88. Photochemical Reactions

135th Communication[1])

Photochemistry of Homoconjugated Cyclobutanones. II. Decisive Effect of *gem*-Dimethyl Substitution on the Course of the Oxa-di-π-methane Rearrangement[2])

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Dedicated to Prof. *W. S. Johnson* on the occasion of his 71st birthday

(2.I.84)

Summary

The synthesis and photolysis of the spirocyclobutanones **4**–**7** incorporating a cyclohexa-, cycloheptа- and cyclooctadiene moiety, respectively, is described. On triplet excitation, these compounds undergo isomerization *via* a 1,2-acyl shift involving one or both double bonds of the diene system. The presence of a *gem*-dimethyl group as in **1**, **4** and **7** dramatically changes the photoproduct distribution, since only these substrates lead to the products **3**, **29** and **34** resulting from vinylogous ring closure *(Scheme 5)*. Those substrates without methyl substitution (**5** and **6**) give only products of a rearrangement involving one double bond.

1. Introduction. – It was previously reported that on triplet excitation ($\lambda > 280$ nm, acetone) the spirocyclic compound **1**, with a 1,3-diene system in homoconjugation with the cyclobutanone, undergoes a 1,2-acyl shift leading to products **2** (46%) and **3** (18%). Compound **2** is formed by a normal oxa-di-π-methane rearrangement (*i.e.* involving only one double bond of the diene system), whereas **3** results from vinylogous ring closure [2] *(*see *Scheme 1)*.

To gain some information about the structural requirements of the process leading to products of type **3**, the photochemical behaviour of the cyclobutanones **4**–**7** *(Scheme 1)* was investigated. These compounds were thought to be suitable models to delineate the influence of the ring size of the diene system, and of the *gem*-dimethyl group on the course of the product formation.

2. Preparation of the Starting Materials. – 2.1. *Spirocyclobutanone* **4**. The synthesis of **4** was achieved as depicted in *Scheme 2*. Initial attempts to prepare **4** by the method

[1]) 134th Communication: [1].

[2]) Part I: [2].

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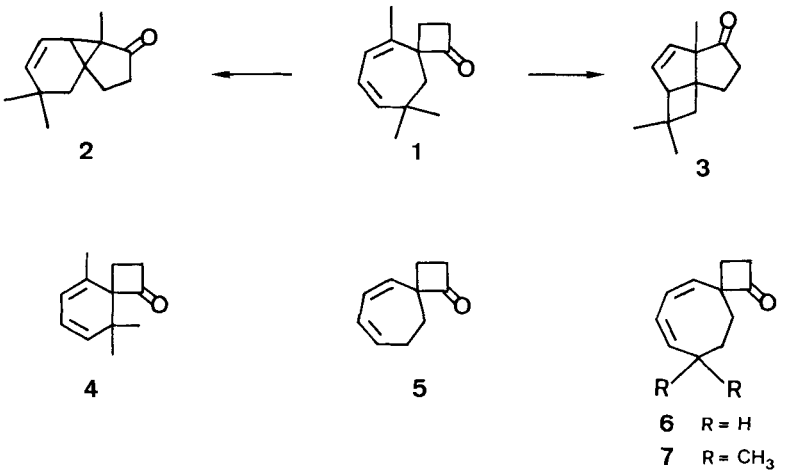
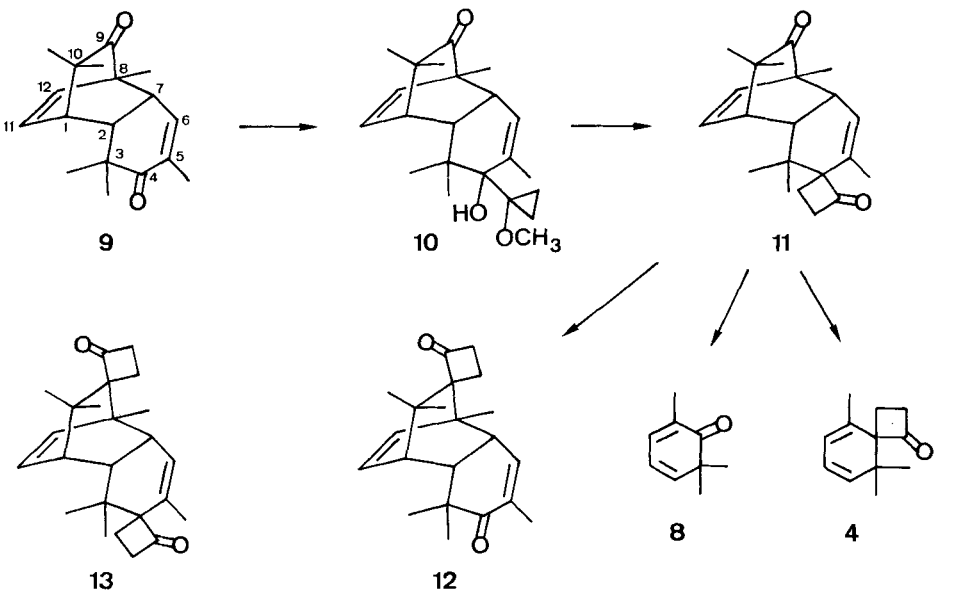
Scheme 1



of *Cohen & Matz* [3] from the cyclohexadienone **8**, which was obtained by thermolysis of the dimer **9** [4], failed. Reaction of **8** with 1-lithio-1-methoxycyclopropane [3] and subsequent treatment of the alkylation product with 50% aq. HBF_4 led only to unidentified aromatic compounds. Therefore, the cyclobutanone moiety was introduced into the dimer **9**. 1-Lithio-1-methoxycyclopropane reacted preferentially with the enone carbonyl group of **9** affording **10**, which was treated with 50% aq. HBF_4/THF (1:1.7) to

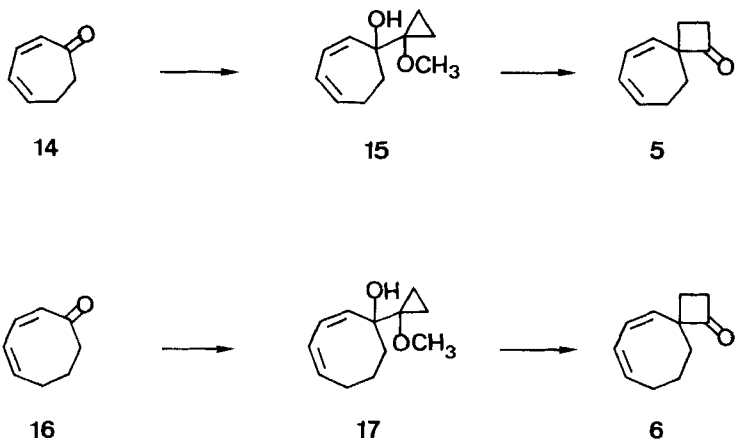
Scheme 2



give compound **11**[4]) (95%). Thermolysis at 350° (15 Torr, 55% conversion) gave the cleavage products **4** and **8** in 47% yield[5]) each as well as the isomeric cyclobutanone **12**[4])[6]) in 8% yield[7]).

2.2. *Spirocyclobutanones* **5** *and* **6** *(Scheme 3).* Compound **5** was obtained in 34% overall yield by reaction of 2,4-cycloheptadienone (**14**) [6] with 1-lithio-1-methoxycyclopropane and transformation of **15** with 50% aq. HBF_4/THF (1:4). Analogously, **6** was synthesized from 2,4-cyclooctadienone (**16**) [7] in 71% yield (**16**→**17**→**6**, *Scheme 3*).

Scheme 3



2.3. *Spirocyclobutanone* **7**. Compound **7** was synthesized starting from 3-methylcrotonaldehyde (**18**) in 1.2% overall yield *(Scheme 4).* Reaction of **18** with 1-lithio-1-methoxycyclopropane gave **19** (65%), which was treated with 50% aq. HBF_4/Et_2O (*ca.* 1:13) to afford the cyclobutanone **20** in 67% yield. Addition of lithium trimethylsilylacetylide[8]) to **20** gave **21A** + **B** (87%) as a mixture of two diastereomers in the ratio of *ca.* 1:3, which on desilylation (aq. KOH/MeOH) [9] gave **22A** + **B** (90%), and subsequent catalytic hydrogenation (*Lindlar* catalyst [10]) afforded **23A** + **B** in 97% yield.

Anionic oxy-*Cope* rearrangement of **23A** + **B** with KH in THF according to the procedure described by *Gadwood & Lett* [11] gave the cyclooctenone (*E*)-**24**[9]) in 56% yield, which on triplet sensitization ($\lambda > 280$ nm, acetone) was transformed to (*Z*)-**24** in 60% yield. The C(2)=C(3) bond was introduced by the method of *Reich* [12]: reac-

[4]) The configuration at the spiro-center was not assigned.

[5]) Yields are based on converted starting material.

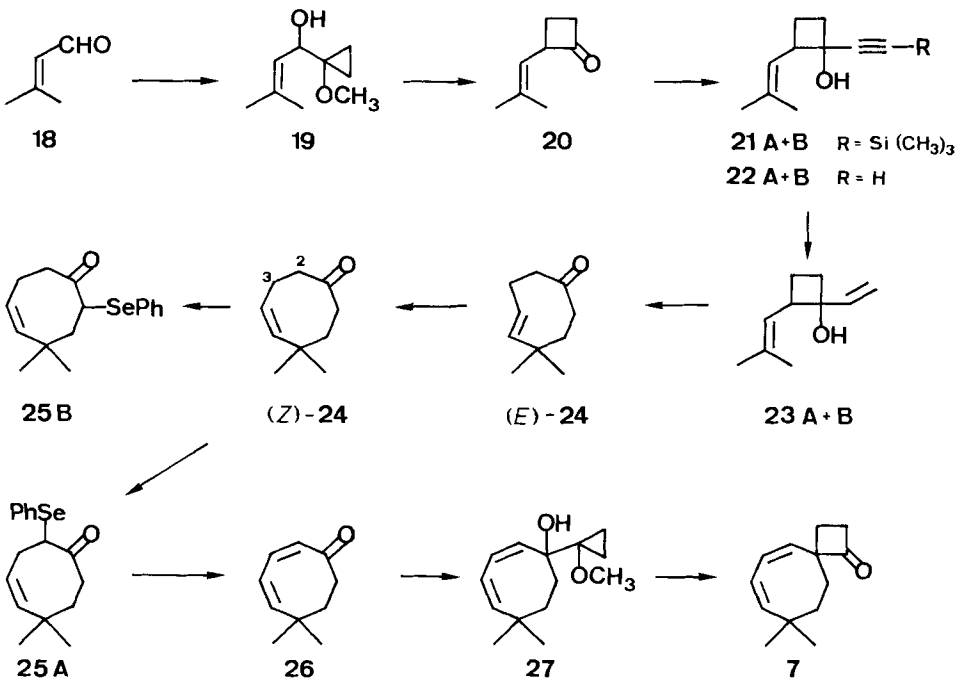
[6]) The transformation of **11**→**12** is presumably a type of *Woodward-Katz* rearrangement [5]. The authors thank the referee for suggesting this mechanism.

[7]) Thermolysis (350°) of the bis-spirocyclobutanone **13**[4]) (*Scheme 2;* obtained by reaction of **9** with 5 equiv. of 1-lithio-1-methoxycyclopropane and subsequent rearrangement with HBF_4) gave only the starting material. Thermolysis of **13** at higher temperature (up to 500°) gave rise to unidentified decomposition products, among which the monomer **4** could not be detected.

[8]) Prepared by metallation of bis-trimethylsilylacetylene with BuLi [8].

[9]) In contrast to analogous substrates, which produced mainly (*Z*)-cyclooctenone systems [11], on rearrangement of **23A** + **B**, less than 5% of (*Z*)-**24** was detected.

Scheme 4



tion of (*Z*)-**24** (*ca.* 0.1M THF solution) with 1.2 equiv. of LDA at −78° and trapping of the enolate with PhSeCl gave a *ca.* 5:1 mixture of the isomers **25A** + **B** in 39% yield and 30% of starting material[10]). Oxidation of the mixture of **25A** + **B** with H_2O_2 [12] afforded the cyclooctadienone **26** in 45% yield (based on **25A**)[11]). The cyclobutanone moiety was introduced in the usual way: the reaction sequence **26**→**27**→**7** afforded the spirocyclobutanone in 61% overall yield.

