Photocycloaddition of Cyclohex-2-enones to Penta-1,2,4-triene

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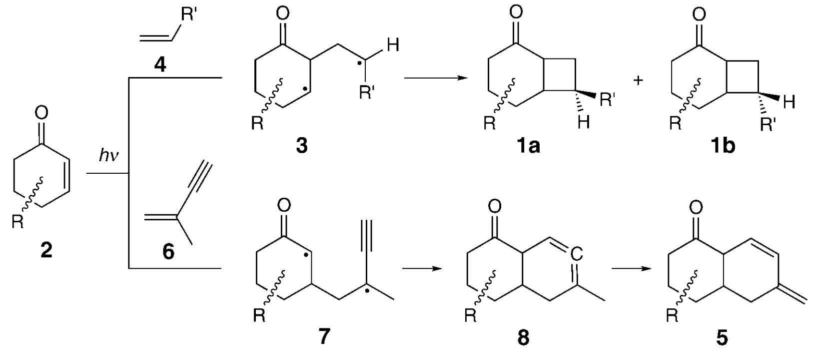
Dedicated to Professor *Henning Hopf* on the occasion of his 65th birthday

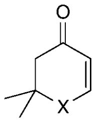
Dihydrothiinone **9a** undergoes photocycloaddition regioselectively to all three C=C bonds of penta-1,2,4-triene (**10**), the relative stabilities of the biradical intermediates determining the product distribution. In contrast, cyclohexenone **9b** and dihydropyranone **9c** afford more complex mixtures of bicyclo[4.2.0]octanones, which also turn out to be less stable on chromatographic workup, reflecting the higher strain due to the shorter bond lengths (C–O and C–C *vs.* C–S) in the six-membered rings, respectively.

1. Introduction. – Bicyclo[4.2.0]octan-2-ones **1**, resulting from photocycloaddition of cyclohex-2-enones **2** to alkenes, represent important synthons, as they are easily transformed into a plethora of natural and nonnatural target molecules [1]. As these light induced conversions proceed in a stepwise manner *via* 1,4-biradicals as **3**, they tend to afford diastereoisomeric mixtures as **1a** and **1b**, when the alkene **4** is unsymmetrically substituted. Recently, we extended the scope of such photoannelations by obtaining naphthalenones **5** in reactions of **2** with conjugated enynes, *e.g.*, 2-methylbut-1-en-3-yne (**6**), as (photo-inert) alkene partner [2][3]. Bicyclic ketones **5** result from 1,6-cyclization of alkyl propargyl biradical **7**, followed by a 1,3-H-shift in the cyclohexa-1,2-diene **8** (*Scheme 1*). In pursuing related examples wherein 1,4- and 1,6-cyclization of the biradical intermediate could compete, we investigated the reaction of cyclohex-2-enones **9a**–**9c** in the presence of the conjugated en-allene penta-1,2,4-triene (**10**).

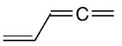
2. Results. – Irradiation (λ 350 nm) of cyclohexenones **9** (0.4M) and penta-1,2,4-triene (**10**; 4.0M) in benzene affords mixtures of six (**9a**), eight (**9b**), and eight (**9c**) [1+1] adducts as monitored by GC and GC/MS. In addition, during the irradiation of **9c**, considerable amounts of dimers (M_r 132) and trimers (M_r 198) of **10** are formed, the overall efficiency in product formation for this last reaction being *ca.* 30 times lower than for the first two ones. ^{1}H-NMR Analyses of the crude reaction mixtures confirm this complexity, but nevertheless characteristic olefinic signals typical for *a*) ethenyl, *b*) buta-1,3-dienyl, and *c*) propa-1,2-dienyl substructures (*cf.* the *Table*) are easily recognized in the mixtures from **9a** and **9b**. On standing in $CDCl_3$ or on stirring the product mixture from **9a** over SiO_2, the signals typical for the buta-1,3-dienyl substructures disappear, whereas, in the mixture from **9b**, all products seem to be affected. Similar preliminary measurements with the product mixture of **9c** are meaningless, as the overlapping sig-

Scheme 1





9a X = S
9b X = CH_2
9c X = O



10

nals of the allene dimers and trimers prevent such a comparison. Column chromatography (SiO_2; pentane/Et_2O 3 : 1) of the product mixture from **9a** allows the partial isolation and identification of five of the six products, **11a** (30%), **12a** (12%), **13a** (22%), **14a** (14%), and **15a** (8%), whereas the sixth product (**16a**, 14%) can be identified directly from the original product mixture (*Scheme 2*).

