Interconversion of *cis*- and *trans*-Fused Oxabicyclo[5.2.0]nonan-2-ones

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Dedicated to Professor *Kurt Schaffner* on the occasion of his 80th birthday

On irradiation (350 nm) in the presence of alkenes (2,3-dimethylbut-2-ene, 1,1-dimethoxyethene, and 2,4,4-trimethylpent-1-ene), benzoxepinone **1** and dioxepinone **2** are converted into mixtures of *cis*- and *trans*-fused oxabicyclo[5.2.0]nonan-2-ones. Their relative thermodynamic stabilities (as reflected by the observed diastereoisomer ratios after equilibration with basic alumina) depend on the substitution pattern of the alkene moiety.

Introduction. – Stepwise [2+2] photocycloaddition of five- or six-membered cyclic enones to alkenes to afford bicyclo[3.2.0]heptan-2-ones or bicyclo[4.2.0]octan-2-ones represents one of the most commonly used preparative light-induced reactions [1][2]. Whereas, for the former bicycles, only *cis*-fused examples are known, the latter exist in both forms, although the *trans*-fused diastereoisomers are converted quantitatively to the *cis*-bicycles under basic conditions. No similar approach to the homologous bicyclo[5.2.0]nonan-2-ones has been reported in the literature, most probably due to the fact that, on irradiation, cyclohept-2-enones undergo efficient (*Z*/*E*)-isomerization, followed by (thermal) dimerization of the so formed (*E*)-diastereoisomers [3–5]. Interestingly, calculations on such 7/4 bicycles suggest that both diastereoisomers should be of approximately equal energy [6][7]. Very recently, we have reported that seven-membered cyclic oxaenones undergo [2+2] photocycloaddition to 2,3-dimethylbuta-1,3-diene efficiently [8]. Here, we report on the reactions of (excited) cyclic oxaenones **1**–**3** in the presence of alkenes **4**–**6**, respectively, and on the subsequent base-induced equilibration of the resulting photocycloadducts (*Fig.*).

Results. – Irradiation of benzoxepinone **1** in the presence of a tenfold molar excess of 2,3-dimethylbut-2-ene (**4**) in benzene as solvent afforded a 1:5:5 mixture of adduct **7**, and of cycloadducts *cis*-**8** and *trans*-**8** (40% overall) in addition to tricyclic photodimers of **1**. Isolation of the 1:1 mixture *cis*-**8**/*trans*-**8** was achieved by chromatography. Irradiation of **1** in the presence of 1,1-dimethoxyethene (**5**) afforded a 2:3 mixture of cycloadducts, *cis*-**9**/*trans*-**9** (90% overall), with only traces of dimers of **1** being detected. Irradiation of **1** in the presence of 2,4,4-trimethylpent-1-ene (**6**) gave a 25:9:15:30:21 mixture **10**/*cis*-**11**/*cis*-**12**/*trans*-**11**/*trans*-**12** (70% overall) as monitored by ^{1}H-NMR spectroscopy, again in addition to photodimers of **1** (*Scheme 1*).

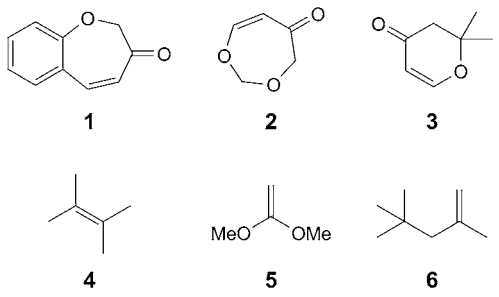
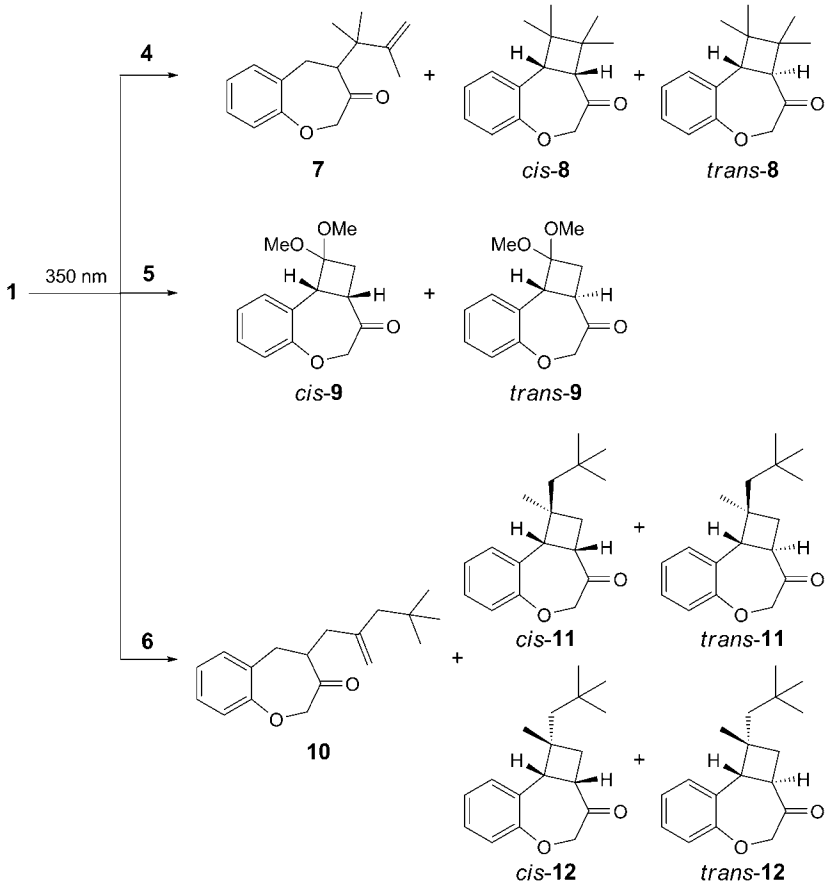


