Photocycloaddition of Conjugated Cyclohex-2-enones to 2,3-Dimethylbuta-1,3-diene

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Dedicated to Prof. *David I. Schuster*, NYU, at the occasion of his 75th birthday

On irradiation, in the presence of 2,3-dimethylbuta-1,3-diene, naphthalen-2-ones **1** are quantitatively and regioselectively converted to mixtures of diastereoisomeric cyclobutane adducts **3** and **4**, whereas, under these conditions, 3-(alk-1-ynyl)cyclohex-2-enones **5** give only one cyclobutane adduct **6** regio- and diastereoselectively. In contrast, 3-(alk-1-ynyl)-2-methylcyclohex-2-enones **10** undergo [2+2]-cycloaddition to the same diene exclusively at the C≡C bond to afford hitherto unknown 3-cyclobutenylcyclohex-2-enones **11**.

Introduction. – The (stepwise) formation of cyclobutanes *via* photocycloaddition of a cyclic α,β-unsaturated ketone to an alkene represents one of the synthetically most useful light-induced reactions [1][2]. Conjugated dienes have very seldom been utilized as the 'alkene' component, as their triplet energy values (E_T *ca.* 255 kJ/mol) correspond to that of cyclohex-2-enone itself, and, therefore, energy transfer from the (triplet)-excited enone to the diene occurs efficiently [3]. Nevertheless, it has been observed that irradiation of cyclohex-2-enone itself in neat buta-1,3-diene resulted in the formation of a mixture of [2+2]-cycloadducts [4]. Subsequently, it has been shown that cyclic enones with lower E_T values, *e.g.*, 2,3-dihydro-2,2-dimethyl-4*H*-thiopyran-4-one [5], 3-(alk-1-ynyl)cyclohept-2-enones [6], and even acyclic 4-acylbut-1-en-3-ynes [7] undergo efficient [2+2]-photocycloadditions to 1,3-dienes under 'standard' enone + alkene reaction conditions, *i.e.*, by using a slight excess of alkene. Very recently, the [2+2]-photocycloaddition of 5-phenylfuran-3(2*H*)-ones to cyclohexa-1,3-dienes has been successfully applied as key step in the total synthesis of biyouyanagin A and its analogs [8]. Here, we report *a*) further examples of such reactions between cyclohex-2-enones – wherein the C=C bond is further conjugated – and 2,3- dimethylbuta-1,3-diene, and *b*) on a novel cyclobutene-forming reaction by cycloaddition of one of the C=C bonds of the same ground-state diene to the C≡C bond of excited 3-(alk-1-ynyl)cyclohex-2-enones.

Results. – Irradiation (350 nm) of 1,2-dihydro-1,1-dimethoxynaphthalen-2-one (**1a**) in the presence of a tenfold molar excess of 2,3-dimethylbuta-1,3-diene (**2**) afforded regioselectively a 2:1 mixture of diastereoisomeric cyclobutane adducts **3a** and **4a**. Similarly, 1,1,7-trimethoxynaphthalenone **1b** was quantitatively converted to a 2:1

