Photoreactions of Enones with Amines – Cyclization of Unsaturated Enones and Reductive Ring Opening by Photoinduced Electron Transfer (PET)[1]☆

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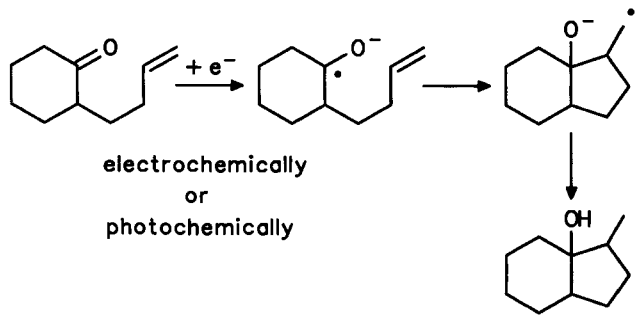
Photolysis of the unsaturated enones **1** yields [2 + 2] cycloaddition products **2** and **3** with varying regioselectivity. Under electron-transfer conditions (PET) spirocyclic products **4** are formed. The *straight* [2 + 2] cycloaddition products **2b,c,f** are converted to the spirocyclic products **4b,c,f** under the same reaction conditions. The cyclobutane **5** and the cyclopropane **11** also undergo this new reductive ring opening reaction, while the stabilized system **7** is converted to reduced ring-enlarged triquinane **10** which may be interesting in natural product synthesis. – Irradiation of 2-cyclohexen-1-one (**14**) in the presence of *N,N*-dimethylallylamine (**15**) leads to the decahydroisoquinoline **18**. A mechanism involving radical intermediates is discussed.

Radical reactions have opened a wide scope of applications in organic synthesis[5] and radical cyclizations are well documented[6]. Cyclization of radical anions can be achieved electrochemically[7] as well as by photochemically[8] induced electron transfer (Scheme 1).

Scheme 1



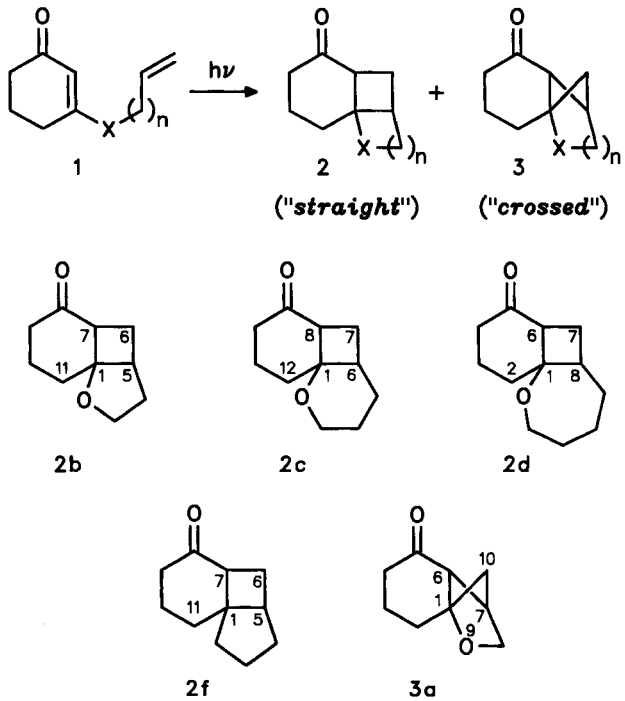
On the other hand, radical reactions have been used for reductive ring opening processes of strained systems[9] leading to medium-sized rings.

We now report on the cyclization of olefinic enones, which yields new spirocyclic compounds[10], and on the reductive ring opening of strained systems, both induced by photoinduced electron transfer (PET).

1. Unsaturated Enones: Intramolecular [2 + 2] Cycloaddition and Formation of Spirocyclic Products

3-(Alkenyloxy)-2-cyclohexen-1-ones and 3-alkenyl-2-cyclohexen-1-ones (**1a–g**) are readily accessible with variable length of the side chain. The enone moiety is easily excited and deactivation by twisting of the C–C double bond is hindered by the cyclic structure[11]. The intramolecular [2 + 2] cycloaddition of these compounds has been extensively studied in particular concerning its regioselectivity, which is influenced by the chain length as well as by substituents[12].

Scheme 2



[+] New address: c/o Bayer AG, LS-P, D-5090 Leverkusen Bayerwerk.

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Regiochemical orientation and yields of intramolecular [2+2] cycloaddition products obtained by irradiation of compounds **1a–g** in the absence of a donor are presented in Table 1. The mode of cycloaddition, *straight* versus *crossed* (Scheme 2), has been assigned by NMR analysis of the isolated products **2b–d**, **2f** and **3a**.

Table 1. Yields of [2 + 2] cycloadducts in the absence of a donor[a]

Enone	X	n	[2+2] Cycloadduct	Yield [b]
1a	O	1	**3a** (crossed)	46 % [c]
1b	O	2	**2b** (straight)	82 %
1c	O	3	**2c** (straight)	65 %
1d	O	4	**2d** (straight)	25 %
1e	CH_2	1	mixture 55 %, 22 %, 20 % [d,e]	
1f	CH_2	2	**2f** (straight)	90 % [f]
1g [g]	CH_2	3	mixture 60 %, 15 %, 15 % [d]	

[a] Irradiation of a 0.1 M solution in CH_3CN with a Philips HPK 125 W lamp. – [b] Isolated yield; no other product >5% detected by GLC. – [c] In accordance with a previous report[13]. – [d] Yield determined by GLC with internal standard. – [e] Wolff and Agosta[14] report a *cis*-fused *straight* product as well as *cis*- and *trans*-fused *crossed* products. – [f] In accordance with a previous report[15]. – [g] GLC-MS shows 20% of an isomeric compound with similar boiling point.

Irradiation in the presence of the donor triethylamine yields new spirocyclic products (Scheme 3). The formation of five- and six-membered rings is restricted by the length of the side chain, while short as well as long chains exclusively yield the [2 + 2] cycloaddition products. In Table 2 are compiled the yields of the spirocyclic compounds **4b**, **c** and **f** obtained by irradiation of **1b,c** and **f** in the presence of triethylamine. In all other cases no new products exceeding 5% yield can be detected by GLC in addition to the [2 + 2] cycloadducts.

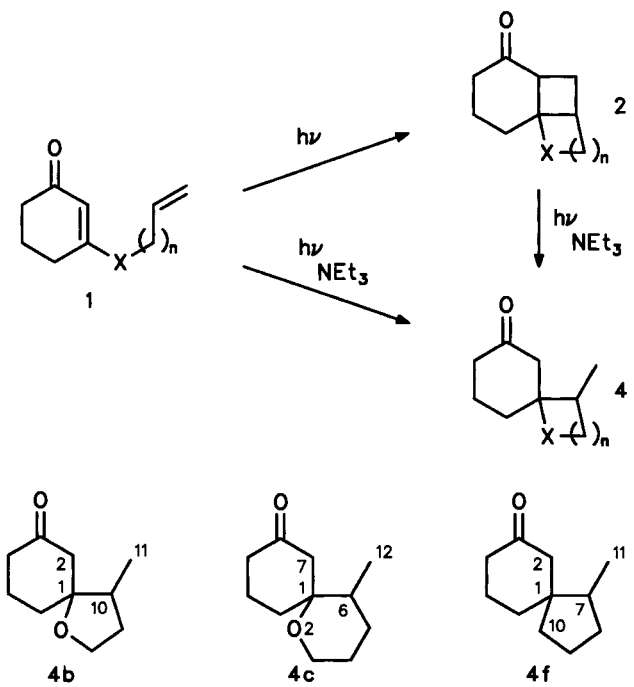
Table 2. Yields of spirocyclic products upon irradiation in the presence of NEt_3[a]

Enone	X	n	Spirocyclic Product	Yield [b]
1b	O	2	**4b**	50 %
1c	O	3	**4c**	53 %
1f	CH_2	2	**4f**	40 %

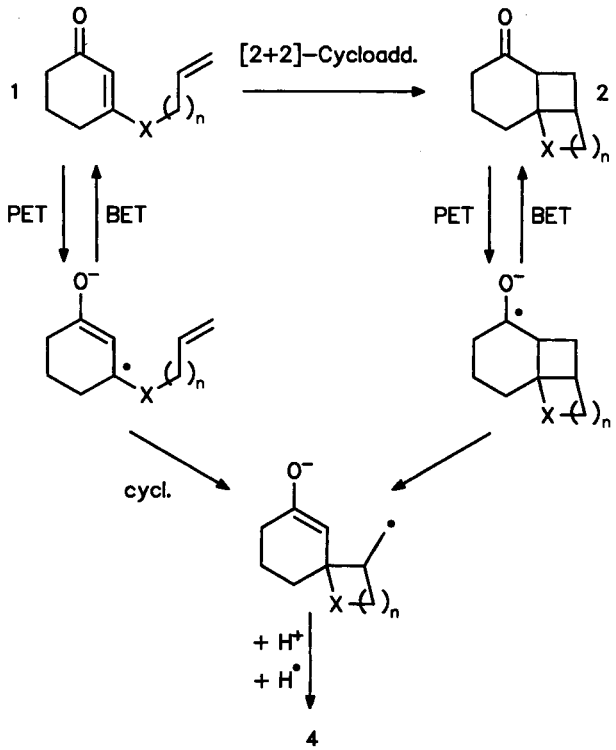
[a] A 0.5 mM solution of the starting material in CH_3CN containing triethylamine (0.5 mM) and *n*-decane (internal standard) sealed in Duran glass tubes under argon was irradiated in a Rayonet reactor fitted with a merry-go-round inset. – [b] Yields were determined by GLC with an internal standard.

