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Regioselectivity in the ene-reaction of singlet oxygen with cyclic alkenes: photooxygenation of methyl-substituted 1,4-cyclohexadiene derivatives

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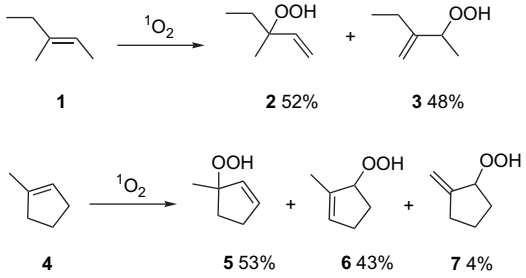
Abstract—The photooxygenation of the 1-methyl-, 2,3-dimethyl-, and 1,4-dimethylcyclohexa-1,4-dienes, which are readily available through Birch reduction, yielded the corresponding ene-products. The formed endocyclic dienes were trapped by the addition of singlet oxygen to give the corresponding bicyclic endoperoxy hydroperoxides. In the case of 1-methylcyclohexa-1,4-diene and 1,4-dimethylcyclohexa-1,4,-diene, the cis-effect determined the product distribution. Photooxygenation of 2,3-dimethylcyclohexa-1,4-dienes gave mainly exocyclic olefin, which was attributed to the lowered rotational barrier of the methyl group and increased reactivity of the methyl groups.

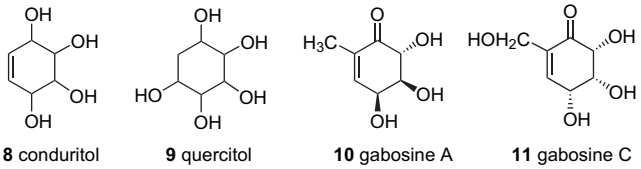
1. Introduction

Singlet oxygen is an important and reactive specie in oxidation reactions and has received remarkable attention by chemists.[1] It exhibits a diverse reactivity with organic unsaturated molecules, giving in particular [4+2] and [2+2] cycloaddition reactions.[2] Wherever an allylic hydrogen is available, an additional reaction channel forming a hydroperoxide is available: this is called the ene-reaction.[3] The ene-reaction was originally discovered by Schenck in 1953.[4] The ene-reaction has attracted major interest due to its controversial reaction mechanism and fascinating regiochemistry and stereochemistry. Various reaction mechanisms have been proposed, which vary from the concerted[5] to non-concerted and include diradical,[6] open-chain zwitterionic,[7] and perepoxide[8] intermediates. Perepoxide or exciplex intermediates have been proposed in some cases and a transition state in others.[3c,9] The reaction of trisubstituted olefins with singlet oxygen gave products derived from the most substituted side of the olefin. For example, the photooxygenation of (*E*)-3-methylpent-2-ene (**1**) formed ene-products **2** and **3** (Scheme 1). These products are derived from the hydrogen abstraction from the side of the olefin with two substituents. This selectivity is referred to as the cis-effect.[10] For the singlet oxygen reaction of cyclic alkenes; it was proposed that the geometry of the allylic hydrogen in the ground state determines the regioselectivity (Scheme 1).



Scheme 1.

The reaction of singlet oxygen with 1-methyl-cyclopent-1-ene (**4**) produced ene-products **5** and **6** where the proton abstraction took place from the allylic protons located in the five-membered ring.[11] The exocyclic olefin **7** was only formed in 4% yield. It has been proposed that the stabilizing effect by the interaction of singlet oxygen with two allylic hydrogens on the same side of the molecule during the formation of the perepoxide plays an important role in determining the regioselectivity.[12]



As an extension of our work that is directed toward to the synthesis of highly hydroxylated cyclohexene derivatives

Keywords: Singlet oxygen; Endoperoxide; Hydroperoxide; Photooxygenation; Ene-reaction; Hydrocarbons.
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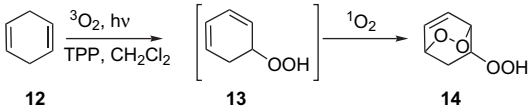
such as conduritols **8**, quercitols **9**,[13] and gabosines **10/11**[14] we were interested in the singlet oxygen ene-reaction of the methyl substituted 1,4-cyclohexadiene derivatives. Herein we report our results.

