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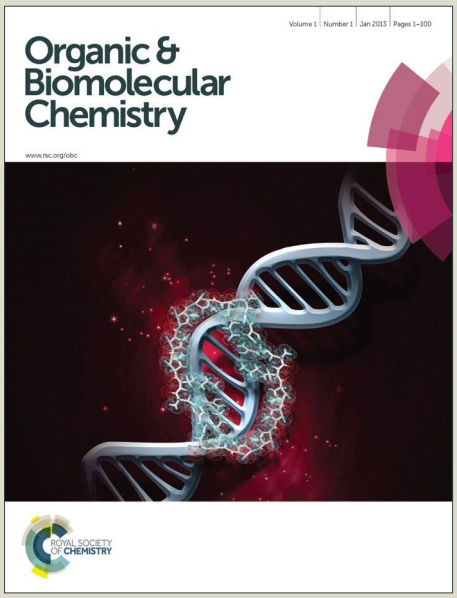

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Efficient Generation of Perfluoroalkyl Radicals from Sodium Perfluoroalkanesulfinates and a Hypervalent Iodine(III) Reagent: Mild, Metal-free Synthesis of Perfluoroalkylated Organic Molecules

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This article describes an efficient method for the introduction of perfluoroalkyl groups into *N*-acrylamides, 2-isocyanides, olefins, and other heterocycles using perfluoroalkyl radicals that were generated from the reaction between sodium perfluoroalkanesulfinates and a hypervalent iodine(III) reagent. This approach represents a simple, scalable perfluoroalkylation method under mild and metal-free conditions.

Over the last decades, the development of cost-effective, efficient, and environmentally benign synthetic methods for the preparation of perfluoroalkylated organic molecules has attracted much attention in pharmaceutical and agrochemical research, as well as in materials science. This is predominantly due to the fact that the introduction of fluoro substituents into organic molecules has a significant positive impact on their physical properties, including metabolic stability, solubility, and lipophilicity.[1,2] To date, various methods for the introduction of trifluoromethyl groups into organic molecules have been developed,[3] and several trifluoromethylating reagents, such as the Ruppert–Prakash reagent, Togni's reagent, and Umemoto's reagent, are now commercially available.[4-6] However, the efficient introduction of longer perfluoroalkyl groups (C_nF_{2n+1}, $n \geq 2$) still remains a substantial challenge in current organic synthesis.

Recently, the *in situ* generation of perfluoroalkyl radicals has been recognized as an attractive method for the direct insertion of perfluoroalkyl groups. This commonly encountered approach is based on perfluoroalkyl halides (C_nF_{2n+1}–X; X = I, Cl, Br) as radical sources, as these are widely available and easily handled.[7] Alternatively, perfluoroalkyl analogs of Togni's or Ruppert–Prakash trifluoromethylating reagents, have recently been used for radical-based perfluoroalkylations.[8] However, the generation of perfluoroalkyl radicals from these reagents often

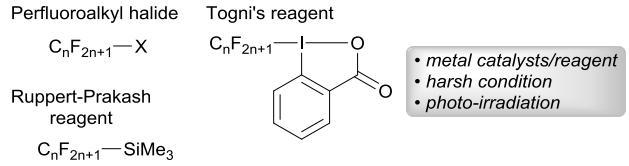
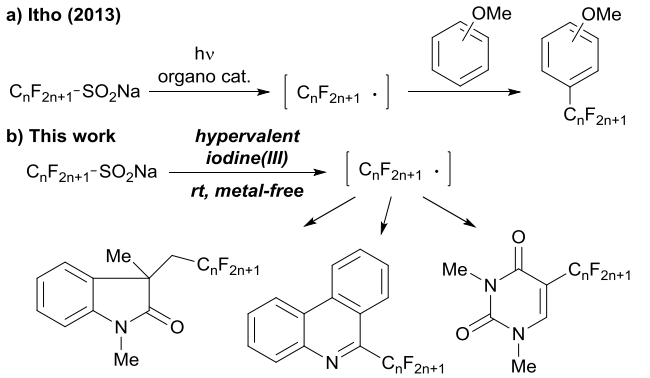


Figure 1. Commonly used, commercially available perfluoroalkylating reagents and their shortcomings.



Scheme 1. Perfluoroalkylations using perfluoroalkyl analogs of the Langlois reagent.

requires transition metal catalysts, high temperatures, and/or photo-irradiation, resulting in limitations with respect to the substrate scope and the practical utility in organic synthesis in general (Figure 1). Thus, the development of efficient perfluoroalkylation reactions under mild, metal-free conditions represents a highly desirable research target.

