119. 2-Alkynylcyclopent-2-enols from 2-Alkynylcyclohex-2-enones *via* 1-Alkynyl-7-oxabicyclo[4.1.0]heptan-2-ones

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2-Alkynylcyclohex-2-enones **1a–c** and **2a–c** react with H_2O_2/NaOH in MeOH to afford 1-alkynyl-7-oxabicyclo[4.1.0]heptan-2-ones **3a–c** and **4a–c**, respectively. The 3-unsubstituted bicyclic epoxy ketones **3a**, **3b**, and **4a**, **4b** react further with H_2O_2/NaOH, undergoing ring contraction and (formal) decarbonylation to give 2-alkynylcyclopent-2-enols **5a**, **5b**, and **6a**, **6b**, respectively. Epoxy ketones **3** are also obtained under neutral conditions on irradiation (λ = 350 nm) of cyclohexenones **1** in air-saturated benzene solution. Similarly, under neutral conditions oxo-cycloalkenecarbonitriles **8** react (thermally) with H_2O_2 in MeCN to give the oxabicyclic carbonitriles **9**.

Introduction. – In our studies on light-induced reactions of 2-alkynylcyclohex-2-enones with alkenes [1–3], we had noticed that, in order to avoid the formation of side products of molecular weight [*M*(enone) + 16], thorough degassing was necessary. Assuming these products to be bicyclic epoxy ketones, we tried to synthesize them by the classical treatment [4–6] of the enones with H_2O_2/NaOH in MeOH. Much to our surprise, this reaction proved to be complex as consecutive reactions occurred under these conditions. Here, we report on the conversion of 2-alkynylcyclohex-2-enones **1** and **2** to 1-alkynyl-7-oxabicyclo[4.1.0]heptan-2-ones **3** and **4**, respectively, and on the reaction of these epoxy ketones with H_2O_2/NaOH to afford 2-alkynylcyclopent-2-enols **5** and **6**, respectively.

Results. – Monitoring the reaction of 2-alkynylcyclohex-2-enones **1** or **2** with 3 equiv. of H_2O_2 and 0.5 equiv. of NaOH in MeOH, which are conditions commonly applied for the epoxidation of cyclohex-2-enones [4–6], by GC/MS shows the primary formation of epoxy ketones **3** and **4**, respectively. While **3c** and **4c** are stable under these conditions, compounds **3a**, **3b**, and **4a**, **4b** rearrange further. By lowering the relative amounts of NaOH (0.25 equiv.) and H_2O_2 (1.5 equiv.), we were able to obtain **3a**, **4a**, and **4b** in good yields, but the formation of **3b** from **1b** is much slower so that the consecutive rearrangement (to **5b**) occurs even under these conditions (*Scheme 1*). Further treatment of **3a** and **3b** with larger amounts of H_2O_2 and base affords cyclopentenols **5a** and **5b**, respectively, in 50–70% isolated yield, while similar treatment of epoxy ketones **4a** and **4b** gives mixtures **6a**/**7a** and **6b**/**7b**, respectively. Stirring of **4a** and **4b** in methanolic NaOH in the absence of H_2O_2 gives only **7a** or **7b**, respectively.

Irradiation (λ = 350 nm) of cyclohexenones **1** in air-saturated benzene solution affords epoxy ketones **3**, albeit in low yields (*Scheme 2*), while irradiation of **2** under the

