103. On the Photochemistry of 12,13-Didehydrosqualene

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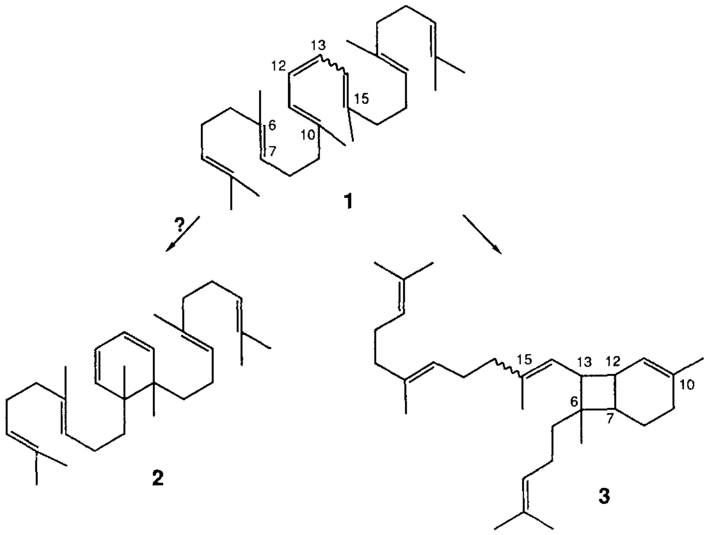
The photochemical formation of bicyclooctenes **3** from 12,13-didehydrosqualene (**1**) upon irradiation at wavelengths longer than 290 nm is reported. The same photoreaction is also observed with trienes **7** and **8** which like **1** have a remote double bond two C-atoms removed from the triene system. A configurational assignment for bicyclooctene **10** obtained from **8** and a mechanism for the observed photochemical reaction are proposed.

1. Introduction. – This paper reports results of the photochemistry of 12,13-didehydrosqualene (**1**). The research has been carried out in the laboratories of Prof. *A. Eschenmoser* at the ETH in Zürich as part of an effort to prepare the squalenoid cyclohexadiene derivative **2** from **1**. A literature search revealed that *Mandell, Miller* and *Faulkner* [1] had attempted to bring about the photochemical electrocyclic ring closure of didehydrosqualene **1** to cyclohexadiene **2**; however, no products from the irradiation of **1** could be identified.

Scheme 1



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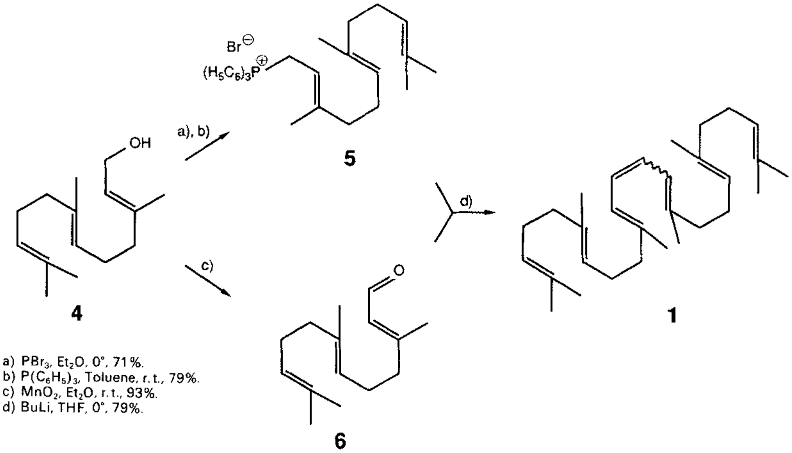
We have observed the formation of a mixture of isomeric bicyclooctenes **3** upon direct irradiation of 12,13-didehydrosqualene (**1**; the squalene numbering is indicated in both **1** and **3** of *Scheme 1*). This reaction is the formal equivalent of a [2 + 2] cycloaddition involving the 6,7- and 12,13-double bonds of didehydrosqualene **1**.

2. Results. – Didehydrosqualene **1** was prepared as shown in *Scheme 2*. This reaction sequence is essentially the same as that used by *Mandell* and *Miller* [1a]. *trans,trans*-Farnesol (**4**)[2]) was reacted with PBr_3 in Et_2O to yield farnesyl bromide which was in turn reacted with triphenylphosphine to form farnesyl(triphenyl)phosphonium bromide (**5**). Phosphonium salt **5** was deprotonated with BuLi and reacted with farnesal (**6**), prepared by the oxidation of *trans,trans*-farnesol (**4**) with active MnO_2 [2], to give didehydrosqualene **1**. GC analysis of **1** showed it to be a 1:1 mixture of two isomers. Based on the method of preparation, these represent the (*E*) and (*Z*) isomers about the 12,13-double bond.

