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Novel Generation, Characterization, and Trapping of 2-Methylene-3-cyclobutene-1-selones

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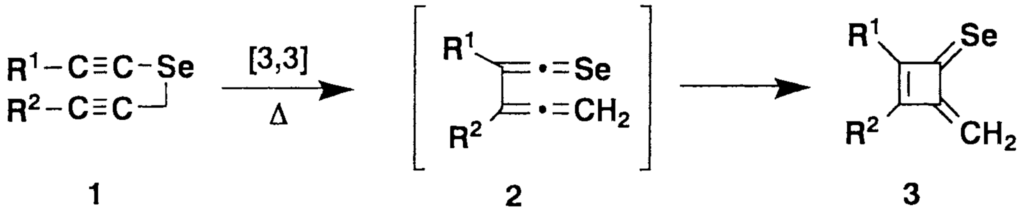
Heating of alkynyl propargyl selenides afforded a stereoisomeric mixture of 5,10-diselenadispiro[3.1.3.1]deca-1,7-dienes. The 1,3-diselenetane rings of the products caused cycloreversion by heating to generate 2-methylene-3-cyclobutene-1-selones and the selones were trapped with diene to give [4+2] cycloadducts.

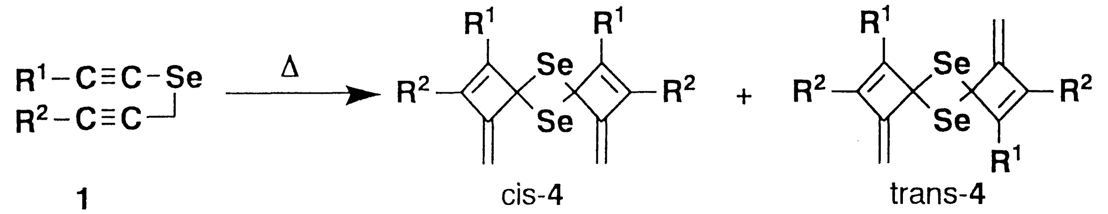
Recently, 2-cyclobuten-1-ones and 3-cyclobutene-1,2-diones are widely used as the intermediates for the organic syntheses. However, to date, no approaches for the generation and structural inspection of 2-methylene-3-cyclobutene-1-selones **3** have been achieved in spite of the expectation to behave not only as acceptors of nucleophiles but also as novel heterodienes or heterodienophiles for the synthesis of heterocycles. As a part of our studies on the synthesis of selenocarbonyl compounds by using unusual reactive species, we have previously reported a synthesis of α,β,γ,δ-unsaturated selenoamides by heating alkynyl propargyl selenides **1** in the presence of primary or secondary amines,1) in which 1,2-propadienylselenoketenes **2** generated by [3,3] sigmatropic rearrangement of alkynyl propargyl selenides **1**2,3) were postulated to behave as the precursors of the selenoamides. It was expected that the facile ring closure of selenoketenes **2** would occur under the thermal reaction condition in the absence of nuclephiles to afford 2-methylene-3-cyclobutene-1-selones **3**, as were reported in the conversion of bisketenes to 3-cyclobutene-1,2-diones.4,5) In this paper, we wish to report the generation, characterization, and trapping of 3,4-disubstituted 2-methylene-3-cyclobutene-1-selones **3** by the thermal reaction of **1**. Generation of the selones **3** by thermal cycloreversion of 1,3-diselenetanes **4**, the dimers of the selones **3**, is also described.



Alkynyl propargyl selenides **1** were prepared from acetylenes, selenium powder, a base, and propargyl bromides according to Brandsma's method.1-3) Heating of a benzene or toluene solution of **1** in an Ar atmosphere afforded two air-stable separable compounds. Mass spectra of both compounds revealed molecular ion peaks at the dimeric regions of the starting selenide **1**, and their ^1H and ^{13}C NMR spectra also revealed similar symmetrical signal patterns to each other including the characteristic signals of exo methylene group. IR spectra of both compounds lacked the allenic or acetylenic stretching bands.