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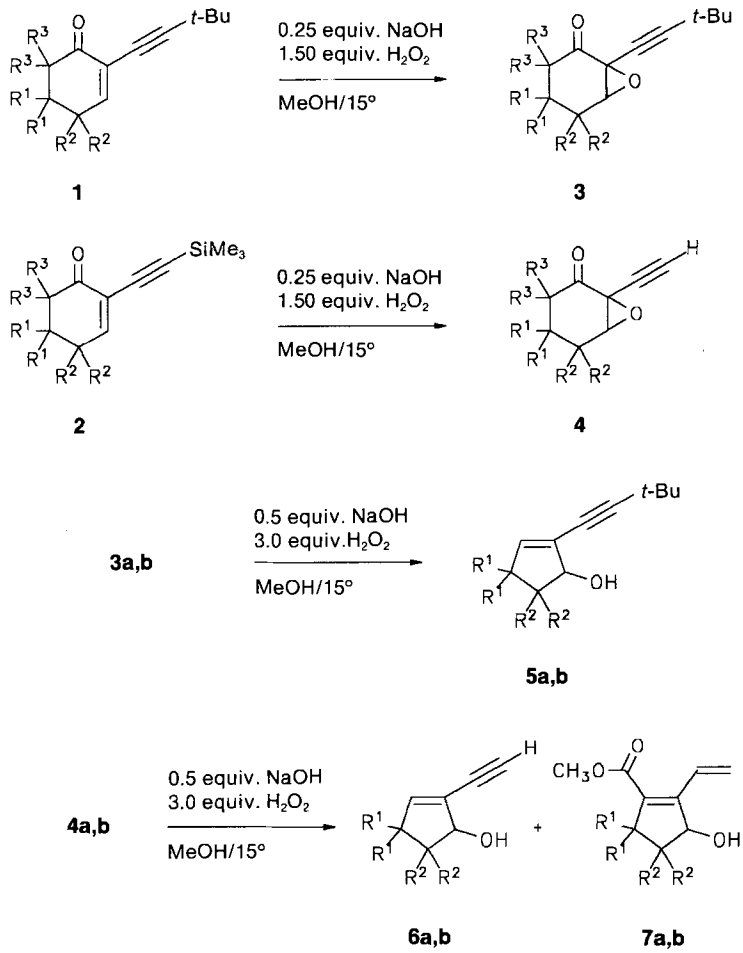
Scheme 1

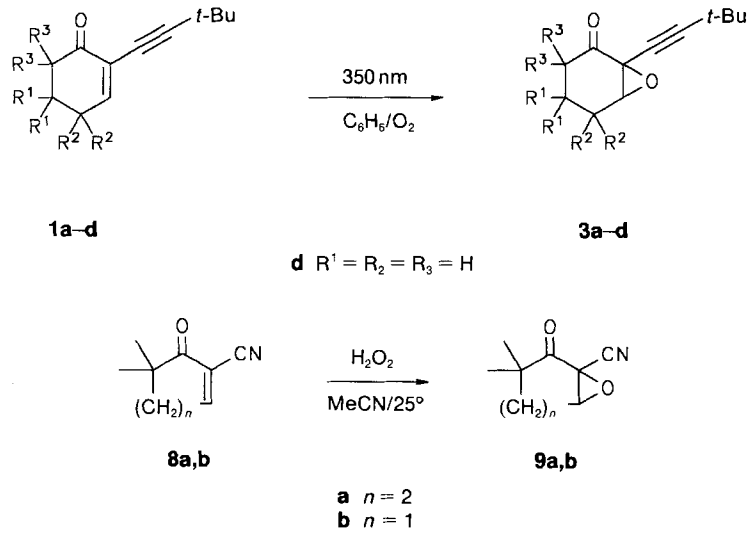


same conditions leads exclusively to slow decomposition of starting material. No conversion of **1** to **3** is observed in parallel dark reactions.

Finally, treatment of oxo-cycloalk-2-enecarbonitriles **8** with H_2O_2 in MeCN in the absence of NaOH gives epoxy ketones **9** in almost quantitative yields (*Scheme 2*).

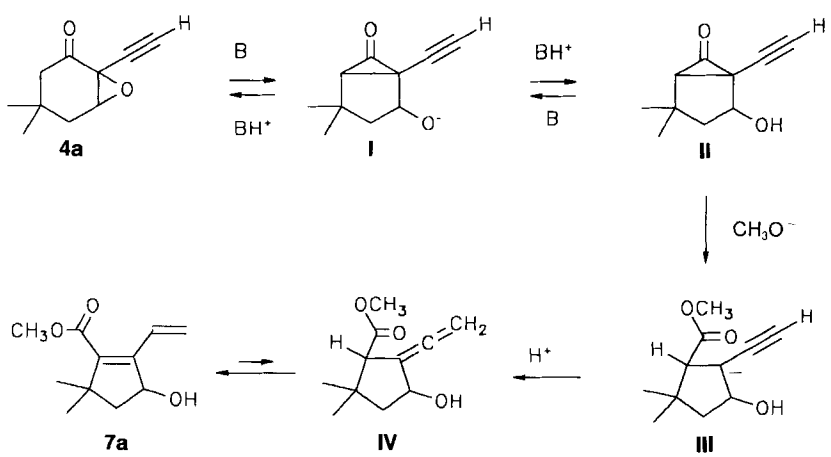
Discussion. – Regarding the non-photochemical reactions presented, both the apparent lability of 1-alkynyl-7-oxabicyclo[4.1.0]heptan-2-ones **3a**, **3b**, and **4a**, **4b** to base and the subsequent formation of 2-alkynylcyclopentenols **5** and **6** are noteworthy, as treatment of bicyclic α,β-epoxy ketones with methanolic bases usually leads to either ring