3. Photolysis Experiments. – To avoid direct irradiation, which occurred partially on photolysis of compound **1** in acetone ($\lambda > 280$ nm)[12]), *Michler*'s ketone was chosen as a triplet sensitizer. MeCN solutions (*ca.* 0.01–0.08M) of the substrates were irradiated ($\lambda > 347$ nm) in the presence of *ca.* 0.15 equiv. of *Michler*'s ketone.

3.1. *Triplet excitation of* **1** (*ca.* 100% conversion) gave **2** and **3** (see *Scheme 1*) in 54 and 25% yield, respectively[13]).

3.2. *Triplet excitation of* **4** (*ca.* 100% conversion) gave **28** in 58% and **29** in 24% yield[13]) (see *Scheme 5*).

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[10]) Using a larger excess of LDA (up to 40%) and/or adding (*Z*)-**24** in more dilute solution (up to five times) did not improve the yield; however, the ratio of **25A**:**25B** became worse (*e.g.* 2:1).

[11]) 4,4-Dimethyl-2,5-cyclooctadienone, the product derived from **25B** was not detected.

[12]) Direct irradiation of **1** ($\lambda = 254$ nm or $\lambda = 327$ nm, pentane) gives rise to decarbonylation and ketene elimination accompanied by electrocyclization [2].

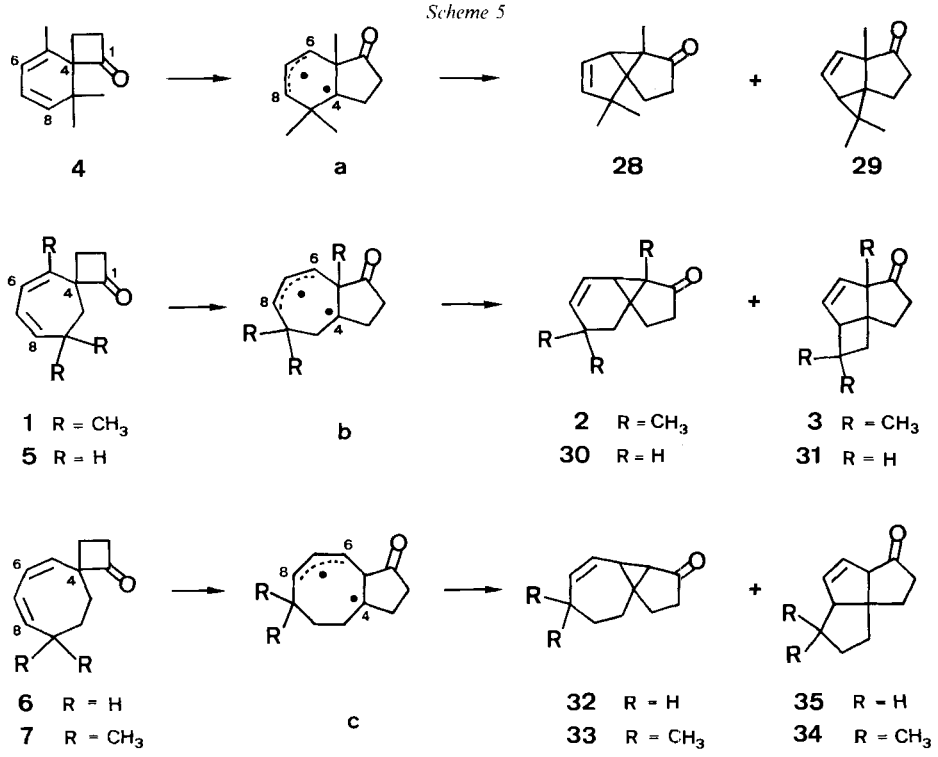
[13]) In addition, only intractable material (presumably polymers) was detected.

3.3. *Triplet excitation of* **5** (80% conversion) gave **30** in 28% yield[5]) and only traces of **31**[13]) (see *Scheme 5*).

3.4. *Triplet excitation of* **6** (89% conversion) produced **32** as the only product in 64% yield[5])[13]) (see *Scheme 5*).

3.5. *Triplet excitation of* **7** (81% conversion) furnished **33** in 19% and **34** in 21% yield[5])[13]) (see *Scheme 5*).

Scheme 5



4. Structure of the Compounds. – *Spirocyclobutanones* **4–7**. The main structural features of these compounds are evidenced by their spectral data. In particular, the IR band in the region of 1770 to 1780 cm^{-1} signifies the cyclobutanone moiety. The UV spectra include π,π^*-bands of the diene systems at 271 (**4**), 255 (**5**), and 237 nm (**6** and **7**), which in the case of **4** and **5** show structures typical for homoconjugated diene chromophores[14]).

Cyclobutanones **11**, **12** *and* **13**. The structures of **11** and **13** are based on the fact that they were obtained in the usual way from **9** by spiroannulation. On the other hand, the proposed structure of **12** was derived by comparison of its NMR spectrum with those of **9** and **11**. The IR spectrum of **11** shows bands of the cyclobutanone (1770 cm^{-1}) and cyclohexanone (1715 cm^{-1}) moieties, whereas **12** shows the cyclobutanone band at 1760 cm^{-1} and an enone band at 1675 cm^{-1}. The bis-spirocyclobutanone **13** exhibits only a strong band at 1760 cm^{-1} in the carbonyl region. Most of the evidence for the structures of **11** and **12** stems from their 300-MHz ^{1}H-NMR spectra, where all the signals could be assigned (see *Exper. Part*). However, the configuration at the spiro-centers was not assigned.

Cyclooctadienone **26**. The dienone moiety is evidenced by a UV maximum at 268 nm (ε = 6800) and a strong IR band at 1660 cm^{-1}[14]).

[14]) Full data and the assignment of the ^{1}H-NMR and ^{13}C-NMR signals are given in the *Exper. Part*.

Tricyclo[4.3.0.0^{1,5}]nonenone **28**. The structure of **28** was elucidated from its spectral data. In particular, the IR band at 1720 cm^{-1} and the UV maximum at 226 nm ($\varepsilon = 7000$) are indicative of a conjugated vinylcyclopropyl carbonyl moiety[14]).

Tricyclo[4.3.0.0^{1,3}]nonenone **29**. The spectral evidence for the homoconjugated cyclopentanone moiety includes a structured n,π^*-band at 316 nm with a large ε in the UV spectrum and an IR band at 1740 cm^{-1} [14]).

Tricyclo[4.4.0.0^{1,5}]decenone **30**. The structure of **30** was elucidated by comparison of its spectral data with those of **2** *(Scheme 1)*. In particular, the conjugated vinylcyclopropyl carbonyl moiety is evidenced by an IR band at 1720 cm^{-1} and a UV maximum at 227 nm ($\varepsilon = 6500$)[14]).

Tricyclo[5.3.0.0^{1,4}]decenone **31**. The structure of **31**, which was only obtained in 0.2% yield, was deduced by comparison of its IR and 300-MHz ^{1}H-NMR spectrum with that of **3** (see *Exper. Part*).

Tricyclo[5.4.0.0^{1,8}]undecenone **32**. The spectral evidence for the conjugated vinylcyclopropyl carbonyl system includes an IR band at 1725 cm^{-1} and a UV maximum at 214 nm ($\varepsilon = 10\,100$)[14]).

Tricyclo[5.4.0.0^{1,8}]undecenone **33**. Analogous to compounds **2**, **28**, **30** and **32**, which also include a conjugated vinyl cyclopropyl moiety, **33** shows an IR band at 1720 cm^{-1} and a UV maximum at 214 nm ($\varepsilon = 11\,600$)[14]).

Tricyclo[6.3.0.0^{1,5}]undecenone **34**. The cyclopentanone moiety is indicated by the IR band at 1735 cm^{-1}. Most of the structural evidence, however, stems from the 300-MHz ^{1}H-NMR spectrum (see the *Figure*).

Decoupling experiments included irradiation at 2.52 ppm which changed the *ddd* of H–C(6) and H–C(7) to *dd* indicating the vicinal and allylic coupling of H–C(8). Analogously, irradiation at 2.91 ppm simplified the signals of H–C(6) and H–C(7), and in addition, the two *dddd* of 2H–C(3) were changed to *ddd* indicating a long-range coupling of H–C(5) with 2H–C(3)[14]).

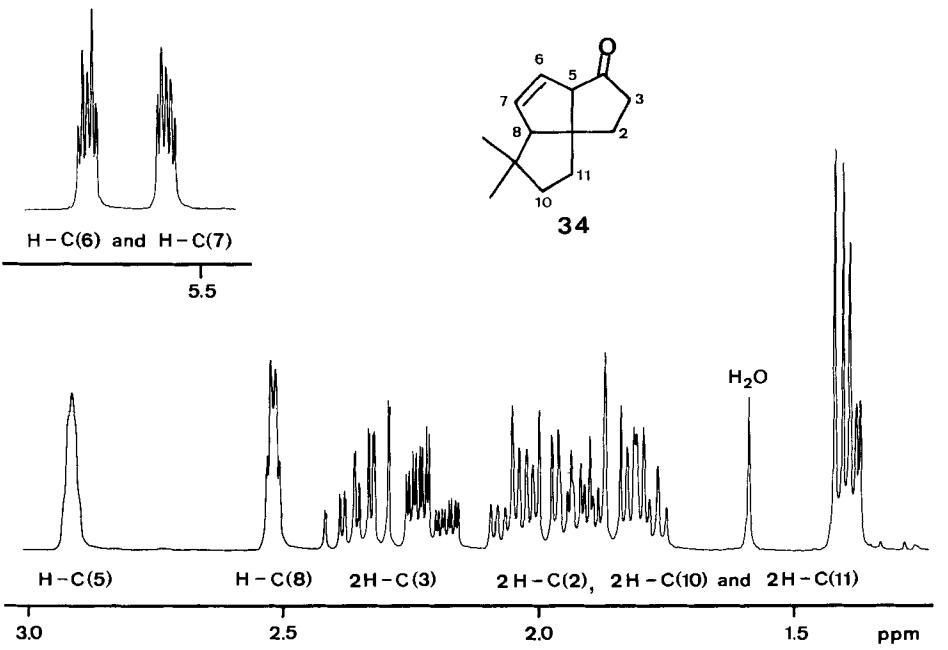


Figure. *300-MHz ^{1}H-NMR Spectrum* ($CDCl_3$) *of* **34**

5. Discussion. – On triplet excitation ($\lambda > 347$ nm, *Michler*'s ketone), the compounds **4**–**7** undergo an oxa-di-π-methane rearrangement [13] which includes as primary steps a 1,2-acyl shift leading to the intermediates **a**, **b** and **c** (see *Scheme 5)*. Compounds **28**, **30**, **32** and **33** arise from these intermediates by the bond formation between *C*(4) and *C*(6). In an analogous manner to the photoisomerization of **1**→**3** [2],

the spirocyclobutanone **4** also undergoes rearrangement with vinyl-analog product formation. Thus, the 1,2-acyl shift (**4**→**a**) is followed by ring closure between C(4) and C(8) leading to compound **29**[15]). However, on photolysis of **5**, the low yield (0.2%) of the product **31** formed by C(4)–C(8) bonding was not expected, since on triplet sensitization (acetone or *Michler*'s ketone) of **1** (the trimethyl analog of **5**) the corresponding compound **3** is produced in 18 and 25% yield, respectively. Therefore, it was assumed that the differing behavior of **1** and **5** is due to the presence of methyl substituents in **1**. Further evidence for this effect was obtained by the investigation of compound **7**, a *gem*-dimethyl analog of **6**. The spirocyclobutanone **6** gives compound **32** arising from **c** by bond formation between C(4) and C(6) in 64% yield, but the hypothetical product of the oxa-di-π-methane rearrangement with vinylogous bond formation (**35**) was not detected. However, the photolysis of its dimethyl analog **7** affords a 19% yield of **33** (the product corresponding to **32**) and, indeed, a 21% yield of **34** arising from **c** by ring closure between C(4) and C(8).