The [2 + 2] cycloaddition products **2b**, **c** and **f**, initially formed as side products when irradiating **1b,c** and **f** in the presence of NEt_3, are consumed during prolonged irradiation. This indicates that conversion of the [2 + 2] cycloadducts **2** to the spirocyclic products **4** takes place under these reaction conditions (Scheme 3). Indeed, irradiation of pure isolated [2 + 2] cycloaddition products **2b,c** and **f** in the presence of NEt_3 leads to the spirocyclic products **4b,c** and **f** (see Scheme 3 and Table 3). The [2 + 2] cycloadducts **3a**, **2d** and the mixtures **2/3e** and **g** (Table 1), however, cannot be converted to the corresponding spirocyclic compounds by this method.

Scheme 3



Scheme 4. Reaction pathways leading to spiro product formation (PET = photoinduced electron transfer, BET = back electron transfer)



The mechanism presented in Scheme 4 shows two possible pathways for the conversion of olefinic enones **1** to spirocyclic products **4**, both involving electron-transfer steps. The time dependence of product formation (Figure 1) indicates that direct cyclization of **1** to **4** is of minor importance only, while spiro-product formation almost entirely takes place by [2 + 2] cycloaddition with subsequent reductive ring opening. This is further supported by the exclusive formation of one stereoisomer only, as discussed more detailed in the following chapter.

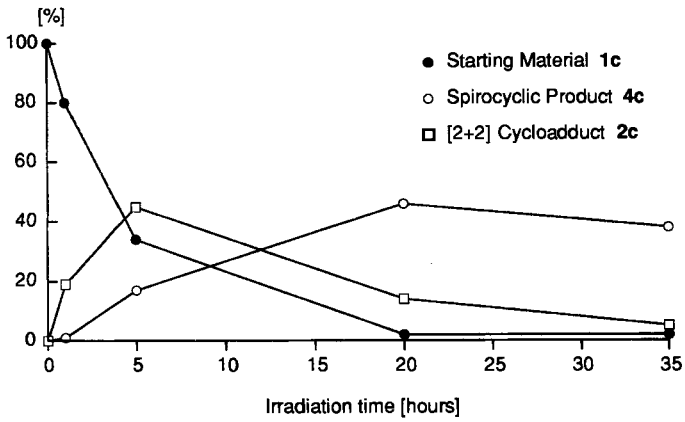
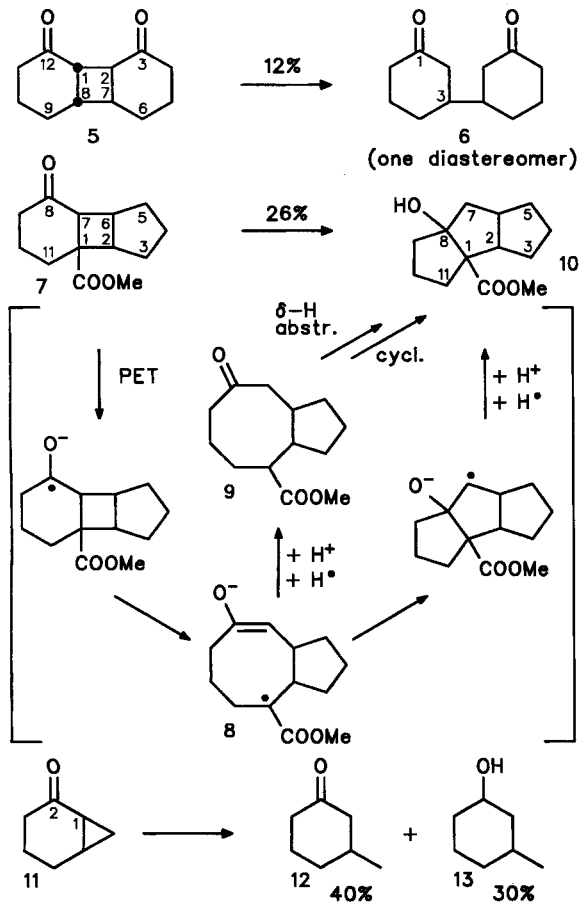


Figure 1. Time dependence of yields of **2c** and **4c** on irradiation of **1c** in the presence of NEt_3 at 300 nm

Scheme 5



2. Reductive Ring Opening of Anellated Cyclobutanes and Cyclopropanes

The new reductive ring cleavage reaction (**2** → **4**) can be extended to other ring systems with a carbonyl group in α-position to a strained ring (Scheme 5 and Table 3)[16,17].

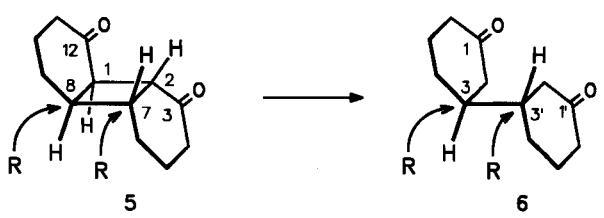
Table 3. Reductive ring cleavage by irradiation in the presence of NEt_3[a]

Starting Material	Ring-Opened Product	Yield [b]
2b	**4b**	80 %
2c	**4c**	60 %
2f	**4f**	40 %
5	**6**	12 %
7	**10**	26 %
11	**12** [c]	40 %

[a] A 0.5 mM solution of the starting material in CH_3CN containing triethylamine (0.5 mM) and *n*-decane (internal standard) sealed in Duran glass tubes under argon were irradiated in a Rayonet reactor fitted with a merry-go-round inset. — [b] Yields were determined by GLC with internal standard. — [c] In addition 30% of 3-methylcyclohexanol (**13**) is formed.

The two main photodimers of 2-cyclohexen-1-one, the head-to-head and head-to-tail *cis-anti-cis* isomers, are easily accessible by irradiation of neat 2-cyclohexen-1-one and subsequent chromatographic separation[18]. While reductive ring opening of isolated head-to-tail isomer by irradiation in the presence of NEt_3 has not been successful (no products in excess of 5% found by GLC), the pure head-to-head isomer **5** has been converted to 3,3′-bicyclohexanone (**6**) in 12% yield by this method. Direct irradiation of 2-cyclohexen-1-one in the presence of triethylamine not only leads to the dimerization, reduction, and addition products[19], but also yields two diastereomeric 3,3′-bicyclohexanones[20] (yields obtained under our reaction conditions are 5% each). The reduced dimer **6** obtained by reductive ring opening of **5** corresponds to the 3,3′-bicyclohexanone with the higher GLC retention time. The reason why only one diastereomer is formed by reductive ring opening is that the relative configuration of the two asymmetric C atoms is already fixed in the 2-cyclohexen-1-one dimer **5**. As shown in the formula the relative configuration of **6** must therefore be (3*RS*,3′*RS*).

Assuming almost certainly *cis*-anellated cyclohexane rings in compounds **2b**, **2c**, and **2f** one can analogously deduce the relative configurations (1*RS*,10*RS*), (1*RS*,6*RS*) and (1*RS*,7*RS*) for the ring-opened products **4b**, **4c**, and **4f**, respectively.



The fact that only one diastereomer is formed here as well, is a further indication that the spirocyclic products might be exclusively formed by [2 + 2] cycloaddition followed by reductive ring opening.