Scheme 2



opening of the oxirane ring or to ring contraction (*Favorskii* rearrangement) of the cycloalkanone moiety with formation of hydroxy-cycloalkanecarboxylic acids or -carboxylates [7]. Indeed, the formation of, *e.g.*, ester **7a** from **4a** fits well into the assumed path for this latter reaction, *i.e.*, formation of **I** and **II**, wherein **II** undergoes ring opening by methoxide to give the propargylic carbanion **III**; protonation of **III** on the terminal C-atom gives the allene ester **IV** which then tautomerizes to the (final) conjugated ester **7**. The ease of the ring opening **II** → **III** as compared to the back reaction to alcoholate **I** is probably due to the stabilization by charge delocalization in the (propargyl-allenyl) carbanion **III** (*Scheme 3*).

Scheme 3

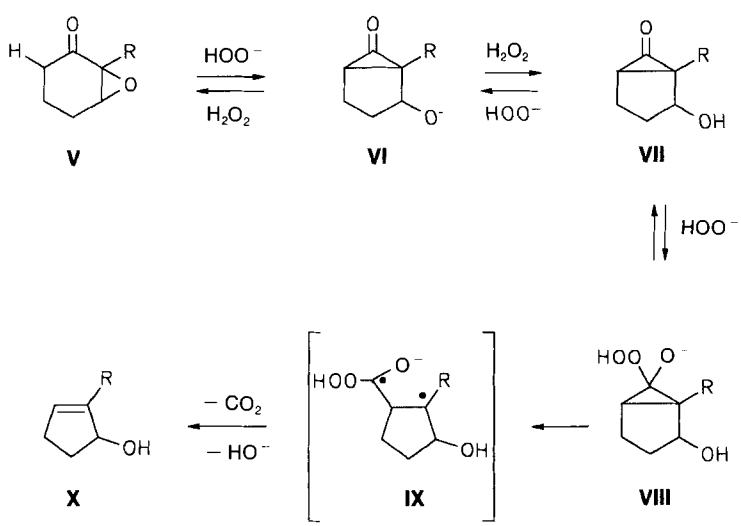


A plausible reaction sequence for the formation of 2-alkynylcyclopentenols **5** and **6** is presented in *Scheme 4*. Because of the stability of compounds **3c** and **4c** towards any excess of base, it can be safely assument, that the first step in the further conversion of those epoxy ketones **3** or **4** (**V**), bearing at least one H-atom on C(3), is again a *Favorskii* rearrangement to the bicycle **VII** *via* the alcoholate **VI**. Trapping this intermediate with the nucleophilic hydroperoxide anion affords anion **VIII**; this species can either undergo a direct homolytic cleavage of the cyclopropane ring, or a heterolytic cleavage followed by a one-electron transfer from the carbanion centre to the peroxy-acid group, to give the anionic 1,3-biradical **IX**, which then affords the final enyne **X**. Here again, the driving force lies in the stabilization due to the propargylic radical moiety in intermediate **IX**. One example of such an oxidative decarbonylation of a cyclopropanone, *i.e.*, where the formal loss of CO is achieved by the extrusion of a CO_2 molecule, has been reported by *Baldwin* and *Cardellina* [8], describing a new olefin synthesis from α-halogeno ketones, H_2O_2 and base. The pathway by which an intermediate analogous to **VIII** should decompose to the olefin was not discussed, but the authors refer to earlier work by *Treibs* [9] wherein a 1,3-dihydroxycyclopentanecarboxylic acid is proposed as – unstable – intermediate in the reaction of the epoxide of piperitone with H_2O_2 in alcaline MeOH.

An additional (minor) difficulty arises from the sensitivity of the Me_3Si group towards nucleophiles in the base-catalyzed epoxidation of enones **2**, as only the ethynyl-substituted epoxy ketones **4** are formed, most probably *via* displacement of the sp-hybridized carbanion by HOO^- on silicon. On the other hand, no problems of interaction with bases arise in the epoxidation of oxo-cycloalkenecarbonitriles **8**. Due to the very high electrophilicity of the olefinic β-C-atom, H_2O_2 reacts even in the absence of added base [10] [11].

