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Synthesis of Primary *gem*-Dihydroperoxides and Their Peroxycarbenium [3 + 2] Cycloaddition Reactions with Alkenes

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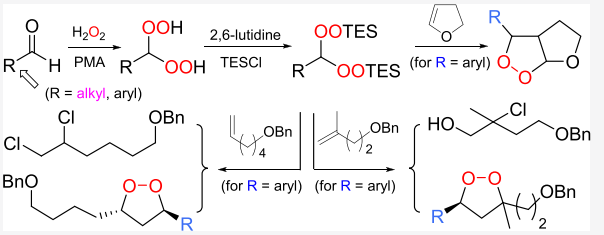
ABSTRACT: It is long known that dihydroperoxidation of aliphatic aldehydes is extremely difficult and normally stops halfway at the hydroxyhydroperoxide stage. This strange phenomenon now has been explored, and a highly effective protocol for conversion of aliphatic aldehydes into *gem*-dihydroperoxides has been developed. Silyl protection of primary *gem*-dihydroperoxides, which is also a challenge due to unexpected based-induced decomposition, was achieved using 2,6-lutidine as the base. The silyl-protected *gem*-dihydroperoxides were then examined in a peroxycarbenium [3 + 2] cycloaddition reaction with alkenes for the first time. Aromatic substrates normally reacted smoothly, affording the expected 1,2-dioxolanes smoothly. Aliphatic aldehydes generally failed to yield 1,2-dioxolane. In all cases, unexpected formation of either a chlorohydrin or a 1,2-dichloride (with Cl atoms derived from $TiCl_4$) depending on the alkene employed was observed, which displays some so far unknown facets of the cycloaddition and helped to gain many mechanistic insights.



INTRODUCTION

In some reactions such as those with esters, epoxides, chlorosilanes, etc., hydrogen peroxide (H_2O_2) and water (H_2O) behave similarly, giving the main products differing only at the incorporated group, i.e., OH from H_2O or OOH from H_2O_2. However, due to the so called α-effect, H_2O_2 may behave radically different from H_2O in some other reactions. For instance, it is normally impossible to add water to ketones to afford *gem*-dihydroxy ketals (unless strongly electron-withdrawing groups such as CF_3 are attached to the carbonyl group), but corresponding *gem*-dihydroperoxides can be synthesized from H_2O_2 (Figure 1A) smoothly using a proper catalyst (e.g., $HClO_4$,[1] H_2SO_4,[2] H_2WO_4,[3] HCO_2H,[4] I_2,[5] BF_3·Et_2O,[6] CAN,[7] Re_2O_7,[8] PMA,[9] silica-supported $NaHSO_4$,[10] silica-supported H_2SO_4,[11] heteropoly acid/NaY zeolite,[12] $SnCl_2$,[13] $SrCl_2$,[14] $AlCl_3$,[15] $ZnCl_2$,[16] $Bi(OTf)_3$,[17] γ-Fe_2O_3@SiO_2-TfOH,[18] MTO (methyltrioxorythnium),[19] CSA[20] (70% aq. H_2O_2), or even catalyst free[21] (35% H_2O_2-DME)). Thanks to this useful difference, many perketal-related organic peroxides including antimalarial,[22a−c] anti-Lieshmaniasis,[23] and antioncogenic[24a] tetraoxanes and 1,2-dioxolanes could be accessed more easily.

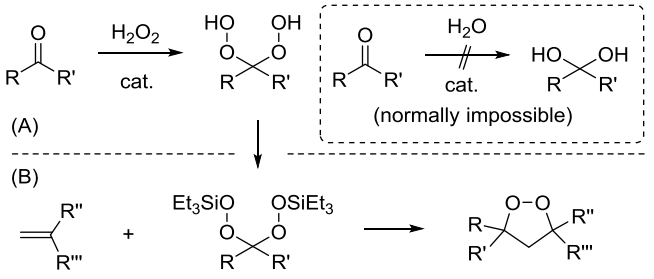


Figure 1. (A) Conversion of ketones into *gem*-dihydroperoxides and subsequent silyl protection and (B) peroxycarbenium [3 + 2] cycloaddition reaction with alkenes.

The peroxycarbenium [3 + 2] cycloaddition reaction with alkenes represents a rapid access to 1,2-dioxolanes (Figure 1B).[4,25] However, to date this interesting reaction was explored mostly using 1,1-disubstituted ethylenes and peroxycarbenium ions derived from ketones. In a previous study,[26] we examined 1,2-disubstituted alkenes in this reaction and found that the failure of these types of alkenes to undergo the peroxycarbenium cation [3 + 2] cycloaddition was caused by the in situ decomposition of the cycloaddition products. However, if there existed an oxygen or nitrogen atom directly attached to the C=C bond, the expected [3 + 2] cycloaddition products still could be obtained in good yield. In the present endeavor, we synthesized a range of primary *gem*-dihydroperoxides and explored their peroxycarbenium [3 + 2] cycloaddition reaction, which has never been documented to date. It was then found that primary *gem*-dihydroperoxides were quite different from the secondary ones, not only in their preparation but also in

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the subsequent silyl protection and the cycloaddition. Some previously unknown side reactions were observed, and many mechanistic insights were thus gained. All the details are given below.

RESULTS AND DISCUSSION

The present study began with the synthesis of primary *gem*-dihydroperoxides. A range of aromatic aldehydes were smoothly converted[5a,c,7,8a,10−18,20,21] into corresponding *gem*-dihydroperoxides via reaction with ethereal H_2O_2 with PMA (phosphomolybdic acid) or $MoO_2(acac)_2$ as the catalyst (Table 1). Generally, the reaction was remarkably faster with PMA as the catalyst. Also, those aldehydes with an electron-donating group at the phenyl ring normally led to faster reactions and higher yields of **2**. Notably, in unconcentrated ethereal H_2O_2 (~1 M) with either PMA or $MoO_2(acac)_2$ as the catalyst, benzaldehyde (**1a**) reacted apparently slower than its dimethyl acetal **1a′**; to obtain **2a** from **1a**, concentrated H_2O_2 must be used (Table 1, entry 1). When using the less potent catalyst $MoO_2(acac)_2$ as the catalyst, it was possible to acquire the intermediate **2a′** (Table 1, entry 3).

All products, except for **2b** and **2d**, showed spectroscopic data in excellent agreement with those in the literature. In our hands, the ^1H and ^{13}C NMR data for **2b** and **2d** obtained using either catalyst are highly reproducible yet not compatible with those documented[11,15,16] in three published articles.[27]

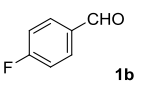
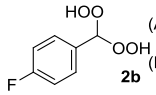
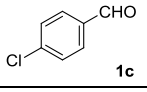
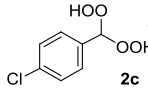
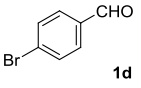
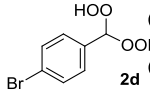
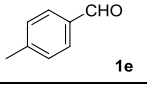
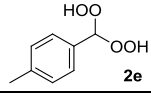
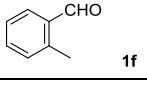
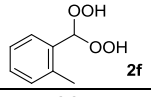
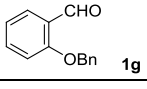
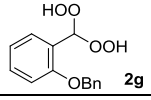
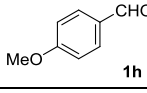
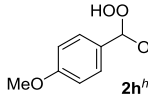
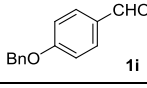
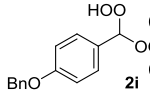
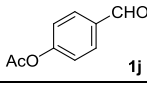
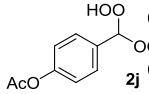
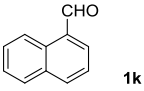
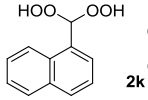
Aliphatic aldehydes failed to give any **2** under the same conditions. In most cases, the only identifiable products were hydroxyhydroperoxides (with only one OOH incorporated), although there were two[18,20] exceptions (vide infra). Such difficulty has long been known,[5c,14,16,20,28] but to date, the phenomenon still does not seem to be understood yet.

Judging from the reaction mechanism (Figure 2), the stability of the carbocation (or the ease with which the carbocation is generated) seems to play a critical role: The carbocation derived from aliphatic hydroxyhydroperoxides (bottom left, Figure 2, stabilized only by one weakly electron-donating alkyl group) is expected to be less stable and thus more difficult to form than that from aromatic precursors (where the positive charge is much better stabilized through delocalization onto the aromatic ring). Similarly, the smooth conversion of aliphatic ketones into secondary *gem*-dihydroperoxides may also be interpreted as a consequence of better stabilization of the carbocation due to the presence of an additional alkyl group.

It should be noted that the above rationalization based on carbocation stability is not contradicted by the facile dialkylacetalization (a process that occurs via a mechanism similar to that in Figure 2) as it seems at a glance. This is because dialkylacetalization conditions are normally more forcing than those for dihydroperoxidation. In addition, as will be reasoned below, dihydroperoxidation may indeed suffer some so far unnoticed additional (compared with dialkylacetalization) difficulty caused by the OOH in the intermediate hydroxyhydroperoxides.

As shown in Figure 3, the OOH and OH might intramolecularly hydrogen-bond to one another and facilitate the reverse of the carbocation generation (i.e., the return of an OH to re-generate the hydroxyhydroperoxide), making generation of the carbocation more difficult than otherwise. In the case of aromatic hydroxyhydroperoxides, the end products can be formed smoothly simply because the positive charge delocalization is powerful enough to ensure a facile

Table 1. Synthesis of 2 from Aromatic 1[a]

entry	1	2 (cat. mol%,[b] time, yield)
1	PhCHO **1a**	$PhCH(OOH)_2$ **2a** (B 5%, 18 h, 75%)[c]
2	$PhCH(OMe)_2$ **1a'**	$PhCH(OOH)_2$ **2a** (A 0.4%, 12 h, 76%)
3	$PhCH(OMe)_2$ **1a'**	PhCH(OMe)OOH **2a'** (B 5%, 2 h, 66%)[c]
4	 **1b**	 **2b** (A 0.4%, 17 h, 80%) (B 5%, 28 h, 77%)[c]
5	 **1c**	 **2c** (A 1.5%, 20 h, 76%) (B 10%, 38 h, 58%)[d,e]
6	 **1d**	 **2d** (A 1.5%, 21 h, 75%) (B 10%, 38 h, 66%)[d,f]
7	 **1e**	 **2e** (A 0.4%, 12 h, 82%) (B 5%, 12 h, 93%)[c]
8	 **1f**	 **2f** (A 0.4%, 13 h, 88%) (B 5%, 11 h, 94%)[c]
9	 **1g**	 **2g** (A 0.4%, 9 h, 87%) (B 5%, 9 h, 84%)[g]
10	 **1h**	 **2h**[h] (A 0.4%, 14 h, 40%) (B 5%, 6 h, 68%)[g]
11	 **1i**	 **2i** (A 0.4%, 6 h, 74%) (B 5%, 8 h, 75%)[g]
12	 **1j**	 **2j** (A 0.4%, 23 h, 50%) (B 5%, 27 h, 65%)[c]
13	 **1k**	 **2k** (A 0.4%, 13 h, 68%) (B 5%, 14 h, 85%)[c]

[a]All experiments were performed at rt in ethereal H_2O_2 containing the indicated catalyst; A = PMA, B = $MoO_2(acac)_2$. [b]With respect to the molar quantity of the substrate. [c]The ethereal H_2O_2 was concentrated to 1/5 of the original volume by bubbling N_2 into the solution before use. [d]The ethereal H_2O_2 was concentrated to 1/10 of the original volume before use. [e]20% of starting **1** was recovered. [f]15% of starting **1** was recovered. [g]The ethereal H_2O_2 was concentrated to 1/3 of the original volume before use. [h]Decomposed on standing at ambient temperature.

generation of the carbocation. In the aliphatic cases, the electron-donating effect of an alkyl group is too weak to confront the adverse effect of the hydrogen bonding associated with OOH; practically no carbocation can be generated, and the reaction halts at the hydroxyhydroperoxide stage.[29]

Although so far there is no definite evidence for such adverse effect of the OOH in hydroxyhydroperoxides yet, both of the two known syntheses of (monofunctional) aliphatic primary *gem*-dihydroperoxides do contain some factors that may counter-balance the adverse effect caused by the OOH. In

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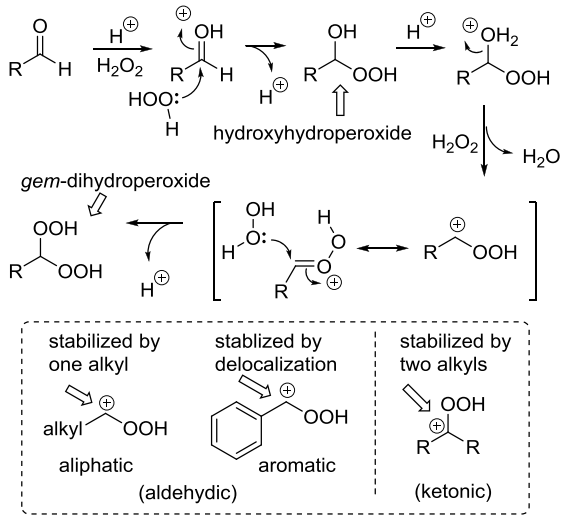

Figure 2. Mechanism for the formation of *gem*-dihydroperoxides, with the stabilizing factors for the positive charge in carbocations derived from different carbonyl species shown at the bottom (boxed).

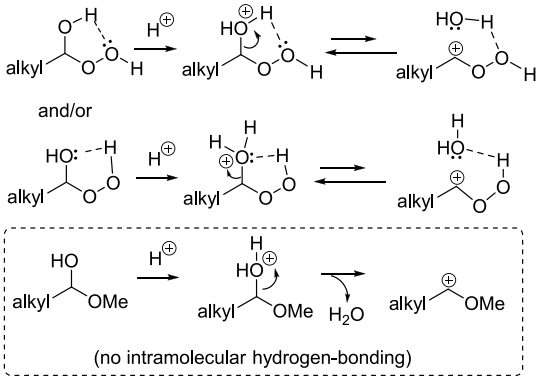

Figure 3. Because of the possible intramolecular H bonding between the OOH and OH in hydroxyhydroperoxides, generation of carbocations from hydroxyhydroperoxides in dihydroperoxidation could be more difficult than from hydroxyalkoxides in dialkylacetalization.

Hamann and Liebscher's conditions[20] (the first ever known study that actually obtained aliphatic primary *gem*-dihydroperoxides via reaction with H_2O_2, which used an 70% aq. H_2O_2-Et_2O biphasic system with 0.1 mol equiv of camphorsulfonic acid (CSA) as the catalyst), the presence of a H_2O_2 phase (containing 30% of H_2O) may facilitate breakage of the intramolecular hydrogen bonding shown in Figure 3 (through formation of intermolecular hydrogen bonding to H_2O_2 or H_2O) and thus promote generation of the carbocation, while still providing a large amount of H_2O_2 as the reactant.[30] Similarly, in Zhang's protocol[18,31] (which utilized a homogeneous mixture consisting of 30% aq. H_2O_2 and MeCN, with 0.1 mol equiv of insoluble γ-Fe_2O_3@SiO_2-TfOH as the catalyst), the reaction occurred on the surface of the magnetic nanoparticles, where Si-OH and/or Fe_2O_3 may also interfere with the intramolecular hydrogen bonding in aliphatic hydroxyhydroperoxides and thus make the generation of the carbocation easier.

All the above suggested that use of more forcing conditions might solve the problem with aliphatic aldehydes. Although for safety concerns, higher reaction temperatures do not seem to appeal, it is feasible to use more catalysts and H_2O_2 (*vide infra*). Then, by chance,[32] we observed that prolonged stirring of a solution of **1l** (Figure 4) under the PMA(0.4 mol %)/two-fold concentrated ethereal H_2O_2/rt/5 day conditions led to formation of traces of **2l** along with **2l′** and the "dimers" (Figure 4, boxed).

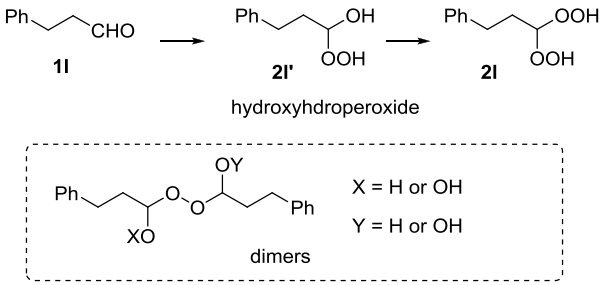

Figure 4. Formation of **2l** from **1l** via hydroxyhydroperoxide **2l′**, with possible dimers shown at the bottom (boxed). Similar "dimers" were also observed in reactions using other substrates as reported in ref 20; cf. the text.

Encouraged by the first promising sign for achieving the almost hopeless goal under conventional homogeneous conditions back at that time, we next examined the conversion of **1l** into **2l** with different amounts of PMA and water scavenger ($MgSO_4$). The representative results are shown in Table 2, which showed that use of larger amounts of PMA and

Table 2. Conversion of 1l into 2l under Different Conditions[a]

entry	conditions (PMA[b], $MgSO_4$[b])	outcome (other species/**2l′**/**2l**)[c]
1	1%, 0	1.5:1:0.3
2	1%, 0.8	0:1:1
3[d]	0.4%, 0.8	1:1:0.4
4	2%, 0.8	0:0.4:1
5[e]	2%, 0.8	1:1:0.4
6[f]	2%, 0.8	0:0.4:1
7	2%, 1.5	0:0:1

[a]All experiments were performed using three-fold concentrated ethereal H_2O_2 (~3 M) at ambient temperature for 23 h unless otherwise stated. [b]Molar equiv (with respect to the peroxy substrate). [c]Molar ratios as measured by the integrals in ^{1}H NMR, with "other species" referring to the "dimers". [d]In the absence of $MgSO_4$, the reaction under otherwise the same conditions for 23 h failed to yield any discernible amounts of **2l**. [e]Na_2SO_4 was used instead of $MgSO_4$. [f]Five-fold concentrated ethereal H_2O_2 (~5 M) was employed instead of the three-fold concentrated one.

H_2O_2 together with stoichiometric amounts of $MgSO_4$ greatly accelerated the reaction. However, more than three-fold concentration of H_2O_2 was not rewarding, indicating that successful acquisition of aliphatic *gem*-dihydroperoxides at high concentrations of H_2O_2 might not be a simple consequence of a kinetic advantage (e.g., rate = k[carbocation][H_2O_2]) but might be a result of breaking the intramolecular hydrogen bonds in the hydroxyhydroperoxides (Figure 3) and/or stabilization[30] of the intermediate carbocation by H_2O_2.

We also examined the reaction using octanal under Hamann and Liebscher's[20] conditions[33] in parallel to a homogeneous experiment (which had the same amounts of substrate, CSA, and H_2O_2 but no water in the reaction mixture); while the former gave a mixture of the primary *gem*-dihydroperoxide along with some other species, the latter (proceeded much

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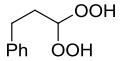
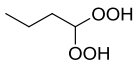
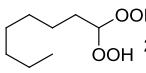
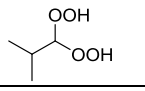
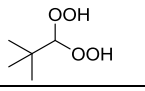
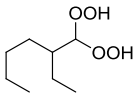
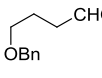
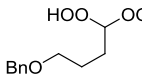
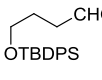
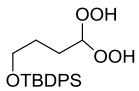
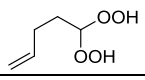
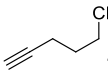
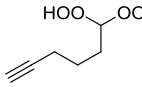
faster and much cleaner than the corresponding biphasic run) afforded the *gem*-dihydroperoxide in 80% yield. Although this result (using ~ten-fold concentrated H_2O_2) was as good as that with PMA as the catalyst, out of safety concerns, we still prefer the PMA protocol (using 0.02 mol equiv of PMA, three-fold concentrated H_2O_2, and 1.5 mol equiv of $MgSO_4$).

