Synthesis of nine-, ten-, and fifteen-membered alkenolides by the oxidative cleavage of the bridging C=C bond in 2-oxabicycloalkenes

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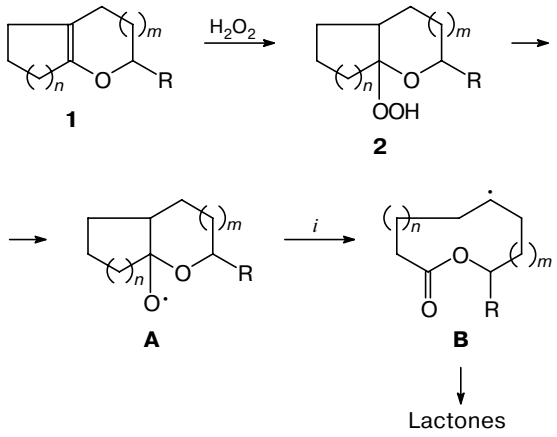
Hydroperoxidation of C=C-bridged 2-oxabicycloalkenes in which the five- or six-membered oxacycle is fused with the five-, six-, or twelve-membered hydrocarbon ring was studied. The $Cu(OAc)_2$-catalyzed decomposition of the resulting hydroperoxides afforded nine-, ten-, or fifteen-membered *trans*-alkenolides, respectively. The latter compounds were obtained as pairs of regioisomers, with the isomers in which the double bond is more remote from the ether oxygen atom predominating.

Key words: synthesis, nine-, ten-, and fifteen-membered alkenolides, 2-oxabicycloalkenes, hydroperoxidation, hydrogen peroxide, 1-hydroperoxy-2-oxabicycloalkanes, catalytic decomposition of hydroperoxides, copper diacetate.

Known procedures for the syntheses of lactones starting from 2-oxabicycloalkenes are based on hydroperoxidation of the latter followed by thermal or catalytic decomposition of the resulting hydroperoxides with the homolytic cleavage of the bridging carbon—carbon bond. This decomposition affords lactones through intermediate stages of generation of tertiary cycloalkoxy (**A**) and alkanolide radicals (**B**) (Scheme 1).[1—6]

Scheme 1

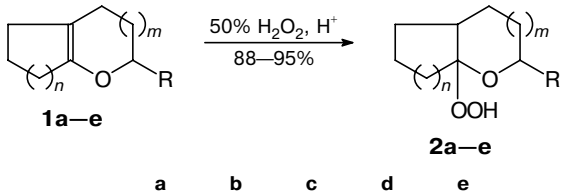


i. β-scission.

The high selectivity of the process can be achieved with the use of the redox $FeSO_4$—$Cu(OAc)_2$ system (1—1.5 equiv. each)[3—5] or a catalytic amount of $Cu(OAc)_2$ (0.0015—0.05 equiv.)[6] for decomposition of hydroperoxides **1**. Previously, we have used the catalytic version of this transformation in the synthesis of 15-pentadecanolide from oxabicyclo[10.4.0]hexadecene.[6]

The aim of the present study was to elucidate the effect of the structures of 2-oxabicycloalkenes on their hydroperoxidation and decomposition of the resulting hydroperoxides catalyzed by copper ions and to extend the scope of this synthetic procedure. 2-Oxabicycloalkenes **1a—e** were used as the starting compounds (Scheme 2).

Scheme 2



	a	b	c	d	e
R	H	H	Me	H	H
m	0	0	0	1	1
n	2	8	8	1	2

Hydroperoxidation of oxabicycloalkenes **1a—e** was carried out at 0—5 °C. The reactions of **1a**, **1d**, and **1e** were performed in Et_2O or MeOH, whereas the reactions of **1b** and **1c** were carried out in MeOH because they virtually did not undergo hydroperoxidation in Et_2O under the conditions used. In MeOH, the transformations of the above-mentioned two groups of the starting substrates into the reaction products also proceeded with substantially different rates. Thus, the reactions of **1a**, **1d**, and **1e** were completed in 30 min, whereas the reactions of **1b** and **1c** were completed in 90 min. Hydroperoxidation of these groups differs also

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Table 1. Hydroperoxidation of oxabicycloalkenes **1a—e**[a]

Substrate	Solvent	τ /min	Product	M.p. /°C	Yield (%)	O_{act}[b] (%)
1a	Et_2O	30	**2a**	Oil	88	90.3
1b	MeOH	90	**2b**	98—100[c]	92	95.9
1c	MeOH	90	**2c**	106—108[c]	94	96.9
1d	Et_2O	30	**2d**	Oil	95	96.6
1d	MeOH	15	**2d**	Oil	83[d]	97.2[f]
1e	Et_2O	30	**2e**	Oil	93	97.5
1e	MeOH	30	**2e**	Oil	84[e]	98.0[f]

[a] Reaction conditions: 9—14 mmol of the substrate; 1.5—2 equiv. of 50% H_2O_2; 15 mL of the solvent; 15—30 mol.% of H_2SO_4; 0—5 °C.
[b] The content of the active oxygen (O_{act}) is given in percentage of the theoretical value according to the data from iodometric titration.
[c] After recrystallization from MeOH.
[d] In addition, 1-methoxy-2-oxabicyclo[4.3.0]nonane was obtained (the yield was 9%).
[e] In addition, 1-methoxy-2-oxabicyclo[4.4.0]decane was obtained (8%).
[f] The O_{act} values in hydroperoxides were determined after treatment with hexane.