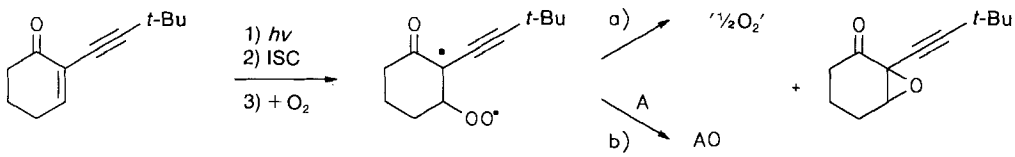
The light-induced conversion of 2-alkynylcyclohexenones **1** to epoxy ketones **3** is of interest too, as, up to now, it has been assumed that triplet cycloalkenones might be quenched by O_2, but that they did not react chemically with it. One exception to this is

Scheme 4



2-phenylbicyclo[3.3.1]non-1-en-3-one, an enone with a strained C=C bond, which behaves like a biradical in reacting with O_2 at −20° in the dark [12]. Whereas the resulting intermediate in this reaction has a (stabilizing) benzyl-radical moiety, bonding between the triplet 2-alkynylcyclohexenone and O_2 affords biradical **XI** containing a highly delocalized propargylic radical moiety. Instead of dissociating into (ground state) enone and $^1O_2$ – a chemical quenching sequence – cyclization of **XI** to **3** occurs either *via* a monomolecular (*Path a*) or a bimolecular (*Path b*) reaction sequence (*Scheme 5*). Although the yields of epoxy ketones **3** by this route are only modest, the advantage of the photochemical epoxidation is that compounds **3** are now formed in the absence of base. The finding that **1b** does not undergo this reaction might be explained by steric hindrance due to the Me groups on C(4) of the enone. Any reasoning to interpret the finding that the analogous conversion **2**→**4** is not observed would presently be purely speculative.

Scheme 5



1d **XI** **3d**

In conclusion, the stepwise conversion of 2-alkynylcyclohex-2-enones to 2-alkynylcyclopent-2-enols *via* 1-alkynyl-7-oxabicyclo[4.1.0]heptan-2-ones represents a synthetically useful path to these highly functionalized allylic alcohols, as the $LiAlH_4$ reduction of 2-alkynylcyclopent-2-enones in our hands turns out to be rather complex.

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Experimental Part

General. Photolyses: *Rayonet RPR-100* photoreactor equipped with 350-nm lamps. GC: 30-m *SE 30* capillary column. UV Spectra: in nm (log ε). IR Spectra: in cm^{-1}. ^1H- and ^{13}C-NMR Spectra: at 400 and 100.63 MHz, resp.; chemical shifts in ppm rel. to TMS (= 0 ppm), coupling constants *J* in Hz. MS: at 70 eV; in *m/z* (rel. intensity in %).

Cycloalkenones. The 2-(3,3-dimethylbut-1-ynyl)cyclohexenones **1a–d** [3]. 5,5-dimethyl-6-oxocyclohex-1-ene-1-carbonitrile (**8a**), and 4,4-dimethyl-5-oxocyclopent-1-ene-1-carbonitrile (**8b**) [13] were synthesized according to the literature. The 2-[2-(trimethylsilyl)ethynyl]cyclohexenones **2** were synthesized according to [3] from the corresponding 2-iodocyclohexenones [3] and tributyl[2-(trimethylsilyl)ethynyl]stannane [14] and purified by chromatography (SiO_2, hexane/AcOEt 8:1).

5,5-Dimethyl-2-[2-(trimethylsilyl)ethynyl]cyclohex-2-enone (**2a**): 69%. M.p. 69°. UV (cyclohexane): 311 (1.98), 264 (3.89). IR (KBr): 2153, 1683. ^1H-NMR ($CDCl_3$): 7.16 (*t*, *J* = 4.6); 2.31 (*d*, *J* = 4.6, 2 H); 2.30 (*s*, 2 H); 1.02 (*s*, 6 H); 0.19 (*s*, 9 H). ^{13}C-NMR ((D_6)benzene): 193.6 (*s*); 151.6 (*d*); 125.2 (*s*); 100.6 (*s*); 97.5 (*s*); 51.5 (*t*); 39.9 (*t*); 33.3 (*s*); 27.8 (*q*); 0.0 (*q*). MS: 220 (10, M^+), *205*.

