

STUDIES ON SAMARIUM DIIODIDE INITIATED ADDITION REACTION OF FLUOROALKYL IODIDES TO ALKYNES AND ITS MECHANISM

Shengming Ma and Xiyan Lu*

Shanghai Institute of Organic Chemistry, Academia Sinica,
345 Lingling Lu, Shanghai 200032, China

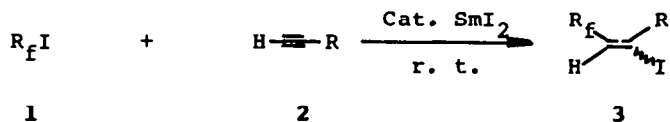
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Abstract: Samarium diiodide was found to be an effective initiator in the addition reaction of fluoroalkyl iodides to alkynes. A single electron-transfer radical chain mechanism was proposed for the reaction based on ESR studies and other experimental results.

Samarium diiodide, a strong single-electron donor, has shown its versatile synthetic utility in organic chemistry.¹ In all the reactions reported so far, samarium diiodide has been used in excess amount as a reductant, while its catalytic property in radical reaction has not been disclosed. Recently, we reported the first example of using samarium diiodide as a catalyst to promote the radical addition reaction,² in which samarium diiodide was found to be able to initiate the addition reaction of fluoroalkyl iodides to olefins under very mild condition with high chemical reactivity and regioselectivity in fairly good yield. In this paper, we wish to report the addition reaction of fluoroalkyl iodides to alkynes.

Results and discussion:

The addition reaction of fluoroalkyl iodides⁴ to alkynes⁶ using photo-irradiated,³ radical initiated,⁷ thermal, electrochemical and transition metal catalyzed methods has been reported, but usually the reaction was carried out at a much higher temperature. Recently, Kitazume et al. found that an enzyme can catalyze the addition reaction of fluoroalkyl iodides to alkynes at room temperature, but it⁸ gives product only in low yield with terminal alkyl substituted alkynes. In our continuing study of the reaction of samarium diiodide, it was found that a catalytic amount of samarium diiodide could initiate the addition reaction of fluoroalkyl iodides to alkynes not only at room temperature but also with excellent yield. The results are shown in Table 1.


 $\text{R}_f = \text{Cl}(\text{CF}_2)_n -$

a: n=2

b: n=4

c: n=6

a: R=n-C₄H₉b: R=n-C₅H₁₁c: R=n-C₈H₁₇d: R=C₆H₅

Table 1. Samarium diiodide initiated addition reaction of fluoroalkyl iodides to alkynes^a

Entry	1	Alkyne	Product	Conversion ^b (%)	Yield ^c (%)
1	1a	2a	3aa	83	76(86:14)
2	1b	2a	3ba	100	90(86:14)
3	1c	2a	3ca	92	86(86:14)
4 ^d	1b	2c	3bc	100	95(88:12)
5 ^d	1c	2c	3cc	92	90(85:15)
6	1b	2b	3bb	91	89(87:13)
7	1b	2d	3bd	40	30(93: 7)
8	1b	Ph-C≡C-Ph	-	0	0

a: All the products gave satisfactory IR, MS, ¹H NMR and ¹⁹F NMR data, and the new compounds gave satisfactory elementary analytical data.

b: Determined by ¹⁹F NMR spectra.

c: Isolated yield based on the alkyne used, the numbers in parentheses are ratios of E-isomer to Z-isomer.

d: 10% samarium diiodide was used.

From Table 1, it was shown that samarium diiodide did initiate the addition reaction of fluoroalkyl iodides to alkynes effectively. This reaction provides an excellent method for the synthesis of fluoroalkyl substituted alkenyl iodides from fluoroalkyl iodides and terminal alkyl substituted alkynes in high yield at mild condition. The yield for phenylacetylene is lower due to the steric or/and electronic effect(entry 7). With diphenylacetylene, the reaction did not afford the expected 1:1 addition product(entry 8). In similar to the results of samarium diiodide initiated

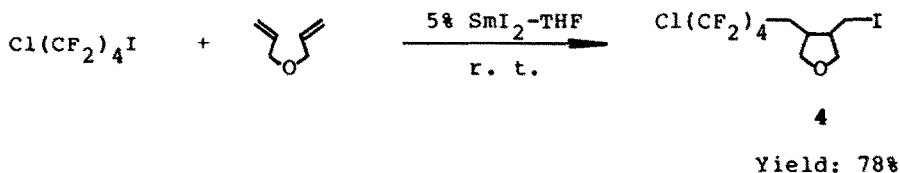
addition reaction of fluoroalkyl iodides to olefins,² the fluoroalkyl group also attacks at the 1-position of alkynes regioselectively. The ratio of E-isomer to Z-isomer is about 85 to 15, while that of phenylacetylene is higher (entry 7). Table 2 shows the comparison of the addition reaction of fluoroalkyl iodides to alkynes under different catalytic systems.