Scheme 2



a) PBr_3, Et_2O, 0°, 71%.
b) $P(C_6H_5)_3$, Toluene, r.t., 79%.
c) MnO_2, Et_2O, r.t., 93%.
d) BuLi, THF, 0°, 79%.

Direct irradiation of a hexane solution of didehydrosqualene **1** at wavelengths longer than 290 nm yielded material that was less polar on TLC than **1**. GC analysis of the product showed it to be primarily a mixture of 4 compounds in a 13:21:43:23 ratio with only trace amounts of other products being present. Flash column chromatography on $AgNO_3$-impregnated 10% silica gel [3] allowed the partial separation of this mixture. ^1H-NMR and MS analysis of the purified products showed them to be stereoisomers of bicyclooctene **3**.

In the NMR spectra, 2 signals (1H each) lying between 2.4 and 2.9 ppm can be assigned to H–C(1) and H–C(8) in 3 of the 4 isomers. These 3 isomers each show a CH_3 group bound to a quaternary center, 7 olefinic CH_3 groups and 5 olefinic protons. The peak at *m/z* 314 in the MS is explained by fragmentation of the cyclobutane ring and loss of a C_7H_{10} unit (see *Fig. 1*).

The partial chromatographic separation yielded isomers **3b** and **3c** as pure compounds and **3d** as the major component (82%) of a mixture containing minor amounts of **3a** and **3c**. Compound **3a** could not be obtained pure.

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[2]) Gift from *F. Hoffmann-La Roche & Co. AG*, Basel, Switzerland. Available from *Aldrich Chemical Co., Inc.*, Milwaukee, WI, USA.

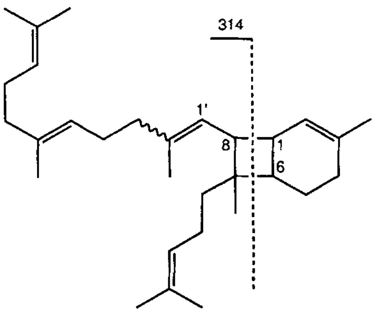

Fig. 1. *Bicyclooctene* **3** *with MS fragmentation*

Attempts to better understand this apparently new reactivity of trienes led to the preparation of trienes **7** and **8** by reaction sequences analogous to that shown in *Scheme 2*. Triene **7** [4] was prepared from geraniol and was determined by GC to be a 1:1 *(E/Z)* mixture about the 8,9-double bond. Triene **8** was obtained by a *Wittig* reaction employing (3-methylbut-2-enyl)triphenylphosphonium bromide [5] and geranial. It too was a 1:1 mixture of geometric isomers about the newly formed double bond.

Chromatographic purification [3] and spectroscopic identification of the 4 less polar compounds produced upon irradiation of triene **7** showed them to be isomers of bicyclooctene **9** (see *Scheme 3* and *Table*). Isomers **9a** and **9c** could be completely purified by

Scheme 3

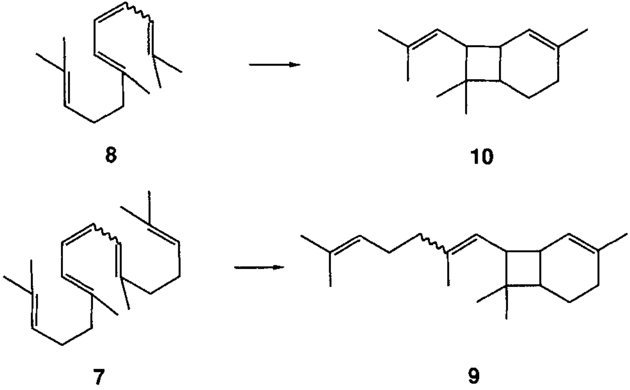

Table. *Photocyclization Reactions of* **1**, **7**, *and* **8**

Starting compound	Product(s)	Isomer ratio	Isolated yield[a])
C$_{15}$-Triene **8**	C$_{15}$-Bicyclooctene **10**	1[b])	37–41%
C$_{20}$-Triene **7**	C$_{20}$-Bicyclooctenes **9**	**a**/**b**/**c**/**d**[c])[d])17:12:23:45	74%
Didehydrosqualene **1**	C$_{30}$-Bicyclooctenes **3**	**a**/**b**/**c**/**d**[c])[d])13:21:43:23	51%

[a]) Yield of bicyclooctene isomer(s) after chromatography on silica gel.

[b]) The ratio of bicyclooctene **10** to 3 unidentified, minor products which were detected by GC was 89:4:5:2.

[c]) The lettering system indicates the order of elution upon GC (**a**, first; *etc.*).

[d]) Trace amounts of unidentified products were detected by GC which showed these minor products to comprise less than 4% of the mixture.

chromatography, but **9b** and **9d** were obtained from chromatography and spectroscopically analyzed as a 1:4 mixture. Surprisingly, irradiation of triene **8** led to the formation of less polar material which proved to be essentially one isomer of bicyclooctene **10**. Bicyclooctene **10** was purified chromatographically [3].