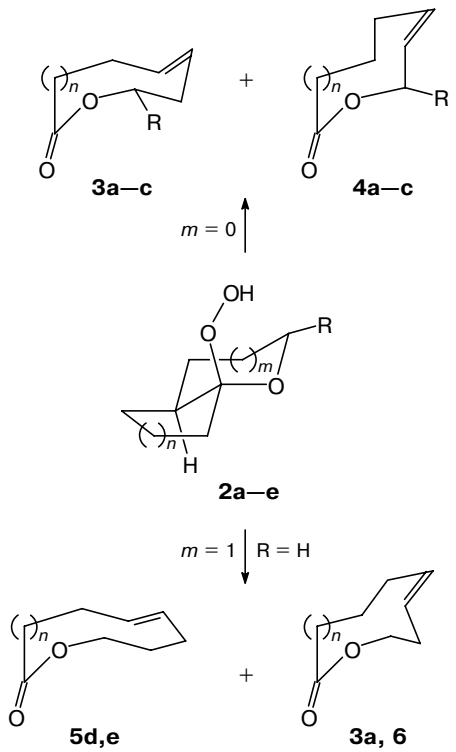
in that the reactions of **1a**, **1d**, and **1e** were accompanied by the side formation of adducts of these substrates with methanol (Table 1), whereas these adducts were not observed upon hydroperoxidation of substrates **1b** and **1c**. The highest selectivity of the reactions was achieved in the presence of 15—30 mol.% of H_2SO_4 (the reactions in the presence of a smaller amount of H_2SO_4 proceeded much more slowly, whereas the use of a larger amount of H_2SO_4 led to a decrease in the yield of hydroperoxides) (see Table 1).

The IR spectra of hydroperoxides **2a—e** have an absorption band at 3355—3365 cm^{-1} characteristic of (*E*)-1-hydroperoxy-2-oxabicycloalkanes (3300 cm^{-1} for *Z* isomers),[4] which indicates that hydroperoxidation proceeded as the electrophilic *trans*-addition to give (*E*)-hydroperoxyoxabicycloalkanes **2a—e**.

The resulting hydroperoxides (except for **2a**) are rather stable and can be kept at below-zero temperatures for several weeks without noticeable decomposition. Hydroperoxides **2b** and **2c** remained unchanged even upon heating to 50 °C over a short period (30 min), whereas hydroperoxides **2d** and **2e** rapidly decomposed upon heating above 40 °C. Hydroperoxide **2a** decomposed even at ~20 °C, but it remained virtually unchanged upon storage at 10 °C for several days. Yet another characteristic property of hydroperoxides **2a—e** is the fact that they are virtually insoluble in cooled (0—10 °C) hexane due to which they can be rather readily purified from hexane-soluble organic impurities.

Hydroperoxides **2a—e** were decomposed using copper ions as a catalyst by the gradual addition of their solutions or suspensions in $MeCOPr^n$ to a solution of 0.05 equiv. of $Cu(OAc)_2$ in the same solvent followed by refluxing of the reaction mixture until hydroperoxides were completely decomposed. The reactions resulted in the cleavage of the bridging C—C bonds in hydroperoxides giving rise to regioisomeric alkenolides containing the double bond in the γ,δ (**3**) or β,γ (**4**) positions with respect to the ether oxygen atom in the cases of hydroperoxides **2a—c** or containing the double bond in the δ,ε (**5**) or γ,δ (**6**) positions in the cases of hydroperoxides **2d,e** (Scheme 3). Hydroperoxides **2a—c** produced alkenolides **3a—c** in which the double bond is more remote from the ether oxygen atom, the reactions proceeding with high regioselectivity (85—97%). The regioselectivity is enhanced upon the replacement of one H atom of the CH_2O group in hydroperoxide by the methyl group (R = Me). For example, the ratio between the corresponding regioisomers **3** and **4** increases from 6 : 1 to >30 : 1 on going from hydroperoxide **2b** to **2c** (Table 2).

Scheme 3



Reagents and conditions: $MeCOPr^n$, $Cu(OAc)_2$ (0.05 equiv.), 100 °C, 1.5—3 h. (For literal notations, see Scheme 2; **6**, *n* = 2.)

The fractions of regioisomers **5d** and **5e** in their mixtures with alkenolides **3a** and **6** were 50 and 73%, respectively. These reactions are also characterized by stereoselectivity producing alkenolides with the *trans* configuration of the double bond as the major isomers.