A range of aliphatic aldehydes was then converted into the corresponding *gem*-dihydroperoxides. As shown in Table 3,

Table 3. Synthesis of *gem*-Dihydroperoxides of Aliphatic Aldehydes[a]

entry	Aldehyde **1**	Product **2** (time, yield)
1	 **1l**	 **2l** (30 h, 70%)
2	 **1m**	 **2m** (24 h, 81%)
3	 **1n**	 **2n** (26 h, 84%)
4	 **1o**	 **2o** (24 h, 78%)
5	 **1p**	 **2p** (36 h, 50%)
6	 **1q**	 **2q** (26 h, 91%)
7	 **1r**	 **2r** (22 h, 83%)
8	 **1s**	 **2s** (25 h, 72%)
9	 **1t**	 **2t** (28 h, 65%)
10	 **1u**	 **2u** (27 h, 69%)

[a]All experiments were performed at rt in ethereal H_2O_2 (initially 30 mL, ~1.0 M, concentrated to ~10 mL prior to reaction) containing 1.0 mmol of **1** using 0.02 mmol of PMA and 1.5 mmol of anhydrous $MgSO_4$. TBDPS = *t*-butyldiphenylsilyl.

under the newly established standard conditions (0.02 mol equiv of PMA, three-fold concentrated ethereal H_2O_2, rt), most of the aliphatic aldehydes could be converted into their *gem*-dihydroperoxides in good to excellent yields within 30 h. Linear or branched aldehydes all reacted well (Table 3, entries 1–6). Protecting groups such as Bn and TBDPS survived (Table 3, entries 7 and 8). Alkenyl or alkynyl groups were also well tolerated (entries 9 and 10).

Silyl protection of the primary *gem*-dihydroperoxides was then attempted with **2a** under the conditions reported by Ramirez and Woerpel[4] (TESCl/imidazole/CH_2Cl_2), which indeed worked very well for all secondary *gem*-dihydroperoxide substrates. The starting **2** was fully consumed, but no silyl-protected products **3** could be detected. Replacement of imidazole with Et_3N, DMAP, or DBU all led to the same results. The only isolable/identifiable species was benzoic acid. Several other *gem*-dihydroperoxides also gave similar results. Stirring of **2a** with the above mentioned bases, separately, under the otherwise identical conditions for the TES protection led to full consumption of **2a** and formation of benzoic acid, most likely occurred through a Bayer–Villiger-type mechanism triggered by deprotonation, as shown in Figure 5.

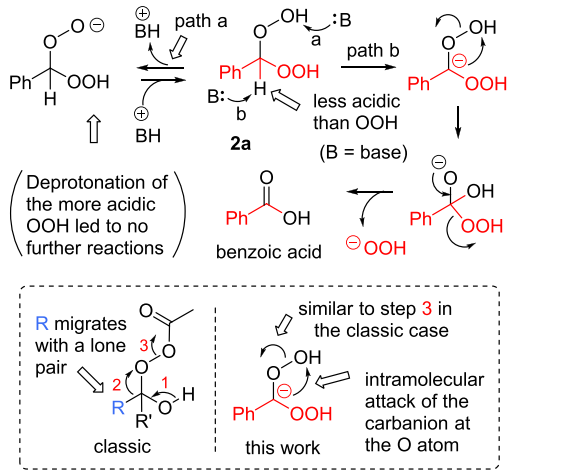


Figure 5. Schematic rationalization (not a proven mechanism) of the base-induced decomposition of primary *gem*-dihydroperoxides (exemplified through reaction of **2a**), with the key events and the sequence in classic Bayer–Villiger oxidation of ketones shown at the bottom left for comparison. The transformation is depicted as a stepwise process (which may not necessarily be true) only for the convenience of description.

To avoid the deprotonation at the acetal carbon atom, we next tested 2,6-lutidine, which has a sterically hindered base and did not lead to any discernible decomposition of **2a** under otherwise the same conditions. Subsequent protection of **2a** with TESCl at 0 °C in the presence of 2,6-lutidine indeed led to clean formation of the expected silylated *gem*-dihydroperoxide **3a**.

It is worthy of note that TES-protected primary *gem*-dihydroperoxides are much less stable than the secondary ones. Unexpected decomposition of such species was observed during the silyl protection reaction at ambient temperature, in the delayed workup, and on silica gel during chromatography if it was not done rapidly enough. To avoid unnecessary loss, the silyl protection should be performed in an ice-water bath, the crude products should be worked up as soon as possible, and chromatographic purification must be performed quickly on a relatively short column. With all these precautions, a range of *gem*-dihydroperoxides could be successfully silylated and isolated (Tables 4 and 5).

The peroxycarbenium [3 + 2] cycloaddition reaction using silyl-protected primary *gem*-dihydroperoxides, which to date has never been documented (to our knowledge), was then examined using several alkenes. 1,1-Disubstituted ethylenes are the most suitable type for peroxycarbenium [3 + 2] cycloaddition as shown by Ramirez and Woerpel's[4] work. In the present context, the reaction of **3a** with **4** (Scheme 1) indeed proceeded well just like those involving secondary *gem*-

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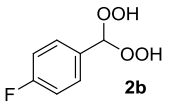
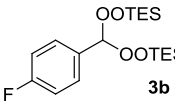
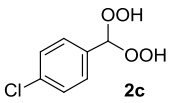
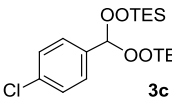
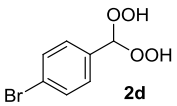
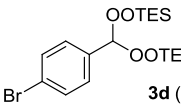
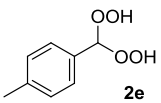
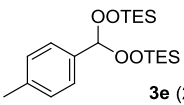
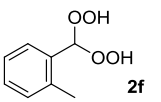
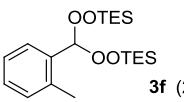
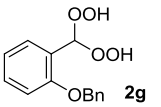
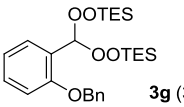
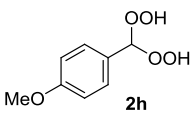
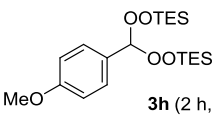
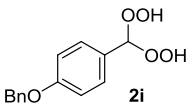
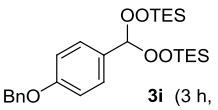
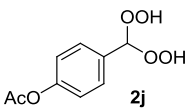
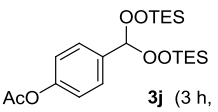
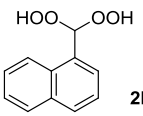
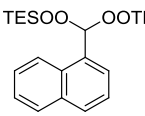
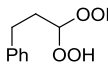
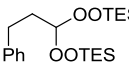
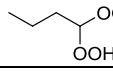
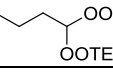
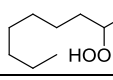
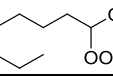
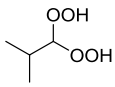
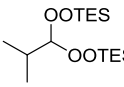
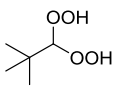
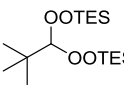
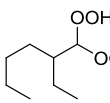
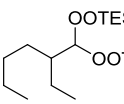
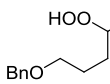
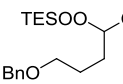
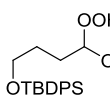
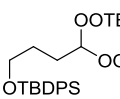
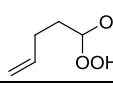
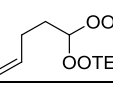
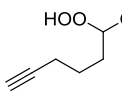
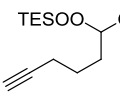
Table 4. TES Protection of *gem*-Dihydroperoxides 2 to Afford 3[a]

entry	substrate **2**	Product **3** (time, yield)
1	$PhCH(OOH)_2$ **2a**	$PhCH(O_2TES)_2$ **3a** (2 h, 86%)
2	 **2b**	 **3b** (2 h, 92%)
3	 **2c**	 **3c** (3 h, 70%)
4	 **2d**	 **3d** (2 h, 68%)
5	 **2e**	 **3e** (2.5 h, 86%)
6	 **2f**	 **3f** (2.5 h, 83%)
7	 **2g**	 **3g** (3 h, 80%)
8	 **2h**	 **3h** (2 h, 53%)
9	 **2i**	 **3i** (3 h, 74%)
10	 **2j**	 **3j** (3 h, 69%)
11	 **2k**	 **3k** (2.5 h, 60%)

[a]All experiments were performed in CH_2Cl_2 at 0 °C using 3 mol equiv (with respect to **2**) of 2,6-lutidine and 2.5 mol equiv (with respect to **2**) of TESCl. TES = triethylsilyl.

Table 5. TES Protection of *gem*-Dihydroperoxides 2 to Afford 3[a]

entry	substrate **2**	Product **3** (time, yield)
1	 **2l**	 **3l** (3 h, 81%)
2	 **2m**	 **3m** (3 h, 91%)
3	 **2n**	 **3n** (3 h, 82%)
4	 **2o**	 **3o** (3 h, 90%)
5	 **2p**	 **3p** (3 h, 77%)
6	 **2q**	 **3q** (3 h, 88%)
7	 **2r**	 **3r** (3 h, 80%)
8	 **2s**	 **3s** (3 h, 79%)
9	 **2t**	 **3t** (3 h, 82%)
10	 **2u**	 **3u** (3 h, 85%)

[a]All experiments were performed in CH_2Cl_2 at 0 °C using 3 mol equiv (with respect to **2**) of 2,6-lutidine and 2.5 mol equiv (with respect to **2**) of TESCl. TES = triethylsilyl.

Scheme 1. Formation of 5a and 6 from 3a and 4

dihydroperoxy substrates in previous studies, giving **5a** as a 1:0.25 inseparable mixture of (*Z*)/(*E*) isomers (cf. the Supporting Information) in 90% total yield.

The only unexpected event was formation of chlorohydrin **6**. Judging from the molar amounts of **5a** and **6**, conversion of **4** into **6** should be a reaction that occurred in parallel to the formation of **5a** and was most likely mediated by epoxide **7** (which was indeed isolated later in another case). Treatment of **7** with $TiCl_4$ under the cycloaddition conditions (CH_2Cl_2, −78 °C, without adding any **3a**) indeed afforded **6** in 81% yield. Since generation of the peroxycarbenium ion was accompanied by formation of a TESOO-Ti, a formal hydroperoxide under the cycloaddition conditions, conversion of **4** into **7** appears to be reasonable. A possible route is shown in Figure 6.

Monosubstituted ethylenes (except allylsilane, which is unique because of its stabilizing effect on the carbocation *β* to the silicon atom) have never been explored in the peroxycarbenium [3 + 2] cycloaddition. Therefore, much of our attention was paid to this type of alkene, which as will be shown below, indeed behaved quite differently from 1,1-disubstituted ethylenes.

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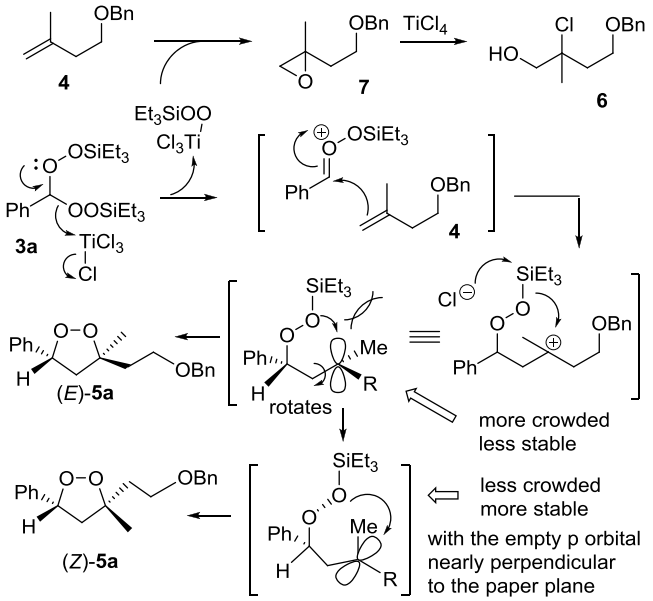
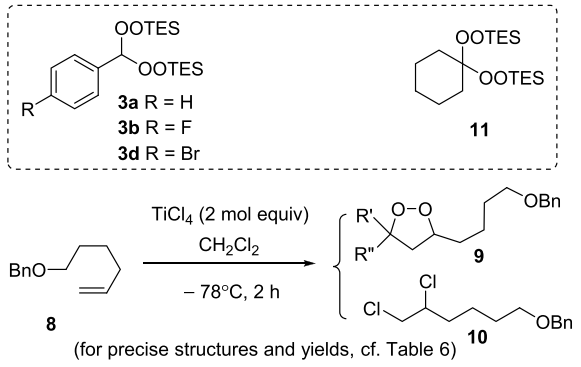


Figure 6. Formation of chlorohydrin **6** and cycloaddition product **5a**.

Treatment of **3a** with **8** in the presence of $TiCl_4$ did afford cycloaddition product **9a** as expected (Scheme 2). Unlike

Scheme 2. Formation of 9 and 10 from 3a-b, 3d, and 11 via Reaction with 8



similar products derived from secondary *gem*-dihydroperoxides, 1,2-dioxolane generated in the reaction with monosubstituted alkene had a *trans* configuration. More interestingly, dichloride **10** was isolated unexpectedly along with the aldehyde **1a** (whose presence was clearly seen in the ^{1}H NMR of the crude product mixture).

Similar results were observed with several other peroxy substrates derived from aromatic aldehydes (**3b**, **3d**) and aliphatic secondary dihydroperoxide **11** to replace **3a**, confirming that formation of such a dichloride (also the corresponding aldehydes **1b**, **1d**) must be a common feature of using monosubstituted alkenes.[34] In all cases, the sums of molar quantity of the cycloaddition product **9** and dichloride **10** were always smaller than that of the starting peroxy substrate (Table 6).

In an effort to rationalize the formation of dichloride **10**, addition of Cl_2 (which might be generated via oxidation of the chloride anion) to alkene **8** was first considered because both (formal) chloride anion and oxidant(s) were present in the reaction mixture. It follows that addition of Cl_2 to alkene **8** is a process in parallel to the addition of the peroxycarbenium ion

Table 6. Reaction of 3 or 11 with Alkene 8 (cf. Scheme 2)[a]

entry	substrate	products (time, yield)
1	**3a** (0.26 mmol)	**9a** (0.13 mmol, 50%) + **10** (0.092 mmol) (35% from **3a**) (12% from **8**)
2	**3b** (0.25 mmol)	R = *p*-F-Ph; **9b** (0.12 mmol, 48%) + **10** (0.084 mmol) (34% from **3b**) (11% from **8**)
3	**3d** (0.22 mmol)	R = *p*-Br-Ph; **9c** (0.13 mmol, 59%) + **10** (0.069 mmol) (31% from **3d**) (10% from **8**)
4	**11** (0.21 mmol)	**9d** (0.026 mmol, 12%) + **10** (0.077 mmol) (37% from **11**) (12% from **8**)

[a]All experiments were performed in CH_2Cl_2 at −78 °C for 2 h using 2 mol equiv (with respect to the peroxy substrate) of $TiCl_4$ and 3 mol equiv (with respect to the peroxy substrate) of **8**.

to **8**—these two reactions must be independent of one another. Therefore, a change in the amount of the added **8** should not lead to any significant change in the products ratio (i.e., **9**/**10**). However, reducing the amount of the added starting **8** (with a molar ratio of **8**/**3a**/$TiCl_4$ = 0.66:1:2 instead of the 3:1:2 as shown in Scheme 2 and Table 6) led to a significantly increased yield of dichloride **10** (60% from **8**) along with full disappearance of the cycloaddition product **9** in the crude product mixture. In addition, the absence of any similar dichloride in the reactions using alkene **4** (more reactive than **8**) instead of **8** also provided supporting evidence for the absence of any Cl_2 in the cycloaddition reaction mixture. Thus, the possibility of addition of Cl_2 to **8** could be excluded.

On the basis all these observations, especially the observation that the sum of the molar amounts of **9** and **10** was always less than the molar amount of the starting peroxy substrate (a sign for the existence of a common intermediate for the formation of both **9** and **10**), we worked out a plausible mechanism for the formation of **10**, with the main features shown in Figure 7: Because in such a case, the carbocation is secondary, which is sterically less crowded than the tertiary ones in previous studies, a Cl^- ion of $TiCl_4$ may thus be incorporated (likely occurred in association with ligand exchange such as the first step in Figure 7) into the alkene chain at the carbocation position to give intermediate C. Then, attack of another chloride anion at the terminal carbon of the alkenic residue (with concurrent formation of **1a**) affords the end product dichloride **10**. The raised yield of **10** in the run with a reduced amount of starting **8** can also be interpreted as a result of the greatly increased amount of (formal) chloride anion. Although conversion of **8** into **10** is not really relevant as far as cycloaddition is concerned, such one-pot transformation without involving hazardous Cl_2 might find utility under certain circumstances because of the mildness of the conditions.

The [3 + 2] cycloaddition of aliphatic peroxy substrates was explored for the first time using **3l**. To our surprise, the reaction with **4** or **8** under the same conditions used for aromatic substrates led to only chlorohydrin **6** or dichloride

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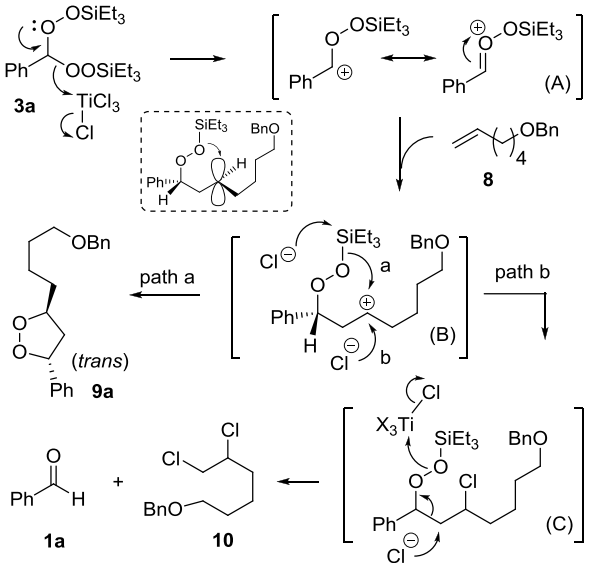
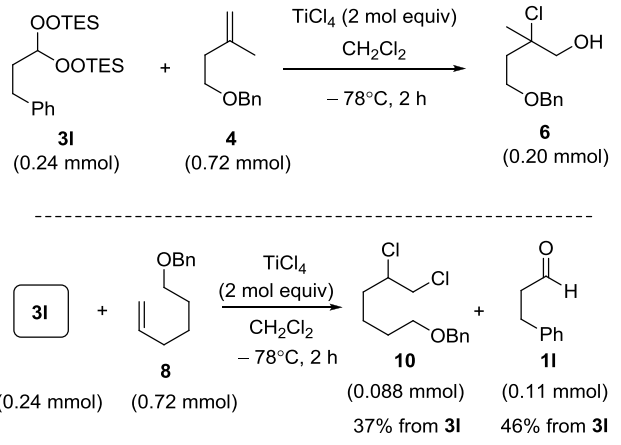


Figure 7. Schematic explanation for the formation of dichloride **10**. For clarity, the source of Cl^- is depicted as an anion although in CH_2Cl_2 it might not exist as a really free moving anion but was delivered onto the carbocation in association with ligand exchange at $TiCl_4$.

10, respectively, as the isolable/identifiable products (Scheme 3). In either case, no cycloaddition products could be detected.

Scheme 3. Reaction of 3l with 4 or 8



At first glance, these results were rather confusing because there seemed to be no reasons for these reactions to fail. Formation of chlorohydrin **6** clearly shows that the peroxycarbenium ion was indeed generated (because its precursor epoxide **7** was derived from alkene **4** via reaction with a hydroperoxy species generated at the same time as the peroxycarbenium ion, cf. Figure 6). Isolation of dichloride **10** unmistakably reflects that the peroxycarbenium ion had successfully added to the C=C in alkene **8** (cf. Figure 7). As alkene **4** is more reactive than **8** in the [3 + 2] cycloaddition, there is no reason to doubt that addition of the peroxycarbenium ion to the C=C in **4** did not occur. Then, the question became why did the final cyclization (corresponding to "path a" for intermediate B in Figure 7) not occur?