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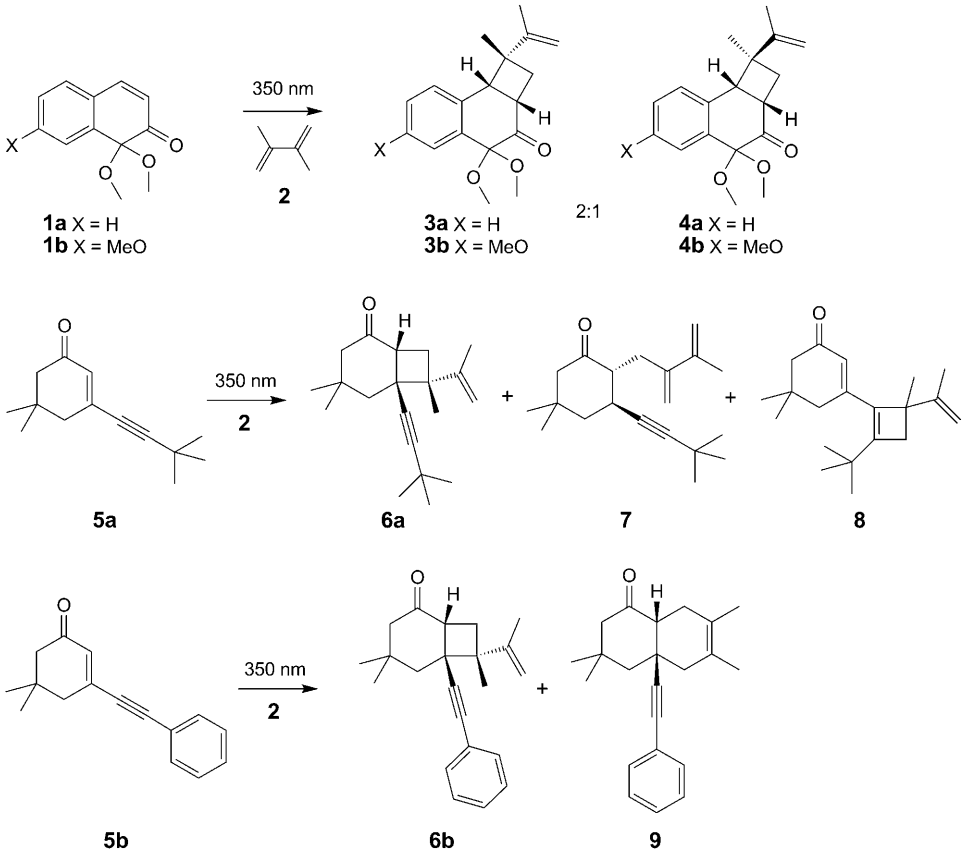
mixture of **3b** and **4b**. Irradiation of 3-(3,3-dimethylbut-1-yn-1-yl)-5,5-dimethylcyclohex-2-enone (**5a**) in the presence of **2** also proceeded with total conversion of starting enone to afford a 2:1 mixture of cyclobutane adduct **6a** and cyclohexanone **7**. Monitoring the reaction by ^{1}H-NMR spectroscopy indicated the formation of an additional minor product **8**, which underwent (photo)decomposition on lenghtened irradiation. Photoproduct **8** was isolated in low yield in an experiment with a low degree of conversion of enone **5a** and identified as a 3-cyclobutenyl-cyclohex-2-enone resulting from cycloaddition of a C=C bond of **2** to the C≡C bond of excited **5a**. Under the same conditions, the 3-(2-phenylethynyl) derivative **5b** gave a 2:1:1 mixture of cyclobutane adduct **6b** (regio- and diastereoselectively as for **6a**) of the 1,4-cyclization product **9** and an additional minor product, which could be neither isolated nor identified directly from the product mixture (*Scheme 1*).

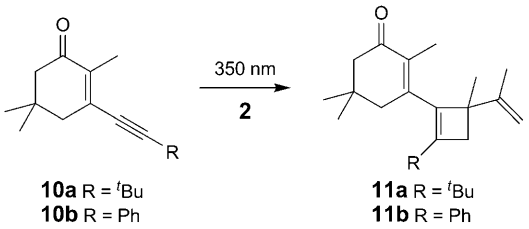
Scheme 1



Encouraged by the finding of a novel cyclobutene-forming reaction, 3-alkynyl-2,5,5-trimethylcyclohex-2-enones **10a** and **10b** were synthesized anew. Irradiation of these enones in the presence of **2** gave 3-cyclobutenylcyclohex-2-enones **11a** and **11b** *via*

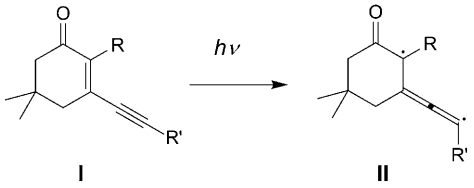
[2 + 2]-cycloaddition to the C≡C bond exclusively (*Scheme 2*). For preparative purposes, these latter reactions required slightly longer (*ca.* 30%) irradiation times as compared to those for cyclohexenones **5** and could only be run up to 75–85% conversion of starting material, since the resulting (conjugated) dienones **11**, which also absorb the incident light, then start to undergo secondary light-induced reactions. All new photoproducts were isolated and purified by chromatography, and fully characterized by one- and two-dimensional NMR spectroscopy. The structures of **6a** and **6b** were additionally established by X-ray analysis.

