JOURNAL OF PHYSICAL ORGANIC CHEMISTRY, VOL. 1, 317–332 (1988)

NOVEL REACTIONS OF STERICALLY PROTECTED FUSED 1,2,3-SELENADIAZOLE. A NEW ASPECT OF REACTIVITY OF ORGANOSELENIUM INTERMEDIATES

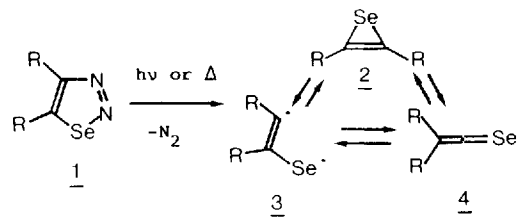
WATARU ANDO,* YORIO KUMAMOTO AND NORIHIRO TOKITOH
Department of Chemistry, The University of Tsukuba, Tsukuba 305, Japan

ABSTRACT

Light- and heat-induced decompositions and reactions with nucleophiles of 6,6,8,8-tetramethyl-2-selena-3,4-diaza-7-oxabicyclo[3.3.0]octa-1(5),3-diene have been studied. In contrast with the conversion to the cyclopentyne derivative (**9**), selenium containing intermediates (**6a**, **6b**, and **7**) were efficiently trapped using several reagents to give various kinds of organoselenium compounds. Of particular note is the isolation of a stable selenirane derivative (**16**) obtained by the cycloaddition of the photochemically generated selenirene intermediate (**7**) with furan. The character and reactivity of the intermediates are also discussed.

INTRODUCTION

The 1,2,3-selenadiazole ring system (**1**) has been widely applied to the synthesis of alkynes.[1] Recent years have seen great interest in the reaction of 1,2,3-selenadiazoles from the viewpoint of a facile formation of reactive intermediates containing a selenium atom such as selenirene (**2**), diradical (**3**), and selenoketene (**4**), which are expected to be useful synthetic blocks for organoselenium compounds.[2]



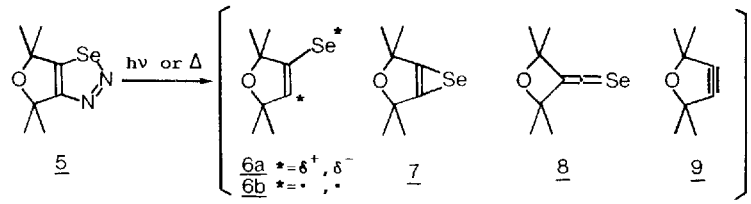
Although the pyrolysis and photolysis of some 1,2,3-selenadiazoles have been well investigated for the purpose of the generation and matrix isolation[3] of selenirene (**2**) and selenoketene (**4**), little is known concerning their character and reactivity in their

*Author for correspondence.

0894–3230/88/060317–16$08.00

Received 11 January 1988
Revised 28 March 1988

intermolecular reactions.[3c,4] The difficulty of the formation and trapping of **2** and **4** is due to their tendency to decompose to selenium and alkynes, as generally known for monocyclic 1,2,3-selenadiazoles. In contrast, the reaction of the 1,2,3-selenadiazoles fused to a less than 8-membered ring gives 1,4-diselenin derivatives as major products instead of the strained cycloalkynes.[5] Therefore, one could use a fused 1,2,3-selenadiazole with a 5-membered ring to study reactive organoselenium species (**6**, **7**, and **8**). In addition, steric protection is effective for stabilizing not only the highly reactive moiety but also the reaction products as described in a number of successful, recent works which isolate rather unstable species by the assistance of bulky groups.[6]



Consequently, here we prepared a sterically protected bicyclic 1,2,3-selenadiazole (**5**) and studies its light- and heat-induced decompositions[7] and its reactions with nucleophiles.[8] Among the expected species (**6–9**), the zwitterion intermediate (**6a**) was formed in the thermolysis and the photolysis of **5** with light of $\lambda = 365$ nm, while the photolysis of **5** with light of $\lambda = 254$ nm generated selenirene (**7**) and diradical (**6b**). The reactions of **5** with nucleophiles afforded the vinylselenide derivatives via the attack of the nucleophile on the selenium atom. In no case were products found which derived from the selenoketene (**8**) or cyclopentyne (**9**).

RESULTS AND DISCUSSION

Photolysis of 1,2,3-selenadiazole (5) with light of $\lambda = 365$ nm

When the 1,2,3-selenadiazole (**5**) was photolyzed in acrylonitrile through a pyrex vessel by a medium pressure mercury lamp at room temperature, nitrogen gas was evolved for 5 hours. Colorless crystalline dihydroselenole (**10a**) was isolated in 94% yield by column chromatographic separation with satisfactory spectral data. Similar adducts (**10b–e**) were obtained in the reactions with electronically activated olefins and strained olefins as shown in Table 1, while 1,4-diselenin (**11**) was formed in a high yield in the absence of any trapping reagents.

The regiospecificity in the cycloaddition reaction with asymmetric olefins indicated that the intermediate here formed was a zwitterionic one (**6a**) in contrast with a well-documented diradical (**6b**).[9] Under the above reaction conditions no derivative of the selenirene (**7**) or the selenoketene (**8**) were obtained.

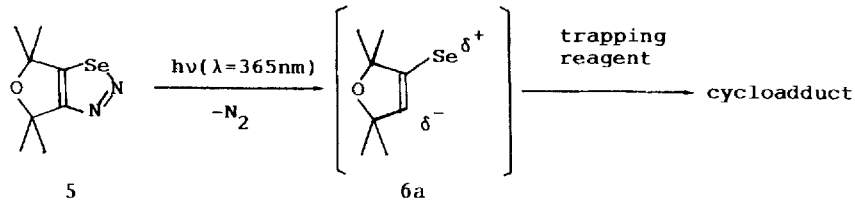
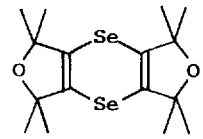
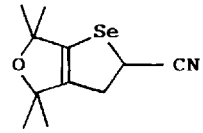
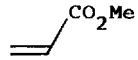
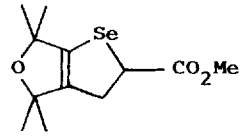
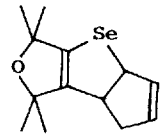
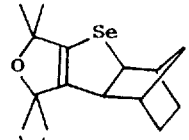
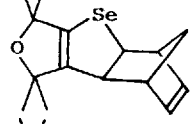
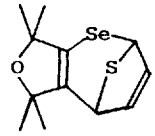
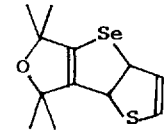
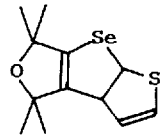
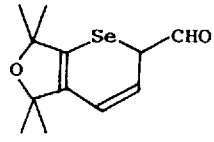
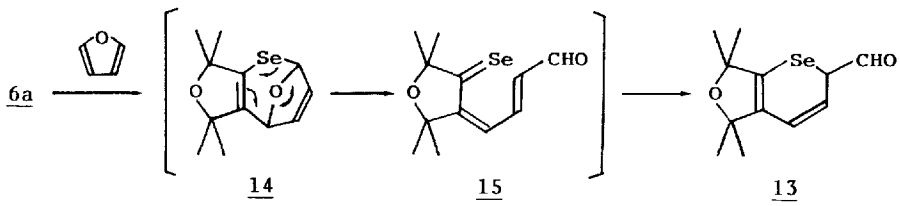


Table 1. Photolysis of the 1,2,3-selenadiazole (**5**) with light of $\lambda = 365$ nm

Run	Trapping Reagent	Products and Yields
1	none (benzene)	 11, 95%
2		 10a, 94%
3		 10b, 87%
4		 10c, 70% + 11, 12%
5		 10d, 27% + 11, 65%
6		 10e, 33% + 11, 61%
7		 12a, 11%  12b, 7%
		 12c, 2% + 11, 39%
8		 13, 18% + 11, 40%

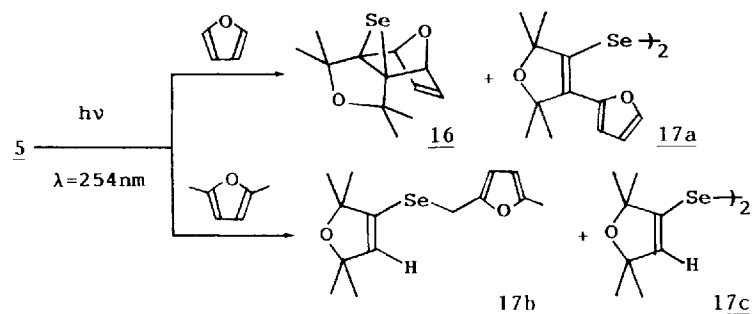
In contrast, the photochemical reaction with thiopene and furan gave characteristic and interesting products. Thiophene gave three isomeric addition products, i.e. [4+3] adduct (**12a**) and [2+3] adducts (**12b** and **12c**). **12a** slowly isomerized into **12b** at room temperature in chloroform, probably to release the ring strain. On the other hand, furan gave a bicyclic aldehyde (**13**) via the initial [4+3] cycloadduct (**14**), followed by the electrocyclic ring transformation through the conjugated selone (**15**).



