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Synthesis of Alkyl Hydroperoxides via Alkylation of *gem*-Dihydroperoxides

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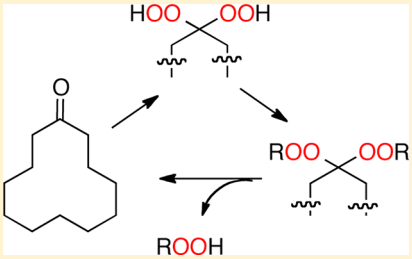
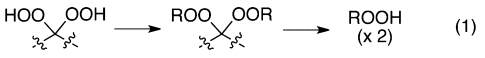
Supporting Information

ABSTRACT: 2-Fold alkylation of 1,1-dihydroperoxides, followed by hydrolysis of the resulting bisperoxyacetals, provides a convenient method for synthesis of primary and secondary alkyl hydroperoxides.



A number of methods have been reported for the synthesis of alkyl hydroperoxides,[1] with some of the most widely used based upon displacement of a leaving group by a peroxide nucleophile.[1b,2] Some years ago, we reported a convenient approach to alkyl hydroperoxides based upon alkylation of 2-methoxypropyl-2-yl hydroperoxide followed by deprotection of the resulting monoperoxyacetals.[3] Although the method has seen significant use,[4] it is limited by the need to generate and concentrate a low molecular weight hydroperoxyacetal.[5] Our recent experiences with the synthesis and reactivity of 1,1-dihydroperoxides (DHPs) led us to hypothesize that these species might offer useful alternatives as precursors for alkyl hydroperoxides.[6] We were encouraged by a report from Nojima and co-workers demonstrating alkylations of 1,1-DHPs,[7] and by the demonstrated stability of 1,1-bisperoxyacetals.[7,8] We now report a convenient procedure for synthesis of alkyl hydroperoxides via alkylation of 1,1-dihydroperoxides followed by acidic deprotection of the derived bisperoxyacetals (eq 1). As



(1)

initial substrates, we selected cyclododecanone 1,1-dihydroperoxide (**1a**) and 4-*tert*-butylcyclohexanone dihydroperoxide (**1b**), known DHPs possessing sufficient mass to simplify isolation and mitigate safety concerns.[9] Compounds **1a** and **1b** were readily prepared via Re_2O_7-catalyzed condensation of the corresponding ketone with aqueous hydrogen peroxide (eq 2).[6a] We chose to initially focus on the cyclododecanone-derived **1a** on the basis of upon previous reports demonstrating that this DHP more readily undergoes acid hydrolysis compared with DHPs derived from strain-free ketones; it was our hope that this increased reactivity would extend to derived bisperoxyacetals.[10] Investigations of conditions for alkylation of **1a** are summarized in Table 1. There have been only a few reports describing alkylation of 1,1-dihydroperoxides.[6b,7] The bisalkylation of **1a** with primary iodides was achieved in good yield using Ag_2O;[7,11] although the reaction was successful in several solvents, the best yields were obtained in ethyl acetate. The corresponding reaction with a primary bromide was unsuccessful. Attempted alkylation of **1a** by a primary iodide in the presence of cesium hydroxide or cesium carbonate resulted in decomposition with formation of ketone.[7] Silver-promoted benzylation proceeded in modest yield due to facile Kornblum fragmentation of the peroxide product.[12] No product was observed upon attempted alkylation in the presence of potassium *tert*-butoxide in THF or under phase-transfer conditions proven effective for alkylation of simple hydroperoxides.[13] Neither Ag_2O nor base was successful in promoting alkylation with a secondary iodide. In search of electrophiles that would allow synthesis of secondary peroxides, we investigated alkyl triflates, which have been successfully applied to alkylation of alkyl hydroperoxides.[2e] Alkylation of **1a** with a slight excess (nominally 2.2−3.0 equiv) of primary or secondary triflates took place rapidly in the presence of potassium *tert*-butoxide (entries 10, 11, 14, 15).[14] We were unable to find any method for 2-fold alkylation with a tertiary electrophile. Ag-promoted alkylation with *tert*-butyl bromide furnished a mixture containing mostly recovered starting material and monoalkylated product; only a trace of the desired bisperoxyacetal was observed (entry 16). Attempted alkylation of **1a** with *tert*-butyl bromide in the presence of base resulted in no reaction or decomposition (entries 17, 18).

