Pressure-Induced Diastereoselectivity in Photochemical [2 + 2] Cycloaddition Reactions

Michael Buback*[a], **Joachim Bünger**[b], and **Lutz F. Tietze***[b]

Institut für Physikalische Chemie der Universität Göttingen[a],
Tammannstraße 6, W-3400 Göttingen, F.R.G.

Institut für Organische Chemie der Universität Göttingen[b],
Tammannstraße 2, W-3400 Göttingen, F.R.G.

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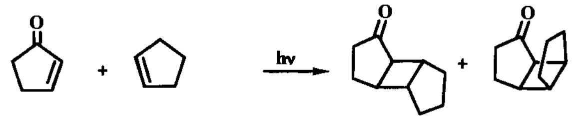
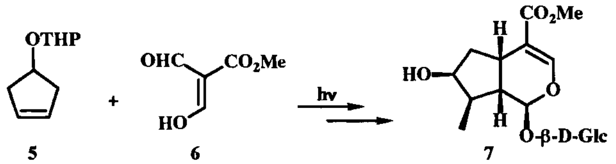
Photochemical [2 + 2] cycloaddition reactions under high pressure of cyclopentenone **1a** or cyclohexenone **15**, as well as of **1a** or 3-substituted cyclopentenones **1b – d** with cyclopentene (**2**), and of **1b** with 3,3-dimethyl-1-butene (**18**) are described. Whereas the pressure dependence on the regioselectivity in the photoaddition of **1a** and **15** is very small, $\Delta\Delta V^{\neq}$ values up to 2.0 ± 0.3 $cm^3 \cdot mol^{-1}$ have been found for the diastereoselectivity in the reactions of **1a – d** with **2** and of **1b** with **18**.

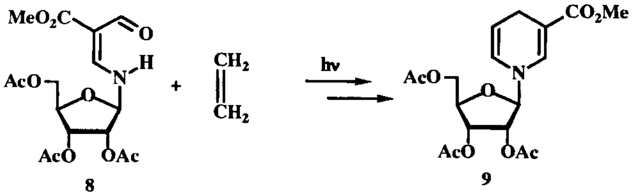
The [2 + 2] cycloaddition of enones to alkenes is one of the most useful photochemical transformations. Thus, irradiation of 2-cyclopentenone (**1a**) and cyclopentene (**2**) with a high-pressure mercury lamp gives the tricyclic ketones **3a** and **4a** in a 30.3:1 ratio in 67% yield[1]. In a similar way, diformylacetate **6** as a 1,3-dicarbonyl compound has been used in a photochemical cycloaddition reaction with **5** according to de Mayo[2] for the synthesis of loganin (**7**)[3], and recently it has been shown by us that enamine carbaldehydes **8** can be employed in the formation of the NADH analogs **9**[4] and annulated pyridine derivatives[5]. In this paper we describe the influence of high pressure[6] on the regio- and stereoselectivity in photochemical cycloadditions of enones.



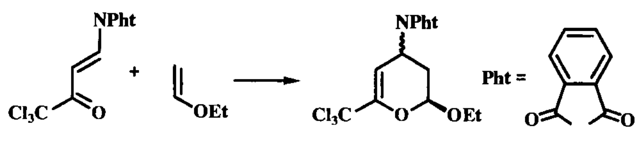
1a **2** **3a** **4a**



5 **6** **7**



8 **9**



10 **11** **12**

For the thermal hetero Diels-Alder reactions of enamino ketones such as **10** with enol ethers such as **11** to give **12** we have found for the first time for a chemical transformation that the stereoselectivity can be improved under high pressure, in this example, from 1:1.67 at 90°C and ambient pressure to 1:13.6 at 0.5°C and 7 kbar[7]. Since very little was known about the influence of pressure on photochemical cycloadditions[8] we irradiated (a) 2-cyclopentenone (**1a**) and (b) 2-cyclohexenone (**15**), (c) the cyclopentenones **1a – d** together with cyclopentene (**2**), as well as (d) 3-methylcyclopentenone (**1b**) together with 3,3-dimethyl-1-butene (**18**) at pressures up to 3000 bar. In (a) and (b) the influence of high pressure on the regioselectivity and in (c) and (d) on the stereoselectivity was of interest.

The reactions were carried out on an analytical scale in a high-pressure cell with optical windows from synthetic sapphire. The cell was placed in the beam of a pulsed XeF excimer laser (wavelength λ = 351 nm) and irradiated for five minutes with a frequency of 60 Hz. With 351-nm light which induces the n-π* transition of enones consecutive reactions like Norrish-type I cleavage due to "secondary irradiation"[9] from absorption of the formed cycloalkanones can be avoided. After release of pressure, the reaction mixture was removed from the cell and the ratio of the regioisomers and diastereomers was determined by capillary gas-liquid (GC) chromatography. Measurements were carried out at ambient temperature (296 K) and at pressures varied in intervals of 200 – 300 bar in the range from 1 to 3000 bar.

