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LETTERS

Synthesis of perfluorinated allylic compounds by radical allylation and their purification over fluorous reverse-phase silica

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Abstract—A simple free-radical method for the preparation of a variety of perfluorinated allylic compounds has been developed starting from perfluoroalkyl iodides and allyltins. Allyltributyltin, methallyltributyltin and crotyltributyltin all proved to be useful for the transformation. The desired perfluorinated allylic compound was conveniently isolated from the crude mixture by solid-phase extraction with fluorous reverse-phase silica (FRPS). © 2001 Elsevier Science Ltd. All rights reserved.

Fluorous techniques constitute a rapidly growing area in synthetic organic chemistry.[1] One of our interests is in the application of this technique to radical carbonylation chemistry,[2] and we have recently reported that fluorous allyltin reagents serve as useful unimolecular chain carriers for a four component coupling system leading to β-functionalized δ,ε-unsaturated ketones.[3,4] In this system, a fluorous/organic biphase workup is conveniently used for separating the fluorous tin residues and the carbonylated products. During the course of a study to extend the four component coupling reaction to include perfluoroalkyl iodides as substrates, we found that no carbonylated product was formed and, instead, allylated perfluoroalkanes were obtained in good yields.[5] A literature survey showed that two precedent studies exist for this perfluoro version of a Keck type radical allylation reaction.[6] Yoshida and co-workers reported the efficient allylation of (chlorodifluoromethyl)arenes by allyltributyltin.[7a] A closer example to the present work was reported very recently by Gladysz and co-workers who have shown that 3-(perfluorooctyl)prop-1-ene can be obtained in good yield by the photolysis of perfluorooctyl iodide with allyltributyltin followed by fluorous/organic biphase workup.[7b] We became interested in determining (i) whether the scope of this rapid S_H2 type reaction is similar to the ordinary Keck type reaction of alkyl radicals, and (ii) whether the recently developed solid-phase extraction method[8] for the separation of perfluorinated compounds might be useful for the separation of allylated perfluoroalkanes from tributyltin compounds. In this letter, we report that radical addition reactions of perfluoroalkyl iodides to allyltributyltin, methallyltributyltin, and crotyltributyltin all work well and using fluorous reverse-phase silica (FRPS) allylated perfluoroalkanes were conveniently isolated.

In a typical reaction procedure, perfluorodecyl iodide (323 mg, 0.5 mmol), allyltributyltin (330 mg, 1 mmol), AIBN (9 mg, 0.05 mmol) and hexane (5 mL) were placed in a flask under a nitrogen atmosphere and the mixture was refluxed for 2 hours. The crude mixture was analyzed by gas chromatography to verify that the perfluorodecyl iodide was completely consumed. After removal of the volatiles, the mixture was submitted to separation over FRPS (Scheme 1). A short column was packed with FRPS (6.5 g) using ether as solvent, before washing with MeCN. The crude reaction mixture was then loaded onto this column and eluted first with MeCN (100 mL) to give the tin products (excess allyltributyltin and tributyltin iodide). In a further elution with ether (30 mL), 3-(perfluorodecyl)prop-1-ene was obtained in 90% yield (252 mg).

Similar reactions were carried out using perfluorooctyl iodide, 7-methylperfluorooctyl iodide and 9-methylperfluorodecyl iodide and the results are presented in Table 1. In all cases the perfluorinated olefins were

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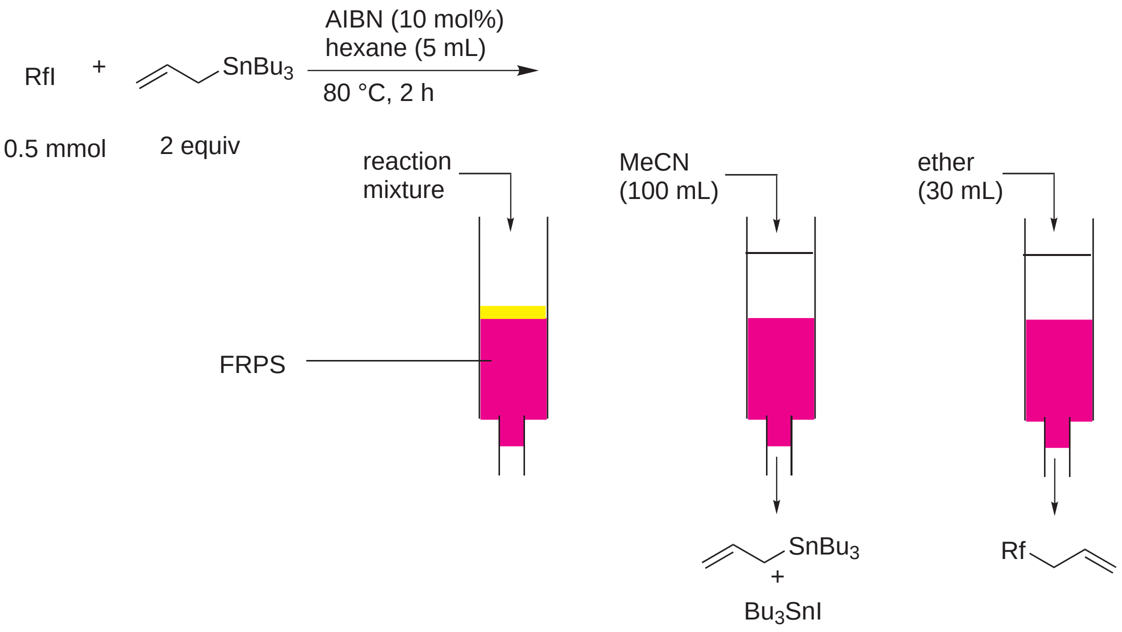
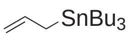
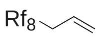
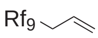
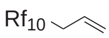
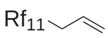
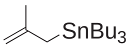
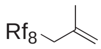
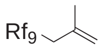
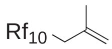
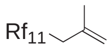
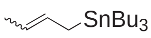
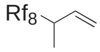
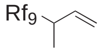
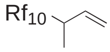
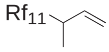