On the basis of these results, it is evident that the transformations **1**→**b**→**3** and **7**→**c**→**34**, which both include bond formation between C(4) and C(8), are promoted by the presence of a *gem*-dimethyl group. The *gem*-dimethyl groups in **1** and **7** may exert similar effects as discussed for the cyclization of acyclic systems[16]). Thus, *e.g.* the *gem*-dimethyl substitution may increase the population of conformations of the seven- and eight-membered rings of compounds **1** and **7** or of the intermediates **b** and **c** ($R=CH_3$), respectively, which favor vinylogous ring closure. On the other hand, in the unsubstituted compounds **5** and **6** or in the corresponding intermediates **b** and **c** (R=H), such conformations may be much less populated and, due to proximity of C(4) and C(6), compounds **30** and **32** are formed preferentially.

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Experimental Part

General. See [16] except as noted below. Analytical gas chromatography (GC) was performed using a 25 m × 0.36 mm *Ucon 50 HB 5100* capillary glass column. Column chromatography was carried out on silica gel (SiO_2 *60 Merck*, 0.040–0.036 mm 230–400 mesh ASTM) according to [17]. Except as noted below, all NMR spectra were taken in $CDCl_3$ solution. 300-MHz ^{1}H-NMR spectra were recorded on a *Bruker WM 300* instrument, and 80-MHz ^{1}H-NMR spectra were taken on a *Bruker WP 80/CW* instrument. Unless otherwise stated, photolysis experiments were carried out under Ar using a 125-W Hg medium-pressure lamp [16] behind a $Pb(NO_3)_2$/KBr filter solution [18] ($\lambda > 347$ nm).

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[15]) A similar rearrangement has been previously reported for spiro[5.5]undeca-1,3-dien-7-one [14].

[16]) It is well-known that when *gem*-dimethyl groups are introduced into a polymethylene chain, the equilibrium and rate constants for cyclization are frequently increased. For examples and discussions of the *gem*-dimethyl effect see [15] and references therein.

3,3,5,8,10,10-Hexamethyltricyclo[6.2.2.0^{2,7}]dodeca-5,11-dien-4,9-dione (**9**) [4]. ^{1}H-NMR (300 MHz): 1.03, 1.13, 1.14, 1.16, 1.30 (5*s*, CH_3–C(8), 2 CH_3–C(3), 2 CH_3–C(10)); 1.78 (*m*, $w_{1/2}$ = 3.5, CH_3–C(5)); 2.51 (*dd*, J_1 = 8, J_2 = 2, H–C(2)); 2.63 (*ddd*, J_1 = 6.5, J_2 = J_3 = 2, H–C(1)); 2.65–2.70 (*m*, H–C(7)); 5.46 (*dd*, J_1 = 8, J_2 = 2, H–C(12)); 6.20–6.25 (*m*, H–C(6)); 6.30 (*dd*, J_1 = 8, J_2 = 6.5, H–C(11)). ^{13}C-NMR: 16.3, 16.8, 22.3, 23.6, 28.0, 32.3 (6*q*, CH_3–C(8), CH_3–C(5), 2 CH_3–C(3), 2 CH_3–C(10)); 40.9, 45.2, 46.7 (3*d*, C(1), C(2), C(7)); 43.9, 44.2, 54.6 (3*s*, C(3), C(8), C(10)); 132.7, 135.7, 137.1 (3*d*, C(6), C(11), C(12)); 135.8 (*s*, C(5)); 204.1, 216.1 (2*s*, C(4), C(9)).

1. Preparation of 4. – 1.1. *Reaction of* **9** *with 1-Lithio-1-methoxycyclopropane.* A stirred solution of 1-(dimethylamino)naphthalene (17.46 g, 102 mmol) in abs. THF (150 ml) was cooled to −45°, and Li-wire (645 mg, 96 mmol) was added in small pieces under Ar. The mixture was stirred for 4.5 h to ensure complete reaction of Li; after cooling to −78°, a solution of 1-methoxy-1-(phenylthio)cyclopropane [3b] (8.4 g, 46.5 mmol) in THF (15 ml) was added, and the mixture was stirred for 90 min. Then a solution of **9** [4] (9.6 g, 35 mmol) in THF (20 ml) was added dropwise. The mixture was stirred for 40 min, quenched by the addition of MeOH, poured into a chilled solution of 5% HCl, and extracted with pentane and CH_2Cl_2. After drying over K_2CO_3, the solvents were removed, and after addition of pentane, compound **10** (9.0 g, 66%) separated on cooling.

4-Hydroxy-4-(1'-methoxy-1'-cyclopropyl)-3,3,5,8,10,10-hexamethyltricyclo[6.2.2.0^{2,7}]dodeca-5,11-diene-9-one (**10**). M.p. 165° (from Et_2O/pentane). UV (5.268 mg in 5 ml MeCN): 302 (94), 312 sh (70). IR ($CHCl_3$): 3635*w*, 3500*w* br., 3020*w*, 2970*s*, 2935*s*, 2870*m*, 2830*m*, 1705*s*, 1465*m* sh, 1445*m*, 1380*m*, 1360*m*, 1075*m*, 1050*m* sh, 1025*m*, 950*w*. ^{1}H-NMR: 0.5–1.0 (*m*, 2H–C(2'), 2H–C(3')); 0.70, 1.10, 1.14, 1.20, 1.26 (5*s*, CH_3–C(8), 2 CH_3–C(3), 2 CH_3–C(10)); 1.41 (*s*, HO–C(4)); 1.76 (*m*, $w_{1/2}$ = 5.5, CH_3–C(5)); 2.18–2.42 (*m*, H–C(2)); 2.56–2.72 (*m*, H–C(7)); 2.96–3.16 (*m*, H–C(1)); 3.06 (*s*, CH_3O); 5.56 (*d*, *J* = 8, H–C(12)); 5.62 (*m*, $w_{1/2}$ = 6.0, H–C(6)); 6.33 (*dd*, J_1 = 8, J_2 = 6, H–C(11)). ^{13}C-NMR: 6.0, 9.9 (2*t*, C(2'), C(3')); 15.9, 20.2, 24.9, 25.1, 25.6, 28.9 (6*q*, CH_3–C(8), CH_3–C(5), 2 CH_3–C(3), 2 CH_3–C(10)); 42.5, 44.5, 46.4 (3*d*, C(1), C(2), C(7)); 42.5, 44.2, 52.6 (3*s*, C(3), C(8), C(10)); 55.1 (*q*, CH_3O); 66.1 (*s*, C(4)); 124.1, 128.4, 139.8 (3*d*, C(6), C(11), C(12)); 139.3 (*s*, C(5)); 218.5 (*s*, C(9)). MS: 344 (6, M^+, $C_{22}H_{32}O_3$), 273 (7), 208 (8), 193 (8), 180 (12), 175 (10), 165 (8), 161 (8), 153 (14), 142 (7), 138 (11), *137* (100), 133 (8), 127 (15), 122 (7), 121 (9), 105 (9), 91 (10), 43 (10), 41 (13). Anal. calc. for $C_{22}H_{32}O_3$ (344.48): C 76.70, H 9.36; found: C 76.56, H 9.44.

1.2. *Transformation of* **10** *into* **11**. The α-methoxy-alcohol **10** (4.6 g, 13.3 mmol) was treated with 50% aq. HBF_4/THF 1:1.7 (230 mmol) for 30 min at 25°. After dilution with H_2O, the mixture was extracted with CH_2Cl_2, and the org. layers were washed with H_2O and dried over K_2CO_3. Removal of the solvent afforded pure **11** (3.6 g, 95%).

3,3,5,8,10,10-Hexamethyl-9-oxotricyclo[6.2.2.0^{2,7}]dodeca-5,11-diene-4-spiro-1'-cyclobutan-2'-one (**11**). M.p. 123° (from CH_2Cl_2/pentane). UV (5.79 mg in 5 ml MeCN): 304 (130), 312 sh (120), 324 sh (60). IR ($CHCl_3$): 3040*w*, 2970*s*, 2930*s*, 2870*m*, 2830*w* sh, 1770*s*, 1715*s*, 1465*m*, 1445*m*, 1435*m*, 1390*m*, 1380*s*, 1365*m*, 1350*w*, 1290*w*, 1240*m*, 1215*w*, 1200*w*, 1185*w*, 1160*w*, 1100*m*, 1045*m*, 1030*m*, 1020*m* sh, 955*w*, 920*w*, 885*w*, 860*w*. ^{1}H-NMR (300 MHz): 0.89, 1.09, 1.11, 1.16, 1.30 (5*s*, CH_3–C(8), 2 CH_3–C(3), 2 CH_3–C(10)); 1.72 (*m*, $w_{1/2}$ = 5.5, CH_3–C(5)); 1.64–1.84 (*m*, H–C(4')); 2.20 (*dm*, *J* = 10, H–C(7)); 2.25–2.45 (*m*, H–C(4')); 2.50 (*d*, *J* = 10, H–C(2)); 2.55 (*d*, *J* = 7, H–C(1)); 2.7–3.0 (*m*, 2 H–C(3')); 5.36 (*m*, $w_{1/2}$ = 6, H–C(6)); 5.69 (*d*, *J* = 8, H–C(12)); 6.32 (*dd*, J_1 = 8, J_2 = 7, H–C(11)). ^{13}C-NMR (75 MHz): 16.0, 21.2, 23.4, 24.4, 24.6, 28.7 (6*q*, CH_3–C(5), CH_3–C(8), CH_3–C(3), 2 CH_3–C(10)); 21.2 (*t*, C(3')); 43.0, 43.8, 44.9 (3*d*, C(1), C(2), C(7)); 43.8 (*t*, C(4')); 38.3, 44.8, 52.6 (3*s*, C(3), C(8), C(10)); 77.0 (*s*, C(4)); 120.0, 130.2, 138.6 (3*d*, C(6), C(11), C(12)); 139.5 (*s*, C(5)); 213.5, 218.4 (2*s*, C(2'), C(9)). MS: 312 (2, M^+, $C_{21}H_{28}O_2$), 185 (8), 176 (11), 157 (8), 135 (12), *134* (100), 133 (13), 120 (16), 119 (33), 105 (12), 91 (8). Anal. calc. for $C_{21}H_{28}O_2$ (312.44): C 80.73, H 9.03; found: C 80.68, H 9.13.

1.3. *Pyrolysis of* **11**. Pyrolysis of **11** (1.5 g, 4.8 mmol) at 350°/15 Torr and chromatography (Et_2O/hexane 1:9) of the reaction mixture gave starting material **11** (685 mg), the spirocyclobutanone **4** (220 mg, 47%), the cyclohexadienone **8** (170 mg, 47%), and the isomer **12** (65 mg, 8%).

5,9,9-Trimethylspiro[3.5]nona-5,7-dien-1-one (**4**). B.p. 150°/14 Torr. UV (0.211 mg in 10 ml pentane): 250 sh (3470), 260 (3800), 271 (3970), 281 sh (3470). UV (2.0 mg in 2 ml): 329 (148), 341 (153), 359 sh (54). IR: 3035*m* sh, 3025*m*, 3000*w*, 2970*m*, 2925*m*, 2910*m*, 2870*m*, 2855*w* sh, 1770*s*, 1585*w*, 1460*m* br., 1440*m* br., 1390*m*, 1380*w* sh, 1375*w*, 1360*m*, 1320*w*, 1250*w* sh, 1235*w* br., 1200*w* sh, 1190*w*, 1180*w*, 1160*w*, 1110*m*, 1095*w* sh, 1075*w*, 1055*w*, 1040*m*, 1020*m*, 1005*w*, 980*w*, 915*w*, 890*w*, 850*w*, 720*m*. ^{1}H-NMR: 1.04, 1.10 (2*s*, 2 CH_3–C(9)); 1.67–2.49 (*m*, 2H–C(3)); 1.78 (*m*, $w_{1/2}$ = 2.5, CH_3–C(5)); 2.84 (*t*, J = 8.3, 2H–C(2)); 5.33 (*dm*, *J* = 9, $w_{1/2}$ = 3.0, H–C(6)); 5.52–5.84 (*m*, H–C(7), H–C(8)). ^{13}C-NMR (75 MHz): 20.3, 22.6, 22.8 (3*q*, CH_3–C(5), 2 CH_3–C(9)); 17.5 (*t*, C(3)); 44.7 (*t*, C(2)); 119.3, 122.2, 135.0 (3*d*, C(6), C(7), C(8); 36.3 (*s*, C(9)); 77.0 (*s*, C(4)); 135.0 (*s*, C(5)); 212.8

(*s*, C(1)). MS: 176 (3, M^+, $C_{12}H_{16}O$), 134 (64), 133 (25), 120 (27), *119* (100), 105 (41), 91 (18), 77 (16), 41 (10). Anal. calc. for $C_{12}H_{16}O$ (176.26): C 81.77, H 9.15; found: C 81.65, H 9.01.