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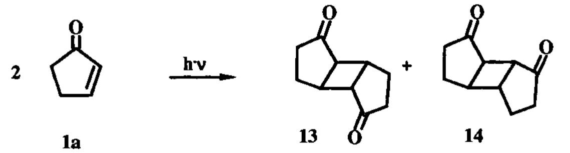
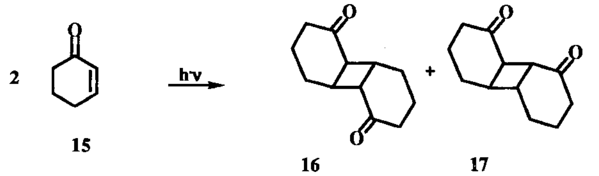
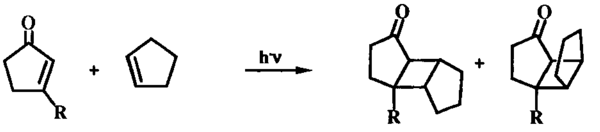


1a 13 14

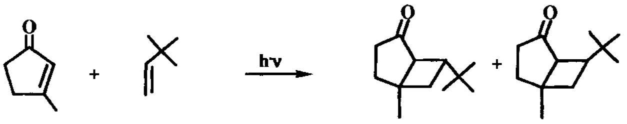


15 16 17



1a-d 2 3a-d 4a-d

1, 3, 4	a	b	c	d
R	H	CH_3	$CH(CH_3)_2$	$C(CH_3)_3$



1b 18 19 20

The photochemical homocycloadditions of **1a** and **15** were performed in dichloromethane. In the cycloaddition reactions of **1a–d** with **2** and of **1b** with **18** the respective olefins, **2** or **18**, were used as solvents to avoid the homoaddition. For the GC and GC-MS analysis the syntheses were also performed on a preparative scale by irradiating a solution of the enones in the corresponding olefins in a ring reactor[10].

Except for **1c** and **1d** all compounds were commercially available; **1c** was obtained by reaction of 3-ethoxy-2-cyclopentenone with isopropylmagnesium chloride in THF at 0°C for 24 h in 75% yield after acidic workup and **1d** by treatment of 3-ethoxy-2-cyclopentenone with *tert*-butyllithium at −78°C → 0°C for 4 h in 78% yield.

At ambient pressure and room temperature the photochemical cycloaddition of **1a** in dichloromethane gives the two known cycloadducts **13** and **14** in a 2.1:1 ratio and 76% yield[11]. Similarly, **16** and **17** which could be separated by chromatography were obtained from **15** in a 1.3:1 ratio and 80% yield[12]. As expected, in the [2 + 2] cycloaddition of **1a** to **2** the *anti* product **3a** is preferred. However, with growing bulkiness of the substituent R the amount of the *syn* product **4** increases. A separation of the formed diastereomers was not possible except for **3b**, **3c**, **4c**, and **4d** which could be obtained in a pure form by column chromatography.

In the reaction of **1b** with **18** the two diastereomers **19** and **20** were formed in a 0.8:1 ratio in 66% yield and could also be separated by column chromatography. The regioisomers were not found in this reaction.

The structure of the cycloadducts was mainly determined by NMR and GC-MS analysis. Compounds **13** and **14** have already been described[12], **3a** as the main adduct of **1a** and **2** was also known[1].

The ^{1}H-NMR spectrum of **16** shows for 2-H and 8-H a doublet of doublets at $\delta = 2.63$ with $J = 6.5$ Hz and 8.5 Hz; for 1-H and 2-H of the corresponding regioisomer **17** a doublet at $\delta = 3.12$ with $J = 8$ Hz is observed, clearly indicating that **16** is the *head-to-tail* and **17** the *head-to-head* cycloadduct.

As already pointed out, the isomers **4a**, **4b**, and **3d** could not be obtained in pure form. Therefore, the structure determination was performed on the product mixtures. The corresponding diastereomers **3a** and **4a**, **3b** and **4b**, **3c** and **4c** as well as **3d** and **4d** show nearly the same fragmentation patterns in their mass spectra resulting from CO extrusion and cleavage of C_5H_8 and very similar ^{13}C-NMR spectra. The assignment for the *syn* and *anti* series is based on the coupling constants of the α-methine proton. This signal shows a coupling contant of $J_{2,1} = 10-11$ Hz for the *syn* products (**4c**: $\delta = 2.48$; **4d**: $\delta = 2.55$) and of $J_{2,1} = 4.5-5$ Hz for the *anti* products (**3b**: $\delta = 1.79-1.87$; **3c**: $\delta = 1.92$). The signal for 2-H of **3b** was not resolved, but the coupling constant could be derived from ^{1}H-^{1}H- and ^{1}H-^{13}C-correlated spectra.

The determination of the structure of **19** and **20** is based on the multiplicity of the signal at $\delta = 2.25$ for **19** and $\delta = 2.11$ for **20** for the methine protons in α-position to the carbonyl group which appear as slightly broadened doublets, indicating that the *tert*-butyl group must be in the β- and not in the γ-position to the carbonyl group. The coupling constants of $J_{2,1} = 6.5$ Hz for **19** and $J_{2,1} = 10$ Hz for **20** are in accord with the data found for **3** and **4** and are in good agreement with results previously published by Berenjian, de Mayo et al.[13].

Under the reasonable assumption that the substitution at the cyclobutane moiety is *cis*-oriented, the configuration must be as described. The existence of an oxetane moiety is unlikely, since the formation of those compounds is disfavored for cyclic enones. Moreover, the NMR and mass spectra should also be different.