Furthermore, the equilibrated mixture of the isomers was afforded by heating of a benzene solution of each isomer at refluxing temperature and the subsequent cooling to room temperature. From these results, it was suggested that these compounds were the stereoisomers of 1,3-diselenetanes **4**(6) afforded by the dimerization of 2-methylene-3-cyclobutene-1-selones **3** *in situ* generated. The structure of the minor isomer of **4c**(R^1=TMS, R^2=Me) was finally determined by X-ray diffraction study, and the ORTEP drawing of **4c** is shown in Figure 1. **4c** has a 5,10-diselenadispiro[3.1.3.1]deca-1,7-diene ring system possessing cis configuration. Thus, the relative stereochemistry of the major isomer of **4c** was assumed to be trans.7) Table 1 summarizes the results of the thermal reactions of **1**.

Table 1. Thermal reactions of alkynyl propargyl selenides **1**



R^1	R^2		Solvent	Temp	Time /h	Product	Yield /%	Major : Minor
Ph	Me	**1a**	benzene	reflux	2	**4a**	18	50 : 50
t-Bu	Me	**1b**	toluene	reflux	15	**4b**	0 a)	-
TMS	Me	**1c**	benzene	reflux	3	**4c**	40	95 : 5 b)
Ph	H	**1d**	benzene	reflux	1	**4d**	0 a)	-

a) A complex mixture was obtained. b) The minor isomer possessed the cis configuration.

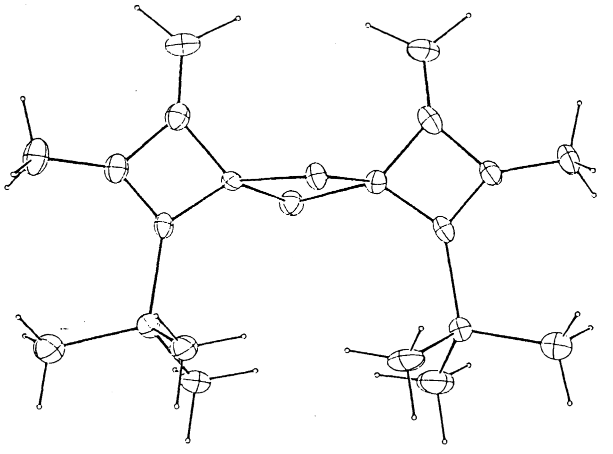


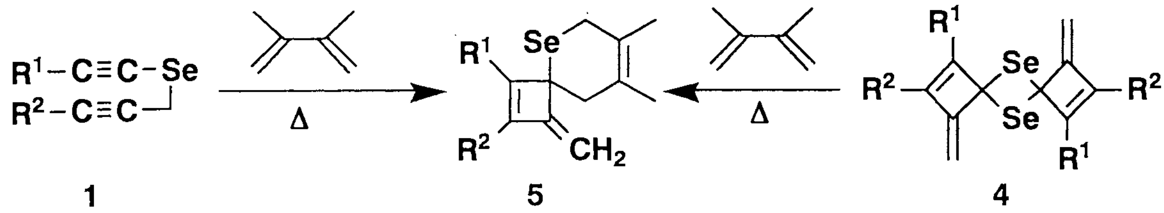
Fig. 1. An ORTEP view of cis-**4c**.

Crystal data for cis-**4c**: $C_{18}H_{28}Se_2Si_2$, F.W.=458.51, Yellow prisms, triclinic, $P\bar{1}$(No.2), a=10.522(2), b=11.931(2), c=9.682(1) Å, α=94.60(2), β=93.00(3), γ=108.94(3) °, V=1142(1) $Å^3$, Z=2, D_{calc}=1.333 g/cm^3, μ(MoKα)=33.04 cm^{-1}, R=0.083, R_w=0.078

