Novel, intramolecular hydrogen-transfer and cyclo-addition photochemistry of cyclic 1,3-dienes

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With use of one- and two-dimensional NMR spectroscopy and deuterium labelling, the photochemistry of 9-*endo*-hydroxy-9-*exo*-vinyl-bicyclo[4.2.1]nonadiene (**1**) and the 9-*exo*-(11-dimethylvinyl)- (**2**) and 9-*exo*-ethyl- (**3**) analogues has been studied. Irradiation of **1–3** gave novel 8-membered ring systems **4–6** by a light-induced rearrangement process, in which the hydroxyl proton is transferred on one side of the molecule toward one of the termini of the endocyclic diene. This rearrangement process thus involves a formal hydrogen transfer, during which either H^+ or $H^\bullet$ may be transferred to a reactive diene intermediate. Replacement of the hydroxyl proton by deuterium in **1–3**, and ^2H NMR of the corresponding photoproducts, confirmed that the hydrogen translocation occurs intramolecularly. Prolonged irradiation of **4** and **5** results in the formation of pyran products **10** and **11** by an intramolecular photocycloaddition of the triplet excited state of the α,β-unsaturated ketone to 1,3-*cis,cis*-cyclooctadiene, via a stabilized bisallylic biradical intermediate. Conformational studies of the structurally more rigid system **10**, which is derived from **4**, revealed that the hydroxyl proton was transferred on the *endo* side of the molecule.

Key words: intramolecular hydrogen transfer, photochemistry of hydroxy-alkyl-bicyclononadienes, intramolecular photocycloaddition, conformational studies.

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Faisant appel à la spectroscopie RMN en une ou en deux dimensions et au marquage par le deutérium, on a étudié la photochimie du 9-*endo*-hydroxy-9-*exo*-vinyl-bicyclo[4.2.1]nonadiène (**1**) et de ses analogues 9-*exo*-(11-diméthylvinyl)- (**2**) et 9-*exo*-éthyl- (**3**). L'irradiation des composés **1–3** conduit à de nouveaux systèmes cycliques à 8 chaînons (**4–6**) par un processus de transposition induit par la lumière dans lequel le proton hydroxylique est transféré d'un côte de la molécule vers l'une des extrémités du diène endocyclique. Ce réarrangement implique donc un transfert formel d'hydrogène au cours duquel soit un H^+ ou un $H^\bullet$ est transféré vers un intermédiaire diénique réactif. Le remplacement du proton hydroxylique des composés **1–3** par du deutérium et la RMN du ^2H des photoproduits correspondants a permis de confirmer que la translocation de l'hydrogène se produit d'une façon intramoléculaire. Une irradiation prolongée des composés **4** et **5** conduit à la formation des pyranes **10** et **11** qui résultent d'une photocycloaddition intramoléculaire de l'état triplet de la cétone α,β-insaturée sur le 1,3-*cis,cis*-cyclooctadiène, par le biais d'un intermédiaire biradicalaire bisallylique stabilisé. Des études conformationnelles du système plus rigide du composé **10** dérivé du produit **4** révèlent que le proton hydroxylique est transféré vers la face *endo* de la molécule.

Mots clés: transfert d'hydrogène intramoléculaire, photochimie d'hydroxy-alkyl-bicyclononadiènes, photocycloaddition intramoléculaire, études conformationnelles.

[Traduit par la rédaction]

Introduction

Photo-excitation of cycloalkenes may result in a substantial apparent increase of molecular basicity, leading in protic media to light-induced protonation of the olefin. On direct and sensitized irradiation in methanol, cyclohexenes, cycloheptenes, and cyclooctenes show initial *cis/trans* isomerization followed by protonation of the resulting highly strained isomers (1–5). This process is facilitated by the concomitant relief of strain in this intermediate (6). In striking constrast, cyclopentenes do not undergo photoprotonation on direct irradiation in methanol (7), but afford a mixture of products as a result of trapping a radical-cation intermediate. Such a radical cation may be the result of an electron ejection from a Rydberg excited state, rather than a ($\pi\pi^*$) state (8–10). On sensitized irradiation, cyclopentenes and other highly constrained cyclic olefins exhibit reactions involving radical intermediates, which probably originate from intermolecular reactions by the ($\pi\pi^*$) excited state itself (5, 11). This behaviour is thought to be associated with the inability of these olefins to undergo *cis/trans* isomerization. Although photoprotonation of cycloalkenes in protic media is thus well documented, the photochemistry of compounds combining such chromophores and suitably positioned hydroxyl groups enjoyed only limited study (12, 13). Under UV irradiation alcohols add to olefins in two modes: (a) the addition takes place at the hydroxyl group or (b) the addition takes place at the carbon atom to which the hydroxyl group is attached.

In the present paper we describe a photochemical study of 9-*endo*-hydroxy-9-*exo*-vinyl-bicylo[4.2.1]nona-2,4-diene (**1**), and the 9-*exo*-(2′-methylpropenyl)- (**2**) and 9-*exo*-ethyl- (**3**) analogues. We have studied the photochemistry of these compounds partly on the basis of deuterium labelling experiments. The structural and conformational properties of the isolated photoproducts were investigated with one- and two-dimensional NMR techniques, low temperature ^{13}C NMR, and semi-empirical AM1 quantum-chemical calculations.

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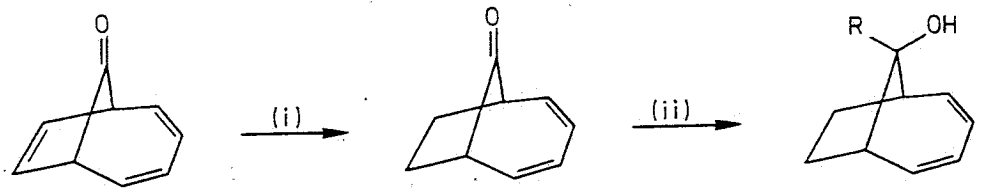


1 R = $-CH=CH_2$

2 R = $-CH=C(CH_3)_2$

3 R = $-CH_2CH_3$

SCHEME 1. (i) H_2/Ni_2B, see refs. 15–17; (ii) (a) RMgBr in THF, (b) H^+.

Results and discussion

Synthesis, purification, and identification

Compounds **1–3** were prepared in two steps from bicyclo-[4.2.1]nona-2,4,7-triene-9-one (Scheme 1) (14). The first step involves selective hydrogenation of the C(7)—C(8) bond, using Ni_2B as a catalyst (15–17). The product, bicyclo[4.2.1]nona-2,4-diene-9-one, was obtained in pure form after silica gel column chromatography. The second step in the synthesis of **1–3** is a Grignard reaction with vinyl-, 2,2-dimethylvinyl-, or ethylmagnesium bromide, respectively. It should be noted that this reaction affords the 9-*endo*-hydroxy epimers exclusively (18, 19). Compounds **1–3** were purified by silica gel column chromatography; their identity and purity were assessed by one- and two-dimensional ^1H NMR (COSY), ^{13}C NMR (including INEPTP), and two-dimensional $^1H/^{13}C$ correlation (for a survey of these techniques see ref. 20), and mass spectrometry. All photoproducts were isolated via preparative HPLC separation of the crude reaction mixtures. Molecular structures could be unequivocally established by the above-mentioned methods.

Photochemistry

UV irradiation of compounds **1–3** in *n*-hexane led to the formation of the novel 8-membered ring systems **4–6**, resulting from a new intramolecular formal hydrogen-transfer reaction (Scheme 2). Simultaneously, the expected products of a disrotatory electrocyclic ring closure reaction **7–9** were formed. Prolonged irradiation of photoproducts **4** and **5** led to the strained pyran structures **10** and **11** (Scheme 3).