14 15 13

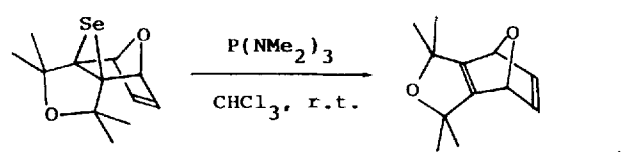
Photolysis of 1,2,3-selenadiazole (5) with light of λ = 254 nm

Selenirene (**2**) has been of special interest as a type of antiaromatic 3-membered heterocycles.[10] However, no example is known of chemical trapping evidence retaining the 3-membered ring structure. We have succeeded in the trapping of the selenirene (**7**) by the photolysis of **5** in furan with light of λ = 254 nm to give selenirane (**16**, 12%), a cycloadduct of the selenirene (**7**) as a single stereoisomer along with the diselenide (**17a**, 41%) and the aldehyde (**13**, 11%).



16 17a 17b 17c

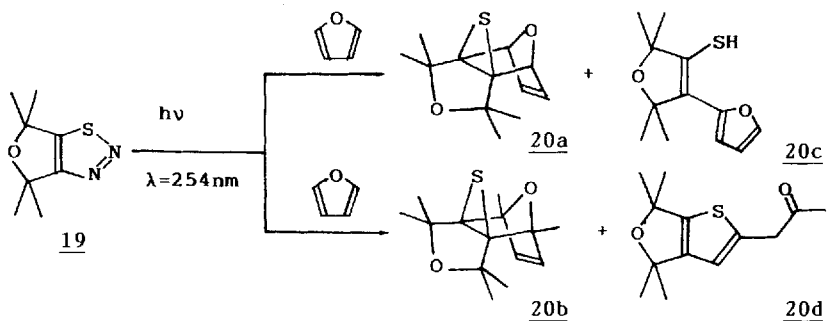
The structure of the furan adduct (**16**), the first example of a stable selenirane, was confirmed by the symmetry of the NMR spectrum and high resolution mass spectra, and the chemical proof in the facile reaction with tris(dimethylamino)phosphine in chloroform at room temperature to give the corresponding deselenated product (**18**) quantitatively accompanied with tris(dimethylamino)phosphine selenide. The selenirane (**16**) is stable in benzene at room temperature and decomposes to a polymeric product with a little bit of acid.



16 18 quant.

In the reaction with 2,5-dimethylfuran, none of the Diels–Alder type adduct of selenirene (**7**) was found, and only the hydrogen abstraction products (**17b**, 14% and **17c**, 20%) of the radical intermediate (**6b**) were obtained. The high reactivity of (**6b**) toward the alkyl C—H bond was ascertained by the reaction with hexane, where the diselenide (**17c**) was obtained in 82% yield, while photolysis with light of λ = 365 nm in hexane or 2,5-dimethylfuran gave only 1,4-diselenin (**11**). These results imply that the selenirene (**7**) and the diradical (**6b**) coexist as intermediates in the photolysis of **5** with light of λ = 254 nm.

The analogous 1,2,3-thiadiazole (**19**),[11] which was inert to light of λ = 365 nm, was irradiated similarly by the low pressure mercury lamp (λ = 254 nm) in either furan or 2,5-dimethylfuran to give the Diels–Alder type adducts (**20a**, 11%) and (**20b**, 12%) along with diradical adducts (**20c**, 30%) and (**20d**, 22%), respectively.



Thermolysis of 1,2,3-selenadiazole (5)

Since the 1,2,3-selenadiazole (**5**) has a weakened Se—N bond due to the strained bicyclic structure, it decomposed thermally at relatively low temperature, *ca.* 75 °C, with evolution of nitrogen gas. Refluxing of **5** in benzene for 24 hours afforded the 1,4-diselenin (**11**) almost

Scheme 1

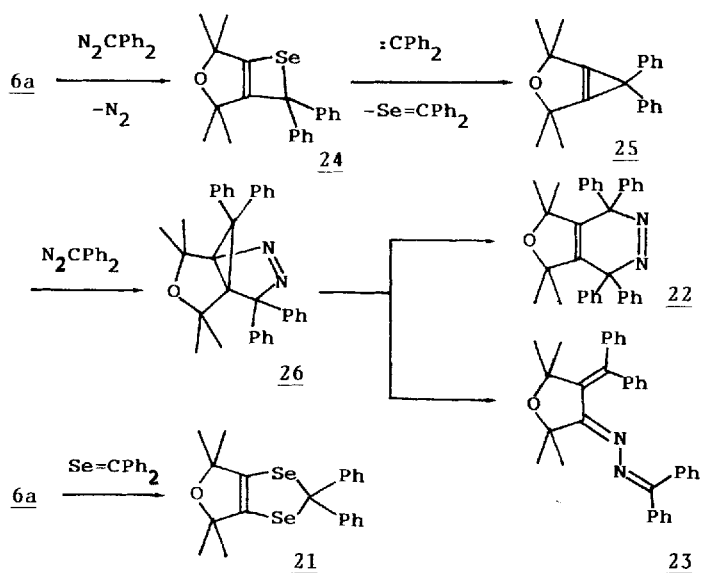
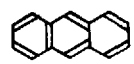
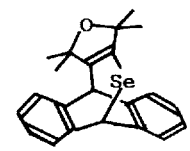
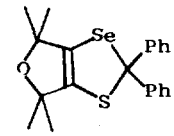
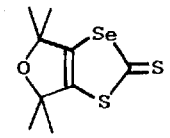
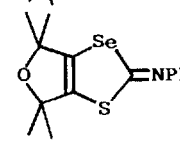
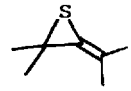
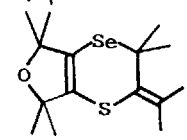
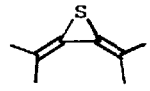
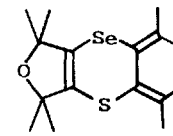


Table 2. Thermolysis of the 1,2,3-selenadiazole (**5**)

Run	Trapping Reagents	Reaction Conditions	Products and Yields
1	none(benzene)	80°C, 24h	11, 96%
2	CH_2=CHCN	77°C, 48h	10a, 85%
3	CH_2=$CHCO_2Me$	86°C, 12h	10b, 91%
4		220°C, 5m	 10f, 26% + 11, 30%
5		80°C, 24h	 10g, 70%
6	CS_2	90°C, 24h	 10h, 75%
7	PhNCS	90°C, 12h	 10i, 61%
8		80°C, 24h	 10j, 31% + 11, 65%
9		80°C, 24h	 10k, 22% + 11, 73%

quantitatively and neither the selenoketene (**8**) nor its dimer, 1,3-diselenetane derivative, were formed. The thermolysis of the 1,2,3-selenadiazole (**5**) in the presence of several olefins and thiocarbonyl compounds afforded the corresponding dihydroselenole (**10a** and **10b**) and 1,3-thiaselenole derivatives (**10g–i**) regiospecifically as shown in Table 2.

