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Oxidations of Secondary Alcohols to Ketones Using Easily Recyclable Bis(trifluoroacetate) Adducts of Fluorous Alkyl Iodides, $CF_3(CF_2)_{n-1}I(OCOCF_3)_2$

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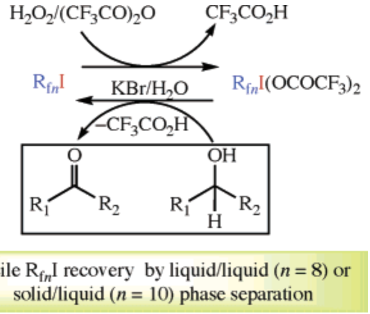

Reactions of commercial fluorous alkyl iodides $R_{fn}I$ (**1**-R_{fn}; $R_{fn} = CF_3(CF_2)_{n-1}$; $n = 7, 8, 10, 12$) with 80% H_2O_2 and trifluoroacetic anhydride give $R_{fn}I(OCOCF_3)_2$ (**2**-R_{fn}; 97−89%). These efficiently oxidize aliphatic and benzylic secondary alcohols to the corresponding ketones (92−57%) in the presence of aqueous KBr and absence of organic or fluorous solvents. Bromide ion activates the reagents and/or generates a relay oxidant such as a functional equivalent of Br^+. Oxidations are much more rapid (<30 min, **2**-R_{f8}; <70 min, **2**-R_{f10}) than with other iodine(III) compounds under similar conditions. The coproducts **1**-R_{fn} can be recovered by adding 3−5 volumes of methanol to the reaction mixtures. Fluorous/methanolic liquid/liquid (**1**-R_{f8}) or solid/liquid (**1**-R_{f10}) biphase systems result. The recovered **1**-R_{fn} can be reoxidized to **2**-R_{fn} and reused. Three cycles are conducted with 1-phenyl-1-propanol and **2**-R_{f10}. The propiophenone yields range from 92% to 83% per cycle, and after the final cycle 59−57% of the original charge of the fluorous iodide species is recovered.

Introduction

Hypervalent iodide compounds play increasingly important roles in organic synthesis.[1] As summarized in a recent critique, many of the most frequently utilized reagents, for example IBX or the Dess−Martin reagent, rate poorly from the standpoint of atom economy and Sheldon's environmental factor *E*.[2] Stoichiometric amounts of waste products with relatively high molecular weights, iodine-containing arenes, are commonly produced. Hence, a number of approaches to recyclable hypervalent iodide reagents have been reported.[3−9] These involve both polymeric and molecular species, and representatives of various classes are illustrated in Figure 1 (**I**−**X**). Protocols that involve

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(1) (a) Wirth, T. *Angew. Chem., Int. Ed.* **2005**, *44*, 3656; *Angew. Chem.* **2005**, *117*, 3722 and earlier review literature cited therein. (b) Tohma, H.; Kita, Y. *Adv. Synth. Catal.* **2004**, *346*, 111. (c) Zhdankin, V. V.; Stang, P. J. *Chem. Rev.* **2002**, *102*, 2523.

(2) Lenoir, D. *Angew. Chem., Int. Ed.* **2006**, *45*, 3206; *Angew. Chem.* **2006**, *118*, 3280.

(3) Togo, H.; Sakuratani, K. *Synlett* **2002**, 1966 and earlier work cited in this account dealing with polymer supported hypervalent iodine reagents.

(4) Polymer supported $PhI(OCOCH_3)_2$: (a) Ficht, S.; Mülbaier, M.; Giannis, A. *Tetrahedron* **2001**, *57*, 4863. (b) Teduka, T.; Togo, H. *Synlett* **2005**, 923. (c) Hossain, Md. D.; Kitamura, T. *Synthesis* **2006**, 1253.

(5) Polymer supported IBX: (a) Mülbaier, M.; Giannis, A. *Angew. Chem., Int. Ed.* **2001**, *40*, 4393; *Angew. Chem.* **2001**, *113*, 4530. (b) Sorg, G.; Mengel, A.; Jung, G.; Rademann, J. *Angew. Chem., Int. Ed.* **2001**, *40*, 4395; *Angew. Chem.* **2001**, *113*, 4532. (c) Lei, Z.; Denecker, C.; Jegasothy, S.; Sherrington, D. C.; Slater, N. K. H.; Sutherland, A. J. *Tetrahedron Lett.* **2003**, *44*, 1635. (d) Chung, W.-J.; Kim, D.-K.; Lee, Y.-S. *Tetrahedron Lett.* **2003**, *44*, 9251.

(6) Reagents recoverable via solid/liquid-phase separations: (a) Tohma, H.; Maruyama, A.; Maeda, A.; Maegawa, T.; Dohi, T.; Shiro, M.; Morita, T.; Kita, Y. *Angew. Chem., Int. Ed.* **2004**, *43*, 3595; *Angew. Chem.* **2004**, *116*, 3679. (b) Dohi, T.; Maruyama, A.; Yoshimura, M.; Morimoto, K.; Tohma, H.; Shiro, M.; Kita, Y. *Chem. Commun.* **2005**, 2205.

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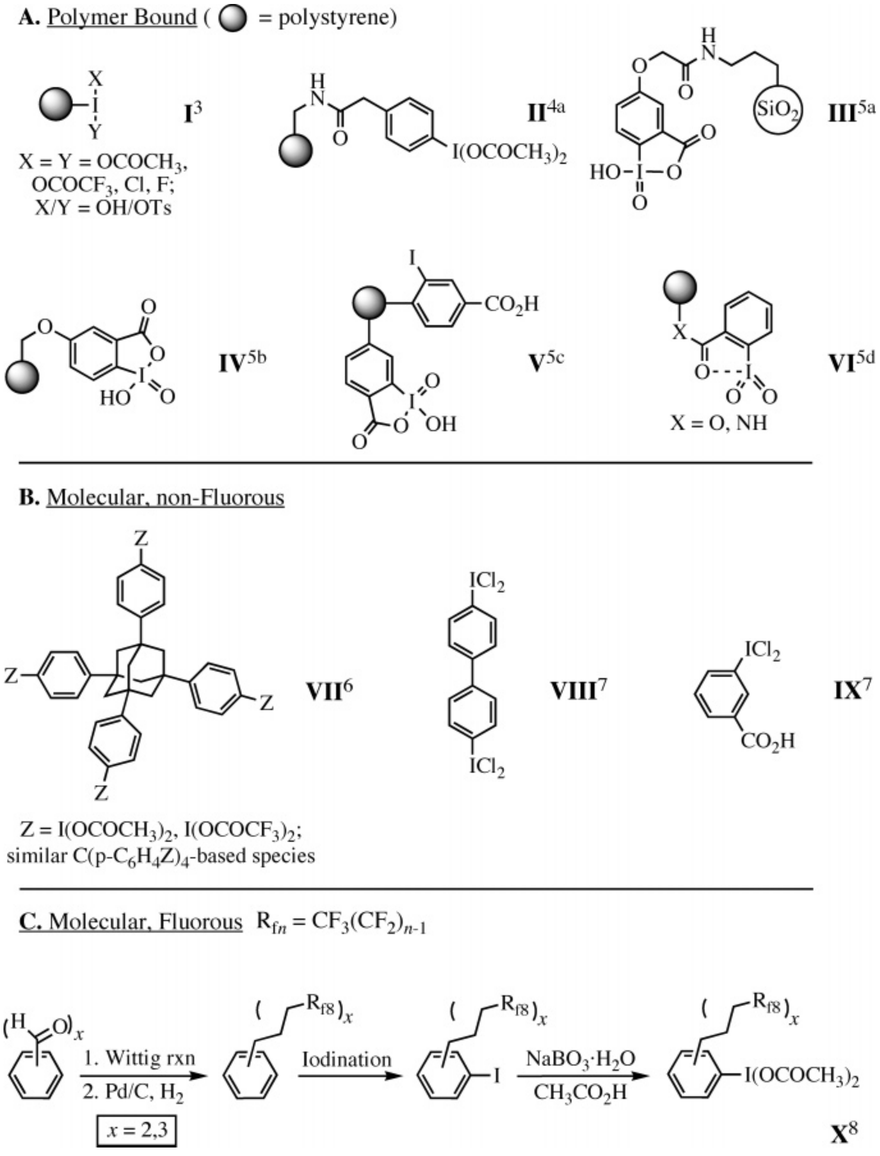