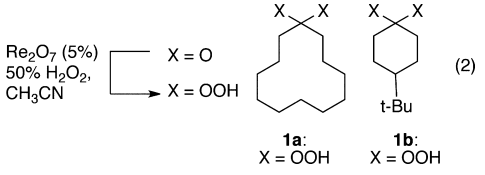


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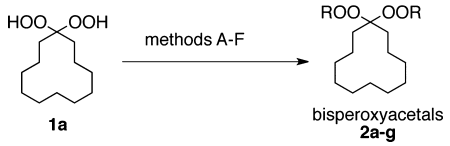
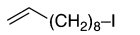
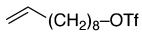
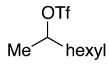
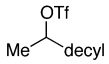
Table 1. Alkylation of Dihydroperoxide 1a

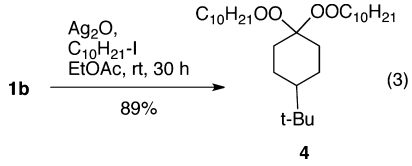


entry	electrophile	method[a]	product (yield)
1	*n*-$C_{10}H_{21}I$	A	**2a** (93%)
2	*n*-$C_{10}H_{21}I$	C	**2a** (19%)[b,c]
3	*n*-$C_{10}H_{21}I$	D	**2a** (7%) [b,c]
4	*n*-$C_{10}H_{21}Br$	A or F	-
5	*n*-$C_{10}H_{21}I$	E	-
7	*n*-$C_6H_{13}I$	A	**2b** (79%)
8	BnBr	A	**2c** (56%)
9		A	**2d** (79%)
10		B	**2d** (80%)
11	$Ph(CH_2)_4$–OTf	B	**2e** (68%)
12	2-iodooctane	A	-
13	2-iodooctane	C	**2f** (trace)[c]
14		B	**2f** (53%)
15		B	**2g** (42%)
16	*t*-BuBr	A	monoalkylation (35%)
17	*t*-BuBr	G	NR
18	*t*-BuBr	H	-[c]

[a]A: Ag_2O, RBr or RI, EtOAc. B: KO*t*Bu, ROTf, THF. C: $CsOH·H_2O$ (2 equiv), RI (2 equiv) DMF. D: $CsCO_3$ (2 equiv), RI (2 equiv), DMF. E: KO*t*Bu (2.1 equiv), RI (2equiv), THF. F: 50% KOH (4 equiv), RBr (2 equiv), *n*-Bu_4NBr (10%), cyclohexane, 50 °C. G: K_2CO_3, acetone. H: K_2CO_3, DMF, 70 °C. [b]NMR-based yield (internal standard). [c]Decomposition of **1a** with formation of ketone.

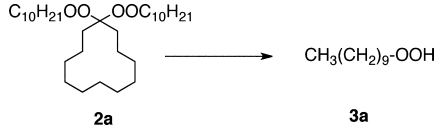
Differential scanning calorimetry/thermal gravimetric analysis (DSC/TGA) demonstrated that the product bisperoxyacetal (**2a**) undergoes exothermic decomposition, but only upon heating to above 120−125 °C (Figure 1).

The cyclohexanone-derived DHP **1b** also underwent Ag-promoted alkylation with iododecane to generate a good yield of bisperoxyacetal **4** (eq 3).



