

139. The Photochemical Behaviour of 5,5-Dimethyl-2(5*H*)-furanone

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Summary

The photochemical behaviour of the title compound **2c** was investigated in various solvents. In benzene and *t*-butanol photodimerization affords the *cis-anti-cis* *HH*- and *HT*-dimers (H = head, T = tail). In acetonitrile, cyclohexane and 2-propanol, photoreduction competes with photodimerization. The photoreduction products are hydrodimers, solvent adducts and the saturated lactone (the 2H-reduction product). In acetonitrile and cyclohexane H-abstraction by the β -C-atom of the C=C bond is the predominant reduction process. In 2-propanol, solvent adducts to the α - and β -C-atoms are formed in equal amounts. In xanthone-sensitized irradiations the ratio of *HH*- to *HT*-dimer is the same as on direct irradiation and the relative rates of conversion of **2c** to products in different solvents are also similar under both conditions.

Irradiation of five-membered cyclic α,β -unsaturated carbonyl compounds, e.g. 2-cyclopentenones [1] [2], 2(5*H*)-furanones [3] [4] and 3(2*H*)-furanones [5] [6], in various solvents usually leads to the formation of tricyclic dimers containing a cyclobutane ring. In addition, H-abstraction from the solvent, either by the carbonyl O-atom or by the β -C-atom of the C=C bond affords solvent adducts, the saturated carbonyl compound and hydrodimers, all these reduction products stemming from the corresponding radical intermediates (*Scheme 1*).

For 2-cyclopentenones (**1**) the introduction of alkyl groups on C(3) or C(4) apparently has a pronounced influence on the reaction path, *i.e.* photodimerization *vs.* photoreduction²). Thus, irradiation of 2-cyclopentenone (**1a**) in toluene affords the *cis-anti-cis* *HH*- and *HT*-dimers³) exclusively, but 3-*t*-butyl-2-cyclopentenone (**1b**) gives only reduction products [2]. When irradiated neat 4,4-dimethyl-2-cyclopentenone (**1c**) affords dimers analogous to those of **1a** but already in *t*-BuOH, a rather poor hydrogen-donating solvent, the ratio of reduction products to dimers is 1:2 [9].

In this connection little is known about 2(5*H*)-furanones **2**. According to *Ohga & Matsuo* [3] [4] irradiation of **2a** in acetonitrile affords the *cis-anti-cis* *HH*- and

¹) Part of the planned doctoral thesis, University of Hamburg.

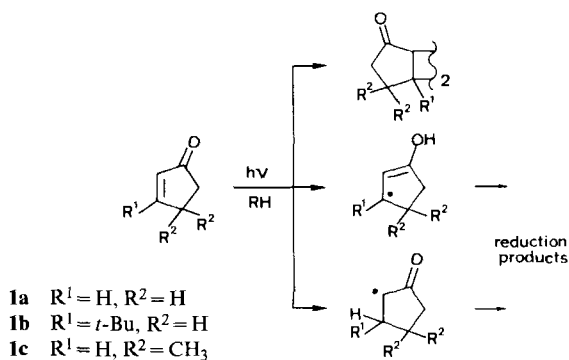
²) For a general discussion of the photoreduction of carbonyl compounds, *cf.* [7].

³) *HH*: head-to-head; *HT*: head-to-tail.

HT-dimers **3** and **4** in 20–30% overall yield, but no photoreduction products have been detected in these experiments. In 2-propanol **2a** and **2b** give the solvent adduct **5** at C(β)-atom exclusively [10], and in cyclohexane a 1:1 mixture of the solvent adducts at α -C- and β -C-atoms is obtained from **2a** [11] [12]. No other reduction products have been observed (*Scheme 2*).