The structures of alkenolides **3—6** and the ratios of the regioisomers were established by ^1H and ^{13}C NMR spectroscopy. The ratios of regioisomeric alkenolides **3** and **4** were determined from the intensities of the signals

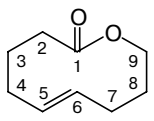
Table 2. $Cu(OAc)_2$-Catalyzed transformations of hydroperoxyoxabicycloalkanes **2** into alkenolides **3—6** [a]

Hydroperoxide	τ/h	Products and their ratio[b]	Total yield[c] (%)
2a	1.5	**3a** : **4a** = 20	90
2b	3	**3b** : **4b** = 6	91
2c	3	**3c** : **4c** > 30	87
2d	1.5	**5d** : **3a** ≈ 1	93[d]
2e	1.5	**5e** : **6** = 2.7	94

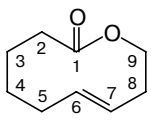
[a] Reaction conditions: hydroperoxide (5—10 mmol); $Cu(OAc)_2$ (0.25—0.5 mmol); $MeCOPr^n$ as the solvent; 100 °C.
[b] ^1H NMR data.
[c] With respect to the product isolated.
[d] GLC data.

for the protons in their CH_2O fragments (in the cases of **3c** and **4c**, in the CHMeO fragments), which differ in the chemical shift and multiplicity. According to the results of the earlier studies,[4,7,8] the complex multiplet signal for the protons of this fragment in the regioisomers of type **3** is shifted upfield with respect to the doublet signal for the regioisomers of type **4**. The regioisomeric compositions of the products generated from hydroperoxides **2a—e** are also evidenced by the doubled numbers of the signals in their ^{13}C NMR spectra and the appearance of two peaks in their GLC chromatograms, except for the pair of alkenolides **5e/6**, which we failed to separate according to this procedure. The effect of the double bond on the chemical shifts of the NMR signals belonging to the CH_2O fragment of the regioisomeric alkenolides **5d,e**, **3a**, and **6** is essentially weakened because these groups are more remote from each other. As a result, it was impossible to estimate the ratios of the pairs of alkenolides **5d/3a** and **5e/6** by the procedure used in the case of the pairs **3/4**. Hence, we employed 2D NMR procedures, *viz.* the gsCOSY[9] and $^1H—^{13}C$ gsHSQC and gsHMBC pulse sequences,[10] for making these estimates, establishing the spatial configurations of the double bonds in alkenolides, and assigning the signals in the ^1H and ^{13}C NMR spectra of alkenolides **5d,e**, **3a**, and **6** to the CH_2O, CH=CH, and other groups.

Below are given the results of analysis of the NMR spectra of a mixture of alkenolides **5e** and **6**:



5e



6

The assignments of the signals, which were made based on the 2D gsCOSY NMR spectrum of these compounds, are shown in Fig. 1. It can be seen that the H(9) and H(9′) protons of the CH_2O group (whose positions can be readily determined based on the comparison of the 2D gsHSQC and DEPT-135 NMR spectra, which allows one to distinguish the signals of the CH_2 groups bound to the O atom and possessing the characteristic chemical shift $\delta_C \simeq 64$) in alkenolides **5e** and **6** are nonequivalent (the difference between the chemical shifts is larger than 0.9 ppm), whereas the signals for the H(6) and H(7) protons of the CH=CH group in alkenolides **6**, unlike the signals for the analogous H(5) and H(6) protons in alkenolide **5e**, completely overlap. The nonequivalence of the protons of the CH_2O groups enabled us to estimate the ratio of compounds **5e** and **6** (2.7) based on the intensities of their signals. In alkenolide **6**, the double bond is located in the 6,7 position, which was confirmed by the 2D gsHSQC NMR spectrum (Fig. 2). Thus, the signals for the H(6) and H(7) protons at the double bond of alkenolide **6** coincide.

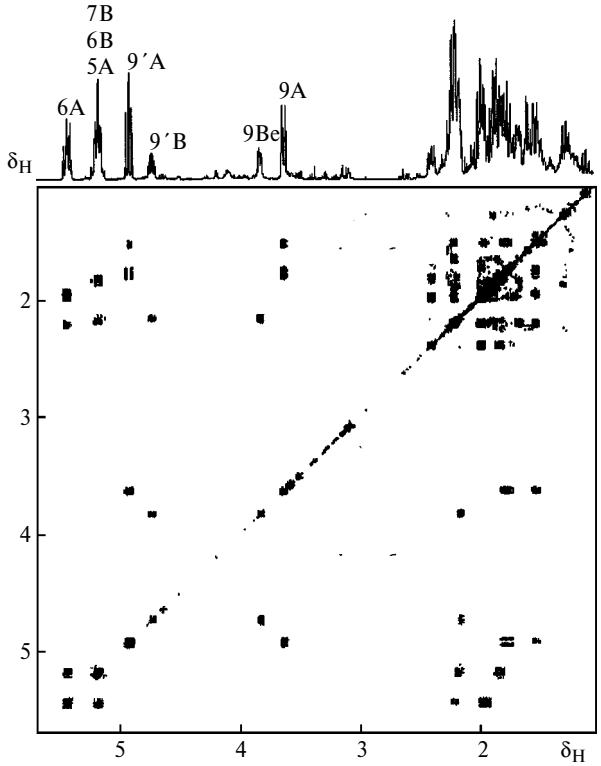


Fig. 1. The 2D gsCOSY spectrum of compounds **5e** (A) and **6** (B).