Hydrolysis of Bisperoxyacetals. Synthesis of Alkyl Hydroperoxides. Table 2 illustrates screening of conditions for deprotection of bisperoxyacetal **2a**. Little deprotection was observed upon exposure of **2a** to a room temperature ethanolic solution of dilute aqueous H_2SO_4 or even upon heating with an excess of sulfuric acid in methanol. In contrast, refluxing **2a** in a methanolic solution containing 50% aqueous H_2SO_4 resulted in rapid deprotection to furnish a high yield of decyl hydroperoxide and recovered ketone (entry 3). Application of the same reagent but at room temperature resulted in only a

Table 2. Optimization of Hydrolysis Conditions



entry	solvent	acid (equiv)	*T* (°C)	*t* (h)	yield[a] (%)
1	EtOH	1 M aq H_2SO_4 (6)	rt	8	NR
2	MeOH	H_2SO_4 (6)	reflux	1	8
3	MeOH	50% aq H_2SO_4 (6)	reflux	0.16	84
4	MeOH	50% aq H_2SO_4 (6)	rt	48	19
5	MeOH	30% aq H_2SO_4 (6)	rt	1.5	NR
6	THF	camphorsulfonic (2)	rt	3	NR
7	THF	50% aq H_2SO_4 (6)	55	3	78
8	THF	50% aq H_2SO_4 (6)	rt	24	20

[a]Isolated yields. Cyclododecanone recovered in comparable yields.

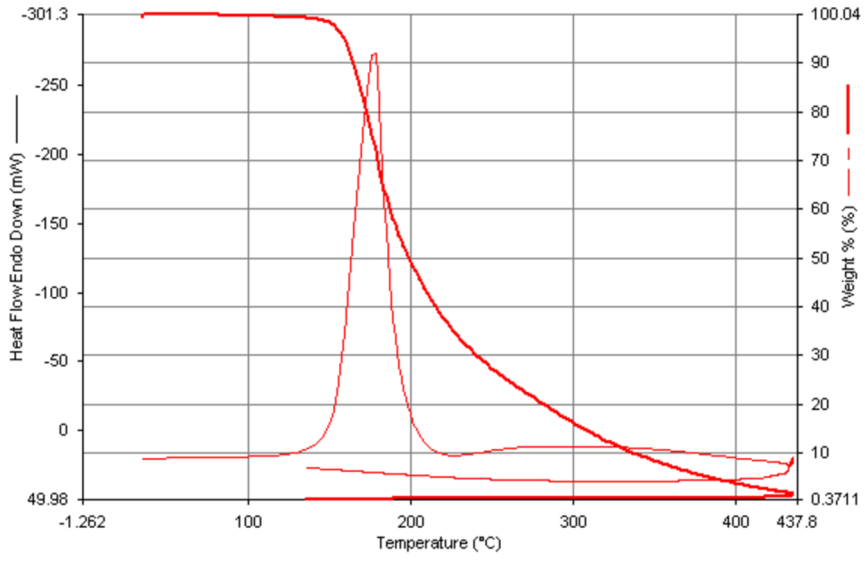


Figure 1. Thermal stability of peroxide **2a**. Upper curve is percent of original mass; lower curve indicates heat flow.

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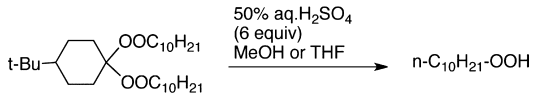
modest yield even after 2 days of reaction (entry 4). A THF solution of **2a** also proved unreactive toward anhydrous acid (entry 6) but rapidly underwent complete deprotection upon heating with a slight excess of 50% aqueous H_2SO_4 (entry 7). Application of the same conditions at room temperature resulted in a prolonged reaction time and lower yield (entry 8). In no case could we detect any ring-expanded lactone. DSC/TGA analysis of a sample of the purified decyl hydroperoxide product (**3a**) revealed a profile for thermal stability very similar to that described earlier for bisperoxyacetal **2a**, with onset of decomposition occurring well above the temperatures required for acid hydrolysis; details are provided in Supporting Information.