Scheme 2



Discussion. – The outcome of the irradiations of both naphthalenones **1** and (alkynyl)cyclohexenones **5** in the presence of diene **2** correlates perfectly with the assumption that the regiochemistry of such [2 + 2]-photocycloadditions reflects the formation of the most stable 1,4-biradical intermediate. The higher diastereoselectivity in the ring-closure step to cyclobutanes **6** (no second diastereoisomer observed) as compared to that for cyclobutanes **3** and **4** (ratio 2 : 1) is most probably due to the higher flexibility of the cyclohexenone ring in **5** as compared to that in – almost rigid – **1**. The configuration of cyclobutane adducts **6** was established by X-ray analysis, whereas the differentiation between diastereoisomers **3** and **4** became unequivocal by comparing the chemical shifts of the methyl and methylethenyl Me signals in the ^{1}H-NMR spectra. In the major products **3**, the former resonates at *ca.* 1.60 ppm and the latter at *ca.* 1.10 ppm, whereas, in the minor adducts **4**, the shielding/deshielding effect of the aromatic ring inverts this sequence, and therefore the former now resonates at 0.65 ppm and the latter at 1.85 ppm. In contrast, the site-selective cyclobutene formation in the reaction of (alkynyl)cyclohexenones **10** with the same diene is remarkable, as cyclobutene-forming cycloadditions between an excited alkyne and a (ground-state) alkene are rather uncommon [9] and have up to now been limited to (excited) aryl- [10] or diarylacetylenes [11], respectively. Apparently, conjugation of the C≡C bond with a C=C bond of an enone moiety (as in **I**) induces an enhancement in photoreactivity towards an alkene partner due to high spin densities (*i.e.*, **II**) at both C(α) of the enone system and C(2) of the alkyne moiety (*Scheme 3*). Upon hindering the primary binding step at C(α) of the excited enone by introducing an additional Me group, as in cyclohexenones **10**, cyclobutene formation now becomes the exclusive reaction.

Scheme 3



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): *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. X-Ray analyses: *Bruker SMART APEX II* three-circle diffractometer at 153 K with MoK_α radiation (λ 0.71073 Å).

2. *Starting Materials.* Naphthalen-2-ones **1** were synthesized according to [12], and cyclohexenones **5a** and **5b** according to [13] and [14], resp.

2.1. *Synthesis of 3-Alkynyl-2,5,5-trimethylcyclohex-2-enones* **10**. In analogy to [13] from 3-ethoxy-2,5,5-trimethylcyclohex-2-enone [15] and 3,3-dimethylbut-1-yn-1-yl or phenylethynyl magnesium bromide.

3-(3,3-Dimethylbut-1-yn-1-yl)-2,5,5-trimethylcyclohex-2-en-1-one (**10a**). CC (SiO_2; pentane/Et_2O 1:1): R_f 0.60. Yield: 30%. Light yellow oil. ^{1}H-NMR ($CDCl_3$): 2.33 (*d*, *J* = 1.9, 2 H); 2.27 (*s*, 2 H); 1.93 (*t*, *J* = 1.9, 3 H); 1.29 (*s*, 9 H); 1.02 (*s*, 6 H). ^{13}C-NMR ($CDCl_3$): 199.7 (*s*); 137.2 (*s*); 136.4 (*s*); 112.2 (*s*); 78.7 (*s*); 51.6 (*t*); 45.3 (*t*); 33.0 (*s*); 31.0 (*q*); 30.2 (*s*); 29.9 (*q*); 12.9 (*q*). EI-MS: 218 (100, M^+).

2,5,5-Trimethyl-3-(2-phenylethynyl)cyclohex-2-en-1-one (**10b**): CC (SiO_2; pentane/Et_2O 3:2): R_f 0.41. Yield: 35%. Light yellow oil. ^{1}H-NMR ($CDCl_3$): 7.50–7.48 (*m*, 2 H); 7.38–7.35 (*m*, 3 H); 2.47 (*d*, *J* = 1.8, 2 H); 2.33 (*s*, 2 H); 2.06 (*t*, *J* = 1.9, 3 H); 1.07 (*s*, 6 H). ^{13}C-NMR ($CDCl_3$): 198.6 (*s*); 137.9 (*s*); 135.1 (*s*); 131.7 (*d*); 128.5 (*d*); 126.1 (*d*); 122.5 (*s*); 102.5 (*s*); 88.6 (*s*); 51.5 (*t*); 44.8 (*t*); 33.5 (*s*); 28.1 (*q*); 13.7 (*q*). EI-MS: 238 (100, M^+).

3. *Photocycloadditions to* **2**. Ar-degassed solns. of either **1**, **5**, or **9** (1 mmol) and 2,3-dimethylbuta-1,3-diene (**2**) (0.82 g, 10 mmol) in benzene (5 ml) were irradiated for the time indicated. Workup (CC; SiO_2) as given below.

