

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

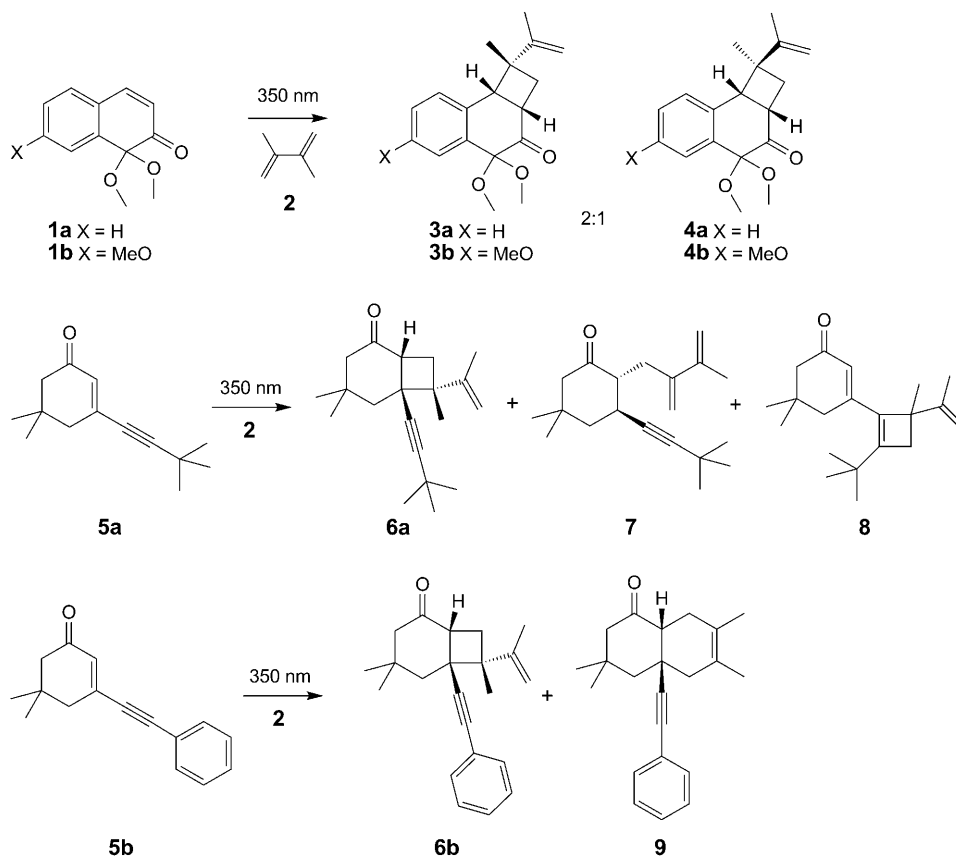
On irradiation, in the presence of 2,3-dimethylbuta-1,3-diene, naphthalen-2-ones **1** are quantitatively and regioselectively converted to mixtures of diastereoisomeric cyclobutane adducts **3** and **4**, whereas, under these conditions, 3-(alk-1-ynyl)cyclohex-2-enones **5** give only one cyclobutane 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 $\equiv$ 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-yne [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 $\equiv$ 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

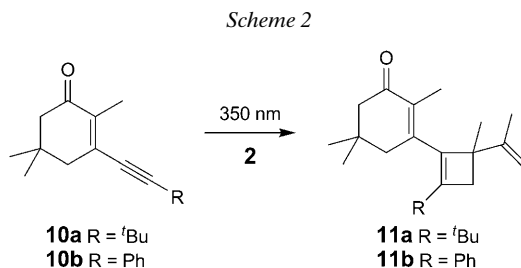
mixture of **3b** and **4b**. Irradiation of 3-(3,3-dimethylbut-1-yn-1-yl)-5,5-dimethylcyclohex-2-enone (**5a**) in the presence of **2** also proceeded with total conversion of starting enone to afford a 2:1 mixture of cyclobutane adduct **6a** and cyclohexanone **7**. Monitoring the reaction by $^1\text{H-NMR}$ spectroscopy indicated the formation of an additional minor product **8**, which underwent (photo)decomposition on lengthened 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 $\text{C}\equiv\text{C}$ 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