Results and Discussion

The effect of high pressure on the regioselectivity of the photochemical dimerization of cyclic enones such as cyclopentenone **1a** and cyclohexenone **15** is very small. The ratio of **13**:**14** changes from 2.17:1 at 200 bar to 2.34:1 at 2800 bar. The difference in the activation volumes for the reaction leading to the *head-to-tail* and *head-to-head* isomers is $\Delta\Delta V^{\neq} = -0.4 \pm 0.2\,\mathrm{cm}^3 \cdot \mathrm{mol}^{-1}$. This value was calculated from the slope of the straight line in a plot of ln(**13**:**14**) versus p [bar]. The ratio of **16**:**17** = 1.3:1 is nearly constant in the range from 200 to 3000 bar.

The ratio of the *syn* and *anti* isomers in the photochemical cycloaddition of substituted cyclopentenones **1a–d** to cyclopentene (**2**) as a function of pressure depends on the steric demand of the substituents in the 3-position of the cyclopentenones **1a**−**d**. Under high pressure for all compounds **1a**−**d** the formation of the *syn* products **4a**−**d** is favored, however to different extents (Table 1).

Table 1. Ratios of **3**:**4** and **19**:**20** in the laser-induced photochemical cycloaddition reaction of cyclopentenones **1a**−**d** with **2** and of **1b** with 3,3-dimethyl-1-buten (**18**) at variable pressure

Ratio of **3** : **4** (pressure [bar])				Ratio of **19** : **20** (pressure [bar])
a	**b**	**c**	**d**	
30.3 (1)	7.85 (1)	6.42 (300)	0.88 (200)	0.85 (300)
29.3 (2140)	8.07 (500)	6.30 (600)	0.87 (400)	0.85 (500)
29.9 (3150)	7.69 (1020)	6.36 (800)	0.87 (600)	0.83 (700)
	7.46 (1310)	6.23 (1100)	0.85 (800)	0.82 (1000)
	7.29 (1500)	6.11 (1300)	0.84 (1000)	0.81 (1200)
	7.39 (1760)	6.05 (1600)	0.84 (1200)	0.78 (1500)
	7.15 (2000)	5.99 (1800)	0.82 (1400)	0.75 (1700)
	7.32 (2260)	5.99 (2100)	0.82 (1600)	0.74 (2000)
	7.39 (2560)	5.82 (2300)	0.79 (1800)	0.73 (2200)
	6.98 (2760)	6.05 (2600)	0.76 (2000)	0.71 (2500)
	6.83 (2980)	5.82 (2800)	0.77 (2400)	0.71 (2700)
		5.87 (3000)	0.74 (2600)	0.70 (3000)
			0.70 (2800)	

The greatest influence of pressure on the diastereoselectivity is found for **1d** with a *tert*-butyl group and the smallest for the unsubstituted cyclopentenone **1a**. Whereas in the photochemical cycloaddition of **1a**−**c** to **2** under ambient pressure the *anti* products **3a**−**c** are formed preferentially, in the reaction of **1d** with **2** the *syn* product **4d** is found as the main product. Thus, the application of high pressure to this system increases the selectivity. A similar effect is observed in the photochemical cycloaddition of 3-methylcyclopentenone **1b** to 3,3-dimethyl-1-butene (**18**). The ratio of **19**:**20** shows a linear change from 0.85:1 at 300 bar to 0.70:1 at 3000 bar. A value for $\Delta\Delta V^{+} = 2.0 \pm 0.2\ \text{cm}^3 \cdot \text{mol}^{-1}$ is calculated for this reaction.

Table 2. $\Delta\Delta V^{+}$ values for the photochemical cycloadditions of **1a**−**d** to **2** as well as **1b** to **18**; the numbers were calculated from the slope of the straight lines in the plots of ln(*anti*:*syn* product) versus *p* [bar] as shown in Figures 1−3

Products	$\Delta\Delta V^{\#}$ [$\text{cm}^3 \cdot \text{mol}^{-1}$]
3a / **4a**	≈ 0
3b / **4b**	1.2 ± 0.3
3c / **4c**	0.8 ± 0.3
3d / **4d**	2.0 ± 0.3
19 / **20**	2.0 ± 0.2

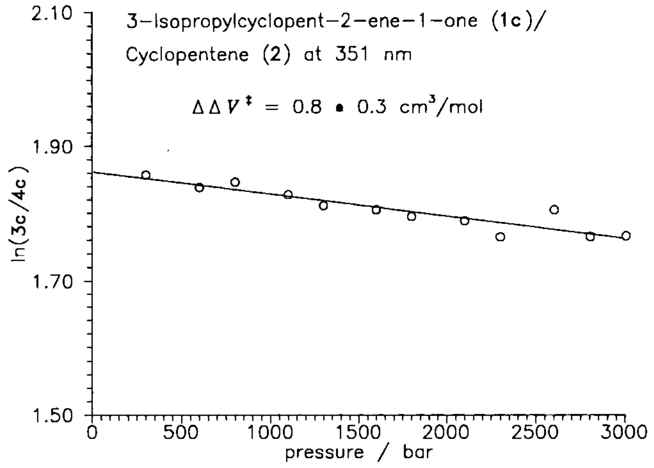


Figure 1. Diastereoselectivity ln[**3c**:**4c**] of the laser-induced photochemical cycloaddition of 3-isopropyl-2-cyclopentenone (**1c**) to cyclopentene (**2**) as a function of reaction pressure (T = 296 K)