A plausible rationalization is shown in Figure 8. Because of the stabilization via charge delocalization, the aromatic ring

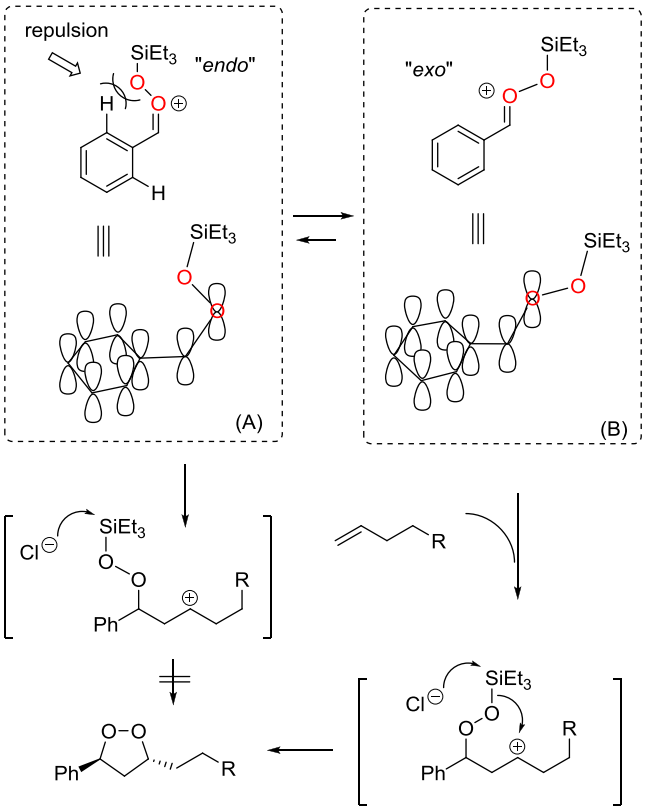


Figure 8. Aromatic peroxycarbenium ions (exemplified here through that derived from **3a**) may enjoy a conformational advantage in the [3 + 2] cycloaddition reaction, with the Ph–O–O– in the same plane and in an "*exo*" chain conformation suitable for the final cyclization to give 1,2-dioxolane; cf. the text.

and the C–O–O– chain may lie in the same plane. This leaves only two possible conformations for the chain: "*endo*" or "*exo*". The "*endo*" conformation is disfavored as a consequence of repulsion between the TESO- and the *o*-H on the phenyl ring. It thus seems that the aromatic peroxycarbenium ions would react mostly in the "*exo*" conformation, the one suitable for the final cyclization (cf. path a, Figure 7).

For aliphatic peroxycarbenium ions such as that derived from **3l**, there is no longer such conformational restriction associated with the positive charge delocalization onto the phenyl ring. The peroxycarbenium ion thus may exist in many different conformations, and practically no peroxycarbenium ions are in the "*exo*" conformation within their short life span (due to lack of strong stabilization); no final cyclization may occur.

It is interesting to note that results of using **3p** to replace **3l** to run the same reaction with **4** led to the expected cycloaddition product **5b** in 7% yield, along with chlorohydrin **6** and epoxide **7** (which provided a strong piece of evidence for the mechanism in Figure 6). As the *t*-Bu group is sterically much bulkier than the linear chain ($PhCH_2CH_2$-) in **3l**, the population of the peroxycarbenium ion of the conformation suitable for the cyclization (similar to the "*exo*" one in Figure 8) may thus be somewhat larger and the increased steric crowding may also lengthen the lifetime of the peroxycarbenium ion (creating more chances for ring closure). Probably because of the existence of these factors, the [3 + 2] cycloaddition reaction of **3p** (affording **5b**) was less difficult than that of **3l**. The reaction of **3p** with alkene **8** failed to give

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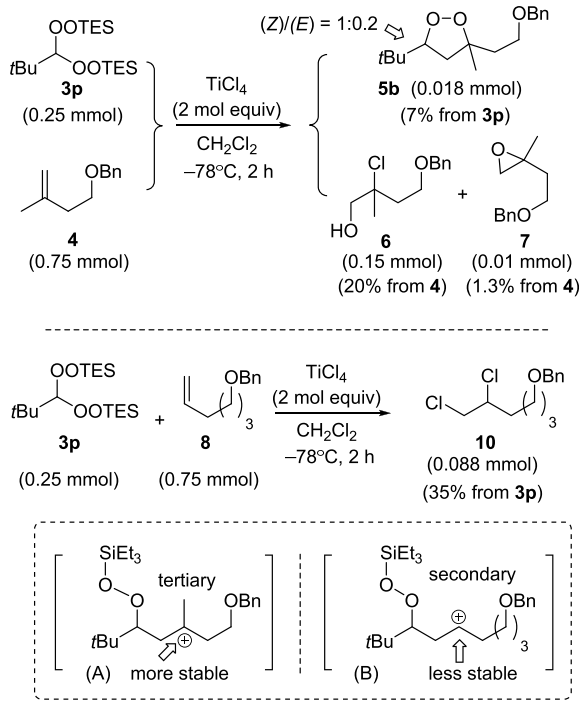
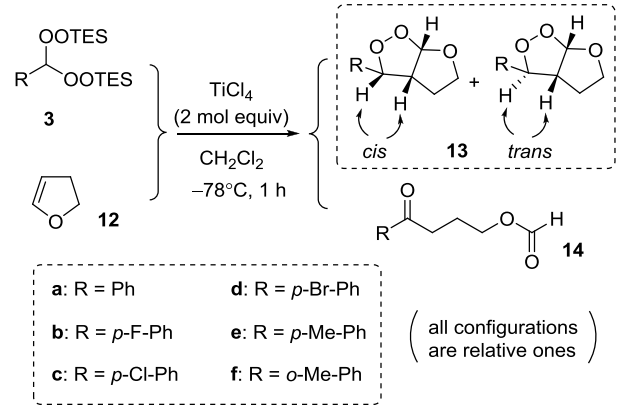
any detectable amounts of cycloaddition product (with the only isolable product being dichloride **10**), most likely because the lifetime of the carbocation B in Scheme 4 (bottom right) was not long enough to allow for the species to adopt a suitable conformation to complete the final ring closure.

Scheme 4. Reaction of 3p with 4 or 8



The third type of alkene we examined was **12**, one of the 1,2-disubstituted ethylenes that had been shown[26] to react smoothly with *gem*-dihydroperoxy substrates derived from ketones. The initial test using **3a** (with R = Ph) as the peroxy substrate under the standard conditions of this work (i.e., 2 mol equiv of $TiCl_4$, CH_2Cl_2, −78 °C)[35] gave a mixture containing three major components, which were very difficult to separate from one another. Similar results were also observed with **3b–f** (Scheme 5). However, after repeated chromatographic purification, we managed to obtain *cis*-**13a–f** (slightly less polar than the corresponding *trans* isomers) and **14a–e** (no **14f** was observed), which made it possible to acquire clean ^1H and ^{13}C NMR of these compounds. In the case of *cis*-**13a**, even the X-ray structure[36] was successfully obtained, which allowed us to assign the *cis* configuration to **13a** beyond all doubt. The relative configurations of *cis*-**13b–f** were subsequently assigned by comparison of their ^1H and ^{13}C NMR spectra with that of *cis*-**13a**.

Scheme 5. Reaction of 3a-f with 12



With the aid of the spectroscopic data of pure *cis*-**13a–f** and **14a–e**, the "extra" signals in the NMR of the mixture of **13** and **14** in each reaction could be readily recognized; the identity of the *trans*-isomer in each case was thus established and the yield of **14a–e** (10–20%) could be estimated from the ^1H NMR of the mixture.

Later, by chance, we noticed that the cleavage products **14a–e** were not present in the crude product mixtures before chromatographic purification; they appeared only after chromatography. Also, the ratio of *cis*-**13**/*trans*-**13** also changed from 1:1 to ∼2.8:1 after chromatography (except for **13f**, in which case no change in *cis*-**13f**/*trans*-**13f** was observed after chromatography and no **14f** could be detected). Apparently, *trans*-**13a–e** were more labile (than *cis*-isomers) to decomposition on silica gel. In addition, generation of **14** might be avoidable if purification was performed under milder conditions. Indeed, when chromatography was performed at lower temperatures (−20 to −30 °C, cf. the Supporting Information for the setup), generation of **14** was greatly suppressed and 1:1 *cis*-**13a-f**/*trans*-**13a-f** could be obtained in substantially raised yields (Table 7).

Table 7. Reaction of 3a-f with 12 (for Structures, cf. Scheme 5)[a]

entry	substrate	products (total yield of the 1:1 mixture)
1	**3a**	1:1 of *cis*-**13a** and *trans*-**13a** (81%)
2	**3b**	1:1 of *cis*-**13b** and *trans*-**13b** (68%)
3	**3c**	1:1 of *cis*-**13c** and *trans* **13c** (73%)
4	**3d**	1:1 of *cis*-**13d** and *trans*-**13d** (65%)
5	**3e**	1:1 of *cis*-**13e** and *trans*-**13e** (76%)
6	**3f**	1:1 of *cis*-**13f** and *trans*-**13f** (80%)

[a]All experiments were performed in CH_2Cl_2 at −78 °C for 1 h using 2 mol equiv (with respect to **3**) of $TiCl_4$ and 3 mol equiv (with respect to **3**) of **12**.

The reactions of **12** with **3g**, **3h**, **3i**, and **3k** all led to rather complex mixtures. Although in these cases, the peroxycarbenium cycloaddition products were likely present, the quantity was too small to allow for isolation of pure samples. Aliphatic substrate **3l** failed to give any isolable products in reaction with **12**; no obvious spots of substantial intensity could be seen on TLC, and the ^1H NMR spectra of the crude product mixture were rather complex, with the only identifiable component being aldehyde **1l**.

CONCLUSIONS

The long-observed yet still not understood resistance of aliphatic hydroxyhydroperoxides to further reaction with H_2O_2 has been explored, and a highly effective protocol (which shows good substrate scope/functional group compatibility and completely avoids the inconveniences caused by the tedious preparation of magnetic nanoparticle catalyst, or purchasing, storage, and use of hazardous high-concentration H_2O_2) for conversion of aliphatic aldehydes into corresponding *gem*-dihydroperoxides has been developed; the up-until-now challenging transformation thus becomes readily achievable. Full decomposition of primary *gem*-dihydroperoxides

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during silyl protection under the well-established conditions, a totally unexpected and frustrating problem, was solved by using 2,6-lutidine instead of imidazole as the base; an array of TES-protected primary *gem*-dihydroperoxides was thus readily prepared. Useful knowledge and techniques of handling such unstable species were also gained. The peroxycarbenium [3 + 2] cycloaddition reaction of the silyl-protected primary *gem*-dihydroperoxy substrates with alkenes was then examined for the first time, using three alkenes of different structural types, including a non-silylated monosubstituted ethylene (which to date has never been examined in such reactions). Aromatic substrates normally underwent the [3 + 2] cycloaddition and afforded 1,2-dioxolanes smoothly but the aliphatic ones generally failed to give any cycloaddition products. All the results, including the unexpected formation of chlorohydrin **6** and 1,2-dihydrochloride **10**, revealed some so far unknown facets of the peroxycarbenium [3 + 2] cycloaddition; many mechanistic insights into the cycloaddition reaction were also gained.

EXPERIMENTAL SECTION

Safety Warning. Although no explosions were experienced in this work, generally speaking, organic peroxides are potentially hazardous compounds and must be handled with great care: Avoid direct exposure to strong heat or light, mechanical shock etc. A safety shield should be used for all operations involving H_2O_2.

Preparation of Ethereal H_2O_2.[37] NaCl (47 g) was added to commercially available 30% aq H_2O_2 (150 mL). The mixture was stirred at ambient temperature for 20 min (when most of the NaCl was dissolved) and then allowed to stand for 5 min to give the H_2O_2 stock solution for the following extraction with Et_2O. A portion of the H_2O_2 stock solution (the supernatant, 50 mL) was transferred into a separatory funnel containing Et_2O (150 mL). The funnel was shaken several times and then allowed to stand. The lower "muddy phase" (containing undissolved NaCl) was drained through the stopcock, and another portion of the above H_2O_2 stock solution (50 mL) was charged into the funnel. The process was repeated three times (i.e., three portions of the H_2O_2 stock solution, 50 mL each, were extracted in turn with the same 150 mL volume of Et_2O). The ethereal phase was then dried over anhydrous $MgSO_4$ (6 g) at ambient temperature with stirring overnight. The supernatant (with the H_2O_2 concentration being ~ 1 M) was then used in the dihydroperoxidation.

Concentration of Ethereal H_2O_2. The ethereal H_2O_2 prepared above was placed in a round-bottom flask (with the desired end volume position marked beforehand) equipped with a rubber stopper and a short needle as the vent. N_2 was bubbled slowly into the solution through a long needle with the tip inserted into the solution until the total volume was reduced to the desired value (e.g., from the initial 50 mL to 10 mL in the case of five-fold concentration). It normally took 1−2 h for vaporizing ~40 mL of Et_2O when the ambient temperature was 20−25 °C.

*(Dihydroperoxymethyl)Benzene (**2a**): $MoO_2(acac)_2$-Catalyzed Conversion of Benzaldehyde **1a** into **2a** ($MoO_2(acac)_2$ Typical Procedure 1 Using Five-fold Concentrated H_2O_2).* A (yellowish transparent) solution of benzaldehyde **1a** (106 mg, 1 mmol) and $MoO_2(acac)_2$ (16.3 mg, 0.05 mmol) in ethereal H_2O_2 (five-fold concentrated, 5 mL) was stirred at ambient temperature for 18 h. The mixture was diluted with Et_2O (10 mL) and washed with water (5 mL). The aqueous layer was back-extracted with Et_2O (10 mL × 2). The combined organic layers were washed with water (5 mL) and brine (5 mL) and dried over anhydrous Na_2SO_4. Removal of the drying agent by filtration and the solvent by rotary evaporation left a crude oil, which was purified by column chromatography (3:1 PE/EtOAc, R_f = 0.3) on silica gel to give the known[5a] **2a** as a colorless oil (117 mg, 0.75 mmol, 75% from **1a**). Data for **2a**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.49 (br s, 2H), 7.45−7.35 (m, 5H), 6.32 (s, 1H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 132.4, 130.0, 128.7, 127.1, 110.2.

*1-(Dihydroperoxymethyl)-4-fluorobenzene (**2b**): PMA-Catalyzed Conversion of **1b** into **2b** (PMA General Procedure).* A (yellowish transparent) solution of **1b** (0.43 mL, 4.0 mmol) and PMA (29 mg, 0.016 mmol, 0.4 mol % with respect to **1b**) in ethereal H_2O_2 (not concentrated, 40 mL) was stirred at ambient temperature for 17 h (when TLC showed full consumption of the starting **1b**). To the mixture were added EtOAc (20 mL) and water (10 mL). The phases were separated. The aqueous layer was back-extracted with EtOAc (20 mL × 2). The combined organic layers were washed with water (5 mL × 2) and brine (10 mL) and dried over anhydrous Na_2SO_4. Filtration and rotary evaporation left a crude oil, which was purified by column chromatography (3:1 PE/EtOAc, R_f = 0.2) on silica gel to give **2b**[11,15,16] as a white solid (557 mg, 3.2 mmol, 80% from **1b**). Data for **2b**: M.p. 42−44 °C. (lit.[16] M.p. 110−112 °C). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.16 (br s, 2H), 7.44−7.39 (m, 2H), 7.09−7.03 (m, 2H), 6.30 (s, 1H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 164.6, 162.6, 129.24, 129.17, 128.39, 128.36, 115.8, 115.7, 109.7; FT-IR (KBr) 3277, 3145, 2946, 2754, 1612, 1600, 1513, 1407, 1392, 1351, 1321, 1247, 1160, 1047, 1014, 987, 858, 830, 798 cm^{-1}; MS (ESI) *m/z*: 219.05 ($[M + HCOO]^-$); HRMS (ESI) *m/z*: $[M - H]^-$ calcd. for $C_7H_6FO_4$ 173.0256; found 173.0258.

*1-Chloro-4-(dihydroperoxymethyl)benzene (**2c**): $MoO_2(acac)_2$-Catalyzed Conversion of **1c** into **2c** ($MoO_2(acac)_2$ Typical Procedure 2 Using 10-Fold Concentrated H_2O_2).* A (yellowish transparent) solution of **1c** (140.5 mg, 1 mmol) and $MoO_2(acac)_2$ (33 mg, 0.1 mmol) in ethereal H_2O_2 (10-fold concentrated, 5 mL) was stirred at ambient temperature for 38 h. The mixture was diluted with Et_2O (10 mL) and washed with water (5 mL). The aqueous layer was back-extracted with Et_2O (10 mL × 2). The combined organic layers were washed with water (5 mL) and brine (5 mL) and dried over anhydrous Na_2SO_4. Removal of the drying agent by filtration and the solvent by rotary evaporation left a crude oil, which was purified by column chromatography (5:1 to 2:1 PE/EtOAc; 3:1 PE/EtOAc R_f = 0.2) on silica gel to give the known[8a] **2c** as a white solid (111 mg, 0.58 mmol, 58% from **1c**) along with recovered **1c** (28 mg, 0.2 mmol). M.p. 71−73 °C (lit.[8a] M.p. 69−71 °C). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.99 (br s, 2H), 7.37 (s, 4H), 6.29 (s, 1H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 136.0, 130.9, 129.0, 128.6, 109.5.

*1-(Dihydroperoxymethyl)-4-methoxybenzene (**2h**): $MoO_2(acac)_2$-Catalyzed Conversion of **1h** into **2h** ($MoO_2(acac)_2$ Typical Procedure 3 Using Three-Fold Concentrated H_2O_2).* A (yellowish transparent) solution of **1h** (136 mg, 1 mmol) and $MoO_2(acac)_2$ (16.3 mg, 0.05 mmol) in ethereal H_2O_2 (three-fold concentrated, 5 mL) was stirred at ambient temperature for 6 h. The mixture was diluted with Et_2O (10 mL) and washed with water (5 mL). The aqueous layer was back-extracted with Et_2O (10 mL × 2). The combined organic layers were washed with water (5 mL) and brine (5 mL) and dried over anhydrous Na_2SO_4. Removal of the drying agent by filtration and the solvent by rotary evaporation left a crude oil, which was purified by column chromatography (3:1 PE/EtOAc, R_f = 0.3) on silica gel to give the known[3a] **2h** (unstable, partially decomposed on standing for 2 h at ambient temperature) as a yellowish oil (127 mg, 0.68 mmol, 68% from **1h**). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.15 (br s, 2H), 7.36 (d, J = 8.9 Hz, 2H), 6.90 (d, J = 8.8 Hz, 2H), 6.29 (s, 1H), 3.81 (s, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 160.8, 128.6, 124.6, 114.1, 110.3, 55.5.

*(Hydroperoxy(methoxy)methyl)benzene (**2a′**): $MoO_2(acac)_2$ catalyzed conversion of **1a′** into **2a′**.* Compound **2a′**[5c] (a colorless oil, 102 mg, 0.66 mmol, 66% from **1a′**) was obtained using "Typical procedure 1" given above (except for using **1a′** to replace **1a**) with the reaction time being 2 h and chromatography eluent being 8:1 PE/EtOAc (10:1 PE/EtOAc R_f = 0.4). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.19 (br s, 1H), 7.50−7.46 (m, 2H), 7.42−7.36 (m, 3H), 5.74 (s, 1H), 3.64 (s, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 135.5, 129.4, 128.5, 127.1, 107.8, 56.2.

