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Generation of allenylthioketene *S*,*S*-dioxides through [3,3] sigmatropic rearrangement of alkynyl propargyl sulfones

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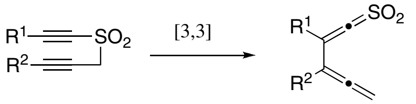
Abstract—Thioketene *S*,*S*-dioxides **2** were successfully generated through [3,3] sigmatropic rearrangement of alkynyl propargyl sulfones **1** and the formation of **2** was confirmed by trapping experiment using cyclohexene or allyltrimethylsilane affording a [2+2] cycloadduct **5**. In situ generated thioketene *S*,*S*-dioxides **2** underwent facile conversion into allenynes **3** in moderate yields, via formation and subsequent [1,2] shift of vinylidene carbenes.

Recently, application of highly reactive species to organic synthesis is desired to the end of efficient and straightforward transformation of complicated target molecules. Particularly our interest was concentrated in the field of generation of reactive species containing chalcogen atom, thiones, and selones, and their cumulene analogues, thioketenes, and selenoketenes. Moreover, chemistry of monooxidized thiones and thioketenes, sulfines[1] and thioketene *S*-oxides,[2] respectively, is also well established by kinetic or thermodynamic stabilization of the reactive species. In contrast, fully oxidized thiones, sulfenes[3] have been recognized as reactive intermediates resulting from β-elimination of sulfonyl chloride by treatment of base and isolation of sulfenes was unsuccessful due to spontaneous decomposition leading to SO_2 and carbenes. Therefore, cumulated sulfenes, thioketene *S*,*S*-dioxides have been regarded to be more difficult to isolate and even to generate up to date. Previously, generation and trapping of chalcogenoketenes from alkynyl propargyl chalcogenides or alkynyl allyl chalcogenides by [3,3] sigmatropic rearrangement in the presence of amine or imine were reported by Schaumann, Brandsma, Koketsu and our group.[4,5] Analogously, generation and trapping of a sulfene by [3,3] sigmatropic rearrangement of allyl vinyl sulfone in the presence of EtOH were reported by King.[6] On the basis of these results, thermal reaction of alkynyl propargyl sulfones seems to be a promising method to generate thioketene *S*,*S*-dioxides, as shown in Eq. 1. In this paper, we wish to describe a novel generation and trapping of allenylthioketene *S*,*S*-dioxides **2** by thermal reaction of alkynyl propargyl sulfones **1**, and the formation of allenynes **4** through spontaneous SO_2 extrusion of **2**. Trapping of an intermediary vinylidene carbene and unexpected formation of furans through electrophilic aromatic substitution of **2** are also described.



1 **2**

(1)

Alkynyl propargyl sulfones **1a**–**j** were readily prepared in excellent yields by treatment of alkynyl propargyl sulfides[5e,f] with *m*-CPBA (2.2 equiv) in chloroform at 0 °C for 30 min. Sulfone **1a** was used for thermal reaction without further purification due to protodesilylation on silica gel to afford **1d**. A benzene or toluene solution of alkynyl propargyl sulfone **1** was refluxed to complete consumption of **1**, and purification of resulting reaction mixture was performed by flash column chromatography on silica gel to give allenynes **3** or furans **4** as colorless oils in moderate yields. All results are summarized in Table 1. Allenynes **3** were identified by MS, IR, ^{1}H NMR, ^{13}C NMR, and elemental analysis. The spectral data of **3e** was in good accordance with those reported.[7]

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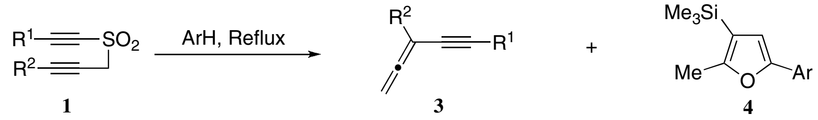
Table 1. Thermal reaction of alkynyl propargyl sulfone **1**