In studying the photochemistry of **1–3**, we monitored the kinetics of formation and disappearance of materials at different photolysis time intervals (GC analysis). The results for the irradiation of **1** are presented in Fig. 1. Our data clearly show that **1** is initially converted to **4** and **7**; compound **10** is formed from **4** in a secondary photoreaction.

Analogously, irradiation of compound **2** initially produces **5** and **8**, and compound **5** is converted to **11** upon prolonged irradiation. The experiments with compound **3** merely showed formation of **6** and **9**, i.e., compound **6** does not show the secondary photoreaction.

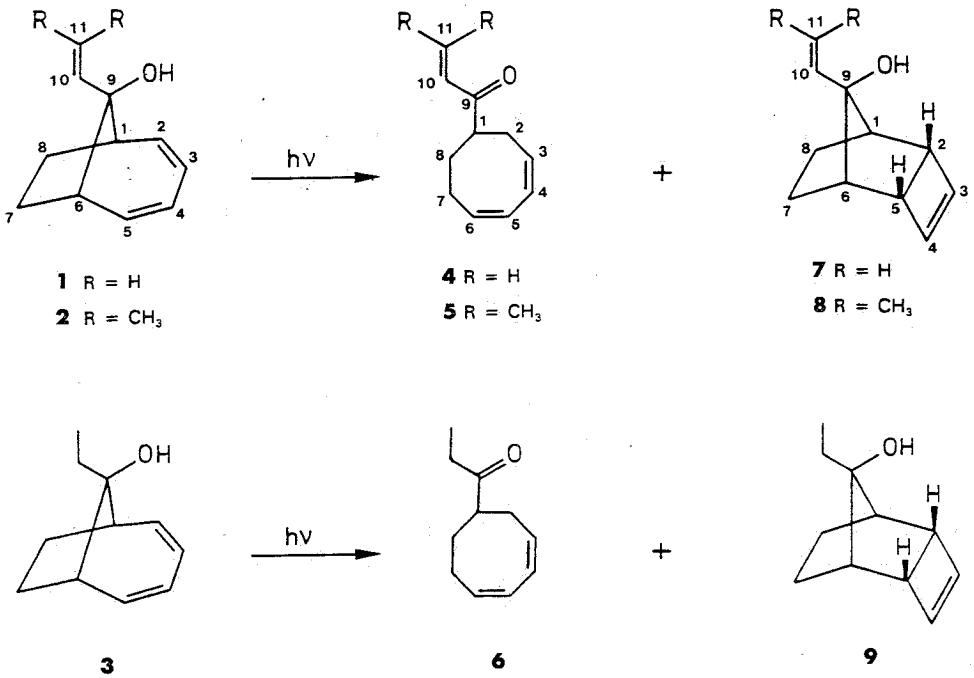
Verification of the stereochemistry of these reactions could be obtained with compound **1***a* (Scheme 4). Transfer of deuterium toward C(2) was evident from the ^1H and ^{13}C NMR spectra of **4***a*. The ^2H NMR spectrum of **4***a*, recorded at 77 MHz, showed a singlet signal at δ 2.3 ppm, exactly at the position of one of the H(2) protons in compound **4** (compare Figs. 2a and 2b). This demonstrates that the transfer of deuterium occurs at one face of the molecule exclusively.

The light-induced conversions **1**→**4**, **2**→**5**, and **3**→**6** may be formulated as proceeding via an initial photoprotonation process followed by a collapse of the resulting carbocation intermediate (cf. the photofragmentation of homoallylic alcohols (7, 21, 22)). Such a photoprotonation process, concomitant with the breaking of one of the bridgehead bonds, would be in line with the involvement of an olefinic intermediate exhibiting enhanced reactivity (6, 7). However, at present the exact nature of this intermediate cannot be defined and transfer of the hydroxylic hydrogen in the form of $H^\bullet$ or even H^- cannot be excluded. Even the cyclic reorganization of electrons (as shown in Fig. 3) involved in the overall reaction may be formulated as an 8-electron analogue of an oxy-retro-ene reaction (23).[2]

Concerning the stereochemistry, we could not establish *exo* or *endo* orientation of deuterium in **4***a*, since the conformational flexibility of the 8-membered ring precludes the application of Karplus-type equations to translate the vicinal proton–proton *J*-coupling constants into proton–proton dihedral angles (24). However, for the structurally more rigid system **10***a*, which is derived from **4***a* (Scheme 4), it could be unequivocally established that deuterium is located on the *endo* face of **10***a* and hence also on the *endo* face of **4***a* (see section of conformational studies). Additional evidence for the presence of deuterium on C(2) was obtained from a comparison of the ^{13}C NMR spectra of **4** and **4***a*. In **4***a*, the C(2) signal is split into three lines of equal intensity and $J = 19.4$ Hz due to one-band *J*-coupling with deuterium ($I = 1$). Interestingly, a small signal is also visible at δ 1.6 ppm in the ^2H NMR spectrum of **4***a*. The small peak is found exactly at the position of one of the H(8) protons in compound **4** (compare Figs. 3a and 3b). The explanation for the appearance of the small peak in Fig. 3b may lie in the occurrence of a thermal suprafacial [1,5]-H sigmatropic shift, occurring during the thermal isomerization of *cis,trans*-cyclooctadiene (COD) to *cis,cis*-COD, according to Scheme 5 (25, 26). Evidently this [1,5]-H shift would place deuterium in an isochronous position in the ^2H NMR spectrum, when compared with the *endo*-located H(8) in compound **4**.

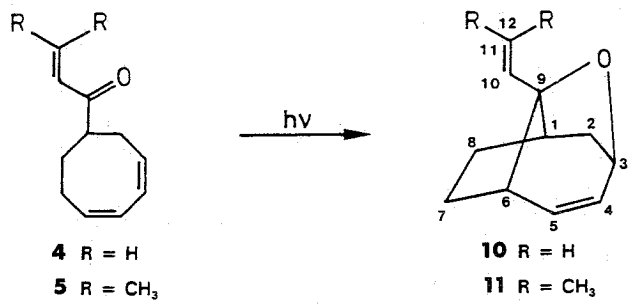
Of course, the occurrence of this [1,5]-H shift is not detectable from the ^1H and ^{13}C NMR spectra of compound **4**. It may be noted that the UV irradiation of **1** and **2** does not induce a sigmatropic [1,3]-OH shift in the head group. In fact, we anticipated that this reaction could occur, in analogy with the previous work of our group on the photochemistry of 8-hydroxygermacrene B (12) and 4-methyl, 4-ethyl disubstituted 3-alkylidene 2-naphthalenol compounds (13, 27). For these

[2]We wish to thank one of the reviewers for suggesting this possible explanation.



1 R = H
2 R = CH_3
4 R = H
5 R = CH_3
7 R = H
8 R = CH_3
3
6
9

SCHEME 2



4 R = H
5 R = CH_3
10 R = H
11 R = CH_3

SCHEME 3

systems, the occurrence of a planar photochemical [1,3]-OH shift was firmly established on the basis of experimental and theoretical data (27–29).