When a toluene solution of either trans- or cis isomer of **4c** was heated to 70-80 °C for about 15 min in a sealed tube, the initial pale yellow solutions gradually turned deep blue,8) and the ^1H NMR spectra of the solution showed new signals at δ 4.62 ppm(d, J=1.5 Hz) and 5.10 ppm(d, J=1.5 Hz), which were assigned to the protons of exo methylene group. ^{13}C NMR spectra of the solution exhibited new characteristic signal of selenocarbonyl carbon at δ 239.9 ppm(s) along with the signals of **4c**, and UV spectrum of the solution also showed the absorption of n-π^* transition of C=Se at 650.0 nm (ε ~150). These results showed that selone **3c** was generated by the cycloreversion of the 1,3-diselenetane ring of **4c**.9) However, **3c** was afforded as the minor component of the equilibrated mixture, and the blue solution of **3c** gradually discolored by standing for a short time at 70–80 °C or even at room temperature to give a complex mixture owing to the re-dimerization and the decomposition of **3c**. All attempts to isolate **3c** were unsuccessful because of the facile conversion to the mixture of cis- and trans-**4c** during the usual workup.

Trapping of selones **3** was succeeded by heating a xylene or benzene solution of **4** in the presence of an excess amount of 2,3-dimethyl-1,3-butadiene to give air-unstable [4+2] cycloadducts **5** in good yields,10–14) and the same cycloadducts **5** were obtained as the main products by heating the starting selenides **1** in a benzene or toluene solution in the presence of the diene. These results demonstrated that the facile ring closure of *in situ* generated 1,2-propadienylselenoketenes **2** afforded selones **3** under the conditions of thermal reaction of **1** in the absence of nucleophiles. Table 2 shows the results of the trapping of selones **3**. On the other hand, heating of a toluene solution of **4c** in the presence of an excess amount of Et$_2$NH afforded a complex mixture, and the products originated from 1,2-propadienenylselenoketene **2c**, such as N,N-diethyl-2-trimethylsilyl-3-methyl-2,4-pentadieneselenoamide,1) were not found at all in the crude reaction product. This result suggested that the conversion of **2c** to **3c** was irreversible under such a reaction condition.

Table 2. Trapping of selones **3** with 2,3-dimethyl-1,3-butadiene.



Substrate	R^1	R^2	Solvent	Temp	Time /h	Product 5	Yield a) /%
1a	Ph	Me	benzene	reflux	2	**5a**	81
1b	t-Bu	Me	toluene	reflux	15	**5b**	79
1c	TMS	Me	benzene	reflux	3	**5c**	75
1d	Ph	H	benzene	reflux	1	**5d**	0 b)
4a(mixture)	Ph	Me	xylene	reflux	0.5	**5a**	71
trans-**4c**	TMS	Me	benzene	reflux	4	**5c**	72
cis-**4c**	TMS	Me	benzene	reflux	1	**5c**	68

a) Isolated yields. b) A complex mixture was obtained.

In conclusion, we have accomplished the generation, characterization, and trapping of 2-methylene-3-cyclobutene-1-selones **3**. Further chemical conversion of the selones **3** is in progress in our laboratory.

References

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6) **4a**(R^1=Ph, R^2=Me): Pale yellow needles, mp 160.0–160.5 °C(dec.); MS(*m/z*) 468(M^+, 1.5%, ^{80}Se), 234(M^+/2, bp, ^{80}Se); IR(KBr) 1674, 1491, 846 cm^{-1}; ^{1}H NMR($CDCl_3$) δ 2.10(6H, s), 4.86(2H, d, J=1.5 Hz), 5.55(2H, d, J=1.5 Hz), 7.37–7.71(6H, m), 8.37–8.52(4H, m). Found: C, 61.81; H, 4.32%. Calcd for $C_{24}H_{20}Se_2$: C, 61.51; H, 4.31%. trans-**4c**(R^1=TMS, R^2=Me): Yellow prisms, mp 135.0–136.0 °C; MS(*m/z*) 460(M^+, 6%, ^{80}Se), 230(M^+/2, bp, ^{80}Se); IR(KBr) 1664, 1556, 820 cm^{-1}; ^{1}H NMR($CDCl_3$) δ 0.47(18H, s), 1.84(6H, s), 4.60(2H, d, J=1.5 Hz), 5.18(2H, d, J=1.5 Hz); ^{13}C NMR($CDCl_3$) δ 0.0(q), 12.7(q), 94.2(t), 94.2(s), 158.1(s), 158.8(s), 161.0(s). Found: C, 46.15; H, 6.15%. Calcd for $C_{18}H_{28}Se_2Si_2$: C, 46.12; H, 6.30%. cis-**4c**(R^1=TMS, R^2=Me): Green yellow prisms, mp 105.0–108.0 °C; MS(*m/z*) 460(M^+, 16%, ^{80}Se), 230(M^+/2, 78%, ^{80}Se); IR(KBr) 1666, 1557, 1244, 846 cm^{-1}; ^{1}H NMR($CDCl_3$) δ 0.38(18H, s), 1.87(6H, s), 4.66(2H, d, J=1.5 Hz), 5.40(2H, d, J=1.5 Hz); ^{13}C NMR($CDCl_3$) δ 0.2(q), 12.8(q), 93.4(t), 93.5(s), 157.5(s), 159.1(s), 163.0(s). Found: C, 46.20; H, 6.25%. Calcd for $C_{18}H_{28}Se_2Si_2$: C, 46.12; H, 6.30%.