Methyl 8-oxotricyclo[5.4.0.0^{2,6}]undecane-1-carboxylate (**7**)[21] contains an additional ester group. The stabilization of a radical in the position 1 by the ester group, as in the intermediate **8** (Scheme 5), now controls the regioselectivity of the β-cleavage reaction. Thus, the opening of the 1,7-C–C bond is enhanced, leading to ring-expanded products. However, in contrast to the radical ring expansion of a similar compound to give eight-membered rings[9], a rearranged ring system **10** is formed in 26% yield (Scheme 5). The formation of this linearly fused triquinane may proceed via **9** with subsequent δ-H abstraction and cyclization, or by direct cyclization of the intermediate radical **8**, as indicated in Scheme 5. Further experimental studies are necessary to ascertain the mechanism and to assess the scope of this reaction.

Bicyclo[4.1.0]heptan-2-one (**11**, Scheme 5) has an increased strain in the three-membered ring. Reductive ring opening of **11** by irradiation in the presence of NEt_3 leads to 3-methylcyclohexanone (**12**) in 40% yield, as independently reported by Cossy[16]. In addition, the two diastereomeric 3-methylcyclohexanols are formed in 15% yield each.

3. Photoinduced Addition of *N,N*-Dimethylallylamine to Cyclohexenone: A New Approach to the Decahydroisoquinoline System

The results on the cyclization of unsaturated enones (Chapter 1) have prompted us to study similar bimolecular photoreactions of 2-cyclohexen-1-one with *N,N*-dimethylallylamine as an unsaturated electron donor. Pienta[19], Schuster[20], and Mariano[34] have already reported on the addition of amines to cyclic enones by PET. However, no unsaturated amines have been found to be involved in these examples. The only comparable case has recently been published by Zhang and Mariano[35] with *N,N*-dimethylaniline as an electron donor.

Direct irradiation (λ > 300 nm) of 2-cyclohexen-1-one (**14**) in the presence of *N,N*-dimethylallylamine (**15**) leads to 2,4β-dimethyl-*cis*-decahydro-5-isoquinolinone (**18**) in yields up to 20%, depending on the polarity of the medium (Table 4)[3].

We assume a PET between the excited enone and amine followed by deprotonation of the amine radical cation (Scheme 6). The derived α-aminoalkyl radical **16** is suggested to react with the ground-state enone to form the α-keto radical **17** which can undergo efficient radical cyclization to form the heterocyclic compound **18**. Hydrogen transfer from excess amine may regenerate the starting α-aminoalkyl radical **16**.

In polar solvent like CH_3CN containing 10% H_2O this PET-promoted addition-cyclization process competes effectively with [2 + 2] cycloaddition pathways leading to dimers of **14**.

Scheme 6. Proposed mechanism of the photoinduced addition of *N,N*-dimethylallylamine to 2-cyclohexen-1-one

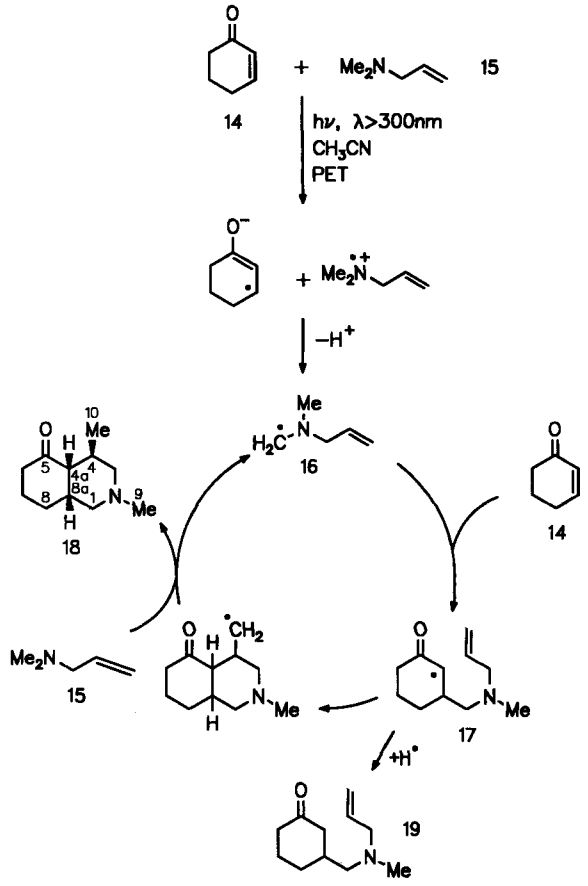


Table 4. Solvent effects on the product yields[a] in various photoadditions[3] of *N,N*-dimethylallylamine (**15**) to 2-cyclohexen-1-one (**14**)

Solvent	**18**	**19**	[2+2] dimers of **14**	cyclohexanone
Cyclohexane	2.6 %	traces	3.5 %	
THF	8.2 %	3.9 %	2.9 %	
MeOH; 20 °C	7.6 %	traces	5.5 %	
MeOH; - 25 °C	5.8 %	3.3 %	2.4 %	
MeOH; - 70 °C	3.7 %	10.4 %	traces	
CH_3CN	3.0 %	traces	2.1 %	
CH_3CN; 0.1 eq. $LiClO_4$	7.4 %	traces	traces	7.5 %
CH_3CN; DCN; λ > 350 nm	traces	3.8 %	2.2 %	
CH_3CN / 10 % H_2O	20.0 %	traces	traces	

[a] Yields determined by capillary GLC at 100% conversion.

Under conditions which favor the separation of the radical ion pair arising from PET (addition of $LiClO_4$, "special salt effect"[36]) yields are diminished. At the same time the yield of cyclohexanone increases indicating reduction of the enone radical anion. Low temperatures reduce effective cyclization of the α-keto radical **17**. Hydrogen transfer leads to the monocyclic adduct **19**.

Upon irradiation in the presence of PET sensitizers such as 1,4-dicyanonaphthalene (DCN) only traces of products are formed.

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Experimental

IR: Shimadzu IR-408. – ^{1}H-NMR: Bruker WM 300 (300 MHz), Varian VXR-300 (300 MHz). – ^{13}C-NMR: Bruker WM 300 (75 MHz), Varian VXR 300 (75 MHz): – MS: Varian MAT CH 7A (GLC-MS coupling) or Finnigan MAT 312. – HPLC: Kontron pump 420, RI detector Bischoff RI 8110, column 250 × 20 mm, LiChrosorb Si 60-5 (Fa. Merck). – Column chromatography: Merck Kieselgel 60, Art. 7734. – GLC: Siemens Sichromat 3 with FID detector and Spectra physics integrator SP 4290 or Siemens Sichromat 4 with FID detector and Spectra physics integrator SP 4400, capillary column Hewlett Packard Ultra 2.

3-(ω-Alkenyloxy)-2-cyclohexen-1-ones **1a–d** – *General Procedure:* 20 g (0.18 mol) of 1,3-cyclohexanedione (Janssen), 0.6 g (3 mmol) of *p*-toluenesulfonic acid, 0.20 mol of the respective ω-unsaturated alcohol, and 250 ml of cyclohexane are refluxed in a Dean-Stark-type apparatus for 36 h. The resulting solution is dried with magnesium sulfate, and the solvent is removed. The crude product is then distilled under reduced pressure.

3-(Allyloxy)-2-cyclohexen-1-one (**1a**)[12f]: 40 g (0.36 mol) of 1,3-cyclohexanedione and 44 ml (38 g; 0.65 mol) of allyl alcohol yield 29.9 g (53%) of **1a**; b.p. 48°C/0.1 Torr. – IR ($CDCl_3$): $\tilde{\nu}$ = 3080 cm^{-1}, 3020, 2950, 2900, 2880, 2840, 1655, 1605. – UV (CH_3CN): λ_{max} (lg ε) = 243 nm (4.229), 303 (1.851). – ^{1}H NMR ($CDCl_3$): δ = 1.99 (quint, *J* = 6.5 Hz, 2H, 5-H), 2.34 (t, *J* = 6.5 Hz, 2H, 4-H), 2.45 (t, *J* = 6.5 Hz, 2H, 6-H), 4.38 (d/t, *J* = 5.5/1.5 Hz, 2H, 1′-H), 5.31 (d/m, *J* = 10.5 Hz, 1H, 3′-H, *cis*), 5.36 (s, 1H, 2-H), 5.38 (d/m, *J* = 17 Hz, 1H, 3′-H, *trans*), 5.97 (d/d/t, *J* = 17/10.5/5 Hz, 1H, 2′-H). – ^{13}C NMR ($CDCl_3$): δ = 21.2 (CH_2), 29.0 (CH_2), 36.8 (CH_2), 69.1 (C-1′), 103.1 (C-2), 118.8 (C-3′), 131.5 (C-2′), 177.3 (C-3), 199.4 (C-1). – MS (70 eV): *m/z* (%) = 153 (4.8) [M^+ + 1], 152 (36.2) [M^+], 124 (28.8) [M^+ – CO], 96 (90.9), 95 (21.2), 84 (15.3), 83 (21.6), 82 (27.6), 81 (16.2), 69 (100), 68 (18.2), 67 (14.1), 56 (11.9), 55 (31.8), 54 (17.0).