Figure. *Starting materials for the described reactions*

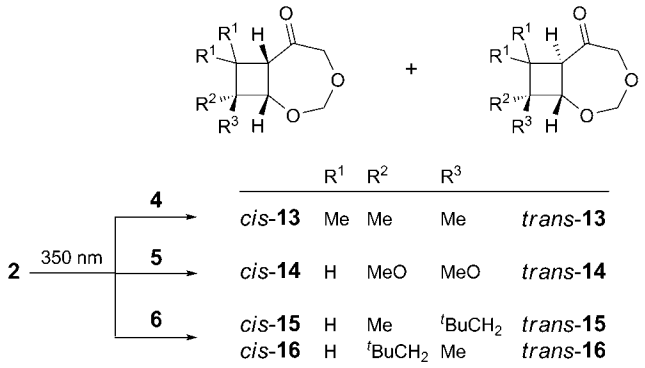
Scheme 1



Similarly, irradiation of dioxepinone **2** in the presence of **4** afforded a 2 : 3 mixture of cycloadducts *cis*-**13**/*trans*-**13**, while, in the presence of **5**, a 1 : 4 mixture *cis*-**14**/*trans*-**14**

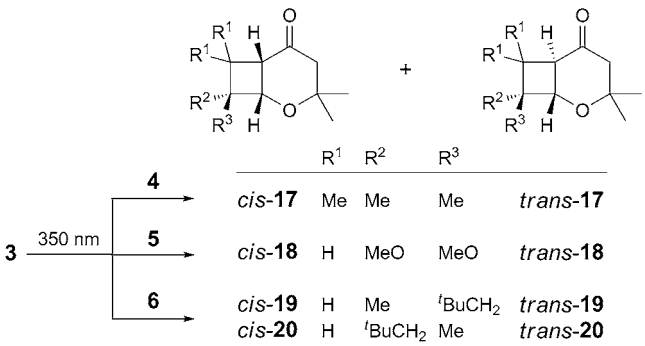
was formed. From **2** and **6**, a 20:5:70:5 mixture *cis*-**15**/*cis*-**16**/*trans*-**15**/*trans*-**16** was obtained. In contrast to the reactions with **1**, no dimers were formed in these irradiations of **2**, the formation of mixed cycloadducts, therefore, being quantitative (*Scheme 2*).

Scheme 2



Finally, irradiation of pyranone **3** in the presence of **4** gave a 3:2 cycloadduct mixture *cis*-**17**/*trans*-**17**, while, in the presence of **5**, a 1:1 mixture *cis*-**18**/*trans*-**18** was obtained [9]. Irradiation in the presence of **6** yielded a 13:27:45:15 cycloadduct mixture *cis*-**19**/*cis*-**20**/*trans*-**19**/*trans*-**20**, respectively (*Scheme 3*).

Scheme 3



Equilibration of the so formed mixtures of diastereoisomeric cycloadducts with basic alumina in CH_2Cl_2, as monitored by ^{1}H-NMR spectroscopy, proceeded in a diversified manner. As expected, all *trans*-fused oxabicyclooctanones, *trans*-**17**, *trans*-**18**, *trans*-**19**, and *trans*-**20**, underwent isomerization quantitatively to the corresponding *cis*-fused diastereoisomers. Regarding the oxabicyclononanones, both dimethoxyethene *trans*-cycloadducts, *trans*-**9** and *trans*-**14**, again isomerized quantitatively to the corresponding *cis*-fused diastereoisomers, respectively. In contrast, the tetramethylethene cycloadducts exhibited a different behavior, as *cis*-**8** isomerized nearly quantitatively to *trans*-**8**, whereas the diastereoisomer ratio *cis*-**13**/*trans*-**13** remained

almost unaffected changing from 2:3 to 1:1. Finally, for the cycloadducts of alkene **6**, a partial but not quantitative isomerization of all *trans*-fused diastereoisomers to the corresponding *cis*-fused cycloadducts was observed (*Table*).

Table. *Percentages of* trans-*Fused Diastereoisomers after Equilibration with Basic Alumina in* CH_2Cl_2 (reaction of enones **1**–**3** with alkenes **4**–**6**, resp.)

