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Samarium(II) Iodide Catalyzed Addition of CCl_3Br and CBr_4 to Olefinic Compounds: Synthesis of the Key Intermediates for Synthetic Pyrethroids

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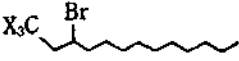

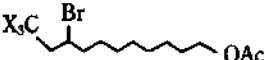

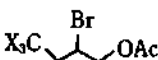

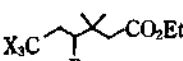
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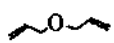
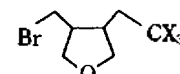

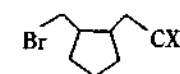
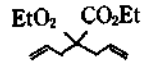
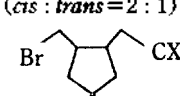
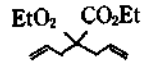
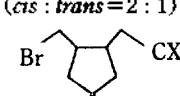
The addition reaction of polyhaloalkanes to olefins is catalyzed by free-radical initiators such as dibenzoyl peroxide

or azoisobutyronitrile (AIBN).¹ A range of transition metal (e.g., Cu, Fe, Co, V, Pd, Cr, Ru, and Re) complexes and salts has also been found to act as catalysts for these addition reactions.² Recently, samarium(II) iodide is known to be a useful reducing reagent. Its synthetic utility has been studied³ and found to be an effective initiator in the addition of fluoroalkyl iodide to terminal alkenes and alkynes.⁴ As the regioselective addition of polyhaloalkanes to terminal olefins is of interest in wide synthetic application, we describe here the samarium(II) iodide catalyzed regioselective addition of bromotrichloromethane and tetrabromomethane to olefinic compounds.

We have investigated the reaction of several terminal olefins with CCl_3Br and CBr_4 by using SmI_2 as a catalyst (0.1 equiv) in dimethylformide at 80–90°C. The results are summarized in Table 1. The terminal olefins **1a–c** were treated with bromotrichloromethane and tetrabromomethane in DMF at 80°C or 90°C to produce the adducts **2a–c** or **3a–c**, respectively (Entries 1–3). The adducts **2d** and **3d** (Entry 4) thus obtained by this method are the key intermediates in the synthesis of synthetic pyrethroids, such as cypermethrin and decamethrin.⁵ In the case of terminal 1,6-dienes, initial formation of radical followed by cyclization by 5-*exo-trig* mode afforded the cyclized products **4e–g** and **5e–f** (Entry 5–7). The reaction of diallyl ether (**1e**) with CCl_3Br and CBr_4 gave the tetrahydrofuran (**4e** and **5e**) with low *cis* (1 : 1) selectivities (Entry 5). In the addition of CCl_3Br and CBr_4 to 1,6-heptadiene (**1f**), the regioselective radical cyclization proceeded more stereoselectively for *cis*-isomers (2 : 1) (Entry 6). The addition reaction of **1f** with CBr_4 afforded cyclopentane (**5f**) and the simple addition product as the minor and major product, respectively. This could imply that the simple addition and cyclization are competing in the radical chain propagating step (Entry 6). On the other hand, the cyclization reaction of the disubstituted dienes (**1g**) with CCl_3Br and CBr_4 occurred without the monoadducts with higher *cis*-stereose-

Table 1. Samarium (II) Iodide Catalyzed Addition of Bromotrichloromethane and Tetrabromomethane to Olefinic Compounds^a

Entry	Substrate	Haloalkanes	Product ^b	Reaction Temp (°C)	Conditions ^b Temp (°C)	Isolated Yield ^c (%)
1		CCl_3Br CBr_4		90	16	74
			2a X=Cl 3a X=Br	80	10	73
2		CCl_3Br CBr_4		90	24	71
			2b X=Cl 3b X=Br	80	24	60
3		CCl_3Br CBr_4		90	24	81
			2c X=Cl 3c X=Br	90	14	72
4		CCl_3Br CBr_4		90	12	65
			2d ^b X=Cl 3d ^b X=Br	80	24	53

5		CCl ₃ Br		90	18	55(∼0) ^e
				(<i>cis</i> : <i>trans</i> = 1 : 1) ^d		
6		CCl ₃ Br		90	8	53(37) ^e
				(<i>cis</i> : <i>trans</i> = 2 : 1) ^d		
7		CCl ₃ Br		100	18	45(9) ^e
				(<i>cis</i> : <i>trans</i> = 3 : 1) ^d		
7		CBr ₄		100	18	25(45) ^e
				(<i>cis</i> : <i>trans</i> = 4 : 1)		

^aReactions were carried out in the presence of SmI₂ (0.1 equiv, 0.1 mmol) with the substrate (1 mmol) in DMF (1 ml) (0.1 M).

^bThe products **2a-2d** and **3a-3d** were confirmed by comparison with the authentic compounds prepared by AIBN initiated radical additions. ^cThe yields have not been optimized. ^dThe ratio of monoadduct. ^eThe yield of the remained starting material.

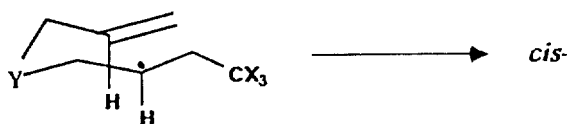


Figure 1.

lectives (3-4 : 1) probably because of the steric effect (Figure 1) in the transition state (Entry 7).

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- The following procedure was typical. To a solution of alkene [**1d**], 5 mmol] and CCl₃Br (5 mmol) in dry DMF (10 ml) was added SmI₂ (0.1 M, 5 ml, 0.1 eq.) and heated at 90°C for 12 h. Aqueous 5% HCl was added and the product (**2d**) was obtained by work-up and separated by column chromatography on silica gel.
- The *cis*-stereochemistry of **4g** was identified by comparison of the data reported in the reference **2f**. ¹H-NMR data of **5c**: ¹H-NMR (500 MHz, CDCl₃) 1.26(t, 6H), 2.50(m, 6H), 2.98(m, 2H), 3.50(q, 2H, *cis*-, major), 3.60(q, 2H, *trans*-, minor), 4.20(q, 4H).