Selectivity in Lewis acid-mediated fragmentations of peroxides and ozonides: application to the synthesis of alkenes, homoallyl ethers, and 1,2-dioxolanes †

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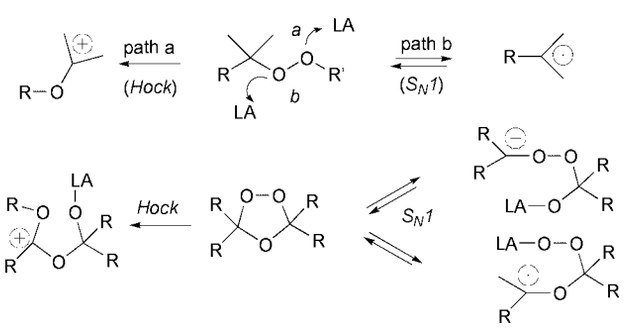
Fragmentation of dialkyl peroxides and ozonides is strongly influenced by the choice of Lewis acid. $TiCl_4$ promotes C–O ionization (S_N1 reaction) of tertiary peroxides while $SnCl_4$ and $BF_3{\cdot}OEt_2$ promote O–O heterolysis (Hock reaction). The cationic intermediates are trapped with allyltrimethylsilane to afford allylated alkanes and homoallyl ethers. In the absence of a nucleophile, ozonides (1,2,4-trioxolanes) invariably undergo O–O heterolysis. However, the combination of allyltrimethylsilane and $SnCl_4$ results in formation of 1,2-dioxolanes *via* trapping of intermediates derived from S_N1 ionization.

Introduction

The acid-catalyzed decomposition of peroxides is an important synthetic process for which two major modes of reaction are typically observed. Heterolysis of the O–O bond (Hock cleavage) produces oxycarbenium ion intermediates *via* migration of a neighboring substituent, while acid-catalyzed C–O ionization furnishes carbenium ions (Scheme 1). Selectivity between these



Scheme 1 Modes of Lewis acid (LA) mediated activation.

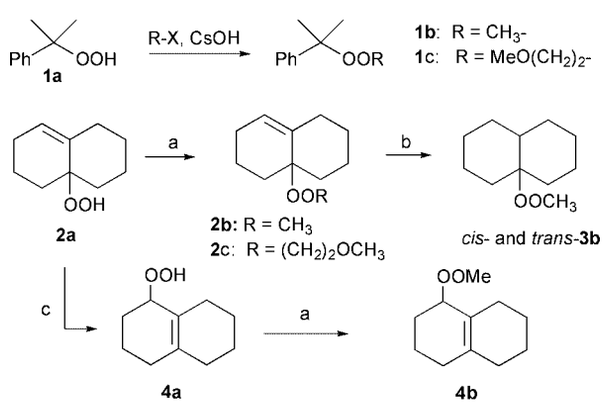
pathways is largely dependent on substrate structure,[1–5] with C–O ionization favored by stabilization of the resulting carbocation and O–O heterolysis favored by neighboring groups of high migratory aptitude. Although there have been a number of reports involving Lewis acid-mediated decomposition of peroxides, there are few data regarding reagent-directed selectivity.[6,7] Our interest arose from studies of Lewis acid-mediated allylation of monoperoxyacetals. $TiCl_4$-promoted reactions were found to proceed with selective displacement of the peroxide to form ethers, whereas $SnCl_4$-promoted reactions resulted in selective displacement of the alkoxide to form allylated peroxides.[8,9] We were interested in using similar methodology to explore the fragmentations of highly substituted peroxides and ozonides, using the relative yields of allylated products as an indicator of the ability of individual Lewis acids to dictate a particular pathway. We now report the effect of peroxide structure and Lewis acid on the fragmentation of dialkyl peroxides and ozonides.

† Experimental results for **22l**, **26** and **27** are available as supplementary data. For direct electronic access see http://www.rsc.org/suppdata/p1/b0/b001391i/

Results and discussion

Substrate preparation

Dialkyl peroxides were prepared by alkylation of the appropriate hydroperoxide with an alkyl halide or sulfonate in the presence of CsOH (Scheme 2).[10] The selective saturation of



Scheme 2 Preparation of peroxide substrates. *Reagents and conditions*: a. CsOH, DMF, MeI or $MeO(CH_2)_2OTs$; b. PtO_2, H_2; c. di-*tert*-butyl hyponitrite, C_6H_6, 60 °C.

unsaturated peroxide is based upon reported work from our group.[11]

Ozonides **5a**–**m** were prepared by co-ozonolysis of oximes and ketones,[12] co-ozonolysis of enol ethers and ketones,[13] or by ozonolysis of alkenes (Table 1).

Fragmentation of hydroperoxides and peroxides

Reaction of 2-phenyl-2-propyl hydroperoxide with Lewis acids in the presence of allyltrimethylsilane furnished low yields of allylcumene **6** (Table 2). 2-Phenyl-2-propyl methyl peroxide (**1b**) underwent $TiCl_4$-mediated allylation to furnish a good yield of **6**, while the corresponding reaction with $SnCl_4$ afforded only allylated phenyl ether **7**. Interestingly, reaction with allyltrimethylsilane and $BF_3{\cdot}OEt_2$ promoted formation of methyl ether **8b**. Methoxyethyl peroxide **1c** was anticipated to favor heterolysis based upon the ability to enter into a five-membered chelate,[14,15] and this outcome was observed in the presence of $SnCl_4$. However, both S_N1 and Hock products were obtained in the presence of $BF_3{\cdot}OEt_2$ or $TiCl_4$.

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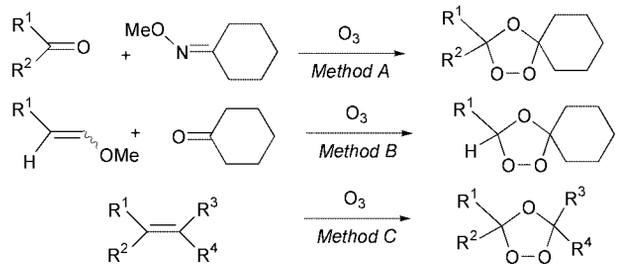
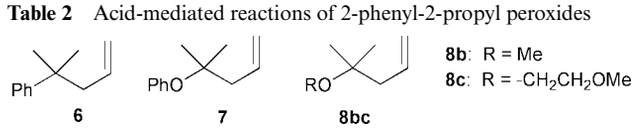
Table 1 Synthesis of ozonides



Ozonide	R^1	R^2	R^3	R^4	Method	Yield (%)
5a	–$(CH_2)_4$–		–$(CH_2)_5$–		A	60
5b	–$(CH_2)_5$–		–$(CH_2)_5$–		A	67
5c	–$(CH_2)_6$–		–$(CH_2)_5$–		A	63
5d	CH_3	Ph	–$(CH_2)_5$–		A	57
5e	C_4H_9	C_4H_9	–$(CH_2)_5$–		A	47
5f	C_8H_{17}	H	–$(CH_2)_5$–		B	47
5g	Ph	H	–$(CH_2)_5$–		B	65
5h	H	H	–$(CH_2)_5$–		C	78
5i	CH_3	$C(CH_3)_3$	–$(CH_2)_5$–		A	53
5j	H	Ph	H	C_3H_7	C	73
5k	H	Ph	H	H	C	77
5l	CH_3	Ph	H	H	C	61
5m	H	–$(CH_2)_3$–		CH_3	C	73

Table 2 Acid-mediated reactions of 2-phenyl-2-propyl peroxides



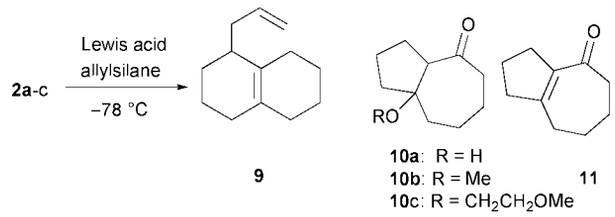
6 **7** **8bc**

Peroxide	Acid	*T*/°C	*t*/min	**6** (%)	**7** (%)	**8** (%)
1a	$BF_3{\cdot}OEt_2$	RT	30	9	—	—
1a	$TiCl_4$	−78	10	18	—	—
1a	$SnCl_4$	−78	30	34	—	—
1b	$BF_3{\cdot}OEt_2$	0–RT	120	—	—	55
1b	$TiCl_4$	−78	10	54	15	—
1b	$SnCl_4$	−40	30	—	64	—
1b	$SnCl_4$	−78	60	—	74	—
1c	$BF_3{\cdot}OEt_2$	RT	90	10	—	30
1c	$TiCl_4$	−78	1	56	36	—
1c	$SnCl_4$	−20	1	—	17	42
1c	$SnCl_4$	−40	2	—	37	37
1c	$SnCl_4$	−78	10	—	80	20