The regiospecific formation of olefin adducts (**10a,b**) suggests that the intermediate here formed was the same zwitterionic species (**6a**) as with the photolysis with light of $\lambda = 365$ nm. The formation of the 1,3-thiaselenoles (**10g–i**) might be interpreted with the thiophilic attack of the intermediate (**6a**) which behaves as a soft nucleophile. Similar reactions also occurred with some thiiranes to give the dihydro-1,4-thiaselenin derivatives (**10j** and **10k**). Treatment of **5** in the presence of an excess of diphenyldiazomethane at 80°C afforded the three products

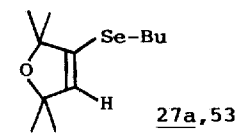
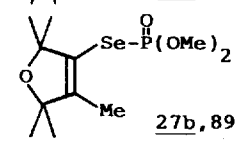
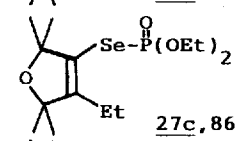
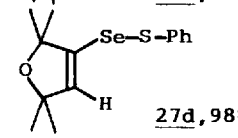
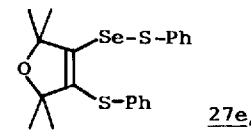
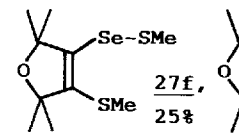
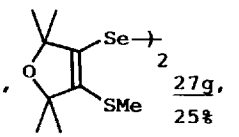
(**21**, **22**, and **23**). Of particular note is that **21** has two selenium atoms while **22** and **23** involve no selenium atom, but nitrogen instead. According to the susceptible generation of selenobenzophenone, we would propose a possible mechanism as shown in Scheme 1.

One would expect that the zwitterionic intermediate (**6a**) initially formed reacted with diphenyldiazomethane to give selenete (**24**) with the extraction of nitrogen. **24** was subjected to the attack of diphenylcarbene formed in these thermal conditions and the succeeding elimination of selenobenzophenone gave the strained cyclopropene (**25**), and the 1,3-diselenole (**21**) was formed by the addition of selenobenzophenone with the intermediate (**6a**). The formation of **22** and **23** can be well explained with the ring transformation of the [2+3] adduct (**26**) of the strained cyclopropene (**25**) with an excess of diphenyldiazomethane.

Reaction of 1,2,3-selenadiazole (5) with nucleophiles

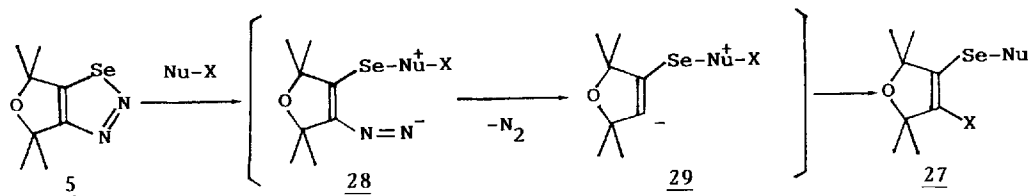
In contrast to the active research on the photolysis and thermolysis of 1,2,3-selenadiazoles little has been reported for the reaction with nucleophiles. Meier *et al.* reported the reaction of

Table 3. Reaction of the 1,2,3-selenadiazole (**5**) with nucleophiles

Run	Nucleophiles	Reaction Conditions	Products and Yields
1	$BuLi/H_2O$	-70°C, 30m	 **27a**, 53%
2	$P(OMe)_3$	50°C, 24h	 **27b**, 89%
3	$P(OEt)_3$	50°C, 36h	 **27c**, 86%
4	Ph-SH	r.t., 12h	 **27d**, 98%
5	PhSSPh	60°C, 48h	 **27e**, 32% + **11**, 45%
6	MeSSMe	60°C, 24h	 **27f**, 25%  **27g**, 25% + **11**, 13%

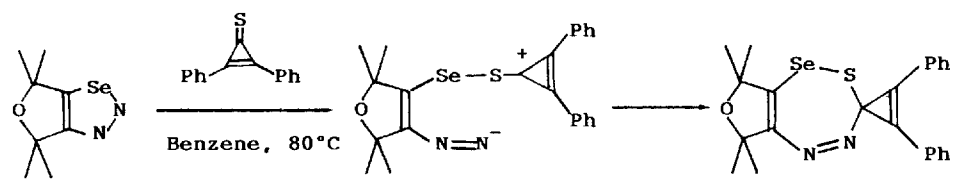
cycloalkeno-1,2,3-selenadiazoles with butyllithium to afford the corresponding cycloalkyne or butyl selenide derivatives via the nucleophilic attack of butyl anion on the selenium atom followed by the extraction of nitrogen.[12] According to the notorious instability of cyclopentyne, selenium atom might be expected to be preserved in the reaction of the 1,2,3-selenadiazole (**5**) with nucleophiles.

Treatment of a tetrahydrofuran solution of **5** with an equimolar amount of butyllithium at −70°C gave the butyl selenide (**27a**) in 53% yield. This type of reaction is general in the reaction with rather soft nucleophiles and proceeded readily below the decomposition temperature of **5** to give the corresponding vinyl selenide derivatives (**27**) as shown in Table 3. These reactions can be rationalized by the initial attack of the nucleophile on the selenium atom leading to the zwitterion (**28**) followed by the loss of nitrogen and intramolecular nucleophilic attack of alkenyl anion (**29**).



5 28 29 27

In addition, a treatment of **5** with diphenylcyclopropenethione afforded a novel 7-membered heterocycle (**30**) as a result of intramolecular cyclization of the initially formed nitrogen containing intermediate (**31**).



5 31 30

Summary

New types of reactions of the 1,2,3-selenadiazole were found using a sterically protected bicyclic system resulting in a novel formation of various organoselenium compounds including the first isolation of a stable selenirane derivative (**16**). The results reported here shed light on the unique and interesting character of selenium containing reactive intermediates (**6a**, **6b**, and **7**). It is clear that the selenoketene (**8**) and the cyclopentyne (**9**) are not involved in the reaction of the 5-membered ring fused 1,2,3-selenadiazole (**5**). The facility and regiospecificity of the photochemical and thermal cycloaddition reactions of **5** with olefins provides a new approach to synthesizing organoselenium compounds.

EXPERIMENTAL SECTION

Melting points were taken with a Yanaco micro melting point apparatus and are uncorrected. IR spectra were obtained on a Hitachi 260-50 infrared spectrometer. ^{1}H-NMR spectra were recorded with a JEOL FX-100 spectrometer and ^{13}C-NMR spectra were recorded with a

JEOL FX-90Q spectrometer; Chemical shifts (δ) are shown in part par million downfield from internal tetramethylsilane. Mass spectra were measured on a Hitachi RMU-6M mass spectrometer. High resolution mass spectra were measured on a JEOL JMS-D300 mass spectrometer. Elemental analyses were determined by our own analysis group.

Preparation of 6,6,8,8-tetramethyl-2-selena-3,4-diaza-7-oxabicyclo[3.2.0]octa-1(5),3-diene (5)

A mixture of 2,2,5,5-tetramethyldihydrofuran-3-one (15·2 g, 0·1 mol), semicarbazide hydrochloride (11·2 g, 0·1 mol), and triethylamine (10·1 g, 0·1 mol) in 30 ml of ethanol with 1 ml of boron trifluoride etherate as catalyst was refluxed for 24 hours. The reaction mixture was cooled and filtered. The residue was dissolved in 100 ml of acetonitrile and to the solution was added selenium dioxide (22·2 g, 0·2 mol) and the mixture was stirred for 3 days at room temperature. After filtration, the filtrate was evaporated and submitted to silica gel column chromatography (Merck Kieselgel 60; eluent dichloromethane) to afford 1,2,3-selenadiazole in 60–70% yield: colorless crystals, mp. 71–72 °C, ^{1}H-NMR($CDCl_3$) δ 1·69(s,6H) 1·62(s,6H), ^{13}C-NMR($CDCl_3$) δ 171·6(s) 165·6(s) 81·2(s) 78·4 (s) 31·7(q) 29·9(q). E.A. Found C,41·62; H,5·24; N,12·07% (Calculated for $C_8H_{12}N_2OSe$ C,41·56; H,5·23; N,12·11%). UV(MeOH) 293 nm(ε = 1440), 218 nm(ε = 10000).