*1-(Dihydroperoxymethyl)-4-fluorobenzene (**2b**).* Experiment A (using PMA): performed using the "PMA General procedure" given

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above, affording **2b** (557 mg, 3.2 mmol, 80% from **1b**). Data for **2b**: cf. above. Experiment B (using $MoO_2(acac)_2$): performed using "$MoO_2(acac)_2$ Typical procedure 1" given above (except for using **1b** to replace **1a**) with the reaction time being 28 h, affording **2b** (135 mg, 0.77 mmol, 77% from **1b**).

*1-Chloro-4-(dihydroperoxymethyl)benzene (**2c**).* Experiment A (using PMA): performed using the "PMA General procedure" above but with **1c** to replace **1b**, the amount of PMA = 1.5 mol %, and the reaction time being 20 h, affording **2c** (1.037 g, 5.44 mmol, 76% from **1c**). Data for **2c**: cf. above. Experiment B (using $MoO_2(acac)_2$): cf. the $MoO_2(acac)_2$ Typical procedure 2 given above, with the reaction time being 38 h, affording **2c** (111 mg, 0.58 mmol, 58% from **1c**).

*1-Bromo-4-(dihydroperoxymethyl)benzene (**2d**).* Experiment A (using PMA): performed using the "PMA General procedure" above but with **1d** to replace **1b**, the amount of PMA = 1.5 mol %, and the reaction time being 21 h, affording **2d** (1.152 g, 4.90 mmol, 75% from **1d**). Data for **2d**[11,15,16] (a white solid, chromatography using 3:1 PE/EtOAc, R_f = 0.3): M.p. 85−87 °C (lit.[11] M.p. 88−90 °C). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.89 (br s, 2H), 7.53 (d, J = 8.5 Hz, 2H), 7.32 (d, J = 8.5 Hz, 2H), 6.27 (s, 1H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 131.9, 131.5, 128.9, 124.3, 109.5. FT-IR (KBr) 3263, 2944, 2751, 1592, 1571, 1487, 1437, 1399, 1341, 1315, 1298, 071, 1043, 1013, 978, 917, 869, 820, 796, 736, 690 cm^{-1}; MS (ESI) m/z: 278.90 ([M + HCOO]$^-$), 280.80 ([M + HCOO]$^-$); HRMS (ESI) m/z: [M + Na]$^+$ calcd. for $C_7H_7BrNaO_4$ 256.9420; found 256.9422. Experiment B (using $MoO_2(acac)_2$): performed using $MoO_2(acac)_2$ Typical procedure 2 given above (except for using **1d** to replace **1c**) with the reaction time being 38 h, affording **2d** (155 mg, 0.66 mmol, 66% from **1d**) along with recovered unreacted **1d** (28 mg, 0.15 mmol).

*1-(Dihydroperoxymethyl)-4-methylbenzene (**2e**).* Experiment A (using PMA): performed using the "PMA General procedure" above but with **1e** to replace **1b**, and the reaction time being 12 h, affording the known[5c] **2e** (279 mg, 1.64 mmol, 82% from **1e**). Data for **2e** (a white solid, chromatography using 3:1 PE/EtOAc, R_f = 0.3): M.p. 51−53 °C; (lit.[5c] M.p. 55−56 °C). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.81 (br s, 2H), 7.33 (d, J = 8.1 Hz, 2H), 7.20 (d, J = 7.8 Hz, 2H), 6.31 (s, 1H), 2.36 (s, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 140.1, 129.4, 127.1, 110.4, 21.5. Experiment B (using $MoO_2(acac)_2$): performed using $MoO_2(acac)_2$ Typical procedure 1 given above (except for using **1e** to replace **1a**) with the reaction time being 12 h, affording **2e** (158 mg, 0.93 mmol, 93% from **1e**).

*1-(Dihydroperoxymethyl)-2-methylbenzene (**2f**).* Experiment A (using PMA): performed using the "PMA General procedure" above but with **1f** to replace **1b**, and the reaction time being 13 h, affording **2f** (449 mg, 2.64 mmol, 88% from **1f**). Data for **2f** (a colorless oil, chromatography using 3:1 PE/EtOAc, R_f = 0.3): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.91 (br s, 2H), 7.40−7.37 (m, 1H), 7.31−7.27 (m, 1H), 7.22−7.17 (m, 2H), 6.50 (s, 1H), 2.43 (s, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 136.6, 130.9, 130.5130.0, 127.0, 126.0, 109.2, 19.3; FT-IR (film of a concd solution in CH_2Cl_2) 3283, 3029, 2961, 2926, 2852, 1604, 1489, 1462, 1384, 1289, 1215, 1035, 988 cm^{-1}; MS (ESI) m/z: 214.95 ([M + HCOO]$^-$); HRMS (ESI) m/z: [M + Na]$^+$ calcd. for $C_8H_{10}O_4Na$ 193.0471; found 193.0465. Experiment B (using $MoO_2(acac)_2$): performed using $MoO_2(acac)_2$ Typical procedure 1 given above (except for using **1f** to replace **1a**) with the reaction time being 11 h, affording **2f** (160 mg, 0.94 mmol, 94% from **1f**).

*1-(Benzyloxy)-2-(dihydroperoxymethyl)benzene (**2g**).* Experiment A (using PMA): performed using the "PMA General procedure" above but with **1g** to replace **1b**, and the reaction time being 9 h, affording **2g** (682 mg, 2.60 mmol, 87% from **1g**). Data for **2g** (a colorless sticky oil, chromatography using 3:1 PE/EtOAc, R_f = 0.3): ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.31 (br s, 2H), 7.46−7.42 (m, 2H), 7.42−7.37 (m, 3H), 7.36−7.31 (m, 2H), 6.99−6.94 (m, 2H), 6.74 (s, 1H), 5.12 (s, 2H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 155.9, 136.6, 131.3, 128.8, 128.3, 128.2, 127.5, 121.2, 120.9, 112.6, 106.3, 70.7; FT-IR (film of a concd solution in CH_2Cl_2) 3420, 3058, 3032, 2923, 2860, 1602, 1495, 1452, 1382, 1294.67, 1250, 1024, 754, 697 cm^{-1}; MS (ESI) m/z: 285.05 ([M + Na]$^+$); HRMS (ESI) m/z: [M + Na]$^+$ calcd. for $C_{14}H_{14}O_5Na$ 285.0733; found 285.0737. Experiment B (using $MoO_2(acac)_2$): performed using $MoO_2(acac)_2$ Typical procedure 3 given above (except for using **1g** to replace **1h**) with the reaction time being 9 h, affording **2g** (220 mg, 0.84 mmol, 84% from **1g**).

*1-(Dihydroperoxymethyl)-4-methoxybenzene (**2h**).* Experiment A (using PMA): performed using the "PMA General procedure" above but with **1h** to replace **1b**, and the reaction time being 14 h, affording **2h** (223 mg, 1.20 mmol, 40% from **1h**). Data for **2h**: cf. the above. Experiment B (using $MoO_2(acac)_2$): cf. the above "$MoO_2(acac)_2$ Typical procedure 3".

*1-(Benzyloxy)-4-(dihydroperoxymethyl)benzene (**2i**).* Experiment A (using PMA): performed using the "PMA General procedure" above but with **1i** to replace **1b**, and the reaction time being 6 h, affording **2i** (485 mg, 1.85 mmol, 74% from **1i**). Data for **2i** (a white solid, chromatography using 2:1 PE/EtOAc; 3:1 PE/EtOAc R_f = 0.3): M.p. 91−92 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.74 (br s, 2H), 7.43−7.31 (m, 7H), 7.00−6.97 (m, 2H), 6.29 (s, 1H), 5.08 (s, 2H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 160.0, 136.7, 128.8, 128.7, 128.2, 127.6, 124.8, 115.0, 110.3, 70.2; FT-IR (KBr) 3261, 3047, 2908, 2867, 1676, 1609, 1585, 1513, 1454, 1432, 1414, 1379, 1318, 1301, 1250, 1173, 1029, 1016, 918, 863, 814, 773, 743, 698 cm^{-1}; MS (ESI) m/z: 285.05 ([M + Na]$^+$); HRMS (ESI) m/z: [M + Na]$^+$ calcd. for $C_{14}H_{14}O_5Na$ 285.0733; found 285.0741. Experiment B (using $MoO_2(acac)_2$): performed using $MoO_2(acac)_2$ Typical procedure 3 given above (except for using **1i** to replace **1h**) with the reaction time being 8 h, affording **2i** (197 mg, 0.75 mmol, 75% from **1i**).

*4-(Dihydroperoxymethyl)phenyl acetate (**2j**).* Experiment A (using PMA): performed using the "PMA General procedure" above but with **1j** to replace **1b**, and the reaction time being 23 h, affording **2j** (323 mg, 1.51 mmol, 50% from **1j**). Data for **2j** (a white solid, chromatography using 4:1 to 2:1 PE/EtOAc, 2:1 PE/EtOAc R_f = 0.2): M.p. 95−98 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.92 (br s, 2H), 7.45 (d, J = 8.7 Hz, 2H), 7.12 (d, J = 8.7 Hz, 2H), 6.27 (s, 1H), 2.31 (s, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 170.5, 151.4, 130.7, 128.6, 121.8, 109.3, 21.3; FT-IR (KBr) 3424, 3351, 1714, 1599, 1507, 1417, 1379, 1338, 1313, 1299, 1257, 1197, 1163, 1052, 1017, 990, 964, 936, 868, 852, 780, 691, 661 cm^{-1}; MS (ESI) m/z: 259.05 ([M + HCOO]$^-$); HRMS (ESI) m/z: [M + Na]$^+$ calcd. for $C_9H_{10}O_6Na$ 237.0370; found 237.0373. Experiment B (using $MoO_2(acac)_2$): performed using $MoO_2(acac)_2$ Typical procedure 1 given above (except for **1j** to replace **1a**) with the reaction time being 27 h, affording **2j** (126 mg, 0.65 mmol, 65% from **1j**).

*1-(Dihydroperoxymethyl)naphthalene (**2k**).* Experiment A (using PMA): performed using the "PMA General procedure" above but with **1k** to replace **1b**, and the reaction time being 13 h, affording **2k** (280 mg, 1.36 mmol, 68% from **1k**). Data for **2k** (an orange oil, chromatography using 3:1 PE/EtOAc, R_f = 0.3): ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.26 (br s, 2H), 8.14 (d, J = 8.4 Hz, 1H), 7.89 (dd, J = 10.6, 8.2 Hz, 2H), 7.63 (d, J = 7.2, 1H), 7.59−7.54 (m, 1H), 7.54−7.50 (m, 1H), 7.45 (dd, J = 8.2, 7.2 Hz, 1H), 6.96 (s, 1H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 133.8, 130.8, 130.5, 128.9, 127.9, 127.1, 126.2, 125.8, 125.0, 123.6, 109.4; FT-IR (film of a concd solution in CH_2Cl_2) 3258, 3054, 2824, 1671, 1580, 1512, 1373, 1260, 1166, 1061, 1008, 984, 800, 786, 776 cm^{-1}; MS (ESI) m/z: 229.00 ([M + Na]$^+$); HRMS (ESI) m/z: [M + Na]$^+$ calcd. For $C_{11}H_{10}O_4Na$ 229.0471; found 229.0471. Experiment B (using $MoO_2(acac)_2$): performed using $MoO_2(acac)_2$ Typical procedure 1 given above (except for using **1k** to replace **1a**) with the reaction time being 14 h, affording **2k** (175 mg, 0.85 mmol, 85% from **1k**).

*(Hydroperoxy(methoxy)methyl)benzene (**2a′**): PMA-Catalyzed Conversion of **1a′** into **2a** and **2a′**.* A (yellowish transparent) solution of **1a′** (0.90 mL, 6.0 mmol) and PMA (45 mg, 0.025 mmol, 0.4 mol % with respect to **1a′**) in ethereal H_2O_2 (not concentrated, 60 mL) was stirred at ambient temperature for 12 h (when TLC showed full consumption of the starting **1a′**). To the mixture were added EtOAc (20 mL) and water (15 mL). The phases were separated. The aqueous layer was back-extracted with EtOAc (20 mL × 2). The combined organic layers were washed with water (10 mL × 2) and brine (10 mL) and dried over anhydrous Na_2SO_4. Filtration and

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rotary evaporation left a crude oil, which was purified by column chromatography (first 8:1 then 3:1 PE/EtOAc; 10:1 PE/EtOAc R_f = 0.4) on silica gel to give first **2a′** as a colorless oil (80 mg, 0.52 mmol, 9% from **1a′**) and then **2a** as a colorless oil (712 mg, 4.56 mmol, 76% from **1a′**). Data for **2a′** and **2a**: cf. the above.

*(3,3-Dihydroperoxypropyl)benzene (**2l**): PMA-Catalyzed Conversion of **1l** into **2l** (General Procedure for Aliphatic Aldehydes).* A (yellowish transparent) mixture of **1l** (268 mg, 2.0 mmol), PMA (73 mg, 0.04 mmol, 2 mol % with respect to **1l**) and anhydrous $MgSO_4$ (361 mg, 3.0 mmol, 1.5 mol equiv. with respect to **1l**) in three-fold concentrated ethereal H_2O_2 (20 mL) was stirred at ambient temperature for ∼30 h (when TLC showed full consumption of the starting **1l**). Solids were filtered off through Celite (washing with EtOAc (10 mL × 3)). To the filtrate/washings were added EtOAc (10 mL) and water (10 mL). The phases were separated. The aqueous layer was back-extracted with EtOAc (20 mL × 2). The combined organic layers were washed with water (10 mL) and brine (10 mL) and dried over anhydrous Na_2SO_4. Filtration and rotary evaporation left a crude oil, which was purified by column chromatography (3:1 PE/EtOAc, R_f = 0.2) on silica gel to give **2l** as a colorless oil (258 mg, 1.4 mmol, 70% from **1l**). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.39 (br s, 2H), 7.32−7.28 (m, 2H), 7.24−7.19 (m, 3H), 5.27 (t, J = 6.2 Hz, 1H), 2.80−2.75 (m, 2H), 2.09−2.03 (m, 2H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 140.6, 128.7, 128.6, 126.4, 110.5, 30.9, 30.2; FT-IR (film of a concd solution in CH_2Cl_2) 3283, 3084, 3063, 3028, 2970, 2932, 2863, 1603, 1497, 1454, 1369, 1188, 1102, 993, 750, 700 cm^{-1}. MS (ESI) m/z: 207.10 ([M + Na]$^+$); HRMS (ESI) m/z: [M − H]$^-$ calcd. for $C_9H_{11}O_4$ 183.0663; found 183.0660.

Synthesis of 2m−u. These aliphatic *gem*-dihydroperoxides were all prepared using the "General procedure for aliphatic aldehydes" given above (with **1m−u** to replace **1l**, respectively, and the corresponding reaction time indicated in each individual case below).

Data for 1,1-dihydroperoxybutane (**2m**,[20] a colorless oil, 217 mg, 1.78 mmol, 81% from **1m**; reaction time = 24 h; chromatography using 4:1 PE/EtOAc; 3:1 PE/EtOAc R_f = 0.3): ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.20 (br s, 2H), 5.31 (t, J = 6.1 Hz, 1H), 1.73−1.68 (m, 2H), 1.52−1.44 (m, 1H), 0.95 (t, J = 7.4 Hz, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 111.3, 30.6, 18.2, 13.9; FT-IR (film of a concd solution in CH_2Cl_2) 3280, 2965, 2937, 2876, 1625, 1466, 1380, 1369, 1158, 1140, 1119, 1073, 1041, 980, 814 cm^{-1}. MS (ESI) m/z: 167.10 ([M + HCOO]$^-$); HRMS (ESI) m/z: [M + 2Na − H]$^+$ calcd. for $C_4H_9Na_2O_4$ 167.0291; found 167.0295.

Data for 1,1-dihydroperoxyoctane (**2n**,[20] a colorless oil, 300 mg, 1.68 mmol, 84% from **1n**; reaction time = 26 h; chromatography using 3:1 PE/EtOAc, R_f = 0.3): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.95 (br s, 2H), 5.30 (t, J = 6.1 Hz, 1H), 1.74−1.67 (m, 2H), 1.48−1.40 (m, 2H), 1.35−1.22 (m, 8H), 0.91−0.85 (m, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 111.6, 31.8, 29.3, 29.2, 28.8, 24.9, 22.8, 14.2; FT-IR (film of a concd solution in CH_2Cl_2) 3284, 2956, 2925, 2856, 1624, 1467, 1377, 1125, 1084, 971, 812, 723, 668 cm^{-1}. MS (ESI) m/z: 223.20 ([M + HCOO]$^-$); HRMS (ESI) m/z: [M + 2Na − H]$^+$ calcd. for $C_8H_{17}Na_2O_4$ 223.0917; found 223.0919.

Data for 1,1-dihydroperoxy-2-methylpropane (**2o**,[20] a white solid which melt at ambient temperature, 190 mg, 1.56 mmol, 78% from **1o**; reaction time = 24 h; chromatography using 4:1 PE/EtOAc; 3:1 PE/EtOAc R_f = 0.3): ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.36 (br s, 2H), 4.99 (d, J = 7.7 Hz, 1H), 2.15−2.04 (m, 1H), 1.02 (d, J = 6.9 Hz, 6H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 115.7, 28.7, 18.3; FT-IR (film of a concd solution in CH_2Cl_2) 3284, 2969, 2937, 2879, 1628, 1473, 1391, 1371, 1330, 1270, 1127, 1030, 1008, 959, 854 cm^{-1}. MS (ESI) m/z: 167.10 ([M + HCOO]$^-$); HRMS (ESI) m/z: [M + 2Na − H]$^+$ calcd. for $C_4H_9Na_2O_4$ 167.0291; found 167.0294.

Data for 1,1-dihydroperoxy-2,2-dimethylpropane (**2p**,[20] a white solid, 173 mg, 1.0 mmol, 50% from **1p**; reaction time = 36 h; chromatography using 4:1 PE/EtOAc; 3:1 PE/EtOAc R_f = 0.3): M.p. 59−61 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.82 (br s, 2H), 5.18 (s, 1H), 1.00 (s, 9H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 117.3, 35.7, 25.7; FT-IR (KBr) 3216, 2975, 2906, 2872, 2795, 1482, 1457, 1397, 1367, 1348, 130, 1050, 1007, 983, 953, 876 cm^{-1}. MS (ESI) m/z: 181.05 ([M + HCOO]$^-$); HRMS (ESI) m/z: [M − H]$^-$ calcd. for $C_5H_{11}O_4$ 135.0663; found 135.0662.

Data for 3-(dihydroperoxymethyl)heptane (**2q**, a colorless oil, 324 mg, 1.82 mmol, 91% from **1q**; reaction time = 26 h; chromatography using 5:1 PE/EtOAc; 3:1 PE/EtOAc R_f = 0.3): ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.00 (br s, 2H), 5.26 (d, J = 6.8 Hz, 1H), 1.81−1.73 (m, 1H), 1.58−1.45 (m, 2H), 1.45−1.39 (m, 1H), 1.39−1.33 (m, 1H), 1.33−1.23 (m, 4H), 0.93−0.86 (m, 6H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 113.8, 39.9, 28.9, 28.3, 23.1, 21.9, 14.2, 11.0; FT-IR (film of a concd solution in CH_2Cl_2) 3365, 2960, 2935, 2873, 1621, 1464, 1381, 1247, 1155, 1124, 1038, 1005, 966, 814 cm^{-1}. MS (ESI) m/z: 223.15 ([M + HCOO]$^-$); HRMS (ESI) m/z: [M + 2Na − H]$^+$ calcd. for $C_8H_{17}Na_2O_4$ 223.0917; found 223.0920.

