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REACTIONS OF CYCLOALKENO-1,2,3-SELENADIAZOLE WITH NUCLEOPHILES

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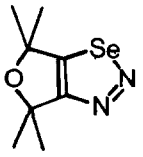
Summary: Reactions of cycloalkeno-1,2,3-selenadiazole and various nucleophiles were studied. In the case of 5-membered ring fused 1,2,3-selenadiazole nucleophilic attack on selenium atom exclusively resulted in a formation of vinyl selenide derivatives.

The photolysis and thermolysis of 1,2,3-selenadiazoles are attractive as potential source of alkynes and widely applied in organic synthesis.[1] In addition, the reactions of cycloalkeno-1,2,3-selenadiazoles with alkyllithium were also reported to form the corresponding cycloalkynes in consequence of the extrusion of nitrogen and selenium.[2] Although the notorious instability of cyclopentyne might suggestively make the reactions of cyclopenteno-1,2,3-selenadiazole unlike those of 4,5-disubstituted 1,2,3-selenadiazoles and 1,2,3-selenadiazoles fused with more than 7-membered ring, there have been no systematic studies on the reactions of medium size ring-fused 1,2,3-selenadiazoles.

Recently we reported that the photolysis of 4,4,6,6-tetramethyldihydrofurano[3,4-d][1,2,3]selenadiazole (**1**) gave the cycloadducts containing the selenium atom opposed to the conversion to cyclopentyne (**3**).[3] Now, we wish to report the reaction of cycloalkeno-1,2,3-selenadiazoles (**1** and **2**[4]) with various nucleophiles which sufficiently reflected the effect of their fused ring structures.



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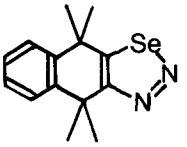

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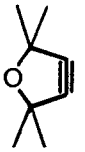

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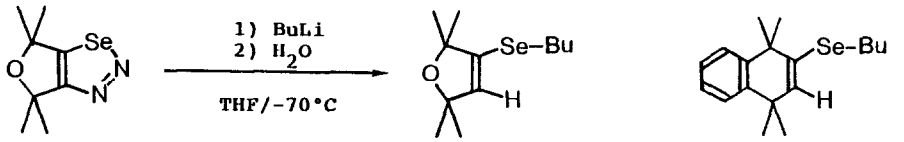
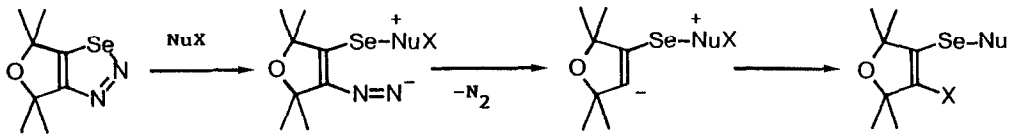
To a 5 ml of tetrahydrofuran solution of **1** (1 mmol) was added butyllithium (1 mmol, in hexane) in portions at -70°C and stirred for 30 minutes at this temperature. After quenching with 5 ml of water and a usual work-up, the residual oil was submitted to high pressure liquid chromatography to give the butyl vinyl selenide (**4**,53%).[5] Similarly in the reaction of **2** with butyllithium the same type of product **5** was obtained in 47% yield.



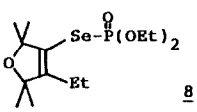
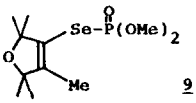
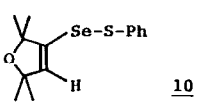
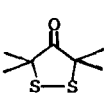
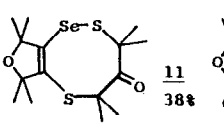
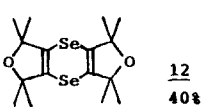
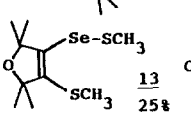
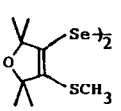
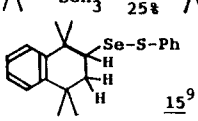
1 4 5

This type of reaction is general in the reactions of 1 with rather soft nucleophiles, trialkyl phosphite, thiol, and disulfide, which gave the ring-opened products containing selenium atom as shown in Table 1.[7] The reaction with dimethyl disulfide afforded the compounds (13) and (14) as principal products along with some dimerization product (12). The product (14) probably arose from the cleavage of week S-Se bond followed by recombination under the reaction conditions.[8] These results can be rationalized by the initial attack of the nucleophile on the selenium atom leading to the zwitter ion (6) followed by the denitrogenation and intramolecular nucleophilic attack of alkenyl anion (7).