7) Heating of a toluene solution of either trans- or cis-**4c** at 100 °C for 2 h and the subsequent cooling to room temperature afforded the equilibrated mixture of **4c**(trans-**4c**:cis-**4c**=~90:10) in modest yields along with the unidentified several products.

8) A $CDCl_3$ solution of **1c** or **4c** in a sealed tube was heated at 80 °C for 2 h and was cooled and subjected to UV and NMR measurement. In all cases, the resulting solution was the mixture of **3c**, cis-**4c**, and trans-**4c** (**3c**:cis-**4c**:trans-**4c**=~1:1:5). **3c**(R^1=TMS, R^2=Me): UV(toluene) λ_{max} 350 nm (ε ~10000), 650 nm (ε ~150); ^{1}H NMR($CDCl_3$) δ 0.31(s), 1.79(s), 4.62(d, J=1.5 Hz), 5.10(d, J=1.5 Hz); ^{13}C NMR($CDCl_3$) δ 239.9(s).

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14) **5a**(R^1=Ph, R^2=Me): Pale yellow prisms, mp 55.0–57.0 °C; MS(*m/z*) 316(M^+, bp, ^{80}Se), 236(M^+-Se, 98%); IR(KBr) 2910, 1490 cm^{-1}; ^{1}H NMR($CDCl_3$) δ 1.73(3H, s), 1.87(3H, s), 2.01(3H, s), 2.35(1H, d, J=15 Hz), 2.94(1H, d, J=15 Hz), 3.35(2H, br.s), 4.63(2H, s), 7.22-7.46(3H, m), 7.55–7.71(2H, m). Found: C, 67.86; H, 6.39%. Calcd for $C_{18}H_{20}Se$: C, 68.03; H, 6.44%. **5b**(R^1=t-Bu, R^2=Me): Pale yellow oil; MS(*m/z*) 296(M^+, 45%, ^{80}Se), 215(M^+-Se, 95%); IR(neat) 2966, 1459 cm^{-1}; ^{1}H NMR($CDCl_3$) δ 1.25(9H, s), 1.75(3H, s), 1.80(6H, s), 2.20(1H, d, J=15 Hz), 2.90(1H, d, J=15 Hz), 3.25(2H, br.s), 4.33 (2H, s). Found: C, 64.85; H, 8.12%. Calcd for $C_{16}H_{24}Se$: C, 65.07; H, 8.19%. **5c**(R^1=TMS, R^2=Me): Pale yellow oil; MS(*m/z*) 312(M^+, 86%, ^{80}Se), 239(M^+-TMS, 43%, ^{80}Se); IR(neat) 2955, 1660, 1240 cm^{-1}; ^{1}H NMR($CDCl_3$) δ 0.22(9H, s), 1.75(3H, s), 1.78(3H, s), 1.82(3H, s), 2.28(1H, d, J=15 Hz), 2.73(1H, d, J=15 Hz), 3.24(2H, br.s), 4.43(2H, s). Found: C, 57.68; H, 7.72%. Calcd for $C_{15}H_{24}SeSi$: C, 57.86; H, 7.77%.

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