Photoannelation Reactions of 3-(Alk-1-ynyl)cyclohept-2-en-1-ones

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Dedicated to Prof. *Jean-Marie Lehn* on the occasion of his 70th birthday

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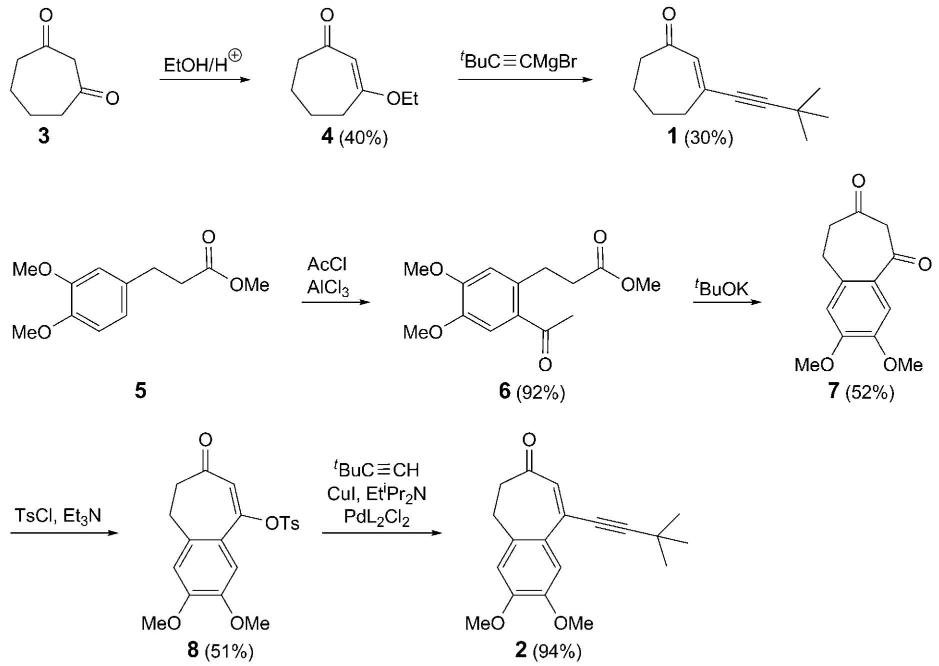
Irradiation (350 nm) of the newly synthesized 3-(alk-1-ynyl)cyclohept-2-en-1-ones **1** and **2** leads to the selective formation of tricyclic *head-to-head* dimers. In the presence of 2,3-dimethylbuta-1,3-diene, the (monocyclic) enone **1** affords *trans*-fused 7-alkynyl-bicyclo[5.2.0]nonan-2-ones as major photoproducts, whereas photocycloaddition of benzocyclohept-5-en-7-one **2** to the same diene gives preferentially the eight-membered cyclic allene **16** *via* 'end-to-end' cyclization of the intermediate allyl-propargyl biradical **22**. On contact with acid, cycloocta-1,2,5-triene **16** isomerizes to cycloocta-1,3,5-triene **18**.

Introduction. – Whereas five- and six-membered cyclic enones undergo efficient photocycloadditions to alkenes [1][2], similar reactions of their seven-membered ring counterparts have so far remained unknown. This is most probably due to the fact that the more flexible cyclohept-2-enones *a*) undergo efficient $(Z) \rightarrow (E)$ photoisomerization [3][4], and *b*) exhibit lower E_T values than the corresponding smaller cycloenones. The only established cyclobutane forming reaction of cyclohept-2-enones is photodimerization to afford tricyclo[7.5.0.0^{2,8}]tetradecanediones. Interestingly, the configuration of the major dimer in all reported examples [5–7] is (*transoid-anti-transoid*), corresponding to a ${}_{\pi}2_a + {}_{\pi}2_s$ ground-state cycloaddition between an (E)- and a (Z)-diastereoisomer. We had previously shown that incorporating an alk-1-ynyl group at C(3) of cyclohex-2-enones or cyclopent-2-enones has a strong influence on their behavior in light-induced reactions, as such compounds, in the presence of alkenes, undergo (triplet-) spin selective annelation reactions *via* cyclopentenyl carbenes as intermediates [8][9]. Here, we report results on photochemical reactions of newly synthesized alkynylcycloheptenones **1** and **2**.

Results. – The common 1,3-diketone → enol ether/ester → alkyne-coupling sequence for the synthesis of both 3-(3,3-dimethylbut-1-ynyl)cyclohept-2-enone (**1**) and of 2,3-dimethoxy-5-(3,3-dimethylbut-1-ynyl)benzocyclohept-5-en-7-one (**2**) is depicted in *Scheme 1*. Thus, cycloheptane-1,3-dione (**3**) was converted into enol ether **4**, which then reacted with (3,3-dimethylbut-1-ynyl)magnesium bromide to afford **1** in 12% overall yield. The synthesis of **2** started with the *Friedel–Crafts*-acylation of **5** to **6**, followed by aldol cyclization to diketone **7**, which, after transformation into toluene-4-sulfonate **8**, finally afforded **2** by a *Sonogashira*-type coupling reaction in 25% overall yield.

