

149. Light-Induced Cycloaddition of Furan and Addition of Methanol to a 4-Thiacyclohex-2-enone (= 2,3-Dihydro-4*H*-thiin-4-one) and a 4-Thiacyclopent-2-enone (= Thiophen-3(2*H*)-one)

by Ronald Kowalewski and Paul Margaretha*

Institut für Organische Chemie der Universität, D-2000 Hamburg 13

(25.VI.92)

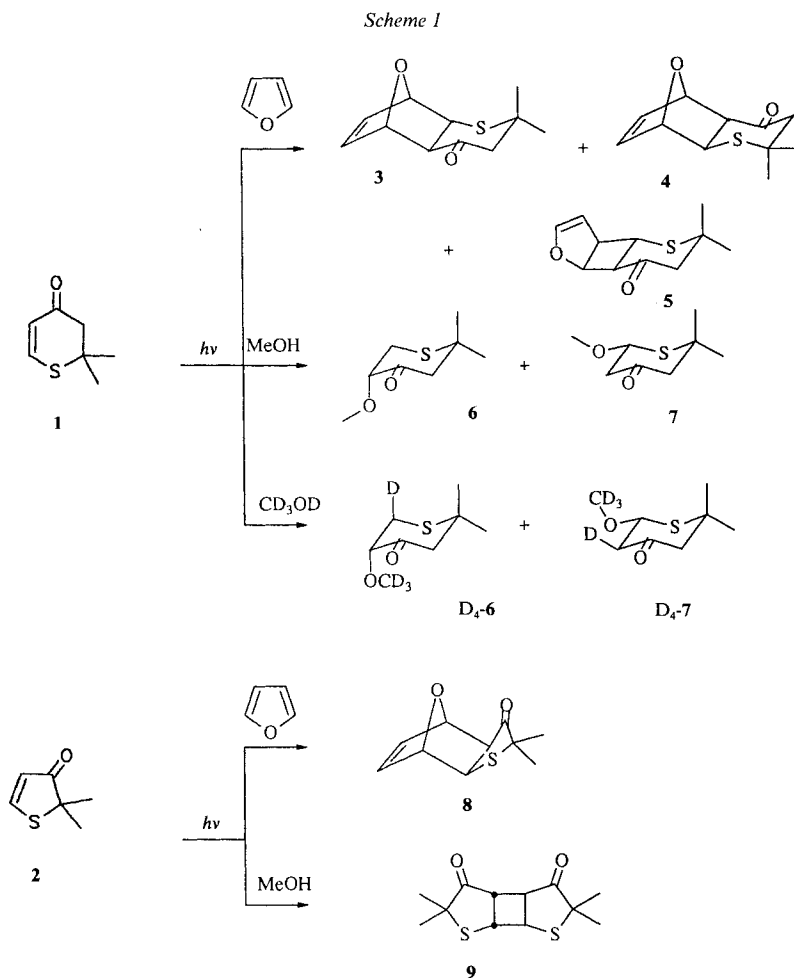
Irradiation of newly synthesized 2,2-dimethyl-2,3-dihydro-4*H*-thiin-4-one (**1**) in furan affords the two [4 + 2] cycloadducts **3** and **4** and the [2 + 2] cycloadduct **5** in a 5:4:1 ratio (*Scheme 1*). Irradiation of **1** in MeOH gives a 3:2 mixture of 5- and 6-methoxy-2,2-dimethylthian-4-ones **6** and **7**. Irradiation in CD₃OD affords the same (deuterated) adducts with the CD₃O and D groups *trans* to each other, results compatible with *cis*-addition of MeOH to a *trans*-configured ground-state enone. Irradiation of the same enone in furan/MeOH 1:1 gives *only* the furan cycloadducts **3–5** and *no* MeOH adducts, suggesting that furan interacts with the (excited) triplet enone *before* the deactivation of this species to a ground-state (*E*)-cyclohexenone, which then reacts with MeOH. On irradiation in furan, the corresponding five-membered thiaenone, 2,2-dimethylthiophen-3(2*H*)-one (**2**) affords *only one, cis*-fused, [4 + 2] cycloadduct with '*exo*'-configuration, *i.e.* **8**, and **2** does *not* undergo solvent addition but rather cyclodimerization (\rightarrow **9**) on irradiation in MeOH (*Scheme 1*).