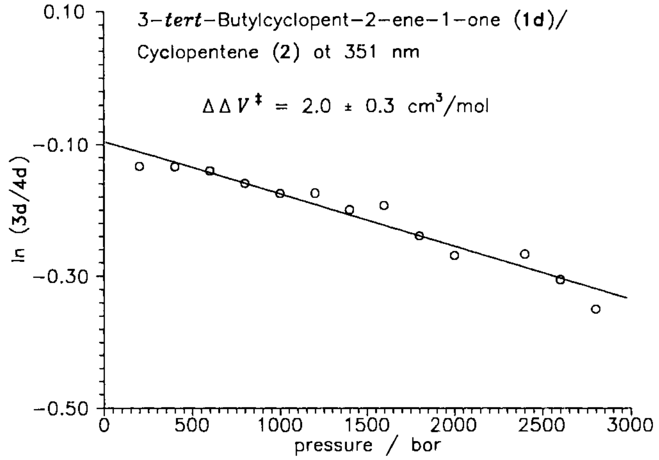


Figure 2. Diastereoselectivity ln[**3d**:**4d**] of the laser-induced photochemical cycloaddition of 3-*tert*-butyl-2-cyclopentenone (**1d**) to cyclopentene (**2**) as a function of reaction pressure (T = 296 K)

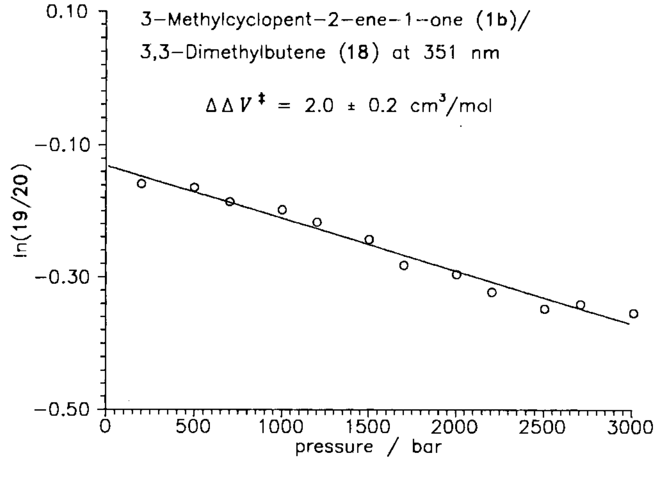
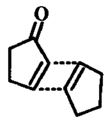
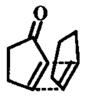


Figure 3. Diastereoselectivity ln[**19**:**20**] of the laser-induced photochemical cycloaddition of 3-methyl-2-cyclopentenone (**1b**) to 3,3-dimethyl-1-butene (**18**) as a function of reaction pressure (T = 296 K)

For the photochemical cycloaddition of cyclic enones to alkenes the following mechanism has been established (simple representation). After absorption of a photon, the enone is transferred into the S_1 state which undergoes a fast intersystem crossing to afford a 1,2-diradical. With the alkene this may form an exciplex and finally give a 1,4-diradical which is either converted into the stable cycloadducts or decomposes to the starting material. It seems clear that a possible influence of high pressure on the photochemical excitation should not affect the selectivity of the cycloaddition. However, the formation of the exciplex[8e] and of the cycloadducts as well as the cleavage of the 1,4-diradical may display a pressure-dependent selectivity. The configuration of the final products **3** and **4** as well as of **19** and **20** is defined in the 1,4-diradical (or possibly already in the exciplex if diastereomeric exciplexes are formed), and thus we have to focus on its formation. On the other hand, the ratio of the products can also be influenced by a different pressure dependence on the cleavage of the 1,4-diradicals[8d]. The transition state TS II leading to a *syn* 1,4-diradical and finally to the *syn* product **4** should have a smaller volume and should therefore be more favored under high pressure than the corresponding transition state TS I which leads to the *anti* 1,4-diradical. A similar argument may be valid for the decomposition of the two intermediately formed 1,4-diradicals. Since the *syn* 1,4-diradical should be stabilized under high pressure, its rate of decomposition should be lower compared to that of the *anti* 1,4-diradical, thereby favoring the formation of the *syn* products.


TS I


TS II

This way of arguing is of course only valid if the quantum yield is well below 1, which is in fact the case. The quantum yield e.g. for the reaction of **1a** with **2** was determined to be ca. 0.2[14]. Thus, both explanations are in agreement with the observed *syn* preference in the cycloadditions proceeding under high pressure. To obtain a better insight in the different effects the described reactions should be investigated at various temperatures. This may allow us to distinguish between the different states of selections according to the isoinversion principle[15]. Moreover, it seems interesting to study the photochemical cycloadditions in different solvents.

