Photocycloaddition Reactions of 5,5-Dimethyl-3-(3-methylbut-3-en-1-ynyl)cyclohex-2-en-1-one

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Dedicated to Professor *William C. Agosta* on the occasion of his 75th birthday

The title cyclohexenone **1d** undergoes photodimerization selectively at the exocyclic C=C bond to give a 1:1 mixture of 1,2-dialkynyl-1,2-dimethylcyclobutanes **6** and **7**. On irradiation in the presence of 2,3-dimethylbuta-1,3-diene, **1d** affords bicyclo[8.4.0]tetradeca-1,2,3,7-tetraen-11-one **9**. This – formal – (6 + 4)-cycloadduct undergoes quantitative isomerization to 3-cycloheptadienyl-2,5,5-trimethylcyclohex-2-enone **11** on treatment with basic silica gel.

1. Introduction. – Cyclohex-2-enones **1** undergo photodimerization to mixtures of (regioisomeric) tricyclo[6.4.0.0^{2,7}]dodecanediones **2** and **3**, the relative ratio of these tricyclic dimers depending on the polarity of the solvent [1 – 3]. This is exemplified in *Scheme 1* for 5,5-dimethylcyclohex-2-enone (**1a**) [4] or isophorone (= 3,5,5-trimethyl-cyclohex-2-enone; **1b**) [5][6]. Both of these photoexcited enones also react efficiently with alkenes [7] to afford bicyclo[4.2.0]octan-2-ones **4**. We had previously shown [8] that replacing the Me group at C(3) of **1b** by an alkynyl group had a pronounced effect on the photocycloaddition of, *e.g.*, **1c** to 2,3-dimethylbut-2-ene, as now the intermediate triplet 1,4-biradical undergoes selective 1,5-cyclization to afford cyclopentenyl carbene **5** as a reactive intermediate. We have now focussed on extending the conjugation of this C(3)-side chain by an additional C=C bond. Here, we report on the results of photocycloaddition reactions of 5,5-dimethyl-3-(3-methylbut-3-en-1-ynyl)cyclohex-2-enone (**1d**).

2. Results. – Irradiation (350 nm) of 0.5M solutions of **1d** in either benzene or in MeCN afford 1:5:4 mixtures of three dimers **2d**, **6**, and **7**, respectively (*Scheme 2*). The same product mixture is obtained when **1d** is irradiated in the presence of a tenfold molar excess of 2,3-dimethylbut-2-ene, *i.e.*, cycloaddition of **1d** to this alkene is totally suppressed by photodimerization. Whereas the assignment of the constitution of **6** and **7** as 1,2-dialkynyl-1,2-dimethylcyclobutanes is unambiguous on the basis of their ^{1}H-NMR spectra, the determination of both constitution and configuration of the minor dimer **2d** is not straightforward. Indeed, the assignment of the structural parameters for such tricyclic photodimers of cyclohexenones and related molecules by ^{1}H-NMR spectroscopy is only unequivocal for cyclic enones bearing no substituents on the olefinic C-atoms, by analysis of the corresponding $AA'XX'$ patterns [9][10]. For