Introduction. – Cyclooct-2-enone and cyclohept-2-enone undergo (*Z*) \rightarrow (*E*) isomerization on irradiation. While (*E*)-cycloocten-2-enone can be characterized spectroscopically at room temperature, (*E*)-cyclohept-2-enone is stable only at temperatures between -190° and -160° , but can be trapped with cyclopentadiene in a dark reaction at -78° . The (*Z*) \rightarrow (*E*) isomerization of these medium-ring cycloalkenones seems to occur much faster than intermolecular processes, *e.g.* cycloaddition to alkenes or energy transfer to perylene or cyclopentadiene [1–4]. Another seven-membered ring enone, 2,3-benzocyclohepta-2,6-dienone, was found to afford *trans*-fused [4 + 2] cycloadducts on irradiation in furan, and, on irradiation in MeOH, a 5-MeO adduct wherein the MeO group and the (new) H-atom are *trans* to each other [5] [6]. The authors inferred from these results that the primary photoprocess was again (*Z*) \rightarrow (*E*) isomerization of the C=C bond in the seven-membered ring and that the (*E*)-enone was then trapped by either furan or MeOH.

As for six-membered enones, cyclohex-2-enone on irradiation in furan afforded both [4 + 2] and [2 + 2] cycloadducts [7]. Although the configuration of these products has not been determined, the author [7] found these results consistent with a mechanism involving attack of an enone triplet on a ground-state diene molecule. Triplet biradicals formed in such a reaction have also been proposed as intermediates in the photocycloaddition of *Pummerer's* ketone (= 4a,9b-dihydro-8,9b-dimethyldibenzofuran-3(4*H*)-one) with furan [8] [9]. On irradiation in MeOH, cyclohex-2-enone gave less than 1% of 3-methoxycyclohexanone [10]; *Pummerer's* ketone, on the other hand, gave a MeOH adduct in 79% yield, with the MeO group and the (new) H-atom are again *trans* to each other [11]. The authors proposed a reactive excited molecule or an intermediate in which the C=C bond is twisted by more than 90° to which MeOH undergoes a regio- and stereospecific nucleophilic *cis*-addition.

Some time ago, we published results [12] on the photochemistry of 2,3-dihydro-4*H*-thiin-4-one. In these investigations, we had obtained low yields of photoproducts and observed extensive polymer formation. Obviously, the longer C–S bonds (as compared to C–C bonds) make such dihydrothiinones ideal model compounds for investigating photochemically generated highly twisted monocyclic cyclohex-2-enones. In this paper, we report on results of irradiations of newly synthesized 2,2-dimethyl-2,3-dihydro-4*H*-thiin-4-one (**1**) in furan, in MeOH, and in furan/MeOH mixture and compare the results with those obtained from irradiations of the corresponding thiacyclopentenone, *i.e.* 2,2-dimethyl-3(2*H*)-thiophenone (**2**).

Results. – Dihydro-4*H*-thiin-4-one **1** was synthesized from the saturated precursor 2,2-dimethylthian-4-one *via* *N*-chlorosuccinimide (NCS) dehydrogenation, in close analogy to the synthesis of the parent 2,3-dihydro-4*H*-thiin-4-one [13] and of thiophen-3(2*H*)-one **2** [14].

