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Synthesis of Ethers via Reaction of Carbanions and Monoperoxyacetals

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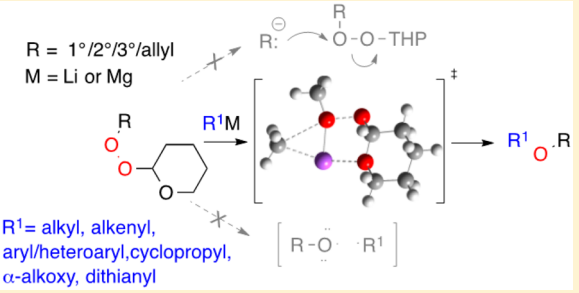
Supporting Information

ABSTRACT: Although transfer of electrophilic alkoxyl ("RO+") from organic peroxides to organometallics offers a complement to traditional methods for etherification, application has been limited by constraints associated with peroxide reactivity and stability. We now demonstrate that readily prepared tetrahydropyranyl monoperoxyacetals react with sp^3 and sp^2 organolithium and organomagnesium reagents to furnish moderate to high yields of ethers. The method is successfully applied to the synthesis of alkyl, alkenyl, aryl, heteroaryl, and cyclopropyl ethers, mixed *O,O*-acetals, and *S,S,O*-orthoesters. In contrast to reactions of dialkyl and alkyl/silyl peroxides, the displacements of monoperoxyacetals provide no evidence for alkoxy radical intermediates. At the same time, the high yields observed for transfer of primary, secondary, or tertiary alkoxides, the latter involving attack on neopentyl oxygen, are inconsistent with an S_N2 mechanism. Theoretical studies suggest a mechanism involving Lewis acid promoted insertion of organometallics into the O−O bond.



INTRODUCTION

Methods for ether synthesis are overwhelmingly based upon the attack of nucleophilic oxygen on electrophilic carbon.[1−4] Our lab has been interested in expanding the scope of an umpoled strategy based upon reaction of carbanions with electrophilic oxygen.[5] The reaction of dialkyl peroxides with carbanions, while long known,[6] has largely remained a curiosity applied mainly to transfer of methoxyl and other unhindered alkoxides.[7,8] Even a slight increase in steric bulk results in reduced yields,[7] and reactions of di-*t*-butyl peroxide furnish multiple products.[9,10] We became interested in a general method for selective transfer of 1°, 2°, or 3° alkoxides from a mixed peroxide to a carbanion. In approaching this problem, we were encouraged by evidence for the strong influence of substituent groups on peroxide reactivity. Bistrimethylsilyl peroxide efficiently transfers $OSiMe_3$ to a variety of organometallic reagents;[11] curiously, *t*BuOOSiMe$_3$ transfers neither $OSiMe_3$ nor *t*BuO.[12] Lithiated peroxides, sometimes described as "oxenoid" in character, transfer LiO to a variety of carbanions,[13] and similar reactivity patterns have been observed with other metalloperoxides.[14] Bisacyl peroxides even transfer acyloxy groups to enolates and enamines.[15] However, transfer of alkoxide is more challenging. The strain within bicyclic peroxides has been harnessed to facilitate reaction of more hindered peroxides; unfortunately, the presence of the scaffold limits the range of potential targets.[16] Electronic activation in the form of peresters has been employed to achieve transfer of tertiary alkoxides to Grignard reagents,[17] but broad application is limited by the propensity of peresters to undergo *C-to-O* rearrangement or fragmentation to carbonyls.[18,19] We were particularly intrigued by reports describing enhanced reactivity of acyclic peroxyacetals and peroxyaminals with Grignard reagents.[20,21] However, the reactions of peroxyaminals displayed variable regioselectivity,[20] while reactions of a mixed ethoxy/peroxy acetal required a significant excess of the Grignard reagent.[21] In preliminary work, we discovered that tetrahydropyranyl (THP) monoperoxyacetals selectively transfer the attached OR to lithiated 1,3-dithianes.[5b] We now describe investigations of reactions between carbanions and several classes of organic peroxides, with an emphasis on monoperoxyacetals. (Figure 1).

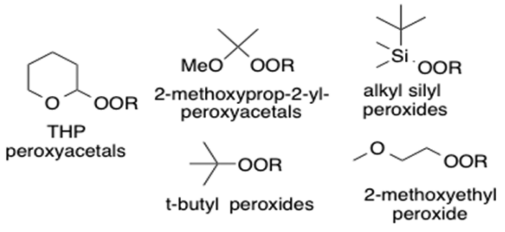


Figure 1. Substrate classes.

RESULTS

Table 1 illustrates preparation of substrates. Base-promoted alkylation of hydroperoxides with primary and secondary

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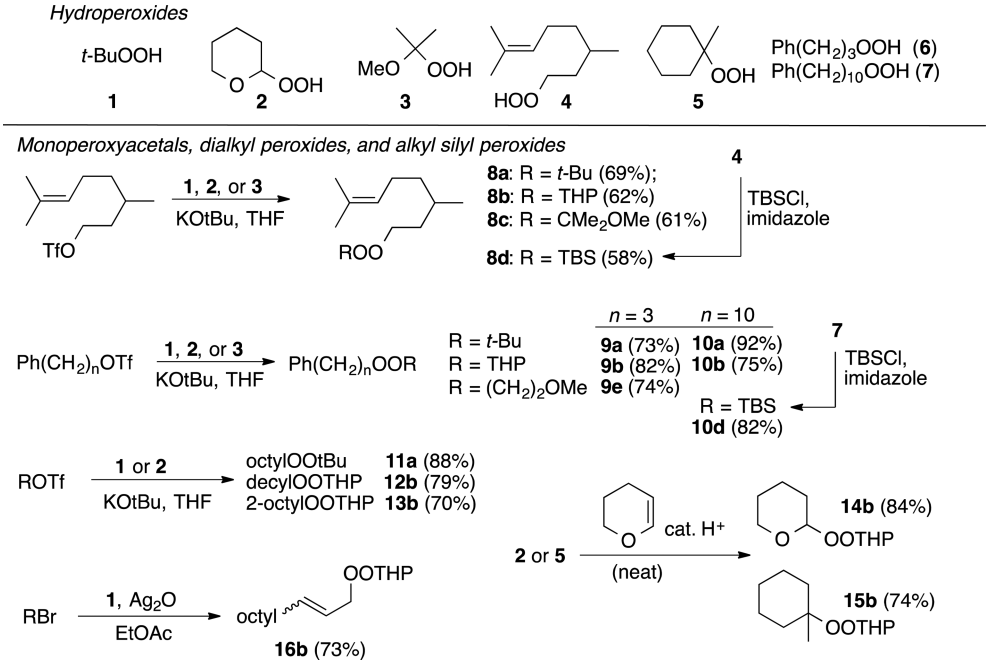
Table 1. Substrate Synthesis



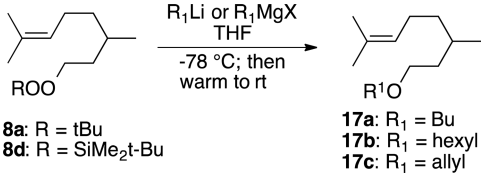
triflates[22] provided good yields of *t*-butyl/alkyl peroxides (**8a**–**11a**), monoperoxyacetals (**8c**,[23] **8b**–**10b**, **12b**, **13b**[24]), and a 2-methoxyethyl peroxide (**9e**). Tetrahydropyranyl monoperoxyacetals (**14b**, **15b**) were also prepared through acetalization of hydroperoxides with dihydropyran.[25] Ag(I)-promoted hydroperoxide alkylation was used to prepare allyl peroxide **16b**.[26] Alkyl/silyl peroxides **8d** and **10d** were prepared through silylation of hydroperoxides.[27]

Thermal Stability. Thermal analysis was conducted on one of the dialkyl peroxides (**10a**) and one of the monoperoxyacetals (**10b**) to provide some baseline stability data for each class. The results, detailed in Supporting Information, revealed that **10a** and **10b** are relatively stable, undergoing exothermic decomposition only once heated past 170 and 120 °C, respectively.

Table 2 illustrates the reactivity of *t*-butyl/alkyl and trialkylsilyl/alkyl peroxides toward sp^3 organometallics. *t*-Butyl peroxide **8a** reacted with an excess of RLi over a period of several hours to furnish ethers derived from selective attack on the less hindered oxygen. The corresponding reactions with Grignard reagents were successful, but somewhat slower. The corresponding trialkylsilyl peroxide (**8d**) reacted slowly with *n*-BuLi to furnish a large number of products (TLC).

Scheme 1 summarizes reactions of THP monoperoxyacetals with sp^3 organometallics. Reactions with RLi proceeded slowly at −78 °C but were complete within minutes at 0 °C. The monoperoxyacetals failed to react with Grignard reagents

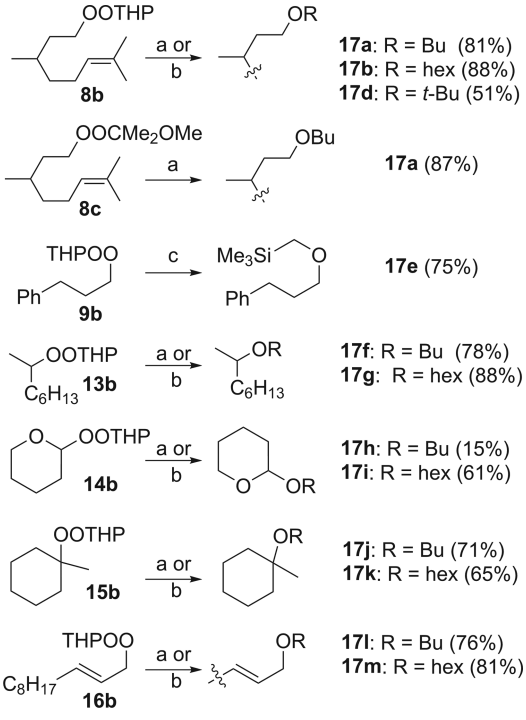
Table 2. Reactions of Dialkyl and Alkyl/Silyl Peroxides



substrate	R_1M (equiv)	time (h)	product	yield (%)
8a	*n-BuLi* (2)	4	**17a**	70
8a	hexMgBr (3)	8	**17b**	42
8a	allylMgBr (2)	0.5	**17c**	27
8a	allylLi (2.5)[a]	4	**17c**	70
8d	*n-BuLi* (2)	8	multiple	

[a]From allylSnBu$_3$ and *n*-BuLi.

Scheme 1. Reaction of sp^3 RM with Peroxyacetals[a]



[a](a) RLi (1.1 equiv), −78 °C; (b) hexylMgBr (1.1 equiv), 0 °C; (c) Me_3SiCH_2MgCl (1.3 equiv), 0 °C.

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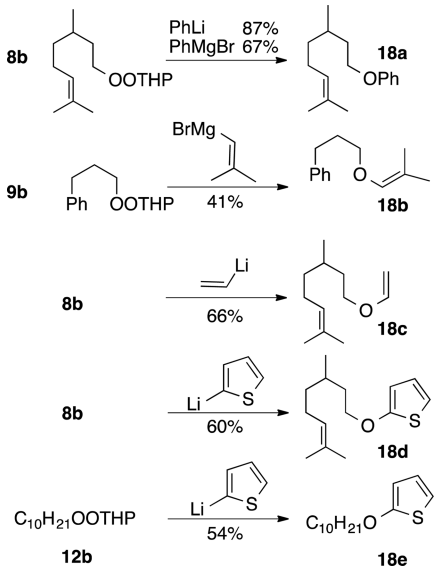
at −78 °C but were consumed rapidly at 0 °C, providing ethers in yields equal or superior to those obtained with RLi. Transfer of 1°, 2°, or 3° alkoxides occurred with similar yields; in each case; we observed only the products of regioselective displacement of OTHP.

Reactions with sp² Organometallics. Monoperoxyacetal **8b** reacted readily with PhLi (−78 °C) and PhMgBr (0 °C) to furnish good yields of the phenyl ether (**18a**, Scheme 2).

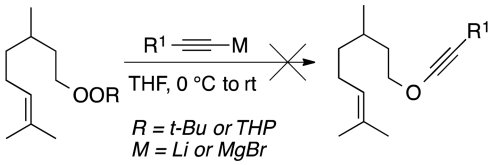
Scheme 2. Reaction of Peroxyacetals with *sp*² RM[a]



[a]THF, −78 to rt (RLi) or 0 °C to rt (RMgX).

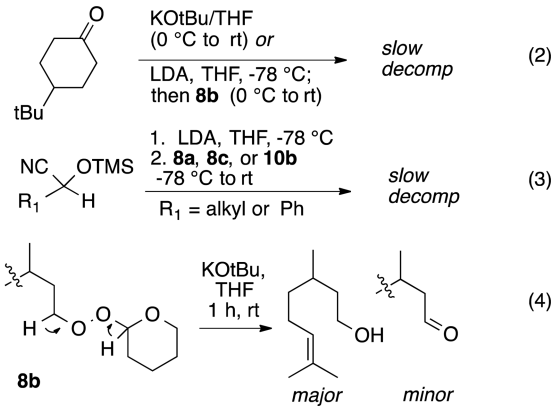
Reaction with an alkenyl magnesium bromide or vinyl lithium, the latter generated in situ, furnished the corresponding enol ethers; the moderate yields may in part reflect decomposition during purification. Reaction of 2-thienyl lithium with primary monoperoxyacetals furnished a moderate yield of 2-alkoxythiophenes **18d** and **18e**, representatives of a class of molecules previously explored only to a limited extent.[28]

Metalated Alkynes. Alkynyllithium or alkynylmagnesium reagents failed to react with a dialkyl peroxide (**8a**) or a monoperoxyacetal (**8b**); starting materials could be recovered even after prolonged reaction periods (eq 1).



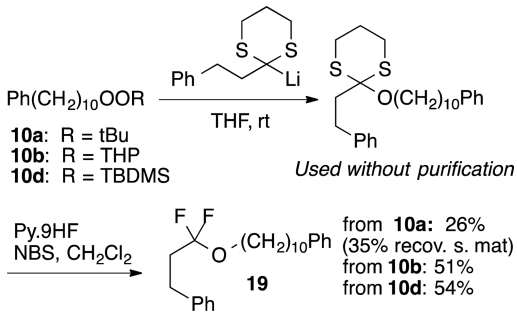
(1)

Reaction with Resonance-Stabilized Nucleophiles. Neither monoperoxyacetals nor a dialkyl peroxide underwent intermolecular C−O bond formation with enolates (eq 2) or azaenolates (eq 3); only slow decomposition was observed. The results were not entirely unexpected given our observations during tandem reactions of enolates with iodoperoxides.[5a] In a control experiment, reaction of a THF solution of **8b** with stoichiometric potassium *t*-butoxide (eq 4) resulted in slow formation of byproducts indicative of E_1CB fragmentation.[19,29] The corresponding *t*-butyl peroxide **8a** (not shown) decomposed more slowly to furnish citronellal.