The 8-membered ring systems **4** and **5** are converted into the strained pyrans **10** and **11** in a secondary photoreaction (in ≈16 and 6% yields respectively). To the best of our knowledge, this reaction represents a novel photocycloaddition, which is reminiscent of the Paterno–Buchi reaction of ketones with alkenes, leading to the formation of oxetanes (30, 31). These reactions generally proceed from an attack of an (n,π^*) state of the carbonyl compound on an unsaturated substrate. In general, photocycloadditions of (n,π^*) states are expected to proceed via diradical intermediates (32, 33). These intermediates are produced either directly or indirectly from $S_1(n,\pi^*)$ or $T_1(n,\pi^*)$ states in the oxetane formation.

In our system the α,β-unsaturated ketone would have a singlet (n,π^*) state of lower energy than the singlet state of the conjugated *cis,cis*-COD system, while the triplet (n,π^*) state is almost equal to the triplet of the *cis,cis*-COD system. For the saturated ketone, however, the photocycloaddition is absent, and its triplet state is considerably higher than the triplet of the *cis,cis*-COD system. Consequently the triplet of the saturated ketone would be quenched by energy transfer many times faster than the α,β-unsaturated ketones, because of the large exothermicity of the process. For approximate energy levels see Table 1.

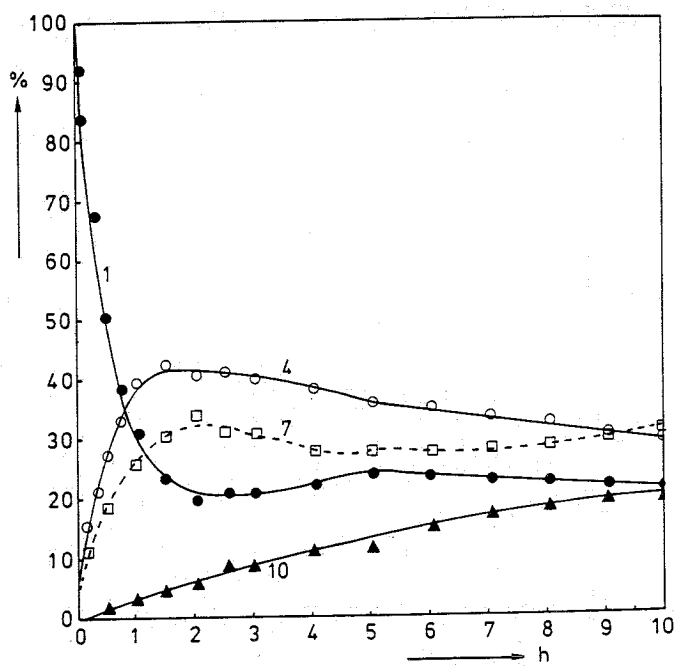


FIG. 1. Plot for conversion (%) of compound **1** to photoproducts **4**, **7**, and **10** as function of time (h).

Energy transfer to the *cis,cis*- or *cis,trans*-COD system results in a photostationary state composition of *cis,cis*- and *cis,trans*-cyclooctadienes (35, 36). It should be noted that the *cis,trans* isomer may isomerize to *cis,cis* either by a *cis/trans* isomerization about the *trans* double bond or by a [1,5]-H shift for the thermal isomerization (25, 26).

Since intersystem crossing (ISC) is very fast in α,β-unsaturated ketones, and singlet processes are normally too slow to compete, a mechanism involving a triplet excited state is

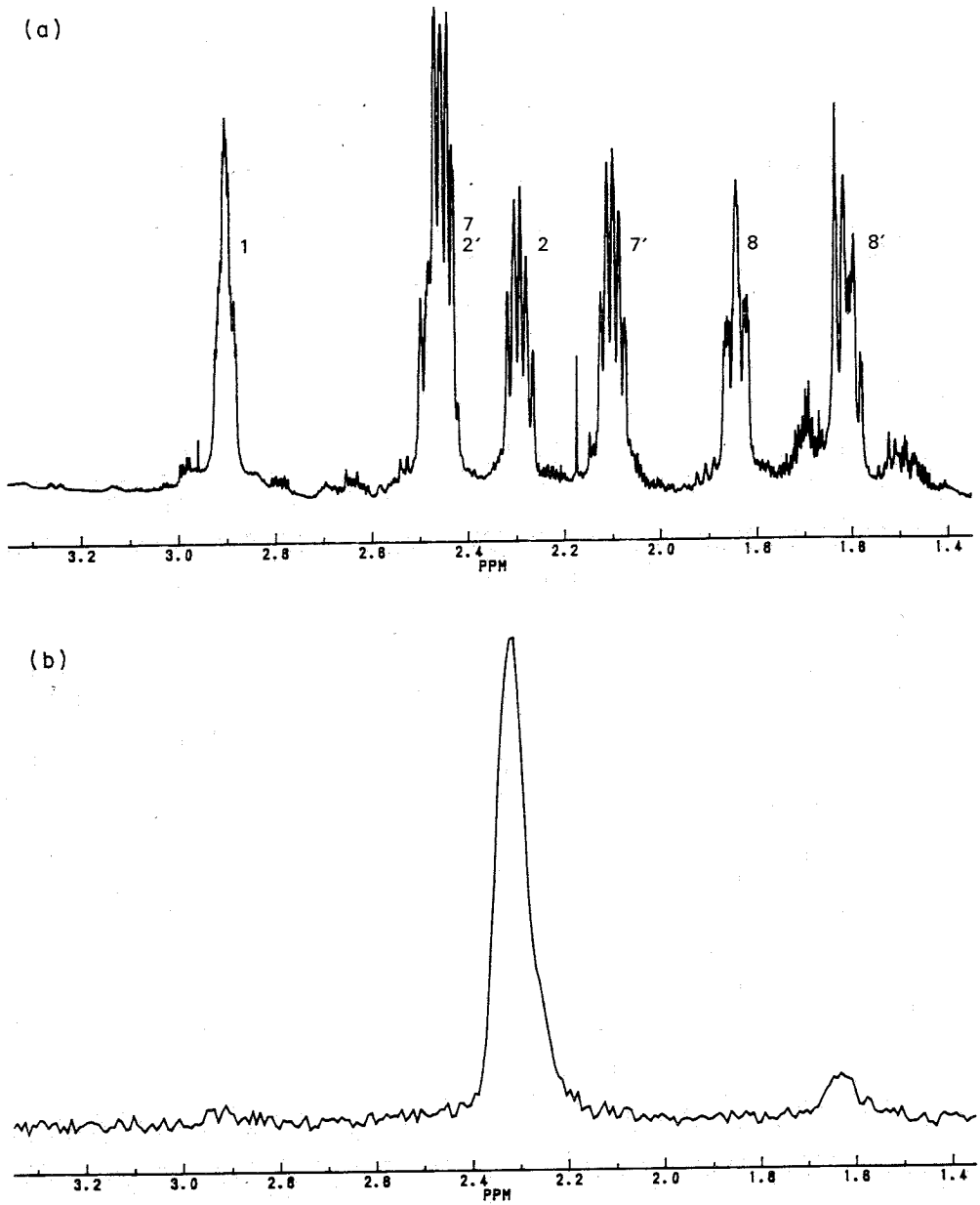
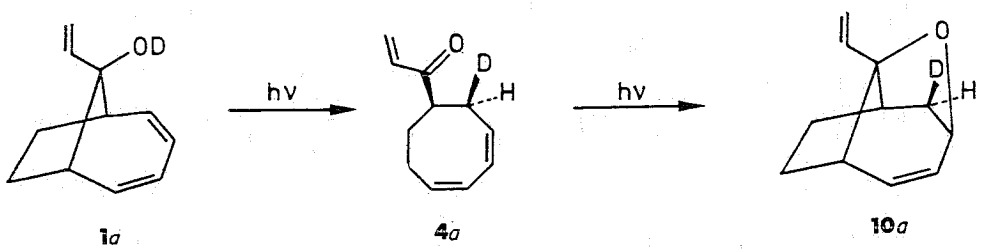


FIG. 2(a). The ^1H NMR (400 MHz) and (b) the ^2H NMR (77 MHz) spectrum of **4***a* in $CDCl_3$. The assignments of protons were obtained from two-dimensional homonuclear NMR spectra (COSY).