2. Results and discussions

Recently, we reported that the tetraphenylporphyrin-sensitized photooxygenation of 1,4-cyclohexadiene (**12**) resulted in the formation of the bicyclic endoperoxide **14**.[15] The singlet oxygen first undergoes an ene-reaction to give **13**. The conjugated diene system in **13** is then easily trapped by a second mole of singlet oxygen to give isomeric **14**. Similar reactions have been observed by the reaction of singlet oxygen with isotetraline (Scheme 2).[16]

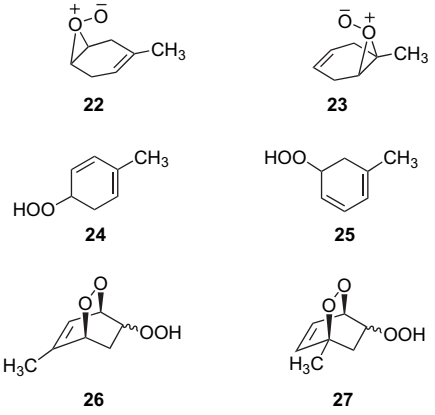


Scheme 2.

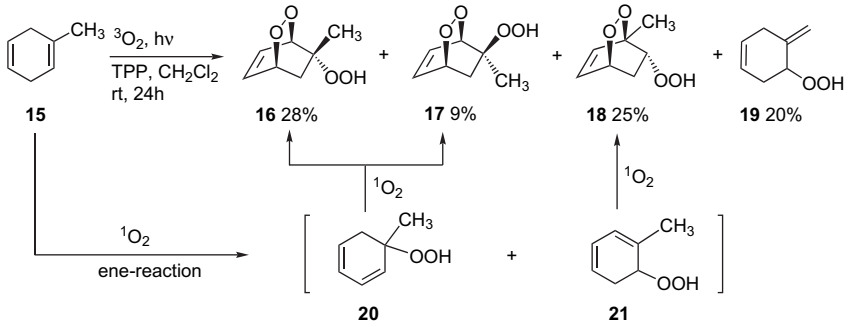
As the first reaction, 1-methylcyclohexa-1,4-diene (**15**)[17] was reacted with singlet oxygen. Tetraphenylporphyrin-sensitized photooxygenation of **15** in methylene chloride at room temperature produced three bicyclic endoperoxides **16–18** and a monocyclic hydroperoxide **19** in a ratio of 3:1:2.5:2. The isolated endoperoxides are quite stable at room temperature for many days.

The structures of **16** and **17** were assigned by ^1H and ^{13}C NMR spectra. The most conspicuous features in the ^1H NMR spectra of the endoperoxide **16** and **17** are the presence of double bond protons and two bridgehead protons along with one AB-system that corresponds to methylenic protons. This clearly indicates that the methyl group is attached to the carbon-atom bearing the hydroperoxide. The presence of two olefinic protons and one bridgehead proton in the ^1H NMR spectrum of **18** showed that the methyl group is attached to the bridgehead carbon atom. The structure of **19** was established based on the presence of four olefinic protons (two of them are methylenic) and two methylene groups with large geminal couplings ($J_{5a,5e}$=21.0 Hz, $J_{2a,2e}$= 20.1 Hz) that indicate the location of these methylene groups between the double bonds.[18] For the mechanism of the formation of these interesting endoperoxides containing hydroperoxide groups, we assume that the 1,4-cyclohexadiene unit in **15** first undergoes an ene-reaction with the double bond activated methylene and methyl groups. The addition of singlet oxygen to diene units in **20** and **21** results in the formation of the isolated products **16–18**. The proposed intermediates **20** and **21** were not detected. Probably, the rate of the cycloaddition of singlet oxygen to the diene unit in **20** and **21** is most likely much faster than the rate of the ene-reaction with **15** (Scheme 3).