The structural assignment of compounds **11a**–**16a** stems from both NMR and MS data. The fact that all bicycles are *cis*-fused results from the magnitude of the vicinal coupling constant for the bridgehead H-atoms, $J = 6.6–8.5$ Hz. The differentiation of the three substitution patterns in compound pairs **11**/**12**, **13**/**16**, and **14**/**15**, respectively, is straightforward not only from NMR (*cf.* the *Table*), but also from MS. For both formal allene cycloaddition pairs **11**/**12** and **13**/**16**, the molecular ions cleave preferentially by elimination of the $SCMe_2$ and CH_2CO fragments to afford intense peaks of m/z 92

Scheme 2

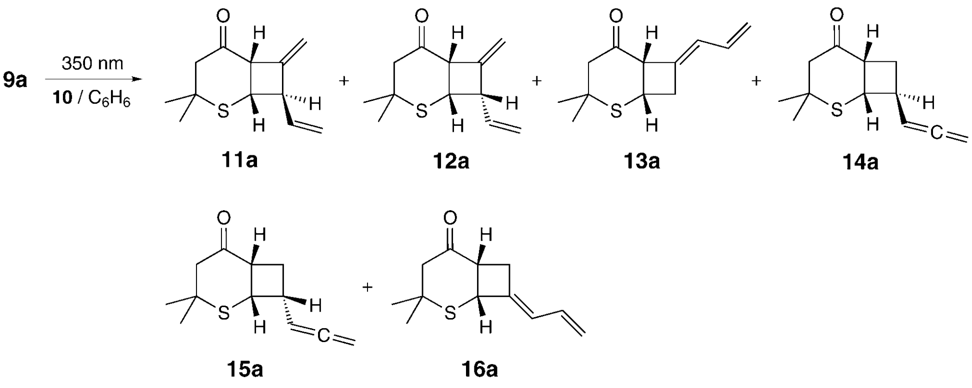
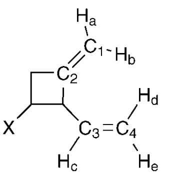


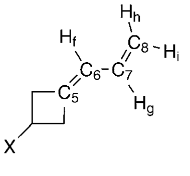
Table. *Selected NMR Data* ($CDCl_3$) *of Major Photocycloadducts* **11a**, **13a** *and* **14a**[a]). δ in ppm, *J* in Hz.

I	δ	II	δ	III	δ
H_a	5.22–5.21 (*m*)	H_f	6.06 (*d*, *J*=10)	H_j	5.25 (*q*, *J*=6.5)
H_b	5.04–5.03 (*m*)	H_g	6.23 (*td*, *J*=10, 17)	H_k	4.82 (*ddd*, *J*=2.5, 6.6, 9.7)
H_c	5.92 (*ddd*, *J*=7, 11, 17)	H_h	5.15 (*d*, *J*=17)	H_l	4.81 (*ddd*, *J*=2.5, 6.6, 9.7)
H_d	5.19 (*d*, *J*=17)	H_i	5.06 (*d*, *J*=10)		
H_e	5.11 (*d*, *J*=11)				
C_1	112	C_5	139	C_9	93
C_2	146	C_6	128	C_{10}	208
C_3	137	C_7	132	C_{11}	78
C_4	118	C_8	117		

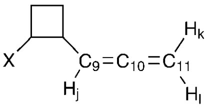
[a]) For convenience, the numbering of the olefinic H- and C-atoms is arbitrary; see **I**–**III**:



I



II

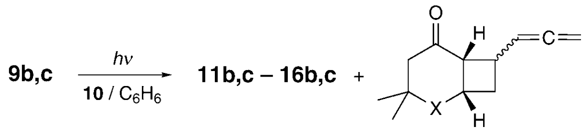


III

and 91, corresponding to $C_7H_8^+$ and $C_7H_7^+$, respectively. In contrast, the molecular ions of formal vinyl cycloadducts **14/15** undergo cycloreversion to give peaks corresponding to either protonated **9a** (*m*/*z* 143) or the molecular ion of **10** (*m*/*z* 66), respectively. Finally, GC analysis reveals that compounds **11/12** exhibit the shortest, and allenes **14/15** the longest retention times. As a matter of fact, all these analytic differentiations can be applied as well for the structural assignments of the photocycloadducts of **9b** and **9c**.