Scheme 1

a R = H
b R = Me
c R = *t*Bu–C≡C
**d** R = H$_2$C=C(Me)–C≡C
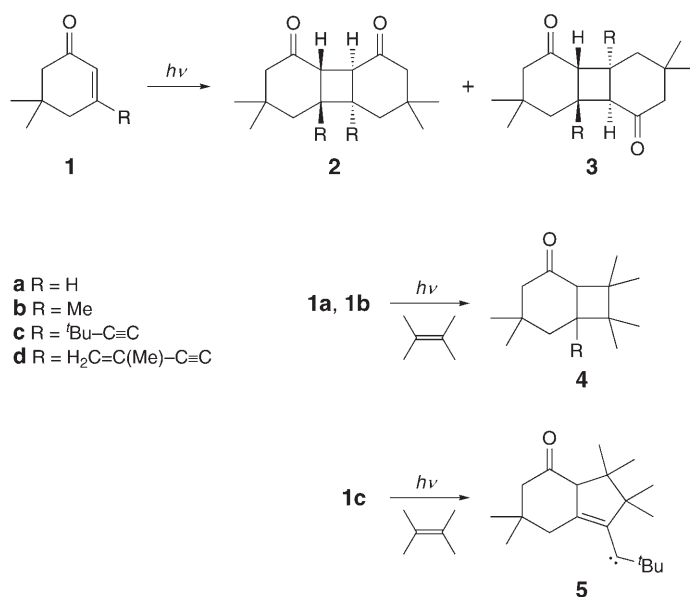
structure determination of the corresponding dimers of cyclic enones bearing a substituent on one of the olefinic C-atoms, a combination of enantioselective gas chromatography and GC/MS analysis [11] can be helpful, but only if these dimers are stable enough under these (thermal) conditions. In this context, it seemed appropriate to select ^{13}C-NMR spectroscopy as possible tool for the differentiation of such dimers. Therefore, we prepared dimers **2b** and **3b**, and the new dimer **2c** by irradiation of **1b** and **1c** (*cf. Scheme 1*), confirmed their structures by X-ray crystal-structure analysis, and recorded their ^{13}C-NMR spectra. Comparison of the ^{13}C-NMR parameters of these dimers with those of **2d** allows the structural assignment of the latter.

As we already had observed [12] that cyclic enones with low triplet energies (< 55 kcal/mol) undergo photoaddition to 'normal' alkenes, *e.g.*, 2,3-dimethylbut-2-ene, very inefficiently if at all, but in contrast very efficiently to dienes or unsaturated nitriles, we irradiated **1d** in the presence of a tenfold molar excess of 2,3-dimethylbuta-1,3-diene (**8**; *Scheme 3*). NMR Analysis indicates the – quantitative – formation of two new products, **9** and **10**, in a 4:1 ratio, respectively. Whereas the minor cycloadduct **10**, which still contains a C≡C bond, can be isolated by chromatography, the major product **9**, which shows no NMR signals for either acetylenic C-atoms or olefinic H-atoms, turns out to be very sensitive towards SiO$_2$. Indeed, stirring of a CH$_2$Cl$_2$ soln. of **9** over SiO$_2$ for *ca.* 30 min leads to its total decomposition. In contrast, on contact with Et$_3$N-neutralized SiO$_2$, **9** isomerizes quantitatively to **11** (*Scheme 3*).

3. Discussion. – The most striking feature in the photochemical behavior of **1d** is the fact that the initial addition step occurs at the terminal olefinic C-atom of the side chain and not at the unsubstituted – *i.e.*, C(2) – C-atom of the cyclohexenone moiety, as

Scheme 2
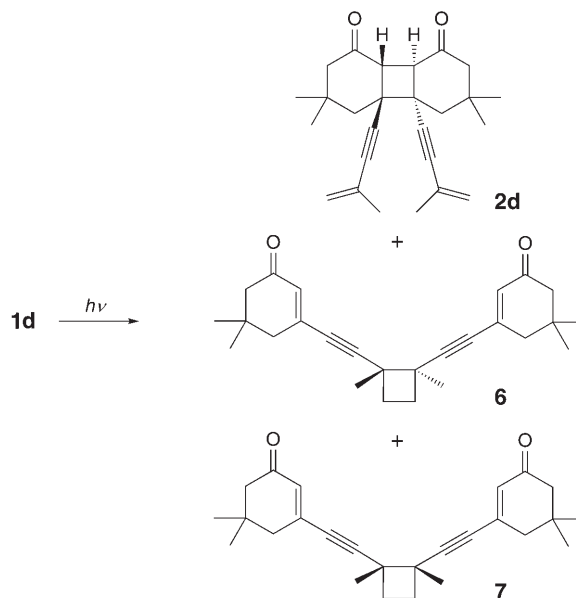
Scheme 3
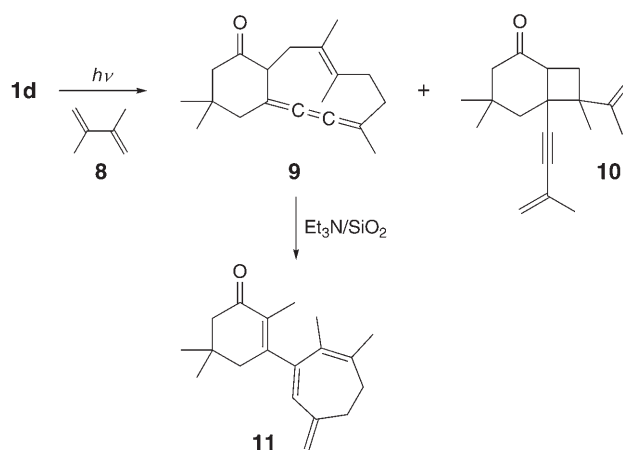
reflected by the preferential formation of (**6** + **7**) *vs.* **2d** in the photodimerization and of **9** *vs.* **10** in the mixed cycloaddition. This feature can be best explained by comparing the relative stabilities of the resulting intermediates resulting from the addition of, *e.g.*, an alkyl radical to a 1-acylhexa-1,5-dien-3-yne **I**. Whereas pent-4-en-2-yn-1-yl radical **II** (and the mesomeric penta-2,3,4-trien-1-yl radical **IIa** [13–15]) are additionally stabilized by the adjacent C=O group, this is not the case for **III** and **IIIa**, respectively