Because of the unsymmetrical arrangement of the double bonds in **15**, singlet oxygen can attack two double bonds. If the singlet oxygen would attack the sterically less crowded double bond, the perepoxide **22** would be formed, which would then rearrange to the hydroperoxides **24** and **25**. Trapping of the diene units in **24** and **25** would end up with the formation of the bicyclic endoperoxides **26** and **27**. However, careful analysis of the different fractions did not reveal the formation of any trace of the endoperoxides **26** and **27**. The structures of the isolated products clearly show that singlet oxygen exclusively attacks the higher substituted double bond in **15**.[19]



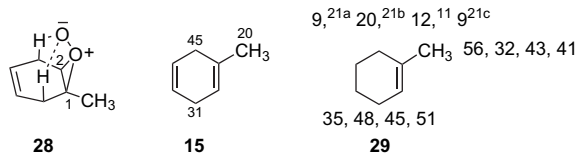
The site selection of singlet oxygen for the higher substituted double bond in **15** can be rationalized in terms of the electrophilic character of this species. The product distribution shows that the ratio of the products (**16**, **17**, and **18**), which were derived from the cis-effect to the product from the *anti*-side is 76:24, and in turn indicates that the more-substituted side of the double bond is more reactive. The formation of the perepoxide on the more-substituted side is



Scheme 3.

favored. Thus, the stabilizing interaction of oxygen with two allylic hydrogens on the same side of the double bond determines the mode of singlet oxygen attack to the double bond. Once the singlet oxygen has selected the favored face of the double bond by hydrogen bonding, it still has the choice for hydrogen abstraction between the two sides of two different allylic hydrogens.

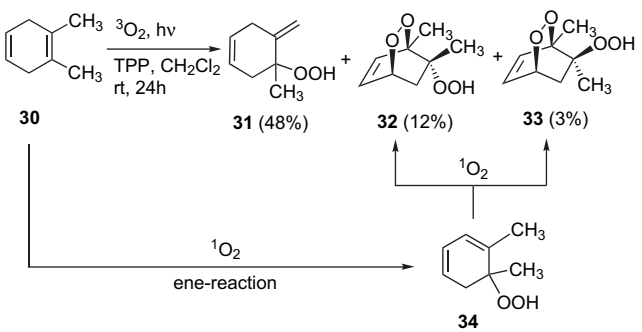
Geminal selectivity was also observed in this case. The product distribution ratio was 45:31. The factors affecting the geminal regioselectivity have been studied by several groups.[3b,3c,20] A methyl group can interact with the perepoxide ring system (1,3-repulsion between the oxygen atom and methyl group) and lengthen the $^{+}O–C_1$ bond. As a consequence of this interaction the hydrogen abstraction from the end of the double bond bearing the methyl group will take place as shown in **28**.



28 **15** **29**

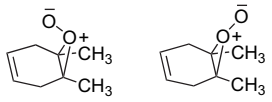
It is worth comparing the results of the photooxygenation of **15** with that of 1-methylcyclohexene (**29**). 1-Methylcyclohexene reacts with singlet oxygen and furnishes a mixture of three hydroperoxides, whereas the major product is the *exo*-cyclic alkene.[21] Methylcyclohexene exhibits anti 'cis-effect' selectivity. The stabilizing interaction between the pendant oxygen and two allylic hydrogens is probably not the dominating interaction in **29**. This can be attributed to the unfavorable conformation of the molecule. Probably the conformation of 1,4-cyclohexadiene in **15** allows the orthogonal orientation of the allylic hydrogen to the double bond plane much better than in **29**.

Next, the 1,2-dimethylcyclohexa-1,4-diene (**30**)[22] was submitted to the photooxygenation reaction under the same reaction conditions as described above. After the separation of the reaction mixture on silica gel, three peroxides **31**, **32**, and **33** were separated. The structures were determined by NMR spectral data. The major product was identified as the exocyclic ene-product **31**. The minor products **32** and **33** were formed by the ene-reaction of singlet oxygen with **30** followed by the [2+4] cycloaddition reaction of singlet oxygen with the primarily formed diene **34** (Scheme 4).



Scheme 4.

The structures of the products show that singlet oxygen exclusively attacks the more-substituted double bond. Any product derived from the attack of the less-substituted double bond was not detected. Singlet oxygen reacts with the tetrasubstituted double bond in **30** and forms two diastereomeric perepoxides **35** and **36** as illustrated below.