Consistent with our hypothesis regarding the contribution of ring strain to peroxyacetal hydrolysis,[10] bisperoxyacetal **4** could not be completely hydrolyzed under conditions that had proven effective for **2a** (Table 3).

Table 3. Hydrolysis of Cyclohexanone-Derived Bisperoxyacetal 4



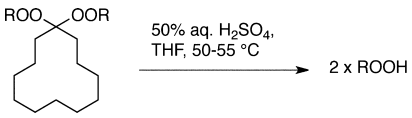
4 **3a**

solvent	T (°C)	t (h)	yield (%)
MeOH	reflux	0.25	21
THF	50–55	6	34[a]

[a]NMR-based yield.

The optimized conditions were next applied to deprotection of bisperoxyacetals **2a–2g** (Table 4) to furnish moderate to good yields of hydroperoxides in highly pure form.

Table 4. Hydrolysis To Form Hydroperoxides



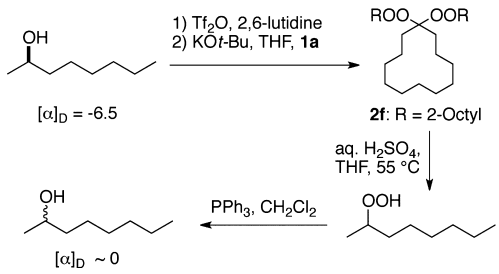
entry	acetal	R	hydroperoxide	yield (%)
1	**2a**	decyl	**3a**	78
2	**2b**	hexyl	**3b**	49[a]
3	**2c**	benzyl	**3c**	60
4	**2d**	9-decenyl	**3d**	62
5	**2e**	$Ph(CH_2)_3$	**3e**	79
6	**2f**	2-octyl	**3f**	48
7	**2g**	2-dodecyl	**3g**	63

[a]Volatile product.

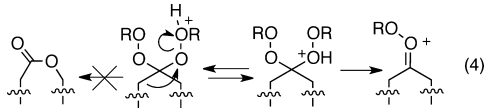
Curious as to the potential for stereospecific displacement of secondary substrates, we repeated the synthesis of 2-hydroperoxyoctane (**3f**) beginning with the triflate derived from enantiomerically enriched (*R*)-(−)-2-octanol (Scheme 1). Phosphine reduction of the derived hydroperoxide furnished 2-octanol possessing a very low specific rotation, suggesting that the displacement of secondary triflates proceeds with little if any stereospecificity.[15]

Discussion. Our decision to focus on the use of a cyclododecanone-derived bishydroperoxide was based upon the report by Terent'ev investigating hydrolysis of analogous 1,1-dihydroperoxides. In that work, the bis-hydroperoxyacetals

Scheme 1. Lack of Stereospecificity in Alkylation with a Secondary Triflate



derived from bulky alicyclic or strained cyclic frameworks underwent hydrolysis more rapidly than those based upon a strain-free backbone.[10] Our results demonstrate that these trends extend to bisperoxyacetals, with **2a** undergoing complete hydrolysis under relatively mild conditions that fail to completely deprotect cyclohexanone-derived **4**. The lack of ring-expanded products observed during acid hydrolysis suggests that ionization of the acetal center is greatly favored relative to C-to-O migration (eq 4). The displacements of



primary halides are anticipated to proceed through an S_N2-type transition state. In contrast, the displacements of secondary triflates appear to involve a transition state with significant cationic character. Although the successful displacement of highly reactive secondary electrophiles suggests the potential for extension to tertiary systems, this proved not to be the case (Table 1, entries 16–18), presumably due to rapid elimination.