(*Scheme 4*). Indeed, this correlation between *a*) stabilization of the biradical intermediate and *b*) product ratio is already reflected by the fact that **1b** affords mixtures of **2b** and **3b**, depending on the polarity of the solvent, whereas **1c** affords dimer **2c** (stemming from a bis-propargyl biradical intermediate) selectively, both in polar and in nonpolar solvents.

Scheme 4
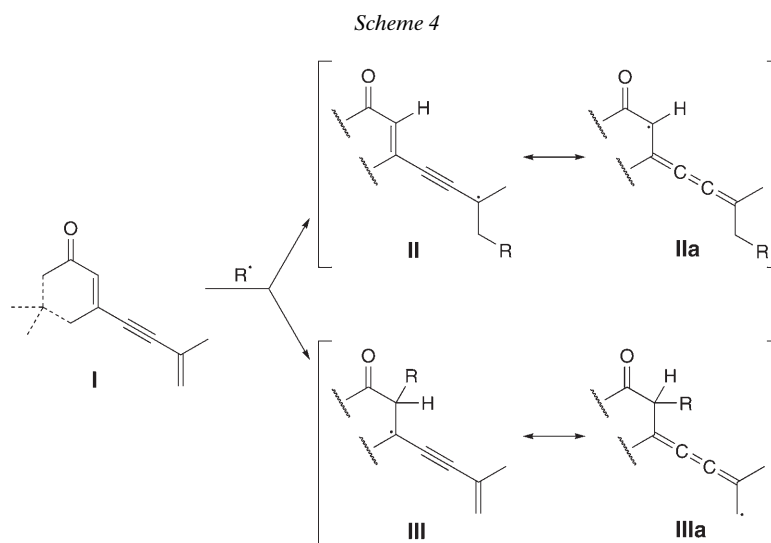
Differentiation between **6** and **7**, *i.e.*, the assignment of *trans*- and *cis*-configuration, stems from NMR analysis alone, as we were not able to obtain crystals suited for X-ray crystal-structure determination for neither of these dimers. Therefore, the *AA′XX′* patterns of the CH_2CH_2 unit in the cyclobutane ring was simulated by SpinWorks [16], assuming the vicinal coupling constant ^3J for the *cis*-H-atoms to be by *ca.* 3 Hz larger than for the corresponding *trans*-H-atoms, and these results were then compared with the recorded data. Further evidence comes from ^{13}C-NMR data of methylated cyclobutanes [17], where Me shifts for *cis*- (δ 15 ppm) and *trans*-1,2-dimethylcyclobutanes (δ 20 ppm) differ by *ca.* 5 ppm. The constitutional assignment (**2d** and not **3d**) for the minor tricyclic dimer of **1d** stems from comparison of the ^{13}C-NMR chemical shifts of the cyclobutane C-atoms. Typical chemical shifts for the tertiary C-atoms of **2** are 50–53 ppm, and 62 ppm for the corresponding C-atoms in **3**, while, for the quaternary C-atoms, the relative chemical shifts are inverted, *i.e.*, 43–45 ppm for **2** and 37–38 ppm for **3** (*cf. Exper. Part*). The selective formation of the formal [6 + 4] photocycloadduct **9** from **1d** and 2,3-dimethylbuta-1,3-diene (**8**) is unprecedented. Apparently, the two radical centres in the biradical intermediate (structure type **II/IIa**; *cf. Scheme 4*) formed by addition of a methylidene unit of **8** to the (exocyclic) methylidene unit of **1d** are located at bonding distance already, thus facilitating the second cyclization step, the (*E*)-configuration of the C(7)=C(8) bond reflecting the preferential s-*trans*-conformation of **8**. Symmetrically substituted 1,1,4,4-tetraalkylbuta-1,2,3-trienes exhibit typical ^{13}C-NMR shifts [18][19], the central olefinic C-atoms resonating at δ 160 ppm, and the external ones at δ 110 ppm. Referring thereto, the values found for