The assignments of the chemical shifts, which were made based on the 2D gsCOSY and 2D $^1H—^{13}C$ gsHSQC NMR spectra of alkenolides **5e** and **6**, are summarized in Table 3.

The *trans* configuration of the double bond in alkenolide **5e** is confirmed by the spin-spin coupling constant between the protons in the CH=CH group (^3J = 15.5 Hz). For this purpose, we used 2D $^1H—^1H$ double quantum filtered correlation (DQF-COSY) spectroscopy[11] because it was impossible to determine the spin-spin coupling constants from the ^1H NMR spectrum of alkenolide **5e** due to the complex multiplet structure of the spectrum and overlapping of the signals.

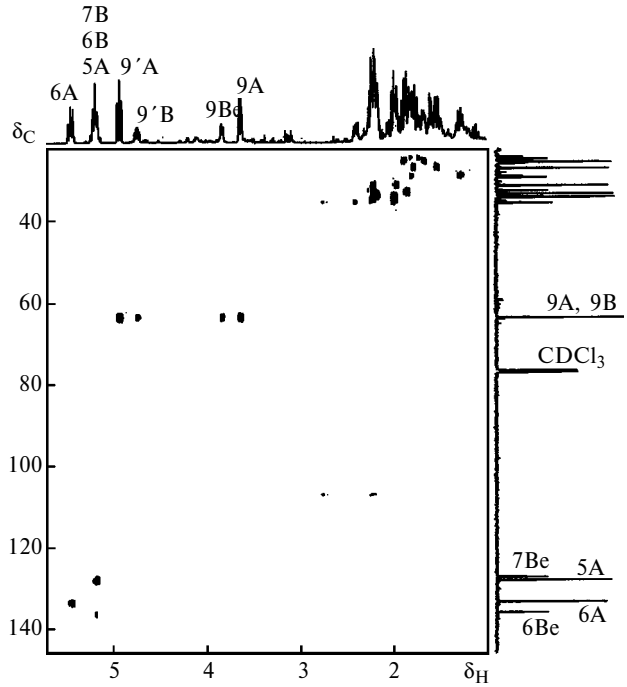


Fig. 2. The 2D $^{1}H—^{13}C$ gsHSQC spectrum of compounds **5e** (A) and **6** (B).

The fragment of the 2D COSY-DQF spectrum corresponding to the region of the protons of the CH=CH group and a one-dimensional projection of the active constant between the protons at the C(5) and C(6) atoms is shown in Fig. 3. In the case of alkenolide **6**, we failed to determine the spin-spin coupling constant according to this procedure because the signals for the protons at the C(6) and C(7) atoms almost completely overlap. However, taking into account the results of the investigation on decomposition of related hydroperoxides induced by the binary $FeSO_4—Cu(OAc)_2$ system,[4] one can say with a fair degree of assurance that alkenolide **6**, like other alkenolides, adopts the *trans* configuration. The *E* configurations of alkenolides **3—6** are also supported by the facts that their IR spectra have a charac-

Table 3. Chemical shifts (δ) in the ^{1}H and ^{13}C NMR spectra of alkenolides **5e** and **6** [a]

Atom	**5e**		**6**	
	^{1}H	^{13}C	^{1}H	^{13}C
1	—	175.9	—	175.5
2	2.00, 2.20	34.5	1.98, 2.38	36.0
3	1.66, 1.89	25.9	1.30, 1.79[b]	29.6
4	1.82	33.6	1.72, 1.81[b]	25.1
5	5.16[c]	128.0	2.21	32.9
6	5.44[c]	133.3	5.20	135.9
7	1.95, 2.22	31.7	5.16	127.2
8	1.53, 1.77	27.4	2.15	34.3
9	3.63, 4.92	63.9	4.73, 3.83	63.8

[a] The integral intensity of the signals corresponds to the expected value.
[b] The chemical shifts were estimated only approximately due to substantial overlapping of the signals for the H(3) and H(4) protons in the ^{1}H NMR spectrum of alkenolide **6**.
[c] $^{3}J_{H(5),H(6)}$ = 15.5 Hz.