Bicyclooctenes **9a** and **9d** showed very similar signal patterns in the ^{1}H-NMR spectra, as did **9d** and **9c**. Each pair of related isomers seems to be isomeric about the C(1')=C(2') bond. Bicyclooctenes **9a** and **9d** are probably configurationally related to **10** because of a correspondence of signal patterns in the ^{1}H-NMR of these three compounds. The bicyclooctenes **3** are hard to correlate with bicyclooctenes **9** and **10** on the basis of NMR spectra because of the increased molecular complexity.

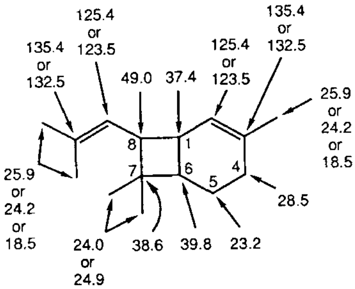

Fig. 2. *^{13}C-NMR (75 MHz) assignments of bicyclooctene* **10**. Chemical shifts in ppm.

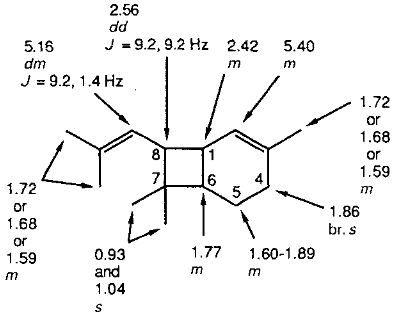

Fig. 3. *^{1}H-NMR (300 MHz) assignments of bicyclooctene* **10**. Chemical shifts in ppm.

We chose to determine the configuration of the simplest of the bicyclooctenes, photoproduct **10**. The 75-MHz ^{13}C-NMR and the 300-MHz ^{1}H-NMR of this compound have been assigned as shown in *Fig. 2* and *3*, respectively. These assignments were made by means of COSY, DEPT, and ^{13}C,^{1}H heteronuclear-shift-correlated 2D spectra (HETCOR, version with H,H couplings), and the configuration of **10** was determined by NOE experiments.

The important NMR assignments were made as follows. The single ^{1}H-NMR signal at 2.56 ppm is assigned to H–C(8). Decoupling experiments show it to be coupled with resonances at 2.42 and 5.16 ppm which are assigned to H–C(1) and H–C(1'), respectively. The COSY experiment confirms these assignments. The COSY also shows that H–C(1) is coupled with a proton which resonates in the region of 1.6–1.9 ppm and that a complex coupling system exists within this 1.6–1.9 ppm region. A DEPT experiment shows that 3 methine C-atoms (49.0, 39.8, and 37.4 ppm) are present in **10**. The HETCOR experiment reveals that the signals of 2 of these 3 methine C-atoms correlate with the H–C(1) and H–C(8) resonances. Therefore, the 3rd methine ^{13}C-signal must be that of C(6), and HETCOR shows it to correlate with a ^{1}H-signal at 1.77 ppm having roughly the form of a *dd*. A second DEPT experiment shows that 2 methylene C-atoms (28.5 and 23.2 ppm) are present in **10**. HETCOR reveals that 1 ^{13}C-resonance (28.5 ppm) correlates with a ^{1}H-resonance appearing as a br. *s* centered at 1.86 ppm (CH_2(4)). The other ^{13}C-resonance (23.2 ppm) correlates with the resonances of 2 chemically non-equivalent protons at 1.6–1.89 ppm. This broad signal is assigned to CH_2(5).

The configuration at C(1) and C(8) is determined by NOE experiments. As shown in *Fig. 4*, irradiation at one of the CH_3 groups at C(7) produces a NOE at H–C(8). Irradiation at the other CH_3 group at C(7) causes a NOE at H–C(1) and H–C(1'). Thus, H–C(1) and H–C(8) are *trans* to each other.

The assignment of the configuration at C(6) is made complex as the *m* in the ^{1}H-NMR for H–C(6) and the 2 H–C(5) overlap in the 1.6–1.9 ppm region³). The HETCOR spectrum (as mentioned above) reveals that the

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³) These signals also overlap when the ^{1}H-NMR is measured in C_6D_6.

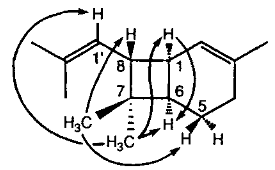


Fig. 4. *Partial results of the NOE experiments with* **10**

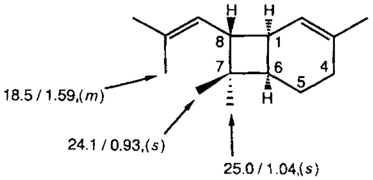


Fig. 5. *Additional* ^{13}*C-NMR/*^{1}*H-NMR assignments based on the NOE experiments with* **10**. Chemical shifts in ppm.