Lithiated Dithianes. Lithiated 1,3-dithianes have been widely applied as acyl anion equivalents for reaction with carbon electrophiles.[30] In the only report of their reactivity toward peroxides, reaction with bistrimethylsilyl peroxide results in preferential transfer of a silyl group.[11a] We recently demonstrated successful reaction of THP monoperoxyacetals with lithiated dithianes to furnish *S,S,O*-orthoesters and derived difluoroalkyl ethers.[5b] Being curious about the influence of the peroxide electrophile on the reactivity toward inductively stabilized anions, we investigated reactions of a monoperoxyacetal, a silyl/alkyl peroxide, and a dialkyl peroxide toward a common lithiated dithiane (Scheme 3). The monoperoxyacetal

Scheme 3. Reactivity towards Lithiated Dithianes



10b and alkyl/silyl peroxide **10d** gave similar yields of difluoroether **19**, isolated following fluorodesulfurization of the initial orthoester products. In contrast, the mixed alkyl/*t*-butyl peroxide **10a** was much less reactive. Reactions were conducted exclusively in THF; previous investigations of reactions of lithiated trithianes[5b] observed no benefit from the presence of additives (LiCl, $MgBr_2$) or polar cosolvents (HMPA).

Attempted Synthesis of Trihaloethers. Trifluoromethyl ethers are of interest as degradation-resistant structural components in agrochemicals and drug molecules.[31] However, methods for their introduction remain limited.[32] We recently reported an indirect approach to introduction of OCF_3 groups via reaction of a monoperoxyacetal with a lithiated trithiane, followed by fluorodesulfurization of the resulting *S,S,O*-orthocarbonate,[5b] and we became interested in a more direct approach based upon reaction of a peroxide with a trifluoromethyl anion. This approach requires the targeted C−O bond formation to occur more rapidly than α-elimination of the nucleophile.[33] We began our investigations with the Ruppert-Prakash reagent, CF_3SiMe_3.[32,33] The trifluoromethyl ether was not observed despite application of different activators, solvents

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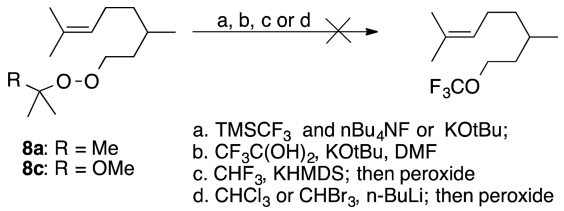
(DMF, THF), or reaction temperatures (Scheme 4). We also failed to detect ether formation for base-promoted reaction

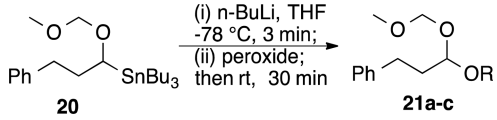
Scheme 4. Attempted Synthesis of Trihalomethyl Ethers



with trifluoroacetaldehyde hydrate,[34] or with KCF_3 generated via low temperature deprotonation of fluoroform.[35] Formation of aldehydes derived from Kornblum fragmentation of the peroxide (see eq 4) was observed in some of these reactions. Interested in whether the displacements might be more successful in the presence of a lithium cation, we investigated reactions with lithiated trihalomethanes but saw no reaction at temperatures (−110 °C for $LiCCl_3$, −50 °C for $LiCBr_3$) where the reagents were stable.

Reaction with α-Alkoxylithium Reagents. Lithiated ethers (α-alkoxylithiums) have been employed as synthons for acyl anions and hydroxymethyl anions.[36] As illustrated in Table 3, the alkoxylithium reagent generated from a

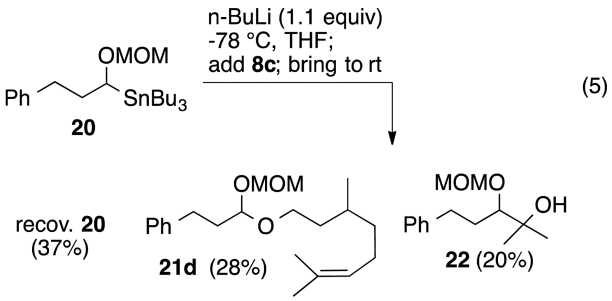
Table 3. Synthesis of *O,O*-Acetals



peroxide	acetal	yield (%)
$C_8H_{17}OOtBu$ (**11a**)	**21a**: R = octyl	57
$Ph(CH_2)_3OOtBu$ (**9a**)	**21b**: R = $(CH_2)_3Ph$	55
$C_{10}H_{21}OOTHP$ (**12b**)	**21c**: R = decyl	55

tributylstannyl MOM ether (**20**) reacted with primary alkyl/*t*-butyl peroxides or a monoperoxyacetal to give moderate yields of the mixed *O,O*-acetals.

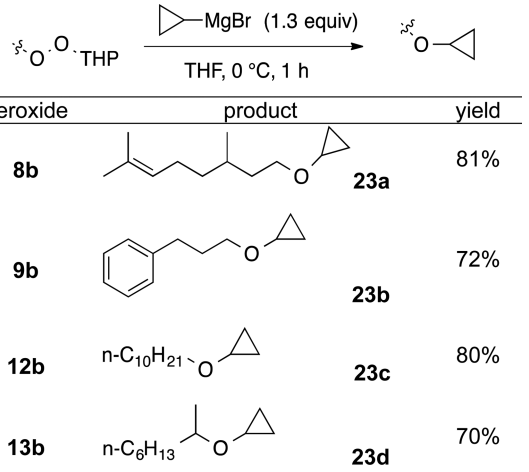
The same reaction, when repeated with methoxypropyl peroxyacetal **8c**, did not proceed to completion. The mixed acetal (**21d**) was isolated in low yield and accompanied by the tertiary alcohol (**22**) derived from trapping of acetone generated from the cleaved acetal (eq 5).



(5)

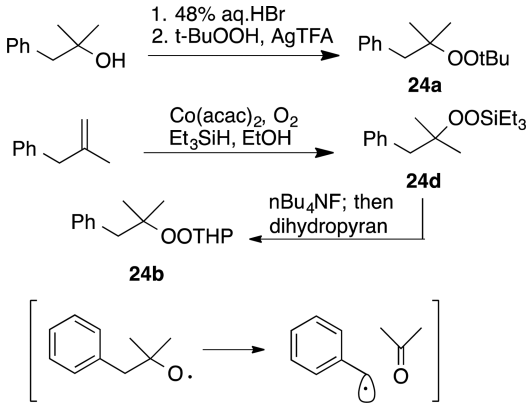
Application to Cyclopropyl Ethers. We were interested in application of the reaction of monoperoxyacetals and organometallics as an approach to cyclopropyl ethers, a relatively challenging class of targets for which multiple approaches have been reported.[37] In approaching this class of reactions, we were encouraged by the reported reaction of *t*-butyl perbenzoates with cyclopropyl magnesium bromide.[38] We found that the reaction of monoperoxyacetals with cyclopropyl magnesium bromide furnishes an efficient approach to primary and secondary cyclopropyl alkyl ethers (Table 4).

Table 4. Synthesis of Cyclopropyl Ethers



Mechanistic Investigations. In an effort to gain information about the possible role of single electron transfer in the C−O bond-forming step, we investigated reactions of phenylmethylpropyl peroxides; the derived alkoxy radical undergoes cleavage to acetone and benzyl radical at $\sim 10^8$/s (Scheme 5).[39] Dialkyl peroxide **24a** was prepared through a known procedure.[40] Silyl peroxide **24d** was prepared through

Scheme 5. Preparation of Radical Probes



Co(II)-mediated peroxidation of methallyl benzene with oxygen and triethylsilane.[41] THP acetal **24b** was prepared by deprotection of the silyl peroxide and acetalization of the intermediate hydroperoxide.[25]

Monoperoxyacetal **24b** underwent rapid reaction with *n*-BuLi to furnish mainly the butyl ether (**25a**), accompanied by smaller amounts of the tertiary alcohol **26** and recovered starting material (Table 5). The corresponding reaction with excess hexylMgBr furnished only the hexyl ether (**25b**) resulting from displacement of OTHP. In contrast, reaction of di-*t*-alkyl peroxide **24a** with *n*-BuLi generated multiple products and only trace amounts of the ether. The reaction of silyl peroxide **24d** with *n*-BuLi provided the most convincing

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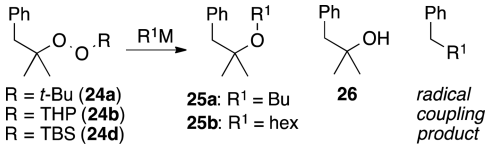
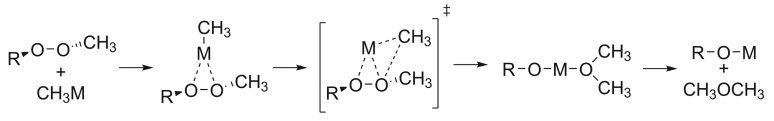
Table 5. RM Reactions with Radical Probes[a]



subs	R^1M	conv. (%)	ether	alcohol	coupling
24b	*n*-BuLi	93	R^1 = Bu (55%)	15%	
24b	hexMgBr	100	R^1 = hex (75%)		
24a	*n*-BuLi	55		32%	PhC_5H_{11} (3%)
24d	*n*-BuLi	59		11%[b]	PhC_5H_{11} (10%)

[a]Conditions: *n*-BuLi (1 equiv), THF, −78 °C, allow to warm to rt; hexylMgBr (2 equiv), 0 °C, allow to warm to rt. [b]Et_3SiOH isolated in 24% yield.

Scheme 6. Predicted Relative Gas-Phase Energies[a] and Solution-Phase Enthalpies[b] of Intermediates and Transition States

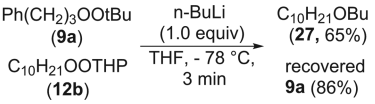


M	R	I	II	TS III	IV	V
Li	t-Bu	0.0	-18.1	-8.0	-105.4	-86.8
		(0.0)	(-13.7)	(5.2)	(-97.6)	(-83.6)
Li	THP	0.0	-28.5	-25.6	-123.5	-106.4
		(0.0)	(-23.1)	(-14.1)	(-111.5)	(-99.4)
Na	t-Bu	0.0	-10.4	2.2	-91.1	-76.9
		(0.0)	(-9.5)	(8.6)	(-86.6)	(-78.2)
Na	THP	0.0	-19.3	-14.8	-112.0	-98.6
		(0.0)	(-17.7)	(-7.2)	(-104.0)	(-95.7)

[a]B3LYP/6-31+G(d,p), 0 K; units in kcal/mol. [b]THF at 298 K with the SMD continuum solvent model; units in kcal/mol and enthalpies in parentheses.

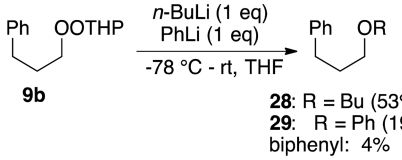
evidence for the intermediacy of radicals in the form of a significant amount of pentylbenzene product of radical−radical coupling.

Competition between a Dialkyl Peroxide and a Monoperoxyacetal. A competition between a dialkyl peroxide and a monoperoxyacetal for capture of a limiting quantity of *n*-BuLi generated only the ether (**27**) derived from the monoperoxyacetal (eq 6).



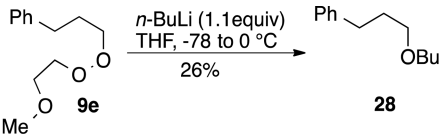
(6)

sp³ vs sp² RLi. A competition between *n-BuLi* and PhLi for a limiting quantity of a monoperoxyacetal revealed a strong preference for reaction with the sp^3 reagent (eq 7).



(7)

Importance of Chelation vs Acetal Structure. In an effort to probe the basis for the enhanced reactivity of the monoperoxyacetals, we investigated C−O bond formation with 2-methoxyethyl peroxide **9e**. This substrate, which possesses the potential for metal chelation but lacks a peroxyacetal, provided the corresponding either in lower yields than had been observed even with simple *t*-butyl peroxides (eq 8).



(8)

Theoretical Investigations. In an effort to gain better understanding of the reactions described above and the influence of reaction conditions on product formation, we conducted B3LYP/6-31+G(d,p) calculations for the simple model reaction of the transfer of methoxide from a methyl peroxide or peroxyacetal to a methyl anion (Scheme 6). Our calculations focused on the impact of changing the metal from Li to Na and of changing the leaving group from O*t*-Bu to OTHP.

All four sets of conditions appear to favor the same mechanism: first, formation of a metal-peroxy complex (**II**), second, passage through a four-centered transition state (**TS III**), third, formation of a complex of the incipient ether with the metal alkoxide (**IV**), and, finally, cleavage to final products (**V**). (Early calculations found the same mechanism for the addition of alkyl lithium reagents to carbon−carbon and carbon−oxygen multiple bonds.)[42,43] The calculations predict that the lithiated system is significantly more reactive than the sodiated system. This suggests that the metal ion's interaction with the peroxy moiety is primarily electrostatic;[42] the greater charge density on the smaller Li^+ leads to greater stabilization.

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The presence of the THP group is found to stabilize the initial organometallic-peroxide complex (**II**) and to dramatically lower the energy for insertion into the peroxide bond. An approximate treatment of THF solvation using the SMD continuum model predicts the relative enthalpies of most intermediates and transition states to be several kcal/mol higher in energy than the gas-phase calculations. However, the solvation calculations predict the same trends in reactivity: the Li^+ ion and the THP substituent both significantly stabilize both the reactive complex and the transition state for insertion.

DISCUSSION

Whereas reactions of dialkyl peroxides are largely limited to transfer of methoxide or primary alkoxide,[6−8,10] monoperoxyacetals have significantly enhanced reactivity toward unstabilized carbanions, transferring primary, secondary, or tertiary alkoxides through highly regioselective attack on the nonacetal oxygen of the peroxide. In contrast to peresters, monoperoxyacetals appear to promote alkoxide transfer without significantly destabilizing the peroxide.[44]

Reaction is observed between monoperoxyacetals and sp^3 and sp^2 RLi and RMgX reagents at −78 °C (organolithium reagents) or 0 °C (Grignard reagents). Both acyclic (2-methoxyprop-2-yl) and cyclic (THP) peroxyacetals offer good reactivity; however, the acyclic peoxyacetals sometime generate side products derived from liberation of a reactive carbonyl group in the presence of the organometallic. The monoperoxyacetals do not undergo intermolecular reactions with enolates or similar stabilized carbanions, paralleling earlier observations from our lab.[5a] The monoperoxyacetals also fail to react with metalated alkynes, an interesting outcome given the reported reactivity of lithiated hydroperoxides toward carbanions,[13,45] as well as our observation of successful reaction of peroxyacetals with inductively stabilized anions such as lithiated dithianes and lithiated ethers. However, the lack of reactivity toward *sp* carbanions is consistent with results observed with bistrimethylsilyl peroxide, which undergoes mainly silyl exchange with lithiated alkynes.[12]

Several mechanisms have been discussed with regard to the reaction of dialkyl peroxides with unstabilized organometallics. While early results with unhindered peroxides were consistent with S_N2-type attack on the O−O bond,[7] reactions of di-*t*-alkyl peroxides have been reported to proceed via intermediate alkoxy radicals.[10,46] Our work found no evidence for radical intermediates in attack of organolithium reagents on THP peroxyacetals.

