Intramolecular Homolytic Displacements. 24. Simple Access to Glycidic Esters via Induced Decomposition of Peroxyketals Derived from Ethyl 2-(1-Hydroperoxyethyl)propenoate

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The synthetic potential of the homolytic-induced decomposition of peroxyketals derived from ethyl 2-(1-hydroperoxyethyl)propenoate to access glycidic esters was demonstrated. The propagation step of this free radical chain reaction proceeds via the addition of an alkyl radical to the double bond followed by S_Hi on the peroxidic bond with the production of an oxy radical, regenerating rapidly by β-elimination the alkyl radical responsible for the induced reaction. These reactions of elimination produce two fragments, an alkyl radical and an ester molecule, from linear "acetalic" radical, or they could be isomerizations in the case of cyclanyloxy radicals. In these last cases, the isomerization creates an ester function corresponding to a new protected functionality as aldehyde, acid, or alcohol.

Introduction

Over the past decade, a resurgence in free radical chemistry was observed.[1,2] The reactivity of carbon-centered radicals toward unsaturation to create carbon–carbon bonds has primarily focused attention on synthetic applications, particularly to prepare cyclic molecules.[2] Carbon-centered radicals were usually generated by homolytic substitutions (direct attack on halogen, sulfur, or selenium by organometallic radicals, or hydrogen abstraction by oxy radicals), while recently, Barton and co-workers[3] have opened new routes to carbon-centered radicals and developed new free radical chain reactions with "thiohydroxamic esters". More recently, the older method of production of carbon centered-radicals from oxy radicals, pioneered by Walling,[4] was considered by other researchers.[5]

Over the last 10 years, we have studied homolytic-induced decomposition of unsaturated peroxy derivatives as sources of oxygenated heterocycles.[6] The propagation step of this chain reaction (Figure 1) relies on an S_Hi reaction on the peroxidic moiety for the generation of an oxy radical, YO•. This latter species is the precursor of the alkyl radical Z•, which provokes the induced decomposition of the unsaturated peroxides. In the last few years, we have particularly studied *tert*-butylperoxy derivatives and used the hydrogen abstraction capacity of the *tert*-butoxy radical toward substrate ZH to generate the expected radical. This method for the production of carbon-centered radicals is however not always selective.[7] A second limitation corresponded to the necessity for a large excess of ZH (the precursor of the radical Z•), which was commonly used as solvent, in order to decrease the importance of allylic hydrogen abstraction from the unsaturated peroxy derivative. These drawbacks prompted us to consider several modifications to produce the expected radical Z•, in the propagation step, by the use of a mediator (suitably designed to react rapidly with alkoxyl radicals, which in so doing generate a radical of suitable selectivity to abstract a halogen[8] from ZX) or of a rearrangement of oxy radicals.[9] Such reactions require a solvent inert toward free radical attack; benzene is generally an acceptable solvent for all these reactions.

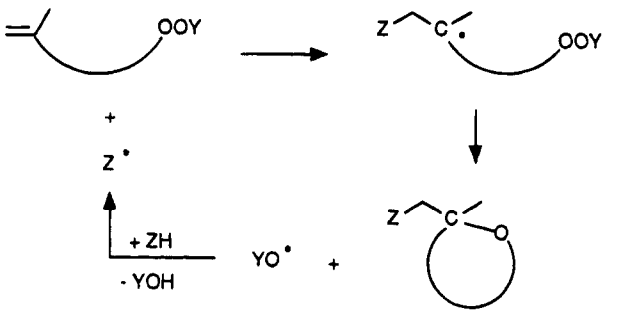

Figure 1. Induced decomposition of unsaturated peroxides in hydrogen donor solvent ZH.

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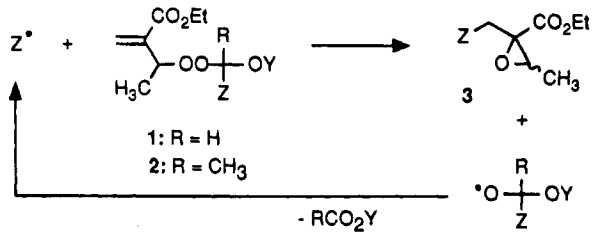
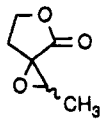


	Z	Y		Z	Y
a	Me	Me[d], Et[a]	h	CH_2OMe	Me
b	Et	Me	i[a]	CH_2Cl	Et
c[a]	n-C_6H_{13}	Me	j	CH_2Br	Me[d], Et[a]
d	i-Pr	Me	k[a]	CH_2CN	Me
e[a]	t-Bu	Me	l[d]	$CH_2C_6H_5$	Me
f, f'	CH_2CO_2R'[b]	Me[a], Et[b]	m[d]	CO_2Me	Me
g[a]	CH_2OH[c]	Et	n[d]	n-C_4H_9-CH(MeO_2C)	Me

[a] only for compounds 1 and / or 3 [b] 1f, 3f: R' = Me ; 2f', 3f': R' = Et
[c] 3g is not stable in conditions of the reaction and reacts by intramolecular transesterification to provide



[d] only for compounds 2 and / or 3

Figure 2. Synthesis of glycidic esters from peroxyketals of aldehydes and linear ketones.

This paper completes the preliminary results[9] obtained according to this strategy of rearrangement of oxy radicals.

Efficient reaction of β-elimination, observed for 1-methoxy-1-methylethoxy radicals derived from "acrylic" peroxyketals (**2a**, Figure 2), has been extended to show the general synthetic potential of such unsaturated peroxy derivate induced decompositions.

Results and Discussion

Peroxyketals were easily obtained by the classical reactions of an hydroperoxide (in this instance ethyl 2-(1-hydroperoxyethyl)propenoate) with the ketal of an aldehyde or a ketone[10] or with the corresponding enol ether.[11] Peroxy compounds **1** and **2** derived from aldehydes and linear ketones (Figure 2), when heated at 110 °C in benzene with *tert*-butyl peracetate (benzene/**1** or **2**/*tert*-butyl peracetate = 20/1/0.2), suffered an induced decomposition to provide epoxides, generally with good yields (Table 1).

Peroxides **1** gave a single epoxide. One could see from these results a decrease in the yield of epoxide **3** with increasing bulk of the alkyl group of the aldehydic precursor of the peroxide. This was attributed to the existence of a secondary reaction of the peroxy derivative (Figure 3) due to a direct elimination of dihydrogen (GC identification) with formation of the corresponding al-

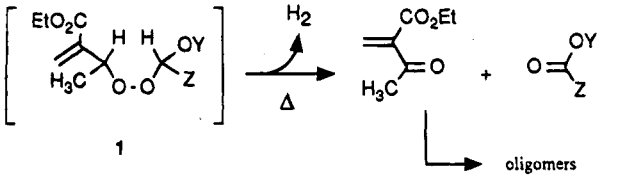


Figure 3. Hydrogen elimination from peroxyketals of aldehydes.

Table 1. Yields of Isolated Epoxides 3[a] from Induced Decomposition of 1 and 2 in Benzene at 110 °C (benzene/1 or 2/*tert*-butyl peracetate = 20/1/0.1)

	yield of 3 (%)[a] starting peroxyketal 1	2		yield of 3 (%)[a] starting peroxyketal 1	2
a	72	90	h	87	83 (1)[c]
b	71	85[b] (10)[c]	i	75	
c	65		j	84	83 (3)[c]
d	40[d]	90[b] (5)[c]	k	62	
e	5[d]		l		46 (traces)[c]
f•	65	85 (traces)[c]	m		45 (traces)[c]
g	79		n		74 (5)[c]

[a] Relative to **1** or **2**. [b] GC yields. [c] Yield of **3a** (GC yields determined on the reaction mixture). [d] For reaction performed at 20 °C with initiation by BEt_3/O_2; yields of isolated **3d** (95%) and **3e** (93%).

kanoate and ethyl 2-acetylpropenoate (which polymerizes under the free radical conditions; identified by ^1H and ^{13}C NMR study of the residue). Such dihydrogen elimination was previously noted during thermal decomposition of hemiperoxyketals.[12] Changing the initiation system (BEt_3 in presence of oxygen[13] instead of *tert*-butyl peracetate) and reaction temperature (20 °C instead of 110 °C) suppressed this secondary reaction and higher yields of epoxides **3d** (95%) and **3e** (93%) were then obtained.

