a five-membered ring were first described in 1909 by Thiele and Peter.[13] Subsequent experiments by Andrews and Keefer[11] led to the synthesis of the chloroacyloxyiodinane **10**. Although acyclic phenyliodine dichloride has been shown to be a synthetically useful reagent,[14] **10** has not proved to be useful in synthesis. Our report here is of a series of cyclic alkoxyiodinanes, including the first stable, isolable bromoiodinanes and dialkoxyiodinanes. The former have proved to be synthetically useful as selective, free-radical brominating agents.

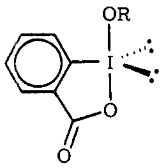
Structure and Bonding. The bonding in iodinanes, like that of sulfuranes and phosphoranes, may be termed hypervalent.[15] A bonding model which is qualitatively correct for iodinanes, as well as for XeF_2,[16] ClF_3, and BrF_3,[17] is similar to the one proposed by Pimentel for HF_2^-.[18] A molecular orbital model which approximates the three-center–four-electron (3c–4e) bonding in iodinanes places four electrons into the two lower energy MOs made of linear combinations of p orbitals on iodine and its two apical ligands.[17a,18]

Two electrons in the second, roughly nonbonding, molecular orbital are associated only with the apical ligands and introduce negative charge on these ligands. This explains the preference observed for the most electronegative substituents to occupy the apical positions.[19]

This theory predicts an approximate bond order of 0.5 for apical iodine–X bonds, which is reflected in an elongation of such bonds relative to the sum of their single-bond covalent radii.[20] Such an elongation (0.22 Å) is observed for the I–Cl bond of $PhCl_2$,[21] corresponding to a bond order of 0.45.[22]

Iodine Mössbauer spectroscopy and chlorine nuclear quadrupole resonance spectroscopy[23] provide experimental data which justify the 3c–4e model without involving significant d-orbital character. Recent calculations[24] indicate that d orbitals do not make energetically significant contributions to hypervalent wave functions in related systems.

The structures of our iodinanes are expected to show the trigonal-bipyramidal (TBP) geometry that has already been observed by X-ray crystallography for interhalogens,[25] for iodobenzene dichloride,[26] and for compounds **11**.[27] Our use



R = CH_3-, CH_3CO-, etc.

11

of the term trigonal bipyramidal includes the three ligands on iodine plus its two electron pairs, in analogy to the terminology used to describe tetracoordinate sulfur(IV) species (sulfuranes). The TBP structure of the iodinanes is slightly distorted from the ideal geometry, with X–I–X apical bonds bent no more than 6° from collinearity. Distortions of the TBP geometry are dependent on the nature of the apical substituents and the presence or absence of the five-membered ring.

Five-Membered Ring Effect. The stabilization of both hypervalent phosphorus compounds (phosphoranes) and hypervalent sulfur compounds (sulfuranes) by the bridging of an apical and an equatorial position by a five-membered ring has been well documented.[28] In the case of phosphoranes, the stabilization is relative to the corresponding four-coordinate tetrahedral phosphorus(V) species, and the large effects of the ring on both rate and equilibrium constants have been attributed to ring strain.[28,29] Similar large effects have been observed in sulfuranes as well.[30]

In the case of iodinanes no quantitative measurements have been made of the magnitude of this effect. A qualitative measure of the degree of stabilization, and of the changes in reactivity which the ring engenders, may be obtained by comparison of several similar iodinanes already known in the literature.[1,31] Several acetoxyiodinanes were found to react with aqueous KOH or NaOH with rates in the order acyclic > monocyclic ≫ bicyclic. This order of reactivity is the same as that which has been observed for a series of sulfuranes.[30]

In our work, the stabilization imparted by the ring is evidenced by our ability to isolate stable bromoiodinanes and dialkoxyiodinanes.

Bromo- and Chloroiodinanes. Iodinanes **1a** and **2a** are isolable, crystalline solids, a presumed manifestation of the stabilizing influence of the five-membered ring effect. The increased stability which occurs on replacement of methyl groups in **2a** by trifluoromethyl groups in **1a** is evidenced in several reactions. (Trifluoromethyl)iodinane **1a** does not react with water under conditions in which *gem*-dimethyliodinane **2a** hydrolyzes rapidly to **7**. Reaction of **1a** with aqueous KOH is very slow under conditions which give complete hydrolysis of **2a**, and the reaction time (5–15 min) of **2a** on irradiation in the presence of substituted toluenes increases to 60 min for **1a**.

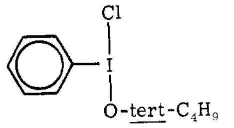
Three factors contribute to the stability of iodinanes **1a,b**: (1) the stabilizing influence of the five-membered ring, (2) the stabilization imparted by the *gem*-dialkyl substituents (Thorpe–Ingold effect),[32] and (3) the presence of electron-withdrawing CF_3 substituents in apical positions. Replacement of apical CH_3 groups in **2a** by apical CF_3 substituents in **1a** markedly increases apical ligand electronegativity and hence stabilizes the 3c–4e bond.

Both bromoiodinanes **1a** and **2a** give highly selective allylic and benzylic free-radical brominations. The irradiation of **1a** or **2a** in the presence of toluene or cyclohexene gives benzyl bromide or 3-cyclohexenyl bromide, respectively. The fact that existing methods for allylic bromination are often of low selectivity, of low yield, or both suggests a possible use for bromoiodinanes in synthesis.

