123. Photochemistry of 4-Thia-2-cycloalkenones

Part 2[1])

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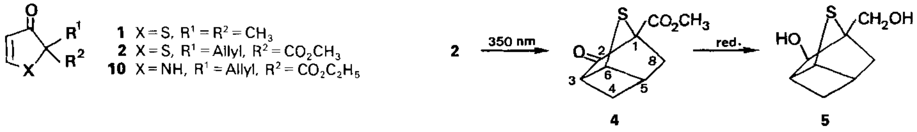
Methyl 2-allyl-3-oxo-2,3-dihydrothiophene-2-carboxylate (**2**) photocyclizes selectively to methyl 2-oxo-7-thiatricyclo[3.2.1.0^{3,6}]octane-1-carboxylate (**4**). In contrast, 4-thia-2-cyclohexenone **3**, on irradiation, affords only low yields of dimers, cycloadducts (2-methylpropene) or RH reduction products (i-ProH).

In the course of our investigations on the photochemistry of heterocyclic enones we have recently published [1] results on cycloadditions of 2,2-dimethyl-3(2*H*)-thiophenone (**1**). We now report on light-induced reactions of methyl 2-allyl-3-oxo-2,3-dihydrothiophene-2-carboxylate (**2**) and of 2,3-dihydrothiopyran-4-one (**3**).

Irradiation (λ = 350 nm) of **2** in various solvents (benzene, MeCN, i-ProH) affords selectively the new product **4**. The quantum yield for this reaction (Φ = 0.21 in benzene) was determined using 8,8,9,9-tetramethyl-1,3,4,6,7,8-hexahydro-1,4-ethanonaphthalene-2,5-dione as chemical actinometer [2]. The structure of **4** was established by its spectra as well as by its reduction to diol **5** *(Scheme 1)*.

Scheme 1



Under similar conditions **3** undergoes photodecomposition to a large extent. Prolonged irradiation affords only traces of a photodimer **6**, whose constitution (head-to-head) and configuration (*cis-anti-cis*) were assigned according to its ^{1}H-NMR spectrum. The rate of consumption of **3** is 4.3 times slower than that of **1**. Irradiation of **3** (benzene, 120 h) in the presence of an excess of 2-methylpropene affords two products, **7** and **8**, in 25% overall yield. This photo-addition reaction of **3** again is 3.8 times slower than that of **1** (in benzene). Irradiation of **3** in i-ProH affords 25% of the addition product **9** *(Scheme 2)*. The spectral data of the new products are summarized in the *Table*.

The behaviour of **2** contrasts that of the analogous pyrrole **10**, which on irradiation rearranges into ethyl 4-allyl-3-hydroxy-1-methylpyrrole-2-carboxylate (**11**) exclusively [3]. On the other hand, it parallels that of 3,4,4- and 2,4,4-trimethyl-5-(2-propenyl)-2-cy-

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[1]) Part 1: [1].

