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A general, efficient approach for the synthesis of fluorocarbon iodides and di-iodides bearing hydrocarbon groups is described and the synthetic utility of these new systems is demonstrated in reactions with thiols.

Perfluorocarbon iodides (R_FI) have been important for many years as 'building blocks' for the synthesis of various organic compounds containing fluorine.^{1–3} For example, they are crucial components in the synthesis of highly efficient surfactants on the industrial scale.⁴ Here, we report an approach to the synthesis of fluorocarbon iodides that bear hydrocarbon endgroups and demonstrate the potential of these systems for further synthesis of fluorinated derivatives.

We are exploring the use of the carbon-hydrogen bond as a functional group in efficient free radical chain reactions with fluorinated alkenes,⁵ *e.g.* formation of **1** and **2** from cyclohexane,[‡] and have begun to explore the chemistry of the resultant fluorinated adducts. It has been demonstrated that stereospecific elimination of hydrogen fluoride⁵ from **1** and **2** leads to unsaturated derivatives **3** and **4** respectively. We now find that alkene derivatives **3** and **4** react with a stoichiometric mixture of iodine pentafluoride and iodine, that corresponds to iodine monofluoride, giving fluorinated iodide **5** and di-iodide **6** respectively in efficient processes (Scheme 1).

The mechanism of iodine monofluoride addition is of interest because the process is regiospecific, to the limits of detection by ¹⁹F NMR. In principle, we could envisage two possible mechanisms for addition of I–F to **3** (Scheme 2). Route B involves first addition of iodine to the double bond, but the next step would then require selective replacement of iodine at the R–CFI site by fluorine and we see no convincing reason for this to occur. Furthermore, we have been unable to add iodine to **3** to give a di-iodide. In contrast, we find that other additions to **3** involving bromine, iodine monochloride and iodine monobromide are efficient processes and moreover, additions



Scheme 1 Reagents and conditions: i, CF₂=CF–CF₃, (*t*-BuO)₂, 140 °C; ii, t-BuOK, 0 °C; iii, I₂, IF₅, 0 °C.

† Electronic supplementary information (ESI) available: characterisation of new fluorocarbon iodides 5–9. See http://www.rsc.org/suppdata/cc/b1/ b107565a/



involving ICl and IBr are regiospecific. It is surprising that these electrophilic additions proceed so readily with electron deficient double bonds but the regioselectivity is entirely consistent with an electrophilic process. The developing carbocationic site in intermediate **7a** is stabilised by cyclohexyl and by fluorine, whereas **7b** would be strongly destabilised by the attached trifluoromethyl group and so, consequently, we favour Route A.

Novel iodides **5** and **6** react with thiols and di-thiols, most likely *via* an S_{RN} 1 mechanism,⁶ giving thioethers **8a–d**⁷ and di-thioethers **9**, mostly in high yields (Scheme 3) and oxidation of the thioether products to the corresponding sulphones was possible using chromium trioxide in acetic acid.

These preliminary results demonstrate that these unusual fluorocarbon iodide 'building blocks' could be used for approaches to a variety of new systems containing fluorinated groups.

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Notes and references

‡ Reaction of cyclohexane with two equiv. of hexafluoropropene yields a mixture of 1,3- and 1,4- dihexafluoropropylcyclohexane adducts. However, the *trans*-1,4-diadduct **2** crystallises from the diadduct mixture and can, therefore be readily separated and purified by filtration (see ref. 5).

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- 7 All compounds were characterised by elemental analysis, NMR and mass spectrometry. For example, **8d**; a yellow oil; bp 292 °C; (Found: C, 48.7; H, 6.3. $C_{26}H_{38}F_{12}S_2$ requires C, 48.6; H, 5.9%); v_{max}/cm^{-1} 2857 and 2932 (C–H); δ_{H} 1.0 –2.0 (32H, m, CH₂), 2.20 (2H, m, CHCF₂), 2.8 (4H, m, CH₂S); δ_{C} 24.7 (t, ${}^{3}J_{CF}$ 4.2, CH₂CH), 25.4 (s, CH₂), 25.5 (s, CH₂), 25.5 (t, ${}^{3}J_{CF}$ 4.2, CH₂CH), 25.7 (s, CH₂), 28.5 (s, C-4), 28.8 (s, C-3), 28.9 (s, C-2), 39.0 (s, CH₂S), 42.4 (t, ${}^{2}J_{CF}$ 21.7, CHCF₂), 101.4 (dm, ${}^{1}J_{CF}$ 242.7, CF), 120.6 (ddd, ${}^{1}J_{CF}$ 263.1, ${}^{1}J_{CF}$ 253.7, ${}^{2}J_{CF}$ 24, CF₂), 122.3 (qd, ${}^{1}J_{CF}$ 287.6, ${}^{2}J_{CF}$ 35.2, CF₃); δ_{F} –72.8 (3F, m, CF₃), −112.0 and −112.7 (2F, AB, J_{AB} 267.6, CF₂), −158.4 (m, CFS); m/z (EI+) 642 (M+, 1%), 409 (40), 227 (65), 143 (100).



Scheme 3 Reagents and conditions: i, PhSNa, DMF, rt; ii, C₈H₁₇SNa, DMF, rt; iii, NaS–C₈H₁₆–SNa, DMF, rt; iv, NaS–C₂H₄–SNa, DMF, rt; v, CrO₃, CH₃COOH, reflux, 3 h.