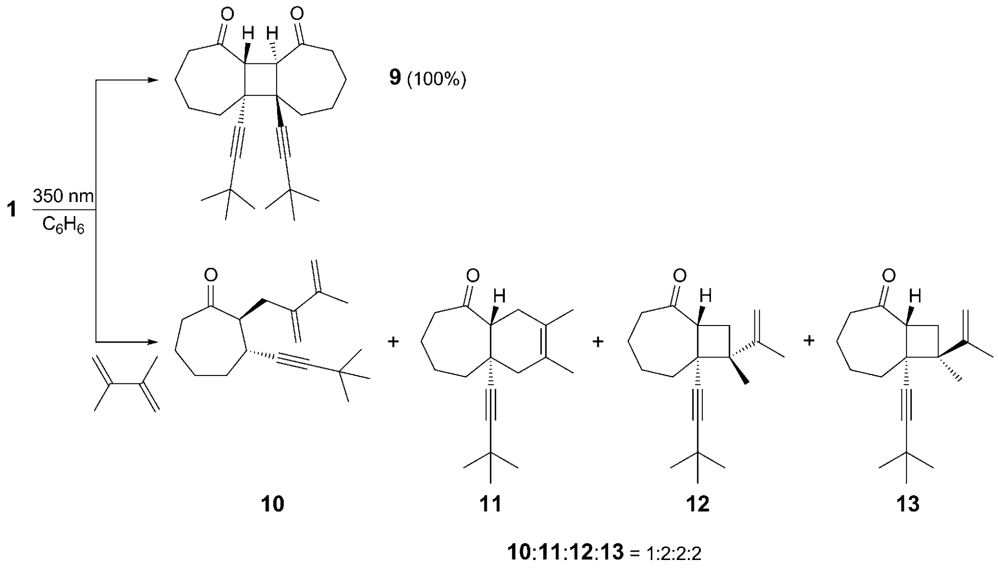
Scheme 1



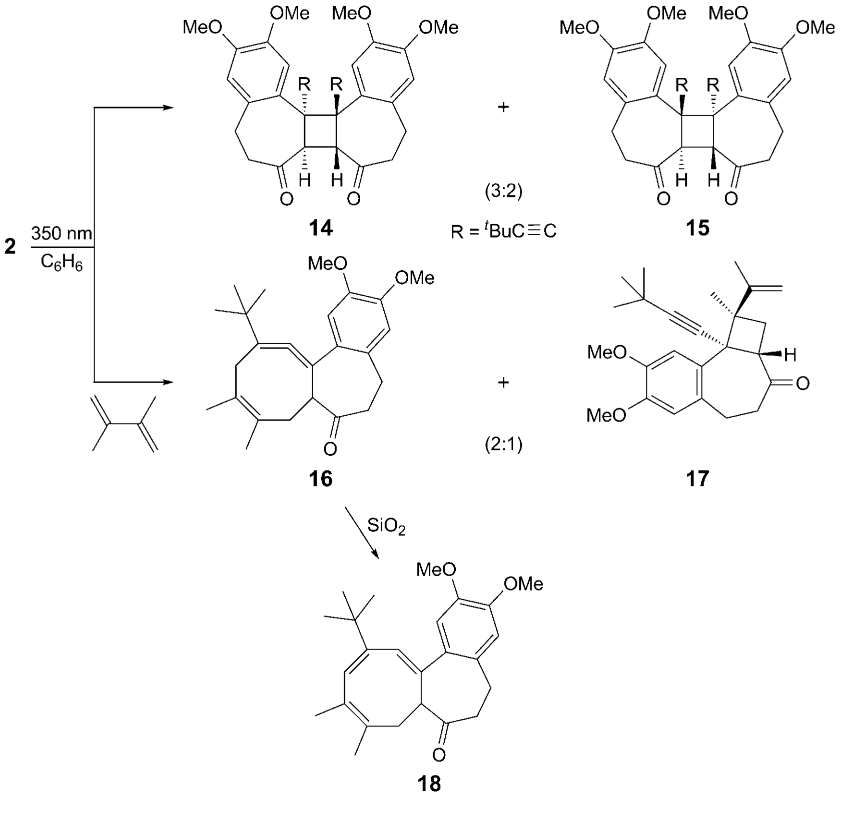
Irradiation (350 nm) of **1** in benzene afforded tricyclic dimer **9** exclusively, the same dimer being formed – again selectively – in other solvents as well. In the presence of a tenfold molar excess of 2,3-dimethylbuta-1,3-diene, **1** afforded a 1 : 2 : 2 : 2 mixture of $1 + 1$ photoadducts **10**, **11**, **12**, and **13**, respectively (*Scheme 2*). In contrast, irradiation of **2** in benzene gives a 3 : 2 mixture of pentacyclic dimers **14** and **15**, the ratio again not being affected by the choice of the solvent, whereas, in the presence of 2,3-dimethylbuta-1,3-diene, a 2 : 1 mixture of photocycloadducts **16** and **17** is obtained. On contact with silica gel or traces of acid, the cyclic allene **16** (^{13}C-NMR shifts for the allenic C-atoms in $CDCl_3$: 126, 201, and 105 ppm) cleanly isomerized to – the fully conjugated – cyclooctatriene **18** (*Scheme 3*). All the photoproducts were purified and isolated by column chromatography and characterized spectroscopically. The structures of enone **2**, of dimers **9**, **14**, and **15**, as well as that of photocycloadduct **17** were established by X-ray analysis. The assignment of a *trans*-fusion between the seven- and the four-membered rings in bicyclononanones **12** and **13** was achieved on the basis of the size of the vicinal coupling constants of the bridgehead H-atom ($J = 7$ and 11 Hz), identical to those observed in compound **17**, which indicated a rigid puckered conformation of the four-membered ring.

Discussion. – Regarding the conversion to tricyclic dimer **9**, cycloheptenone **1** behaved exactly like its six-membered analogue, which also gave a *head-to-head* dimer selectively. This can be explained by the stability of the bis-propargylic 1,4-biradical resulting from the primary binding between the C(2)-atoms of the cycloalkenone units.