In contrast, column chromatography of the product mixture from **9b** does not afford any pure fraction containing a (or several) primary photoproducts, as these decompose under acidic conditions. Therefore, the product distribution was determined directly from the product mixture with the help of both the GC/MS and ^{1}H-NMR data, by correlating them with those of the known products **11a**–**16a**. In addition to (presumptive) compounds **11b** (19%), **12b** (7%), **13b** (7%), **14b** (28%), **15b** (15%), and **16b** (7%), two additional regioisomeric 8-(propa-2,3-dien-1-yl)bicyclo[4.2.0]octan-2-ones, **17b** (8%) and **18b** (8%), are formed in this reaction. Finally, chromatographic workup of the product mixture from **9c** affords first a complex mixture of dimers and trimers of vinylallene **10**, followed by pure **11c**. No further primary photoproduct could be isolated from the following fractions, and, therefore, the product distribution was again determined from the GC/MS data of the mixture. Thus, besides **11c** (10%), (presumptive) cycloadducts **12c** (10%), **13c** (6%), **14c** (20%), **15c** (20%), **16c** (6%), and again two additional regioisomeric propa-2,3-dien-1-yl derivatives, **17c** (14%) and **18c** (14%), are formed (*Scheme 3*).

Scheme 3

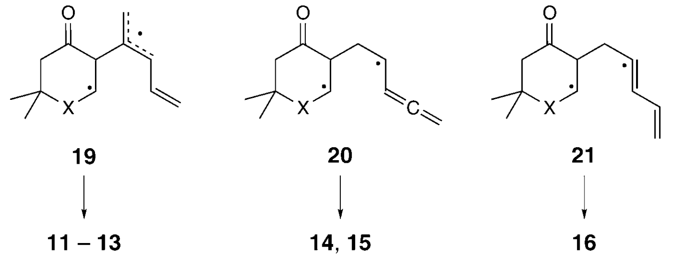


17b,c + 18b,c

3. Discussion. – In the preparative application of photocycloadditions, two factors concerning product formation are of decisive relevance, namely the efficiency and the selectivity. Regarding this second factor, the reactions of excited enones with penta-1,2,4-triene **10** are (unfortunately) much more complex than those with enynes, where primary bonding of the excited enone occurs almost exclusively at C(1) of **6**, cyclobutene formation by cycloaddition to the C≡C bond only being observed exceptionally, *e.g.*, when a contact ion pair is formed between the (electron deficient) enone and the enyne [3]. Nevertheless, the reactions of cyclohexenones **9** with **10** afford bicyclooctanones as **11**, **13**, or **14** with so far unknown substitution patterns on the four-membered ring. In this context, several aspects are of interest, some of them are related to the differential behavior of the cyclohexenones **9a**–**9c** themselves, some others to the outcome of the reactions in general. Regarding cyclohex-2-enones **9a**–**9c**, they differ mainly by their rigidity, *i.e.*, the ease with which the triplet enone relaxes by twisting around the C=C bond, this being due to the differences in C–S, C–C and C–O bond lengths. Although the triplet energies of **9a**–**9c** are unknown, that of **9b** must be very similar to the triplet energy of the parent (unsubstituted) cyclohex-2-enone ($E_T = 63$ kcal/mol), whereas those for **9a** and **9c** can be assumed in a first approximation to be similar to those of cyclohept-2-enone ($E_T = 43$ kcal/mol) and cyclopent-2-enone ($E_T = 74$ kcal/mol), respectively [4]. The fact that the triplet energy of **10** (estimated to be very similar to that of buta-1,3-diene) corresponds to a value slightly below 60 kcal/mol [5], explains why efficient energy transfer to **10** with concomitant dimerization only occurs from **9c**, but not from the other two enones **9a** and **9b**. This correlates with the finding that cyclohex-2-enone undergoes a photocycloaddition to buta-1,3-diene with almost the same efficiency as it does to simple alkenes, whereas cyclopent-2-enone reacts much more slowly with the same diene, at the same time affording relatively large amounts of the diene dimer *via* energy transfer [6]. This 'ring-size effect' due to the differences in bond lengths also reflects the relative stabilities of the bicyclooctanones formed. Whereas the – less strained – photoproducts derived from **9a** are reasonably stable towards acid, the corresponding photocycloadducts derived from **9b** and **9c** decompose partially or almost totally on prolonged contact to SiO_2.