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Experimental

High-pressure reactions were carried out with an optical cell previously described[7b]. The solution was placed directly between the optical sapphire windows without using poly(tetrafluoroethylene) bags to ensure a maximum irradiation. – Laser: EMG 102 MSC from Lambda Physik using a $Xe/F_2/He$ gas mixture (λ = 351 nm). – All values of $\Delta\Delta V^{\neq}$ were calculated from the slopes of the straight lines in the corresponding plots of ln(selectivity) versus pressure. Cyclopentene, cyclopentenone and cyclohexene were purchased from Merck-Schuchardt, 3,3-dimethyl-1-butene was purchased from Aldrich. Solvents and reagents were distilled prior to use. – GC: Varian 3700 with FID and Merck-Hitachi D2000 integrator using a SE 30 permabond, 0.32 mm × 50 m, 0.25 μm film from Macherey, Nagel und Co; carrier gas nitrogen (1 atm). Compounds **3d** and **4d** could not be separated under the above-described conditions; separation was performed by using a Carlo Erba Mega 5300 with FID, Shimadzu C-RSA integrator, Chrompack WCOT CPSil 5CB 0.22 mm × 25 m, 0.13 μm film and hydrogen as carrier gas (2 atm). – ^1H and ^{13}C NMR: Varian XL-200, VXR-200, VXR-500S (internal TMS); multiplicities were determined with the APT pulse sequence; assignments marked with an asterisk may be interchanged. – IR: Bruker IFS 25. – Melting points (corrected values): Kofler melting point apparatus. – Elemental analysis were carried out in the analytical laboratory of the university. – Solutions of the enones in the olefins (1:100 mol) were used for high-pressure reactions as well as for the preparative transformations. For homodimers a solution of the enones in dichloromethane (0.5 M) was used; **3a** was prepared according to ref.[1], **13** and **14** were synthesized according to ref.[11], **16** and **17** according to ref.[12].

Synthesis of the Cycloadducts **16**, **17**, **3b–d**, **4b–d** *by Photochemical [2 + 2] Cycloadditions. – General Procedure:* A solution of the enones **1a** or **15** in dichloromethane or of **1b–d** in cyclopentene (**2**) or of **1b** in 3,3-dimethyl-1-butene (**18**) was placed in a pyrex ring reactor, and argon was bubbled through the mixture for 10 min. Afterwards, the solution was irradiated at 0°C with a high-pressure mercury lamp (Heraeus TQ 718 or TQ 150) for 3–6 h according to the reaction scale. A longer irradiation time favors side reactions like the α-cleavage. The progress of the reactions was monitored by TLC or GC. For the workup the solvent was removed in vacuo and the residue distilled and purified by chromatography on silica gel. Yields ranged from 60 to 80%.

(1α,2β,7β,8α)-Tricyclo[6.4.0.0^{2,7}]dodeca-3,9-dione (**16**) *and (±)-(1α,2β,7β,8α)-Tricyclo[6.4.0.0^{2,7}]dodeca-3,12-dione* (**17**): The photochemical cycloaddition of **15** (1.50 g, 15.6 mmol) according to the general procedure gave 0.98 g (65%) of **16** and **17** as a 1.3:1 (GC) mixture which was separated by column chromatography.

16: M.p. 45°C. – R_f = 0.26 [ethyl acetate/petroleum ether (1:2)]. – t_r = 29.59 (initial temp.: 50°C; 5°C/min). – ^1H NMR ($CDCl_3$): δ = 1.60–2.30 (m, 8H, 5-H_2, 6-H_2, 11-H_2, 12-H_2), 2.14–2.56 (m, 4H, 4-H_2, 10-H_2), 2.66 (dd, *J* = 8.5 Hz, *J* = 6.5 Hz, 2H, 2-H, 8-H), 3.04 (m_c, 2H, 1-H, 7-H). – ^{13}C NMR ($CDCl_3$): δ = 21.21 (C-5, C-11), 26.79 (C-6, C-12), 38.17 (C-1, C-7), 39.96 (C-4, C-11), 47.35 (C-2, C-8), 213.0 (C-3, C-9). – MS (70 eV): *m/z* (%) = 192 (48) [M^+], 96 (32) [cyclohexenone$^+$], 68 (100) [cyclohexenone$^+$ – CO].

17: M.p. 57–59°C. – R_f = 0.42 [ethyl acetate/petroleum ether (1:2)]. – t_r = 30.43 min (initial temp.: 50°C; 5°C/min). – ^1H NMR ($CDCl_3$): δ = 1.52 (ddd, *J* = 14 Hz, *J* = 5 Hz, *J* = 4 Hz, 2H, 6-H^b, 9-H^b), 1.66–1.75 (m, 2H, 6-H^a, 9-H^a), 1.87 (dtt, *J* = 14 Hz, *J* = 12 Hz, *J* = 4 Hz, 2H, 5-H^b, 10-H^b), 1.98 (ddddd, *J* = 14 Hz, *J* = 5 Hz, *J* = 5 Hz, *J* = 5 Hz, *J* = 5 Hz, 2H, 5-H^a, 10-H^a), 2.29 (ddd, *J* = 14 Hz, *J* = 12 Hz, *J* = 5 Hz, 2H, 4-H^b, 11-H^b), 2.42 (dddd, *J* = 14 Hz, *J* = 5 Hz, *J* = 4 Hz, *J* = 1 Hz, 2H, 4-H^a, 11-H^a), 2.83 (ddd, *J* = 7.5 Hz, *J* = 5.5 Hz, *J* = 2 Hz, 2H, 7-H, 8-H), 3.11 (d, *J* = 8 Hz, 2H, 1-H, 2-H). – ^{13}C NMR ($CDCl_3$): δ = 22.66 (C-5, C-10), 24.92 (C-6, C-9), 40.02 (C-7, C-8), 40.96 (C-4, C-11), 47.51 (C-1, C-2), 213.2 (C-3, C-12). – MS (70 eV): *m/z* (%) = 192 (60) [M^+], 96 (64) [cyclohexenone$^+$], 68 (100) [cyclohexenone$^+$ – CO].