Octahydronaphthyl hydroperoxide **2a** underwent rapid fragmentation in the presence of $SnCl_4$ and allylsilane to afford a mixture of an elimination-prone hydroxyketone (**10a**) and enone **11** (Table 3). The corresponding reaction in the presence of $EtAlCl_2$ and allylsilane furnished **10a/11** accompanied by a small amount of the allylated S_N1 adduct **9**.[16] The methyl peroxide, **2b**, underwent $TiCl_4$-promoted allylation to afford only **9** whereas reaction with stoichiometric $SnCl_4$ or catalytic TMSOTf resulted in nearly exclusive ($SnCl_4$) or exclusive (TMSOTf) formation of **10b/11**. Reaction of the methoxyethyl peroxide **2c** gave predominately ($TiCl_4$) or exclusively ($SnCl_4$) the rearrangement-derived ring expansion products **9c/10**. Higher yields of rearrangement product were observed in the presence of tetra-*n*-butylammonium perchlorate, with or without acetonitrile as a cosolvent. No reaction was observed in the presence of allyltributylstannane, presumably reflecting rapid metathesis with $SnCl_4$ to form a less reactive allylstannane–Lewis acid pair.[17]

The isomeric octahydronaphthyl peroxide (**4b**) underwent $SnCl_4$-mediated reaction to furnish a mixture of the allylated octahydronaphthalene and the spirodecanone **12** (Scheme 3). The saturated analog **3** underwent selective consumption of the *cis* isomer to form an allylated epoxycyclodecane (**13**) derived from migration of the central C–C bond, accompanied by smaller amounts of an allylated oxepane (**14**) derived from migration of a peripheral C–C bond.

Table 3 Allylation of octahydronaphthyl peroxides

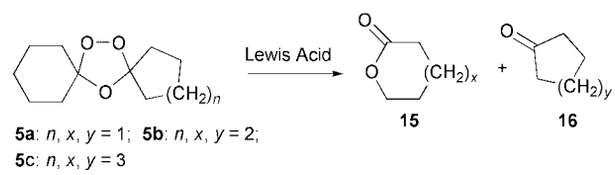


9 **11**

Peroxide	L. acid (equiv.)	*t*/min	**9** (%)	[**10** + **11**] (%)
2a	$SnCl_4$ (1.0)	5	Decomp.	53
2a	$EtAlCl_2$ (1.0)	5	18	76
2b	$TiCl_4$ (1.0)	1	68	—
2b	$SnCl_4$ (1.0)	3	8	74
2b	TMSOTf (0.1)	5	—	80
2c	$TiCl_4$ (1.0)	1	11	45
2c	$SnCl_4$ (1.0)	1	—	67
2c	$SnCl_4$ (1.0)[a]	5	—	98
2c	$SnCl_4$ (1.0)	5	—	45
2c	$SnCl_4$ (1.0)[a,b]	5	—	89

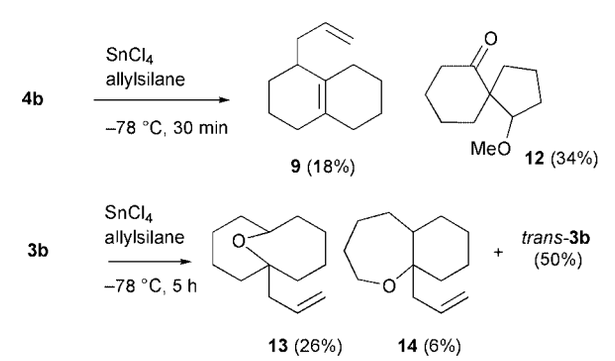
[a] Presence of stoichiometric n-Bu_4NClO_4. [b] 20% $MeCN–CH_2Cl_2$ as solvent.

Table 4 Lewis acid-mediated fragmentation of ozonides



15 **16**

Ozonide	Lewis acid	*T*/°C	Yield (%) **15a**	**15b**	**15c**	**16a**	**16b**	**16c**
5a	$TiCl_4$	−78	18	32		30	20	
	$SnCl_4$	0	5	39		45	11	
	TMSOTf	RT	14	36		36	14	
5b	$TiCl_4$	−78		52			48	
	$SnCl_4$	0		49			51	
	TMSOTf	RT		50			50	
5c	$TiCl_4$	−78		43	5		11	41
	$SnCl_4$	0		44	5		6	45
	TMSOTf	RT		49	1		1	49

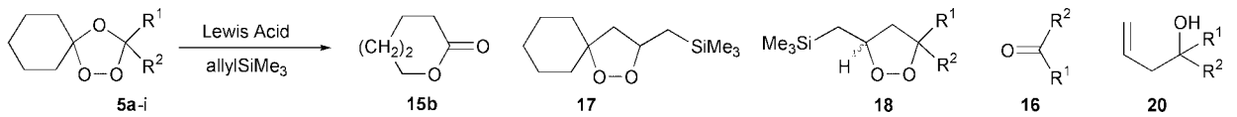


Scheme 3 Rearrangement of octa- and decahydronaphthyl peroxides.

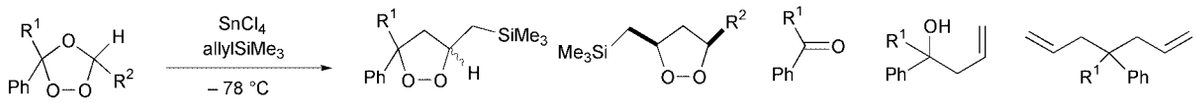
Fragmentation of ozonides

Table 4 summarizes Lewis acid-promoted decomposition of ozonides **5a–c**. The spiro-6,6-ozonide **5b** invariably underwent Hock-type decomposition to afford a 1 : 1 mixture of caprolactone (**15b**) and cyclohexanone (**16b**). The spiro-6,5- and -6,7-

Table 5 Lewis acid-mediated allylation of ozonides



Ozonide	R^1	R^2	Lewis acid	*T*/°C	Yield (%) 15b	17	18	Ketones	20
5a		$-(CH_2)_4-$	$SnCl_4$	−78–0	11	50	—	**16a**,**b** (trace)	—
5b		$-(CH_2)_5-$	$TiCl_4$	−78	9	0	—	**16b**,**c** (35% combined)	—
5b		$-(CH_2)_5-$	$SnCl_4$	−78–0	17	57	—	**16c** (trace)	—
5b		$-(CH_2)_5-$	TMSOTf	−78–0	—	NR	—	—	—
5b		$-(CH_2)_5-$	$SbCl_5$	−78–RT	Major	Decomp.	—	**16b** (major, as mixture)	—
5c		$-(CH_2)_6-$	$SnCl_4$	−78–0	39	24	—	**16c** (trace)	—
5d	CH_3	Ph	$SnCl_4$	−78–0	25	61	—	**16d** (93%)	—
5e	C_4H_9	C_4H_9	$SnCl_4$	−78–0	40	14	—	**16e** (70%)	75
5f	H	C_8H_{17}	$SnCl_4$	−78	—	56	—	—	50
5g	H	Ph	$SnCl_4$	−78	—	79	—	—	13
5h	H	H	$SnCl_4$	−78	—	10	—	—	—
5i	CH_3	$C(CH_3)_3$	$SnCl_4$	−78–0	31	21	9 (*cis*)	—	—



Ozonide	R^1	R^2	**22** (%, *cis*:*trans*)	**23** (%)	Ketones (%)	**20j** (%)	**24** (%)
5j	H	C_3H_7	15 (1:1)	7	39	20	—
5k	H	H	15 (1:1)	—	22	24	—
5l	CH_3	H	9 (1:1)	—	43	—	2.5

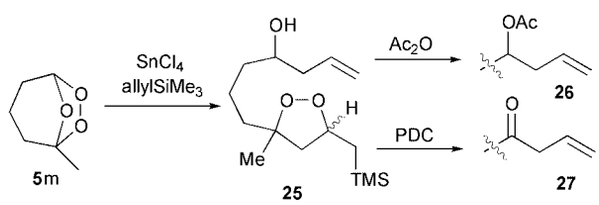
analogs **5a** and **5c** underwent similar reactions, again favoring the product derived from migration of a cyclohexyl C–C bond. $TiCl_4$-promoted reactions occurred at much lower temperatures than those promoted by $SnCl_4$ or TMSOTf.