	4	**5**	**6** (*anti*)	**6** (*syn*)
1	**8** (85%)	**9** (0%)	**11** (40%)	**12** (40%)
2	**13** (50%)	**14** (0%)	**15** (10%)	**16** (40%)
3	**17** (0%)	**18** (0%)	**19** (0%)	**20** (0%)

Discussion. – The replacement of C- by O-atoms in a seven-membered cyclic enone increases the ring rigidity due to the shorter C–O *vs.* C–C bonds and thus slows down the relaxation of the triplet enone by twisting around the C=C bond, allowing its partial (compound **1** with one O-atom) or quantitative (compound **2** with two O-atoms) trapping by alkenes. Photocycloadducts *trans*-**8**, *cis*-**9**, and *cis*-**14** represent the first examples of isolated and purified, both *cis*- and *trans*-fused, bicyclo[5.2.0]nonan-6-one derivatives[1]). Differentiation between these diastereoisomers stems from both ^{1}H- and ^{13}C-NMR spectra. Regarding the cycloadducts of **2**, the acetal CH_2 group represents an excellent indicator, both *via* the geminal H,H-coupling constant (^2J of *ca.* 5 for *cis*-fused, and *ca.* 7.5 Hz for *trans*-fused diastereoisomers), and the difference in chemical shifts of the H-atoms (<0.1 for *cis*-fused, and ≥ 0.8 ppm for *trans*-fused diastereoisomers), reflecting the corresponding preferential conformation of the dioxepane ring [10]. In addition, the chemical shifts of the acetal C-atoms also differ distinctly (δ *ca.* 95 for *cis*-fused, and *ca.* 100 ppm for *trans*-fused diastereoisomers). In contrast, the differentiation between the corresponding cycloadducts of **1** is more subtle, the best indicators being the vicinal H,H-coupling constant of the bridgehead H-atoms (^3J of *ca.* 11 for *cis*-fused, and *ca.* 13 Hz for *trans*-fused diastereoisomers), as well as the chemical shifts of the CH_2O C-atoms ($\delta \geq 80$ for *cis*-fused, and ≤ 79 ppm for *trans*-fused diastereoisomers). Finally the differentiation of diastereoisomeric oxabicyclooctanones **17**–**20** is straightforward following the indicators established before [11]. Adducts **7** and **10** exhibit spectroscopic data very similar to those for the (known) 4-methyl derivative [12].

Interestingly, alkene **6**, which we employed as higher-boiling substitute for (gaseous) isobutene, has so far only been reported twice as reactant in enone + alkene cycloadditions [13][14], although the differentiation between the resulting *syn*- and *anti*-diastereoisomers was not possible at that time. Here, in addition to NOE measurements, the chemical shifts of the neopentyl CH_2 C-atoms represents an excellent indicator ($\delta \geq 55$ for *anti*-cycloadducts and ≤ 50 ppm for *syn*-cycloadducts, resp.).

Whereas calculations on the stability relationship of diastereoisomeric bicyclic ketones such as bicyclo[3.3.0]octanones and bicyclo[4.3.0]nonanones have been

[1]) No references were found for the parent bicycle although a *CAS* registry is present (105104-52-7).

performed recently [15], only little corresponding information exists for bicyclo[5.2.0]- or oxabicyclo[5.2.0]nonanones, except, as already mentioned in the *Introduction*, for the assumption that here *cis*- and *trans*-fused diastereoisomers should be of approximately equal energy [6][7].The experimental isomerization conditions used here were optimized (complete equilibration without decomposition of a diastereoisomer) with oxabicyclooctanone mixtures *cis*-**17**/*trans*-**17** – *cis*-**20**/*trans*-**20**.

Our results (*cf. Table*) do confirm this hypothesis, as indeed *both diastereoisomers are present after equilibration* for all 9,9-dialkyl- or 8,8,9,9-tetraalkyl-substituted oxabicyclo[5.2.0]nonan-2-ones, and, surprisingly, for compounds **8**, *i.e.*, **1** + **4** cycloadducts, the *trans*-fused diastereoisomer is the one of higher stability. The observation that the corresponding dimethoxy-substituted *trans*-fused diastereoisomers *trans*-**9** and *trans*-**14** do again quantitatively isomerize to the corresponding *cis*-diastereoisomers could be due to the fact that here the anomeric effect [16] represents a more important factor than conformational strain.

Experimental Part

1. *General.* Photolyses were conducted in a *Rayonet RPR-100* photoreactor equipped with 350-nm lamps, and with solvents of spectrophotometric grade. Column chromatography (CC): silica gel *60* (SiO_2; *Merck*; 230–400 mesh). ^{1}H- and ^{13}C-NMR spectra (including 2D plots): in $CDCl_3$; *Bruker WM-500*; at 500.13 and 125.8 MHz, resp.; δ in ppm rel. to Me_4Si as internal standard, J in Hz. GC/EI-MS: *Varian MAT-311A* at 70 eV.

2. *Starting Materials. 1-Benzoxepin-3(2*H*)-one* (**1**) was synthesized according to [17] and *2,3-dihydro-2,2-dimethyl-4*H*-pyran-4-one* (**3**) according to [18]. *1,3-Dioxepin-5(4*H*)-one* (**2**) was obtained by oxidation of the corresponding allylic alcohol [19] using pyridinium dichromate (PDC) as oxidant in DMF as solvent [20] instead of MnO_2 [19]. The alkenes **4**–**6** were commercially available. Basic alumina (pH 8.0; *Woelm*).

2.1. *Synthesis of* **2**. A mixture of 10.6 g of PDC and 2.32 g (20 mmol) of 4,5-dihydro-5-hydroxy-1,3-dioxepine in DMF (40 ml) was stirred for 30 min at 0°, then for 6 h at r.t., poured into H_2O (500 ml), and then extracted (5 × 50 ml) with Et_2O/pentane 2:1. The combined org. layers were dried ($MgSO_4$), and the solvent was distilled off using a *Vigreux* column. The residue (600 mg, 22%), consisted of **2** (80%) and DMF (20%), and was used as such for the irradiations described below. Pure (> 95%) **2** could only be obtained by prep. GC.