In conclusion, we have demonstrated a convenient synthesis of primary and secondary alkyl hydroperoxides based upon use of 1,1-dihydroperoxides. The reagents are available in one step from commercially available ketones, which can be recovered from the hydrolysis/deprotection step. The ease of generating 1,1-dihydroperoxides and of handling the bisperoxyacetal intermediates suggests the potential for extension of the methodology to solid-phase organic synthesis.

Note on Safety. Although no safety issues were encountered in the course of this work, any preparative work with peroxides should be conducted with an awareness of the potential for spontaneous and exothermic decomposition reactions.[16]

EXPERIMENTAL SECTION

1,1-Dihydroperoxides were prepared using a literature procedure.[6a] Alkyl triflates were prepared according to a published procedure and used without column purification.[14] EA = ethyl acetate; Hex = hexane. NMR spectra were acquired at 400 MHz (^1H) or 100 MHz (^{13}C) in $CDCl_3$ unless noted.

General Procedure (Method A): Synthesis of 1,1-Bisperoxyacetals. To a 0 °C solution of cyclododecanone 1,1-dihydroperoxide (1 mmol) in ethyl acetate (10 mL) was added freshly prepared Ag_2O (3 mmol) followed by alkyl iodide (2.2 mmol). The reaction was stirred at room temperature until starting material could no longer be detected (TLC, 5–30 h).[17] The reaction solution was filtered though a small pad of Celite, and the filtrate was concentrated *in vacuo*. The residue was purified by silica chromatography using 1% EA/Hex to furnish pure samples of the bisperoxyacetal.

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General Procedure (Method B): Synthesis of Bisperoxyacetal from Alkyl Triflates. To a 0 °C solution of 1,1-dihydroperoxide (0.5 mmol) in dry THF was added KO*t*Bu (2.1 equiv) followed by alkyl triflate (2.2 equiv/equiv DHP for primary triflates, 3 equiv/equiv DHP for secondary triflates). The reaction was allowed to stir until starting material was no longer visible (TLC, 20 min to 1 h) and then quenched with water (15 mL).[17] The combined EA extracts (25 mL × 2) were dried over Na_2SO_4 and concentrated on a rotary evaporator. The crude product was purified by silica chromatography using 1% diethyl ether and hexane.

General Procedure: Synthesis of Alkyl Hydroperoxides from 1,1-Dihydroperoxides. To a room temperature solution of bisperoxyacetal (0.3 mmol) in tetrahydrofuran (3 mL) was added 50% aqueous H_2SO_4 (1.8 mmol, 6 equiv). The reaction was heated at 50−55 °C until starting material could no longer be detected (TLC, 1−3 h).[17] The reaction was then allowed to cool to room temperature and quenched with saturated aqueous Na_2CO_3 (15 mL). The combined EA extracts (25 mL × 2) were dried over Na_2SO_4 and concentrated. The residue was purified by silica chromatography using 1−3% EA/Hex.

1,1-Dihydroperoxy Cyclododecane (1a). White solid, mp 139−141 °C, yield 78% (909 mg). R_f (20% EA/Hex) 0.54; ^{1}H NMR δ (MeOH-d_4, 300 MHz) 4.84 (s, 2H), 1.59−1.52 (m, 8H), 1.39 (m, 14H); ^{13}C NMR δ (MeOH-d_4, 75 MHz) 113.3, 25.8, 25.7, 21.9, 21.6, 18.9.

4-*tert*-Butyl 1,1-Dihydroperoxy Cyclohexane (1b). White solid, mp 78−80 °C, yield 85% (174 mg). R_f (20% EA/Hex) 0.54; ^{1}H NMR δ (300 MHz) 8.95 (bs, 2H), 2.33 (bd, J = 12 Hz, 2H), 1.75 (bd, J = 12 Hz, 2H), 1.48 (dt, J = 13.3, 3.6 Hz, 2H), 1.27 (dq, J = 13.3, 3.6 Hz, 2H), 1.06 (tt, J = 12.0, 2.9 Hz, 1H), 0.88 (s, 9H); ^{13}C NMR δ 111.0, 47.4, 32.3, 29.7, 27.6, 23.4.