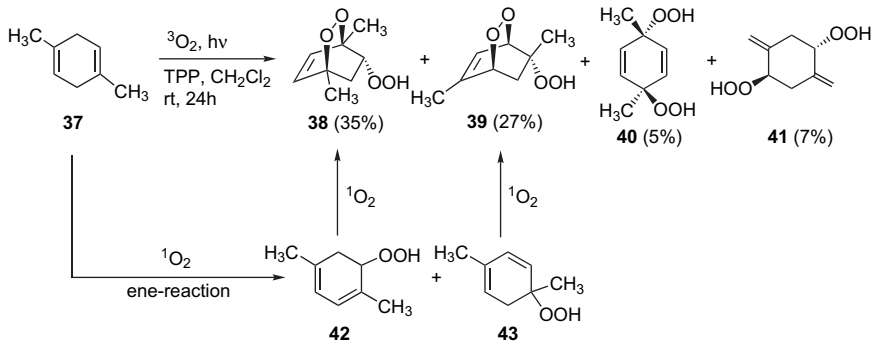


35 **36**

Because of the symmetrical environment in **35** as well as in **36**, the pendant oxygen can abstract the allylic hydrogen from one of the neighboring allyl hydrogens and form the corresponding products **32** and **33**. The product distribution shows that the diastereoisomer **36** was formed as the major intermediate. Houk et al.[12a] suggested that the barrier to rotate the allylic hydrogen to the perpendicular geometry desired for hydrogen abstraction determines the mode of singlet oxygen attack. Thus, the greater reactivity of the methyl groups of this molecule may arise from the relative ease of rotating one C–H bond on one of these methyls to the perpendicular conformation in the transition state. The presence of a second methyl group at the C-2 position in **30** most likely decreases the rotational barrier of the methyl group and increases their reactivity.

As the last compound, we searched the photooxygenation of 1,4-dimethylcyclohexa-1,4-diene (**37**).[17a] We isolated four products **38**–**41**. Two of them were bicyclic endoperoxides **38** and **39**, which were formed by an ene-reaction followed by the [2+4] cycloaddition reaction of singlet oxygen. The diene **43** also undergoes an ene-reaction besides the cycloaddition reaction to form **40**. Singlet oxygen attacks the trisubstituted double bond in **43** and forms a *syn*-perepoxide, which is responsible for the formation of **40**. The hydroperoxide **41** is derived from the formation of an *exo*-perepoxide formed by the reaction of singlet oxygen with one of the double bonds in **37**. Based on the product distribution it can be easily rationalized that the major products are derived from the *endo*-perepoxide (10:1). The reaction of singlet oxygen with dienes **30** and **37** clearly demonstrates that the position of the second methyl group in 1,4-cyclohexadiene unit has a dramatic effect on product distribution. In the case of **30** the products derived from the *exo*-perepoxide were major (1:4); however, in the case of **37**, the major products are derived from the *endo*-peroxide (10:1). The product distribution is completely reversed. On the other hand, the product distribution of **37** resembles the product distribution from **15** as expected (Scheme 5).

In conclusion, the photooxygenation of three different methyl substituted cyclohexa-1,4-dienes shows complete side-selectivity. The more-substituted double bond is preferentially attacked. The cis-effect is mainly observed. In the case of 2,3-dimethylcyclohexa-1,4-diene **37** the major products are derived from the *exo*-perepoxide. It has attributed to the lower rotational barrier of the methyl groups that in turn increases their reactivity. Further work with different substituents are currently under progress.



Scheme 5.

3. Experimental

3.1. General

Melting points are uncorrected. Infrared spectra were obtained from a solution in 0.1-mm cells or KBr pellets on a regular instrument. The ^1H and ^{13}C NMR spectra were recorded on 400 (100) MHz spectrometers. Apparent splitting is given in all cases. Column chromatography was performed on silica gel (60-mesh, Merck). TLC was carried out on Merck 0.2-mm silica gel 60 F_{254} analytical aluminum plates. All of the substances reported in this paper are in their racemic form.