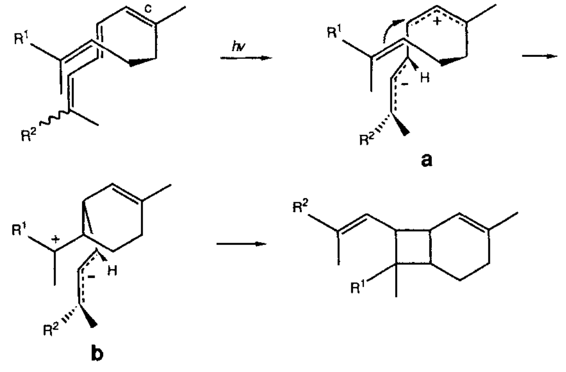
H–C(6) signal appears between 1.71 and 1.84 ppm and has roughly the form of a *dd*. This signal lies across the signal for the 2 non-isochronous H–C(5) at 1.6–1.89 ppm (centered at 1.74 ppm). Almost identically shaped NOE signals at 1.72–1.82 ppm result, when either H–C(1) or the CH_3 group at C(7) '*syn*' to H–C(1) are irradiated. The position and shape of the NOE signals correspond to the position and general shape of the *m* observed for H–C(6). A broader NOE signal at 1.60–1.76 ppm results, when the CH_3 group at C(7) '*syn*' to H–C(8) is irradiated. This NOE signal corresponds to the more shielded of the 2 H–C(5). Based on these results, the bicyclooctene is assigned a *cis*-ring fusion as shown in *Fig. 4*.

Some further support for this configuration comes from the ^{13}C- and ^{1}H-NMR data for the CH_3 groups at C(7) which can now be assigned as shown in *Fig. 5* on the basis of the NOE experiments. The β-CH_3 is '*syn*' to the vicinal C(5) and the α-CH_3 is '*syn*' to the vicinal C(1'). Such an arrangement should produce the observed similarity in the ^{13}C-NMR chemical shifts for the 2 CH_3–C(7). If the opposite configuration were present at C(6), then very different chemical shifts would be expected for the 2 CH_3–C(7) as one of them would be '*syn*' to both C(1') and C(5). The β-CH_3–C(7) which is more shielded by virtue of its position on the concave face of the bicyclooctene appears at higher field in the ^{1}H-NMR than the α-CH_3–C(7). This observation is also consistent with the assigned configuration.

The course of the photolysis of **1**, **7**, and **8** has been followed by GC. This technique furnished evidence that upon irradiation, a rapid double-bond isomerization of the triene starting materials occurs to give a large mixture of double-bond isomers followed by a relatively slow formation of the bicyclooctenes.

3. Discussion. – We propose the mechanism shown in *Scheme 4* to explain the formation of these bicyclooctenes. Presumably, only those isomers in which the double bond designated c is (*Z*) are capable of reacting to yield a bicyclooctene. *Dauben* and *Kellogg* have proposed that bisallylic excited states of trienes in which twisting has occurred about the central double bond of the triene unit are involved in the photocyclization of certain trienes to bicyclo[3.1.0]hexanes [6]. Calculations have shown that, if

Scheme 4



the two allylic systems of such an excited-state triene are perpendicular to one another, then a charge-separated excited state results [7]. With these ideas in mind, we suggest that formation of a planar excited-state singlet of the triene possessing bisallylic character [6] occurs upon direct irradiation, and this electronically excited triene yields the charge-separated (zwitterionic) intermediate **a** with twisting about the central bond of the excited triene until the two allylic systems are orthogonal to each other [7] *(Scheme 4)*. Trapping of the positively charged allylic system by an isolated double bond leads to cyclohexenyl zwitterion **b**. Ring closure producing a cyclobutane by bond formation between the allylic anion and the tertiary carbonium ion gives the observed bicyclooctenes.

This reaction between trienes and a remote double bond has apparently not been previously observed. The known reactions of triene photochemistry are: *1)* electrocyclic ring closure to give cyclobutenes, *2)* formation of derivatives of bicyclo[3.1.0]hexene, *3)* 1,5-H shift to yield allenes, *4)* electrocyclic ring closure to give cyclohexadienes, and *5)* double-bond isomerizations [8].

The concept of ground-state conformational control of triene photochemistry has been advanced by *Dauben et al* [8]. A study by *Havinga* and coworkers [9] showed that the product distribution obtained upon photolysis of a simple acyclic triene is very strongly influenced by the ground-state conformational equilibrium of the triene which is in turn determined by the substitution pattern of the triene. The trienes used in our study were all disubstituted at the terminal positions of the triene and were 1:1 *(Z/E)* mixtures about the central double bond of the triene. The most stable ground-state conformations of such trienes will be the *'tZt'* (s-*trans*, s-*trans*) and *'tEt'* (s-*trans*,s-*trans*) conformations. *Havinga*'s study [9] indicated that the major photochemical reaction pathway of trienes having the *'tZt'* and *'tEt'* conformations will be double-bond isomerization. Thus, it is reasonable for double-bond isomerization to be the major reaction pathway upon photolysis of trienes **1**, **7**, and **8**.