Two different epoxides were generally isolated during the induced decomposition of peroxy derivatives **2**, prepared from linear ketones, by virtue of the reactions of radicals Z• and CH_3• with the substrate **2**. Indeed, oxy radical $CH_3OZ(CH_3)CO$• could evolve by two competitive processes of elimination with formation of such radicals; the relative amounts of epoxides formed in these induced decompositions show that the most stable radical was predominantly eliminated. From a synthetic point of view, production of epoxide **3a** (due to methyl radical formation), competitively with expected epoxides **3**, was not generally a serious drawback, due to the easy removal of the small amounts of lower boiling epoxide **3a** (Table 1).

Comparison of yields of the same epoxides **3** produced by induced decomposition of peroxy derivatives of aldehydes **1** and ketones **2** indicates similar efficiency for both synthetic routes. Thus, both reactions appear complementary and the choice of the peroxyketal, in terms of synthetic application, will be driven by the easier access to the precursor methyl ketone or aldehyde.

In all of the reactions described above, the entity Z "grafted" on the epoxy ester is native to the starting molecule and is liberated in the course of the rearrangement of the oxy radical with the elimination of a molecule

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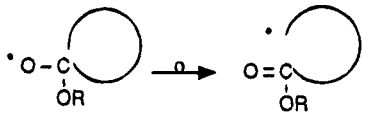
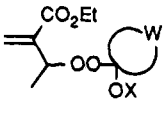


Figure 4. Free radical rearrangement of cyclic oxy radicals derived from peroxyketals of cyclanones.



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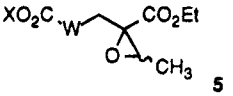

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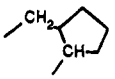
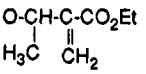
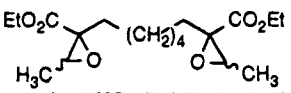
	W	X	Yield of 5 (%)[a]
a	$-(CH_2)_4-$	CH_3	88
b[b]		CH_3	85
c	$-(CH_2)_5-$	CH_3	76(13)[c]
d	$-(CH_2)_5-$	OtBu	90[e]
e[d]	$-(CH_2)_5-$		62[e]
f[f]	$-CH_2-CH=CH-(CH_2)_2-$	CH_3	30(2)[g]

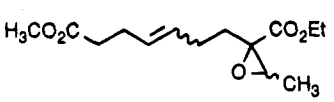
[a] relative to **4**

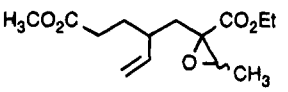
[b] **5b**: CO_2CH_3 linked to CH_2 from W and glycidyl fragment to CH

[c] presence of **3n** (gc yield determined on the reaction mixture)

[d] **5e**: 

[e] reaction performed at 20°C with initiation by Et_3B/O_2

[f] **5f**: 

5f': 

[g] presence of **5f'** (yield determined by ^1H NMR based on ethylenic H)

Figure 5. Synthesis of glycidic esters from cyclic peroxyketals of cyclanones.

of ester. Depending upon the existence of a chain W in either Z or R, elimination from the oxy radical will evolve by isomerization to produce an ester function and an alkyl radical in the same entity (Figure 4). To demonstrate this, peroxyketals **4**, prepared from cyclic ketones, were isomerized in benzene at 110 °C in presence of *tert*-butyl peracetate (Figure 5).

In the case of cyclopentanone derivative **4a** and 2-norbornanone derivative **4b**, single compounds (**5a** and **5b**, respectively) were isolated in fair yields. For cyclohexanone peroxy derivative **4c**, two isomeric epoxy esters **5c** and **3n** were obtained according to the behavior of the alkyl radicals produced in the β-scission of the oxy radical via free radical addition to the unsaturation of **4c** either before or after 1,5-hydrogen transfer (Figure 6). Another peroxy derivative **4d** prepared from cyclohexanone gave epoxy peroxy ester **5d**. In contrast to the case of peroxyketal **4c**, no adduct corresponding to the isomerization of the intermediate alkyl radical, by 1,5-hydrogen transfer, was identified. Three different explanations

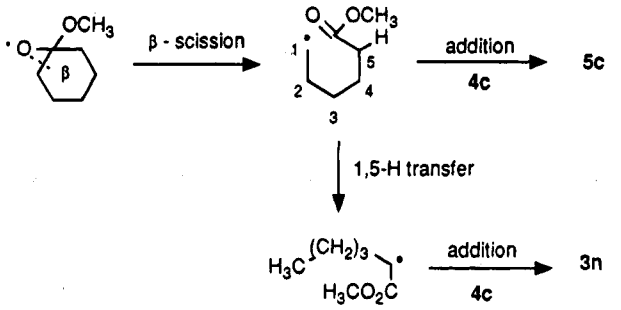


Figure 6. Formation of epoxides **5c** and **3n** from peroxyketal **4c**.

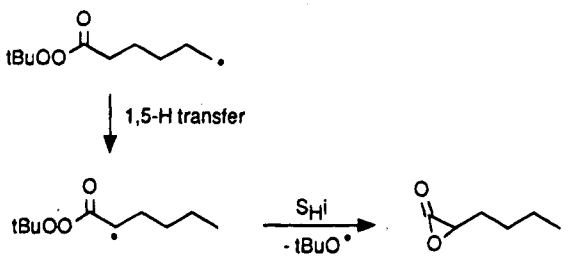


Figure 7. Free radical rearrangement in the induced decomposition of diperoxyketal **4d**.

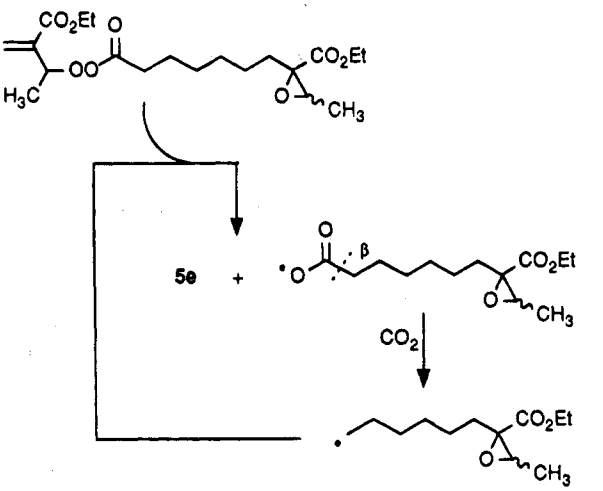


Figure 8. Formation of epoxide **5e** from diperoxyketal **4e**.

could account for this result: (1) the competition between the intramolecular 1,5-hydrogen transfer and the intermolecular addition to the double bond of a molecule of peroxide could hardly be influenced by the temperature of the reaction (20 °C for **4c** and 110 °C for **4d**); (2) the radical produced by 1,5-hydrogen transfer in the case of **4d** would react uniquely by the S_Hi reaction identified by Milas and Golubovic[14] (Figure 7); (3) the different bulk of *tert*-butylperoxy and methoxy groups attached to the carbonyl would affect the efficiency of the 1,5-hydrogen transfer.

Induced decomposition of the symmetrical diperoxyketal **4e** directly provided the diepoxide **5e**. This is not surprising if we consider that the intermediate unsaturated peroxy ester ought to suffer induced decomposition by alkyl radical to give the product (Figure 8). In the reaction of the peroxyketal of cyclohex-2-enone **4f**, products **5f** and **5f'**, corresponding to reaction of the allylic radical formed in the β-elimination were isolated (Figure

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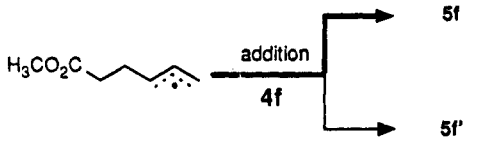


Figure 9. Formation of epoxide **5f** and **5f'** from peroxyketal **4f**.