3. *Photocycloadditions.* Ar Degassed solns. of enone **1**, **2**, or **3** (1 mmol) and alkene **4**, **5**, or **6** (10 mmol) in benzene (10 ml) were irradiated for 4–14 h until total conversion (monitoring by GC). After evaporation of the solvent and excess alkene, the residue was subjected to CC (SiO_2).

3.1. *Irradiation of* **1** *in the Presence of* **4**. A soln. of **1** (160 mg) and **4** (840 mg) was irradiated for 14 h. CC (pentane/Et_2O 4:1) afforded first 15 mg (6%) of *4,5-dihydro-4-(1,1,2-trimethylprop-2-en-1-yl)-1-benzoxepin-3(2*H*)-one* (**7**; R_f 0.51). Colorless liquid. ^{1}H-NMR: 7.35–7.05 (*m*, 4 H); 4.87 (*s*, 2 H); 4.44 (*s*, 2 H); 3.61 (*dd*, *J* = 3.6, 12.4, 1 H); 2.95 (*dd*, *J* = 12.4, 16.4, 1 H); 2.83 (*dd*, *J* = 3.6, 16.4, 1 H); 1.72, 1.28, 1.25 (3*s*, 9 H). ^{13}C-NMR: 213.1 (*s*); 159.9 (*s*); 150.1 (*s*); 130.3 (*s*); 128.7 (*d*); 128.6 (*d*); 127.9 (*d*); 126.3 (*d*); 111.7 (*t*); 79.1 (*t*); 52.1 (*d*); 40.7 (*s*); 31.7 (*t*); 25.5 (*q*); 22.2 (*q*); 19.9 (*q*).

The second fraction (63 mg, 27%, R_f 0.41) consisted of a 1:1 mixture cis/trans-*1,2,2a,9b-tetrahydro-1,1,2,2-tetramethylcyclobuta*[d]*[1]benzoxepin-3(4*H*)-one (cis-***8**/*trans-***8**). The isolation of *trans*-**8** is described in *Sect. 4.1*; the following data for *cis*-**8** stem from the oily product mixture: ^{1}H-NMR: 7.35–7.05 (*m*, 4 H); 4.40, 4.27 (*AB*, *J* = 17.2, 2 H); 3.87 (*d*, *J* = 10.9, 1 H); 3.38 (*d*, *J* = 10.9, 1 H); 1.30, 1.20, 1.18, 0.88 (4*s*, 12 H). ^{13}C-NMR: 214.1 (*s*); 160.0 (*s*); 131.2 (*s*); 128.1 (*d*); 127.9 (*d*); 127.2 (*d*); 126.6 (*d*); 79.9 (*t*); 56.1 (*d*); 46.1 (*d*); 41.2 (*s*); 41.1 (*s*); 27.0 (*q*); 24.9 (*q*); 22.1 (*q*); 21.9 (*q*).

3.2. *Irradiation of* **1** *in the Presence of* **5**. A soln. of **1** (160 mg) and **5** (880 mg) was irradiated for 14 h. CC (pentane/Et_2O 1:1) afforded 205 mg (80%) of a 2:3 mixture cis/trans *1,2,2a,9b-tetrahydro-1,1-*

*dimethoxycyclobuta[*d*][1]benzoxepin-3(4*H*)-one (cis-***9***/trans-***9***;* R_f 0.48). The isolation of *cis*-**9** is described in *Sect. 4.2*; the following data for *trans*-**9** stem from the oily product mixture: ^{1}H-NMR: 7.35–7.05 (*m*, 4 H); 4.62, 4.48 (*AB*, *J* = 16.6, 2 H); 3.65 (*m*, 2 H); 3.40, 3.28 (2*s*, 6 H); 2.40 (*dd*, *J* = 7.8, 12.0, 1 H); 2.35 (*dd*, *J* = 9.6, 12.0, 1 H). ^{13}C-NMR: 209.1 (*s*); 159.9 (*s*); 130.3 (*s*); 128.7 (*d*); 128.6 (*d*); 127.9 (*d*); 126.3 (*d*); 101.3 (*s*); 78.0 (*t*); 50.5 (*d*); 50.4 (*q*); 50.2 (*q*); 42.5 (*d*); 30.2 (*t*).

3.3. *Irradiation of* **1** *in the Presence of* **6**. A soln. of **1** (160 mg) and **6** (1120 mg) was irradiated for 14 h. CC (pentane/Et_2O 7:1) afforded first 50 mg (19%) of *4,5-dihydro-4-(4,4-dimethyl-2-methylidene-pentyl)-1-benzoxepin-3(2*H*)-one* (**10**; R_f 0.54). Colorless liquid. ^{1}H-NMR: 7.35–7.05 (*m*, 4 H); 4.90 (*s*, 1 H); 4.80 (*s*, 1 H); 4.58, 4.42 (*AB*, *J* = 17.2, 2 H); 3.67 (*m*, 1 H); 3.12 (*dd*, *J* = 4.1, 17.0, 1 H); 2.75 (*dd*, *J* = 12.0, 17.0, 1 H); 2.67 (*dd*, *J* = 4.9, 15.2, 1 H); 2.06 (*dd*, *J* = 9.1, 15.2, 1 H); 1.94 (*s*, 2 H); 0.93 (*s*, 9 H). ^{13}C-NMR: 213.9 (*s*); 159.9 (*s*); 146.1 (*s*); 130.3 (*s*); 128.7 (*d*); 128.6 (*d*); 127.9 (*d*); 126.3 (*d*); 117.1 (*t*); 79.1 (*t*); 50.1 (t); 47.3 (*d*); 37.1 (*t*); 32.9 (*t*); 30.9 (*s*); 29.6 (*q*).

