Isolation and Characterization of an Allenylthioketene and 4-Methylenecyclobutenethiones Generated by Thermal Reaction of Alkynyl Propargyl Sulfides

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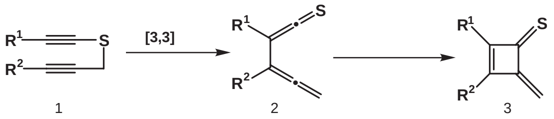
Alkynyl propargyl sulfides underwent [3,3] sigmatropic rearrangement followed by ring closure to afford isolable 4-methylenecyclobutenethiones, and an intermediary allenylthioketene **2** was isolated by heating *t*-butyldimethylsilylethynyl propargyl sulfide.

For a few decades, generation and trapping of chalcogenoketenes[1–5] have been widely investigated and their high reactivity to amines and imines has been providing efficient approaches to the corresponding chalcogenoamides and β-chalcogenolactams, respectively.[2] Furthermore, isolations of thermodynamically and/or kinetically stabilized chalcogenoketenes were performed to reveal their unique structures and reactivities.[3] Among the reported methods for generation of chalcogenoketenes, [3,3] sigmatropic rearrangement of alkynyl propargyl chalcogenides and alkynyl allyl chalcogenides was recognized to be the most convenient way in the light of relatively mild reaction condition and easy access to their precursors.[4,5] We reported an efficient generation and trapping of allenylselenoketenes by [3,3] sigmatropic rearrangement of alkynyl propargyl selenides,[5c] and Koketsu et al. also observed allenylselenoketene generated through a similar route.[5f] Accordingly, these results prompted us to isolation of intermediary allenylchalcogenoketenes and cyclobutenechalcogenones to confirm the formation pathway involving [3,3] sigmatropic rearrangement and the subsequent ring closure. Considering the relative stability, less dimerizing natures, and the synthetic applicability of cyclobutenethiones,[6] thermal reaction of alkynyl propargyl sulfides seems to be a promising way to isolate 4-methylenecyclobutenethiones **3** as a monomeric form. Herein, we wish to report the first isolation of an allenylthioketene **2** and 4-methylenecyclobutenethiones **3** by thermal reaction of alkynyl propargyl sulfides **1**, as well as the reactivity of **2** and **3**.



(1)

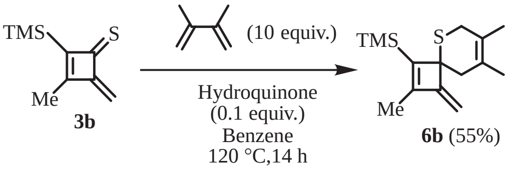
Alkynyl propargyl sulfides **1a**–**1f** were readily prepared as a slightly air-sensitive pale yellow oil in an analogous manner reported for alkynyl propargyl selenides.[5c] After heating a solution of sulfides **1** in the absence of a trapping agent up to complete consumption of **1**, the resultant reaction mixture was subjected to column chromatography on silica gel for purification. Sulfides **1a**–**1d** bearing a bulky substituent, *t*-Bu, Me_3Si, or *t*-$BuMe_2Si$, at R^1 were efficiently converted into cyclobutenethiones **3** as air-sensitive reddish oils (Table 1). The required reaction temperature and time were affected by the bulkiness of R^1 and R^2 of **1** due to the formation of almost planar transition state in [3,3] sigmatropic rearrangement of **1**. Thermal reaction of **1c** in refluxing MeCN for 14 h afforded thione **3c** in 54% yield along with polymeric products, presumably formed by further reaction of **3c** in the polar solvent. In contrast with the analogous reactions in the selenium series, 1,3-dithietanes, dimers of **3**, were not found at all in the crude product. The structures of thiones **3** were fully characterized by means of MS, IR, ^{1}H NMR, ^{13}C NMR spectra, and elemental analysis. While **3a**–**3d** were relatively stable in hexane solution to be stored for a week, exposure of neat thiones **3a**–**3d** to air caused gradual decomposition to give uncharacterizable insoluble solid. Because of lability of **3e** relative to **3a**–**3d**, thermal reaction of **1e** was carried out in an NMR tube. The ^{13}C NMR signals of **3a**–**3e** in the range of $\delta = 230$–236 ppm are assigned to thiocarbonyl carbons and characteristic electronic absorptions of **3a**–**3d** in Et_2O ranging from 528 to 560 nm were assigned to n–π^* transitions of thiocarbonyl groups (Table 1). Thiones **3a**, **3c**, and **3d** showed red shift in electronic absorption in comparison with **3b**, presumably due to the higher π-conjugation involving a phenyl group.

Table 1. Thermal reaction of **1** and the selected spectral data of **2** and **3**

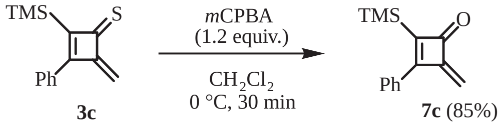
Substrate	R^1	R^2	Solvent	Temp/°C	Time	Yield/%[a]		^{13}C NMR[b]	UV–vis[c]
						2	**3**		
1a	*t*-Bu	Ph	Toluene	Reflux	72 h	0	57 (**3a**)	230.2	560 ($\varepsilon = 126$)
1b	TMS	Me	Hexane	Reflux	10 h	0	64 (**3b**)	234.8	528 ($\varepsilon = 13$)
1c	TMS	Ph	Benzene	Reflux	14 h	0	85 (**3c**)	234.3	555 ($\varepsilon = 59$)
1d	TBS	Ph	Benzene	Reflux	48 h	0	52 (**3d**)	235.2	558 ($\varepsilon = 52$)
1e[d]	9-Triptycyl	H	$CDCl_3$	50	50 min	0	68 (**3e**)[e]	231.3	540[f]
1f[g]	TBS	H	THF	50	10 min	51 (**2f**)	0	242.3	532 ($\varepsilon = 24$)

[a]Isolated yield. [b]The signal assigned to thiocarbonyl carbons. δ value in ppm measured in $CDCl_3$. [c]Selected λ_{max} value in nm measured in Et_2O. [d]Thermal reaction of **1e** was carried out in an NMR tube. [e]Estimated by integration of ^{1}H NMR spectrum using dichloroethane as an internal standard. [f]Electronic absorption of crude **3e**. [g]**1f** was prepared in THF and the resulting solution was subjected to thermal reaction without isolation of **1f**.

