

Generation of Alkylidenecarbenes from 1,1-Dibromoalk-1-enes by the Reaction with Samarium Diiodide in Hexamethylphosphoric Triamide–Benzene†

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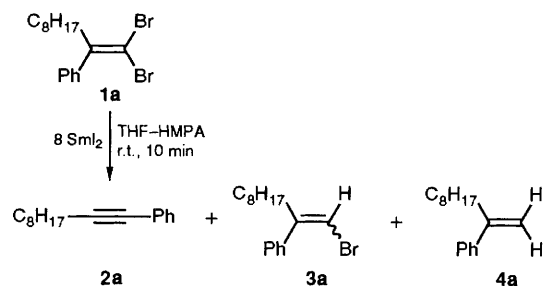
Reaction of 1,1-dibromoalk-1-enes with samarium diiodide in benzene containing 10% of hexamethylphosphoric triamide (HMPA) affords rearranged alkynes; generation of alkylidenecarbenes is probably involved.

Samarium diiodide (SmI_2) has been shown to be a useful reagent for organic synthesis.¹ Barbier-type C–C bond formations, β -eliminations, and simple reductions of organic monohalides with SmI_2 have been widely investigated.^{1d, 2} In contrast to the reactions of monohalides, reactions of *gem*-dihalides with SmI_2 generating carbenes or carbenoids are very limited. SmI_2 -induced Simmons–Smith-type cyclopro-

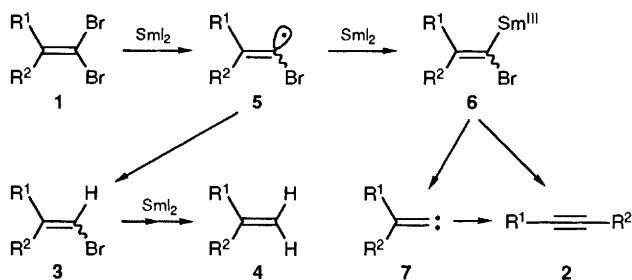
panation using methylene diiodide and 1,3-dipolar addition of an α -ketocarbenoid generated from an α,α -dibromoketone have been reported.³ We report for the first time generation of alkylidenecarbenes (or alkylidenecarbenoids) from 1,1-dibromoalk-1-enes **1** by the reaction with SmI_2 in benzene–HMPA, which affords the rearranged alkynes **2**.⁴

Exposure of 1,1-dibromo-2-phenyldec-1-ene **1a** to 8 equiv. of SmI_2 in THF–HMPA (THF = tetrahydrofuran) (9:1) at room temperature under nitrogen gave the rearranged 1-phenyldec-1-yne **2a**, albeit in low yield (27%) (Scheme 1).⁵ In this reaction, hydrogenative debromination was found to be

† CAUTION: Solvents used in this work, such as HMPA, are highly toxic and care should be taken in their use.



Scheme 1



Scheme 2

a major reaction course; thus, we obtained the partially reduced bromoalkene **3a** in 39% yield as a 1:1 mixture of stereoisomers, and the fully reduced alkene **4a** in 6% yield. It has been shown that the reduction of aryl halides to arenes with SmI_2 in THF involves a hydrogen atom abstraction from the solvent by an intermediate radical, generated by a single electron transfer (SET) from SmI_2 to halides.^{2d} This process may lead to the formation of reduction products **3a** and **4a** in this reaction in THF. In order to decrease the rate of hydrogen atom abstraction from solvents by an intermediate α -bromovinyl radical generated from **1a**, the solvent THF was replaced by benzene, which was frequently used as a solvent in radical reactions.

A solution of diiodoethane (3.55 mmol) in benzene (32 ml) and HMPA (3.6 ml) was added to samarium powder (40 mesh, 5.32 mmol) under nitrogen.[‡] Gentle heating was required to initiate the reaction. The reaction mixture was stirred for 5 days at room temperature to afford a purple solution of SmI_2 in benzene-HMPA. The concentration of SmI_2 was determined by titration using iodine under nitrogen.⁶ The reaction of **1a** with 2.5 equiv. of SmI_2 in benzene-HMPA gave **2a** in 67% yield, along with the formation of **4a** (8%).[§] The bromoalkene **3a** was not detected. Similarly, the reaction of dibromoalkenes **1b–e** gave the rearranged alkynes **2b–e** and the results are summarized in Table 1.⁷

Scheme 2 illustrates possible mechanistic pathways for the reductive alkyne-forming rearrangement of **1**. The formation

[‡] All the attempts to prepare SmI_2 in benzene using samarium and diiodoethane or iodine were found to be fruitless. We found that the addition of 10% of HMPA as a cosolvent to benzene promoted the reaction of samarium and diiodoethane.

[§] For a typical procedure: to a purple solution of SmI_2 (0.094 mol dm^{-3} in benzene-HMPA, 4 ml, 0.38 mmol), a solution of **1a** (50 mg, 0.13 mmol) in benzene (1.2 ml) was added at room temperature under nitrogen. After stirring for 10 min, the mixture was quenched with dilute HCl, and then extracted with diethyl ether. The organic layer was dried and concentrated to afford a crude mixture, which was purified on preparative TLC to give **2a** and **4a**.

Table 1 Reactions of dibromoalkenes with SmI_2 in HMPA-benzene

		Yield of 2 (%) ^a
1a : $\text{R}^1 = \text{C}_8\text{H}_{17}$,	$\text{R}^2 = \text{Ph}$	2a 67
1b : $\text{R}^1 = \text{Me}$,	$\text{R}^2 =$	2b 41
1c : $\text{R}^1 = \text{C}_6\text{H}_{13}$,	$\text{R}^2 = \text{H}$	2c (90)
1d : $\text{R}^1 = \text{C}_8\text{H}_{17}$,	$\text{R}^2 = \text{H}$	2d (74)
1e : $\text{R}^1 = \text{cyclo-C}_6\text{H}_{11}$	$\text{R}^2 = \text{H}$	2e (86)

^a Isolated yield. GLC yields are given in parentheses.

of the alkenylsamarium(III) **6** by the reaction of SmI_2 with the alkenyl radical **5**, generated by a SET from SmI_2 to **1** may compete with a hydrogen atom abstraction by **5** from solvents. When THF is used as a solvent, the latter process becomes predominant to undergo hydrogenative debromination to afford **3** and **4**. In benzene, the rate of this hydrogen atom abstraction is decreased more than that of the formation of **6**. The alkenylsamarium(III) **6** would generate the alkydlenecarbene **7**. Intramolecular C-H insertions of alkydlenecarbenes leading to the formation of cyclopentenes are well established.⁸ However, when the alkydlenecarbenes have hydrogens or aryl groups at the α -position, the intramolecular C-H insertions can no longer compete with a 1,2-shift of these groups.⁸ Thus, the alkydlenecarbene **7** selectively undergoes a 1,2-shift of an α -hydrogen or an α -aryl group to afford the rearranged alkyne **2**. Alternatively, the alkydlenecarbenoid **6** could directly rearrange to **2**.

Thus, the reaction of 1,1-dibromoalkenes **1** with SmI_2 in benzene-HMPA provides a useful tool for the generation of alkydlenecarbenes.

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