SCHEME 4

preferred over a singlet excited process. A mechanism involving the formation of a charge-transfer, stabilized exciplex, leading to a biradical that can collapse to the strained pyrans or undergo radiationless decay to the ground-state molecules, is rather remote for the *cis,cis*-COD system (37, 38). In the oxetane formation of acetone and COD (ISC is slower in this case) the total rate of fluorescence quenching of the ketone is significantly slower than the rate of ISC (38). Therefore we consider the pyran formation to occur predominantly from the triplet state of the α,β-unsaturated ketone, and a chemical reaction can indeed compete with the triplet energy transfer to the COD, because of the decrease in diene character of the 8-membered ring. Based on an alkoxy model (39), the intramolecular pyran formation, like intramolecular cycloaddition, is

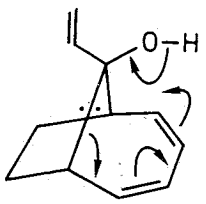
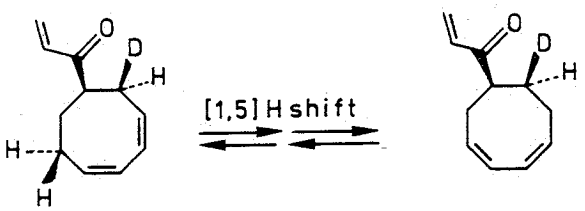


FIG. 3. Schematic representation for the formal hydrogen-transfer reaction.



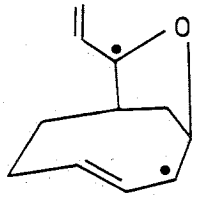
SCHEME 5

TABLE 1. Approximate singlet and triplet energy levels

Compound	S_1 (kcal/mol)	T_1 (kcal/mol)
α,β-Unsaturated ketone[a]	74	70
Saturated ketone[a]	84	78
cis,cis-Cyclooctadiene[b]	>80	70–73
cis,trans-Cyclooctadiene[b]	—	<70

[a]Data obtained from N. J. Turro (34).
[b]Data obtained from R. S. H. Liu (in ref. 36).

expected to obey a "rule of five" (40), involving the stabilized diradicaloid intermediate:

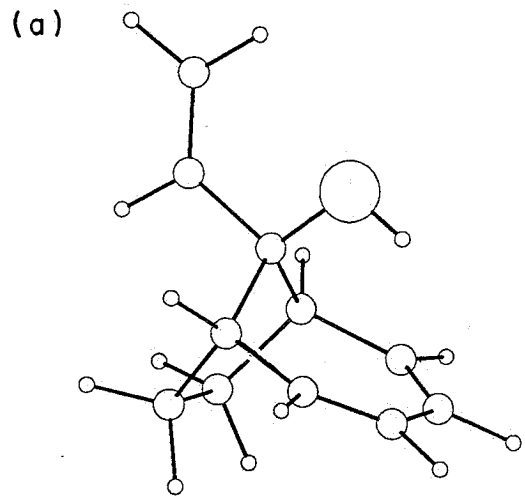


The formation of photoproducts **7–9** involves a ring closure of the endocylic dienes in **1–3**. As can be seen in Fig. 1, the photoprotonation reaction and the ring closure occur with approximately equal probability during the irradiation of **1**. Similar results were obtained for **2** and **3**. The photochemical ring closure of **1–3** follows a disrotatory route, as predicted by the Woodward and Hoffmann rules (41). The *endo* orientation of the protons H(2) and H(5) was established on the basis of the NMR spin–spin coupling constant $J_{H(1)-H(2)}$, and comparison with literature data (42).

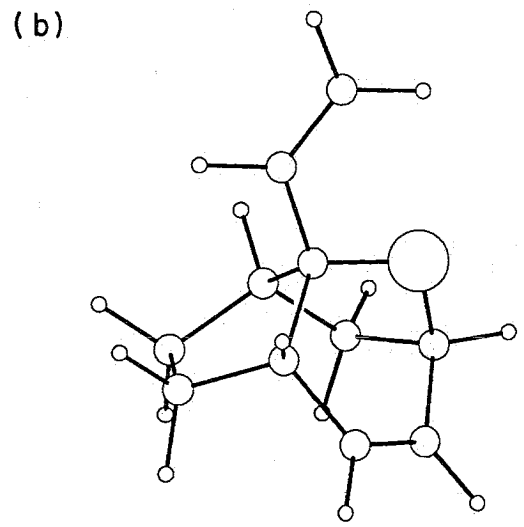
Conformational studies

The ^{1}H NMR spectrum of the compounds **1–3** in the ground state showed a long-range spin–spin coupling between H(10) and the hydroxyl proton ($^4J_{HCCOH} \approx 1.5$ Hz). This reveals that the coupling path is in all-*trans* ("W") conformation, i.e., the OH group resides in the plane of C(9), C(10), and C(11). The C(10)—C(11) double bond in **1** and **2** is therefore approximately orthogonal with respect to the endocyclic diene system. The conformational properties of **1–3** were investigated further on the basis of semi-empirical MO calculations. Dreiding models of **1–3** provided initial starting conformations. The geometries of **1–3** were optimized using the AM1 Hamiltonian of the AMPAC program (43, 44). The optimized conformations of **1–3** showed *trans* conformation of the coupling path H-O-C(9)-C(10)-H(10) in the head group (Fig. 4a).

Inspection of the AM1-optimized conformation of **1** confirms that the hydroxyl proton is proximate to C(2) ($r_{OH-proton-C(2)} = 2.52$ Å). Essentially the same conformation was found in the AM1 calculation on structures **2** and **3**. (The AM1 calculations on **1–3**, **10**, and **11** resulted in the following enthalpies of formation (ΔH_f): ΔH_f(**1**) = −2.78 kcal/mol, ΔH_f(**2**) = −17.80 kcal/mol, ΔH_f(**3**) = −34.67 kcal/mol, ΔH_f(**10**) = −8.03 kcal/mol, ΔH_f(**11**) = −23.47 kcal/mol.)



1



10

FIG. 4(a). Optimized conformation of **1** studied with AM1 calculation method showing *trans* conformation of the coupling path in the head group (ΔH_f = −2.78 kcal/mol). (b) Optimized conformation of **10** from which proton–proton torsion angles for the Karplus relations have been extracted (ΔH_f = −8.03 kcal/mol).