The second fraction (133 mg, 47%; R_f 0.41) consisted of a 1:2:4:2 diastereoisomer mixture of *1-(2,2-dimethylpropyl)-1,2,2a,9b-tetrahydro-1-methyl-cyclobuta[*d*][1]benzoxepin-3(4*H*)-one (cis-***11***/cis-***12***/trans-***11***/trans-***12***)*. The following data stem from the product mixture (aromatic H- and C-atoms not indicated).

cis-**11**: ^{1}H-NMR: 4.60, 4.35 (*AB*, *J* = 17.4, 2 H); 3.85 (*d*, *J* = 11.4, 1 H); 3.80 (*m*, 1 H); 2.58 (*dd*, *J* = 3.3, 11.9, 1 H); 2.30 (*dd*, *J* = 9.8, 11.9, 1 H); 1.85, 1.75 (*AB*, *J* = 14.1, 2 H); 1.49 (*s*, 3 H); 1.02 (*s*, 9 H). ^{13}C-NMR: 82.0 (*t*); 57.1 (*t*); 51.0 (*d*); 47.1 (*d*); 42.1 (*s*); 34.2 (*t*); 30.5 (*s*); 29.4 (*q*); 26.4 (*q*).

cis-**12**: ^{1}H-NMR: 4.67, 4.35 (*AB*, *J* = 17.4, 2 H); 3.83 (*d*, *J* = 11.4, 1 H); 3.80 (*m*, 1 H); 2.33 (*dd*, *J* = 3.3, 11.9, 1 H); 1.97 (*dd*, *J* = 9.8, 11.9, 1 H); 1.30, 0.92 (*AB*, *J* = 14.1, 2 H); 1.27 (*s*, 3 H); 0.84 (*s*, 9 H). ^{13}C-NMR: 82.0 (*t*); 51.1 (*d*); 48.0 (*t*); 47.1 (*d*); 42.1 (*s*); 33.2 (*t*); 30.5 (*s*); 29.4 (*q*); 22.4 (*q*).

trans-**11**: ^{1}H-NMR: 4.50 (*s*, 2 H); 4.10 (*m*, 1 H); 3.18 (*d*, *J* = 12.4, 1 H); 2.32 (*dd*, *J* = 8.8, 12.0, 1 H); 1.96 (*dd*, *J* = 11.5, 12.0, 1 H); 1.95, 1.64 (*AB*, *J* = 13.8, 2 H); 1.53 (*s*, 3 H); 1.01 (*s*, 9 H). ^{13}C-NMR: 79.9 (*t*); 57.9 (*t*); 53.0 (*d*); 46.1 (*d*); 42.1 (*s*); 35.0 (*t*); 30.5 (*s*); 29.4 (*q*); 25.4 (*q*).

trans-**12**: ^{1}H-NMR: 4.53, 4.46 (*AB*, *J* = 17.4, 2 H); 3.67 (*m*, 1 H); 3.41 (*d*, *J* = 12.2, 1 H); 3.08 (*dd*, *J* = 8.3, 11.9, 1 H); 2.08 (*dd*, *J* = 9.2, 11.9, 1 H); 1.52 (*s*, 2 H); 1.24 (*s*, 3 H); 0.98 (*s*, 9 H). ^{13}C-NMR: 80.0 (*t*); 53.0 (*d*); 46.2 (*d*); 46.2 (*t*); 42.1 (*s*); 34.9 (*t*); 30.5 (*s*); 29.4 (*q*); 25.2 (*q*).

3.4. *Irradiation of* **2** *in the Presence of* **4**. A soln. of **2** (114 mg) and **4** (840 mg) was irradiated for 14 h to afford, in quant. yield, a 2:3 diastereoisomer mixture of *8,8,9,9-tetramethyl-2,4-dioxabicyclo[5.2.0]-nonan-6-one* (*cis*-**13**/*trans*-**13**). The following data all stem from the product mixture.

cis-**13**: 4.92, 4.84 (*AB*, *J* = 4.7, 2 H); 4.12, 3.93 (*AB*, *J* = 17.7, 2 H); 3.95 (*d*, *J* = 6.3, 1 H); 3.07 (*d*, *J* = 6.3, 1 H); 1.16, 1.08, 1.07, 0.95 (4*s*, 12 H). ^{13}C-NMR: 211.1 (*s*); 97.1 (*t*); 79.1 (*d*); 74.5 (*t*); 57.2 (*d*); 45.0 (*s*); 44.5 (*s*); 28.2 (*q*); 26.4 (*q*); 25.2 (*q*); 24.4 (*q*).

trans-**13**: 5.39, 4.63 (*AB*, *J* = 7.4, 2 H); 4.33, 4.12 (*AB*, *J* = 17.8, 2 H); 3.70 (*d*, *J* = 9.1, 1 H); 3.30 (*d*, *J* = 9.1, 1 H); 1.14, 1.12, 1.03, 1.02 (4*s*, 12 H). ^{13}C-NMR: 210.8 (*s*); 100.1 (*t*); 80.2 (*d*); 80.1 (*t*); 61.0 (*d*); 44.2 (*s*); 42.8 (*s*); 28.4 (*q*); 26.8 (*q*); 25.4 (*q*); 25.2 (*q*).