9 (δ 112 ppm for C(1), 116 ppm for C(4), 156 ppm for C(3), and 158 ppm for C(2)) give indeed a very good fit. Interestingly, cyclodeca-1,2,3-triene has already been synthesized [20], but no ^{13}C-NMR spectroscopy was available at that time. Such [3]cumulenes are known to dimerize to radialenes and to react readily with atmospheric oxygen [18]. It is, therefore, not surprising that attempts to purify **9** by chromatography failed. As for the minor cycloadduct **10**, the relative configuration of the Me and the methylethenyl group on the cyclobutane ring is unknown. Finally, the base-catalyzed isomerization **9** → **11** is intriguing, since very few reports on carbanionic rearrangements are found in the literature, and only one of them is classified as 'ring-strain-promoted' [21]. A tentative mechanistic interpretation involves an addition/elimination sequence followed by a (formal) 1-methylpropa-1,2-diene → buta-1,3-diene tautomerization involving intermediates **IV** – **VI**, the isomerization of a (β,γ-unsaturated) 3-methylidenecyclohexanone to a (fully conjugated) cyclohexenone representing the driving force (*Scheme 5*).

Scheme 5
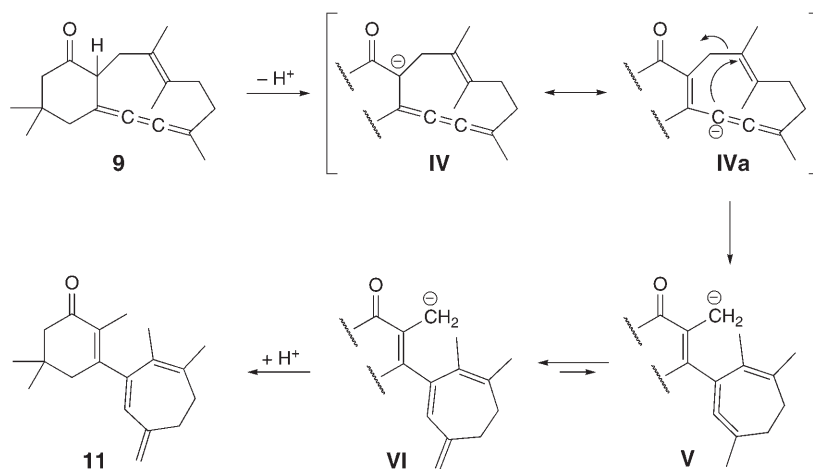
Experimental Part

1. *General.* Photolyses were conducted in a *Rayonet RPR-100* photoreactor equipped with (16) 350-nm lamps and solvents of spectrophotometric grade. Column chromatography (CC): silica gel *60* (*Merck*; 230 – 400 mesh). Gas chromatography (GC): 30-m *SE-30* capillary column. ^{1}H- and ^{13}C-NMR Spectra (including two-dimensional plots): *Bruker WM-500*; at 500.13 and 125.8 MHz, resp., δ in ppm, J in Hz. GC/EI-MS: at 70 eV. X-Ray analyses: *Bruker APEX CCD* three-circle diffractometer at 153 K with MoK_α radiation (λ 0.71073 Å).