Entry	Sulfone	R^1	R^2	Solvent	Time (h)	Product	Yield[a] (%)	
							3	**4**
1	**1a**[b]	Me_3Si	Me_3Si	Toluene	14	**3a**	76 (95)[c]	0
2	**1b**	*t*-$BuMe_2Si$	Me_3Si	Toluene	14	**3b**	56 (77)[c]	0
3	**1c**	*n*-C_4H_9	Me_3Si	Toluene	24	**3c**	32 (41)	0
4	**1d**	H	Me_3Si	Toluene	6	**4d** ($Ar = MeC_6H_4$)	0	52[d]
5	**1d**	H	Me_3Si	Benzene	10	**4d′** ($Ar = C_6H_5$)	0	56
6	**1e**	Me_3Si	*n*-C_5H_{11}	Toluene	14	**3e**	60	0
7	**1f**	C_6H_5	CH_3	Toluene	14	**3f**	26	0
8	**1g**	*p*-$MeOC_6H_4$	Me_3Si	Toluene	10	**3g**	57 (76)[c]	0
9	**1h**	*p*-MeC_6H_4	Me_3Si	Toluene	10	**3h**	41 (74)[c]	0
10	**1i**	C_6H_5	Me_3Si	Toluene	14	**3i**	53 (61)[c]	0
11	**1j**	*p*-ClC_6H_4	Me_3Si	Toluene	14	**3j**	44 (63)[c]	0

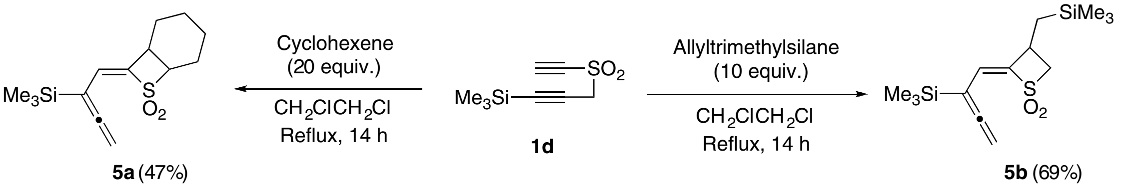
[a] Isolated yield.

[b] Compound **1a** was used without further purification.

[c] Thermal reaction of **1** was carried out in $CDCl_3$ at 100 °C for 14 h in an NMR tube and the yield of **3** was estimated by ^1H NMR using 1,2-dichloroethane as an internal standard.

[d] Compound **4d** was afforded as a mixture of *o*-, *m*-, and *p*-isomers.

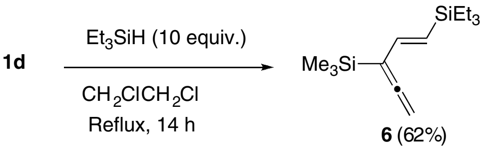
Allenynes **3** having trimethylsilyl group at R^2 were more stable than **3e** and **3f**. The thermal reaction of **1a–c**, and **1g–j** in $CDCl_3$ at 100 °C for 14 h in a sealed tube also afforded alleneyne **3** in good yield. Allenynes **3** would be products derived from thioketene *S*,*S*-dioxides **2**. It is noteworthy that thermal reaction of **1c** and **1e** afforded no cycloolefin expected to be formed through intramolecular carbene insertion into a C–H bond of the alkyl chain.[9,10a] Interestingly, thermal reaction of **1d** in refluxing toluene afforded unexpected products of solvent incorporation, an inseparable isomeric mixture of 2-methyl-3-trimethylsilyl-5-tolylfurans **4d** in 52% combined yield. Analogously when benzene was used as a solvent, furan **4d′** was isolated in 56% yield. In these cases, thioketene *S*,*S*-dioxide **2d** was successfully trapped by aromatic solvent to give furan **4** presumably due to slow SO_2 extrusion and/or 1,2-shift of hydrogen atom of **2d**. Thus, we undertook thermal reaction of **1d** in the presence of other trapping reagents.