Aside from double-bond isomerizations, we have not detected any of the traditional products of triene photochemistry, although their formation in trace amounts cannot be excluded at this time. The observed bicyclooctene formation fits in well with the mechanistic scheme [6] [7] that has been established in this area.

We would like to thank Prof. *A. Eschenmoser* for allowing us to report these results that were obtained during the post-doctoral stay of *W. M.* at the ETH and for financial support. *W. M.* gratefully acknowledges the *Swiss National Science Foundation* for an international postdoctoral fellowship (1984–1986). Ms. *B. Brandenburg* and Mr. *F. Fehr* kindly acquired the NMR spectra and Ms. *L. Golgowski* kindly measured the mass spectra. Dr. *D. Felix* and Mr. *P. Hess* expertly prepared the GC columns.

Experimental Part

1. *General.* GC: *Carlo Erba Fractovap (*series *4160)* instrument. Chromatography columns were prepared in house and are described below. UV spectra (nm): *Kontron-Uvikon-860* instrument and *Perkin-Elmer-402* spectrophotometer. IR spectra (cm^{-1}): *Perkin-Elmer-781* spectrophotometer. NMR spectra (δ in ppm): *Bruker-WM-300* and *Varian-XL-300* instruments. MS (m/z (rel. %)): *Hitachi-Perkin-Elmer-RMU-6M* instrument.

2. *NMR Experiments. NOE-difference spectra* were obtained by alternative accumulation of an FID with the decoupler on resonance (*ca.* 80% saturation) and an FID with the decoupler at the high-field end of the spectrum (control). Typically, 200 to 400 scans in blocks of 16 were acquired per FID. The FID were subtracted and processed with a line broadening of 1.5 Hz. Individual lines of *m* were separately irradiated and the FID added in order to surpress SPT-side effects.

The *COSY* was a double quantum filtered, phased 2D experiment with a 16-membered phase cycle and having 512 × 512 data points.

The *HETCOR* spectrum was acquired using a standard pulse sequence without ^{1}H,^{1}H decoupling. The 1024 × 512 data points obtained were transformed to give a 1024 × 1024 matrix. Cross sections along the proton dimension were plotted at the frequency of all ^{13}C-signals.

3. *General Procedure for the Preparation of Trienes* **1**, **7** *and* **8**. The phosphonium salt (1.3 mmol) was suspended in THF (9 ml) under Ar. At 0°, a soln. of BuLi (1.4 mmol) in hexane was added to this suspension and the temp. maintained at 0°. After 1 h, a soln. of the aldehyde (1.8 mmol) in THF (3 ml) was added by cannula. After 1 h at 0°, the mixture was poured into H$_2$O and the resulting mixture extracted with Et$_2$O (2 ×). The combined org. layers were washed with brine (1 ×), dried (MgSO$_4$), filtered, and evaporated. The residue was taken up in hexane and the triphenylphosphine oxide removed by filtration. Concentration of the filtrate yielded the crude trienes.

12,13-Didehydrosqualene (= (6E,10E,12E/Z,14E,18E)-2,6,10,15,19,23-Hexamethyl-2,6,10,12,14,18,22-tetracosaheptaene; **1**) [1] was prepared from *trans,trans*-farnesal (**6**) and *trans,trans*-farnesyl(triphenyl)phosphonium bromide (**5**) and isolated as a 1:1 (12*E*/*Z*) mixture by chromatography (silica gel, 0.063–0.200 mm; hexane/EtOAc 99:1) in 79% yield.

(6E,8E/Z,10E)-2,6,11,15-Tetramethyl-2,6,8,10,14-hexadecapentaene (**7**) [4] was prepared from geranial and geranyl(triphenyl)phosphonium chloride and isolated as a 1:1 (8*E*/*Z*) mixture by bulb-to-bulb distillation (135° (max. oven temp.)/0.5 Torr) in 95% yield.

(4E/Z,6E)-2,7,11-Trimethyl-2,4,6,10-dodecatetraene (**8**) was prepared from geranial and (3-methylbut-2-enyl)triphenylphosphonium bromide [5] and isolated as a 1:1 (4*E*/*Z*) mixture by bulb-to-bulb distillation (150° (max. oven temp.)/0.5 Torr) in 96% yield.