Sodium trifluoromethanesulfinate (CF_3SO_2Na, Langlois reagent), a stable and inexpensive solid reagent, has recently received attention as a convenient trifluoromethylating reagent, which generates trifluoromethyl radicals under mild conditions upon reaction with several oxidants.[9,10] To our surprise, only a few perfluoroalkylations using higher perfluoroalkyl analogs of the Langlois reagent ($C_nF_{2n+1}SO_2Na$, $n \geq 2$) have been reported so far.[11] For example, in 2013, Itho and co-workers reported the

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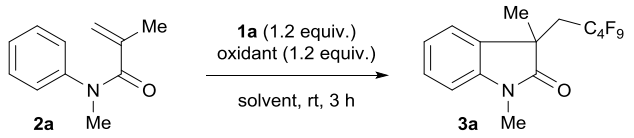
photolytic radical perfluoroalkylation of arenes using sodium perfluoroalkanesulfinates and an organocatalyst. However, this system also required photo-irradiation and the substrate scope was limited to electron-rich arenes (Scheme 1a).[11a] In this context, we would like to report herein the efficient generation of perfluoroalkyl radicals from sodium perfluoroalkanesulfinates, using a hypervalent iodine(III) reagent as the oxidant. The present system generates perfluoroalkyl radicals under mild, metal-free conditions, and it can be used for the radical-based perfluoroalkylation of *N*-acrylamides, 2-isocyanides, olefins, and heterocycles (Scheme 1b).

Sodium perfluoroalkanesulfinates **1** ($C_nF_{2n+1}SO_2Na$; $n \geq 2$) were easily prepared as stable solids in large quantities according to the procedure reported by Hu and DesMarteau.[12] With these sulfinates in hand, we initially examined the perfluoroalkylation/cyclization of *N*-arylacrylamide **2** to afford the corresponding perfluorinated oxindole as a model reaction.[13] When the reaction between $C_4F_9SO_2Na$ (**1a**) and *N*-methyl-*N*-phenylacrylamide (**2a**) was carried out in the presence of oxidants such as $K_2S_2O_8$, 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ), or *tert*-butylhydroperoxide (TBHP), only trace amounts of the desired product (**3a**) were obtained (Table 1, entries 1–3). Under Baran's conditions (TBHP in DCM/H_2O),[10a] the reaction furnished **3a** in merely 22% yield (entry 4). Therefore, we subsequently tested hypervalent iodine(III) oxidants:[14] while (diacetoxyiodo)benzene (DIB) did not generate any **3a** (entry 5), [bis(trifluoroacetoxy)iodo]benzene (PIFA) afforded **3a** in 72% yield (entry 6). Moreover, we tested several solvents for this reaction, and acetonitrile was identified as the most efficient.[15] By slow addition of the PIFA solution using a syringe pump, the yield of **3a** could be improved to 83% (entry 7). It should also be noted that the reaction could be scaled up to 3 mmol without any loss in efficiency, generating **3a** (1.03 g) in 87% yield (entry 8).

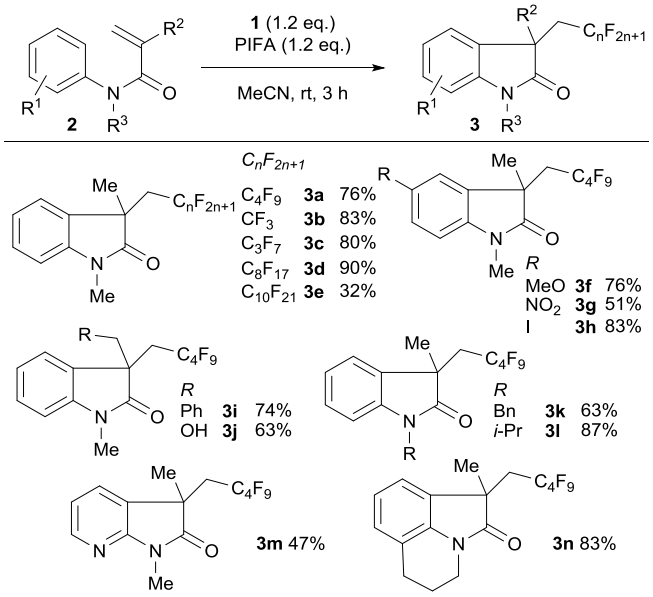
Table 1. Perfluoroalkylation/cyclization of *N*-methyl-*N*-phenylacrylamide **2a** with $C_4F_9SO_2Na$ **1a**.[a]