3.1. *Photocycloaddition of* **1a**. Total conversion of starting material was achieved after irradiation for 3 h. CC: SiO_2; pentane/Et_2O 9:1. The minor product, rel-*(1*R*,2a*R*,8b*R*)-2,2a,4,8b-tetrahydro-4,4-dimethoxy-1-methyl-1-(1-methylethenyl)cyclobuta[*a*]naphthalen-3(1*H*)-one* (**4a**), eluted first (R_f 0.67). Yield: 40 mg (14%). Yellow oil. ^{1}H-NMR ($CDCl_3$): 7.72 (*d*, *J* = 8.4, 1 H); 7.28–7.25 (*m*, 2 H); 7.07 (*d*, *J* = 8.4, 1 H); 4.97 (br. *s*, 1 H), 4.86 (br. *s*, 1 H); 4.50 (*d*, *J* = 11.0, 1 H); 3.65 (*ddd*, *J* = 4.3, 9.5, 11.0, 1 H); 3.55, 2.95 (2*s*, 3 H); 2.30 (*dd*, *J* = 4.3, 12.0, 1 H); 2.26 (*dd*, *J* = 9.5, 12.0, 1 H); 1.83 (*s*, 3 H); 0.65 (*s*, 3 H). ^{13}C-NMR ($CDCl_3$): 207.1 (*s*); 152.2 (*s*); 136.2 (*s*); 134.3 (*s*); 128.1 (*d*); 127.6 (*d*); 127.2 (*d*); 126.4 (*d*); 110.2 (*t*); 100.5 (*s*); 53.1, 49.2 (2*q*); 48.1 (*s*); 47.2 (*d*); 38.3 (*d*); 32.4 (*t*); 24.2 (*q*); 19.1 (*q*).

Compound **4a** was followed by rel-*(1*R*,2a*S*,8b*S*)-2,2a,4,8b-tetrahydro-4,4-dimethoxy-1-methyl-1-(1-methylethenyl)cyclobuta[*a*]naphthalen-3(1*H*)-one* (**3a**; R_f 0.61). Yield: 123 mg (43%). Yellow oil. ^{1}H-NMR ($CDCl_3$): 7.67 (*d*, *J* = 8.4, 1 H); 7.26–7.24 (*m*, 2 H); 7.03 (*d*, *J* = 8.4, 1 H); 4.77 (br. *s*, 1 H), 4.76 (br. *s*, 1 H); 4.08 (*d*, *J* = 10.5, 1 H); 3.70 (*ddd*, *J* = 6.2, 10.2, 10.5, 1 H); 3.55, 2.94 (2*s*, 3 H); 2.68 (*dd*, *J* = 6.2, 12.6, 1 H); 2.00 (*dd*, *J* = 10.2, 12.6, 1 H); 1.61 (*s*, 3 H); 1.09 (*s*, 3 H). ^{13}C-NMR ($CDCl_3$): 207.1 (*s*); 148.2 (*s*); 138.0 (*s*); 135.5 (*s*); 128.1 (*d*); 127.2 (*d*); 126.5 (*d*); 125.7 (*d*); 113.1 (*t*); 100.5 (*s*); 53.0 (*d*); 52.1, 48.7 (2*q*); 47.1 (*s*); 36.5 (*d*); 31.7 (*t*); 29.9 (*q*); 21.1 (*q*).

3.2. *Photocycloaddition of* **1b**. Total conversion of starting material was achieved after irradiation for 3 h. CC: SiO_2; pentane/Et_2O 9:1. The minor product, rel-*(1*R*,2a*R*,8b*R*)-2,2a,4,8b-tetrahydro-4,4,6-trimethoxy-1-methyl-1-(1-methylethenyl)cyclobuta[*a*]naphthalen-3(1*H*)-one* (**4b**), eluted first (R_f 0.36).

Yield: 48 mg (15%). Yellow oil. ^{1}H-NMR ($CDCl_3$): 7.18 (*d*, *J* = 2.7, 1 H); 7.00 (*d*, *J* = 8.5, 1 H); 6.88 (*dd*, *J* = 2.7, 8.5, 1 H); 4.98 (*s*, 1 H); 4.89 (*s*, 1 H); 4.42 (*d*, *J* = 10.8, 1 H); 3.85 (*s*, 3 H); 3.60 (*ddd*, *J* = 4.3, 9.5, 11.0, 1 H); 3.55, 3.00 (2*s*, 3 H); 2.29 (*m*, 2 H); 1.82 (*s*, 3 H); 0.68 (*s*, 3 H). ^{13}C-NMR ($CDCl_3$): 207.1 (*s*); 159.2 (*s*); 152.1 (*s*); 139.2 (*s*); 132.2 (*s*); 129.9 (*d*); 116.9 (*d*); 112.1 (*d*); 110.1 (*t*); 99.9 (*s*); 55.9 (*q*); 51.0 (*q*); 49.1 (*q*); 48.2 (*s*); 46.1 (*d*); 37.1 (*d*); 30.0 (*t*); 23.7 (*q*); 19.1 (*q*).