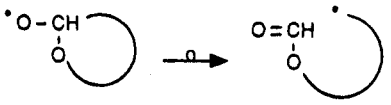
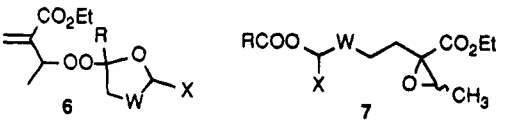


Figure 10. Free radical rearrangement of cyclic oxy radicals derived from cyclic peroxyketals containing an oxygen atom in the ring.



	R	W	X	Yield of 7(%)[a]
a	H	CH_2	H	80
b	CH_3	CH_2	H	87
c	H	CH_2	OMe	78
d	H	$(CH_2)_2$	H	86
e	H	$(CH_2)_2$	OEt	65

[a] relative to 6

Figure 11. Synthesis of glycidic esters from cyclic peroxyketals containing an oxygen atom in the ring.

9). The low yield observed could be attributed to two main causes: induced decomposition of the peroxy derivative by allylic attack (several kinds of allylic hydrogens) and/or dimerization of allylic radicals being more efficient than addition to the unsaturation of the peroxide, a circumstance observed earlier.[15]

Other cyclic peroxyketals **6** were designed where the alkoxy moiety was connected to one of the alkyl groups to provide oxacycloalkoxy radicals, which would then isomerize to carbon-centered radicals (Figure 10). Several such materials were prepared and decomposed in benzene at 110 °C in presence of *tert*-butyl peracetate to yield glycidic esters **7** on which protected alcohol and aldehyde functions were therefore "grafted" (Figure 11).

Conclusion

The strategy of alkyl radical generation by β-elimination from 1-alkoxyalkyloxy radicals, to provide alkyl radicals which promote induced decomposition of unsaturated "acrylic" peroxyketals to yield glycidic esters, appears to be facile and thus potentially useful in synthesis. Such reactions allow liberation of alkyl radicals native to the carbonyl precursor of the peroxyketal. Novel functionalized alkyl radicals can also be generated by isomerization of the 1-alkoxycycloalkoxy and 1-oxacycloalkoxy radicals with the formation of esters as protected acids, alcohols, or aldehydes. Homolytic-induced decompositions could also be performed on unsaturated diperoxyketals at room temperature to yield peresters or compounds containing two glycidyl moieties linked by an alkyl chain. The efficiency of such a method of production of alkyl radicals from α-alkoxyalkoxy radicals underlines the need for a deep knowledge of the reactivity of these transients with particular attention to the kinetic parameters of their reactions which are under investigation at the moment.

Experimental Section

General Procedure and Materials. ^1H NMR spectra were recorded at 250 MHz and the ^{13}C NMR data obtained at 62.9 MHz on a Bruker AC 250. ^1H and ^{13}C NMR chemical shifts of major diastereoisomer(s) are mentioned in *italic* when possible. Elemental analyses were performed at the Laboratoire Central de Microanalyse (CNRS), Vernaison, France. Flash column chromatographic purifications of peroxyketals were carried out on Merck silica gel 60 (60–200 mesh) and monitored by TLC using Merck precoated silica gel 60 F-250 (0.25-mm thickness) aluminium-backed plates. The plates were visualized under UV or iodine vapor. Mixtures of Et_2O and light petroleum ether (bp 45–55 °C) were used as eluant. Evaporative distillation refers to bulb-to-bulb distillation under reduced pressure using a Büchi Kugelrohr oven. Petroleum ether was distilled whereas diethyl ether and benzene were reagent grade and simply dried prior to use. Commercial compounds were used without any further purification.

General Procedure for the Preparation of Peroxyketals. (a) From Acetal (Method A). To a mixture of an acetal (30 mmol) and p-toluenesulfonic acid monohydrate (50 mg, 0.2 mmol) was added in small portions ethyl 2-(1-hydroperoxyethyl)propenoate[16] (4.8 g, 30 mmol) over 1 h. Liberated alcohol (methanol or ethanol) was eliminated under reduced pressure (20 mmHg). The reaction was monitored by ^1H NMR (disappearance of alcohol signals). The residue was then transfered to a column of silica gel and eluted with 12–20% Et_2O in petroleum ether to furnish pure peroxyketal.

(b) From Ketone, Trimethyl Orthoformate (Method A'). To a mixture of ketone (30 mmol), trimethyl orthoformate (3.18 g, 30 mmol) and p-toluenesulfonic acid monohydrate (50 mg, 0.2 mmol) was added in small portions ethyl 2-(1-hydroperoxyethyl)propenoate[16] (4.8 g, 30 mmol). Liberated methanol and methyl formate were evaporated under reduced pressure (20 mmHg) and the reaction was monitored by ^1H NMR tracking the disappearance of the methoxy signals (3.2 and 3.7 ppm) from methanol and methyl formate, respectively. Peroxyketal was then purified by flash chromatography on silica gel.

(c) From Enol Ether (Method B). A solution of ethyl 2-(1-hydroperoxyethyl) propenoate[16] (4.8 g, 30 mmol) and *p*-toluenesulfonic acid monohydrate (50 mg, 0.2 mmol) in Et_2O (50 mL) was cooled with stirring at −10 °C. To the cooled solution was added a solution of enol ether (30 mmol) in Et_2O (10 mL) dropwise. The stirred reaction mixture was then allowed to warm slowly at room temperature and washed with an aqueous solution of Na_2CO_3 (10 mL) and water (2 × 10 mL). The combined organic layers were dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure and peroxyketal purified by flash chromatography on a column of silica gel. Retention factor t_R (on TLC) for solvents petroleum ether/ether are mentioned for each peroxyketal.

Ethyl 2-[1-[(1-ethoxyethyl)peroxy]ethyl]propenoate (1a): method B, 70%; t_R = 0.43 (88/12); ^1H NMR δ 6.17 (s, 1H), 5.78–5.75 (m, 1H), 4.88 (dq, J = 7 Hz, 2H), 4.06 (q, J = 7 Hz, 2H), 3.39–3.25 (m, 1H), 3.08–2.95 (m, 1H), 0.78–0.60 (m, 12H); ^{13}C NMR δ 165.6, 140.9, 140.8, 124.8, 103.1, 103.0, 77.6, 77.4, 63.8, 60.4, 18.9, 18.7, 18.4, 18.2, 15.2, 15.1, 13.9. Anal. Calcd for $C_{11}H_{20}O_5$: C, 56.88; H, 8.68. Found: C, 57.03; H, 8.88.

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Ethyl 2-[1-[(1-methoxypropyl)peroxy]ethyl]propenoate (1b): method A with 1,1-dimethoxypropane,[17] 80%; t_R = 0.46 (88/12); ^{1}H NMR δ 6.25 (m, 1H) 5.86 (m, 1H), 4.67 (q, J = 6.6 Hz, 1H), 4.64 (t, J = 5.9 Hz, 1H), 4.15 (q, J = 7.1 Hz, 2H), 3.41 (s, 3H), 1.6–1.45 (m, 2H), 1.26 (d, J = 6.6 Hz, 3H), 1.23 (t, J = 7.1 Hz, 3H), 0.84 (t, J = 7.5 Hz, 3H); ^{13}C NMR δ 165.7, 140.9, 125.1, 125.0, 108.9, 108.8, 77.6, 77.4, 60.6, 60.5, 56.0, 55.9, 25.1, 19.1, 18.8, 14.1, 9.1. Anal. Calcd for $C_{11}H_{20}O_5$: C, 56.88; H, 8.68. Found: C, 57.03; H, 8.88.

Ethyl 2-[1-[(1-methoxyheptyl)peroxy]ethyl]propenoate (1c): method A with 1,1-dimethoxyheptane,[18] 78%; t_R = 0.48 (88/12); ^{1}H NMR δ 6.26 (m, 1H) 5.85 (m, 1H), 4.87 (q, J = 6.6 Hz, 1H), 4.72 (dt, J = 5.8 Hz, 1H), 4.16 (q, J = 7.1 Hz, 2H), 3.42 (s, 3H), 1.68–1.3 (m, 16H), 1.26 (d, J = 6.6 Hz, 3H), 1.24 (t, J = 7.1 Hz, 3H), 0.8 (br t, 3H); ^{13}C NMR δ 165.8, 165.7, 141.0, 140.9, 125.2, 125.0, 107.8, 107.7, 77.6, 77.4, 60.6, 60.5, 56.0, 55.9, 31.9, 31.6, 29.0, 24.7, 22.5, 19.1, 18.8, 15.2, 14.1, 13.9. Anal. Calcd for $C_{15}H_{28}O_5$: C, 62.47; H, 9.79. Found: C, 62.80; H, 10.02.