Data for ((4,4-dihydroperoxybutoxy)methyl)benzene (**2r**, a colorless oil, 190 mg, 0.83 mmol, 83% from **1r**; reaction time = 22 h; chromatography using 3:1 PE/EtOAc, R_f = 0.3): ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.15 (br s, 2H), 7.38−7.28 (m, 5H), 5.29 (t, J = 6.1 Hz, 1H), 4.53 (s, 2H), 3.56 (t, J = 5.9 Hz, 2H), 1.88−1.82(m, 2H), 1.82−1.75 (m, 2H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 137.8, 128.7, 128.1, 128.0, 111.0, 73.3, 69.8, 25.3, 24.6; FT-IR (film of a concd solution in CH_2Cl_2) 3263, 3087, 3062, 3031, 2941, 2865, 1496, 1454, 1363, 1208, 1090, 1072, 1027, 988, 813, 740, 699 cm^{-1}. MS (ESI) m/z: 251.05 ([M + Na]$^+$); HRMS (ESI) m/z: [M + Na]$^+$ calcd. for $C_{11}H_{16}NaO_5$ 251.0890; found 251.0892.

Data for *tert*-butyl(4,4-dihydroperoxybutoxy)diphenylsilane (**2s**, a colorless oil, 271 mg, 0.72 mmol, 72% from **1s**; reaction time = 25 h; chromatography using 3:1 PE/EtOAc, R_f = 0.2): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.76 (br s, 2H), 7.69−7.63 (m, 4H), 7.47−7.35 (m, 6H), 5.31 (t, J = 6.2 Hz, 1H), 3.73 (t, J = 6.0 Hz, 2H), 1.87 (dt, J = 7.9, 6.4 Hz, 2H), 1.73−1.65 (m, 2H), 1.05 (s, 9H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 135.7, 133.6, 129.9, 127.9, 111.2, 63.4, 27.5, 27.0, 25.0, 19.3; FT-IR (film of a concd solution in CH_2Cl_2) 3335, 3071, 3045, 2957, 2931, 2890, 2858, 1472, 1428, 1390, 1362, 1111, 1007, 994, 823, 740, 702, 688, 614, 506 cm^{-1}. MS (ESI) m/z: 399.45 ([M + Na]$^+$); HRMS (ESI) m/z: [M + Na]$^+$ calcd. for $C_{20}H_{28}NaO_5Si$ 399.1597; found 399.1598.

Data for 5,5-dihydroperoxypent-1-ene (**2t**, a colorless oil, 174 mg, 1.3 mmol, 65% from **1t**; reaction time = 28 h; chromatography using 3:1 PE/EtOAc, R_f = 0.3): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.70 (br s, 2H), 5.81 (ddt, J = 16.9, 10.2, 6.7 Hz, 1H), 5.32 (t, J = 6.1 Hz, 1H), 5.09 (dq, J = 17.2, 1.7 Hz, 1H), 5.04 (dq, J = 10.3, 1.5 Hz, 1H), 2.26−2.18 (m, 2H), 1.86−1.79 (m, 2H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 137.0, 116.1, 110.9, 28.9, 27.9; FT-IR (film of a concd solution in CH_2Cl_2) 3272, 3081, 3003, 2978, 2941, 2856, 1642, 1448, 1419, 1367, 1216, 1129, 1080, 1050, 1019, 993, 916, 860, 816 cm^{-1}. MS (ESI) m/z: 179.00 ([M + HCOO]$^-$); HRMS (ESI) m/z: [M − H]$^-$ calcd. for $C_5H_9O_4$ 133.0506; found 133.0504.

Data for 6,6-dihydroperoxyhex-1-yne (**2u**, a colorless oil, 201 mg, 1.38 mmol, 69% from **1u**; reaction time = 27 h; chromatography using 3:1 PE/EtOAc, R_f = 0.3): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.81 (br s, 2H), 5.34 (t, J = 6.1 Hz, 1H), 2.26 (dt, J = 2.7, 6.9 Hz, 2H), 1.99 (t, J = 2.7 Hz, 1H), 1.90−1.84 (m, 2H), 1.73−1.65 (m, 2H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 110.9, 83.6, 69.3, 27.7, 23.6, 18.2; FT-IR (film of a concd solution in CH_2Cl_2) 3291, 2940, 2872, 1623, 1457, 1434, 1375, 1191, 1110, 1074, 969, 649 cm^{-1}. MS (ESI) m/z: 169.05 ([M + Na]$^+$); HRMS (ESI) m/z: [M + Na]$^+$ calcd. for $C_6H_{10}NaO_4$ 169.0471; found 169.0469.

*(Bis(triethylsilylperoxy)methyl)benzene (**3a**): Conversion of **2a** into **3a** (General Procedure for TES Protection).* To a solution of **2a** (650 mg, 4.16 mmol) in dry CH_2Cl_2 (40 mL) stirred in an ice-water bath under argon (balloon) were added 2,6-lutidine (1.45 mL, 12.48 mmol) and Et_3SiCl (1.75 mL, 10.4 mmol). After completion of the addition, the mixture was stirred at the same temperature for 2 h (when TLC showed full consumption of the starting **2a**). Ice-water-cooled CH_2Cl_2 (10 mL) was added followed by cold water (15 mL). Phases were separated. The aqueous layer was back-extracted with CH_2Cl_2 (15 mL × 2). The combined organic layers were quickly washed with brine (10 mL) and dried over anhydrous Na_2SO_4 for ∼ 20 min (to avoid decomposition). Filtration and rotary evaporation left a crude oil, which was purified immediately by flash column

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chromatography (with silica gel column height <10 cm; eluting with 50:1 PE/EtOAc as quickly as possible to avoid decomposition, R_f = 0.6) to give **3a** as a colorless oil (1.373 g, 3.57 mmol, 86% from **2a**). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42−7.38 (m, 2H), 7.37−7.34 (m, 3H), 6.13 (s, 1H), 0.98 (t, J = 7.9 Hz, 18H), 0.74−0.68 (m, 12H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 134.5, 129.4, 128.3, 127.5, 110.4, 6.83, 3.9 ppm; FT-IR (film of a concd solution in CH_2Cl_2) 3067, 3036, 2956, 2913, 2878, 1495, 1457, 1413, 1299, 1240, 1007, 974, 854, 789, 742 cm^{-1}; MS (ESI) m/z: 407.25 ([M + Na]$^+$); HRMS (ESI) m/z: [M + Na]$^+$ calcd. for $C_{19}H_{36}O_4NaSi_2$ 407.2044; found 407.2046.

*Conversion of **2b−u** into **3b−u**.* These compounds were synthesized using the "General procedure for TES protection" given above (with **2b−u** to replace **2a**, respectively, and the corresponding reaction time indicated in each individual case below).

Data for 1-(bis(triethylsilylperoxy)methyl)-4-fluorobenzene (**3b**, a colorless oil, 1.067 g, 2.65 mmol, 92% from **2b**; reaction time = 2 h; chromatography using 50:1 PE/EtOAc, R_f = 0.6): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41−7.36 (m, 2H), 7.06−7.01 (m, 2H), 6.09 (s, 1H), 0.98 (t, J = 8.0 Hz, 18H), 0.74−0.68 (m, 12H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 164.3, 162.4, 130.6, 130.5, 129.5, 129.4, 115.3, 115.2, 109.6, 6.8, 3.9; FT-IR (film of a concd solution in CH_2Cl_2) 2957, 2935, 2914, 2879, 1608, 1512, 1460, 1413, 1296, 1231, 1158, 1006, 829, 741 cm^{-1}; MS (ESI) m/z: 425.30 ([M + Na]$^+$); HRMS (ESI) m/z: [M + Na]$^+$ calcd. For $C_{19}H_{35}FO_4NaSi_2$ 425.1950; found 425.1954.

Data for 1-(bis(triethylsilylperoxy)methyl)-4-chlorobenzene (**3c**, a colorless oil, 368 mg, 0.88 mmol, 70% from **2c**; reaction time = 3 h; chromatography using 50:1 PE/EtOAc, R_f = 0.6): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36−7.31 (m, 4H), 6.08 (s, 1H), 0.98 (t, J = 8.0 Hz, 18H), 0.74−0.67 (m, 12H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 135.3, 133.1, 128.9, 128.5, 109.6, 6.8, 3.9; FT-IR (film of a concd solution in CH_2Cl_2) 2937, 2956, 2913, 2878, 1603, 1492, 1459, 1411, 1296, 1240, 1092, 1018, 1006, 974, 860, 818, 785, 742 cm^{-1}. MS (ESI) m/z: 441.20 ([M + Na]$^+$), 443.25 ([M + Na]$^+$); HRMS (ESI) m/z: [M + Na]$^+$ calcd. for $C_{19}H_{35}ClO_4NaSi_2$ 441.1655; found 441.1664.

Data for 1-(bis(triethylsilylperoxy)methyl)-4-bromobenzene (**3d**, a colorless oil, 450 mg, 0.97 mmol, 68% from **2d**; reaction time = 2 h; chromatography using 50:1 PE/EtOAc, R_f = 0.6): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50−7.48 (m, 2H), 7.29−7.27 (m, 2H), 6.06 (s, 1H), 0.97 (t, J = 7.9 Hz, 18H), 0.74−0.67 (m, 12H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 133.6, 131.5, 129.2, 123.6, 109.6, 6.8, 3.9; FT-IR (film of a concd solution in CH_2Cl_2) 2956, 2913, 2934, 2878, 1595, 1488, 1458.70, 1412, 1295, 1240, 1071, 1013, 860, 816, 769, 742 cm^{-1}. MS (ESI) m/z: 485.20 ([M + Na]$^+$) 487.20 ([M + Na]$^+$); HRMS (ESI) m/z: [M + Na]$^+$ calcd. for $C_{19}H_{35}BrO_4NaSi_2$ 485.1149; found 485.1153.

Data for 1-(bis(triethylsilylperoxy)methyl)-4-methylbenzene (**3e**, a colorless oil, 445 mg, 1.12 mmol, 86% from **2e**; reaction time = 2.5 h; chromatography using 50:1 PE/EtOAc, R_f = 0.6): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 (d, J = 8.1 Hz, 2H), 7.17 (d, J = 7.9 Hz, 2H), 6.11 (s, 1H), 2.36 (s, 3H), 0.99 (t, J = 7.9 Hz, 18H), 0.76−0.69 (m, 12H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 139.2, 131.6, 129.0, 127.4, 110.5, 21.5, 6.8, 3.9; FT-IR (film of a concd solution in CH_2Cl_2) 2955, 2935, 2914, 2878, 1619, 1517, 1460, 1414, 1303, 1240, 1020, 1006, 859, 812, 741 cm^{-1}. MS (ESI) m/z: 421.30 ([M + Na]$^+$); HRMS (ESI) m/z: [M + Na]$^+$ calcd. for $C_{20}H_{38}O_4NaSi_2$ 421.2201; found 421.2200.

Data for 1-(bis(triethylsilylperoxy)methyl)-2-methylbenzene (**3f**, a colorless oil, 804 mg, 2.02 mmol, 83% from **2f**; reaction time = 2.5 h; chromatography using 50:1 PE/EtOAc, R_f = 0.6): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 (d, J = 7.8 Hz, 1H), 7.24 (dd, J = 7.4, 1.5 Hz, 1H), 7.19−7.14 (m, 2H), 6.30 (s, 1H), 2.41 (s, 3H), 0.97 (t, J = 8.0 Hz, 18H), 0.73−0.66 (m, 12H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 136.4, 132.9, 130.6, 129.2, 127.8, 125.6, 109.2, 19.4, 6.8, 3.9; FT-IR (film of a concd solution in CH_2Cl_2) 3070, 3032, 2956, 2914, 2879, 1604, 1489, 1460, 1413, 1240, 1021, 1006, 974, 853, 789, 743 cm^{-1}. EMS (ESI) m/z: 421.20 ([M + Na]$^+$); HRMS (ESI) m/z: [M + Na]$^+$ calcd. for $C_{20}H_{38}O_4NaSi_2$ 421.2201; found 421.2208.

Data for 1-(benzyloxy)-2-(bis(triethylsilylperoxy)methyl)benzene (**3g**, a colorless oil, 567 mg, 1.16 mmol, 80% from **2g**; reaction time = 3 h; chromatography using 50:1 PE/EtOAc, R_f = 0.6): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.46−7.41 (m, 3H), 7.40−7.35 (m, 2H), 7.33−7.27 (m, 2H), 6.97−6.90 (m, 2H), 6.63 (s, 1H), 5.11 (s, 1H), 0.94 (t, J = 7.9 Hz, 18H), 0.71−0.62 (m, 12H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 155.8, 137.00, 130.5, 129.1, 128.6, 128.0, 127.4, 123.2, 120.5, 112.0, 105.3, 70.3, 6.8, 3.8; FT-IR (film of a concd solution in CH_2Cl_2) 3064, 3032, 2955, 2937, 2913, 2877.18, 1604, 1493, 1453, 1413, 1294, 1244, 1114, 1021, 974, 858, 841, 788, 740, 696 cm^{-1}. MS (ESI) m/z: 513.45 ([M + Na]$^+$); HRMS (ESI) m/z: [M + Na]$^+$ calcd. for $C_{26}H_{42}O_5NaSi_2$ 513.2463; found 513.2467.

Data for 1-(bis(triethylsilylperoxy)methyl)-4-methoxybenzene (**3h**, a colorless oil, 149 mg, 0.36 mmol, 53% from **2h**; reaction time = 2 h; chromatography using 50:1 PE/EtOAc, R_f = 0.6): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 (d, J = 8.4 Hz, 2H), 6.88 (d, J = 8.8 Hz, 2H), 6.08 (s, 1H), 3.81 (s, 3H), 0.98 (t, J = 7.9 Hz, 18H), 0.74−0.67 (m, 12H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 160.4, 128.9, 126.8, 113.7, 110.3, 55.4, 6.8, 3.9; FT-IR (film of a concd solution in CH_2Cl_2) 2956, 2935, 2913, 2878, 2836, 1697, 1613, 1514, 1460, 1414, 1302, 1252, 1174, 1037, 1019, 1006, 858, 826, 799, 787, 741 cm^{-1}. MS (ESI) m/z: 437.25 ([M + Na]$^+$); HRMS (ESI) m/z: [M + Na]$^+$ calcd. for $C_{20}H_{38}O_5NaSi_2$ 437.2150; found 437.2151.

Data for 1-(benzyloxy)-4-(bis(triethylsilylperoxy)methyl)benzene (**3i**, a colorless oil, 412 mg, 0.84 mmol, 74% from **2i**; reaction time = 3 h; chromatography using 50:1 PE/EtOAc, R_f = 0.6): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45−7.36 (m, 4H), 7.35−7.31 (m, 2H), 6.97−6.93 (m, 2H), 6.08 (s, 1H), 5.07 (s, 2H), 0.98 (t, J = 8.0 Hz, 18H), 0.74−0.67 (m, 12H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 159.6, 137.0, 128.9, 128.7, 128.2, 127.6, 127.1, 114.6, 110.3, 70.1, 6.8, 3.9; FT-IR (film of a concd solution in CH_2Cl_2) 3058, 3032, 2955, 2937, 2913, 2877, 1612, 1586, 1513, 1457, 1413, 1380, 1300, 1245, 1173, 1019, 974.50, 859, 787, 734, 696 cm^{-1}. MS (ESI) m/z: 513.45 ([M + Na]$^+$); HRMS (ESI) m/z: [M + Na]$^+$ calcd. for $C_{26}H_{42}O_5NaSi_2$ 513.2463; found 513.2470.

Data for 4-(bis(triethylsilylperoxy)methyl)phenyl acetate (**3j**): (a colorless oil, 143 mg, 0.32 mmol, 69% from **2j**; reaction time = 3 h; chromatography using 50:1 PE/EtOAc, R_f = 0.6): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43−7.41 (m, 2H), 7.09−7.07 (m, 2H), 6.11 (s, 1H), 2.30 (s, 3H), 0.98 (t, J = 7.9 Hz, 18H), 0.74−0.68 (m, 12H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 169.3, 151.4, 132.2, 128.7, 121.4, 109.7, 21.3, 6.8, 3.9; FT-IR (film of a concd solution in CH_2Cl_2) 2956, 2932, 2955, 2914, 2878, 1771, 1607, 1509, 1460, 1414, 1369, 1299, 1201, 1166, 1007, 975, 911, 872, 838, 788, 742 cm^{-1}. MS (ESI) m/z: 465.35 ([M + Na]$^+$); HRMS (ESI) m/z: [M + Na]$^+$ calcd. for $C_{21}H_{38}O_6NaSi_2$ 465.2099; found 465.2103.

Data for 1-(bis(triethylsilylperoxy)methyl)naphthalene (**3k**, a colorless oil, 741 mg, 1.70 mmol, 60% from **2k**; reaction time = 2.5 h; chromatography using 50:1 PE/EtOAc, R_f = 0.6): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.18 (d, J = 8.6 Hz, 1H), 8.87−7.81 (m, 2H), 7.61 (d, J = 7.3 Hz, 1H), 7.54−7.49 (m, 1H), 7.49−7.43 (m, 2H), 6.76 (s, 1H), 0.95 (t, J = 7.9 Hz, 18H), 0.72−0.66 (m, 12H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 133.9, 130.9, 130.5, 130.0, 128.6, 126.4, 126.0, 125.9, 125.1, 124.6, 110.0, 6.8, 3.9; FT-IR (film of a concd solution in CH_2Cl_2) 3056, 2956, 2913, 2878, 1599, 1512, 1459, 1413, 1374, 1304, 1239, 1169, 1063, 1006, 973, 883, 849, 799, 773, 742 cm^{-1}. MS (ESI) m/z: 457.25 ([M + Na]$^+$); HRMS (ESI) m/z: [M + Na]$^+$ calcd. for $C_{23}H_{38}O_4NaSi_2$ 457.2201; found 457.2207.

Data for (3,3-bis(triethylsilylperoxy)propyl)benzene (**3l**, a colorless oil, 1.111 g, 2.69 mmol, 81% from **2l**; reaction time = 3 h; chromatography using 65:1 PE/EtOAc, R_f = 0.6): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31−7.26 (m, 2H), 7.22−7.17 (m, 3H), 5.16 (t, J = 6.0 Hz, 1H), 2.78−2.72 (m, 2H), 2.10−2.03 (m, 2H), 1.00 (t, J = 7.9 Hz, 18H), 0.76−0.69 (m, 12H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 141.4, 128.6, 128.5, 126.1, 110.1, 31.4, 31.3, 6.9, 3.9; FT-IR (film of a concd solution in CH_2Cl_2) 3028, 2955, 2913, 2878, 1457, 1413, 1239, 1022, 1006, 850, 790, 741, 698 cm^{-1}. MS (ESI) m/z: 435.55 ([M + Na]$^+$), HRMS (ESI) m/z: [M + Na]$^+$ calcd. for $C_{21}H_{40}O_4NaSi_2$ 435.2357; found 435.2360.

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Data for 1,1-bis(triethylsilylperoxy)butane (**3m**, a colorless oil, 581 mg, 1.66 mmol, 91% from **2m**; reaction time = 3 h; chromatography using 60:1 PE/EtOAc, R_f = 0.6): ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.15 (t, J = 6.0 Hz, 1H), 1.73−1.67 (m, 2H), 1.49−1.39 (m, 2H), 1.00 (t, J = 8.0 Hz, 18H), 0.93 (t, J = 7.4 Hz, 3H), 0.78−0.65 (m, 12H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 110.8, 32.0, 18.5, 14.1, 6.9, 3.9; FT-IR (film of a concd solution in CH_2Cl_2) 2957, 2937, 2914, 2878, 1459, 1413, 1379, 1239, 1119, 1072, 1016, 1006, 972, 858, 831, 787, 740 cm^{-1}. MS (ESI) m/z: 373.40 ([M + Na]$^+$); HRMS (ESI) m/z: [M + Na]$^+$ calcd. for $C_{16}H_{38}O_4NaSi_2$ 373.2201; found 373.2197.