Photolysis of 5 with light of λ = 265 nm

The procedure with acrylonitrile is typical.

3-Cyano-6,6,8,8-tetramethyl-2-selena-7-oxabicyclo[3.3.0]oct-1(5)-ene ***(10a)*** The 1,2,3-selenadiazole (**5**, 231 mg, 1 mmol) dissolved in 3 ml of acrylonitrile was irradiated using a pyrex vessel by a medium pressure mercury lamp (Riken 400W) through a filter solution (phenanthrene/methanol, 5 g/1000 ml) at room temperature. The irradiation induced nitrogen evolution which 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 as colorless crystals in 94% yield. A sample further purified by recrystallization from hexane had mp 53·5–54·5 °C; ^{1}H-NMR($CDCl_3$) δ 4·71(dd,*J* = 7Hz, 8Hz, 1H) 2·87(d,*J* = 8Hz, 1 H) 2·84(d,*J* = 7Hz, 1H) 1·40(s,3H) 1·36(s,3H×2) 1·39(s,3H), ^{13}C-NMR($CDCl_3$) δ 141·8(s) 138·0(s) 120·3(s) 84·6(s) 84·2(s) 77·3(d) 35·2(t) 29·2(q×2) 28·4(q×2). IR(NaCl) 2240(C≡N) cm^{-1}. MS, *m/z* 257 [M^+]. HRMS, *m/z* Found 257·0303 (Calculated for $C_{11}H_{15}NOSe$ 257·0318).

The photolyses of **5** in the presence of other trapping reagents listed in Table 1 were carried out in a similar way. The spectral data of the products (**10b–10e**, and **11**) are as follows.

3-Methoxycarbonyl-6,6,8,8-tetramethyl-2-selena-7-oxabicyclo[3.3.0]oct-1(5)-ene ***(10b)*** Colorless crystals, mp 56–57 °C, ^{1}H-NMR($CDCl_3$) δ 5·03(dd, *J*=6Hz, 9Hz, 1H) 3·76(s,3H) 3·00(dd, *J*=6Hz, 16Hz, 1H) 2·72(dd, *J* = 9Hz, 16Hz, 1H) 1·36(s,3H×3) 1·33(s,3H), ^{13}C-NMR($CDCl_3$) δ 173·2(s) 143·3(s) 135·9(s) 84·7(s) 84·1(s) 52·6(q) 47·5(d) 31·7(t) 29·3(q) 29·1(q) 28·4(q) 28·3(q). IR(NaCl) 1725(C=O) cm^{-1}. E.A. Found C,49·69; H,6·32% (Calculated for $C_{12}H_{18}O_3Se$ C,49·83; H,6·27%). MS, *m/z* 290 [M^+]. HRMS, *m/z* Found 290·0406 (Calculated for $C_{12}H_{18}O_3Se$ 290·0419).

4,4,6,6-Tetramethyl-2-selena-5-oxatricyclo[6.3.0.0^{3,7}]undeca-3(7),10-diene ***(10c)*** Colorless oil, ^{1}H-NMR($CDCl_3$) δ 5·7–5·9(m,3H) 3·4–3·6(m,1H) 2·5–2·7(m,2H) 1·37(s,3H×2)) 1·35(s,3H×2), ^{13}C-NMR($CDCl_3$) δ 144·4(s) 137·4(s) 132·2(d) 130·9(d) 84·8(s) 83·6(s) 62·8(d) 46·8(d) 37·9(t) 29·5(q) 29·4(q) 29·2(q) 28·8 (q). MS, *m/z* 270 [M^+]. HRMS, *m/z* Found 270·0562 (Calculated for $C_{13}H_{18}OSe$ 270·0522).

5,5,7,7-Tetramethyl-3-selena-6-oxa-tetracyclo[8.2.1.0^{2,9}.0^{4,8}]tridec-4(8)-ene ***(10d)*** Colorless oil, ^{1}H-NMR($CDCl_3$) δ 4·45(dd, *J* = 8Hz,2Hz,1H) 2·79(dd, *J* = 8Hz,1Hz,1H) 2·3–2·4(m,2H) 1·9–2·1(m,1H) 1·1–1·8(m,5H) 1·36(s,3H×2) 1·33(s,3H) 1·31(s,3H), ^{13}C-NMR($CDCl_3$) δ 144·3(s) 140·3(s) 84·7(s) 83·2(s) 59·7(d) 54·2(d) 45·5(d) 41·5(d) 33·3(t×2) 30·0(q) 29·7(q) 29·6(q) 28·9(t) 28·6(q). HRMS, *m/z* Found 298·0823 (Calculated for $C_{15}H_{22}OSe$ 298·0833).

5,5,7,7-Tetramethyl-3-selena-6-oxatetracyclo[8.2.1.0^{2,9}.0^{4,8}]trideca-4(8),11-diene ***(10e)*** Colorless oil, ^{1}H-NMR($CDCl_3$) δ 6·0–6·2(m,2H) 4·40(dd, *J*=8Hz,2Hz,1H) 2·9–3·1(m,2H) 2·84(dd, *J*=8Hz,1Hz,1H) 2·0–2·2(m,1H) 1·6–1·8(m,1H) 1·40(s,3H) 1·36(s,3H×2) 1·34(s,3H), ^{13}C-NMR($CDCl_3$) δ 141·8(s) 141·2(s) 137·8(d) 136·3(d) 84·9(s) 83·2(s) 56·9(d) 50·5(d) 50·3(d) 43·1(t) 29·8(q) 29·1(q) 29·0(q) 28·4(q). HRMS, *m/z* Found 296·0704 (Calculated for $C_{15}H_{20}OSe$ 296·0679).

4,4,6,6,10,10,12,12- Octamethyl -5,11- dioxa -2,8 - diselenatricyclo[7.3.0.0^{3,7}]dodeca -1(9),3(7) - diene ***(11)*** Colorless crystals, mp 172–174 °C, ^{1}H-NMR($CDCl_3$) δ 1·37(s,24H), ^{13}C-NMR($CDCl_3$) δ 132·3(s) 88·3(s) 28·8(q). E.A. Found C,47·60; H,6·05% (Calculated for $C_{16}H_{24}O_2Se_2$ C,47·30; H,5·95%).

4,4,6,6-Tetramethyl-2-selena-5-oxa-11-thiatricyclo[6.2.1.0^{3,7}]undeca-3(7),9-diene ***(12a)*** The 1,2,3-selenadiazole (**5**, 231 mg, 1 mmol) dissolved in 3 ml of thiophene was irradiated by a medium pressure mercury lamp through a filter solution (phenanthrene/methanol, 5 g/1000 ml) at room temperature until the nitrogen gas finished evolving after about 5 hours. Then the mixture was evaporated and the residue was submitted to high pressure liquid chromatography to give three adducts (**12a**, 32 mg, 11%), (**12b**, 20 mg, 7%), and (**12c**, 6 mg, 2%) along with 1,4-diselenin (**11**, 65 mg, 39%). **12a**: pale yellow oil, ^{1}H-NMR($CDCl_3$) δ 6·60(d, *J*=6Hz,1H) 5·98(dd, *J*=6Hz, 3Hz, 1H) 4·52(dd, *J*=5Hz,3Hz,1H) 4·33(d, *J*=5Hz,1H) 1·51(s,3H) 1·46(s,3H) 1·41(s,3H) 1·31(s,3H), ^{13}C-NMR($CDCl_3$) δ 137·0(s) 133·0(s) 132·8(d) 122·5(d) 89·1(s) 88·2(s) 50·4(d) 49·2(d) 29·6(q) 29·3(q) 29·0(q) 28·8(q).