Scheme 2

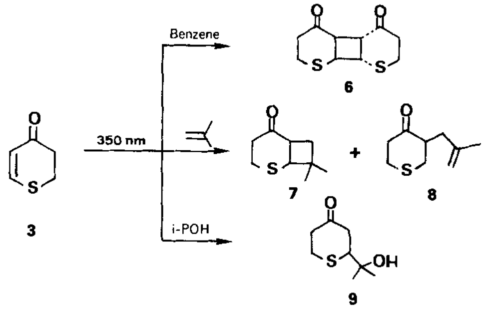


Table. *Spectral Data of Compounds 2-9*

Compound	UV (Cyclohexane)	^{1}H-NMR (CDCl$_3$)	MS
2	312 (3.75)	8.40, 6.16 (*AB*, J = 5.8); 5.73 (*m*, 1H); 5.20 (*m*, 2H); 3.77 (*s*, 3H); 2.94 (*m*, 2H)	198 (M^+) 85
3	295 (3.99)	7.45, 6.15 (*AB*, J = 11.1); 3.23 (*m*, 2H); 2.70 (*m*, 2H)	114 (M^+) 86
4[a])		4.33 (*t*, J = 4.5, H–C(6)); 3.88 (*s*, CH$_3$O); 3.08 (*dddd*, J = 7.0, 6.0, 5.9, 4.5, H–C(5)); 287 (*ddd*, J = 7.0, 5.4, 4.5, H–C(3)); 2.64 (*d*, J = 12.6, H–C(8)); 2.47 (*ddd*, J = 12.5, 6.0, 3.0, H–C(8)); 2.42 (*dddd*, J = 10.8, 6.0, 5.4, 3.0, H–C(4)); 1.67 (*d*, J = 10.8, H–C(4))	198 (M^+) 55
5		4.20 (*s*, 2H); 4.02 (*t*, J = 4.5); 3.88 (*s*, 1H); 2.69 (*m*, 1H); 2.46 (*m*, 1H); 2.10 (*m*, 1H); 2.01 (*m*, 1H); 1.83 (*d*, J = 12.0); 1.30 (*m*, 2H)	172 (M^+) 85
6[b])		3.93, 3.63 (*AA'XX'*, J_{AX} = 8.4, $J_{AX'}$ = 0.1, $J_{AA'}$ = 4.4, $J_{XX'}$ = 1.9); 3.10 (*m*, 4H); 2.90 (*m*, 4H)	228 (M^+) 86
7[c])		3.21 (*ddd*, J = 11.7, 10.6, 6.8); 3.12 (*d*, J = 11.7); 3.10–2.50 (*m*, 4H); 2.04 (*t*, J = 10.6); 1.89 (*dd*, J = 10.6, 6.8); 1.32, 1.17 (*s*, CH$_3$)	170 (M^+) 86
8[c])		4.80, 4.70 (=CH$_2$); 2.80 (*dt*, J = 9.6, 4.8); 3.10–2.60 (*m*, 6H); 2.58 (*dd*, J = 14.6, 4.8); 2.10 (*dd*, J = 14.6, 9.6); 1.71 (*s*, CH$_3$)	170 (M^+) 82
9		3.76 (*dd*, J = 7.2, 2.7); 3.00 (*ddd*, J = 11.4, 10.6, 5.4); 2.73 (*ddd*, J = 10.6, 7.0, 2.0); 2.40 (*dd*, J = 13.4, 7.2); 2.37 (*ddd*, J = 12.6, 5.4, 2.0); 2.19 (*ddd*, J = 12.6, 11.4, 7.0); 2.05 (*dd*, J = 13.4, 2.7); 1.44, 1.41 (*s*, CH$_3$)	174 (M^+) 59

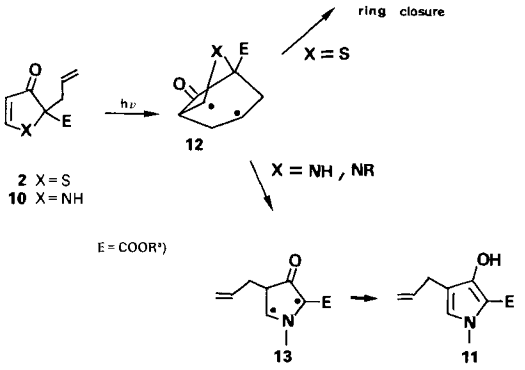
[a]) ^{13}C-NMR (CDCl$_3$): 201.2 (C(2)); 166.9 (*C*OOR); 70.0 (C(1)); 52.9 (CH$_3$O); 47.3; 47.1; 42.4; 39.8; 33.9.

[b]) Not isolated; NMR from mixture, MS from GC/MS.

[c]) Mixture (55:45) of **7** and **8** not separated; NMR from mixture, MS from GC/MS.

clopentenones which again give the appropriate trimethyltricyclo[3.2.1.0^{3,6}]octan-2-ones [4]. From these results, it becomes apparent that it is not the alkoxycarbonyl group which facilitates the conversion of the diradical **12** to **13** as originally proposed [3], but that

Scheme 3



[a]) See *Scheme 1*.

either the formation of **11** is favoured due to a specific stabilization of **13** by the nitrogen lone-pair [5], or diradical **12** is not an intermediate in the photorearrangement **10**$\to$**11** *(Scheme 3)*.

To differentiate between the proposed structure **4** and that of an isomeric 2-thiatricyclo[3.2.1.0^{3,6}]octan-7-one, we tried to reduce the carbonyl group of **4** to observe the additional coupling and change in chemical shift for either H–C(3) or H–C(6) in the corresponding alcohol. While the reduction of **4** with $NaBH_4$ in either MeOH or EtOH led to destruction of the tricyclic skeleton, the reduction with $NaBH_4$ in i-ProH afforded diol **5** although in moderate yield. Probably due to the thio group on C(α), the ester function is reduced as easily as the carbonyl group. The fact that the signal of H–C(3) in **5** is slightly broadened and shifted from 2.87 (in **4**) to 2.46 ppm is in agreement with the proposed structure of **4**.