FIGURE 1. Representative Recyclable Hypervalent Iodide Reagents.

catalytic quantities of the hypervalent iodide compound have also been recently described.[10]

However, many of the recyclable reagents require multistep syntheses. For example, in our own first efforts, we were interested in exploiting fluorous recovery strategies,[11] which commonly employ "ponytailed" species with substituents $R_{fn}(CH_2)_m$ ($R_{fn} = CF_3(CF_2)_{n-1}$). Toward this end, fluorous aryl iodides of the formula $(R_{f8}(CH_2)_3)_xC_6H_{5-x}I$ ($x = 2, 3$) were prepared as shown in Figure 1C and converted to the iodine(III) bis(acetate) adducts $(R_{f8}(CH_2)_3)_xC_6H_{5-x}I(OCOCH_3)_2$ (**X**).[8] The latter proved to be excellent reagents for oxidations of hydroquinones to quinones. The aryl iodide coproducts could be recovered in >99−98% yields via fluorous/organic liquid/liquid biphase workups and reoxidized to the iodine(III) compounds. Nonetheless, the syntheses of these reagents required four steps from the aromatic aldehydes $(O{=}CH)_xC_6H_{6-x}$.

We therefore sought fluorous hypervalent iodide compounds that could be more readily accessed. Our attention was attracted by the commercial availability of numerous fluorous primary alkyl iodides of the formula $R_{fn}I$ (**1**-R_{fn}). These can be oxidized with H_2O_2 in trifluoroacetic anhydride to iodine(III) bis(trifluoroacetate) adducts, $R_{fn}I(OCOCF_3)_2$ (**2**-R_{fn}),[12,13] as reported earlier for $n = 2, 3, 4, 6$, and 8.[13b] Importantly, H_2O_2 is an optimal oxidant from the green chemistry standpoint.[14] Compounds **2**-R_{fn} have seen extensive use for the conversion of

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(7) Reagents recoverable via solid/liquid-phase separations: (a) More, J. D.; Finney, N. S. *Org. Lett.* **2002**, *4*, 3001. (b) Yusubov, M. S.; Drygunova, L. A.; Zhdankin, V. V. *Synthesis* **2004**, 2289.

(8) Rocaboy, C.; Gladysz, J. A. *Chem.*−*Eur. J.* **2003**, *9*, 88.

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(10) (a) Thottumkara, A. P.; Bowsher, M. S.; Vinod, T. K. *Org. Lett.* **2005**, *7*, 2933. (b) Ochiai, M.; Takeuchi, Y.; Katayama, T.; Sueda, T.; Miyamoto, K. *J. Am. Chem. Soc.* **2005**, *127*, 12244. (c) Schulze, A.; Giannis, A. *Synthesis* **2006**, 257.

(11) *Handbook of Fluorous Chemistry*, Gladysz, J. A., Curran, D. P., Horváth, I. T., Eds.; Wiley/VCH: Weinheim, Germany, 2004, pp 1−4.

(12) Umemoto, T. *Chem. Rev.* **1996**, *96*, 1757.

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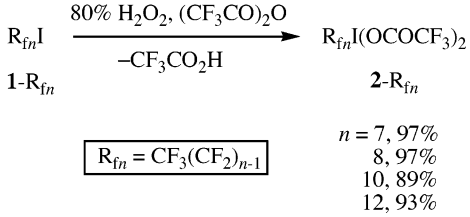
(14) Noyori, R.; Aoki, M.; Sato, K. *Chem. Commun.* **2003**, 1977 (feature article).

SCHEME 1. Syntheses of Title Compounds



arenes to derivatives $R_{fn}I(Ar)(X)$ and subsequent transformations.[12] However, they have not to our knowledge been applied in functional group oxidations or even spectroscopically characterized.

Compounds of the type **2**-R_{fn} offer other potential advantages as reagents. Unlike many fluorous systems, there is no intrinsic need for insulating methylene groups; the directly bound, highly electronegative R_{fn} moieties maximize the oxidizing power of the iodine center. Crich has employed similar strategies with selenium-based fluorous oxidants.[15] Also, the trifluoroacetate moieties might be replaced by heavier fluorous carboxylates (e.g., $OCOR_{f10}$), such that all coproducts would be fluorophilic and together recoverable. We note in passing that other types of fluorous iodine(III) compounds, designed for applications in peptide synthesis, have been reported.[16]

In this paper, we describe the syntheses and physical characterization of the "heavier" fluorous iodine(III) species **2**-R_{fn} with $n = 7$, 8, 10, and 12, and their application under environmentally friendly aqueous and methanolic conditions as recoverable reagents for oxidations of secondary alcohols to ketones. A portion of this work has been communicated, together with complementary oxidations of hydroquinones to quinones.[17] Additional details are supplied elsewhere.[18]

Results

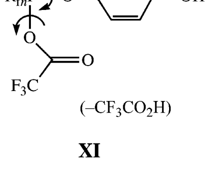
1. Syntheses and Phase Properties of Iodine-Containing Fluorous Compounds. As shown in Scheme 1, the fluorous primary alkyl iodides **1**-R_{f7}, **1**-R_{f8}, **1**-R_{f10}, and **1**-R_{f12}[19] were treated with 80% H_2O_2[20] and trifluoroacetic anhydride (ca. 1.0:1.8 mol ratio). These conditions generate the peracid CF_3CO_3H and have been applied by Zhdankin to **1**-R_{f8} previously.[13b] A ca. 4-fold excess of H_2O_2 sufficed with **1**-R_{f7} and **1**-R_{f8}, but 20−30-fold excesses were required with **1**-R_{f10} and **1**-R_{f12}, presumably because of less efficient phase mixing. Workups gave the bis(trifluoroacetate) adducts **2**-R_{fn} in 97−89% yields, which were characterized by IR and NMR (^{13}C, ^{19}F) spectroscopy and mass spectrometry. Data are summarized in the Experimental Section. Typical IR and ^{13}C NMR spectra, which feature ν_{CO} bands and downfield signals diagnostic of $OCCF_3$ groups, are depicted in the Supporting Information.[18]