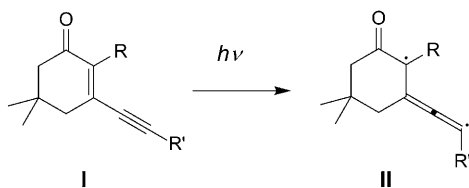
Encouraged by the finding of a novel cyclobutene-forming reaction, 3-alkynyl-2,5,5-trimethylcyclohex-2-enones **10a** and **10b** were synthesized anew. Irradiation of these enones in the presence of **2** gave 3-cyclobutenylcyclohex-2-enones **11a** and **11b** via

[2 + 2]-cycloaddition to the $C\equiv C$ 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.



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 ^1H -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 $C\equiv C$ 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 $C(\alpha)$ of the enone system and $C(2)$ of the alkyne moiety (*Scheme 3*). Upon hindering the primary binding step at $C(\alpha)$ 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). ^1H - 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. ^1H -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. ^1H -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*,2*aR*,8*bR*)-2,2*a*,4,8*b*-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. ^1H -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 (2s, 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 (2q); 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*,2*aS*,8*bS*)-2,2*a*,4,8*b*-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. ^1H -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 (2s, 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 (2q); 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*,2*aR*,8*bR*)-2,2*a*,4,8*b*-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. $^1\text{H-NMR}$ (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). $^{13}\text{C-NMR}$ (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*,2*aS*,8*bS*)-2,2*a*,4,8*b*-tetrahydro-4,4,6-trimethoxy-1-methyl-1-(1-methylethenyl)cyclobutaf[naphthalen-3(1*H*)-one (**3b**; R_f 0.31). Yield: 141 mg (44%). Yellow oil. $^1\text{H-NMR}$ (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). $^{13}\text{C-NMR}$ (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 $^1\text{H-NMR}$) 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. $^1\text{H-NMR}$ (CDCl_3): 5.10 (*s*, 1 H); 5.07 (*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). $^{13}\text{C-NMR}$ (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°. $^1\text{H-NMR}$ (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). $^{13}\text{C-NMR}$ (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, $\text{C}_{20}\text{H}_{30}\text{O}$, M_r 286.44, monoclinic, space group $P2(1)/c$; $Z = 4$, $a = 15.942(3)$ Å, $b = 9.1199(1)$ Å, $c = 12.1515(19)$ Å, $\beta = 90.944(3)^\circ$; $V = 1766.5(5)$ Å³, $D_x = 1.077$ 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. $^1\text{H-NMR}$ (CDCl_3): 5.90 (br. *s*, 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). $^{13}\text{C-NMR}$ (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 $^1\text{H-NMR}$) with formation of a 1:2 mixture of 1:1 photoproducts **9** and **6b**. CC (SiO_2 ; pentane/Et₂O 2:1) afforded first *rel*-(4*aR*,8*aR*)-3,4,4*a*,5,8*a*-hexahydro-3,3,6,7-tetramethyl-4*a*-(phenylethynyl)naphthalen-1(2*H*)-one (**9**; R_f 0.61). Yield: 55 mg (18%). Light yellow oil. $^1\text{H-NMR}$ (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). $^{13}\text{C-NMR}$ (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°. $^1\text{H-NMR}$ (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,

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). ¹³C-NMR (CDCl₃): 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 CH₂Cl₂, C₂₂H₂₆O, *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) Å³, *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 ¹H-NMR). CC (SiO₂; CH₂Cl₂/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. ¹H-NMR (CDCl₃): 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). ¹³C-NMR (CDCl₃): 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 ¹H-NMR). CC (SiO₂; CH₂Cl₂/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. ¹H-NMR (CDCl₃): 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). ¹³C-NMR (CDCl₃): 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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