4,4-Dimethyl-2-[2-(trimethylsilyl)ethynyl]cyclohex-2-enone (**2b**): 81%. M.p. 79°. ^1H-NMR ($CDCl_3$): 6.98 (*s*); 2.47, 1.83 (*AA'BB'*, 4 H); 1.16 (*s*, 6 H); 0.19 (*s*, 9 H). ^{13}C-NMR ($CDCl_3$): 195.1 (*s*); 163.9 (*d*); 122.5 (*s*); 99.2 (*s*); 97.2 (*s*); 35.5 (*t*); 34.3 (*t*); 33.7 (*s*); 27.6 (*q*); 0.0 (*q*). MS: 220 (9, M^+), *205*.

6,6-Dimethyl-2-[2-(trimethylsilyl)ethynyl]cyclohex-2-enone (**2c**): 77%. M.p. 67°. UV (cyclohexane): 327 (1.85), 263 (3.89). IR (KBr): 2153, 1679. ^{1}H-NMR ($CDCl_3$): 7.19 (*t*, *J* = 4.6); 2.42 (*dt*, *J* = 4.6, 6.1, 2 H); 1.80 (*t*, *J* = 6.1, 2 H); 1.10 (*s*, 6 H); 0.18 (*s*, 9 H). ^{13}C-NMR ($CDCl_3$): 200.3 (*s*); 153.5 (*d*); 123.5 (*s*); 99.8 (*s*); 96.8 (*s*); 41.5 (*s*); 35.6 (*t*); 24.1 (*q*); 23.6 (*t*); −0.1 (*q*). MS: 220 (9, M^+), *205*.

Preparation of Epoxy Ketones **3** *and* **4**. To a soln. of 0.01 mol **1** or **2** and 1.43 ml (0.015 mol) of 30% H_2O_2 in 20 ml of MeOH at 15° is added dropwise 0.5 ml (0.0025 mol) of 5N aq. NaOH during 10 min. After the addition is complete, the resulting mixture is stirred for 40 min at 20°. The mixture is then poured into 30 ml of H_2O, and the resulting mixture is extracted twice with 10 ml of Et_2O. The combined extracts are washed with H_2O and dried ($MgSO_4$). After evaporation, the residue is purified by chromatography (SiO_2; hexane/AcOEt 2:1).

4,4-Dimethyl-1-(3,3-dimethylbut-1-ynyl)-7-oxabicyclo[4.1.0]heptan-2-one (**3a**): 74%. Oil. ^{1}H-NMR ((D$_6$)benzene): 3.41 (*d*, *J* = 4.6); 2.43 (*d*, *J* = 13.2); 1.69 (*dd*, *J* = 2.5, 13.2); 1.53 (*d*, *J* = 15.3); 1.26 (*ddd*, *J* = 2.5, 4.6, 15.3); 1.21 (*s*, 9 H); 0.62 (*s*, 3 H); 0.57 (*s*, 3 H). ^{13}C-NMR ((D$_6$)benzene): 201.0 (*s*); 96.3 (*s*); 72.6 (*s*); 64.9 (*d*); 54.2 (*s*); 48.3 (*t*); 37.3 (*t*); 36.0 (*s*); 30.8 (*q*); 30.5 (*q*); 27.9 (*q*); 27.7 (*s*). MS: 220 (14, M^+), *83*.

5,5-Dimethyl-1-(3,3-dimethylbut-1-ynyl)-7-oxabicyclo[4.1.0]heptan-2-one (**3b**): 16%. Oil. ^{1}H-NMR ($CDCl_3$): 3.30 (*s*); 2.42 (*ddd*, *J* = 3.5, 6.0, 18.5); 2.19 (*ddd*, *J* = 7.0, 11.5, 18.5); 1.79 (*ddd*, *J* = 6.0, 11.5, 13.5); 1.33 (*ddd*, *J* = 3.5, 7.0, 13.5); 1.22 (*s*, 9 H); 1.17 (*s*, 3 H); 1.09 (*s*, 3 H). ^{13}C-NMR ($CDCl_3$): 200.8 (*s*); 96.1 (*s*); 72.3 (*d*); 71.9 (*s*); 54.9 (*s*); 33.2 (*t*); 31.0 (*s*); 30.6 (*q*); 27.5 (*s*); 27.1 (*q*); 23.2 (*q*). MS: 220 (2, M^+), *69*.