Scheme 2



Scheme 3



As for the higher flexibility of cycloheptenones as compared to that of cyclohexenones, it is not surprising that **9** had *trans-anti-trans* configuration, whereas the corresponding 6/4/6 tricycle had *cis-anti-cis* configuration [10]. Similarly, **2** behaved like (the parent) benzocyclohept-5-en-7-one [5] by affording a roughly 1:1 mixture of *head-to-head* dimers with the two above mentioned configurations. In its reaction with 2,3-dimethylbuta-1,3-diene, (monocyclic) enone **1** behaved very similarly to 2,3-dihydro-6,6-dimethylthiin-4-one (**19**) [11] by affording both [2 + 2] and [2 + 4] photocycloadducts *via* biradicals **20** and **21**, respectively. Again, the higher flexibility of **1** as compared to that of thiacyclohexenone **19** is the reason for the relatively higher overall ratio of *trans*-fused bicycles from **20** (56%) as compared to those from **21** (10%). The ease of access to cyclic allene **16** in the photocycloaddition of **2** to 2,3-dimethylbuta-1,3-diene is remarkable. The parent cycloocta-1,2,5-triene has been reported to be formed by thermolysis of *cis*-1-ethenyl-2-ethynylcyclobutane and to dimerize rapidly in solution at low temperatures [12]. Obviously, the bulky ^{t}Bu group in **16** prevents such a dimerization, as it does for 1-(*tert*-butyl)cycloocta-1,2-diene itself [13]. This cyclic allene isomerizes to a mixture of conjugated cyclooctadienes in the presence of acid, as observed here in the conversion **16** → **18**.

Examples of cyclizations of alkyl propargyl biradicals on C(3) of the propargylic moiety to afford cyclic allenes are highly uncommon. A six-membered cyclic allene, which undergoes a subsequent 1,3-H shift, has been proposed as intermediate in the photocycloaddition of 2-methylcyclohex-2-enones to 2-methylbut-1-en-3-yne [14][15], and a seven-membered cyclic allene, which cyclodimerizes, is formed by photoisomerization of 2,5,5-trimethyl-2-(prop-1-yn-1-yl)cyclopentanone [16]. Obviously, allyl-propargyl biradical **22** strongly differs in its cyclization behavior from its (monocyclic) counterpart **20** (*Scheme 4*), and the main reason for this seems to be the – additional – benzylic character of the propargyl radical moiety which apparently induces an increased spin density on the 'allenic' C-atom [17].

Unfortunately, so far we have not been able to obtain crystals of **18** suitable for X-ray analysis. For the moment, we propose that the C(5)=C(6) bond in both cycloocta-1,2,5- and -1,3,5-trienes, **16** and **18**, respectively, has (*Z*)-configuration, as DFT studies indicate that a (*Z*,*Z*,*E*)-cycloocta-1,3,5-triene should be more strained by *ca.* 80 kJ/mol than the corresponding (all-*Z*)-isomer [18].

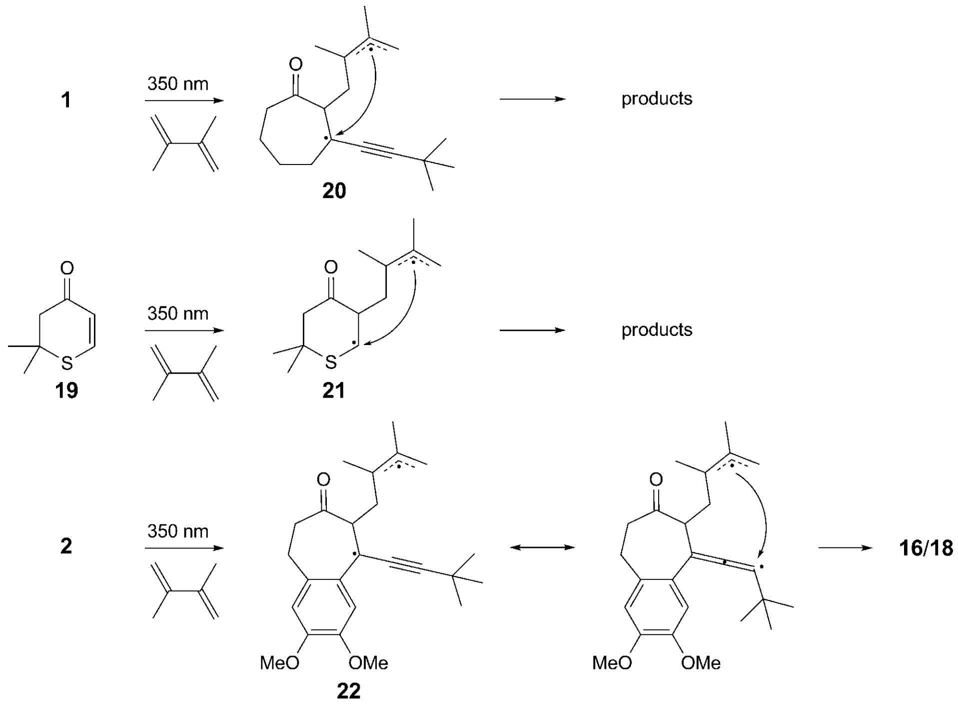
Experimental Part

1. *General.* Photolyses were conducted in a *Rayonet RPR-100* photoreactor equipped with 350-nm lamps and 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. Cycloheptane-1,3-dione* (**3**) was synthesized according to [19], and *methyl 3-(3,4-dimethoxyphenyl)propanoate* (**5**) was prepared from the commercially available acid *via* the corresponding acid chloride.