The compounds **2**-R_{fn} were white solids, and a satisfactory carbon analysis was obtained for **2**-R_{f8}. As summarized in Table 1, the melting points clustered into a quite narrow range, from ca. 110 to 122 °C. The absolute solubilities of **2**-R_{fn}, like those of many other fluorous compounds,[21] decreased as the lengths of the ponytails were increased. Solubilities were highest in DMSO, acetone, methanol, and ether and somewhat lower in CH_2Cl_2 and $CHCl_3$ (Table 1). In contrast, **2**-R_{fn} compounds were not very soluble in fluorous solvents, for example $CF_3C_6F_{11}$ (perfluoro(methylcyclohexane)). In response to a point of reviewer (and frequent reader) confusion, we emphasize that perfluoroarenes such as perfluorotoluene ($CF_3C_6F_5$) are not (for well-defined physical reasons)[11,22] fluorous solvents.

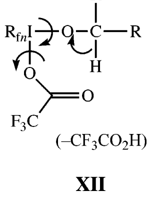
From the standpoint of recycling, the phase properties of the precursors **1**-R_{fn} are also critical. As summarized in Table 1, **1**-R_{f7}, and **1**-R_{f8} exhibited high solubilities in a broad spectrum of organic and fluorous solvents. However, the longer ponytail in **1**-R_{f12} distinctly decreases solubilities. The appreciable volatility of **1**-R_{f7} (Table 1) presented difficulties in an earlier study,[17] so **2**-R_{f7} was not screened in this work. The volatility of **1**-R_{f8} can also be problematic,[17] and it should be noted that the recovery protocols developed below never require solvent evaporation.

The $CF_3C_6F_{11}$/toluene partition coefficients of **1**-R_{f8} and **1**-R_{f10} have been reported as 88.5:11.5 and 94.5:5.5 (GLC).[23] As described in the Experimental Section, we independently measured 87.7:12.3 and 94.3:5.7, which can be considered good agreement. Partition coefficients of fluorophilic substances become more biased when the polarity of the organic solvent is increased. Accordingly, values of 89.4:10.6 and 97.6:2.4 were obtained with $CF_3C_6F_{11}$/methanol. Because of the low solubilities of **2**-R_{fn} in fluorous solvents, partition coefficients could not be measured. However, since **2**-R_{fn} are more polar than **1**-R_{fn}, they should be less fluorophilic.

2. Oxidation of Secondary Alcohols: Screening. As described earlier,[17] **2**-R_{fn} are excellent reagents for oxidations of hydroquinones to quinones in methanol at room temperature. These likely involve the intermediacy of $R_{fn}I(OCOCF_3)(OAr)$ species (**XI**), which then undergo formal eliminations of $R_{fn}I$ and trifluoroacetic acid. In principle, the same type of mechanism should be available to alcohols (e.g., **XII**). However, when **2**-R_{f8} and 1-phenyl-1-propanol (**3a**) or 1-phenylethanol (**3b**) were similarly reacted, only sluggish oxidations occurred. After 20−25 h, ^1H NMR spectra showed 35−32% conversions to the corresponding ketones. Only in the case of the doubly benzylic alcohol diphenylcarbinol could a good yield of ketone (benzophenone) be realized (80% conversion, 72 h). Reactions in ether were comparable to those in methanol, but other solvents (CH_2Cl_2, CD_3CN, THF, acetone-d_6, DMSO-d_6) were less effective.



XI



XII

Similar results have been reported with bis(carboxylate) adducts of phenyl iodide.[1b] We therefore investigated a strategy

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(15) (a) Crich, D.; Zou Y. *Org. Lett.* **2004**, *6*, 775. (b) Crich, D.; Zou, Y. *J. Org. Chem.* **2005**, *70*, 3309.

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(19) Typical prices/100 g in year 2006: **1**-R_{f7}, \$1030 (FTI); **1**-R_{f8}, \$52/144 Euros (FTI/ABCR); **1**-R_{f10}, \$412/397 Euros (FTI/ABCR), **1**-R_{f12}, 734 Euros (ABCR).

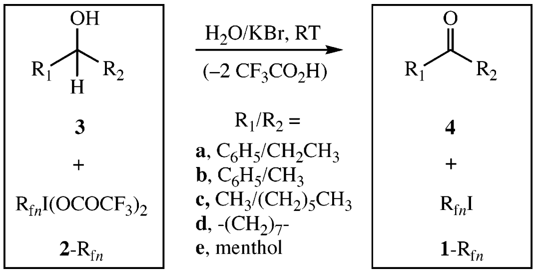
(20) **CAUTION**: Concentrated H_2O_2 may decompose violently in contact with iron, copper, chromium, and most other metals and their salts and dust. Absolute cleanliness, suitable equipment (uncontaminated PVC, butyl or Neoprene rubber, Teflon), and personal protection are essential for safe handling. See *Bretherick's Handbook of Reactive Chemical Hazards*, 6th ed.; Urben, P. G., Ed.; Butterworth-Heinemann: Oxford, 1999; Vol. 1, p 1624.

TABLE 1. Phase Properties of 1-R_{fn} and 2-R_{fn}

	$R_{fn}I(OCOCF_3)_2$ (**2**-R_{fn})				$R_{fn}I$ (**1**-R_{fn})			
	$n = 7$	$n = 8$	$n = 10$	$n = 12$	$n = 7$	$n = 8$	$n = 10$	$n = 12$
mp (°C)	110.0−111.5[a]	112.0−113.5[a]	115.0−116.5[a]	121−122.5[a]			65−67	99−101
bp (°C)					137−138	160−161	195−200	132 (34 mm)
				Solubility				
DMSO	high	high	low	low	high	high	low	v. low
methanol	high	high	low	low	high	high	low	v. low
acetone	high	high	high	med	high	high	high	med
CH_2Cl_2	med	med	v. low	v. low	high	high	med	med
$CHCl_3$	med	med	v. low	v. low	high	high	high	med
ether	high	high	med	med	high	high	high	med
hexane	low	low	v. low	v. low	high	high	high	med
toluene	low	low	v. low	v. low	high	high	high	v. low
$CF_3C_6F_5$	high	high	med	med	high	high	high	med
$CF_3C_6F_{11}$	low	low	v. low	v. low	high	high	high	med

[a] dec.

