Samarium Di-iodide Initiated Addition of Polyhalogenomethanes to Olefins

Shengming Ma and Xiyan Lu *
Shanghai Institute of Organic Chemistry, Academia Sinica, 345 Lingling Lu, Shanghai 200032, China

Samarium di-iodide is different from other inorganic metallic salts, in the catalytic properties of the addition of polyhalogenomethanes to olefins. The reaction mechanism is briefly discussed.

Addition of polyhalogenomethanes to olefins is both effective for forming carbon–carbon bonds and also has important synthetic potential because it results in elaboration of the polyhalogenomethyl group. Such reactions can be initiated by photoirradiation,[1] radical initiators,[2] inorganic metallic salts,[3] ruthenium complexes[4–7] and other transition metal complexes.[8,9] In contrast to the photo- or peroxide-initiated reactions, copper chloride[3] completely suppresses telomerization because the metal chloride participates in the propagation step, and in the case of transition metal complexes,[4] the radical intermediates involved in the reaction process are assumed to be complexed with the metal species, and thus show their unique stereoselectivity. Samarium di-iodide has been found to be a strong single-electron donor and its versatile utility as a reductant in organic synthesis has been demonstrated.[10] During studies of the catalytic properties of samarium di-iodide in radical reactions, we found that it is an excellent catalyst for the addition of fluoroalkyl iodides to olefins[11] or alkynes.[12]

Results and Discussion

Samarium di-iodide catalyses the addition of fluoroalkyl iodides to olefins or alkynes at room temperature with high chemical reactivity and regioselectivity.[11,12] Addition of samarium di-iodide to a mixture of oct-1-ene and carbon tetrachloride at room temperature (Scheme 1), failed to give a 1:1 adduct although the typical deep-blue colour of samarium di-iodide disappeared immediately. The 1:1 adduct (3ab) was obtained in 25% yield under reflux conditions. Bromotrichloromethane was found to be more reactive than carbon tetrachloride and Table 1 lists the results of addition of the former to oct-1-ene under different reaction conditions. It can be seen that samarium di-iodide initiates the addition of bromotrichloromethane to oct-1-ene in low yield at room temperature and in moderate yield at a higher temperature.

The results in Table 2 show that samarium di-iodide-initiated addition of polyhalogenomethanes to olefins affords the 1:1 adduct (3) in moderate yield. The trihalogenomethyl group also attacks the 1-position of the olefins exclusively. As in the addition of fluoroalkyl iodides to olefins,[11] the reaction failed to afford the expected 1:1 adduct for electron-deficient olefins due to the electronic effect. Further, for a 1,1-disubstituted olefin, the reaction again failed to afford the expected 1:1 adduct, thus showing its unique chemical selectivity.

Table 1. The addition reaction of bromotrichloromethane to oct-1-ene initiated by samarium di-iodide.

Entry	Ratio (1b)/(2b)	SmI$_2$ (%)	Solvent	Reaction conditions	Yield (%)
1	2:1	10	MeCN	R.t., 10 h	23
2	2:1	10	MeCN	70 °C, 10 h	71
3	2:1	5	MeCN	50 °C, 10 h	35
4	3:1	5	MeCN	50 °C, 10 h, then r.t., 10 d	71
5	3:1	5	MeCN	60 °C, 10 h, then r.t., 10 d	81
6	2:1	10	THF	70 °C, 10 h	52

3243.79 G   3293.225 G

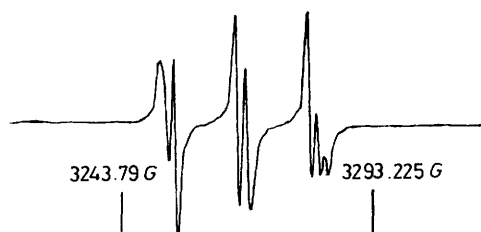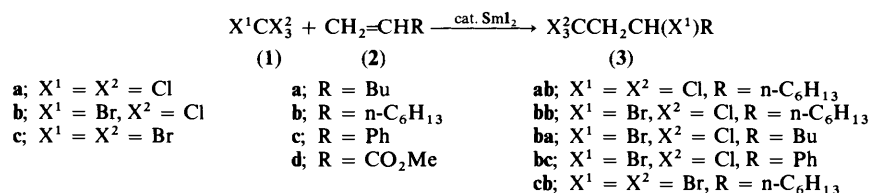**Figure.** ESR spectrum of radical species (9).