The irradiation of **1b** or **2b** with substituted toluenes at 50 °C in benzene gives more than 95% of the benzyl chloride as determined by ^1H NMR spectroscopy. Photolysis of **1b** or **2b** in the presence of cyclohexene gives 95% 3-chlorocyclohexene. While phenyliodine dichloride gives free-radical benzylic chlorination of toluene, it does not give allylic chlorinations of olefins. Instead, it adds the elements of chlorine to the double bonds of allylic substrates.[14b]

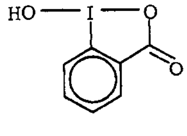
Compound **10** has been found in our work to give neither selective benzylic nor selective allylic chlorinations. Both nuclear and benzylic monochlorination products as well as presumed polychlorination products are formed with toluene. Olefins react with **10** to give addition of chlorine to the double bond.

Tanner[33] has demonstrated that **12** acts as a selective, free-radical chlorinating agent for several alkane substrates. No attempts to effect allylic or benzylic chlorinations were reported with this reagent although benzylic iodination is reported[33b] with the use of another reagent postulated to contain an iodoiodinane, the dimer of *tert*-butyl hypoiodite. No evidence for the structure of this postulated intermediate was reported.



12

Alkoxyiodinanes. Aryliodoso compounds generally have a characteristic odor, decompose explosively on melting, and show a very characteristic I=O stretching frequency of 650–700 cm^{-1}.[14a] However, the presence of an ortho carboxyl function dramatically alters the properties of iodosobenzene. The characteristic odor vanishes, the compound is stable at its melting point, and the I=O bond at 687 cm^{-1} disappears.[14a] The carbonyl stretching frequency, which is normally 1680–1750 cm^{-1}, falls to 1615–1650 cm^{-1} for *o*-iodosobenzoic acid. [14a,34] These data suggest that the acid exists as the hydroxyiodinane **13**.[31b] Recent X-ray structure work by Etter[27e,35] on the methoxy analogue of **13** indicates that these species do exist as the hydroxy- (or alkoxy-) iodinanes.

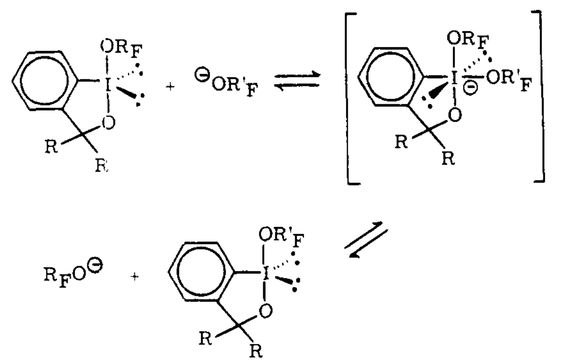


13

Although X-ray structural data are not available for compound **7**, it is expected that, by analogy to **13**, the iodoso alcohol exists primarily as the hydroxyiodinane form in the solid state. This is supported by the absence of a strong band in the IR between 650 and 700 cm^{-1}, the region generally characteristic of the iodoso species (I=O stretch).

Like the parent hydroxy compounds, the hexafluorocumyl ethers **8** and **9** are expected to exist as cyclic dialkoxyiodinanes. Both **8** and **9** are similar to a series of dialkoxysulfuranes[36] which have been shown by X-ray crystallography to exist as the cyclic species. Evidence in support of the structures **8** and **9** may also be adduced from their proton magnetic resonance spectra. The aromatic proton ortho to the ring iodine in **8** shows a marked downfield shift relative to the acyclic iodo alcohol **4** (**8**, 8.05 ppm, vs. **4**, 6.90 ppm). Similar shifts are observed for bromoiodinane **1a** (**1a**, 7.85 ppm, vs. **4**, 6.90 ppm) and for chloroiodinane **1b** (**1b**, 7.90 ppm, vs. **4**, 6.90 ppm). This ortho proton shift has been found to be characteristic for the presence of the hypervalent bond in cyclic sulfuranes,[30d,37] although in this case the downfield shift is much larger (1.24 ppm). Since the ortho shift is a through-space interaction, dependent on the distance of an apical ligand from the ortho hydrogen, the differences in the magnitude of the shifts for sulfuranes and for iodinanes may be attributed in part to differences in the average C–S bond lengths (1.79 Å)[37] and the longer average C–I bond length (2.16 Å for compounds **11** and **13**).[27,35] The increase of the C–I bond length over that of the C–S bond length moves the apical iodinane ligand farther from the ortho proton, which reduces the effect of the through-space interaction and the magnitude of the ortho shift.

Exchange Reactions. Dialkoxyiodinanes **8** and **9** undergo rapid degenerate ligand exchange on the NMR time scale in the presence of R_FOK (~0.10 M). The analogous exchange with R_FOH at comparable concentrations occurs slowly on the NMR time scale at temperatures up to 175 °C. Coalescence occurs at a lower temperature ($T \approx 56$ °C) for the trifluoromethyl compound **8** than for the *gem*-dimethyl analogue **9** ($T \approx 93$ °C). This is not surprising in light of the fact that CF_3 substituents, which lower the electron density on iodine relative to CH_3 substituents, make the iodine more susceptible to attack by alkoxide in an associative mechanism[38] of the type pictured below.



Because similar exchange processes have not been observed in other iodinanes, direct comparisons of iodine species cannot be made. This result is in contrast to that reported[39] for similar degenerate exchanges in an analogous acyclic dialkoxysulfurane for which alkoxy ligand exchange was found to occur via a rapid dissociative process in the presence of R_FOH.

