SAMARIUM DIIODIDE INITIATED ADDITION REACTION OF FLUOROALKYL IODIDES TO OLEFINS

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Abstract: Samarium diiodide was found to be an effective initiator in the addition reaction of fluoroalkyl iodides to olefins.

Since Kagan et al. published their first paper¹ on the applications of divalent lanthanoids in organic synthesis in 1980, samarium diiodide has shown its versatile synthetic utility in organic synthesis². In all the reactions reported, samarium diiodide has been used in excess amount as a reductant. Although perfluoroalkylation of a carbon-carbon double bond, an valuable reaction in organic synthesis, has been realized using photoirradiated³, radical initiated⁴, thermal⁵, electrochemical⁶ and transition metal catalyzed methods⁷, it is still desirable to develop an excellent means for introducing a fluoroalkyl group to organic molecules. We wish to report here the use of a catalytic amount of samarium diiodide as an initiator in addition reaction of fluoroalkyl iodides to olefins.

$$R_{fI} + \underline{\qquad} R \qquad \underbrace{Cat. SmI_2}_{r.t.} \qquad R_{f} \qquad I$$

 $R_{f}=Cl(CF_{2})_{n}-R=alkyl$ n=2,4,6

The procedure is simple: To a mixture of olefin (1 mmol) and fluoroalkyliodide (1 mmol) was added 1 ml of 0.05 M SmI_2 solution in THF⁸ at room temperature. After stirring for 1 h at room temperature, the product was isolated by SiO_2 -chromatography. The results are summarized in the table.

| Entry | Cl(CF2) _n I | Olefin | Conversionb | Yield ^C |
|-------|------------------------|--------------|-------------|---------------------|
| 1 | 2 | 1-hevene | 62 | (%) |
| 2 | 2 | 1-octene | 90 | 80 |
| 3 | 4 | 1-hexene | 75 | 75 |
| 4 | 4 | 1-octene | 91 | 91 |
| 5d | 4 | cyclohexene | 50 | 36(trans:cis=68:32) |
| 6 | 6 | 1-hexene | 85 | 79 |
| 7 | 6 | 1-octene | 96 | 95 |
| 8 | 4 | diallyl ethe | r 86e | 78 |
| 9 | 6 | diallyl ethe | r 80e | 80 |

Table. Samarium Diiodide Initiated Addition Reaction of Fluoroalkyl Iodides to Olefins^a

a: All products gave satisfactory IR, MS and ¹H NMR data, and the new compounds gave satisfactory elementary analytical data; b: Determined by ¹⁹F NMR spectra; c: Isolated yield based on the olefin used; d: Reaction time: 12 h; e: The product is 3-Fluoroalkylmethyl-4-iodomethyl-tetrahydro-furan.

In all cases in the table, the fluoroalkyl group attacks at the 1-position of the olefin. Even β -chloroperfluoroethyliodide (n=2), which gave products in lower yield when some other initiators were empolyed⁹, was used, the reaction affords the addition products in good yield under mild condition (entries 1 and 2).

We propose a radical mechanism for the present reaction on the following basis. Diallyl ether, an excellent radical probe¹⁰, afforded 3-fluoroalkylmethyl-4-iodomethyltetrahydrofuran(entries 8 and 9). Furthermore the reaction can be inhibited by the electron transfer inhibitor, p-dinitrobenzene.



To the best of our knowledge, it is the first example to use SmI_2 as a catalyst to promote the radical addition reactions. The reaction failed to take place for olefins with electronwithdrawing group such as methyl acrylate. No reaction was observed when allyl alcohol was used. The catalyst also showed significant difference in reactivity between monosubstituted and disubstituted olefins. Product was isolated in lower yield from an 1,2-disubstituted olefins probably due to the steric effect (entry 5). 1,1-Disubstituted olefin failed to react. These might be due to the difficulty of the sterically hindered radical to abstract the bulky iodine atom from the fluoroalkyl iodide.

This procedure appears to offer an useful method in the synthesis of organofluoro compounds from monosubstituted olefins.

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