3,3,5,8,10,10-Hexamethyl-4-oxotricyclo[6.2.2.0^{2,7}]dodeca-5,11-diene-9-spiro-1'-cyclobutan-2'-one (**12**). M.p. 130° (from hexane). UV (0.234 mg in 10 ml MeCN): 232 (6700). UV (4.076 mg in 5 ml MeCN): 232 (135), 344 (65) sh. IR: 3035*w*, 2980*m*, 2960*s*, 2920*m*, 2870*m*, 2840*w* sh, 1760*s*, 1675*s*, 1470*w*, 1450*m*, 1435*w* sh, 1385*m*, 1360*m*, 1330*w*, 1240*w*, 1200*m*, 1180*w*, 1165*w*, 1150*w*, 1120*w*, 1090*m*, 1075*w*, 1030*m*, 1010*w*, 990*w*, 925*w*, 915*w*, 855*w*. ^{1}H-NMR (300 MHz): 0.89 (3H), 1.06 (3H), 1.11 (6H), 1.31 (3H) (4*s*, CH_3–C(8), 2 CH_3–C(3), 2 CH_3–C(10)); 1.71 (*dd*, $J_1 = 5$, $J_2 = 1$, CH_3–C(5)); 1.76–1.90, 1.98–2.12 (2*m*, 2 H–C(4')); 2.36 (*d*, $J = 7$, H–C(1)); 2.56 (*d*, $J = 8.5$, H–C(2)); 2.64–2.84 (*m*, 2H–C(3')); 3.10–3.20 (*m*, H–C(7)); 5.46 (*d*, $J = 8$, H–C(12)); 6.17 (*dd*, $J_1 = 8.5$, $J_2 = 7$, H–C(11)); 6.21 (*dd*, $J_1 = 4$, $J_2 = 1.5$, H–C(6)). ^{13}C-NMR (75 MHz): 16.8, 18.9, 22.3, 25.5, 29.9, 32.0 (6*q*, CH_3–C(5), CH_3–C(8), 2 CH_3–C(3), 2 CH_3–C(10)); 17.9 (*t*, C(4')); 39.3, 44.6, 47.1 (3*d*, C(1), C(2), C(7)); 44.3 (*t*, C(3')); 41.1, 43.8, 45.6 (3*s*, C(3), C(8), C(10)); 77.1 (*s*, C(9)); 134.7, 135.2, 140.1 (3*d*, C(6), C(11), C(12)); 134.9 (*s*, C(5)), 205.0, 214.6 (2*s*, C(4), C(2')). MS: 312 (1.8, M^+, $C_{21}H_{28}O_2$), 176 (9), *134* (100), 133 (13), 120 (22), 119 (32), 105 (11). Anal. calc. for $C_{21}H_{28}O_2$ (312.44): C 80.73, H 9.03; found: C 80.73, H 9.17.

1.4. *Bis-spirocyclobutanone* **13**. To a stirred solution of 1-lithio-1-methoxycyclopropane in THF prepared as described in *Sect. 1.1* [from 1-methoxy-1-(phenylthio)cyclopropane [3b] (7.2 g, 39.8 mmol) in THF (15 ml) with 1-(dimethylamino)naphthalene (3.46 g, 20.2 mmol) and Li-wire (266 mg, 39.9 mmol) in THF (40 ml)] was added **9** (2.0 g, 7.3 mmol) in THF (10 ml) at −78°. The mixture was stirred for 6 h, quenched by the addition of MeOH, poured into H_2O, extracted with Et_2O/hexane 1:1 and dried over K_2CO_3. Chromatography (Et_2O/hexane 1:2) gave the crude bis-α-methoxyalcohol, which was treated directly with 50% aq. HBF_4/THF 1:4 (75 ml) for 20 min. at 25°. After dilution with H_2O, the mixture was extracted with hexane/AcOEt 1:1, and the org. layers were washed with H_2O and dried over K_2CO_3. Removal of the solvent followed by crystallization yielded pure **13** (850 mg, 33%).

3,3,5,8,10,10-Hexamethyltricyclo[6.2.2.0^{2,7}]dodeca-5,11-diene-4-spiro-1'-cyclobutan-2'-one-9-spiro-1''-cyclobutan-2''-one (**13**). M.p. 173–74° (from CH_2Cl_2/hexane). UV (2.069 mg in 2 ml MeCN): 301 (228), 311 (225), 322 (160) sh, 350 (27) sh. IR ($CHCl_3$): 3030*w*, 2960*m*, 2920*m*, 2870*w*, 2840*w* sh, 1760*s*, 1465*w*, 1440*w*, 1385*w*, 1365*w*, 1180*w*, 1165*w*, 1135*w*, 1105*w* sh, 1090*w*, 1070*w*, 1050*w*, 1005*w*, 890*w*. ^{1}H-NMR: 0.72 (3H), 0.89 (3H), 1.03 (3H), 1.20 (6H) (4*s*, CH_3–C(8), 2 CH_3–C(3), 2 CH_3–C(10)); 1.68 (*m*, $w_{1/2} = 6$, CH_3–C(5)); 1.5–2.9 (*m*, 11H, H–C(1), H–C(2), H–C(7), 2H–C(3'), 2H–C(4'), 2H–C(3''), 2H–C(4'')); 5.30 (*m*, $w_{1/2} = 4$, H–C(6)); 5.74 (*d*, $J = 8$, H–C(12)); 6.16 (*dd*, $J_1 = 8$, $J_2 = 7$, H–C(11)). ^{13}C-NMR: 18.4, 21.1, 22.7, 24.4, 27.1, 30.2 (6*q*, CH_3–C(5), CH_3–C(8), 2 CH_3–C(3), 2 CH_3–C(10)); 17.1, 21.0 (2*t*, C(4'), C(4'')); 38.4, 41.7, 42.4 (3*s*, C(3), C(8), C(10)); 41.0, 42.7, 46.0 (3*d*, C(1), C(2), C(7)); 43.5, 44.2 (2*t*, C(3'), C(3'')); 76.9, 79.0 (2*s*, C(4), C(9)); 120.6, 133.0, 136.3 (3*d*, C(6), C(11), C(12)); 138.5 (*s*, C(5)); 213.3, 213.6 (2*s*, C(2'), C(2'')). MS: 352 (1, M^+, $C_{24}H_{32}O_2$), 310 (6), 176 (4), 135 (15), *134* (100), 133 (28), 120 (31), 119 (49), 105 (19), 91 (10). Anal. calc. for $C_{24}H_{32}O_2$ (352.50): C 81.77, H 9.15; found: C 81.62, H 9.19.

2. Preparation of 5. – To a solution of 1-(dimethylamino)naphthalene (6.73 g, 39.35 mmol) in dry THF cooled to −45° was added under Ar with vigorous stirring small pieces of Li-wire (0.27 g, 39.35 mmol). After stirring for 4.5 h, the mixture was cooled to −78° and a solution of 1-methoxy-1-(phenylthio)cyclopropane (3.68 g, 20.46 mmol) in THF (5 ml) was added. After stirring for 90 min at −78°, a solution of 2,4-cycloheptadienone (**14**) [6] (1.70 g, 15.74 mmol) in THF (5 ml) was added and the mixture stirred for 40 min. The reaction was quenched with MeOH (10 ml), the mixture was poured into ice/H_2O and worked up with hexane to give an oil, which was filtered through *Florisil* (hexane/Et_2O 10:1). The crude cyclopropyl methoxyalcohol **15** (1.3 g) was directly treated with 50% aq. HBF_4/THF 1:4 (42.5 ml) for 20 min at 0°. After dilution of the reaction mixture with water, workup and distillation (130°/0.3 Torr) afforded **5** (0.80 g, 34%).

Spiro[3.6]deca-5,7-dien-1-one (**5**). B.p. 100°/0.3 Torr. UV (0.242 mg in 10 ml MeCN): 246 sh (7600), 255 (8200), 263 sh (6400), 271 sh (2400), 310 (550). UV (1.72 mg in 2 ml): end absorption to 350. IR: 3010*m*, 2995*w* sh, 2950*w* sh, 2920*m*, 2850*w*, 1775*s*, 1600*w*, 1430*w*, 1395*w*, 1230*w*, 1170*w*, 1100*w*, 1060*w*, 1040*w* br., 840*w*, 690*m*, 650*w*. ^{1}H-NMR: 1.70–2.25 (*m*, 2H–C(9), 2H–C(10)); 2.25–2.90 (*m*, 2H–C(3)); 2.95–3.50 (*m*, 2H–C(2)); 5.50–6.10 (*m*, H–C(4), H–C(5), H–C(6), H–C(7)); ^{13}C-NMR (75 MHz): 26.7, 27.2, 31.0 (3*t*, C(3), C(9), C(10)); 42.6 (*t*, C(2)); 124.4, 125.8, 131.7, 134.9 (4*d*, C(5), C(6), C(7), C(8)); 72.0 (*s*, C(4)); 211.1 (*s*, C(1)). MS: 148 (4, M^+, $C_{10}H_{12}O$), 106 (38), 105 (22), 92 (17), *91* (100), 79 (17), 78 (54), 77 (12), 65 (11), 39 (15). Anal. calc. for $C_{10}H_{12}O$ (148.20): C 81.04, H 8.16; found: C 80.76, H 8.05.

3. Preparation of 6. – A solution of 1-(dimethylamino)naphthalene (17.1 g, 100 mmol) in dry THF (100 ml) was cooled to −45° and Li-wire (0.62 g, 90 mmol) was added in small pieces. After stirring for 5 h at −45°, the mixture was cooled to −78° and a solution of 1-methoxy-1-(phenylthio)cyclopropane (7.3 g, 41 mmol) in THF

(10 ml) was added over 3 min. After stirring at −78° for 45 min, a solution of 2,4-cyclooctadienone (**16**) (4.03 g, 33 mmol) [7] in dry THF (10 ml) was added and the mixture stirred at −78° for 20 min. The reaction was quenched with 4 ml of $MeOH/H_2O$ 1:1 and worked up with hexane/Et_2O to give an oil which was treated directly with 50% aq. HBF_4/THF 1:4 (125 ml) at 0–10° for 20 min. After pouring the reaction mixture into 5% HCl, workup with hexane and chromatography (SiO_2, hexane/Et_2O 87:13) gave **6** (3.78 g, 71%).

Spiro[3.7]undeca-5,7-dien-1-one (**6**). B.p. 75°/0.03 Torr. UV (0.290 mg in 10 ml): 237 (6100). UV (2.0 mg in 2 ml): 304 (190). IR: 3000*m*, 2960*m* sh, 2930*s*, 2860*m*, 1780*s*, 1625*w*, 1450*m*, 1440*m* sh, 1430*w* sh, 1395*m*, 1245*w* sh, 1235*w* br., 1180*w* br., 1120*m*, 1095*m*, 1080*m*, 1060*m*, 1045*m* sh, 1040*m*, 1000*w* br., 845*w*, 715*w*. ^{1}H-NMR: 1.20–2.42 (*m*, 8 aliph. H); 2.80–3.21 (*m*, 2H–C(2)); 5.42–5.87 (*m*, 3 olef. H); 6.01 (*dd*, $J_1 = 11$, $J_2 = 4$, 1 olef. H). ^{13}C-NMR: 20.9, 25.1, 26.3, 26.8 (4*t*, C(3), C(9), C(10), C(11)); 42.3 (*t*, C(2)); 125.1, 127.7, 130.8 (4*d*, 2*d* at 130.8, C(5), C(6), C(7), C(8)); 70.3 (*s*, C(4)); 210.4 (*s*, C(1)). MS: 162 (16, M^+, $C_{11}H_{14}O$), 120 (31), 119 (13), 106 (16), 105 (54), 93 (15), *92* (100), 91 (98), 80 (17), 79 (59), 78 (38), 77 (30), 65 (14), 53 (11), 51 (13), 41 (17). Anal. calc. for $C_{11}H_{14}O$ (162.23): C 81.44, H 8.70; found: C 81.56, H 8.84.