3,3-Dimethyl-1-(3,3-dimethylbut-1-ynyl)-7-oxabicyclo[4.1.0]heptan-2-one (**3c**): 82%. M.p. 29°. ^{1}H-NMR ($CDCl_3$): 3.62 (*d*, *J* = 2.5); 2.12 (*dddd*, *J* = 2.5, 2.5, 5.1, 15.5); 2.03 (*ddd*, *J* = 4.1, 13.4, 15.5); 1.76 (*ddd*, *J* = 5.1, 13.1, 13.4); 1.28 (*ddd*, *J* = 2.5, 4.1, 13.1); 1.18 (*s*, 9 H); 1.07 (*s*, 3 H); 1.01 (*s*, 3 H). ^{13}C-NMR ($CDCl_3$): 204.1 (*s*); 95.4 (*s*); 72.4 (*s*); 62.7 (*d*); 52.2 (*s*); 41.8 (*s*); 30.6 (*q*); 29.7 (*t*); 27.4 (*q*); 24.7 (*q*); 20.3 (*t*). MS: 220 (3, M^+), *121*.

4,4-Dimethyl-1-ethynyl-7-oxabicyclo[4.1.0]heptan-2-one (**4a**): 75%. M.p. 73°. ^{1}H-NMR ((D$_6$)benzene): 3.30 (*d*, *J* = 4.6); 2.33 (*d*, *J* = 13.7); 2.08 (*s*); 1.62 (*dd*, *J* = 2.5, 13.7); 1.40 (*d*, *J* = 15.3); 1.12 (*ddd*, *J* = 2.5, 4.6, 15.3); 0.53 (*s*, 3 H); 0.47 (*s*, 3 H). ^{13}C-NMR ((D$_6$)benzene): 200.2 (*s*); 77.7 (*s*); 75.6 (*d*); 64.6 (*d*); 53.6 (*s*); 48.0 (*t*); 36.9 (*t*); 36.0 (*s*); 30.3 (*q*); 27.6 (*q*). MS: 164 (6, M^+), *83*.

5,5-Dimethyl-1-ethynyl-7-oxabicyclo[4.1.0]heptan-2-one (**4b**): 73%. M.p. 58°. ^{1}H-NMR ($CDCl_3$): 3.40 (*s*); 2.51 (*s*); 2.46 (*ddd*, *J* = 3.6, 6.1, 18.6); 2.24 (*ddd*, *J* = 7.1, 11.7, 18.6); 1.82 (*ddd*, *J* = 6.1, 11.7, 13.5); 1.36 (*ddd*, *J* = 3.6, 7.1, 13.5); 1.19 (*s*, 3 H); 1.10 (*s*, 3 H). ^{13}C-NMR ($CDCl_3$): 200.2 (*s*); 77.7 (*s*); 75.6 (*d*); 64.6 (*d*); 53.6 (*s*); 48.0 (*t*); 36.9 (*t*); 30.3 (*q*); 27.6 (*q*). MS: 164 (0.5, M^+), *69*.

6,6-Dimethyl-1-ethynyl-7-oxabicyclo[4.1.0]heptan-2-one (**4c**): 42%. Colorless liquid. ^{1}H-NMR ($CDCl_3$): 3.75 (*dd*, *J* = 1.0, 2.5); 2.47 (*s*); 2.19 (*dddd*, *J* = 2.5, 2.5, 5.0, 14.8); 2.08 (*dddd*, *J* = 1.0, 4.3, 14.1, 14.8); 1.81 (*ddd*, *J* = 5.0, 13.7, 14.1); 1.33 (*ddd*, *J* = 2.5, 4.3, 13.7); 1.13 (*s*, 3 H); 1.05 (*s*, 3 H). ^{13}C-NMR ($CDCl_3$): 203.6 (*s*); 77.6 (*s*); 74.6 (*d*); 62.5 (*d*); 51.7 (*s*); 41.9 (*s*); 29.4 (*t*); 25.3 (*q*); 24.8 (*q*); 20.3 (*t*). MS: 164 (0.5, M^+), *56*.