4,4,6,6-Tetramethyl-2-selena-5-oxa-9-thiatricyclo[6.3.0.0^{3,7}]undeca-3(7),10-diene ***(12b)*** Pale yellow oil, ^{1}H-NMR($CDCl_3$) δ 6·40(dd, *J*=6Hz,1Hz,1H) 6·22 (ddd, *J*=9Hz,3Hz,1Hz,1H) 5·70(dd, *J*=6Hz,3Hz,1H) 4·92(d, *J*=9Hz,1H) 1·41(s,3H) 1·39(s,3H) 1·36(s,3H×2), ^{13}C-NMR($CDCl_3$) δ 142·3(s) 141·7(s) 129·2(d) 121·8(d) 84·6(s) 84·5(s) 66·6(d) 57·2(d) 29·3(q) 29·0(q) 28·9(q) 28·5(q).

9,9,11,11-Tetramethyl-2-selena-4-thia-10-oxatricyclo[6.3.0.0^{3,7}]undeca-1(8),5-diene ***(12c)*** Pale yellow oil, ^{1}H-NMR($CDCl_3$) δ 6·53(d, *J*=8Hz,1H) 6·34(dd, *J*=6Hz,3Hz,1H) 5·62(dd, *J*=

6Hz,2Hz,1H) 4·13(ddd, J = 8Hz,3Hz,2Hz,1H) 1·38(s,3H×4), ^{13}C-NMR($CDCl_3$) δ 142·2(s) 139·7(s) 125·7(d) 121·0(d) 85·2(s) 85·1(s) 61·6(d) 29·4(q) 29·2(q) 28·9(q) 28·8(q). HRMS, *m/z* Found 288·0067 (Calculated for $C_{12}H_{16}OSSe$ 288·0085).

3-Formyl-7,7,9,9-tetramethyl-5-selena-8-oxabicyclo[4.3.0]nona-1(6),2-diene (13) This was obtained in 18% yield along with 40% yield of the 1,4-diselenin (**11**) according to the procedure for **12** using furan as a solvent. **13** Colorless oil, ^{1}H-NMR(C_6D_6) δ 9·00(d, J=2Hz,1H) 5·81(d, J=10Hz,1H) 4·97(dd, J=10Hz,7Hz,1H) 3·10(dd, J=7Hz,2Hz,1H) 1·32(s,3H) 1·26(s,3H) 1·25(s,3H) 1·22(s,3H), ^{13}C-NMR(C_6D_6) δ 186·9(d) 142·7(s) 137·1(s) 126·1(d) 114·2(d) 87·6(s) 89·6(s) 42·0(d) 30·7(q) 29·6(q) 28·5(q) 27·1(q). IR(CCl_4) 1715(C=O) cm^{-1}.

Photolysis of 1,2,3-Selenadiazole (5) with Light of λ = 254 nm with Furan

A furan solution (5 ml) of the 1,2,3-selenadiazole (**5**, 231 mg, 1 mmol) was irradiated in a quartz vessel by a low pressure mercury lamp (Ushio 120W) at room temperature. After 5 hours, the mixture was evaporated and the residual oil was submitted to high pressure liquid chromatography to afford the selenirane (**16**, 33 mg, 12%), disulfide (**17a**, 111 mg, 41%), and aldehyde (**13**, 30 mg, 11%).

1,6-Episeleno-2,5-epoxy-7,7,9,9-tetramethyl-8-oxabicyclo[4.3.0]non-3-ene (16) Colorless oil, ^{1}H-NMR($CDCl_3$) δ 6·22(m,2H) 5·13(m,2H) 1·70(s,6H) 1·48(s,6H), ^{13}C-NMR(C_6D_6) δ 135·9(d) 81·0(s) 80·3(d) 71·8(s) 31·5(q) 30·0(q). HRMS, *m/z* Found 272·0323 (Calculated for $C_{12}H_{16}O_2Se$ 272·03160).

3,3'-Bis(4,2''furyl-2,2,5,5-tetramethyl-3-oxolenyl)diselenide (17a) Yellow crystals, mp 87–89 °C. ^{1}H-NMR($CDCl_3$) δ 7·41(d, J=2Hz,2H) 7·05(d, J=3Hz,2H) 6·39(dd, J=3Hz,2Hz,2H) 1·50(s,12H) 1·40 (s,12H), ^{13}C-NMR($CDCl_3$) δ 148·1(s) 142·2(d) 141·8(s) 128·2(s) 112·7(d) 111·3(d) 89·9(s) 87·1(s) 29·6(q) 29·4(q). HRMS, *m/z* Found 542·0498 (Calculated for $C_{24}H_{30}O_4Se_2$ 542·0473).

5-Methylfurfuryl-2',2',5',5'-tetramethyl-3'-oxolenyl-3'-selenide (17b) This was obtained in 14% yield along with diselenide (**17c**, 20%) according to the procedure for **16** using 2,5-dimethylfuran as a solvent. **17b**: pale yellow oil, ^{1}H-NMR($CDCl_3$) δ 6·05(m,1H) 5·87(m,1H) 5·34(s,1H) 3·93(s,2H) 2·27(s,3H) 1·31(s,6H) 1·30(s,6H), ^{13}C-NMR($CDCl_3$) δ 151·9(s) 149·3(s) 134·9(d) 134·4(s) 108·8(d) 106·5(d) 89·7(s) 86·4(s) 29·7(q) 29·1(q) 22·4(t) 13·7(q). HRMS, *m/z* Found 300·0606 (Calculated for $C_{14}H_{20}O_2Se$ 300·0586).

3,3'-Bis(2,2,5,5-tetramethyl-3-oxolenyl)diselenide (17c) Colorless oil, ^{1}H-NMR($CDCl_3$) δ 5·90(s,2H) 1·41(s,12H) 1·34(s,12H), ^{13}C-NMR($CDCl_3$) δ 138·9(d) 133·4(s) 89·3(s) 85·7(s) 29·5(q) 29·4(q). HRMS, *m/z* Found 410·0284 (Calculated for $C_{16}H_{26}O_2Se_2$ 410·0263).

*2,5-Epoxy-7,7,9,9-tetramethyl-8-oxabicyclo[4.3.0]nona-1(6),3-diene (**18**)* To a chloroform solution (0·5 ml) of the selenirane (**16**, 27 mg, 0·1 mmol) was added an excess amount of tris(dimethylamino)phosphine at room temperature. After 5 minutes the mixture was submitted to high pressure liquid chromatography to afford the corresponding deselenated product quantitatively with tris(dimethylamino)phosphine selenide. Colorless oil, ^{1}H-NMR($CDCl_3$) δ 7·16(m,2H) 5·25(m,2H) 1·48(s,6H) 1·08(s,6H), ^{13}C-NMR($CDCl_3$) δ 163·9(s) 143·8(d) 83·2(s) 81·3(d) 29·4(q) 25·0(q). HRMS, *m/z* Found 192·1146 (Calculated for $C_{12}H_{16}O_2$ 192·1149).

*Photolysis of the 1,2,3-thiadiazole (**19**) with light of λ = 254 nm*

*1,6-Epithio-2,5-epoxy-7,7,9,9-tetramethyl-8-oxabicyclo[4.3.0]non-3-ene (**20a**)* This was obtained in the reaction of the 1,2,3-thiadiazole (**19**) with furan in 11% yield according to the procedure of **16** along with the thiol (**20c**, 30%). **20a**: colorless crystals, mp 104–105 °C, ^{1}H-NMR($CDCl_3$) δ 6·23(m,2H) 5·07(m,2H) 1·66(s,6H) 1·39(s,6H), ^{13}C-NMR($CDCl_3$) δ 135·0(d) 81·5(s) 81·2(s) 66·4(s) 30·3(q) 25·8(q). HRMS, *m/z* Found 224·0855 (Calculated for $C_{12}H_{16}O_2S$ 224·0870). E.A. Found C,64·00; H,7·16% (Calculated for $C_{12}H_{16}O_2S$ C,64·25; H,7·18%).