(±)-(1α,2β,6β,7α)-6-Methyltricyclo[5.3.0.0^{2,6}]decan-3-one (**3b**) *and (±)-(1α,2α,6α,7α)-6-Methyltricyclo[5.3.0.0^{2,6}]decan-3-one* (**4b**): The photochemical cycloaddition of **1b** (750 mg, 7.81 mmol) to **2** according to the general procedure gave 832 mg (65%) of **3b** and **4b** as a 7.3:1 (GC) mixture from which **3b** could be obtained in a pure form by column chromatography.

3b and **4b**: IR (film): $\tilde{\nu}$ = 2942 cm^{-1} (C—H), 2864 (C—H), 1732 (C=O).

$C_{11}H_{16}O$ Calcd. 164.1201 Found 164.1201 (MS)

3b: t_r = 19.50 min (initial temp.: 45°C; 5°C/min). — ^{1}H NMR ($CDCl_3$): δ = 1.00 (s, 3H, CH_3), 1.40—1.55 (m, 2H, 8-H, 10-H), 1.60—1.74 (m, 2H, 9-H, 10-H), 1.79—1.87 (m, 4H, 2-H, 5-H, 8-H, 9-H), 2.01 (ddd, *J* = 14.7 Hz, *J* = 9.4 Hz, *J* = 5.5 Hz, 1H, 5-H), 2.30 (dddd, *J* = 17.4 Hz, *J* = 9.4 Hz, *J* = 5.5 Hz, *J* = 1.8 Hz, 1H, 4-H), 2.48 (dd, *J* = 7.0 Hz, *J* = 7.0 Hz, 1H, 7-H), 2.56 (ddd, *J* = 7.0 Hz, *J* = 7 Hz, *J* = 4.5 Hz, 1H, 1-H), 2.72 (dddd, *J* = 17.4 Hz, *J* = 9.4 Hz, *J* = 9.4 Hz, *J* = 0.7 Hz, 1H, 4-H). — ^{13}C NMR ($CDCl_3$): δ = 20.29 (CH_3), 25.84 (C-9), 28.05 (C-8), 32.50 (C-10), 37.59 (C-4), 37.81 (C-5), 39.42 (C-1), 39.47 (C-6), 46.74 (C-7), 55.66 (C-2), 221.3 (C-3). — MS (70 eV): *m/z* (%) = 164 (15) $[M^+]$, 122 (50) $[M^+ - CO]$, 97 (100) $[C_6H_8O^+ + 1]$, 68 (36) $[C_5H_8^+]$.

4b: t_r = 19.10 min (initial temp.: 45°C; 5°C/min). — ^{1}H NMR ($CDCl_3$): δ = 1.32 (s, 3H, CH_3), 1.30—2.80 (m, 12H), 2.98 (ddd, *J* = 17 Hz, *J* = 9 Hz, *J* = 9 Hz, 1H, 4-H). — MS (70 eV): *m/z* (%) = 164 (11) $[M^+]$, 122 (14) $[M^+ - CO]$, 97 (100) $[M^+ - C_6H_8O]$, 68 (36) $[C_5H_8^+]$.

(±)-(1α,2β,6β,7α)-6-Isopropyltricyclo[5.3.0.0^{2,6}]decan-3-one (**3c**) *and (±)-(1α,2α,6α,7α)-6-Isopropyltricyclo[5.3.0.0^{2,6}]decan-3-one* (**4c**): The photochemical cycloaddition of **1c** (500 mg, 4.03 mmol) to **2** according to the general procedure gave 542 mg (70%) of **3c** and **4c** as a 3.5:1 (GC) mixture from which **3c** and **4c** could be obtained in a pure form by column chromatography.

3c and **4c**: B.p. 100°C/0.1 mbar (Kugelrohr). — IR (film): $\tilde{\nu}$ = 2952 cm^{-1} (C—H), 2874 (C—H), 1730 (C=O), 1468 (C—H), 1448 (C—H), 1386 (C—H), 1368 (C—H).

3c: t_r = 25.09 min (initial temp.: 50°C; 5°C/min). — ^{1}H NMR ($CDCl_3$): δ = 0.68 (d, *J* = 7 Hz, 3H, CH_3), 0.81 (d, *J* = 7 Hz, 3H, CH_3), 1.40—1.90 (m, 8H), 1.93 (br. d, *J* = 5 Hz, 1H, 2-H), 2.47 (br. d, *J* = 7 Hz, 1H, 7-H), 2.60 (br. ddd, *J* = 7 Hz, *J* = 7 Hz, *J* = 5 Hz, 1H, 1-H), 2.70 (dddd, *J* = 18 Hz, *J* = 10 Hz, *J* = 7 Hz, *J* = 1 Hz, 1H, 4-H), 2.14 (ddd, *J* = 13 Hz, *J* = 10 Hz, *J* = 7 Hz, 1H), 2.24 (dddd, *J* = 17 Hz, *J* = 12 Hz, *J* = 6 Hz, *J* = 1 Hz, 1H, 4-H). — ^{13}C NMR ($CDCl_3$): δ = 15.72 (CH_3), 16.46 (CH_3), 26.12 (CH_2), 28.09 (CH_2), 28.09 $[C(CH_3)_2]$, 28.99 (C-10), 32.55 (CH_2), 38.12 (C-4), 38.71 (C-1), 46.44 (C-6), 47.50 (C-7), 54.17 (C-2), 222.7 (C-3). — MS (70 eV): *m/z* (%) = 192 (30) $[M^+]$, 149 (44) $[M^+ - C(CH_3)_2]$, 125 (100) [isopropylcyclopentenone$^+$ + 1], 68 (70) [cyclopentene$^+$].

