

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

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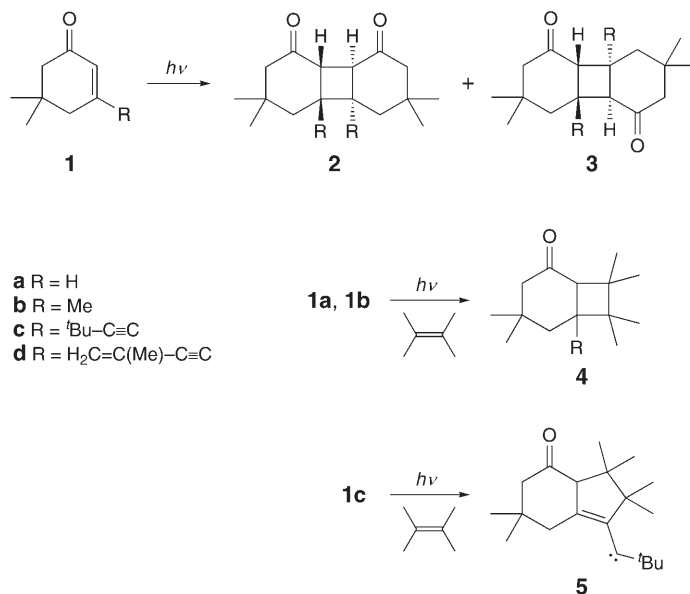
Dedicated to Professor William C. Agosta on the occasion of his 75th birthday

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-trimethylcyclohex-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 ¹H-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 ¹H-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

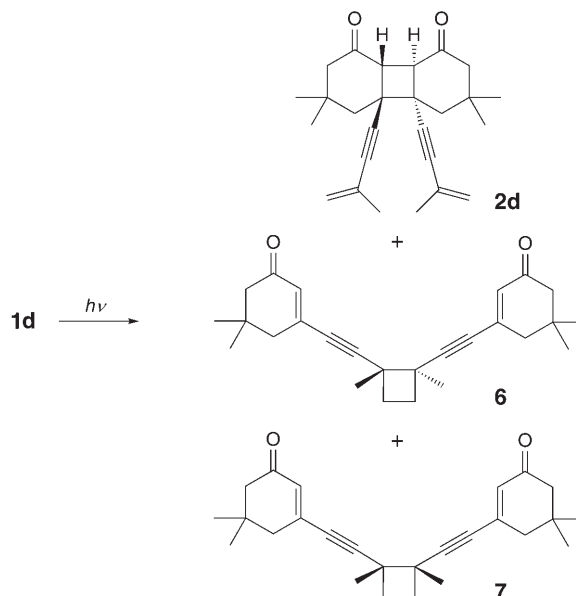


structure determination of the corresponding dimers of cyclic enones bearing a substituent on one of the olefinic C-atoms, a combination of enantioselective gas chromatography and GC/MS analysis [11] can be helpful, but only if these dimers are stable enough under these (thermal) conditions. In this context, it seemed appropriate to select ¹³C-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 ¹³C-NMR spectra. Comparison of the ¹³C-NMR parameters of these dimers with those of **2d** allows the structural assignment of the latter.

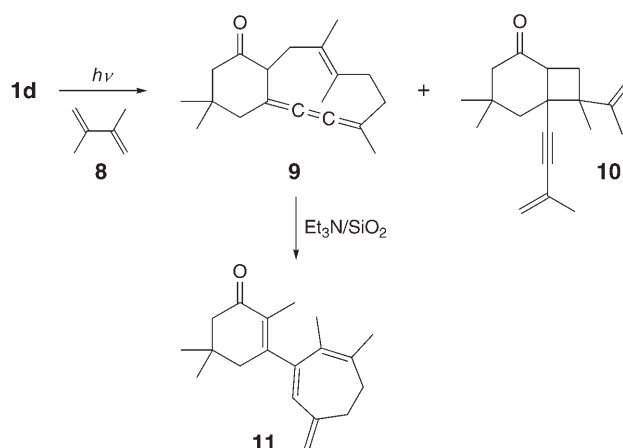
As we already had observed [12] that cyclic enones with low triplet energies (< 55 kcal/mol) undergo photoaddition to ‘normal’ alkenes, e.g., 2,3-dimethylbut-2-ene, very inefficiently if at all, but in contrast very efficiently to dienes or unsaturated nitriles, we irradiated **1d** in the presence of 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 SiO₂. Indeed, stirring of a CH₂Cl₂ soln. of **9** over SiO₂ for ca. 30 min leads to its total decomposition. In contrast, on contact with Et₃N-neutralized SiO₂, **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



