

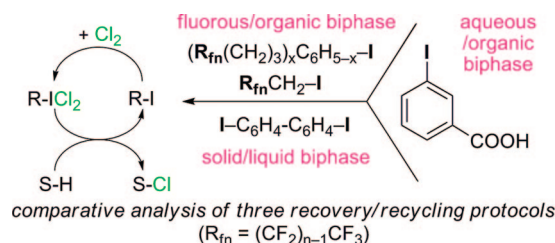
Synthesis and Reactivity of Fluorous and Nonfluorous Aryl and Alkyl Iodine(III) Dichlorides: New Chlorinating Reagents that are Easily Recycled using Biphasic Protocols

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Received February 3, 2009



Fluorous aryl and alkyl iodine(III) dichlorides of the formulas $(R_{fn}(CH_2)_3)_2C_6H_3ICl_2$ ($R_{fn} = CF_3(CF_2)_{n-1}$; $n = 8$ for 3,5-disubstituted and $n = 6, 8, 10$ for 2,4-disubstituted) and $R_{fn}CH_2ICl_2$ ($n = 8, 10$) are prepared in 71–98% yields by reactions of Cl_2 and the corresponding fluorous iodides. These are effective reagents for the conversions of cyclooctene to *trans*-1,2-dichlorocyclooctene, anisole to 4-chloro- and 2-chloroanisole, 4-*tert*-butylphenol to 2-chloro-4-*tert*-butylphenol, $PhCOCH_2COPh$ to $PhCOCHClCOPh$, and $PhCOCH_3$ to $PhCOCH_2Cl$ and $PhCOCHCl_2$ (CH_3CN , rt to 40 °C, 100–64% conversions). The chlorinated products and fluorous iodide coproducts are easily separated by organic/fluorous liquid/liquid biphasic workups. The latter are obtained in 97–90% yields and reoxidized with Cl_2 . Analogous chlorinations are conducted with 3- $Cl_2IC_6H_4COOH$ (**16**) and 4,4'- $Cl_2IC_6H_4C_6H_4ICl_2$. With the former, the products and coproduct 3- IC_6H_4COOH (91–85% recoveries) are easily separated by organic/aqueous $NaHCO_3$ liquid/liquid biphasic workups. The coproduct from the latter, 4,4'- $IC_6H_4C_6H_4I$, is insoluble in common organic solvents, allowing separation by liquid/solid phase workups (91–89% recoveries). The effect of the structure of the iodine(III) dichloride upon reactivity is analyzed in detail. The fluorous systems with R_{f8} substituents are generally superior, but **16** is more reactive and gives higher selectivities.

1. Introduction

Hypervalent iodine reagents have been recognized as exceedingly useful tools in synthesis and promising candidates for environmentally benign processes. In the latter context, they have received growing interest due to their useful oxidizing properties, combined with their low toxicity, ready availability,

easy handling, high efficiency, and mild reaction conditions.¹ They constitute safe alternatives to heavy metal reagents for a wide range of transformations, especially oxidations.² Despite their increasingly wide application, their low atom economy

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remains a major drawback, as stoichiometric amounts of aryl iodides or similar waste products are produced.³ This represents a distinct debit from a “green” chemistry viewpoint. A possible solution would be the recycling and reuse of reaction coproducts, which reduces Sheldon’s environmental factor *E*.⁴ Accordingly, a number of approaches to recyclable hypervalent iodine reagents have been reported involving both polymeric^{5–10} (polystyrene or silica supports) and molecular species,^{11–13} among which iodine(III) bis(acetates) and bis(trifluoroacetates) dominate.

Recently, several recyclable hypervalent iodine reagents based on fluororous chemistry principles have been developed.¹¹ Fluororous chemistry, an important part of “green” chemistry,¹⁴ exploits the combined lipophobicity and hydrophobicity of fluororous molecules to effect cleaner reactions and separation processes. Liquid/liquid or liquid/solid biphasic conditions are commonly employed to remove “phase tagged” or “ponytailed” coproducts or catalysts from the product.¹⁵ As a case in point, fluororous aryl iodine(III) bis(acetates) have been shown to be excellent reagents for oxidations of hydroquinones to quinones under homogeneous conditions. The resulting fluororous aryl iodides can be recovered by simple fluororous/organic liquid/liquid

phase separations and reoxidized to the iodine(III) bis(acetates).^{11a} Many fluororous alkyl iodides $R_{fn}I$ ($R_{fn} = CF_3(CF_2)_{n-1}$) are commercially available and can similarly be converted to fluororous alkyl iodine(III) bis(trifluoroacetates). These reagents also efficiently oxidize hydroquinones to quinones, as well as secondary aliphatic and benzylic alcohols to ketones, and the $R_{fn}I$ coproducts are easily recovered and reoxidized (for less volatile species with $n > 8$).^{11b,c}

Chlorination constitutes one of the most important transformations in organic synthesis.¹⁶ Molecular chlorine, the most commonly used chlorinating agent, is a hazardous, toxic, and corrosive chemical whose high reactivity and highly exothermic reactions cause difficulties in effecting selective conversions. Consequently, alternative chlorination reagents (e.g., NCS) and reaction systems have been developed with increased ease of handling and selectivity.¹⁷ However, drawbacks such as low atom economy and the need to remove spent reagent remain. As the chemistry of hypervalent iodine(III) dihalides has expanded, they have received increasing attention as halogenating and oxidizing agents, as well as building blocks for other hypervalent iodine compounds.¹ The most frequently encountered representative is (dichloroiodo)benzene, a molecule that was first prepared in 1886 by Willgerodt by passing chlorine through a solution of iodobenzene in an organic solvent.¹⁸ This is still the most general method for preparing (dichloroiodo)arenes.

Despite the synthetic importance of (dichloroiodo)benzene, its broader application as a reagent has been restricted due to the often tedious separation of the coproduct iodobenzene from the desired products. To circumvent this problem, a polymer-supported version has been developed.^{9a} Furthermore, a recent report described the use of 4,4'-bis(dichloroiodo)biphenyl and 3-(dichloroiodo)benzoic acid for iodochlorinations and iodoalkoxylations of unsaturated compounds.^{13d} The former gives a coproduct that is insoluble in most organic solvents, 4,4'-bis(iodo)biphenyl. The latter gives a coproduct that can be extracted with aqueous base, 3-iodobenzoic acid. Accordingly, these have been efficiently recovered by solid/liquid and organic/aqueous $NaHCO_3$ liquid/liquid biphasic protocols, respectively, and reoxidized to the dichlorides and reused.

Surprisingly, there have not been any reports of fluororous (dichloroiodo)arenes. However, a few fluororous aliphatic iodine(III) chlorides of the formulas $R_{fn}CH_2ICl_2$ ($n = 1–3$) have been synthesized, as well as the related species $H(CF_2)_6CH_2ICl_2$.¹⁹ Importantly, these feature a methylene “spacer” between the iodine and the highly electron-withdrawing R_{fn} moiety. The apparent absence of the spacerless analogues $R_{fn}ICl_2$ in the literature may reflect unfavorable thermodynamics for the chlorination, or a kinetic barrier. These iodine(III) compounds have been shown to efficiently dichlorinate alkenes and monochlorinate 1,3-diketones. However, the $R_{fn}CH_2I$ ($n = 1–3$) coproducts are too volatile for easy recycling.