If the reactions involve neither simple displacement nor cleavage to alkoxy radicals, then what? Lithiated peroxides are often thought to react with nucleophiles through oxenoid-type insertion into the C−Li bond; attack on alkenyl lithium and cyclopropyl lithium appears to occur without loss of stereochemistry.[13] However, whereas the transfer of LiO from lithiated hydroperoxides to organolithium reagents has been calculated to involve in-line arrangement of the carbanion, the lithiated oxygen, and the departing oxygen,[13b] our calculations suggest side-on insertion of the RLi into the Lewis acid activated O−O bond. This theoretical result is supported by the similar yields obtained for transfer of primary, secondary, and tertiary alkoxides, a result which would seem to rule out an S_N2-type attack on the backside of the breaking O−O bond. Calculations predict, and experiments confirm, that the presence of the acetal group significantly lowers the energy for insertion of unstabilized organometallics and directs the reaction toward exclusive transfer of the nonanomeric oxygen. The bidentate coordination available to the organometallic/Lewis acid is not sufficient to explain the results, as evidenced by the poor reactivity of the methoxyethyl peroxide. However, the interaction of Lewis acids with peroxyacetals and ozonides (1,2,4-trioxolanes) has been previously demonstrated to activate both C−O and O−O bonds.[47]

In conclusion, we have shown that monoperoxyacetals, readily prepared and easily handled derivatives of hydroperoxides, enable highly efficient intermolecular transfer of alkoxide to unstabilized organolithium and organomagnesium reagents along with some inductively stabilized organolithium species. The peroxyacetal activating group promotes highly selective transfer of the nonanomeric OR, regardless of steric bulk. The bond-forming process, which appears to involve metal-promoted insertion into the O−O linkage, appears to be mechanistically distinct from similar reactions of alkyl or alkyl silyl peroxides. The new methodology offers a new tool with which to approach ethers, including some poorly accessible through existing methods.

EXPERIMENTAL PROCEDURES

General Experimental. Reagents and solvents were used as supplied commercially, except for DCM and THF, which were distilled from CaH_2 and Na/Ph_2CO, respectively. Reagents supplied as solutions were dispensed based upon manufacturer-supplied concentrations. Reactions were conducted under an atmosphere of N_2 except where noted. Thin-layer chromatography (TLC) was performed on 0.25 mm hard-layer silica G plates visualized with a UV lamp or by staining: 1% ceric sulfate and 10% ammonium molybdate in 10% H_2SO_4 (general stain, after heating); 3% vanillin in 3% H_2SO_4 in EtOH (general stain, after heating); or a 1% *N*,*N*′-dimethyl-*p*-phenylenediamine in 1:20:100 acetic acid/water/methanol (specific for peroxides).[48] Unless otherwise noted, NMR spectra were acquired in $CDCl_3$; ^1H spectra are reported as chemical shift (multiplicity, *J* couplings in Hz, number of protons). IR spectra were recorded as neat films on a ZrSe crystal; selected absorbances are reported in cm^{-1}. Abbreviations: hexane = Hex; EA = ethyl acetate; THF = tetrahydrofuran; TBDMS (or TBS) = *tert*-butyldimethylsilyl; THP = tetrahydropyranyl.

Calculations. Optimized geometries, harmonic vibrational frequencies, and electronic energies of all structures in Scheme 6 were obtained with the B3LYP level of density functional theory and the 6-31+G(d,p) basis set.[49,50−52] All minima reported (structures **I**, **II**, **IV**, and **V**) contain all real frequencies, and all transition states (structures **TS III**) contain one imaginary frequency. Intrinsic reaction coordinate calculations confirmed that each transition state connected a metal-peroxy complex **II** and the corresponding metal alkoxide-ether complex **IV**. The relative electronic energies were corrected by the differences in zero-point vibrational energy scaled by 0.9806.[53] Solution-phase enthalpies were determined as follows: The thermal corrections to the electronic energies were calculated based on the B3LYP/6-31+G(d,p) geometries and harmonic frequencies. Solvation corrections were based on single-point energy calculations using the continuum SMD model of Truhlar and co-workers.[54]

***t*-Butyl Hydroperoxide (1).** [75-91-2], 5.5 M in decane, was used as purchased.

2-Tetrahydropyranyl (THP) Hydroperoxide (2). [4676-84-0] was synthesized using a modified version of a known procedure.[24] To a 0 °C solution of 50 wt % aq. H_2O_2 (6.66 mL, ∼118 mmol) was added 10% aq. H_2SO_4 (0.1 mL) The mixture was stirred for 10 min, after which 3,4-dihydro-2*H*-pyran (4.94 g, 58.8 mmol) was added over a period of 3 min. The reaction was stirred for 1 h at 0 °C and then diluted with sat. aq. NH_4Cl (15 mL). The solution was extracted with ether (150 mL), and the organic layer was washed with aq. sat. $(NH_4)_2SO_4$ (5 × 10 mL). The resulting solution was dried over Na_2SO_4 and concentrated on a rotary evaporator. The residue obtained

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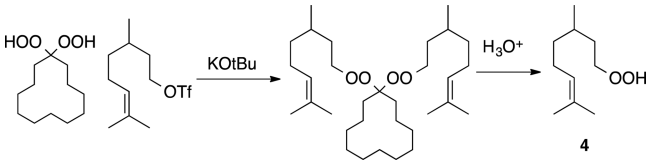
was purified by silica gel flash chromatography using a gradient of 4−25% EA/Hex to afford the hydroperoxide as a thick and colorless oil (4.60 g, 66%). Spectral data were identical to those previously reported.[19]

2-Methoxyprop-2-yl Hydroperoxide (3). [10027-74-4] was prepared as a colorless oil (82%, 878 mg) from 2,3-dimethyl-2-butene (10.0 mmol, 841 mg) using a known procedure.[23,55] R_f = 0.3 (15% EA:Hex).

8-Hydroperoxy-2,6-dimethyloct-2-ene (4). [123369-58-4] was prepared by alkylation of a 1,1-dihydroperoxycyclodecane, followed by hydrolysis of the resulting bisperoxyacetal.[22]



A solution of 3,7-dimethyloct-6-en-1-ol (0.936 g, 6 mmol) in dry DCM (18 mL) was cooled to 0 °C, and triflic anhydride (1.4 equiv) and 2,6-lutidine (1.5 equiv) were sequentially added via syringe. The reaction was stirred for 15 min at 0 °C and then diluted with ice-cold hexane (∼40 mL). The resulting solution was washed with ice cold 0.1 M aq. $KHSO_4$ (40 mL), and the separated aqueous layer was extracted with another portion of cold Hex (25 mL). The combined organic layers were dried over Na_2SO_4 and concentrated on a rotary evaporator (bath temperature 10 °C). The residue was subjected to 0.5 mmHg for approximately 5 min to generate nearly pure 3,7-dimethyloct-6-en-1-yl trifluoromethanesulfonate (1.693 g, 98%) as a light brown oil, which was placed in a −20 °C freezer and used within an hour:[56] R_f = 0.59 (10% EA/Hex); ^{1}H NMR: 5.11−5.07 (m, 1H), 4.61−4.57 (m, 2H), 2.06−1.96 (m, 2H), 1.93−1.85 (m, 1H), 1.72−1.68 (m, 1H), 1.70 (s, 3H), 1.66−1.64 (m, 1H), 1.62 (s, 3H), 1.42−1.32 (m, 1H), 1.29−1.20 (m, 1H), 0.96 (d, J = 6.3 Hz, 3H); ^{13}C NMR: 131.8, 123.9, 118.5 (q, J = 323 Hz), 76.2, 36.6, 36.0, 28.6, 25.6, 25.1, 19.0, 17.6.

To a 0 °C solution of cyclododecanone-1,1-dihydroperoxide (2.196 g, 9.469 mmol, synthesized as previously described)[57] in dry THF (50 mL) was added KO*t*Bu (2 equiv), followed by the triflate described above (6.0 g, 20.8 mmol). The reaction mixture was stirred until the starting material was no longer visible (TLC, ∼20 min). The reaction mixture was then quenched with water (25 mL) and extracted with EA (50 mL × 2). The combined organic layers were dried over Na_2SO_4 and concentrated on a rotary evaporator. The residue was purified by silica chromatography using 1% EA/hex to furnish 1,1-bis-(3,7 dimethyl-6-octenylperoxy) cyclododecane (2.84 g, 59%) as a colorless oil: R_f = 0.75 (10% EA:Hex); ^{1}H NMR: 5.10 (m, 2H), 4.17−3.99 (m, 4H), 2.07−1.91 (m, 4H), 1.72−1.64 (m, 9H), 1.69 (s, 3H), 1.61 (s, 3H), 1.58−1.53 (m, 7H), 1.48−1.28 (m, 20H), 1.24−1.15 (m, 2H), 0.92 (d, J = 6.5, 6H); ^{13}C NMR: 131.2, 124.6, 113.1, 73.4, 37.1, 34.6, 29.7, 27.0, 26.1, 25.7, 25.4, 22.3, 21.9, 19.6, 19.4, 17.6; HRMS (TOFMS-ES): Calcd for $C_{32}H_{60}O_4Na$ $(M + Na)^+$ 531.4389 found: 531.4373; IR: 2926, 2850, 1445, 1052.

To a room temperature solution of the bisperoxyacetal (1.01 g, 2 mmol) in THF (20 mL) was added a solution of 50% aq. H_2SO_4 (1.8 mmol, 6 equiv), and the reaction mixture was stirred at 55 °C until starting material was nearly consumed (TLC, 1−3 h). The reaction was then quenched with saturated aq. Na_2CO_3 (25 mL), and the resulting mixture was extracted with EA (30 mL × 2). The combined organic layers were dried over Na_2SO_4 and concentrated on a rotary evaporator. The crude product was purified by silica chromatography using 1−3% EA/Hex to furnish hydroperoxide **4** as a colorless oil (0.364 mg, 53%). The molecule has previously been reported without characterization:[58] R_f = 0.4 (10% EA/Hex); ^{1}H NMR: 8.53 (s, 1H), 5.09 (m, 1H), 4.10−4.00 (m, 2H), 2.06−1.93 (m, 2H), 1.73−1.63 (m, 1H), 1.68 (s, 3H), 1.60 (s, 3H), 1.54−1.35 (m, 2H), 1.33−1.14 (m, 2H), 0.91 (d, J = 6.5, 3H); ^{13}C NMR: 131.3, 124.6, 75.5, 37.1, 34.3, 29.5, 25.7, 25.4, 19.5, 17.6. IR: 3617−3101 (broad peak), 2915, 1455, 1377, 1053 (mass spec not attempted due to volatility).

1-Hydroperoxy-1-methylcyclohexane (5). [4952-03-8] was prepared through a two-step procedure.

Triethyl(1-methylcyclohexylperoxy)silane. (CAS 634600-89-8) was prepared through a modification of a reported procedure.[59] 1-Methyl cyclohexene (0.96 g, 10 mmol) and Et_3SiH (2.32 g., 20 mmol) were sequentially added to a solution of $Co(acac)_2$ (1 mmol) in ethanol (35 mL). The reaction mixture was placed under an atmosphere of O_2 (balloon) until no starting material was observed (TLC, ∼14 h). The residue obtained upon concentration in vacuo was purified by silica gel chromatography using 1−8% EA:Hex to furnish the 1-methyl-1-cyclohexyl triethylsilyl peroxide as a as colorless oil (0.844 g, 34%): R_f = 0.7 (10% EA/Hex). Spectral data matched those previously reported.[60]

To a solution of the triethylsilylperoxide (0.78 g, 3.19 mmol) in THF (10 mL) was added tetra *n*-butyl ammonium fluoride (1 M solution in THF, 1.2 equiv).[47] The reaction was stirred at room temperature until no starting material could be observed (TLC, ∼5 min). The residue obtained upon concentration in vacuo was diluted with hexane (30 mL) and washed with water (10 mL). The combined organic layers were dried over Na_2SO_4 and concentrated. The residue was purified by short-column (3″) flash chromatography with 5% EA/Hex (two iterations were required to remove silanol/siloxane byproducts) to furnish the hydroperoxide **5** as a colorless oil (0.266 g, 64%). Although the hydroperoxide is commercially available, NMR data are difficult to access and are provided here for convenience: R_f = 0.4 (10% EA:Hex); ^{1}H NMR: 7.34 (s, 1H), 1.80−1.74 (m, 2H), 1.63−1.53 (m, 2H), 1.51−1.38 (m, 5H), 1.34−1.29 (m, 1H), 1.25 (s, 3H); ^{13}C NMR: 81.7, 34.4, 25.6, 23.8, 22.2, 6.55, 5.76.

3-Phenylpropyl Hydroperoxide (6). [60956-33-4] was prepared using a route analogous to that employed for hydroperoxide **4**.

3-Phenylpropyl trifluoromethanesulfonate [66950-73-0] was prepared (1.34 g, quant.) as a light brown oil from 3-phenylpropanol (0.681 g, 5 mmol) using the procedure described above: R_f = 0.5 (10% EA/Hex). Other spectral data matched those in a previous report.[5b]

Using a similar procedure as described earlier, cyclododecanone 1,1-dihydroperoxide (1.05 g, 4.545 mmol) was reacted with the 3-phenylpropyl triflate (2.6 g, 10 mmol) to furnish the bisperoxyacetal (1.4381 g, 67%) as a colorless oil: R_f = 0.6 (15% EA/Hex); ^{1}H NMR: 7.32−7.29 (m, 4H), 7.23−7.21 (m, 6H), 4.11 (t, J = 6.4, 4H), 2.73 (t, J = 7.5, 4H), 2.02−1.95 (m, 4H), 1.74−1.70 (m, 4H), 1.56−1.46 (m, 4H), 1.45−1.31 (m, 14H); ^{13}C NMR: 141.7, 128.4, 128.3, 125.8, 113.3, 74.2, 32.3, 29.5, 27.1, 26.1, 22.3, 22.0, 19.4; IR: 2914, 2845, 1462, 1053

Hydrolysis of the bisperoxyacetal (1.35 g, 2.88 mmol) by a similar procedure as described above furnished hydroperoxide **6** as a colorless oil (0.725 g, 82%): R_f = 0.57 (20% EA/Hex). Spectral data matched those previously reported.[61]

10-Phenyldecane Hydroperoxide (7). The title compound was prepared by an analogous strategy as described for hydroperoxides **4** and **6**.