1,1-Bis(decylperoxy) Cyclododecane (2a). Thick colorless liquid, yield 93% (553 mg). R_f (10% EA/Hex) 0.74; ^{1}H NMR δ 4.07 (t, J = 6.8 Hz, 4H), 1.75−1.58 (m, 8H), 1.48 (m, 4H), 1.35−1.27 (m, 42H), 0.88 (t, J = 6.8 Hz, 6H); ^{13}C NMR δ 113.1, 75.0, 31.9, 29.6, 29.5, 29.3, 27.9, 27.0, 26.2, 26.11, 22.7, 22.3, 21.9, 19.4, 14.1; IR (neat) 2922, 2851, 1468, 1054, 989; HRMS (ESI$^+$, TOF) calcd for $C_{32}H_{64}NaO_4$ $(M + Na)^+$ 535.4702, found 535.4727.

1,1-Bis(hexylperoxy) Cyclododecane (2b). Thick colorless liquid, yield 79% (317 mg). R_f (10% EA/Hex) 0.65; ^{1}H NMR δ 4.05 (t, J = 6.7 Hz, 4H), 1.67−1.57 (m, 8H), 1.50−1.41 (m, 4H), 1.39−1.27 (m, 26H), 0.88 (t, J = 6.8 Hz, 6H); ^{13}C NMR δ 113.1, 75.0, 31.6, 27.8, 27.0, 26.0, 25.9, 25.7, 22.6, 22.3, 21.9, 19.3, 13.99; IR (neat) 2927, 2852, 1468, 1052, 989; HRMS (ESI$^+$, TOF calcd for $C_{24}H_{48}NaO_4$ $(M + Na)^+$ 423.3450, found 423.3465.

1,1-Bis(benzylperoxy) Cyclododecane: (2c). White solid, yield 56% (232 mg). Mp 68−70 °C; R_f (10% EA/Hex) 0.69; ^{1}H NMR δ 7.41−7.32 (m, 10H), 5.11 (s, 4H), 1.73−1.69 (m, 4H), 1.52−1.42 (m, 4H), 1.35 (m, 14H); ^{13}C NMR δ 136.0, 129.2, 128.3, 128.2, 113.8, 27.1, 26.1, 22.3, 21.9, 19.4; IR (neat) 2927, 2850, 1706, 1469, 1453, 964; HRMS (ESI$^+$, TOF) calcd for $C_{26}H_{36}NaO_4$ $(M + Na)^+$ 435.2511, found 435.2508.

1,1-Bis(9-decenylperoxy) Cyclododecane (2d). Thick colorless liquid, yield (method B) 80% (122 mg), (method A) 79% (400 mg). R_f (10% EA/Hex) 0.81; ^{1}H NMR δ 5.81 (m, 2H), 5.02−4.91 (m, 4H), 4.07 (t, J =6.6 Hz, 4H), 2.04 (q, J = 6.8 Hz, 4H), 1.70−1.58 (m, 8H), 1.49−1.31 (m, 38H); ^{13}C NMR δ 139.1, 114.3, 113.1, 75.0, 33.8, 29.4, 29.1, 28.9, 27.9, 27.1, 26.2, 26.1, 22.3, 21.98, 19.4; IR (neat) 3076 (week), 2924, 2852, 1468, 990, 907; HRMS (ESI$^+$, TOF) calcd for $C_{32}H_{60}NaO_4$ $(M + Na)^+$ 531.4389, found 531.4385.