Data for 1,1-bis(triethylsilylperoxy)octane (**3n**, a colorless oil, 800 mg, 1.97 mmol, 82% from **2n**; reaction time = 3 h; chromatography using 65:1 PE/EtOAc, R_f = 0.6): ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.14 (t, J = 6.0 Hz, 1H), 1.74−1.68 (m, 2H), 1.44−1.37 (m, 2H), 1.34−1.22 (m, 8H), 1.00 (t, J = 7.9 Hz, 18H), 0.90−0.86 (m, 3H), 0.76−0.69 (m, 12H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 111.1, 31.9, 29.9, 29.5, 29.2, 25.1, 22.8, 14.2, 6.9, 3.9; FT-IR (film of a concd solution in CH_2Cl_2) 2956, 2925, 2877, 2856, 1459, 1413, 1240, 1022, 1007, 972, 853, 1007, 972, 853, 790, 740 cm^{-1}. MS (ESI) m/z: 429.55 ([M + Na]$^+$); HRMS (ESI) m/z: [M + Na]$^+$ calcd. for $C_{20}H_{46}O_4NaSi_2$ 429.2827; found 429.2830.

Data for 2-methyl-1,1-bis(triethylsilylperoxy)propane (**3o**, a colorless oil, 529 mg, 1.51 mmol, 90% from **2o**; reaction time = 3 h; chromatography using 65:1 PE/EtOAc, R_f = 0.6): ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.87 (d, J = 6.7 Hz, 1H), 2.21−2.08 (m, 1H), 1.03−0.96 (m, 24H), 0.79−0.66 (m, 12H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 114.6, 29.7, 18.4, 6.9, 3.9; FT-IR (film of a concd solution in CH_2Cl_2) 2957, 2940, 2914, 2878, 1460, 1413, 1240, 1020, 1006, 975, 853, 789, 771, 741 cm^{-1}. MS (ESI) m/z: 373.40 ([M + Na]$^+$); HRMS (ESI) m/z: [M + Na]$^+$ calcd. for $C_{16}H_{38}O_4NaSi_2$ 373.2201; found 373.2194.

Data for 2,2-dimethyl-1,1-bis(triethylsilylperoxy)propane (**3p**, a colorless oil, 454 mg, 1.25 mmol, 77% from **2p**; reaction time = 3 h; chromatography using 65:1 PE/EtOAc, R_f = 0.6): ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.00 (s, 1H), 1.03−0.95 (m, 27H), 0.81−0.64 (m, 12H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 116.0, 36.7, 26.1, 6.9, 4.0; FT-IR (film of a concd solution in CH_2Cl_2) 2957, 2937, 2914, 2878, 1459, 1413, 1365, 1240, 1019, 1008, 974, 867, 823, 791, 741 cm^{-1}. MS (ESI) m/z: 387.50 ([M + Na]$^+$); HRMS (ESI) m/z: [M + Na]$^+$ calcd. For $C_{17}H_{40}O_4NaSi_2$ 387.2357; found 387.2364.

Data for 3-(bis(triethylsilylperoxy)methyl)heptane (**3q**, a colorless oil, 865 mg, 2.13 mmol, 88% from **2q**; reaction time = 3 h; chromatography using 65:1 PE/EtOAc, R_f = 0.6): ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.14 (d, J = 5.5 Hz, 1H), 1.83−175 (m, 1H), 1.54−1.42 (m, 2H), 1.40−1.32 (m, 1H), 1.32−1.24 (m, 5H), 1.00 (t, J = 8.0 Hz, 18H), 0.89 (t, J = 7.3 Hz, 6H), 0.78−0.65 (m, 12H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 112.8, 41.39, 29.3, 28.6, 23.1, 22.2, 14.2, 11.5, 6.9, 4.0; FT-IR (film of a concd solution in CH_2Cl_2) 2957, 2938, 2912, 2877, 1459, 1413, 1380, 1240, 1022, 1006, 973, 857, 791, 741 cm^{-1}. MS (ESI) m/z: 429.55 ([M + Na]$^+$); HRMS (ESI) m/z: [M + Na]$^+$ calcd. for $C_{20}H_{46}O_4NaSi_2$ 429.2827; found 429.2825.

Data for ((4,4-bis(triethylsilylperoxy)butoxy)methyl)benzene (**3r**, a colorless oil, 283 mg, 0.62 mmol, 80% from **2r**; reaction time = 3 h; chromatography using 40:1 PE/EtOAc; 60:1 PE/EtOAc R_f = 0.5): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37−7.31 (m, 4H), 7.31−7.26 (m, 1H), 5.18 (t, J = 5.9 Hz, 1H), 4.50 (s, 2H), 3.49 (t, J = 6.3 Hz, 1H), 1.88−1.81 (m, 2H), 1.78−1.70 (m, 2H), 0.99 (t, J = 7.9 Hz, 18H), 0.76−0.67 (m, 12H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 138.7, 128.5, 127.8, 127.7, 110.6, 73.0, 70.0, 26.8, 25.3, 6.9, 3.9; FT-IR (film of a concd solution in CH_2Cl_2) 2955, 2940, 2913, 2877, 1457, 1412, 1361, 1240, 1101, 1022, 1006, 972, 858, 840, 788, 733, 697 cm^{-1}. MS (ESI) m/z: 479.60 ([M + Na]$^+$); HRMS (ESI) m/z: [M + Na]$^+$ calcd. for $C_{23}H_{44}O_5NaSi_2$ 479.2619; found 479.2624.

Data for (4,4-bis(triethylsilylperoxy)butoxy)(*tert*-butyl)-diphenylsilane (**3s**) (a colorless oil, 277 mg, 0.46 mmol, 79% from **2s**; reaction time = 3 h; chromatography using 50:1 PE/EtOAc; 60:1 PE/EtOAc R_f = 0.6): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69−7.64 (m, 4H), 7.46−7.32 (m, 6H), 5.18 (t, J = 6.0 Hz, 1H), 3.67 (t, J = 6.2 Hz, 1H), 1.90−1.82 (m, 2H), 1.72−1.64 (m, 2H), 1.05 (s, 9H), 0.99 (t, J = 7.9 Hz, 18H), 0.79−0.65 (m, 12H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 135.7, 134.1, 129.7, 127.8, 110.8, 63.6, 28.2, 27.0, 26.6, 19.4, 6.9, 3.9; FT-IR (film of a concd solution in CH_2Cl_2) 3071, 2955, 2937, 2913, 2877, 1460, 1428, 1240, 1111, 1019, 1006, 973, 854, 823, 785, 739, 701 cm^{-1}. MS (ESI) m/z: 627.80 ([M + Na]$^+$); HRMS (ESI) m/z: [M + Na]$^+$ calcd. for $C_{32}H_{56}O_5NaSi_3$ 627.3328; found 627.3331.

Data for 5,5-bis(triethylsilylperoxy)pent-1-ene (**3t**, a colorless oil, 244 mg, 0.67 mmol, 82% from **2t**; reaction time = 3 h; chromatography using 50:1 PE/EtOAc; 60:1 PE/EtOAc R_f = 0.6): ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.81 (ddt, J = 16.9, 10.2, 6.5 Hz, 1H), 5.16 (t, J = 5.9 Hz, 1H), 5.05 (dq, J = 17.1, 1.7 Hz, 1H), 4.99 (dq, J = 10.2, 1.4 Hz, 1H), 2.21−2.14 (m, 2H), 1.86−1.80 (m, 2H), 1.00 (t, J = 7.9 Hz, 18H), 0.79−0.66 (m, 12H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 137.7, 115.3, 110.2, 29.2, 29.1, 6.8, 3.9 ppm; FT-IR (film of a concd solution in CH_2Cl_2) 3080, 2956, 2937, 2914, 2878, 1643, 1459, 1414, 1240, 1019, 1005, 975, 914, 849, 790, 740 cm^{-1}. MS (ESI) m/z: 385.50 ([M + Na]$^+$); HRMS (ESI) m/z: [M + Na]$^+$ calcd. for $C_{17}H_{38}O_4NaSi_2$ 385.2201; found 385.2202.

Data for 6,6-bis(triethylsilylperoxy)hex-1-yne (**3u**, a colorless oil, 294 mg, 0.78 mmol, 85% from **2u**; reaction time = 3 h; chromatography using 50:1 PE/EtOAc; 60:1 PE/EtOAc R_f = 0.6): ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.16 (t, J = 6.0 Hz, 1H), 2.23 (dt, J = 2.6, 7.1 Hz, 2H), 1.95 (t, J = 2.6 Hz, 1H), 1.89−1.83 (m, 2H), 1.70−1.61 (m, 2H), 1.00 (t, J = 7.9 Hz, 18H), 0.76−0.69 (m, 12H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 110.4, 83.9, 68.9, 28.9, 24.0, 18.4, 6.8, 3.9; FT-IR (film of a concd solution in CH_2Cl_2) 3313, 2956, 2937, 2914, 2878, 1459, 1413, 1240, 1075, 1019, 1007, 973, 855, 786, 740 cm^{-1}. MS (ESI) m/z: 397.50 ([M + Na]$^+$); HRMS (ESI) m/z: [M + Na]$^+$ calcd. for $C_{18}H_{38}O_4NaSi_2$ 397.2201; found 397.2202.

*3-(2-(Benzyloxy)ethyl)-3-methyl-5-phenyl-1,2-dioxolane (**5a**): Reaction of **3a** with Alkene **4** to Afford 1,2-Dioxolane **5a** and Chlorohydrin **6** (General Procedure for Peroxycarbenium [3 + 2] Cycloaddition Reaction with Alkenes).* To a solution of silyl protected *gem*-dihydroperoxides **3a** (100 mg, 0.26 mmol) in dry CH_2Cl_2 (2 mL) stirred in a dry ice-acetone bath (−78 °C) under argon (balloon) were added (via syringes) in turn a solution of alkene **4** (137 mg, 0.78 mmol) in dry CH_2Cl_2 (3 mL) and a solution of $TiCl_4$ (1.0 M, in CH_2Cl_2, 0.52 mL, 0.52 mmol). After completion of the additions, the yellow mixture was stirred at −78 °C for 2 h (when TLC showed disappearance of the **3a**). Aq. sat. $NaHCO_3$ (5 mL) was added quickly. The cooling bath was then removed and the reaction mixture was allowed to warm to ambient temperature before being filtered through Celite (washing with 3 × 10 mL of CH_2Cl_2). The combined filtrate/washings were washed with water (30 mL). The aqueous layer was back extracted with CH_2Cl_2 (10 mL × 2). The combined organic layers were washed with brine (10 mL) and dried over anhydrous Na_2SO_4. Filtration and rotary evaporation left a crude oil, which was purified by column chromatography (45:1 to 10:1 PE/EtOAc; 20:1 PE/EtOAc R_f = 0.5) on silica gel to give first **5a** (a 1:0.25 inseparable mixture of two diastereomers, 70 mg, 0.235 mmol, 90% from **3a**) and then chlorohydrin **6** (58 mg, 0.25 mmol, 96% from **3a**).

Data for **5a** (a colorless oil): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41−7.28 (m, 12.5H), 5.32 (t, J = 7.7 Hz, 0.25H), 5.25 (t, J = 7.7 Hz, 1H), 4.54 (s, 2H), 4.48 (s, 0.5H), 3.74−3.61 (m, 2.5H), 3.06 (dd, J = 12.2, 7.8 Hz, 1H), 2.77 (dd, J = 12.2, 7.6 Hz, 0.25H), 2.63 (dd, J = 12.2, 7.8 Hz, 0.25H), 2.38 (dd, J = 12.2, 7.8 Hz, 1H), 2.18−2.11 (m, 0.25H), 2.09−2.05 (m, 2H), 2.05−2.02 (m, 0.25H), 1.45 (s, 3H), 1.44 (s, 0.75H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 139.0, 138.8, 138.4, 128.7, 128.6, 128.5, 128.30, 128.28, 127.78, 127.76, 127.7, 126.71, 126.67, 85.4, 83.5, 83.2, 73.3, 73.2, 66.8, 66.7, 54.0, 39.2, 38.4, 25.1, 24.3; FT-IR (film of a concd solution in CH_2Cl_2) 3087, 3063, 3030, 2974, 2928, 2868, 2795, 1497, 1453, 1366, 1307, 1100, 1077, 1028, 737, 698 cm^{-1}. MS (ESI) m/z: 321.30 ([M + Na]$^+$); HRMS (ESI) m/z: [M + Na]$^+$ calcd. For $C_{19}H_{22}NaO_3$ 321.1461; found 321.1465.

Data for **6** (a colorless oil, 20:1 PE/EtOAc R_f = 0.1): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38−7.34 (m, 2H), 7.34−7.28 (m, 3H), 4.55 (d, J = 11.6 Hz, 1H), 4.51 (d, J = 11.6 Hz, 1H), 3.78−3.70 (m, 2H), 3.63 (ddd, J = 10.0, 6.4, 3.8 Hz, 1H), 3.57 (dd, J = 11.9, 8.5 Hz, 1H), 3.11 (dd, J = 8.6, 6.4 Hz, 1H), 2.20 (ddd, J = 15.4, 8.0, 3.8 Hz, 1H),

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2.08 (ddd, J = 15.4, 6.4, 3.5 Hz, 1H), 1.60 (s, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 137.5, 128.7, 128.1, 128.0, 73.6, 72.8, 70.5, 66.8, 40.9, 28.3; FT-IR (film of a concd solution in CH_2Cl_2) 3434, 2062, 3031, 2973, 2929, 2870, 1496, 1451, 1366, 1096, 1077, 1050, 738, 698 cm^{-1}. MS (ESI) m/z: 251.15 ($[M + Na]^+$), 249.15 ($[M + Na]^+$); HRMS (ESI) m/z: $[M + Na]^+$ calcd. for $C_{12}H_{17}ClNaO_2$ 251.0809; found 251.0809.

The relative configurations of the two diastereomers of **5a** were assigned according to the literature[38] rule; cf. also Figure S2 below. Other 1,2-dioxolanes were also assigned similarly.

*4-(Benzyloxy)-2-chloro-2-methylbutan-1-ol (**6**): Reaction of **3l** with Alkene **4** to Afford Chlorohydrin **6**.* The "General procedure for peroxycarbenium [3 + 2] cycloaddition reaction with alkenes" given above was used, with **3l** to replace **3a**. The reaction of **3l** with alkene **4** afforded (after chromatography using 60:1 to 10:1 PE/EtOAc; 20:1 PE/EtOAc R_f = 0.1) **6** as a colorless oil (46 mg, 0.20 mmol, 83% from **3l**). Data for **6**: cf. above.

*3-(2-(Benzyloxy)ethyl)-5-(tert-butyl)-3-methyl-1,2-dioxolane (**5b**): Reaction of **3p** with Alkene **4** to Afford 1,2-Dioxolane **5b** and Chlorohydrin **6**.* The "General procedure for peroxycarbenium [3 + 2] cycloaddition reaction with alkenes" given above was used, with **3p** to replace **3a**. The reaction of **3p** with alkene **4** afforded (after chromatography using 60:1 to 10:1 PE/EtOAc) **5b** (a 1:0.2 inseparable mixture of two diastereomers, 5 mg, 0.018 mmol, 7% from **3p**) first, then epoxide **7** (2 mg, 0.01 mmol), and finally **6** as a colorless oil (much more polar than **5b**, 35 mg, 0.15 mmol, 60% from **3p**).

Data for **5b** (a colorless oil, 20:1 PE/EtOAc R_f = 0.5): ^1H NMR (500 MHz, $CDCl_3$) δ 7.36−7.30 (m, 5H), 7.30−7.27 (m, 1H), 4.50 (s, 2.6H), 4.04 (dd, J = 8.7, 7.5 Hz, 0.2H), 3.98 (t, J = 8.1 Hz, 1H), 3.66−3.56 (m, 2.6H), 2.45 (dd, J = 12.1, 7.7 Hz, 1H), 2.27 (dd, J = 12.1, 8.7 Hz, 0.2H), 2.19 (dd, J = 12.0, 7.4 Hz, 0.2H), 2.07 (dd, J = 12.1, 8.4 Hz, 1H), 2.03−1.89 (m, 2.6H), 1.33 (s, 3.6H), 0.93 (s, 11H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 138.5, 128.5, 127.8, 127.7, 89.3, 89.1, 84.68, 84.66, 73.3, 73.3, 66.9, 66.8, 47.0, 46.7, 38.9, 38.2, 33.27, 33.25, 26.12, 26.07, 24.7, 24.0; FT-IR (film of a concd solution in CH_2Cl_2) 3087, 3064, 3031, 2958, 2931, 2869, 1496, 1477, 1455, 1396, 1366, 1111, 1101, 1028, 1008, 736, 697 cm^{-1}. MS (ESI) m/z: 301.2 ($[M + Na]^+$); HRMS (ESI) m/z: $[M + Na]^+$ calcd. for $C_{17}H_{26}NaO_3$ 301.1774; found 301.1773.

Data for **6** (a colorless oil): cf. above.

Data for 2-(2-(benzyloxy)ethyl)-2-methyloxirane (**7**,[39] a colorless oil, 20:1 PE/EtOAc R_f = 0.3): ^1H NMR (500 MHz, $CDCl_3$) δ 7.37−7.31 (m, 4H), 7.30−7.27 (m, 1H), 4.50 (s, 2H), 3.62−3.53 (m, 2H), 2.70 (d, J = 4.8 Hz, 1H), 2.60 (d, J = 4.9 Hz, 1H), 1.98−1.91 (m, 1H), 1.88−1.80 (m, 1H), 1.34 (s, 3H).

(3R,5S*)-3-(4-(Benzyloxy)butyl)-5-phenyl-1,2-dioxolane (**9a**): Reaction of **3a** with Alkene **8** to Afford 1,2-Dioxolane **9a** and Dichloride **10**.* The "General procedure for peroxycarbenium [3 + 2] cycloaddition reaction with alkenes" given above was used, with alkene **8** (3 mol equiv with respect to **3a**) to replace alkene **4**. The reaction of **3a** (100 mg, 0.26 mmol) with alkene **8** afforded (after chromatography using 60:1 to 20:1 PE/EtOAc) **10** (24 mg, 0.092 mmol, 35% from **3a**, 12% from **8**) first and then **9a** (40 mg, 0.13 mmol, 50% from **3a**).

Data for dichloride (((5,6-dichlorohexyl)oxy)methyl)benzene (**10**, a colorless oil, 20:1 PE/EtOAc R_f = 0.6): ^1H NMR (500 MHz, $CDCl_3$) δ 7.38−7.33 (m, 4H), 7.31−7.29 (m, 1H), 4.51 (s, 2H), 4.07−4.00 (m, 1H), 3.76 (dd, J = 11.3, 5.1 Hz, 1H), 3.65 (dd, J = 11.3, 7.4, 1H), 3.50 (t, J = 6.2 Hz, 2H), 2.06−1.97 (m, 1H), 1.78−1.60 (m, 4H), 1.58−1.48 (m, 1H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 138.6, 128.5, 127.8, 127.7, 73.1, 70.0, 61.2, 48.3, 35.0, 29.3, 22.8; FT-IR (film of a concd solution in CH_2Cl_2) 3087, 3064, 3030, 2943, 2862, 2794, 1496, 1479, 1454, 1363, 1205, 1102, 1028, 735, 698 cm^{-1}. MS (ESI) m/z: 283.25 ($[M + Na]^+$), 285.05 ($[M + Na]^+$); HRMS (ESI) m/z: $[M + Na]^+$ calcd. for $C_{13}H_{18}Cl_2NaO$ 283.0627; found 283.0625.

Data for (3R*,5S*)-3-(4-(benzyloxy)butyl)-5-phenyl-1,2-dioxolane (**9a**, a colorless oil, 20:1 PE/EtOAc R_f = 0.2): ^1H NMR (500 MHz, $CDCl_3$) δ 7.40−7.33 (m, 8H), 7.33−7.27 (m, 2H), 5.27 (dd, J = 8.0, 6.1 Hz, 1H), 4.51 (s, 2H), 4.45 (quint, J = 6.8 Hz, 1H), 3.49 (t, J = 6.4 Hz, 2H), 2.70 (ddd, J = 12.0, 7.3, 6.1 Hz, 1H), 2.64 (ddd, J = 12.0, 8.1, 6.5 Hz, 1H), 1.81−1.72 (m, 1H), 1.68 (quint, J = 7.1 Hz, 2H), 1.64−1.57 (m, 1H), 1.55−1.43 (m, 2H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 139.2, 138.7, 128.7, 128.5, 128.4, 127.8, 127.7, 126.7, 82.4, 81.5, 73.1, 70.2, 48.5, 33.1, 29.8, 23.1; FT-IR (film of a concd solution in CH_2Cl_2) 3086, 3062, 3030, 2938, 2862, 2793, 1721, 1605, 1494, 1453, 1363, 1329, 1308, 1288, 1205, 1101, 1028, 736, 698 cm^{-1}. MS (ESI) m/z: 335.10 ($[M + Na]^+$); HRMS (ESI) m/z: $[M + Na]^+$ calcd. for $C_{20}H_{24}NaO_3$ 335.1618; found 353.1621.