10-phenyldecyl trifluoromethanesulfonate (1.098 g, quant.) was prepared from 10-phenyldecanol (0.70 g, 3 mmol) as a light brown oil: R_f = 0.65 (10% EA/Hex); ^{1}H NMR: 7.33−7.28 (m, 2H), 7.22−7.18 (m, 3H), 4.56 (t, J = 6.5 Hz, 2H), 2.63 (t, J = 7.7 Hz, 2H), 1.85 (m, 2H), 1.69−1.59 (m, 2H), 1.46−1.33 (m, 12H); ^{13}C NMR: 142, 128.4, 128.2, 125.5, 118.6 (q, J = 320 Hz), 77.7, 35.9, 31.5, 29.4, 29.37, 29.30, 29.27, 29.22, 28.8, 25.0. HRMS (ESI): Calcd for $C_{17}H_{25}F_3NaO_3$ S (M + Na) 389.1374, found 389.1369.

Using a similar procedure as described above, reaction of 1,1-dihydroperoxycyclododecanone (0.293 g, 1.26 mmol) and the 10-phenyl decyl triflate (1.02 g, 2.787 mmol) was used to prepare 1,1-bis-(10-phenyldecyldioxy)cyclodecanone: (0.834 g, 99%) as a colorless oil: R_f = 0.74 (15% EA/Hex); ^{1}H NMR: 7.32−7.29 (m, 4H), 7.21−7.19 (m, 6H), 4.09 (t, J = 6.6, 4H), 2.62 (t, J = 7.7, 4H), 1.72−1.59 (m, 12H), 1.37−1.30 (m, 42H); ^{13}C NMR: 142.9, 128.4, 128.2, 125.5, 113.1, 75.0, 36.0, 31.5, 29.57, 29.53, 29.48, 29.36, 27.8, 27.0, 26.2, 26.1, 22.3, 21.9, 19.4. HRMS (TOF-MS-ES+): Calcd for

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$C_{44}H_{72}O_4Na$ $(M + Na)^+$ 687.5328 found 687.5300; IR: 2914, 2845, 1462, 1053.

Using a procedure similar to that described above, hydrolysis of the bis-(10-phenyldecyl)peroxyacetal (0.755 g, 1.14 mmol) furnished 10-phenyldecyl hydroperoxide as a colorless oil (0.243 g, 64%): R_f = 0.55 (15% EA/Hex); ^{1}H NMR: 8.04 (t, J = 6.5, 1H), 7.33−7.28 (m, 2H), 7.22−7.20 (m, 3H), 4.04 (t, J = 6.6, 2H), 2.63 (t, J = 7.7, 2H), 1.68−1.61 (m, 4H), 1.32 (m, 12H); ^{13}C NMR: 142.9, 128.4, 128.2, 125.5, 76.6, 36.0, 31.5, 29.5, 29.4, 29.3, 27.5, 25.9; HRMS (TOF-MS-EI+): Calcd for $C_{16}H_{25}O$ $(M - OH)^+$ 233.1905; found: 233.1920; IR: 3390, 2922, 2852, 1453, 696.

Synthesis of Peroxides via Alkylation of Hydroperoxides with Triflates (Method A). Synthesis of dialkyl peroxides from alkyl triflates was based upon reported procedures.[22] The hydroperoxide (10 mmol in a minimum amount of THF) was added under nitrogen to a 0 °C solution of KO*t*Bu (10 mmol) in dry THF (50 mL). The reaction mixture was stirred for 3 min, after which was added preformed alkyl triflate (10 mmol, neat from syringe, remaining triflate rinsed into the reaction using 1 mL of THF). The reaction was stirred for 15 min at the same temperature and then quenched with water (20 mL). The mixture was extracted with 10% EA/Hex (50 mL × 2), and the organic layer was dried over Na_2SO_4. The residue obtained upon concentration was purified by flash silica chromatography using 1% EA/Hex.

Peroxides via Acetalization (Method B). Acetalization of alkyl hydroperoxides to form tetrahydropyranyl (THP) monoperoxyacetals employed a modification of a reported procedure.[25] A mixture of alkyl hydroperoxide (1.0 mmol) and 2,3-dihydropyran (1.0 mmol) was cooled to 0 °C, after which was added 0.05 mL of a solution of 10% H_2SO_4 in THF. The stirred reaction mixture was allowed to warm to rt over a period of 45 min. The reaction was diluted with 10% ether/Hex (15 mL), and the resulting solution was washed with water (2 mL). The separated organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by silica gel chromatography using 4% EA/Hex.

Ag-Promoted Alkylation (Method C). Dialkyl peroxide synthesis using silver oxide was based upon a modification of reported procedures.[26b,c] The alkyl hydroperoxide (1.0 mmol) was added to a suspension (EA, 10 mL) of freshly prepared silver oxide (1.2 mmol). Alkyl halide (1.0 mmol) was added, and the reaction was stirred at rt until no starting material could be observed (TLC, approximately 4−10 h). The reaction mixture was filtered through a small pad of Celite, and the residue was washed with EA (10−20 mL). The combined filtrates were concentrated, and the residue was purified by silica gel chromatography using 1−3% EA/Hex.

Trialkylsilylation of Hydroperoxides (Method D). Trialkylsilylation was performed based upon a reported procedure, except for a different order of addition and the use of water rather than aqueous acid for the wash.[27] To a room temperature solution of alkyl hydroperoxide (1.0 mmol) in DMF (2 mL) was added *tert*-butyl dimethylsilyl chloride (1.2 mmol), followed by imidazole (1.4 mmol). The reaction was stirred for 1 h and then diluted with water (10 mL). The hexane extracts (1 × 50, 1 × 10 mL) were dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by silica gel chromatography (4.0 in. tall × 0.5 in. column) using 1% ether/Hex.

8-(*tert*-Butylperoxy)-2,6-dimethyloct-2-ene (8a). [1592933-34-0]: Using method A (above), *t*-butyl hydroperoxide (5.5 M in decane, 0.588 mL, 3.24 mmol) was reacted with 3,7-dimethyl-6-octenyl triflate (described above in relation to preparation of peroxide **4**, 1.025 g, 3.559 mmol) to furnish **8a** as a colorless oil (0.511 g, 69%); R_f = 0.6 (10% EA/Hex). Spectral data matched those in literature reports.[5a]

2-(3,7-Dimethyloct-6-ene-1-yl)peroxy)-tetrahydro-2*H*-pyran (8b). Using method A, THP hydroperoxide **1** (0.63 g, 5.34 mmol) was reacted with 3,7-dimethyl-6-octenyl triflate (1.69 g, 5.87 mmol) to furnish peroxide **9a** as a colorless oil (0.854 g, yield: 62%) R_f = 0.42 (10% EA/Hex); ^{1}H NMR: 5.15 (t, J = 3.5 Hz, 1H), 5.10 (m, 1H), 4.19−4.00 (m, 2H), 4.02 (m, 1H), 3.66−3.61 (m, 1H), 1.98 (m, 2H), 1.78−1.71 (m, 2H), 1.70−1.65 (m, 1H), 1.68 (s, 3H), 1.64−1.53 (m, 5H), 1.60 (s, 3H), 1.49−1.42 (m, 1H), 1.41−1.32 (m, 1H), 1.23−1.1 (m, 1H), 0.92 (d, J = 6.6 Hz, 3H); ^{13}C NMR: δ: 131.2, 124.7, 100.8, 73.7, 62.5, 37.1, 34.6, 29.6, 27.96, 25.7, 25.4, 25.1, 19.7, 19.5, 17.6. HRMS (ESI$^+$ TOF) calcd for $C_{15}H_{28}NaO_3$ (M + Na): 279.1931; found: 279.1934; IR: 2923, 2861, 1440, 1040.

8-((2-Methoxypropan-2-yl)peroxy)-2,6-dimethyloct-2-ene (8c). Using method A, hydroperoxide **3** (0.674 g, 6.35 mmol, 1.5 equiv) was reacted with 3,7-dimethyl-6-octenyl triflate (1.21 g, 4.2 mmol) to furnish **8c** as a colorless oil (0.627 g, yield: 61%); R_f = 0.4 (10% EA/Hex); ^{1}H NMR: 5.1 (m, 1H), 4.11−4.01 (m, 2H), 3.33 (s, 3H), 2.06−1.91 (m, 2H), 1.71−1.64 (m, 1H), 1.69 (s, 3H), 1.61 (s, 3H), 1.62−1.54 (m, 1H), 1.47−1.31 (m, 2H), 1.40 (s, 6H), 1.24−1.10 (m, 1H), 0.91 (d, J = 6.5 Hz, 3H); ^{13}C NMR131.2, 124.7, 104.5, 73.4, 49.2, 37.1, 34.6, 29.6, 25.7, 25.4, 22.76, 22.74, 19.5, 17.6; HRMS (TOF-MS-ES+) calcd for $C_{14}H_{28}NaO_3$ (M + Na): 267.1931; found: 267.1926; IR: 2954, 2874, 1457, 836.

***t*-Butyldimethylsilyl 3,7-Dimethyl-6-octenyl Peroxide (8d).** Using method D, alkyl hydroperoxide **4** (0.22 g, 1.279 mmol) was silylated with *t*-butyldimethylsilyl chloride (TBS-Cl) to furnish **8d** as a colorless oil (0.212 g, 58%): R_f = 0.75 (10% EA/Hex); ^{1}H NMR: 5.12 (m, 1H), 4.06−3.97 (2H), 2.06−1.91 (m, 2H), 1.69 (s, 3H), 1.67−1.59 (m, 1H), 1.61 (s, 3H), 1.59−1.51 (m, 1H), 1.46−1.30 (m, 2H), 1.22−1.15 (m, 1H), 0.95 (s, 9H), 0.91 (d, J = 6.6), 0.17 (s, 6H); ^{13}C NMR: 131.2, 124.6, 75.3, 37.1, 34.5, 29.6, 26.1, 25.7, 25.4, 19.6, 18.1, 17.6, −5.9; HRMS (TOF-MS-EI+) calcd for $C_{16}H_{34}NaO_2Si$ (M + Na): 309.2220; found: 309.2218; IR: 2928, 2857, 1461, 834.

3-*tert*-Butylperoxypropyl Benzene (9a). [419568-76-6]: Using method A, *tert*-butyl hydroperoxide (1.8 mL, 5.0−6.0 M in decane, 10 mmol) was reacted with 3-phenyl propyl triflate (2.68 g, 10 mmol) to furnish **9a** as a colorless liquid (1.5151 g. 73%). R_f (10% EA/Hex) = 0.65. Spectral data matched those in a literature report.[62]

2-(3-Phenylpropylperoxy)tetrahydro-2*H*-pyran (9b). [1630792-49-2]: Using method A, THP hydroperoxide **1** (1.18 g, 10 mmol) was reacted with 3-phenylpropyl triflate (2.68 g, 10 mmol) to furnish peroxide **9b** as a colorless oil (1.937 g, 82%); R_f = 0.66 (15% EA/Hex). Spectral properties matched those in a literature report.[5b]

3-(2-Methoxyethylperoxy)propyl Benzene (9e). The title compound was prepared in two steps.

2-Methoxyethyl trifluoromethanesulfonate [112981-50-7] was prepared (2.08 g, ∼quant) from 2-methoxyethanol (760 mg, 10.0 mmol) using the procedure described above and used without purification. Spectral data matched those reported.[63] R_f = 0.5 (30% EA/hex).

Using method A, alkyl hydroperoxide **6** (0.70 g, 4.6 mmol) was reacted with 2-methoxyethyl trifluoromethanesulfonate (0.956 g, 4.6 mmol) to furnish **9e** as a colorless oil (0.723 g, 74%): R_f = 0.62 (20% EA/Hex); ^{1}H NMR: 7.32−7.27 (2H), 7.22−7.18 (3H), 4.15 (m, 2H), 4.05 (t, J = 6.4, 2H), 3.62 (m, 2H), 3.40 (s, 3H), 2.71 (t, J = 7.8, 2H), 2.01−1.93 (2H); ^{13}C NMR: 141.6, 128.46, 128.39, 125.9, 73.59, 73.54, 69.8, 59.1, 32.2, 29.4; HRMS (TOF-MS-CI+) calcd for $C_{12}H_{18}O_3Na$ $[M + Na]^+$: 233.1154; found: 233.1152; IR: 2924, 1496, 1453, 745.

10-(*tert*-Butylperoxy)decylbenzene (10a). Using method A, *t*-butyl hydroperoxide (1.41 mL, 5.0−6.0 M in decane, 7.76 mmol) was reacted with 10-phenyldecyl triflate (3.125 g, 8.54 mmol) to furnish **10a** as a colorless oil (2.42 g, 92%). R_f = 0.73 (10% EA/Hex); ^{1}H NMR: 7.33−7.20 (m, 2H), 7.22−7.17 (m, 3H), 3.96 (t, J = 6.7 Hz, 2H), 2.62 (t, J = 7.8 Hz, 2H), 1.69−1.56 (m, 4H), 1.32−1.28 (m, 12H), 1.27 (s, 9H); ^{13}C NMR: δ: 142.9, 128.4, 128.2, 125.5, 80.0, 75.1, 36.0, 31.5, 29.5, 29.3, 27.8, 26.3, 26.2. HRMS (ESI$^+$ TOF): Calcd for $C_{20}H_{34}NaO_2$ (M + Na): 329.2451; found: 329.2470; IR: 2924.8, 2853.72, 1361.5, 697.

2-(10-Phenyldecylperoxy)tetrahydro-2*H*-pyran (10b). [1630792-52-7]: Using method A, THP hydroperoxide **2** (0.20 g, 1.77 mmol) was reacted with 10-phenyldecyl triflate (0.65 g, 1.775 mmol) to furnish **10b** as a colorless oil (0.448 g, 75%); R_f = 0.42 (10% EA/Hex). Spectral properties matched those in a literature report.[5b]

***t*-Butyldimethylsilyl 10-Phenyldecyl Peroxide (10d).** Using method D, alkyl hydroperoxide **7** (0.22 g, 0.89 mmol) was converted into the corresponding silyl peroxide **10d**, which was obtained as a colorless oil (0.267 g, 82%): R_f = 0.8 (10% EA/Hex); ^{1}H NMR: 7.32−7.28 (m, 2H), 7.22−7.19 (m, 3H), 3.99 (t, J = 6.6 Hz, 2H),

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2.63 (t, J = 7.7 Hz, 2H), 1.66−1.56 (m, 4H), 1.32 (m, 12H), 0.97 (s, 9H), 0.19 (s, 6H); ^{13}C NMR: 142.9, 128.4, 128.2, 125.5, 76.6, 36.0, 31.5, 29.5, 29.3, 27.7, 26.2, 26.1, 18.1, −5.8; HRMS (ESI$^+$ TOF) calcd for $C_{22}H_{40}NaO_2Si$ (M + Na): 387.2690; found: 387.2677; IR: 2925, 2854, 1462, 1248.

