Light-induced reactions of 2,2-bis(2,2-dimethylethyl)-6*H*-1,3-oxaselenin-6-one in methanol

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**Dedicated to Professor Waldemar Adam on the occasion of his 70th birthday**

Abstract

On irradiation (λ = 300 nm) in methanol the title compound **1** undergoes both solvent addition to α-methoxylactone **3** and cycloreversion to a mixture of the diastereomeric *Z,Z- E,Z-* and *E,E-*dimethyl 3,3'-diselenodipropenoates **4-6** and to 2,2,4,4-tetramethylpentan-2-one (**7**), whereas on solid state irradiation only ketone **7** and polymeric material are detected.

Keywords: Organoselenium compounds, photoaddition, selenoformylketene

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Introduction

Whereas the outcome of detailed investigations on the photochemical behaviour of (S-hetero)cyclic unsaturated carbonyl compounds has been subject of a review,[1] only very few results on light-induced reactions of the corresponding selenium compounds have been published.[2] One such comparative study deals with the behaviour of 2-acetylthiophene and of 2-acetylselenophene in the presence of 2,3-dimethylbut-2-ene. Interestingly, the major photoproduct from the S-heterocycle is a [4+2]-cycloadduct, while the selenium derivative affords a mixture of a cyclobutane and an oxetane, i.e. [2+2]-cycloadducts exclusively.[3,4] In the last few years, one of us has developed an easy synthetic approach to 1,3-oxathiin-6-ones and 1,3-oxaselenin-6-ones by heating propiolic acid with an appropriate thione or selenone, respectively.[5,6] Here we report results on the photochemical behaviour of the title compound **1** and compare them (Figure 1) to those recently published for spiro[6H-[1,3]oxathiin-2,2'-tricyclo[3.3.1.1^{3,7}]decan]-6-one (**2**). [7]

1   **2**
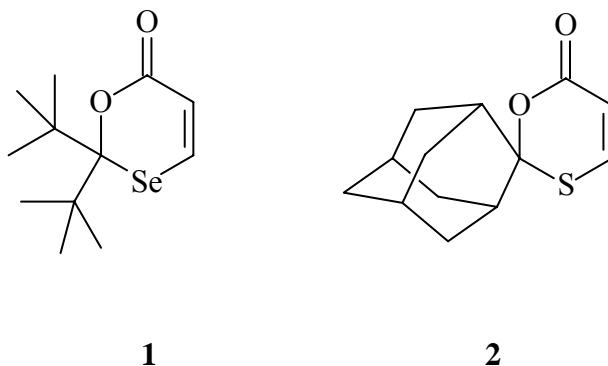
Figure 1

Results and Discussion

Irradiation of **1** (0.5M) in methanol and subsequent evaporation of the solvent affords a 1:1 mixture of   the (formal) methanol adduct **3** and a mixture of all three diastereomeric dimethyl 3,3'-diselenodipropenoates **4-6**. Monitoring the reaction by GC/MS indicates the additional formation of 2,2,4,4-tetramethylpentan-3-one (**7**). Monitoring the reaction by ^{1}H-NMR in CD$_3$OD confirms the formation of (tetradeutero)-**3** and **7** in about equal amounts and shows in addition that on continuing irradiation the primarily formed *Z,Z*-diastereomer **4** is converted into the *E,Z*-diastereomer **5**, and that on prolonged irradiation the *E,E*-diastereomer **6** becomes the predominant stereoisomer. The 5-methoxy-1,3-oxaselenanone **3** can be purified by column chromatography and is isolated in 25% yield. When the irradiation of **1** is performed without solvent the ^{1}H-NMR of the photolysate shows signals due to ketone **7** and to (unreacted) **1** only, no traces of the second cycloreversion product, i.e. selenoformylketene (**8**) nor of any dimer of **8** being detectable (Scheme 1). The structure of the methanol adduct **3** is straightforward from both its mass spectral data (308, M$^+$, ^{80}Se) and its NMR spectral data (δ CH$_2$ = 75 ppm, $^2J_{H,H}$ = 9.4 Hz), which establishes the methylene group as being adjacent to the selenium atom. The MS- and NMR-data of diselenide **4** match those reported in the literature,[8] while those for **5** and **6** exhibit the expected changes in both vicinal coupling constants of the olefinic H- and chemical shifts of the olefinic C-atoms. Finally, MS- and NMR-data of **7** are again identical with those reported in the literature.[9]