Summary

We have prepared organic derivatives of iodine(III) incorporating structural features known to stabilize TBP molecules, namely, the inclusion of the hypervalent central iodine in a five-membered ring with a bidentate ligand which provides an electronegative site (oxygen) which can occupy an apical position and an electropositive site (carbon) which can occupy an equatorial position. The *gem*-dialkyl effect (Thorpe–Ingold effect)[32] also provides stability to these cyclic structures. This has allowed us to isolate, for the first time, stable bromoiodinanes. We have also prepared stable dialkoxyiodinanes. The bromo compounds and their chloro analogues show promise as synthetically useful, free-radical halogenating agents. They are highly selective in this respect toward benzylic and allylic hydrogens. Further work on the chemistry of the iodinanes is currently underway.

Experimental Section

Fluorine chemical shifts are reported on the ϕ scale (ppm upfield from fluorotrichloromethane) and proton and carbon chemical shifts on the δ scale (ppm downfield from Me_4Si). Elemental analyses of new compounds are within 0.4% of theoretical values.

1-(2-Iodo-5-methylphenyl)-1-(trifluoromethyl)-2,2,2-trifluoroethanol (4). *p*-Toluidine (100 g, 0.93 mol) and *p*-toluenesulfonic acid (2.3 g) in 90 mL of chlorobenzene were heated to 145 °C, and hexafluoroacetone (145.4 g, 0.88 mol) was distilled into the stirred reaction mixture over a 5-h period (a dry ice condenser was used). Solvent was removed under vacuum (100 °C, 20 torr), and the resulting solid was recrystallized from ether to give 191.8 g (80%) of white crystals of **3**, mp 111–112 °C (lit.[5] 109–110 °C).

To a solution of the amino alcohol **3** (13.7 g, 0.05 mol) in 100 mL of water containing 4.5 mL of H_2SO_4 at 0 °C was added 15 mL of aqueous $NaNO_2$ solution (3.6 g, 50 mmol), and then H_2SO_4 (4.5 mL), with stirring over a 30-min period. This mixture was added dropwise to aqueous KI solution (9.96 g, 60 mmol, in 20 mL of water) at 0 °C and then stirred with 0.1 g of copper bronze. The reaction mixture was warmed for 20 min at 80 °C and extracted with ether. The extract was washed twice with 10% aqueous HCl, once with 1 N H_2SO_4, and once with water, dried, and stripped of solvent in vacuo. Sublimation (40 °C, 0.5 torr) of the resultant brown solid gave 7.0 g (40%) of yellow needles of **4:** mp 32.0–33.5 °C; IR (KBr) 3470 (m, OH), 1265–1110 (s), 965 (s), 832 (s), 819 (s), 751 (s), 735 cm^{-1} (s); ^1H NMR (CCl_4) δ 2.30 (s, 3, CH_3), 4.0–4.2 (br s, 0.7, O*H*), 6.8–8.0 (m, 2.7, Ar*H*); ^{19}F NMR (CCl_4) ϕ 74.04 (s, CF_3); ^{13}C NMR ($CDCl_3$) δ 21.20 (s, CH_3), 86.48 (s), 113.01 (s, C-1), 129.66 (s, C-3), 130.74 (s, C-2), 132.51 (s, C-5), 138.29 (s, C-4), 144.36 (C-6); mass spectrum (70 eV) *m/e* (rel intensity) 384 (100, $M^{+\cdot}$), 315 (54, M – CF_3), 245 (22.4), 159 (16.6), 119 (88), 91 (21.4); UV (pentane) λ_{max} 199 (ϵ 20 300), 229 (9760), 275 nm (1260). Anal. ($C_{10}H_7IF_6O$) C, H, I.

1-Bromo-1,3-dihydro-5-methyl-3,3-bis(trifluoromethyl)-1,2-benziodoxole (1a). Iodo alcohol **4** was converted to its potassium salt in ether by reaction with excess potassium hydride. The salt was dried at 30 °C (0.075 torr) (12 h). A suspension of 1.05 g (2.5 mmol) of the salt in CCl_4 (10 mL) was mixed with 0.4 g (2.5 mmol) of bromine. The precipitated potassium bromide was removed, and the solvent was stripped from the filtrate to give a bright yellow solid, **1a,** which was washed with hexane and vacuum dried (1.0 g, 2.25 mmol, 90%): mp 173–175 °C; IR (KBr) 1278 (m), 1262 (s), 1225 (s), 1170 (s), 1149 (s), 1122 (s), 1015 (m), 966 (s), 957 (m), 819 (s), 732 cm^{-1} (s); ^1H NMR (220 MHz, $CDCl_3$) δ 2.55 (s, 3, CH_3), 7.47 (s, 1, H ortho to $C(CF_3)_2$), 7.60 (d, 1.1, J = 8.6 Hz, H para to $C(CF_3)_2$), 7.85 (d, 0.98, J = 8.5 Hz, H ortho to I); ^{19}F NMR ($CDCl_3$) ϕ 76.08 (d, CF_3, J = 1.35 Hz); ^{13}C NMR ($CDCl_3$) δ 20.93 (s, CH_3), 106.32 (s), 113.12 (s, C-1), 129.54 (s, C-5), 130.23 (s, C-3), 132.51 (s, C-4), 134.63 (s, C-6), 142.92 (s, C-2); mass spectrum (10 eV) *m/e* (rel intensity) 464 (1.7, P + 2), 462 (1.7, $M^{+\cdot}$), 395 (53.6, P + 2), 393 (53.7, M – CF_3), 383 (22.1, M – Br), 314 (37.3), 245 (100), 217 (20.8); UV (pentane) λ_{max} 200 (ϵ 18 600), 235 (13 300), 332 nm (136). Anal. ($C_{10}H_6BrF_6IO$) C, H, Br.

