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A Novel Synthesis of α,β,γ,δ-Unsaturated Selenoamides by Using [3,3] Sigmatropic Rearrangement of Alkynyl Propargyl Selenides in the Presence of Diethylamine

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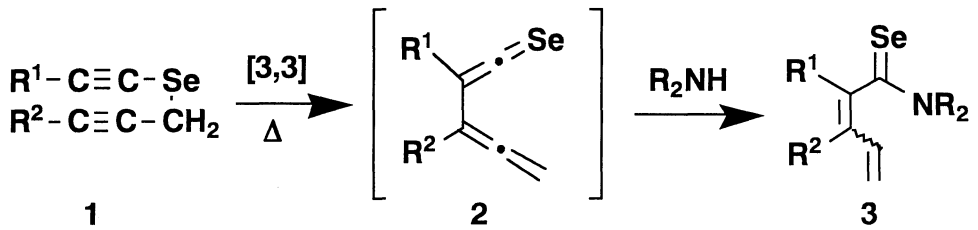
[3,3] Sigmatropic rearrangement of alkynyl propargyl selenides in the presence of an excess amount of Et_2NH afforded N,N-diethyl-2,4-pentadiene-selenoamides in modest yields.

Recently, highly reactive species related to heterocumulenes are of great interest for their roles as novel reactive intermediates of the organic reactions. However, methods for the generation of selenoketenes have not been extensively studied except for the ring cleavage of 1,2,3-selenadiazole derivatives,[1-7] acid hydrolysis of alkynyl selenolates,[8-11] and [3,3] sigmatropic rearrangement of allyl alkynyl selenides.[12,13] In particular, the third method has revealed the synthetic preference in the light of the isolation of selenoketenes. It was expected that the thermal reaction of alkynyl propargyl selenides **1** would generate 1,2-propadienylselenoketenes **2**, which would give the highly conjugated selenoamides **3** by the addition of amines and subsequent isomerization. In this paper, we wish to report a novel synthesis of N,N-diethyl-2,4-pentadieneselenoamides starting from alkynyl propargyl selenides **1**.

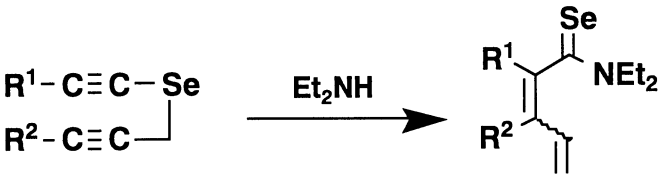


1 **2** **3**

Alkynyl propargyl selenides **1** were prepared according to Schaumann's method,[13] and the structures of the selenides **1** were determined by the physical data including MS, IR, and ^1H NMR spectra.[14] Heating of the benzene or THF solution of selenides **1** in the presence of an excess amount of Et_2NH under an Ar

atmosphere and the subsequent purification of the resulting crude products by SiO_2 column chromatography afforded 2,3-disubstituted N,N-diethyl-2,4-pentadieneselenoamides **3** in modest yields as an inseparable mixture of double bond isomers besides the recovery of **1**. Physical properties of the products including MS, IR, and ^1H NMR spectra are fully consistent with the structures of **3**.[15] The structure of **3a** and **3b** were also confirmed by conversion to the corresponding N,N-diethyl-2,4-pentadienamides **4** by treatment with 1.1 molar anount of mCPBA in CH_2Cl_2.[16-18] These results showed that the 1,2-propadienylselenoketenes **2** were generated *in situ* by the [3,3] sigmatropic rearrangement of **1**, and that the α,β,γ,δ-unsaturated selenoamides **3** were obtained by the addition of Et_2NH to **2** followed by the base-induced isomerization. However, in contrast to the α-allyl analogues,[13] all attempts to isolate the 1,2-propadienylselenoketenes **2** were not successful.

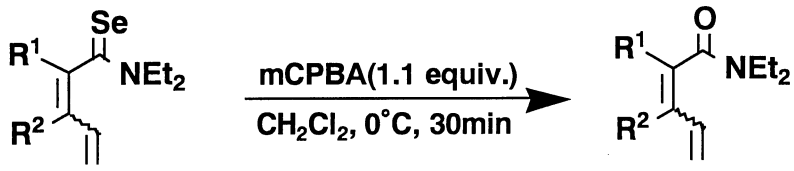
Table 1. Synthesis of N,N-diethyl-2,4-pentadieneselenoamides **3**