(3R,5S*)-3-(4-(Benzyloxy)butyl)-5-(4-fluorophenyl)-1,2-dioxolane (**9b**): Reaction of **3b** with **8** to Afford **9b** and Dichloride **10**.* This transformation was achieved using the "General procedure for peroxycarbenium [3 + 2] cycloaddition reaction with alkenes" given above, with **3b** and alkene **8** to replace **3a** and alkene **4**, respectively, affording **9b** (41 mg, 0.12 mmol, 48% from **3b**) and **10** (22 mg, 0.084 mmol, 34% from **3b**, 11% from **8**).

Data for **9b** (a white solid, 20:1 PE/EtOAc R_f = 0.2): M.p. 34−36 °C. ^1H NMR (500 MHz, $CDCl_3$) δ 7.37−7.31 (m, 6H), 7.30−7.26 (m, 1H), 7.07−7.02 (m, 2H), 5.24 (dd, J = 7.7, 6.3 Hz, 1H), 4.50 (s, 2H), 4.48−4.41 (m, 1H), 3.49 (t, J = 6.4 Hz, 2H), 2.69−2.60 (m, 2H),1.80−1.72 (m, 1H), 1.67 (quint, J = 7.0 Hz, 2H), 1.64−1.43 (m, 3H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 163.7, 161.8, 138.7, 134.91, 134.88, 128.6, 128.52, 128.49, 127.8, 127.7, 115.7, 115.6, 81.8, 81.6, 73.1, 70.2, 48.5, 33.1, 29.8, 23.1; FT-IR (KBr) 3062, 3034, 2985, 2935, 2908, 2865, 2795, 1604, 1512, 1498, 1482, 1456, 1358, 1261, 1221, 1160, 1124, 1105, 1030, 833, 734, 696 cm^{-1}. MS (ESI) m/z: 353.15 ($[M + Na]^+$); HRMS (ESI) m/z: $[M + Na]^+$ calcd. for $C_{20}H_{23}FNaO_3$ 353.1523; found 353.1533.

Data for dichloride **10** (a colorless oil): cf. the above.

(3R,5S*)-3-(4-(Benzyloxy)butyl)-5-(4-bromophenyl)-1,2-dioxolane (**9c**): Reaction of **3d** with **8** to Afford **9c** and Dichloride **10**.* This transformation was achieved using the "General procedure for peroxycarbenium [3 + 2] cycloaddition reaction with alkenes" given above, with **3d** and alkene **8** to replace **3a** and alkene **4**, respectively, affording **9c** (50 mg, 0.13 mmol, 59% from **3d**) and **10** (18 mg, 0.069 mmol, 31% from **3d**, 10% from **8**).

Data for **9c** (a white solid, 20:1 PE/EtOAc R_f = 0.2): M.p. 40−42 °C. ^1H NMR (500 MHz, $CDCl_3$) δ 7.50−7.46 (m, 2H), 7.36−7.31 (m, 4H), 7.29−7.26 (m, 1H), 7.25−7.23 (m, 1H), 7.24−7.23 (m, 1H), 5.22 (t, J = 6.9 Hz, 1H), 4.50 (s, 2H), 4.44−4.38 (m, 1H), 3.49 (t, J = 6.4 Hz, 1H), 2.70−2.60 (m, 2H), 1.79−1.71 (m, 1H), 1.70−1.63 (m, 1H), 1.63−1.55 (m, 1H), 1.54−1.43 (m, 2H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 138.7, 138.6, 131.9, 128.5, 128.3, 127.8, 127.7, 122.2, 81.6, 81.4, 73.1, 70.2, 48.5, 33.2, 29.8, 23.1; FT-IR (KBr) 3093, 3067, 3028, 2936, 2912, 2853, 2797, 1595, 1489, 1479, 1453, 1412, 1383, 1359, 1311, 1298, 1259, 1118, 1094, 1071, 1027, 1009, 932, 841, 786, 736 cm^{-1}. MS (ESI) m/z: 413.05 ($[M + Na]^+$), 415.15 ($[M + Na]^+$); HRMS (ESI) m/z: $[M + Na]^+$ calcd. for $C_{20}H_{23}BrO_3Na$ 413.0723; found 413.0730.

Data for dichloride **10** (a colorless oil): cf. the above.

*3-(4-(Benzyloxy)butyl)-1,2-dioxaspiro[4.5]decane (**9d**): Reaction of **11** with **8** to Afford **9d** and Dichloride **10**.* This transformation was achieved using the "General procedure for peroxycarbenium [3 + 2] cycloaddition reaction with alkenes" given above, with **11** and alkene **8** to replace **3a** and alkene **4**, respectively, affording first **10** (20 mg, 0.077 mmol, 37% from **11**, 12% from **8**) and then **9d** (8 mg, 0.026 mmol, 12% from **11**).

Data for **9d** (a colorless oil, more polar than **10**, chromatography using 50:1 to 30:1 PE/EtOAc; 30:1 PE/EtOAc R_f = 0.2): ^1H NMR (500 MHz, $CDCl_3$) δ 7.36−7.31 (m, 4H), 7.30−7.27 (m, 1H), 4.49 (s, 2H), 4.24 (dq, J = 5.3, 7.2 Hz, 1H), 3.47 (t, J = 6.5 Hz, 2H), 2.39 (dd, J = 11.8, 7.3 Hz, 1H), 1.89 (dd, J = 11.8, 7.0 Hz, 1H), 1.74−1.57 (m, 9H), 1.55−1.34 (m, 7H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 138.7, 128.5, 127.8, 127.7, 85.1, 81.5, 73.1, 70.1, 50.8, 36.3, 35.5, 33.5, 29.8, 25.5, 24.0, 23.8, 23.2; FT-IR (film of a concd solution in CH_2Cl_2) 3090, 3063, 3030, 2934, 2858, 2790, 1496, 1452, 1362, 1302, 1260, 1204, 1102, 1028, 914, 818, 735, 697 cm^{-1}. MS (ESI) m/z: 327.20 ($[M + Na]^+$); HRMS (ESI) m/z: $[M + Na]^+$ calcd. for $C_{19}H_{28}NaO_3$ 327.1931; found 327.1935.

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*Reaction of **3l** with Alkene **8** to Afford Dichloride **10** and Phenylpropionaldehyde **1l**.* The "General procedure for peroxycarbenium [3 + 2] cycloaddition reaction with alkenes" given above was used, with **3l** and alkene **8** to replace **3a** and alkene **4**, respectively. The reaction of **3l** with alkene **8** afforded (after chromatography using 60:1 to 20:1 PE/EtOAc) **10** first as a colorless oil (23 mg, 0.088 mmol, 37% from **3l**) and then **1l** (more polar than **10**, 15 mg, 0.11 mmol, 46% from **3l**).

Data for **10** (a colorless oil): cf. above.

*Reaction of **3p** with Alkene **8** to Afford Dichloride **10**.* The "General procedure for peroxycarbenium [3 + 2] cycloaddition reaction with alkenes" given above was used, with **3p** and alkene **8** to replace **3a** and alkene **4**, respectively. The reaction of **3p** with alkene **8** afforded (after chromatography using 60:1 to 20:1 PE/EtOAc) **10** (a colorless oil, 23 mg, 0.088 mmol, 35% from **3p**) as the only isolable/identifiable product.

Data for **10** (a colorless oil): cf. above.

(3R,3aR*,6aS*)- and (3S*,3aR*,6aS*)-3-Phenyltetrahydro-3H-furo[2,3-c][1,2]dioxole (cis-**13a** and trans-**13a**) and 4-Oxo-4-phenylbutyl Formate (**14a**): Reaction of **3a** with 2,3-Dihydrofuran **12** to Afford **13a** and **14a** (General Procedure for Peroxycarbenium [3 + 2] Cycloaddition Reaction with **12**).* To a solution of silyl protected *gem*-dihydroperoxides **3a** (100 mg, 0.26 mmol) in dry CH_2Cl_2 (10 mL) stirred in a dry ice-acetone bath (−78 °C) under argon (balloon) were added (via a syringes) in turn a solution of 2,3-dihydrofuran **12** (57 μL, 0.78 mmol) and a solution of $TiCl_4$ (1.0 M, in CH_2Cl_2, 0.52 mL, 0.52 mmol). After completion of the additions, the mixture was stirred at −78 °C for 1 h (when TLC showed disappearance of **3a**; initially orange-yellow then it gradually changed to pale yellow) and diluted with CH_2Cl_2 (10 mL). Aq. sat. $NaHCO_3$ (10 mL) was added quickly. The cooling bath was then removed and the reaction mixture was allowed to warm to ambient temperature before being filtered through Celite (washing with 3 × 10 mL of CH_2Cl_2). The combined filtrate/washings were washed with water (20 mL, led to formation of a lot of white floccules suspended in the aqueous phase). The aqueous layer was back-extracted with CH_2Cl_2 (10 mL × 2). The combined organic layers were washed with brine (10 mL) and dried over anhydrous Na_2SO_4. Filtration and rotary evaporation left a crude oil (^{1}H NMR of which showed the ratio of the two diastereomers being 1:1), which was purified by column chromatography (first 15:1 HPLC-grade *n*-hexane/EtOAc, then 10:1:1 *n*-hexane/EtOAc/CH_2Cl_2; with the column cooled to −20 to −30 °C with ice-water/dry ice placed in the cooling jacket made of a truncated water bottle; all eluents were also pre-cooled in an ice-EtOH bath) on silica gel to give **13a** (1:1 mixture of the *cis/trans* isomers, the effluent was filtered through two layers of slow-speed filtration paper to remove traces of silica gel before rotary evaporation to avoid decomposition of **13a**, 40 mg, 0.21 mmol, 81% from **3a**). After repeated chromatography, a small sample of *cis*-**13a** was obtained, which allowed for collection of physical and spectroscopic data for the *cis* isomer (*cis*-**13a**). If the experiment was done with less care in cooling (e.g., performing the chromatography at ambient temperature), varying amounts of the cleavage product **14a** could be obtained depending on the conditions in the individual run.

Data for *cis*-**13a** (a white solid, 10:1 PE/EtOAc R_f = 0.3): M.p. 77−80 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40−7.36 (m, 2H), 7.34−7.30 (m, 1H), 7.23−7.20 (m, 2H), 6.06 (d, *J* = 5.2 Hz, 1H), 5.36 (d, *J* = 6.2 Hz, 1H), 4.01 (ddd, *J* = 11.4, 8.2, 5.8 Hz, 1H), 3.94 (dt, *J* = 1.7, 8.3 Hz, 1H), 3.66−3.60 (m, 1H), 1.2−1.72 (m, 1H), 1.63−1.58 (m, 1H), ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 134.6, 128.8, 128.3, 126.2, 109.0, 85.6, 69.9, 56.7, 27.3 ppm; FT-IR (KBr) 2984, 2965, 2954, 2924, 2880, 1496, 1452, 1366, 1349, 1253, 1072, 1012, 984, 960, 928, 748, 715 cm^{-1}. MS (ESI) *m/z*: 215.05 ([M + Na]$^+$); HRMS (ESI) *m/z*: [M + Na]$^+$ calcd. for $C_{11}H_{12}NaO_3$ 215.0679; found 215.0682.

Data for a 1:1.5 (because some of the *cis*-isomer was already removed) mixture of *cis*-**13**/*trans*-**13a** (a colorless oil, 10:1 PE/EtOAc R_f = 0.3): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43−7.28 (m, 11H), 7.23−7.20 (m, 2H), 6.05 (d, *J* = 5.2 Hz, 1H), 5.93 (d, *J* = 5.0 Hz, 1.5H), 5.36 (d, *J* = 6.2 Hz, 1H), 5.14 (br s, 1.5H), 4.20 (ddd, *J* = 11.1, 8.4, 6.0 Hz, 1.5H), 4.09 (dt, *J* = 2.1, 8.1 Hz, 1.5H), 4.01 (ddd, *J* = 11.4, 8.2, 5.7 Hz, 1H), 3.94 (dt, *J* = 1.7, 8.3 Hz, 1H), 3.74−3.70 (m, 1.5H), 3.66−3.60 (m, 1H), 2.33−2.20 (m, 3H), 1.82−1.71 (m, 1H), 1.63−1.57 (m, 1H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 140.1 (*trans*), 134.6, 128.8, 128.7 (*trans*) 128.2, 128.0 (*trans*), 126.2, 125.7 (*trans*), 109.0, 107.6 (*trans*), 88.3 (*trans*), 85.6, 69.8, 69.1 (*trans*), 60.7 (*trans*), 56.6, 32.4 (*trans*), 27.2. FT-IR (film of a concd solution in CH_2Cl_2) 3062, 3030, 2978, 2889, 1496, 1450, 1365, 1074, 978, 958, 926, 846, 699 cm^{-1}; MS (ESI) *m/z*: 215.05 ([M + Na]$^+$); HRMS (ESI) *m/z*: [M + Na]$^+$ calcd. for $C_{11}H_{12}NaO_3$ 215.0679; found 215.0684.

Data for **14a** (a colorless oil, less polar than *trans*-**13a** but more polar than *cis*-**13a**, 10:1 PE/EtOAc R_f = 0.3): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 (s, 1H), 7.99−7.94 (m, 2H), 7.60−7.55 (m, 1H), 7.49−7.45 (m, 2H), 4.29 (t, *J* = 6.3 Hz, 2H), 3.10 (t, *J* = 7.2 Hz, 2H), 2.14 (quint, *J* = 6.7 Hz, 2H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 199.0, 161.1, 136.9, 133.4, 128.8, 128.1, 63.4, 34.8, 23.2; FT-IR (film of a concd solution in CH_2Cl_2) 3059, 2962, 2933, 2892, 1724, 1686, 1597, 1580, 1449, 1412, 1369, 1324, 1273, 1169, 1001, 754, 739, 690 cm^{-1}. MS (ESI) *m/z*: 215.05 ([M + Na]$^+$); HRMS (ESI) *m/z*: [M + NH_4]$^+$ calcd. for $C_{11}H_{16}NO_3$ 210.1125; found 210.1136.

(3R,3aR*,6aS*)- and (3S*,3aR*,6aS*)-3-(4-Fluorophenyl)-tetrahydro-3H-furo[2,3-c][1,2]dioxole (cis-**13b** and trans-**13b**) and 4-(4-Fluorophenyl)-4-oxobutyl Formate (**14b**): Reaction of **3b** with 2,3-Dihydrofuran **12** to Afford **13b** and **14b**.* The "General procedure for peroxycarbenium [3 + 2] cycloaddition reaction with **12**" given above was used, with **3b** to replace **3a**. The reaction of **3b** with dihydrofuran **12** afforded **13b** (a colorless oil, 35 mg, 0.17 mmol, 68% from **3b**). If the experiment was done with less care in cooling (e.g., performing the chromatography at ambient temperature), varying amounts of the cleavage product **14b** could be obtained depending on the conditions in the individual run.

Data for *cis*-**13b** (a colorless oil, 10:1 PE/EtOAc R_f = 0.3): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.22−7.18 (m, 2H), 7.11−7.05 (m, 2H), 6.06 (d, *J* = 5.2 Hz, 1H), 5.34 (d, *J* = 6.2 Hz, 1H), 4.01−3.92 (m, 2H), 3.64−3.57 (m, 1H), 1.83−1.73 (m, 1H), 1.61−1.57 (m, 1H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 163.5, 161.6, 130.31, 130.29, 128.0, 127.9, 116.0, 115.8, 109.1, 85.1, 69.8, 56.6, 27.2; FT-IR (film of a concd solution in CH_2Cl_2) 2957, 2921, 2892, 2851, 1608, 1512, 1457, 1224, 1159, 1077, 977, 958, 925, 839, 808 cm^{-1}. MS (ESI) *m/z*: 233.15 ([M + Na]$^+$); HRMS (ESI) *m/z*: [M + Na]$^+$ calcd. for $C_{11}H_{11}FNaO_3$ 233.0584; found 233.0590.

Data for a 1:1 mixture of *cis*-**13b**/*trans*-**13b** (a colorless oil, 10:1 PE/EtOAc R_f = 0.3): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38−7.33 (m, 2H), 7.22−7.17 (m, 2H), 7.11−7.01 (m, 4H), 6.06 (d, *J* = 5.1 Hz, 1H), 5.92 (d, *J* = 5.0 Hz, 1H), 5.33 (d, *J* = 6.2 Hz, 1H), 5.11 (br s, 1H), 4.19 (ddd, *J* = 11.1, 8.4, 5.9 Hz, 1H), 4.08 (dt, *J* = 2.0, 8.2 Hz, 1H), 4.01−3.92 (m, 2H), 3.70−3.65 (m, 1H), 3.64−3.58 (m, 1H), 2.32−2.25 (m, 1H), 2.24−2.19 (m, 1H), 1.83−1.73 (m, 1H), 1.61−1.55 (m, 1H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 163.5, 161.53, 135.98 (*trans*), 135.95 (*trans*), 130.30, 130.27, 128.0, 127.9, 127.62 (*trans*), 127.56 (*trans*), 116.0, 115.8, 115.7 (*trans*), 115.5 (*trans*), 109.1, 107.5 (*trans*), 87.8 (*trans*), 85.1, 70.0, 69.1 (*trans*), 60.8 (*trans*), 56.5, 32.3 (*trans*), 27.2; FT-IR (film of a concd solution in CH_2Cl_2) 2979, 2959, 2891, 1607, 1511, 1224, 1160, 1076, 979, 958, 926, 843 cm^{-1}. MS (ESI) *m/z*: 233.0 ([M + Na]$^+$); HRMS (ESI) *m/z*: [M + Na]$^+$ calcd. for $C_{11}H_{11}FNaO_3$ 233.0584; found 233.0591.

Data for **14b** (a white solid, less polar than *trans*-**13b** but more polar than *cis*-**13b**, 10:1 PE/EtOAc R_f = 0.3): M.p. 45−47 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 (s, 1H), 8.02−7.97 (m, 2H), 7.14 (t, *J* = 8.7 Hz, 2H), 4.28 (t, *J* = 6.4 Hz, 2H), 3.07 (t, *J* = 7.1 Hz, 2H), 2.14 (quint, *J* = 6.7 Hz, 2H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 197.3, 167.0, 164.9, 161.1, 133.33, 133.30, 130.8, 130.7, 116.0, 115.8, 63.3, 34.7, 23.1; FT-IR (KBr) 3072, 2976, 2955, 2896, 1715, 1679, 1598, 1507, 1474, 1468, 1411, 1368, 1303, 1275, 1231, 1208, 1192, 1168, 1099, 990, 932, 844 cm^{-1}. MS (ESI) *m/z*: 233.00 ([M + Na]$^+$); HRMS (ESI) *m/z*: [M + Na]$^+$ calcd. for $C_{11}H_{11}FNaO_3$ 233.0584; found 233.0582.

(3R,3aR*,6aS*)- and (3S*,3aR*,6aS*)-3-(4-Chlorophenyl)-tetrahydro-3H-furo[2,3-c][1,2]dioxole (cis-**13c** and trans-**13c**) and 4-(4-Chlorophenyl)-4-oxobutyl Formate (**14c**): Reaction of **3c** with*

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*2,3-Dihydrofuran **12** to Afford **13c** and **14c**.* The "General procedure for peroxycarbenium [3 + 2] cycloaddition reaction with **12**" given above was used, with **3c** to replace **3a**. The reaction of **3c** with dihydrofuran **12** afforded **13c** (a colorless oil, 44 mg, 0.19 mmol, 73% from **3c**). If the experiment was done with less care in cooling (e.g., performing the chromatography at ambient temperature), varying amounts of the cleavage product **14c** could be obtained depending on the conditions in the individual run.