To clarify the aspect of photodimerization *vs.* photoreduction for this class of compounds, we investigated the photochemical behaviour of 5,5-dimethyl-2(5*H*)-furanone (**2c**) in different solvents. Irradiation ($\lambda=254$ nm) of **2c** (10^{-2} – 10^{-1} M) in acetonitrile afforded a mixture of six products, the *cis-anti-cis* *HH*- and *HT*-dimers **3c** and **4c**, the diastereoisomeric hydrodimers **8c** and **9c**, the saturated lactone **10c** and the solvent adduct **11c**. Only the two dimers were formed when

Scheme 1



Scheme 2

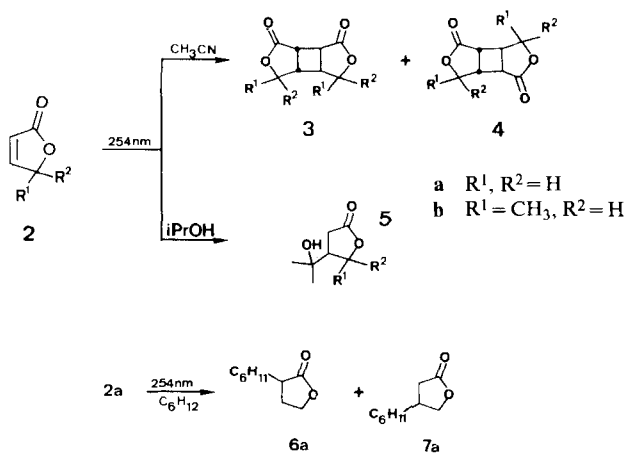


Table 2. Product distribution for irradiation ($\lambda = 254$ nm) of **2c** ($2 \cdot 10^{-2}$ M) in different solvents and relative reactivities

Solvent	Dimers		Reduction products					$R_{\alpha}H/10 + R_{\beta}H$		Relative degree of conversion
	3c	4c	8c	9c	10c	$R_{\alpha}H^a$	$R_{\beta}H^b$	2c	2a	
CH ₃ CN	16	16	15	15	12	25 (11c)	-	2.1	1.1 ^c	8
C ₆ H ₆	23	77	-	-	-	-	-	-	-	1
(CH ₃) ₃ COH	26	74	-	-	-	-	-	-	-	12
(CH ₃) ₂ CHOH	-	-	-	-	35	35 (13c)	30 (5c)	0.5	0.0 ^d	24
C ₆ H ₁₂ ^e	2	5	9	9	16	35 (6c)	5 (7c)	1.7	1.0 ^f	17

^a) Solvent adduct at α -C-atom. ^b) Solvent adduct at β -C-atom. ^c) This work, *Scheme 5*. ^d) [10].

^e) In addition 10% **12c** and 5% higher molecular weight products are formed. ^f) [11] and [12].

The spectroscopic data for photoproducts **3c-13c** are summarized in *Table 3*. In the ¹H-NMR spectra of dimers **3c** and **4c** and of hydrodimers **8c** and **9c** the $AA'XX'$ and $AA'BB'XX'$ systems, respectively, could be analyzed and the calculated coupling constants were successfully used to simulate these spectra. As neither **8c** nor **9c** could be resolved into enantiomers by GC on a chiral stationary phase, the assignment of D,L- or meso-configuration to **8c** and **9c** is tentative. The different coupling constants between the α -carbonyl protons of the two rings ($J(XX') = 8.4$ Hz for **8c** and 5.4 Hz for **9c**) also did not allow a clear decision. An easy way of differentiating between the solvent adducts at α -C- and β -C-atoms was based on the fact, that the geminal coupling constant for a CH₂-group in a five-membered ring α to a carbonyl group is larger than for a CH₂-group at β -position (16 vs. 12 Hz) [13].

Irradiation ($\lambda \geq 300$ nm) of **2c** (0.02 M) in the presence of xanthone (0.002 M) as sensitizer afforded the *HH*- and *HT*-dimers in the same ratio as above. The relative rates of conversion of **2c** in different solvents were also similar to those on direct irradiation (*Table 4*).

Irradiation of **2a** (10^{-2} M in CH₃CN, $\lambda = 254$ nm) afforded two solvent adducts **11a** and **14a** and the saturated lactone **10a** in addition to the dimers **3a** and **4a** (*Scheme 5*). The original experiments leading to the exclusive detection of dimers **3a** and **4a** had been performed in more concentrated (0.2-0.6 M) solutions [3]. In *Table 5* are summarized the relative reactivities for **2c** and **2a** on direct irradiation in acetonitrile and *t*-BuOH, and for **2c**, **2a**, cyclopentenones **1a** and **1c** and 2,2-dimethyl-3(2*H*)-furanone **15** in *t*-BuOH in the presence of xanthone as sensitizer.