4. *Data for* **1**. UV (pentane): 276 (35000), 286 (47000), 298 (38000). IR (neat): 2960, 2920, 2850, 1640, 1440, 1380, 1370, 960, 760. ^{1}H-NMR (CDCl$_3$, 300 MHz): 1.61 (br. *s*, 9 H); 1.62 (*m*, 3 H); 1.68 (br. *s*, 6 H); 1.78 (*m*, 6 H); 1.96–2.18 (*m*, 16 H); 5.08–5.18 (*m*, 4 H); 5.90–5.94 (*m*, 1 H); 6.06–6.16 (*m*, 1 H); 6.26–6.40 (*m*, 2H). MS: 410 (0.4, $M^{+\cdot}$+2), 409 (2.9, $M^{+\cdot}$+1), 408 (9.1, $M^{+\cdot}$), 272 (5.3), 271 (24.0), 137 (19.1), 119 (11.6), 95 (9.5), 81 (53.2), 69 (100).

5. *Data for* **7**. UV (hexane): 275 (42000), 285 (53000), 296 (39000). IR (neat): 2960, 2920, 2860, 1640, 1445, 1375, 960, 765. ^{1}H-NMR (CDCl$_3$, 300 MHz): 1.61–1.62 (*m*, 6 H); 1.68 (br. *s*, 6 H); 1.77 (*m*, 6 H); 2.09–2.13 (*m*, 4 H); 5.09–5.12 (*m*, 2 H); 5.89–5.92 (*m*, 1 H); 6.08–6.12 (*m*, 1 H); 6.28–6.35 (*m*, 2 H). MS: 273 (1.6, $M^{+\cdot}$+1), 272 (6.7, $M^{+\cdot}$), 203 (19.8), 147 (11.1), 135 (5.3), 133 (6.9), 121 (10.7), 119 (14.1), 109 (14.8), 105 (13.8), 93 (13.0), 91 (10.4), 81 (16.0), 69 (100).

6. *Data for* **8**. UV (hexane): 271 (40000), 282 (51000), 293 (38000). IR (neat): 2960, 2910, 2850, 1640, 1445, 1375, 950, 760. ^{1}H-NMR (CDCl$_3$, 300 MHz): 1.61–1.62 (*m*, 3 H); 1.69 (br. *s*, 3 H); 1.77 (*m*, 3 H); 1.79 (br. *s*, 1.5 H); 1.84 (br. *s*, 1.5 H); 2.0–2.3 (*m*, 4 H); 5.10–5.13 (*m*, 1 H); 5.88–5.92 (*m*, 1 H); 6.07–6.10 (*m*, 1 H); 6.28–6.33 (*m*, 2 H). MS: 205 (4.6, $M^{+\cdot}$+1), 204 (26.4, $M^{+\cdot}$), 135 (100), 69 (38).

7. *General Procedure for the Photolysis of Trienes* **1**, **7**, *and* **8**. The concentration of the triene in UV spectroscopic-grade hexane (*Fluka*) varied from 10^{-4} to 10^{-2}M. N$_2$ was bubbled through the mixture in a standard photochemical immersion unit [10] for 10 min, before the irradiation was started. At r.t., the mixture was irradiated through *Pyrex* with a 125-W medium-pressure Hg lamp, as N$_2$ was bubbled slowly through the mixture (monitoring by GC). After complete disappearance of all triene isomers, the mixture was evaporated. The crude product was chromatographed (silica gel, 0.063–0.200 mm; hexane/EtOAc 99:1) to yield the bicyclooctene(s). This purification removed unidentified compounds appearing at the base line of a TLC upon elution with hexane/EtOAc 99:1.

3,7-Dimethyl-7-(4-methyl-3-pentenyl)-8-(2,6,10-trimethyl-1,5,9-undecatrienyl)bicyclo[4.2.0]oct-2-enes (**3**) were separated by flash chromatography [3] (AgNO$_3$-impregnated (10% *w/w*) silica gel; gradient: 0.5–17% of Et$_2$O in hexane/benzene 1:1). *8-(2,6-Dimethyl-1,5-heptadienyl)-3,7,7-trimethylbicyclo[4.2.0]oct-2-enes* (**9**) were separated by the same procedure (gradient: 0.25–3% of Et$_2$O in *hexane/benzene* 1:1). *3,7,7-Trimethyl-8-(2-methyl-1-propenyl)bicyclo[4.2.0]oct-2-ene* (**10**) was also further purified by this procedure (0.25% of Et$_2$O in hexane/benzene 1:1).