1-Chloro-1,3-dihydro-5-methyl-3,3-bis(trifluoromethyl)-1,2-benziodoxole (1b). A solution of 0.95 g (2.5 mmol) of **4** in 0.5 mL of CCl_4 with 0.29 mL (0.27 g, 2.5 mmol) of *tert*-butyl hypochlorite gave, after 20 min, yellow needles which were collected and sublimed (75 °C, 0.2 torr) to give **1b** (1.0 g, 2.4 mmol, 96%): mp 179–180 °C; IR (KBr) 1279 (m), 1262 (m), 1225 (s), 1169 (s), 1149 (s), 1120 (s), 968 (s), 815 (s), 750 (s), 730 cm^{-1} (s); ^1H NMR (220 MHz, $CDCl_3$) δ 2.55 (s, 3, CH_3), 7.50 (s, 0.9, H ortho to $C(CF_3)_2$), 7.63 (d, 1.1, H para to $C(CF_3)_2$, J = 9.0 Hz), 7.90 (d, 1, J = 8.5 Hz, H ortho to I); ^{19}F NMR ($CDCl_3$) ϕ 76.13 (d, CF_3, J = 1.38 Hz); ^{13}C NMR ($CDCl_3$) δ 20.94 (s, CH_3), 109.87 (s), 113.29 (s, C-1), 128.17 (s, C-5), 130.37 (s, C-3), 132.31 (s, C-4), 134.75 (s, C-6), 142.69 (s, C-2); mass spectrum (70 eV) *m/e* (rel intensity) 418 (4, $M^{+\cdot}$), 383 (24, M – Cl), 349 (100, M – CF_3), 314 (28, M – CF_3, Cl), 245 (92, M – CF_3, CF_3), 217 (23), 90 (79), 69 (39, CF_3), 28 (26, CO); UV (pentane) λ_{max} 200 (ϵ 16 400), 223 (19 500), 329 nm (100). Anal. ($C_{10}H_6ClF_6IO$) C, H, Cl.

1-Fluoro-1,3-dihydro-5-methyl-3,3-bis(trifluoromethyl)-1,2-benziodoxole (1c). (a) Iodo alcohol **4** (0.38 g, 1.0 mmol) in 10 mL of Freon-11 was mixed at –78 °C with excess trifluoromethyl hypofluorite. The resulting solid was collected by filtration, washed with cold hexane, and dried under vacuum to give a white powder (0.38 g, 0.95 mmol, 95%): mp 179–181 °C (dec); IR (KBr) 1530 (m), 1298 (s), 1250–1210 (s), 1170 (s), 1120 (s), 1038 (m), 970 (s), 889 (w), 819 (s), 756 (s), 735 cm^{-1} (s); ^{1}H NMR (CCl_4) δ 2.58 (s, 3, $\mathrm{C}H_3$), 7.4–7.7 (m, 2, ArH), 7.92 (d, 1, H ortho to I, J = 7.5 Hz); ^{19}F NMR (CCl_4) ϕ 75.8 (m, 6, $\mathrm{C}F_3$, J_{HF} = 1.4 Hz, J_{FF} = 2.5 Hz), 161.3 (m, 1, F–I, J_{HF} = 1.35 Hz, J_{FF} = 3.0 Hz); ^{13}C NMR ($CDCl_3$) δ 20.93 (s, CH_3), 109.81 (s), 114.0 (s, C-1), 128.17 (s, C-5), 130.29 (s, C-3), 132.11 (s, C-4), 135.72 (s, C-6), 143.69 (s, C-2); mass spectrum (70 eV) *m/e* (rel intensity) 402 (0.2, $M^{+\cdot}$), 383 (9, M − F), 314 (6, M − CF_3, F), 189 (28), 119 (12.6), 31 (100), 28 (25, CO); UV (pentane) $\lambda_{\max}$ 209 (ϵ 9000), 223 (9000), 325 nm (40). Anal. ($C_{10}H_6F_7IO$) C, H, F.

(b) A solution of **1b** (0.69 g, 1.65 mmol) in 15 mL of CH_2Cl_2 was mixed with yellow mercuric oxide (0.18 g, 0.83 mmol) and 0.2 mL of 48% aqueous HF. The solution was stirred 10 min, filtered, and washed with dilute aqueous $NaHCO_3$. Removal of the solvent in vacuo gave white plates of **1c** (0.60 g, 1.50 mmol, 94%): mp 179–181 °C dec.

1-(2-Iodophenyl)-1-methylethanol (5). The compound was prepared from methyl *o*-iodobenzoate by the Grignard addition method of Brown and Okamoto:[8a] bp 118–121 °C (5 torr) [lit.[8a,b] 121 °C (5.5 torr)]; 70% yield. Because the Grignard reaction gave impurities which proved difficult to remove by distillation, a new method of purification was used. In a typical experiment, 5.0 g (19 mmol) of crude **5** dissolved in 15 mL of CCl_4 was treated with 2.07 g (19 mmol) of *tert*-butyl hypochlorite. The precipitate of **2b** which formed (3.38 g, 11.4 mmol, 60%) was collected, dried, and dissolved in $CHCl_3$ (~20 mL). This solution was treated with H_2S until an aliquot no longer showed the presence of **2b** by ^{1}H NMR. Filtration of the mixture and removal of solvent from the filtrate gave pure **5** (2.54 g, 9.7 mmol, 85%): bp 120–121 °C, 5 torr.