3.5. *Irradiation of* **2** *in the Presence of* **5**. A soln. of **2** (114 mg) and **4** (880 mg) was irradiated for 14 h to give, in quant. yield, a 1:4 diastereoisomer mixture of *9,9-dimethoxy-2,4-dioxabicyclo[5.2.0]nonan-6-one* (*cis*-**14**/*trans*-**14**). The isolation of *cis*-**14** is described in *Sect. 4.3*; the following data for *trans*-**14** stem from the oily product mixture: ^{1}H-NMR: 5.45, 4.65 (*AB*, *J* = 7.3, 2 H); 4.50, 4.17 (*AB*, *J* = 18.4, 2 H); 3.75 (*d*, *J* = 9.4, 1 H); 3.57 (*ddd*, *J* = 8.8, 9.4, 10.9, 1 H); 3.38, 3.22 (2*s*, 6 H); 2.21 (*dd*, *J* = 8.8, 11.5, 1 H); 1.93 (*dd*, *J* = 10.9, 11.5, 1 H). ^{13}C-NMR: 209.1 (*s*); 101.0 (*s*); 100.1 (*t*); 80.2 (*d*); 79.2 (*t*); 50.8 (*q*); 50.2 (*q*); 48.1 (*d*); 26.3 (*t*).

3.6. *Irradiation of* **2** *in the Presence of* **6**. A soln. of **2** (114 mg) and **4** (1120 mg) was irradiated for 14 h to afford, in quant. yield, a 20:5:70:5 diastereoisomer mixture of *9-(2,2-dimethylpropyl)-9-methyl-2,4-dioxabicyclo[5.2.0]nonan-6-one* (*cis*-**15**/*cis*-**16**/*trans*-**15**/*trans*-**16**; monitoring by GC/MS). The data of the two main products stem from this mixture.

cis-**15**: 4.93, 4.83 (*AB*, *J* = 4.9, 2 H); 4.25, 3.97 (*AB*, *J* = 17.7, 2 H); 4.10 (*d*, *J* = 8.8, 1 H); 3.50 (*m*, 1 H); 2.25 (*dd*, *J* = 4.2, 12.0, 1 H); 1.75 (*dd*, *J* = 9.5, 12.0, 1 H); 1.56, 1.44 (*AB*, *J* = 14.1, 2 H); 1.10 (*s*, 3 H); 0.96 (*s*, 9 H). ^{13}C-NMR: 212.1 (*s*); 96.1 (*t*); 79.1 (*d*); 73.5 (*t*); 54.1 (*t*); 47.2 (*d*); 42.8 (*s*); 32.1 (*t*); 30.4 (*s*); 30.3 (*q*); 29.5 (*q*).

trans-**15**: 5.41, 4.57 (*AB*, *J* = 7.4, 2 H); 4.45, 4.15 (*AB*, *J* = 17.8, 2 H); 3.71 (*ddd*, *J* = 8.8, 9.1, 10.8, 1 H); 3.42 (*d*, *J* = 9.1, 1 H); 1.67–1.65 (*m*, 2 H); 1.55, 1.40 (*AB*, *J* = 14.3, 2 H); 1.35 (*s*, 3 H); 0.96 (*s*, 9 H). ^{13}C-NMR: 210.2 (*s*); 101.1 (*t*); 82.5 (*d*); 79.5 (*t*); 57.1 (*t*); 52.0 (*d*); 44.1 (*s*); 32.1 (*t*); 30.4 (*s*); 30.3 (*q*); 29.6 (*q*).

3.7. *Irradiation of* **3** *in the Presence of* **4**. A soln. of **3** (126 mg) and **4** (840 mg) was irradiated for 4 h to give, in quant. yield, a 5 : 3 diastereoisomer mixture of *3,3,7,7,8,8-hexamethyl-2-oxabicyclo[4.2.0]octan-5-one* (*cis*-**17**/*trans*-**17**). The isolation of *cis*-**17** is described in *Sect. 4.4*; the following data for *trans*-**17** stem from the oily product mixture: ^{1}H-NMR: 3.82 (*d*, *J* = 11.0, 1 H); 2.65 (*d*, *J* = 11.0, 1 H); 2.30, 2.13 (*AB*, *J* = 14.2, 2 H); 1.38, 1.33, 1.18, 1.13, 1.02, 1.00 (6*s*, 18 H). ^{13}C-NMR: 204.2 (*s*); 80.9 (*s*); 80.1 (*d*); 59.1 (*d*); 53.8 (*t*); 44.1 (*s*); 43.8 (*s*); 27.2 (*q*); 26.4 (*q*); 24.3 (*q*); 23.2 (*q*); 22.8 (*q*); 20.2 (*q*).