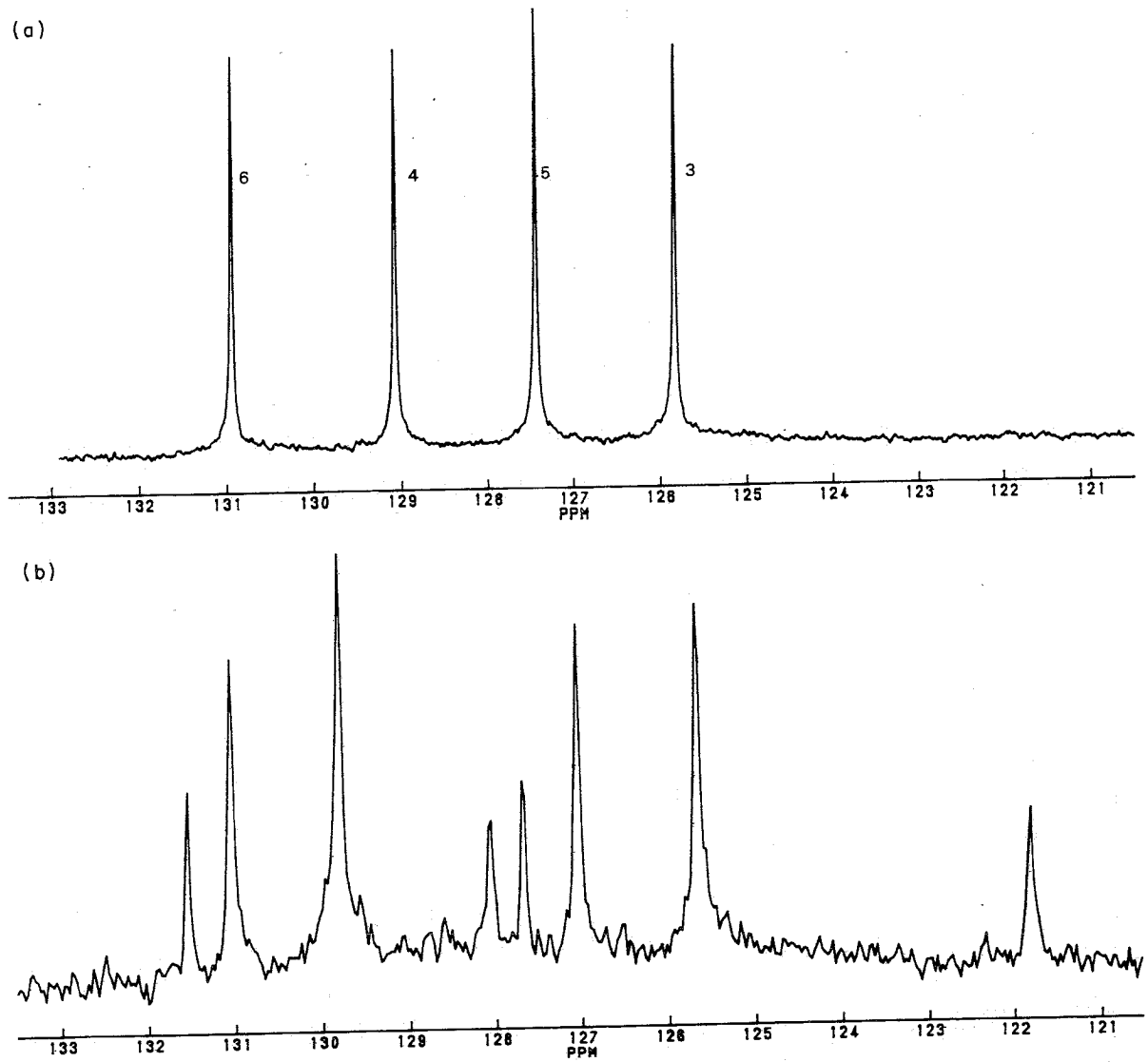


FIG. 5.(a). Olefinic region of the ^{13}C NMR spectrum in of **6** at 20°C (100 MHz, solvent CD_2Cl_2). The assignments are based on a ^{13}C–^{1}H correlation experiment. (b) Decoalescence in the olefinic region of ^{13}C NMR spectrum of **6** at −90°C (100 MHz, solvent CD_2Cl_2). Clearly, two distinct molecular conformations are present in a ratio of approximately 1:2 at this temperature. These observations closely resemble the data of Anet *et al.* on *cis,cis*-cyclooctadiene, and *cis,cis*-cyclooctadiene mono-epoxide (refs. 45–47).

The conformational properties of the 8-membered ring compounds **4–6** are more difficult to characterize, since there is no obvious starting geometry for the AM1 calculations. Rather it must be expected from the work of Anet and Yavari on *cis,cis*-1,3-cyclooctadiene and *cis,cis*-cyclooctadiene mono-epoxide (45–47) that compounds **4–6** are involved in a complex conformational equilibrium. We obtained convincing evidence for the flexible nature of compounds **4–6** from variable-temperature ^{13}C NMR measurements. Upon lowering the sample temperature from 20 to −90°C in CD_2Cl_2 we observed decoalescence phenomena for **4–6**. As a typical example, Figs. 5a and 5b show the olefinic regions in the ^{13}C NMR spectra of compound **6**, as measured at 20°C and −90°C.

The observation of two sets of ^{13}C NMR peaks at −90°C clearly shows that at least two distinct conformations coexist at this temperature. It should be noted that our ^{13}C NMR spectral data on compounds **4–6** closely resemble the data of Anet and Yavari on *cis,cis*-1,3-cyclooctadiene and *cis,cis*-cyclooctadiene mono-epoxide (45–47). The conformational properties of the strained pyrans **10** and **11** were again studied with the AM1 calculation method. Starting geometries were obtained from Dreiding molecular models. In the optimized conformation of **10** (Fig. 4b) we especially focused on the proton–proton torsion angles Φ_1 (H(1)-C(1)—C(2)-H(2)) = −2.2°; Φ_2 (H(1)-C(1)—C(2)-H(2′)) = 119.2°; Φ_3 (H(3)-C(3)—C(2)-H(2)) = −23.6°; Φ_4 (H(3)-C(3)—C(2)-H(2′)) = 96.4°. Thus, from a simple Karplus dependency of $^{3}J_{HH}$ on the proton–proton torsion angle (24), one expects that $^{3}J_{H(1)-H(2,endo)}$ and $^{3}J_{H(3)-H(2,endo)}$ are substantially larger than $^{3}J_{H(1)-H(2',exo)}$ and $^{3}J_{H(3)-H(2',exo)}$. Interestingly, these tentative conclusions are in line with the experimental ^{1}H NMR data on compound **10**, which show that the downfield H(2) proton (δ 2.24 ppm) has relatively large coupling constants with its vicinal neighbours H(1) and H(3) (i.e., 10.1 and 6.2 Hz, respectively, see experimental section), while the upfield H(2) proton (δ 1.63 ppm) shows much smaller $^{3}J_{HH}$ couplings with H(1) and H(3) (i.e., <1 Hz in both cases). Therefore, we tentatively assign the downfield H(2) proton as H(2,*endo*), and the upfield H(2′) proton as H(2′,*exo*). Having

this assignment, it is worthwhile to reexamine the ^{1}H NMR spectrum of the C(2)-deuterated compound **10***a*. Now it seems likely that it is H(2,*endo*) and not H(2′,*exo*) that is replaced by deuterium in **10***a*. Thus the photochemical formal proton transfer reaction **1** → **4** proceeded *exclusively* on the *endo* face of the molecule. We anticipate that this holds also for the analogous photochemical reactions **2** → **5** and **3** → **6**.

Concluding remarks

UV irradiation of compounds **1**–**3** leads to a new photochemical rearrangement process, in which the hydroxyl hydrogen is transferred on the *endo* side of the molecule toward one of the terminals of the endocyclic diene. This reaction is probably driven by the enhanced reactivity of the diene moiety after photo-excitation, leading to a protonation of the olefin. However, the reaction can also be considered as an oxy-retro-ene type reaction. The 8-membered ring structures **4** and **5** are converted relatively slowly to the strained pyrans **10** and **11** in a secondary photoreaction. This reaction is not observed for the ethyl counterpart **6**. Most likely, the reaction of **4** and **5** is a photo-cycloaddition, resembling the Paterno–Buchi reaction. We believe that the reaction develops from the T_1 excited state of the α,β-unsaturated ketone, leading to the strained pyran products, which may arise from a bisallylic radical intermediate.