On a first view, the 4-thia-2-cyclohexenone **3** also exhibits normal enone behaviour, the four-times lower efficiency of conversion as compared to **1** reflecting the greater ease of radiationless decay of cyclohexenones *vs.* cyclopentenones [6]. Nevertheless, the low yields of photoproducts and the strongly marked polymer formation indicates an additional reactive path for excited **3**. It is known [7] that 4-thiacyclohexanones afford thietanones on irradiation [8], and that larger ring ketosulfides also afford the corresponding thiolactones with elimination of a C_2 fragment [9] [10]. A similar sequence for **3** would give the saturated or unsaturated β-thiolactone, which most probably is unstable under the reaction conditions, and thus would not be observed.

Experimental Part

General. See [1]. GC was performed on a *SE-30* capillary column. Enones **2** and **3** were synthesized according to [11] and [12], resp. 2-Methylpropene was purchased from *Fluka AG.* All solvents used for photolyses were of spectral grade. Irradiations were performed in a *Rayonet RPR-100* photoreactor (3500-Å lamps) with a built in merry-go-round setup.

Methyl 2-Oxo-7-thiatricyclo[3.2.1.0^{3,6}]octane-1-carboxylate (**4**). An Ar-degassed soln. of **2** (396 mg, $2 \cdot 10^{-3}$ mol) in benzene (10 ml) was irradiated for 16 h. Evaporation of the solvent and bulb-to-bulb distillation (150°/0.1 Torr) afforded **4** (360 mg, 91%).

1-Hydroxymethyl-2-hydroxy-7-thiatricyclo[3.2.1.0^{3,6}]octane (**5**). A soln. of **4** (99 mg, $5 \cdot 10^{-4}$ mol) and $NaBH_4$ (10 mg) in i-ProH (2 ml) was stirred at r.t. for 8 h. The solvent was evaporated, the residue treated with 10%

aq. AcOH and CH_2Cl_2, the aq. phase extracted several times with CH_2Cl_2, the combined org. phases washed with sat. $NaHCO_3$ and NaCl solns., and dried ($MgSO_4$). Evaporation of the solvent afforded **5** (21 mg, 25%) as a colourless oil (GC-purity 90%). The 2-OH group is most probably *exo*-configurated as deduced from the very small coupling constant between H–C(2) and H–C(3).

Irradiation of 2,3-Dihydrothiopyran-4-one (**3**). An Ar-degassed soln. of **3** (114 mg, 10^{-3} mol) in benzene (5 ml) was irradiated for 120 h. After filtration from polymeric material and evaporation of the solvent, the residue (50 mg) consisted of **3** (90%) and cis-anti-cis *3,12-dithiatricyclo[6.4.0.0^{2,7}]dodecan-6,9-dione* (**6**; 10%), which were not further separated.

7,7-Dimethyl-5-thiabicyclo[4.2.0]octan-2-one (**7**) and *3-(2-methyl-3-propenyl)tetrahydrothiopyran-4-one* (**8**). A soln. of **3** (114 mg, 10^{-3} mol) in benzene (10 ml) was saturated with 2-methylpropene and irradiated for 120 h. After filtration from polymeric material and evaporation of the solvent, bulb-to-bulb distillation (150°/0.1 Torr) afforded 45 mg (25%) of a 55:45 mixture **7/8** which was not further separated.

2-(1-Hydroxy-1-methylethyl)tetrahydrothiopyran-4-one (**9**). An Ar-degassed soln. of **3** (114 mg, 10^{-3} mol) in i-ProH (10 ml) was irradiated for 48 h. After filtration from polymeric material and evaporation of the solvent, bulb-to-bulb distillation (140°/0.1 Torr) afforded **9** (50 mg, 28%).

Actinometry and Relative Rates of Consumption. The quantum yield for the conversion **2**→**4** (benzene, $\lambda = 366$ nm) was determined by UV spectroscopy using 8,8,9,9-tetramethyl-1,3,4,6,7,8-hexahydro-1,4-ethanonaphthalene-2,5-dione as chemical actinometer [2]. The relative rates of consumption of **3** *vs.* **1** in benzene soln. were measured by GC using decane as internal standard.

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