1,3-Dihydro-1-hydroxy-3,3-dimethyl-1,2-benziodoxole (7). Treatment of 0.685 g (2.32 mmol) of **2b** in 10 mL of CH_2Cl_2 with 0.16 g (2.32 mmol) of potassium hydroxide in 5 mL of water affords, after separation of layers and removal of solvent from the organic phase, 0.32 g (50%, 1.16 mmol) of white, crystalline **7**: mp 126.0–128.0 °C; IR ($CHCl_3$) 2970 (s), 2870 (m), 2440 (w), 1568 (w), 1465 (s), 1440 (s), 1382 (s), 1361 (s), 1260 (m), 1162 (s), 1113 (m), 1036 (s), 1009 (m), 956 (s), 871 (s), 611 (s), 564 cm^{-1} (s); ^{1}H NMR (CCl_4) δ 1.47 (s, 6, $\mathrm{C}H_3$), 7.20–7.50 (m, 1, H ortho to alkyl group), 7.54–7.80 (m, 2, H para to iodine, H para to alkyl group), 8.00–8.20 (m, 1, H ortho to iodine); mass spectrum (10 eV) *m/e* (rel intensity) 278 (4.64, $M^{+\cdot}$), 263 (10.5, M − CH_3), 262 (46.6), 261 (15.4, M − OH), 247 (50.9), 246 (77.3, M − CH_3, OH), 231 (100, M − CH_3, CH_3, OH), 203 (16.7); UV (pentane) $\lambda_{\max}$ 205 (ϵ 12 995), 235 nm (10 465). Anal. ($C_9H_{11}IO_2$) C, H, I.

1-Bromo-1,3-dihydro-3,3-dimethyl-1,2-benziodoxole (2a). A solution of 0.1 g (3.61 mmol) of **7** in 5 mL of methylene chloride was treated with excess hydrogen bromide in the presence of a pellet of P_2O_5. The yellow crystals obtained by removal of solvent in vacuo were recrystallized from CCl_4 to give **2a** (0.1 g, 70%): mp 98.0–100.0 °C; IR (CCl_4) 2990 (m), 1585 (w), 1465 (m), 1440 (m), 1381 (w), 1363 (w), 1255 (m), 1160 (s), 1112 (m), 1080 (m), 1045 (m), 1000 (m), 949 (s), 867 (s), 610 cm^{-1} (s); ^{1}H NMR (CCl_4) δ 1.57 (s, 6, $\mathrm{C}H_3$), 7.23–7.40 (m, 1, H ortho to CMe_2), 7.68–7.83 (m, 2, H para to I, H para to CMe_2), 8.18–8.32 (m, 1, H ortho to I); mass spectrum (10 eV) *m/e* (rel intensity) 327 (80), 325 (100, M − CH_3), 324 (42.9), 261 (62.3, M − Br), 246 (71.9, M − Br, CH_3, CH_3), 243 (86.4), 231 (68.4); UV (pentane) $\lambda_{\max}$ 204 (ϵ 10 370), 235 nm (6190). Anal. ($C_9H_{10}BrIO$) C, H, Br.

1-Chloro-1,3-dihydro-3,3-dimethyl-1,2-benziodoxole (2b). Iodo alcohol **5** (10.0 g, 38.2 mmol) was dissolved in 30 mL of CCl_4, and 4.14 g (38.2 mmol) of *tert*-butyl hypochlorite was added. After 30 min, a pale yellow powder was collected by filtration. Recrystallization from CCl_4 gave 10.0 g (88%) of **2b**: mp 143–145 °C; IR ($CHCl_3$) 3030 (s), 1599 (w), 1568 (w), 1468 (m), 1442 (m), 1385 (w), 1260 (m), 1161 (s), 1115 (m), 1002 (m), 946 (s), 863 cm^{-1} (s); ^{1}H NMR ($CDCl_3$) δ 1.58 (s, 6, $\mathrm{C}H_3$), 7.15 (m, 1, H ortho to CMe_2), 7.49 (m, 2, H para to I, H para to CMe_2), 8.00 (m, 1, H ortho to I); ^{13}C NMR ($CDCl_3$) δ 29.19 (s, CH_3), 85.12 (s, CMe_2), 114.63 (s, C-1), 126.09 (s, C-4), 128.44 (s, C-3), 130.44 (s, C-6), 130.92 (s, C-5), 149.52 (s, C-2); mass spectrum (70 eV) *m/e* (rel intensity) 298 (0.2, P + 2), 296 (0.6, $M^{+\cdot}$), 283 (31), 281 (100, M − CH_3), 261 (32, M − Cl), 246 (51, M − Cl, CH_3), 231 (70, M − CH_3, CH_3, Cl), 203 (27), 139 (10); UV (pentane) $\lambda_{\max}$ 200 (ϵ 16 000), 232 (15 000), 329 nm (190). Anal. ($C_9H_{10}ClIO$) C, H, Cl.