In this paper, we present the synthesis and characterization of several fluororous aryl and alkyl iodine(III) dichlorides and detail their use as recyclable chlorinating reagents for alkenes,

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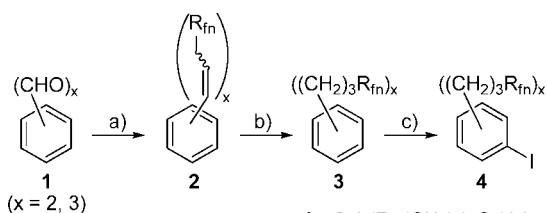
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SCHEME 1^a

- 4a:** 3,4- $(\text{R}_{18}(\text{CH}_2)_3)_2\text{C}_6\text{H}_3\text{I}$
4b: 2,4- $(\text{R}_{16}(\text{CH}_2)_3)_2\text{C}_6\text{H}_3\text{I}$
4c: 2,4- $(\text{R}_{18}(\text{CH}_2)_3)_2\text{C}_6\text{H}_3\text{I}$
4d: 2,4- $(\text{R}_{10}(\text{CH}_2)_3)_2\text{C}_6\text{H}_3\text{I}$
4e: 2,4,6- $(\text{R}_{18}(\text{CH}_2)_3)_3\text{C}_6\text{H}_2\text{I}$

^a Key: (a) $(\text{R}_{\text{fn}}\text{CH}_2\text{CH}_2)\text{Ph}_3\text{P}^+\text{I}^-$, K_2CO_3 , *p*-dioxane/ H_2O , 95 °C; (b) 10% Pd/C, 1 atm H_2 , ethanol/ $\text{CF}_3\text{C}_6\text{H}_5$; (c) $\text{I}_2/\text{H}_5\text{IO}_6$, AcOH/ $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$ /reflux or I_2 , $\text{PhI}(\text{OAc})_2$, AcOEt/reflux.

arenes, and ketones. The effect of the structures of the aryl and alkyl iodine(III) dichlorides upon their stabilities and reactivities are carefully defined. Complementary experiments are conducted with the nonfluorous iodine(III) dichlorides derived from 4,4'-bis(iodo)biphenyl and 3-iodobenzoic acid.^{13d} As noted above, these iodoarenes can be recovered by solid/liquid and aqueous/organic liquid/liquid biphasic protocols. Thus, this study represents one of the few in which the effectiveness of several competing reagent recycling strategies are compared and contrasted.

2. Results and Discussion

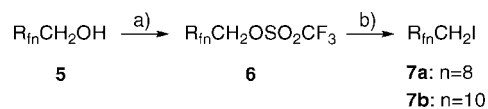
2.1. Syntheses of Fluorous Aryl Iodides 4 and Alkyl Iodides 7. The fluorous aryl iodides 3,4- $(\text{R}_{18}(\text{CH}_2)_3)_2\text{C}_6\text{H}_3\text{I}$ (**4a**), 2,4- $(\text{R}_{16}(\text{CH}_2)_3)_2\text{C}_6\text{H}_3\text{I}$ (**4b**), 2,4- $(\text{R}_{18}(\text{CH}_2)_3)_2\text{C}_6\text{H}_3\text{I}$ (**4c**), 2,4- $(\text{R}_{10}(\text{CH}_2)_3)_2\text{C}_6\text{H}_3\text{I}$ (**4d**), and 2,4,6- $(\text{R}_{18}(\text{CH}_2)_3)_3\text{C}_6\text{H}_2\text{I}$ (**4e**) can be synthesized in several simple steps from benzene di- or tricarbaldehydes $\text{C}_6\text{H}_{6-x}(\text{CHO})_x$ (**1**). As summarized in Scheme 1, Wittig reactions with the appropriate fluorous triphenylphosphonium salts were followed by side-chain hydrogenations and then iodinations of the arene cores. The resulting fluorous aryl iodides feature two or three ponytails, each with three methylene spacers. The homologous series **4b,c,d** contain increasingly long R_{fn} segments, which results in progressively lower absolute solubilities.¹⁴

The syntheses of **2a,c,e**, **3a,c,e**, and **4a,c,e** have been reported previously,^{11a,20} and data for the new compounds **2b,d**, **3b,d**, and **4b,d** are summarized in the Experimental Section and Supporting Information. While **2b**, **3b**, and **4b** were isolated in analytically pure form in 78%, 97%, and 75% yields, respectively, **2d**, **3d**, and **4d** could only be obtained in crude form. The solubilities of compounds with multiple R_{10} -containing ponytails can be especially low, complicating both reactions and workups.

The fluorous alkyl iodides $\text{R}_{\text{fn}}\text{CH}_2\text{I}$ (**7**) were prepared in two simple steps from the commercially available alcohols $\text{R}_{\text{fn}}\text{CH}_2\text{OH}$ (**5**). As shown in Scheme 2, this involved initial conversion to the corresponding triflates **6** and subsequent iodination to give **7**. The syntheses of **6a** and **7a** have been reported previously.²¹ Details for **6b** and **7b**, which were isolated in analytically pure form in 99% and 87% yields, respectively, are provided in the Experimental Section.

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SCHEME 2^a

^a Key: (a) $(\text{CF}_3\text{SO}_2)_2\text{O}$, pyridine/ PhCF_3 , 0 °C to rt, 12 h; (b) KI, $\text{HOCH}_2\text{CH}_2\text{OH}$, reflux, 12 h.

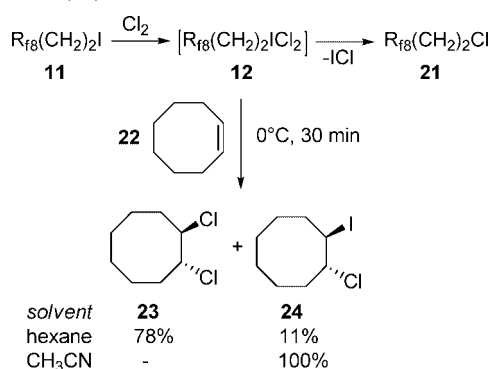
TABLE 1. Synthesis of Various Iodine(III) Dichloride Reagents Using Molecular Chlorine^a