$C_9H_{12}O_2$ (152.2) Calcd. C 71.03 H 7.95
Found C 71.01 H 7.85

3-(3-Butenyloxy)-2-cyclohexen-1-one (**1b**): In addition to literature procedures treating allylmagnesium bromide with paraformaldehyde[22], 3-buten-1-ol is accessible by hydrolysis of 4-bromo-1-buten: 10 g (74 mmol) of 4-bromo-1-butene (see below) is stirred with 6.5 g (74 mmol) of sodium carbonate and 100 ml of water. Refluxing for 15 h gives a clear solution which is extracted 5 times with ether. Drying of the combined extracts with magnesium sulfate and removal of the solvent by distillation yield 2.4 g (45%) of GLC-pure product. 20 g (0.18 mol) of 1,3-cyclohexanedione and 13 g (0.18 mol) of 3-buten-1-ol give 19 g (63%) of product **1b** according to the general procedure; b.p. 60°C/0.1 Torr. – IR ($CDCl_3$): $\tilde{\nu}$ = 3080 cm^{-1}, 2950, 2900, 2840, 1670, 1650, 1645, 1605. – UV (CH_3CN): λ_{max} (lg ε) = 243 nm (4.233), 294 (1.886). – ^{1}H NMR ($CDCl_3$): δ = 1.98 (quint, *J* = 6.5 Hz, 2H, 5-H), 2.33 (t, *J* = 6.5 Hz, 2H, 4-H), 2.41 (t, *J* = 6.5 Hz, 2H, 6-H), 2.49 (q/t, *J* = 7/1.5 Hz, 2H, 2′-H), 3.89 (t, *J* = 6.5 Hz, 2H, 1′-H), 5.10 (d/m, *J* = 10 Hz, 1H, 4′-H, *cis*), 5.14 (d/m, *J* = 17 Hz, 1H, 4′-H, *trans*), 5.35 (s, 1H, 2-H), 5.82 (d/d/t, *J* = 17/10/6.5 Hz, 1H, 3′-H). – ^{13}C NMR ($CDCl_3$): δ = 21.2 (CH_2), 27.0 (CH_2), 32.8 (CH_2), 36.7 (CH_2), 67.5 (C-1′), 102.8 (C-2), 117.5 (C-4′), 133.6 (C-3′), 177.8 (C-3), 199.6 (C-1). – MS (70 eV): *m/z* (%) = 167 (2.4) [M^+ + 1], 166 (16.8) [M^+], 110 (21.8), 96 (17.9), 94 (11.4), 84 (21.2), 69 (18.2), 55 (100), 54 (53.4).

$C_{10}H_{14}O_2$ (166.2) Calcd. C 72.26 H 8.49
Found C 71.51 H 8.26

3-(4-Pentenyloxy)-2-cyclohexen-1-one (**1c**): 4-Penten-1-ol is accessible via tetrahydrofurfuryl chloride[23] by a literature procedure[24]. 20 g (0.18 mol) of 1,3-cyclohexanedione and 17 g (0.20 mol) of 4-penten-1-ol give 27.3 g (84%) of **1c** according to the general procedure; b.p. 95°C/0.1 Torr. – IR ($CDCl_3$): $\tilde{\nu}$ = 3080 cm^{-1}, 2950, 2890, 1665, 1650, 1605. – UV (CH_3CN): λ_{max} (lg ε) = 244 nm (4.201), 294 (1.892). – ^{1}H NMR ($CDCl_3$): δ = 1.83 (quint, *J* = 7 Hz, 2H, 2′-H), 1.93 (quint, *J* = 6.5 Hz, 2H, 5-H), 2.18 (q, *J* = 7 Hz, 2H, 3′-H), 2.34 (t, *J* = 6.5 Hz, 2H, 4-H), 2.41 (t, *J* = 6.5 Hz, 2H, 6-H), 3.82 (t, *J* = 7 Hz, 2H, 1′-H), 4.98 (m, 1H, 5′-H), 5.50 (m, 1H, 5′-H), 5.34 (s, 1H, 2-H), 5.78 (d/d/t, *J* = 17/10/6.5 Hz, 1H, 4′-H). – ^{13}C NMR ($CDCl_3$): δ = 21.3 (CH_2), 27.7 (CH_2), 29.0 (CH_2), 30.0 (CH_2), 36.8 (CH_2), 67.7 (C-1′), 102.7 (C-2), 115.5 (C-5′), 137.2 (C-4′), 177.8 (C-3), 199.5 (C-1). – MS (70 eV): *m/z* (%) = 181 (4.3) [M^+ + 1], 180 (26.5) [M^+], 124 (12.5), 123 (15.7), 113 (11.1), 110 (43.6), 85 (16.4), 84 (33.5), 69 (29.1), 68 (100), 67 (56.5), 55 (12.7).

$C_{11}H_{16}O_2$ (180.2) Calcd. C 73.30 H 8.95
Found C 73.14 H 8.87

3-(5-Hexenyloxy)-2-cyclohexen-1-one (**1d**): 11.5 g (0.10 mol) of 1,3-cyclohexanedione and 10 g (0.10 mol) of 5-hexen-1-ol give 9 g (46%) of **1d** according to the general procedure; b.p. 85–90°C/0.03 Torr. – IR ($CDCl_3$): $\tilde{\nu}$ = 3080 cm^{-1}, 2950, 2895, 1665, 1655, 1605. – UV (CH_3CN): λ_{max} (lg ε) = 244 nm (4.210), 296 (1.792). – ^{1}H NMR ($CDCl_3$): δ = 1.51 (quint, *J* = 7 Hz, 2H, 3′-H), 1.74 (quint, *J* = 7 Hz, 2H, 2′-H), 1.98 (quint, *J* = 6 Hz, 2H, 5-H), 2.09 (q, *J* = 7 Hz, 2H, 4′-H), 2.34 (t, *J* = 7 Hz, 2H, 4-H), 2.41 (t, *J* = 6 Hz, 2H, 6-H), 3.83 (t, *J* = 6 Hz, 2H, 1′-H), 4.98 (d, *J* = 10 Hz, 1H, 6′-H, *cis*), 5.03 (d, *J* = 17 Hz, 1H, 6′-H, *trans*), 5.35 (s, 1H, 2-H), 5.80 (d/d/t, *J* = 17/10/7 Hz, 1H, 5′-H). – ^{13}C NMR ($CDCl_3$): δ = 20.2 (CH_2), 24.1 (CH_2), 26.9 (CH_2), 27.8 (CH_2), 32.2 (CH_2), 35.6 (CH_2), 67.1 (C-1′), 101.4 (C-2), 113.7 (C-6′), 137.0 (C-5′), 176.5 (C-3), 197.5 (C-1). – MS (70 eV): *m/z* (%) = 194 (12) [M^+], 113 (38), 95 (10), 85 (26), 84 (49), 83 (14), 82 (30), 69 (18), 67 (72), 55 (100), 54 (74), 43 (10), 41 (72).

$C_{12}H_{18}O_2$ (194.3) Calcd. C 74.19 H 9.34
Found C 73.47 H 9.33

3-(ω-Alkenyl)-2-cyclohexen-1-ones **1e–g**. – *ω-Unsaturated Bromoalkanes*[25,26]: Except for allyl bromide the ω-unsaturated bromoalkanes are prepared by adding 1 equivalent of hexamethylphosphoric triamide to the respective 1,ω-dibromoalkane at 195°C during which time the product distills into an ice-cooled trap. The crude product is redistilled over a Vigreux column[25]. In order to avoid the mutagenic 1,5-dibromopentane the latter compound is also prepared from 4-pentene-1-ol[26,29].

3-Ethoxy-2-cyclohexen-1-one[27]: 56 g (0.5 mol) of 1,3-cyclohexanedione, 45 g (1 mol) of ethanol, 1 g of *p*-toluenesulfonic acid, and 250 ml of chloroform are refluxed in a Dean-Stark-type apparatus for 15 h. Drying of the solutions with magnesium sulfate, evaporation of the solvent and distillation of the crude product under reduced pressure provide 59 g (84%) of pure product; b.p. 88°C/2.5 Torr.

