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PHOTOLYSIS OF STERICALLY PROTECTED BICYCLIC 1,2,3-SELENADIAZOLE

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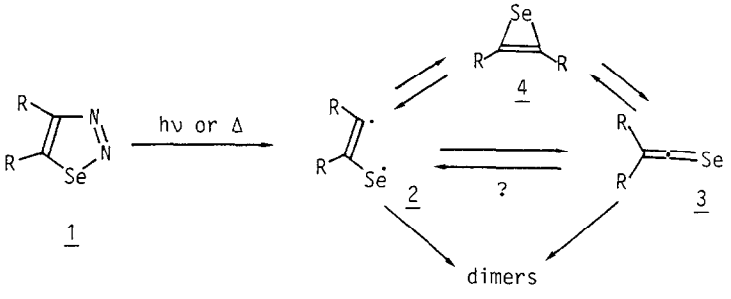
Summary: The photolysis of sterically protected 1,2,3-selenadiazole in the presence of olefin was studied. The regioselective cycloadducts were obtained via the initially formed zwitter-ionic intermediate.

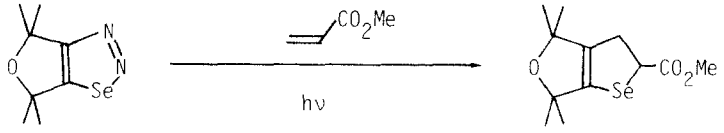
The photolysis of the 1,2,3-selenadiazole ring system (1) has attracted much attention from a viewpoint of studying the character of 3 and 4.[1-6] However, no chemistry has been reported for the intermolecular reaction so far as we know probably due to the highly reactive intermediates resulting from the lack of effective protection. In most cases the intermediates such as 2, 3, and 4 from photolysis and thermolysis of selenadiazole are very unstable and gave only dimerization products.[7-10]



Here we introduce a new bicyclic selenadiazole fused system with tetramethyl dihydrofuran ring (5)[11] and delineate its photochemical reaction in the presence of olefin. We expected that the steric protection by the geminal methyl groups is effective enough not only to stabilize the highly reactive intermediates but also to suppress the further decomposition of the reaction products.

Typical example is as follows: The selenadiazole (5) (1 mmol) dissolved in 3 ml of methyl acrylate was irradiated in a pyrex vessel by a medium pressure

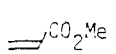
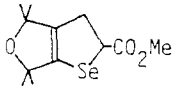
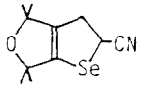
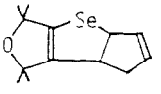
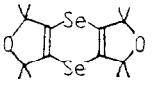
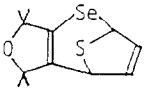
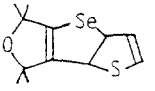
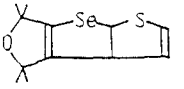
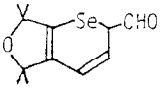
mercury lamp at room temperature. The irradiation evoked the nitrogen gas evolution and it ceased in about 5 hours. Then the mixture was evaporated and the residue was submitted to column chromatography (silica gel/dichloromethane) to afford a single adduct (6), the structure of which was confirmed by ^{1}H-NMR, ^{13}C-NMR, IR, and MS spectra.[12]



5 6

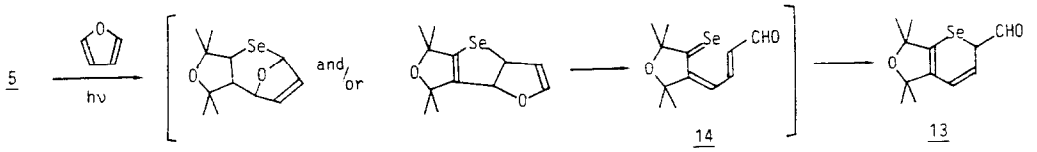
Similarly the regioselective adducts (7[13] and 8[14]) were obtained from acrylonitrile and cyclopentadiene, although the diselenin (9)[15] was formed as a by-product in the latter case, shown in Table 1. No product derived from the reaction with selenirene or selenoketene was obtained.

Table 1. Photolysis of 1,2,3-selenadiazole (5) in olefin.

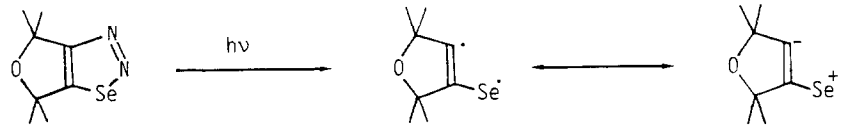
	Olefin	Products and Yield
1		 6 (87%)
2		 7 (94%)
3		 8 (70%),  9 (12%)
4		 10 (11%),  11 (7%),  12 (2%), 9 (39%)
5		 13 (18%), 9 (40%)

On the contrary, the reaction with thiophene and furan gave characteristic and interesting products. Thiophene gave three regio-isomers, i.e. [4+3]adduct (10)[16](7%) and [2+3]adducts (11)[17] and (12)[18] (11 and 2% respectively), along with diselenin (9) as a major product (39%). Adduct 10 underwent a slow ring conversion into adduct 11 on standing as a chloroform solution. On the other hand, a bicyclic aldehyde (13)[19] was obtained from

furan. The formation of 13 might be the initial cycloaddition of 15 to furan yielding the [4+3]- and/or [2+3]adducts, followed by the intramolecular electrocyclic ring transformation leading to the bicyclic aldehyde (13) via the conjugated selenoketone intermediate (14).



On the basis of above results, we can rationalize the photolysis of 5 is interpreted with an open-chained intermediate such as 15a or 15b, which is successfully protected by the neighboring geminal methyl groups to have an enough life-time for the intermolecular cycloaddition.



