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 chalcogenoketenes¹⁻⁵ 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.



Alkynyl propargyl sulfides 1a-1f were readily prepared as a slightly air-sensitive pale vellow 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, Me₃Si, or t-BuMe₂Si, at R¹ 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 14h 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, ¹HNMR, ¹³CNMR 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 ¹³C 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 Et₂O ranging from 528 to 560 nm were assigned to $n-\pi^*$ 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	\mathbb{R}^1	R ²	Solvent	Temp/°C	Time	Yield/% ^a		13C NIMP	IW vice
						2	3	CINNIK	UV - VIS
1a	<i>t</i> -Bu	Ph	Toluene	Reflux	72 h	0	57 (3a)	230.2	$560 \ (\mathcal{E} = 126)$
1b	TMS	Me	Hexane	Reflux	10 h	0	64 (3b)	234.8	528 ($\mathcal{E} = 13$)
1c	TMS	Ph	Benzene	Reflux	14 h	0	85 (3c)	234.3	555 ($\mathcal{E} = 59$)
1d	TBS	Ph	Benzene	Reflux	48 h	0	52 (3d)	235.2	558 ($\mathcal{E} = 52$)
1e ^d	9-Triptycyl	Η	CDCl ₃	50	50 min	0	68 (3e) ^e	231.3	540 ^f
$1f^{g}$	TBS	Η	THF	50	10 min	51 (2f)	0	242.3	532 ($\mathcal{E} = 24$)

^aIsolated yield. ^bThe signal assigned to thiocarbonyl carbons. δ value in ppm measured in CDCl₃. ^cSelected λ_{max} value in nm measured in Et₂O. ^dThermal reaction of **1e** was carried out in an NMR tube. ^eEstimated by integration of ¹H NMR spectrum using dichloroethane as an internal standard. ^fElectronic absorption of crude **3e**. ^g**1f** was prepared in THF and the resulting solution was subjected to thermal reaction without isolation of **1f**.

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[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 CH₂Cl₂ at 0 °C for 30 min furnished 4-methylenecyclobutenone **7c** in 85% yield. The spectroscopic properties of **7c** were identical with the reported data⁸ and the structures of **3** were finally confirmed to be 4-methylenecyclobutenethiones.



Thermal reaction of **1b** in the presence of Et_2NH (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.



Interestingly, thermal reaction of 1f in THF at 50 °C for 10 min afforded allenyl(*t*-butyldimethylsilyl)thioketene $2\mathbf{f}^7$ in 51% yield as an air-sensitive reddish oil. The ¹³C 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] signatropic 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 R¹ 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 \mathbb{R}^1 , **3f** was assumed to be unstable. Actually, throughout the NMR monitoring of a CDCl₃ 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 BnNH₂ (1.5 equiv.) or Et₂NH (1.5 equiv.) in CHCl₃ 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 generat-

ed 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.

$$TBS \underbrace{\overset{S}{\underset{(1.5 \text{ equiv.})}{}}_{\text{NHBn}} \underbrace{\overset{BnNH_2}{\underset{(1.5 \text{ equiv.})}{}}_{\text{CHCl}_3,}}_{CHCl_3,} \underbrace{\overset{S}{\underset{(1.5 \text{ equiv.})}{}}_{CHCl_3,}} \underbrace{\overset{Et_2NH}{\underset{(1.5 \text{ equiv.})}{}}_{CHCl_3,}}_{CHCl_3,} \underbrace{\overset{S}{\underset{(1.5 \text{ equiv.})}{}}_{CHCl_3,}}_{(E)-5f(88\%)} \underbrace{\overset{S}{\underset{(1.5 \text{ equiv.})}{}}_{NEt_2}(5)}_{CHCl_3,}$$

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.

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- 7 Compound **2f**: Reddish oil; UV–vis (Et₂O) $\lambda_{max} = 299 \text{ nm}$ ($\varepsilon = 363$), $\lambda_{max} = 532 \text{ nm}$ ($\varepsilon = 24$); MS (m/z) 210 (M⁺; 29%), 153 (M⁺ – t-Bu; bp); IR (neat) 2957, 2930, 1946, 1722, 1251, 840 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) 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); ¹³C NMR (100 MHz, CDCl₃) 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 C₁₁H₁₈SSi: C, 62.79; H, 8.62%. Found: C, 62.53; H, 8.71%.
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