General Procedure[28]: To a Grignard reagent prepared from 0.1 mol of ω-bromo-1-alkene and 2.7 g (0.11 mol) of magnesium turn-

ings in 100 ml of ether a solution of 14 g (0.1 mol) of 3-ethoxy-2-cyclohexen-1-one in 40 ml of ether is added dropwise at 0°C. After the addition is complete the reaction mixture is stirred at room temp. for 30 min followed by refluxing for 60 min. The cooled reaction mixture is poured into 300 ml of an ice/water mixture, acidified with 5% hydrochloric acid and extracted 5 times with ether. The combined organic layers are dried with magnesium sulfate, and the solvent is evaporated. The crude product (ca. 10 g) is dissolved in 40 ml of methanol and after the addition of 2.5 g of potassium hydroxide the mixture is stirred overnight in order to decompose side products and unreacted starting material. After acidification with 10% hydrochloric acid and removal of the solvent by evaporation, 20 ml of ether as well as the amount of water necessary to dissolve the remaining salts (ca. 10 ml of H_2O) are added to the residue. The layers are separated and the aqueous phase is extracted 3 times with ether. The combined organic extracts are washed with water, dried with magnesium sulfate and distilled under reduced pressure.

3-(3-Butenyl)-2-cyclohexen-1-one (**1e**) was prepared according to a literature procedure reported by Wolff and Agosta[14a]. – UV (CH_3CN): λ_{max} (lg ε) = 232 nm (4.143), 311 (1.462), 338 (1.477). – ^{13}C NMR ($CDCl_3$): δ = 22.6 (CH_2), 29.6 (CH_2), 30.5 (CH_2), 37.2 (CH_2), 37.9 (CH_2), 115.5 (C-4′), 125.9 (C-2), 137.0 (C-3′), 165.4 (C-3), 199.5 (C-1). – MS (70 eV): *m/z* (%) = 150 (28) [M^+], 132 (16), 121 (16), 107 (15), 104 (15), 94 (36), 93 (19), 91 (13), 80 (46), 79 (100), 77 (15), 53 (15).

3-(4-Pentenyl)-2-cyclohexen-1-one (**1f**)[14b]: 22 g (150 mmol) of 5-bromo-1-penten, 4.3 g (180 mmol) of magnesium turnings, and 21 g (150 mmol) of 3-ethoxy-2-cyclohexen-1-one yield 14 g of **1f** with b.p. 50–60°C/0.08 Torr, which is further purified by MPLC (eluent: ethyl acetate/cyclohexane, 40:60). Yield 11.6 g (47%) of pure **1f**. – IR (cap.): $\tilde{\nu}$ = 3080 cm^{-1}, 3030, 2980, 2940, 2890, 2870, 1670, 1645, 1628. – UV (CH_2CN): λ_{max} (lg ε) = 232 nm (4.146), 308 (1.279), 340 (1.398). – ^1H NMR ($CDCl_3$): δ = 1.61 (quint, *J* = 8 Hz, 2H, 2′-H), 1.99 (quint, *J* = 6.5 Hz, 2H, 5-H), 2.08 (q, *J* = 7 Hz, 2H, 3H, 3 CH_2), 2.55 (d/d, *J* = 2.5/1.5 Hz, 1H, 7-H), 3.17 (d/d, *J* = 3/2.5 Hz, 1H, 6-H), 3.65 (d, *J* = 6 Hz, 1H, 8-H), 3.87 (d, *J* = 6 Hz, 5.02 (d, *J* = 16 Hz, 1H, 5′-H, *trans*), 5.78 (d/d/t, *J* = 17/10/6.5 Hz, 1H, 4′-H), 5.87 (s, 1H, 2-H). – ^{13}C NMR ($CDCl_3$): δ = 22.7 (CH_2), 26.1 (CH_2), 29.7 (CH_2), 33.2 (CH_2), 37.3 (CH_2), 37.4 (CH_2), 115.2 (C-5′), 125.8 (C-2), 137.8 (C-4′), 166.1 (C-3), 199.6 (C-1). – MS (70 eV): *m/z* (%) = 164 (18) [M^+], 136 (23), 135 (13), 123 (11), 121 (13), 110 (18), 108 (25), 94 (16), 93 (23), 82 (100), 80 (16), 79 (26), 67 (30), 55 (18), 54 (17), 53 (17).

$C_{11}H_{16}O$ (164.2) Calcd. C 80.44 H 9.82
Found C 79.78 H 9.91

3-(5-Hexenyl)-2-cyclohexen-1-one (**1g**): 16.3 g (0.1 mol) of 6-bromo-1-hexene, 2.7 g (0.11 mol) of magnesium turnings, and 14 g (0.1 mol) of 3-ethoxy-2-cyclohexen-1-one yield 6 g (34%) of **1g** after column chromatography (eluent: ethyl acetate/cyclohexane, 20:80); b.p. 70–80/0.04 Torr. – IR (cap.): $\tilde{\nu}$ = 2920 cm^{-1}, 2860, 1660, 1620, 1425, 1250, 1190, 910, 885. – ^1H NMR ($CDCl_3$): δ = 1.35–1.70 (m, 4H), 1.92–2.13 (m, 4H), 2.17–2.42 (m, 6H), 4.96 (d, *J* = 10 Hz, 1H, 6′-H, *cis*), 5.01 (d, *J* = 17 Hz, 1H, 6′-H, *trans*), 5.79 (d/d/t, *J* = 17/10/7 Hz, 1H, 5′-H), 5.87 (s, 1H, 2-H). – ^{13}C NMR ($CDCl_3$): δ = 22.2 (CH_2), 25.7 (CH_2), 27.8 (CH_2), 29.1 (CH_2), 32.9 (CH_2), 36.8 (CH_2), 37.2 (CH_2), 114.2 (C-12), 125.2 (C-2), 137.9 (C-5′), 166.2 (C-3), 199.1 (C-1). – MS (70 eV): *m/z* (%) = 179 (6) [M^+ + 1], 178 (44) [M^+], 177 (5) [M^+ – 1], 150 (22), 149 (19), 136 (23), 135 (18), 123 (30), 122 (36), 121 (20), 110 (48), 108 (24), 107 (24), 97 (13), 96 (13), 95 (60), 94 (21), 93 (25), 82 (100).

$C_{12}H_{18}O$ (178.3) Calcd. C 80.85 H 10.18
Found C 80.94 H 10.40

Photochemical Cyclizations – General Procedure: The calculated amounts of the starting materials are dissolved in the appropriate solvent together with *n*-decane as an internal standard. After introduction into the reaction vessel (300 ml max. capacity) the solution is purged with dry Ar for 1 min. Irradiation is carried out with a Philips mercury high-pressure lamp HPK 125 W which is in a quartz or Duran immersion well. During the irradiation the apparatus which is fitted with a condenser is flushed with Ar and the solution continuously stirred with a magnetic stirrer. The reaction is monitored by GLC. After irradiation the solvent is removed by evaporation and the crude product purified by column chromatography. If necessary the products are separated by HPLC.

Photo Product **3a** *of 3-(Allyloxy)-2-cyclohexen-1-one* (**1a**): Irradiation of 4 g (26 mmol) of **1a**, 2.9 g (29 mmol) of triethylamine, and 1 ml of *n*-decane in 200 ml of acetonitrile during 19 h by using a quartz immersion well and subsequent purification by HPLC (eluent: ethyl acetate/cyclohexane, 30:70) yield 1.85 g (46%) of the *crossed* [2 + 2] cycloaddition product *9-oxatricyclo[5.2.1.0^{1,6}]decan-5-one* (**3a**). – IR (cap.): $\tilde{\nu}$ = 3000 cm^{-1}, 2950, 2890, 1750. – ^1H NMR ($CDCl_3$): δ = 1.64 (d/d, *J* = 7/1.5 Hz, 1H, 10-H), 1.87 (d/d, *J* = 3/7 Hz, 1H, 10-H), 1.91–2.11 and 2.16–2.38 (2 m, 3H/3H, 3 CH_2), 2.55 (d/d, *J* = 2.5/1.5 Hz, 1H, 7-H), 3.17 (d/d, *J* = 3/2.5 Hz, 1H, 6-H), 3.65 (d, *J* = 6 Hz, 1H, 8-H), 3.87 (d, *J* = 6 Hz, 1H, 8-H). – ^{13}C NMR ($CDCl_3$): δ = 25.1 (CH_2), 26.7 (CH_2), 39.8 (CH_2), 42.2 (C-6), 42.2 (C-10), 56.9 (C-7), 65.2 (C-8), 92.2 (C-1), 207.6 (C-5). – MS (70 eV): *m/z* (%) = 152 (3.3) [M^+], 96 (100), 95 (41), 85 (21), 83 (32), 82 (43), 81 (28), 69 (20), 68 (23), 67 (45).