4. Preparation of 7. – 4.1. *Reaction of* **18** *with 1-Lithio-1-methoxycyclopropane.* To a solution of 1-lithio-1-methoxycyclopropane in THF, prepared as described in *Sect. 1.1* [from 1-methoxy-1-(phenylthio)cyclopropane (88.5 g, 0.492 mol) in THF (400 ml) with 1-(dimethylamino)naphthalene (263 g, 1.535 mol) and Li-wire (8.05 g, 1.150 mol) in THF (1250 ml)] was added 3-methylcrotonaldehyde (**18**; 32.2 g, 0.384 mol; *Merck*) in THF (400 ml) at −78°. After 45 min, the reaction was quenched by the addition of MeOH and worked up in Et_2O/hexane 2:1. After drying over Na_2SO_4, the solvents were removed, and the residue chromatographed, first with CH_2Cl_2, to remove 1-(dimethylamino)naphthalene, and then twice with Et_2O/CH_2Cl_2 1:2 to yield **19** (39.0 g, 65%).

3-Methyl-1-(1'-methoxycyclopropyl)-2-buten-1-ol (**19**). B.p. 40–45°/0.01 Torr. IR: 3620*m*, 3580*m*, 3470*w* br., 3090*w*, 3010*m*, 2970*m*, 2930*s*, 2910*s*, 2820*m*, 1670*w*, 1460*m* sh, 1445*s*, 1435*m* sh, 1410*m*, 1380*m* sh, 1375*m*, 1330*m*, 1315*m* sh, 1285*m*, 1250*m*, 1220*s*, 1170*m*, 1110*w*, 1060*s*, 1025*s* sh, 1015*s*, 975*m*, 960*w*, 910*w*, 890*w*, 870*w*, 840*w*. ^{1}H-NMR (80 MHz): 0.37–0.92 (*m*, 2H–C(2'), 2H–C(3')); 1.73 (*m*, $w_{1/2} = 5$, 3H–C(4), CH_3–C(3)); 2.10 (*m*, $w_{1/2} = 5$, OH); 3.38 (*s*, CH_3O); 4.90 (*AB*-system, $J = 8$, $\delta_A = 4.68$, H–C(1), $\delta_B = 5.12$, split into *m*, H–C(2)). ^{13}C-NMR: 18.5, 25.9 (2*q*, C(4), CH_3–C(3)); 55.3 (*q*, CH_3O); 9.4 (2*t* overlapped, C(2'), C(3')); 68.6 (*d*, C(1)); 124.5 (*d*, C(2)); 65.5 (*s*, C(1')); 135.6 (*s*, C(3)). MS: 156 (1, M^+, $C_9H_{16}O_2$), 128 (25), 127 (18), 123 (12), 113 (31), 112 (33), 109 (14), 96 (12), 95 (22), 87 (59), 85 (68), 83 (24), 82 (20), 81 (23), 72 (12), 71 (19), 70 (50), 67 (55), 65 (10), 59 (18), 57 (28), 55 (41), 53 (20), 43 (30), 42 (14), *41* (100).

4.2. *Transformation of* **19** *to the Cyclobutanone* **20**. To a solution of **19** (62.0 g, 0.398 mol) in Et_2O (*ca.* 2 l) was added a 50% aq. HBF_4-solution (150 ml) at 0°. After stirring for 20 min at r.t., the mixture was washed with H_2O and sat. $NaHCO_3$-solution. After drying over $MgSO_4$, the solvent was removed, and the residue distilled affording **20** (33.0 g, 67%) as a colorless oil.

2-(2'-Methyl-1'-propenyl)cyclobutanone (**20**). B.p. 90°/25 Torr. IR: 3550*w*, 3050*w* sh, 2990*m* sh, 2970*m*, 2930*m*, 2910*m*, 2880*w*, 2860*w*, 1780*s*, 1670*w* br., 1450*w*, 1435*w* sh, 1430*w* sh, 1390*w*, 1380*w*, 1375*m*, 1345*w*, 1270*w*, 1235*w*, 1195*w*, 1175*w*, 1125*w*, 1070*m*, 1020*w*, 990*w*, 890*w*. ^{1}H-NMR (80 MHz): 1.38–2.70 (*m*, structured, 2H–C(3)); 1.67, 1.74 (2*s*, 3H–C(3'), CH_3–C(2')); 2.70–3.42 (*m*, 2H–C(4)); 3.90–4.35 (*m*, H–C(2)); 5.18 (*d*, $J = 8$, split into *m*, H–C(1')). MS: 124 (3, M^+, $C_8H_{12}O$), 96 (7), 82 (78), 81 (45), 79 (12), 68 (10), *67* (100), 65 (8), 55 (10), 54 (14), 53 (28), 51 (14), 50 (8), 42 (16), 41 (43).

4.3. *Reaction of* **20** *with Lithio(trimethylsilyl)acetylide.* To a solution of bis(trimethylsilyl)acetylene (84.3 g, 0.495 mol) in dry dimethoxyethane (600 ml) was added BuLi (322 ml of a 1.6N solution in hexane, 0.515 mol) at r.t. under Ar. After 2.5 h, a solution of **20** (32.8 g, 0.264 mol) in dimethoxyethane (20 ml) was added, and the mixture was stirred for 3 h. After cooling to −30°, 2N HCl (250 ml) was added carefully, and the mixture was let to warm to r.t. overnight. After evaporating most of the dimethoxyethane, the residue was worked up in Et_2O giving a *ca.* 1:3 mixture of **21A** + **B** (51.0 g, 87%). Analytically pure samples of **21A** and **21B** were obtained by chromatography (CH_2Cl_2).

1-(Trimethylsilylethynyl)-2-(2'-methyl-1'-propenyl)cyclobutanol (isomer A, **21A**). B.p. 55°/0.1 Torr. IR: 3580*w* br., 2990*m* sh, 2960*m*, 2950*m*, 2910*m*, 2860*w*, 2160*m*, 1445*m*, 1405*w*, 1380*w*, 1375*w*, 1320*m*, 1300*w* sh, 1250*s*, 1225*m*, 1145*m*, 1120*m*, 1105*m*, 1070*w*, 970*m*, 950*w*, 905*m*, 855*s*, 840*s*. ^{1}H-NMR (80 MHz): 0.16 (*s*, 3 CH_3–Si); 1.58–2.68 (*m*, 2H–C(3), 2H–C(4)); 1.71, 1.78 (2*s*, 3H–C(3'), CH_3–C(2')); 2.17 (*s*, OH); 3.22–3.62 (*m*, H–C(2)); 5.20 (*d*, $J = 8$, split into *m*, H–C(1')). ^{13}C-NMR: 18.9, 25.8 (2*q*, C(3'), CH_3–C(2')); 23.0, 34.8 (2*t*, C(3), C(4)); 46.1 (*d*, C(2)); 122.7 (*d*, C(1')); 70.3 (*s*, C(1)); 87.4, 109.6 (2*s*, C(1''), C(2'')); 137.1 (*s*, C(2')). MS: 222 (1, M^+, $C_{13}H_{22}OSi$), 207 (7), 126 (8), 125 (64), 97 (18), 83 (33), *82* (100), 81 (10), 75 (19), 73 (37), 67 (49), 55 (9), 53 (8), 43 (15), 41 (22). Anal. calc. for $C_{13}H_{22}OSi$ (222.41): C 70.21, H 9.97; found: C 70.35, H 9.86.

Isomer B (**21B**). B.p. 55°/0.1 Torr. IR: 3600*m*, 3440*w* br., 2990 *m* sh, 2960*m*, 2950 sh, 2930*m*, 2910*m*, 2860*w*, 2160*w*, 1445*w*, 1435*w*, 1405*w*, 1380*w*, 1370*w*, 1325*m*, 1260*w* sh, 1250*s*, 1220*w*, 1180*w*, 1145*w*, 1120*m* sh, 1090*m*,

1040*w*, 980*w*, 955*w*, 925*w*, 900*s*, 850*s* sh, 840*s*, 700*w*, 670*w*. ^{1}H-NMR (80 MHz): 0.20 (*s*, 3 CH_3–Si); 1.16–2.55 (*m*, 2H–C(3), 2H–C(4)); 1.66, 1.73 (2*s*, 3H–C(3'), CH_3–C(2')); 2.59 (*s*, OH); 2.86–3.30 (*m*, H–C(2)); 5.33 (*d*, J = 9, split into *m*, H–C(1')). ^{13}C-NMR: 18.6, 25.8 (2*q*, C(3'), CH_3–C(2')); 20.2, 35.6 (2*t*, C(3), C(4)); 47.4 (*d*, C(2)); 125.0 (*d*, C(1')); 73.0 (*s*, C(1)); 90.7, 107.1 (2*s*, C(1''), C(2'')); 133.4 (*s*, C(2')). MS: 222 (0.5, M^+, $C_{13}H_{22}OSi$), 207 (6), 125 (58), 97 (16), 83 (32), *82* (100), 81 (8), 75 (18), 74 (16), 73 (32), 67 (50), 55 (8), 53 (8), 43 (14), 41 (19). Anal. calc. for $C_{13}H_{22}OSi$ (222.41): C 70.21, H 9.97; found: C 70.64, H 9.82.

4.4. *Desilylation of* **21A + B**. To a solution of **21A + B** (50.6 g, 0.288 mol) in MeOH (1 l) was added 5% aq. KOH (500 ml) at 0°. After stirring for 20 min at r.t., MeOH was evaporated and the residue worked up in Et_2O giving a *ca.* 1:3 mixture of **22A + B** (30.8 g, 90%).

1-Ethynyl-2-(2'-methyl-1'-propenyl)cyclobutanol (**22A + B**). (Mixture of 2 diastereoisomers in proportion *ca.* 3:1). IR: 3600*m*, 3450*w* br., 3310*s*, 2980*s*, 2940*s*, 2910*s*, 2860*m*, 1660*w*, 1445*m*, 1435*m*, 1380*m*, 1375*m*, 1360*m*, 1320*m*, 1245*m*, 1225*m*, 1180*w*, 1145*m*, 1115*s* sh, 1090*s*, 1040*w*, 980*m*, 950*w*, 905*w*, 870*w*, 835*m*, 660*s*, 620*s*. ^{1}H-NMR (80 MHz, $CDCl_3$): 1.05–2.43 (*m*, 2H–C(3), 2H–C(4), H–O); 1.67, 1.74 (2*s*, 3H–C(3'), CH_3–C(2'), major isomer); 1,70, 1.79 (2*s*, 3H–C(3'), CH_3–C(2'), minor isomer); 2.57 (*s*, H–C≡C, minor isomer); 2.60 (*s*, H–C≡C, major isomer); 2.87–3.60 (*m*, H–C(2)); 5.21 (*d*, J = 8, split into *m*, H–C(1'), minor isomer); 5.35 (*d*, J = 9, split into *m*, H–C(1'), major isomer). MS: 150 (8, M^+, $C_{10}H_{14}O$), 135 (28), 122 (18), 117 (8), 109 (11), 108 (40), 107 (48), 105 (10), 95 (23), 94 (25), 93 (50), 91 (39), 83 (10), *82* (100), 81 (23), 79 (77), 77 (32), 68 (12), 67 (82), 66 (10), 65 (15), 55 (27), 54 (12), 53 (36), 51 (17), 43 (14), 41 (54).

4.5. *Hydrogenation of* **22A + B**. A solution of **22A + B** (15.4 g, 0.102 mol) and quinoline (60 ml) in hexane (1.2 l) was stirred with *Lindlar* catalyst (5.3 g) [10] under H_2. After 2 h the reaction was complete (GC analysis); the mixture was filtered through *Celite*, the solvent was evaporated and the residue chromatographed in two parts (550 g SiO_2; CH_2Cl_2) affording a *ca.* 1:3 mixture of **23A + B** (15.0 g, 97%). Analytically pure samples of **23A** and **23B** were obtained by chromatography (CH_2Cl_2).