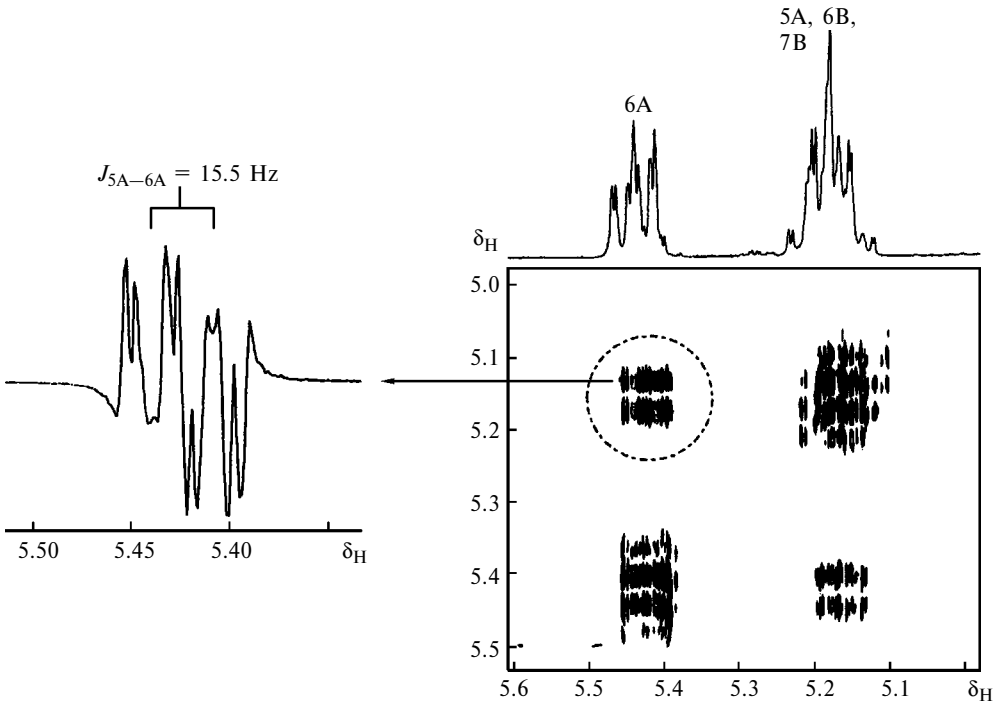


Fig. 3. Fragment of the 2D COSY-DQF spectrum of compounds **5e** (A) and **6** (B).

teristic absorption band at 960—970 cm^{-1} and that exclusively (*E*)-alkenolides were formed upon the cleavage of the bridging C—C bond in bicyclic hydroperoxides related to hydroperoxides **2a—e** under the action of the $FeSO_4$—$Cu(OAc)_2$ system.[4,7,8]

The observed regio- and stereoselectivities of the $Cu(OAc)_2$-catalyzed transformations of hydroperoxides **2** into alkenolides **3—6** are determined by rapid oxidative coupling of the carbon radicals of type **B** (see Scheme 1) with $Cu(OAc)_2$ giving rise to alkyl copper intermediates with the C—Cu^{III} σ-pseudobond (see Ref. 12) followed by their subsequent cleavage according to the mechanism of *syn*-E2 elimination.[4]

Hence, hydroperoxidation of oxabicycloalkenes containing the bridging C=C bond and the five- or six-membered oxacycle fused with the five-, six-, or twelve-membered hydrocarbon ring followed by $Cu(OAc)_2$-catalyzed decomposition of the resulting hydroperoxides makes it possible to perform the oxidative cleavage of the C=C bond giving rise to nine-, ten-, or fifteen-membered *trans*-alkenolides, respectively, as pairs of regioisomers in high yields, with the isomers in which the double bond is more remote from the ether oxygen atom predominating.

Experimental

The 1D NMR spectra were recorded on Bruker WM-250 (250 MHz for ^1H) and Bruker AM-300 (75.4 MHz for ^{13}C) spectrometers in solutions in $CDCl_3$ with Me_4Si as the internal standard. The 2D NMR spectra were measured on a Bruker DRX-500 spectrometer operating at 500 and 125 MHz for ^1H and ^{13}C, respectively. The spectra were accumulated and processed on a Silicon Graphics workstation using the XWINNMR 2.0 program package. The signals of the residual protons of the solvent and the signals of the carbon atoms of the solvent were used as the standards for the ^1H (δ_H 7.27) and ^{13}C (δ_C 77.0) NMR spectra, respectively. The 2D NMR experiments were carried out at ~20 °C using the gsCOSY[9] and ^1H—^{13}C gsHSQC pulse sequences,[10] which employ the pulse field gradients for choosing the path of the magnetization transfer (gs signifies gradient selected), and the COSY-DQF pulse sequence.[11] The parameters of accumulation and processing of the NMR spectra corresponded to those described in the literature.[13] The IR spectra were recorded on a UR-20 spectrometer (Carl Zeiss, Jena) in thin layers. The GLC analysis was carried out on Varian-3700 (flame ionization detector, 2000×3-mm glass column, 5% Carbowax 20M on Inerton) and LKhM-80 (flame ionization detector, 1000×4-mm steel column, 5% XE-60 on Chromaton N-AW) chromatographs. Regioisomeric alkenolides **3a** and **5d** were separated by GLC on a Biokhrom-21 chromatograph (flame ionization detector, 30-m×0.25-mm quartz capillary column, β-cyclodextrin, 0.25 μm, 110 °C, helium). The TLC analysis was carried out on chromatographic Silufol UV-254 plates. Flash chromatography was performed using silica gel L 40—100 μm and an AcOEt—hexane mixture (1—5% AcOEt) as the eluent. Commercial $Cu(OAc)_2$ hydrate and a 50% aqueous solution of H_2O_2 were used. The solvents were purified according to standard procedures: MeOH was distilled over $Mg(OMe)_2$ and Et_2O was distilled over $LiAlH_4$.