***tert*-Butylperoxy Octane (11a).** [38375-34-7]: 1-Octyl trifluoromethanesulfonate [71091-89-9] was prepared (3.08 g, 98%) as a light brown oil from 1-octanol (1.56 g, 12 mmol) using the general procedure described above. The ^{1}H NMR spectrum matched data previously reported:[64] R_f = 0.52 (10% EA/Hex); ^{1}H NMR: 4.55 (t, J = 6.54, 2H), 1.84 (m, 2H), 1.46−1.40 (m, 2H), 1.36−1.29 (m, 8H), 0.90 (t, J = 6.9, 3H); ^{13}C NMR: 118.2 (q, J = 320.1 Hz), 76.7, 31.6, 29.2, 28.9, 28.8, 25.0, 22.5, 14.0.

t-Butyl hydroperoxide (1.81 mL, 5.5 M in decane, 10 mmol) was reacted with octyl triflate (2.88 g, 11 mmol) to furnish **11a** as a colorless oil (1.78 g, 88%): R_f = 0.79 (10% EA/Hex). The molecule has been previously reported without spectral characterization:[65] ^{1}H NMR: 3.93 (t, J = 6.7 Hz, 2H), 1.63−1.55 (m, 2H), 1.34−1.26 (m, 10H), 1.25 (s, 9H), 0.88 (t, J = 6.9 Hz, 3H); ^{13}C NMR: 79.9, 75.1, 31.8, 29.4, 29.2, 27.8, 26.3, 26.2, 22.6, 14.0; HRMS (ESI-TOF-MS) Calcd for $C_{12}H_{26}NaO_2$ (M + Na): 225.1825; found: 225.1840; IR: 2924, 2856, 1361, 1197.

2-(Decylperoxy)-tetrahydro-2*H*-pyran (12b). [1630792-51-6]: Decyl trifluoromethanesulfonate [53059-89-5] was prepared (3.1 g, quant = 2.9 g) as a light brown oil from 1-decanol (1.58 g, 10.0 mmol) using the procedure described above. Spectra closely matched those in previous reports:[66] R_f = 0.52 (10% EA/Hex); ^{1}H NMR: 4.55 (t, J = 6.5 Hz, 2H), 1.84 (m, 2H), 1.43 (m, 2H), 1.36−1.28 (m, 12H), 0.9 (t, J = 6.8 Hz, 3H); ^{13}C NMR: 118.6 (q, J_{C-F} = 320 Hz), 77.7, 31.8, 29.4, 29.3, 29.2, 28.8, 25.0, 22.6, 14.0.

Using method A, 2-tetrahydropyranyl hydroperoxide **2** (1.18 g, 10 mmol) was reacted with decyl triflate (2.98 g, 10 mmol) to furnish peroxide **12b** as a colorless oil (2.05 g, 79%); R_f = 0.56 (15% EA/Hex). Spectral properties matched those in a literature report.[5b]

2-(2-Octylperoxy)-tetrahydro-2*H*-pyran (13b). [1630792-50-5]: 2-Octyl trifluoromethanesulfonate [58864-30-5] was prepared (3.58 g, estimated 91%) as a light brown oil from 2-octanol (2.0 g, 15 mmol) using the procedure described above. R_f = 0.3 (10% EA/Hex). Spectral properties matched those in a previous report.[5b]

Using method A, hydroperoxide **2** (0.595 g, 5.01 mmol) was reacted with 2-octyl triflate (1.47 g, 5.61 mmol) to furnish **13b** as a colorless oil (0.808 g, 70%) R_f = 0.61 (20% EA/Hex). Spectral properties matched those in a literature report.[5b]

Bis-(tetrahydro-2*H*-pyranyl) Peroxide (14b). [685877-38-7]: Using method B, acetalization of 2-tetrahydropyranyl hydroperoxide **2** (0.35 g, 2.97 mmol) with dihydropyran (0.249 g, 2.97 mmol) furnished peroxide **14b** as a colorless oil (0.493 g, 84%). This molecule has been previously prepared without NMR characterization:[67] R_f = 0.50 (10% EA/Hex); ^{1}H NMR: 5.22 (m, 2H), 4.09 (m, 1H), 4.00 (m, 1H), 3.63−3.60 (m, 2H), 1.76−1.74 (m, 4H), 1.66−1.53 (m, 8H); ^{13}C NMR: 101.8, 100.2, 62.5, 62,1, 27.9, 27.7, 25.1, 25.0, 19.6, 19.4.

2-(1-Methylcyclohexylperoxy)-tetrahydro-2*H*-pyran (15b). Using method B, hydroperoxide **5** (0.266 g, 2.04 mmol) was reacted with dihydropyran (0.171 g, 2.04 mmol) to furnish **15b** as a colorless oil (0.326 g, 74%). R_f = 0.50 (10% EA/Hex); ^{1}H NMR: 5.04 (broad triplet, 1H), 4.02 (m, 1H), 3.60 (m, 1H), 1.75 (m, 5H), 1.68−1.53 (m, 6H), 1.47−1.35 (m, 6H), 1.26 (s, 3H); ^{13}C NMR: 101.0, 81.5, 62.7, 35.0, 27.8, 25.7, 25.1, 24.3, 22.5, 22.3, 20.0; HRMS (ESI$^+$ TOF) calcd for $C_{12}H_{22}NaO_3$ (M + Na): 237.1461; found: 237.1469; IR: 2931, 2852, 1443, 962.

(*E*,*Z*)-2-(Undec-2-en-1-yl peroxy)tetrahydro-2*H*-pyran (16b). Using a known procedure,[68] cross-metathesis of 1-octene (6.72 g, 4.8 mmol) and allyl bromide (1.45 g, 12 mmol) in the presence of the Grubbs II catalyst furnished 1-bromo-2-undecene (1.109 g, 80%) as a colorless oil consisting of a 84:16 E/Z mixture using a known procedure. The portions of the spectra corresponding to the major (E) isomer closely matched a previous report [67952-61-8]:[69] R_f = 0.8 (hexane); ^{1}H NMR: (both isomers, partial integrals given): 5.82−5.58 (m, 2H), 4.01 (d, J = 8.3 Hz, 0.32 H), 3.96 (d, J = 8.2 Hz, 1.68 H), 2.14 (m, 0.32H), 2.07 (m, 1.68), 1.40−1.35 (m, 2H), 1.34−1.28 (m, 10H),5.82− 0.89 (t, J = 6.8 Hz, 3H); ^{13}C NMR: (*major isomer*): 136.7, 126.2, 33,6, 32.0, 31.9, 29.4, 29.2, 29.1, 28.8, 22.7, 14.1.

Using method C, hydroperoxide **2** (0.118 mg, 1 mmol) was reacted with an E/Z-mixture of 2-undecenyl bromide (0.232 g, 1.0 mmol) to furnish peroxide **16b** as a colorless oil (0.197 mg, 73%) consisting of an inseparable 84:16 E/Z mixture: R_f = 0.42 (10% EA/Hex); ^{1}H NMR: 5.82−5.74 (m, 1H), 5.69−5.55 (m, 1H), 5.16 (m, 1H), 5.64 (d, J = 6.8 Hz, 0.24 H), 4.51 (d, J = 6.8 Hz, 1.76 H), 4.01 (m, 1H), 3.64−3.60 (m, 1H), 2.13−2.02 (m, 2H), 1.73−1.68 (m, 2H), 1.65−1.53 (m, 4H), 1.38−1.35 (m, 2H), 1.31−1.26 (m, 10H), 0.87 (t, J = 6.8 Hz, 3H); ^{13}C NMR: 137.8, 123.7, 100.8, 76.2, 62.4, 32.3, 31.8, 29.4, 29.2, 29.1, 28.8, 27.8, 25.1, 22.6, 19.6, 14.0. HRMS (TOF-MS-ES+) calcd for $C_{16}H_{30}NaO_3$ (M + Na): 293.2087; found: 293.2087; IR: 2923, 2851, 1202, 962.

Etherification of Peroxides with sp^3 RM. The alkyllithium (0.55 mmol, 1.1 equiv, typically as a solution in Hex) was added to the solution of peroxide (0.50 mmol) in dry THF (3 mL) at −78 °C, and the reaction was stirred for 15 min. For THP monoperoxyacetals, the reaction was brought to room temperature for 15 min and then quenched with water (2 mL); for other peroxides, the reaction was allowed to stir at room temperature for the time indicated. The mixture was extracted with 20% ether in Hex (1 × 25, 1 × 5 mL), and the combined organic layers were dried over Na_2SO_4 and concentrated. The residue was purified by silica gel chromatography (0.5 × 4 in. column) using 1% ether in hexane. Note: For volatile ethers, column fractions were carefully concentrated on a rotary evaporator at 20 °C bath temperature and then briefly (1 min) concentrated on high vacuum while held in an ice bath.

For reaction with Grignard reagents, a solution of the alkyl magnesium bromide (0.55 mmol, 1.1 equiv) in diethyl ether was added to a 0 °C solution of the THP monoperoxyacetal (0.5 mmol) in dry THF (3 mL). The reaction was stirred for 15 min and then brought to room temperature. After 15 min, the reaction was quenched with water (2 mL) and extracted with 20% ether/Hex (1 × 25, 1 × 5 mL). The combined organic layers were dried over Na_2SO_4, and the concentrated residue was purified by silica gel chromatography (0.5 × 4 in. column) using 1% ether/Hex. In the case of volatile ethers, column fractions were concentrated on a rotary evaporator at 20 °C bath temperature and subsequently subjected to high vacuum (<1 mm) for 1 min while placed in an ice bath.

8-Butoxy-2,6-dimethyloct-2-ene (17a). [71077-30-0]: Using the general procedure described above, THP monoperoxyacetal **8b** (128 mg, 0.5 mmol) was reacted with *n*-BuLi (0.34 mL, 1.6 M in Hex, 0.55 mmol) to furnish ether **17a** as a colorless oil (86 mg, 81%). The same procedure, when applied to dialkyl peroxide **8b** or 2-methoxypropyl peroxyacetal **8c** furnished **17a** in 70% and 87% yields, respectively. Spectral data matched those in previous reports.[5a] R_f = 0.6 (5% EA/Hex).

8-Hexyloxy-2,6-dimethyl-2-octene (17b). Using the general procedure for Grignard-promoted etherification described above, monoperoxacetal **8b** (128 mg, 0.5 mmol) was reacted with *n*-hexyl magnesium bromide (0.27 mL, 2 M in diethyl ether, 0.55 mmol) to furnish hexyl ether **17b** as a colorless oil (106 mg, 88%). The same product could be obtained from dialkyl peroxide **8a** except in 42% yield: R_f = 0.70 (10% EA/Hex); ^{1}H NMR: 5.11 (m, 1H), 3.47−3.38 (m, 4H), 2.08−1.94 (m, 2H), 1.69 (s, 3H), 1.65−1.53 (m, 4H), 1.61 (s, 3H), 1.45−1.31 (m, 8H), 1.23−1.11 (m, 1H), 0.91−0.88 (m, 6H); ^{13}C NMR: 131.1, 124.8, 71.0, 69.1, 37.2, 36.7, 31.7, 29.7, 29.6, 25.9, 25.7, 25.4, 22.6, 19.6, 17.6, and 14.0. HRMS (TOF-MS-EI$^+$) calcd for $C_{16}H_{32}O$: 240.2453; found: 240.2453; IR: 2954, 2927, 2858, 1455, 1376, 1112.

8-Allyloxy-2,6-dimethyloct-2-ene (17c). [139694-24-9]: To a 0.2 M solution of peroxide **8a** (229 mg, 1.0 mmol) in THF was added allyltributyl tin (0.62 mL, 2.0 mmol). The solution was cooled to −78 °C, and *n*-BuLi (2.5 mmol, 1.0 mL, 2.5 M in Hex) was added dropwise. After 30 min, the reaction was quenched with 10 mL of water and extracted with ether. The combined organic layer was dried with Na_2SO, and concentrated under reduced pressure. The residue was then purified by column chromatography (2.5% EA/Hex) to yield 137 mg (70%) of **17c** as a colorless oil. The ^{1}H NMR spectrum

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matched the listing in a previous report.[70] R_f = 0.25 (5% EA/Hex); ^{1}H NMR: 0.92 (d, 3H, J = 6.7), 1.18 (m, 1H), 1.39 (m, 1H), 1.52−1.68 (s at 1.62 overlapping unresolved signal, 6H), 1.70 (s, 3H), 2.00 (m, 2H), 3.48 (m, 2H), 3.98 (dt, 2H, J = 5.6, 1.4), 5.14−5.08 (m 1H), 5.19 (app. dq, H_{cis}, J = 10.6, 1.3, 1H), 5.29 (app. dq, H_{trans}, J = 17.2, 1.6, 1H), 5.9 (m, 1H); ^{13}C NMR: 17.6, 19.6, 25.5, 25.7, 29.6, 36.7, 37.2, 68.7, 71.8, 116.7, 124.8, 131.2, 135.1.

8-*tert*-Butoxy-2,6-dimethyl-2-octene (17d). [436141-44-5]: Using the general procedure for etherification described above, peroxyacetal **8b** (128 mg, 0.5 mmol) was reacted with *t*-BuLi (0.32 mL 1.7 M in pentane, 0.55 mmol) to furnish **17d** as a colorless oil (55 mg, 51%). Spectral data were nearly identical to those previously described:[71] R_f = 0.6 (5% EA/Hex); ^{1}H NMR: 5.11 (m, 1H), 3.42−3.31 (m, 2H), 2.06−1.91 (m, 2H), 1.69 (s, 3H), 1.61 (m, 3H), 1.59−1.51 (m, 2H), 1.39−1.27 (m, 2H), 1.19 (s, 9H), 1.17−1.10 (m, 1H), 0.90 (d, J = 6.5 Hz, 3H); ^{13}C NMR: 131.0, 124.9, 72.3, 59.7, 37.7, 37.2, 29.6, 27.5, 25.7, 25.4, 19.6, 17.6.

3-Phenylpropyl Trimethylsilylmethyl Ether (17e). Using the general procedure for etherification described above, peroxide **9b** (118 mg, 0.50 mmol) was reacted with 2-trimethylsilyl methyl magnesium chloride (0.65 mL, 1 M in ether, 0.65 mmol) to furnish ether **17e** as a colorless oil (84 mg, 75%): R_f = 0.8 (10% EA/Hex); ^{1}H NMR: 7.31−7.29 (m, 2H), 7.22−7.19 (m, 3H), 3.42 (t, J = 6.3 Hz, 2H), 3.12 (s, 2H), 2.70 (t, J = 7.7 Hz, 2H), 1.91−1.87 (m, 2H), 0.09 (s, 9H); ^{13}C NMR: 142.3, 128.5, 128.2, 125.6, 74.2, 64.7, 32.3, 31.2, −2.98; HRMS(TOF-MS-EI+) calcd for $C_{13}H_{22}OSi$ $(M)^+$: 222.1440; found: 222.1442; IR: 2955, 2845, 1246, 839.

2-Butoxy Octane (17f). [110458-41-8]: Using the general procedure for etherification described above, peroxide **13b** (115 mg, 0.5 mmol) was reacted with *n*-BuLi (0.34 mL 1.6 M in Hex, 0.55 mmol) to furnish ether **17f** as a colorless oil (73 mg, 78%). The ^{1}H NMR data matched those previously reported:[72] R_f = 0.6 (5% EA/Hex); ^{13}C NMR: 75.3, 68.1, 36.7, 32.3, 31.8, 29.4, 25.6, 22.6, 19.7, 19.4, 14.0, 13.9.