Ethyl 2-[1-[(1-methoxy-2-methylpropyl)peroxy]ethyl]-propenoate (1d): method A with 1,1-dimethoxy-2-methylpropane,[18] 75%; t_R = 0.45 (88/12); ^{1}H NMR δ 6.25 (m, 1H) 5.89–5.83 (m, 1H), 4.97 (q, J = 6.7 Hz, 1H), 4.4 (dd, J = 6.6 Hz, 1H), 4.15 (q, J = 7.1 Hz, 2H), 3.45 (s, 3H), 1.81 (oct, J = 6.6 Hz, 1H), 1.27 (d, J = 6.7 Hz, 3H), 1.24 (t, J = 7.1 Hz, 3H), 0.84 (d, J = 6.6 Hz, 6H); ^{13}C NMR δ 165.8, 165.7, 140.9, 125.3, 125.1, 111.9, 111.7, 77.4, 77.3, 60.6, 60.5, 57.1, 56.9, 30.9, 30.7, 19.2, 18.8, 17.85, 17.8, 17.7, 17.5, 15.2, 14.1. Anal. Calcd for $C_{12}H_{22}O_5$: C, 58.52; H, 9.00. Found: C, 58.42; H, 8.93.

Ethyl 2-[1-[(1-methoxy-2,2-dimethylpropyl)peroxy]ethyl]propenoate (1e): method A with 1,1-dimethoxy-2,2-dimethylpropane,[19] 88%; t_R = 0.44 (88/12); ^{1}H NMR δ 6.25 (m, 1H) 5.89–5.82 (m, 1H), 5.03–4.94 (m, 1H), 4.4 (m, 1H), 4.15 (dq, J = 7.1 Hz, 2H), 3.54 (m, 3H), 1.28 (dd, J = 6.6 Hz, 3H), 1.24 (dt, J = 7.1 Hz, 3H), 0.83 (s, 9H); ^{13}C NMR δ 165.8, 165.7, 140.7, 140.6, 125.5, 125.2, 113.7, 113.6, 77.3, 76.9, 60.6, 60.5, 59.4, 59.2, 35.8, 35.7, 25.1, 19.3, 18.8, 14.1. Anal. Calcd for $C_{13}H_{24}O_5$: C, 59.98; H, 9.29. Found: C, 59.92; H, 9.20.

Ethyl 2-[1-[[1-methoxy-2-(methoxycarbonyl)ethyl]-peroxy]ethyl]propenoate (1f): method A, 70%; t_R = 0.27 (85/15); ^{1}H NMR δ 6.20 (m, 1H) 5.79 (m, 1H), 5.08 (dt, J = 6 Hz, 1H), 4.92 (dq, J = 6.5 Hz, 1H), 4.10 (q, J = 7 Hz, 2H), 3.56 (ds, 3H), 3.38 (ds, 3H), 2.60 (dd, J = 6 Hz, 2H), 1.21 (d, J = 6.5 Hz, 3H), 1.18 (t, J = 7 Hz, 3H); ^{13}C NMR δ 169.7, 169.6, 165.7, 165.6, 140.6, 140.5, 125.4, 125.2, 104.1, 104.0, 77.87, 77.76, 60.6, 56.6, 56.5, 51.7, 51.6, 37.7, 37.6, 18.9, 18.7, 14.0. Anal. Calcd for $C_{12}H_{20}O_7$: C, 52.17; H, 7.30. Found: C, 52.03; H, 7.39.

Ethyl 2-[1-[(1-ethoxy-2-hydroxyethyl)peroxy]ethyl]-propenoate (1g): method A, 63%; t_R = 0.17 (80/20); ^{1}H NMR δ 6.21–6.18 (m, 1H) 6.06–5.72 (m, 1H), 4.96–4.91 (m, 1H), 4.84 (t, J = 7.5 Hz, 1H), 4.09 (dq, J = 7.05 Hz, 2H), 3.86–3.40 (m, 4H), 2.83 (s, 1H), 1.23–1.13 (m, 6H), 1.08 (dt, J = 7.05 Hz, 3H); ^{13}C NMR δ 166.0, 165.7, 140.6, 140.4, 125.7, 125.5, 105.8, 105.6, 77.8, 65.0, 64.9, 61.3, 61.2, 60.8, 60.7, 18.6, 18.5, 15.0, 14.9, 14.0. Anal. Calcd for $C_{11}H_{20}O_6$: C, 53.22; H, 8.12. Found: C, 53.12; H, 8.20.

Ethyl 2-[1-[(1,2-dimethoxyethyl)peroxy]ethyl]propenoate (1h): method A, 92%; t_R = 0.33 (83/17); ^{1}H NMR δ 6.19 (m, 1H) 5.8 (m, 1H), 4.63 (dq, J = 6.4 Hz, 1H), 4.7 (dt, J = 5.1 Hz, 1H), 4.08 (q, J = 7.1 Hz, 2H), 3.35 (dd, J = 5.1 Hz, 2H), 3.38 (s, 3H), 3.23 (s, 3H), 1.2 (dd, J = 6.4 Hz, 3H), 1.17 (t, J = 7.1 Hz, 3H); ^{13}C NMR δ 165.6, 165.5, 140.7, 140.6, 125.2, 125.1, 105.8, 105.5, 77.9, 77.8, 71.1, 71.0, 60.5, 59.1, 56.3. Anal. Calcd for $C_{11}H_{20}O_6$: C, 53.22; H, 8.12. Found: C, 53.13; H, 8.21.

General Procedure for the Preparation of Halogeno Peroxy Derivatives 1i, 1j, and 2j from Enol Ether and *tert*-Butyl Hypochlorite (Method C) or *N*-halogenosuccinimide (Method D). To a cooled (−10 °C) and stirred mixture of ethyl 2-(1-hydroperoxyethyl)propenoate (4.8 g, 30 mmol) and vinyl alkyl ether (30 mmol) in Et_2O (20 mL) was added analytical grade $NaHCO_3$ (8.4 mg, 1 mmol) and *tert*-butyl hypochlorite (3.26 g, 30 mmol) or *N*-halogenosuccinimide (5.34 g of NBS or 4 g of NCS, 30 mmol) in small portions over 1 h. Stirring was continued for 2 h in the case of tBuOCl and overnight when *N*-halogenosuccinimide was used. The reaction mixture was then washed with a saturated aqueous solution of $NaHCO_3$ (10 mL), extracted with Et_2O (2 × 10 mL), and dried over anhydrous $MgSO_4$. The solvent was evaporated under reduced pressure and the residue was chromatographed on silica to give pure peroxyketals **1i**, **1j**, and **2j**.

Ethyl 2-[1-[(2-chloro-1-ethoxyethyl)peroxy]ethyl]propenoate (1i): method C, 35% or method D, 50%; t_R = 0.54 (88/12); ^{1}H NMR δ 6.20 (m, 1H), 5.81 (m, 1H), 5–4.8 (m, 2H), 4.12 (q, J = 7 Hz, 2H), 3.86–3.7 (m, 1H), 3.6–3.4 (m, 3H), 1.3–1.1 (m, 9H); ^{13}C NMR δ 165.7, 165.6, 141.0, 140.9, 125.5, 125.4, 105.0, 104.8, 78.1, 78.0, 65.0, 64.9, 60.6, 60.5, 42.1, 41.9, 18.7, 18.6, 15.2, 15.1, 14.0. Anal. Calcd for $C_{11}H_{19}O_5Cl$: C, 49.54; H, 7.18; O, 29.99. Found: C, 49.48; H, 7.07; O, 30.12.