2.1. *Synthesis of 3-(3,3-Dimethylbut-1-yn-1-yl)cyclohept-2-enone* (**1**). 2.1.1. *Synthesis of 3-Ethoxycyclohept-2-enone* (**4**). A soln. of 12.8 g (0.1 mol) of **3** and 0.1 g of 4-TsOH in a mixture of EtOH (100 ml) and $CHCl_3$ (200 ml) was refluxed for 15 h on a *Dean–Stark* trap, and additional TsOH (0.1 g)

Scheme 4



was added after 5 and 10 h, resp. Subsequent workup as described for similar 3-ethoxycycloalk-2-enones [20] afforded 6.4 g (40%) of **4**. Light yellow oil. NMR Data: identical to those reported in [21].

2.1.2. *Synthesis of* **1**. In analogy to [22], the addition of (3,3-dimethylbut-1-ynyl)magnesium bromide (from 4.2 g (0.05 mol) of 3,3-dimethylbut-1-yne and 6.2 g (0.05 mol) of EtMgBr) to 7.8 g (0.05 mol) of **4**, and subsequent workup, followed by CC (SiO_2; pentane/Et_2O 3 : 2), afforded 2.85 g (30%) of **1** (R_f 0.36). Light yellow liquid. ^{1}H-NMR ($CDCl_3$): 6.23 (*s*); 2.61–2.56 (*m*, 4 H); 1.88–1.77 (*m*, 4 H); 1.26 (*s*, 9 H). ^{13}C-NMR ($CDCl_3$): 203.2 (*s*); 141.4 (*s*); 135.6 (*d*); 106.3 (*s*); 81.3 (*s*); 42.5 (*t*); 34.9 (*7*); 30.6 (*q*); 28.3 (*s*); 25.1 (*t*); 21.5 (*t*). EI-MS: 190 (100, M^+).

2.2. *Synthesis of 5-(3,3-Dimethylbut-1-yn-1-yl)-5,6-dihydro-2,3-dimethoxy-7*H*-benzocyclohepten-7-one* (**2**). 2.2.1. *Synthesis of Methyl 3-(2-Acetyl-4,5-dimethoxyphenyl)propanoate* (**6**). To a soln. of 7.0 g (31.2 mmol) of **5** in CH_2Cl_2 (140 ml) were added AcCl (3.4 ml, 46.8 mmol) and $AlCl_3$ (6.2 g, 46.8 mmol), and the mixture was stirred for 4 h at r.t. After addition of ice cold H_2O (200 ml), the org. phase was separated and washed twice with 10% HCl. The aq. phase was extracted with CH_2Cl_2, and the combined org. phases were dried (Na_2SO_4). After evaporation of the solvent, the residue was purified by CC (SiO_2; hexane/AcOEt 6 : 1) to afford 7.6 g (92%) of **6** (R_f 0.42). White solid. M.p. 71–72°. ^{1}H-NMR ($CDCl_3$): 7.24 (*s*); 6.78 (*s*); 3.92 (*s*, 3 H); 3.91 (*s*, 3 H); 3.65 (*s*, 3 H); 3.17 (*t*, $J = 7.0$, 2 H); 2.65 (*t*, $J = 7.0$, 2 H); 2.57 (*s*, 3 H). ^{13}C-NMR ($CDCl_3$): 199.2 (*s*); 173.7 (*s*); 151.8 (*s*); 146.7 (*s*); 136.2 (*s*); 129.1 (*s*); 114.3 (*d*); 113.6 (*d*); 56.2 (*q*); 56.0 (*q*); 51.5 (*q*); 35.7 (*t*); 29.9 (*t*); 29.2 (*q*). EI-MS: 266 (90, M^+), 43 (100).

2.2.2. *Synthesis of 5,6,8,9-Tetrahydro-2,3-dimethoxy-7*H*-benzocycloheptene-5,7-dione* (**7**). In analogy to [23], **6** (4.5 g, 17 mmol) was reacted with 2 equiv. of ^{t}BuOK. After workup, the residue was dissolved in CH_2Cl_2 and filtered from insoluble material. After evaporation, the residue was purified by CC (SiO_2; Et_2O/AcOEt 9 : 1) to afford 2.07 g (52%) of **7** (R_f 0.37). White solid. M.p. 131–132°. ^{1}H-NMR ($CDCl_3$): 7.54 (*s*); 6.70 (*s*); 4.13 (*s*, 2 H); 3.96 (*s*, 3 H); 3.91 (*s*, 3 H); 3.32, 2.73 (*AA'XX'*, $J_{AA'} =$

$J_{XX'} = 15.0$, $J_{AX} = J_{AX'} = 7.0$, 4 H). ^{13}C-NMR ($CDCl_3$): 203.7 (*s*); 189.5 (*s*); 153.4 (*s*); 148.2 (*s*); 136.9 (*s*); 128.3 (*s*); 112.7 (*d*); 112.1 (*d*); 60.3 (*t*); 56.1 (*q*); 56.0 (*q*); 41.6 (*t*); 30.9 (*t*). EI-MS: 234 (100, M^+).