1 **3**

Substrate			Solvent	Temp.	Time	Product	Yield [a]	Major : Minor[b]
R^1	R^2	**1**		/°C	/h	**3**	/%	
Ph	Me	**1a**	benzene	reflux	2	**3a**	58	84 : 16
Ph	H	**1b** [c]	THF	r.t.	1	**3b**	33 [d]	100 : 0 [e]
t-Bu	H	**1c**	benzene	r.t.	12	**3c**	32	100 : 0
TMS	Me	**1d**	benzene	reflux	3	**3d**	64	58 : 42
TMS	H	**1e** [c]	THF	r.t.	3	**3e**	28 [f]	100 : 0

a) Isolated yields. b) Determined by the ^1H NMR measurement. c) In-situ generated selenides **1** were treated with Et_2NH. d) Overall yield from phenylacetylene. e) Freshly obtained product was the isomeric mixture of selenoamides. After standing the mixture at room temperature, the minor products gradually isomerized to the major product. f) Overall yield from trimethylsilylacetylene.



3a(R^1=Ph, R^2=Me) **4a(77%)**
3b(R^1=Ph, R^2=H) **4b(86%)**

When selenides **1a** and **1b** were treated with an excess amount of Et_2NH at the lower temperature, the substrates were completely recovered. Treatment of methyl 2-phenylethynyl selenide with Et_2NH under similar reaction conditions as shown above also afforded the recovery of the starting selenide. These results excluded out the alternative mechanism including the addition of amines to **1** and the subsequent [3,3] sigmatropic rearrangement of the resulting aminoselenoketeneacetal.

In conclusion, this work has provided a novel method for the conversion of alkynyl propargyl selenides to α,β,γ,δ-unsaturated selenoamides through [3,3] sigmatropic rearrangement. Further attempts for the isolation or trapping of the reactive intermediates **2**, along with the application toward the synthesis of selenium-containing heterocycles by the use of **2**, are in progress in our laboratory.

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14) **1a**(R^1=Ph, R^2=Me): Orange oil; MS(*m/z*) 234(M^+, bp, ^{80}Se), 154(M^+-Se, 79%); IR(neat) 2236, 2158, 1594 cm^{-1}; ^1H NMR($CDCl_3$) δ 1.85(3H, t, J=3 Hz), 3.57(2H, q, J=3 Hz), 7.26-7.56(5H, m). **1c**(R^1=t-Bu, R^2=H): Red oil; MS(*m/z*) 289(M^+, 60%, ^{80}Se), 209(M^+-Se, bp); IR(neat) 2156, 1458 cm^{-1}; ^1H NMR($CDCl_3$) δ 1.25(9H, s), 2.34(1H, t, J=3 Hz), 3.46 (2H, d, J=3 Hz). **1d**(R^1=TMS, R^2=Me): Pale yellow oil; MS(m/z) 230(M^+, 23%, ^{80}Se), 150(M^+-Se, 13%); IR(neat) 2237, 2089 cm^{-1}; ^1H NMR($CDCl_3$) δ 0.19(9H, s), 1.85(3H, t, J=3 Hz), 3.53(2H, q, J=3 Hz).

15) **3a**(R^1=Ph, R^2=Me): Orange oil; MS(*m/z*) 307(M^+, 84%, ^{80}Se), 278(M^+-Et, 50%, ^{80}Se); IR(neat) 2930, 1490 cm^{-1}; ^1H NMR($CDCl_3$) major isomer δ 0.95(3H, t, J=7 Hz), 1.33(3H, t, J=7 Hz),