R-I	R-ICl ₂	Time	Yield
4a	8a , <i>Ar</i> _{3,4} - <i>R</i> ₁₈ 	18 h	98 %
4b	8b , $n=6$, <i>Ar</i> _{2,4} - <i>R</i> ₁₆ 	18 h	71 %
4c	8c , $n=8$, <i>Ar</i> _{2,4} - <i>R</i> ₁₈ 	24 h	88 %
4d	8d , $n=10$, <i>Ar</i> _{2,4} - <i>R</i> ₁₀ 	19 h	75 %
4e	8e , <i>Ar</i> _{2,4,6} - <i>R</i> ₁₈ 	19 h	/
10	9a , $n=8$, $m=0$, <i>R</i> ₁₈ $\text{R}_{\text{fn}}-(\text{CH}_2)_m-\text{ICl}_2$	19 h ^b	/
7a	9b , $n=8$, $m=1$, <i>R</i> ₁₈ <i>CH</i> ₂ $\text{R}_{\text{fn}}-(\text{CH}_2)_m-\text{ICl}_2$	3 h ^b	78 %
7b	9c , $n=10$, $m=1$, <i>R</i> ₁₀ <i>CH</i> ₂ $\text{R}_{\text{fn}}-(\text{CH}_2)_m-\text{ICl}_2$	2 h ^b	84 %
11	12 , $n=8$, $m=2$, <i>R</i> ₁₈ <i>CH</i> ₂ <i>CH</i> ₂ $\text{R}_{\text{fn}}-(\text{CH}_2)_m-\text{ICl}_2$	5 h ^c	
13	14 , $n=0$, $m=8$ $\text{R}_{\text{fn}}-(\text{CH}_2)_m-\text{ICl}_2$	5 h ^c	
15	16 , <i>Ar</i> _{aq} HOOC 	19 h ^d	82 %
17	18 , <i>Ar</i> _{solid} 	3 h ^d	96 %
19	20 , <i>Ar</i> Ph-ICl ₂	2 h	95 %

^a Hexane solvent unless noted. ^b 0.3 equiv of $\text{CF}_3\text{SO}_3\text{H}$ was added. ^c Unstable product. ^d CHCl_3 solvent.

2.2. Syntheses and Properties of Aryl and Alkyl Iodine(III) Dichlorides. The corresponding fluorous aryl iodine(III) dichlorides were sought next. Thus, gaseous chlorine was bubbled through hexane solutions of **4a–e**. Workups of the resulting yellowish precipitates gave the target molecules **8a–d** in 98–71% yields as summarized in Table 1. No conversion was observed in the case of **4e**, showing that two substituents *ortho* to the iodine atom suppress chlorination under these conditions. Accordingly, the yields with the substrates with one *ortho* (and one *para*) substituent (denoted *Ar*_{2,4}-*R*_{fn}) were slightly lower than that without (*Ar*_{3,4}-*R*₁₈). The dichlorides **8a–c** were isolated in analytically pure form, and **8d** was of >98% purity.

The fluorous aryl iodine(III) dichlorides **8a–d** are pale yellow solids that are stable in a freezer for weeks. They exhibit good solubilities in CHCl_3 , decreasing as expected for **8b–d** as the

SCHEME 3. Trapping of Unstable $R_{18}CH_2CH_2ICl_2$ with Cyclooctene (22**)**


R_{18} segment is lengthened. They are slightly soluble in methanol, CH_2Cl_2 , Et_2O , and C_6F_{14} .

Related aliphatic fluorine(III) dichlorides would offer several potential advantages, such as shorter syntheses and lower molecular weights. Therefore, the chlorination of fluorine alkyl iodides with varying R_{18} segment and methylene spacer lengths was investigated. As can be seen from the results in Table 1, the number of methylene groups has a marked effect upon the reactivity with chlorine and on the stability of the resulting iodine(III) dichlorides. In the absence of a methylene spacer ($R_{18}I$, **10**), chlorination did not occur, presumably due to the electron-withdrawing effect of the perfluoroalkyl chain. Even the presence of 1 equiv of CF_3SO_3H as a catalyst did not activate **10** for chlorination. In contrast, and in accord with literature precedent noted above,¹⁹ the single methylene spacer in **7a,b** provided sufficient insulation, enabling chlorination to **9a,b** to proceed in the presence of 0.3 equiv of CF_3SO_3H . These compounds were isolated as analytically pure yellow solids that were stable in a freezer for weeks. However, they had very low solubilities in common organic solvents. The chlorination of commercial $R_{18}CH_2CH_2I$ (**11**), which features two methylene spacers, was studied next. Chlorine addition occurred in the absence of any CF_3SO_3H catalyst, but the presumed product $R_{18}CH_2CH_2ICl_2$ (**12**) rapidly decomposed upon attempted isolation, with evolution of gaseous iodine chloride and formation of the fluorine alkyl chloride $R_{18}CH_2CH_2Cl$ (**21**)²² (Scheme 3). A related nonfluorous substrate, octyl iodide (**13**), behaved similarly. The formation of **12** was strongly supported by a trapping reaction with cyclooctene (**22**) (Scheme 3). When the chlorination of **11** was performed at 0 °C in hexane, **12** precipitated. An equimolar amount of **22** was then added. The precipitate vanished and **22** was transformed mainly to *trans*-1,2-dichloro-cyclooctane (**23**; 78%). Some *trans*-1-chloro-2-iodocyclooctane (**24**; 11%) also formed as assayed by ¹H NMR spectroscopy of the crude reaction mixture. When an analogous experiment was conducted in acetonitrile, which yielded a brown solution characteristic of ICl , **24** was obtained as the sole product.

Next, the nonfluorous aryl iodine(III) dichlorides, 3-(dichloroiodo)benzoic acid (**16**) and 4,4'-bis(dichloroiodo)biphenyl (**18**), required for the alternative recycling protocols noted above, were prepared as described earlier.^{13d} Since the former slowly equilibrates in acetic acid with 3-iodobenzoic acid (**15**) and

TABLE 2. Reactions of Aryl and Alkyl Iodine(III) Dichlorides with Cyclooctene: Conditions Required for Complete Conversion^a

reagent	conditions (time, h; T, °C)
8a , $Ar_{3,4}-R_{18}$	8, rt
8b , $Ar_{2,4}-R_{16}$	8, rt
8c , $Ar_{2,4}-R_{18}$	8, 40
8d , $Ar_{2,4}-R_{10}$	8, 40
9a , $R_{18}CH_2$	3, 40
9b , $R_{10}CH_2$	10, 40
16 , Ar_{aq}	0.5, rt
18 , Ar_{solid}	8, 40
20 , Ar	2, rt

^a Determined by ¹H NMR spectroscopy.

chlorine,²³ it was stored as a solid in the freezer. The parent compound (dichloroiodo)benzene (**20**) was also prepared for reference experiments. This light- and heat-sensitive yellow crystalline solid can be stored in a freezer for approximately 2 weeks.^{1c} Although all of these reactions are known, the syntheses are detailed in the Supporting Information and the yields incorporated into Table 1 to facilitate comparisons with the fluorine reagents.