2.2.3. *Synthesis of 5,6-Dihydro-2,3-dimethoxy-7-oxo-7*H*-benzocyclohept-5-yl 4-Methylbenzenesulfonate* (**8**). To a soln. of **7** (1.5 g, 6.3 mmol) in CH_2Cl_2 (75 ml) were added equivalent amounts of TsCl and Et_3N. After hydrolytic workup, drying ($MgSO_4$), and evaporation of the solvent, the residue was purified by CC (SiO_2; Et_2O/AcOEt 7:2) to afford 1.26 g (51%) of **8** (R_f 0.38). Yellow solid. M.p. 121–122°. ^{1}H-NMR ($CDCl_3$): 7.76 (*d*, $J = 8.3$, 2 H); 7.31 (*d*, $J = 8.3$, 2 H); 7.08 (*s*); 6.70 (*s*); 5.97 (*s*); 3.92 (*s*, 3 H); 3.80 (*s*, 3 H); 2.92, 2.66 (*AA'XX'*, $J_{AA'} = J_{XX'} = 15.0$, $J_{AX} = J_{AX'} = 7.0$, 4 H); 2.43 (*s*). ^{13}C-NMR ($CDCl_3$): 199.7 (*s*); 156.8 (*s*); 151.1 (*s*); 147.7 (*s*); 135.2 (*s*); 133.4 (*s*); 129.9 (*d*); 128.4 (*d*); 123.7 (*s*); 120.7 (*d*); 111.8 (*d*); 111.7 (*d*); 56.1 (*q*); 56.0 (*q*); 42.6 (*t*); 29.9 (*t*); 21.7 (*q*). EI-MS: 388 (37, M^+); 191 (100).

2.2.4. *Synthesis of* **2**. To a soln. of **8** (1.26 g, 3.3 mmol) in dry MeCN (50 ml) were added 3,3-dimethylbut-1-yne (0.95 ml, 7.5 mmol), EtN^iPr_2 (0.9 ml, 5 mmol), CuI (60 mg, 0.33 mmol), and bis(triphenylphosphine)palladium chloride (230 mg, 0.33 mmol). After stirring the mixture overnight at r.t., the suspension was filtered over *Celite*, and the solvent was evaporated. The residue was purified by CC (SiO_2; Et_2O/AcOEt 9:1) to afford 0.91 g (94%) of **2** (R_f 0.44). Yellow solid. M.p. 108–109°. ^{1}H-NMR ($CDCl_3$): 7.47 (*s*); 6.72 (*s*); 6.49 (*s*); 3.93 (*s*, 3 H); 3.90 (*s*, 3 H); 2.93, 2.69 (*AA'XX'*, $J_{AA'} = J_{XX'} = 15.0$, $J_{AX} = J_{AX'} = 7.0$, 4 H); 1.34 (*s*, 9 H). ^{13}C-NMR ($CDCl_3$): 200.9 (*s*); 149.9 (*s*); 147.2 (*s*); 135.5 (*s*); 135.0 (*s*); 131.2 (*d*); 127.1 (*s*); 114.5 (*d*); 111.7 (*d*); 106.4 (*s*); 81.0 (*s*); 56.0 (*q*); 55.8 (*q*); 43.4 (*t*); 30.7 (*t*); 29.2 (*q*); 28.4 (*s*). EI-MS: 298 (100, M^+).

X-Ray Crystal-Structure Determination of **2**[1]). Pale colorless blocks (0.46 × 0.26 × 0.07 mm) from hexane, $C_{19}H_{22}O_3$, M_r 298.37; monoclinic, space group $P2(1)/c$; $Z = 4$, $a = 13.5310(17)$, $b = 9.8353(12)$, $c = 14.0853$ Å, $\beta = 116.567(2)°$; $V = 1676.6(4)$ Å^3, $D_x = 1.182$ g cm^{-3}.

3. *Photochemical Reactions.* Ar-Degassed solns. of **1** or **2** were irradiated (concentration, solvent, added reaction partner, duration, degree of conversion, and workup as described).

3.1. *Photodimerizations.* Solns. of either **1** or **2** in benzene (0.5 mmol/ml) were irradiated for 5–6 h.

3.1.1. *Photodimerization of* **1**. Leads to selective and quantitative conversion into *(1α,2β,8α,9β)-8,9-bis(3,3-dimethylbut-1-yn-1-yl)tricyclo[7.5.0.0^{2,8}]tetradecane-3,14-dione* (**9**). White crystals. M.p. 55–57°. ^{1}H-NMR ($CDCl_3$): 3.58 (*s*, 2 H); 2.53–2.33 (*m*, 4 H); 2.06–1.99 (*m*, 2 H); 1.99–1.96 (*m*, 2 H); 1.89–1.83 (*m*, 4 H); 1.81–1.78 (*m*, 2 H); 1.78–1.73 (*m*, 2 H); 1.21 (*s*, 18 H). ^{13}C-NMR ($CDCl_3$): 209.4 (*s*); 98.0 (*s*); 76.5 (*s*); 53.6 (*d*); 46.7 (*s*); 42.6 (*t*); 36.5 (*t*); 31.4 (*q*); 27.5 (*s*); 26.2 (*t*); 23.1 (*t*). EI-MS: 380 (100, M^+).

X-Ray Crystal-Structure Determination of **9**[1]). Pale colorless blocks (0.50 × 0.29 × 0.10 mm) from hexane, $C_{26}H_{36}O_2$, M_r 380.55; monoclinic, space group $P2(1)/n$; $Z = 4$, $a = 11.078(4)$, $b = 11.586(4)$, $c = 17.747(7)$ Å, $\beta = 93.055(5)°$; $V = 22.74.8(15)$ Å^3, $D_x = 1.111$ g cm^{-3}.