1.95(3H, s), 3.40-3.83(2H, m), 3.83-4.45(2H, m), 5.10(1H, d, J=11 Hz), 5.30(1H, d, J=17 Hz), 6.56(1H, dd, J=17, 11 Hz), 7.25-7.40(3H, m), 7.55-7.70(2H, m), minor isomer δ 0.97(3H, t, J=7 Hz), 1.33(3H, t, J=7 Hz), 1.90(3H, s), 3.40-3.83(2H, m), 3.83-4.45(2H, m), 5.10(1H, d, J=11 Hz), 5.33(1H, d, J= 17 Hz), 6.83(1H, dd, J=17, 11 Hz), 7.32(5H, br.s). Found: C, 62.64; H, 7.01; N, 4.47%. Calcd for $C_{16}H_{21}NSe$: C, 62.74; H, 6.91; N, 4.57%. **3b**(R^1=Ph, R^2=H): Orange oil; MS(*m/z*) 293(M^+, bp, ^{80}Se), 213(M^+-Se, 93%); IR(neat) 1500, 1440 cm^{-1}; ^1H NMR($CDCl_3$) δ 1.02(3H, t), 1.42(3H, t), 3.45(2H, q, J=7 Hz), 3.85-4.65(2H, m), 5.26(1H, d, J=9 Hz), 5.41(1H, d, H=14 Hz), 6.38(1H, d, J=10 Hz), 6.63(1H, ddd, J=14, 10, 9 Hz), 7.22-7.37(3H, m), 7.48-7.62(2H, m). Found: C, 62.01; H, 6.72; N, 4.64%. Calcd for $C_{15}H_{19}NSe$: C, 61.64; H, 6.55; N, 4.79%. **3c**(R^1=t-Bu, R^2=H): Orange needles; mp 78.0-80.0 °C; MS(*m/z*) 289(M^+, 65%, ^{80}Se), 209(M^+-Se, bp); IR(KBr) 2972, 1502 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.20(3H, t, J=7 Hz), 1.28(9H, s), 1.36(3H, t, J=7 Hz), 3.15-4.00(3H, m), 4.60(1H, dq, J=15, 7 Hz), 5.08(1H, dd, J=10, 1.5 Hz), 5.18(1H, dd, J=17, 1.5 Hz), 5.85(1H, d, J=11 Hz), 6.40(1H, ddd, J=17, 11, 10 Hz). Found: C, 57.07; H, 8.44; N, 5.48%. Calcd for $C_{13}H_{23}NSe$: C, 57.34; H, 8.51; N, 5.14%. **3d**(R^1=TMS, R^2=Me): Orange oil; MS(*m/z*) 303(M^+, 25%, ^{80}Se), 223(M^+-Se, 48%); IR(neat) 2950, 1490 cm^{-1}; ^1H NMR($CDCl_3$) major isomer δ 0.30(9H, s), 1.18(3H, t, J=7 Hz), 1.36(3H, t, J=7 Hz), 1.99(3H, s), 3.20-4.70(4H, m), 5.13(1H, d, J=12 Hz), 5.26(1H, d, J=18 Hz), 6.63(1H, dd, J=18, 12 Hz), minor isomer δ 0.30(9H, s), 1.20(3H, t, J=7 Hz), 1.36(3H, t, J=7 Hz), 1.82(3H, s), 3.20-4.70(4H, m), 5.15(1H, d, J=12 Hz), 5.26(1H, d, J=18 Hz), 6.72(1H, dd, J=18, 12 Hz). Found: C, 51.47; H, 8.44; N, 4.55%. Calcd for $C_{13}H_{25}NSeSi$: C, 51.68; H, 8.33; N, 4.63%. **3e**(R^1=TMS, R^2=H): Yellow needles, mp 58.0-60.0 °C; MS(*m/z*) 289(M^+, 65%, ^{80}Se), 209(M^+-Se, bp); IR(KBr) 2957, 1496 cm^{-1}; ^1H NMR($CDCl_3$) δ 0.24(9H, s), 1.28(3H, t, J=7 Hz), 1.35(3H, t, J=7 Hz), 3.33(1H, dq, J=15, 7 Hz), 3.63(1H, dq, J=15, 7 Hz), 3.81(1H, dq, J=15, 7 Hz), 4.46(1H, dq, J=15, 7 Hz), 5.18(1H, dd, J=10, 1.5 Hz), 5.28(1H, dd, J=16, 1.5 Hz), 5.96(1H, d, J=12 Hz), 6.42(1H, ddd, J=16, 12, 10 Hz); ^{13}C NMR ($CDCl_3$) δ 0.1(q), 11.3(q), 12.9(q), 47.7(t), 48.0(t), 119.9(t), 131.6(d), 131.6(d), 133.6(d), 150.9(s), 203.8(s). Found: C, 48.67; H, 8.12; N, 4.77%. Calcd for $C_{12}H_{23}NSeSi$: C, 48.98; H, 8.04; N, 4.86%.

16) The resulting amide **4b** was identical in all respects with N,N-diethyl-2-phenyl-2,4-pentadienamide prepared by the independent [3,3] sigmatropic route from 1-phenyl-2-(N,N-diethylamino)acetylene **5** reported by Ficini. J. Ficini, N. Lumbroso-Bader, and J. Pouliquen, *Tetrahedron Lett.*, **1968**, 4139.

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18) Treatment of **3d** or **3e** with mCPBA(1.1 equiv.) afforded a mixture of a small amount of **4d** or **4e**, respectively, and the corresponding desilylated amides.

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