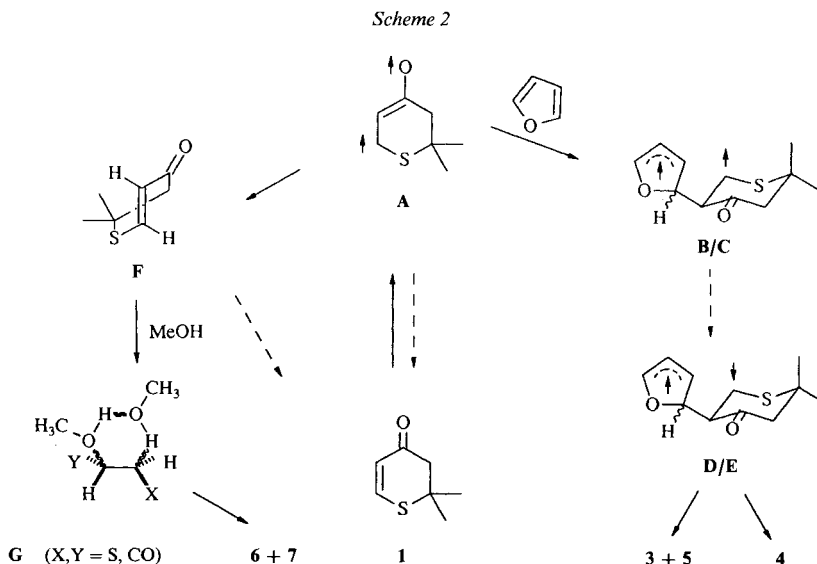


Irradiation (λ 350 nm) of **1** (10^{-1} M) in neat furan or in furan/MeCN 1:1 affords three cycloadducts **3**, **4**, and **5** in a 5:4:1 ratio, whose formation is quenched by (*E*)-stilbene. Irradiation of **1** (10^{-1} M) in MeOH affords a 3:2 mixture of ether **6** and O,S-acetal **7**, and in CD₃OD a similar mixture of D₄-**6** and D₄-**7**. Irradiation of **1** (10^{-1} M) in furan/MeOH 1:1 gives only cycloadducts **3–5**, but no adducts **6** and **7**. In contrast, **2** affords a 1:1 mixture of cycloadduct **8** and tricyclic dimer **9** on irradiation in furan, this latter product being formed exclusively on irradiation of **2** in MeOH (no methanol addition products). (*E*)-Stilbene again quenches the formation of both **8** and **9** from **2**. As all [4 + 2] cycloadducts **3**, **4**, and **8** undergo easily *retro-Diels-Alder* reaction, no satisfactory *Stern-Volmer* plots could be obtained by means of GC analysis.

Discussion. – In the light-induced reactions of cycloalkenones in MeOH studied [5] [6] [11], the formation of 3-methoxycycloalkanones (with H or D on C(α) and MeO or CD₃O on C(β) *trans* to each other) has been usually taken as evidence for the intermediacy of an (*E*)-cycloalkenone, the yield of ethers giving an indirect measure for the lifetime of these species. In this context, it becomes obvious that **1** is a very suitable model compound for such studies, as it represents the first example of a monocyclic cyclohex-2-enone analogue undergoing efficient MeOH photoaddition. Thiaenone **2** apparently cannot undergo (*Z*) \rightarrow (*E*) isomerization efficiently any more and, therefore, on irradiation in MeOH, cyclodimer **9** is formed exclusively.

There seem to be two reaction paths leading to the *trans*-fused [4 + 2] cycloadducts formed in the irradiation of cycloalkenones in furan. On the one side, (*E*)-cyclooct-2-enone or (*E*)-cyclohept-2-enone can be generated photochemically from the corresponding (*Z*)-cycloalkenones and then be trapped *in the dark* by furan, the experiment with the seven-membered ring having to be performed at temperatures below -78° . On the other hand, *Pummerer's* ketone or even cyclohex-2-enone itself afford *trans*-fused [4 + 2] cycloadducts with furan at room temperature. The facts that for **1 a)** a similar behaviour is observed, *b)* [4 + 2] and [2 + 2] photocycloadducts are formed from a common intermediate, as suggested by the quenching experiments with (*E*)-stilbene, and *c)* in furan/MeOH 1:1, *only* the furan cycloadducts are formed, strongly suggest that for cyclohex-2-enones, the enone triplet, *i.e.* the *precursor* of the (*E*)-cycloalkenone, is trapped by furan. It can be safely assumed that enone triplets will interact with furan ($E_T = 76$ kcal/mol [15]) in a similar way they do with simple alkenes, affording triplet 1,4-biradicals *via* a possible exciplex intermediate [16]. After intersystem crossing, the singlet biradicals – with an allylic radical moiety in the furan ring – will then undergo both [4 + 2] and [2 + 2] ring closure, the observed *trans*-fusion reflecting the more stable equatorial, equatorial ring fusion to the thiaenone ring in a chair conformation. Five-membered thiaenone **2** also reacts with furan (as an alkene, *cf.* [14]), but here, the *exo*-adduct **8** is *cis*-fused due to the higher strain in a *trans*-fused bicyclo[3.3.0]octane system.