3.2. Photooxygenation of 1-methylcyclohexa-1,4-diene (15)

To a stirred solution of 1-methylcyclohex-1,4-diene (**15**) (5.0 g, 53.14 mmol) in 500 mL of CH_2Cl_2 was added 85 mg of tetraphenylporphyrin (TPP). The resulting mixture was irradiated with a projection lamp (500 W) while oxygen was passed through solution, in which the mixture was stirred for 24 h at room temperature. The ^1H NMR spectrum of the mixture showed that the conversion was approximately 80% and the products **16**, **17**, **18**, and **19** were formed in a ratio of 3:1:2.5:2, respectively (6.5 g). Evaporation of the solvent (30 °C, 20 mmHg) and chromatography of the residue on a silica gel column (200 g) eluting with hexane/ether (3:2) gave as the first fraction hydroperoxide **19**, the second fraction a mixture of the endoperoxide **16** and **18**, and as the third fraction **17**, **16**, and **18** were separated by crystallization from hexane/ether mixture. Pure samples were obtained by repeated column chromatography.

3.2.1. (1*R*(*S*),4*S*(*R*),5*R*(*S*))-5-Methyl-2,3-dioxabicyclo-[2.2.2]oct-7-en-5 hydroperoxide (16). Colorless solid, mp 108–109 °C from ether/hexane (28%); ^1H NMR (400 MHz, $CDCl_3$) δ 7.52 (br s, 1H, –OOH), 6.68 (quasi t, 2H, H_7 and H_8), 4.70 (m, 2H, H_1 and H_4), 2.10 (dd, A-part of AB-system, $^2J_{gem}$=14.1 Hz, $^3J_{1,6endo}$=3.7 Hz, 1H, H_{6endo}), 1.70 (s, 3H, –CH_3), 1.42 (dd, B-part of AB-system, $^2J_{gem}$=14.1 Hz, $^3J_{1,6exo}$=1.9 Hz, 1H, H_{6exo}). ^{13}C NMR (100 MHz, $CDCl_3$) δ 131.8, 130.7, 78.6, 75.7, 71.0, 36.5, 21.8. IR (KBr, cm^{-1}) 3339, 2979, 2935, 1368, 1105, 925, 707. Anal. Calcd for $C_7H_{10}O_4$: C, 53.16; H, 6.37. Found: C, 53.01; H, 6.51.

3.2.2. (1*R*(*S*),4*S*(*R*),5*S*(*R*))-5-Methyl-2,3-dioxabicyclo-[2.2.2]oct-7-en-5-yl hydroperoxide (17). Colorless liquid, purity 95% (9%). ^1H NMR (400 MHz, $CDCl_3$) δ 8.17 (br s, 1H, –OOH), 6.60 (m, 2H, H_7 and H_8), 4.75 (m, 1H, H_4), 4.64 (m, 1H, H_1), 2.1 (dd, A-part of AB-system, $^2J_{gem}$=14.2 Hz, $^3J_{1,6endo}$=4.1 Hz, 1H, H_{6endo}), 1.45 (dd, B-part of AB-system, $^2J_{gem}$=14.1 Hz, $^3J_{1,6exo}$=1.8 Hz, 1H, H_{6exo}), 1.25 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 133.0, 130.9, 80.2, 74.9, 70.9, 35.2, 23.3. IR (KBr, cm^{-1}) 3402, 2976, 2930, 1369, 1103, 974, 762. Anal. Calcd for $C_7H_{10}O_4$: C, 53.16; H, 6.37. Found: C, 52.90; H, 6.49.

3.2.3. (1*R*(*S*),4*S*(*R*),5*R*(*S*))-4-Methyl-2,3-dioxabicyclo-[2.2.2]oct-7-en-5-yl hydroperoxide (18). Viscous liquid (25%). ^1H NMR (400 MHz, $CDCl_3$) δ 8.1 (br s, 1H), 6.66 (dd, A-part of AB-system, $J_{7,8}$=8.3 Hz, $J_{7,6}$=6.1 Hz, 1H, H_7), 6.21 (br d, B-part of AB-system, $J_{7,8}$=8.3 Hz, 1H, H_8), 4.65 (m, 1H, H_1), 4.32 (dd, $J_{5,6endo}$=8.1 Hz, $J_{5,6exo}$=2.3 Hz, 1H_5), 2.55 (ddd, A-part of AB-system, $^2J_{gem}$=14.8 Hz, $J_{5,6endo}$=8.1 Hz, $J_{1,6endo}$=3.7 Hz, 1H, H_{6endo}), 1.50 (s, 3H, –CH_3), 1.41 (dt, B-part of AB-system, $^2J_{gem}$=14.8 Hz, $J_{5,6exo}$=$J_{1,6exo}$=2.2 Hz, 1H, H_{6exo}). ^{13}C NMR (100 MHz, $CDCl_3$) δ 133.6, 133.1, 80.9, 76.0, 70.9, 31.6, 19.8. IR (KBr, cm^{-1}) 3403, 2979, 2940, 1432, 1381, 1105. Anal. Calcd for $C_7H_{10}O_4$: C, 53.16; H, 6.37. Found: C, 53.45; H, 6.56.