Isolation of 4-bromomethyl-3-(2,2,2-trichloroethyl)methyltetrahydrofuran (4) from the addition of bromotrichloromethane to diallyl ether, revealed the radical nature of the mechanism (Entry 6, Table 2). The results in Tables 1 and 2, show that bromotrichloromethane is more reactive than carbon tetrachloride, a result similar to that reported by Kharasch et al.[2] The results are different from those obtained for metal salts or complex-catalysed reactions, in which bromotrichloromethane and carbon tetrachloride have almost the same reactivity because of the metal–halogen species involved in the propagation step.[8,13] The conversion of trivalent samarium into divalent samarium under normal conditions is precluded by its high redox potential $[E^{\circ}(Sm^{3+}/Sm^{2+}) = -1.55 \text{ V}]$. Thus, it is concluded that abstraction of a halogen atom by the newly formed radical (7) from the polyhalogenomethane molecule rather than from the samarium trihalide formed in step (2) constitutes the chain-transfer step (4). This result is different

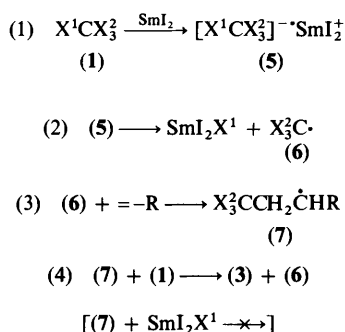$$X^1CX_3^2 + CH_2=CHR \xrightarrow{\text{cat. SmI}_2} X_3^2CCH_2CH(X^1)R$$

(1)   (2)   (3)

a; X^1 = X^2 = Cl   a; R = Bu   ab; X^1 = X^2 = Cl, R = n-C$_6$H$_{13}$
b; X^1 = Br, X^2 = Cl   b; R = n-C$_6$H$_{13}$ bb; X^1 = Br, X^2 = Cl, R = n-C$_6$H$_{13}$
c; X^1 = X^2 = Br   c; R = Ph   ba; X^1 = Br, X^2 = Cl, R = Bu
                            d; R = CO$_2$Me   bc; X^1 = Br, X^2 = Cl, R = Ph
                                               cb; X^1 = X^2 = Br, R = n-C$_6$H$_{13}$

Scheme 1.

Table 2. Samarium di-iodide-initiated addition of polyhalogenomethanes to olefins.[a]

Entry	Compounds		Ratio (1)/(2)	Product	Reaction temp. (°C)	Yield[b] (%)
1	(1a)	(2b)	2:1	(3ab)	Reflux	25
2	(1b)	(2b)	2:1	(3bb)	70	71
3	(1b)	(2a)	3:1	(3ba)	60	71
4	(1b)	(2c)	3:1	(3bc)	60	46
5	(1c)	(2b)	2:1	(3cb)	60	68
6	(1b)	(2e)[c]	1:1	(4)[c]	60	60
7	(1b)	Cyclohexene	3:1	mixture[d]	60	—
8	(1b)	(2d)	3:1	—	60	0
9	(1b)	3-Methyleneheptane	3:1	—	60	0

[a] All products gave satisfactory IR, MS and ^{1}H NMR data, and the new compounds gave satisfactory elementary analytical data. Reaction time: 10 h; solvent: CH_3CN; SmI_2: 10%. [b] Isolated yield based on the olefin used. [c] (2e): diallyl ether; (4) is characterized as 4-bromomethyl-3-(2′,2′,2′-trichloroethyl)tetrahydrofuran. [d] There are other products besides the expected 1:1 adduct in the mixture.