Experimental

General procedures

All solvents and commercial reagents were reagent grade and dried with the appropriate drying agents. Argon was dried over Drierite pellets. Column chromatography was performed using Silica-60 as the stationary phase. Proton, deuterium, and carbon-13 NMR spectra were recorded on a Bruker AM400[3] or a Bruker AM600[4] spectrometer in $CDCl_3$ solution. Chemical shifts are reported in ppm (δ), relative to tetramethylsilane as an internal standard. Coupling constants (*J*) are given in Hz. GC analyses were performed on a Kipp Analytica 8200 instrument with FID detection (25 m × 0.22 mm i.d.; column type: WCOT fused silica; stationary phase CP WAX 51). All HPLC separations were run on a system that consists of a Waters 6000A pump, a 4 × 100 mm Lichrosorb 60 (5 μm) column, and a Philips Unicam PU4020 UV detector (254 nm). Mass spectral data were obtained on a Hewlett Packard 5970A system by electron ionization at 70 eV.

Synthesis

Bicyclo[4.2.1]nona-2,4-diene-9-one

This compound was prepared via selective hydrogenation of the C(7)—C(8) bond in bicyclo[4.2.1]nona-2,4,7-triene-9-one (**14**) (Scheme 3). This reaction is not straightforward, as is evident from the work of Brown (15), Gilissen *et al.* (16,17), and Schuster and Kim (18). We used Ni_2B as hydrogenation catalyst, which was prepared as follows: $Ni(Ac)_2 \cdot 4\ H_2O$ (230 mg, 0.92 mmol) was dissolved under an argon atmosphere with magnetic stirring in 20 mL of ethanol in a 500-mL Erlenmeyer flask. A solution of 33 mg $NaBH_4$ in 20 mL of ethanol was transferred dropwise into the reaction vessel, yielding a black suspension of Ni_2B. Subsequently, bicylo[4.2.1]nona-2,4,7-triene-9-one (1 g, 7.4 mmol) was added, and hydrogen gas was allowed into the flask (atmospheric pressure). Stirring was continued until 170 mL (6.9 mmol) hydrogen gas was absorbed. Ethanol was evaporated, and the residue was dissolved in 100 mL of dry ether. Standard work-up (addition of 50 mL saturated aqueous $NaHCO_3$, filtration, and repeated washing of the aqueous phase with ether) yielded a mixture of the desired diene, and the starting compound (ratio ≈ 5:1), which was chromatographed on a silica gel column using CH_2Cl_2 as eluent (R_f diene = 0.43; R_f triene = 0.49). This afforded 460 mg of the desired product (yield 45%). ^{1}H NMR ($CDCl_3$) δ: 5.58–5.96 (4H, m, H(2–5)), 2.69–2.87 (2H, m, H(1,6)), 2.10–2.46 (4H, m, H(7,8)). ^{13}C NMR ($CDCl_3$) δ: 216.44 (s, C(9)), 129.55 (d, C(2,5)), 126.12 (d, C(3,4)), 50.35 (d, C(1,6)). 34.55 (t, C(7,8)). EI-MS; 134 (m^+), 106, 91, 78 (base peak), 51, 39, 27.

*9-endo-Hydroxy-9-exo-vinyl-bicyclo[4.2.1]nona-2,4-diene (**1**)*

Magnesium turnings (1.27 g, 52.7 mmol) and 15 mL of dry THF were transferred into a 250-mL reaction flask equipped with a reflux cooler (connected with a methanol cryostat (−60°C)), a dropping funnel, and a mechanical stirrer. During the experiment, dry argon was slowly passed through the reaction vessel. Vinyl bromide (0.5 g, 4.7 mmol) and a small iodine crystal were added. After start-up of the reaction, 15 mL of dry THF was added immediately, followed by the main portion of vinyl bromide (6.25 g, 58.3 mmol) in 10 mL of dry THF, over a period of 1 h. After completion of the addition, the mixture was stirred for 1 h, and cooled to 0°C with an ice bath. Bicyclo[4.2.1]-nona-2,4-diene-9-one (1.68 g, 12.5 mmol), dissolved in 15 mL of dry THF, was added dropwise over a period of 1 h. The reaction was allowed to proceed for 6 h at 0°C, and for 14 h at ambient temperature. Then, the reaction was finished through addition of 35 mL of 3 N HCl at 0°C. THF was removed and the residue was mixed with 100 mL of diethyl ether. The organic layer was washed with $NaHCO_3$, dried over $MgSO_4$, and concentrated. Column chromatography using CH_2Cl_2 as eluent afforded 5.19 g of pure **1** (R_f 0.35, yield 91%). ^{1}H NMR ($CDCl_3$) δ: 6.18–6.34 (1H, dd, H(10)), 5.75–6.01 (4H, m, H(2–5)), 5.38–5.49 (1H, dd, H(11, *trans*)), 5.12–5.22 (1H, dd, H(11, *cis*)), 3.07 (1H, d, OH), 2.48–2.58 (2H, m, H(1,6)), 2.02–2.08 (4H, m, H(7,8)). ^{13}C NMR ($CDCl_3$) δ: 142.81 (d, C(10)), 136.13 (d, C(2,5)), 126,14 (d, C(3,4)), 113.88 (t, C(11)), 77.49 (s, C(9)), 49.44 (t, C(1,6)), 38.17 (t, C(7,8)). EI-MS: 147, 115, 107, 95, 91, 79 (base peak), 65, 55, 39, 27.

*9-endo-Hydroxy-9-exo-(2′-methylpropenyl)-bicyclo[4.2.1]nona-2,4-diene (**2**)*

The Grignard reagent was prepared from 1-bromo-2-methylpropene (2.35 g, 17.4 mmol) and magnesium turnings (0.37 g, 15.2 mmol) in 30 mL of dry THF. The reaction was allowed to proceed for 6 h at 40°C. Bicyclo[4.2.1]nona-2,4-diene-9-one (1 g, 7.45 mmol) in 10 mL of dry THF was slowly added in 30 min. The reaction mixture was stirred for 48 h, poured onto crushed ice, and 100 mL 1 N NH_4Cl solution was added. Subsequently, the pH of the solution was lowered to 5, via addition of 1 N HCl solution. Usual work-up procedure and repeated column chromatography, using hexane–dichloromethane (30:70) as eluent, afforded pure **3** (R_f 0.20, yield 0.44 g, 31%). ^{1}H NMR ($CDCl_3$) δ: 5.70–6.11 (4H, m, H(2–5)), 5.45–5.55 (1H, m, H(10)), 2.87–2.88 (1H, d, OH), 2.55–2.72 (2H, m, H(1,6)), 1.95–2.04 (4H, m, H(7,8)), 1.91–1.92 (3H, d, CH_3), 1.77–1.78 (3H, d, CH_3). ^{13}C NMR ($CDCl_3$) δ: 138.21 (s, C(11)), 136.37 (d, C(2,5)), 130.59 (d, C(10)), 125.76 (d, C(3,4)), 76.57 (s, C(9)), 48.58 (d, C(1,6)), 37.92 (t, C(7,8)), 27.83 and 20.60 (q, CH_3). EI-MS: 190 (m^+), 175, 147, 105, 83 (base peak), 55, 41, 39, 29, 27.