$C_9H_{12}O_2$ (152.2) Calcd. C 71.03 H 7.95
Found C 70.49 H 8.18

Photoproducts **2b** *and* **4b** *of 3-(3-butenyloxy)-2-cyclohexen-1-one* (**1b**): Irradiation of 8.3 g (50 mmol) of **1b**, 5.1 g (50 mmol) of triethylamine, and 1 ml of *n*-decane in 200 ml of acetonitrile during 8 h by using a quartz immersion well and subsequent purification by HPLC (eluent: ethyl acetate/cyclohexane, 40:60) yield 6.8 g (82%) of *straight* [2 + 2] cycloaddition product *2-oxatricyclo[5.4.0.0^{1,5}]undecan-8-one* (**2b**). – IR (CH_2Cl_2): $\tilde{\nu}$ = 3030 cm^{-1}, 2560, 2290, 1690, 1410, 1245, 1060, 885, 680. – ^1H NMR ($CDCl_3$): δ = 1.67–2.15 (m, 8H, 4 × CH_2), 2.20–2.32 and 2.46–2.56 (2 m, 2H, CH_2), 2.71 (d/t, *J* = 5/8 Hz, 1H, CH), 2.83 (d/d, *J* = 7/11.5 Hz, 1H, CH), 4.00 (d/d/d, *J* = 9/15/9 Hz, 1H, 3-H), 4.16 (d/d/d, *J* = 1.2/8/9 Hz, 1H, 3-H). – ^{13}C NMR ($CDCl_3$): δ = 19.6 (CH_2), 24.2 (CH_2), 31.2 (CH_2), 31.4 (CH_2), 39.1 (CH_2), 40.0 (C-5), 49.3 (C-7), 66.8 (C-3), 87.4 (C-1), 212.3 (C-8). – A ^{13}C-^1H-correlated spectrum helps to assign the CH groups in the ^1H-NMR spectrum. Decoupling of the two CH signals confirms the indicated structure since both couple with a CH_2 group at δ = 1.80–1.94. Between the two CH hydrogen atoms only a long-range coupling of approx. 1 Hz is observed. – MS (70 eV): *m/z* (%) = 166 (25) [M^+], 97 (22), 96 (87), 94 (27), 84 (27), 68 (149, 55 (100).

$C_{10}H_{14}O_2$ (166.2) Calcd. C 72.26 H 8.49
Found C 72.01 H 8.88

Irradiation of 3.3 g (20 mmol) of **1b**, 10 g (100 mmol) of triethylamine, and 0.5 ml of *n*-decane in 250 ml of acetonitrile during 87 h by using a quartz immersion well and subsequent purification by column chromatography (eluent: ethyl acetate/cyclohexane, 20:80) yield 1.6 g (48%) of *10-methyl-7-oxaspiro[5.4]decan-3-one* (**4b**). – IR (cap.): $\tilde{\nu}$ = 2930 cm^{-1}, 2850, 1710, 1445, 1410, 1370, 1350, 1330, 1305, 1280, 1255, 1215, 1165, 1105, 1030, 1010, 965, 935, 905, 895, 765, 725. – ^1H NMR ($CDCl_3$): δ = 1.01 (d, *J* = 7 Hz, 1H, 11-H), 1.55–2.19 (m, 7H), 2.20–2.38 (m, 4H), 3.73 (d/t, *J* = 7/8 Hz, 1H, 8-H), 3.88 (d/t, *J* = 4/8 Hz, 1H, 8-H). – ^{13}C NMR ($CDCl_3$): δ = 14.8 (C-11), 21.9 (CH_2), 33.5 (CH_2), 34.8 (CH_2), 40.7 (C-4), 42.4 (C-

10), 47.1 (C-2), 65.0 (C-8), 86.7 (C-1), 211.6 (C-3). – MS (70 eV): *m/z* (%) = 169 (6) [M^+ + 1], 168 (54) [M^+], 140 (14), 125 (89), 113 (16), 111 (100), 110 (22), 98 (40), 97 (8), 85 (15), 56 (58), 55 (52), 43 (48), 42 (30), 41 (50).

$C_{10}H_{16}O_2$ (168.2) Calcd. C 71.39 H 9.59
Found C 71.04 H 9.59

Photoproducts **2c** *and* **4c** *of 3-(4-Pentenyloxy)-2-cyclohexen-1-one* (**1c**): Irradiation of 3.6 g (20 mmol) of **1c**, 1.4 g (20 mmol) of triethylamine, and 250 µl of *n*-decane in 100 ml of acetonitrile during 12 h by using a quartz immersion well and subsequent separation of the products by HPLC (eluent: ethyl acetate/cyclohexane, 40:60) yield 1.0 g (28%) of **2c**, 400 mg (11%) of **4c**, and 430 mg (12%) of the starting material **1c**.

2-Oxatricyclo[6.4.0.0^{1,6}]dodecan-9-one (**2c**): IR (cap.): $\tilde{\nu}$ = 2940 cm^{-1}, 2850, 1710. – ^1H NMR ($CDCl_3$): δ = 1.37–1.57 (m, 2H), 1.72 (m, 4H), 2.00 (m, 2H), 2.10 (m, 2H, 7-H), 2.19 (m, 1H, 6-H), 2.34 (m, 2H, 10-H), 2.87 (d/d, *J* = 5.5/9 Hz, 1H, 8-H), 3.58 (d/d/d, *J* = 2.5/9/11.5 Hz, 1H, 3-H), 3.73 (d/m, *J* = 11.5 Hz, 1H, 3-H). – ^{13}C NMR ($CDCl_3$): δ = 21.1 (CH_2), 21.7 (CH_2), 23.8 (CH_2), 25.5 (C-7), 31.8 (Ch_2), 34.5 (C-6), 40.0 (C-10), 49.3 (C-8), 62.2 (C-3), 79.2 (C-1), 212.7 (C-9). – MS (70 eV): *m/z* (%) = 180 (24) [M^+], 124 (12), 123 (22), 111 (17), 110 (100), 109 (27), 98 (16), 95 (15), 84 (12), 69 (16), 67 (29), 55 (67), 53 (12), 43 (14).

$C_{11}H_{16}O_2$ (180.2) Calcd. C 73.30 H 8.95
Found C 72.70 H 9.12

6-Methyl-2-oxaspiro[5.5]undecan-8-one (**4c**): IR (cap.): $\tilde{\nu}$ = 2960 cm^{-1}, 2940, 2870, 1715. – ^1H NMR ($CDCl_3$): δ = 0.91 (d, *J* = 7 Hz, 3H, 12-H), 1.34 (m, 1H), 1.58 (m, 5H), 1.86 (m, 1H), 1.98 (d/t, *J* = 4/12 Hz, 1H), 2.04–2.40 (m, 2H), 2.22 (d, *J* = 13.5 Hz, 1H), 2.84 (d/t, *J* = 13.5/2.5 Hz, 1H), 3.60 (m, 2H, 3-H). – ^{13}C NMR ($CDCl_3$): δ = 17.2 (C-12), 20.6 (CH_2), 25.6 (CH_2), 27.3 (CH_2), 34.9 (CH_2), 38.9 (C-6), 40.8 (C-9), 41.8 (C-7), 60.9 (C-3), 80.0 (C-1), 210.8 (C-8). – MS (70 eV): *m/z* (%) = 182 (38) [M^+], 139 (51), 125 (73), 124 (65), 113 (65), 112 (34), 97 (31), 85 (61), 84 (56), 83 (24), 70 (33), 69 (16), 67 (15).