Scheme 1.

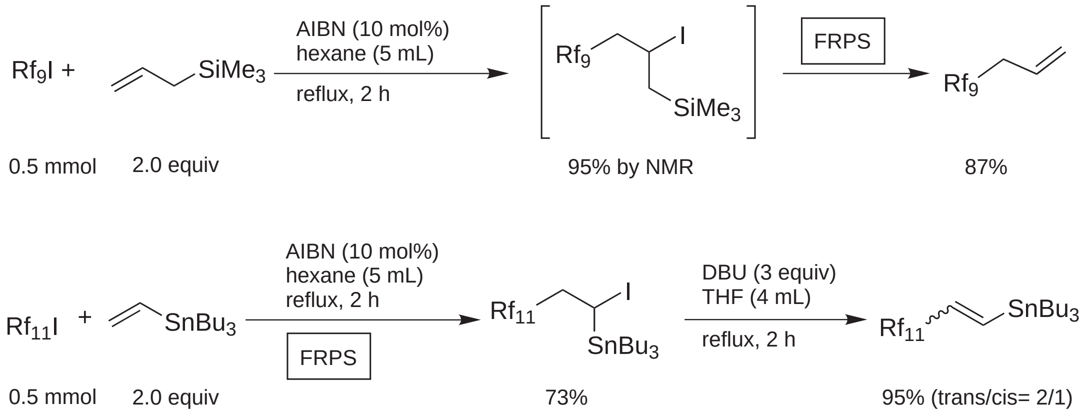
isolated in good to excellent yields.[9] Methallyltributyltin also worked well as the radical chain carrier. It has been reported that crotyltributyltin is not a good radical chain carrier for radical allylation reactions due to a steric reason.[6] However, to our gratification, when crotyltributyltin was used as the chain carrier, the perfluoroallylic compounds were obtained in good yields. In this experiment, after 2 hours some starting material still remained, extra AIBN was added and the mixture was refluxed for an additional 2 hours; the perfluoroalkyl iodides being completely consumed at this time. Unlike the case of alkyl radicals,[6a] only trace amounts of the reduced product were found in the crude mixture of the reaction with crotyltributyltin, as evidenced by GC analysis.

It should be noted that comparable yields were obtained when the reactions were carried out using an automated synthetic apparatus and some of the results are also given in Table 1.

Table 1. Preparation of 3-(perfluoroalkyl)prop-1-enes

	$C_8F_{17}I$ (Rf_8I)	$(CF_3)_2CF(CF_2)_6I$ (Rf_9I)	$C_{10}F_{21}I$ ($Rf_{10}I$)	$(CF_3)_2CF(CF_2)_8I$ ($Rf_{11}I$)
	 **1**, 83%	 **2**, 86%	 **3**, 90%	 **4**, 91% (90%)
	 **5**, 81%	 **6**, 82%	 **7**, 87%	 **8**, 95% (91%)
	 **9**, 69%	 **10**, 74%	 **11**, 73%	 **12**, 78% (82%)

(a) Conditions: RfI (0.5 mmol), allyltributyltin or methallyltin (2.0 equiv.) or crotyltributyltin (2.5 equiv.), AIBN (10 mol%), hexane (5 mL), reflux, 2 or 4 h (crotyltributyltin). (b) Isolated yields by FRPS workup procedure. (c) The results in parenthesis were obtained using JEOL JNM-PTW100 Bohdan Automation equipment.



Scheme 2.