*9-endo-Hydroxy-9-exo-ethyl-bicyclo[4.2.1]nona-2,4-diene (**3**)*

The Grignard reagent was prepared from ethyl bromide (1.21 g, 11.1 mmol) and magnesium turnings (0.27 g, 11.1 mmol) in 30 mL of dry diethyl ether. Bicyclo[4.2.1]nona-2,4-diene-9-one (1.36 g, 10.1 mmol), dissolved in 15 mL of dry diethyl ether, was added dropwise in 30 min at 0°C. After completion of the reaction (30 min at 0°C and 90 min at ambient temperature), the suspension was poured onto 30 g of crushed ice. Hydrochloric acid (25 mL of a 1 N solution) was slowly added. Standard work-up and column chromatography with CH_2Cl_2 as eluent yielded 0.92 g (54%) of pure **2** (R_f 0.33). ^{1}H NMR ($CDCl_3$) δ: 5.80–6.05 (4H, m, H(2–5)), 2.84 (1H, s, OH), 2.40–2.55 (2H, m, H(1,6)), 1.95–2.05 (4H, m, H(7,8)), 1.69–1.86 (2H, q, H(10)), 0.92–1.11 (3H, t, H(11)). ^{13}C NMR ($CDCl_3$) δ: 136.45 (d, C(2,5)), 125.71 (d, C(3,4)), 77.44 (s, C(9)), 48.17 (d, C(1,6)), 37.83 (t, C(10)), 32.05 (t, C(7,8)), 9.34 (q, C(11)). EI-MS: 164 (m^+), 135, 117, 107, 91, 79, 65, 57 (base peak), 41, 39, 29.

[3]NMR facility of the Eindhoven University of Technology.

[4]The 600-MHz ^{1}H NMR spectra were recorded on the Bruker AM600 NMR spectrometer of the Dutch National hf NMR facility at Nijmegen, The Netherlands.

TABLE 2. Irradiation of bicyclononadienes[a]

Olefin	Amount (mg)	Time (h)	Yield (%)[b] 1–3	4–6	7–9	10,11
1	460	1.5	22	41	30	4
		10	21	30	30	16
2	440	1.5	23	18	56	—
		8	1	15	73	6
3	460	1.5	16	34	50	0
		10	1	34	65	0

[a]Irradiations were conducted as described in this section using ≈500 mL of *n*-hexane containing ≈3 mmol of olefin.

[b]Yields were determined by gas-chromatographic analysis of aliquots removed periodically from the irradiation mixture.

Irradiation procedure

All photochemical experiments (as shown in Table 2) on **1–3** were performed in ≈500 mL of *n*-hexane (concentration ≈6 mM), which was dried over sodium prior to use.

Irradiations were performed using a 500-W medium Hg lamp (Hanau TQ78) through quartz. Cooling of the lamp and the reaction mixture was accomplished by means of a closed circuit filled with methanol. In this way, the temperature in the reaction vessel was maintained around 0°C. Before and during irradiation, the reaction mixture was purged by a stream of dry argon, to remove all traces of oxygen. All photoreactions were monitored by means of gas chromatography. After irradiation, the solvent was removed on a rotatory evaporator. The reaction mixture was separated by HPLC using CH_2Cl_2/hexane (10:90 or 15:85) as eluent. Isolation of products was continued until sufficient material was obtained for NMR characterization.

Spectral and analytical data of photoproducts

The nomenclature of compounds is according to the IUPAC convention. However, to obtain as much consistency as possible, the numbers in the NMR data were assigned as in Schemes 2 and 3, and may differ from IUPAC convention.

*6-(1'-Oxo-propenyl)-1,3-*cis,cis*-cyclooctadiene (**4**)*

^{1}H NMR ($CDCl_3$) δ: 6.46 (1H, dd, H(10)), 6.26 (1H, dd, H(11, *trans*)), 5.95–5.84 (2H, m, H(4,5), $^3J_{H(4)-H(3)}$ = 11.3 Hz, $^3J_{H(4)-H(5)}$ = 4.28 Hz, $^3J_{H(5)-H(6)}$ = 11.3 Hz), 5.76 (1H, dd, H(11, *cis*)), 5.65 (2H, m, H(3,6), $^3J_{H(3)-H(2)}$ = 7.12 Hz, $^3J_{H(3)-H(2')}$ = 2.5 Hz, $^3J_{H(6)-H(7)}$ = 7.04 Hz, $^3J_{H(6)-H(7')}$ = 2.50 Hz), 2.93 (1H, m, H(1), $^3J_{H(1)-H(2)}$ = 9.13 Hz, $^3J_{H(1)-H(2')}$ = 2.27 Hz, $^3J_{H(1)-H(8)}$ = 4.36 Hz, $^3J_{H(1)-H(8')}$ = 8.86 Hz), 2.48 (1H, m, H(2')), 2.48 (1H, m, H(7) or H(7')), 2.30 (1H, m, H(2), $^2J_{H(2)-H(2')}$ = 15.29 Hz), 2.12 (1H, m, H(7') or H(7)), 1.85 (1H, m, H(8) or H(8')), 1.63 (1H, m, H(8') or H(8)). ^{13}C NMR ($CDCl_3$) δ: 204.50 (s, C(9)), 136.11 (d, C(10)), 132.06 (d, C(3) or C(6)), 130.17 (d, C(6) or C(3)), 129.03 (t, C(11)), 128.64 (d, C(4) or C(5)), 127.15 (d, C(5) or C(4)), 45.48 (d, C(1)), 30.60 (t, C(2)), 27.67 (t, C(7)), 26.75 (t, C(8)). EI-MS: 162 (m^+), 147, 145, 107, 91, 79 (base peak), 55, 41, 39, 27.

*(2-Deutero)-6-(1'-oxo-propenyl)-1,3-*cis,cis*-cyclooctadiene (**4**a)*

^{1}H NMR ($CDCl_3$): identical to **4** except for the H(2) signal at δ = 2.30, which is lacking. ^{2}H NMR ($CDCl_3$) δ: 2.32 (1D, s, D(2)), 1.64 (1D, s, D(2)[5]). ^{13}C NMR ($CDCl_3$); identical to **4** except for the C(2) signal: δ = 30.66 (m, C(2)). EI-MS: 163 (m_D^+), 162 (m_H^+), 148, 147, 107, 91, 79 (base peak), 55, 39, 27.

*6-(3'-Methyl-1'-oxo-but-2'-enyl)-1,3-*cis,cis*-cyclooctadiene (**5**)*

^{1}H NMR ($CDCl_3$) δ: 6.12 (1H, m, H(10)), 5.93–5.80 (2H, m, H(4,5)), 5.64 (2H, m, H(3,6)), 2.58 (1H, m, H(1)), 2.45 (1H, m, H(2')), 2.45 (1H, m, H(7) or H(7')), 2.24 (1H, m, H(2)), 2.14 (3H, d, H(12) or H(13)), 2.07 (1H, m, H(7') or H(7)), 1.90 (3H, d, H(13) or H(12)), 1.83 (1H, m, H(8) or H(8')), 1.57 (1H, m, H(8') or H(8)). ^{13}C NMR ($CDCl_3$) δ: 205.30 (s, C(9)), 156.77 (s, C(11)), 132.18 (d, C(10)), 130.64, 128.35 (d, C(3,6)), 126.99, 124.5 (d, C(4,5)), 48.73 (d, C(1)), 30.66 (t, C(2)), 28.86, 21.85 (q, C(12, 3)), 27.80 (t, C(7)), 26.59 (t, C(8)). EI-MS: 190 (m^+), 175, 147, 83 (base peak), 55, 39.