Preparation of Cyclopentenols **5**. To a soln. of 0.004 mol of **3a** or **3b**, and 1.43 ml (0.015 mol) of 30% H_2O_2 in 10 ml of MeOH at 15° is added dropwise 1 ml (0.003 mol) of 3N NaOH during 5 min. After the addition is complete, the resulting mixture is stirred for 30 min at 15–20°. The mixture is then poured into 20 ml of H_2O and extracted twice with 10 ml of Et_2O. The combined extracts are washed with sat. aq. NaCl and dried ($MgSO_4$). After evaporation, the residue is purified by chromatography (SiO_2; hexane/AcOEt 2:1).

4,4-Dimethyl-2-(3,3-dimethylbut-1-ynyl)cyclopent-2-en-1-ol (**5a**): 63%. Colorless liquid. ^{1}H-NMR ($CDCl_3$): 5.86 (*d*, *J* = 1.0); 4.72 (*ddd*, *J* = 1.0, 5.1, 7.1); 2.10 (*dd*, *J* = 7.1, 13.2); 1.58 (*dd*, *J* = 5.1, 13.2); 1.24 (*s*, 9 H); 1.13 (*s*, 3 H); 1.03 (*s*, 3 H). ^{13}C-NMR ($CDCl_3$): 148.0 (*d*); 125.1 (*s*); 101.6 (*s*); 78.7 (*d*); 73.8 (*s*); 48.2 (*t*); 43.9 (*s*); 31.1 (*q*); 29.6 (*q*); 28.6 (*q*); 28.1 (*s*). MS: 192 (32, M^+), *159*.

5,5-Dimethyl-2-(3,3-dimethylbut-1-ynyl)cyclopent-2-en-1-ol (**5b**): 51%. Colorless liquid. ^{1}H-NMR ($CDCl_3$): 5.75 (*t*, *J* = 4.5); 4.80 (*s*); 2.30 (*d*, *J* = 4.5, 2 H); 1.25 (*s*, 9 H); 1.23 (*s*, 3 H); 1.13 (*s*, 3 H). MS: 192 (82, M^+), *177*.

Reaction of **4a** *and* **4b** *with* H_2O_2/*NaOH*. Similar treatment and workup as described above for **3** affords mixtures **6a**/**7a** (4:1), and **6b**/**7b** (2:1), respectively. Compounds **6** having higher R_f values than **7** are separated and isolated by chromatography (SiO_2; hexane/AcOEt 2:1).

4,4-Dimethyl-2-ethynylcyclopent-2-en-1-ol (**6a**): 58%. Colorless liquid. ^{1}H-NMR ($CDCl_3$): 6.07 (*s*); 4.81 (*dd*, *J* = 5.1, 7.1); 3.00 (*s*); 2.14 (*dd*, *J* = 7.1, 13.2); 1.61 (*dd*, *J* = 5.1, 13.2); 1.15 (*s*, 3 H); 1.05 (*s*, 3 H). MS: 136 (15, M^+), *77*.

5,5-Dimethyl-2-ethynylcyclopent-2-en-1-ol (**6b**): 32%. Colorless liquid. ^{1}H-NMR ($CDCl_3$): 5.87 (*t*, *J* = 4.5); 4.85 (*s*); 2.98 (*s*); 2.35 (*d*, *J* = 4.5, 2 H); 1.28 (*s*, 3 H); 1.18 (*s*, 3 H). MS: 136 (22, M^+), *121*.

Preparation of Cyclopent-1-enecarboxylates **7**. To a soln. of 0.004 mol of **4a** or **4b** in 10 ml of MeOH at 15° is added 2 ml (0.012 mol) of 6N NaOH. The resulting mixture is stirred for 30 min at r.t. The mixture is then poured into 20 ml of H_2O and extracted twice with 10 ml of Et_2O. The combined extracts are washed with sat. aq. NaCl and dried ($MgSO_4$). After evaporation, the residue is purified by chromatography (SiO_2; hexane/AcOEt 2:1).

Methyl 5,5-Dimethyl-2-ethenyl-3-hydroxycyclopent-1-ene-1-carboxylate (**7a**): 28%. Colorless liquid. ^{1}H-NMR ($CDCl_3$): 7.06 (*dd*, J = 11.2, 17.8); 5.71 (*dd*, J = 1.5, 17.8); 5.44 (*dd*, J = 1.5, 11.2); 5.03 (*dd*, J = 3.1, 7.1); 3.76 (*s*, 3 H); 2.08 (*dd*, J = 3.1, 13.5); 1.72 (*dd*, J = 7.1, 13.5); 1.34 (*s*, 3 H); 1.18 (*s*, 3 H). ^{13}C-NMR ($CDCl_3$): 166.4 (*s*); 148.0 (*s*); 140.6 (*s*); 130.4 (*d*); 121.0 (*t*); 74.6 (*d*); 51.2 (*q*); 49.3 (*t*); 45.7 (*s*); 29.0 (*q*); 27.9 (*q*). MS: 196 (15, M^+), *93*.