1,1-Bis(4-phenylbutylperoxy) Cyclododecane (2e). Thick colorless liquid, yield 68% (340 mg). R_f (10% EA/Hex) 0.82; ^{1}H NMR δ 7.30 (m, 4H), 7.21 (m, 6H), 4.13 (t, J = 6.0, 4H), 2.67 (t, J = 7.1 Hz, 4H), 1.76−1.69 (m, 12H), 1.51 (m, 4H), 1.39 (m, 14H); ^{13}C NMR δ 142.3, 128.4, 128.3, 125.7, 113.2, 74.8, 35.7, 28.0, 27.5, 27.1, 26.1, 22.4, 22.0, 19.4; IR (neat) 2927, 2860, 1495, 1469, 1452, 989; HRMS (ESI$^+$, TOF) calcd for $C_{32}H_{48}NaO_4$ $(M + Na)^+$ 519.3450 found 519.3439.

1,1-Bis(2-octyl peroxy) Cyclododecane (2f). Thick colorless liquid, yield 53% (417 mg). R_f (10% EA/Hex) 0.85; ^{1}H NMR δ 4.25−4.06 (m, 2H), 1.71−1.58 (m, 7H), 1.48 (m, 5H), 1.36−1.20 (m, 30H), 1.21 (d, J = 6.2 Hz, 6H), 0.90 (t, J = 6.4 Hz, 6H); ^{13}C NMR δ 112.8, 79.6, 79.5, 34.7, 32.1, 31.8, 31.5, 29.4, 27.3, 27.2, 26.2, 26.1, 25.6, 25.5, 25.3, 22.6, 22.4, 22.0, 19.4, 18.8, 14.0; IR (neat) 2927, 2855, 1468, 1055, 989; HRMS (ESI$^+$, TOF) calcd for $C_{28}H_{56}NaO_4$ $(M + Na)^+$ 479.4076, found 479.4068.

1,1-Bis(2-dodecyl peroxy) Cyclododecane (2g). Thick colorless liquid, yield 42% (252 mg). R_f (15% EA/Hex) 0.84; ^{1}H NMR δ 4.23 (m, 2H), 1.71−1.59 (m, 6H), 1.48 (m, 4H), 1.36 (m, 18H), 1.28 (m, 30H), 1.21 (d, J = 6.3 Hz, 6H), 0.90 (t, J = 6.3 Hz, 6H); ^{13}C NMR δ 112.8, 79.6, 79.5, 34.7, 31.9, 29.8, 29.6, 29.3, 27.3, 26.2, 26.1, 25.7, 25.6, 22.7, 22.3, 22.0, 19.4, 18.86, 18.83, 14.1; IR (neat) 2922, 2851, 1467, 989; HRMS (ESI$^+$, TOF) calcd for $C_{36}H_{72}NaO_4$ $(M + Na)^+$ 591.5328, found 591.5319.

4-*tert*-Butyl-1,1-bis(decylperoxy) Cyclohexane (4). Thick colorless liquid, yield 89% (866 mg). R_f (10% EA/Hex) 0.71; ^{1}H NMR δ 4.11 (t, J = 6.7 Hz, 2H), 4.06 (t, J = 6.7 Hz, 2H), 2.29 (bd, J = 12.0 Hz, 2H), 1.69−1.58 (m, 6H), 1.44−1.19 (m, 33H), 0.89 (t, J = 0.89 Hz, 6H), 0.87 (s, 9H); ^{13}C NMR δ 108.9, 75.4, 75.1, 47.5, 32.3, 31.9, 30.6, 29.6, 29.48, 29.47, 29.3, 27.89. 27.83, 27.6, 26.18, 26.16, 23.5, 22.7, 14.1; IR (neat) 2922, 2853, 1466, 1365, 1060; HRMS (ESI$^+$, TOF) calcd for $C_{30}H_{60}NaO_4$ $(M + Na)^+$ 507.4389, found 507.4384.