Table 2. Comparison of the addition reaction of fluoroalkyl iodides and terminal alkylsubstituted alkynes initiated by different methods

Catalytic system	Reaction temperature	time(h)	Yield (%)
light ³	r. t.	1.5-72	29-26
heat ⁵	>160°C	-	70-80
radical initiator ⁴	70°C	20	70-80
Pd(PPh ₃) ₄ ^{7b,7c}	70°C	3-6	60-75
enzyme ⁸	r. t.	14-25	25-35
SmI ₂	r. t.	1	76-95

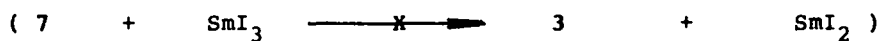
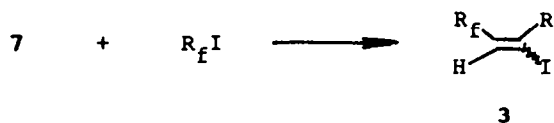
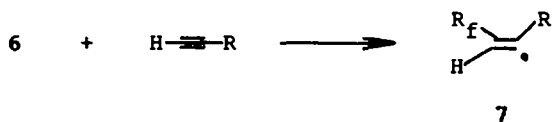
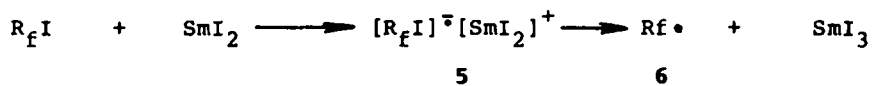
Table 2 shows that the present method has several advantages over the methods reported so far.

In order to study the mechanism of this reaction, diallyl ether was used as a radical probe.^{2,9} The isolation of the cyclic product, 3-(4-(chlorodifluoromethyl)-4-iodomethyl)tetrahydrofuran **4**, from the samarium diiodide initiated reaction of diallyl ether and 4-chlorooctafluorobutyl iodide, revealed its radical pathway.



A single-electron transfer process accounted for the formation of the radical anion **5** was confirmed by the fact that the reaction can be suppressed by a single-electron transfer inhibitor, e.g., p-dinitrobenzene. The fact that the characteristic deep-blue colour of samarium diiodide has not reappeared either during the reaction or after the reaction ruled out the possibility of the abstraction of an iodine atom from samarium triiodide by the newly formed radical **7** in the chain-transfer step. Then a single-electron transfer radical chain mechanism was proposed for this addition reaction as shown in

the following:



This mechanism was further confirmed by the ESR studies. In order to trap the radical intermediate formed during the reaction, *N*-tert-butyl- α -phenyl nitron **8** was chosen as a scavenger. As a control experiment, a THF solution of **8** was proved first to give no ESR signal (Fig. 1).