   In an additional experiment, spiro[2,3-dihydrothiin-2,2'-tricyclo[3.3.1.1^{3,7}]decan]-4-one (**9**) was irradiated in methanol to afford quantitatively a 4:1 mixture of methanol adducts **10** and **11**, respectively (Scheme 2). Differentiation between **10** and **11** as well as their structural assignment is straightforward by ^{1}H-NMR. Whereas the thiacyclohexanone ring in the minor adduct **11** exists in a chair conformation as reflected by the geminal coupling constants of the methylene H-atoms adjacent to the carbonyl group, ^2J = -12.3 Hz and -13.7 Hz, respectively, the same ring in the major adduct **10** adopts a twist boat conformation (^2J = 17.2 Hz).[10] Moreover,

the methoxy group in **11** is in equatorial position as shown by the vicinal coupling constants of the methine H-atom $(\Sigma\,^3J = 16.0\ \text{Hz})$ whereas in **10** it is axial $(\Sigma\,^3J = 10.6\ \text{Hz})$.[11]

Scheme 1

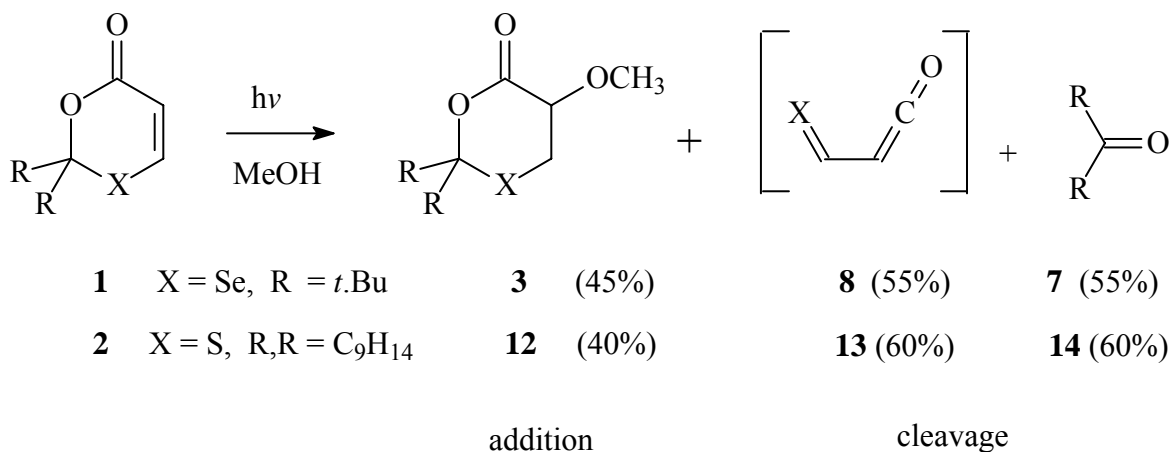**9**   **10** (80 %)   **11** (20 %)
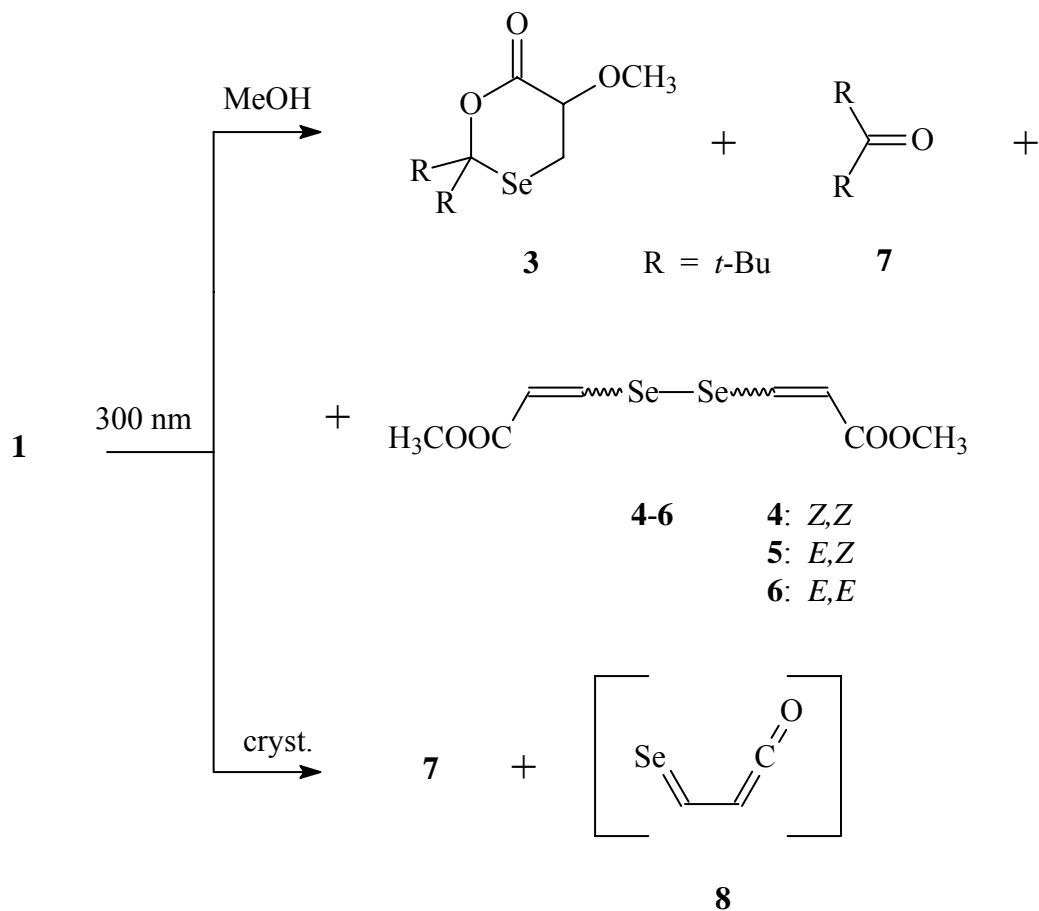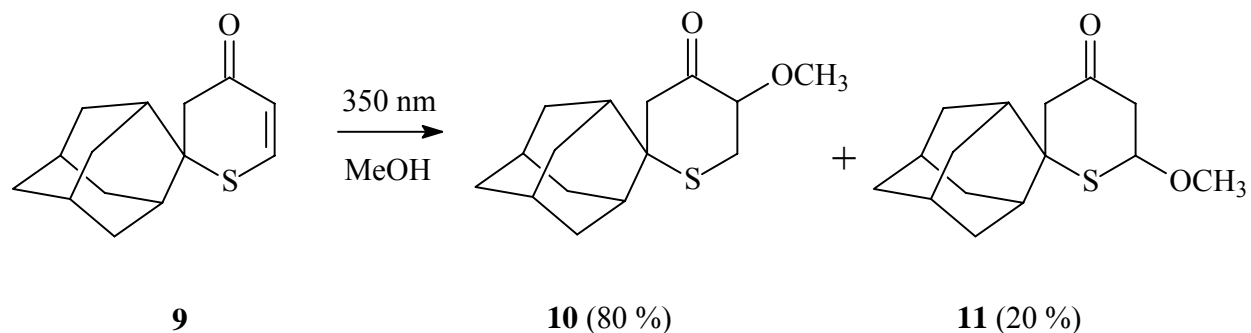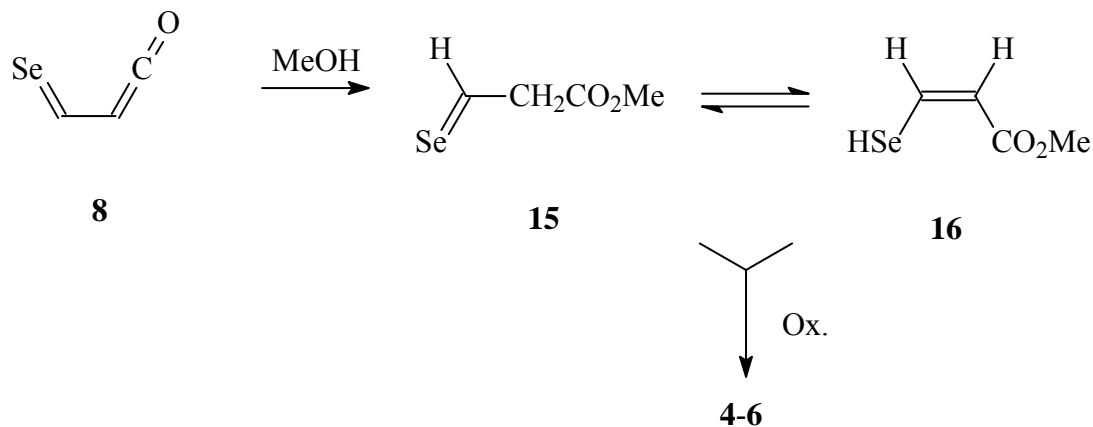
Scheme 2