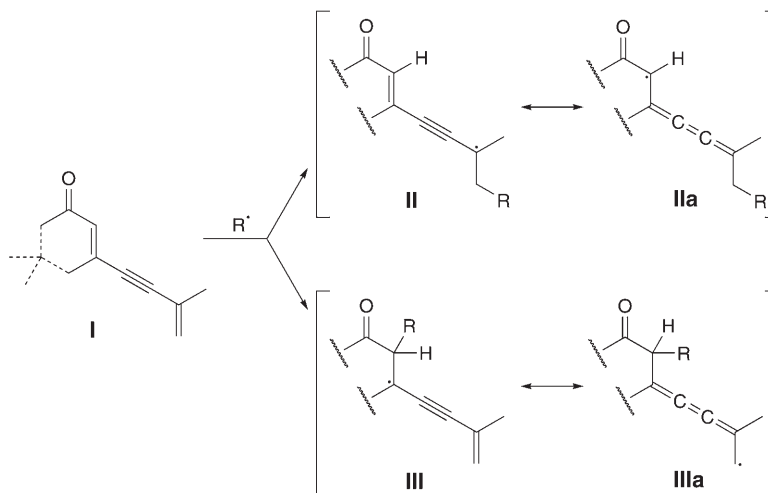
Scheme 3



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.

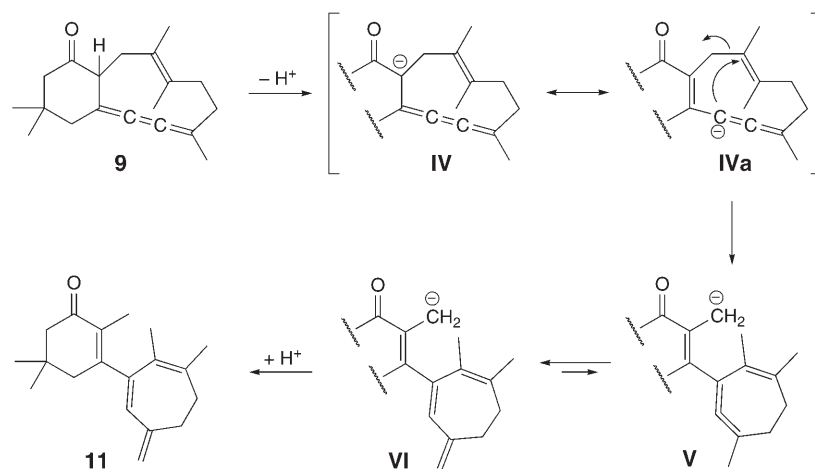
Scheme 4



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) methyldiene 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** $\rightarrow$ **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 $\rightarrow$ buta-1,3-diene tautomerization involving intermediates **IV**–**VI**, the isomerization of a (β,γ -unsaturated) 3-methylenecyclohexanone 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. ^1H - 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-dimethylcyclohex-2-enone and the Grignard derivative of 2-methylbut-1-en-3-yne in analogy to **1c** [22] in 45% yield after CC (Et_2O /pentane 1:1) as colorless oil. ^1H -NMR

(CDCl₃): 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). ¹³C-NMR (CDCl₃): 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*⁺), 132 (100).

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

3.1. Photodimerization of **1b** in H₂O. A soln. of 18.22 mg (0.13 mmol) of **1b** in H₂O (2 ml) is irradiated for 48 h. The white precipitate is filtered, dried, and recrystallized from Et₂O 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°. ¹H-NMR (CDCl₃): 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). ¹³C-NMR (CDCl₃): 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 Et₂O, C₁₈H₂₈O₂, *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) Å³, *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 Et₂O 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°. ¹H-NMR (CDCl₃): 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). ¹³C-NMR (CDCl₃): 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 Et₂O, C₁₈H₂₈O₂, *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) Å³, *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 Et₂O 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°. ¹H-NMR (CDCl₃): 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). ¹³C-NMR (CDCl₃): 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 Et₂O, C₂₈H₄₀O₂ + 0.5 (C₂H₃N) + 0.5 (C₂H₃N), *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) Å³, *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 ¹H-NMR: 10% of **1d**, 9% of **2d**, 45% of **6**, and 36% of **7**) is subjected to CC (SiO₂; pentane/Et₂O 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. ¹H-NMR (CDCl₃): 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). ¹³C-NMR (CDCl₃): 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°. ¹H-NMR (C₆D₆): 6.41 (*t*, *J* = 1.7, 2 H); 2.15 (*AA'**XX'*, *J*_{AX} ≈ 11, *J*_{AA'} = *J*_{XX'} ≈ 7, *J*_{AX'} ≈ 10, 2 H); 1.97 (*s*, 4 H); 1.93 (*d*, *J* = 1.7, 4 H); 1.66 (*AA'**XX'*, *J*_{AX} ≈ 11, *J*_{AA'} = *J*_{XX'} ≈ 7, *J*_{AX'} ≈ 10, 2 H); 1.55 (*s*, 6 H); 0.65 (*s*, 12 H). ¹³C-NMR (C₆D₆): 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*).