Ethyl 2-[1-[(2-bromo-1-ethoxyethyl)peroxy]ethyl]propenoate (1j): method D, 65%; t_R = 0.47 (88/12); ^{1}H NMR δ 6.23 (m, 1H) 5.83 (m, 1H), 5.0 (qd, J = 6.5 Hz, 1H), 4.90 (td, J = 5.5 Hz, 1H), 4.12 (q, J = 7.1 Hz, 2H), 3.85–3.23 (m, 4H), 1.25 (d, J = 6.5 Hz, 3H), 1.20 (t, J = 7.1 Hz, 3H), 1.13 (td, J = 7 Hz, 3H); ^{13}C NMR δ 165.5, 165.4, 140.5, 140.4, 125.4, 125.3, 104.9, 104.7, 78.1, 77.9, 65.1, 65.0, 60.6, 60.55, 29.6, 29.4, 18.8, 18.6, 15.1, 14.9, 14.1. Anal. Calcd for $C_{11}H_{19}O_5Br$: C, 42.46; H, 6.15; O, 25.71. Found: C, 42.33; H, 6.21; O, 25.90.

Ethyl 2-[1-[(1-methoxy-2-cyanoethyl)peroxy]ethyl]propenoate (1k): method A, 30%; t_R = 0.21 (80/20); ^{1}H NMR δ 6.17 (m, 1H) 5.79–5.75 (m, 1H), 4.9 (q, J = 6.5 Hz, 1H), 4.87 (t, J = 5.6 Hz, 1H), 4.05 (q, J = 7.1 Hz, 2H), 3.33 (ds, 3H), 2.7–2.6 (m, 2H), 1.18 (dd, J = 6.5 Hz, 3H), 1.13 (t, J = 7.1 Hz, 3H); ^{13}C NMR δ 165.4, 165.3, 140.1, 125.7, 125.6, 115.8, 115.6, 102.1, 101.8, 78.3, 78.1, 60.6, 56.6, 56.4, 21.9, 21.8, 18.4, 18.3, 13.9. Anal. Calcd for $C_{11}H_{17}NO_5$: C, 54.31; H, 7.04; O, 32.88. Found: C, 54.34; H, 7.11; O, 33.02.

Ethyl 2-[1-[(1-methoxy-1-methylethyl)peroxy]ethyl]-propenoate (2a): method B, 81%; t_R = 0.37 (88/12); ^{1}H NMR δ 6.27 (m, 1H), 5.90 (m, 1H), 4.93 (q, J = 6.6 Hz, 1H), 4.16 (q, J = 7.1 Hz, 2H), 3.22 (s, 3H), 1.34–1.21 (m, 12H); ^{13}C NMR δ 165.9, 141.2, 124.9, 104.6, 77.6, 60.6, 49.1, 22.8, 22.6, 18.7, 14.1. Anal. Calcd for $C_{11}H_{20}O_5$: C, 56.88; H, 8.68. Found: C, 56.81; H, 8.75.

Ethyl 2-[1-[(1-methoxy-1-methylpropyl)peroxy]ethyl]-propenoate (2b): method A′, 80%; t_R = 0.43 (88/12); ^{1}H NMR δ 6.22 (m, 1H) 5.85 (m, 1H), 4.90 (dq, J = 6.6 Hz, 1H), 4.13 (q, J = 7.1 Hz, 2H), 3.17 (s, 3H), 1.64–1.52 (m, 2H), 1.24–1.18 (m, 6H), 1.21 (t, J = 7.1 Hz, 3H), 0.82 (dt, J = 7.5 Hz, 3H); ^{13}C NMR δ 165.9, 141.2, 124.8, 124.7, 106.9, 106.8, 77.3, 77.1, 60.5, 48.8, 48.7, 28.1, 27.8, 19.1, 19.0, 18.9, 14.1, 8.3. Anal. Calcd for $C_{12}H_{22}O_5$: C, 58.52; H, 9.00. Found: C, 58.48; H, 9.11.

Ethyl 2-[1-[(1,2-dimethyl-1-methoxypropyl)peroxy]ethyl]propenoate (2d): method A′, 86%; t_R = 0.48 (88/12); ^{1}H NMR δ 6.17 (m, 1H) 5.82–5.79 (m, 1H), 4.91–4.81 (m, 1H), 4.08 (q, J = 7.1 Hz, 2H), 3.13 (s, 3H), 2.08–1.98 (m, 1H), 1.20 (d, J = 6.6 Hz, 3H), 1.17 (t, J = 7.1 Hz, 3H), 1.04 (s, 3H), 0.77 (d, J = 6.9 Hz, 6H); ^{13}C NMR δ 165.8, 165.7, 141.2, 124.7, 124.6, 108.9, 108.7, 77.1, 76.8, 60.45, 60.4, 48.5, 48.4, 31.7, 31.5, 19.0, 18.9, 17.6, 17.5, 17.4, 17.3, 14.6, 14.5, 14.0. Anal. Calcd for $C_{13}H_{24}O_5$: C, 59.17; H, 9.07. Found: C, 59.02; H, 9.09.

Ethyl 2-[1-[[1-ethoxy-1-methyl-2-(ethoxycarbonyl)ethyl]peroxy]ethyl]propenoate (2f): method B, 73%; t_R = 0.29 (88/12); ^{1}H NMR δ 6.09 (m, 1H) 5.82 (m, 1H), 4.77 (q, J = 6.5 Hz, 1H), 4.11 (q, J = 7 Hz, 2H), 4.02 (dq, J = 7.1 Hz, 2H), 3.58–3.34 (m, 2H), 2.78–2.57 (m, 2H), 1.38 (s, 3H), 1.23–1.13 (m, 9H), 1.08 (t, J = 7.1 Hz, 3H); ^{13}C NMR δ 169.2, 165.7, 165.6, 141.0, 140.9, 124.9, 124.7, 104.1, 103.9, 77.6, 77.4, 60.5, 60.3, 60.2, 57.0, 56.9, 41.7, 20.3, 18.9, 15.1, 14.0. Anal. Calcd for $C_{15}H_{26}O_7$: C, 56.59; H, 8.23; C, 56.65; H, 8.21.

Ethyl 2-[1-[(1,2-dimethoxy-1-methylethyl)peroxy]ethyl]propenoate (2h): method A′, 74%; t_R = 0.43 (88/12); ^{1}H NMR δ 6.2 (m, 1H) 5.85 (m, 1H), 4.85 (q, J = 7 Hz, 1H), 4.15 (q, J = 7 Hz, 2H), 3.3 (ds, 6H), 3.15–3.0 (m, 2H), 1.5–1.1 (m,

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9H). Anal. Calcd for $C_{12}H_{22}O_6$: C, 54.95; H, 8.45. Found: C, 54.87; H, 8.56.

Ethyl 2-[1-[(2-bromo-1-methoxy-1-methylethyl)peroxy]ethyl]propenoate (2j): method D, 74%; t_R = 0.43 (88/12); ^{1}H NMR δ 6.22 (m, 1H), 5.84 (m, 1H), 4.97 (qd, J = 6.5 Hz, 1H), 4.12 (q, J = 7.1 Hz, 2H), 3.6–3.3 (m, 2H), 3.23 (sd, 3H), 1.27 (d, J = 6.5 Hz, 3H), 1.23 (s, 3H), 1.21 (t, J = 7.1 Hz, 3H); ^{13}C NMR δ 165.7, 165.6, 140.9, 140.6, 125.4, 124.9, 104.5, 104.4, 77.9, 77.7, 60.5, 49.8, 49.7, 34.2, 34.1, 22.7, 22.5, 18.9, 18.8, 14.1. Anal. Calcd for $C_{11}H_{19}O_5Br$: C, 42.46; H, 6.15; O, 25.71. Found: C, 42.30; H, 5.88; O, 25.53.

Ethyl 2-[1-[(1-benzyl-1-methoxyethyl)peroxy]ethyl]-propenoate (2l): method A', 65%; t_R = 0.35 (88/12); ^{1}H NMR δ 7.3–7.16 (m, 5H), 6.25 (m, 1H), 5.97 (m, 1H), 5.08 (qd, J = 6.6 Hz, 1H), 4.22 (dq, J = 7.1 Hz, 2H), 3.35 (s, 3H), 3.09–2.92 (m, 2H), 1.38 (d, J = 6.6 Hz, 3H), 1.29 (t, J = 7.1 Hz, 3H), 1.15 (s, 3H); ^{13}C NMR δ 165.9, 141.2, 136.8, 130.5, 130.4, 128.0, 126.4, 125.1, 106.6, 106.4, 77.8, 77.4, 60.6, 49.3, 49.2, 42.5, 42.2, 19.4, 19.2, 19.1, 14.2. Anal. Calcd for $C_{17}H_{24}O_5$: C, 66.21; H, 7.84. Found: C, 66.44; H, 7.55.