2. *Starting Materials.* 3,5,5-Trimethylcyclohex-2-enone (**1b**) is commercially available. *3-(3,3-Dimethylbut-1-ynyl)-5,5-dimethylcyclohex-2-enone* (**1c**) was synthesized according to [22]. *5,5-Dimethyl-3-(3-methylbut-3-en-1-ynyl)cyclohex-2-enone* (**1d**) has been prepared by a Pd/Ag-catalyzed vinyl triflate/1-(trimethylsilyl)alkyne coupling in 94% yield [23], but no data of this compound have been reported. We obtained **1d** from 3-ethoxy-5,5-dimethyl-cyclohex-2-enone and the *Grignard* derivative of 2-methylbut-1-en-3-yne in analogy to **1c** [22] in 45% yield after CC (Et$_2$O/pentane 1:1) as colorless oil. ^{1}H-NMR

(CDCl$_3$): 6.20 (*t*, *J* = 1.5); 5.43, 5.38 (br. *s*, 2 H); 2.35 (*d*, *J* = 1.5, 2 H); 2.21 (*s*, 2 H); 1.95 (br. *s*, 3 H); 1.07 (*s*, 6 H). ^{13}C-NMR (CDCl$_3$): 199.3 (*s*); 153.2 (*s*); 141.5 (*s*); 131.7 (*d*); 124.7 (*t*); 100.8 (*s*); 88.0 (*s*); 51.4 (*t*); 44.7 (*t*); 34.1 (*s*); 28.5 (*q*); 23.4 (*q*). EI-MS: 188 (79, $M^{+\cdot}$), 132 (100).

3. *Photodimerizations.* Ar-Degassed solns. of **1** are irradiated (concentration, solvent, duration, and workup as described).

3.1. *Photodimerization of* **1b** *in* H$_2$O. A soln. of 18.22 mg (0.13 mmol) of **1b** in H$_2$O (2 ml) is irradiated for 48 h. The white precipitate is filtered, dried, and recrystallized from Et$_2$O to afford 12.7 mg (71%) of cis-transoid-cis-*5,5,7,8,10,10-hexamethyltricyclo[6.4.0.0^{2,7}]dodecane-3,12-dione* (**2b**). M.p. 159°. ^{1}H-NMR (CDCl$_3$): 2.81 (*s*, 2 H); 2.47 (*d*, *J* = 14.8, 2 H); 2.08 (*d*, *J* = 14.2, 2 H); 2.06 (*dd*, *J* = 2.4, 14.9, 2 H); 1.36 (*dd*, *J* = 2.4, 14.2, 2 H); 1.17 (*s*, 6 H); 1.10 (*s*, 6 H); 0.93 (*s*, 6 H). ^{13}C-NMR (CDCl$_3$): 209.9 (*s*); 53.2 (*d*); 51.4 (*t*); 45.1 (*s*); 43.1 (*t*); 35.9 (*s*); 33.5 (*q*); 27.5 (*q*); 23.5 (*q*).

X-Ray Crystal-Structure Determination of **2b**[1]). Pale colorless blocks (0.07 × 0.17 × 0.52 mm) from Et$_2$O, C$_{18}$H$_{28}$O$_2$, M_r 276.40; monoclinic, space group *C2/c*, *Z* = 8, *a* = 12.3453(15), *b* = 17.248(2), *c* = 15.982(2) Å, β = 106.307(2)°, *V* = 3266.2(7) Å^3, D_x = 1.124 g cm^{-3}.

3.2. *Photodimerization of* **1b** *in Cyclohexane.* A soln. of 138 mg (1 mmol) of **1b** in cyclohexane (2 ml) is irradiated for 48 h. After evaporation of the solvent, the crystalline residue is washed with cyclohexane and recrystallized from Et$_2$O to afford 60.6 mg (88%) of cis-transoid-cis-*1,5,5,7,11,11-hexamethyltricyclo[6.4.0.0^{2,7}]dodecane-3,9-dione* (**3b**). M.p. 207°. ^{1}H-NMR (CDCl$_3$): 2.50 (*s*, 2 H); 2.26 (*dd*, *J* = 2.4, 16.2, 2 H); 2.11 (*d*, *J* = 14.2, 2 H); 1.87 (*d*, *J* = 16.2, 2 H); 1.79 (*dd*, *J* = 2.4, 14.2, 2 H); 1.20 (*s*, 6 H); 1.03 (*s*, 6 H); 0.87 (*s*, 6 H). ^{13}C-NMR (CDCl$_3$): 212.5 (*s*); 62.4 (*d*); 53.8 (*t*); 52.7 (*t*); 37.6 (*s*); 33.9 (*s*); 31.7 (*q*); 28.5 (*q*); 27.5 (*q*).