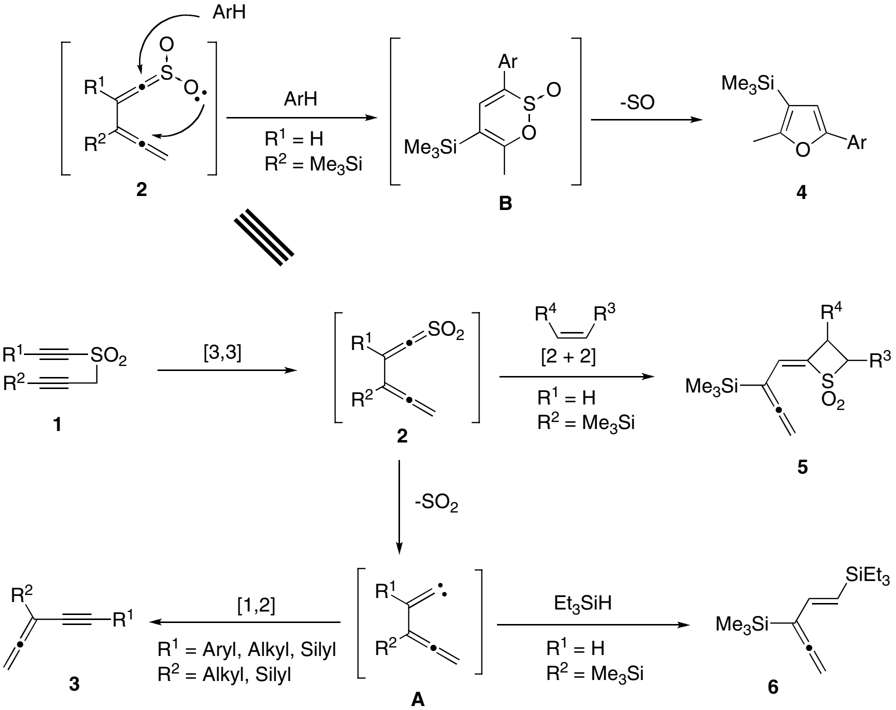
(2)

Thermal reaction of **1d** in the presence of cyclohexene (20 equiv) in 1,2-dichloroethane at refluxing temperature afforded cycloadduct **5a**[11] in 47% yield through [2+2] cycloaddition of sulfene moiety of **2d** and cyclohexene (Eq. 2). Geometry of the double bond of **5a** was confirmed to be (*Z*) by means of NOE experiment (14%, vinylic proton and allylic proton). Analogous reaction using allyltrimethylsilane (10 equiv) afforded [2+2] cycloadduct **5b**[12] in 69% yield as a single isomer through the reaction of γ-position of allylsilane with sulfur atom of sulfene moiety of **2d**. Geometry of **5b** was also confirmed to be (*Z*) by means of NOE experiment (11%, vinylic proton and allylic proton). Formation of **5a** and **5b** intensively supported the generation of allenylthioketene *S*,*S*-dioxides **2**. Interestingly, thermal reaction of **1a** in the presence of cyclohexene as a trapping reagent gave only allenyne **3a** as a single product instead of [2+2] adduct, presumably due to steric hindrance of trimethylsilyl group at R^1.

Heating of a 1,2-dichloroethane solution of **1d** and triethylsilane (10 equiv) at refluxing temperature for 14 h gave triene **6** as a single (*E*)-isomer in 62% yield, which would be formed by the insertion of intermediary vinylidene carbene **A** into Si–H bond of Et_3SiH[10b] (Eq. 3). It is noteworthy that thermal reaction of **1a** in the presence of triethylsilane as a trapping reagent gave only allenyne **3a** as a single product, presumably due to the rapid migration of R^1 after SO_2 extrusion from **2a**.



(3)



Scheme 1. Plausible formation pathway of allenyne **3** and trapping products **4**–**6**.