Our results combined with those reported in the literature [7–9] [11] are compatible with the mechanistic sequence for excited cyclohex-2-enones, as shown in *Scheme 2* for thiacyclohexenone **1**. Excitation followed by intersystem crossing gives triplet enone **A** which reacts with furan to give two diastereoisomeric triplet 1,4-biradicals **B**, **C** which then undergo intersystem crossing to singlet 1,4-biradicals **D** and **E**, the one being precursor to cycloadducts **3** and **5** and the other one to cycloadduct **4**. In the absence of furan, the triplet enone undergoes internal conversion to (*E*)-cyclohexanone **F** which



either re-isomerizes to **1** or is trapped by MeOH to give ether **6** or O,S-acetal **7**. In contrast to (carbocyclic) cyclohexanones, *two* regioisomers are formed from **1** as both the carbonyl group *and* the S-atom stabilize an adjacent carbanionic center. The selective *trans*-configuration of the MeO group and the H-atom in these adducts is, maybe, best explained by a mechanism wherein two molecules of MeOH are linked by a H-bond and add to the (*E*)-double bond of **F** via a six-atom transition state **G**.

The authors are grateful to the *Deutsche Forschungsgemeinschaft* and the *Fonds der Chemischen Industrie* for financial support of this work, and to Dr. *George Lenz* (BOC, Murray Hill, NJ) for enlightening discussions.

Experimental Part

1. *General*. Photolyses: *Rayonet-RPR-100* photoreactor equipped with 350 nm lamps using a liquid filter with cut-off at 340 nm. Qual. GC: 30-m *SE 30* capillary column. ^1H - and ^{13}C -NMR Spectra: at 400 and 100.63 MHz, resp.; chemical shifts in ppm rel. to TMS (= 0 ppm), coupling constants *J* in Hz. MS: at 70 eV; in *m/z* (rel. intensity in %).

2. *2,2-Dimethyl-2,3-dihydro-4H-thiophen-4-one (1)*. To an ice-cooled, well stirred soln. of 2,2-dimethylthian-4-one [17] (7.2 g, 50 mmol), and pyridine (4 g, 50 mmol) in CH_2Cl_2 (100 ml), *N*-chlorosuccinimide (6.75 g, 50 mmol) is added within 20 min. Stirring is continued for 7 h at r.t., the solvent evaporated and replaced with Et_2O (100 ml), and the precipitate filtered off and washed with Et_2O (10 ml). The combined Et_2O extracts are dried (MgSO_4) and chromatographed (SiO_2 , CH_2Cl_2): 5.8 g (81%) of **1**. ^1H -NMR (CDCl_3): 7.42, 6.19 (2d, *J* = 10.0); 2.64 (s, 2 H); 1.46 (s, 6 H). ^{13}C -NMR (CDCl_3): 195 (s); 145 (d); 122 (d); 52 (t); 46 (s); 28 (q). MS: 142 (46, M^+), 86.

2,2-Dimethyl-3(2H)-thiophenone (2) was synthesized according to [14].

3. *Photochemistry*. Ar-degassed 2.10^{-1} M solns. of **1** or **2** are irradiated up to total conversion of starting material (GC monitoring) and worked up as described below.