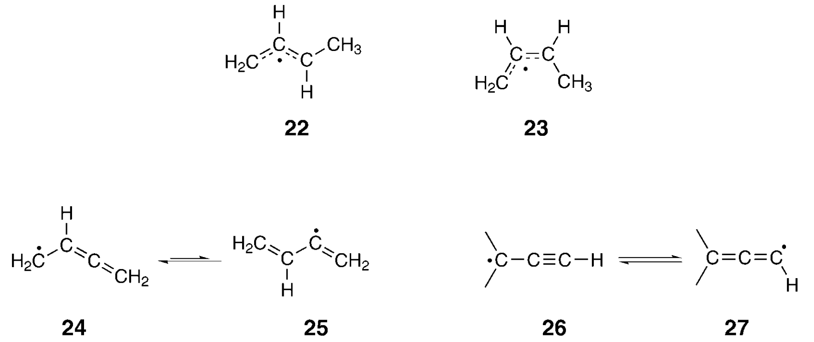
Regarding the product distribution itself, it can be safely assumed that bicyclooctanones **11**, **12**, and **13** stem from a common biradical precursor **19**, bicyclooctanones **14** and **15** from a common biradical **20** and **16** from biradical **21** (*Scheme 4*). In the sulfur series (starting material: **9a**), these three intermediates account quantitatively for all products formed and thus reflect the importance of the C-radical stabilization by the (vicinal) S-atom. The much better delocalization of the second radical center in the penta-1,4-dien-2-yl moiety in **19** as compared to that in the (formal) penta-3,4-dien-2-yl moiety in **20** then explains the much higher yield of **11a**–**13a** (64%) as compared to that of **14a**–**15a** (22%). In the CH_2 (**9b**) and the oxygen (**9c**) series, the first radical stabilizing effect is by far not so influent, and, therefore, regioisomeric bicyclooctanones **17** and **18** are formed as well, thus increasing the overall (relative) amount of cyclobutanes bearing an allenyl side chain.

Scheme 4



A final point involves the observation that biradicals **19** and **20** undergo 1,4-cyclization exclusively, whereas alkyl-propargyl biradical **7** (*cf. Scheme 1*) undergoes both 1,4- and 1,6-cyclizations, leading to the question '*Why do biradicals such as* **19** *and* **20** *not cyclize to naphthalenones ?*' The answer for **19** can be found in theoretical calculations on relative stabilities of the two conformers of the 1-methylallyl radical [7]. The *s-trans*-conformer **22** (*Scheme 5*; $\Delta H_f = 36.7$ kcal/mol) is slightly more stable than the corresponding *s-cis*-conformer **23** ($\Delta H_f = 37.4$ kcal/mol), and the activation barrier for interconversion of **22** to **23** ($E_a \approx 13$ kcal/mol) is relatively high, and, therefore, biradical **19** will exist mainly as the *s-trans*-conformer, unable to undergo 1,6-cyclization. In addition, calculations predict the buta-1,2-dien-4-yl radical (**24**) to be more stable than the isomeric buta-1,3-dien-2-yl radical (**25**) by *ca.* 9–10 kcal/mol [8]. This implies that in **20** the spin density on C(4) of the biradical will be much higher than on C(6), again excluding any 1,6-cyclization. In contrast, there is experimental evidence [9] that propargyl and allenyl radicals, *e.g.*, **26** and **27**, have very similar stabilities, which explains why biradical **7** does indeed undergo both cyclization modes.

Scheme 5



Experimental Part

1. *General.* Photolyses were run in a *Rayonet RPR-100* photoreactor equipped with (16) 350-nm lamps and a merry-go-round setup, with solvents of spectrophotometric grade. Column chromatography (CC): silica gel *60* (*Merck*; 230–400 mesh). ^{1}H- and ^{13}C-NMR spectra (including two-dimensional plots): in $CDCl_3$ at 500.13 and 125.8 MHz, resp., δ in ppm, *J* in Hz. GC/EI-MS: at 70 eV; 30-m *SE-30* cap. column.

