2,3-Sigmatropic Rearrangement of Sulfonium Ylides Generated by Addition of Samarium Carbenoids

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Received 26 August 1998

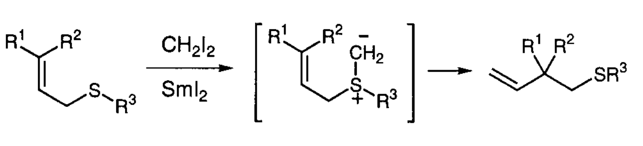
Abstract: Allylic sulfides are transformed into homoallylic sulfides with complete allylic inversion by treatment with SmI_2 and CH_2I_2 in THF. The reaction will involve allylic sulfonium ylides as an intermediate, which undergoes 2,3-rearrangement.

2,3-Sigmatropic rearrangement of allylic compounds is a useful method for the synthesis of functionalized alkenes.[1] Recently, we demonstrated that samarium iodide (SmI_2) is highly useful to effect 2,3-Wittig rearrangement. Metalated ethers undergoing 2,3-rearrangement were regioselectively generated by either an intramolecular 1,5-hydrogen transfer of a vinyl radical, generated by a single electron transfer from SmI_2 to γ-halogenoallyl ethers,[2a] or a net two-electron reduction of diallyl acetals with the liberation of an allyloxy samarium by SmI_2 in acetonitrile.[2b] In connection with this research, our attention has been focused on development of SmI_2-mediated 2,3-rearrangement of allylic sulfonium ylides.

Among the methods for generation of allylic sulfonium ylides, carbenoids addition to allylic sulfides has been shown to be a useful method.[3] In contrast to reactions utilizing carbenoids possessing α-carbonyl groups generated by decomposition of diazocompounds,[3,4] there is only one report for utilizing a Simmons-Smith type reagent, a simple methylene carbenoid, for generation of allylic sulfonium ylides.[5] Recently, SmI_2 has been shown to be useful for generation of several types of carbenoids from organo-*gem*-dihalogen compounds under mild conditions.[6, 7, 8] However, application of samarium carbenoids to 2,3-rearrangement of sulfonium ylides has not been reported.

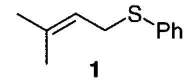
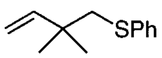
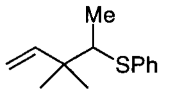
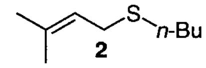
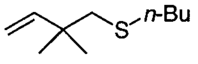
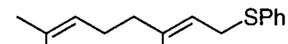
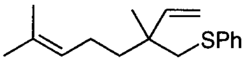
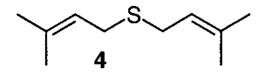
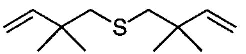
After several attempts using phenyl prenyl sulfide (**1**) as a substrate, we found that reaction of **1** with 3 equiv of CH_2I_2 and 6 equiv of SmI_2 in THF at room temperature gave 2,2-dimethyl-3-butenyl phenyl sulfide (**5**) in 97% yield.[9] Results are summarized in Table 1. The reaction took place in good yield by using dibromomethane instead of the iodide while dichloromethane gave a moderate yield of **2a** by heating at 40°C for 4 days (runs 2, 3). Ethylidene bromides was also found to be effective for the reaction, giving **6**. Similarly, transformation of the allylic sulfides (**2**–**4**) to the homoallylic sulfides (**7**–**9**) was achieved in good to excellent yield.

The reaction involves addition of a samarium carbenoid, arising from CH_2I_2 and SmI_2, to a divalent sulfur leading to the formation of a sulfonium ylide, which rearranged to a homoallylic sulfide (Scheme 1). As an alkene is less reactive than a sulfide towards a carbene,[3] no cyclopropanation of alkenes was observed in any case. Imamoto and his coworker reported that Stevens rearrangement occurred by the reaction of phenylthioacetic acid methyl ester with a samarium carbenoid generated from samarium metal and diiodomethane.[7] However, no evidence for compounds formed by 1,2-rearrangement was obtained in our case.



Scheme 1

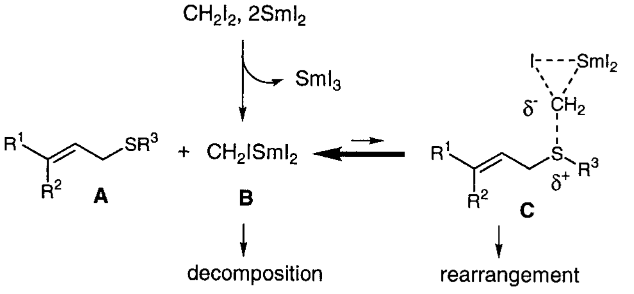
Table 1. 2,3-Rearrangement of (γ,γ-Dialkylallyl)sulfonium Ylides Generated by Addition of Samarium Carbenoids

Run	Reactant	$RCHX_2$	Product[a]	Time	Yield (%)[c]
1	 **1**	CH_2I_2	 **5**	1.5 h	97
2		CH_2Br_2		2 h	86
3[b]		CH_2Cl_2		4 days	41[d,e]
4		CH_3CHBr_2	 **6**	1.5 h	72[e]
5	 **2**	CH_2I_2	 **7**	15 min	79[e]
6	 **3**	CH_2I_2	 **8**	15 min	92
7	 **4**	CH_2I_2	 **9**	15 min	80

[a] All compounds were identified by ^1H- and ^{13}C NMR. [b] Reaction temp. = 40°. [c] Isolated yield. [d] The starting sulfide was recovered in 58%. [e] Since the starting sulfide was included even after silica gel column chromatography, yield was determined by NMR

When an allylic sulfide with a hydrogen at the γ-vinylic position was used, the yield of the rearranged product dropped to about 50%, most likely due to intramolecular elimination of the sulfonium ylide resulting from addition of the carbenoid to the rearranged homoallyl sulfide (Table 2, runs 1, 5, 7).[10] Since an excess carbenoid would cause the elimination, attempts were again made either by decreasing the amount of generating carbenoid or at a lower temperature (0°C). However, the yields of the rearranged product decreased (runs 2, 3). Shortening the reaction time to 1 min at room temperature resulted in a decrease of the elimination, and homoallylic sulfides (**13–15**) were obtained in somewhat higher yield (runs 4, 6, 8).

