Photochemistry of Spiro[6H-[1,3]Oxathiin-2,2′-tricyclo[3.3.1.1^{3,7}]decan]-6-one

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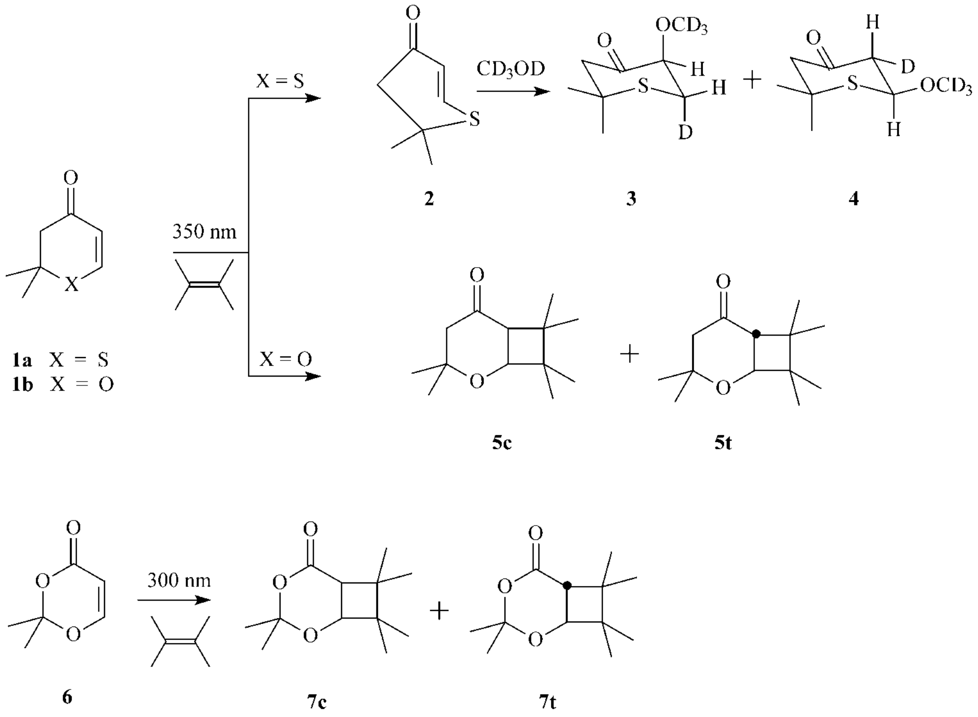
Dedicated to Professor *Amos B. Smith III* on the occasion of his 60th birthday

On irradiation (300 nm) in the solid state, the title compound **8** affords tricyclo[3.3.1.1^{3,7}]decan-2-one (=adamantan-2-one; **9**) selectively *via* [4+2] cycloreversion. A similar result is obtained on photolysis in solution (MeCN or acetone), also in the presence of added alkenes. On irradiation in MeOH, a solvent adduct **11** is isolated in addition to **9**. From experiments in CD_3OD, it can be inferred that **11** is formed *via syn*-addition of MeOH to the ground-state (E)-heterocycle **16**.

Introduction. – In the course of our investigations on the photochemistry of (S-hetero)cyclic unsaturated carbonyl compounds [1], we had observed that the photochemical behavior of 3,4-dihydro-2H-thiin-4-ones, *e.g.*, **1a**, resembles strongly that of cyclohept-2-enones: due to the longer bond length of the C−S bond, these rings become less rigid, and, therefore, the twisting around the C=C bond in the excited state is facilitated (*Scheme 1*). This is the reason why photodimerization and photocycloaddition to simple alkenes occurs with very low efficiency [2], whereas the so formed ground-state (E)-diastereoisomer **2** is efficiently trapped by MeOH to afford a 3:2 mixture of **3** and **4**, respectively [3]. This behavior is indeed typical for 3,4-dihydro-2H-thiin-4-one, as the corresponding oxa-enones, *e.g.*, **1b**, exhibit typical enone behavior by undergoing efficient [2+2] photocycloaddition to alkenes to afford oxabicyclooctanones **5** [4]. The transition from a cyclic oxa-enone to an unsaturated 'oxa-lactone', *e.g.*, **6**, does not alter this typical enone behavior, as this latter dioxinone is cleanly converted to bicycles **7** on long-wavelength irradiation in the presence of 2,3-dimethylbut-2-ene [5]. A recently reported easy synthetic access to 2,2-dialkyl-6H-1,3-oxathiin-6-ones [6] prompted us to investigate the photochemical behavior of such analogous thiacycles. Here, we report the photochemical behavior of the title compound **8** (*Scheme 2*).