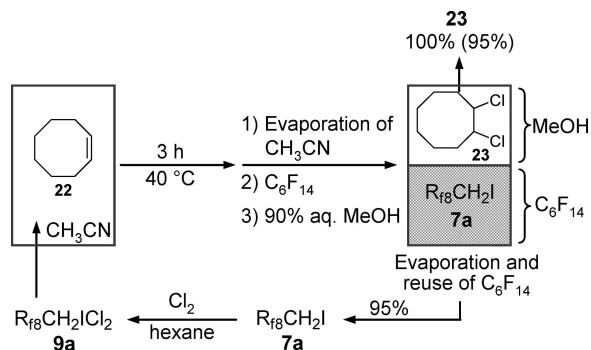
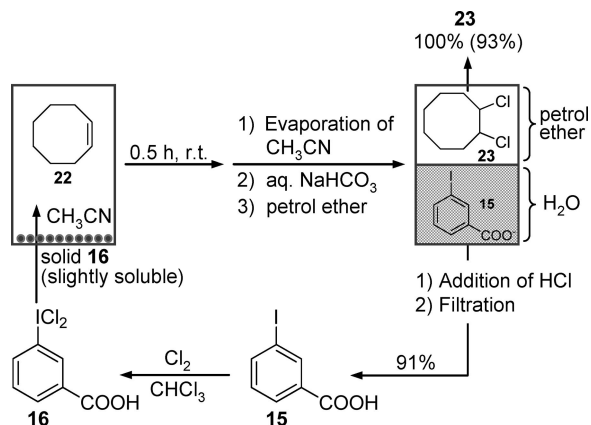
2.3. Aryl and Alkyl Iodine(III) Dichlorides As Recyclable Chlorinating Reagents. Several representative organic substrates were selected for chlorination studies: cyclooctene (**22**), anisole (**25**), 4-*tert*-butylphenol (**28**), 1,3-diphenylpropane-1,3-dione (**30**), and acetophenone (**32**). Reactions with the alkene **22** were screened first. In all experiments, 0.10 mmol of **22** was dissolved in 1.0 mL of acetonitrile, and 0.10 mmol of the iodine(III) reagent was added. The mixture was then stirred at room temperature or 40 °C until the reagent was consumed. The acetonitrile was replaced by a deuterated solvent and the conversion assayed by ¹H NMR. As summarized in Table 2, all iodine(III) reagents quantitatively transformed **22** into *trans*-1,2-dichlorocyclooctane (**23**). However, the aryl or alkyl substituent greatly affected reactivity. The resulting aryl and alkyl iodides were then recovered via various procedures as described below.

With the fluorine iodine(III) dichlorides **8** and **9**, a fluorine/organic liquid/liquid biphasic system was employed for separation of the product from the spent reagent. In the case of $Ar_{3,4}-R_{18}$ **8a**, which is soluble in acetonitrile, the chlorination was performed at room temperature under homogeneous conditions. After 8 h, the acetonitrile was replaced by C_6F_{14} and 80–90% aqueous methanol. The product **23** partitioned into the upper aqueous methanol phase, whereas the iodine(I) coproduct **4a** partitioned into the lower fluorine phase. In this context, the perfluoromethylcyclohexane/methanol partition coefficients of **4a,c** have been reported as (97.0–98.6):(3.0–1.4).^{11a} After phase separation, workup (Experimental Section) gave **23** in 95% yield and **4a** in 95% yields. The C_6F_{14} was recovered and reused.

The reagent $Ar_{2,4}-R_{16}$ **8b** could be employed in exactly the same way. However, the other fluorine iodine(III) dichlorides **8c,d** and **9a,b** were not as soluble in acetonitrile at room temperature. In the case of $Ar_{2,4}-R_{18}$ **8c**, homogeneous conditions could be achieved at 40 °C. Although $R_{18}CH_2$ **9a** remained incompletely soluble at 40 °C, the reaction mixture became

(22) (a) Consorti, C. S.; Jurisch, M.; Gladysz, J. A. *Org. Lett.* **2007**, *9*, 2309–2312. (b) Mandal, D.; Jurisch, M.; Consorti, C. S.; Gladysz, J. A. *Chem. Asian J.* **2008**, *3*, 1772–1782.

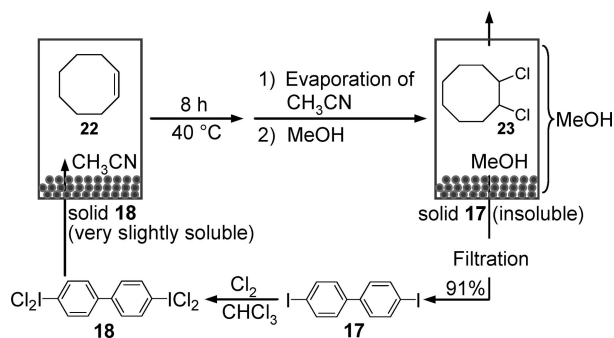
(23) Andrews, L. J.; Keefer, R. M. *J. Am. Chem. Soc.* **1959**, *81*, 4218–4223.

SCHEME 4. Schematic Representation of Chlorination with Fluorous Iodine(III) Dichlorides **8** and **9**, Illustrated for **9a**SCHEME 5. Schematic Representation of Chlorination with 3-(Dichloroiodo)benzoic Acid (**16**)

homogeneous as **22** was consumed. In contrast, in chlorinations involving reagents with longer R_{F10} perfluoroalkyl chains, Ar_{2,4}-R_{F10} **8d** and R_{F10}CH₂ **9b**, white solids persisted throughout the reaction, consistent with the low solubilities of the coproducts **4d** and **7b**. However, all of the fluorous aryl and alkyl iodides could be recycled exactly as **4a**, as illustrated for **7a** in Scheme 4. Yields were 97–90%.

Next, the analogous reaction of 3-(dichloroiodo)benzoic acid (Ar_{aq}, **16**) was investigated. This reagent did not completely dissolve in acetonitrile at room temperature. Nevertheless, it gave the fastest chlorination of **22**, requiring only 0.5 h. The acetonitrile was replaced by an aqueous/organic biphasic system consisting of 5% aqueous NaHCO₃ and petroleum ether. After phase separation, workup (Experimental Section) gave **23** in 93% yield and 3-iodobenzoic acid (**15**) in 91% yield (isolated by filtration of the acidified aqueous phase). The recycling procedure is summarized in Scheme 5. With all of the substrates that follow below, recoveries of **15** were 91–85%.

The reagent 4,4'-bis(dichloroiodo)biphenyl (Ar_{solid}, **18**) was then studied. Chlorinations were conducted at 40 °C due to the very low solubility of **18** in acetonitrile at room temperature. However, the reaction mixture remained heterogeneous. Over the course of 8 h, undissolved pale yellow **18** was replaced by the white 4,4'-diiodobiphenyl (**17**) coproduct. The acetonitrile was then replaced by methanol, in which **17** is poorly soluble. Simple filtration gave **17** in 91% yield. The product **23** remained dissolved in the filtrate, which also contained traces of **17**. When hexane was used in place of methanol, recoveries of **17** were lower. The recycling procedure is summarized in Scheme 6. With all of the substrates that follow, recoveries of **17** were 91–89%.