2-(2'-Methyl-1'-propenyl)-1-vinylcyclobutanol (isomer A, **23A**). IR: 3560*m* br., 3080*w*, 2970*s*, 2940*s*, 2910*s*, 2860*m*, 1635*w*, 1440*m*, 1435*m* sh, 1410*m*, 1380*m*, 1375*m*, 1290*m* br., 1265*m* sh, 1240*m* sh, 1230*m*, 1195*m*, 1140*m*, 1110*m*, 1090*w* sh, 1070*w*, 1020*w*, 990*m*, 945*w*, 920*s*, 910*m* sh, 665*w*. ^{1}H-NMR (80 MHz): 1.60, 1.79 (2*s*, 3H–C(3'), CH_3–C(2')); 1.50–2.40 (*m*, 2H–C(3), 2H–C(4), OH); 2.95–3.32 (*m*, H–C(2)); 4.93–5.18 (*m*, H–C(1'), 2H–C(2'')); 6.11 (*dd*, J_1 = 17, J_2 = 10, H–C(1'')). MS: 152 (15, M^+, $C_{10}H_{16}O$), 109 (8), 96 (15), 95 (34), 83 (11), *82* (100), 81 (22), 79 (8), 70 (8), 69 (9), 67 (60), 57 (13), 55 (37), 54 (9), 53 (12), 43 (13), 41 (33).

Isomer B (**23B**). IR: 3600*m*, 3470*w* br., 3080*w*, 2980*s* sh, 2960*s*, 2930*s*, 2910*s*, 2860*m*, 1640*w*, 1615*m*, 1460*m* sh, 1440*m*, 1410*m*, 1380*m*, 1375*m*, 1325*m* sh, 1310*m*, 1270*m*, 1235*m*, 1220*m* sh, 1180*m* sh, 1175*m*, 1145*m*, 1105*m*, 1030*m*, 1020*m*, 990*m*, 920*s*, 685*w*. ^{1}H-NMR (80 MHz, *ca.* 80% pure): 1.64, 1.68 (2*s*, 3H–C(3'), CH_3–C(2')); 1.50–2.30 (*m*, 2H–C(3), 2H–C(4), OH); 2.95–3.35 (*m*, H–C(2)); 4.93–5.41 (*m*, H–C(1'), 2H–C(2'')); 6.07 (*dd*, J_1 = 17, J_2 = 11, H–C(1'')). MS: 152 (14, M^+, $C_{10}H_{16}O$), 121 (23), 120 (14), 109 (9), 106 (12), 97 (15), 95 (37), 83 (11), *82* (100), 81 (23), 79 (10), 69 (9), 67 (60), 57 (15), 55 (29), 54 (10), 53 (13), 43 (11), 41 (32).

4.6. *Rearrangement of* **23A + B** *to* (E)-**24**. A solution of **23A + B** (30.0 g, 0.197 mol) in abs. THF (1 l) was transferred *via* a cannula to a suspension of KH (30 g powder; the commercially available oil suspension was washed 3 times with hexane) in THF (1 l) over a period of 30 min at r.t. After stirring for 1 h, AcOH (140 ml) was added very slowly with cooling, then the mixture was neutralized with solid $NaHCO_3$ and filtered through a small path of *Celite*. Evaporation of the solvent followed by chromatography of the residue in two parts (550 g SiO_2; CH_2Cl_2) gave (*E*)-**24** (16.5 g, 56%).

(E)-6,6-Dimethylcyclooct-4-en-1-one ((E)-**24**). IR: 3020*w*, 2960*s*, 2920*m*, 2910*m* sh, 2860*m*, 2840*w*, 1700*s*, 1615*m*, 1595*w* sh, 1465*w*, 1450*m*, 1435*m*, 1420*w*, 1385*w*, 1365*m*, 1335*w* sh, 1325*m*, 1290*w*, 1270*w*, 1195*w* sh, 1185*w* sh, 1175*m*, 1155*w*, 1125*w*, 1105*s*, 1040*w*, 1010*w*, 990*m*, 935*w*, 920*w*, 910*w*, 860*w*, 685*w*. ^{1}H-NMR (300 MHz): 1.07, 1.10 (2*s*, 2 CH_3–C(6)); 1.45 (*dd*, J_1 = 13.0, J_2 = 5,7, H–C(7)); 1.77 (*dd*, split into *m*, $w_{1/2}$ = 3.5, $J_1 = J_2$ = 13.0, H–C(7)); 1.83 (*dddd*, J_1 = 13.0, J_2 = 5.7, $J_3 = J_4$ = 1.6, H–C(8)); 2.35 (*ddd*, $J_1 = J_2$ = 13.0, J_3 = 1.8, H–C(8)); 2.41–2.62 (*m*, H–C(2), 2H–C(3)); 2.90 (*ddd*, J_1 = 16.9, J_2 = 10.0, J_3 = 6.8, H–C(2)); 5.19 (*d*, J = 16.6, H–C(5)); 5.85 (*ddd*, J_1 = 16.6, J_2 = 10.0, J_3 = 4.7, H–C(4)). ^{13}C-NMR: 20.7, 28.8 (2*q*, 2 CH_3–C(6)); 33.8, 40.9, 42.0, 49.9 (4*t*, C(2), C(3), C(7), C(8)); 126.4 (*d*, C(4)); 142.0 (*d*, C(5)); 38.1 (*s*, C(6)); 216.3 (*s*, C(1)). MS: 152 (22, M^+, $C_{10}H_{16}O$), 137 (11), 124 (9), 110 (9), 109 (18), 97 (10), 96 (24), 95 (77), 83 (12), *82* (100), 81 (39), 79 (13), 69 (12), 68 (10), 67 (56), 57 (25), 55 (27), 54 (10), 53 (16), 41 (36).

4.7. *Isomerization of* (E)-**24** *to* (Z)-**24**. A solution of (*E*)-**24** (5.0 g, 32.9 mmol) in actone (500 ml) was irradiated (125-W Hg medium-pressure lamp [16]. *Pyrex; ca.* 100% conversion). Evaporation of the solvent and distillation (105°/14 Torr) of the residue afforded (*Z*)-**24** (3.0 g, 60%) as a colorless oil. An analytical sample of (*Z*)-**24** was obtained by chromatography (Et_2O/hexane 1:1) and distillation.

*(Z)-6,6-Dimethylcyclooct-4-en-1-one ((Z))-***24**. B.p.: 105°/14 Torr. IR: 3010*m*, 2960*s*, 2930*s* sh, 2900*m*, 2870*m*, 1700*s*, 1480*w*, 1470*m*, 1455*w*, 1445*w*, 1435*w*, 1430*w* sh, 1420*w*, 1405*w*, 1380*w*, 1360*w*, 1340*m*, 1325*w*, 1260*w*, 1240*w*, 1205*w*, 1170*w*, 1160*w*, 1145*w*, 1120*w*, 1105*w*, 1040*w*, 920*w*, 890*w*, 870*w*. ^{1}H-NMR (300 MHz): 1.12 (*s*, 2 CH_3–C(6)); 1.86–1.90 (*m*, 2H–C(7)); 2.51–2.58 (*m*, 2H–C(2), 2H–C(3), 2H–C(8)); 5.32 (*d*, J = 11.8, H–C(5)); 5.43–5.53 (*m*, H–C(4)). ^{13}C-NMR: 30.3 (2*q* overlapped, 2 CH_3–C(6)); 22.3 (*t*, C(7)); 37.7, 38.9, 44.9 (3*t*, C(2), C(3), C(8)); 126.7 (*d*, C(4)); 140.1 (*d*, C(5)); 36.5 (*s*, C(6)); 213.4 (*s*, C(1)). MS: 152 (31, M^+, $C_{10}H_{16}O$), 137 (24), 124 (18), 123 (12), 110 (14), 109 (30), 97 (51), 96 (45), 95 (95), 93 (16), 83 (22), *82* (100), 81 (51), 79 (21), 77 (14), 69 (22), 68 (15), 67 (71), 57 (24), 55 (50), 54 (12), 53 (24), 43 (13), 41 (56). Anal. calc. for $C_{10}H_{16}O$ (152.25): C 78.89, H 10.59; found: C 78.76, H 10.68.

4.8. *Transformation of (Z)-***24** *to* **25A** + **B**. To 140 ml of abs. THF was added a 1M LDA-solution [12] in THF (27.8 ml, 27.8 mmol) at 0° under Ar. After cooling the mixture to −78°, a solution of (*Z*)-**24** (3.5 g, 23.0 mmol) in THF (7 ml) was added dropwise with stirring. After 2 h, a solution of phenylselenyl chloride (4.41 g, 23.0 mmol) in THF (17.5 ml) was added dropwise. After stirring for 20 min at −78°, the mixture was allowed to warm up to r.t. overnight, poured into pentane/0.5N HCl and worked up. Chromatography (400 g SiO_2; Et_2O/hexane 1:3) gave starting material (1.10 g) and a *ca.* 5:1 mixture of **25A** + **B** (2.76 g, 39%).

(Z)-6,6-Dimethyl-2-phenylselenylcyclooct-4-en-1-one (**25A**) (contaminated with *ca.* 10% of **25B**). IR: 3070*w*, 3060*w*, 3010*m*, 2960*s*, 2930*s* sh, 2900*m*, 2860*w*, 1695*s*, 1580*w*, 1480*s*, 1460*m*, 1440*s*, 1410*w*, 1385*w*, 1365*w*, 1340*m*, 1305*w*, 1245*m*, 1210*w*, 1200*w*, 1165*w*, 1155*w*, 1140*w*, 1110*m*, 1070*w*, 1025*m*, 1005*w*, 965*w*, 915*w*, 880*w*, 870*w*, 695*s*, 675*w*. ^{1}H-NMR (80 MHz); 1.05, 1.18 (2*s*, 2 CH_3–C(6)); 1.38–3.40 (*m*, 2H–C(3), 2H–C(7), 2H–C(8)); 3.83 (*dd*, J_1 = 12.5, J_2 = 6.0, H–C(2)); 5.25–5.75 (structured *m*, H–C(4), H–C(5)); 7.15–7.75 (*m*, PhSe). MS: 310 (13), 309 (12), 308 (65, M^+, $C_{16}H_{20}OSe$), 306 (33), 305 (12), 304 (12), 184 (19), 182 (10), 158 (10), 157 (21), 155 (12), 152 (12), *151* (100), 133 (32), 123 (26), 109 (67), 107 (64), 105 (15), 97 (35), 96 (10), 95 (81), 94 (13), 93 (39), 91 (28), 83 (12), 82 (11), 81 (79), 79 (31), 78 (19), 77 (47), 69 (39), 67 (60), 65 (15), 57 (12), 55 (92), 53 (26), 51 (20), 43 (30), 41 (60).

4.9. *Transformation of* **25A** + **B** *to* **26**. To a solution of a *ca.* 5:1 mixture of **25A** + **B** (2.76 g, 8.99 mmol) in CH_2Cl_2 (32 ml) and pyridine (1.5 ml) was added dropwise an aq. 14% H_2O_2-solution (5.0 ml) at 15°. After stirring for 30 min at r.t., solid $NaHCO_3$ (5 g) was added, and the mixture was worked up by washing the org. layer with 5% aq. HCl-, sat. aq. $NaHCO_3$- and NaCl-solution. Chromatography (75 g SiO_2; Et_2O/hexane 1:3) afforded the cyclooctadienone **26** (0.51 g, 45% based on **25A**).