Results. – Irradiation (300 nm) of **8** (0.1 – 1M) in MeCN led to the exclusive formation of adamantan-2-one (**9**) besides some polymeric precipitate. Changing the solvent to acetone hindered this precipitation but, again, **9** was the only detectable (GC, NMR) product, which was isolated by chromatography in yields up to 90%. Iradiation of **8** in MeCN in the presence of a 20-fold molar excess of either 2,3-dimethylbut-2-ene or furan led to results identical to those mentioned above, *i.e.*, exclusive formation of **9** as detectable product. Interestingly, this same reactive behavior was also observed on irradiation of **8** as solid film, the selective conversion to **9** occuring without any

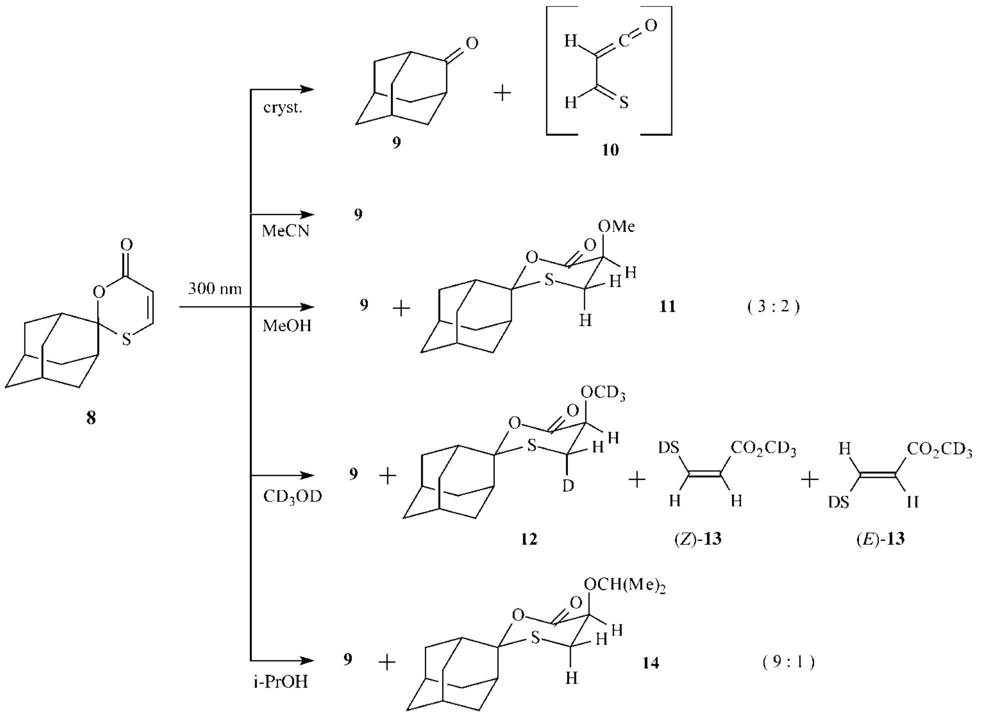
Scheme 1



liquefaction. In all these experiments, no evidence for any low-molecular-weight derivative of thioacylketene **10** was obtained. Irradiation of **8** in MeOH afforded a 3:2 mixture (^{1}H-NMR) of **9** and the MeOH adduct **11**, whose separation/isolation was achieved by column chromatography. The assignment of the MeO group location stems from the ^{1}H-NMR spectrum, wherein the geminal coupling constant of the new CH_2 group ($J = 9.8$ Hz) evidences a CH_2 group adjacent to a S-atom (*Scheme 2*).

