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Alkylidenecarbenes from 1,1-Dihalogenoalkenes with Samarium Diiodide: Mild and Efficient Method for the Synthesis of Cyclopentenes

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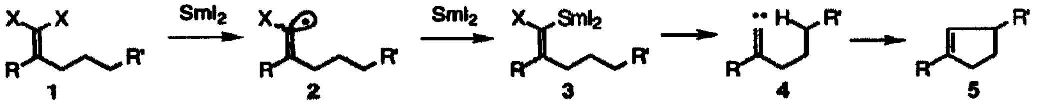
Abstract: A new mild method for construction of cyclopentenes *via* 1,5-C—H insertion of alkylidenecarbenes by the reaction of 2,2-dialkyl-1,1-dihalogenoalkenes with SmI_2 in benzene—hexamethylphosphoric triamide (HMPA) was developed.

The intramolecular 1,5-C—H insertion of alkylidenecarbenes is an efficient and convenient method for construction of five-membered ring because the carbenes are capable of undergoing regioselective carbon—carbon bond formation on non-activated carbon centers. Several mild methods for generation of alkylidenecarbenes; fluoride-induced α-elimination of α-chlorovinylsilanes or silylvinyl triflates,[1a,b] thermal decomposition of tosylazoalkenes[1c] or diazoalkenes[1d] and weak base-induced α-elimination of alkenyliodonium salts,[1e] have been developed. Here we report a new mild method for construction of cyclopentenes (**5**) *via* 1,5-C—H insertions of alkylidenecarbenes (**4**) (or carbenoids (**3**)) generated from 1,1-dihalogenoalkenes (**1**) by the reaction with SmI_2.[2]

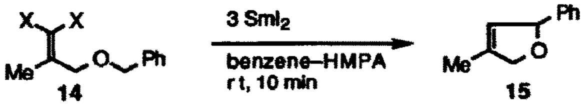
Scheme 1



The reaction will proceed by a route illustrated in Scheme 1. Since alkyl groups at α position to carbenic center are loath to migrate leading to alkynes in alkylidenecarbenes,[1d, 1e, 3] we examined the reaction of 2,2-*dialkyl*-1,1-dibromoalkene with SmI_2 in *benzene*—HMPA.[4] Exposure of **6** (X = Br) in benzene to SmI_2 (2.5 equvi.) in benzene—HMPA (9 : 1) at room temperature under nitrogen flow for 10 min gave cyclopentene (**7**) in 59 % yield (Table 1). Diiodide (**6**, X = I) also afforded **7** in 76 % yield whereas the reactivity of dichloride toward SmI_2 was very low. Another product of these reactions was fully reduced alkene (**6**, X = H) and no rearranged alkynes were detected. As summarized in Table 1, diiodides generally gave the corresponding insertion product more than dibromides. The reactions of dihalides (**8**) and (**10**) afforded fused bicyclic (**9**) and spiro (**11**) compounds, respectively. Although a heteroatom activates C—H bond at α position to it toward insertion by carbenes,[5] the reaction of benzyl ether (**14**) with SmI_2 afforded dihydrofuran derivative (**15**) in somewhat low yield (Scheme 2). Since the activation of C—H bond is ascribed to weakening of it by α-heteroatoms, an intramolecular hydrogen abstraction by an α-halovinyl radical corresponding to **2** from the activated bond probably competes with the generation of carbenoid.[6]

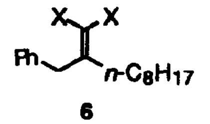
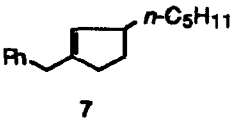
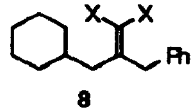
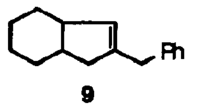
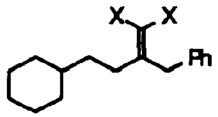
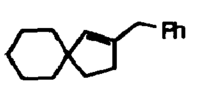
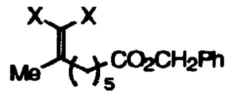
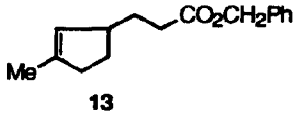
It should be noted that not only mildness and simplicity of the reaction but also stability and accessibility of *gem*-dihalogenoalkenes make the present reaction useful for synthesis of five-membered ring especially substituted cyclopentenes *via* alkylidenecarbenes.