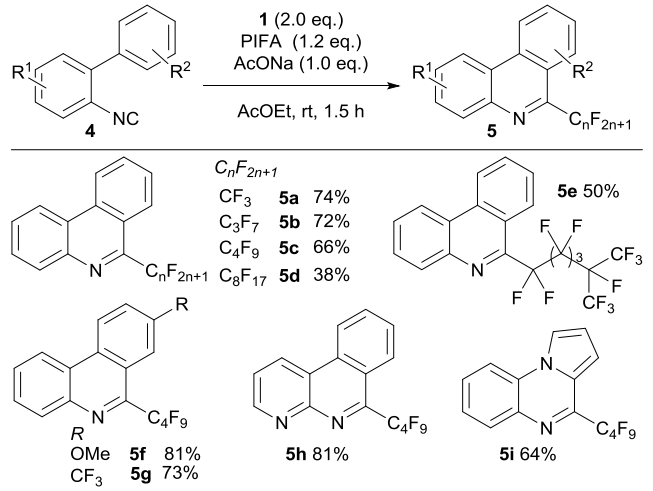
entry	oxidant	solvent	Yield **3a** (%)[b]
1	$K_2S_2O_8$	MeCN	<5
2	DDQ	MeCN	<5
3	TBHP	MeCN	<5
4[c]	TBHP	DCM/H_2O	22
5	DIB	MeCN	<5
6	PIFA	MeCN	72
7[d]	PIFA	MeCN	83 (76)[e]
8[f]	PIFA	MeCN	87[e]

[a] Unless otherwise specified, reactions were carried out in the presence of **1a** (1.2 equiv), **2a** (0.1 mmol), oxidant (1.2 equiv.), and the respective solvent (0.05 M). [b] The yield was determined by ^1H NMR spectroscopy using 1,1,2,2-tetrachloroethane as the internal standard. [c] The reaction between **2a** and **1a** (3.0 equiv.) was carried out in the presence of TBHP (5.0 equiv.) in DCM/H_2O (2.5/1). [d] A solution of PIFA in acetonitrile was added to the reaction mixture with a syringe pump over 20 min. [e] Isolated yield. [f] The reaction was conducted on a 3 mmol scale.

With optimized conditions in hand, we examined the substrate scope of the perfluoroalkylation/cyclization of *N*-arylacrylamides (**2**) with $C_nF_{2n+1}SO_2Na$ (**1**) (Scheme 2). The reaction of **2a** with various sodium perfluoroalkanesulfinates proceeded smoothly and furnished the corresponding perfluorinated oxindoles (**3a–e**) in moderate to high yield. Both electron-donating and electron-withdrawing substituents on the aryl moiety of **2** did not significantly affect the yield (**3f–h**), and α-substituents on the alkenes, e.g. phenyl and alcohol groups (**3i** and **3j**) were also tolerated well. The reactions of *N*-benzyl and *N*-isopropyl acrylamides (**2k** and **2l**) also afforded the corresponding products (**3k** and **3l**) in good yield. The use of heterocycle **2m** slightly decreased the yield of **3m** (47%). Furthermore, the reaction could also be carried out in the presence of a tetrahydroquinoline moiety (**2n**), affording tricyclic oxytetrahydroquinoline **3n** in 83% yield.



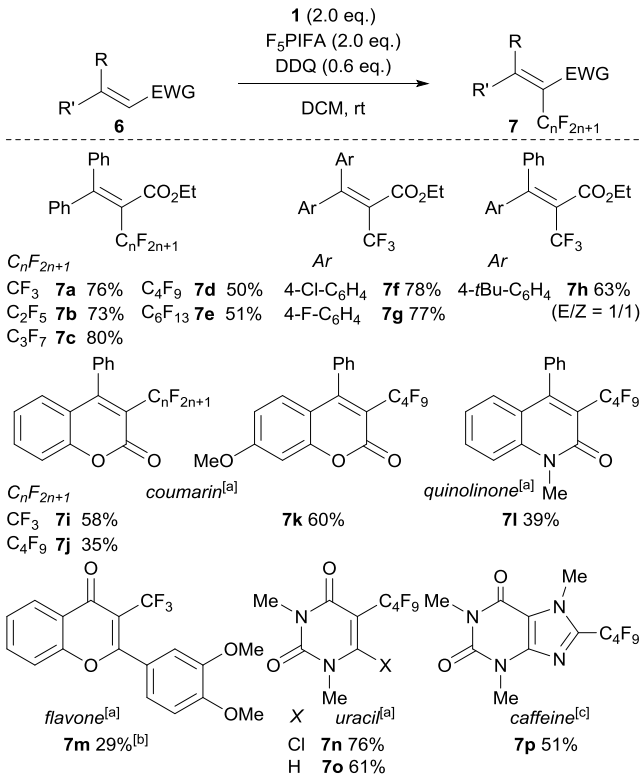
Scheme 2. Perfluoroalkylation/cyclization of *N*-Arylacrylamide (**2**).