Irradiation of 1 in MeOH. For 16 h, **1** (284 mg) in MeOH (10 ml) is irradiated, then the solvent evaporated, and the residue chromatographed (SiO_2 ; $\text{CH}_2\text{Cl}_2/\text{MeOH}$ 99:1): 49 mg (14%) *6-methoxy-2,2-dimethylthian-4-one (7)*. ^1H -NMR (CDCl_3): 3.96 (dd, *J* = 5.5, 10.0); 3.45 (s, 3 H); 3.05 (dd, *J* = 5.5, 14.0); 2.96 (dd, *J* = 10.0, 14.0); 2.58 (s,

2 H); 1.39 (s, 3 H); 1.36 (s, 3 H). $^{13}\text{C-NMR}$ (CDCl_3): 212 (s); 73 (t); 59 (q); 56 (t); 54 (d); 47 (s); 31 (q); 30 (q). MS: 174 (98, M^+), 45.

The 2nd fraction consists of 70 mg (20%) of 5-methoxy-2,2-dimethylthian-4-one (6). $^1\text{H-NMR}$ (CDCl_3): 3.92 (dd, $J = 4.0, 6.5$); 3.76 (dd, $J = 4.0, 10.0$); 3.67 (dd, $J = 6.5, 10.0$); 3.35 (s, 3 H); 2.76, 2.64 (2d, $J = 12.0$); 1.51 (s, 3 H); 1.48 (s, 3 H). $^{13}\text{C-NMR}$ (CDCl_3): 206 (s); 84 (d); 58 (q); 57 (t); 48 (s); 38 (t); 30 (q); 28 (q). MS: 174 (11, M^+), 58.

Irradiation of 1 in CD_3OD . In a quartz NMR tube, **1** (14.2 mg) in CD_3OD (0.5 ml) is irradiated for 8 h, followed by direct measurement of the $^1\text{H-NMR}$ spectrum of the mixture $\text{D}_4\text{-6}/\text{D}_4\text{-7}$: $\text{D}_4\text{-6}$: 3.92 (d, $J = 4.0$); 3.76 (d, $J = 4.0$); $\text{D}_4\text{-7}$: 3.96 (d, $J = 10.0$); 3.05 (d, $J = 10.0$).

Irradiation of 1 in Furan. For 16 h, **1** (568 mg) in furan (20 ml) is irradiated, excess furan evaporated, and the residue chromatographed (SiO_2 , $\text{CH}_2\text{Cl}_2/\text{MeOH}$ 99:1): 42 mg (5%) of 9,9-dimethyl-cis-cisoid-trans-3-oxa-8-thiatricyclo[5.4.0.0^{2,6}]undec-4-en-11-one (5). $^1\text{H-NMR}$ (C_6D_6): 6.09 (dd, $J = 1.5, 2.5$); 5.18 (dd, $J = 4.0, 7.0$); 4.66 (t, $J = 2.5$); 3.45 (dd, $J = 2.0, 7.5$); 3.24 (ddd, $J = 1.5, 4.5, 7.5$); 3.01 (ttt, $J = 1.5, 2.5, 7.0$); 2.17, 2.02 (2d, $J = 15.5$); 1.02 (s, 3 H); 0.93 (s, 3 H). $^{13}\text{C-NMR}$ (C_6D_6): 206 (s); 148 (d); 104 (d); 83 (d); 54 (t); 53 (d); 49 (d); 45 (s); 42 (d); 31 (q); 30 (q). MS: 210 (10, M^+), 86.