1,3-Dihydro-5-methyl-1-[1-phenyl-1-(trifluoromethyl)-2,2,2-trifluoroethoxy)-3,3-bis(trifluoromethyl]-1,2-benziodoxole (8). A solution of **1b** (0.26 g, 0.62 mmol) in 30 mL of CH_2Cl_2 was stirred 3 h with 0.175 g (0.62 mmol) of the potassium salt of 1-phenyl-1-trifluoromethyl-2,2,2-trifluoroethanol (KOR_F).[9] The solution was filtered to remove KCl, and the solvent was removed under vacuum (0.3 torr, 25 °C). Compound **8** was obtained as a white powder (0.30 g, 0.48 mmol, 77%): mp 161–163.5 °C; IR (Nujol mull) 2680 (w), 2050 (w), 1580 (w), 1370 (m), 1275 (s), 1220 (s), 1180 (s), 1160 (m), 1130 (s), 1080 (m), 970 (m), 940 (m), 855 (m), 760 (s), 715 cm^{-1} (s); ^{1}H NMR (CD_2Cl_2) δ 2.55 (s, 3, $\mathrm{C}H_3$), 7.40–8.05 (m, 8, ArH), ^{19}F NMR (CD_2Cl_2) ϕ 72.9 (s, 6, R_FO–), 76.1 (s, 6, O–C($\mathrm{C}F_3$)$_2$); mass spectrum (70 eV) *m/e* (rel intensity) 626 (3.0, $M^{+\cdot}$), 557 (20.5, M − CF_3), 418 (7.7), 383 (85.0), 351 (28.0), 349 (85.8), 314 (46.9), 245 (100.0), 217 (27.6), 137 (39.1), 122 (10.1), 119 (36.0), 109 (11.0), 105 (11.5), 91 (12.1), 90 (52.7), 89 (29.7), 77 (37.8), 69 (12.8, CF_3), 63 (18.3). Anal. ($C_{19}H_{11}F_{12}IO$) C, H, I.

1,3-Dihydro-3,3-dimethyl-1-[1-phenyl-1-(trifluoromethyl)-2,2,2-trifluoroethoxy]-1,2-benziodoxole (9). Addition of 0.49 g (1.76 mmol) of potassium hexafluorocumyl oxide (KOR_F)[9] to 0.52 g (1.76 mmol) of **2b** in 30 mL of dry CCl_4 caused an immediate formation of potassium chloride. After the precipitate was removed by filtration under nitrogen, the filtrate was stripped to dryness. The resultant beige powder was then recrystallized from pentane to give 0.80 g (1.6 mmol, 90%) of white crystalline **9**: mp 94.0–96.0 °C; IR ($CHCl_3$) 2980 (s), 1460 (m), 1437 (m), 1379 (m), 1360 (m), 1268 (s), 1182 (s), 1102 (s), 1077 (s), 1033 (s), 968 (s), 942 (s), 921 (m), 869 (s), 825 (s), 725 (m), 620 (s), 563 cm^{-1} (m); ^{1}H NMR (CCl_4) δ 1.48 (s, 6, $\mathrm{C}H_3$), 7.05–8.14 (m, 10, ArH); ^{19}F NMR (CCl_4) ϕ 72.92 (s, $\mathrm{C}F_3$); mass spectrum (70 eV) *m/e* (rel intensity) 504 (2.1, $M^{+\cdot}$), 489 (100, M − CH_3), 261 (54.5, M − R_F, CH_3), 246 (91.8, M − R_F, CH_3, CH_3), 231 (90.2), 203 (26.4), 175 (30.1), 105 (59.9), 77 (99.9), 43 (99.9); UV (pentane) $\lambda_{\max}$ 195 (ϵ 34 955), 225 (18 584), 295 nm (796). Anal. ($C_{18}H_{15}IF_6O_2$) C, H, I.

1-Chloro-1,2-benziodoxol-3(1*H*)-one (10). Excess chlorine was bubbled into a suspension of *o*-iodobenzoic acid (1.0 g, 4.0 mmol) in 20 mL of nitromethane at 25 °C (a modification of the method of Keefer and Andrews).[11] The precipitate of dichloride was collected by filtration, washed with CCl_4, and placed under vacuum (0.1 torr, 25 °C) to remove HCl formed during cyclization. This treatment results in a pale yellow powder, **10** (1.0 g, 3.6 mmol, 89%): mp 167–170 °C (lit.[10] 169–171 °C); IR (Nujol) 1680 (s, C=O), 1475 (s), 1380 (m), 1120 cm^{-1} (w); ^{1}H NMR (CH_3NO_2) δ 7.1–8.2 (m, 4, ArH).

Exchange of Iodinanes 8 and 9 with KOR_F. (a) Iodinane 8 (12.4 mg, 0.019 mmol) was added to 0.5 mL of CCl_4. Addition of 16.5 mg (0.059 mmol) of KOR_F (0.118 M KOR_F, 0.038 M 8) caused the ^{19}F peak of the R_FO–ligand to broaden into the base line at 56 °C.

(b) The addition of 12.7 mg (0.043 mmol) of KOR_F to a solution of iodinane **9** (10.6 mg, 0.021 mmol) in 0.5 mL of CCl_4 causes the ^{19}F peak coalescence at 93 °C. The solution is 0.086 M in KOR_F and 0.042 M in **9**.

Benzylic Halogenations, General. Reactions of **1a,b, 2a,b,** and **10** were carried out in sealed NMR tubes with substituted toluenes and benzene solvent. Degassed samples (at least three freeze–thaw cycles) were placed in a constant-temperature bath at 50.0 ± 0.1 °C and irradiated with a 275-W GE sunlamp.

In a typical experiment, 0.02 g (0.05 mmol) of **1a** and 0.07 g (0.75 mmol) of toluene were mixed with 0.5 mL of dry benzene and the sample was sealed and irradiated 30 min. Products were analyzed by ^{1}H NMR spectroscopy and identified on the basis of their known chemical shifts.

Allylic Halogenations, General. Allylic halogenations with **1a,b, 2a,b,** and **10** were performed in sealed NMR tubes with cyclohexene and carbon tetrachloride solvent. Samples were evacuated, sealed (three freeze–thaw cycles), and placed in a constant-temperature bath at 50.0 ± 0.1 °C. Photolyses, carried out with a 275-W GE sunlamp, were complete within 60 min.