Compound **4b** was followed by rel-*(1*R*,2a*S*,8b*S*)-2,2a,4,8b-tetrahydro-4,4,6-trimethoxy-1-methyl-1-(1-methylethenyl)cyclobuta[*a*]naphthalen-3(1*H*)-one* (**3b**; R_f 0.31). Yield: 141 mg (44%). Yellow oil. ^{1}H-NMR ($CDCl_3$): 7.21 (*d*, *J* = 2.7, 1 H); 6.99 (*d*, *J* = 8.5, 1 H); 6.82 (*dd*, *J* = 2.7, 8.5, 1 H); 4.75 (br. *s*, 2 H); 4.00 (*d*, *J* = 11.0, 1 H); 3.84 (*s*, 3 H); 3.66 (*ddd*, *J* = 6.2, 10.0, 11.0, 1 H); 3.57, 3.00 (2*s*, 3 H); 2.70 (*dd*, *J* = 6.2, 12.5, 1 H); 2.08 (*dd*, *J* = 10.0, 12.5, 1 H); 1.62 (*s*, 3 H); 1.21 (*s*, 3 H). ^{13}C-NMR ($CDCl_3$): 207.1 (*s*); 159.2 (*s*); 148.1 (*s*); 136.1 (*s*); 130.1 (*s*); 128.2 (*d*); 114.3 (*d*); 111.1 (*t*); 109.5 (*d*); 100.0 (*s*); 55.1 (*q*); 52.1 (*q*); 52.0 (*d*); 49.1 (*q*); 47.2 (*s*); 38.4 (*d*); 31.1 (*t*); 30.9 (*q*); 22.1 (*q*).

3.3. *Photocycloaddition of* **5a**. Irradiation for 3 h led to total conversion (monitoring by ^{1}H-NMR) with formation of a 1:2 mixture of 1:1 photoproducts **7** and **6a**. CC (SiO_2; pentane/2:1) afforded first trans-*3-(3,3-dimethylbut-1-yn-1-yl)-5,5-dimethyl-2-(3-methyl-2-methylidenebut-3-en-1-yl)cyclohexanone* (**7**; R_f 0.64). Yield: 23 mg (8%). Light yellow oil. ^{1}H-NMR ($CDCl_3$): 5.10 (*s*, 1 H); 5.07 (*s*, 1 H); 5.01 (*s*, 1 H); 4.98 (*s*, 1 H); 3.05 (*ddd*, *J* = 5.0, 5.1, 7.3, 1 H); 2.80 (*dd*, *J* = 6.9, 14.1, 1 H); 2.68 (*dd*, *J* = 7.5, 14.1, 1 H); 2.59 (*m*, 1 H); 2.36 (*d*, *J* = 13.6, 1 H); 2.14 (*m*, 1 H); 1.90 (*s*, 3 H); 1.85 (*m*, 1 H), 1.70 (*d*, *J* = 13.8, 1 H); 1.13 (*s*, 3 H); 1.08 (*s*, 9 H); 0.96 (*s*, 3 H). ^{13}C-NMR ($CDCl_3$): 212.8 (*s*); 145.1 (*s*); 142.4 (*s*); 114.0 (*t*); 113.0 (*t*); 92.3 (*s*); 78.2 (*s*); 52.2 (*t*); 51.0 (*d*); 41.3 (*t*); 36.0 (*s*); 31.5 (*d*); 31.2 (*t*); 31.0 (*q*); 30.2 (*q*); 29.5 (*q*); 27.4 (*s*); 21.5 (*q*). EI-MS: 286 (20, M^+), 41 (100).