$C_{11}H_{18}O_2$ (182.3) Calcd. C 72.49 H 9.96
Found C 71.95 H 10.00

Photoproduct **2d** *of 3-(5-Hexenyloxy)-2-cyclohexen-1-one* (**1d**): Irradiation of 2 g (10 mmol) of **1d**, 200 µl of *n*-decane, and 100 ml of acetonitrile during 17 d by using a quartz immersion well and subsequent purification by column chromatography (eluent: ethyl acetate/cyclohexane, 40:60) yield 0.5 g (25%) of the *straight* [2 + 2] cycloaddition product *13-oxatricyclo[6.5.0.0^{1,6}]tridecan-5-one* (**2d**). – IR (cap.): $\tilde{\nu}$ = 2920 cm^{-1}, 2840, 1690, 1440, 1340, 1320, 1290, 1240, 1175, 1120, 1100, 1075, 1015, 870, 800, 670. – ^1H NMR ($CDCl_3$): δ = 1.15–1.35 (m, 1H), 1.55–2.00 (m, 10H), 2.00–2.20 (m, 2H), 2.35 (m, 2H), 2.96 (t, *J* = 10 Hz, 1H, 6-H), 3.40 (d/m, *J* = 13 Hz, 1H, 12-H), 3.67 (d/m, *J* = 13 Hz, 1H, 12-H). – ^{13}C NMR ($CDCl_3$): δ = 19.3 (CH_2), 23.4 (CH_2), 28.7 (CH_2), 30.4 (CH_2), 31.4 (CH_2), 32.2 (CH_2), 38.3 (CH_2), 44.7 (C-8), 49.5 (C-6), 65.3 (C-12), 79.5 (C-1), 212 (C-5). – ^{13}C-^1H-correlated spectrum: decoupling of the CH signal at δ = 2.96 confirms the indicated structure since the CH signal at δ = 2.0–2.2 is not influenced. – MS (70 eV): *m/z* (%) = 194 (8.4) [M^+], 113 (38), 85 (18), 84 (29), 82 (32), 67 (60), 55 (100), 54 (93), 43 (22), 41 (70), 40 (82), 39 (25).

$C_{12}H_{18}O_2$ Calcd. 194.1307 Found 194.1302 (MS)

Photoproducts **2f** *and* **4f** *of 3-(4-Pentenyl)-2-cyclohexen-1-one* (**1f**): Irradiation of 4 g (23 mmol) of **1f**, 2.5 g (25 mmol) of triethylamine, und 1 ml of *n*-decane in 200 ml of acetonitrile during 3 h by using a quartz immersion well and subsequent separation of the products by HPLC (eluent: ethyl acetate/cyclohexane, 40:60) yield 0.5 g (25%) of the analytically pure *straight* [2 + 2] cycloaddition product **2f** as well as 180 mg (4%) of **4f**.

Tricyclo[5.4.0.0^{1,5}]undecan-8-one (**2f**): IR (cap.): $\tilde{\nu}$ = 2940 cm^{-1}, 2870, 2850, 1700. – ^1H NMR ($CDCl_3$): δ = 1.35 (d/t, *J* = 7/12 Hz, 1H), 1.59 (m, 5H), 1.85 (m, 3H), 1.92–2.25 (m, 4H), 2.35–2.62 (m, 3H). – Decoupling of the CH signals shows the following coupling patterns: 1.82 (d/d/d, *J* = 4.6/11.5/13 Hz, 1H, 6-H), 2.08 (d/d/d, *J* = 7.0/9.6/13 Hz, 1H, 6-H), 2.40 (d/d/d, *J* = 4.6/6/9.6 Hz, 1H, 5-H), 2.48 (d/d/d, *J* = 1/7/11.5 Hz, 1H, 7-H). – ^{13}C NMR ($CDCl_3$): δ = 21.1 (CH_2), 25.0 (CH_2), 26.8 (C-6), 32.8 (CH_2), 33.0 (CH_2), 39.5 (C-5), 39.5 (CH_2), 40.3 (CH_2), 47.2 (C-7), 49.9 (C-1), 215.1 (C-8). – MS (70 eV): *m/z* (%) = 164 (5.8) [M^+], 123 (25), 122 (20), 121 (57), 110 (46), 108 (50), 107 (21), 97 (32), 94 (79), 93 (61), 91 (28), 83 (20), 82 (95), 81 (20), 80 (37), 79 (100), 77 (23), 67 (37), 55 (32).

$C_{11}H_{16}O$ (164.2) Calcd. C 80.44 H 9.82
Found C 80.36 H 10.09

7-Methylspiro[5.4]decan-3-one (**4f**): IR (cap.): $\tilde{\nu}$ = 2930 cm^{-1}, 2860, 1690, 1435, 1420, 1370, 1335, 1310, 1220, 1170, 1120, 1090, 1040, 1020, 945, 840, 665. – ^1H NMR ($CDCl_3$): δ = 0.91 (d, *J* = 7 Hz, 3H, 11-H), 1.15–1.45 (m, 3H), 1.50–1.90 (m, 7H), 1.99 (d/m, *J* = 13 Hz, 2H), 2.13–2.33 (m, 3H). – ^{13}C NMR ($CDCl_3$): δ = 14.4 (C-11), 21.0 (CH_2), 23.8 (CH_2), 32.2 (CH_2), 35.8 (CH_2), 35.8 (CH_2), 41.4 (CH_2), 43.9 (C-7), 46.2 (CH_2), 49.4 (C-1), 215.1 (C-3). – MS (70 eV): *m/z* (%) = 166 (46) [M^+], 137 (14), 124 (20), 123 (65), 110 (100), 108 (37), 97 (25), 96 (18), 95 (44), 82 (35), 81 (39), 79 (139, 68 (23), 67 (54), 55 (44), 53 (15), 41 (43).

$C_{10}H_{18}O$ (166.2) Calcd. C 79.47 H 10.91
Found C 78.87 H 11.10

Photodimers of 2-Cyclohexen-1-one: 20 g of 2-cyclohexen-1-one is distributed among two 10-ml Duran glass tubes, purged with dry Ar for 1 min and sealed with a septum. Irradiation in a Rayonet reactor fitted with 350-nm tubes and a merry-go-round inset leads to total consumption of the starting material after 5 d. Column chromatography (eluent: ethyl acetate/cyclohexane, 40:60) of the crude product gives 10 g (50%) of a mixture of dimers. GLC analysis shows the head-to-head and head-to-tail isomers in a ratio of 53:47. Analytically pure samples of the two main isomers, the two *cis-anti-cis* isomers[18,30], are obtained by HPLC (eluent: ethyl acetate/cyclohexane, 30:70).

cis-anti-cis-Tricyclo[6.4.0.0^{2,7}]dodecane-3,12-dione (**5**): M.p. 74 to 75°C (refs.[30,31]: 77–78°C). – IR (KBr): $\tilde{\nu}$ = 2900 cm^{-1}, 2800, 1690, 1410, 1300, 1250, 1220, 1170, 1120, 960. – ^1H NMR ($CDCl_3$): δ = 1.55 (d, *J* = 14 Hz, 2H), 1.6–1.8 (m, 2H), 1.8–2.1 (m, 4H), 2.3 (d/d/d, *J* = 14/11.5/5 Hz, 2H), 2.4 (d/d/t, *J* = 4/1/14 Hz, 2H), 2.8 (s (br.), 2H), 3.1 (d, *J* = 8 Hz, 2H). – ^{13}C NMR ($CDCl_3$): δ = 22.7 (CH_2), 25.0 (CH_2), 40.1 (C-7, -8), 41.0 (C-4, -11), 47.5 (C-1, -2), 213.2 (C-3, -12). – MS (70 eV): *m/z* (%) = 192 (60) [M^+], 136 (40), 135 (25), 121 (20), 109 (28), 108 (30), 97 (68), 96 (84), 80 (28), 79 (38), 68 (100), 67 (20), 55 (38).

cis-anti-cis-Tricyclo[6.4.0.0^{2,7}]dodecane-3,9-dione: M.p. 46°C (refs.[30,31]: 51–52°C). – IR (KBr): $\tilde{\nu}$ = 2900 cm^{-1}, 2850, 1695, 1480, 1375, 1190. – ^1H NMR ($CDCl_3$): δ = 1.8 (m, 2H), 1.9–2.1 (m, 6H), 2.3 (m, 2H), 2.5 (m, 2H), 2.7 (t, *J* = 7.5 Hz, 2H), 3.1 (m, 2H). – ^{13}C NMR ($CDCl_3$): δ = 21.3 (CH_2), 29.9 (CH_2), 38.2 (C-1, -7), 40.0 (C-4, -10), 47.4 (C-2, -8), 213.0 (C-3, -9). – MS (70 eV): *m/z* (%) = 192 (43) [M^+], 150 (44), 99 (65), 98 (82), 97 (100), 96 (67), 81 (63), 68 (99), 55 (56), 41 (51).