In a typical experiment, **1a** (0.028 g, 0.07 mmol), cyclohexene (0.008 g, 0.1 mmol), and 0.5 mL of CCl_4 were irradiated 15 min. 3-Cyclohexenyl chloride was identified as the sole product by ^{1}H NMR spectroscopy.

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References and Notes

(1) (a) C. Willgerodt, *J. Prakt. Chem.*, [2]**33,** 154 (1886); (b) C. Willgerodt, *Chem. Ber.*, **29**, 1567 (1896); (c) B. S. Garvey, Jr., L. F. Halley, and C. F. H. Allen, *J. Am. Chem. Soc.*, **59,** 1827 (1937).

(2) J. Thiele and W. Peter, *Chem. Ber.*, **38**, 2842 (1905).
(3) G. S. Forbes and J. H. Faull, Jr., *J. Am. Chem. Soc.*, **55**, 1820 (1933).
(4) G. A. Melent'eva, I. I. Dozorova, and M. A. Salimov, *Farmatsiya (Moscow)*, **20**, 31 (1971); *Chem. Abstr.*, **74**, 130414 (1971).
(5) E. E. Gilbert, E. S. Jones, and J. P. Sibilia, *J. Org. Chem.*, **30**, 1001 (1965).
(6) R. L. Amey and J. C. Martin, *J. Am. Chem. Soc.*, **100**, 300 (1978).
(7) W. Carpenter, *J. Org. Chem.*, **31**, 2688 (1966).
(8) (a) H. C. Brown, Y. Okamoto, and G. Ham, *J. Am. Chem. Soc.*, **79**, 1906 (1957); (b) E. Bergmann and A. Weizmann, *Trans. Faraday Soc.*, **32**, 1318 (1936).
(9) J. C. Martin, R. J. Arhart, J. A. Franz, E. F. Perozzi, and L. J. Kaplan, *Org. Synth.*, **57**, 22 (1977).
(10) (a) H. S. Gutowsky and C. H. Holm, *J. Chem. Phys.*, **25**, 1228 (1956); (b) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance", McGraw-Hill, New York, 1959, p 223.
(11) L. J. Andrews and R. M. Keefer, *J. Am. Chem. Soc.*, **81**, 2374 (1959).
(12) R. L. Amey and J. C. Martin, *J. Am. Chem. Soc.*, in press.
(13) J. Thiele and W. Peter, *Justus Liebigs Ann. Chem.*, **369**, 119 (1909).
(14) For example see (a) D. F. Banks, *Chem. Rev.*, **66**, 243 (1966); (b) D. D. Tanner and G. C. Gidley, *J. Org. Chem.*, **33**, 38 (1968); (c) D. D. Tanner and P. B. Van Bostelen, *ibid.*, **32**, 1517 (1967).
(15) (a) J. I. Musher, *Angew. Chem., Int. Ed. Engl.*, **8**, 54 (1969); (b) J. I. Musher in "Sulfur Research Trends", Vol. 110, R. F. Gould, Ed., American Chemical Society, Washington, D.C., 1972, pp 44–52.
(16) J. G. Malm, H. Selig, J. Jortner, and S. A. Rice, *Chem. Rev.*, **65**, 199 (1965).
(17) (a) R. E. Rundle, *Surv. Prog. Chem.*, **1**, 81 (1963); (b) E. E. Havinga and E. H. Wiebenga, *Recl. Trav. Chim. Pays-Bas*, **78**, 724 (1959).
(18) G. C. Pimentel, *J. Chem. Phys.*, **19**, 446 (1951).
(19) E. L. Muetterties and R. A. Schunn, *Q. Rev. Chem. Soc.*, **20**, 245 (1966).
(20) L. Pauling, "The Nature of the Chemical Bond and the Structure of Molecules and Crystals", 3rd ed., Cornell University Press, Ithaca, NY, 1960, pp 221–228.
(21) J. D. McCullough, *Acta Crystallogr.*, **6**, 746 (1953).
(22) L. Pauling, *J. Am. Chem. Soc.*, **69**, 542 (1947).
(23) (a) B. S. Ehrlich and M. Kaplan, *J. Chem. Phys.*, **54**, 612 (1971); (b) J. C. Evans and G. Y.-S. Lo, *J. Phys. Chem.*, **71**, 2730 (1967).
(24) (a) A. Rauk, L. C. Allen, and K. Mislow, *J. Am. Chem. Soc.*, **94**, 3035 (1972); (b) J. B. Florey and L. C. Cusachs, *ibid.*, **94**, 3040 (1972); (c) R. Hoffman, J. M. Howell, and E. L. Muetterties, *ibid.*, **94**, 3047 (1972); (d) P. J. Hay, *ibid.*, **99**, 1003 (1977); (e) J. M. Howell and J. F. Olsen, *ibid.*, **98**, 7119 (1976); (f) J. M. Howell, *ibid.*, **97**, 3930 (1975); (g) J. M. F. van Dijk, J. F. M. Pennings, and H. M. Buck, *ibid.*, **97**, 4836 (1975); (h) M. M. L. Chen and R. Hoffmann, *ibid.*, **98**, 1647 (1976); (i) S. R. Ungemach and H. F. Schaefer III, *ibid.*, **98**, 1658 (1976).
(25) (a) R. D. Burbank and F. N. Bensey, *J. Chem. Phys.*, **21**, 602 (1953); (b) E. L. Muetterties and W. D. Phillips, *J. Am. Chem. Soc.*, **79**, 322 (1957).
(26) E. M. Archer and T. G. D. van Schalkwyk, *Acta Crystallogr.*, **6**, 88 (1953).
(27) (a) J. Z. Gougoutas and J. C. Clardy, *J. Solid State Chem.*, **4**, 226, 230 (1972); (b) J. Z. Gougoutas and L. Lessinger, *ibid.*, **7**, 175 (1973); (c) J. Z. Gougoutas and L. Lessinger, *ibid.*, **9**, 155 (1974); (d) J. Z. Gougoutas, K. H. Chang, and M. C. Etter, *ibid.*, **16**, 283 (1976); (e) M. C. Etter, *ibid.*, **16**, 399 (1976); (f) M. C. Etter, *J. Am. Chem. Soc.*, **98**, 5326, 5331 (1976); (g) For an X-ray structure of a related acyclic dioxyiodinane see G. F. Koser, R. H. Wettach, J. M. Troup, and B. A. Frenz, *J. Org. Chem.*, **41**, 3609 (1976).
(28) (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., Elsevier, New York, 1972, pp 1–56.
(29) (a) I. Ugi and F. Ramirez, *Chem. Br.*, 198 (1972); (b) P. A. Bristow, J. G. Tillett, and D. E. Wiggins, *J. Chem. Soc. B*, 1360 (1968).
(30) (a) G. W. Astrologes and J. C. Martin, *J. Am. Chem. Soc.*, **99**, 4390 (1977); (b) G. W. Astrologes and J. C. Martin, *ibid.*, **97**, 6909 (1975); (c) E. F. Perozzi and J. C. Martin, *ibid.*, **94**, 5519 (1972); (d) L. J. Kaplan and J. C. Martin, *ibid.*, **95**, 793 (1973); (e) J. C. Martin and E. F. Perozzi, *ibid.*, **96**, 3155 (1974).
(31) For a qualitative comparison of iodinane reactivities, compare the following: (a) G. P. Baker, F. G. Mann, N. Sheppard, and A. J. Tetlow, *J. Chem. Soc.*, 3721 (1965); (b) W. C. Agosta, *Tetrahedron Lett.*, 2681 (1965).
(32) See E. L. Eliel, "Stereochemistry of Carbon Compounds", McGraw-Hill, New York, 1962, p 196 ff.
(33) (a) D. D. Tanner and G. C. Gidley, *Can. J. Chem.*, **46**, 3537 (1968); (b) *J. Am. Chem. Soc.*, **90**, 808 (1968).
(34) J. R. Dyer, "Applications of Absorption Spectroscopy of Organic Compounds", Prentice-Hall, Englewood Cliffs, NJ, 1965, pp 34–5.
(35) M. C. Etter, Ph.D. Thesis, University of Minnesota, 1974.
(36) For a review see J. C. Martin and E. F. Perozzi, *Science*, **191**, 154 (1976).
(37) E. F. Perozzi, J. C. Martin, and I. C. Paul, *J. Am. Chem. Soc.*, **96**, 578, 6735 (1974).
(38) C. H. Langford and H. B. Gray, "Ligand Substitution Processes", W. A. Benjamin, New York, 1965.
(39) R. J. Arhart and J. C. Martin, *J. Am. Chem. Soc.*, **94**, 4997 (1972).