The second fraction consisted of rel-*(1*R*,6*R*,7*R*)-6-(3,3-dimethylbut-1-yn-1-yl)-4,4,7-trimethyl-7-(1-methylethenyl)bicyclo[4.2.0]octan-2-one* (**6a**; R_f 0.43). Yield: 80 mg (28%). White crystals. M.p. 65°. ^{1}H-NMR ($CDCl_3$): 4.83 (br. *s*, 1 H); 4.59 (*s*, 1 H); 2.95 (*dd*, *J* = 9.5, 9.8, 1 H); 2.30 (*d*, *J* = 14.8, 1 H); 2.21 (*dd*, *J* = 9.8, 10.8, 1 H); 2.06 (*dd*, *J* = 1.3, 14.8, 1 H); 1.91 (*d*, *J* = 12.8, 1 H); 1.89 (*dd*, *J* = 9.5, 10.8, 1 H); 1.63 (*dd*, *J* = 1.5, 12.8, 1 H); 1.67 (*s*, 3 H); 1.35 (*s*, 3 H); 1.17 (*s*, 9 H); 1.03 (*s*, 3 H); 1.02 (*s*, 3 H). ^{13}C-NMR ($CDCl_3$): 210.8 (*s*); 150.3 (*s*); 109.6 (*t*); 92.4 (*s*); 82.6 (*s*); 51.4 (*t*); 48.5 (*s*); 45.2 (*d*); 42.6 (*s*); 41.9 (*t*); 35.3 (*s*); 32.7 (*t*); 31.7 (*q*); 31.1 (*q*); 27.9 (*s*); 26.3 (*q*); 23.7 (*t*); 18.7 (*q*). EI-MS: 286 (9, M^+), 205 (100).

X-Ray Crystal-Structure Determination of **6a**[1]). Pale colorless blocks (0.36 × 0.17 × 0.05 mm) from hexane, $C_{20}H_{30}O$, M_r 286.44, monoclinic, space group *P*2(1)/*c*; *Z* = 4, *a* = 15.942(3) Å, *b* = 9.1199(1) Å, *c* = 12.1515(19) Å, *β* = 90.944(3)°; *V* = 1766.5(5) Å^3, D_x = 1.077 g cm^{-3}.

3.4. *Photocycloaddition of* **5a** *at Low Degree of Conversion.* Irradiation for 60 min and subsequent CC as described above afforded *3-[2-(*tert*-butyl)-4-methyl-4-(1-methylethenyl)cyclobut-1-en-1-yl]-5,5-dimethylcyclohex-2-en-1-one* (**8**; R_f 0.30). Yield: 6 mg (2%). Light yellow oil. ^{1}H-NMR ($CDCl_3$): 5.90 (br., 1 H); 4.82 (*s*, 1 H); 4.80 (*s*, 1 H); 2.41 (*d*, *J* = 14.5, 1 H); 2.27 (*d*, *J* = 1.4, 2 H); 2.22 (*s*, 2 H); 2.14 (*d*, *J* = 14.5, 1 H); 1.71 (*s*, 3 H); 1.38 (*s*, 3 H); 1.12 (*s*, 9 H); 1.035 (*s*, 3 H), 1.032 (*s*, 3 H). ^{13}C-NMR ($CDCl_3$): 199.9 (*s*); 155.3 (*s*); 149.4 (*s*); 142.5 (*s*); 142.2 (*s*); 126.3 (*d*); 110.2 (*t*); 50.9 (*t*); 47.5 (*s*); 42.5 (*t*); 40.1 (*t*); 33.5 (*s*); 33.4 (*s*); 29.4 (*q*); 28.1 (*q*); 23.4 (*q*); 18.4 (*q*). EI-MS: 286 (40, M^+), 229 (100).

3.5. *Photocycloaddition of* **5b**. Irradiation for 3 h led to total conversion (monitoring by ^{1}H-NMR) with formation of a 1:2 mixture of 1:1 photoproducts **9** and **6b**. CC (SiO_2; pentane/Et_2O 2:1) afforded first rel-*(4a*R*,8a*R*)-3,4,4a,5,8,8a-hexahydro-3,3,6,7-tetramethyl-4a-(phenylethynyl)naphthalen-1(2*H*)-one* (**9**; R_f 0.61). Yield: 55 mg (18%). Light yellow oil. ^{1}H-NMR ($CDCl_3$): 7.30–7.28 (*m*, 2 H); 7.24–7.22 (*m*, 3 H); 2.42 (*dd*, *J* = 1.2, 5.2, 1 H); 2.30 (*dd*, *J* = 1.0, 5.0, 1 H); 2.27 (br. *s*, 2 H); 2.20 (*d*, *J* = 12.8, 1 H); 2.18 (*dd*, *J* = 2.0, 12.8, 1 H); 2.04 (*d*, *J* = 12.8, 1 H); 2.01 (*dd*, *J* = 2.0, 13.0, 1 H); 1.69 (*s*, 3 H); 1.64 (*d*, *J* = 13.0, 1 H); 1.62 (*s*, 3 H); 1.21 (*s*, 3 H); 1.07 (*s*, 3 H). ^{13}C-NMR ($CDCl_3$): 209.7 (*s*); 131.7 (*d*); 128.7 (*d*); 126.9 (*d*), 124.1 (*s*); 123.0 (*s*); 122.7 (*s*); 91.3 (*s*); 85.3 (*s*); 54.3 (*t*); 52.3 (*d*); 49.3 (*t*); 48.9 (*s*); 48.5 (*t*); 35.7 (*s*); 33.1 (*q*); 28.7 (*q*); 27.0 (*q*); 18.7 (*q*); 18.5 (*q*). EI-MS: 306 (51, M^+), 168 (100).