SCHEME 6. Schematic Representation of Chlorination with 4,4'-Bis(dichloroiodo)biphenyl (**18**)TABLE 3. Reactions of Aryl and Alkyl Iodine(III) Dichlorides with Anisole (**25**)

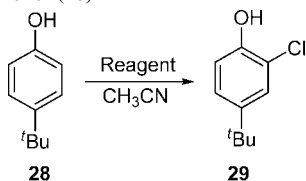
reagent	conditions (time, h; T, °C)	conv ^a (%)	ratio 26/27	selectivity 26/27
8a , Ar _{3,4} -R _{F8}	24, rt	100	48:52	0.92
8b , Ar _{2,4} -R _{F6}	8, rt	100	57:43	1.33
8c , Ar _{2,4} -R _{F8}	24, 40	92	87:13	6.69
8d , Ar _{2,4} -R _{F10}	8, 40	100	71:29	2.45
9a , R _{F8} CH ₂	8, 40	100	86:14	6.14
9b , R _{F10} CH ₂	24, 40	100	79:21	3.76
16 , Ar _{aq}	1, rt	100	88:12	7.33
18 , Ar _{solid}	24, 40	100	82:18	4.56
20 , Ar	2, rt	95	80:20	4.00

^a Determined by ¹H NMR spectroscopy.

An analogous reaction with (dichloroiodo)benzene **20** proceeded quite rapidly (2 h) under homogeneous conditions at room temperature. However, **23** could only be separated from the coproduct iodobenzene (**19**) by column chromatography.

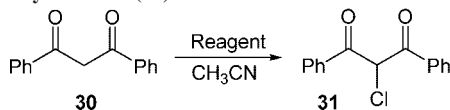
In order to gauge the generality of the preceding chlorination and recovery protocols, organic substrates bearing other functional groups were investigated. The chlorination of anisole (**25**) normally gives a mixture of *p*-chloroanisole (**26**) and *o*-chloroanisole (**27**). As shown in Table 3, reaction with Ar_{3,4}-R_{F8} **8a** in acetonitrile required ca. 24 h at room temperature and afforded a 48:52 **26/27** ratio. Conversions were assayed as in Table 2. With Ar_{2,4}-R_{F6} **8b**, which features a substituent *ortho* to the iodine, the selectivity for *para* chlorination was slightly higher (57:43). When the lengths of the ponytails were extended (Ar_{2,4}-R_{F8} **8c** and Ar_{2,4}-R_{F10} **8d**) *para* selectivities increased further (87:13 and 71:29), despite the higher reaction temperatures (40 °C). Curiously, selectivities with the fluorous alkyl iodine(III) dichlorides R_{F8}CH₂ **9a** and R_{F10}CH₂ **9b** (86:14 and 79:21) were similar. Interestingly, the nonfluorous reagent Ar_{aq} **16** proved to be the most reactive and selective of all, giving a complete reaction within 1 h at room temperature and a 88:12 **26/27** ratio. Ar_{solid} **18**, being very poorly soluble in acetonitrile, required heating and longer reaction times, while **20** was more reactive and gave a selectivity similar to that of **18** (80:20 vs 82:18).

The chlorination of another arene, 4-*tert*-butylphenol (**28**, Table 4), was analogously investigated. In all cases, only 2-chloro-4-*tert*-butylphenol (**29**) was observed. No dichlorination

TABLE 4. Reactions of Aryl and Alkyl Iodine(III) Dichlorides with 4-*tert*-Butylphenol (**28**)

reagent	conditions (time, h; T, °C)	conv ^a (%)
8a , Ar _{3,4} -R ₁₈	24, rt	76
8b , Ar _{2,4} -R ₁₆	9, rt	81
8c , Ar _{2,4} -R ₁₈	24, 40	75
8d , Ar _{2,4} -R ₁₀	24, 40	64
9a , R ₁₈ CH ₂	8, 40	78
9b , R ₁₀ CH ₂	25, 40	64
16 , Ar _{aq}	24, rt	85
18 , Ar _{solid}	24, 75	66
20 , Ar	8, rt	95

^a Determined by ¹H NMR spectroscopy.

TABLE 5. Reactions of Aryl and Alkyl Iodine(III) Dichlorides with Dibenzoylmethane (**30**)

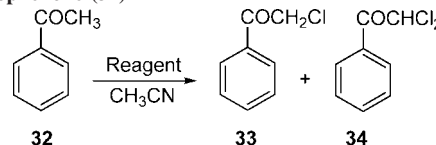
reagent	conditions (time, h; T, °C)	conv ^a (%)
8a , Ar _{3,4} -R ₁₈	26, rt	100
8b , Ar _{2,4} -R ₁₆	20, rt	100
8c , Ar _{2,4} -R ₁₈	24, 40	94
8d , Ar _{2,4} -R ₁₀	24, 40	100
9a , R ₁₈ CH ₂	6, 40	100
9b , R ₁₀ CH ₂	24, 40	91
16 , Ar _{aq}	3, 0	95
18 , Ar _{solid}	24, 75	95
20 , Ar	3, rt	100

^a Determined by ¹H NMR spectroscopy.

products were detected. The fluorous reagents **8** and **9** showed similar reactivity patterns as with anisole (**25**). Conversions with the R₁₀ species **8d** and **9b** were lower than those with the R₁₈ analogues **8c** and **9a**. Chlorinations with Ar_{aq} **16** and Ar_{solid} **18** required longer reaction times and/or higher temperatures. The conversion with **20** was particularly high (95%), but as with **16** and **18** a longer reaction time was required as compared to Table 3.

The same series of reagents was next assayed for the chlorination of the 1,3-diketone **30**. As summarized in Table 5, all afforded 2-chloro-1,3-diphenylpropane-1,3-dione (**31**) with good conversions and selectivities. No dichlorinated product was detected. The overall reactivity pattern was similar to those in Tables 3 and 4. Among the fluorous reagents, the aliphatic species R₁₈CH₂ **9a** again exhibited one of the higher reactivities. But Ar_{aq} **16** was distinctly more reactive, chlorinating **30** even at 0 °C. The poorly soluble reagent **18** again needed higher reaction temperatures for efficient conversion. As with **25** (Table 3), **20** gave the highest conversion.

Analogous chlorinations of acetophenone (**32**, Table 6) afforded both monochlorinated and dichlorinated products (**33**, **34**). With Ar_{3,4}-R₁₈ **8a**, **33** and **34** were obtained in almost equal amounts. When *ortho*-substituted Ar_{2,4}-R₁₆ **8b** and Ar_{2,4}-R₁₈ **8c** were used, selectivities for monochlorinated **33** increased to ca. 70:30. Very similar ratios were obtained with the fluorous alkyl iodine(III) dichlorides **9**. As in Table 3, 3-(dichloroiodo)benzoic

TABLE 6. Reactions of Aryl and Alkyl Iodine(III) Dichlorides with Acetophenone (**32**)

reagent	conditions (time, h; T, °C)	conv ^a (%)	ratio 33/34	selectivity 33/34
8a , Ar _{3,4} -R ₁₈	26, rt	67	49:51	0.97
8b , Ar _{2,4} -R ₁₆	8, rt	76	69:31	2.26
8c , Ar _{2,4} -R ₁₈	24, 40	78	72:28	2.57
8d , Ar _{2,4} -R ₁₀	8, 40	74	61:39	1.55
9a , R ₁₈ CH ₂	5, 40	78	70:30	2.34
9b , R ₁₀ CH ₂	24, 40	67	72:28	2.57
16 , Ar _{aq}	3, 0	80	95:5	19.00
18 , Ar _{solid}	24, 75	65	60:40	1.50
20 , Ar	20, rt	79	75:25	3.00

^a Determined by ¹H NMR spectroscopy.

acid (**16**) afforded the highest selectivity (95:5). Furthermore, **16** was completely consumed after only 3 h at 0 °C. When the same reaction was repeated at room temperature, the selectivity decreased to 80:20. The poorly soluble reagent Ar_{solid} **18** was again the least reactive. Extended periods at 75 °C were required to achieve comparable conversions, and this was likely responsible for the meager selectivity (60:40).