Fig. 1

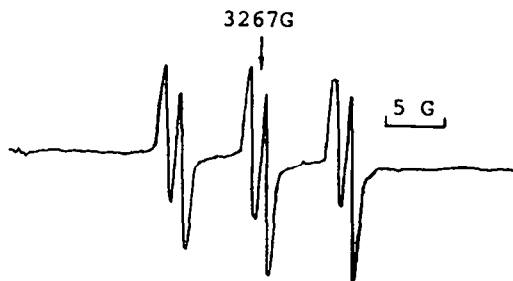


Fig. 2

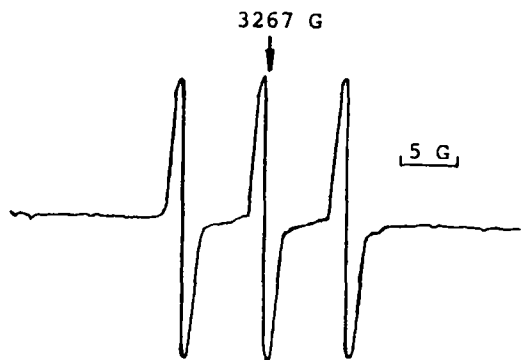


Fig. 3

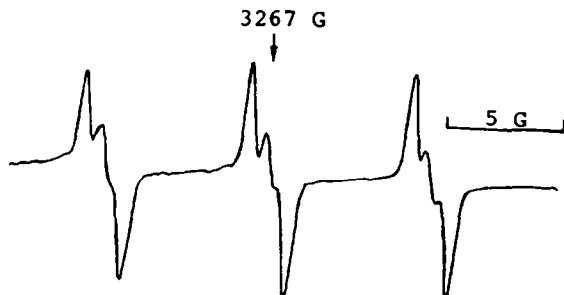
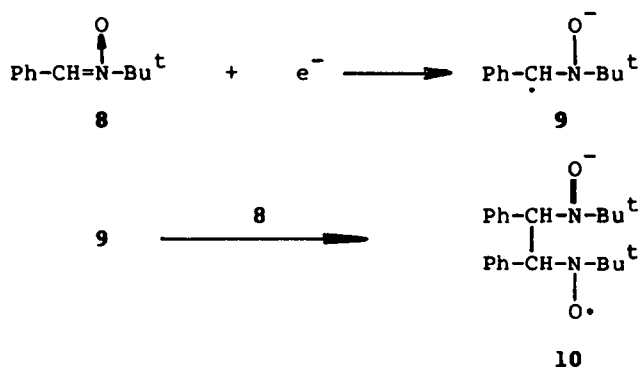
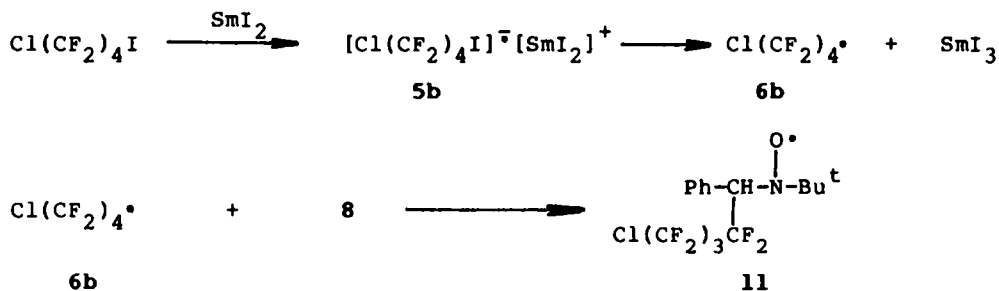


Fig. 4

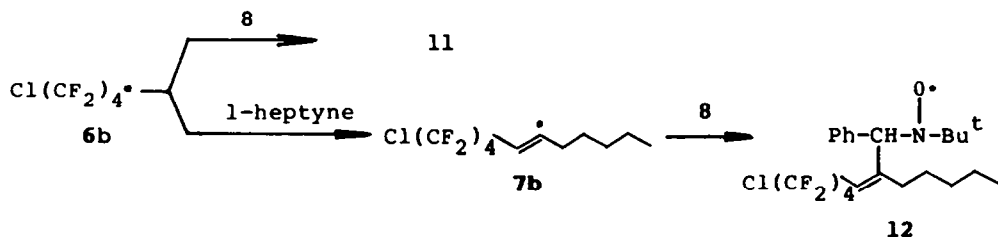
When a THF solution of samarium diiodide was added to the THF solution of **8**, the ESR signal, which was attributed to be the signal of radical **10** ($\alpha_N = 14.63$ G, $\alpha_{\beta-H} = 2.75$ G), was observed as shown in Fig. 2, indicating that samarium diiodide is a strong single-electron donor.



Similarly, if samarium diiodide was added to the THF solution of **8** and 4-chlorooctafluorobutyl iodide, a simple triplet signal, which is attributed to be the spectra of radical **11** ($\alpha_N = 14.50$ G),¹⁰ was observed (Fig. 3).



As a THF solution of samarium diiodide was added to the THF solution of **8**, 4-chlorooctafluorobutyl iodide and 1-heptyne, a signal largely different from Figure 3 was observed (Fig. 4). It can be regarded as the composition of the signals of radicals **11** and **12** ($\alpha_N = 14.13$ G, $\alpha_{\beta-H} = 3.00$ G).



The radical 11 shows a simple triplet signal because the highly electron-withdrawing fluoroalkyl group reduces the interaction of the β -H with the electron spin in radical 11. For radical 12, the fluoroalkyl group and the β -C are separated by a carbon-carbon double bond, thus the β -H shows its original interaction to the electron spin in the radical 12, and its spectra is considered to be similar to that of the radical 10, which shows a group of double-triplet signal (Fig 2). Thus, it is supposed that Figure 4 is the vector composition of the ESR spectra of radicals 11 and 12.