[4 + 2] cycloaddition of isolated cyclobutenethione **3b** with 2,3-dimethyl-1,3-butadiene (10 equiv.) in the presence of hydroquinone (0.1 equiv.) in benzene solution at 120 °C for 14 h in a sealed tube afforded cycloadduct **6b** in 55% yield. Treatment of thione **3c** with *m*CPBA (1.2 equiv.) in CH$_2$Cl$_2$ at 0 °C for 30 min furnished 4-methylenecyclobutenone **7c** in 85% yield. The spectroscopic properties of **7c** were identical with the reported data[8] and the structures of **3** were finally confirmed to be 4-methylenecyclobutenethiones.

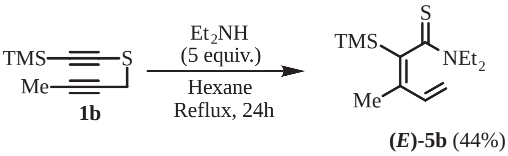


(2)



(3)

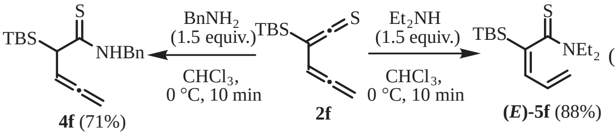
Thermal reaction of **1b** in the presence of Et$_2$NH (5 equiv.) in refluxing hexane for 24 h afforded 2,4-pentadienethioamide (***E***)–**5b**, trapping product of allenylthioketene **2b**, in 44% yield as a single isomer.



(4)

Interestingly, thermal reaction of **1f** in THF at 50 °C for 10 min afforded allenyl(*t*-butyldimethylsilyl)thioketene **2f**[7] in 51% yield as an air-sensitive reddish oil. The ^{13}C NMR signals at $\delta = 242.3$ and 210.9 ppm, assignable to thiocarbonyl carbon and allenyl center carbon, respectively, strongly supported the structure of **2f**. The successful isolation of **2f** would be due to smooth [3,3] sigmatropic rearrangement of **1f** without further reaction under relatively mild condition. In contrast, sulfide **1e** bearing a 9-triptycyl group at the R^1 position underwent [3,3] sigmatropic rearrangement followed by facile ring closure to give 4-cyclobutenethione **3e** by heating, and intermediary **2e** was not observed at all throughout the NMR monitoring of the reaction. These results suggest that TBS group at R^1 stabilizes allenylthioketene **2f** and decelerates the ring closure.[3a] Considering the lability of **3e**, substitution at R^2 would also play an important role of stabilizing **3**. Therefore, despite substitution of TBS group at R^1, **3f** was assumed to be unstable. Actually, throughout the NMR monitoring of a CDCl$_3$ solution of **2f** in a sealed tube under heating at 80 °C, formation of a complex matter, instead of **3f**, was only observed, and thermal reaction of **2f** in the presence of 2,3-dimethyl-1,3-butadiene (5 equiv.) in refluxing benzene did not afford the [4 + 2] cycloadduct of **3f** and the diene.[5d]

Treatment of **2f** with BnNH$_2$ (1.5 equiv.) or Et$_2$NH (1.5 equiv.) in CHCl$_3$ at 0 °C for 10 min afforded **4f** and (***E***)–**5f** as a single isomer in 71 and 88% yields, respectively. Analogous results were given in the trapping reaction of thermally generated allenylselenoketenes using a primary or secondary amine affording 3,4-pentadieneselenoamide or 2,4-pentadieneselenoamide, respectively.[5c,5e] These results also supported the conversion pathway from **1** into **3** involving the generation of intermediary allenylthioketenes **2**.



(5)

In summary, we found a new and convenient preparation of 4-methylenecyclobutenethiones **3** having various substituents through thermal reaction of substituted alkynyl propargyl sulfides **1**, and the isolation and characterization of relatively-stable allenylthioketene **2f** afforded by heating of **1f**. Further synthetic application of **2f** and **3** is under way in our laboratory.

References and Notes

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7 Compound **2f**: Reddish oil; UV–vis (Et$_2$O) $\lambda_{\max} = 299$ nm ($\varepsilon = 363$), $\lambda_{\max} = 532$ nm ($\varepsilon = 24$); MS (m/z) 210 (M$^+$; 29%), 153 (M$^+$ − *t*-Bu; bp); IR (neat) 2957, 2930, 1946, 1722, 1251, 840 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$) δ 0.13 (s, 6H), 0.89 (s, 9H), 4.88 (d, $J = 6.7$ Hz, 2H), 5.30 (t, $J = 6.7$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl$_3$) δ −5.6(q), 19.6(s), 26.6(q), 60.5(s), 77.8(s), 81.3(d), 210.9(s), 242.3(s). Anal. calcd for C$_{11}$H$_{18}$SSi: C, 62.79; H, 8.62%. Found: C, 62.53; H, 8.71%.

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