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°. ¹H-NMR (C₆D₆): 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). ¹³C-NMR (C₆D₆): 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, ¹H-NMR analysis indicates the residue (140 mg) to be a 4:1 mixture of **9** and **10**. The following data of (7E)-4,7,8,13,13-pentamethylbicyclo[8.4.0]tetradeca-1,2,3,7-tetraen-11-one (**9**) stem directly from the crude photolysate. ¹H-NMR (CDCl₃): 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)). ¹³C-NMR (CDCl₃): 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 SiO₂ in CH₂Cl₂ for 3 h, followed by filtration, washing with CH₂Cl₂, and evaporation of the solvent. CC (SiO₂; CH₂Cl₂/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. ¹H-NMR (C₆D₆): 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). ¹³C-NMR (C₆D₆): 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 SiO₂ pretreated with 1% Et₃N in CH₂Cl₂. After filtration and evaporation of the solvent, the residue is subjected to CC (SiO₂ pretreated with 1% Et₃N in CH₂Cl₂; CHCl₃) 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. ¹H-NMR (CDCl₃): 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). ¹³C-NMR (CDCl₃): 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).

REFERENCES

- [1] K. Schmidt, J. Kopf, P. Margaretha, *Helv. Chim. Acta* **2007**, *90*, 1667.
- [2] D. I. Schuster, M. M. Greenberg, I. M. Nunez, P. C. Tucker, *J. Org. Chem.* **1983**, *48*, 2615.
- [3] Y. Y. Lam, E. Valentine, G. S. Hammond, *J. Am. Chem. Soc.* **1967**, *89*, 3482.
- [4] W. G. Dauben, G. W. Shaffer, N. D. Vietmeyer, *J. Org. Chem.* **1968**, *33*, 4060.
- [5] B. J. Hrnjez, A. J. Mehta, M. A. Fox, K. P. Johnston, *J. Am. Chem. Soc.* **1989**, *111*, 2662.
- [6] H. Goncalves, G. Robinet, M. Barthelot, A. Lattes, *J. Phys. Chem., A* **1998**, *102*, 1279.
- [7] P. Margaretha, in 'Molecular and Supramolecular Photochemistry', Vol. 12, Eds. A. G. Griesbeck, J. Mattay, Marcel Dekker, New York, 2005, p. 211–238, and refs. cit. therein.
- [8] W. C. Agosta, P. Margaretha, *Acc. Chem. Res.* **1996**, *29*, 179.
- [9] K. Schmidt, J. Kopf, P. Margaretha, *Helv. Chim. Acta* **2006**, *89*, 1927.
- [10] C. P. Klaus, C. Thiemann, J. Kopf, P. Margaretha, *Helv. Chim. Acta* **1995**, *78*, 1079.
- [11] E. Anklam, W. A. König, P. Margaretha, *Tetrahedron Lett.* **1983**, *24*, 5851.
- [12] P. Margaretha, K. Schmidt, J. Kopf, V. Sinnwell, *Synthesis* **2007**, 1426.
- [13] B. Yang, C. Huang, L. Wie, J. Wang, L. Sheng, Y. Zhang, F. Qi, W. Zheng, W. K. Li, *Chem. Phys. Lett.* **2006**, *423*, 321.
- [14] F. Stahl, P. v. R. Schleyer, H. F. Bettinger, R. I. Kaiser, Y. T. Lee, H. F. Schaefer III, *J. Chem. Phys.* **2001**, *114*, 3476.
- [15] C. Roberts, J. C. Walton, *J. Chem. Soc., Perkin Trans. II* **1981**, 553.

- [16] K. Marat, <http://www.umanitoba.ca/chemistry/nmr/spinworks>.
- [17] E. L. Eliel, K. M. Pietruszewicz, *Org. Magn. Reson.* **1980**, 13, 193.
- [18] M. Iyoda, S. Tanaka, H. Otani, M. Nose, M. Oda, *J. Am. Chem. Soc.* **1988**, 110, 8494.
- [19] A. Maercker, R. Dujardin, *Angew. Chem.* **1985**, 97, 612.
- [20] W. R. Moore, T. M. Ozretich, *Tetrahedron Lett.* **1967**, 8, 3205.
- [21] J. R. Scheffer, R. E. Gayler, T. Zakouras, A. A. Dzakpasu, *J. Am. Chem. Soc.* **1977**, 99, 7726.
- [22] P. Margaretha, H. J. Rathjen, W. C. Agosta, *Tetrahedron Lett.* **1990**, 31, 3245.
- [23] P. Bertus, U. Halbes, P. Pale, *Eur. J. Org. Chem.* **2001**, 4391.

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