Scheme 2



X = Br; y. 28 %
X = I; y. 42 %

Table 1. 1,5-C—H Insertion of alkylidenecarbenes derived from 1,1-dihalogenoalkenes with SmI_2.

1,1-dihalogenoalkene		cyclization product		yield of reduced product (X = H)
	X	yield (%)^a		
 **6**	Cl	3	 **7**	19^d
	Cl	15^b		20
	Cl	40^c		23
	Br	59		10
	I	76		8
 **8**	Br	56	 **9**	6
	I	79		3
 **10**	Br	51	 **11**	6
	I	65		5
 **12**	Br	32	 **13**	
	I	52		

a) Reactions were carried out in benzene—HMPA (9 : 1) for 10 min at r.t. under nitrogen flow. b) The reaction was carried out for 3 h at r.t. c) The reaction was carried out for 3 h at reflux temp. d) 48 % of **6** was recovered.

References and Notes

1 (a) Cunico, R. F.; Han, Y. K. *J. Organomet. Chem.* **1976**, *105*, C29-C31. (b) Stang, P. J.; Christensen, S. B. *J. Org. Chem.* **1981**, *46*, 823-824. (c) Stang, P. J.; Fox, D. P. *J. Org. Chem.* **1977**, *42*, 1667-1669. (d) Gilbert, J. C.; Giamalva, D. H.; Weerasooriya, U. *J. Org. Chem.* **1983**, *48*, 5251-5256. (e) Ochiai, M.; Takaoka, Y.; Nagao, Y. *J. Am. Chem. Soc.* **1988**, *110*, 6565-6566.

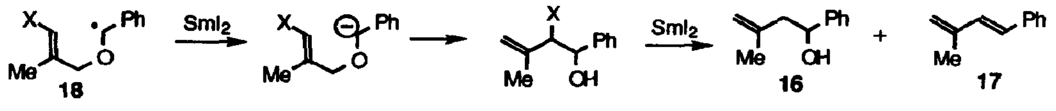
2 Recently, we have found that the reaction of *gem*-dibromoalkenes having hydrogen or aryl group at β-position with SmI_2 in benzene—HMPA generates alkylidenecarbenes, which undergo 1,2-rearrangement of an α-substituent to lead alkynes, under mild conditions, see Kunishima, M.; Hioki, K.; Ohara, T.; Tani, S. *J. Chem Soc., Chem. Commun.* **1992**, 219-220.

3 Gilbert, J. C.; Weerasooriya, U. *J. Org. Chem.* **1982**, *47*, 1837-1845.

4 It is important to use benzene to avoid a hydrogen atom abstraction, which occurs predominantly in tetrahydrofuran (THF) to give reduced alkenes, from solvent by an α-halogenovinyl radical (**2**).^{2}

5 Gilbert, J. C.; Blackburn B. K. *J. Org. Chem.* **1986**, *51*, 3656-3663, and references cited therein.

6 In the reaction of **14** (X = Br), alcohol (**16**, 28%) and diene (**17**, 17%) were produced. Formation of these products would be attributed to the intramolecular hydrogen abstraction of α-halovinyl radical from the C—H bond α to the etheral oxygen. The resulting α-oxyradical (**18**) would be then reduced to the carbanion followed by 2,3-rearrangement, and final reductive dehalogenation afforded **16** and **17**.



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