2-Hexyloxy Octane (17g). [51182-98-0]: Using the general procedure for etherification using a Grignard reagent, peroxide **13b** (115 mg, 0.50 mmol) was reacted with *n*-hexyl magnesium bromide (0.27 mL, 2 M in diethyl ether, 0.54 mmol) to furnish hexyl ether **17g** as a colorless oil (95 mg, 88%). The product has been partially characterized:[72] R_f = 0.6 (5% EA/Hex); ^{1}H NMR: 3.51−3.29 (m, 1H), 3.40−3.29 (m, 2H), 1.57−1.53 (m, 3H), 1.41−1.29 (m, 15H), 1.12 (d, J = 6.1 Hz, 3H), 0.9 (m, 6H); ^{13}C NMR: 75.3, 68.4, 36.7, 31.8, 31.7, 30.1, 29.4, 25.9, 25.6, 22.63, 22.62, 19.7, 14.05, 14.02.

2-Butoxy-tetrahydro-2*H*-pyran (17h). [1927-68-0]: Using the general procedure for etherification described above, peroxide **14b** (101 mg, 0.50 mmol) was reacted with *n*-BuLi (0.31 mL 1.6 M in hexane, 0.5 mmol) to furnish ether **17h** (12 mg, 15%) accompanied by 16 mg (15%) of recovered **14b**. Partial spectral characterization has been reported.[73] R_f = 0.5 (15% EA/Hex); ^{1}H NMR: 4.59 (m, 1H), 3.89 (m, 1H), 3.76 (m, 1H), 3.52 (m, 1H), 3.40 (m, 1H), 1.84 (m, 1H), 1.72 (m, 1H), 1.65−1.49 (m, 6H), 1.45−1.35 (m, 2H), 0.94 (t, J = 7.3 Hz, 3H); ^{13}C NMR: 98.8, 67.3, 62.3, 31.8, 30.8, 25.5, 19.7, 1.4, 13.9.

2-Hexyloxy-tetrahydro-2*H*-pyran (17i). [1927-63-5] Using the general procedure for etherification with alkyl magnesium bromide described above, peroxide **14b** (107 mg, 0.5 mmol) was reacted with *n*-hexyl magnesium bromide (0.25 mL, 2 M in diethyl ether, 0.50 mmol) to furnish hexyl ether **17i** as a colorless oil (57 mg, 61%). The ^{1}H NMR data matched those in a previous report.[74] R_f = 0.5 (15% EA/Hex); ^{1}H NMR: 4.57 (m, 1H), 3.90−3.84 (m, 1H), 3.76−3.70 (m, 1H), 3.52−3.47 (m, 1H), 3.41−3.35 (m, 1H), 1.87−1.79 (m, 1H), 1.74−1.68 (m, 1H), 1.62−1.50 (m, 6H), 1.42−1.26 (m, 6H), 0.89 (t, J = 6.8 Hz, 3H); ^{13}C NMR: 98.8, 67.6, 62.3, 31.7, 30.8, 29.7, 25.9, 25.5, 22.6, 19.6, 14.0.

1-Butoxy-1-methyl Cyclohexane (17j). Using the general procedure for etherification described above, peroxide **15b** (107 mg, 0.50 mmol) was reacted with *n*-BuLi (0.34 mL, 1.6 M in Hex, 0.55 mmol) to furnish ether **17j** as a colorless oil (61 mg, 71%): R_f = 0.70 (10% EA/Hex); ^{1}H NMR: 3.32 (t, J = 6.4 Hz, 2H), 1.71−1.64 (m, 2H), 1.61−1.45 (m, 5H), 1.43−1.19 (m, 7H), 1.10 (s, 3H), 0.93 (t, J = 7.20 Hz, 3H); ^{13}C NMR: 72.8, 59.9, 36.5, 32.8, 25.86, 24.6, 22.2, 19.6, 13.99. HRMS (TOF-MS-EI$^+$) calcd for $C_{11}H_{22}O$: 170.1671; found: 170.1671; IR: 2962, 2925, 2862, 1447, 1081.

1-Hexyloxy 1-Methyl Cyclohexane (17k). Using the general procedure for etherification described above, peroxide **15b** (107 mg, 0.50 mmol) was reacted with *n*-hexyl magnesium bromide (0.27 mL, 2 M in ether, 0.54 mmol) to furnish hexyl ether **17k** as a colorless oil (64 mg, 65%): R_f = 0.65 (5% EA/Hex); ^{1}H NMR: 3.29 (t, J = 6.7 Hz, 2H), 1.71−1.66 (m, 2H), 1.64−1.47 (m, 5H), 1.44−1.27 (m, 11H), 1.11 (s, 3H), 0.90 (t, J = 6.9 Hz, 3H); ^{13}C NMR: 72.9, 60.2, 36.5, 31.8, 30.7, 26.1, 25.8, 24.6, 22.6, 22.2, 14.0; HRMS (TOF-MS-EI$^+$) calcd for $C_{13}H_{26}O$: 198.1984; found: 198.1992; IR: 2962, 2925, 2862, 1447, 1081.

(*E*/*Z*)-1-Butoxyundec-2-ene (17l). Using the general procedure for etherification described above, peroxide **16b** (135 mg, 0.50 mmol) was reacted with *n*-BuLi (0.34 mL, 1.6 M in Hex, 0.55 mmol) to furnish ether **17l** as a colorless oil (86 mg, 76%): R_f = 0.63 (10% EA/Hex); ^{1}H NMR: 5.73−5.66 (m, 1H), 5.59−5.52 (m, 1H), 4.01 (m, 0.23 H), 3.91 (dd, J = 0.6, 6.15, 1.76 H), 3.41 (t, J = 6.6 Hz, 2H), 2.05 (m, 2H), 1.61−1.54 (m, 2H), 1.43−1.35 (m, 4H), 1.33−1.27 (m, 10H), 0.93 (t, J = 7.4 Hz, 3H), 0.89 (t, J = 7.1 Hz, 3H); ^{13}C NMR: 134.5, 126.4, 71.6, 69.8, 32.3, 31.88, 31.87, 29.4, 29.27, 29.21, 29.0, 22.7, 19.3, 14.0, 13.9; HRMS (TOF-MS-EI$^+$): Calcd for $C_{15}H_{30}O$: 226.2297; found: 226.2297; IR: 2954, 2923, 2852, 1465, 1105.

(*E*/*Z*)-Hexyl 2-Undecenyl Ether (17m). Using the general procedure for etherification described above, peroxide **16b** (115 mg, 0.50 mmol) was reacted with *n*-hexyl magnesium bromide (0.27 mL, 2 M in ether, 0.54 mmol) to furnish hexyl ether **17m** as a colorless oil (104 mg, 81%): R_f = 0.67 (10% EA/Hex); ^{1}H NMR: 5.73−5.66 (m, 1H), 5.59−5.52 (m, 1H), 4.01 (m, 0.24 H), 3.91 (dd, J = 0.6, 6.2, 1.76 H), 3.40 (t, J = 6.7, 2H), 2.05 (m, 2H), 1.58 (m, 2H), 1.43−1.27 (m, 18H), 0.90−0.87 (6H); ^{13}C NMR: 134.5, 126.4, 71.6, 70.2, 32.3, 31.88, 31.74, 29.76, 29.46, 29.28, 29.22, 29.1, 25.9, 22.67, 22.62, 14.08, 14.03. HRMS (TOF-MS-EI$^+$) calcd for $C_{17}H_{34}O$: 254.2610; found: 254.2610; IR: 2954, 2923, 2852, 1465, 1105.

General Procedure for sp^2 C−O Bond Formation. Reactions involving commercially available reagents were conducted as described above for sp^3 C−O bond formations except that reaction times were approximately 1 h. Reactions involving in situ formation of vinyl or heteroaryllithium reagents from the corresponding tributylstannanes were conducted as described below.

To a −78 °C solution of alkenyl- or aryltributyltin (0.55 mmol) in dry THF (3 mL) was added *n*-BuLi (0.55 mmol, 1.6 M in Hex). The reaction mixture was stirred for 10 min, after which was added a solution of the monoperoxyacetal (0.50 mmol) in THF (1 mL). The reaction mixture was stirred until no starting material could be detected on TLC (approximately 60 min) and then diluted with Hex (10 mL). The resulting solution was passed though a column of neutral alumina (1 × 2 in.) and then concentrated (an aqueous workup could also be conducted employing aq. carbonate to minimize hydrolysis). The residue was purified by silica flash chromatography using 1% ether/Hex; chromatography of enol and thienyl ethers included 0.2% triethylamine.

3,7-Dimethyl-6-octen-1-yl Phenyl Ether (18a). [51113-53-2]: Using the general procedure described above, peroxide **8b** (128 mg, 0.5 mmol) was reacted with phenyl lithium (0.30 mL, 1.8 M in dibutyl ether, 0.54 mmol) to furnish phenyl ether **18a** as a colorless oil (102 mg, 87%).[75] The same product was available (78 mg, 67%) by reaction of peroxide **8b** (128 mg, 0.50 mmol) with phenyl magnesium bromide (0.18 mL, 3.0 M in ether, 0.54 mmol):

R_f = 0.66 (10% EA/Hex); ^{1}H NMR: 7.32−7.30 (m, 2H), 6.97−6.93 (m, 3H), 5.15 (m, 1H), 4.03 (m, 2H), 2.08 (m, 1H), 2.02 (m, 1H), 1.88 (m, 1H), 1.75−1.71 (m, 1H), 1.73 (s, 3H), 1.65 (s, 3H), 1.64−1.61 (m, 1H), 1.46−1.41 (m, 1H), 1.30−1.24 (m, 1H), 0.98 (d, J = 6.9 Hz, 3H); ^{13}C NMR: 151.1, 131.3, 129.4, 124.7, 120.5, 114.5, 66.1, 37.2, 36.1, 29.6, 25.8, 25.5, 19.6, 17.7.

2-Methylprop-1-en-1-yl 3-Phenylpropyl Ether (18b). Using the general procedure described above, peroxide **9b** (118 mg, 0.5 mmol) was reacted with 2-methyl-1-propenyl magnesium bromide (1.3 mL, 0.5 M in THF, 0.65 mmol) to furnish ether **18b** as a colorless

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oil (39 mg, 41%), which decomposed during chromatography: ^{1}H NMR: 7.34−7.30 (m, 2H), 7.26−7.21 (m, 3H), 5.83−5.82 (m, 1H), 3.72 (t, J = 6.4 Hz, 2H), 2.75 (t, J = 7.8 Hz, 2H), 2.00−1.93 (m, 2H), 1.68 (s, 3H), 1.59 (s, 3H); ^{13}C NMR: 141.8, 140.0, 128.5, 128.4, 125.8, 110.5, 70.7, 32.0, 31.4, 19.5, 15.0. HRMS (TOF-MS-EI$^+$) calcd for $C_{13}H_{18}O$ $(M)^+$: 190.1358; found: 190.1363; IR: 2918, 2865, 1689, 1496, 1159.

3,7-Dimethyl-6-octen-1-yl Vinyl Ether (18c). Using the procedure described above for etherifications with in situ generated sp^2 RLi, peroxyacetal **8b** (128 mg, 0.5 mmol) was reacted with the reagent generated from tributyl vinylstannane (237 mg, 0.75 mmol) and *n*-BuLi (0.47 mL, 1.6 M in Hex, 0.75 mmol) to furnish ether **18c** as a colorless oil (62 mg, 66%), which partially decomposed upon thin-layer or column chromatography: R_f = 0.7 (10% EA/Hex); ^{1}H NMR: 6.48 (dd, J = 6.8, 14.1 Hz, 1H), 5.12 (t, J = 7.0 Hz, 1H), 4.19 (d, J = 14.1 Hz, 1H), 3.99 (d, J = 6.8 Hz, 1H), 3.78−3.68 (m, 2H), 2.08−1.93 (m, 2H), 1.77−1.69 (m, 1H), 1.70 (s, 3H), 1.65−1.58 (m, 1H), 1.62 (s, 3H), 1.54−1.44 (m, 1H), 1.42−1.33 (m, 1H), 1.25−1.16 (m, 1H), 0.93 (d, J = 6.6 Hz, 3H); ^{13}C NMR: 152.0, 131.3, 124.7, 86.2, 66.3, 37.1, 35.9, 29.5, 25.7, 25.4, 19.5, 17.6. HRMS (TOF-MS-EI$^+$ calcd for $C_{12}H_{22}O$ $(M - H)^+$: 181.1598; found: 181.1602; IR: 2961, 2913, 2871, 1647, 1609, 1200.

2-(3,7-Dimethyloct-6-en-1-oxy)-thiophene (18d). Using the procedure described above for etherifications with in situ generated sp^2 RLi, peroxyacetal **8b** (128 mg, 0.50 mmol) was reacted with the reagent generated from 2-(tributylstannyl)thiophene (279 mg, 0.75 mmol) and *n*-BuLi (0.47 mL, 1.6 M in Hex, 0.75 mmol) to furnish ether **18d** as a colorless oil (72 mg, 60%): R_f = 0.75 (10% EA/Hex); ^{1}H NMR: 6.73 (dd, J = 3.7, 6.0 Hz, 1H), 6.56 (dd, J = 1.2, 6.0 Hz, 1H), 6.22 (dd, J = 1.2, 3.7 Hz, 1H), 5.13 (t, J = 7.1 Hz, 1H), 4.10−4.06 (m, 2H), 2.08−1.98 (m, 2H), 1.89−1.84 (m, 1H), 1.74−1.67 (m, 1H), 1.72 (s, 3H), 1.64 (s, 3H), 1.62−1.59 (m, 1H), 1.43−1.38 (m, 1H), 1.27−1.22 (m, 1H), 0.97 (d, J = 6.6 Hz, 3H); ^{13}C NMR: 165.8, 131.4, 124.7, 124.6, 111.7, 104.6, 72.3, 37.0, 36.0, 29.4, 25.7, 25.4, 19.5,17.7; HRMS (TOF-MS-EI$^+$) calcd for $C_{14}H_{22}OS$ $(M)^+$: 238.1391; found: 238.1390; IR: 2963, 2925, 2913, 2871, 1536, 1193.

2-(Decyloxy)-thiophene (18e). Using the procedure described above, peroxide **12b** (129 mg, 0.50 mmol) was reacted with the reagent generated from 2-(tributylstannyl)thiophene (279 mg, 0.75 mmol) and *n*-BuLi (0.47 mL, 1.6 M in Hex, 0.75 mmol) to furnish ether **18e** as a colorless oil (65 mg, 54%): R_f = 0.7 (10% EA/Hex); ^{1}H NMR: 6.74−6.72 (m, 1H), 6.56−6.54 (m, 1H), 6.23−6.21 (m, 1H), 4.04 (t, J = 6.4 Hz, 2H), 1.83−1.76 (m, 2H), 1.48−1.44 (m, 2H), 1.38−1.30 (m, 12H), 0.91 (t, J = 6.8 Hz, 3H); ^{13}C NMR: 165.9, 124.6, 111.6, 104.5, 74.0, 31.9, 29.5, 29.3, 29.2, 25.8, 22.7, 14.1. HRMS (TOF-MS-EI$^+$) calcd for $C_{14}H_{24}OS$ $(M)^+$: 240.1548; found: 240.1548; IR: 2920, 2853, 1536, 1456, 1193.