3.1.2. *Photodimerization of* **2**. Quant. conversion afforded a 3:2 mixture of **14** and **15** (monitoring by ^{1}H-NMR). CC (SiO_2; hexane/AcOEt 2:1) afforded first 74 mg (50%) of *(7aα,7bβ,14bβ,14cα)-14b,14c-bis(3,3-dimethylbut-1-yn-1-yl)-5,6,7a,7b,9,10,14b,14c-octahydro-2,3,12,13-tetramethoxy-dibenzo[*c,c*]cyclobuta[1,4-*a:*2,3-*a'*]dicyclohept-5-ene-7,8-dione* (**14**; R_f 0.45). Light yellow solid. M.p. 85–86°. ^{1}H-NMR ($CDCl_3$): 7.18 (*s*, 2 H); 6.67 (*s*, 2 H); 4.49 (*s*, 2 H); 3.90 (*s*, 6 H); 3.81 (*s*, 6 H); 3.71 (*ddd*, $J = 4.0, 9.0, 10.0$, 2 H); 2.80–2.62 (*m*, 4 H); 2.58 (*ddd*, $J = 4.0, 13.0, 17.0$, 2 H); 0.93 (*s*, 18 H). ^{13}C-NMR ($CDCl_3$): 205.8 (*s*); 147.5 (*s*); 146.3 (*s*); 132.0 (*s*); 131.8 (*s*); 113.0 (*d*); 112.1 (*d*); 97.3 (*s*); 81.7 (*s*); 55.8 (*q*); 55.6 (*q*); 53.9 (*d*); 51.1 (*s*); 44.1 (*t*); 30.4 (*q*); 29.7 (*t*); 28.1 (*s*). FAB-MS: 597.4 ($[M + H]^+$).

X-Ray Crystal-Structure Determination of **14**[1]). Pale colorless blocks (0.50 × 0.17 × 0.03 mm) from hexane, $C_{38}H_{44}O_6$, M_r 596.73; monoclinic, space group $P2(1)/n$; $Z = 8$, $a = 17.401(4)$, $b = 23.086(5)$, $c = 20.478(3)$ Å, $\beta = 124.261(12)°$; $V = 680.1$ Å^3, $D_x = 1.166$ g cm^{-3}.

This is followed by 42 mg (29%) of *(7aα,7bβ,14bα,14cβ)-14b,14c-bis(3,3-dimethylbut-1-yn-1-yl)-5,6,7a,7b,9,10,14b,14c-octahydro-2,3,12,13-tetramethoxy-dibenzo[*c,c'*]cyclobuta[1,4-*a;*2,3-*a'*]dicyclohept-5-ene-7,8-dione* (**15**; R_f 0.27). Light yellow solid. M.p. 188–189°. ^{1}H-NMR ($CDCl_3$): 7.25 (*s*, 2 H); 6.77 (*s*, 2 H); 3.90 (*s*, 6 H); 3.87 (*s*, 2 H); 3.84 (*s*, 6 H); 3.26 (*ddd*, $J = 2.0, 11.0, 13.0$, 2 H); 3.02 (*ddd*, $J = 2.0, 7.0, 15.0$, 2 H); 2.78 (*ddd*, $J = 2.0, 7.0, 15.0$, 2 H); 2.65 (*ddd*, $J = 2.0, 11.0, 13.0$, 2 H); 0.96 (*s*, 18 H).

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[1]) CCDC-734158–734162 contain the supplementary crystallographic data for **2**, **9**, **14**, **15**, and **17**, resp. These data can be obtained free of charge *via* www.ccdc.cam.ac.uk/data_request/cif.

^{13}C-NMR ($CDCl_3$): 206.3 (*s*); 147.3 (*s*); 146.6 (*s*); 132.8 (*s*); 131.0 (*s*); 114.8 (*d*); 111.0 (*d*); 98.2 (*s*); 77.3 (*s*); 55.9 (*q*); 55.8 (*q*); 54.7 (*d*); 51.8 (*s*); 41.9 (*t*); 30.9 (*t*); 30.5 (*q*); 27.5 (*s*). FAB-MS: 597.4 ([*M* + H]$^+$).

X-Ray Crystal-Structure Determination of **15**[1]). Pale colorless blocks (0.50 × 0.17 × 0.03 mm) from hexane, $C_{38}H_{44}O_6$, M_r 596.73; monoclinic, space group $P2(1)/c$; $Z = 4$, $a = 12.348(3)$, $b = 10.460(3)$, $c = 25.793(7)$ Å, $\beta = 101.647(52)°$; $V = 3262.8(15)$ Å^3, $D_x = 1.215$ g cm^{-3}.

3.2. *Photocycloadditions to 2,3-Dimethylbuta-1,3-diene.* Solns. of either **1** or **2** (0.5 mmol) and 2,3-dimethylbuta-1,3-diene (0.41 g, 5 mmol) in benzene (5 ml) were irradiated for 6–7 h.