from that of catalysts such as copper or ferric chloride. It is still not apparent whether the radical intermediates (6) and (7) are co-ordinated with samarium or not. A single-electron transfer radical-chain addition mechanism is proposed for this reaction (see Scheme 2).

$$(1) \quad X^1CX_3^2 \xrightarrow{\ SmI_2\ } [X^1CX_3^2]^{-\cdot}SmI_2^+$$
$$\qquad\quad (1) \qquad\qquad\qquad\quad (5)$$

$$(2) \quad (5) \longrightarrow SmI_2X^1 + X_3^2C\cdot$$
$$\qquad\qquad\qquad\qquad\qquad\quad (6)$$

$$(3) \quad (6) + \mathrm{=}{-}R \longrightarrow X_3^2CCH_2\dot{C}HR$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\quad (7)$$

$$(4) \quad (7) + (1) \longrightarrow (3) + (6)$$

$$[(7) + SmI_2X^1 \nrightarrow]$$

Scheme 2.

This mechanism was further supported by an ESR study. The trichloromethyl radical formed by the dissociation of the radical anion (5a) was scavenged by N-t-butyl-α-phenylnitrone in the form of the stable radical (9) (Scheme 3), which shows the ESR signal shown in the Figure ($a_N = 14.07$ G, $a_\beta^H = 1.74$ G; lit.,[14] $a_N = 14.00$ G, $a_\beta^H = 1.71$ G).

$$\mathrm{Ph{-}CH{=}\overset{\overset{O}{\uparrow}}{N}{-}Bu^t} + \cdot CCl_3 \longrightarrow \mathrm{Ph{-}CH{-}\overset{\overset{O^\cdot}{\uparrow}}{N}{-}Bu^t}$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad |$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad Cl_3C$$
$$\quad (8) \qquad\qquad (6a) \qquad\qquad\qquad (9)$$
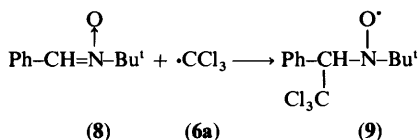
Scheme 3.

Experimental

All the materials used were freshly distilled immediately before use. Tetrahydrofuran (THF) was freshly distilled from sodium ketyl. Acetonitrile was freshly distilled from P_2O_5. The ^{1}H NMR spectra were measured on a Varian EM-360 (60 MHz) spectrometer using tetramethylsilane (TMS) as an internal standard. The ESR spectra were recorded with a Varian E-112 EPR spectrometer, IR spectra on a Perkin-Elmer 983 spectrometer, and mass spectra on a Finnigan GC-MS-4021 instrument. The THF or acetonitrile solutions of samarium di-iodide were prepared by the literature methods.[15] All the reactions were carried out in a pre-purified nitrogen atmosphere.

Typical Procedure for Addition of Polyhalogenomethanes to Olefins.—Samarium di-iodide (1 ml) in MeCN (0.1M) was added to a mixture of oct-1-ene (1 mmol) and bromotrichloromethane (2 mmol) under a nitrogen atmosphere at 70 °C. The mixture was heated for 10 h at this temperature, after which the reaction was stopped, the catalyst was removed by a short column of silica gel using light petroleum (b.p. 60–90 °C) as the eluant, and the product was obtained by removal of solvent.

1,1,1,3-*Tetrachlorononane* (3ab). δ_H(60 MHz; CCl_4) 4.37 (1 H, m), 3.40 (2 H, m), 2.03–1.70 (2 H, m), 1.37 (8 H, m), and 0.90 (3 H, t); m/z 231 (M^+ − Cl, 0.35%), 229 (M^+ − Cl, 0.62), 195 (M^+ − HCl − Cl, 3.81), 193 (M^+ − HCl − Cl, 9.18), 159 (M^+ − 3Cl, 15.76), 157 (M^+ − 3Cl, 52.79), and 121 (100.00); v_{max} 2 958, 2 925, 1 261, 1 038, 793, and 701 cm^{-1}.