Fragmentations of ozonides in the presence of allyltrimethylsilane

Reaction of ozonide **5b** with $TiCl_4$ in the presence of allyltrimethylsilane occurred at −78 °C, producing caprolactone, cyclohexanone, and cycloheptanone (Table 5). However, the corresponding reaction with $SnCl_4$ occurred only upon warming to ~0 °C and furnished spirodioxolane **17** accompanied by small amounts of cycloheptanone. No reaction was observed in the presence of TMSOTf. Application of the most favorable conditions ($SnCl_4$, −78 to 0 °C, allyltrimethylsilane) to a series of tri- and tetrasubstituted ozonides invariably led to the predominant formation of dioxolane **17**. Decomposition of several styrene ozonides proceeded in low yield to furnish as the major product the dioxolane derived from attack on the center better able to stabilize positive charge. Reaction of **5j** also produced significant quantities of benzaldehyde and 1-phenylbut-3-enol while the reaction of **5l** furnished 43% of acetophenone and traces of 4-methyl-4-phenylhepta-1,6-diene.

Allylation of a bicyclic ozonide

The $SnCl_4$-mediated allylation of a bicyclic ozonide was investigated to determine whether the S_N1-type reaction proceeded *via* initial ionization of the C–O (ethereal) or C–OO (peroxide) linkage. Treatment of ozonide **5m** with $SnCl_4$ and allyltrimethylsilane produced a good yield of 3,5,5-trisubstituted 1,2-dioxolane (**25**) as a single regioisomer consisting of two separate *cis* and two separate *trans* diastereomers in a 35:35:15:15 ratio (Scheme 4). The presence of a secondary

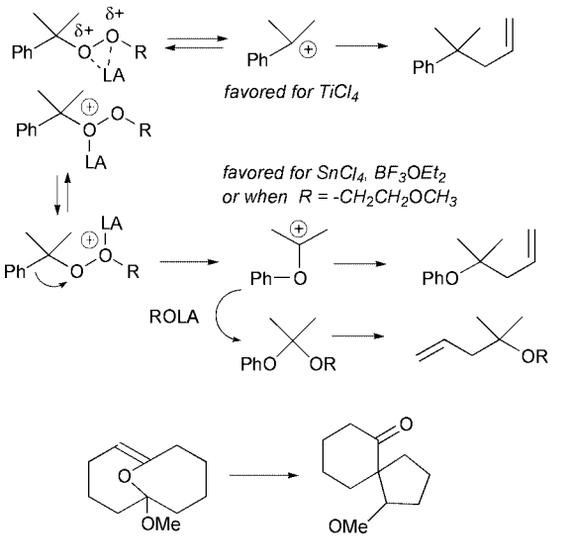


Scheme 4 Allylation of a bicyclic ozonide.

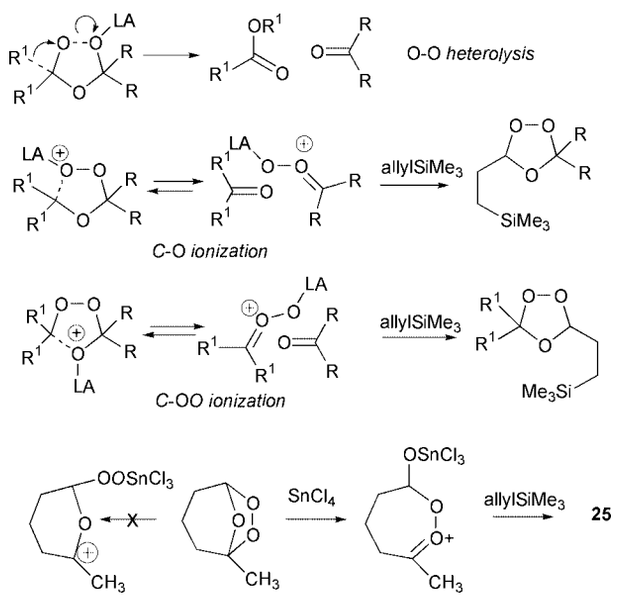
alcohol was confirmed by the downfield shift of the H–C–O signal upon formation of acetate **26** and by the disappearance of the same signal upon oxidation to ketone **27**. The stereochemical assignment was supported by the observation of a 70:30 mixture of *cis*/*trans* two diastereomers upon oxidation to ketone **27**.

Discussion

The selective formation of allylcumene and allyloctahydronaphthalene provides clear evidence for the ability of $TiCl_4$ to selectively promote S_N1-type C–O ionization of dialkyl peroxides (Scheme 5). $SnCl_4$-mediated allylations proceed with a strong preference for Hock rearrangement. In some cases, the intermediate oxycarbenium ion is diverted into other pathways too rapidly for trapping by allylsilane. For example, the failure to observe ring-expanded allyl ethers from **2a**–**c** or **4b** reflects rapid intramolecular closure of the intermediate vinyl ketals, an outcome previously observed for $Cu(OTf)_2$-mediated rearrangement of allyl hydroperoxides.[18] Similarly, the conversion of 2-phenyl-2-propyl alkyl peroxides to alkyl allyl ethers results from formation and subsequent reaction of mixed acetals; the greater extent of this process in the presence of $BF_3{\cdot}OEt_2$ may indicate the higher nucleophilicity of alkoxyboranes relative to alkoxystannanes.



Scheme 5 Overview of peroxide fragmentation.



Scheme 6 Pathways for ozonide ionization.

Ozonides (1,2,4-trioxolanes) can in principle undergo acid-catalyzed decomposition through ionization of peroxide, ionization of alkoxide, or oxygen–oxygen heterolysis (Scheme 6).[19] Acidolysis of ozonides with $ClSO_3H$ or $SbCl_5$ has been reported to produce metalated or protonated carbonyl oxides through ionization of the C–OO linkage, followed by loss of carbonyl from the oxycarbenium ion intermediate.[20–22] Self-reaction and/or attack on another ozonide results in formation of cyclic peroxides, while trapping of the metalated carbonyl oxide with 1,1-substituted alkenes produces 1,2-dioxolanes.[23] Related work from our group has demonstrated $SnCl_4$-mediated allylation of ozonides furnishes 1,2-dioxolanes, presumably *via* similar intermediates. In the current study, both $SnCl_4$ and $TiCl_4$ promote O–O heterolysis. However, in the presence of allyltrimethylsilane, only $SnCl_4$ promotes formation of 1,2-dioxolanes. This result indicates that $SnCl_4$ is more efficient in promoting reversible ionization of the C–O linkage, that $TiCl_4$ promotes more rapid O–O heterolysis, or some combination of these factors. The regioselectivity in allylation of unsymmetrical ozonides supports a mechanism involving ionization of both the C–O and C–OO linkages. In the case of a bicyclic ozonide, only the products corresponding to initial C–O ionization were observed.

In conclusion, $SnCl_4$ and $TiCl_4$ provide alternate low energy pathways for activation of dialkyl peroxides. $TiCl_4$ tends to promote S_N1 ionization, even when this requires activation of the more hindered oxygen. In contrast, $SnCl_4$ generally promotes selective O–O heterolysis through activation of the less hindered peroxide oxygen. Allyltrimethylsilane is an effective trapping agent generally able to capture the carbenium or oxycarbenium intermediates. In the absence of a nucleophile, both $TiCl_4$ and $SnCl_4$ promote O–O heterolysis of ozonides, while the combination of $SnCl_4$ and allyltrimethylsilane furnishes 1,2-dioxolanes through capture of an intermediate peroxycarbenium ion. Our results demonstrate the ability to dictate the mode of peroxide and ozonide decomposition through selection of Lewis acid, as well as the ability to employ this decomposition for the controlled synthesis of alkenes and allyl ethers.