Photoproduct **6** *of the 2-Cyclohexen-1-one Dimer Mixture:* 3.8 g (20 mmol) of the mixture and 4.0 g (40 mmol) of triethylamine as well as 0.5 ml of *n*-decane are dissolved in 20 ml of acetonitrile. The solution is distributed among Duran glass tubes and purged

with Ar for 1 min. The tubes are sealed with a septum and placed in a Rayonet reactor, fitted with 300-nm tubes and a merry-go-round inset. After 200 h of irradiation 65% of the starting material are consumed. Purification by HPLC (Eluent: ethyl acetate/cyclohexane, 30:70) yields 460 mg (12%) of analytically pure *3,3'-bicyclohexanone([1,1'-Bicyclohexyl]-3,3'-dione)* (**6**), m.p. 76–80°C. – IR (KBr): $\tilde{\nu}$ = 2960 cm^{-1}, 2870, 1710, 1450, 1430, 1415, 1385, 1350, 1325, 1270, 1225, 1190, 1115, 1055, 1035, 970, 910, 870, 760, 645. – ^1H NMR ($CDCl_3$): δ = 0.8–2.5 (m). – ^{13}C NMR ($CDCl_3$): δ = 24.7 (C-5, -5'), 27.7 (C-4, -4'), 40.7 (C-6, -6'), 43.1 (C-3, -3'), 44.3 (C-2, -2'), 210.3 (C-1, -1'). – MS (70 eV): *m/z* (%) = 195 (3) [M^+ + 1], 194 (18) [M^+], 136 (20), 123 (6), 110 (5), 98 (16), 97 (100), 95 (8), 81 (5), 79 (5), 69 (24), 67 (7), 55 (37), 42 (7), 41 (32). – The MS data of **6** are identical with those of one of the reductive dimerization products which were obtained by Schuster and Isogna[20,37] by irradiation of 2-cyclohexen-1-one in the presence of triethylamine.

$C_{12}H_{18}O_2$ (194.3) Calcd. C 74.19 H 9.34
Found C 73.59 H 9.28

Methyl 8-Oxotricyclo[5.4.0.0^{2,6}]undecane-1-carboxylate (7)[21]: A mixture of the *cis-anti-cis* and *cis-syn-cis* isomers (87:13) is accessible in two steps by starting from methyl 1-cyclohexene-1-carboxylate according to a literature procedure[21,32] in 50% yield: b.p. 89–94°C/0.08 Torr. – IR (cap.): $\tilde{\nu}$ = 2940 cm^{-1}, 2860, 1725, 1695, 1450, 1430. – ^1H NMR ($CDCl_3$): δ = 1.45–2.15 (m, 10H), 2.31 (d/t, *J* = 18/7 Hz, 1H), 2.46 (d/t, *J* = 18/6 Hz, 1H), 2.65 (t, *J* = 7.5 Hz, 1H), 2.78 (m, 1H), 3.01 (d, *J* = 6.5 Hz, 1H), 3.75 (s, 3H). – ^{13}C NMR ($CDCl_3$): δ = 19.6 (C-10), 25.2 (C-11), 29.0 (C-4), 32.36 (C-3), 32.39 (C-5), 38.1 (C-9), 39.8 (C-6), 46.8 (C-2), 48.3 (C-1), 49.0 (C-7), 51.5 (C-13), 174.4 (C-12), 211.9 (C-8). – MS (70 eV): *m/z* (%) = 223 (1.3) [M^+ + 1], 222 (8) [M^+], 163 (12), 156 (21), 155 (100), 134 (15), 127 (18), 123 (39), 95 (31), 91 (20), 79 (19), 77 (16), 68 (37), 67 (43), 65 (12), 55 (16), 53 (14), 41 (27), 39 (22).

$C_{13}H_{18}O_3$ (222.3) Calcd. C 70.24 H 8.16
Found C 70.21 H 8.39

Photoproduct **10** *of Ester* 7: 2.5 g (11 mmol) of 7 and 1.6 ml (11 mmol) of triethylamine as well as 1.5 ml of *n*-decane are dissolved in 30 ml of acetonitrile and placed into Duran glass tubes. After purging with Ar for 1 min the tubes are sealed with a septum and irradiated in a Rayonet reactor, which is fitted with 300-nm tubes and a merry-go-round inset. After 96 h 91% of the starting material is consumed. Purification by HPLC (eluent: ethyl acetate/cyclohexane, 25:75) yields 350 mg (14%) of analytically pure *methyl 8-hydroxytricyclo[6.3.0.0^{2,6}]undecan-1-carboxylate* (**10**): – IR (cap.): $\tilde{\nu}$ = 3510 cm^{-1}, 2940, 1705, 1445, 1430, 1375. – ^1H NMR ($CDCl_3$): δ = 1.32–1.55 (m, 3H), 1.55–1.95 (m, 9H), 1.95–2.10 (m, 1H), 2.10–2.25 (m, 1H), 2.35–2.55 (m, 2H), 3.71 (s, 3H), 3.91 (s, 1H). – ^{13}C NMR ($CDCl_3$): δ = 21.3 (CH_2), 26.6 (CH_2), 30.4 (CH_2), 33.0 (CH_2), 37.0 (CH_2), 39.6 (CH_2), 40.8 (CH), 46.4 (CH_2), 51.2 (OCH_3), 53.6 (CH), 63.1 (C-1), 91.2 (C-8), 177.4 (C=O). – MS (70 eV): *m/z* (%) = 224 (3) [M^+], 192 (40), 182 (79), 164 (32), 150 (44), 149 (32), 148 (100), 147 (32), 140 (23), 137 (23), 135 (30), 121 (22), 119 (33), 107 (20), 95 (22), 93 (22), 91 (39), 81 (40), 79 (46), 77 (24), 67 (50), 55 (36), 53 (22), 43 (28), 41 (44), 40 (29).

$C_{13}H_{20}O_3$ (224.3) Calcd. C 69.61 H 8.99
Found C 69.56 H 9.22

Photoproducts **12** *and* **13** *of Bicyclo[4.1.0]heptan-2-one* (**11**): A solution of 2 g (18 mmol) of **11**[33] and 2.5 ml (18 mmol) of triethylamine as well as 1.5 ml of *n*-decane in 60 ml of acetonitrile is distributed in 6 Duran glass tubes. After purging with Ar for 1 min the tubes are sealed with a septum and irradiated in a Rayonet-reactor fitted with 300-nm tubes and a merry-go-round inset. After 84 h the starting material is almost completely consumed. Three products can be isolated by HPLC (eluent: ethyl acetate/cyclohexane, 25:75), which are assigned to **12** and two diastereomers of **13** by a comparison with authentic samples (MS).

2,4β-Dimethyl-cis-decahydro-5-isoquinoline (**18**): Solutions of 2-cyclohexen-1-one **14** (5×10^{-3} M) and *N,N*-dimethylallylamine (**15**) (2.5×10^{-2} M) in the specified solvent (Table 4) are degassed by argon bubbling and irradiated in a Rayonet photoreactor by using 300-nm mercury lamps. Yields are determined by capillary GC with *n*-decane as an internal standard. An analytically pure sample of **18** is obtained as a yellow oil by HPLC on a LiChrosorb Si 60-5 column by using cyclohexane/ethyl acetate/triethylamine (59:40:1) as an eluent. The structure of **18** is assigned according to H,H- and H,C-COSY NMR as well as ^1H-NOE experiments. – IR (neat): $\tilde{\nu}$ = 2940 cm^{-1} (s), 2870, 2780 (s), 1700 (s), 1460 (s), 1390, 1250, 1155, 1075, 850. – ^1H NMR (300 MHz, C_6D_6): δ = 0.73 (d, *J* = 6.7 Hz, 3H, 10-H), 1.2–1.5 (m, 3H, 8_{eq}-H, 3_{ax}-H, 7-H), 1.6–1.8 (m, 3H, 8a-H, 5_{ax}-H, 7-H), 1.86 (dd, *J* = 10.3/4.7 Hz, 1H, 4a-H), 2.00 (s, 3H, 9-H), 2.0–2.1 (m, 4H, 6_{ax}-H, 6_{eq}-H, 8_{ax}-H, 4-H), 2.28 (d, *J* = 9.04 Hz, 1H, 1_{eq}-H), 2.48 (ddd, *J* = 10.9/3.8/1.3 Hz, 1H, 3_{eq}-H). – ^{13}C NMR (75 MHz, $CDCl_3$): δ = 211.1 (C-5), 63.1 (C-3), 60.2 (C-1), 57.8 (C-4a), 46.7 (C-9), 38.7 (C-6), 38.5 (C-8a), 29.2 (C-4), 26.5 (C-8), 25.7 (C-7), 17.2 (C-10). – MS (70 eV): *m/z* (%) = 181 (18) [M^+], 84 (100), 72 (20), 57 (17).

$C_{11}H_{19}NO$ (181.3) Calcd. C 72.88 H 10.56 N 7.73
Found C 72.65 H 10.77 N 7.81

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