We also examined two additional perfluoroalkylation reactions using trimethylallylsilane and tributylvinyltin (Scheme 2). In the former reaction, the formation of carboiodination intermediate was confirmed by ^{1}H NMR (95%). The fluorinated allylic product was isolated by FRPS in 87% yield, which was obtained by an in situ elimination of silyl iodide.[10] The carboiodination reaction of vinyltin proceeds in 73% yield after FRPS workup. The subsequent treatment with DBU gave the vinyltin compound having a perfluoroalkyl chain at the β position.[11]

In summary, allylic perfluorinated compounds were prepared using perfluorinated alkyl iodides and allyltins as the allyl source and radical chain carrier.[12] It is noteworthy that, in addition to allyltributyltin and methallyltributyltin, crotyltributyltin can also be successfully used in this S_H2 type radical addition reaction. The use of FRPS allows for a fast and convenient purification of the products. Based on the findings herein, we conclude that the method has broader scope than the standard Keck reaction of alkyl radical and is highly useful for the preparation of allylated perfluoroalkanes.

Acknowledgements

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9. Selected spectral data. 3-(Perfluorodecyl)prop-1-ene (**3**): ^{1}H NMR (270 MHz, $CDCl_3$) δ 2.86 (dt $J=6.9$ and 18.2 Hz, 2H), 5.30–5.38 (m, 2H), 5.76–5.89 (m, 1H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 35.95 (t, $J=22.4$ Hz), 107.61–124.88 (m, CF_2, CF_3), 122.35, 125.07; EIMS (relative intensity) m/z 561 (M^++1, 11), 560 (M^+, 71), 541 (21), 495 (57), 477 (7), 131 (16), 119 (10), 91 (100), 69 (18), 41 (52); HRMS calcd for $C_{13}H_5F_{21}$ m/z 560.0056, found: 560.0054. 2-Methyl-3-(9-methylperfluorodecyl)prop-1-ene (**8**): ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.88 (s, 3H), 2.78 (t, $J=19.3$, 2H), 4.97 (s, 1H), 5.11 (s, 1H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 23.48, 38.78 (t, $J=21.8$ Hz), 110.80–120.86 (m, CF_2, CF_3), 118.85, 134.06; EIMS (relative intensity) m/z 625 (M^++1, 17), 624 (M^+, 100), 605 (15), 591 (19), 545 (6), 105 (23), 69 (11), 65 (12), 60 (12), 55 (68); HRMS calcd for $C_{15}H_7F_{23}$: m/z 624.01804, found: 624.0175. 3-Methyl-3-(7-methylperfluorooctyl)prop-1-ene (**10**): ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.26 (d, $J=6.9$ Hz, 3H), 2.99–3.09 (m, 1H), 5.22–5.28 (m, 2H), 5.72–5.85 (m, 1H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 13.18, 41.45 (t, $J=21.5$ Hz), 109.9–120.35 (m, CF_2, CF_3), 118.85, 132.88; EIMS (relative intensity) m/z 524 (M^+, 5), 505 (11), 585 (7), 477 (4), 105 (55), 69 (14), 65 (12), 55 (100); HRMS calcd for $C_{13}H_7F_{19}$: m/z 524.0244, found: 524.0248.
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12. Perfluorinated olefins are important building blocks for the preparation of more complex organofluorine systems.[a] Previous methods for the synthesis of 3-(perfluoroalkyl)prop-1-enes include metal catalyzed reactions of perfluoroalkyl iodides with allyl halides,[b] allyltrimethylsilane[c] and allyltributyltin compounds.[d] A synthesis involving the use of perfluoroalkanesulfinates as intermediates, has also been reported.[e] Perfluoroalkylation by radical addition into allylic halides has been reported.[f,g] (a) Ameduri, B.; Boutevin, B.; Guida-Piertrasanta, F.; Manseri, A.; Ratsimihety, A.; Caporiccio, G. *J. Polym. Sci., Part A: Polym. Chem.* **1996**, *34*, 3077–3090 (see also Ref. 7b); (b) Kitazume, T.; Ishikawa, N. *J. Am. Chem. Soc.* **1985**, *107*, 5186–5191; (c) Fuchikami, T.; Ojima, I. *Tetrahedron Lett.* **1984**, *25*, 307–308; (d) Matsubara, S.; Mitani, M.; Utimoto, K. *Tetrahedron Lett.* **1987**, *28*, 5857–5860; (e) Hu, C.-M.; Qing, F.-L.; Huang, W.-Y. *J. Org. Chem.* **1991**, *56*, 2801–2804; (f) Rubio, S.; Blancou, H.; Commeyras, A. *J. Fluorine Chem.* **1999**, *99*, 171–175; (g) Napoli, M.; Gambaretto, G. P. *J. Fluorine Chem.* **1997**, *84*, 111–120.