On comparing the photochemical behaviour of **1**, **2** and **9** in methanol it becomes apparent (Scheme 3) that both lactones **1** and **2** afford very similar (1:1) solvent addition (**3** and **12**)   *vs*

cleavage (**8** + **7** and **13** +**14**) product ratios, independent of the chalcogen atom, whereas ketone **9** undergoes methanol addition exclusively. These results support a synchronous cycloreversion mechanism, wherein ketone extrusion represents the overall driving force. A stepwise mechanism with cleavage of the (weakest) chalcogen – C(2) bond as rate determining step becomes highly improbable, as the dissociation energies for C-Se bonds are generally 10 kcal/mol lower than for the corresponding C-S bonds, and therefore much more cycloreversion should be observed from excited **1** than from **2**.

1	X = Se, R = *t*.Bu	**3**	(45%)	**8** (55%)	**7** (55%)
2	X = S, R,R = C$_9$H$_{14}$	**12**	(40%)	**13** (60%)	**14** (60%)

addition   cleavage

Scheme 3

While nothing is known about selenoformylketene (**8**), its sulfur analogue, i.e. thioformylketene (**13**), has been predicted to undergo [4+4]-cyclodimerization to a 1,5-dithiocin-2,6-dione.[12] No traces of **8** or any possible dimer were observed during solid state irradiation of **1**, whereas in methanol this intermediate might be trapped to afford the – unstable – selenoaldehyde **15**.[13] This intermediate, in equilibrium with the tautomeric 3-selenanylacrylate **16**, then undergoes quantitative dehydrodimerization to **4-6** (Scheme 4), which is not surprising since selenols are generally more sensitive to air than thiols. On the other hand, the fact that on irradiation in CD$_3$OD only hexadeuterated **4-6** are formed suggests, that the solvent does undergo 1,4-addition to **8** to afford (tetradeuterated) **16** directly, which is then oxidized to the hexadeuterated diselenides.