Experimental

Standard conditions have been described.[24] As in any work involving peroxides, standard precautions (safety shields, avoidance of heat, light, or metal salts, use of minimal scale) should be faithfully observed.[25–27] NMR spectra were acquired at 300 MHz (^{1}H) and 75 MHz (^{13}C) in $CDCl_3$ unless otherwise noted; *J* values are given in Hz; DEPT135 assignments are indicated with (+) or (−) where relevant. IR spectra were recorded as neat oils; C=O and O–H stretches are reported. "Standard work-up" refers to aqueous quench, two-fold ether extraction (25–100 mL, depending upon scale), drying over Na_2SO_4, and concentration *in vacuo*. Unless otherwise indicated, compounds were purified by silica flash chromatography.

Methyl 2-phenyl-2-propyl peroxide (1b)

To a 0 °C solution of iodomethane (0.84 mL, 13.5 mmol) in DMF (30 mL) under N_2 was added cumene hydroperoxide **1a** (1.2 mL, 6.8 mmol) followed by CsOH (1.7 g, 8.1 mmol). The resulting solution was stirred for 2 h at 0 °C and then submitted to a standard workup, followed by flash chromatography (2.5% ether–pentane) to afford methyl 2-phenyl-2-propyl peroxide **1b** (0.70 g, 63%) as a colorless oil: $R_f = 0.24$ (2.5% EA–hex); ^{1}H NMR δ 7.54–7.27 (m, 5 H), 3.82 (s, 3 H), 1.64 (s, 6 H); ^{13}C NMR δ 145.3, 128.1, 127.0, 125.4, 82.9, 62.9, 26.4; Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 72.22; H, 8.41%.

2-Methoxyethyl 2-phenyl-2-propyl peroxide (1c)

To a 0 °C solution of 2-methoxyethanol (1.0 mL, 12.7 mmol), and pyridine (2.1 mL, 25.4 mmol) under N_2 was added *p*-tolylsulfonyl chloride (2.40 g, 12.7 mmol). After stirring for 1 h, the reaction was quenched with ice-cold 10% HCl (100 mL). The ether extracts (3 × 100 mL) were washed with aqueous saturated NaCl solution (3 × 100 mL) and dried over Na_2SO_4. After removal of solvent *in vacuo*, flash chromatography (20% EA–hex) afforded 2-methoxyethyl toluene-*p*-sulfonate ester (2.5 g, 86%) as a colorless oil: $R_f = 0.23$ (5% EA–hex); ^{1}H NMR δ 7.76 (d, 2 H, $J = 8.4$), 7.31 (d, 2 H, $J = 8.1$), 4.12 (t, 2 H, $J = 4.5$), 3.54 (t, 2 H, $J = 4.5$), 3.27 (s, 3 H), 2.41 (s, 3 H); ^{13}C NMR δ 144.8, 132.9, 129.7, 127.8, 69.9, 69.0, 58.9, 21.5; Anal. Calcd for $C_{10}H_{14}SO_4$: C, 52.16; H, 6.13. Found: C, 51.99; H, 6.05%.

Alkylation of cumene hydroperoxide (1.7 mL, 9 mmol) with the methoxyethyl toluene-*p*-sulfonate (2.10 g, 9 mmol) as for **1b**, furnished, after standard work-up and flash chromatography (10% EA–hex), peroxide **1c** (0.96 g, 51%) as a colorless oil: $R_f = 0.63$ (20% EA–hex); ^{1}H NMR δ 7.52–7.25 (m, 5 H), 4.09 (t, 2 H, $J = 4.8$), 3.59 (t, 2 H, $J = 5.0$), 3.35 (s, 3 H), 1.63 (s, 6 H); ^{13}C NMR δ 145.2, 128.0, 127.1, 125.5, 83.0, 74.2, 69.8, 58.9, 26.4; Anal. Calcd for $C_{12}H_{18}O_3$: C, 68.55; H, 8.63. Found: C, 68.36; H, 8.39%.

4a-Hydroperoxy-1,2,3,4,4a,5,6,7-octahydronaphthalene (2a)

Compound **2a** was prepared using a reported procedure.[28]

4a-Methyldioxy-1,2,3,4,4a,5,6,7-octahydronaphthalene (2b)

Compound **2b** was prepared in 93% yield from **2a** (142 mg, 0.85 mmol) and iodomethane (0.11 mL, 1.7 mmol) by a similar procedure as for **1b**: $R_f = 0.50$ (0.25% EA–hex); ^{1}H NMR δ 5.63 (app. quintet, 1 H, $J = 2.3$), 3.82 (s, 3 H), 2.33–2.16 (m, 3 H), 2.04–1.85 (m, 3 H), 1.79–1.63 (m, 3 H), 1.59–1.48 (m, 2 H), 1.29–1.12 (m, 3 H); ^{13}C NMR δ 136.7, 126.7, 80.7, 62.9, 35.7, 32.9, 32.3, 27.5, 25.8, 21.7, 18.7; Anal. Calcd for $C_{11}H_{18}O_2$: C, 72.49; H, 9.95. Found: C, 72.36; H, 9.87%.

4a-(2-Methoxyethyl)dioxy-1,2,3,4,4a,5,6,7-octahydronaphthalene (2d)

Compound **2d** was prepared in 61% yield from **2a** (78.8 mg, 0.47 mmol) and 2-methoxyethoxy toluene-*p*-sulfonate (108.1 mg, 0.47 mmol) as for **1d**: $R_f = 0.37$ (5% EA–hex); ^{1}H NMR δ 5.63 (app. quintet, 1 H, $J = 2.2$), 4.11 (t, 2 H, $J = 4.8$), 3.60 (t, 2 H, $J = 4.9$), 3.37 (s, 3 H), 2.29–2.20 (m, 3 H), 2.03–1.84 (m, 3 H), 1.77–1.61 (m, 3 H), 1.56–1.48 (m, 2 H), 1.29–1.10 (m, 3 H); ^{13}C NMR δ 136.6, 126.8, 80.7, 74.0, 70.1, 59.0, 35.7, 32.8, 32.4, 27.4, 25.9, 21.7, 18.7; Anal. Calcd for $C_{13}H_{22}O_3$: C, 68.99; H, 9.80. Found: C, 68.78; H, 10.00%.

***cis* and *trans*-1-Methyldioxy-1,2,3,4,4a,5,6,7,8,8a-decahydronaphthalene (3b)**

An ethyl acetate suspension of PtO_2 (81 mg, 0.36 mmol) and **2b** (443.4 mg, 2.4 mmol) was placed under an atmosphere of hydrogen for 1 h. The solution was filtered through Celite and then concentrated *in vacuo*. Filtration through silica (5% EA–hexane) and HPLC (0.1% EA–hexane) isolated **3b** (415.7 mg, 93%) as a 1 : 1 mixture of *cis* (5.3 min) and *trans* (7.5 min) isomers. Assignments are based on literature reports for related compounds. *trans*: $R_f = 0.60$ (5% EA–hex); ^{1}H NMR (500 MHz) δ 3.81 (s, 3 H), 2.04 (dq, 2 H, $J = 13.7, 2.8$), 1.73–1.62 (m, 4 H), 1.50–1.44 (m, 2 H), 1.40–1.18 (m, 7 H), 1.00 (td, 2 H, $J = 13.7, 4.0$); ^{13}C NMR (125 MHz) δ 80.8, 62.6, 45.3, 34.3, 28.4, 26.5, 21.7; HRMS Calcd for $C_{11}H_{20}O_2$ (M^+): 184.1463. Found: 184.1463. *cis*: $R_f = 0.60$ (5% EA–hex); ^{1}H NMR (500 MHz) δ 3.80 (s, 3 H), 1.76–1.70 (m, 3 H), 1.68–1.48 (m, 8 H), 1.44–1.27 (m, 6 H); ^{13}C NMR (125 MHz) δ 83.6, 62.9, 37.7, 28.1, 22.7.

1-Hydroperoxy-1,2,3,4,5,6,7,8-octahydronaphthalene (4a)[29]

This was prepared from **2a** by a reported method.[30]

1-Methyldioxy-1,2,3,4,5,6,7,8-octahydronaphthalene (4b)

Alkylation of **4a** (977.4 mg, 5.8 mmol) with MeI as for **1b** furnished **4b** (819.5 mg, 77%) as a colorless oil: $R_f = 0.50$ (2.5% EA–hex); ^{1}H NMR δ 4.21 (br s, 1 H) 3.83 (s, 3 H), 2.27 (d, 1 H, J =16.2), 2.19–2.11 (m, 1 H), 1.94–1.80 (m, 5 H), 1.78–1.62 (m, 3 H), 1.59–1.41 (m, 4 H); ^{13}C NMR δ 137.7, 124.8, 80.1, 62.2, 30.7, 30.6, 27.8, 27.0, 22.9, 22.7, 17.7; Anal. Calcd for $C_{11}H_{18}O_2$: C, 72.49; H, 9.95. Found: C, 72.69; H, 9.70%.