Formation and Rearrangement of Ipso Intermediates in Aromatic Free-Radical Chlorination Reactions[1]

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Photoinitiated chlorination of *p*-chloronitrobenzene (1) in carbon tetrachloride at room temperature produces mainly *p*-dichlorobenzene (2) plus some 1,2,4-trichlorobenzene (3). Reaction of *p*-bromonitrobenzene (7) under the same conditions also produces 2 and 3 plus a small amount of 1-chloro-2-bromo-4-nitrobenzene (9). The presence of rearrangement product 9 and the greater ratio of 3/2 from 7 than from 1 are strong evidence for the formation and rearrangement of an ipso intermediate (10) in these aromatic free-radical chlorinations.

Only during the past decade has the importance of ipso attack in aromatic substitution reactions been appreciated.[2] Although replacements of a substituent during aromatic free-radical substitution reactions have been reported by several investigators during the past 75 years, the substantial volume of current literature about ipso attack has been largely confined to electrophilic substitutions.[2] Cationic ipso intermediates have been trapped, and their rearrangements have been shown to account for as much as half of the ortho substitution products obtained in some nitrations.[2] We have now obtained evidence for the formation and rearrangement of an ipso intermediate during free-radical chlorination of *p*-bromonitrobenzene.

Although the ipso position has been regarded by some investigators as the most unlikely position for attack by a free radical and although a significant role for an ipso intermediate in the mechanism of aromatic free-radical substitution reactions has been advocated only recently,[1b,3-5] the chemical literature includes a number of reports of free-radical ipso substitutions. The earliest one appears to be about the formation (in 50% yield) of chlorobenzene by the chlorination of bromobenzene,[6] and several reports of similar halogen exchanges in preference to or at least competitive with hydrogen replacement have followed.[7] Replacements of halo substituents in benzene derivatives by (4-bromophenyl)diphenylmethyl radical,[8] by aryl radicals,[9] by cyclohexyl radical,[10] by elemental sulfur (presumably as a diradical intermediate),[11] by benzenesulfenyl and benzenesulfonyl radicals,[12] and by hydrogen atom,[13] replacement of the chloro substituent in 9-chloroanthracene by phenyl radical,[14a] and replacements

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