The mass spectra were measured on a Varian MAT-311A instrument (EI, 70 eV).

The starting oxabicycloalkenes **1a—e** were prepared according to known two- and three-step procedures[14—19] from cyclohexanone, cyclododecanone, or cyclopentanone in the following yields (% with respect to the starting cycloalkanones): 21 (**1a**); 24 (**1b**); 22 (**1c**); 28 (**1d**); and 28 (**1e**).

7-Oxabicyclo[4.3.0]non-1(6)-ene[14] (1a). B.p. 115—120 °C (30 Torr). ^1H NMR, δ: 1.31—2.42 (m, 10 H, CH_2); 3.95 (t, 2 H, CH_2O, J = 5.8 Hz).

13-Oxabicyclo[10.3.0]pentadec-1(12)-ene[15,16] (1b). B.p. 115—120 °C (1.5 Torr). ^1H NMR, δ: 1.18—1.61 (m, 16 H, CH_2); 2.06—2.19 (m, 4 H, CH_2C=); 2.44—2.55 (m, 2 H, CH_2C=); 4.20 (t, 2 H, CH_2O, J = 5.8 Hz).

14-Methyl-13-oxabicyclo[10.3.0]pentadec-1(12)-ene[16,17] (1c). B.p. 135—145 °C (1.5 Torr). ^1H NMR, δ: 1.12—1.50 (m, 25 H, CH_3, CH_2, CH); 2.03—2.20 (m, 4 H, CH_2C=); 4.47—4.61 (m, 1 H, CHO).

2-Oxabicyclo[4.3.0]non-1(6)-ene[18] (1d). B.p. 105—110 °C (20 Torr). ^1H NMR, δ: 1.70—1.85 (m, 4 H, CH_2); 1.85—1.98 (m, 2 H, CH_2C=); 2.12—2.33 (m, 4 H, CH_2C=); 3.87—3.97 (t, 2 H, CH_2O, J = 5.8 Hz). ^{13}C NMR, δ: 19.1, 21.7, 22.6, 30.8, 32.2 (CH_2); 64.6 (CH_2O); 106.5 (C=); 150.9 (=C—O).

2-Oxabicyclo[4.4.0]dec-1(6)-ene[19] (1e). B.p. 70—75 °C (10 Torr). ^1H NMR, δ: 1.50—1.72 (m, 6 H, CH_2); 1.75—2.05 (m, 6 H, CH_2C=); 3.92 (t, 2 H, CH_2O, J = 5.8 Hz). ^{13}C NMR, δ: 23.0, 23.2, 23.3, 25.3, 27.3, 29.0 (CH_2); 65.6 (CH_2O); 104.3 (C=); 146.9 (=C—O).

Hydroperoxidation of oxabicycloalkenes 1a—e (general procedure). A 50% aqueous solution of H_2O_2 (1.5—2.0 equiv.), which was cooled to 0 °C and contained a catalytic amount of concentrated H_2SO_4 (0.05—0.1 g), was added dropwise to an intensively stirred solution of oxabicycloalkene (5—15 mmol) in MeOH or Et_2O (10—15 mL) cooled to 0 °C at such a rate as to maintain the temperature of the reaction mixture below 5 °C (generally, during at most 5 min). The reaction mixture was stirred at 0—5 °C until the complete conversion of the substrate was achieved (0.5—1.5 h), the latter being monitored by TLC (AcOEt—hexane), and then neutralized with solid $NaHCO_3$. The liquid phase was separated by decantation and concentrated *in vacuo* at 0—10 °C until the solvent, water, and an excess of H_2O_2 were completely, where possible, removed (8—10 Torr, 2 h). Then the residual impurities were removed *in vacuo* (1 Torr) at 0 °C during 0.5 h to obtain hydroperoxides **2a—e**, which were analyzed by IR and ^1H NMR spectroscopy. The active oxygen in **2a—e** was determined by iodometric titration.[20] The results of analysis and the yields of compounds **2a—e** are given in Table 1. The resulting hydroperoxides were used without additional purification.

(*E*)-6-Hydroperoxy-7-oxabicyclo[4.3.0]nonane (2a). IR, ν/cm^{-1}: 3360, 2950, 2860, 1700, 1450, 1355, 1175, 1140, 1005, 930, 650. ^1H NMR, δ: 0.90—2.40 (m, 11 H, CH_2, CH); 3.88—4.12 (m, 2 H, CH_2O); 8.70—9.70 (br.s, 1 H, OOH).

(*E*)-12-Hydroperoxy-13-oxabicyclo[10.3.0]pentadecane[15,16] (2b). IR, ν/cm^{-1}: 3355, 2935, 2860, 1635, 1430, 1090. ^1H NMR, δ: 0.95—2.10 (m, 23 H, CH_2, CH); 3.90—4.15 (m, 2 H, CH_2O); 8.70—9.20 (br.s, 1 H, OOH).