3. Conclusion

This study has established that the fluorous aryl and alkyl iodine(III) dichlorides **8a–d** and **9a,b** are easily synthesized by chlorinations of the corresponding aryl and alkyl iodides and are effective and conveniently recycled chlorinating agents for a variety of aliphatic and aromatic unsaturated organic substrates. They can be isolated in yields ranging from 98% to 71% (Table 1), for which we consider the precipitation conditions amenable to further optimization. However, analogues of **9a,b** that lack or have longer methylene spacers are either not accessible via chlorination or rapidly decompose at room temperature (Scheme 3). We speculate in passing that it still may be possible to access species of the type R_nI(OC(=O)CF₃)₂.^{11b,c} The bis(acetate) of the doubly *ortho*-substituted fluorous aryl iodide **4e** (Table 1), which also resists direct chlorination, is also easily prepared.^{11a}

Among the aromatic fluorous reagents, **8a,b** generally show the highest reactivity. This may be due to the lack of an *ortho* substituent in **8a**, and the greater solubility of **8b** vs **8c,d**. The aliphatic fluorous reagents **9a,b** are also less reactive, but all substrates investigated can be chlorinated with all of the fluorous iodine(III) reagents on convenient time scales between room temperature and 40 °C. One advantage of the *ortho*-substituted reagents is the higher selectivities in Tables 3 and 6. The recoveries of the fluorous iodide coproducts per Scheme 4 are uniformly high (97–90%). Overall, we judge the best combination of performance characteristics to be found with **8c** and **9a**.

This work also significantly extends past studies with the nonfluorous recyclable aryl iodine(III) reagents Ar_{aq} **16** and Ar_{solid} **18** (Table 1), providing the first simple mono- and dichlorinations. The complementary protocols in Schemes 5 and 6 return the aryl iodide coproducts in 91–85% and 91–89% yields, respectively. We do not view these yield ranges as much different than those with the fluorous iodides. Nonetheless,

unless multirun averaging and/or optimization were to alter this picture, a slight recycling edge seems to lie with the fluorous reagents. Of course, the traditional reagent (dichloriodo)benzene (Ar **20**), for which the coproduct must be recovered chromatographically from the reactions in Tables 2–6, is not competitive with any of these.

The reactivities of Ar_{aq} **16**, Ar_{solid} **18**, and Ar **20** provide a number of interesting contrasts with the fluorous reagents. In general, the carboxylic acid containing reagent Ar_{aq} **16** is the most reactive (Tables 2, 3, 5, 6). Often Ar **20** is the next most reactive (Tables 2, 3, 5), and edges out Ar_{aq} **16** in Table 4. The reactivity of poorly soluble Ar_{solid} **18** generally parallels that of the least soluble fluorous reagents, but can be much lower (Tables 4–6). This is clearly the least promising reagent for further development. In the two reactions that give product mixtures (Tables 3, 6) Ar_{aq} **16** also provides the highest selectivities, perhaps in part as it can be employed at lower temperatures.

In summary, this work has contributed to the development of both hypervalent iodine and green chemistry through the synthesis of new fluorous aryl and alkyl iodine(III) dichlorides that are effective and easily recyclable chlorinating agents and by careful comparisons to known nonfluorous analogues that can be recycled by alternative protocols. Additional efforts involving recyclable reagents and catalysts are underway in all of the authors' laboratories and will be reported in due course.

4. Experimental Section

4.1. Representative Synthesis of a Fluorous Aryl Iodine(III) Dichloride 8 (Others Are Supplied in the Supporting Information). **1,3-(R₁₆CH₂CH=CH)₂C₆H₄ (2b).** A three-necked flask was charged with (R₁₆CH₂CH₂)₂Ph₃P⁺I⁻ (22.32 g, 30.5 mmol),²⁰ K₂CO₃ (8.28 g, 60.0 mmol), isophthalaldehyde (1.97 g, 14.7 mmol), *p*-dioxane (200 mL), and distilled water (0.6 mL). The mixture was stirred overnight at 95 °C and cooled to room temperature. All volatiles were removed by rotary evaporation. Then CH₂Cl₂ (200 mL) and water (200 mL) were added. The organic phase was separated and dried (MgSO₄). The solvent was removed by rotary evaporation, and the residue was dissolved in petroleum ether and chromatographed (silica gel column, CH₂Cl₂/hexane, 1:1 v/v, R_f(TLC) = 0.95). The solvent was removed from the product containing fractions by rotary evaporation to give **2b** as a yellow oil of moderate purity (9.087 g, 11.44 mmol, 78%). ¹H NMR (400 MHz, CDCl₃): δ = 7.38–7.36 (m, 1H), 7.16–7.14 (m, 2H), 7.07–7.05 (m, 1H), 6.84–6.81 (m, 2H), 5.80–5.77 (m, 2H), 3.13–2.92 (m, 4H). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ = 136.2, 135.1, 128.7, 128.2, 127.6, 118.4 (t, ³J_{CF} = 4 Hz), 30.6 (t, ²J_{CF} = 23 Hz). IR (oil film, cm⁻¹): 3038 (w), 2347 (w), 1447 (w), 1200 (s), 1146 (s), 969 (w), 899 (m), 814 (w).

1,3-(R₁₆(CH₂)₃)₂C₆H₄ (3b). A round-bottom flask with a gas inlet was charged with Pd/C 10% (0.400 g, 0.37 mmol), **2b** (9.087 g, 11.44 mmol), hexane (35 mL), and ethanol (35 mL). The mixture was flushed with hydrogen and connected to a thick-walled hydrogen balloon with a PVC hose. The mixture was stirred at room temperature overnight and then filtered through a plug of Celite. The plug was washed with hexane (80 mL). The filtrate was concentrated, and CH₂Cl₂/hexane (1:1 v/v) was added. The sample was filtered through a silica gel plug. The solvent was removed by rotary evaporation to give **3b** as a clear oil (8.853 g, 11.09 mmol, 97%). Anal. Calcd for C₂₄H₁₆F₂₆: C, 36.09; H, 2.01. Found: C, 35.80; H, 1.99. ¹H NMR (400 MHz, CDCl₃): δ = 7.28–7.24 (m, 1H), 7.06–7.00 (m, 3H), 2.72–2.69 (m, 4H), 2.08–1.95 (m, 8H). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ = 140.9, 128.8, 128.4, 126.4, 34.9, 30.2 (t, ²J_{CF} = 23 Hz), 21.8. IR (oil film, cm⁻¹): 2961 (w), 2347 (w), 1467 (w), 1366 (w), 1316 (w), 1231

(s), 1189 (s), 1143 (s), 1119 (s), 1077 (w), 1015 (m), 810 (m), 791 (m). MS (FAB): 798 (70) [**3b**]⁺, 451 (100) [**3b** – CH₂CH₂R₁₆]⁺.