*4,2'-Furyl-2,2,5,5-tetramethyl-3-oxolene-3-thiol (**20c**)* Colorless oil, ^{1}H-NMR($CDCl_3$) δ 7·45(d, *J*=2Hz,1H) 6·54(d, *J*=3Hz,1H) 6·47(dd, *J*=3Hz,2Hz,1H) 3·21(s,1H) 1·53(s,6H) 1·44(s,6H), ^{13}C–NMR($CDCl_3$) δ 141·3(d) 129·0(s) 113·3(s) 111·1(d) 109·0(d) 96·1(s) 88·2(s) 87·4(s) 29·4(q) 28·5(q). HRMS, *m/z* Found 224·0888 (Calculated for $C_{12}H_{16}O_2S$ 224·0871).

*1,6-Epithio-2,5-epoxy-2,4,7,7,9,9-hexamethyl-8-oxabicyclo[4.3.0]non-3-ene (**20b**)* Colorless crystals, mp 88–90 °C ^{1}H-NMR($CDCl_3$) δ 6·54(s,2H) 1·52(s,6H) 1·47(s,6H) 1·38(s,6H), ^{13}C-NMR($CDCl_3$) δ 142·0(d) 87·4(s) 82·0(s) 80·4(s) 31·7(q) 27·2(q) 16·1(q). HRMS, *m/z* Found 252·1185 (Calculated for $C_{14}H_{20}O_2S$ 252·1184). E.A. Found C,66·40; H,8·07% (Calculated for $C_{14}H_{20}O_2S$ C,66·62; H,7·98%).

*1,1,3,3,6-Pentamethyl-4,2'-oxopropylthieno[2,3-c]dihydrofuran (**20d**)* Colorless oil, ^{1}H-NMR($CDCl_3$) δ 3·74(s,2H) 2·21(s,3H) 2·04(s,3H) 1·52(s,6H) 1·51(s,6H), ^{13}C-NMR($CDCl_3$) δ 204·5(s) 148·1(s) 143·3(s) 132·7(s) 127·2(s) 83·5(s) 82·8(s) 43·4(t) 31·2(q) 29·3(q) 29·1(q) 11·6(q). HRMS, *m/z* Found 252·1184 (Calculated for $C_{14}H_{20}O_2S$ 252·1184). IR(NaCl) 1715(C=O) cm^{-1}.

*Thermolysis of 1,2,3-selenadiazole (**5**)*

The procedure with thiobenzophenone is typical.

*6,6,8,8-Tetramethyl-3,3-diphenyl-2-thia-4-selena-7-oxabicyclo[3.3.0]oct-1(5)-ene (**10g**)* The mixture of the 1,2,3-selenadiazole (**5**, 231 mg, 1 mmol) and thiobenzophenone (400 mg, 2 mmol) was heated at 80 °C for 24 hours. Then the mixture was submitted to column

chromatography (silica gel/benzene) to afford 1,3-dithiole (**10g**, 150 mg, 75%). Yellow oil, ^{1}H-NMR($CDCl_3$) δ 7·1–7·7(m,5H) 1·39(s,6H) 1·37(s,6H), ^{13}C-NMR($CDCl_3$) δ 144·4(s) 138·2(s) 134·1(s) 128·0(d×2) 127·7(d) 86·1(s) 85·7(s) 85·2(s) 29·4(q) 29·1(q). HRMS, *m/z* Found 402·0531 (Calculated for $C_{21}H_{22}OSSe$ 402·0556).

*6,6,8,8-Tetramethyl-N-phenyl-2-thia-4-selena-7-oxabicyclo[3.3.0]oct-1(5)-ene-3-imine (**10i**)* Pale yellow crystals, mp 122–123 °C, ^{1}H-NMR($CDCl_3$) δ 6·9–7·5(m,5H) 1·50(s,6H) 1·45(s,6H), ^{13}C-NMR($CDCl_3$) δ 168·8(s) 152·3(s) 146·7(s) 132·1(s) 129·8(d) 125·4(d) 119·1(d) 87·7(s) 87·1(s) 29·9(q) 29·6(q). IR(KBr) 1565(C=N) cm^{-1}. MS, *m/z* 339 [M^+]. E.A. Found C,53·20; H,5·02; N,4·17% (Calculated for $C_{15}H_{17}ONSSe$ C,53·25; H,5·06; N,4·14%).

*3-Isopropylidene-4,4,7,7,9,9-hexamethyl-2-thia-5-selena-8-oxabicyclo[4.3.0]non-1(6)-ene (**10j**)* Colorless oil, ^{1}H-NMR($CDCl_3$) δ 2·05(s,3H) 2·00(s,3H) 1·88(s,6H) 1·41(s,6H) 1·34(s,6H), ^{13}C-NMR($CDCl_3$) δ 130·0(s) 127·7(s) 127·5(s) 123·2(s) 88·8(s) 88·7(s) 43·5(s) 31·5(q) 29·4(q) 29·2(q) 27·5(q) 23·7(q). HRMS, *m/z* 332·0734 (Calculated for $C_{15}H_{24}OSSe$ 332·0679).

*3,4-Diisopropylidene-7,7,9,9,-tetramethyl-2-thia-5-selena-8-oxabicyclo[4.3.0]non-1(6)-ene (**10k**)* Colorless crystals, mp 140–141 °C, ^{1}H-NMR($CDCl_3$) δ 2·01(s,3H) 1·98(s,3H) 1·73(s,3H×2) 1·40(s,3H) 1·39(s,3H) 1·32(s,3H×2), ^{13}C-NMR($CDCl_3$) δ 136·6(s) 135·7(s) 129·1(s) 122·3(s) 118·7(s) 115·4(s) 88·5(s) 88·4(s) 29·9(q) 29·3(q) 28·9(q) 28·5(q) 24·0(q) 22·1(q) 21·7(q) 21·5(q). MS, *m/z* 344 [M^+]. E.A. Found C,55·99; H,7·03% (Calculated for $C_{16}H_{24}OSSe$ C,55·96; H,7·04%).

*6,6,8,8-Tetramethyl-2-thia-4-selena-7-oxabicyclo[3.3.0]oct-1(5)-ene-3-thione (**10h**)* The 1,2,3-selenadiazole (**5**, 115 mg, 0·5 mmol) dissolved in 2 ml of carbon disulfide was heated at 90 °C in a sealed pyrex tube for 24 hours. The mixture was then evaporated and the residue was submitted to column chromatography (silica gel/benzene) to afford 75% of yellow–orange crystalline 1,3-thiaselenole-2-thione (**10h**) having mp 121–122 °C, ^{1}H-NMR($CDCl_3$) δ 1·54(s,6H) 1·52(s,6H), ^{13}C-NMR($CDCl_3$) δ 219·3(s) 146·5(s) 144·7(s) 87·5(s) 86·6(s) 30·5(q) 30·2(q). Mass, *m/z* 280 [M^+]. E.A. Found C, 38·56; H,4·30% (Calculated for $C_8H_{12}OS_2Se$ C,38·70; H,4·33%).

*Dibenzo[i,l]-4,4,6,6-tetramethyl-2-selena-5-oxatricyclo[6.2.2.0^{3,7}]dec-3(7)-ene (**10f**)* To 3·56 g (20 mmol) of anthracene was added 1,2,3-selenadiazole(**5**, 462 mg, 2 mmol) in portions at 220 °C and stirred, the vigorous nitrogen gas evolution ceased within 5 minutes. The reaction mixture was poured into 20 ml of ethanol and filtered to remove the excess of anthracene. Then the solution was evaporated and the residue was submitted to column chromatography (silica gel/dichloromethane) to give 26% yield of pale yellow crystalline [3+4] adduct (**10f**) along with 30% of 1,4-diselenin (**11**). A sample further purified by recrystallization from hexane had mp, 148–150 °C. ^{1}H-NMR($CDCl_3$) δ 7·1–7·5(m,8H) 5·00(s,1H) 4·24(s,1H) 1·44(s,6H) 1·07(s,6H), ^{13}C-NMR($CDCl_3$) δ 140·1(s) 137·6(s) 129·2(s) 126·9(d) 126·7(d) 126·0(s) 125·0(d) 124·9(d) 90·1(s) 87·7(s) 43·1(d) 39·6(d) 29·7(q) 28·3(q). MS, *m/z* 382 [M^+]. E.A. Found C,69·27; H,5·90% (Calculated for $C_{22}H_{22}OSe$ C,69·28; H,5·81%).