3.2.1. *Photocycloaddition of* **1**. After total conversion, monitoring by ^{1}H-NMR indicates the formation of a 1:2:2:2 mixture of 1:1 photoproducts **10**–**13** (numbering by CC-elution order). CC (SiO_2; CH_2Cl_2) afforded first 23 mg (11%) of cis-*3-(3,3-dimethylbut-1-ynyl)-2-(3-methyl-2-methylidenebut-3-en-1-yl)cycloheptan-1-one* (**10**; R_f 0.54). Light yellow oil. ^{1}H-NMR ($CDCl_3$): 5.17 (*s*); 5.06 (*s*); 5.01 (*s*); 4.97 (*s*); 2.94 (*ddd*, *J* = 1.0, 3.5, 14.5); 2.85 (*ddd*, *J* = 3.0, 3.0, 6.0); 2.74 (*ddd*, *J* = 3.0, 3.0, 10.2); 2.58–2.54 (*m*, 2 H); 2.32 (*dd*, *J* = 10.2, 14.5); 2.10–2.02 (*m*, 2 H); 1.89 (*s*, 3 H); 1.84–1.73 (*m*, 2 H); 1.55–1.47 (*m*, 2 H); 1.19 (*s*, 9 H). ^{13}C-NMR ($CDCl_3$): 212.8 (*s*); 145.8 (*s*); 142.3 (*s*); 114.7 (*t*); 113.0 (*t*); 94.0 (*s*); 77.4 (*s*); 54.4 (*d*); 43.8 (*t*); 35.3 (*t*); 34.8 (*t*); 32.0 (*q*); 30.5 (*d*); 27.4 (*s*); 26.1 (*t*); 25.4 (*t*); 21.3 (*q*). EI-MS: 272 (6, M^+), 178 (100).

The second fraction consists of 35 mg (25%) of *7-(3,3-dimethylbut-1-yn-1-yl)-9,10-dimethylbicyclo[5.4.0]undec-9-en-2-one* (**11**; R_f 0.49). Light yellow oil. ^{1}H-NMR ($CDCl_3$): 3.12 (*ddd*, *J* = 2.8, 12.0, 12.0); 2.38–2.35 (*m*); 2.34–2.32 (*m*); 2.27 (*dd*, *J* = 0.5, 12.0); 2.10–2.05 (*m*, 2 H); 2.05–2.02 (*m*, 2 H); 1.95 (*d*, *J* = 15.4); 1.86–1.83 (*m*); 1.81–1.75 (*m*, 2 H); 1.68 (*s*, 3 H); 1.58 (*s*, 3 H); 1.39–1.33 (*m*); 1.17 (*s*, 9 H). ^{13}C-NMR ($CDCl_3$): 215.5 (*s*); 124.4 (*s*); 123.2 (*s*); 93.8 (*s*); 80.1 (*s*); 57.0 (*d*); 48.6 (*s*); 47.7 (*t*); 42.3 (*t*); 34.5 (*t*); 34.3 (*t*); 31.4 (*s*); 27.5 (*q*); 25.0 (*t*); 24.5 (*t*); 18.1 (*q*); 17.7 (*q*). EI-MS: 272 (89, M^+), 215 (100).

The third fraction (70 mg, 50%) is a 5:4 mixture of diastereoisomeric *(1α,7β)-7-(3,3-dimethylbut-1-ynyl)-8-methyl-8-(1-methylethenyl)bicyclo[5.2.0]nonan-2-ones* **12** and **13** (R_f 0.32), which can be differentiated by NOE. The major component is the 8β-diastereoisomer **12**. ^{1}H-NMR ($CDCl_3$): 4.73 (*s*); 4.61 (*s*); 3.25 (*dd*, *J* = 7.3, 10.4); 2.51 (*dd*, *J* = 10.4, 10.4); 2.45 (*ddd*, *J* = 2.8, 12.0, 12.1); 1.89–1.88 (*m*); 1.81–1.75 (*m*, 4 H); 1.72–1.69 (*m*, 2 H); 1.66 (*s*, 3 H); 1.63 (*dd*, *J* = 7.3, 10.4); 1.26 (*s*, 3 H); 1.20 (*s*, 9 H). ^{13}C-NMR ($CDCl_3$): 212.1 (*s*); 151.3 (*s*); 108.8 (*t*); 91.9 (*s*); 79.0 (*s*); 50.4 (*d*); 47.9 (*s*); 46.7 (*s*); 43.3 (*t*); 36.7 (*t*); 30.5 (*t*); 30.4 (*s*); 27.4 (*q*); 26.5 (*t*); 24.5 (*t*); 21.8 (*q*); 18.4 (*q*).

Data of the 8α-Diastereoisomer **13**. ^{1}H-NMR ($CDCl_3$): 5.02 (*s*); 4.96 (*s*); 3.28 (*dd*, *J* = 7.5, 10.8); 2.28 (*ddd*, *J* = 2.8, 12.0, 12.1); 2.15 (*dd*, *J* = 7.5, 12.5); 2.11 (*dd*, *J* = 10.9, 12.5); 1.81–1.75 (*m*, 5 H); 1.74 (*s*, 3 H); 1.72–1.69 (*m*, 2 H); 1.27 (*s*, 3 H); 1.21 (*s*, 9 H). ^{13}C-NMR ($CDCl_3$): 212.1 (*s*); 147.1 (*s*); 110.7 (*t*); 98.6 (*s*); 80.1 (*s*); 50.9 (*d*); 47.7 (*s*); 47.5 (*s*); 43.2 (*t*); 36.5 (*t*); 31.4 (*s*); 29.1 (*t*); 27.7 (*q*); 26.7 (*t*); 23.9 (*q*); 21.8 (*q*).