2,4-(R₁₆(CH₂)₃)₂C₆H₃I (4b). A flask was charged with **3b** (8.853 g, 11.09 mmol), I₂ (11.1 g, 44.0 mmol), H₃IO₆ (9.50 g, 42.0 mmol), and a mixture of H₂SO₄, acetic acid, and water (3:100:20 v/v/v, 100 mL). The mixture was stirred overnight at 65 °C and cooled to room temperature. Water (100 mL) and ether (500 mL) were added. The organic phase was separated, washed with aqueous Na₂S₂O₃ (1.0 M, 200 mL), and dried (MgSO₄). After solvent removal, hexane/CH₂Cl₂ (1:1 v/v) was added, and the mixture was filtered through a silica gel plug. The solvent was removed from the filtrate by rotary evaporation to give **4b** as a yellow solid (7.690 g, 8.32 mmol, 75%). Mp (capillary): 31.5–31.8 °C. Anal. Calcd for C₂₄H₁₅F₂₆I: C, 31.17; H, 1.62. Found: C, 31.29; H, 1.83. ¹H NMR (400 MHz, CDCl₃): δ = 7.75 (d, ³J_{HH} = 8 Hz, 1H), 7.03 (s, 1H), 6.76 (d, ³J_{HH} = 8 Hz, 1H), 2.96, 2.67 (2t, ³J_{HH} = 8 Hz, 4H), 2.19–1.88 (m, 8H). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ = 143.5, 141.3, 140.0, 129.5, 128.4, 97.5, 39.7, 34.4, 30.1–30.0 (apparent m), 21.7, 20.8. IR (oil film, cm⁻¹): 2957 (w), 2872 (w), 2347 (w), 1463 (w), 1366 (w), 1320 (w), 1231 (s), 1189 (s), 1143 (s), 1119 (s), 1077 (m), 1011 (m), 845 (m). MS (EI): 924 (100) [**4b**]⁺, 923 (80) [**4b** – H]⁺, 797 (20) [**4b** – I], 703 (80), 577 (40).

2,4-(R₁₆(CH₂)₃)₂C₆H₃ICl₂ (8b). Hexane (40 mL), **4b** (0.924 g, 1.00 mmol), and chlorine were combined in a procedure analogous to that for **8a**. An identical workup gave **8b** as a yellow solid (0.706 g, 0.71 mmol, 71%). Mp (capillary): 68–70 °C. Iodometric titration: 99% purity. Anal. Calcd for C₂₄H₁₅Cl₂F₂₆I: C, 28.97; H, 1.52. Found: C, 29.32; H, 1.43. ¹H NMR (300 MHz, CDCl₃): δ = 8.20 (d, ³J_{HH} = 8.4 Hz, 1H), 7.29 (d, ⁴J_{HH} = 2.2 Hz, 1H), 7.14 (dd, ³J_{HH} = 8.4 Hz, ⁴J_{HH} = 2.2 Hz, 1H), 3.19 (t, ³J_{HH} = 7.5 Hz, 2H), 2.81 (t, ³J_{HH} = 7.7 Hz, 2H), 1.92–2.35 (m, 8H). ¹³C{¹H} NMR (76 MHz, CDCl₃): δ = 147.2, 141.2, 137.3, 130.3, 130.2, 38.3, 34.8, 30.3 (t, ²J_{CF} = 22 Hz), 21.7, 21.3. ¹⁹F NMR (282 MHz, CDCl₃): δ = -81.4 (t, ³J_{FF} = 10 Hz, 6F), -114.6 (m, 4F), -122.4 (m, 4F), -123.4 (m, 4F), -123.9 (m, 4F), -126.7 (m, 4F).

4.2. Representative Synthesis of a Fluorous Alkyl Iodine(III) Dichloride 9. **R₁₀CH₂OSO₂CF₃ (6b).** A three-necked flask was fitted with a nitrogen inlet and dropping funnel and charged with R₁₀CH₂OH (**5b**; 5.107 g, 9.29 mmol), pyridine (1.12 g, 1.15 mL, 14.0 mmol), and CF₃C₆H₅ (50 mL) under nitrogen. The flask was cooled to 0 °C, and after 30 min, (CF₃SO₂)₂O (4.23 g, 3.44 mL, 15.0 mmol) was slowly added. The cold bath was removed, and the light red suspension was stirred overnight. Water was added (60 mL), and the organic phase was separated and dried (MgSO₄). The solvent was removed by rotary evaporation, and the solid residue was dissolved in petroleum ether and chromatographed (silica gel column, petroleum ether/ethyl acetate, 4:1 v/v, R_f(TLC) = 0.95). The solvent was removed from the product containing fractions by rotary evaporation to give **6b** as a white solid (6.261 g, 9.18 mmol, 99%). Mp (capillary): 84.4 °C. Anal. Calcd for C₁₂H₂F₂₄O₃S: C, 21.11; H, 0.29; S, 4.69. Found: C, 20.60; H, 0.35; S, 4.87. ¹H NMR (400 MHz, acetone-*d*₆): δ = 5.52 (t, ³J_{HF} = 15 Hz, 2H). ¹³C{¹H} NMR (100 MHz, C₆F₁₄, internal lock C₆D₆): δ = 71.0 (t, ²J_{CF} = 27 Hz). IR (powder film, cm⁻¹): 2961 (w), 2926 (w), 2856 (w), 1420 (m), 1204 (s), 1139 (s), 1081 (w), 1027 (m), 883 (m), 822 (m). MS (EI): 663 (15) [**6b** – HF]⁺, 613 (30), 549 (15), 511 (35), 463 (100).

R₁₀CH₂I (7b). A flask was charged with **6b** (6.261 g, 9.18 mmol), KI (7.60 g, 45.78 mmol), and ethylene glycol (35 mL). The mixture was refluxed at 200 °C overnight and allowed to cool to room temperature. Water (100 mL) and hexane (40 mL) were added. The organic phase was separated and dried (MgSO₄). The solvent was removed by rotary evaporation. The white solid was dissolved in petroleum ether and chromatographed (silica gel column, petroleum ether/ethyl acetate, 20:1 v/v). The solvent was removed from the product containing fractions by rotary evaporation to give **7b** as a white solid (5.297 g, 8.03 mmol, 87%). Mp (capillary): 80.8 °C. Anal. Calcd for C₁₁H₂F₂₁I: C, 20.00; H, 0.30. Found: C, 20.05; H, 0.49. ¹H NMR (400 MHz, acetone-*d*₆): δ =

4.06 (t, $^3J_{\text{HF}} = 18$ Hz, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, acetone- d_6): $\delta = -2.79$ (t, $^2J_{\text{CF}} = 25$ Hz). IR (powder film, cm^{-1}): 1420 (w), 1374 (w), 1343 (w), 1204 (s), 1146 (s), 1069 (w), 1046 (m), 891 (m).