Preparation of ozonides

Method A. Into a 0 °C hexane solution of *O*-methyl oxime and ketone was bubbled O_3–O_2 until a light blue was observed. Residual O_3 was sparged with O_2 and solvent was removed *in vacuo*. The residue was subjected to flash chromatography.

Method B. Similar to method A, except a −78 °C solution of vinyl ether (1 equiv.) and cyclohexanone (2 equiv.) in 2 : 1 hexane–CH_2Cl_2 was used.

Method C. Similar to method A, except a −78 °C solution of alkene in hexane was used. The ^{1}H and ^{13}C NMR data of **5a** (60%), **5b** (67%), **5c** (63%), **5d** (57%), and **5m** were identical to literature reports.[12,13]

3,3-Dibutyl-1,2,4-trioxaspiro[5.4]decane (5e)

Yield 47%; $R_f = 0.77$ (10% EA–hex); ^{1}H NMR δ 1.80–1.50 (m, 12 H), 1.50–1.25 (m, 10 H), 0.87 (t, 6 H, $J = 4.5$); ^{13}C NMR δ 111.7, 108.9, 35.1, 34.7, 26.1, 25.0, 23.8, 22.9, 14.0.

3-Octyl-1,2,4-trioxaspiro[5.4]decane (5f)

Yield 47%; $R_f = 0.76$ (10% EA–hex); ^{1}H NMR δ 5.20 (t, 1 H, $J = 4.5$), 1.75–1.50 (m, 8 H), 1.50–1.20 (m, 16 H), 0.87 (t, 3 H, $J = 4.5$); ^{13}C NMR δ 109.2, 103.9, 35.5, 33.4, 32.6, 31.8, 31.2, 29.5, 29.4, 29.2, 24.9, 24.0, 23.9, 14.1, 22.7.

3-Phenyl-1,2,4-trioxaspiro[5.4]decane (5g)

Yield 65%; $R_f = 0.65$ (10% EA–hex); ^{1}H NMR δ 7.60–7.50 (m, 2 H), 7.50–7.38 (m, 3 H), 6.08 (s, 1 H), 2.00–1.80 (m, 4 H), 1.80–1.60 (m, 4 H), 1.60–1.40 (m, 2 H); ^{13}C NMR δ 132.6, 130.4, 128.6, 127.9, 110.6, 103.5, 35.7, 33.6, 25.0, 24.0, 23.8.

1,2,4-Trioxaspiro[5.4]decane (5h)

Yield 78%; $R_f = 0.67$ (10% EA–hex); ^{1}H NMR δ 5.10 (s, 2 H), 1.75–1.55 (m, 8 H), 1.45–1.35 (m, 2 H); ^{13}C NMR δ 108.8, 93.6, 33.8, 24.8, 23.8.

3-*tert*-Butyl-3-methyl-1,2,4-trioxaspiro[5.4]decane (5i)

Yield 53%; $R_f = 0.75$ (10% EA–hex); ^{1}H NMR δ 1.70–1.50 (m, 8 H), 1.50–1.30 (m, 2 H), 1.44 (s, 3 H), 1.03 (s, 9 H); ^{13}C NMR δ 112.3, 110.0, 37.5, 35.4, 35.3, 26.5, 25.6, 24.5, 24.2, 20.6.

3-Phenyl-5-propyl-1,2,4-trioxolane (5j)

Yield 73%, 1 : 1 *cis–trans* mixture $R_f = 0.63$ (10% EA–hex); *first eluting*: ^{1}H NMR δ 7.62–7.40 (m, 5 H), 6.15 (s, 1 H), 5.47 (t, 1 H, $J = 5.25$), 1.87 (m, 2 H), 1.60 (m, 2 H), 1.03 (t, 3 H, $J = 7.4$); ^{13}C NMR δ 134.3, 130.1, 128.5, 127.3, 105.1, 103.30, 103.27, 34.4, 17.5, 13.9. *Second eluting*: ^{1}H NMR same except δ 7.62–7.40, 6.09 (s, 1 H), 5.54 (t, 1 H, $J = 4.8$), 1.05 (t, 3 H, $J = 7.4$); ^{13}C NMR δ 132.6, 130.5, 128.6, 127.8, 105.6, 103.81, 103.78, 32.9, 17.2, 14.0.

3-Phenyl-1,2,4-trioxolane (5k)

Yield 77%; $R_f = 0.60$ (10% EA–hex); ^{1}H NMR δ 7.60–7.40 (m, 5 H), 6.07 (s, 1 H), 5.44 (s, 1 H), 5.36 (s, 1 H); ^{13}C NMR δ 132.9, 130.4, 128.6, 127.5, 103.08, 103.05, 95.2.

3-Methyl-3-phenyl-1,2,4-trioxolane (5l)

Yield 61%; $R_f = 0.62$ (10% EA–hex); ^{1}H NMR δ 7.60–7.28 (m, 5 H), 5.28 (d, 1 H, $J = 4.0$), 1.84 (s, 3 H); ^{13}C NMR δ 140.7, 128.6, 128.3, 125.2, 108.3, 94.5, 24.3.

General procedure for allylation

To a 0 °C (BF_3·OEt_2) or −78 °C ($SnCl_4$ or $TiCl_4$) solution of cumene hydroperoxide (0.24 mL, 1.4 mmol) and allylsilane (0.22 mL, 1.4 mmol) in CH_2Cl_2 (6 mL) under N_2 was added Lewis acid (1.2 mmol). After stirring for 5–30 min at the initial temperature, the reaction was brought to RT, and subjected to a standard work-up and flash chromatography. Allylations of **1b** were analyzed by ^{1}H NMR. Allylations of **1c** were performed in the presence of 2-methylnaphthalene as an internal standard; the products were quantified by ^{1}H NMR. Fragmentations of **2a**–**d** were performed as for **1b**–**d** except that chromatography was performed using alumina (ether–pentane) and hydroxy- or alkoxybicyclo[5.3.0]decanones **10a/b** were quantified together with bicyclodecenone **11**.

4-Methyl-4-phenylpent-1-ene (6)

R_f = 0.81 (2.5% EA–hex); ^{1}H NMR (500 MHz) δ 7.36–7.16 (m, 5 H), 5.60–5.51 (m, 1 H), 4.98 (s, 1 H), 4.94 (d, 1 H, J = 8.1), 2.36 (d, 2 H, J = 7.3), 1.31 (s, 6 H); ^{13}C NMR (125 MHz) δ 149.3, 135.5, 128.0, 125.8, 125.5, 116.9, 48.8, 37.6, 28.5; Anal. Calcd for $C_{12}H_{16}$: C, 89.94; H, 10.06. Found: C, 90.13; H, 10.04%.

4-Methyl-4-phenoxypent-1-ene (7)

R_f = 0.48 (2.5% EA–hex); ^{1}H NMR (500 MHz) δ 7.27–6.98 (m, 5 H), 5.95 (m, 1 H), 5.12 (s, 1 H), 5.09 (d, 1 H, J = 11.3), 2.41 (d, 2 H, J = 7.3), 1.27 (s, 6 H); ^{13}C NMR (125 MHz) δ 155.2, 134.5, 128.9, 124.2, 123.3, 117.7, 80.0, 46.7, 26.4; Anal. Calcd for $C_{12}H_{16}O$: C, 81.77; H, 9.15. Found: C, 81.75; H, 8.94%.

4-Methoxy-4-methylpent-1-ene (8b)

R_f = 0.45 (5% EA–hex); ^{1}H NMR δ 5.86 (m, 1 H), 5.13 (s, 1 H), 5.09 (d, 1 H, J = 7.4), 3.29 (s, 3 H), 2.31 (d, 2 H, J = 7.2), 1.23 (s, 6 H); ^{13}C NMR δ 134.1, 117.6, 75.4, 49.1, 44.2, 24.7.