6,6-Dimethylcycloocta-2,4-dien-1-one (**26**). B.p. 100°/14 Torr. UV (0.192 mg in 10 ml): 268 (6800). IR: 3000*m*, 2960*s*, 2920*m*, 2910*m* sh, 2860*m*, 1715*w*, 1700*w*, 1660*s*, 1620*w*, 1600*w*, 1465*m*, 1450*w*, 1440*w*, 1430*m*, 1420*w*, 1390*w*, 1380*w*, 1365*w*, 1355*w*, 1310*w*, 1260*m*, 1230*w*, 1180*m*, 1135*m*, 1125*m*, 1030*w*, 990*w*, 960*w*, 885*w*, 850*w*, 705*w*, 650*m*. ^{1}H-NMR (300 MHz): 1.12 (*s*, 2 CH_3–C(6)); 1.97–2.01 (*m*, 2H–C(7)); 2.63–2.67 (*m*, 2H–C(8)); 5.81 (*d*, J = 12.7, H–C(5)); 5.87–5.97 (*m*, H–C(2), H–C(4)); 6.44 (*ddd*, J_1 = 12.7, J_2 = 3.9, J_3 = 1.8, H–C(3)). ^{13}C-NMR: 29.5 (2*q* overlapping 2 CH_3–C(6)); 39.4, 43.7 (2*t*, C(7), C(8)); 124.4, 129.8, 137.0, 147.7 (4*d*, C(2), C(3), C(4), C(5)); 38.2 (*s*, C(6)); 205.4 (*s*, C(1)). MS: 150 (13, M^+, $C_{10}H_{14}O$), 135 (11), 122 (22), 109 (10), 108 (70), 107 (84), 95 (41), 94 (65), 93 (62), 91 (35), 81 (13), 80 (14), *79* (100), 78 (13), 77 (35), 67 (18), 66 (16), 65 (12), 55 (16), 53 (16), 51 (15), 41 (27).

4.10. *Reaction of* **26** *with 1-Lithio-1-methoxycyclopropane*. To a solution of 1-lithio-1-methoxycyclopropane in THF, prepared as described in *Sect.* 1.1 [from 1-methoxy-1-(phenylthio)cyclopropane (1.54 g, 8.54 mmol) in THF (9 ml) with 1-(dimethylamino)naphthalene (4.57 g, 26.7 mmol) and Li-wire (141 mg, 20.1 mmol) in THF (22 ml)] was added a solution of **26** (1.00 g, 6.67 mmol) in THF (9 ml) at −78°. After 45 min, the reaction was quenched with MeOH (3.6 ml) and worked up in Et_2O/hexane. Chromatography (160 g SiO_2; Et_2O/hexane 1:4→1:2) afforded **27** (0.98 g, 66%).

1-(1'-Methoxycyclopropyl)-6,6-dimethyl-2,4-cyclooctadien-1-ol (**27**). IR: 3550*m* br., 3090*w*, 3010*m* sh, 2990*m*, 2950*s*, 2930*s* sh, 2910*m* sh, 2860*m*, 2820*m*, 1470*m*, 1455*m*, 1445*m*, 1435*m* sh, 1420*w*, 1400*w*, 1375*w*, 1360*m*, 1340*w*, 1270*m* sh, 1240*s*, 1170*w*, 1150*w*, 1100*m* sh, 1080*m* sh, 1070*s*, 1045*m* sh, 1020*m*, 975*w*, 900*w*, 870*w*, 715*w*, 650*w*. ^{1}H-NMR (80 MHz): 0.75 (*s*, 2H–C(2'), 2H–C(3')); 1.01, 1.07 (2*s*, 2 CH_3–C(6)); 1.40–2.75 (*m*, 2H–C(7), 2H–C(8), OH); 3.35 (*s*, CH_3O); 5.15–6.00 (*m*, H–C(2), H–C(3), H–C(4), H–C(5)). MS: 222 (1, M^+, $C_{14}H_{22}O_2$), 204 (10), 189 (12), 161 (13), 151 (13), 149 (16), 148 (48), 147 (71), 135 (35), 134 (26), 133 (64), 131 (10), 129 (10), 123 (13), 121 (24), 120 (17), 119 (41), 117 (31), 115 (15), 110 (11), 109 (13), 107 (23), 106 (22), 105 (74), 103 (12), 95 (17), 93 (38), 92 (97), *91* (100), 79 (48), 78 (36), 77 (45), 71 (10), 69 (25), 67 (17), 65 (21), 57 (17), 55 (37), 53 (20), 51 (16), 43 (15), 41 (61).

4.11. *Transformation of* **27** *to the Cyclobutanone* **7**. To a solution of **27** (0.95 g, 4.28 mmol) in THF (10 ml) was added dropwise 50% aq. HBF_4/THF 1:10 (30 ml) at 15°. After stirring at r.t. for 20 min, the mixture was poured into H_2O and worked up in Et_2O. Distillation (60°/0.03 Torr) gave 7 (0.75 g, 93%).

9,9-Dimethylspiro[3.7]undeca-5,7-dien-1-one (**7**). B.p. 60°/0.03 Torr. UV (0.350 mg in 10 ml MeCN): 237 (5500); UV (1.750 mg in 10 ml MeCN): 300 (270). IR: 3540*w*, 3000*m* sh, 2990*m*, 2960*s*, 2940*m*, 2920*m*, 2910*m*, 2860*w*, 2840*w*, 1775*s*, 1630*w*, 1470*w*, 1455*w*, 1445*w*, 1430*w*, 1385*w*, 1360*w*, 1280*w*, 1235*w*, 1180*w*, 1150*w*, 1100*m*, 1070*m*, 1035*w*, 1000*w*, 895*w*, 710*m*, 675*w*, 670*w*. ^{1}H-NMR (300 MHz): 0.98, 1.09 (2*s*, 2 CH_3–C(9)); 1.34–2.27 (*m*, 2H–C(3), 2H–C(10), 2H–C(11)); 2.97 (*AB*-system, J = 18.0, δ_A = 2.92, split into *dd*, J_1 = 10.0, J_2 = 6.5; δ_B = 3.02 split into *dd*, J_1 = 10.0, J_2 = 7.4, 2H–C(2)); 5.22 (*d*, J = 12.5) and 5.54 (*d*, J = 11.2) (H–C(5) and H–C(8)); 5.65 (*dd*, br., J_1 = 12.5, J_2 = 4.3) and 5.97 (*ddd*, J_1 = 11.2, J_2 = 4.3, J_3 = 0.7) (H–C(6) and H–C(7)). ^{13}C-NMR (35°): 30.3, 30.4 (2*q* br., 2 CH_3–C(9)); 26.5, 27.9, 34.8, 42.7 (4*t*, C(2), C(3), C(10), C(11)); 122.9, 128.7, 129.5, 140.6 (4*d*, C(5), C(6), C(7), C(8)); 36.7 (*s*, C(9)); 69.4(*s*, C(4)); 213.0 (*s*, C(1)). MS: 205 (4), 190 (4, M^+, $C_{13}H_{18}O$), 148 (23), 147 (10), 134 (13), 133 (56), 121 (12), 120 (14), 119 (30), 106 (18), 105 (56), 93 (22), *92* (100), 91 (69), 79 (27), 78 (31), 77 (21), 65 (11), 55 (14), 41 (27). Anal. calc. for $C_{13}H_{18}O$ (190.29): C 82.06, H 9.54; found: C 82.02, H 9.65.

5. Photolysis Experiments. – 5.1. *Triplet Sensitization of* **1**. A solution of *Michler*'s ketone (20 mg, 0.075 mmol) and **1** (100 mg, 0.53 mmol) in MeCN (*ca.* 100 ml) was irradiated (λ > 347 nm, *ca.* 100% conversion). Chromatography (SiO_2, hexane/AcOEt 24:1) gave **2** [2] (54 mg, 54%), **3** [2] (25 mg, 25%), and intractable material.

5.2. *Triplet Sensitization of* **4**. A solution of *Michler*'s ketone (21 mg, 0.078 mmol) and **4** (98 mg, 0.56 mmol) in MeCN (125 ml) was irradiated (λ > 347 nm, *ca.* 100% conversion). Chromatography (SiO_2, hexane/AcOEt 9:1) and distillation (150°/12 Torr) afforded **29** (24 mg, 24%), **28** (57 mg, 58%), and intractable material.

5,9,9-Trimethyltricyclo[4.3.0.0^{1,5}]non-7-en-4-one (**28**). B.p. 155°/14 Torr. UV (0.236 mg in 10 ml): 226 (7000). UV (1.9 mg in 2 ml): 276 (88), 286 (92), 300 sh, (63). IR: 3060*w*, 3045*w*, 3010*w* sh, 2990*m*, 2960*s*, 2935*s*, 2900*m*, 2865*m*, 1720*s*, 1595*w*, 1465*m* sh, 1460*m* sh, 1455*m*, 1440*w* sh, 1420*m*, 1380*w*, 1375*w* sh, 1360*m*, 1345*w*, 1320*w* sh, 1305*m*, 1295*m*, 1270*w*, 1220*w*, 1205*m*, 1165*w* sh, 1160*m*, 1080*m*, 1065*w*, 1045*w*, 1030*m*, 1015*w*, 995*w*, 985*w*, 965*w*, 885*m*, 875*w* sh, 825*w*. ^{1}H-NMR: 1.02, 1.10 (2*s*, CH_3–C(5), 2 CH_3–C(9)); 1.88–2.16 (*m*, 2H–C(2), 2H–C(3)); 2.20 (*d*, *X*-part of *ABX*-system, J = 2, H–C(6)); 5.56 (*dd*, *A*-part of *ABX*-system, J_1 = 5.5, J_2 = 2.0, H–C(7)); 5.67 (*d*, *B*-part of *ABX*-system, J = 5.5, H–C(8)). ^{13}C-NMR: 8.2, 20.0, 27.1 (3*q*, 2 CH_3–C(9), CH_3–C(5)); 21.1 (*t*, C(2)); 33.4 (*t*, C(3)); 38.9 (*d*, C(6)); 42.8, 47.0, 49.7 (3*s*, C(1), C(5), C(9)); 125.4, 144.5 (2*d*, C(7), C(8)); 215.2 (*s*, C(4)). MS: 176 (10, M^+, $C_{12}H_{16}O$), 161 (16), 134 (70), 133 (34), 120 (59), *119* (100), 117 (10), 105 (67), 91 (33), 79 (13), 77 (22), 65 (11), 51 (10), 41 (17). Anal. calc. for $C_{12}H_{16}O$ (176.26): C 81.77, H 9.15; found: C 81.66, H 9.19.

2,2,6-Trimethyltricyclo[4.3.0.0^{1,3}]non-4-en-7-one (**29**). B.p. 155°/14 Torr. UV (2.0 mg in 2 ml): 275 (186), 285 (217), 295 (234), 305 (257), 316 (257), 328 (184), 334 (69). IR: 3055*w*, 3005*w* sh, 2995*m*, 2975*m* sh, 2965*m*, 2950*m*, 2930*m*, 2910*m* sh, 2870*m*, 1740*s*, 1590*w*, 1475*w* sh, 1465*w*, 1455*w*, 1450*w* sh, 1405*w*, 1385*w*, 1370*w*, 1340*w*, 1295*w*, 1280*w*, 1270*w*, 1200*w* br., 1160*w*, 1140*w*, 1120*w* br., 1070*m*, 1050*m*, 1025*w*, 1005*w* sh, 990*w*, 975*w*, 955*w*, 930*w*, 920*w*, 900*w*, 880*w*, 700*w*. ^{1}H-NMR: 0.99, 1.13, 1.18 (3*s*, 2 CH_3–C(2), CH_3–C(6)); 1.47 (*d*, *X*-part of *ABX*-system, J = 2.0, H–C(3)); 1.73–2.48 (*m*, 2H–C(8), 2H–C(9)); 5.47 (*d*, *A*-part of *ABX*-system, J = 5.5, H–C(5)); 5.70 (*dd*, *B*-part of *ABX*-system, J_1 = 5.5, J_2 = 2.0, H–C(4)). ^{13}C-NMR (75 MHz): 16.3, 22.9, 24.1 (3*q*, 2 CH_3–C(2), CH_3–C(6)); 26.6, 36.7 (2*d*, C(8), C(9)); 42.0 (*d*, C(3)); 132.1, 134.3 (2*d*, C(4), C(5)); 26.9, 40.7 (2*s*, C(1), C(2)); 62.1 (*s*, C(6)); 220.9 (*s*, C(7)). MS: 176 (10, M^+, $C_{12}H_{16}O$), 161 (11), 134 (71), 133 (38), 121 (11), 120 (61), *119* (100), 117 (10), 106 (12), 105 (74), 103 (10), 92 (10), 91 (43), 79 (15), 78 (10), 77 (24), 65 (13), 53 (10), 51 (12), 41 (20). Anal. calc. for $C_{12}H_{16}O$ (176.26): C 81.77, H 9.15; found: C 81.48, H 9.26.