SCHEME 2. Oxidation of Alcohols by 2-R_{fn}; General Conditions



that has been used with other iodine(III) reagents, that of an activator or relay oxidant.[1b] Both Kita[6,24] and Zheng[9] obtained much improved results when reactions were conducted in the presence of bromide ions (aqueous KBr or NaBr in an ionic liquid). Mechanisms involving the addition of bromide to iodine and/or generation of a functional equivalent of "Br^+" were proposed. As shown in Scheme 2, the neat secondary alcohols **3a**−**e** were combined with aqueous KBr (1 equiv), and the resulting biphasic systems were treated with 1.24 equiv of **2**-R_{f8} or **2**-R_{f10}. Note that no organic or fluorous solvents are present.

The colorless samples immediately turned orange, but after some time (5−20 min for **2**-R_{f8}; 45−70 min for **2**-R_{f10}) bleached back to colorless or pale yellow. New multiphase systems formed as diagrammed in Chart 1. Those generated from **2**-R_{f8} (**XIV**) were fluorous/organic/aqueous liquid/liquid/liquid triphasic, with fluorous iodide **1**-R_{f8} as the bottom layer. Those generated from **1**-R_{f10} (**XV**) were solid/liquid/liquid triphasic, with solid **1**-R_{f10} as the bottom layer. After 30 min (**2**-R_{f8}) or 70 min (**2**-R_{f10}), hexane and the GC standard undecane were added. Consistent with the appreciable solubilities of **1**-R_{fn} in hexane (Table 1), organic/aqueous liquid/liquid biphase systems formed (**XVI**).

As summarized in Chart 1, GC analyses showed 92−57% yields of the corresponding ketones **4a**−**e**. No starting alcohols remained. Product identities were confirmed by comparisons to commercial samples. When substoichiometric quantities of KBr were utilized, complete oxidations could still be effected. However, much longer reaction times were required, as noted earlier with other iodine(III) reagents.[9,24] ^{1}H NMR analyses of crude ketones from larger scale reactions (below) often showed signals consistent with minor amounts of α-hydroxyketones (e.g., δ 4.86 (s, CH_2; $CDCl_3$) for α-hydroxyacetophenone).[25] The independent oxidation of ketones to α-hydroxyketones by $PhI(OCOCF_3)_2$/trifluoroacetic acid in refluxing aqueous acetonitrile has been studied.[25a] In accord with the trends in our data, yields decreased in the order cycloheptanone > acetophenone > propiophenone (94%, 69%, 36%).

3. Product/Reagent Separation and Recycling. To optimize conditions for separating the spent reagents **1**-R_{fn} from the ketone products, experiments were repeated on larger scales. Chart 2 illustrates the procedure developed for **2**-R_{f8}. After reactions as described above (30 min), 3−5 volumes of methanol were added. This gave fluorous/methanolic liquid/liquid biphase systems, with **1**-R_{f8} as the bottom layer (**XVII**). The methanolic phase was separated and extracted with hexane. Chromatography gave 86−53% yields of the ketones **4a**−**e** (Chart 2), which were pure by ^{1}H NMR. Crude **1**-R_{f8} was recovered in 98−95% yields. These samples were treated with hexane and undecane and analyzed by GC. In all cases, some additional ketone was detected (4−10%). Hence, the ketones do not completely partition into the polar methanolic phase. Importantly, the aqueous component of this phase suppresses the loss of **1**-R_{f8}, which as noted in Table 1 is soluble in methanol.

Chart 3 illustrates the procedure developed for **2**-R_{f10}. After reactions with **3a**,**c**−**e** as described above (70 min), 3−5 volumes of methanol were added. The resulting fluorous/methanolic solid/liquid biphase systems (**XVIII**) were centrifuged, and the residues separated. These (**XIX**) were washed with methanol/H_2O, giving **1**-R_{f10} as a white solid in ≥99.5% yields. The combined methanol/H_2O phases (**XX**) were extracted with hexane. Chromatography gave the ketones **4a**,**c**−**e** in 92−51% yields, as summarized in Chart 3. The samples of **1**-R_{f10} were checked for residual ketone as described above. Much

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(21) (a) Hughes, R. P.; Trujillo, H. A. *Organometallics* **1996**, *15*, 286. (b) Alvey, L. J.; Rutherford, D.; Juliette, J. J. J.; Gladysz, J. A. *J. Org. Chem.* **1998**, *63*, 6302.

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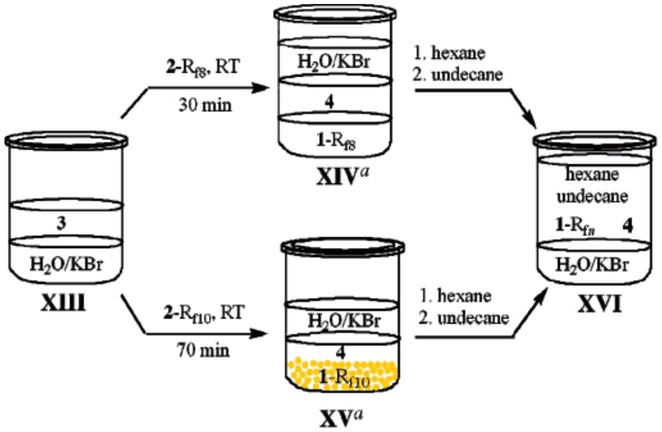
(25) (a) Moriarty, R. M.; Berglund, B. A.; Penmasta, R. *Tetrahedron Lett.* **1992**, *33*, 6065. (b) Moriarty, R. M.; Hou, K.-C.; Prakash, I.; Arora, S. K. *Org. Synth.* **1985**, *64*, 138 (Coll. Vol. 7, p 263).

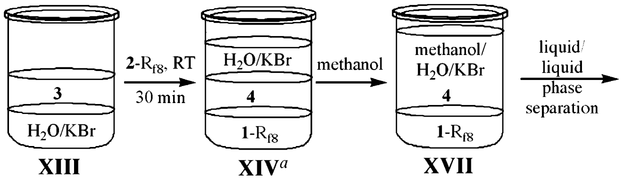
CHART 1. Phase and Yield Data for Oxidations



Entry	Oxidant	Alcohol / Ketone	Yield, **4** (%, GC)
1	**2**-R_{f8}	**3a / 4a**	92
2	**2**-R_{f8}	**3b / 4b**	78
3	**2**-R_{f8}	**3c / 4c**	88
4	**2**-R_{f8}	**3d / 4d**	59
5	**2**-R_{f8}	**3e / 4e**	80
6	**2**-R_{f10}	**3a / 4a**	90
7	**2**-R_{f10}	**3b / 4b**	73
8	**2**-R_{f10}	**3c / 4c**	71
9	**2**-R_{f10}	**3d / 4d**	57
10	**2**-R_{f10}	**3e / 4e**	70

[a] The aqueous phase in **XIV** and **XV** is above ketone **4a** but under ketones **4b**−**e**.