The second fraction consisted of rel-*(1*R*,6*R*,7*R*)-4,4,7-trimethyl-6-(phenylethynyl)-7-(1-methylethenyl)bicyclo[4.2.0]octan-2-one* (**6b**; R_f 0.36). Yield: 67 mg (22%). White crystals. M.p. 144°. ^{1}H-NMR ($CDCl_3$): 7.36–7.34 (*m*, 2 H); 7.26–7.24 (*m*, 3 H); 4.88 (br. *s*, 1 H); 4.64 (*s*, 1 H); 3.11 (*dd*, *J* = 9.3, 10.5,

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[1]) CCDC-764276 and -764277 contain the supplementary crystallographic data for **6a** and **6b**, respectively. These data can be obtained free of charge *via* www.ccdc.cam.ac.uk/data_request/cif.

1 H); 2.35 (*d*, *J* = 14.8, 1 H); 2.28 (*dd*, *J* = 10.5, 11.0, 1 H); 2.11 (*dd*, *J* = 1.3, 14.8, 1 H); 2.01 (*d*, *J* = 14.0, 1 H); 1.98 (*dd*, *J* = 9.3, 11.0, 1 H); 1.84 (*dd*, *J* = 1.3, 14.0, 1 H); 1.73 (*s*, 3 H); 1.47 (*s*, 3 H); 1.11 (*s*, 3 H); 1.06 (*s*, 3 H). ^{13}C-NMR ($CDCl_3$): 210.7 (*s*); 149.9 (*s*); 131.1 (*d*); 127.9 (*d*); 126.5 (*d*); 123.4 (*s*); 109.9 (*t*); 91.1 (*s*); 86.4 (*s*); 51.2 (*t*); 49.4 (*s*); 44.8 (*d*); 43.7 (*s*); 41.8 (*t*); 35.1 (*q*); 32.7 (*t*); 31.1 (*q*); 26.2 (*q*); 23.5 (*q*); 19.0 (*q*). EI-MS: 306 (20, M^+), 168 (100).

X-Ray Crystal-Structure Determination of **6b**[1]). Pale colorless blocks (0.48 × 0.41 × 0.07 mm) from CH_2Cl_2, $C_{22}H_{26}O$, M_r 306.43, trigonal, space group *P*32; *Z* = 3, *a* = *b* = 9.6842(10) Å, *c* = 16.744(2) Å, γ = 120°; *V* = 1359.9(3) Å^3, D_x = 1.122 g cm^{-3}.

3.6. *Photocycloaddition to* **10a**. Irradiation for 4 h led to *ca.* 85% conversion to **11a** (monitoring by ^{1}H-NMR). CC (SiO_2; CH_2Cl_2/toluene 90:1) afforded *3-[2-(*tert*-butyl)-4-methyl-4-(1-methylethenyl)cyclobut-1-en-1-yl]-2,5,5-trimethylcyclohex-2-en-1-one* (**11a**; R_f 0.48). Yield: 147 mg (49%). Light yellow oil. ^{1}H-NMR ($CDCl_3$): 4.80 (*s*, 2 H); 2.55 (*d*, *J* = 13.1, 1 H); 2.25 (*s*, 2 H); 2.19 (*s*, 2 H); 2.07 (*d*, *J* = 13.1, 1 H); 1.81 (*s*, 3 H); 1.78 (*s*, 3 H); 1.36 (*s*, 3 H); 1.02 (*s*, 9 H); 1.015 (*s*, 3 H); 0.98 (*s*, 3 H). ^{13}C-NMR ($CDCl_3$): 199.9 (*s*); 151.0 (*s*); 149.4 (*s*); 147.9 (*s*); 141.4 (*s*); 131.5 (*s*); 110.5 (*t*); 51.5 (*t*); 50.5 (*s*); 43.8 (*t*); 38.1 (*t*); 33.5 (*s*); 33.1 (*s*); 28.6 (*q*); 28.0 (*q*); 27.6 (*q*); 24.3 (*q*); 19.2 (*q*); 13.8 (*q*). EI-MS: 300 (35, M^+), 218 (100).