The 2nd fraction, a mixture 3/4, is rechromatographed (SiO_2 ; pentane/MeOH 93:7): 168 mg (20%) of (1RS,2SR,7SR,8SR)-4,4-dimethyl-trans-11-oxa-3-thiatricyclo[6.2.1.0^{2,7}]undec-9-en-6-one (4). $^1\text{H-NMR}$ (C_6D_6): 6.10 (dd, $J = 1.5, 5.5$); 5.90 (dd, $J = 1.5, 5.5$); 4.82 (dd, $J = 1.5, 3.5$); 4.51 (d, $J = 1.5$); 2.99 (d, $J = 3.5, 9.0$); 2.55 (d, $J = 9.0$); 2.12, 2.08 (2d, $J = 14.0$); 1.13 (s, 3 H); 1.12 (s, 3 H). $^{13}\text{C-NMR}$ (C_6D_6): 204 (s); 139 (d); 129 (d); 80 (d); 75 (d); 61 (d); 59 (t); 45 (d); 31 (q); 30 (q). MS: 210 (0.8, M^+), 81.

The final fraction consists of 210 mg (25%) of (1RS,2RS,7RS,8SR)-4,4-dimethyl-trans-11-oxa-3-thiatricyclo[6.2.1.0^{2,7}]undec-9-en-6-one (3). $^1\text{H-NMR}$ (C_6D_6): 6.14 (dd, $J = 1.5, 5.5$); 5.66 (dd, $J = 1.5, 5.5$); 4.98 (d, $J = 1.5$); 4.73 (dd, $J = 1.5, 3.5$); 3.20 (dd, $J = 3.5, 9.0$); 2.24, 2.17 (2d, $J = 14.0$); 2.11 (d, $J = 9.0$); 1.21 (s, 3 H); 1.08 (s, 3 H). $^{13}\text{C-NMR}$ (C_6D_6): 204 (s); 141 (d); 131 (d); 81 (d); 79 (d); 62 (d); 59 (t); 48 (d); 32 (q); 31 (q). MS: 210 (0.66, M^+), 81.

Irradiation of 1 in Furan/MeOH. For 8 h, **1** (142 mg) is irradiated in furan/MeOH 1:1. GC: 4/5/3 4:1:5, no detectable trace of either **6** or **7**.

Irradiation of 2 in Furan. For 16 h, **2** (256 mg) is irradiated in furan (10 ml). Evaporation of excess furan and chromatography (SiO_2 ; pentane/MeOH 99:5) afford first 26 mg (10%) cis-transoid-cis-perhydro-2,2,5,5-tetramethylcyclobuta[1,2-b:4,3-b']dithiophene-3,4-dione (9), identical with the major photocyclodimer obtained on irradiation of **2** in benzene [14].

The 2nd fraction consists of 129 mg (36%) of (1RS,2SR,6RS,7SR)-4,4-dimethyl-cis-10-oxa-3-thiatricyclo[5.2.1.0^{2,6}]dec-8-en-5-one (8). $^1\text{H-NMR}$ (C_6D_6): 5.68 (s, 2 H); 5.23 (s, 2 H); 4.40 (s, 2 H); 2.71, 2.12 (2d, $J = 7.0$); 1.47 (s, 3 H); 1.30 (s, 3 H). $^{13}\text{C-NMR}$ (C_6D_6): 212 (s); 137 (d); 136 (d); 84 (d); 82 (d); 59 (s); 53 (d); 42 (d); 29 (q); 28 (q). MS: 196 (0.2, M^+), 128.

Irradiation of 2 in MeOH. For 18 h, **2** (128 mg) in MeOH (5 ml) is irradiated. GC: only **9**.

Quenching Experiments. Solns. of **1** or **2** in furan containing varying amounts (up to 1M) of (*E*)-stilbene ($E_\tau = 52$ kcal/mol) are irradiated in as 'merry-go-round' setup. Stern-Volmer plots for the formation of **3-5** from **1** and of **8** from **2** are rather inaccurate (error $\pm 50\%$) as cycloadducts **3, 4**, and **8** undergo retro-Diels-Alder reaction under the GC conditions used. The $k_q \cdot \tau$ values found are 13.2 M^{-1} for **1** and 65 M^{-1} for **2**. This latter value is in good agreement with the one reported [18] for quenching **2** with naphthalene (71 M^{-1}).

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