CHART 2. Phase and Yield Data for Oxidations with Recovery of 1-R_{f8}



Starting alcohol	Yield **4** (%, isolated)	Yield **1**-R_{f8} (%, isolated)[b]	Residual **4** in **1**-R_{f8} (%, GC)
3a	86	97	5.8
3b	73	98	4.4
3c	78	96	9.4
3d	53	98	5.2
3e	70	95	10

[a] The aqueous phase in **XIV** is above ketone **4a** but under ketones **4b**−**e**. [b] The yields of **1**-R_{f8} decrease by 0.5−2.5% when corrected for the mass of residual **4**.

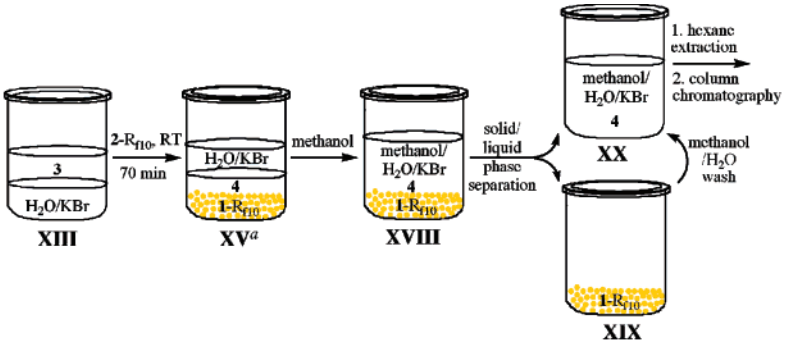
lower levels were present (≤1.3%). Hence, the solid/liquid-phase separation is more efficient with respect to the ketone products.

Since the alcohol **3a** gave the highest yields of ketone and the reagent **2**-R_{f10} the more effective phase separations, they were selected for recycling experiments. As summarized in Chart 4, sequences analogous to Chart 3 were conducted. Following hexane extraction of the methanol/H_2O phases (**XXa**), the yield of ketone **4a** was determined by GC. The recovered **1**-R_{f10} was reoxidized to **2**-R_{f10} (80%) as in Scheme 1. Then a fresh charge of **3a** and aqueous KBr were added, with the quantities adjusted to the amount of **2**-R_{f10}. Two analogous cycles were conducted, and the entire sequence was carried out in duplicate (cycles 1a−3a and 1b−3b). Overall, 59% to 57% of the original charge of the fluorous iodide species could be recovered (e.g., calculated from $0.952 \times 0.80 \times 0.966 \times 0.81 \times 0.989 = 0.59$).

Discussion

The preceding data establish that **2**-R_{f8} and **2**-R_{f10} are highly effective and easily recovered reagents for oxidations of secondary alcohols to ketones in the presence of aqueous KBr.

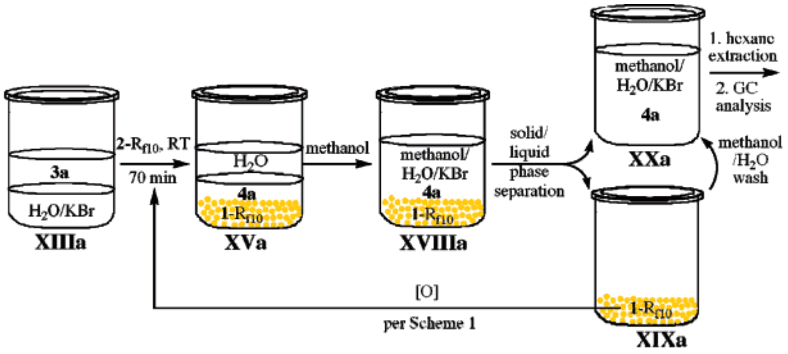
CHART 3. Phase and Yield Data for Oxidations with Recovery of 1-R$_{f10}$



Starting alcohol	Yield **4** (%, isolated)	Yield **1**-R$_{f10}$ (%, isolated)	Residual **4** in **1**-R$_{f8}$ (%, GC)
3a	92	99.3	not found
3c	69	>99	1.3
3d	51	>99	0.6
3e	69	>99	1.1

[a] The aqueous phase in **XV** is above ketone **4a** but under ketones **4b**−**e**.

CHART 4. Phase and Yield Data for Oxidations of 3a with Recycling of 1-R$_{f10}$



Cycle[a]	Yield **4a** (%, GC)	Yield **1**-R$_{f10}$ (%, isolated)	**2**-R$_{f10}$ (%, isolated)
1a	90	95	80
2a	86	97	81
3a	85	99	-
1b	92	99	78
2b	92	98	75
3b	83	>99	-

[a] 1a-3a and 1b-3b denote two separate runs.

No additional solvents are required, and methanolic workups enable efficient separations of the ketones from the recyclable coproducts **1**-R$_{fn}$. Given the excellent results with **2**-R$_{f10}$, no attempts were made to effect analogous reactions with **2**-R$_{f12}$, which is derived from a somewhat more expensive fluorous alkyl iodide.[19] However, **2**-R$_{f12}$ gave superior results in oxidations of hydroquinones,[17] for which other types of workups involving solid/liquid-phase separations were employed.

Interestingly, **2**-R$_{fn}$ oxidized secondary alcohols in the presence of bromide ions much more rapidly than other iodine(III) reagents. For example, Kita reported reaction times of 2−24 h for comparable oxidations with PhIO or reagents of the type **VII** (Figure 1B) in the presence of aqueous KBr.[6,24] Similarly, Zhang reported reaction times of 2−18 h when using an ionic ArI$(OCOCH_3)_2$ species in conjunction with NaBr and an ionic liquid solvent.[9] These trends may in part be ascribed to the directly bound electron-withdrawing perfluoroalkyl substituents in **2**-R$_{fn}$, which as noted above enhance the oxidizing strength.

Compounds **2**-R$_{f10}$ and **2**-R$_{f12}$ belong to the growing numbers of fluorous catalysts[26] and reagents[27] that can be recycled by solid/liquid phase separations, or precipitations. Many of these protocols avoid the use of somewhat costly fluorous solvents. Recently, this approach has also gained popularity with nonfluorous hypervalent iodide reagents. For example, the highly

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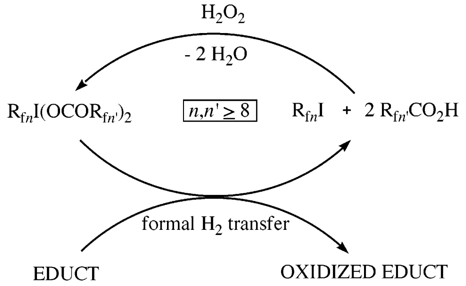
[26] For a recent review, see Gladysz, J. A.; Tesevic, V. *Top. Organomet. Chem.*, DOI 10.1007/3418_043.

[27] Wang, C.-Y.; Meng, W.-D.; Huang, Y.-G.; Qing, F.-L. *J. Fluorine Chem.* **2005**, *126*, 996.