(*E*)-12-Hydroperoxy-14-methyl-13-oxabicyclo[10.3.0]pentadecane[16,17] (2c). IR, ν/cm^{-1}: 3355, 2930, 2860, 1630, 1440, 1080. ^1H NMR, δ: 1.10—2.20 (m, 25 H, CH_3, CH_2, CH); 3.55—3.98 (m, 2 H, CH_2O); 8.75 (br.s, 1 H, OOH).

(*E*)-1-Hydroperoxy-2-oxabicyclo[4.3.0]nonane (2d). IR, ν/cm^{-1}: 3365, 2940, 2860, 1700, 1450, 1175, 1005, 920. ^1H NMR, δ: 1.20—2.20 (m, 11 H, CH_2, CH); 3.55—3.92 (m, 2 H, CH_2O); 9.00—9.50 (br.s, 1 H, OOH). ^{13}C NMR, δ: 19.8,

20.6, 22.2, 28.4 (CH_2); 35.2 (CH); 38.7 (CH_2—C—O); 61.4 (CH_2O); 112.2 (C—O).

(*E*)-1-Hydroperoxy-2-oxabicyclo[4.4.0]decane[21] (2e). IR, ν/cm^{-1}: 3360, 2940, 2860, 1720, 1450, 1180, 1000. ^{1}H NMR, δ: 1.10—1.70 (m, 12 H, CH_2, CH); 3.55—3.98 (m, 2 H, CH_2O); 8.40—8.70 (br.s, 1 H, OOH). ^{13}C NMR, δ: 22.5, 24.6, 25.6, 26.0, 29.2 (CH_2); 32.0 (CH); 43.5 (CH_2—C—O); 61.4 (CH_2O); 103.4 (C—O).

Hydroperoxides **2d** and **2e**, which were prepared from solutions of oxabicycloalkenes **1d** and **1e**, respectively, in MeOH, contained known 1-methoxy-2-oxabicyclo[4.3.0]nonane and 1-methoxy-2-oxabicyclo[4.4.0]decane[22,23] as impurities. The impurities were removed by extraction with hexane. The structures of these by-products were established based on the ^{1}H NMR spectra of the residues, which were obtained by concentrating the residues of the hexane extracts.

$Cu(OAc)_2$-Catalyzed transformations of hydroperoxides into alkenolides (general procedure). A solution or a suspension of hydroperoxide (5—10 mmol) in $MeCOPr^n$ (5—10 mL) was added to a solution of $Cu(OAc)_2 \cdot H_2O$ (5 mol.% with respect to the amount of hydroperoxide) in $MeCOPr^n$ (10—15 mL), which was heated to boiling and vigorously stirred, during 15—30 min. Then the reaction mixture was stirred and refluxed until the hydroperoxide was completely decomposed (1.5—3 h), cooled, diluted with hexane (20—40 mL), and separated from the precipitate that formed by filtration. The precipitate was washed with AcOEt (20 mL), the filtrate was concentrated *in vacuo*, and the residue was analyzed by GLC. Then the reaction mixture was distilled *in vacuo* using a water-cooled distilling head (10—30 Torr, the temperature of the bath was 100—180 °C) and purified by flash chromatography (AcOEt—light petroleum as the eluent). Unlike other lactones, the mixture of alkenolides **5d** and **3a** was isolated using a standard distillation flask. The yields and the ratios of the products are given in Table 2.

(*E*)-Oct-5-eno-8-lactone (3a) and (*E*)-oct-6-eno-8-lactone (4a). IR (KBr, thin layer), ν/cm^{-1}: 1730 (C=O), 960—970 (*trans*-CH=CH). ^{1}H NMR, δ: **3a:** 1.25—2.40 (m, 12 H, CH_2); 4.08—4.30 (m, 2 H, CH_2O); 5.00—5.27 (m, 2 H, CH=CH); **4a:** 1.25—2.40 (m, 12 H, CH_2); 4.62—4.69 (d, 2 H, CH_2O, J = 6.9 Hz); 5.57—5.78 (m, 2 H, CH=CH). ^{13}C NMR, δ: **3a:** 25.2, 26.5, 28.1, 34.2 (CH_2); 62.6 (CH_2O); 127.9, 136.3 (C=C); 177.4 (C=O); **4a:** 27.4, 28.5, 29.5, 35.9 (CH_2); 61.9 (CH_2O); 124.5, 134.6 (C=C); 178.7 (C=O). MS, m/z (I_{rel} (%)): 140 (21.9) $[M]^+$, 126 (9.4), 125 (56.4), 111 (19.1), 110 (39.1), 100 (13.2), 99 (51.1), 95 (36.1), 86 (52.4), 83 (29.8), 82 (62.7), 71 (37.9), 68 (54.5), 67 (63.9), 56 (28.8), 55 (100), 45 (26.3), 43 (95.9). Found (%): C, 68.39; H, 9.03. $C_8H_{12}O_2$. Calculated (%): C, 68.55; H, 8.63.