Ethyl 2-[1-[[1-methoxy-1-(methoxycarbonyl)ethyl]-peroxy]ethyl]propenoate (2m): method A with methyl 2,2-dimethoxypropanoate,[20] 78%; t_R = 0.29 (80/20); ^{1}H NMR δ 6.2 (m, 1H), 5.8 (m, 1H), 4.96–4.76 (m, 1H), 4.0 (dq, J = 7 Hz, 2H), 3.6 (ds, 3H), 3.2 (ds, 3H), 1.3 (s, 3H), 1.2–1.05 (m, 6H); ^{13}C NMR δ 168.8, 168.5, 165.5, 140.6, 140.3, 125.4, 124.8, 103.5, 103.4, 78.1, 78.0, 60.5, 52.5, 50.1, 49.9, 19.0, 18.8, 14.0. Anal. Calcd for $C_{12}H_{20}O_7$: C, 52.17; H, 7.30. Found: C, 52.24; H, 7.24.

Ethyl 2-[1-[[2-(methoxycarbonyl)-1-methoxy-1-methylhexyl]peroxy]ethyl]propenoate (2n): method A' with methyl 2-butylacetoacetate,[21] 72%; t_R = 0.35 (88/12); ^{1}H NMR δ 6.15 (m, 1H) 5.8 (m, 1H), 4.8 (q, J = 7 Hz, 1H), 4.15 (q, J = 7 Hz, 2H), 3.7 (s, 3H), 3.2 (s, 3H), 1.9–1.1 (m, 16H), 0.9 (br t, 3H). Anal. Calcd for $C_{17}H_{30}O_7$: C, 58.94; H, 8.73. Found: C, 59.08; H, 8.64.

Ethyl 2-[1-[(1-methoxy-1-cyclopentyl)peroxy]ethyl]-propenoate (4a): method B with 1-methoxycyclopentene;[22] 65%, t_R = 0.36 (88/12); ^{1}H NMR δ 6.20 (m, 1H) 5.83 (m, 1H), 4.91 (q, J = 6.55 Hz, 1H), 4.11 (q, J = 7.1 Hz, 2H), 3.17 (s, 3H), 1.87–1.48 (m, 8H), 1.21 (d, J = 6.55 Hz, 3H), 1.19 (t, J = 7.1 Hz, 3H); ^{13}C NMR δ 165.8, 141.2, 124.8, 116.4, 77.2, 60.5, 50.2, 33.7, 33.6, 23.6, 18.9, 14.0. Anal. Calcd for $C_{13}H_{22}O_5$: C, 60.45; H, 8.52. Found: C, 60.49; H, 8.37.

Ethyl 2-[1-[(2-methoxy-2-norbornanyl)peroxy]ethyl]-propenoate (4b): method A with 2,2-methoxynorbornane;[23] t_R = 0.42 (88/12); ^{1}H NMR δ 6.15 (m, 1H) 5.75 (m, 1H), 5.1–4.65 (m, 1H), 4.15 (q, J = 7 Hz, 2H), 3.15 (s, 3H), 2.5–0.9 (m, 16H). Anal. Calcd for $C_{15}H_{24}O_5$: C, 63.36; H, 8.51. Found: C, 63.31; H, 8.62.

Ethyl 2-[1-[(1-methoxy-1-cyclohexyl)peroxy]ethyl]propenoate (4c): method B with 1-methoxycyclohexene;[24] t_R = 0.39 (88/12); ^{1}H NMR δ 6.20 (m, 1H) 5.84 (m, 1H), 4.90 (q, J = 6.6 Hz, 1H), 4.11 (q, J = 7.1 Hz, 2H), 3.15 (s, 3H), 1.60–1.25 (m, 10H), 1.20 (d, J = 6.6 Hz, 3H), 1.19 (t, J = 7.1 Hz, 3H); ^{13}C NMR δ 165.8, 141.3, 124.7, 104.7, 77.2, 60.5, 48.0, 31.6, 31.4, 25.4, 22.65, 22.6, 19.0, 14.0. Anal. Calcd for $C_{14}H_{24}O_5$: C, 61.74; H, 8.88. Found: C, 61.59; H, 8.73.

Ethyl 2-[1-[[1-(*tert*-butylperoxy)-1-cyclohexyl]peroxy]-ethyl]propenoate (4d). To a stirred mixture of 1,1-bis(*tert*-butylperoxy)cyclohexane (5.2 g, 20 mmol, prepared from cyclohexanone and *t*-butyl hydroperoxide according to the method of Stocker et al.[25]) and *p*-toluenesulfonic acid monohydrate (50 mg, 0.2 mmol) was added in small portions ethyl 2-(1-hydroperoxyethyl)propenoate (3.2 g, 20 mmol) over 1 h. Liberated *tert*-butyl hydroperoxide was evaporated step by step under reduced pressure (10^{-3} Torr) and the reaction was monitored by ^{1}H NMR tracking the disappearance of the OOH signals (8–9 ppm). The product was then purified on silica (4.88 g, 74%): t_R = 0.55 (88/12); ^{1}H NMR δ 6.23 (m, 1H) 5.90 (m, 1H), 5.16 (q, J = 6.7 Hz, 1H), 4.13 (dq, J = 7.1 Hz, 2H), 1.73–1.65 (m, 4H), 1.53–1.28 (m, 6H), 1.22 (d, J = 6.7 Hz, 3H), 1.23 (t, J = 7.1 Hz, 3H), 1.20 (s, 9H); ^{13}C NMR δ 165.9, 141.5, 124.5, 108.1, 79.0, 77.8, 60.3, 30.7, 30.6, 26.7, 25.5, 22.6, 22.4, 19.0, 14.1. Anal. Calcd for $C_{17}H_{30}O_6$: C, 61.80; H, 9.15. Found: C, 61.65; H, 8.95.

Ethyl 2-[1-[[1-(2-ethoxycarbonyl)-1-methylprop-2-enyl]peroxy]-1-(cyclohexylperoxy)ethyl]propenoate (4e): To a stirred mixture of trimethyl orthoformate (2.12 g, 20 mmol), cyclohexanone (1.96 g, 20 mmol), and *p*-toluenesulfonic acid monohydrate (50 mg, 0.2 mmol) was added in small portions ethyl 2-(1-hydroperoxyethyl)propenoate (6.4 g, 40 mmol) over 1 h. Liberated methanol and methyl formate were evaporated under reduced pressure (20 mmHg) and the reaction was monitored by ^{1}H NMR tracking the disappearance of the methoxy signals (3.2 and 3.7 ppm) from methanol and methyl formate, respectively. Peroxyketal was then purified by flash chromatography on silica: t_R = 0.35 (88/12); ^{1}H NMR δ 6.23–6.21 (m, 2H) 5.88–5.83 (m, 2H), 5.03 (q, J = 6.5 Hz, 2H), 4.13 (dq, J = 7.2 Hz, 4H), 1.74–1.31 (m, 10H), 1.25 (d, J = 6.5 Hz, 6H), 1.21 (t, J = 7.2 Hz, 6H); ^{13}C NMR δ 165.8, 141.1, 141.2, 124.8, 124.7, 109.1, 109.0, 77.7, 77.5, 60.4, 30.4, 25.4, 22.6, 18.9, 14.1. Anal. Calcd for $C_{20}H_{32}O_8$: C, 59.98; H, 8.05. Found: C, 60.07; H, 8.14.