3-*Bromo*-1,1,1-*trichlorononane* (3bb). δ_H(60 MHz; CCl_4) 4.27 (1 H, m), 3.30 (2 H, m), 1.92 (2 H, m), 1.35 (8 H, m), and 0.90 (3 H, t); m/z 275 (M^+ − Cl, 0.15%), 235 (M^+ − Br, 0.22), 233 (M^+ − Br, 0.28), 231 (M^+ − Br, 0.67), 229 (M^+ − Br, 0.72), 195 (M^+ + 1 − Br − Cl, 3.77), 193 (M^+ + 1 − Br − Cl, 6.43), and 159 (M^+ − Br − 2Cl, 18.02), 157 (M^+ − Br − 2Cl, 52.19), 121 (100.00); v_{max} 2 954, 2 927, 787, and 703 cm^{-1}.

3-*Bromo*-1,1,1-*trichloroheptane* (3ba). δ_H(60 MHz; CCl_4) 4.31 (1 H, m), 3.30 (2 H, m), 1.90 (2 H, m), 1.40 (4 H, m), and 0.90 (3 H, t); m/z 265 (M^+ − CH_3, 1.15%), 247 (M^+ − Cl, 0.80), 245 (M^+ − Cl, 0.57), 207 (M^+ − Br, 0.60), 205 (M^+ − Br, 0.44), 203 (M^+ − Br, 0.99), 201 (M^+ − Br, 1.15), 167 (M^+ − HBr − Cl, 7.92), and 93 (100.00); v_{max} 2 957, 2 927, 1 260, 1 177, 1 036, 783, and 701 cm^{-1}.

(1-*Bromo*-3,3,3-*trichloropropyl)benzene* (3bc). δ_H(60 MHz; CCl_4) 7.36 (5 H, m), 5.477 (1 H, m), and 3.73 (2 H, m); m/z 304 (M^+, 0.09%), 302 (M^+, 0.18), 300 (M^+, 0.08), 240 (M^+ − Cl − C_2H_5, 6.17) 238 (M^+ − Cl − C_2H_5, 6.49), 221 (M^+ − Br, 8.61), 125 (100.00), and 77 (Ph^+, 29.26); v_{max} 3 063, 3 029, 2 925, 1 229, 1 056, 766, and 698 cm^{-1}.

1,1,1,3-*Tetrabromononane* (3cb). δ_H(60 MHz; CCl_4) 4.37–3.23 (3 H, m), 2.03 (2 H, m), 1.39 (8 H, m), and 0.90 (3 H, t); m/z 367 (M^+ − Br, 0.12%), 365 (M^+ − Br, 0.49), 363 (M^+ − Br, 0.55), 361 (M^+ − Br, 0.18), 283 (M^+ + 1 − 2Br, 4.79), 241 (M^+ − Br − C_3H_5, 2.78), 203 (M^+ − 3Br, 23.89), 201 (M^+ − 3Br, 29.94), and 55 ($C_4H_7^+$, 100.00); v_{max} 2 925, 2 855, 1 192, 1 030, 720, and 617 cm^{-1}.

4-*Bromomethyl*-3-(2,2,2-*trichloroethyl)tetrahydrofuran* (4). δ_H(60 MHz; CCl_4) 4.25–2.70 (m); m/z 299 (M^+ + 1, 0.94%), 297 (1.66), 296 (0.57), 295 (1.22), 217 (5.25), 215 (5.43), 181 (21.18), 115 (30.70), 113 (53.75), 109 (25.17), and 89 (100.00); HRMS 293.9000 (Calc. for $C_7H_{10}BrCl_3O$: 293.8981); v_{max} 2 960, 1 260, 1 021, 798, and 700 cm^{-1}.

Procedure for the ESR Study.—Carbon tetrachloride, oct-1-

ene, *N*-t-butyl-α-phenylnitrone and THF were placed in an ESR tube, and a THF solution of samarium di-iodide (0.05M) was added to the tube at room temperature. The deep-blue colour rapidly turned to bright yellow; the tube was then sealed and the ESR spectra were recorded at room temperature.

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