To obtain additional information on the mode of the MeOH addition and also to eventually trap the postulated thioacylketene **10**, **8** was irradiated in CD_3OD in an NMR tube, and the reaction was monitored by ^{1}H-NMR (without removal of the solvent). In addition to the signals corresponding to **9** and to the *trans*-4-deuterio-5-(trideuteriomethoxy) adduct **12** (vicinal coupling constant J(eq,eq) = 3.5 Hz), two new sets of *AB* systems, one resonating at 7.77 and 5.80 ppm with $J = 15$ Hz and the other one resonating at 7.27 and 5.96 ppm with $J = 10$ Hz, were observed. Upon allowing the mixture to stand at room temperature, these latter signals gradually disappeared. The original (molar) composition of the mixture corresponds to **9** (1.5), **12** (1.0), (*Z*)-**13** (1.1), and (*E*)-**13** (0.4). The ^{1}H-NMR data for (*Z*)-**13** in CD_3OD are in agreement with the chemical shifts reported for the corresponding non-deuterated ester in $CDCl_3$ (7.10 and 5.98 ppm, $J = 10.4$) [7]. Finally, irradiation of **8** in i-PrOH afforded a 9:1 mixture (^{1}H-NMR) of **9** and alcohol adduct **14**. Due to its very low yield of formation, **14** was not isolated but characterized by ^{1}H-NMR and MS in the mixture.

Scheme 2



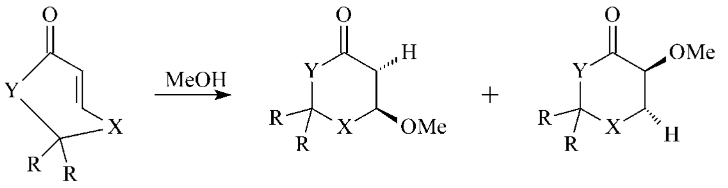
Discussion. – The clean conversion of **8** to **9** is, to our knowledge, one of the very first examples of a formal *Diels–Alder*-type cycloreversion occuring in the solid-state. Fragmentation reactions are relatively rare in the solid state because the crystal lattice holds the fragments together, and they just recombine. This changes when one of the products formed is a gas, which escapes, exemplified by recently reported solid-state photodecarbonylation reactions [8]. In solution, *retro-Diels–Alder* reactions are well-known [9], but most of the reactions in which a C=O compound is formed as 'heterodienophile' are thermal processes, whereby the presence of a second heteroatom in the ring usually allows lowering of the cleavage temperature [10]. Only very few such light-induced reactions have been reported, *i.e.*, the cycloreversion of 2,2,6,6-tetramethyl-2*H*,6*H*-pyran-3-one to 2-methylprop-2-enylketene and acetone, which occurs in dilute solution in competition with photodimerization [11], and the short-wavelength (254 nm) photocleavage of 2,2-dialkyl- and 2,2,6-trialkyl-1,3-dioxin-4-ones to acylketenes and carbonyl compounds, respectively [12][13].

Very little indeed is known about thioacylketenes, *e.g.*, **10**. Flash vacuum pyrolysis studies of either 1,3-dioxin-4-thiones [14] or of 1,6-dioxa-6a-λ^4-thiapentalenes [15] indicate these species to be slightly lower in energy than the isomeric acylthioketenes but nothing is known about their behavior in solution. The alcohol adducts of **10**, *i.e.*, 3-sulfanylacrylates **13**, and the corresponding thiolate ions are known to be stable only at temperatures below 0° [16], as they undergo both rapid oligomerization as well as oxidation to disulfanes [7].