$\text{R}_{10}\text{CH}_2\text{ICl}_2$ (9b). Hexane (30 mL), $\text{R}_{10}\text{CH}_2\text{I}$ (7b; 0.660 g, 1.00 mmol), $\text{CF}_3\text{SO}_3\text{H}$ (0.026 mL, 0.30 mmol), and Cl_2 were combined in a procedure analogous to that for 9a. An identical workup gave 9b as a yellow solid (0.614 g, 0.84 mmol, 84%). Mp (capillary): 135–138 °C. Since 9b was insoluble in all common solvents, it could not be characterized by NMR. Iodometric titration: 98% purity. Anal. Calcd for $\text{C}_{11}\text{H}_2\text{Cl}_2\text{F}_2\text{I}$: C, 18.08; H, 0.28. Found: C, 18.36; H, 0.33.

4.3. Generation of $\text{R}_{18}\text{CH}_2\text{CH}_2\text{ICl}_2$ (12). Chlorination of $\text{R}_{18}\text{CH}_2\text{CH}_2\text{I}$ (11). A flask was charged with acetonitrile (10 mL) and 11 (0.574 g, 1.00 mmol) and cooled to 0 °C. The mixture was saturated with molecular chlorine with stirring. When the sample was warmed to room temperature, rapid decomposition of $\text{R}_{18}\text{CH}_2\text{CH}_2\text{ICl}_2$ (12) was observed with evolution of brown gaseous iodine chloride. After 2 h, the acetonitrile was removed under reduced pressure. ^1H NMR (300 MHz, CDCl_3) analysis revealed the formation of $\text{R}_{18}\text{CH}_2\text{CH}_2\text{Cl}$ (21): $\delta = 3.70$ – 3.75 (m, 2H), 3.22–3.28 (m, 2H).²²

Trapping of $\text{R}_{18}\text{CH}_2\text{CH}_2\text{ICl}_2$ (12). A flask was charged with $\text{R}_{18}\text{CH}_2\text{CH}_2\text{I}$ (11; 0.574 g, 1.00 mmol) and acetonitrile (10 mL). The solution was cooled to 0 °C and saturated with Cl_2 with stirring. Over the course of 15 min, a brown solution was obtained. Then cyclooctene (22; 0.110 g, 1.00 mmol) was added and the mixture decolorized. After 30 min, the acetonitrile was evaporated under reduced pressure. NMR analysis revealed the formation of *trans*-1-chloro-2-iodocyclooctane (24) as the sole product. ^1H NMR (300 MHz, CDCl_3): $\delta = 4.60$ (ddd, $^3J_{\text{HH}} = 9.0, 7.0, 2.3$ Hz, 1H), 4.47 (ddd, $^3J_{\text{HH}} = 9.0, 7.4, 1.7$ Hz, 1H), 1.95–2.15 (m, 2H), 2.22–2.41 (m, 2H), 1.38–1.91 (m, 8H). $^{13}\text{C}\{^1\text{H}\}$ NMR (76 MHz; CDCl_3 ; Me_4Si): $\delta = 70.1, 41.9, 34.5, 33.2, 27.9, 25.6, 25.2, 25.1$. Compound 24 is unstable and decomposes during the purification procedure. Its structure was confirmed by comparison of ^1H NMR chemical shifts of independently prepared sample by reaction of cyclooctene (22) with ICl in CH_3CN .

4.4. Typical Procedure for the Chlorination of 22, 25, 28, 30, and 32 Using the Aryl and Alkyl Iodine(III) Dichlorides 8, 9, 16, 18, and 20. The iodine(III) dichloride (0.10 mmol) was added to 0.10 mmol of the substrate in 1 mL of acetonitrile. As summarized in Tables 2–6, the mixture was stirred at 0–70 °C for 0.5–26 h. The progress of the reaction was monitored by TLC. When the iodine(III) dichloride was consumed, the acetonitrile was evaporated under reduced pressure. Substrate conversions were determined by redissolving the samples in CDCl_3 and integrating characteristic substrate and product signals. Subsequent workup depended upon the chlorinating reagent as detailed below. The identities of the chlorinated products were confirmed by NMR and

comparisons with literature data (see the Supporting Information) or commercial samples (for 26 and 27).

Liquid/Liquid Fluorous/Organic Phase Separation for Chlorination Using Fluorous Iodine(III) Dichlorides (8 and 9). Perfluorohexane (2 mL) and 80–90% aqueous methanol (2 mL) were added to the reaction mixture. The fluorous and organic phases were separated, and the fluorous phase was further washed with 80–90% aqueous methanol (3×2 mL). The combined methanol/ H_2O phases were extracted with hexane (3×3 mL). The solvent was removed from the combined extracts by rotary evaporation, and the crude chlorination product was analyzed by ^1H NMR spectroscopy. Evaporation of the perfluorohexane from the fluorous phase gave the fluorous iodides 4 and 7 in 90–97% yields. The perfluorohexane was recovered and reused as well.

Liquid/Liquid Organic/Aqueous Phase Separation for Chlorination Using *m*- $\text{HOOC}_6\text{H}_4\text{ICl}_2$ (16). The reaction mixture was transferred to a separatory funnel, and 5% aqueous NaHCO_3 (5 mL) was added. The product was extracted with petroleum ether (3×3 mL). The solvent was removed from the combined extracts by rotary evaporation and the crude chlorination product analyzed by ^1H NMR. The aqueous phase was acidified with 5% aqueous HCl (15 mL). The white precipitate was isolated by filtration and air-dried to give 15 in 85–91% yields.

Solid/Liquid Biphasic Separation for Chlorination Using 4,4'- $\text{Cl}_2\text{IC}_6\text{H}_4\text{C}_6\text{H}_4\text{ICl}_2$ (18). Methanol was added to the reaction mixture, and the pale yellow precipitate was isolated by filtration and air-dried to give 4,4'-diiodobiphenyl (17) in 89–91% yields. The methanol was evaporated under reduced pressure, and the crude chlorination product was analyzed by ^1H NMR.

Acknowledgment. This research has been supported by the Ministry of Higher Education, Science and Technology of the Republic of Slovenia, the Young Researcher Program (A.P.) of the Republic of Slovenia, Deutsche Forschungsgemeinschaft (DFG, GL 300/3-3), the Welch Foundation, and the European Union (COST D29 working group 0011-03). We are grateful to the National NMR Centre at the National Institute of Chemistry in Ljubljana, the Mass Spectroscopy Centre at the JSI, and Faculty of Chemistry and Chemical Technology University of Ljubljana for elemental analyses (T. Stipanovič and B. Stanovnik).

Supporting Information Available: Additional experimental procedures for syntheses of analogues of the compounds in sections 4.1 and 4.2 and nonfluorous aryl iodine(III) dichlorides, spectroscopic data of chlorinated products, and copies of NMR spectra for all new compounds. This material is available free of charge via the Internet at <http://pubs.acs.org>.

JO900233H