3.8. *Irradiation of* **3** *in the Presence of* **5**. A soln. of **3** (126 mg) and **5** (880 mg) was irradiated for 4 h to provide, in quant. yield, a 10 : 9 diastereoisomer mixture of *8,8-dimethoxy-3,3-dimethyl-2-oxabicyclo[4.2.0]octan-5-one* (*cis*-**18**/*trans*-**18**). The isolation of *cis*-**18** is described in *Sect. 4.5*; the following data for the *trans*-**18** stem from the oily product mixture: ^{1}H-NMR: 3.82 (*d*, *J* = 11.0, 1 H); 3.39, 3.28 (2*s*, 6 H); 2.87 (*ddd*, *J* = 9.0, 11.0, 11.1, 1 H); 2.46, 2.18 (*AB*, *J* = 13.9, 2 H); 2.15 (*dd*, *J* = 9.0, 11.2, 1 H); 1.89 (*dd*, *J* = 11.0, 11.2, 1 H); 1.46, 1.29 (2*s*, 6 H). ^{13}C-NMR: 204.1 (*s*); 106.0 (*s*); 83.0 (*s*); 82.9 (*d*); 54.1 (*t*); 51.9 (*q*); 51.2 (*q*); 47.5 (*d*); 31.0 (*q*); 29.2 (*t*); 27.4 (*q*).

3.9. *Irradiation of* **3** *in the Presence of* **6**. A soln. of **3** (126 mg) and **6** (1120 mg) was irradiated for 4 h to afford, in quant. yield, a 1 : 2 : 3.1 diastereoisomer mixture of *8-(2′,2′-dimethylpropyl)-3,3,8-trimethyl-2-oxabicyclo[4.2.0]octan-5-one* (*cis*-**19**/*cis*-**20**/*trans*-**19**/*trans*-**20**). The data of all four products stem from this product mixture.

cis-**19**: ^{1}H-NMR: 4.20 (*d*, *J* = 6.7, 1 H); 2.93 (*m*, 1 H); 2.57, 2.28 (*AB*, *J* = 15.5, 2 H); 2.06 (*m*, 1 H); 1.97 (*m*, 1 H); 1.54, 1.47 (*AB*, *J* = 14.5, 2 H); 1.34, 1.26, 1.10 (3*s*, 9 H); 0.96 (*s*, 9 H). ^{13}C-NMR: 210.1 (*s*); 79.2 (*s*); 76.5 (*d*); 53.2 (*t*); 50.5 (*t*); 42.1 (*s*); 41.5 (*d*); 37.2 (*t*); 30.9 (*q*); 30.5 (*s*); 30.4 (*q*); 27.2 (*q*); 26.5 (*q*).

cis-**20**: ^{1}H-NMR: 3.94 (*dd*, *J* = 2.8, 4.0, 1 H); 2.93 (*m*, 1 H); 2.50, 2.28 (*AB*, *J* = 17.0, 2 H); 2.10 (*m*, 1 H); 1.99 (*m*, 1 H); 1.59, 1.47 (*AB*, *J* = 14.5, 2 H); 1.37, 1.29, 1.16 (3*s*, 9 H); 0.94 (*s*, 9 H). ^{13}C-NMR: 210.1 (*s*); 79.2 (*s*); 76.9 (*d*); 50.0 (*t*); 47.1 (*t*); 41.3 (*s*); 41.1 (*d*); 38.1 (*t*); 30.9 (*q*); 30.8 (*s*); 30.4 (*q*); 26.2 (*q*); 24.5 (*q*).

trans-**19**: ^{1}H-NMR: 3.55 (*d*, *J* = 10.7, 1 H); 3.04 (*m*, 1 H); 2.35, 2.15 (*AB*, *J* = 13.5, 2 H); 1.67–1.58 (*m*, 2 H); 1.58, 1.46 (*AB*, *J* = 14.0, 2 H); 1.46, 1.29, 1.04 (3*s*, 9 H); 0.95 (*s*, 9 H). ^{13}C-NMR: 205.4 (*s*); 82.9 (*s*); 80.2 (*d*); 57.1 (*t*); 54.2 (*t*); 52.2 (*d*); 41.9 (*s*); 33.2 (*t*); 30.3 (*q*); 30.3 (*s*); 30.1 (*q*); 30.0 (*q*); 27.2 (*q*).

trans-**20**: ^{1}H-NMR: 3.45 (*d*, *J* = 10.8, 1 H); 3.04 (*m*, 1 H); 2.36, 2.15 (*AB*, *J* = 13.5, 2 H); 2.00 (*dd*, *J* = 8.8, 12.0, 1 H); 1.80, 1.60 (*AB*, *J* = 14.0, 2 H); 1.53 (*dd*, *J* = 11.5, 12.0, 1 H); 1.41, 1.28, 1.00 (*s*, 3 H); 0.96 (*s*, 9 H). ^{13}C-NMR: 205.4 (*s*); 82.7 (*s*); 80.9 (*d*); 54.1 (*t*); 52.2 (*d*); 43.2 (*t*); 41.7 (*s*); 30.3 (*q*); 30.3 (*s*); 30.1 (*q*); 30.0 (*q*); 28.4 (t); 27.2 (*q*).

4. *Equilibration with Basic* Al_2O_3. To a soln. of a diastereoisomer mixture of cycloadducts (0.5 mmol) in CH_2Cl_2 (5 ml) was added basic alumina (800 mg), and the suspension was stirred at r.t. for 3 h. Filtration, washing with an additional ml of CH_2Cl_2, and evaporation of the solvent afforded one pure diastereoisomer or the correspondingly modified product mixtures (*cf. Table*).