4-Methylpent-1-enyl 2-methoxyethyl ether (8c)

R_f = 0.13 (2.5% EA–hex); ^{1}H NMR (500 MHz) δ 5.87–5.79 (m, 1 H), 5.05 (s, 1 H), 5.02 (d, 1 H, J = 6.4), 3.50 (dt, 4 H, J = 2.8, 2.4), 3.37 (s, 3 H), 2.25 (d, 2 H, J = 7.3), 1.16 (s, 6 H); ^{13}C NMR (125 MHz) δ 134.7, 117.1, 74.7, 72.6, 60.8, 59.1, 44.8, 25.3; HRMS Calcd for $C_9H_{18}O_2$ (M^+): 158.1307. Found: ($M - C_3H_5^+$): 117.09146.

1-Allyl-1,2,3,4,5,6,7,8-octahydronaphthalene (9)

R_f = 0.83 (1% EA–hex); ^{1}H NMR δ 5.80–5.72 (m, 1 H), 4.99 (d, 1 H, J = 17.7), 4.97 (d, 1 H, J = 8.5), 2.32–2.28 (m, 1 H), 2.11–2.06 (m, 1 H), 2.00–1.72 (m, 7 H), 1.67–1.43 (m, 8 H); ^{13}C NMR δ 138.2, 130.5, 129.2, 115.4, 38.8, 37.2, 30.9, 30.8, 28.4, 27.6, 23.5, 23.2, 20.0; Anal. Calcd for $C_{13}H_{20}$: C, 88.57; H, 11.43. Found: C, 88.72; H, 11.50%.

7-Hydroxybicyclo[5.3]decan-2-one (10a)

R_f = 0.26 (20% EA–hex); ^{1}H NMR (500 MHz) δ 3.13 (t, 1 H, J = 8.5), 2.53 (d, 1 H, J = 18.9), 2.42–2.36 (m, 2 H), 2.16 (d, 1 H, J = 10.1), 1.93–1.60 (m, 10 H), 1.24 (br s, 1 H); ^{13}C NMR (125 MHz) δ 211.6, 81.8, 59.5, 44.3, 43.7, 41.7, 24.8, 24.1, 23.4, 21.6; IR (neat)/cm^{-1} 3463 (br, OH), 1693 (C=O).

7-Methoxybicyclo[5.3]decan-2-one (10b)

R_f = 0.66 (20% EA–hex); ^{1}H NMR (500 MHz) δ 3.04 (s, 3 H), 2.97 (t, 1 H, J = 8.5), 2.49 (d, 1 H, J = 17.7), 2.41–2.30 (m, 2 H), 2.08 (ddd, 1 H, J = 13.7, 6.9, 3.6), 1.87–1.78 (m, 2 H), 1.70–1.58 (m, 3 H), 1.57–1.30 (m, 4 H); ^{13}C NMR (125 MHz) δ 211.1, 85.9, 60.8, 48.3, 43.6, 36.1, 35.7, 25.0, 24.9, 23.5, 21.6; IR (neat)/cm^{-1} 1700 (C=O).

Bicyclo[5.3]dec-1(7)-en-2-one (11)

R_f = 0.28 (10% EA–hex); ^{1}H NMR (500 MHz) δ 2.65–2.54 (m, 6 H), 2.44 (m, 2 H), 1.82–1.75 (m, 6 H); ^{13}C NMR (125 MHz) δ 201.4, 159.0, 138.4, 43.9, 41.6, 33.9, 31.6, 25.8, 22.4, 21.2; IR (neat)/cm^{-1} 1643 (C=O), 1625 (C=C); Anal. Calcd for $C_{10}H_{14}O$: C, 79.96; H, 9.36. Found: C, 79.99; H, 9.31%.

1-Methoxyspiro[4.5]decan-6-one (12)

Addition of $SnCl_4$ (0.88 mL, 0.88 mmol, 1 M in CH_2Cl_2) to a 78 °C solution of methyl peroxide **4b** (159.7 mg, 0.88 mmol) and allyltrimethylsilane (0.28 mL, 1.7 mmol) in CH_2Cl_2 (4.5 mL), furnished, following a standard work-up and flash chromatography (5% ether–pentane) **9** (27.6 mg, 18%) and **12** (54.0 mg, 34%): R_f = 0.23 (5% EA–hex); ^{1}H NMR (500 MHz) δ 3.84 (dd, 1 H, J = 4.4, 2.8), 3.21 (s, 3 H), 2.55 (dt, 1 H, J = 13.3, 7.3), 2.43 (td, 1 H, J = 13.7, 6.1), 2.39–2.36 (m, 1 H), 2.04 (sextet of d, 1 H, J = 9.7, 2.8), 1.85–1.53 (m, 8 H), 1.42 (td, 1 H, J = 14.1, 4.0), 1.07 (ddd, 1 H, J = 12.9, 7.7, 5.6); ^{13}C NMR (125 MHz) δ 211.5, 87.2, 61.2, 56.5, 41.6, 38.5, 32.0, 29.1, 27.6, 22.6, 21.1; IR (neat)/cm^{-1} 1712 C=O; Anal. Calcd for $C_{11}H_{18}O_2$: C, 72.49; H, 9.95. Found: C, 72.50; H, 9.79%.

1-Allyl-1,6-epoxycyclodecane (13) and 7-allyl-1-oxabicyclo[5.4.0]undecane (14)

$SnCl_4$-mediated allylation (5 h, −78 °C) of a mixture of *cis*- and *trans*-**3b** (369.7 mg, 2.0 mmol) furnished, following chromatography on alumina (1% ether–pentane) and HPLC on silica (hexane), 1-allyl-1,6-epoxycyclodecane **13** (103 mg, 26%, retention time = 21 min), 7-allyl-1-oxabicyclo[5.4.0]undecane **14** (6%, 24 min), and 180 mg of recovered *trans*-**3b**.

1-Allyl-1,6-epoxycyclodecane (13)

R_f = 0.13 (1% EA–hex); ^{1}H NMR (500 MHz) δ 5.77 (m, 1 H), 5.01 (d, 1 H, J = 7.3), 4.99 (d, 1 H, J = 16.9), 4.06 (m, 1 H), 2.23 (d, 2 H, J = 7.7), 1.78–1.49 (m, 16 H); ^{13}C NMR (125 MHz) δ 135.6, 117.2, 80.1, 76.8, 47.6, 37.2, 34.8, 25.3, 24.9; HRMS Calcd for $C_{13}H_{22}O$ (M^+): 194.1671. Found: 194.1671.

7-Allyl-1-oxabicyclo[5.4.0]undecane (14)

R_f = 0.13 (1% EA–hex); ^{1}H NMR (500 MHz) δ 5.87 (m, 1 H), 5.05 (d, 1 H, J = 10.1), 5.03 (d, 1 H, J = 6.9), 3.57 (m, 2 H), 2.47 (dd, 1 H, J = 14.5, 8.1), 2.25 (dd, 1 H, J = 13.3, 4.8), 1.92–1.20 (m, 15 H); ^{13}C NMR (125 MHz) δ 134.7, 116.7, 61.2, 45.1, 38.9, 32.2, 31.5, 31.3, 30.9, 29.2, 23.2, 21.2; HRMS Calcd for $C_{13}H_{22}O$ (M^+): 194.1671. Found ($M - C_3H_5^+$): 153.1280.

Lewis acid-promoted decomposition of ozonides

A −78 °C solution of ozonide in 1 mL of $CDCl_3$ was admixed in an NMR tube with a solution of excess Lewis acid in CD_2Cl_2. The mixture was brought to room temperature and monitored by NMR.

Reaction of ozonides with allylsilane: general procedure

To a −78 °C solution of 200 mg (1 equiv., 1.01 mmol) of ozonide **5a** and 0.20 mL (1.3 equiv., 1.3 mmol) and allylsilane in CH_2Cl_2 (5 mL) was added $SnCl_4$ (1.1 equiv. as a 1 M solution in CH_2Cl_2). A standard work-up (except CH_2Cl_2 extractions) gave 180 mg of a residue, from which was separated 115 mg (0.50 mmol, 50%) of **17**, 13 mg (0.11 mmol, 11%) of **15b** and trace amounts of **16a** and **16b** were isolated. Compounds **15b**, **16a** and **16b** were assigned based upon comparison of ^{1}H and ^{13}C NMR data with authentic samples.