From *Tables 1* and *2* it can be seen that the ratio of *HH/HT* dimers **3c/4c** varies with the polarity of the solvent, the *HH*-dimer **3c** being preferentially formed in the more polar solvent CH₃CN. This aspect has been observed and discussed for several cyclic α,β -unsaturated carbonyl compounds [1] [4] [6]. As expected, the ratio of dimers to reduction products increases with increasing concentration of **2c**.

Hydrodimers **8c** and **9c** are products either from dimerization of the radical formed by β -H-abstraction (**16c**) or from specific addition of **16c** to the α -C-atom of ground state **2c**, the highest yield being obtained in CH₃CN and no such products being detected in 2-propanol. The unsubstituted lactone **2a** did not give hydrodimers when irradiated in dilute CH₃CN-solution. A similar hydrodimer

formation has only been observed in toluene for cyclopentenones **1** bearing a bulky substituent ($R^1 = \text{CH}(\text{CH}_3)_2, \text{C}(\text{CH}_3)_3$) on C(3)-atom [2]. Although it is difficult to propose a rationale for these findings, it becomes obvious that for preparative purposes photochemical hydrodimerization is complementary to electrohydrodimerization, as in the latter reaction dicarbonyl compounds coupled *via* the β -C-atoms are formed exclusively [15].

Table 3. Spectroscopic data for photoproducts of **2c**

Compound	IR ^{a)}	MS	¹ H-NMR (CDCl ₃)
3c	1775	209 ($M^+ - \text{CH}_3$) 79	3.31 ($AA'XX'$, 4 H, $J(AX) = 6.5, J(AX') = -1.5,$ 2.94 ($J(AA') = 5.3, J(XX') = 1.9$) 1.43, 1.35 (4 CH ₃)
4c	1740 ^{b)}	224 (M^+) 209	3.40 ($AA'XX'$, 4 H, $J(AX) = 7.6, J(AX') = 2.8,$ 2.81 ($J(AA') = 3.2, J(XX') = 2.0$) 1.56, 1.39 (4 CH ₃)
5c	3500 1770	157 ($M^+ - \text{CH}_3$) 59	2.85 ($d \times d, J = 17.2$ and 12.8) 2.50 ($d \times d, J = 17.2$ and 8.0) 2.29 ($d \times d, J = 12.8$ and 8.0) 1.55, 1.46, 1.35, 1.26 (4 CH ₃)
6c	1765	181 ($M^+ - \text{CH}_3$) 114	2.69 ($d \times d \times d, J = 11.7, 9.3$ and 5.2) 2.03 ($d \times d, J = 12.5$ and 9.3) 1.84 ($d \times d, J = 12.5$ and 11.7) 1.44, 1.35 (2 CH ₃)
7c		196 (M^+) 110	
8c	1775	226 (M^+) 81	3.41 ($d \times d \times d, J = 12.2, 8.6$ and 8.4) 2.19 ($d \times d, J = 12.6$ and 8.6) 1.87 ($d \times d, J = 12.6$ and 12.2) 1.49, 1.42 (4 CH ₃)
9c	1775	226 (M^+) 43	3.08 ($d \times d \times d, J = 12.2, 8.6$ and 5.0) 2.43 ($d \times d, J = 12.6$ and 8.6) 1.87 ($d \times d, J = 12.6$ and 12.2) 1.48, 1.40 (4 CH ₃)
10c^{c)}	1775	114 (M^+) 43	2.60 (4 H, $J(\text{vic}) = 8.2$) 2.06 1.35 (2 CH ₃)
11c	2240 1770	138 ($M^+ - \text{CH}_3$) 43	3.06 ($d \times d \times d \times d, J = 12.0, 8.9, 8.4$ and 4.6) 2.81 ($d \times d, J = 17.3$ and 4.6) 2.59 ($d \times d, J = 17.3$ and 8.4) 2.41 ($d \times d, J = 12.7$ and 8.9) 1.95 ($d \times d, J = 12.7$ and 12.0) 1.48, 1.38 (2 CH ₃)
12c	1760	263 ($M^+ - \text{CH}_3$) 113	2.40 ($d \times d, J = 10.6$ and 2.4) 1.85 ($d \times d, J = 10.6$ and 2.4); 1.8–1.5 (22 H, cyclohexyl) 1.43 (2 CH ₃)
13c	3500 1760	157 ($M^+ - \text{CH}_3$) 59	2.93 ($d \times d, J = 12.2$ and 9.4) 2.13 ($d \times d, J = 12.6$ and 9.4) 1.84 ($d \times d, J = 12.6$ and 12.2) 1.46, 1.37, 1.25, 1.22 (4 CH ₃)