3.2.4. (1*R*(S))-6-Methylenecyclohex-3-en-1-yl hydroperoxide (19). Colorless liquid (20%), purity 95%. ^1H NMR (400 MHz, $CDCl_3$) δ 7.98 (s, 1H, –OOH), 5.62 (d, AB-system, J_{34}=9.7 Hz, 1H, H_3 or H_4), 5.54 (br d, B-part of AB-system, J=9.9 Hz, 1H, H_3 or H_4), 5.04 (s, 1H, C=CH_2), 5.0 (s, 1H, C=CH_2), 4.60 (t, $J_{1,2a}$=$J_{1,2}$=4.6 Hz, 1H, H_1), 2.96–2.75 (br, AB-system, $J_{5a,5e}$=21.0 Hz, 2H, H_5), 2.5–2.42 (m, AB-system, $J_{2a,2}$=20.1 Hz, 1H, H_2). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.6, 128.5, 126.6, 111.3, 83.3, 30.8, 21.6. IR (KBr, cm^{-1}) 3340, 2936, 1598, 1452, 1400, 1178, 1076.

3.3. Photooxygenation of 1,2-dimethylcyclohexa-1,4-diene (30)

To a stirred solution of 1,2-dimethylcyclohexa-1,4-diene (5.0 g, 46.25 mmol) in 500 mL of CH_2Cl_2 was added 75 mg of tetraphenylporphyrin (TPP). The resulting mixture was irradiated with a projection lamp (500 W) while oxygen was passed through solution, in which the mixture was stirred for 24 h at room temperature. The ^1H NMR spectrum of the mixture showed that the conversion was about 60% and the products **31** and **32/33** were formed in a ratio of 4:1 (4.06 g). Evaporation of the solvent (30 °C, 20 mmHg) and

chromatography of the residue on a silica gel column (200 g) eluting with hexane/ether (3:2) gave as the first fraction hydroperoxide **31**, and as the second fraction endoperoxide **32** and as the third fraction **33**. Pure samples were obtained by repeated column chromatography.

3.3.1. 1*R*(*S*)-1-Methyl-6-methylenecyclohex-3-en-1-yl hydroperoxide (31). Viscous liquid (48%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (s, 1H, –OOH), 5.69 (br d, A-part of AB-system, J=9.8 Hz, 1H, C_3 or C_4), 5.45 (br d, B-part of AB-system, J=9.8 Hz, 1H, C_3 or C_4), 5.06 (s, 1H, –C=CH_2), 5.03 (s, 1H, –C=CH_2), 3.08 (br d, A-part of AB-system, J=18.4 Hz, 1H, H_5), 2.81 (br d, B-part of AB-system, J=18.4 Hz, 1H, $H_{5'}$), 2.44 (br d, A-part of AB-system, J=21.3 Hz, 1H, H_2), 2.23 (br d, B-part of AB-system, J=21.3 Hz, 1H, $H_{2'}$), 1.49 (s, 3H, –CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.9, 126.0, 123.2, 110.1, 82.9, 37.4, 33.1, 21.5. IR (KBr, cm^{-1}) 3400, 3089, 3030, 2979, 2934, 1423, 1370, 912, 744. Anal. Calcd for $C_8H_{12}O_2$: C, 68.54; H, 8.63. Found: C, 68.01; H, 8.44.