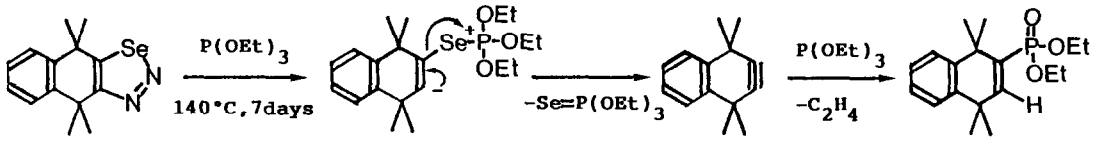


1 6 7

Table 1. Reaction of Cycloalkeno-1,2,3-selenadiazoles with Soft Nucleophiles

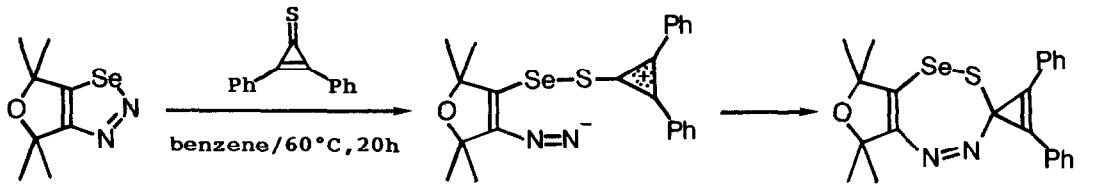
Substrate	Nucleophile	Conditions	Products and Yields
1	$P(OEt)_3$	50°C 36h	 8 86%
1	$P(OMe)_3$	50°C 24h	 9 89%
1	Ph-SH	r.t. 12h	 10 98%
1		60°C 48h	 11 38%  12 40%
1	CH_3SSCH_3	60°C 24h	 13 25%  14 25% 12 13%
2	Ph-SH	125°C 7days	 15[9] 44%

However, the reaction of 2 with triethyl phosphite did proceed in a different fashion. The spectral data of the product (17)[10] confirmed the extrusion of selenium atom, which is almost certainly interpreted with the high leaving ability of the triethyl selenophosphate and the stability of the cyclohexyne intermediate (16) in contrast to cyclopentyne (3).



2 16 17 quant.

Furthermore, treatment of the selenadiazole (1) with diphenylcyclopropenethione also led to a characteristic and interesting cyclization product (19) in 90% yield. The structure of 19 was confirmed by the ^{1}H-NMR, ^{13}C-NMR, elemental analysis, and photon spectroscopy at S-Se bond.[11] Of particular note is that the nitrogen unit is still remained. It is attractive to speculate that the initially formed intermediate (18) similar to 6 readily undergoes an intramolecular collapsing resulting in a formation of a novel 7-membered heterocycle (19).



1 18 19

In sum, it is clear that cyclopentyne is not involved in the reactions of 5-membered ring fused 1,2,3-selenadiazole (1) with nucleophiles, but rather vinyl selenide derivatives.

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3. W. Ando, Y. Kumamoto, and N. Tokitoh, Tetrahedron Lett., **27**, 6107 (1986).

4. Synthesis of the 6-membered ring fused 1,2,3-selenadiazole (**2**).

A mixture of 1,1,4,4-tetramethylbenzcyclohexan-2-one (20 mmol) and semicarbazide hydrochloride (20 mmol) in 10 ml of pyridine was refluxed for 24 hours with catalytic amount of BF_3 etherate. After evaporating the solvent, the residue was dissolved in 50 ml of acetonitrile and to the solution was added selenium dioxide (40 mmol) and the mixture was stirred for 2 days at room temperature. After filtration, the mixture was evaporated and submitted to column chromatography (silica gel/hexane) to afford selenadiazole (**2**) in 80% yield

2 ^{1}H-NMR($CDCl_3$) δ 1.79(s,6H) 1.89(s,6H) 7.4-7.6(m,4H), ^{13}C-NMR($CDCl_3$) δ 33.0(q) 38.5(q) 38.8(s) 40.8(s) 125.8(d) 126.6(d) 127.0(d) 127.2(d) 139.3(s) 141.8(s) 162.9(s) 165.5(s).