a) In CCl₄. b) In KBr. c) Cf. [14].

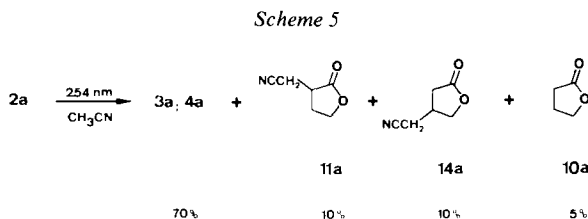
Table 4. Ratio of dimers **3c/4c** and relative reactivity of **2c** ($2 \cdot 10^{-2} \text{M}$) in different solvents on sensitized irradiations (xanthone, $2 \cdot 10^{-3} \text{M}$, $\lambda \geq 300 \text{nm}$)

	CH ₃ CN	C ₆ H ₆	(CH ₃) ₃ COH	(CH ₃) ₂ CHOH	C ₆ H ₁₂
3c/4c	50:50	25:75	25:75	–	33:66
Relative degree of conversion	8	1	10	120	68

Table 5. Relative reactivity (photodimerization) for five-membered cyclic enones

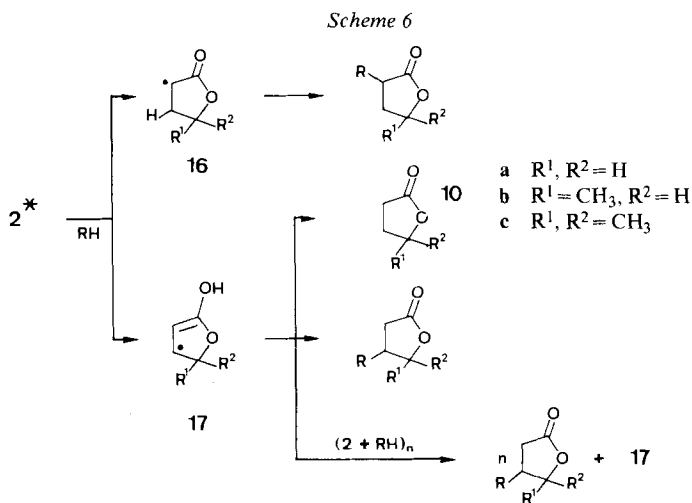
Experimental conditions	Relative degrees of conversion				
	2c	2a	1a	1c	15
10^{-1}M in CH ₃ CN, $\lambda = 254 \text{nm}$	1	:	4		
$2 \cdot 10^{-2} \text{M}$ in <i>t</i> -BuOH, $\lambda = 254 \text{nm}$	1.9	:	1		
10^{-2}M and xanthone ($3 \cdot 10^{-2} \text{M}$) in <i>t</i> -BuOH, $\lambda \geq 300 \text{nm}$	1.8	:	1	:	4.3 : 2.4 : 3.5

a) > 99% light absorbed by sensitizer.



The result that **2c** gave a much higher proportion of the solvent adduct at α -C-atom and also more saturated lactone **10** than **2a** on direct irradiation is easier to explain. If the only key steps for the formation of these products would be H-abstraction by either the β -C-atom (formation of **16**) or by the carbonyl O-atom (formation of **17**), one should rather expect the opposite, as the approach of the H-donor to β -C-atom in **2c** is more hindered by the adjacent CH₃-groups. This leads to the assumption that **2c** and **2a** undergo both types of H-abstraction in equal proportion and that **17** undergoes a free-radical chain reaction with **2** and the solvent to afford solvent adduct at β -C-atom (such a chain mechanism has been proposed to explain the quantum yields exceeding unity for the addition of 2-propanol to **2a** or **2b** giving exclusively the solvent adduct **5** [10]), and therefore the necessary conclusion that this propagation step occurs less efficiently (or not at all) for **17c**. The direct coupling of **17** with a radical R \cdot is less favourable for **17c** than for **17a** owing to the steric hindrance by the CH₃-groups and therefore more 2 H-reduction product **10c** is formed from **2c** than **10a** from **2a** (Scheme 6).