SCHEME 3. A Possible Waste-Free Recycling Protocol



symmetrical tetraiodides derived from **VII** (Figure 1) and the tetraphenylmethane analogue also quantitatively precipitate from methanol, enabling facile recycling.[6a] The diiodide derived from **VIII**, which is commercially available, can be similarly recovered.[7b] Alternatively, IBX can be utilized under solvent-free conditions, and the insoluble coproduct can be isolated by filtration and recycled.[7a]

There are several obvious extensions of the preceding methodology. First, $PhI(OCOCH_3)_2$ has been employed in conjunction with other relay oxidants, one of which is TEMPO.[28] A variety of fluorous TEMPO derivatives are now known, and one has recently been applied in such oxidations of alcohols, with recovery and reuse for six cycles.[29] The combined use of **2**-R_{fn} and a fluorous TEMPO would seem to offer very attractive possibilities. Second, it can be anticipated that **2**-R_{fn}— like other iodine(III) species—will be effective oxidants for a variety of other functional groups.[1a,c,30] In work to date, several nitrogen-containing compounds have been oxidized in high yields.[31]

In our opinion, the ultimate extension of this chemistry would be the sequence illustrated in Scheme 3. As noted in the Introduction, analogous reagents derived from higher and more fluorophilic perfluorocarboxylic acids are likely easily synthesized. The coproducts **1**-R_{fn} and $R_{fn'}CO_2H$ might be recycled together, with dehydration of the latter to give a fluorous anhydride that could mediate the reoxidation of **1**-R_{fn} by H_2O_2 (compare to Scheme 1). The next conceptual step—a functional group oxidation using H_2O_2, with water as the only nonrecycled coproduct—would represent the ultimate in atom economy and a fluorous-based green process worthy of considerable attention.

In summary, this study has shown that fluorous iodine(III) reagents **2**-R_{fn} with longer ponytails (n = 7, 8, 10, 12) are easily prepared from commercially available primary alkyl iodides **1**-R_{fn}. In conjunction with aqueous KBr, they are highly effective reagents for the oxidations of secondary alcohols to ketones. No fluorous or organic solvents are required, and reaction times are shorter than with other types of hypervalent iodide reagents.[6a,9,24] Methanolic workups allow the facile recovery of the coproducts **1**-R_{fn} by liquid/liquid or solid/liquid phase separations. These are easily reoxidized to **2**-R_{fn}.

Experimental Section

General Data. Chemicals were treated as follows: methanol and $CHCl_3$, distilled; $CF_3C_6F_{11}$, $R_{f7}I$ (**1**-R_{f7}), $R_{f8}I$ (**1**-R_{f8}), $R_{f10}I$ (**1**-R_{f10}), $R_{f12}I$ (**1**-R_{f12}),[19] trifluoroacetic anhydride, 1-phenyl-1-propanol (**3a**), 1-phenylethanol (**3b**), menthol (**3e**), propiophenone (**4a**), menthone (**4e**), 2-octanol (**3c**), cyclooctanol (**3d**), 2-octanone (**4c**), cyclooctanone (**4d**), acetophenone (**4b**), acetone-d_6, used as received. The ~80% H_2O_2 was prepared from 30% H_2O_2 by reducing the volume 1/2.7 in vacuo at 50 °C[20] and standardized by titration with $KMnO_4$.[32]

NMR spectra were recorded on standard 400 or 300 MHz FT spectrometers at ambient temperatures and referenced as follows: ^{13}C, internal acetone-d_6 (δ 29.8); ^{19}F, internal C_6F_6 (δ −162.0). GC data were acquired using a capillary column (OPTIMA-5−0.25 μm; 25 m × 0.32 mm). Other instrumentation has been described in earlier papers.[8,17]

$R_{f7}I(OCOCF_3)_2$ (2-R_{f7}). A round-bottom flask was charged with H_2O_2 (~80%; 0.25 mL, 8.00 mmol)[20] and cooled to −10 °C. Then trifluoroacetic anhydride (1.65 mL, 14.9 mmol) was added with stirring. The cold bath was removed. After 30 min, the mixture was cooled to −15 °C, and **1**-R_{f7} (0.45 mL, 0.91 g, 1.83 mmol) was added with stirring. The mixture was stirred for 3 h at 0 °C and then allowed to stand for 48 h at 20 °C. The volatiles were removed by oil pump vacuum (−78 °C trap), and the residue collected to give **2**-R_{f7} as a white solid (1.190 g, 1.648 mmol, 97%), mp 110.0−111.5 °C dec. Anal. Calcd for $C_{11}F_{21}IO_4$: C, 18.28. Found: C, 17.58.[33]MS (FAB$^+$, m/Z): 609 ($M^+{-}OCOCF_3$, 30%), 1330 ($2M^+{-}OCOCF_3$,[34] 100%). IR (cm^{-1}, thin film): υ_{CO} 1739 (ms), 1686 (ms); υ_{CF} 1212−1069 (vs). NMR (δ, acetone-d$_6$): $^{13}C\{^1H\}$ (partial) 114.1 (q, $^1J_{CF}$ = 287.5 Hz, $\mathbf{C}F_3CO$), 160.9 (q, $^2J_{CF}$ = 41.2 Hz, $CF_3\mathbf{C}O$); ^{19}F −73.67 (s, 6F, $C\mathbf{F}_3CO$), −77.79 (t, $^4J_{FF}$ = 15.1 Hz, 2F, $C\mathbf{F}_2I$), −78.97 (t, $^4J_{FF}$ = 10.0 Hz, 3F, $C\mathbf{F}_3CF_2$), −113.42 (m, 2F, $C\mathbf{F}_2$), −119.31 (m, 2F, $C\mathbf{F}_2$), −119.66 (m, 2F, $C\mathbf{F}_2$), −120.55 (m, 2F, $C\mathbf{F}_2$), −124.05 (m, 2F, $C\mathbf{F}_2$).[35]

$R_{f8}I(OCOCF_3)_2$ (2-R_{f8}). H_2O_2 (~80%; 0.25 mL, 8.00 mmol),[20] trifluoroacetic anhydride (1.65 mL, 14.9 mmol), and **1**-R_{f8} (0.50 mL, 1.00 g, 1.83 mmol) were combined in a procedure analogous to that for **2**-R_{f7}. An identical workup gave **2**-R_{f8} as a white solid (1.385 g, 1.795 mmol, 98%), mp 112.0−113.5 °C dec. Anal. Calcd for $C_{12}F_{23}IO_4$: C, 18.65. Found: C, 18.38. MS (FAB$^+$, m/Z): 659 ($M^+{-}OCOCF_3$,[34] 50%), 1431 ($2M^+{-}OCOCF_3$, 100%). IR (cm^{-1}, thin film): υ_{CO} 1741 (ms), 1687 (ms); υ_{CF} 1216−1096 (vs). NMR (δ, acetone-d$_6$): $^{13}C\{^1H\}$ (partial) 114.1 (q, $^1J_{CF}$ = 287.3 Hz, $\mathbf{C}F_3CO$), 160.9 (q, $^2J_{CF}$ = 41.2 Hz, $CF_3\mathbf{C}O$); ^{19}F −73.73 (s, 6F, $C\mathbf{F}_3CO$), −78.10 (t, $^4J_{FF}$ = 14.0 Hz, 2F, $C\mathbf{F}_2I$), −79.02 (t, $^4J_{FF}$ = 10.2 Hz, 3F, $C\mathbf{F}_3CF_2$), −113.44 (m, 2F, $C\mathbf{F}_2$), −119.36 (m, 4F, $C\mathbf{F}_2$), −119.71 (m, 2F, $C\mathbf{F}_2$), −120.55 (m, 2F, $C\mathbf{F}_2$), −124.09 (m, 2F, $C\mathbf{F}_2$).[35]