8. *Data for* **3b**. UV (hexane): end absorption 210. IR (neat): 2960, 2920, 2850, 1445, 1370. ^{1}H-NMR (CDCl$_3$, 300 MHz): 0.94 (*s*, 3 H); 1.39 (*ddd*, J = 6.0, 11.0, 13.5, 1 H); 1.48–1.76 (*m*, 2 H); 1.60 (*m*, 9 H); 1.66 (br. *s*, 3 H); 1.68 (*m*, 3 H); 1.70 (*m*, 6 H); 1.80–2.12 (*m*, 14 H); 2.42 (*m*, 1 H); 2.59 (*dd*, J = 9.5, 9.5, 1 H); 5.09 (*tm*, J = 7.0, 1.4, 1 H); 5.12 (*m*, 1 H); 5.15 (*tm*, J = 7.2, 1.4, 1 H); 5.20 (*dm*, J = 9.8, 1.3, 1 H); 5.38 (*m*, 1 H). MS: 408 (0.3, $M^{+\cdot}$), 314 (13.5), 271 (1.3), 245 (6.0), 177 (15.3), 137 (5.6), 135 (8.0), 121 (22.0), 109 (15.7), 107 (13.6), 95 (14.6), 93 (13.7), 81 (25.0), 69 (100).

9. *Data for* **3c**. UV (hexane): end absorption 210. IR (neat): 2960, 2920, 2850, 1445, 1370. ^{1}H-NMR (CDCl$_3$, 300 MHz): 0.95 (*s*, 3 H); 1.36 (*ddd*, J = 6.5, 10.5, 13.5, 1 H); 1.46–1.77 (*m*, 2 H); 1.58 (*m*, 3 H); 1.60 (br. *s*, 9 H); 1.68 (*m*, 9 H); 1.81–2.15 (*m*, 14 H); 2.43 (*m*, 1 H); 2.59 (*dd*, J = 9.3, 9.3, 1 H); 5.11 (*m*, 1 H); 5.12 (*m*, 1 H); 5.14 (*m*, 1 H); 5.19 (*dm*, J = 9.2, 1.1, 1 H); 5.39 (*m*, 1 H). MS: 408 (0.3, $M^{+\cdot}$), 314 (12.0), 271 (1.3), 245 (3.5), 177 (29.5), 137 (7.7), 135 (6.2), 121 (22.9), 109 (9.7), 107 (14.9), 95 (14.4), 93 (13.8), 81 (29.9), 69 (100).

10. *Data for* **3d** sample containing 82% **3d** and minor amounts of **3a** and **3c** (GC). UV (hexane): end absorption 210. IR (neat): 2960, 2910, 1445, 1370. ^{1}H-NMR (CDCl$_3$, 300 MHz): 0.84 (*s*, 3 H); 1.3–1.8 (*m*, 3 H); 1.57 (*m*, 3 H); 1.60 (br. *s*, 9 H), 1.69 (*m*, 9 H); 1.80–2.16 (*m*, 14 H); 2.81 (*dd*, J = 9, 9, 1 H); 2.88 (*m*, 1 H); 5.06–5.18 (*m*, 3 H); 5.29 (*dm*, J = 9, 1, 1 H); 5.32 (*m*, 1 H). MS: 408 (0.5, $M^{+\cdot}$), 339 (0.3), 314 (7.3), 271 (1.6), 245 (3.4), 177 (18.3), 137 (8.0), 135 (6.7), 121 (16.3), 109 (13.3), 107 (12.8), 95 (15.4), 93 (15.0), 81 (30.5), 69 (100).

11. *Partial Data for* **3a**. ^{1}H-NMR (CDCl$_3$, 300 MHz): 0.94 (*s*, 3 H); 2.42 (*dd*, J = 9.5, 9.5, 1 H).

12. *Data for* **9a**. ^{1}H-NMR (CDCl$_3$, 300 MHz): 0.91 (*s*, 3 H); 1.05 (*s*, 3 H); 1.5–2.1 (*m*, 9 H); 1.61 (*m*, 3 H); 1.66 (*m*, 3 H); 1.68 (br. *s*, 3 H); 1.71 (*m*, 3 H); 2.41 (*m*, 1 H); 2.56 (*dd*, J = 9.5, 9.5, 1 H); 5.11 (*m*, 1 H); 5.17 (*dm*, J = 9.7, 1.3, 1 H); 5.39 (*m*, 1 H). MS: 203 (1.3), 179 (3.3), 178 (23.6), 110 (9.6), 109 (100), 94 (5.3), 69 (17.5).

13. *Data for* **9c**. ^{1}H-NMR (CDCl$_3$, 300 MHz): 0.82 (*s*, 3 H); 1.18 (*s*, 3 H); 1.50–2.15 (*m*, 9 H); 1.55 (*m*, 3 H); 1.61 (br. *s*, 3 H); 1.68 (br. *s*, 3 H); 1.70 (br. *s*, 3 H); 2.80 (*ddd*, J = 9.2, 9.2, 1.0, 1 H); 2.92 (*m*, 1 H); 5.10 (*tm*, J = 6, 1, 1 H); 5.29 (*dm*, J = 9.4, 1.3, 1 H); 5.31 (*m*, 1 H). MS: 272 (0.2, $M^{+\cdot}$), 203 (0.8), 178 (13.9), 110 (9.2), 109 (100), 94 (3.8), 69 (18.1).