The results of the xanthone sensitized experiments with **2c** summarized in Table 4 can be interpreted as follows. As the ratios of *HH*- to *HT*-dimer in the different solvents in the sensitizing experiments are the same as on direct irradiation, it can be assumed that these products are formed *via* the same triplet (T_1) state. For **2b** this triplet reaction has been further supported by quenching experiments with 1,3-pentadiene [4]. In cyclohexane and 2-propanol the xanthone-sensitized reaction proceeds much faster (relative to benzene) than on direct irradiation. This



is probably due to an enhanced formation of intermediate **17c** via H-transfer to the carbonyl O-atom of **2c** by the radical formed from excited xanthone through H-abstraction from the solvent, thus accelerating the free-radical chain reaction described in *Scheme 6*.

Photodimerization of cyclic enones is known to be a multistep process [1] [6] [16]. Whereas a comparison of reactivities of excited enones toward one alkene (or of one enone towards different alkenes) under constant experimental conditions (solvent, concentration, temperature) using an appropriate kinetic scheme [17] [18] is feasible, an extension to photodimerization reactions, e.g. comparing **2b** and **1a** [4], is problematic, as reactivities of various excited molecules toward *different* ground state partners are now compared. Comparing sensitized photodimerizations is obviously even more delicate, as the efficiencies for energy transfer from e.g. triplet xanthone to the different enones are not necessarily alike. The data in *Table 5* merely emphasize the complexity of enone photodimerization, as illustrated by either the fact that on direct irradiation the relative reactivities of lactones **2a** and **2c** invert in changing the solvent from acetonitrile to *t*-BuOH, or by the result that in the sensitized irradiation the 4,4-dimethyl compound **1c** is converted to dimers more slowly than **1a**, as expected on steric arguments, but that lactones **2c** and **2a** show the opposite behaviour.

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Experimental Part

General. Absorptions in the IR spectra are given in cm^{-1} . Chemical shifts in the ^1H -(400 MHz)-NMR spectra are given in ppm relative to TMS (=0 ppm) as internal standard. The GC/MS analyses were carried out on a *Varian MAT CH7* instrument at 70 eV using a 2-m column of 3% *SE 30* on 80/100 *Suppelcoport*.

Starting materials. Furanones **2a** [19] and **2c** [20], cyclopentenone **1c** [17] and 3(2*H*)-furanone **15** [21] were synthesized according to the references indicated. Cyclopentenone **1a** was purchased from Aldrich. All solvents used for photolyses were of spectral grade.

Photolyses. a) Direct irradiations: Ar-degassed solutions of **2c** were irradiated in quartz tubes, either in a Rayonet RPR-100 photoreactor or in a merry-go-round apparatus (Applied Photophysics), with light of $\lambda = 254$ nm. b) Sensitized irradiations: Ar-degassed solutions were irradiated in Pyrex tubes in the photoreactors mentioned above with light of $\lambda \geq 300$ nm.

*Direct ($\lambda = 254$ nm) irradiation of **2c**.* - a) **1M** in acetonitrile. A solution of 224 mg **2c** in 2 ml was irradiated for 12 h. After evaporation of the solvent the solid residue (**3c** and **4c**, 1:1) was dissolved in 1 ml acetone. Slow addition of 1 ml pentane precipitated **4c**. The white crystals were filtered, washed with pentane yielding 90 mg (40%) *cis-anti-cis*-5,5,10,10-tetramethyl-4,9-dioxatricyclo[5.3.0.0^{2,6}]decane-3,8-dione (**4c**, m.p. 248–250°). The filtrate was evaporated and the residue recrystallized 4 times from pentane to afford pure *cis-anti-cis*-5,5,8,8-tetramethyl-4,9-dioxatricyclo[5.3.0.0^{2,6}]decane-3,10-dione (**3c**, m.p. 152–155°).