5 15a 15b

In addition, the high regioselectivity observed in the reaction with unsymmetrical and electron-deficient olefins (entries 1 and 2) strongly suggests that as for the initially formed intermediate the contribution of zwitterionic character (15a) is rather greater than that of a well-documented diradical structure (15b).

REFERENCES AND NOTES

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11) Preparation of 6,6,8,8-tetramethyl-2-selena-3,4-diaza-7-oxabicyclo[3.3.0]-octa-1(5),3-diene (5).

A mixture of 15.2g (0.1 mol) of 2,2,5,5-tetramethyltetrahydrofuran-3-one, 11.2g (0.1 mol) of semicarbazide hydrochloride and 10.1g (0.1 mol) of triethylamine in 30 ml of benzene was refluxed for 12 hours. The reaction mixture was cooled and filtered. The residue was dissolved in 100 ml of dioxane and to the solution was added 22.2g (0.2 mol) of selenium dioxide and the mixture was stirred for 2 days at room temperature. After filtration, the mixture was evaporated and submitted to column chromatography to afford selenadiazole (5) in 30% yield.
5; ^{1}H-NMR(δ,$CDCl_3$) 1.62(s,6H) 1.69(s,6H), ^{13}C-NMR(δ,$CDCl_3$) 29.9(q) 31.7(q) 78.4(s) 81.2(s) 165.6(s) 171.6(s).

12) 6; mp. 56-57°C, ^{1}H-NMR(δ,$CDCl_3$) 1.33(s,3H) 1.36(s,9H) 2.72(dd,1H) 3.00 (dd,1H) 3.76(s,3H) 5.03(dd,1H), ^{13}C-NMR(δ,$CDCl_3$) 28.3(q) 28.4(q) 29.1(q) 29.3(q) 31.7(q) 47.5(d) 52.6(q) 84.1(s) 84.7(s) 135.9(s) 143.3(s) 173.2(s), MS. m/e 288, 290 [M^+], EA. C:49.69 H:6.32 (calcd for $C_{12}H_{18}O_3Se$ C:49.83 H:6.27), IR(NaCl) 1725(C=O).

13) 7; mp. 53.5-54.5°C, IR(NaCl) 2240(C≡N), ^{1}H-NMR(δ,$CDCl_3$) 1.29(s,3H) 1.36(s,6H) 1.40(s,3H) 2.84(d,1H) 2.87(d,1H) 4.71(dd,1H), ^{13}C-NMR(δ,$CDCl_3$) 28.4(q) 29.2(q) 35.2(t) 77.3(d) 84.2(s) 84.6(s) 120.3(s) 138.0(s) 141.8(s), MS. m/e 255, 257 [M^+], HRMS. 257.0303(m/e calcd for $C_{11}H_{15}NOSe$ 257.0318).

14) 8; ^{1}H-NMR(δ,$CDCl_3$) 1.35(s,6H) 1.37(s,6H) 2.54-2.37(m,2H) 3.55(dt,1H) 5.75-5.92(m,3H), ^{13}C-NMR(δ,$CDCl_3$) 28.8(q) 29.2(q) 29.4(q) 29.5(q) 37.9(t) 46.8(d) 62.8(d) 83.6(s) 84.8(s) 130.9(s) 132.2(s) 137.4(s) 144.4(s), HRMS. 270.0562 (calcd for $C_{13}H_{18}OSe$ 270.0522).

15) 9; mp. 172-174°C, ^{1}H-NMR(δ,$CDCl_3$) 1.37(s), ^{13}C-NMR(δ,$CDCl_3$) 28.8(q) 88.3(s) 132.3(s), EA. C:47.60 H:6.05 (calcd for $C_{16}H_{20}O_2Se_2$ C:47.30 H:5.95).

16) 10; ^{1}H-NMR(δ,$CDCl_3$) 1.31(s,3H) 1.41(s,3H) 1.46(s,3H) 1.51(s,3H) 4.33(d,1H) 4.52(dd,1H) 5.98(dd,1H) 6.60(d,1H), ^{13}C-NMR(δ,$CDCl_3$) 29.0(q) 29.3(q) 29.6(q) 49.2(d) 50.4(d) 88.2(s) 89.1(s) 122.5(s) 132.8(s).

17) 11; ^{1}H-NMR(δ,$CDCl_3$) 1.36(s,6H) 1.39(s,3H) 1.41(s,3H) 4.92(d,1H) 5.70(dd,1H) 6.22(ddd,1H) 6.40(dd,1H), ^{13}C-NMR(δ,$CDCl_3$) 28.5(q) 28.9(q) 29.0(q) 29.3(q) 57.2(d) 66.6(d) 84.5(s) 84.6(s) 121.8(d) 129.2(d) 141.7(s) 142.3(s).

18) 12; ^{1}H-NMR(δ,$CDCl_3$) 1.38(s,12H) 4.13(ddd,1H) 5.62(dd,1H) 6.34(dd,1H) 6.53(d,1H), HRMS. 288.0067 (calcd for $C_{12}H_{16}OSSe$ 288.0085).

19) 13; IR(CCl4) 1715(C=O), ^{1}H-NMR(δ,$CDCl_3$) 1.22(s,3H) 1.25(s,3H) 1.26(s,3H) 1.32(s,3H) 3.10(dd,1H) 4.97(dd,1H) 5.81(d,1H) 9.00(d,1H), ^{13}C-NMR(δ,$CDCl_3$) 27.1(q) 28.5(q) 29.6(q) 30.7(q) 42.0(d) 86.9(s) 87.6(s) 114.2(d) 126.1(d) 137.1(s) 142.7(s) 186.9(d).

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