Scheme 3. Radical cyclization of 2-isocyanobiphenyl **4** with sulfinates **1** and PIFA.

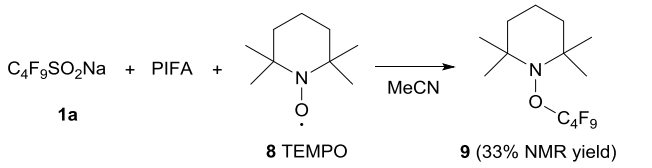
The present system was also utilized for the synthesis of 6-perfluoroalkylated phenanthridines.[16] The radical perfluoroalkylation of 2-isocyanobiphenyl **4** with sulfinates **1** and PIFA proceeded smoothly to give a variety of 6-perfluoroalkylated phenanthridines **5** in moderate to high yields as shown in Scheme 3.[17,18]

To demonstrate the extended utility of this system, we subsequently turned our attention to the direct perfluoroalkylation of sp²–hybridized C–H bonds of olefins and heterocycles (Scheme 4). Even though the direct trifluoromethylation of sp²–hybridized C–H bonds of (hetero)arenes has recently been accomplished by several research groups, the direct perfluoroalkylation and trifluoromethylation of olefinic sp²–hybridized C–H bonds still remains challenging.[19,20] Therefore, we initially examined the trifluoromethylation of 3,3-diphenylacrylate **6a** as a model reaction. The optimization of the reaction conditions revealed that the use of a mixture of [bis(trifluoroacetoxy)iodo]-pentafluorobenzene (F_5-PIFA) and DDQ afforded the corresponding product in good yield.[15] The use of symmetrical 3,3'-diarylacrylates (**6a**–**g**) afforded tetrasubstituted olefins **7a**–**g** in moderate to good yield, and in case of an unsymmetrical 3,3'-diarylacrylate (**6h**), both *E* and *Z* isomers of **7h** were obtained in 63% yield (*E*/*Z* = 1/1). Additionally, the perfluoroalkylation of sp²–hybridized C–H bonds in several heterocycles such as coumarin, flavone, and 2-quinolinone derivatives was studied. The reactions involving coumarin derivatives proceeded well, and the corresponding perfluorinated coumarins (**7i**–**k**) were obtained in moderate to good yield. The use of 2-quinolinone or flavone derivatives afforded **7l** and **7m** in modest yield. Moreover, the introduction of perfluoroalkyl groups into uracil and caffeine derivatives furnished **7n**–**p** in good yield.



Scheme 4. Direct perfluoroalkylation of sp²–hybridized C–H bonds in olefins and heterocycles. [a] 2,6-Lutidine (1.0 equiv.) was added. [b] The yield was determined by ^{1}H NMR spectroscopy using 1,1,2,2-tetrachloroethane as the internal standard. [c] 2,6-Di-*t*butyl-pyridine (1.0 equiv.) was added.

At present, we consider these reactions to proceed via a mechanism that is based on the generation of perfluoroalkyl radicals. In fact, when **1a** was added to a solution containing PIFA and the radical scavenger 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO, **8**), the perfluoroalkyl radical was successfully trapped (Scheme 5).



Scheme 5. Trapping C_4F_9· radicals with TEMPO. [a] The yield was determined by ^{1}H NMR spectroscopy using 1,1,2,2-tetrachloroethane as the internal standard.

Conclusions

In summary, we developed a method for the efficient generation of perfluoroalkyl radicals using readily available sodium perfluoroalkanesulfinates and a hypervalent iodine(III) reagent. This approach allows the introduction of perfluoroalkyl groups into a wide variety of organic molecules under mild and metal-free conditions. Further investigations into the detailed mechanism and synthetic applicability to other, related systems are currently in progress in our laboratory.

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