b) $2 \cdot 10^{-2}$ M in acetonitrile. A solution of 67.2 mg **2c** in 30 ml was irradiated for 3 h. After evaporation of the solvent, **4c** was precipitated by addition of 2 ml acetone/pentane 1:1 and **3c** by adding additional 2 ml pentane. Chromatography of the filtrate on SiO₂ (Et₂O/pentane 2:1) afforded **10c** (cf. d)) and 3-cyanomethyl-5,5-dimethyl-3,4-dihydro-2(5*H*)-furanone (**11c**, *R_f* 0.3, oil). Elution with Et₂O/pentane 9:1 afforded racemic 3-[2-oxo-5,5-dimethyl-3,4-dihydro-(5*H*)-3-furyl]-5,5-dimethyl-3,4-dihydro-2(5*H*)-furanone (**8c**, *R_f* 0.8, m.p. 164–165°) and the *meso* hydrodimer **9c** (*R_f* 0.4, slightly contaminated with dimer **4c**).

c) $2 \cdot 10^{-2}$ M in benzene or *t*-BuOH. A mixture of **3c** and **4c** was obtained (1:3 by ¹H-NMR).

d) $2 \cdot 10^{-2}$ M in 2-propanol. Irradiation of 67.2 mg in 30 ml for 3 h afforded a mixture of **10c**, **13c** and **5c** (35:35:30 by ¹H-NMR). Chromatography on SiO₂ (CH₂Cl₂/AcOEt 2:1) afforded 5,5-dimethyl-3,4-dihydro-2(5*H*)-furanone (**10c**, *R_f* 0.8, oil), 3-(2-hydroxy-2-methyl)ethyl-5,5-dimethyl-3,4-dihydro-2(5*H*)-furanone (**13c**, *R_f* 0.7, m.p. 72–74°), and the 4-substituted compound **5c** (*R_f* 0.5, oil).

e) $2 \cdot 10^{-2}$ M in cyclohexane. Irradiation of 67.2 mg in 30 ml for 3 h, evaporation of the solvent, addition of 3 ml pentane, filtration of the precipitate (dimers **3c** and **4c** and hydrodimers **8c** and **9c**) and chromatography on SiO₂ (hexane/AcOEt 2:1) afforded *trans*-3,4-dicyclohexyl-5,5-dimethyl-3,4-dihydro-2(5*H*)-furanone (**12c**, *R_f* 0.8, oil), traces of the *cis*-compound (*R_f* 0.7, oil. - IR: 1775. - MS: 263 (*M*⁺ - CH₃), 113), 3-cyclohexyl-5,5-dimethyl-3,4-dihydro-2(5*H*)-furanone (**6c**, *R_f* 0.6, m.p. 69–71°), the 4-cyclohexyl compound **7c** (*R_f* 0.5, oil) and **10c** (cf. d)).

*Direct ($\lambda = 254$ nm) irradiation of **2a** (10^{-2} M) in acetonitrile.* GC/MS analysis indicated the formation of 3,4-dihydro-2(5*H*)-furanone **10a** (5%, *M*⁺ = 86), of 3- and 4-cyanomethyl-3,4-dihydro-2(5*H*)-furanone **11a** (10%, *M*⁺ = 125) and **14a** (10%, *M*⁺ = 125) in addition to the known dimers **3a** and **4a** (70%).

*Sensitized irradiation ($\lambda \geq 300$ nm) of **2c**.* After irradiation of **2c** (10^{-2} M) and xanthone (10^{-3} M) in the different solvents, the ratios of dimers **3c/4c** were determined by ¹H-NMR. The relative rates of conversion of starting material were monitored by GC using undecane as internal standard.

Comparative irradiations. Solutions of **2a** and **2c** (10^{-1} M in acetonitrile or $2 \cdot 10^{-2}$ M in *t*-BuOH) or solutions of **1a**, **1c**, **2a**, **2c** and **15** (10^{-2} M) and xanthone ($3 \cdot 10^{-2}$ M) were irradiated in the merry-go-round apparatus and the degree of conversion measured by GC.

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