In spite of generation of a large excess of carbenoids, there is no evidence for the formation of sulfonium salts derived from either the starting or produced sulfide via protonation of sulfonium ylides. Cohen and his co-worker exhibited that poor yields of rearranged products (homoallylic sulfides) were much improved by addition of acetaldehyde, which allows the homoallylic sulfides to regenerate from the corresponding sulfonium ylides. However, acetaldehyde was found to be ineffective in our reaction.[11] Attempts to isolate sulfonium salts derived from either the starting or produced sulfides were unsuccessful.[12] These results would indicate that the formation step of sulfonium ylides (**C**) is reversible and the equilibrium would only favor sulfides (**A**) and carbenoids (**B**) rather than **C**, and that the carbenoids can decompose by itself during the reaction (Scheme 2). Almost quantitative yield of **5** from **1** in the reaction of Table 1, run 1 may be compatible with the assumption, and may indicate the absence of the ylides at the end of reaction.



Scheme 2

In summary, we have developed a samarium carbenoids-induced 2,3-rearrangement of allylic sulfonium ylides. The reaction proceeds quickly at room temperature, and no treatment with acetaldehyde to liberate the product is required. In addition, high yield of the homoallylic sulfides was obtained when the starting sulfides with γ-γ-dialkyl groups were used.

References and Notes

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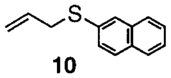
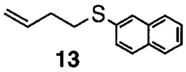
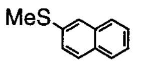
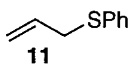
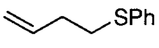
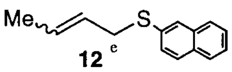
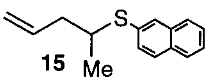
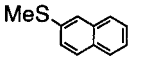
(9) For a typical procedure: To a stirred solution of SmI_2 (0.044 M in THF , 23 mL, 1.01 mmol) containing **1** (30 mg, 0.17 mmol) was

Table 2. Reaction of Allylic Sulfide Possessing γ-Hydrogen

$$\text{allylic sulfide} \xrightarrow{3CH_2I_2,\ 6SmI_2,\ THF} \text{homoallylic sulfide}$$

Run	Reactant (allylic sulfide)	Product (homoallylic sulfide)	Conditions	Yield(%)[a,b]	Recovery(%)	Methyl sulfide (%)[c]
1	 **10**	 **13**	rt, 15 min	58 (70)	17	 23
2[d]			rt, 15 min	33 (57)	42	8
3			0°, 70 min	41 (49)	17	**16** 37
4			rt, 1 min	60 (76)	21	18
5	 **11**	 **14**	rt, 15 min	42 (52)	19	18
6			rt, 1 min	59 (83)	29	Me-S-Ph **17** 7
7	 **12**[e]	 **15**	rt, 15 min	48 (53)	9	 20
8			rt, 1 min	63 (84)	24	**16** 6

[a] Determined by NMR. [b] Yields based on the conversion of starting compounds are given in parentheses. [c] Produced by intramolecular elimination from rearranged homoallylic sulfides. [d] Ratio of $\mathbf{10}/CH_2I_2/SmI_2$ is 1 : 1 : 2. [e] *E/Z* = 5.3 : 1

added CH_2I_2 (135.2 mg, 0.50 mmol) at rt under nitrogen. The greenish-blue color of SmI_2 disappeared within 15 min. After stirring for 1.5 hr., the mixture was poured into water and extracted with ether. The residue was purified by preparative TLC (hexane) to give **5** as a colorless oil. **5**: IR (neat) 3083, 2964, 1637, 1583, 1481, 914, 739 cm^{-1}; ^1H NMR (400 MHz $CDCl_3$) δ 1.15 (s, 6H), 2.96 (s 2H), 5.00 (dd, *J* = 1.2, 10.7 Hz, 1H), 5.03 (dd, *J* = 1.2, 17.4 Hz, 1H), 5.87 (dd, *J* = 10.7, 17.4 Hz, 1H), 7.11-7.16 (m, 1H), 7.22-7.28 (m, 2H), 7.31-7.36 (m, 2H); ^{13}C NMR (100 MHz $CDCl_3$) δ 26.4, 38.0, 47.1, 111.8, 125.6, 128.8, 129.1, 138.2, 146.4; HRMS for $C_{12}H_{16}S$ calcd 192.0973, found 192.0956.

(10) Though 1,3-dienes could not be isolated due to their low boiling point, the formation of methyl aryl sulfides, another product formed by elimination, could be detected.

(11) In order to examine the effect of acetaldehyde on our reaction, acetaldehyde was added before quenching the reaction performed under the conditions of **1** (1 eq), CH_2I_2 (2 eq), and SmI_2 (4 eq) at rt where 79% of **5** was obtained without treatment of acetaldehyde. The yield of **5** was found to be 82%.

(12) The reaction of **1** with CH_2I_2 and SmI_2 in the presence of water resulted in recovery of **1** (87%) with no detectable amount of the sulfonium salt (**5**). A further attempt using diphenyl sulfide, which was employed to avoid rearrangement of sulfonium ylides, under the same conditions was unsuccessful.