$C_{13}H_{20}O$ Calcd. 192.1514 Found 192.1514 (MS)

4c: t_r = 25.30 min (initial temp.: 50°C; 5°C/min). — ^{1}H NMR ($CDCl_3$): δ = 0.83 (d, *J* = 7 Hz, 3H, CH_3), 0.90 (d, *J* = 7 Hz, 3H, CH_3), 1.00—1.55 (m, 4H), 1.61 (ddd, *J* = 14.5 Hz, *J* = 12 Hz, *J* = 4.5 Hz, 1H, 5-H), 1.65—1.90 (m, 4H), 2.28 (dddd, *J* = 19 Hz, *J* = 12 Hz, *J* = 9 Hz, *J* = 2 Hz, 1H, 4-H), 2.40 (dddd, *J* = 19 Hz, *J* = 10 Hz, *J* = 4.5 Hz, *J* = 1 Hz, 1H, 4-H), 2.48 (br. dd, *J* = 11 Hz, *J* = 1 Hz, 1H, 2-H), 2.59 (br. dd, *J* = 8 Hz, *J* = 8 Hz, 1H, 7-H), 2.88 (br. ddd, *J* = 11 Hz, *J* = 8 Hz, *J* = 8 Hz, 1H, 1-H). — ^{13}C NMR ($CDCl_3$): δ = 15.95 (CH_3), 16.15 (CH_3), 20.10 (CH_2), 27.13 (CH_2), 27.74 (CH_2), 28.16 (CH_2), 36.56 $[C(CH_3)_2]$, 37.16 (C-1*), 41.15 (C-4), 44.72 (C-7*), 48.39 (C-6), 48.67 (C-2), 221.7 (C-3). — MS (70 eV): *m/z* (%) = 192 (8) $[M^+]$, 149 (15) $[M^+ - C(CH_3)_2]$, 125 (100) [isopropylcyclopentenone$^+$ + 1], 68 (40) [cyclopentene$^+$].

$C_{13}H_{20}O$ Calcd. 192.1514 Found 192.1514 (MS)

(±)-(1α,2β,6β,7α)-6-tert-Butyltricyclo[5.3.0.0^{2,6}]decan-3-one (**3d**) *and (±)-(1α,2α,6α,7α)-6-tert-Butyltricyclo[5.3.0.0^{2,6}]decan-3-one* (**4d**): The photochemical cycloaddition of **1d** (1.10 g, 7.97 mmol) to **2** according to the general procedure gave 0.75 g (68%) of **3d** and **4d** as a 0.8:1 (GC) mixture from which **4d** could be obtained in a pure form by column chromatography.

3d and **4d**: B.p. 100°C/0.1 mbar (Kugelrohr). — IR (film): $\tilde{\nu}$ = 2948 cm^{-1} (C—H), 2868 (C—H), 1728 (C=O), 1478 (C—H), 1396 (C—H), 1366 (C—H).

3d: t_r = 16.98 min (initial temp.: 80°C, 5 min; 5°C/min). — ^{13}C NMR ($CDCl_3$): δ = 21.2 (CH_2), 25.89 $[C(CH_3)_3]$, 25.89 (CH_2), 26.04 (CH_2), 26.64 (CH_2), 34.51 $[C(CH_3)_3]$, 40.76 (CH_2), 41.27 (C-7*), 47.24 (C-1*), 53.5 (C-2), 59.4 (C-6), 219.6 (C=O). — MS (70 eV): *m/z* (%) = 206 (8) $[M^+]$, 150 (46) [M^+ — cyclopentene], 149 (48) $[M^+ - C(CH_3)_3]$, 57 (96) $[C(CH_3)_3^+]$.

4d: t_r = 16.90 min (initial temp.: 80°C, 5 min; 5°C/min). — ^{1}H NMR ($CDCl_3$): δ = 0.96 [s, 9H, $C(CH_3)_3$], 1.19 (m_c, 1H), 1.33 (m_c, 1H), 1.47 (m_c, 1H), 1.66—1.90 (m_c, 5H), 2.27 (dddd, *J* = 18.5 Hz, *J* = 12 Hz, *J* = 10 Hz, *J* = 2 Hz, 1H, 4-H), 2.39 (dddd, *J* = 18.5 Hz, *J* = 9 Hz, *J* = 3.5 Hz, *J* = 1 Hz, 1H, 4-H), 2.55 (br. d, *J* = 10.5 Hz, 1H, 2-H), 2.73—2.82 (m, 2H). — ^{13}C NMR ($CDCl_3$): δ = 20.91 (CH_2), 24.09 $[C(CH_3)_3]$, 27.03 (CH_2), 27.71 (CH_2), 28.58 (CH_2), 34.44 $[C(CH_3)_3]$, 37.82 (C-1*), 41.30 (C-7*), 41.45 (C-4), 46.07 (C-2), 51.30 (C-6), 222.8 (C=O). — MS (70 eV): *m/z* (%) = 206 (8) $[M^+]$, 150 (46) [M^+ — cyclopentene], 149 (48) $[M^+ - C(CH_3)_3]$, 57 (96) $[C(CH_3)_3^+]$.