The above mentioned solid-state photodecarbonylations are known to proceed in two steps, *i.e.*, primary α-cleavage, followed by CO elimination from the intermediate acyl-alkyl biradical [8]. It is, therefore, reasonable to assume that the light-induced cycloreversion of **8** proceeds in a stepwise sequence, in which the cleavage of the (weakest) S–C(2) bond occurs first, followed by cleavage of the O–C(O) bond. Nevertheless, a synchronous process cannot be excluded at the moment, and it is also not evident whether the twisting around the C=C bond in excited **8** facilitates the elimination of **9**.

A final comment regards the regiochemistry of the MeOH addition to highly strained (*E*)-cycloalkenones, *e.g.*, (*E*)-cyclohept-2-enone (**15**), **2**, and **16**, to afford **17** [17, 18], a 3:2 mixture of **3** and **4** [3], and **11**, respectively (*Scheme 3*).

Scheme 3



15	X = CH$_2$CH$_2$, Y = CH$_2$, R = H	**17**		**-**
2	X = S , Y = CH$_2$, R = Me	**4**	(2 : 3)	**3**
16	X = S , Y = O , R–R = adamantane	**-**		**11**

The exclusive formation of 3-methoxycycloheptanone (**17**) from **15** has been explained by assuming a *Michael*-type addition of the alcohol. It is doubtful that this interpretation is correct as, in highly twisted (*E*)-cycloalkenones, conjugation between the C=O and the C=C bond should become negligible. If this conjugative effect would be important, **2** and **16** should also undergo selective MeOH addition at the (vinylogous) C(β)-atom.

The reversal of regioselectivity observed in the reactions above indicates several combined effects, *i.e.*, *a*) higher stabilization of the negative charge at C(α) (resulting from the MeOH addition at C(β)) rather by the ketone than by the carboxy CO group, *b*) hindrance of the approach of MeOH to C(β) by the lone pairs of the S-atom, and *c*) stabilization of the negative charge at C(β) by this same heteroatom. The common feature in all these reactions is the fact that they proceed stereospecifically as *syn*-additions, affording products wherein the MeOH group and the (new) H-atom are *trans*-located.

Experimental Part

1. *General.* ^{1}H- and ^{13}C-NMR Spectra in $(CD_3)_2CO$ (unless otherwise stated): 500 and 125.8 MHz, resp.; chemical shifts in δ in ppm rel. to Me_4Si (=0 ppm). MS: at 70 eV; in *m*/*z* (rel. intensity in %). Photolyses in a *RPR-100 Rayonet* photochemical reactor equipped with 300-nm lamps.

2. *Starting Materials.* The title compound **8** was synthesized according to [6]. UV (MeCN): λ_{max} 300.5 nm, log ε 4.081. *Adamantan-2-one* (=*tricyclo[3.3.1.1^{3,7}]decan-2-one*; **9**) is commercially available.

3. *Photolyses.* 3.1 *Irradiation of* **8** *in Soln.* Ar-Degassed solns. containing 118 mg (0.5 mmol) of **8** in 5 ml of MeCN or acetone were irradiated for 12 h, until monitoring by TLC indicated total consumption of starting material. In MeCN, the formation of a (polymeric) precipitate was observed. Both GC analysis of the crude photolysate and NMR analysis of the residue after evaporation of the solvent indicated the exclusive formation of **9**, isolated in 87% yield by purification (CC) on a short column (SiO_2; CH_2Cl_2).

3.2 *Solid-State Irradiation of* **8**. An Ar-degassed soln. of 118 mg (0.5 mmol) of **8** in CH_2Cl_2 (5 ml) in a 25-ml tapered flask was slowly evaporated to produce a homogeneous solid film. After irradiation for 21 h, the (originally colorless) solid residue had turned yellowish. According to both GC and NMR analysis, the residue consisted of > 90% **9**.

3.3 *Irradiation of* **8** *in the Presence of Alkenes.* Ar-Degassed solns. containing 118 mg (0.5 mmol) of **8** and a 20-fold molar excess of either 2,3-dimethylbut-2-ene or furan in 5 ml of MeCN were irradiated for 12 h, until monitoring by TLC indicated total consumption of starting material. After filtration of the polymeric precipitate and evaporation of the solvent, both GC and NMR analysis of the residue indicated the exclusive formation of **9**.