X-Ray Crystal-Structure Determination of **3b**[1]). Pale colorless needles (0.02 × 0.14 × 0.31 mm) from Et$_2$O, C$_{18}$H$_{28}$O$_2$, M_r 276.40; triclinic, space group *P1*, *Z* = 1, *a* = 5.7811(12), *b* = 8.0588(17), *c* = 9.103(2) Å, α = 84.951(4), β = 76.606(4), γ = 73.635(4)°, *V* = 395.73(15) Å^3, D_x = 1.160 g cm^{-3}.

3.3. *Photodimerization of* **1c** *in MeCN.* A soln. of 25 mg (0.12 mmol) of **1c** in MeCN (1 ml) is irradiated for 24 h. After evaporation of the solvent, the residue is washed with cyclohexane and recrystallized from Et$_2$O to afford 15.7 mg (64%) of cis-transoid-cis-*7,8-bis(3,3-dimethylbut-1-ynyl)-5,5,10,10-tetramethyltricyclo[6.4.0.0^{2,7}]dodecane-3,12-dione* (**2c**). M.p. 150°. ^{1}H-NMR (CDCl$_3$): 2.95 (*s*, 2 H); 2.41 (*d*, *J* = 15.0, 2 H); 2.30 (*d*, *J* = 14.5, 2 H); 2.15 (*dd*, *J* = 2.0, 15.0, 2 H); 1.80 (*dd*, *J* = 2.0, 14.5, 2 H); 1.19 (*s*, 18 H); 1.10 (*s*, 6 H); 0.93 (*s*, 6 H). ^{13}C-NMR (CDCl$_3$): 208.0 (*s*); 96.2 (*s*); 80.9 (*s*); 51.3 (*t*); 50.5 (*d*); 44.0 (*t*); 42.9 (*s*); 35.5 (*s*); 31.0 (*q*); 30.5 (*q*); 27.5 (*s*) 26.9 (*q*).

X-Ray Crystal-Structure Determination of **2c**[1]). Pale colorless blocks (0.19 × 0.24 × 0.50 mm) from Et$_2$O, C$_{28}$H$_{40}$O$_2$ + 0.5 (C$_2$H$_3$N) + 0.5 (C$_2$H$_3$N), M_r 449.65; triclinic, space group *P1*, *Z* = 2, *a* = 10.1044(9), *b* = 11.7421(11), *c* = 15.5705(14) Å, α = 68.906(2), β = 84.965(2), γ = 65.878(2)°, *V* = 1569.3(2) Å^3, D_x = 0.952 g cm^{-3}.

3.4. *Photodimerization of* **1d** *in Benzene.* A soln. of 376 mg (2 mmol) **1d** in benzene (10 ml) is irradiated for 24 h up to 90% conversion. After evaporation of the solvent, the residue (from ^{1}H-NMR: 10% of **1d**, 9% of **2d**, 45% of **6**, and 36% of **7**) is subjected to CC (SiO$_2$; pentane/Et$_2$O 1 : 1) to afford first **1d** (25 mg).