$C_{14}H_{22}O$ (206.3) Calcd. C 81.50 H 10.75
Found C 81.55 H 10.77

(±)-(1α,5α,7α)-7-tert-Butyl-5-methylbicyclo[3.2.0]heptan-2-one (**19**) *and (±)-(1α,5α,7β)-7-tert-Butyl-5-methylbicyclo[3.2.0]heptan-2-one* (**20**): The photochemical cycloaddition of **1b** (1.00 g, 10.4 mmol) to **18** according to the general procedure gave 1.24 g (66%) of **19** and **20** as a 0.8:1 (GC) mixture from which **19** and **20** could be obtained in a pure form by column chromatography.

19 and **20**: B.p. 90°C/1 mbar (Kugelrohr). — IR (film): $\tilde{\nu}$ = 2950 cm^{-1} (C—H), 2868 (C—H), 1732 (C=O), 1470 (C—H), 1458 (C—H), 1366 (C—H).

19: t_r = 16.98 min (initial temp.: 50°C; 5°C/min). — ^{1}H NMR ($CDCl_3$): δ = 0.84 [s, 9H, $C(CH_3)_3$], 1.18 (s, 3H, CH_3), 1.77—1.86 (m, 1H), 1.89—2.06 (m, 3H), 2.25 (br. d, *J* = 6.5 Hz, 1H, 1-H), 2.36 (dddd, *J* = 18 Hz, *J* = 9.5 Hz, *J* = 6.5 Hz, *J* = 2 Hz, 1H, 3-H), 2.69 (dddd, *J* = 18 Hz, *J* = 9 Hz, *J* = 8 Hz, *J* = 1 Hz, 1H, 3-H). — ^{13}C NMR ($CDCl_3$): δ = 26.16 $[C(CH_3)_3]$, 26.49 (CH_3), 31.76 (C-5), 34.10 (C-6*), 35.78 (C-4*), 36.84 $[C(CH_3)_3]$, 38.87 (C-3), 44.24 (C-7), 53.26 (C-1), 221.0 (C-2). — MS (70 eV): *m/z* (%) = 180 (60) $[M^+]$, 123 (70) $[M^+ - C_4H_9]$, 97 (100) $[M^+ - C_6H_{12} + 1]$, 84 (40) $[C_6H_{12}^+]$, 57 (65) $[C_4H_9^+]$.

20: t_r = 19.38 min (initial temp.: 50°C; 5°C/min). — ^{1}H NMR ($CDCl_3$): δ = 0.91 [s, 9H, $C(CH_3)_3$], 1.38 (s, 3H, CH_3), 1.62 (ddd, *J* = 13 Hz, *J* = 10.5 Hz, *J* = 10 Hz, 1H, 4-H), 1.76 (m, 1H), 1.98 (ddd, *J* = 13 Hz, *J* = 9.5 Hz, *J* = 2.5 Hz, 1H, 4-H), 2.05 (dd, *J* = 10.5 Hz, *J* = 8 Hz, 1H, 6-H), 2.11 (br. d, *J* = 10 Hz, 1H, 1-H), 2.15 (m, 1H), 2.45 (dddd, *J* = 20 Hz, *J* = 10 Hz, *J* = 2.5 Hz, *J* = 2 Hz, 1H, 3-H), 2.70 (dddd, *J* = 20 Hz, *J* = 10.5 Hz, *J* = 9.5 Hz, *J* = 1 Hz, 1H, 3-H). — ^{13}C NMR ($CDCl_3$): δ = 21.77 (CH_3), 23.00 (C-6*), 27.83 $[C(CH_3)_3]$, 32.87 $[C(CH_3)_3]$, 36.18 (C-4*), 38.65 (C-3), 48.37 (C-5), 49.08 (C-7), 50.11 (C-1), 220.0 (C-2). — MS (70 eV):

m/*z* (%) = 180 (15) [M^+], 123 (30) [$M^+ - C_4H_9$], 97 (100) [$M^+ - C_6H_{12} + 1$], 84 (65) [$C_6H_{12}^+$], 57 (60) [$C_4H_9^+$].

$C_{12}H_{20}O$ (180.3) Calcd. C 79.94 H 11.18
Found C 79.96 H 11.17

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1a: 930-30-3 / **1b**: 2758-18-1 / **1c**: 1619-28-9 / **1d**: 5682-70-2 / **2**: 142-29-0 / **3a**: 142694-95-9 / **3b**: 123931-74-8 / **3c**: 142581-55-3 / **3d**: 142581-56-4 / **4a**: 142694-96-0 / **4b**: 142694-97-1 / **4c**: 142694-98-2 / **4d**: 142694-99-3 / **13**: 2065-43-2 / **14**: 142695-02-1 / **15**: 930-68-7 / **16**: 142695-00-9 / **17**: 53092-46-9 / **18**: 558-372 / **19**: 142695-01-0 / **20**: 142581-57-5