3.3.2. (1*R*(*S*),4*S*(*R*),5*R*(*S*))-4,5-Dimethyl-2,3-dioxabicyclo-[2.2.2]oct-7-en-5-yl hydroperoxide (32). Viscous liquid (9%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.5 (s, 1H, –OOH), 6.59 (dd, A-part of AB-system, $J_{7,8}$=8.3 Hz, $J_{1,7}$=6.1 Hz, 1H, H_7), 6.25 (dd, B-part of AB-system, $J_{7,8}$=8.31 Hz, $J_{1,8}$=1.4 Hz, 1H, H_8), 4.59 (m, 1H, H_1), 2.08 (dd, A-part of AB-system, $J_{6,6'}$=14.1 Hz, $J_{1,6}$=3.6 Hz, 1H, H_6), 1.74 (dd, B-part of AB-system, $J_{6,6'}$=14.1 Hz, $J_{1,6}$=2.1 Hz, 1H, $H_{6'}$), 1.52 (s, 3H, –CH_3), 1.37 (s, 3H, –CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.8, 131.8, 81.7, 78.3, 71.4, 37.8, 18.9, 16.6. IR (KBr, cm^{-1}) 3421, 2988, 1452, 1380, 1124, 1082, 1059, 835, 748. Anal. Calcd for $C_8H_{12}O_4$: C, 55.81; H, 7.02. Found: C, 55.35; H, 7.01.

3.3.3. (1*R*(*S*),4*S*(*R*),5*S*(*R*))-4,5-Dimethyl-2,3-dioxabicyclo-[2.2.2]oct-7-en-5-yl hydroperoxide (33). Viscous liquid (3%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.13 (s, 1H, –OOH), 6.70 (dd, A-part of AB-system, $J_{7,8}$=8.2 Hz, $J_{1,7}$=5.8 Hz, 1H, H_7), 6.25 (br d, B-part of AB-system, $J_{7,8}$=8.2 Hz, 1H, H_8), 4.76 (m, 1H, H_1), 2.97 (br d, A-part of AB-system, $J_{6,6'}$= 14.2 Hz, 1H, H_6), 1.50 (d, B-part of AB-system, $J_{6,6'}$= 14.2 Hz, 1H, $H_{6'}$), 1.45 (s, 3H, –CH_3), 1.19 (s, 3H, –CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.1, 133.3, 82.9, 81.1, 71.9, 33.1, 24.1, 15.0. IR (KBr, cm^{-1}) 3392, 2984, 2940, 1371, 913, 745. Anal. Calcd for $C_8H_{12}O_4$: C, 55.81; H, 7.02. Found: C, 55.51; H, 7.23.

3.4. Photooxygenation of 1,4-dimethylcyclohexa-1,4-diene (37)

To a stirred solution of 1,4-dimethylcyclohexa-1,4-diene **37** (5.0 g, 46.25 mmol) in 500 mL of CH_2Cl_2 was added 75 mg of tetraphenylporphyrin (TPP). The resulting mixture was irradiated with a projection lamp (500 W) while oxygen was passed through solution, in which the mixture was stirred for 24 h at room temperature. The ^{1}H NMR spectrum of the mixture showed that the conversion was 70% and the products **38**, **39**, **40**, and **41** formed were in a ratio of 1.5:1.0:0.3:0.2, respectively (5.60 g). Evaporation of the solvent (30 °C, 20 mmHg) and chromatography of the residue on a silica gel column (200 g) eluting with hexane/ether (3:2) gave as the first fraction hydroperoxide **38**, the second fraction the endoperoxide **39**, the third fraction **41**, and as the last fraction **40**.

3.4.1. (1*R*(*S*),4*S*(*R*),5*R*(*S*))-1,4-Dimethyl-2,3-dioxabicyclo-[2.2.2]oct-7-en-5-yl hydroperoxide (38). Colorless solid, mp 105–106 °C from ether/hexane (35%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.1 (br s, 1H, –OOH), 6.49 (d, A-part of AB-system, $J_{8,3}$=8.3 Hz, 1H, H_7 or H_8), 6.26 (d, B-part of AB-system, $J_{8,3}$=8.3 Hz, 1H, H_8 or H_7), 4.42 (dd, $J_{5,6}$=8.1 Hz, $J_{5,6'}$=2.5 Hz, 1H, H_5), 2.40 (dd, A-part of AB-system, J_{gem}=14.0 Hz, $J_{5,6}$=8.1 Hz, 1H, H_5), 1.59 (s, 3H, CH_3), 1.58 (dd, B-part of AB-system, J_{gem}=14.0 Hz, $J_{5,6'}$=2.5 Hz, 1H), 1.42 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.8, 132.4, 82.0, 75.5, 74.8, 37.3, 20.3, 18.9. IR (KBr, cm^{-1}) 3429, 2988, 2940, 2916, 1452, 1308, 1124, 1082, 1059, 835, 748. Anal. Calcd for $C_8H_{12}O_4$: C, 55.81; H, 7.02. Found: C, 55.42; H, 7.08.