The second fraction (26.5 mg, 7.7%) contains pure cis-transoid-cis-*7,8-bis(3-methylbut-3-en-1-ynyl)-5,5,10,10-tetramethyltricyclo[6.4.0.0^{2,7}]dodecane-3,12-dione* (**2d**) as light yellow oil. ^{1}H-NMR (CDCl$_3$): 5.24 (*s*, 2 H); 5.22 (*s*, 2 H); 3.06 (*s*, 2 H); 2.45 (*d*, *J* = 15.1, 2 H); 2.36 (*d*, *J* = 13.9, 2 H); 2.18 (*dd*, *J* = 2.0, 15.1, 2 H); 2.01 (*dd*, *J* = 2.0, 13.9, 2 H); 1.87 (*s*, 6 H); 1.13 (*s*, 6 H); 1.07 (*s*, 6 H). ^{13}C-NMR (CDCl$_3$): 207.5 (*s*); 126.3 (*s*); 121.5 (*t*); 90.7 (*s*); 86.9 (*s*); 51.2 (*t*); 49.7 (*d*); 44.2 (*t*); 43.4 (*s*); 35.2 (*s*); 31.5 (*q*); 25.8 (*q*); 24.9 (*q*).

The third fraction (35 mg, 11%) contains pure trans-*1,2-bis[2-(5,5-dimethyl-3-oxocyclohex-1-en-1-yl)ethynyl]-1,2-dimethylcyclobutane* (**6**). M.p. 49°. ^{1}H-NMR (C$_6$D$_6$): 6.41 (*t*, *J* = 1.7, 2 H); 2.15 (*AA′XX′*, $J_{AX} \approx 11$, $J_{AA'} = J_{XX} \approx 7$, $J_{AX'} \approx 10$, 2 H); 1.97 (*s*, 4 H); 1.93 (*d*, *J* = 1.7, 4 H); 1.66 (*AA′XX′*, $J_{AX} \approx 11$, $J_{AA'} = J_{XX} \approx 7$, $J_{AX'} \approx 10$, 2 H); 1.55 (*s*, 6 H); 0.65 (*s*, 12 H). ^{13}C-NMR (C$_6$D$_6$): 196.9 (*s*); 141.5 (*s*); 132.1 (*d*); 102.9 (*s*); 84.6 (*s*); 50.9 (*t*); 44.5 (*t*); 40.2 (*s*); 32.5 (*s*); 31.7 (*t*); 27.8 (*q*); 25.2 (*q*).

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[1])   CCDC-672011, -672012, and -672013 contain the supplementary crystallographic data for **2b**, **3b**, and **2c**, resp. This data can be obtained free of charge *via* www.ccdc.cam.ac.uk/data_request/cif.

The last fraction (60 mg, 18%) contains pure cis-*1,2-bis[2-(5,5-dimethyl-3-oxocyclohex-1-en-1-yl)ethynyl]-1,2-dimethylcyclobutane* (**7**). M.p. 51°. ^{1}H-NMR (C$_6$D$_6$): 6.49 (t, J = 1.7, 2 H); 2.26 (AA'XX', J_{AX} ≈ 11, $J_{AA'}$ = $J_{XX'}$ ≈ 10, $J_{AX'}$ ≈ 7, 2 H); 2.11 (d, J = 1.7, 4 H); 2.02 (s, 4 H); 1.59 (AA'XX', J_{AX} ≈ 11, $J_{AA'}$ = $J_{XX'}$ ≈ 10, $J_{AX'}$ ≈ 7, 2 H); 1.12 (s, 6 H); 0.74 (s, 12 H). ^{13}C-NMR (C$_6$D$_6$): 196.8 (s); 140.5 (s); 131.1 (d); 105.1 (s); 90.5 (s); 51.0 (t); 44.8 (t); 40.7 (s); 33.5 (s); 32.2 (t); 27.9 (q); 22.0 (q).