Decyl Hydroperoxide (3a). CAS no. 4225-91-6. Colorless liquid, yield 78% (64 mg). R_f (10% EA/Hex) 0.44; ^{1}H NMR, δ 8.23 (s, 1H), 4.03 (t, J = 6.7 Hz, 2H), 1.64 (quintet, J = 6.7 Hz, 2H), 1.37−1.27 (m, 14H), 0.89 (t, J = 6.8 Hz, 3H); ^{13}C NMR δ 76.7, 31.9, 29.5, 29.4, 29.3, 27.5, 25.9, 22.7, 14.1.

Hexyl Hydroperoxide (3b). CAS no. 4312-76-9. Colorless liquid, yield 49% (58 mg). R_f (10% EA/Hex) 0.39; ^{1}H NMR δ 8.36 (s, 1H), 4.03 (t, J = 6.7 Hz, 2H), 1.64 (quintet, J = 6.8 Hz, 2H), 1.39−1.26 (m, 6H), 0.89 (t, J = 6.9 Hz, 3H); ^{13}C NMR δ 76.7, 31.6, 27.5, 25.5, 22.5, 13.9.

Benzyl Hydroperoxide (3c). CAS no. 3071-34-9. Colorless liquid, yield 60% (75 mg). R_f (10% EA/Hex) 0.22; ^{1}H NMR δ 8.25 (s, 1H), 7.43−7.39 (m, 5H), 5.02 (s, 2H); ^{13}C NMR δ 135.7, 129.0, 128.6, 79.2.

9-Decenyl Hydroperoxide (3d). CAS no. 123369-53-9. Colorless liquid, yield 62% (107 mg). R_f (10% EA/Hex) 0.37; ^{1}H NMR δ 8.23 (s, 1H), 5.87−5.77 (m, 1H), 5.03−4.92 (m, 2H), 4.03 (t, J = 6.7 Hz, 2H), 2.07−2.02 (m, 2H). 1.64 (quintet, J = 6.9 Hz, 2H), 1.40−1.25 (m, 10H); ^{13}C NMR δ 139.1, 114.1, 76.7, 33.7, 29.35, 29.34, 29.0, 28.9, 27.5, 25.9.

4-Phenylbutyl Hydroperoxide (3e). CAS no. 99172-63-1. Colorless liquid, yield 79% (133 mg). R_f (10% EA/Hex) 0.30; ^{1}H NMR δ 8.44 (s, 1H), 7.37−7.33 (m, 2H), 7.27−7.24 (m, 3H), 4.09 (t, J = 6.1 Hz, 2H), 2.71 (t, J = 7.1 Hz, 2H). 1.80−1.71 (m, 4H); ^{13}C NMR δ 142.2, 128.48, 128.4, 125.8, 76.9, 35.6, 27.7, 27.2.

2-Octyl Hydroperoxide (3f). CAS no. 32956-90-4. Colorless liquid, yield 48% (105 mg). R_f (10% EA/Hex) 0.37; $[\alpha]_D$ −0.5 (c 1.46 g/100 mL, $CHCl_3$);[2g] ^{1}H NMR δ 7.89 (s, 1H), 4.07 (m, 1H), 1.64 (m, 1H), 1.44−1.28 (m, 9H), 1.23 (d, J = 6.1 Hz, 3H), 0.89 (t, J = 6.9 Hz, 3H); ^{13}C NMR δ 84.7, 34.0, 31.7, 29.3, 25.3, 22.5, 18.1, 14.0.

2-Dodecyl Hydroperoxide (3g). CAS no. 123369-50-6. Colorless liquid; yield 63% (94 mg). R_f (15% EA/Hex) 0.33; ^{1}H NMR δ 7.81 (s, 1H), 4.12−4.04 (m, 1H), 1.68−1.61 (m, 1H), 1.45−1.27 (m, 17H), 1.24 (d, J = 6.1 Hz, 3H), 0.89 (t, J = 6.9 Hz, 3H); ^{13}C NMR δ 81.7, 34.0, 31.9, 29.69, 29.61, 29.59, 29.55, 29.33, 25.4, 22.6, 18.1, 14.1.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

^{1}H and ^{13}C NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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