4.1. *Mixture* cis-**8**/trans-**8**. Prep. TLC (pentane/Et_2O 4 : 1) afforded 67 mg (63%) of *(2aα,9bβ)-1,2,2a,9b-tetrahydro-1,1,2,2-tetramethylcyclobuta[*d*][1]benzoxepin-3(4*H*)-one* (*trans*-**8**; R_f 0.41). Light-yellow oil. ^{1}H-NMR: 7.35–7.05 (*m*, 4 H); 4.48, 4.37 (*AB*, *J* = 17.2, 2 H); 3.71 (*d*, *J* = 13.2, 1 H); 3.52 (*d*, *J* = 13.2, 1 H); 1.28, 1.18, 1.00, 0.96 (4*s*, 12 H). ^{13}C-NMR: 212.3 (*s*); 160.0 (*s*); 131.4 (*s*); 128.2 (*d*); 127.9 (*d*); 127.3 (*d*); 126.8 (*d*); 78.5 (*t*); 54.1 (*d*); 47.1 (*d*); 42.2 (*s*); 41.8 (*s*); 27.5 (*q*); 24.3 (*q*); 22.8 (*q*); 21.5 (*q*).

4.2. *Mixture* cis-**9**/trans-**9**. Prep. TLC (pentane/Et_2O 1 : 1) afforded 96 mg (89%) of *(2aα,9bα)-1,2,2a,9b-tetrahydro-1,1-dimethoxycyclobuta[*d*][1]benzoxepin-3(4*H*)-one* (*cis*-**9**; R_f 0.45). Light-yellow waxy solid. M.p. 48–51°. ^{1}H-NMR: 7.35–7.05 (*m*, 4 H); 4.49, 4.40 (*AB*, *J* = 17.1, 2 H); 4.08 (*d*, *J* = 11.0, 1 H); 3.62 (*ddd*, *J* = 6.0, 11.0, 11.0, 1 H); 3.34, 3.10 (2*s*, 6 H); 3.10 (*dd*, *J* = 6.0, 12.0, 1 H); 2.37 (*dd*, *J* = 11.0, 12.0, 1 H). ^{13}C-NMR: 210.1 (*s*); 159.9 (*s*); 130.5 (*s*); 128.8 (*d*); 127.7 (*d*); 126.5 (*d*); 101.1 (*s*); 79.5 (*t*); 50.5 (*d*); 50.4 (*q*); 50.2 (*q*); 50.1 (*d*); 32.2 (*t*).

4.3. *Mixture* cis-**14**/trans-**14**. Prep. TLC (pentane/Et_2O 2 : 1) afforded 88 mg (88%) of *(1α,7α)-9,9-dimethoxy-2,4-dioxabicyclo[5.2.0]nonan-6-one* (*cis*-**14**; R_f 0.46). White solid. M.p. 59–63°. ^{1}H-NMR: 5.06, 4.91 (*AB*, *J* = 5.0, 2 H); 4.39 (*d*, *J* = 8.6, 1 H); 4.31, 4.00 (*AB*, *J* = 17.7, 2 H); 3.37 (*ddd*, *J* = 4.8, 8.8,

9.8, 1 H); 3.26, 3.22 (2*s*, 6 H); 2.80 (*dd*, *J* = 5.0, 13.1, 1 H); 2.07 (*dd*, *J* = 10.1, 13.1, 1 H). ^{13}C-NMR: 210.1 (*s*); 101.2 (*s*); 94.7 (*t*); 77.5 (*d*); 73.3 (*t*); 50.7 (*q*); 50.6 (*q*); 49.9 (*d*); 29.1 (*t*).

4.4. *Mixture* cis-**17**/trans-**17**. Prep. TLC (pentane/Et_2O 3:1) afforded 93 mg (89%) of *(1α,6α)-3,3,7,7,8,8-hexamethyl-2-oxabicyclo[4.2.0]octan-5-one* (*cis*-**17**; R_f 0.42). Colorless oil. ^{1}H-NMR: 3.93 (*d*, *J* = 4.8, 1 H); 2.66 (*d*, *J* = 4.8, 1 H); 2.26 (*s*, 2 H); 1.38, 1.33, 1.18, 1.13, 1.02, 1.00 (6*s*, 18 H). ^{13}C-NMR: 210.2 (*s*); 78.1 (*s*); 75.5 (*d*); 52.1 (*t*); 51.4 (*d*); 43.7 (*s*); 43.2 (*s*); 26.8 (*q*); 26.2 (*q*); 24.8 (*q*); 23.6 (*q*); 22.9 (*q*); 20.5 (*q*).

4.5. *Mixture* cis-**18**/trans-**18**. Prep. TLC (pentane/Et_2O 1:1) afforded 94 mg (89%) *(1α,6α)-8,8-dimethoxy-3,3-dimethyl-2-oxabicyclo[4.2.0]octan-5-one* (*cis*-**18**; R_f 0.45) as white solid. M.p. 56–61°. ^{1}H-NMR: 4.43 (*dd*, *J* = 3.0, 5.5, 1 H); 3.28, 3.23 (2*s*, 6 H); 2.71 (*ddd*, *J* = 5.5, 7.5, 9.0, 1 H); 2.62, 2.25 (*AB*, *J* = 17.2, 2 H); 2.40–2.30 (*m*, 2 H); 1.40, 1.22 (2*s*, 6 H). ^{13}C-NMR: 209.1 (*s*); 102.0 (*s*); 77.5 (*s*); 76.2 (*d*); 51.4 (*t*); 50.9 (*q*); 50.2 (*q*); 36.8 (*d*); 34.0 (*t*); 29.9 (*q*); 27.1 (*q*).

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