Scheme 4

Due to the strong preference of the C-O-C(O)-C unit in lactones in general and in valerolactones in particular to be close to planar and thus preserve the resonance energy of the ester group, there are conformational restrictions for δ-lactones as compared to cyclohexanones, as chair forms are not compatible with this planarity.[14] Interestingly, the ^{1}H-NMR data of methoxylactones **3** and **12**, specifically the vicinal coupling constants of the methine H-atom, indicate that these two compounds exist in distinctly different conformations. Whereas the values found for this H-atom in **12**, i.e. ^3J = 3.5 Hz and 7.0 Hz, are very similar to those observed for ketone **10**, the corresponding values in **3** are substantially larger, i.e. 4.1 and 9.4 Hz, respectively. This would then imply that both saturated S-heterocycles **10** and **12** adopt the same twist boat conformation with an axial MeO-group, whereas the saturated Se-heterocyclic lactone **3** exists in a half-chair conformation with a – now – planar lactone moiety, wherein the methoxy group is (pseudo)equatorial. A plausible explanation for this conformational difference is the increased Se-C *vs* S-C (1.95 Å *vs* 1.80 Å) bond length, which favours such a strainless half-chair conformation. It is noteworthy that all these described coupling constants for **3**, **10**, **11** and **12**, respectively, are identical in both CDCl₃ and CD₃OD. This is good evidence that all these compounds adopt one preferred conformation and that these values do not correspond to mean values reflecting equilibria between two, or possibly even more, conformations.[15] Finally, it is interesting to note, that the (formal) OCH₃-addition to lactones **1** and **2** occurs regiospecifically at C(5) whereas for ketone **9** 20% of the O,S-acetal **11** is also formed. A possible reason for this could be a different degree of twisting around the C-C double bond in the excited unsaturated molecules, the bulky substituents on C(2) totally hindering the approach of methanol to C(6) in the unsaturated lactones, but only partially in the unsaturated ketone, respectively.

Experimental Section

General Procedures. 1H-NMR spectra (500 MHz) and 13C-NMR spectra (125 MHz) were recorded on a Bruker DRX 500 spectrometer. Chemical shifts (δ) are given in ppm rel. to TMS (0 ppm) as internal standard. Mass spectra were measured on a Varian MAT 311 A instrument at 70 eV. Photolyses were run in a Rayonet RPR-100 photochemical reactor equipped with either 300 nm or 350 nm lamps.

Starting materials. Oxaseleninone **1** was synthesized according to the literature.[6] UV (MeCN): λ_{max} = 316 nm, log ε = 4.075. Thiinone **9** was synthesized according to the literature.[16] Methanol (as solvent in photolyses) was of spectroscopic grade.

Irradiation of 1 in MeOH. An Ar-degassed soln. of 138 mg (0.5 mmol) of **1** in 5 ml of MeOH was irradiated (300 nm) for 6 h. ^{1}H-NMR Analysis of the crude photolysate after being aerated indicated the presence of a mixture of esters **4-6** (55%) and **3** (45%). Preparative thin layer chromatography (SiO$_2$; pentane/ether 5:2) afforded first 39 mg (25%) of pure *5-methoxy-2,2-bis(dimethylethyl)-1,3-oxaseleninan-6-one* (**3**, R$_f$ = 0.45), m.p. 35-37 °C. ^{1}H-NMR (CDCl$_3$) δ 1.24 (9H, s), 1.26 (9H, s), 3.40 (3H, s), 3.71 (1H, t, *J* = 9.4 Hz), 4.12 (1H, dd, *J* = 4.1, 9.4 Hz), 4.35 (1H, dd, *J* = 4.1, 9.4 Hz; ^{13}C-NMR (CDCl$_3$) δ 30.1 (q), 45.1 (d), 46.4 (s), 60.2 (q), 75.1 (t), 107.4 (s), 175.3 (s); MS *m/z*: 308 (M$^+$, [80]Se, 0.4%), 57 (100%). The second fraction (16 mg, 18 %) consisted of a mixture of dimethyl 3,3'-diselenodipropenoates **4-6**. R$_f$ = 0.35. The following NMR-spectral data are taken from this diastereomeric mixture. *Z,Z*-Diastereomer **4**: ^{1}H-NMR (CDCl$_3$) δ 3.79 (6H, s), 6.27 (2H, d, *J* = 9.3 Hz), 8.05 (2H, d, *J* = 9.3 Hz); ^{13}C-NMR (CDCl$_3$) δ 53.2 (q), 119.2 (d), 154.1 (d), 169.2 (s); *Z,E*-diastereomer **5**: ^{1}H-NMR (CDCl$_3$) δ 3.74 (3H, s), 3.82 (3H, s), 6.26 (1H, d, *J* = 15.1 Hz), 6.35 (1H, d, *J* = 9.2 Hz), 7.90 (1H, d, *J* = 9.2 Hz), 8.09 (1H, d, *J* = 15.1 Hz); ^{13}C-NMR (CDCl$_3$) δ 53.2 (q), 119.2 (d), 124.1 (d), 141.2 (d), 154.1 (d), 169.2 (s); *E,E*-diastereomer **6**: ^{1}H-NMR (CDCl$_3$) δ 3.75 (6H, s), 6.11 (2H, d, *J* = 15.2 Hz), 8.04 (2H, d, *J* = 15.2 Hz); ^{13}C-NMR (CDCl$_3$) δ 53.2 (q), 124.2 (d), 141.1 (d), 169.2 (s). MS *m/z* of **4-6**: 330 (M$^+$, [80]Se, 10%), 165 (100%).