5. **4** ^{1}H-NMR($CDCl_3$) δ 0.94(t,3H) 1.32(s,6H) 1.36(s,6H) 1.0-1.9(m,4H) 2.79(t,2H) 5.42(s,1H), ^{13}C-NMR($CDCl_3$) δ 13.6(q) 23.0(t) 26.5(t) 29.4(q) 29.8(q) 31.6(t) 86.6(s) 89.4(s) 130.5(s) 135.8(s). MS m/z 262 [M^+].

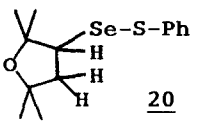
6. **5** ^{1}H-NMR($CDCl_3$) δ 0.94(t,3H) 1.26-1.82(m,4H) 1.36(s,6H) 1.51(s,6H) 2.76(t,2H) 5.48(s,1H) 7.1-7.4(m,4H), ^{13}C-NMR($CDCl_3$) δ 13.8(q) 22.2(t) 30.6(t) 31.2(q) 32.8(q) 33.4(t) 36.6(s) 40.0(s) 125.8(d) 126.0(d) 126.1(d) 126.5(d) 132.0(d) 138.3(s) 141.3(s) 142.5(s).

7. All the compounds listed in Table 1 showed the satisfactory ^{1}H-NMR, ^{13}C-NMR, and mass, spectra. The spectral data of **8** is shown as a representative.

8 ^{1}H-NMR($CDCl_3$) δ 1.37(t,6H) 1.41(s,6H) 1.41(t,3H) 1.48(s,6H) 3.05(q,2H) 4.16 (J_{HP}=7Hz,q,4H), ^{13}C-NMR($CDCl_3$) δ 15.2(q) 16.3(J_{CP}=6Hz,q) 22.5(t) 29.1(q) 29.7(q) 61.8(J_{CP}=6Hz,t) 89.5(J_{CP}=21Hz,s) 90.6(J_{CP}=20Hz,s) 132.2(J_{CP}=27Hz,s) 150.4(J_{CP}=10Hz,s), HRMS 370.0848 (Calcd for $C_{14}H_{27}O_4PSe$ 370.0812).

8. The recombination was observed also in the case of **10** which gave the diselenide and diphenyl disulfide slowly at room temperature in $CDCl_3$.

9. **15** might be thought to be the reduction product of the initial formed vinyl selenide by thiophenol. In the case of the reaction of **10** with thiophenol at 120°C for 70 hours, the reduction also occurred to afford **20** in 70% yield.



20

10. **17** ^{1}H-NMR($CDCl_3$) δ 1.34(t,6H) 1.39(s,6H) 1.70(s,6H) 4.11(J_{HP}=7Hz,q,4H) 5.61 (J_{HP}=10Hz,s,1H) 7.1-7.5(m,4H), ^{13}C-NMR($CDCl_3$) δ 16.4(J_{CP}=6Hz,q) 29.6 (J_{CP}=2Hz,q) 31.9(J_{CP}=2Hz,q) 48.4(J_{CP}=6Hz,s) 50.0(J_{CP}=20Hz,s) 61.3(J_{CP}=6Hz,t) 108.1(J_{CP}=194Hz,d) 122.4(d) 122.5(d) 127.1(d) 127.6(d) 146.6(s) 149.8(s) 185.5 (J_{CP}=6Hz,s), EA Found C,66.91; H,8.40% (Calcd for $C_{18}H_{27}O_3P$: C,67.06; H,8.44%).

11. **19** ^{1}H-NMR($CDCl_3$) δ 1.52(s,6H) 1.74(s,6H) 7.2-7.5(m,10H), ^{13}C-NMR($CDCl_3$) δ 29.1(q) 29.3(q) 86.1(s) 86.9(s) 117.1(s) 121.2(s) 128.1(d) 128.2(d) 130.2(d) 132.1(s) 141.6(s) 150.5(s), EA Found C,61.01; H,4.92; N,6.24% (Calcd for $C_{23}H_{22}ON_2SSe$: C,60.91; H,4.89; N,6.17%).

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