2. *Starting Materials.* Cyclohexenones **9a** [10], **9b** [11], **9c** [12] were synthesized according to literature procedures. *Penta-1,2,4-triene* (**10**) was synthesized according to [13], but, in the last step, extracted into benzene (and not into pentane as described in [13]).

3. *Preparative Photolyses.* 3.1. *General Procedure.* Ar-Degassed solns. of **9** (2 mmol) and **10** (20 mmol) in benzene (5 ml) were irradiated for the time given, up to the degree of conversion indicated (GC monitoring) and then submitted to CC.

3.2. *Photocycloaddition of* **9a** *to* **10**. A soln. of **9a** (284 mg) and **10** (1.32 g) in benzene (10 ml overall) was irradiated for 9 h up to total conversion of **9a**. GC Monitoring (increasing retention times) indicated the formation of products **11a**–**16a** as described under *Results.* After evaporation, the residue (410 mg) was subjected to CC (2.5×40 cm column; pentane/Et_2O 3:1). The first fraction (84 mg) contained pure **11a** (20%; colorless oil). The 2nd fraction (170 mg) consisted of a 2:3:4 mixture of **13a**, **12a**, and **14a**, resp. The 3rd fraction (21 mg) contained pure **15a** (5%; colorless oil). The data given below for **16a** stem from the original product mixture.

Data of (1α,6α,8β)-8-Ethenyl-3,3-dimethyl-7-methylidene-2-thiabicyclo[4.2.0]octan-5-one (**11a**): ^{1}H-NMR: 5.92 (*ddd*, *J*=7.0, 10.5, 17.0); 5.22–5.21 (*m*); 5.19 (*d*, *J*=17.0); 5.11 (*d*, *J*=10.5); 5.04–5.03 (*m*); 3.82 (*d*, *J*=8.5); 3.78 (*dd*, *J*=4.1, 8.5); 3.47–3.43 (*m*); 2.62, 2.52 (*AB*, *J*=15.7, 2 H); 1.40, 1.34 (*s*, 2 Me). ^{13}C-NMR: 208.1 (*s*); 146.2 (*s*); 137.3 (*d*); 118.2 (*t*); 112.7 (*t*); 56.9 (*d*); 56.2 (*t*); 52.1 (*d*); 51.9 (*s*); 41.4 (*d*); 30.9, 30.7 (*q*, 2 Me). MS: 208 (1, $M^{+\cdot}$), 92 (100).

Data of (1α,6α,8α)-8-Ethenyl-3,3-dimethyl-7-methylidene-2-thiabicyclo[4.2.0]octan-5-one (**12a**): ^{1}H-NMR: 5.85 (*ddd*, *J*=7.0, 10.5, 17.0); 5.23 (*d*, *J*=17.0); 5.11 (*d*, *J*=10.5); 5.01–4.99 (*m*); 4.98–4.96 (*m*); 4.16 (*dd*, *J*=7.0, 7.5); 3.90 (*d*, *J*=7.5); 3.76–3.73 (*m*); 2.67, 2.41 (*AB*, *J*=16.4, 2 H); 1.37, 1.30 (*s*, 2 Me). ^{13}C-NMR: 207.9 (*s*); 148.8 (*s*); 134.6 (*d*); 119.9 (*t*); 108.8 (*t*); 56.9 (*t*); 52.2 (*d*); 52.1 (*d*); 46.8 (*s*); 41.4 (*d*); 30.7, 30.6 (*q*, 2 Me). MS: 208 (1, $M^{+\cdot}$), 92 (100).

Data of (1α,6α)-3,3-Dimethyl-7-(prop-2-enylidene)-2-thiabicyclo[4.2.0]octan-5-one (**13a**): ^{1}H-NMR: 6.23 (*td*, *J*=10.0. 17.0); 6.06 (*d*, *J*=10.0); 5.15 (*d*, *J*=17.0); 5.06 (*d*, *J*=10.0); 4.05 (*ddd*, *J*=3.0, 8.0, 9.0); 3.88 (*d*, *J*=8.0); 3.25 (*dd*, *J*=9.0, 10.0); 2.66 (*dd*, *J*=3.0, 10.0); 2.65, 2.46 (*AB*, *J*=16.4, 2 H); 1.36, 1.31 (*s*, 2 Me). ^{13}C-NMR: 207.2 (*s*); 139.1 (*s*); 132.2 (*d*); 126.1 (*d*); 117.3 (*t*); 56.1 (*t*); 52.1 (*d*); 48.7 (*s*); 38.2 (*d*); 36.8 (*d*); 31.5, 30.8 (*q*, 2 Me). MS: 208 (100, $M^{+\cdot}$).