3.7. *Photocycloaddition to* **10b**. Irradiation for 4 h led to *ca.* 70% conversion to **11b** (monitoring by ^{1}H-NMR). CC (SiO_2; CH_2Cl_2/toluene 10:1) afforded *2,5,5-trimethyl-3-[4-methyl-4-(1-methylethenyl-2-phenyl)cyclobut-1-en-1-yl]cyclohex-2-en-1-one* (**11b**; R_f 0.40). Yield: 131 mg (41%). Light yellow oil. ^{1}H-NMR ($CDCl_3$): 7.36–7.19 (*m*, 5 H); 4.85 (*s*, 1 H); 4.83 (*s*, 1 H); 2.89 (*d*, *J* = 13.0, 1 H); 2.49 (*d*, *J* = 13.0, 1 H); 2.38 (*d*, *J* = 17.9, 1 H); 2.34 (*s*, 2 H); 2.32 (*d*, *J* = 17.9, 1 H); 1.80 (*s*, 3 H); 1.68 (br. *s*, 3 H); 1.54 (*s*, 3 H); 1.07 (*s*, 3 H); 1.06 (*s*, 3 H). ^{13}C-NMR ($CDCl_3$): 199.6 (*s*); 149.7 (*s*); 149.2 (*s*); 143.6 (*s*); 139.7 (*s*); 134.8 (*s*); 131.3 (*s*); 128.8 (*d*); 128.2 (*d*); 125.7 (*d*); 109.7 (*t*); 51.5 (*t*); 47.5 (*s*); 41.3 (*t*); 39.8 (*t*); 33.5 (*s*); 29.0 (*q*); 28.6 (*q*); 24.4 (*q*); 19.3 (*q*); 13.0 (*q*). EI-MS: 320 (100, M^+).

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REFERENCES

[1] J. P. Hehn, C. Müller, T. Bach, in 'Handbook of Synthetic Photochemistry', Eds. A. Albini, M. Fagnoni, Wiley-VCH, Weinheim, 2009, pp. 171–215.
[2] P. Margaretha, in 'Molecular and Supramolecular Photochemistry', Vol. 12, Eds. A. G. Griesbeck, J. Mattay, Marcel Dekker, New York, 2005, p. 211–238.
[3] E. Y. Y. Lam, D. Valentine, G. S. Hammond, *J. Am. Chem. Soc.* **1967**, *89*, 3482.
[4] T. S. Cantrell, *J. Org. Chem.* **1974**, *39*, 3063.
[5] P. Margaretha, K. Schmidt, J. Kopf, V. Sinnwell, *Synthesis* **2007**, 1426.
[6] I. Inhülsen, P. Margaretha, *Org. Lett.* **2010**, *12*, 728.
[7] M. R. J. Vallée, I. Inhülsen, P. Margaretha, *Helv. Chim. Acta* **2010**, *93*, 17.
[8] K. C. Nicolau, T. R. Wu, D. Sarlah, D. M. Shaw, E. Rowcliffe, D. R. Burton, *J. Am. Chem. Soc.* **2008**, *130*, 11114.
[9] P. Margaretha, in 'Houben-Weyl', Vol. E17f, Thieme, Stuttgart, 1997, p. 654.
[10] G. Kaupp, M. Stark, *Chem. Ber.* **1981**, *114*, 2217.
[11] T. A. Zeidan, S. V. Kovalenko, M. Manohavan, R. J. Clark, I. Ghiviriga, I. V. Alabugin, *J. Am. Chem. Soc.* **2005**, *127*, 4270.
[12] D. Mal, H. N. Roy, N. K. Hazra, S. Adhikari, *Tetrahedron* **1997**, *53*, 2177.
[13] H. J. Rathjen, P. Margaretha, S. Wolff, W. C. Agosta, *J. Am. Chem. Soc.* **1991**, *113*, 3904.
[14] J. V. Comasseto, W. L. Lo, N. Petragnani, *Tetrahedron* **1997**, *53*, 7445.
[15] E. G. Meek, J. H. Turnbull, W. Wilson, *J. Chem. Soc.* **1953**, 811.

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