Irradiation of 1 in CD$_3$OD. A (partially) Ar-degassed soln. of 13.8 mg (0.05 mmol) of **1** in 1 ml of CD$_3$OD was irradiated (300 nm) for four 30 min periods and the conversion to products monitored by ^{1}H-NMR. Besides (tetradeutero)-**3** and 2,2,4,4-tetramethylpentan-5-one (**7**) in a 1:1 ratio, a mixture of hexadeuterated diesters **4-6** was formed, whose composition varied during the photolysis experiment. After one hour the ratio **4**:**5**:**6** was 5:4:1 and after two hours 3:2:5, respectively.

Solid-state irradiation of 1. An Ar-degassed soln. of 138 mg (0.5 mmol) of **1** in 5 ml of CH$_2$Cl$_2$ in a 25-ml tapered flask was slowly evaporated to produce a homogeneous solid film. After irradiation for 18 h, the (originally colorless) solid residue had become a yellowish oil. According to both GC and NMR analysis, the residue consisted mainly of **7** and some polymeric material.

Irradiation of 9 in MeOH. An Ar-degassed soln. of 23.4 mg (0.1 mmol) of **9** in 3 ml MeOH was irradiated (350 nm) for 6 h. ^{1}H-NMR Analysis of the crude photolysate indicated total

conversion of starting material and exclusive formation of a 4:1 mixture of **10** and **11**. As attempted chromatographic separation failed, the NMR-spectral data were obtained from this mixture of isomers. *Spiro[5-methoxythian-2,2'-tricyclo[3.3.1.1^{3,7}]decan]-4-one* (**10**): ^{1}H-NMR (CDCl$_3$) δ (adamantane signals omitted), 2.74 (1H, d, *J* = 17.2 Hz), 2.94 (1H, d, *J* = 17.2 Hz), 3.37 (3H, s), 3.60 (1H, dd, *J* = 6.5, 9.6 Hz), 3.73 (1H, dd, *J* = 4.1, 9.6 Hz), 3.80 (1H, dd, *J* = 4.1, 6.5 Hz); ^{13}C-NMR δ (adamantane signals omitted), 52.1 (t), 53.2 (d), 58.1 (s), 60.0 (q), 74.2 (t), 212.5 (s); MS *m/z*: 266 (M^{+}, 40%), 45 (100%). *Spiro[6-methoxythian-2,2'-tricyclo[3.3.1.1^{3,7}]decan]-4-one* (**11**): ^{1}H-NMR (CDCl$_3$) δ (adamantane signals omitted), 2.79 (1H, d, *J* = 12.3 Hz), 2.83 (1H, dd, *J* = 10.2, 13.7 Hz), 3.01 (1H, dd, *J* = 5.8, 13.7 Hz), 3.45 (1H, d, *J* = 12.3 Hz), 3.46 (3H, s), 3.97 (1H, dd, *J* = 5.8, 10.2 Hz); ^{13}C-NMR δ (adamantane signals omitted), 30.1 (t), 53.2 (t), 58.1 (s), 59.4 (q), 84.2 (d), 207.5 (s); MS *m/z*: 266 (M^{+}, 20%), 148 (100%).

References and Footnotes

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