Based on the above results, both the radical intermediate 6b formed by the dissociation of radical anion 5b and the newly formed radical intermediate 7b formed by the addition of 6b to 1-heptyne have been scavenged in the form of the stable radicals 11 and 12. Thus, the single-electron transfer radical chain addition mechanism was well confirmed.

Further applications of samarium diiodide to radical reaction are being investigated in our laboratory.

Experimental:

All the materials used were freshly distilled immediately before use. THF was freshly distilled from sodium ketyl. The ^1H NMR spectra were measured on a Varian XL-200 (200 MHz) spectrometer using TMS as an internal standard. ^{19}F NMR spectra were taken on a Varian EM-360 (60MHz) using trifluoroacetic acid as the external standard (positive for upfield shifts). ESR spectra were recorded with a Varian E-112 EPR spectrometer. IR spectra were taken on a Perkin-Elmer 983 spectrometer. MS spectra were taken on a Finnigan GC-MS-4021 instrument. The THF solution of samarium diiodide was prepared by the literature method. All the reactions were carried out in prepurified nitrogen atmosphere.

General procedure for the addition reaction of fluoroalkyl iodides to alkynes:

To a mixture of an alkyne (1 mmol) and a fluoroalkyl iodide (1 mmol) was added 1 ml of 0.05 M samarium diiodide solution in THF at room temperature. After stirring for an additional one hour at room temperature, the pure product was obtained after removing the catalyst by chromatography on a column of silica gel followed by removing the solvent.

3aa: δ : [6.33(t, $J_{\text{H-F}}=14$ Hz), 6.24 (t, $J_{\text{H-F}}=14$ Hz), 1H], 2.64(m, 2H), 1.56(m, 2H), 1.35(m, 2H), 0.94(t, 3H); δ_{F} : -5.7(2F), [+28.0, +31.3, 2F]; m/z: 346(M ^{+37}Cl), 9.64), 344(M ^{+35}Cl), 23.64), 304(M ^{+37}Cl -C $^{35}\text{H}_6$, 13.49), 302 (M ^{+35}Cl -C $^{37}\text{H}_6$, 36.68), 219(M ^{+37}Cl -I, 39.51), 217(M ^{+35}Cl -I, 100.00), 199 (M ^{+37}Cl -I-HF, 5.80), 197(M ^{+35}Cl -I-HF, 19.20); ν_{max} : 2929, 1632, 1458,

1189, 1136, 1094 and 1038 cm^{-1} .

3ba: δ_{H} : [6.32(t, $J_{\text{F-H}} = 14$ Hz), 6.24(t, $J_{\text{F-H}} = 14$ Hz), 1H], 2.64(m, 2H), 1.57(m, 2H), 1.38(m, 2H), 0.94(t, 3H); δ_{F} : -9.0(2F), [+28.5, +31.8, 2F], +42.7(2F), +45.7(2F); m/z: 445(M+1, 4.47), 444(M⁺, 10.11), 319(M⁺(³⁵Cl)-I, 23.19), 317(M⁺(³⁵Cl)-I, 62.07), 299(M⁺(³⁷Cl)-I-HF, 12.30), 297(M⁺(³⁵Cl)-I-HF, 41.17), 41(C₃H₇⁺, 100.00); ν_{max} : 2961, 2937, 2875, 1634, 1467, 1382, 1367, 1342, 1193, 1137, 1101 and 982 cm^{-1} .

3ca: δ_{H} : [6.32(t, $J_{\text{F-H}} = 14$ Hz), 6.24(t, $J_{\text{F-H}} = 14$ Hz), 1H], 2.64(m, 2H), 1.60(m, 2H), 1.39(m, 2H), 0.93(t, 3H); δ_{F} : -9.0(2F), [+28.5, +31.5, 2F], +43.0(2F), 44.5(4F), 45.9(2F); m/z: 546(M⁺, 1.57), 421(M⁺(³⁵Cl)-I, 4.06), 419(M⁺(³⁵Cl)-I, 13.45), 401(M⁺(³⁷Cl)-I-HF, 3.31), 399(M⁺(³⁵Cl)-I-HF, 9.35), 43(C₃H₇⁺, 100.00); ν_{max} : 2962, 2934, 2875, 1634, 1467, 1342, 1318, 1211, 1150 and 997 cm^{-1} .