5.3. *Triplet Sensitization of* **5**. A solution of **5** (1.0 g, 6.76 mmol) and *Michler*'s ketone (260 mg, 0.97 mmol) in MeCN (350 ml) was irradiated (λ > 347 nm, 80% conversion). Chromatography (hexane/Et_2O 2:1) gave **5** (198 mg), **30** (218 mg, 28%), **31** (2 mg, 0.2%), and intractable material.

Tricyclo[4.4.0.0^{1,5}]dec-7-en-4-one (**30**). B.p. 60°/0.01 Torr. UV (0.184 mg in 10 ml MeCN): 227 (6500). UV (2.707 mg in 5 ml MeCN): 279 (180). IR: 3030*m*, 3000*w*, 2925*s*, 2850*m*, 1720*s*, 1640*w*, 1450*w*, 1435*w*, 1415*w*, 1390*w*, 1365*w*, 1315*w*, 1290*w*, 1280*w*, 1260*m*, 1240*m*, 1210*w*, 1185*m*, 1150*m*, 1120*w*, 1065*m*, 1040*w*, 1030*w*, 1020*m*, 985*w*, 950*w*, 930*w*, 885*s*, 870*m*, 720*w*, 700*s*, 600*w*. ^{1}H-NMR: 1.60–2.30 (*m*, 2H–C(2), 2H–C(3), H–C(5), H–C(6), 2H–C(9), 2H–C(10)); 5.45–5.70 and 5.80–6.05 (2*m*, H–C(7), H–C(8)). ^{13}C-NMR: 22.0, 22.9, 28.6, 33.1 (4*t*, C(2), C(3), C(9), C(10)); 26.1 (*d*, C(6)); 41.3 (*d*, C(5)); 125.9, 124.3 (2*d*, C(7), C(8)); 36.5 (*s*, C(1)); 212.3 (*s*, C(4)). MS: 148 (14, M^+, $C_{10}H_{12}O$), 133 (3), 120 (10), 106 (49), 105 (22), 92 (21), *91* (100), 79 (17), 78 (47), 77 (15), 65 (16), 51 (12), 39 (25). Anal. calc. for $C_{10}H_{12}O$ (148.20): C 81.04, H 8.16; found: C 80.83, H 8.25.

Tricyclo[5.3.0.0^{1,4}]dec-5-en-8-one (**31**). IR: 3020*w*, 2960*w*, 2920*m*, 2895*w*, 2840*w*, 1735*s*, 1445*w*, 1440*w*, 1425*w*, 1405*w*, 1390*w*, 1280*w*, 1265*w*, 1250*w*, 1160*w*, 1145*w*, 1135*w* sh, 1125*w* sh, 1090*w*, 1065*w*, 1020*w*, 965*w*, 940*w*. ^{1}H-NMR (300 MHz): 1.6–2.0 (*m*, 2H–C(10)); 2.0–2.5 (*m*, 2H–C(2), 2H–C(3), 2H–C(9)); 2.96 (*ddd*,

$J_1 = 3.0$, $J_2 = J_3 = 2.5$, H–C(7)); 3.00–3.08 (*m*, H–C(4)); 5.72 (*ddd*, $J_1 = 5.5$, $J_2 = 3.0$, $J_3 = 1.3$, H–C(6)); 5.92 (*dddd*, $J_1 = 5.5$, $J_2 = J_3 = 2.5$, $J_4 = 1.0$, H–C(5)).

5.4. *Triplet Sensitization of* **6**. A solution of *Michler*'s ketone (614 mg, 2.3 mmol) and **6** (2.48 g, 15.3 mmol) in MeCN (200 ml) was irradiated ($\lambda > 347$ nm, 89% conversion). Chromatography (SiO_2, hexane/Et_2O 17:3→1:1) afforded **6** (272 mg), **32** (1.41 g, 64%), and intractable material.

Tricyclo[5.4.0.0^{1,8}]undec-5-en-9-one (**32**). B.p. 95°/0.01 Torr. UV (0.212 mg in 10 ml pentane): 214 (10100). UV (2.1 mg in 2 ml): 284 (49), 292 sh (48), 302 sh (34), 313 sh (13). IR: 3020*m*, 2970*m* sh, 2930*s*, 2900*m* sh, 2865*m*, 2840*m*, 1725*s*, 1660*w*, 1450*m*, 1430*w*, 1420*m*, 1410*w*, 1290*w* sh, 1280*m*, 1260*m*, 1240*m*, 1230*m*, 1200*m*, 1185*s*, 1175*s*, 1150*w*, 1130*m*, 1095*w*, 1065*w*, 1050*w*, 1030*w*, 1020*w*, 1000*w*, 970*w*, 950*m*, 935*w*, 920*w*, 900*m*, 890*w*, 865*w*. ^{1}H-NMR: 1.08–2.36 (*m*, 12 aliph. H); 5.42–5.82 (*m*, H–C(5), H–C(6)). ^{13}C-NMR: 24.3, 30.0, 30.5, 33.3, 33.5 (5*t*); 32.2 (*d*, C(7)); 43.6 (*d*, C(8)); 125.5 and 131.5 (2*d*, C(5) and C(6)); 41.0 (*s*, C(1)); 213.0 (*s*, C(9)). MS: 162 (49, M^+, $C_{11}H_{14}O$), 134 (14), 133 (21), 120 (56), 119 (21), 107 (21), 106 (47), 105 (47), 93 (12), 92 (65), *91* (100), 79 (36), 78 (33), 77 (27), 65 (15), 53 (12), 51 (15), 41 (19). Anal. calc. for $C_{11}H_{14}O$ (162.23): C 81.44, H 8.70; found: C 81.39 H 8.74.

5.5. *Triplet Sensitization of* **7**. A solution of **7** (399 mg, 2.10 mmol) and *Michler*'s ketone (100 mg, 0.37 mmol) in MeCN (150 ml) was irradiated ($\lambda > 347$ nm, 81% conversion). After 8 h, the mixture was filtered through *Florisil*, the solvent was evaporated and the residue was chromatographed (20 g SiO_2; Et_2O/hexane 1:4) to give the starting material **7** (76 mg), a mixture, containing *ca.* 80% of **34** (84 mg), **33** (60 mg, 19%), and intractable material. Rechromatography of the mixture (20 g SiO_2; Et_2O/hexane 1:4) afforded pure **34** (66 mg, 21%).

4,4-Dimethyltricyclo[5.4.0.0^{1,8}]undec-5-en-9-one (**33**). B.p. 75°/0.1 Torr. UV (0.373 mg in 25 ml pentane): 214 (11600); (2.198 mg in 10 ml pentane): 286 (95). IR: 3000*m*, 2955*s*, 2930*s*, 2920*s*, 2860*s*, 1720*s*, 1655*w*, 1470*m*, 1460*m*, 1420*m*, 1410*m* sh, 1375*w*, 1360*m*, 1350*w*, 1290*w*, 1275*m*, 1250*w*, 1225*m*, 1220*m* sh, 1190*m* sh, 1185*m*, 1160*m*, 1155*m*, 1120*m*, 1060*w*, 1050*w*, 1040*w*, 1025*w*, 1010*w*, 965*w*, 950*w*, 930*w*, 905*m*, 870*w*. ^{1}H-NMR (300 MHz): 0.96, 1.04 (2*s*, 2 CH_3–C(4)); 1.36–1.48 (*m*, 1H); 1.57–1.67 (*m*, 1H); 1.84–1.94 (*m*, 2H); 2.07–2.26 (*m*, 4H) (2H–C(2), 2H–C(3), 2H–C(10), 2H–C(11)); 1.66 (*d*, $J = 2.9$, H–C(8)); 1.81 (*dd*, $J_1 = 4.7$, $J_2 = 2.9$, H–C(7)); 5.25 (*d*, $J = 11.9$, H–C(5)); 5.48 (*ddd*, $J_1 = 11.9$, $J_2 = 4.7$, $J_3 = 0.6$, H–C(6)). ^{13}C-NMR (75 MHz): 28.8, 31.5 (2*q*, 2 CH_3–C(4)); 28.5, 30.6, 33.2, 38.0 (4*t*, C(2), C(3), C(10), C(11)); 31.3, 43.0 (2*d*, C(5), C(6)); 121.1, 141.5 (2*d*, C(7), C(8)); 37.2, 41.5 (2*s*, C(1), C(4)); 213.1 (*s*, C(9)). MS: 190 (26, M^+, $C_{13}H_{18}O$), 175 (20), 162 (22), 161 (11), 149 (35), 148 (36), 147 (47), 135 (25), 134 (38), 133 (70), 129 (14), 122 (19), 121 (68), 120 (30), 119 (78), 117 (15), 107 (18), 106 (32), 105 (77), 103 (10), 95 (11), 93 (40), 92 (83), *91* (100), 82 (11), 81 (11), 80 (10), 79 (60), 78 (60), 77 (39), 69 (29), 67 (20), 65 (22), 55 (27), 53 (22), 51 (17), 43 (11), 41 (56). Anal. calc. for $C_{13}H_{18}O$ (190.29): C 82.06, H 9.53; found: C 81.91, H 9.64.

9,9-Dimethyltricyclo[6.3.0.0^{1,5}]undec-6-en-4-one (**34**). B.p. 55°/0.1 Torr. UV (1.270 mg in 10 ml pentane): 304 (330). IR: 3050*w*, 2950*s*, 2940*s*, 2900*m* sh, 2860*s*, 1735*s*, 1465*w* sh, 1450*m*, 1410*m*, 1380*w*, 1360*m*, 1340*w*, 1320*w*, 1290*w*, 1275*w*, 1250*w*, 1230*w*, 1220*w*, 1205*w*, 1180*w* sh, 1160*m*, 1145*m*, 1120*w* sh, 1060*w*, 1055*w*, 1020*w*, 980*w*, 955*w*, 920*w*, 895*w*, 880*w*, 715*m*. ^{1}H-NMR (300 MHz): 0.95, 1.07 (2*s*, 2 CH_3–C(9)); 1.36–1.42 (*m*, 2H) and 1.74–2.09 (*m*, 4H) (2H–C(2), 2H–C(10), 2H–C(11)); 2.21 (*dddd*, $J_1 = 17.1$, $J_2 = 7.7$, $J_3 = 3.8$, $J_4 = 1.7$, H–C(3)); 2.35 (*dddd*, $J_1 = 17.1$, $J_2 = 11.5$, $J_3 = 8.4$, $J_4 = 0.6$, H–C(3)); 2.52 (*ddd*, $J_1 = 2.9$, $J_2 = 2.4$, $J_3 = 2.3$, H–C(8)); 2.91 (*m*, $w_{1/2} = 7$, H–C(5)); 5.55 (*ddd*, $J_1 = 5.5$, $J_2 = 2.9$, $J_3 = 1.9$) and 5.7 (*ddd*, $J_1 = 5.5$, $J_2 = 2.3$, $J_3 = 2.3$) (H–C(6), H–C(7)). ^{13}C-NMR (75 MHz): 25.8, 28.9 (2*q*, 2 CH_3–C(9)); 35.4, 37.7, 38.8, 39.5 (4*t*, C(2), C(3), C(10), C(11)); 68.0, 69.2 (2*d*, C(5), C(8)); 128.0, 135.6 (2*d*, C(6), C(7)); 41.8 (*s*, C(9)); 57.2 (*s*, C(1)); 217.7 (*s*, C(4)). MS: 190 (55, M^+, $C_{13}H_{18}O$), 175 (18), 149 (36), 147 (15), 135 (29), 134 (27), 133 (18), 131 (14), 122 (22), *121* (100), 120 (28), 119 (58), 106 (18), 105 (23), 93 (29), 92 (40), 91 (50), 79 (59), 78 (99), 77 (23), 69 (29), 65 (13), 55 (12), 41 (27). Anal. calc. for $C_{13}H_{18}O$ (190.29): C 82.06, H 9.53; found: C 81.99, H 9.58.

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