Data of (1α,6α,8β)-3,3-Dimethyl-8-(propa-1,2-dienyl)-2-thiabicyclo[4.2.0]octan-2-one (**14a**): ^{1}H-NMR: 5.25 (*q*, *J*=6.5); 4.82 (*ddd*, *J*=2.5, 6.6, 9.7); 4.81 (*ddd*, *J*=2.5, 6.6, 9.7); 3.85 (*dd*, *J*=8.2, 8.3); 3.09 (*ddd*, *J*=4.4, 8.3, 8.9); 2.84 2.81 (*m*); 2.72 (*ddd*, *J*=4.4, 9.0, 11.0); 2.64, 2.58 (*AB*, *J*=13.9, 2 H); 2.07 (*ddd*, *J*=8.8, 9.0, 11.0); 1.43, 1.38 (*s*, 2 Me). ^{13}C-NMR: 212.1 (*s*); 208.2 (*s*); 93.1 (*d*); 78.1 (*t*); 56.1 (*t*); 48.1 (*s*); 47.2 (*d*); 43.1 (*d*); 41.9 (*d*); 28.4 (*t*); 31.1, 30.5 (*q*, 2 Me). MS: 208 (1, $M^{+\cdot}$), 143 (60), 86 (100), 66 (30).

Data of (1α,6α,8α)-3,3-Dimethyl-8-(propa-1,2-dienyl)-2-thiabicyclo[4.2.0]octan-2-one (**15a**): ^{1}H-NMR: 5.20 (*q*, *J*=6.5); 4.79 (*ddd*, *J*=2.5, 6.6, 9.7); 4.74 (*ddd*, *J*=2.5, 6.6, 9.7); 4.16 (*ddd*, *J*=3.3, 6.6, 6.6); 3.25 (*m*); 3.06 (*ddd*, *J*=6.6, 9.1, 10.1); 2.72 (*d*, *J*=15.8); 2.59 (*t*, *J*=10.0); 2.44 (*dddd*, *J*=3.3, 4.0, 8.0, 10.0); 2.42 (*d*, *J*=15.8); 1.38, 1.28 (*s*, 2 Me). ^{13}C-NMR: 212.1 (*s*); 208.2 (*s*); 90.2 (*d*); 77.8 (*t*); 55.2 (*t*); 45.8 (*d*); 45.6 (*s*); 42.6 (*d*); 34.4 (*d*); 31.2 (*t*); 31.1, 30.2 (*q*, 2 Me). MS: 208 (1, $M^{+\cdot}$), 143 (60), 86 (100), 66 (30).

Data of (1α,6α)-3,3-Dimethyl-8-(prop-2-enylidene)-2-thiabicyclo[4.2.0]octan-5-one (**16a**): ^{1}H-NMR: 6.45 (*td*, *J*=10.0, 17.0); 6.02 (*d*, *J*=10.0); 5.11 (*d*, *J*=17.0); 5.04 (*d*, *J*=10.0); 3.97–3.94 (*m*); other CH- and CH_2-signals not identified; 1.39, 1.33 (*s*, 2 Me). ^{13}C-NMR (only olefinic C-signals detectable): 138.1 (*s*); 132.1 (*d*); 128.1 (*d*); 117.1 (*t*). MS: 208 (100, $M^{+\cdot}$).

3.3. *Photocycloaddition of* **9b** *and* **10**. A soln. of **9b** (248 mg) and **10** (1.32 g) in benzene (10 ml overall) was irradiated for 12 h up to total conversion of **9b**. GC Monitoring (increasing retention times) indicated the formation of products **11b**–**18b** as described under *Results*. After evaporation, the residue (360 mg) was subjected to CC (2.5×40 cm column; pentane/Et_2O 3 : 1). The first fraction (20 mg) contained **12b** (5%) already slightly contaminated with decomposition products, the next two fractions consisted mainly of (decomposition) products not present in the original product mixture.