14. *Data for* **9d** (4:1 mixture **9d**/**9b** (GC)). UV (hexane): end absorption 210. ^{1}H-NMR (CDCl$_3$, 300 MHz): 0.92 (*s*, 3 H); 1.03 (*s*, 3 H); 1.5–2.15 (*m*, 9 H); 1.58 (*m*, 3 H); 1.61 (br. *s*, 3 H); 1.68 (*m*, 3 H); 1.69 (*m*, 3 H); 2.42 (*m*, 1 H); 2.57 (*dd*, J = 9.2, 9.2, 1 H); 5.10 (*tm*, J = 6.8, 1.4, 1 H); 5.15 (*dm*, J = 9.1, 1.2, 1 H); 5.40 (*m*, 1 H). MS: 272 (0,1, $M^{+\cdot}$), 203 (0.6), 178 (21.2), 110 (9.1), 109 (100), 94 (4.1), 69 (12.7).

15. *Partial Data for* **9b**. ^{1}H-NMR (CDCl$_3$, 300 MHz): 0.84 (*s*, 3 H); 1.15 (*s*, 3 H); 2.82 (*m*, 1 H); 2.90 (*m*, 1 H); 5.28 (*m*, 1 H); 5.33 (*m*, 1 H).

16. *Data for* **9** (mixture of 4 isomers). UV (hexane): end absorption 210. IR (neat): 2920, 1655, 1445, 1375.

17. *Data for* **10**. UV (hexane): end absorption 210. IR (neat): 2920, 1665*w*, 1445, 1370. ^{1}H-NMR (CDCl$_3$, 300 MHz): 0.93 (*s*, 3 H); 1.04 (*s*, 3 H); 1.59 (*m*, 3 H); 1.60–1.89 (*m*, 2 H); 1.68 (*m*, 3 H); 1.72 (*m*, 3 H); 1.77 (*m*, 1 H); 1.86 (br. *s*, 2 H); 2.42 (*m*, 1 H); 2.56 (*dd*, J = 9.2, 9.2, 1 H); 5.16 (*dm*, J = 9.2, 1.4, 1 H); 5.40 (*m*, 1 H). ^{13}C-NMR (CDCl$_3$): 135.4, 132.5, 125.4, 123.5, 49.0, 39.8, 38.6, 37.4, 28.5, 25.9, 24.9, 24.2, 24.0, 23.2, 18.5. MS: 204 (0.6, $M^{+\cdot}$), 135 (6.5), 111 (9.4), 110 (100), 95 (37.2), 94 (10.2), 93 (9.3), 69 (5.8).

18. *NOE Experiments with* **10**. Irradiation at 0.93 (*s*, CH$_3$–C(7))→NOE at 1.59 (*m*, CH$_3$–C(2')), 1.60–1.76 (*m*, H–C(5)), and 2.56 (*dd*, J = 9.2, 9.2, H–C(8)). Irradiation at 1.04 (*s*, CH$_3$–C(7))→NOE at 1.72–1.82 (*m*, H–C(6)), 2.42 (*m*, H–C(1)), and 5.16 (*dm*, J = 9.2, 1.4, H–C(1')). Irradiation at 2.42 (*m*, H–C(1))→NOE at 1.04 (*s*, CH$_3$–C(7)), 1.72–1.82 (*m*, H–C(6)), 5.16 (*dm*, J = 9.2, 1.4, H–C(1')), and 5.40 (*m*, H–C(2)). Irradiation at 2.56 (*dd*, J = 9.2, 9.2, H–C(8))→NOE at 1.59 (*m*, CH$_3$–C(2')), 5.16 (*dm*, J = 9.2, 1.4, H–C(1')), and 5.40 (*m*, H–C(2)).

19. *Preparation of AgNO$_3$-Impregnated (10%) Silica Gel.* AgNO$_3$ (5 g) was dissolved in MeCN [11] (150 ml) in a tared flask. Silica gel (0.040–0.063 mm, 50 g) was added and the MeCN removed from the slurry by means of a rotary evaporator. After 4–5 h on the rotary evaporator, free flowing AgNO$_3$-impregnated silica gel (55 g) was obtained.

20. *GC Conditions.* For the separation of each **7**–**10**: Wide bore capillary column containing immobilized *PS 255* (15 m × 0.6 mm, 1.5μ film thickness), H_2 as carrier gas, 0.15 kg/cm^2 of pressure at the head of the column, flow rate of 9 ml/min, on-column injection, isothermal operation at 110 to 190°.

For the separation of **1** and **3**: Capillary column containing *SP 2340* on $BaCO_3$ (11.5 m × 0.3 mm), H_2 as carrier gas, 0.20 kg/cm^2 of pressure at the head of the column, on-column injection; typical program: initial temp. 65°, temp. allowed to rise 10°/min until it reached 170°, temp. maintained at 170° for 15 min.

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