3-(Trimethylsilylmethyl)-1,2-dioxaspiro[5.4]decane (17)

R_f = 0.72 (10% EA–hex); ^{1}H NMR δ 4.40–4.28 (m, 1 H), 2.36 (dd, 1 H, J = 11.7, 6.9), 1.83 (dd, 1 H, J = 11.7, 8.1), 1.75–1.50 (m, 6 H), 1.50–1.30 (m, 4 H), 1.14 (dd, 1 H, J = 14.1, 5.3), 0.83 (dd, 1 H, J = 14.1, 9.3), 0.05 (s, 9 H); ^{13}C NMR δ 86.2, 80.3, 53.5, 37.6, 36.0, 25.9, 24.6, 24.1, 21.7, −0.4. Anal. Calcd for $C_{12}H_{24}O_2Si$: C, 63.10; H, 10.59. Found: C, 62.89; H, 10.40%. ^{1}H and ^{13}C assignments based on DEPT and HETCOR.

5-(Prop-2-en-1-yl)nonan-5-ol (20e)

R_f = 0.66 (20% EA–hex); ^{1}H NMR δ 5.80 (m, 1 H), 5.11 (m, 2 H), 2.20 (d, 2 H, J = 7.0), 1.62–1.20 (m, 12 H), 0.87 (t, 6 H, J = 7.0).

Dodec-1-en-4-ol (20f)

R_f = 0.50 (20% EA–hex); ^{1}H NMR δ 5.80 (m, 1 H), 5.10 (m, 2 H), 3.62 (m, 1 H), 2.30 (m, 1 H), 2.15 (m, 1 H), 1.60 (s, 1 H, O*H*), 1.50–1.20 (m, 14 H), 0.84 (t, 3 H, J = 7.0).

1-Phenylbut-3-en-1-ol (20j = 20k)

R_f = 0.46 (20% EA–hex); ^{1}H NMR δ 7.40–7.16 (m, 5 H), 5.80 (m, 1 H), 5.15 (m, 2 H), 4.52 (t, 1 H, J = 6.1), 2.50 (m, 2 H).

3-(Trimethylsilylmethyl)-5-*tert*-butyl-5-methyl-1,2-dioxaspiro-[5.4]decane (18)

R_f = 0.72 (10% EA–hex); ^{1}H NMR δ 4.22 (m, 1 H), 2.68 (dd, 1 H, J = 11.7, 6.9), 1.63 (dd, 1 H, J = 11.7, 8.1), 1.35 (s, 3 H), 1.08 (dd, 1 H, J = 14.1, 5.3), 0.98 (s, 9 H), 0.82 (dd, 1 H, J = 14.1, 9.3), 0.04 (s, 9 H); ^{13}C NMR δ 90.92, 80.58, 50.40, 36.12, 25.91, 23.06, 20.42, −0.95. Anal. Calcd for $C_{12}H_{26}O_2Si$: C, 62.56; H, 11.37. Found: C, 62.69; H, 11.41%.

***cis*-3-Phenyl-5-(trimethylsilylmethyl)-1,2-dioxaspiro[5.4]decane (22j = 22k)**

R_f = 0.33 in 5% EA–hexane; ^{1}H NMR (500 MHz) δ 7.45–7.25 (m, 5 H), 5.29 (t, 1 H, J = 7.5), 4.49 (tt, 1 H, J = 9.3, 5.5), 3.14 (ddd, 1 H, J = 11.9, 7.9, 6.0), 2.20 (ddd, 1 H, J = 11.9, 8.5, 6.9), 1.19 (dd, 1 H, J = 14.1, 5.2), 0.90 (dd, 1 H, J = 14.1, 9.3), 0.07 (s, 9 H); ^{13}C NMR δ 141.17, 128.62, 127.88, 126.16, 82.83, 80.11, 51.27, 20.40, −1.01. Anal. Calcd for $C_{13}H_{20}O_2Si$: C, 66.05; H, 8.53. Found: C, 65.94; H, 8.41%.

***trans*-3-Phenyl-5-(trimethylsilylmethyl)-1,2-dioxaspiro[5.4]-decane (22j = 22k)**

R_f = 0.33 (5% EA–hexane); ^{1}H NMR (500 MHz) δ 7.45–7.28 (m, 5 H), 5.30 (dd, 1 H, J = 8.5, 6.0), 4.62–4.55 (m, 1 H), 2.65 (dt, 1 H, J = 11.7, 6.0), 2.55 (dt, 1 H, J = 11.7, 8.5), 1.17 (dd, 1 H, J = 14.1, 5.4), 0.93 (dd, 1 H, J = 14.1, 8.9), 0.08 (s, 9 H); ^{13}C NMR δ 138.81, 128.66, 128.36, 126.83, 83.17, 80.05, 50.05, 20.90, −0.97. Anal. Calcd for $C_{13}H_{20}O_2Si$: C, 66.05; H, 8.53. Found: C, 65.87; H, 8.34%.

3-Methyl-3-phenyl-5-(trimethylsilylmethyl)-1,2-dioxaspiro[5.4]-decane (22l)

Compound **22l** was isolated as a 1 : 1 mixture. Pure *cis*-**22l** and a (1 : 1.5) mixture of *cis*/*trans* **22l** were obtained by HPLC (2% EA–hex). R_f = 0.33 (5% EA–hexane); ^{1}H NMR (500 MHz) δ 7.46–7.42 (m, 2 H), 7.32–7.38 (m, 2 H), 7.30–7.24 (m, 1 H), 4.43–4.36 (m, 1 H), 2.93 (dd, 1 H, J = 11.7, 6.4), 2.27 (dd, 1 H, J = 11.7, 8.1), 1.68 (s, 3 H), 1.17 (dd, 1 H, J = 14.1, 5.6), 0.93 (dd, 1 H, J = 14.1, 9.3), 0.05 (s, 9 H); ^{13}C NMR δ 144.80, 128.36, 127.18, 124.98, 86.79, 79.83, 56.00, 27.83, 21.62, −0.99. DEPT 135 NMR δ 128.36(+), 127.18(+), 124.98(+), 79.83(+), 56.00(−), 27.83(+), 21.62(−), −0.99(+). Anal. Calcd for $C_{14}H_{22}O_2Si$: C, 67.15; H, 8.86. Found: C, 67.22; H, 8.74%.

***cis*-3-Propyl-5-(trimethylsilylmethyl)-1,2-dioxaspiro[5.4]decane (23j)**

R_f = 0.45 (5% EA–hexane); ^{1}H NMR (500 MHz) δ 4.35–4.23 (m, 2 H), 2.77 (dt, 1 H, J = 11.7, 6.9), 1.74 (ddd, 1 H, J = 11.7, 8.1, 6.5), 1.75–1.30 (m, 4 H), 1.11 (dd, 1 H, J = 14.1, 5.4), 0.93 (t, 3 H, J = 6.9), 0.85 (dd, 1 H, J = 14.1, 9.3), 0.06 (s, 9 H); ^{13}C NMR δ 81.42, 79.35, 48.33, 37.15, 21.02, 19.52, 13.99, −1.01. Anal. Calcd for $C_{10}H_{22}O_2Si$: C, 59.35; H, 10.96. Found: C, 59.47; H, 11.04%.

4-Methyl-4-phenylhepta-1,6-diene (24)

R_f = 0.75 in 5% (EA–hex); ^{1}H NMR (500 MHz) δ 7.33–7.17 (m, 5 H), 5.63–5.47 (m, 2 H), 5.05–4.92 (m, 4 H), 2.52 (dd, 1 H, J = 13.7, 6.6), 2.32 (dd, 2 H, J = 11.7, 6.6), 1.29 (s, 3 H); ^{13}C NMR δ 147.1, 135.1, 128.0, 126.4, 125.6, 117.2, 47.0, 24.2.