$R_{f10}I(OCOCF_3)_2$ (2-R_{f10}). H_2O_2 (~80% 1.19 mL, 38.0 mmol),[20] trifluoroacetic anhydride (7.00 mL, 63.2 mmol), and **1**-R_{f10} (1.182 g, 1.830 mmol) were combined in a procedure analogous to that for **2**-R_{f7}. An identical workup gave **2**-R_{f10} as a white solid (1.413 g, 1.620 mmol, 89%), mp 115.0−116.5 °C dec. Anal. Calcd for $C_{14}F_{27}IO_4$: C, 19.27. Found: C, 18.49.[33] MS (FAB$^+$, m/Z): 759 ($M^+{-}OCOCF_3$, 46%), 1631 ($2M^+{-}OCOCF_3$,[34] 100%). IR (cm^{-1}, thin film): υ_{CO} 1745 (ms), 1691 (ms); υ_{CF} 1216−1096 (vs). NMR (δ, acetone-d$_6$): $^{13}C\{^1H\}$ (partial) 114.1 (q, $^1J_{CF}$ = 287.4 Hz, $\mathbf{C}F_3CO$), 160.9 (q, $^2J_{CF}$ = 41.1 Hz, $CF_3\mathbf{C}O$); ^{19}F −73.71 (s, 6F, $C\mathbf{F}_3CO$), −77.77 (t, $^4J_{FF}$ = 13.3 Hz, 2F, $C\mathbf{F}_2I$), −79.04 (t, $^4J_{FF}$ = 10.1

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[32] Huckaba, C. E.; Keyes, F. G. *J. Am. Chem. Soc.* **1948**, *70*, 1640.

[33] Although some microanalyses were marginal, the best available data are given.

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[35] (a) All compounds with $(CF_2)_7CF_3$ ponytails exhibit very similar ^{19}F NMR chemical shifts, which have been assigned by detailed 2D NMR experiments: Gladysz, J. A. In *Handbook of Fluorous Chemistry*; Gladysz, J. A., Curran, D. P., Horváth, I. T., Eds.; Wiley/VCH: Weinheim, Germany, 2004; pp 43−44. (b) The triplets represent $^4J_{FF}$ and not $^3J_{FF}$ values. See: (i) White, H. F. *Anal. Chem.* **1966**, *38*, 625. (ii) Foris, A. *Magn. Reson. Chem.* **2004**, *42*, 534.

Hz, 3F, $C\mathbf{F}_3CF_2$), −113.36 (m, 2F, $C\mathbf{F}_2$), −119.44 (m, 10F, $C\mathbf{F}_2$), −120.54 (m, 2F, $C\mathbf{F}_2$), −124.08 (m, 2F, $C\mathbf{F}_2$).[35]

$R_{f12}I(OCOCF_3)_2$ (2-R_{f12}). H_2O_2 (∼80% 1.64 mL, 52.4 mmol),[20] trifluoroacetic anhydride (7.89 mL, 73.1 mmol), and **1**-R_{f12} (1.365 g, 1.829 mmol) were combined in a procedure analogous to that for **2**-R_{f7}. An identical workup gave **2**-R_{f12} as a white solid (1.654 g, 1.701 mmol, 93%), mp 121.0−122.5 °C dec. Anal. Calcd for $C_{16}F_{31}IO_4$: C, 19.75. Found: C, 19.06.[33] MS (FAB$^+$, m/Z): 859 ($M^+-OCOCF_3$, 80%), 1830 ($2M^+-OCOCF_3$,[34] 100%). IR (cm^{-1}, thin film): υ_{CO} 1742 (ms), 1688 (ms); υ_{CF} 1194−1094 (vs). NMR (δ, acetone-d_6): $^{13}C\{^1H\}$ (partial) 114.1 (q, $^1J_{CF} = 287.5$ Hz, $\mathbf{C}F_3$-CO), 160.9 (q, $^2J_{CF} = 41.3$ Hz, $CF_3\mathbf{C}O$); ^{19}F −73.94 (s, 6F, $C\mathbf{F}_3$-CO), −77.72 (t, $^4J_{FF} = 13.2$ Hz, 2F, $C\mathbf{F}_2I$), −78.97 (t, $^4J_{FF} = 10.0$ Hz, 3F, $C\mathbf{F}_3CF_2$), −113.38 (m, 2F, $C\mathbf{F}_2$), −119.42 (m, 14F, $C\mathbf{F}_2$), −120.54 (m, 2F, $C\mathbf{F}_2$), −124.05 (m, 2F, $C\mathbf{F}_2$).[35]

Oxidations with 2-R_{f8} in Chart 1. The following is representative, and data for the other experiments are provided in the Supporting Information. A 10 mL vial was charged with **3a** (0.0526 g, 0.386 mmol), H_2O (0.10 mL), and KBr (0.0459 g, 0.386 mmol). Then **2**-R_{f8} (0.3692 g, 0.4782 mmol) was added with stirring. The orange suspension became a pale yellow triphasic liquid system. After 30 min, hexane (1 mL) and undecane (0.0388 mL, 0.0287 g, 0.183 mmol) were added to give a biphasic liquid system. GC analysis of a 0.020 mL aliquot of the upper organic phase showed **4a** (0.0474 g, 0.353 mmol, 91.5%).

Oxidations with 2-R_{f10} in Chart 1. The following is representative, and data for the other experiments are provided in the Supporting Information. A 10 mL vial was charged with **3a** (0.1004 g, 0.7371 mmol), H_2O (0.20 mL), and KBr (0.0875 g, 0.735 mmol). Then **2**-R_{f10} (0.7966 g, 0.9135 mmol) was added with stirring. The orange suspension turned pale yellow. After 70 min, hexane (1 mL) and undecane (0.0780 mL, 0.0575 g, 0.368 mmol) were added to give a biphasic liquid system. GC analysis of a 0.020 mL aliquot of the upper organic phase showed **4a** (0.0889 g, 0.663 mmol, 90.0%).