3,3-Difluoro-3-((10-phenyldecyl)oxy)propyl)benzene (19). The difluoroether was prepared applying a previously reported two-step procedure (reaction of lithiated dithiane with the peroxide; fluorodesulfurization of the poorly stable difluoroether products)[5b] to three different precursors: 2-(3-phenylpropyl)-1,3-dithiane and monoperoxyacetal **10b** (100 mg, 51% isolated yield); silyl peroxide **10d** (105 mg, 54% isolated yield); *t*-butyl peroxide **10a** (95 mg, 26%, with 35% recovered starting material). In each case, difluoroether **19** was isolated as a colorless oil with R_f = 0.5 (5% EA/Hex) and with spectra matching literature values.[5b]

Tributyl(1-(methoxymethoxy)-3-phenylpropyl)stannane (20). [123294-00-8] was prepared using a modification of a literature procedure.[76] A solution of diisopropylamine (0.22 g, 1.1 equiv) in 5 mL of THF was cooled to 0 °C, and *n*-BuLi (1.37 mL, 1.6 M in Hex, 2.2 mmol, 1.1 equiv) was added. The reaction was stirred for 10 min, after which was added Bu_3SnH (0.582 g, 2.0 mmol, 1 equiv). The reaction was stirred for 15 min at 0 °C and then cooled to −78 °C, whereupon hydrocinnamaldehyde (268 mg, 2.0 mmol) was added as a solution in THF (10 mL). After stirring at −78 °C for 5 min, the reaction was quenched with sat. aq. NH_4Cl (10 mL), then allowed to warm to room temperature. The separated organic layer was dried over $MgSO_4$ and concentrated (rotary evaporator, followed by high vacuum).

The residue from the step described above was dissolved in DCM (12 mL), and the solution cooled to −10 °C. Diisopropyl ethylamine (0.335 g, 1.3 equiv) was added, followed by chloromethyl methyl ether (0.177 g, 1.1 equiv). The reaction was stirred for 7 h at rt and then washed with water (10 mL). The separated organic layer was dried (Na_2SO_4) and concentrated on a rotary evaporator. The residue was chromatographed on silica gel using 1% EA/Hex to afford **20** as a colorless liquid (63%, 598 mg): R_f = 0.51 (10% EA/Hex); ^{1}H NMR: 7.33−7.27 (m, 2H), 7.23−7.19 (m, 3H), 4.65 (d, J = 6.5 Hz, 1H), 4.62 (d, J = 6.5 Hz, 1H), 4.15−4.11 (m, 1H), 3.41 (s, 3H), 2.82−2.66 (m, 2H), 2.22−2.05 (m, 2H), 1.60−1.49 (m, 6H), 1.39−1.29 (m, 6H), 0.96−0.88 (m, 12H), 0.92 (t, J = 7.3 Hz, 3H); ^{13}C NMR: 142.4, 128.4, 128.3, 125.7, 96.6, 73.7, 55.5, 37.4, 34.5, 29.2, 27.5, 13.7, 9.2.

Benzene, 3-Methoxymethoxy-3-octyloxypropyl (21a). To a −78 °C solution of stannane **20** (235 mg, 0.5 mmol) in dry THF (3 mL) was added a solution of *n*-BuLi in Hex (1.6 M, 0.5 mmol). After the reaction had stirred for 3 min, peroxide **11a** (100 mg, 0.5 mmol) was added as a solution in THF (1 mL), and the reaction was stirred for an additional 30 min at −78 °C. The cold bath was removed, and the reaction was allowed to warm to rt over 30 min. The reaction was quenched with water (1 mL) and diluted with hexane (40 mL). The mixture was washed with water (10 mL), and the separated aqueous layer was extracted with Hex (10 mL). The combined organic layers were dried over Na_2SO_4 and concentrated. The residue was purified by silica gel chromatography using ether/Hex (1−5%) to furnish recovered **11a** (10%) and then the acetal **21a** as a colorless oil (88 mg, 57%): R_f = 0.36 (10% EA/hex); ^{1}H NMR: 7.32−7.27 (m, 2H), 7.24−7.19 (m, 3H), 4.83 (d, J = 6.8 Hz, 1H), 4.70 (d, J = 6.8 Hz, 1H), 4.70−4.66 (m, 1H), 3.68−3.63 (m, 1H), 3.47−3.40 (m, 1H), 3.43 (s, 3H), 2.71−2.72 (m, 2H), 2.04−1.98 (m, 2H), 1.64−1.57 (m, 2H), 1.40−1.30 (m, 10H), 0.91 (t, J = 6.7 Hz, 3H); ^{13}C NMR: 141.7, 128.4, 125.8, 101.4, 93.3, 66.7, 55.7, 36.4, 31.8, 30.8, 29.8, 29.4, 29.2, 26.2, 22.6, 14.1; HRMS (ESI+ TOF) calcd for $C_{19}H_{32}O_3$ $(M + Na)^+$: 331.2249; found: 331.2265; IR: 2925, 2855, 1149, 1002.

3-Methoxymethoxy-3-phenylpropoxy Propylbenzene (21b). The title compound was synthesized as a colorless oil (86 mg, 55%) from reaction of **9a** (104 mg, 0.50 mmol) using the general procedure described above except that 1.2 equiv each of tributylstannane and *n*-BuLi was used: R_f = 0.43 (10% EA/Hex); ^{1}H NMR: 7.35−7.31 (m, 4H), 7.28−7.21 (m, 6H), 4.85 (d,, J = 6.6 Hz, 1H), 4.73 (d, J = 6.6 Hz, 1H), 4.72−4.70 (m, 1H), 3.74−3.69 (m, 1H), 3.51−3.47 (m, 1H), 3.44 (s, 3H), 2.81−2.74 (m, 4H), 2.08−2.02 (m, 2H), 2.00−1.93 (m, 2H); ^{13}C NMR: 141.88, 141.7, 128.5, 128.49, 128.45, 128.42, 128.39, 125.9, 125.8, 101.6, 93.5, 65.8, 55.8, 36.4, 32.4, 31.4, 30.8; HRMS (TOF MS ES+) calcd for $C_{20}H_{26}NaO_3$ $(M + Na)^+$: 337.1780; found: 337.1775; IR: 2927, 1453, 1122, 1000, 697.

3-Decyloxy-3-methoxymethoxy Propyl Benzene (21c). The title compound was synthesized as a colorless oil (89 mg, 53%) from stannane **20** (0.235 g, 0.50 mmol) and peroxyacetal **12b** (0.129 g, 0.50 mmol) using the general procedure described above: R_f = 0.40 (10% EA/Hex); ^{1}H NMR: 7.30−7.26 (m, 2H), 7.21−7.17 (m, 3H), 4.82−4.80 (m, 1H), 4.69−4.63 (m, 2H), 3.66−3.60 (m, 1H), 3.40 (s, 3H), 2.74−2.70 (m, 2H), 2.05−1.95 (m, 2H), 1.60−1.54 (m, 2H), 1.38−1.27 (m, 15H), 0.88 (t, J = 6.80 Hz, 3H); ^{13}C NMR: 141.9, 128.4, 125.9, 101.5, 93.4, 66.9, 55.8, 36.4, 32.0, 30.9, 29.9, 29.7, 29.6, 29.5, 29.4, 26.3, 22.7, 14.2. HRMS (TOF MS ES+) calcd for $C_{21}H_{36}NaO_3$ $(M + Na)^+$: 359.2562; found: 359.2578; IR: 2925, 2856, 1149, 1000.

3-((3,7-Dimethyloct-6-en-1-yl)oxy)-3-(methoxymethoxy) Propylbenzene (21d). Using the general procedure described above, peroxide **8c** (244 mg, 0.50 mmol) was reacted with alkoxylithium generated from reaction of stannane **20** (235 mg, 0.5 mmol) and *n*-BuLi (0.31 mL, 1.6 M in Hex, 0.5 mmol) to furnish a mixture of mixed acetal **21d** (48 mg, 28%) accompanied by 3-methoxymethyloxy-2-methyl-5-phenylpentan-2-ol **22** (23 mg, 20%). NMR analysis of the crude reaction mixture suggested the presence of 40% of mixed acetal **21d**; presumably, some was lost during the separation process. The mixed acetal **16d** was contaminated with a small amount of inseparable byproduct, which could be removed by subjecting a DCM solution of the crude reaction mixture to brief (∼1 min) room temperature

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ozonolysis with 2% O_3/O_2 (1 mmol O_3/min) prior to chromatography. The separated byproduct was determined to be 3-methoxymethoxypropyl benzene (3 mg, ~3%), the product of protonation of the functionalized organolithium reagent.

21d. R_f = 0.5 (5% EA/Hex); ^{1}H NMR: 7.32−7.27 (m, 2H), 7.23−7.19 (m, 3H), 5.12 (m, 1H), 4.83 (d, J = 6.8 Hz, 1H), 4.70 (d, J = 6.8 Hz, 1H), 4.68−4.66 (m, 1H), 3.73−3.64 (m, 1H), 3.52−3.44 (m, 1H), 3.43 (s, 3H), 2.74 (m, 2H), 2.08−1.91 (m, 4H), 1.70 (s, 3H), 1.68−1.56 (m, 2H), 1.62 (s, 3H), 1.49−1.31 (m, 2H), 1.28−1.14 (m, 1H), 0.93−0.91 (m, 3H); ^{13}C NMR: 141.7, 131.2, 128.4, 128.4, 128.39, 125.8, 124.7, 101.5, 101.4, 93.3, 64.9, 64.8, 55.7, 37.2, 37.1, 36.8, 36.78, 36.39, 30.83, 29.5, 25.7, 25.5, 19.6, 19.5, 17.6; HRMS (TOF-ESI$^+$) calcd for $C_{21}H_{34}O_3Na$ $(M + Na)^+$: 357.2406; found 357.2401; IR: 2927, 1454, 1369, 1002.

3-Methoxymethyloxy-2-methyl-5-phenylpentan-2-ol (22). R_f = 0.3 (15% EA/Hex); ^{1}H NMR: 7.33−7.27 (m, 2H), 7.22−7.20 (m, 3H), 4.84 (d, J = 6.7 Hz, 1H), 4.69 (d, J = 6.7 Hz, 1H), 3.58 (s, 1H), 3.49 (s, 3H), 3.29 (m, 1H), 2.94−2.87 (m, 1H), 2.66−2.58 (m, 1H), 1.88−1.81 (m, 1H), 1.78−1.70 (m, 1H), 1.19 (s, 3H), 1.15 (s, 3H); ^{13}C NMR: 141.9, 128.5, 128.4, 125.9, 99.2, 89.9, 72.0, 56.0, 33.5, 32.7, 26.3, 23.7. HRMS (TOF-ESI$^+$) calcd for $C_{14}H_{22}O_3Na$ $(M + Na)^+$: 261.1467; found: 261.1483; IR: 3461, 2930, 2889, 1028.

3-Methoxymethoxypropylbenzene [91898-11-2] has been reported on multiple occasions without NMR characterization: R_f = 0.5 (20% EA/Hex); ^{1}H NMR: 7.33−7.28 (m, 2H), 7.23−7.18 (m, 3H), 4.66 (s, 3H), 3.57 (t, J = 6.4 Hz, 2H), 3.39 (s, 3H), 2.73 (t, J = 7.8 Hz, 2H), 1.99−1.89 (m, 2H); ^{13}C NMR: 141.9, 128.4, 128.3, 125.8, 96.5, 67.1, 55.2, 32.4, 31.4.

General Procedure for Synthesis of Cyclopropyl Ethers. The THP monoperoxyacetal (0.50 mmol) was dissolved in dry THF (5 mL), and the solution cooled to 0 °C. Cyclopropyl magnesium bromide (1.3 mL, 0.5 M in THF, 0.65 mmol) was then added. The cooling bath was removed, and the reaction was stirred for 45 min prior to quenching by sequential dilution with 1 M aq. hydrochloric acid (~2 mL) and water (10 mL). The addition of HCl clarified a previously hazy solution. The combined Hex extracts (20 mL × 2) were dried over Na_2SO_4 and concentrated on a rotary evaporator. The residue was purified by silica gel chromatography (5 in. tall; 0.5 in. diameter) using 1−2% EA/Hex, with fraction concentrated initially at 80−120 mm. (rotary evaporator, rt) and at 0.5 mm (1 min, 0 °C).

3,7-Dimethyloct-6-en-1-yl Cyclopropyl Ether (23a). Using the general procedure described above, THP peroxide **8b** (128 mg, 0.50 mmol) was reacted with cyclopropyl magnesium bromide (1.3 mL, 0.5 M in THF, 0.65 mmol) to furnish cyclopropyl ether **23a** as a colorless oil (80 mg, 80%): R_f = 0.52 (10% EA/Hex); ^{1}H NMR: 5.13−5.09 (m, 1H), 3.58−3.48 (m, 2H), 3.28−3.24 (m, 1H), 2.05−1.91 (m, 2H), 1.70 (s, 3H), 1.62 (s, 3H), 1.58−1.49 (m, 2H), 1.42−1.31 (m, 2H), 1.23−1.09 (m, 1H), 0.91 (d, J = 6.5 Hz, 3H), 0.58−0.54 (m, 2H), 0.48−0.43 (m, 2H); ^{13}C NMR: 131.1, 124.8, 68.9, 52.9, 37.2, 36.6, 29.5, 25.7, 25.4, 19.5, 17.6, 5.45, 5.41; HRMS (TOF-MS CI$^+$) calcd for $C_{13}H_{25}O$ $(M + H)^+$: 197.1905; found: 197.1913; IR: 2960, 2916, 1452, 1342.

Cyclopropyl 3-Phenylpropyl Ether (23b). Using the general procedure described above, THP peroxide **9b** (118 mg, 0.50 mmol) was reacted with cyclopropyl magnesium bromide (1.3 mL, 0.5 M in THF, 0.65 mmol) to furnish cyclopropyl ether **23b** as a colorless oil (64 mg, 72%): R_f = 0.46 (10% EA/Hex); ^{1}H NMR: 7.32−7.29 (m, 2H), 7.22−7.19 (m, 3H), 3.52 (t, J = 6.4 Hz, 2H), 3.28 (app septet, likely tt, J = 3.0, 6.0 Hz, 1H), 2.70 (t, J = 7.7 Hz, 2H), 1.94−1.87 (m, 2H), 0.61−0.57 (m, 2H), 0.49−0.45 (m, 2H); ^{13}C NMR: 141.9, 128.4, 128.3, 125.8, 69.7, 53.0, 32.4, 31.2, 5.5; HRMS: (TOF-MS EI$^+$) calcd for $C_{12}H_{16}O$ (M^+): 176.1201; found: 176.1199; IR: 3031, 2938, 2850, 1452, 1342.