3bc: (Found: C, 34.15, H, 3.60, F, 30.44., calcd. for C₁₄H₁₈ClF I: C, 33.59, H, 3.62, F, 30.36); δ_{H} : [6.38(t, $J_{\text{F-H}} = 14$ Hz), 6.24(t, $J_{\text{F-H}} = 14$ Hz), 1H], 2.62(m, 2H), 1.61(m, 2H), 1.29(m, 10H), 0.90(t, 3H); δ_{F} : -9.0(2F), [+28.3, +31.6, 2F], +42.7(2F), +45.7(2F); m/z: 502(M⁺(³⁵Cl), 2.37), 500(M⁺(³⁵Cl), 7.48), 499(M⁻¹, 16.01), 375(M⁺(³⁷Cl)-I, 9.59), 373(M⁺(³⁵Cl)-I, 57.74), 371(95.34), 57(C₄H₉⁺, 100.00); ν_{max} : 2927, 2856, 1634, 1190, 1136 and 842 cm^{-1} .

3cc: (Found: C, 32.19, H, 2.97, F, 38.48. calcd. for C₁₆H₁₈ClF I: C, 31.99, H, 3.02, F, 37.96); δ_{H} : [6.31(t, $J_{\text{F-H}} = 14$ Hz), 6.24(t, $J_{\text{F-H}} = 14$ Hz), 1H], 2.63(m, 2H), 1.60(m, 2H), 1.29(m, 10H), 0.92(t, 3H); δ_{F} : -9.0(2F), [+28.6, +31.5, 2F], +43.0(2F), +44.6(4F), 46.3(2F); m/z: 602(M⁺(³⁵Cl), 0.38), 600(M⁺(³⁵Cl), 1.42), 599(M⁺(³⁵Cl)-I, 4.33), 475(M⁺(³⁵Cl)-I, 1.86), 473(M⁺(³⁵Cl)-I, 10.32), 455(M⁺(³⁷Cl)-I-HF, 0.26), 453(M⁺(³⁵Cl)-I-HF, 0.32), 57(C₄H₉⁺, 100.00); ν_{max} : 2929, 2857, 1634, 1467, 1212, 1150, 1107 and 998 cm^{-1} .

3bb: (Found: C, 28.85, H, 2.75, F, 32.17, calcd. for C₁₁H₁₂ClF I: C, 28.81, H, 2.64, F, 33.14); δ_{H} : [6.32(t, $J_{\text{F-H}} = 14$ Hz), 6.24(t, $J_{\text{F-H}} = 14$ Hz), 1H], 2.63(m, 2H), 1.60(m, 2H), 1.30(m, 4H), 0.91(t, 3H); δ_{F} : -9.0(2F), [+28.5, +31.7, 2F], +42.7(2F), +45.5(2F); m/z: 460(M⁺(³⁵Cl), 1.17), 458(M⁺(³⁵Cl), 3.75), 333(M⁻¹, 14.14), 313(M⁺(³⁷Cl)-I-HF, 3.21), 311(M⁺(³⁵Cl)-I-HF, 9.70), 55(C₄H₇⁺, 100.00); ν_{max} : 2931, 1633, 1190 and 1136 cm^{-1} .

3bd: δ_{H} : 7.30(m, 5H), 6.60(t, 1H, $J_{\text{F-H}} = 13.6$ Hz); δ_{F} : -9.0(2F), [+28.2, +32.5, 2F], +42.5(2F), +45.0(2F); m/z: 465(M+1, 0.54), 429(M⁻¹Cl, 3.28), 387(M⁺-Ph, 0.23), 339(M⁺(³⁵Cl)-I, 33.26), 337(M⁺(³⁵Cl)-I, 100.00), 319(M⁺(³⁷Cl)-I-HF, 0.81), 317(M⁺(³⁵Cl)-I-HF, 2.25); ν_{max} : 3060, 2925, 1637, 1191 and 1131 cm^{-1} .

Reaction in presence of p-dinitrobenzene:

A THF solution of samarium diiodide (0.05 M, 1 ml) was added to the solution of 1-heptyne (1 mmol), 4-chlorooctafluorobutyl iodide (1 mmol), p-dinitrobenzene (20mg, 0.1 mmol) and THF (1 ml) at room temperature. No reaction occurred as shown by ¹⁹F NMR spectra.

Procedure for ESR studies:

1. N-tert-butyl- α -phenyl nitron was placed in a ESR tube, THF was added to dissolve it, then the tube was sealed and the ESR spectra were recorded at room temperature.

2. The sample (see text) was placed in a ESR tube, a THF solution of samarium diiodide (0.05 M) was added at room temperature. The deep-blue colour turned rapidly into bright yellow, the tube was sealed and the ESR spectra were recorded at room temperature.

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