4. *Photocycloaddition of* **1d** *to 2,3-Dimethylbuta-1,3-diene* (**8**). A soln. containing 94 mg (0.5 mmol) of **1d** and 164 mg (2 mmol) of **8** in benzene (5 ml) is irradiated for 4 h. After evaporation of the solvent, ^{1}H-NMR analysis indicates the residue (140 mg) to be a 4:1 mixture of **9** and **10**. The following data of *(7*E*)-4,7,8,13,13-pentamethylbicyclo[8.4.0]tetradeca-1,2,3,7-tetraen-11-one* (**9**) stem directly from the crude photolysate. ^{1}H-NMR (CDCl$_3$): 3.08 (dd, J = 3.0, 11.0, H−C(10)); 2.92 (dd, J = 11.0, 14.0, H$_{ax}$−C(9)); 2.87 (dt, J = 7.5, 13.5, H$_{ax}$−C(6)); 2.45, 2.22 (AB, J = 14.0, 2 H−C(14)); 2.38, 2.29 (AB, J = 13.5, 2 H−C(12)); 2.34 (m, H$_{eq}$−C(6)); 2.05, 1.95 (m, 2 H−C(5)); 1.82 (s, Me−C(8)); 1.67 (s, Me−C(7)); 1.62 (s, Me−C(4)); 1.08, 0.89 (s, 2 Me−C(13)). ^{13}C-NMR (CDCl$_3$): 209.5 (s, C(11)); 158.1 (s, C(2)); 156.5 (s, C(3)); 127.2 (s, C(8)); 127.0 (s, C(7)); 116.5 (s, C(4)); 111.4 (s, C(1)); 54.5 (t, C(12)); 48.7 (d, C(10)); 48.5 (t, C(14)); 34.9 (s, C(13)); 31.9 (t, C(6)); 30.5 (q, *Me*−C(13)); 30.2 (t, C(9)); 29.5 (t, C(5)); 26.5 (q, *Me*−C(13)); 23.9 (q, *Me*−C(8)); 17.8 (q, *Me*−C(7)); 16.4 (q, *Me*−C(4)).

The crude photolysate is stirred over SiO$_2$ in CH$_2$Cl$_2$ for 3 h, followed by filtration, washing with CH$_2$Cl$_2$, and evaporation of the solvent. CC (SiO$_2$; CH$_2$Cl$_2$/toluene 9:1) affords 8 mg (6%) of *4,4,7-trimethyl-6-(3-methylbut-3-en-1-ynyl)-7-(1-methylethenyl)bicyclo[4.2.0]octan-2-one* (**10**) as colorless oil. ^{1}H-NMR (C$_6$D$_6$): 5.26, 5.00 (s, 2 H); 4.77, 4.52 (s, 2 H); 3.15 (dd, J = 9.5, 10.0); 2.11 (d, J = 14.2); 2.07 (s, 2 H); 2.05 (m, 1 H); 1.87 (d, J = 14.2); 1.73 (s, 3 H); 1.68 (m, 1 H); 1.61 (s, 3 H); 1.33 (s, 3 H); 1.07 (s, 3 H); 0.73 (s, 3 H). ^{13}C-NMR (C$_6$D$_6$): 208.5 (s); 150.1 (s); 126.2 (s); 121.2 (t); 110.1 (t); 92.9 (s); 86.5 (s); 51.5 (t); 49.1 (s); 45.1 (d); 42.5 (s); 41.7 (t); 34.8 (s); 32.1 (t); 31.5 (q); 30.6 (q); 26.5 (q); 24.9 (q); 19.5 (q).

5. *Isomerization of* **9** *to* **11**. The crude photolysate (*cf*. above) is stirred for 3 h over SiO$_2$ pretreated with 1% Et$_3$N in CH$_2$Cl$_2$. After filtration and evaporation of the solvent, the residue is subjected to CC (SiO$_2$ pretreated with 1% Et$_3$N in CH$_2$Cl$_2$; CHCl$_3$) to afford 70 mg (55%) of *3-(6,7-dimethyl-3-methylidenecyclohepta-1,6-dien-1-yl)-2,2,5-trimethylcyclohex-2-enone* (**11**) as colorless oil. ^{1}H-NMR (CDCl$_3$): 6.08 (s, 1 H); 4.89 (s, 1 H); 4.78 (s, 1 H); 2.40 (m, 2 H); 2.33 (s, 2 H); 2.31 (m, 2 H); 2.25 (s, 2 H); 1.87 (s, 3 H); 1.82 (s, 3 H); 1.78 (s, 3 H); 0.99 (s, 6 H). ^{13}C-NMR (CDCl$_3$): 198.9 (s); 153.1 (s); 145.1 (s); 142.2 (s); 135.9 (s); 131.1 (s); 126.9 (s); 122.1 (d); 111.1 (t); 52.1 (t); 42.9 (t); 34.9 (t); 32.5 (s); 32.1 (t); 28.1 (q); 21.1 (q); 14.7 (q); 12.2 (q).

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