3.4 *Irradiation of* **8** *in MeOH.* An Ar-degassed soln of 590 mg (2.5 mmol) of **8** in 10 ml of MeOH was irradiated for 4 h. ^{1}H-NMR Analysis of the crude photolysate indicated the presence of traces of **8** and a mixture of **9** and a novel compound **11** in a 3 : 2 molar ratio. CC (SiO_2; CH_2Cl_2) afforded first 8 mg (1.5%) of **8** (R_f 0.70) then 130 mg (20%) of pure *5-methoxyspiro[[1,3]oxathiane-2,2′-tricyclo[3.3.1.1^{3,7}]decan]-6-one* (**11**; R_f 0.68). Colorless viscous oil. ^{1}H-NMR: 4.40 (*dd*, J = 3.5, 7.0); 3.78 (*dd*, J = 3.5, 9.8); 3.68 (*dd*, J = 7.0, 9.8); 3.34 (*s*, 3 H); 2.19 – 2.01 (*m*, 5 H); 1.88 – 1.73 (*m*, 9 H). ^{13}C-NMR: 172.48 (*s*); 96.27 (*s*); 73.90 (*t*); 59.13 (*q*); 48.23 (*d*); 41.46 (*d*); 41.42 (*d*); 37.80 (*t*); 35.94 (*t*); 35.39 (*t*); 34.84 (*t*); 34.61 (*t*); 27.15 (*d*); 27.04 (*d*). MS: 268 (20, $M^{+\cdot}$), *151*.

The next fraction (R_f 0.66; 205 mg; representing an additional 20% yield of **11**) consisted of a 1 : 1 mixture **11/9**, which was then finally obtained pure (150 mg) in the last fraction (R_f 0.64).

3.5 *Irradiation of* **8** *in CD_3OD.* An Ar-degassed soln. of 23.6 mg (0.1 mmol) of **8** in 1 ml of CD_3OD was irradiated for 1 h. ^{1}H-NMR Analysis indicated on the one hand the expected 3 : 2 mixture of **9** and trans*-5-([$^2H_3$]methoxy)spiro[[4-$^2H_1$][1,3]oxathiane-2,2′-tricyclo[3.3.1.1^{3,7}]decan]-6-one* (**12**): ^{1}H-NMR (CD_3OD): 4.36 (*d*, J = 3.5); 3.74 (*d*, J = 3.5); 2.19 – 2.01 (*m*, 5 H); 1.88 – 1.73 (*m*, 9 H). MS: 272 (20, $M^{+\cdot}$), *151*. In addition, the equivalent amount of a 1 : 3 mixture of (*E*)- and (*Z*)-sulfanylacrylates **13** was observed by their two *AB* systems, resonating at 7.77 and 5.89 (J = 15) and 7.27 and 5.96 (J = 10), respectively.

3.6 *Irradiation of* **8** *in i-PrOH.* An Ar-degassed soln. of 47.2 mg (0.2 mmol) of **8** in 2 ml of i-PrOH was irradiated for 3 h. After evaporation of the solvent, ^{1}H-NMR analysis indicated a 9 : 1 molar ratio of **9** and *5-(1-Methylethoxy)spiro[[1,3]oxathiane-2,2′-tricyclo[3.3.1.1^{3,7}]decan]-6-one* (**14**): ^{1}H-NMR: 4.35 (*dd*, J = 3.5, 6.7); 3.83 (*dd*, J = 3.5, 9.8); 3.74 (*dd*, J = 6.7, 9.8); 3.65 (*sept.*, J = 6.0) ; 2.19 – 2.01 (*m*, 5 H); 1.88 – 1.73 (*m*, 9 H); 1.13 (*d*, J = 6.0, 3 H); 1.12 (*d*, J = 6.0, 3 H). MS: 296 (5, $M^{+\cdot}$), *224*.

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