Ethyl 2-[1-[(1-methoxy-1-cyclohex-3-enyl)peroxy]ethyl]propenoate (4f): method B with 1-methoxycyclohexa-1,4-diene, 60% or 1-methoxycyclohexa-1,3-diene, 30%; t_R = 0.33 (88/12); ^{1}H NMR δ 6.23 (m, 1H) 5.86 (m, 1H), 5.51 (br AX system, J = 9.9 Hz, 2H), 4.3 (q, J = 6.6 Hz, 1H), 4.13 (q, J = 7.1 Hz, 2H), 3.22 (s, 3H), 2.40–1.29 (m, 6H), 1.25 (br d, 3H), 1.22 (t, J = 7.1 Hz, 3H); ^{13}C NMR δ 165.8, 141.2, 141.1, 126.5, 126.4, 125.0, 124.9, 122.8, 122.7, 104.2, 104.1, 77.5, 77.3, 60.5, 48.4, 32.5, 32.4, 27.7, 27.6, 23.4, 19.0, 14.1. Anal. Calcd for $C_{14}H_{22}O_5$: C, 62.20; H, 8.20. Found: C, 61.85; H, 8.46.

Ethyl 2-[1-(2-tetrahydrofuranylperoxy)ethyl]propenoate (6a): method A, 91% or method B, 60%; t_R = 0.35 (85/15); ^{1}H NMR δ 6.19 (m, 1H), 5.8 (m, 1H), 5.55–5.50 (m, 1H), 4.9 (dq, J = 6.5 Hz, 1H), 4.10 (q, J = 7.1 Hz, 2H), 3.85–3.72 (m, 2H), 2.05–1.54 (m, 4H), 1.20 (d, J = 6.5 Hz, 3H), 1.19 (t, J = 7.1 Hz, 3H); ^{13}C NMR δ 165.8, 165.7, 141.1, 140.8, 125.0, 106.7, 106.1, 77.9, 77.3, 67.4, 67.3, 60.5, 60.4, 29.4, 29.3, 23.8, 19.1, 18.7, 14.0. Anal. Calcd for $C_{11}H_{18}O_5$: C, 57.38; H, 7.88. Found: C, 57.26; H, 7.83.

Ethyl 2-[1-[(2-methyl-2-tetrahydrofuranyl)peroxy]ethyl]propenoate (6b): method B, 65%; t_R = 0.38 (85/15); ^{1}H NMR δ 6.18 (m, 1H) 5.83–5.80 (m, 1H), 4.93 and 4.86 (q, J = 6.6 Hz, 1H), 4.10 (q, J = 7.15 Hz, 2H), 3.90–3.80 (m, 2H), 2.10–1.62 (m, 4H), 1.22 (ds, 3H), 1.20 (d, J = 6.6 Hz, 3H), 1.19 (t, J = 7.15 Hz, 3H); ^{13}C NMR δ 165.9, 165.8, 141.3, 141.1, 124.9, 124.8, 112.6, 112.3, 78.0, 77.9, 68.4, 68.3, 22.2, 22.1, 19.0, 18.9, 14.0. Anal. Calcd for $C_{12}H_{20}O_5$: C, 59.00; H, 8.25. Found: C, 58.93; H, 8.21.

Ethyl 2-[1-[(5-methoxy-2-tetrahydrofuranyl)peroxy]-ethyl]propenoate (6c): method A, 83%; t_R = 0.32 (83/17); ^{1}H NMR δ 6.15 (m, 1H) 5.76 (m, 1H), 5.51–5.48 (m, 1H), 5.0 (m, 1H), 4.9 (dq, J = 6.6 Hz, 1H), 4.05 (q, J = 7.1 Hz, 2H), 3.20 (s, 3H), 2.03–1.59 (m, 4H), 1.17 (d, J = 6.6 Hz, 3H), 1.15 (t, J = 7.1 Hz, 3H); ^{13}C NMR δ 165.6, 140.9, 140.7, 125.1, 125.0, 106.4, 106.1, 105.8, 105.2, 77.8, 77.6, 60.5, 60.4, 54.9, 54.6, 30.3, 30.2, 27.6, 27.5, 19.0, 18.6, 14.0. Anal. Calcd for $C_{12}H_{20}O_6$: C, 55.37; H, 7.75. Found: C, 55.19; H, 7.81.

Ethyl 2-[1-(2-tetrahydropyranylperoxy)ethyl]propenoate (6d): method B, 75%; t_R = 0.35 (85/15); ^{1}H NMR δ 6.11 (m, 1H), 5.79 (m, 1H) 5.71 (m, 1H), 5.0–4.9 (m, 1H), 4.88 (q, J = 6.6 Hz, 1H), 4.03 (q, J = 7.2 Hz, 2H), 3.78–3.26 (m, 2H), 1.50–1.35 (m, 6H), 1.15 (d, J = 6.6 Hz, 3H), 1.12 (t, J = 7.2 Hz, 3H); ^{13}C NMR δ 165.6, 141.0, 140.8, 124.8, 100.9, 100.4, 77.9, 77.1, 62.4, 62.2, 60.4, 27.7, 27.6, 25.0, 24.9, 19.5, 19.0, 18.7, 14.0, 13.9. Anal. Calcd for $C_{12}H_{20}O_5$: C, 59.00; H, 8.25. Found: C, 59.11; H, 8.17.

Ethyl 2-[1-[(6-ethoxy-2-tetrahydropyranyl)peroxy]ethyl]propenoate (6e): method B, 62%; t_R = 0.32 (83/17); ^{1}H NMR δ 6.18 (m, 1H) 5.8 (m, 1H), 5.27–5.21 (m, 1H), 5.0 (dq, J = 6.5 Hz, 1H), 4.84–4.72 (m, 1H), 4.08 (q, J = 7.1 Hz, 2H),

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3.94–3.3 (m, 2H), 1.68–1.26 (m, 6H), 1.19 (d, J = 6.5 Hz, 3H), 1.10 (t, J = 7.1 Hz, 3H), 1.08 (t, J = 7 Hz, 3H); ^{13}C NMR δ 165.6, 141.0, 140.9, 140.8, 140.7, 125.2, 125.0, 124.9, 124.8, 101.6, 101.3, 99.7, 99.0, 97.5, 97.4, 96.9, 78.5, 78.3, 77.5, 77.2, 63.0, 60.5, 29.9, 29.8, 29.6, 29.5, 27.3, 27.1, 26.9, 19.1, 18.9, 18.8, 18.7, 17.9, 17.7, 17.5, 15.0, 14.0. Anal. Calcd for $C_{14}H_{24}O_6$: C, 58.32; H, 8.39. Found: C, 58.30; H, 8.37.

General Procedure for the Synthesis of Glycidic Esters. (a) With *tert*-Butyl Peracetate Initiator. A mixture of peroxyketal (20 mmol) and *tert*-butyl peracetate (0.26 g, 2 mmol) was added to an ampule containing the amount of benzene (31.2 g, 200 mmol) required to produce a molar ratio benzene/peroxyketal/initiator equal to 20/1/0.1. The ampule was then sealed under reduced pressure (10^{-3} Torr) and heated at 110 °C for 12 h. The volatiles were then removed under *vacuum* and the glycidic ester was distilled with a bulb-to-bulb apparatus.

(b) With BEt_3/O_2 Initiating System. To a vigorously stirred solution of peroxyketal (1 mmol) in benzene (1 mL) was added a 0.1 M solution of BEt_3 in hexane (1 mL) over 30 min. Continuous air bubbling was maintained in the reaction medium during the whole procedure.

Product **3a**[7] is a known compound, and the spectral data agree with those reported.

Ethyl 2,3-epoxy-2-propylbutanoate (3b): ^{1}H NMR δ 4.7–3.96 (m, 2H), *3.1* and 2.9 (q, J = 5.5 Hz, 1H), 2.1–1.27 (m, 4H), 1.21 (d, J = 5.5 Hz, 3H), 1.13 (t, J = 7 Hz, 3H), 0.82 (t, J = 7 Hz, 3H); ^{13}C NMR δ *171.0*, 169.5, *61.2*, 61.1, 62.2, *60.8*, 58.2, *57.9*, 35.1, *29.4*, *18.5*, 18.1, *14.2*, 14.1, *14.0*, 13.8, *13.6*, 13.4. Anal. Calcd for $C_9H_{16}O_3$: C, 62.77; H, 9.36. Found: C, 62.82; H, 9.42.