3-Methyl-3-(4-hydroxyhept-6-enyl)-5-(trimethylsilylmethyl)-1,2-dioxolane (25)

To a −78 °C solution of 145 mg (1.1 mmol) of **14m** in 20 mL of CH_2Cl_2 was added 1.1 mL of a 1 M solution of $SnCl_4$. After 2 min, a solution of allylsilane (251 mg, 2 equiv.) in 20 mL of CH_2Cl_2 was added. The reaction mixture was stirred for 30 min and subjected to standard work-up. Flash chromatography on silica gel (10% to 20% EA–hex) afforded 151 mg (48%) of **25** as a colorless mixture of four isomers which could be partially separated by HPLC: (10% EA–hex) into two *cis* isomers (35%, 35%) and a mixture of two *trans* isomers (15%, 15%). *cis*-**25a**: R_f = 0.30 (20% EA–hex); ^{1}H NMR (500 MHz) δ 5.88–5.78 (m, 1 H), 5.14 (m, 2 H), 4.42–4.34 (m, 1 H), 3.71–3.63 (m, 1 H), 2.364 (dd, 1 H, J = 11.7, 6.5), 2.36–2.27 (m, 1 H), 2.20–2.11 (m, 1 H, CH), 1.923 (dd, 1 H, J = 11.7, 8.5), 1.80–1.40 (m, 6 H), 1.28 (s, 3 H), 1.079 (dd, 1 H, J = 14.1, 5.2), 0.815 (dd, 1 H, J = 14.1, 9.3), 0.046 (s, 9 H); ^{13}C NMR δ 134.8(+), 118.3(−), 85.9, 79.8(+), 70.6(+), 53.56(−), 42.1(−), 40.6(−), 37.2(−), 23.31(+), 21.0(−), 20.8(−), −1.0(+). Anal. Calcd for $C_{15}H_{30}O_3Si$: C, 62.63; H, 10.55. Found: C, 62.51; H, 10.46%. *cis*-**25b**: ^{1}H NMR (500 MHz) δ 5.88–5.77 (m, 1 H), 5.17–5.11 (m, 2 H), 4.41–4.33 (m, 1 H), 3.71–3.64 (m, 1 H), 2.357 (dd, 1 H, J = 11.67, 6.5), 2.34–2.27 (m, 1 H), 2.19–2.11 (m, 1 H), 1.929 (dd, 1 H, J = 11.7, 8.5), 1.75–1.35 (m, 6 H), 1.28 (s, 3 H), 1.08 (dd, 1 H, J = 13.7, 5.2), 0.814 (dd, 1 H, J = 13.7, 9.3), 0.045 (s, 9 H); ^{13}C NMR δ 134.8(+), 118.2(−), 85.9, 79.9(+), 70.4(+), 53.5(−), 42.0(−), 40.5(−), 37.0(−), 23.5(+), 20.8(−), 20.6(−), −1.0(+). Anal Calcd for $C_{15}H_{30}O_3Si$: C, 62.63; H, 10.55. Found: C, 62.44; H, 10.32%. *trans*-**25ab** (mixture of diastereomers): R_f = 0.27 (20% EA–hex); ^{1}H NMR (500 MHz) δ 5.87–5.77 (m, 2 H), 5.17–5.11 (m, 4 H), 4.36–4.28 (m, 2 H), 3.70–3.63 (m, 2 H), 2.51–2.45 (m, 2 H), 2.34–2.27 (m, 2 H), 2.19–2.11 (m, 2 H), 1.85–1.80 (m, 2 H), 1.66–1.40 (m, 12 H), 1.34 (s, 3 H), 1.096 (dd, 2 H, J = 14.1, 5.2), 0.840 (dd, 2 H, J = 13.7, 9.3), 0.047 (s, 18 H); ^{13}C NMR δ 134.7 (for 2C), 118.4 (for 2C), 86.1 (for 2C), 80.1 (for 2C), 70.5, 70.4, 53.1, 52.9, 42.1, 42.0, 38.8, 38.7, 37.2, 37.1, 26.0, 25.8, 21.1 (for 2C), 21.0, 20.8, −1.0 (for 2C). Anal. Calcd for $C_{15}H_{30}O_3Si$: C, 62.63; H, 10.55. Found: C, 62.67; H, 10.47%.

3-Methyl-3-(4-acetoxyhept-6-enyl)-5-(trimethylsilylmethyl)-1,2-dioxolane (26)

Acetylation of **25** (23 mg) with DMAP and acetic anhydride in CH_2Cl_2 furnished, after standard work-up and flash chromatography, 25 mg (92%) of **26** as a colorless oil which was resolved by HPLC (3% EA–hex) into two *cis* dioxolanes *cis*-**26a** (35%) and *cis*-**26b** (35%) as well as a mixture of two *trans* dioxolanes *trans*-**26ab** (30%): *cis*-**26a**: R_f = 0.58 (20% EA–hex). ^{1}H NMR (500 MHz) δ 5.80–5.70 (m, 1 H), 5.11–5.04 (m, 2 H), 4.97–4.89 (m, 1 H), 4.40–4.32 (m, 1 H), 2.36 (dd, 1 H, J = 11.7, 6.8), 2.33–2.28 (m, 2 H), 1.89 (dd, 1 H, J = 11.7, 8.5), 2.03 (s, 3 H), 1.75–1.25 (m, 6 H), 1.26 (s, 3 H), 1.08 (dd, 1 H, J = 13.9, 5.0), 0.81 (dd, 1 H, J = 13.9, 9.5), 0.05 (s, 9 H); ^{13}C NMR δ 170.8, 133.7(+), 117.7(−), 85.7, 79.8(+), 73.0(+), 53.7(−), 40.3(−), 38.8(−), 33.9(−), 23.2(+), 21.2(+), 20.8(−), 20.3(−), −1.0(+). Calcd. for $C_{17}H_{32}O_4Si$: C, 62.15; H, 9.82. Found: C, 62.19; H, 9.70%. *cis*-**26b**: R_f = 0.56 (20% EA–hex). ^{1}H NMR (500 MHz) δ 5.80–5.70 (m, 1 H), 5.11–5.03 (m, 2 H), 4.95–4.88 (m, 1 H), 4.40–4.33 (m, 1 H), 2.35 (dd, 1 H, J = 11.7, 6.6), 2.37–2.25 (m, 2 H), 1.90 (dd, 1 H, J = 11.7, 8.3), 2.04 (s, 3 H), 1.75–1.67 (m, 1 H), 1.60–1.34 (m, 4 H), 1.43–1.34 (m, 1 H), 1.27 (s, 3 H), 1.07 (dd, 1 H, J = 13.7, 5.2), 0.81 (dd, 1 H, J = 13.7, 9.5), 0.05 (s, 9 H); ^{13}C NMR δ 170.8, 133.7(+), 117.7(−), 85.7, 79.8(+), 73.2(+), 53.5(−), 40.3(−), 38.6(−), 33.9(−), 23.4(+), 21.3(+), 20.8(−), 20.4(−), −1.0(+). Anal. Calcd for $C_{17}H_{32}O_4Si$: C, 62.2; H, 9.8. Found: C, 62.6; H, 9.7%. Anal. Calcd for $C_{17}H_{32}O_4Si$: C, 62.15; H, 9.82. Found: C, 62.02; H, 9.67%. Spectral listings for *trans*-**26ab** are included in supplementary material.

3-Methyl-3-(4-oxohept-6-enyl)-5-(trimethylsilylmethyl)-1,2-dioxolane (27)

Oxidation of **25** (23 mg) with PDC in CH_2Cl_2, furnished, after

work-up and chromatography (7–16% EA–hex) 19 mg of **27** (83%) and 3.7 mg (16%) of recovered **25**. HPLC (3% EA–hex) resolved the material into pure *cis*-**27** and a mixture of *cis*- and *trans*-**27** (1.9 : 1.0). *cis*-**27** $R_f = 0.77$ (20% EA–hex). ^{1}H NMR (500 MHz) δ 5.97–5.87 (m, 1 H), 5.183 (ddt, 1 H, $J = 10.3, 1.6, 1.2$), 5.141 (ddt, 1 H, $J = 17.3, 1.6, 1.2$), 4.40–4.33 (m, 1 H), 3.171 (dt, 2 H, $J = 6.9, 1.2$), 2.49 (dt, 2 H, $J = 7.3, 6.9$), 2.36 (dd, 1 H, $J = 11.7, 6.5$), 1.93 (dd, 1 H, $J = 11.7, 8.5$), 1.70–1.50 (m, 4 H), 1.28 (s, 3 H), 1.07 (dd, 1 H, $J = 11.7, 5.2$), 0.809 (dd, 1 H, $J = 11.7, 9.3$), 0.05 (s, 9 H); ^{13}C NMR δ 208.5, 130.7(+), 118.8(−), 85.7, 79.9(+), 53.5(−), 47.8(−), 42.3(−), 39.8(−), 23.3(+), 20.8(−), 18.8(−), −1.1(+). Anal. Calcd for $C_{15}H_{28}O_3Si$: C, 63.33; H, 9.92. Found: C, 63.44; H, 9.87%. A spectral listing for the *cis*/*trans*-**27** mixture is included in supplementary material.

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