(*E*)-Tetradecen-11-eno-14-lactone (3b) and (*E*)-tetradecen-12-eno-14-lactone (4b).[15,16,24] IR (KBr, thin layer), ν/cm^{-1}: 1720 (C=O), 960 (*trans*-CH=CH). ^{1}H NMR, δ: **3b:** 1.15—2.40 (m, 40 H, CH_2); 4.10—4.20 (m, 2 H, CH_2O); 5.32—5.78 (m, 2 H, CH=CH); **4b:** 1.15—2.40 (m, 40 H, CH_2); 4.45—4.58 (d, 2 H, CH_2O, J = 7.1 Hz); 5.51—5.80 (m, 2 H, CH=CH). ^{13}C NMR, δ: 21.5, 22.3, 22.4, 22.7, 24.3, 24.5, 24.6, 24.7, 24.9, 25.3, 26.0, 26.1, 26.2, 26.3, 26.8, 26.9, 31.0, 31.4, 33.6, 34.4 (CH_2); 64.0, 64.7 (CH_2O); 125.0, 127.5, 132.6, 137.4 (C=C); 173.5, 174.2 (C=O). MS, m/z (I_{rel} (%)): 224 (52.7) $[M]^+$, 206 (13.9), 195 (11.6), 181 (11.8), 167 (11.8), 164 (18.4), 154 (10.6), 153 (11.9), 151 (15.6), 150 (31.6), 111 (45.0), 110 (50.9), 109 (64.3), 108 (41.8), 96 (69.2), 94 (51.9), 81 (79.7), 80 (77.6), 68 (98.8), 67 (80.3), 55 (100), 54 (82.4).

(*E*)-Pentadecen-11-eno-14-lactone (3c) and (*E*)-pentadecen-12-eno-14-lactone (4c).[15,16] IR (KBr, thin layer), ν/cm^{-1}: 1720 (C=O), 960 (*trans*-CH=CH). ^{1}H NMR, δ: **3c:** 1.05—2.45 (m, 50 H, CH_3, CH_2); 4.92—5.01 (m, 1 H, CH—O); 5.32—5.40 (m, 2 H, CH=CH); **4c:** 1.05—2.45 (m, 50 H, CH_3, CH_2); 5.02—5.12 (d, 1 H, CH—O); 5.60—5.78 (m, 2 H, CH=CH). ^{13}C NMR, δ: **3c:** 20.4, 22.4, 24.3, 24.7, 25.8, 26.0, 27.5, 28.4, 30.8, 33.6, 38.7, 40.3 (CH_2); 70.4 (CH—O); 126.6, 132.6 (C=C); 173.6 (C=O). MS, m/z (I_{rel} (%)): 238 (7.3) $[M]^+$, 221 (3.6), 193 (3.0), 178 (3.1), 163 (3.5), 151 (7.3), 135 (8.0), 123 (1.7), 113 (2.4), 100 (47.6), 95 (42.2), 82 (35.4), 81 (49.5), 71 (25.7), 68 (53.9), 67 (55.8), 57 (29.1), 55 (100).

(*E*)-Oct-4-eno-8-lactone (5d) and (*E*)-oct-5-eno-8-lactone (3a). B.p. 60—65 °C (35 Torr). IR (KBr, thin layer), ν/cm^{-1}: 1730 (C=O), 990 (*trans*-CH=CH). ^{1}H NMR, δ: **5d:** 1.70—2.35 (m, 8 H, CH_2); 4.00—4.45 (m, 2 H, CH_2O); 5.35—5.47 (m, 2 H, CH=CH). MS, m/z (I_{rel} (%)): 140 (7.7) $[M]^+$, 125 (12.2), 124 (9.3), 97 (11.2), 83 (12.9), 82 (11.1), 81 (19.4), 80 (17.6), 78 (13.0), 71 (38.1), 69 (18.5), 68 (26.6), 67 (41.0), 60 (21.5), 56 (27.2), 55 (66.9), 54 (23.9), 53 (18.4), 43 (100). Found (%): C, 69.06; H, 8.65. $C_8H_{12}O_2$. Calculated (%): C, 68.55; H, 8.63. The spectra of compound **3a** were identical with those of the sample prepared from hydroperoxide **2a**.

(*E*)-Non-5-eno-9-lactone (5e) and (*E*)-non-6-eno-9-lactone (6). IR (KBr, thin layer), ν/cm^{-1}: 1735 (C=O), 960, 972 (*trans*-CH=CH). The ^{1}H and ^{13}C NMR spectra are given in Table 3. MS, m/z (I_{rel} (%)): 154 (13.6) $[M^+]$, 136 (9.5), 127 (14.7), 111 (8.4), 110 (12.7), 109 (10.1), 97 (11.2), 95 (32.9), 94 (14.5), 84 (15.6), 82 (15.6), 79 (25.4), 71 (100), 70 (17.8), 67 (39.1), 57 (17.0), 55 (53.3), 53 (14.3), 45 (22.6), 44 (44.2). Found (%): C, 69.81; H, 9.23. $C_9H_{14}O_2$. Calculated (%): C, 70.10; H, 9.15.

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