3.2.2. *Photocycloaddition of* **2**. After total conversion, monitoring by ^{1}H-NMR in benzene indicated the formation of a 2:1 mixture of 1:1 photoproducts **16** an **17**. On contact with SiO_2 or on standing in $CDCl_3$, **16** cleanly isomerized to **18**. The spectroscopic data of 12-(1,1-dimethylethyl)-*5,6,7a,8-tetrahydro-2,3-dimethoxy-9,10-dimethyl-7*H,*11*H*-benzo[3,4]cyclohepta[1,2]cycloocten-7-one* (**16**), therefore, stem directly from the reaction mixture. ^{1}H-NMR (C_6D_6): 6.78 (*s*); 6.65 (*s*); 3.86 (*s*, 3 H); 3.85 (*s*, 3 H); 3.49 (*dd*, *J* = 3.8, 12.0); 3.10, 2.91 (*AB*, *J* = 15.5); 2.90–2.88 (*m*, 3 H); 2.57–2.55 (*m*, 2 H); 2.45 (*dd*, *J* = 3.8, 12.0); 1.88 (*dd*, *J* = 12.0, 12.0); 1.73 (*s*, 3 H); 1.57 (*s*, 3 H); 1.07 (*s*, 9 H). ^{13}C-NMR ((D_6)benzene; allenic C-atoms indicated): 209.7 (*s*); 201.0 (*s*, C(13)); 147.7 (*s*); 147.5 (*s*); 129.4 (*s*); 129.3 (*s*); 127.4 (*s*); 127.0 (*s*); 126.2 (*s*, C(12)); 113.5 (*d*); 111.3 (*d*); 105.5 (*s*, C(13a)); 55.9 (*q*); 55.8 (*q*); 47.5 (*d*); 41.3 (*t*); 33.1 (*t*); 32.1 (*s*); 30.9 (*t*); 30.8 (*t*); 29.2 (*q*); 21.8 (*q*); 20.3 (*q*). CC of the crude reaction mixture (SiO_2; hexane/AcOEt 4:1) afforded first 80 mg (42%) of 12-(1,1-dimethylethyl)-*5,6,7,7a-tetrahydro-2,3-dimethoxy-9,10-dimethyl-7*H*-benzo[3,4]cyclohepta[1,2]cycloocten-7-one* (**18**; R_f 0.30). Colorless solid. M.p. 71–72°. ^{1}H-NMR ($CDCl_3$): 6.67 (*s*); 6.62 (*s*); 6.09 (*s*); 5.67 (*s*); 3.88 (*s*, 3 H); 3.87 (*s*, 3 H); 3.64 (*dd*, *J* = 5.6, 12.5); 3.25 (*dd*, *J* = 5.6, 12.5); 3.06 (*ddd*, *J* = 2.2, 10.3, 16.0); 2.96–2.94 (*m*); 2.91–2.89 (*m*); 2.60–2.58 (*m*); 1.90 (*dd*, *J* = 12.5, 12.5); 1.70 (*s*, 3 H); 1.69 (*s*, 3 H); 1.09 (*s*, 9 H). ^{13}C-NMR ($CDCl_3$): 209.3 (*s*); 148.1 (*s*); 147.4 (*s*); 146.6 (*s*); 140.0 (*s*); 138.4 (*s*); 130.4 (*d*, C(13)); 129.8 (*s*); 129.4 (*s*); 125.1 (*d*, C(11)); 112.7 (*d*); 112.6 (*d*); 56.3 (*q*); 56.0 (*q*); 54.1 (*d*); 42.0 (*t*); 36.3 (*s*); 35.2 (*t*); 30.9 (*t*); 30.0 (*q*); 18.4 (*q*); 17.6 (*q*). FAB-MS: 381.3 ([*M* + H]$^+$).

The second fraction consisted of 42 mg (24%) of *(1α,2aα,9bβ)-9b-(3,3-dimethylbut-1-yn-1-yl)-1,2,2a,4,5,9b-hexahydro-7,8-dimethoxy-1-methyl-1-(1-methylethenyl)-3*H*-benzo[*a*]cyclobuta[*c*]cyclohept-

en-3-one (**17**; R_f 0.24). Colorless solid. M.p. 128–129°. ^{1}H-NMR (CDCl$_3$): 6.59 (*s*); 6.58 (*s*); 4.97 (*s*); 4.90 (*d*); 4.12 (*dd*, $J = 7.7$, 11.1); 3.85 (*s*, 3 H); 3.80 (*s*, 3 H); 3.29 (*ddd*, $J = 2.0$, 12.6, 16.7); 3.00 (*ddd*, $J = 2.2$, 12.6, 17.4); 2.90 (*ddd*, $J = 2.0$, 6.5, 16.7); 2.57 (*ddd*, $J = 2.0$, 6.5, 17.5); 2.32 (*dd*, $J = 11.1$, 11.2); 2.05 (*dd*, $J = 7.7$, 11.2); 1.66 (*s*, 3 H); 1.65 (*s*, 3 H); 1.14 (*s*, 9 H). ^{13}C-NMR (CDCl$_3$): 210.3 (*s*); 148.8 (*s*); 148.7 (*s*); 147.4 (*s*); 134.3 (*s*); 128.5 (*s*); 114.4 (*t*); 114.1 (*d*); 109.9 (*d*); 96.8 (*s*); 81.1 (*s*); 55.8 (*q*); 55.7 (*q*); 51.7 (*s*); 51.3 (*s*); 50.1 (*d*); 41.4 (*t*); 31.5 (*t*); 31.1 (*t*); 30.9 (*q*); 27.6 (*s*); 22.7 (*q*); 22.6 (*q*). FAB-MS: 381.3 ($[M + \mathrm{H}]^+$).

X-Ray Crystal-Structure Determination of **17**[1]). Pale colorless blocks ($0.50 \times 0.21 \times 0.24$ mm) from hexane, $C_{25}H_{32}O_3$, M_r 380.51; monoclinic, space group $P2(1)/c$; $Z = 4$, $a = 14.3801(14)$, $b = 10.8618(10)$, $c = 14.3929(14)$ Å, $\beta = 108.031(10)°$; $V = 2137.7(4)$ Å^3, $D_x = 1.182$ g cm^{-3}.

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