Data of (1α,6α,7α)-7-Ethenyl-4,4-dimethyl-8-methylidenebicyclo[4.2.0]octan-2-one (**12b**): ^{1}H-NMR: 5.82 (*ddd*, *J* = 7.0, 10.5, 17.0); 5.21 (*d*, *J* = 17.0); 5.17 (*d*, *J* = 10.5); 4.85–4.84 (*m*); 4.82–4.81 (*m*); 3.87–3.84 (*m*); 3.50 (*d*, *J* = 9.0); 2.56–2.53 (*m*); 2.25, 2.12 (*AB*, *J* = 16.5, 2 H); 1.79–1.75 (*m*, 2 H); 1.05, 0.91 (*s*, 2 Me). ^{13}C-NMR: 210.2 (*s*); 148.8 (*s*); 134.6 (*d*); 119.1 (*t*); 105.2 (*t*); 54.2 (*t*); 45.6 (*d*); 44.4 (*d*); 43.2 (*d*); 40.4 (*s*); 35.1 (*t*); 30.7, 25.6 (*q*, 2 Me). MS: 190 (12, $M^{+\cdot}$), 91 (100).

MS Data of Other Photocycloadducts (from the original product mixture)*:* **11b**: 190 (12, $M^{+\cdot}$), 91 (100); **13b**: 190 (40, M^{+}), 91 (100); **14b**: 190 (20, $M^{+\cdot}$), 125 (100), 66 (95); **15b**: 190 (20, $M^{+\cdot}$), 125 (95), 66 (100); **16b**: 190 (40, M^{+}), 91 (100); mixture of **17b** and **18b**: 190 (5, M^{+}), 125 (100), 66 (98).

3.4. *Photocycloaddition of* **9c** *and* **10**. A soln. of **9c** (252 mg) and **10** (1.32 g) in benzene (10 ml overall) was irradiated for 72 h up to *ca.* 50% conversion of **9c**. GC Monitoring (increasing retention times) indicated the formation of dimers of **10**, followed by products **11c**–**18c** as described under *Results*. After evaporation, the residue (600 mg) was subjected to CC (2.5×40 cm column, pentane/Et_2O 3 : 1). The first fraction (360 mg) contained a mixture of dimers and trimers of **10**. The 2nd fraction (12 mg) consisted of pure **11c** (3%, colorless oil). The next fraction contained the four allenic derivatives **14c**, **15c**, **17c**, and **18c** contaminated with (decomposition) products not present in the original product mixture.

Data of (1α,6α,8β)-8-Ethenyl-3,3-dimethyl-7-methylidene-2-oxabicyclo[4.2.0]octan-5-one (**11c**): ^{1}H-NMR: 5.95 (*ddd*, *J* = 7.0, 10.5, 17.0); 5.20 (*d*, *J* = 17.0); 5.15–5.14 (*m*); 5.10 (*d*, *J* = 10.5); 5.05–5.04 (*m*); 4.35 (*dd*, *J* = 2.2, 5.7); 3.60 (*d*, *J* = 5.7); 3.40 (*m*); 2.50, 2.25 (*AB*, *J* = 16.4, 2 H); 1.35, 1.21 (*s*, 2 Me). ^{13}C-NMR: 208.1 (*s*); 144.2 (*s*); 137.3 (*d*); 117.6 (*t*); 112.3 (*t*); 76.1 (*s*); 74.2 (*d*); 52.1 (*t*); 51.9 (*d*); 51.2 (*d*); 30.4, 25.9 (*q*, 2 Me). MS: 192 (0.01, $M^{+\cdot}$), 92 (50), 79 (100).

MS Data of Other Photocycloadducts (from the original product mixture)*:* **12c**: 192 (0.01, $M^{+\cdot}$), 92 (50), 79 (100); **13c**: 192 (0.01, M^{+}), 136 (30), 92 (50), 79 (100); **14c**: 192 (0.005, $M^{+\cdot}$), 127 (100), 66 (98); **15c**: 192 (0.005, $M^{+\cdot}$), 127 (100), 66 (98); **16c**: 192 (0.01, M^{+}), 136 (30), 92 (50), 79 (100); mixture of **17c** and **18c**: 192 (0.005, $M^{+\cdot}$), 127 (98), 66 (100).

3.5. *Relative-Efficiency Measurements.* For comparative irradiations of **9a**–**9c** in the presence of **10**, Ar-degassed solns. containing 0.1 mmol of **9** and 1 mmol of **10** in benzene (1 ml) were irradiated in a merry-go-round setup, and the formation of products was monitored by GC, with dodecane as internal standard, after constant time intervals.

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