Oxidations in Chart 2. The following is representative, and data for the other experiments are provided in the Supporting Information. A 10 mL vial was charged with **3a** (0.1501 g, 1.101 mmol), H_2O (0.30 mL), and KBr (0.1310 g, 1.101 mmol). Then **2**-R_{f8} (1.0542 g, 1.3655 mmol) was added with stirring. The orange suspension became a pale yellow triphasic liquid system. After 30 min, methanol (1.3 mL) was added. The two liquid phases were separated by pipet. The fluorous phase was extracted with methanol/H_2O (4.5:1 v/v; 2 × 1 mL), leaving **1**-R_{f8} (0.7245 g, 1.327 mmol, 97.1%). Then hexane (1 mL) and undecane (0.0050 mL, 0.0037 g, 0.024 mmol) were added, giving one phase. GC analysis showed some residual **4a** (0.0085 g, 0.064 mmol, 5.8%). The methanol/H_2O phases were extracted with hexane (3 × 3 mL). The solvent was removed from the combined extracts by rotary evaporation, and the residue was chromatographed (200 × 15 mm silica column, $CHCl_3$) to give **4a** (0.1271 g, 0.9471 mmol, 86.0%) that was pure by ^1H NMR.

Oxidations in Chart 3. The following is representative, and data for the other experiments are provided in the Supporting Information. A 10 mL vial was charged with **3a** (0.1000 g, 0.7342 mmol), H_2O (0.20 mL), and KBr (0.0874 g, 0.734 mmol). Then **2**-R_{f10} (0.7938 g, 0.9104 mmol) was added with stirring. The orange suspension turned pale yellow. After 70 min, methanol (0.9 mL) was added. The suspension was centrifuged. The precipitate was separated, washed with methanol/H_2O (4.5:1 v/v; 3 × 2 mL with centrifugation after each wash), and dissolved in hexane (2 mL); traces of methanol/H_2O were removed by pipet. The hexane was removed by rotary evaporation to give **1**-R_{f10} (0.5839 g, 0.9038 mmol, 99.3%). Then hexane (1 mL) and undecane (0.0050 mL, 0.0037 g, 0.024 mmol) were added. GC analysis showed no **4a** (detection limit based upon solvent impurity: 0.09%). 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 residue was chromatographed (200 × 15 mm silica column, $CHCl_3$) to give **4a** (0.0904 g, 0.674 mmol, 91.7%) that was pure by ^1H NMR.

Recycling (Chart 4). A 10 mL vial was charged with 1-phenyl-1-propanol (**3a**; 0.1000 g, 0.7342 mmol), H_2O (0.20 mL), and KBr (0.0874 g, 0.734 mmol). Then **2**-R_{f10} (0.7938 g, 0.9104 mmol) was added with stirring. The orange suspension turned pale yellow. After 70 min, methanol (0.90 mL) was added. The suspension was centrifuged. The precipitate **1**-R_{f10} was separated, washed with methanol/H_2O (4.5:1 v/v; 3 × 2 mL with centrifugation after each wash), and dissolved in hexane (2 mL); traces of methanol/H_2O were removed by pipet. The hexane was removed by rotary evaporation to give **1**-R_{f10} (0.5600 g, 0.8668 mmol, 95.2%). 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 hexane (1 mL) and undecane (0.0780 mL, 0.0575 g, 0.367 mmol) were added. GC analysis showed **4a** (0.0884 g, 0.659 mmol, 89.7%).

A vial was similarly charged with **3a** (0.0760 g, 0.558 mmol), H_2O (0.15 mL), and KBr (0.0661 g, 0.558 mmol). Then **2**-R_{f10} (0.6050 g, 0.6938 mmol; prepared in 80% yield from the **1**-R_{f10} from the previous cycle) was added with stirring, and the procedure was repeated using methanol (0.7 mL), methanol/H_2O (4.5:1 v/v; 3 × 2 mL), hexane (2 mL), hexane (1 mL), and undecane (0.0570 mL, 0.0422 g, 0.270 mmol) to give **1**-R_{f10} (0.4330 g, 0.6703 mmol, 96.6%) and (following extraction) **4a** (0.0640 g, 0.478 mmol, 85.6%). A vial was similarly charged with **3a** (0.0595 g, 0.437 mmol), H_2O (0.12 mL), and KBr (0.0519 g, 0.437 mmol). Then **2**-R_{f10} (0.4731 g, 0.5424 mmol; prepared in 81% yield from the **1**-R_{f10} from the previous cycle) was added with stirring, and the procedure was repeated using methanol (0.54 mL), methanol/H_2O (4.5:1 v/v; 3 × 2 mL), hexane (2 mL), hexane (1 mL), and undecane (0.0550 mL, 0.0410 g, 0.262 mmol) to give **1**-R_{f10} (0.3468 g, 0.5369 mmol, 98.9%) and (following extraction) **4a** (0.0499 g, 0.372 mmol, 85.2%).

Partition Coefficients. A: A 5 mL vial was charged with **1**-R_{f8} (0.0806 g, 0.147 mmol), $CF_3C_6F_{11}$ (2.00 mL), and toluene (2.00 mL). The mixture was vigorously shaken (2 min) and immersed in a 35 °C oil bath. After 12 h, the bath was removed. After 12 h, a 0.200 mL aliquot of each layer of was added to 0.100 mL of a standard 0.0138 M solution of undecane in hexane. The samples were diluted with ether and GC analysis (average of three injections) showed 0.0128 mmol of **1**-R_{f8} in the $CF_3C_6F_{11}$ aliquot and 0.00180 mmol in the toluene aliquot (87.7:12.3; a 2.00/0.200 scale factor gives a total mass recovery of 0.0786 g, 0.144 mmol, 98%). **B:** An analogous experiment was conducted with **1**-R_{f8} (0.0650 g, 0.119 mmol), $CF_3C_6F_{11}$ (2.00 mL), and methanol (2.00 mL). GC data: 0.0105 and 0.00125 mmol of **1**-R_{f8} in the $CF_3C_6F_{11}$ and methanol aliquots (89.4:10.6; total mass recovery 0.0642 g, 0.118 mmol, 99%). **C:** An analogous experiment was conducted with **1**-R_{f10} (0.0823 g, 0.127 mmol), $CF_3C_6F_{11}$ (2.00 mL), and toluene (2.00 mL), using 0.500 mL aliquots. GC data: 0.0299 and 0.00071 mmol of **1**-R_{f10} in the $CF_3C_6F_{11}$ and toluene aliquots (94.3:5.7; a 2.00/0.500 scale factor gives a total mass recovery of 0.0812 g, 0.125 mmol, 99%). **D:** An analogous experiment was conducted with **1**-R_{f10} (0.0881 g, 0.136 mmol), $CF_3C_6F_{11}$ (2.00 mL), and methanol (2.00 mL). GC data: 0.0322 and 0.00078 mmol of **1**-R_{f10} in the $CF_3C_6F_{11}$ and methanol aliquots (97.6:2.4; total mass recovery 0.0852 g, 0.132 mmol, 97%).

Acknowledgment. We thank the Deutsche Forschungsgemeinschaft (DFG, 300/3-3) and European Union (COST D29 working group 0011-03) for support.

Supporting Information Available: Full data for all experiments in Charts 1−3, and typical IR, $^{13}C\{^1H\}$, and ^{19}F NMR spectra for **2**-R_{fn}. This material is available free of charge via the Internet at http://pubs.acs.org.

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