Plausible formation pathway of allenyne **3** and trapping of intermediates **4**, **5**, and **6** are illustrated in Scheme 1. Thus, highly reactive allenylthioketene *S*,*S*-dioxides **2** were generated by [3,3] sigmatropic rearrangement of sulfones **1**. Sequentially, extrusion of SO_2 from **2** took place to form intermediary vinylidene carbenes **A**. Finally, [1,2] shift of R^1 group occurred to give allenynes **3**.[8] When **1d** ($R^1 = H$) was heated in aromatic solvent, intramolecular domino attack of an oxygen atom of sulfonyl group to allenic center carbon triggered by electrophilic aromatic substitution of sulfene moiety of **2** proceeded to give sultine **B**. Following extrusion of SO from **B** afforded furans **4**. In the case cyclohexene or allenyltrimethylsilane was used as trapping reagent, [2+2] cycloaddition of sulfene moiety of **2d** and olefinic moiety of trapping reagent occurred to give sulfones **5**. In thermal reaction of **1d** in the presence of Et_3SiH, insertion of vinylidene carbene **A** into Si–H bond of Et_3SiH afforded triene **6**.[1]

In conclusion, generation of allenylthioketene *S*,*S*-dioxides **2**, novel highly reactive species, by thermal reaction of alkynyl propargyl sulfones **1** was established. Generation of **2** was supported by isolation of allenynes **3** as well as direct trapping of **2** using cyclohexene or allyltrimethylsilane. Trapping experiments elucidated the formation mechanism of **3** through the generation of vinylidene carbene **A** followed by [1,2] shift of the substituent R^1. Additional studies on mechanistic and preparative aspects of these reactions are underway.

Acknowledgment

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2007.01.087.

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11. Compound **5a**: Colorless oil; MS (*m/z*): 282 (M^+; 18%), 208 (M^+-Me_3Si; bp). IR (neat): 2936, 1926, 1685, 1250, 1120, 846 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.15 (s, 9H), 1.08–1.26 (m, 2H), 1.29–1.43 (m, 2H), 1.49–1.61 (m, 2H), 1.65–1.74 (m, 1H), 1.91–1.96 (m, 1H), 2.72–2.77 (m, 1H), 4.60 (dd, $J = 13.0$, 2.3 Hz, 1H), 4.65 (dd, $J = 13.0$, 2.3 Hz, 1H), 5.01 (br s, 1H), 6.01 (ddd, $J = 2.3$, 2.3, 1.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ -1.9 (q), 19.8 (t), 23.5 (d), 27.6 (t), 29.4 (t), 41.1 (d), 72.0 (t), 80.7 (s), 93.6 (dd), 126.3 (d), 158.5 (s), 210.9 (s). Anal. Calcd for $C_{14}H_{22}O_2SSi$: C, 59.53; H, 7.85. Found: C, 59.32; H, 7.79.
12. Compound **5b**: Colorless oil; MS (*m/z*): 314 (M^+; 2%), 241 (M^+-Me_3Si; 3%), 168 (M^+-2Me_3Si; 58%), 73 (Me_3Si; bp). IR (neat): 2955, 1926, 1471, 1251, 1120, 844 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.84 (s, 9H), 0.16 (s, 9H), 1.05 (dd, $J = 14.0$, 9.2 Hz, 1H), 1.28 (dd, $J = 14.0$, 5.7 Hz, 1H), 2.31 (dd, $J = 15.2$, 9.2 Hz, 1H), 3.07 (dd, $J = 15.2$, 5.7 Hz, 1H), 4.76 (br dd, 2H), 5.24–5.26 (m, 1H), 6.13 (t, $J = 2.1$ Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ -1.8 (q), -1.0 (q), 23.5 (t), 37.9 (dd), 72.0 (t), 82.3 (s), 93.9 (s), 126.2 (d), 153.6 (s), 211.1 (s). Anal. Calcd for $C_{14}H_{26}O_2Si_2$: C, 53.45; H, 8.33. Found: C, 53.00; H, 8.40.