Thermolysis of 1,2,3-selenadiazole (5) in the presence of diphenyldiazomethane

A mixture of 1,2,3-selenadiazole (**5**, 231 g, 1 mmol) and diphenyldiazomethane (970 mg, 5 mmol) dissolved in 10 ml of benzene was refluxed for 12 hours. Then the mixture was evaporated and chromatographed (silica gel/dichloromethane) to remove tetraphenylazine and tetraphenylethylene. The residue was submitted to high pressure liquid chromatography to afford diselenole (**21**, 134 mg, 30%), dihydropyridazine (**22**, 82 mg, 17%), azine (**23**, 44 mg, 9%), and diselenin (**11**, 51 mg, 25%).

6,6,8,8-Tetramethyl-3,3-diphenyl-2,4-diselena-7-oxabicyclo[3.3.0]oct-1(5)-ene (21) Yellow crystals, mp 95–96 °C, ^{1}H-NMR($CDCl_3$) δ 7·2–7·7(m,10H) 1·36(s,12H), ^{13}C-NMR($CDCl_3$) δ 145·3(s) 138·0(s) 128·2(d) 128·1(d) 127·6(d) 87·3(s) 29·5(q). E.A. Found C,56·28; H,5·00% (Calculated for $C_{21}H_{22}OSe_2$ C,56·26; H,4·95%).

7,7,9,9-Tetramethyl-2,2,5,5-tetraphenyl-3,4-diaza-8-oxabicyclo[4.3.0]nona-1(6),3-diene (22) Yellow crystals, mp 185–186 °C, ^{1}H-NMR($CDCl_3$) δ 7·2–7·4(m,20H) 1·27(s,12H), ^{13}C-NMR($CDCl_3$) δ 166·2(s) 136·8(s) 128·6(d) 128·3(d) 127·6(d) 85·6(s) 81·1(s) 28·9(q). Mass, *m/z* 484 [M^+]. E.A. Found C,84·14; H,6·65; N,5·78% (Calculated for $C_{34}H_{32}N_2O$ C,84·26; H,6·65; N,5·78%).

2,2,5,5-Tetramethyl-2-diphenylmethylene-4-diphenylmethylenehydrazonooxolane (23) Yellow–orange crystals, mp 143–144 °C. Mass, *m/z* 484 [M^+]. E.A. Found C,84·29; H,6·78; N,5·74% (Calculated for $C_{34}H_{32}N_2O$ C,84·14; H,6·65; N,5·78%).

In NMR spectra the tautomers, s-*trans* and s-*cis* were observed in the ratio of 1:2. Although only the former was observed just after dissolving the crystals of **23**, the equilibrium was established in about 10 minutes at 35 °C. s-*trans*: ^{1}H-NMR($CDCl_3$) δ 6·7–7·5(m,20) 1·64(s,6H) 1·16(s,6H), ^{13}C-NMR($CDCl_3$) δ 169·6(s) 160·0(s) 143·4(s) 142·4(s) 139·8(s) 138·6(s) 135·1(s) 132·3(s) 127–130(d×12) 81·3(s) 78·8(s) 30·3(q) 27·3(q). s-*cis* ^{1}H-NMR($CDCl_3$) δ 6·7–7·5(m,20H) 1·43(s,6H) 1·07(s,6H), ^{13}C-NMR($CDCl_3$) δ 165·7(s) 156·6(s) 146·7(s) 143·8(s) 142·2(s) 137·5(s) 133·3(s) 127–130(d×12) 128·2(s) 81·0(s) 77·9(s) 29·9(q) 28·5(q).

Reaction of 1,2,3-selenadiazole (2) with nucleophiles

The procedure with trimethylphosphite is typical.

2,2,4,5,5-Pentamethyl-3-dimethylphosphonoseleno-3-oxolene (27b) The mixture of **5** (116-mg, 0·5 mmol) and trimethylphosphite (500 mg, 4 mmol) was heated at 50 °C for 24 hours. During this time nitrogen gas evolution was observed. Then the mixture was submitted to high pressure liquid chromatography to give 89% yield of colorless oily vinylselenide (**27b**, 125 mg). ^{1}H-NMR($CDCl_3$) δ 3·78(J_{CP}=11Hz,s,6H) 2·32(s,3H) 1·46(s,6H) 1·43(s,6H), ^{13}C-NMR($CDCl_3$) δ 152·0(J_{CP}=10Hz,s) 138·5(J_{CP}=30Hz,s) 91·1(J_{CP}=19Hz,s) 89·3(J_{CP}=21Hz,s) 52·3(J_{CP}=6Hz,q) 29·6(q) 29·2(q) 8·45(q). HRMS, *m/z* Found 328·0333 (Calculated for $C_{11}H_{21}O_4Se$ 328·0340).

3-Ethyl-2,2,5,5-tetramethyl-4-diethylphosphonoseleno-3-oxolene (27c) Colorless oil, ^{1}H-NMR($CDCl_3$) δ 4·16(J_{CP}=7Hz, q, J=7Hz, 4H) 3·05(q, J=7Hz,2H) 1·48(s,6H) 1·41(t, J=7Hz,3H) 1·41(s,6H) 1·37(t, J=7Hz,6H), ^{13}C-NMR($CDCl_3$) δ 150·4(J_{CP}=10Hz,s) 132·2(J_{CP} = 27Hz,s) 90·6(J_{CP} = 20Hz,s) 89·5(J_{CP} = 21Hz,s) 61·8(J_{CP} = 6Hz,t) 29·7(q) 29·1(q) 22·5(t) 16·3(J_{CP} = 6Hz,q) 15·2(q). HRMS, *m/z* Found 370·0848 (Calculated for $C_{14}H_{27}O_4PSe$ 370·0812).

2,2,5,5-Tetrametyl-3-phenylthioseleno-3-oxolene (27d) Colorless oil, ^{1}H-NMR($CDCl_3$) δ 7·1–7·6(m,5H) 5·78(s,1H) 1·36(s,6H) 1·27(s,6H), ^{13}C-NMR($CDCl_3$) δ 137·7(s) 135·5(s) 130·6(d) 129·0(d) 128·9(d) 127·7(d) 89·3(s) 85·9(s) 29·5(q) 29·4(q). MS, *m/z* 314 [M^+].

2,2,5,5-Tetramethyl-3-phenylthio-4-phenylthioseleno-3-oxolene (27e) Pale yellow oil, ^{1}H-NMR($CDCl_3$) δ 7·1–7·6(m,10H) 1·44(s,6H) 1·23(s,6H), ^{13}C-NMR($CDCl_3$) δ 142·6(s) 139·1(s) 137·8(s) 135·2(s) 130·4(d) 129·9(d) 129·0(d) 128·9(d) 127·5(d) 127·0(d) 96·2(s) 89·0(s) 29·6(q) 29·2(q). Mass *m/z* 422 [M^+].

2,2,5,5-Tetramethyl-3-methylthio-4-methylthioseleno-3-oxolene (27f) Colorless oil, ^{1}H-NMR($CDCl_3$) δ 2·69(s,3H) 2·40(s,3H) 1·46(s,6H) 1·40(s,6H), ^{13}C-NMR($CDCl_3$) δ 145·3(s) 138·1(s) 88·8(s) 88·2(s) 29·4(q) 29·1(q) 23·0(q) 18·0(q). Mass, *m/z* 298 [M^+].

3,3'-Bis(2,2,5,5-tetramethyl-4-methylthio-3-oxolene)diselenide (27g) Colorless oil, ^{1}H-NMR($CDCl_3$) δ 2·44(s,6H) 1·42(s,12H) 1·40(s,12H), ^{13}C-NMR($CDCl_3$) δ 149·6(s) 133·2(s) 89·3(s) 88·3(s) 29·4(q) 29·2(q) 17·5(q). Mass, *m/z* 502 [M^+]. HMRS, *m/z* Found 502·0080 (Calculated for $C_{18}H_{30}O_2S_2Se_2$ 502·0017).