Cyclopropyl Decyl Ether (23c). Using the general procedure described above, THP peroxide **12b** (129 mg, 0.50 mmol) was reacted with cyclopropyl magnesium bromide (1.3 mL, 0.5 M in THF, 0.65 mmol) to furnish cyclopropyl ether **23c** as a colorless oil (79 mg, 80%): R_f = 0.56 (10% EA/Hex); ^{1}H NMR: 3.49 (t, J = 6.7 Hz, 2H), 3.26 (app septet, likely tt, J = 3.0, 6.0 Hz, 1H), 1.58−1.54 (m, 2H), 1.34−1.27 (m, 14H), 0.89 (t, J = 7.0 Hz, 3H), 0.57−0.55 (m, 2H), 0.47−1.95 (m, 2H); ^{13}C NMR: 70.7, 52.9, 31.9, 29.68, 29.60, 29.57, 29.5, 29.3, 26.2, 22.7, 14.1, 5.4; HRMS: (TOF-MS CI$^+$) calcd for $C_{13}H_{27}O$ $(M + H)^+$: 199.2062; found: 199.2057; IR: 2922, 2853, 1453, 1343.

Cyclopropyl 2-Octyl Ether (23d). Using the general procedure described above, THP peroxide **13b** (115 mg, 0.50 mmol) was reacted with cyclopropyl magnesium bromide (1.3 mL, 0.5 M in THF, 0.65 mmol) to furnish cyclopropyl ether **23d** as a colorless oil (60 mg, 70%): R_f = 0.6 (10% EA/Hex); ^{1}H NMR: 3.57−3.49 (m, 1H), 3.33−3.29 (m, 1H), 1.41−1.23 (m, 10H), 1.18 (d, J = 6.1 Hz, 3H), 0.89 (t, J = 6.8 Hz, 3H), 0.61−0.56 (m, 1H), 0.54−0.51 (m, 1H), 0.49−0.47 (m, 1H), 0.46−0.40 (m, 1H); ^{13}C NMR: 75.7, 50.7, 36.6, 31.8, 29.4, 25.4, 22.6, 19.9, 14.0, 5.96, 5.42; HRMS (TOF-MS EI$^+$) calcd for $C_{11}H_{22}O$ $(M)^+$: 170.1671; found: 170.1678; IR: 2927, 2857, 1452, 1373.

***t*-Butyl 1,1-Dimethyl-2-Phenylethyl Peroxide (24a).** [133476-12-7]: 2-Bromo-2-methylpropyl benzene [23264-13-3] was prepared (3.79 g, 88%) as a colorless liquid from the corresponding alcohol (3 g, 20 mmol) using a modification of a reported procedure.[40b] Spectral data matched those in a previous report.[77] R_f = 0.8 (25% EA/Hex); ^{1}H NMR: 7.35−7.26 (m, 5H), 3.22 (s, 2H), 1.78 (s, 6H); ^{13}C NMR: 137.3, 130.9, 128.0, 127.0, 66.6, 53.4, 33.9.

The *t*-buyl peroxide was prepared from the bromide (1.89 g 8.9 mmol, 1 equiv) through reaction with *t*-BuOOH (1.94 mL, 5.5 M in decane 1.2 equiv, 10.6 mmol), and silver trifluoroacetate (2.34 g, 10.6 mmol 1.2 equiv) using a reported procedure.[40a] Following a workup which includes brief exposure to $NaBH_4$ to destroy the trifluoroacetate ester, peroxide **24a** was isolated as a colorless oil (0.79 g, 40%), which was only modestly responsive to the "peroxide" TLC stain (see the General Experimental section) even after warming: R_f = 0.7 (10% EA/Hex). Spectral properties matched those in literature reports.[40a]

Triethylsilyl (2-Methyl-1-phenylpropan-2-yl) Peroxide (24d). [830345-47]: 2-Methyl-3-phenyl-1-propene (0.66 g, 5 mmol) and Et_3SiH (1.16 g, 10 mmol) were sequentially added to a solution of $Co(acac)_2$ (0.50 mmol) in ethanol (15 mL).[41] The reaction mixture was stirred under an atmosphere of O_2 (balloon) until no starting material was observed (TLC, ~14 h). The residue obtained upon concentration in vacuo was purified by silica gel chromatography using 1−8% EA/Hex to furnish **24d** (0.95 g, 68%) as a colorless oil. The molecule has previously been reported without NMR characterization:[41b] R_f = 0.7 (10% EA/Hex); ^{1}H NMR: 7.28−7.18 (m, 5H), 2.88 (s, 2H), 1.16 (s, 6H), 1.00 (m, J = 7.9 Hz, 9H), 0.70 (q, J = 7.9 Hz, 6H); ^{13}C NMR: 138.3, 130.8, 127.8, 126.1, 82.6, 44.8, 24.3, 6.9, 4.0.

2-((2-Methyl-3-phenylpropan-1-yl)tetrahydro-2*H*-pyranyl Peroxide (24b). To a 0 °C solution of silyl peroxide **24d** (0.70 g, 2.5 mmol) in THF (6 mL) was added *n*-Bu_4NF (3 mL, 1 M in THF, ~3 mmol). After 10 min, the reaction was diluted with 50 mL of Hex and the resulting solution was washed with water (2 × 5 mL). The dried (Na_2SO_4) organic layer was concentrated, and the residue was purified through a short plug of silica (10% EA/hexane) to furnish 2-hydroperoxy-2-methylpropyl)benzene [1944-83-8] as a colorless oil (0.41 g, 98%), which displayed spectral data matching literature reports.[78] R_f = 0.35 (10% EA/hex).

The crude hydroperoxide (0.40 g, 2.4 mmol) and dihydropyran (0.2 g, 2.4 mmol) were reacted using method B to furnish monoperoxyacetal **24b** as a colorless oil (0.397 g, 66%): R_f = 0.42 (10% EA/Hex); ^{1}H NMR: 7.29−7.19 (5H), 5.12 (m, 1H), 4.06 (m, 1H), 3.63 (m, 1H), 2.97 (d, J = 13.5 Hz, 1H), 2.86 (d, J = 13.5 Hz, 1H), 1.79−175 (m, 2H), 1.67−1.59 (m, 4H), 1.25 (s, 3H), 1.18 (s, 3H); ^{13}C NMR: 138.0, 130.7, 127.9, 126.2, 101.2, 82.9, 62.8, 45.0, 27.9, 25.3, 24.7, 24.3, 20.1. HRMS (TOF-MS-ES+) calcd for $C_{15}H_{22}NaO_3$ (M + Na): 273.1461; found: 273.1461; IR: 2928, 2856, 1451.

Reaction of Monoperoxyacetal **24b** *with Organometallic Reagents.*

2-Butoxy-2-methylpropylbenzene (25a). Using the procedure described for reaction of *n*-BuLi with THP monoperoxyacetals, reaction of **24b** (125 mg, 0.50 mmol) with *n*-BuLi (0.34 mL, 1.6 M in Hex, 0.55 mmol) at −78 C for 15 min furnished, after workup and

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chromatography, recovered **24b** (9 mg, 7%), alcohol **26** (15 mg, 10%), and butyl ether **25a** (56 mg, 55%).

25a. Colorless oil; R_f = 0.75 (10% EA/Hex); ^{1}H NMR: 7.29−7.26 (m, 2H), 7.23−7.19 (m, 3H), 3.42 (t, J = 6.6 Hz, 2H), 2.79 (s, 2H), 1.59−1.52 (m, 2H), 1.44−1.35 (m, 2H), 1.14 (s, 6H), 0.94 (t, J = 7.3 Hz, 3H); ^{13}C NMR: 138.8, 130.7, 127.8, 126.0, 74.9, 61.2, 47.2, 32.8, 25.3, 19.6, 14.1; HRMS (TOF MS EI+) calcd for $C_{14}H_{22}O$ $(M)^+$: 206.1671; found: 206.1677; IR: 2956, 2927, 1453, 1362, 1080.

(2-Hexyloxy-2-methylpropyl)benzene (25b). By the general procedure described for reaction of Grignard reagents with monoperoxyacetals, a solution of **24c** (125 mg, 0.5 mmol) in THF (3 mL) was reacted with hexylMgBr (0.60 mL, 2 M in ether, 2.4 equiv) to furnish, after workup and chromatography, hexyl ether **25b** as a colorless oil (88 mg, 75%): R_f = 0.75 (10% EA/Hex); ^{1}H NMR: 7.29−7.25 (m, 2H), 7.22−7.19 (m, 3H), 3.41 (t, J = 6.7 Hz, 2H), 2.78 (s, 2H), 1.60−1.52 (m, 2H), 1.39−1.30 (m, 6H), 1.14 (s, 6H), 0.91 (t, J = 6.8 Hz, 3H); ^{13}C NMR: 138.8, 130.7, 127.8, 126.0, 74.9, 61.5, 47.1, 31.9, 30.7, 26.1, 25.3, 22.7, 14.2. HRMS Calcd for $C_{16}H_{26}ONa$ $(M + Na)^+$: 257.1879; found: 257.1881; IR: 2956, 2927, 1453, 1362, 1080.

*Reaction of t-Butyl Peroxide Probe **24a** with n-BuLi.* Using the general procedure described for reaction of *n*-BuLi with THP peroxides as above, peroxide **24a** (222 mg, 1.0 mmol) was reacted with *n*-BuLi (0.62 mL, 1.6 M in Hex, 1.1 mmol) at room temperature for 5 h to furnish, following workup and chromatography, the following products: unreacted starting material (101 mg, 45%); alcohol **26** (48 mg, 32%); and pentylbenzene (5 mg, 3%): **2-Methyl-1-phenylpropan-2-ol (26)** [100-86-7]: colorless oil; R_f = 0.35 (10% EA/Hex); ^{1}H NMR: 7.33−7.21 (m, 5H), 2.77 (s, 2H), 1.23 (s, 6H); ^{13}C NMR: 137.9, 130.5, 128.3, 126.6, 70.8, 49.8, 29.2. **Pentyl benzene** [538-68-1]: colorless oil; R_f = 0.8 (10% EA/Hex); ^{1}H NMR: 7.31−7.29 (m, 2H), 7.23−7.19 (m, 3H), 2.63 (t, J = 7.7 Hz, 2H), 1.67−1.62 (m, 2H), 1.40−1.33 (m, 4H), 0.93 (t, J = 7.0 Hz, 3H); ^{13}C NMR: 142.9, 128.4, 128.2, 125.5, 35.9, 31.5, 31.2, 22.5, 14.0.

*Reaction of Silyl Peroxide Probe **24d** with n-BuLi.* Peroxide **24d** (280 mg, 1.0 mmol) was reacted with *n*-BuLi (0.62 mL, 1.6 M in Hex, 1 mmol) at room temperature for 6 h, to furnish a mixture of products which were separated by chromatography: recovered **24d** (115 mg, 41%); Et_3SiOH (15 mg, 24%); pentylbenzene (16 mg, 11%) and alcohol **26** (15 mg, 10%).

Triethylsilanol [597-52-4]. Colorless oil; R_f = 0.5 (10% EA/Hex); ^{1}H NMR: 1.49−1.44 (bs, 1H), 0.99 (t, J = 8.0 Hz, 9 H), 0.618 (q, J = 8.0 Hz, 6H); ^{13}C NMR: 6.58, 5.79.

Competition for *n*-BuLi: Monoperoxyacetal vs Peroxide. To a −78 °C solution containing peroxyacetal **12b** (0.50 mmol, 129 mg) and peroxide **9a** (0.50 mmol, 104 mg) in THF (3 mL) was added *n*-BuLi (0.31 mL, 1.6 M in Hex, 0.50 mmol). The reaction was quenched after 3 min with an excess of water to furnish, as a colorless oil, *n*-butyl decyl ether (**27**, 70 mg, 65%) accompanied by recovered **9a** (90 mg, 86%). **Butyl decyl ether (27)** [111082-32-7]: R_f = 0.8 (10% EA/Hex); ^{1}H NMR: 3.41−3.37 (m, 4H), 1.61−1.51 (m, 4H), 1.41−1.26 (m, 16H), 0.91 (t, J = 7.4 Hz, 3H); 0.87 (t, J = 6.8 Hz, 3H); ^{13}C NMR: 71.1. 70.7, 32.02. 32.00, 29.9, 29.73, 29.69, 29.62, 29.4, 26.3, 22.8, 19.5, 14.2, 14.0.

Competition for Monoperoxyacetal: *n*-BuLi vs PhLi. Solutions of *n*-BuLi (0.47 mL, 0.762 mmol, 1.6 M in Hex) and PhLi (0.42 mL, 0.762 mmol, 1.8 M in dibutyl ether, 0.42 mL) were sequentially drawn into the same 1 mL syringe, and the contents were rapidly added to a rapidly stirring −78 °C solution of **9b** (0.762 mmol, 180 mg) in dry THF (5 mL). The reaction was quenched at −78 C after 5 min to furnish dialkyl ether **28** (78 mg, 53%), phenyl alkyl ether **29** (30 mg, 19%), and biphenyl (5 mg, 4%): **3-Butoxypropyl benzene (28)**: Spectral data were nearly identical to those previously reported.[79] R_f = 0.7 (10% EA/Hex); ^{1}H NMR: 7.32−7.28 (m, 2H), 7.23−7.20 (m, 3H), 3.46−3.43 (m, 4H), 2.72 (t, J = 7.6 Hz, 2H), 1.95−1.91 (m, 2H), 1.63−1.57 (m, 2H)1.44−1.40 (m, 2H), 0.96 (t, J = 7.4 Hz, 3H); ^{13}C NMR: 142.1, 128.5, 128.3, 125.7, 70.7, 69.9, 32.4, 31.9, 31.3, 19.4, 14.0. **3-Phenoxy propyl benzene** [64806-63-9] (**29**): Colorless oil; R_f = 0.6 (10% EA/Hex); ^{1}H NMR: 7.34−7.21 (m, 7H); 6.99−6.92 (m, 3H); 4.00 (t, J = 6.3 Hz, 2H), 2.85 (t, J = 7.5 Hz, 2H), 2.18 (m, 2H); ^{13}C NMR: 159.1, 141.7, 129.5, 128.6, 128.5, 126.0, 120.7, 114.7, 66.9, 32.3, 30.9.

Reactivity of Methoxyethoxy Alkyl Peroxide. Using the general procedure for etherification described above, methoxyethoxy peroxide **9e** (105 mg, 0.5 mmol) was reacted with *n*-BuLi (0.34 mL, 1.6 M in Hex, 0.55 mmol) to furnish 3-butoxypropyl benzene (**28**, 25 mg, 26%) as a colorless oil, accompanied by a small amount (4 mg, 6%) of 3-phenyl-1-propanol.

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. The reader is directed to a web-published collection of peroxide-related safety information.[80]

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b02043.

Optimized coordinates, electronic energies, and zero-point vibrational energies of all minima and transition states considered in Scheme 6; thermal analysis of **10a** and **10b**; ^{1}H and ^{13}C spectra of new molecules (PDF)

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Notes

The authors declare no competing financial interest.

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