Data for *cis*-**13c** (a white solid, 10:1 PE/EtOAc R_f = 0.3): M.p. 78−80 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 (d, J = 8.5 Hz, 2H), 7.16 (d, J = 8.4 Hz, 2H), 6.05 (d, J = 5.2 Hz, 1H), 5.33 (d, J = 6.2 Hz, 1H), 4.00−3.91 (m, 2H), 3.65−3.58 (m, 1H), 1.83−1.73 (m, 1H), 1.60−1.54 (m, 1H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 134.2, 133.1, 129.1, 127.6, 109.1, 85.0, 69.8, 56.5, 27.2; FT-IR (KBr) 2980, 2890, 1493, 1449, 1408, 1327, 1300, 1249, 1190, 1079, 1016, 978, 959, 926, 861, 843, 772 cm^{-1}. MS (ESI) m/z: 248.90 ([M + Na]$^+$), 250.60 ([M + Na]$^+$); HRMS (ESI) m/z: [M + Na]$^+$ calcd. for $C_{11}H_{11}ClNaO_3$ 249.0289; found 249.0289.

Data for a 1:1 mixture of *cis*-**13c**/*trans*-**13c** (a colorless oil, 10:1 PE/EtOAc R_f = 0.3): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39−7.31 (m, 6H), 7.17−7.14 (m, 2H), 6.05 (d, J = 5.2 Hz, 1H), 5.90 (d, J = 5.0 Hz, 1H), 5.32 (d, J = 6.2 Hz, 1H), 5.11 (br s, 1H), 4.19 (ddd, J = 11.1, 8.4, 5.9 Hz, 1H), 4.08 (dt, J = 1.9, 8.1 Hz, 1H), 4.00−3.91 (m, 2H), 3.66−3.63 (m, 1H), 3.63−3.59 (m, 1H), 2.33−2.25 (m, 1H), 2.24−2.1 (m, 1H), 1.83−1.73 (m, 1H), 1.60−1.54 (m, 1H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 138.7 (*trans*), 134.1, 133.9 (*trans*), 133.1, 129.1, 128.9 (*trans*), 127.5, 127.2 (*trans*), 109.1, 107.4 (*trans*), 87.6 (*trans*), 85.0, 69.8, 69.2 (*trans*), 60.8 (*trans*), 56.5, 32.4 (*trans*), 27.2; FT-IR (film of a concd solution in CH_2Cl_2) 2979, 2958, 2890, 1722, 1687, 1597, 1493, 1077, 1015, 979, 959, 926, 861, 844 cm^{-1}. MS (ESI) m/z: 249.15 ([M + Na]$^+$), 251.05 ([M + Na]$^+$); HRMS (ESI) m/z: [M + Na]$^+$ calcd. for $C_{11}H_{11}ClNaO_3$ 249.0289; found 249.0292.

Data for **14c** (a white solid, less polar than *trans*-**13c** but more polar than *cis*-**13c**, 10:1 PE/EtOAc R_f = 0.3): M.p. 42−45 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 (s, 1H), 7.90 (d, J = 8.6 Hz, 2H), 7.44 (d, J = 8.6 Hz, 2H), 4.28 (t, J = 6.3 Hz, 2H), 3.06 (t, J = 7.1 Hz, 2H), 2.13 (quint, J = 6.7 Hz, 2H);^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 197.7, 161.1, 139.8, 135.2, 129.5, 129.1, 63.3, 34.8, 23.1; FT-IR (KBr) 3412, 3342, 3092, 2980, 2965, 2933, 2903, 1720, 1680, 1590, 1574, 1490, 1473, 1401, 1369, 1278, 1210.1, 1093, 1013, 989, 928, 840, 831, 807, 775, 765 cm^{-1}. MS (ESI) m/z: 248.90 ([M + Na]$^+$), 250.95 ([M + Na]$^+$); HRMS (ESI) m/z: [M + Na]$^+$ calcd. for $C_{11}H_{11}ClNaO_3$ 249.0289; found 249.0295.

(3R,3aR*,6aS*)- and (3S*,3aR*,6aS*)-3-(4-Bromophenyl)-tetrahydro-3H-furo[2,3-c][1,2]dioxole (cis-**13d** and trans-**13d**) and 4-(4-Bromophenyl)-4-oxobutyl Formate (**14d**): Reaction of **3d** with 2,3-Dihydrofuran **12** to Afford **13d** and **14d**.* The "General procedure for peroxycarbenium [3 + 2] cycloaddition reaction with **12**" given above was used, with **3d** to replace **3a**. The reaction of **3d** with dihydrofuran **12** afforded **13d** (a colorless oil, 46 mg, 0.17 mmol, 65% from **3d**). If the experiment was done with less care in cooling (e.g., performing the chromatography at ambient temperature), varying amounts of the cleavage product **14d** could be obtained depending on the conditions in the individual run.

Data for *cis*-**13d** (a colorless oil, 10:1 PE/EtOAc R_f = 0.3): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54−7.50 (m, 2H), 7.12−7.08 (m, 2H), 6.05 (d, J = 5.2 Hz, 1H), 5.31 (d, J = 6.2 Hz, 1H), 4.00−3.92 (m, 2H), 3.65−3.58 (m, 1H), 1.83−1.73 (m, 1H), 1.60−1.54 (m, 1H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 133.6, 132.0, 127.9, 122.3, 109.1, 85.0, 69.8, 56.5, 27.2; FT-IR (film of a concd solution in CH_2Cl_2) 2980, 2890, 1493, 1449, 1408, 1327, 1300, 1249, 1190, 1079, 1016, 978, 959, 926, 861, 843, 772 cm^{-1}. MS (ESI) m/z: 293.20 ([M + Na]$^+$), 295.10 ([M + Na]$^+$); HRMS (ESI) m/z: [M + Na]$^+$ calcd. for $C_{11}H_{11}BrNaO_3$ 292.9784; found 292.9787.

Data for a 1:1 mixture of *cis*-**13d**/*trans*-**13d** (a colorless oil, 10:1 PE/EtOAc R_f = 0.3): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54−7.47 (m, 4H), 7.28−7.25 (m, 2H), 7.12−7.08 (m, 2H), 6.05 (d, J = 5.2 Hz, 1H), 5.90 (d, J = 5.0 Hz, 1H), 5.30 (d, J = 6.2 Hz, 1H), 5.09 (br s, 1H), 4.19 (ddd, J = 11.2, 8.4, 5.9 Hz, 1H), 4.08 (dt, J = 1.9, 8.1 Hz, 1H), 4.00−3.91 (m, 2H), 3.68−3.63 (m, 1H), 3.63−3.59 (m, 1H), 2.33−2.25 (m, 1H), 2.25−2.19 (m, 1H), 1.83−1.73 (m, 1H), 1.60−1.54 (m, 1H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 139.3 (*trans*), 133.6, 132.0, 131.8 (*trans*), 127.9, 127.5 (*trans*), 122.3, 122.0 (*trans*), 109.1, 107.5 (*trans*), 87.7 (*trans*), 85.0, 69.8, 69.2 (*trans*), 60.8 (*trans*), 56.5, 32.4 (*trans*), 27.2; FT-IR (film of a concd solution in CH_2Cl_2) 2979, 2957, 2889, 1721, 1489, 1401, 1365, 1073, 1011. 979, 958, 926, 844 cm^{-1}. MS (ESI) m/z: 293.10 ([M + Na]$^+$), 295.05 ([M + Na]$^+$); HRMS (ESI) m/z: [M + Na]$^+$ calcd. for $C_{11}H_{11}BrNaO_3$ 292.9784; found 292.9791.

Data for **14d** (a white solid, less polar than *trans*-**13d** but more polar than *cis*-**13d**, 10:1 PE/EtOAc R_f = 0.3): M.p. 58−60 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.07 (s, 1H), 7.83 (d, J = 8.3 Hz, 2H), 7.62 (d, J = 8.2 Hz, 2H), 4.28 (t, J = 6.4 Hz, 2H), 3.06 (t, J = 7.1 Hz, 2H), 2.13 (quint, J = 6.7 Hz, 2H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 197.9, 161.1, 135.6, 132.1, 129.7, 128.6, 63.3, 34.8, 23.0; FT-IR (CH_2Cl_2 film) 2925, 2849, 1717, 1681, 1585, 1472, 1277, 1207, 1071, 988, 827 cm^{-1}. MS (ESI) m/z: 292.85 ([M + Na]$^+$), 294.90 ([M + Na]$^+$); HRMS (ESI) m/z: [M + Na]$^+$ calcd. For $C_{11}H_{11}BrNaO_3$ 292.9784; found 292.9782.

(3R,3aR*,6aS*)- and (3S*,3aR*,6aS*)-3-(p-Tolyl)tetrahydro-3H-furo[2,3-c][1,2]dioxole (cis-**13e** and trans-**13e**) and 4-Oxo-4-(p-tolyl)butyl Formate (**14e**): Reaction of **3e** with 2,3-Dihydrofuran **12** to Afford **13e** and **14e**.* The "General procedure for peroxycarbenium [3 +2] cycloaddition reaction with **12**" given above was used, with **3e** to replace **3a**. The reaction of **3e** with dihydrofuran **12** afforded **13e** (a colorless oil, 40 mg, 0.19 mmol, 76% from **3e**). If the experiment was done with less care in cooling (e.g., performing the chromatography at ambient temperature), varying amounts of the cleavage product **14e** could be obtained depending on the conditions in the individual run.

Data for *cis*-**13e** (a white solid, 10:1 PE/EtOAc R_f = 0.3): M.p. 65−67 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.19 (d, J = 8.0 Hz, 1H), 7.10 (d, J = 8.1 Hz, 1H), 6.05 (d, J = 5.2 Hz, 1H), 5.33 (d, J = 6.3 Hz, 1H), 4.00 (ddd, J = 11.4, 8.2, 5.8 Hz, 1H), 3.94 (dt, J = 1.7, 8.3 Hz, 1H), 3.62−3.57 (m, 1H), 2.35 (s, 3H), 1.80−1.71 (m, 1H), 1.67−1.61 (m, 1H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ = 138.1, 131.4, 129.5, 126.2, 109.1, 85.6, 69.9, 56.6, 27.3, 21.3; FT-IR (KBr) 3002, 2971, 2921, 2885, 2859, 1515, 1488, 1447, 1347, 1327, 1307, 1275, 1247, 1187, 1072, 1016, 977, 953, 925, 863, 845, 828, 810, 760, 727 cm^{-1}. MS (ESI) m/z: 229.15 ([M + Na]$^+$); HRMS (ESI) m/z: [M + Na]$^+$ calcd. for $C_{12}H_{14}NaO_3$ 229.0835; found 229.0834.

Data for a 0.6:1 (because some of the *cis*-isomer was already removed) mixture of *cis*-**13e**/*trans*-**13e** (a colorless oil, 10:1 PE/EtOAc R_f = 0.3): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30−7.26 (m, 2H), 7.20−7.16 (m, 3H), 7.13−7.09 (m, 2H), 6.04 (d, J = 5.2 Hz, 0.6H), 5.93 (d, J = 5.1 Hz, 1H), 5.33 (d, J = 6.2 Hz, 0.6H), 5.10 (br s, 1H), 4.20 (ddd, J = 11.1, 8.3, 5.9 Hz, 1H), 4.08 (dt, J = 2.0, 8.1 Hz, 1H), 4.00 (ddd, J = 11.4, 8.2, 5.8 Hz, 0.6H), 3.94 (dt, J = 1.7, 8.3 Hz, 0.6H), 3.72−3.67 (m, 1H), 3.62−3.56 (m, 0.6H), 2.35 (s, 1.8H), 2.34 (s, 3H), 2.30−2.24 (m, 1H), 2.23−2.18 (m, 1H), 1.81−1.71 (m, 0.6H), 1.66−1.60 (m, 0.6H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 138.0, 137.9 (*trans*), 137.1 (*trans*), 131.4, 129.5, 129.4 (*trans*), 126.1, 125.8 (*trans*), 109.0, 107.6 (*trans*), 88.3 (*trans*), 85.6, 69.8, 69.1 (*trans*), 60.6 (*trans*), 56.6, 32.3 (*trans*), 27.2, 21.3, 21.2 (*trans*); FT-IR (film of a concd solution in CH_2Cl_2) 2955, 2921, 2891, 1721, 1682, 1607, 1515, 1449, 1364, 1182, 1074, 978, 957, 925, 803 cm^{-1}. MS (ESI) m/z: 207.00 ([M + H]$^+$); HRMS (ESI) m/z: [M + Na]$^+$ calcd. for $C_{12}H_{14}NaO_3$ 229.0835; found 229.0838.

Data for **14e** (a colorless oil, less polar than *trans*-**13e** but more polar than *cis*-**13e**, 10:1 PE/EtOAc R_f = 0.3): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 (s, 1H), 7.88−7.86 (m, 2H), 7.28−7.25 (m, 2H), 4.28 (t, J = 6.4 Hz, 2H), 3.06 (t, J = 7.2 Hz, 2H), 2.42 (s, 3H), 2.13 (quint, J = 6.7 Hz, 2H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 198.7, 161.2, 144.2, 134.4, 129.5, 128.3, 63.5, 34.7, 23.2, 21.8; FT-IR (film of a concd solution in CH_2Cl_2) 2958, 2920, 2843, 1723, 1681, 1606, 1574, 1404, 1363, 1178, 811 cm^{-1}. MS (ESI) m/z: 228.95 ([M + Na]$^+$); HRMS (ESI) m/z: [M + Na]$^+$ calcd. for $C_{12}H_{14}NaO_3$ 229.0835; found 229.0839.

(3R,3aR*,6aS*)- and (3S*,3aR*,6aS*)-3-(o-Tolyl)tetrahydro-3H-furo[2,3-c][1,2]dioxole (cis-**13f** and trans-**13f**): Reaction of **3f***

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with 2,3-Dihydrofuran ***12*** *to Afford* ***13f.*** The "General procedure for peroxycarbenium [3 + 2] cycloaddition reaction with **12**" given above was used, with **3f** to replace **3a**. The reaction of **3f** with dihydrofuran **12** afforded **13f** (a colorless oil, 41 mg, 0.20 mmol, 80% from **3f**). In this case, the two diastereomers were relatively easier to separate from one another and after repeated chromatographic separations pure analytical samples of both *cis*-**13f** and *trans*-**13f** were obtained. No cleavage product **14f** was observed.

Data for *cis*-**13f** (a white solid, 10:1 PE/EtOAc R_f = 0.3): M.p. 55−57 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30−7.27 (m, 1H), 7.25−7.19 (m, 3H), 6.07 (d, J = 5.2 Hz, 1H), 5.39 (d, J = 6.2 Hz, 1H), 3.98 (ddd, J = 11.6, 8.2, 5.5 Hz, 1H), 3.92 (dt, J = 1.4, 8.3 Hz, 1H), 3.74−3.69 (m, 1H), 2.28 (s, 3H), 1.80−1.70 (m, 1H), 1.48−1.43 (m, 1H), ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 134.1, 133.3, 130.7, 128.1, 126.2, 125.3, 109.1, 83.3, 70.0, 54.3, 27.3, 19.6; FT-IR (KBr) 3081, 3034, 2963, 2924, 2887, 1489, 1464, 1447, 1364, 1350, 1323, 1251, 1205, 1074, 1010, 979, 959, 926, 847, 745, 731, 707 cm^{-1}. MS (ESI) m/z: 229.10 ([M + Na]$^+$); HRMS (ESI) m/z: [M + Na]$^+$ calcd. for $C_{12}H_{14}NaO_3$ 229.0835; found 229.0835.

Data for *trans*-**13f** (a colorless oil, 10:1 PE/EtOAc R_f = 0.3): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57−7.54 (m, 1H), 7.25−7.19 (m, 2H), 7.20−7.16 (m, 1H), 5.90 (d, J = 5.0 Hz, 1H), 5.22 (br s, 1H), 4.26−4.20 (m, 1H), 4.12−4.08 (m, 1H), 3.55 (dq, J = 1.6, 4.9 Hz, 1H), 2.33 (s, 3H), 2.30−2.26 (m, 2H);^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 138.7, 133.9, 130.6, 127.8, 126.3, 125.0, 107.5, 86.4, 69.1, 60.6, 32.6, 19.7; FT-IR (film of a concd solution in CH_2Cl_2) 3063, 3023, 2975, 2956, 2889, 1485, 1461, 1364, 1291, 1271, 1216, 1187, 1073, 989, 959, 927, 853, 753 cm^{-1}. MS (ESI) m/z: 228.95 ([M + Na]$^+$); HRMS (ESI) m/z: [M + Na]$^+$ calcd. for $C_{12}H_{14}NaO_3$ 229.0835; found 229.0837.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.joc.0c02180.

^{1}H and ^{13}C{^{1}H} NMR, IR spectra for all new compounds, NMR comparison table for **2b−d**, relative configuration of **5a** and ^{1}H NMR, and setup for concentrating ethereal H_2O_2 and low-temperature column chromatography (PDF)

Accession Codes

CCDC 2024241 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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(27) A scrutiny of the literature data revealed that the NMR data listed in these articles (by the same authors) were exactly the same, without any delicate discrepancies normally expected for the data from different measurements. The ^1H and ^{13}C NMR data for **2c** reported (ref 14) by that group were also problematic and incompatible with those reported earlier in ref 7 (which agreed very well with ours). We also tried to repeat the experiments in ref 15. In our hands, the reactions were very incomplete under the conditions of that article, giving ∼30% of the products. Also, **2b** and **2d** thus-obtained showed ^1H and ^{13}C NMR data fully consistent with the data of the samples prepared using the conditions (PMA or $MoO_2(acac)_2$) of this work.
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(29) One of the reviewers suggested that another factor that may contribute to the extra difficulty of dihydroperoxidation (compared with dialkyl acetalization) is the inner oxygen atom in the hydroperoxy group (the one directly connected to the acetal carbon atom) in that a hydroyhydroperoxide is easier to be protonated than the OMe in a nonperoxyhemiacetal.
(30) Alternatively, the facilitated reaction could be a consequence of better stabilization of the intermediate carbocation by H_2O_2.
(31) The physical and spectroscopic data of only one of three primary *gem*-dihydroperoxides (derived from aliphatic aldehydes) reported in that work was provided. The other two were referred to refs 20 and 21, and that in ref 21 (the product of the Table 2, entry 11 therein) turned out to be hydroxyhydropeoxide, not *gem*-dihydroperoxide.
(32) The experiment did not show any discernible reactions after stirring for 1 day and therefore was put aside to be abandoned. Somehow, the stirring was not stopped for 5 days when another TLC examination was made.
(33) Due to safety regulations, H_2O_2 of concentrations higher than 30% is not readily attainable in China (probably also some other countries). For this reason, we prepared the biphasic system of the same composition by mixing a calculated amount of H_2O with a calculated volume of ∼ten-fold concentrated ethereal H_2O_2.
(34) Exposure of the epoxide derived from **8** to the cycloaddition conditions (in the absence of any peroxy substrate) did not afford any **10**.
(35) Use of less $TiCl_4$ (1.2 mol equiv with respect to **3**) led to substantial lowering with partial recovery of the starting **3** despite prolonged reaction time (5 h). Higher reaction temperatures (−40, −25, or 0 °C) all resulted in drastically lowered yields. Alternative workup procedures (quenching with bases such as Et_3N) all led to much less satisfactory results.
(36) The X-structure for *cis*-**13a** has been deposited with Cambridge Structure Center and has been assigned the registration number CCDC 2024241.
(37) For an early (very brief) report on preparation of ethereal H_2O_2, see (a) Saito, I.; Nagata, R.; Yuba, K.; Matsuura, T. Synthesis of α-silyloxyhydroperoxides from the reaction of silyl enol ethers and hydrogen peroxide. *Tetrahedron Lett.* **1983**, *24*, 1737−1740. For a brief report of our modified procedure cf. ref 9.
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