3-Butylseleno-2,2,5,5-tetramethyl-3-oxolene (27a) To a 5 ml of tetrahydrofuran solution of **5** (231 mg, 1 mmol) was added butyllithium (1 mmol, hexane solution) in portions by means of a syringe at −70 °C and stirred for 30 minutes at this temperature. After quenching with 5 ml of water the mixture was extracted with dichloromethane (10 ml × 3), the organic layer was evaporated and the residue was submitted to high pressure liquid chromatography to give colorless oily butyl selenide in 53% yield. ^{1}H-NMR($CDCl_3$) δ 5·42(s,1H) 2·79(t,2H) 1·0–1·9(m,4H) 1·36(s,6H) 1·32(s,6H) 0·94(t,3H), ^{13}C-NMR($CDCl_3$) δ 135·8(s) 130·5(s) 89·4(s) 86·6(s) 31·6(t) 29·8(q) 29·4(q) 26·5(t) 23·0(t) 13·6(q). MS *m/z* 262 [M^+]. HRMS, *m/z* Found 260·0636 (Calculated for $C_{12}H_{26}OSe$ 260·0677).

Spiro[8,8,10,10-tetramethyl-2-selena-3-thia-5,6-diaza-9-oxabicyclo[5.3.0]deca-1(7),5-diene-4,3'-1',2'-diphenylcyclopropene] (30) A mixture of the selenadiazole (**5**, 231 mg, 1 mmol) and diphenylcyclopropenethione (222 mg, 1 mmol) dissolved in 1 ml of benzene was heated at 70 °C for 12 hours. The solvent was then removed under reduced pressure and the residue was submitted to column chromatography (silica gel/dichloromethane) to give an orange crystalline nitrogen containing adduct (**30**) in 90% yield (408 mg). A sample further purified by recrystallization from ethanol had mp 162–164 °C, ^{1}H-NMR($CDCl_3$) δ 7·2–7·5(m,10H)

1·74(s,6H) 1·52(s,6H), ^{13}C-NMR($CDCl_3$) δ 150·5(s) 141·6(s) 132·1(s) 131·5(s) 130·2(d) 128·2(d) 128·1(d) 111·7(s) 86·9(s) 86·1(s) 29·3(q) 29·1(q). MS, *m/z* 454 [M^+]. E.A. Found C,61·01; H,4·92; N,6·24% (Calculated for $C_{23}H_{22}N_2OSSe$ C,60·91; H,4·89; N,6·17%).

REFERENCES

1. (a) I. Lalezari, A. Shafiee and M. Yalpani, *Angew. Chem., Int. Ed. Engl.*, **9**, 464 (1970). (b) H. Meier and I. Menzel *J. Chem. Soc., Chem. Commun.*, 1509 (1971). (c) H. Meier, *Synthesis*, 235 (1972). (d) I. Lalezari, A. Shafiee and H. Golgolab, *J. Heterocyclic Chem.*, 655 (1973). (e) H. Golgolab and I. Lalezari, *J. Heterocyclic Chem.*, 801 (1975). (f) H. Meier and H. Gugel, *Synthesis* 338 (1976). (g) H. Meier, M. Layer, W. Combrink and S. Schniepp, *Chem. Ber.*, **109**, 1650 (1976). (h) H. Meier, T. Echter and H. Petersen, *Angew. Chem., Int. Ed. Engl.*, **17**, 942 (1978). (i) H. Meier, N. Hanold and H. Kolshorn, *Angew. Chem., Int. Ed. Engl.*, **21**, 66 (1982).
2. (a) I. Lalezari, A. Shafiee, F. Rabet and M. Yalpani, *J. Heterocyclic Chem.*, 953 (1973). (b) B. Bak, O. J. Nielsen and H. Svanholt, *Chem. Phys. Lett.*, **53**, 374 (1978). (c) R. Schulz and A. Schweig, *Angew. Chem., Int. Ed. Engl.*, **17**, 942 (1978). (d) A. Holm, *et al.*, *J. Chem. Soc., Chem. Commun.*, 99 (1979). (e) H. Bock, S. Aygen, P. Rosmus and B. Solouki, *Chem. Ber.*, **113**, 3187 (1980). (f) B. Bak, *et al.*, *Chem. Phys. Lett.*, **78**, 301 (1981). (g) W. W. Sander and O. L. Chapman, *J. Org. Chem.*, **50**, 543 (1985).
3. (a) J. Laureni, A. Krantz and R. A. Hajdu, *J. Am. Chem. Soc.*, **98**, 7872 (1976). (b) A. Krantz and J. Laureni, *J. Am. Chem. Soc.* **99**, 4842 (1977). (c) N. Harrit, S. Rosenkilde, B. D. Larsen and A. Holm, *J. Chem. Soc., Perkin Trans. 1*, 907 (1985).
4. I. Johannsen, K. Bechgaard, K. Mortensen and C. Jacobsen, *J. Chem. Soc., Chem. Commun.*, 295 (1983).
5. (a) I. Lalezari, A. Shafiee and M. Yalpani, *J. Heterocyclic Chem.*, 1411 (1972). (b) I. Lalezari and S. Sadeghi-Milani, *J. Heterocyclic Chem.* 501 (1978).
6. (a) R. B. Boar, *et al.*, *J. Chem. Soc., Chem. Commun.*, 756 (1975). (b) R. West, M. J. Fink and J. Michl, *Science*, **214**, 1343 (1981). (c) M. Yoshifuji, *et al.*, *J. Am. Chem. Soc.*, **103**, 4587 (1981). (d) A. Krebs and J. Berndt, *Tetrahedron Lett.*, **24**, 4083 (1983). (e) W. Ando, Y. Hanyu and T. Takata, *J. Am. Chem. Soc.*, **106**, 2216 (1984).
7. W. Ando, Y. Kumamoto and N. Tokitoh, *Tetrahedron Lett.*, **27**, 6107 (1986); W. Ando, Y. Kumamoto and N. Tokitoh, *Tetrahedron Lett.*, **28**, 2867 (1987).
8. W. Ando, Y. Kumamoto, H. Ishizuka and N. Tokitoh, *Tetrahedron Lett.*, **28**, 4707 (1987).
9. (a) H. Meier, T. Molts, U. Merkle and M. Lorch, *Liebigs Ann. Chem.*, 914 (1982). (b) H. Meier and I. Menzel, *Tetrahedron Lett.*, 445 (1972). (c) H. Meier and E. Voight, *Tetrahedron*, **28**, 187 (1972).
10. (a) O. P. Strausz, *et al.*, *J. Am. Chem. Soc.*, **89**, 4805 (1967). (b) D. E. Thornton, R. K. Gosavi and O. P. Strausz, *J. Am. Chem. Soc.*, **92**, 1768 (1970). (c) I. G. Csizmadia, J. Font and O. P. Strausz, *J. Am. Chem. Soc.*, **90**, 7360 (1968). (d) J. Fenwick, G. Frater, K. Ogi and O. P. Strausz, *J. Am. Chem. Soc.*, **95**, 124 (1973). (e) T. L. Gilchrist, G. E. Gymer and C. W. Rees, *J. Chem. Soc., Chem. Commun.*, 1519 (1971). (f) S. Mente and C. W. Rees, *J. Chem. Soc., Chem. Commun.*, 418 (1972). (g) S. A. Matlin and P. S. Sammes, *J. Chem. Soc., Chem. Commun.*, 11 (1972). (h) M. Torres, E. M. Lown, H. E. Gunning and O. P. Strausz, *Pure & Appl. Chem.*, **52**, 1623 (1980). (i) M. L. McKee, *J. Am. Chem. Soc.*, **108**, 5059 (1986).
11. W. Ando, Y. Kumamoto and N. Tokitoh, *Tetrahedron Lett.*, **28**, 2867 (1987).
12. (a) H. Petersen, H. Kolshorn and H. Meier, *Angew. Chem., Int. Ed. Engl.*, **17**, 461 (1976). (b) M. Lorch and H. Meier, *Chem. Ber.*, **114**, 2382 (1981).