*6-(1'-Oxo-propyl)-1,3-*cis,cis*-cyclooctadiene (**6**)*

^{1}H NMR ($CDCl_3$) δ: 5.94–5.80 (2H, m, H(4,5)), 5.60 (2H, m, H(3,6)), 2.63 (1H, m, H(1), $^3J_{H(1)-H(2)}$ = 3.87 Hz), 2.49 (2H, q, H(10)), 2.42 (1H, m, H(2')), 2.42 (1H, m, H(7) or H(7')), 2.27 (1H, m, H(2)), 2.08 (1H, m, H(7') or H(7)), 1.85 (1H, m, H(8) or H(8')), 1.60 (1H, m, H(8') or H(8)), 1.06 (3H, t, H(11)). ^{13}C NMR ($CDCl_3$) δ: 215.77 (s, C(9)), 132.08 (d, C(3) or C(6)), 130.21 (d, C(6) or C(3)), 128.62 (d, C(4) or C(5)), 127.01 (d, C(5) or C(4)), 47.91 (d, C(1)), 35.21 (t, C(10)), 30.56 (t, C(2)), 27.87 (t, C(7)), 26.69 (t, C(8)), 9.06 (q, C(11)). EI-MS: 165, 164 (m^+), 146, 135, 107, 91, 79 (base peak), 57, 41, 39, 29.

*9-*endo*-Hydroxy-9-*exo*-vinyl-tricyclo[4.2.1.0^{2,5}]nona-3-ene (**7**)*

^{1}H NMR ($CDCl_3$) δ: 6.23 (1H, dd, H(10)), 6.23 (2H, m, H(3,4)), 5.40 (1H, dd, H(11, *trans*)), 5.15 (1H, dd, H(11, *cis*)), 3.33 (2H, m, H(2,5)), 1.95 (2H, m, H(1,6)), 1.55 (2H, m, H(7,8) or H(7',8')), 1.42 (2H, m, H(7',8') or H(7,8)). ^{13}C NMR ($CDCl_3$) δ: 142.42 (d, C(10)), 140.70 (d, C(3,4)), 115.66 (t, C(11)), 93.61 (s, C(9)), 50.72 (d, C(2,5)), 47.84 (d, C(1,6)), 24.63 (t, C(7,8)). EI-MS: 161, 147, 134, 107, 96, 91, 79 (base peak), 55, 39, 27.

*9-*endo*-Hydroxy-9-*exo*-(2'-methyl-propenyl)-tricyclo[4.2.1.0^{2,5}]-nona-3-ene (**8**)*

^{1}H NMR ($CDCl_3$) δ: 6.27 (2H, m, H(3,4)), 5.50 (1H, dd, H(10)), 3.29 (2H, dd, H(2,5)), 2.03 (2H, m, H(1,6)), 1.85 (3H, d, H(12) or H(13)), 1.85 (2H, m, H(7,8) or H(7',8')), 1.74 (3H, d, H(13) or H(12)), 1.45 (2H, m, H(7',8') or H(7,8)). ^{13}C NMR ($CDCl_3$) δ: 140.72 (d, C(3,4)), 129.65 (d, C(10)), 50.72 (d, C(2,5)), 47.70 (d, C(1,6)), 27.74 (q, C(12) or C(13)), 24.39 (t, C(7,8)), 20.63 (q, C(13) or C(12)). EI-MS: 190 (m^+), 175, 147, 109, 91, 83 (base peak), 55, 39.

*9-*endo*-Hydroxy-9-*exo*-propyl-tricyclo[4.2.1.0^{2,5}]nona-3-ene (**9**)*

^{1}H NMR ($CDCl_3$) δ: 6.28 (2H, m, H(3,4)), 3.28 (2H, dd, H(2,5)), 1.85 (2H, m, H(1,6)), 1.69 (2H, q, H(10)), 1.51 (2H, m, H(7,8) or H(7',8')), 1.37 (2H, m, H(7',8') or H(7,8)), 1.01 (3H, t, H(11)). ^{13}C NMR ($CDCl_3$) δ: 141.06 (d, C(3,4)), 95.43 (s, C(9)), 50.60 (d, C(2,5)), 45.52 (d, C(1,6)), 30.80 (t, C(10)), 24.73 (t, C(7,8)), 9.47 (q, C(11)). EI-MS: 164 (m^+), 163, 149, 135, 107, 91, 79 (base peak), 57, 41, 39, 29.

*9-Oxa-8-vinyl-tricyclo[5.2.1.0^{4,8}]dec-2-ene (**10**)*

^{1}H NMR ($CDCl_3$) δ: 6.13 (1H, dd, H(10)), 6.13 (1H, dd, H(4), $^3J_{H(4)-H(5)}$ = 4.8 Hz, $^3J_{H(4)-H(3)}$ = 9.6 Hz, $^3J_{H(4)-H(6)}$ = 1.0 Hz), 5.53 (1H, dd, H(5), $^3J_{H(5)-(6)}$ = 3.5 Hz), 5.27 (1H, dd, H(11, *trans*)), 5.12 (1H, dd, H(11, *cis*), 4.44 (1H, m, H(3), $^3J_{H(3)-H(2)}$ = 6.2 Hz, $^3J_{H(3)-H(2')}$ = <0.1 Hz), 2.70 (1H, m, H(6)), 2.34 (1H, m, H(1), $^3J_{H(1)-H(2)}$ = 10.1 Hz, $^3J_{H(1)-H(2')}$ = <0.1 Hz), 2.24 (1H, m, H(2), $^2J_{H(2)-H(2')}$ = 11.7 Hz), 2.10 (1H, m, H(7) or H(8) or H(7') or H(8')), 1.63 (1H, m, H(8) or H(7) or H(7') or H(8')), 1.80 (1H, m, H(7') or H(8) or H(7) or H(8')), 1.51 (1H, m, H(8') or H(8) or H(7') or H(7)). ^{13}C NMR ($CDCl_3$) δ: 140.80 (d, C(10)), 113.92 (t, C(11)), 134.39 (d, C(4)), 129.50 (d, C(5)), 93.51 (s, C(9)), 73.95 (d, C(3)), 45.92 (d, C(6)), 45.63 (t, C(1)), 44.86 (t, C(2)), 32.03 (t, C(7) or C(8)), 29.42 (t, C(8) or C(7)). EI-MS: 163, 162 (m^+), 147, 134, 133, 120, 107, 91, 79 (base peak), 55, 41, 39, 27.

*(10-Deutero)-9-oxa-8-vinyl-tricyclo[5.2.1.0^{4,8}]dec-2-ene (**10**a)*

^{1}H NMR ($CDCl_3$): identical to **10** except for the H(10) signal at δ = 2.24, which is lacking. ^{2}H NMR ($CDCl_3$) δ: 2.21 (1D, s, D(2)). ^{13}C NMR ($CDCl_3$) δ: 141.03 (d, C(10)), 134.20 (d, C(4)), 129.59 (d, C(5)), 113.89 (t, C(11)), 93.53 (s, C(9)), 73.88 (d, C(3)), 46.08 (d, C(6)), 45.78 (t, C(1)), 44.61 (m, C(2)), 32.02, 29.52 (t, C(7,8)). EI-MS: 163 (m_D^+), 162 (m_H^+), 148, 147, 129, 108, 107 (base peak), 92, 91, 79, 55, 39.

*9-Oxa-8-(2'-methyl-propen-1'-yl)-tricyclo[5.2.1.0^{4,8}]dec-2-ene (**11**)*

Could not be isolated as pure (11). Its existence was verified by GC analyses (6.5% after 8 h).

[5]Signal due to [1,5]-H shift.

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