3.4.2. (1*R*(*S*),4*S*(*R*),5*R*(*S*))-5,7-Dimethyl-2,3-dioxabicyclo-[2.2.2]oct-7-en-5-yl hydroperoxide (39). Viscous liquid, (20%). ^{1}H NMR (400 MHz, $CDCl_3$, acetone-d_6) δ 8.71 (s, 1H, –OOH), 6.25 (dq, $J_{4,8}$=6.7 Hz, $^4J_{8,Me}$=1.6 Hz, 1H, H_8), 4.72 (dd, $J_{4,8}$=6.7 Hz, $J_{1,4}$=0.8 Hz, 1H, H_4), 4.45 (br dd, $J_{1,6}$=4.0 Hz, $J_{1,6'}$=1.7 Hz, 1H, H_1), 2.10 (dd, A-part of AB-system, J_{gem}=14.1 Hz, $J_{1,6}$=4.0 Hz, 1H, H_6), 1.93 (d, $J_{1,6}$=1.6 Hz, 3H, –CH_3), 1.49 (dd, B-part of AB-system, J_{gem}= 14.1 Hz, $J_{1,6'}$=1.7 Hz, 1H, $H_{6'}$), 1.27 (s, 3H, –CH_3). ^{13}C NMR (100 MHz, acetone-d_6) δ 138.3, 119.0, 76.2, 71.2, 71.0, 19.1, 19.0, 14.1. IR (KBr, cm^{-1}) 3384, 2981, 2935, 1323, 1124, 913, 744. Anal. Calcd for $C_8H_{12}O_4$: C, 55.81; H, 7.02. Found: C, 55.47; H, 6.79.

3.4.3. 4-Hydroperoxy-2,5-dimethylenecyclohexyl hydroperoxide (40). Colorless solid, mp 123–124 °C from ether/hexane (7%). ^{1}H NMR (400 MHz, $CDCl_3$, acetone-d_6) 9.35 (s, 2H, –OOH), 5.04 (s, 2H, –C=CH_2), 4.99 (s, 2H, –C=CH_2), 4.4 (t, $J_{1,2}$=$J_{1,2'}$=3.1 Hz, 2H, H_1 and H_4), 2.61 (dd, A-part of AB-system, J_{gem}=14.6 Hz, $J_{1,2}$=3.1 Hz, 2H, H_2 and H_4 or ($H_{2'}$ and $H_{4'}$)), 2.15 (dd, B-part of AB-system, J_{gem}=14.6 Hz, $J_{1,2'}$=3.1 Hz, 2H, $H_{2'}$ and $H_{4'}$ (or H_2 and H_4)). ^{13}C NMR (100 MHz, acetone-d_6) δ 136.1, 111.7, 80.3, 30.3. IR (KBr, cm^{-1}) 3342, 3028, 2990, 1404, 1061, 847, 787. Anal. Calcd for $C_8H_{12}O_4$: C, 55.81; H, 7.02. Found: C, 55.50; H, 6.70.

3.4.4. 4-Hydroperoxy-1,4-dimethylcyclohexa-2,5-dien-1-yl hydroperoxide (41). Colorless solid, mp 147–148 °C from ether/hexane (5%). ^{1}H NMR (400 MHz, acetone-d_6) δ 9.9 (s, 2H, –OOH), 5.89 (s, 4H, –CH=CH–), 1.24 (s, 6H, –CH_3). ^{13}C NMR (100 MHz, acetone-d_6) δ 133.9, 77.9, 23.8. IR (KBr, cm^{-1}) 3331, 2930, 1429, 1057, 995, 931, 744. Anal. Calcd for $C_8H_{12}O_4$: C, 55.81; H, 7.02. Found: C, 55.17; H, 6.81.

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