Methyl 4,4-Dimethyl-2-ethenyl-3-hydroxycyclopent-1-ene-1-carboxylate (**7b**): 33%. Oil. ^{1}H-NMR ($CDCl_3$): 7.35 (*dd*, J = 11.5, 17.5); 5.75 (*dd*, J = 1.5, 17.5); 5.45 (*dd*, J = 1.5, 11.5); 4.43 (*s*); 3.75 (*s*, 3 H); 2.61, 2.39 (*AB*, J = 17.4, 2 H); 1.11 (*s*, 3 H); 1.02 (*s*, 3 H). MS: 196 (31, M^+), *121*.

Preparation of Oxa-bicycloalkane-1-carbonitriles **9**. According to [11], to a soln. of **8** ($7 \cdot 10^{-3}$ mol) in 15 ml MeCN was added 35% H_2O_2 (3 ml, 35 mmol) at r.t. under Ar. The mixture was stirred for 30 min (**8b**) or 6 h (**8a**), then 10% $NaHSO_3$ (20 ml) was added, and extracted with CH_2Cl_2. The org. fraction was dried ($MgSO_4$) and evaporated to afford **9a** and **9b**, resp.

3,3-Dimethyl-2-oxo-7-oxabicyclo[4.1.0]heptan-1-carbonitrile (**9a**): 66%. M.p. 33–34° (from pentane). IR (film): 1717. ^{1}H-NMR ($CDCl_3$): 4.03 (*d*, J = 2.4); 2.32, 2.14 (*m*, J_{gem} = 15.8, 2 H); 1.83, 1.42 (*m*, J_{gem} = 13.4, 2 H); 1.17 (*s*, 3 H); 1.10 (*s*, 3 H). ^{13}C-NMR ($CDCl_3$): 201.0 (*s*); 114.5 (*s*); 61.7 (*d*); 50.0 (*s*); 42.1 (*s*); 28.8 (*t*); 25.2 (*q*); 19.8 (*t*). MS: 165 (0.5, M^+), *56*.

3,3-Dimethyl-2-oxo-6-oxabicyclo[3.1.0]hexan-1-carbonitrile (**9b**): 79%. M.p. 72–74° (from pentane). IR (KBr): 1744. ^{1}H-NMR ($CDCl_3$): 4.37 (*d*, J = 2.1); 2.35 (*d*, J = 15.3); 2.13 (*dd*, J = 2.1, 15.3); 1.18 (*s*, 3 H); 1.16 (*s*, 3 H). ^{13}C-NMR ($CDCl_3$): 204.6 (*s*); 112.1 (*s*); 63.4 (*d*); 51.7 (*s*); 42.2 (*s*); 37.6 (*t*); 27.8 (*q*); 25.8 (*q*). MS: 151 (10, M^+), *41*.

Irradiation of **1** *in Aerated Solns.* A soln. of $5 \cdot 10^{-4}$ mol of **1** in 5 ml of benzene is saturated with air and irradiated for 24 h. After evaporation, the residue is purified by chromatography on SiO_2.

1-(3,3-Dimethylbut-1-ynyl)-7-oxabicyclo[4.1.0]heptan-2-one (**3d**): from **1d**, 11% yield. Colorless liquid (hexane/AcOEt 3:1). IR (film): 1723. ^{1}H-NMR ($CDCl_3$): 3.72 (*dd*, J = 2.0, 0.5); 2.58–1.60 (*m*, 6 H); 1.25 (*s*, 9 H). ^{13}C-NMR ($CDCl_3$): 200.8 (*s*); 96.0 (*s*); 71.8 (*s*); 64.4 (*d*); 54.0 (*s*); 36.3 (*t*); 30.7 (*q*); 27.5 (*s*); 23.0 (*t*); 17.8 (*t*). MS: 192 (27, M^+), *121*.

3a: 24% (hexane/AcOEt 8:1); **3b**: < 2% after 48 h; **3c**: 22% (hexane/AcOEt 8:1). No conversion **1** → **3** occurs in samples protected by alumina foil.

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