Ethyl 2,3-epoxy-2-heptylbutanoate (3c): ^{1}H NMR δ 4.10 (q, J = 7.1 Hz, 2H), *3.13* and 2.94 (q, J = 5.5 Hz, 1H), 2.2–1.3 (m, 12H), 1.24 (d, J = 5.5 Hz, 3H), 1.21 (t, J = 7.1 Hz, 3H), 0.80 (br t, 3H); ^{13}C NMR δ *170.9*, 169.5, *61.2*, 61.0, 62.3, *60.9*, 58.3, *57.9*, 33.0, *31.5*, 29.5, *29.2*, *28.9*, *27.3*, 25.0, *24.6*, *22.4*, 14.1, *13.9*, 14.0, 13.6, *13.4*. Anal. Calcd for $C_{13}H_{24}O_3$: C, 68.38; H, 10.60. Found: C, 68.31; H, 10.72.

Ethyl 2,3-epoxy-2-(2-methylpropyl)butanoate (3d): ^{1}H NMR δ 4.09 (q, J = 7.2 Hz, 2H), *3.04* and 2.88 (q, J = 5.5 Hz, 1H), 2.13–1.75 (m, 3H), 1.23 (d, J = 5.5 Hz, 3H), 1.17 (t, J = 7.2 Hz, 3H), 0.86 (dd, J = 5.2 Hz, 6H); ^{13}C NMR δ *171.3*, 169.7, *61.2*, 61.1, 62.0, *60.4*, 58.1, *57.2*, 42.0, *35.4*, 25.8, *25.6*, *22.9*, 22.6, *14.2*, 14.0, 13.6, *13.4*. Anal. Calcd for $C_{10}H_{18}O_3$: C, 64.49; H, 9.74. Found: C, 64.59; H, 9.85.

Ethyl 2,3-epoxy-2-(2,2-dimethylpropyl)butanoate (3e): ^{1}H NMR δ 3.98 (q, J = 7.2 Hz, 2H), *2.78* and 2.70 (q, J = 5.4 Hz, 1H), 2.35–2.27 (m, 2H), 1.13 (d, J = 5.4 Hz, 3H), 1.07 (t, J = 7.2 Hz, 3H), 0.78 (s, 9H); ^{13}C NMR δ *171.9*, 170.2, *61.1*, 60.9, 61.8, *59.6*, 57.9, *56.6*, 46.1, *38.0*, 31.6, *31.4*, *30.1*, 29.9, 14.0, *13.9*, *13.6*, 13.3. Anal. Calcd for $C_{11}H_{20}O_3$: C, 65.97; H, 10.07. Found: C, 66.03; H, 9.98.

Methyl 4,5-epoxy-4-(ethoxycarbonyl)hexanoate (3f): ^{1}H NMR δ 4.16–3.92 (m, 2H), 3.46 (s, 3H), 3.12 (q, J = 5.5 Hz, 1H), 2.50–1.64 (m, 4H), 1.19 (d, J = 5.5 Hz, 3H), 1.08 (t, J = 7.1 Hz, 3H); ^{13}C NMR δ 172.8, 172.7, 170.3, 166.9, 61.8, 59.6, 61.4, 61.3, 58.7, 58.5, 51.5, 29.6, 28.0, 29.0, 22.7, 14.1, 13.9, 13.7, 13.3. Anal. Calcd for $C_{10}H_{16}O_5$: C, 55.55; H, 7.46. Found: C, 55.63; H, 7.52.

Ethyl 4,5-epoxy-4-(ethoxycarbonyl)hexanoate (3f'): ^{1}H NMR δ 4.10–4 (m, 2H), 3.93 (q, J = 7.2 Hz, 2H), *3.12* (dq, J = 5.5 Hz, 1H), 2.41–1.32 (m, 4H), 1.18 (d, J = 5.5 Hz, 3H), 1.09 (t, J = 7.2 Hz, 3H) 1.07 (t, J = 7.4 Hz, 3H); ^{13}C NMR δ *172.3*, 172.2, *170.3*, 169.1, 61.9, *60.3*, *61.4*, 61.3, *59.7*, 58.7, *58.5*, *29.9*, 29.3, 28.1, *22.7*, 14.1, *13.9*, *14.0*, 13.4, *13.4*. Anal. Calcd for $C_{11}H_{18}O_5$: C, 57.88; H, 7.88. Found: C, 58.01; H, 7.94.

2-Methyl-1,5-dioxaspiro[2.5]heptan-4-one (3g): ^{1}H NMR δ 4.45–4.15 (m, 2H), *3.1* (dq, 5.3 Hz, 1H), 2.34–2.12 (m, 2H), 1.20 (dd, J = 5.3 Hz, 3H); ^{13}C NMR δ 174.3, 65.1, 61.5, 57.8, 30.2, 29.8, 14.6. Anal. Calcd for $C_6H_8O_3$: C, 56.25; H, 6.29. Found: C, 56.33; H, 6.36.

Ethyl 2,3-epoxy-2-(2-methoxyethyl)butanoate (3h): ^{1}H NMR δ 4.17 (q, J = 7.1 Hz, 2H), 3.55 (t, J = 6.6 Hz, 2H) 3.30 (s, 3H), *3.23* and 2.90 (q, J = 5.3 Hz, 1H), 2.43–1.74 (m, 2H), 1.35 (d, J = 5.3 Hz, 3H), 1.26 (t, J = 7.1 Hz, 3H); ^{13}C NMR δ *170.5*, 169.2, *68.6*, 68.0, *61.1*, 61.0, 60.9, *58.7*, 58.6, *58.3*, 58.3, *57.7*, 33.1, *27.5*, 14.3, *13.8*, *13.4*, 13.3. Anal. Calcd for $C_9H_{16}O_4$: C, 57.43; H, 8.57. Found: C, 57.31; H, 8.65.

Ethyl 2,3-epoxy-2-(2-chloroethyl)butanoate (3i): ^{1}H NMR δ 4.05 (q, J = 7.1 Hz, 2H), 3.5 (dt, J = 7.4 Hz, 2H), *3.16* and 3.01 (q, J = 5.5 Hz, 1H), 2.5–1.8 (m, 2H), 1.23 (d, J = 5.5 Hz, 3H), 1.12 (t, J = 7.1 Hz, 3H); ^{13}C NMR δ *170.1*, 169.6, *61.6*, 61.5, 60.7, *58.6*, 59.0, *58.2*, 40.1, *39.8*, *36.2*, 30.8, 14.1, *13.9*, *13.6*, 13.3. Anal. Calcd for $C_8H_{13}O_3Cl$: C, 49.88; H, 6.80; O, 24.91. Found: C, 49.97; H, 6.81; O, 24.51.

Ethyl 2,3-epoxy-2-(2-bromoethyl)butanoate (3j): ^{1}H NMR δ 4.15–4.03 (m, 2H), 3.43–3.33 (m, 2H), *3.20* and 3.05 (q, J = 5.5 Hz, 1H), 2.61–1.89 (m, 2H), 1.21 (d, J = 5.5 Hz, 3H), 1.16 (t, J = 7.1 Hz, 3H); ^{13}C NMR δ *170.0*, 168.8, *61.7*, 61.6, 61.5, *59.4*, 58.9, *58.2*, 36.5, *31.2*, *27.2*, 27.0, 14.2, *14.0*, *13.7*, 13.3. Anal. Calcd for $C_8H_{13}O_3Br$: C, 40.53; H, 5.53; O, 20.24. Found: C, 40.45; H, 5.62; O, 20.33.

Ethyl 2,3-epoxy-2-(2-cyanoethyl)butanoate (3k): ^{1}H NMR δ 4.14 (q, J = 7.1 Hz, 2H), *3.32* and 3.11 (q, J = 5.5 Hz, 1H), 2.65–2.50 (m, 2H), 2.47–1.78 (m, 2H), 1.32 (d, J = 5.5 Hz, 3H), 1.21 (t, J = 7.1 Hz, 3H); ^{13}C NMR δ 169.7, 169.2, 125.9, 118.9, 62.0, 61.9, 60.8, 58.4, 59.3, 59.0, 29.3, 24.0, 14.2, 14.1, 13.6, 13.4. Anal. Calcd for $C_9H_{13}O_3N$: C, 59.00; H, 7.15; O, 26.20. Found: C, 58.96; H, 7.10; O, 26.24.

Ethyl 2,3-epoxy-2-(2-phenylethyl)butanoate (3l): ^{1}H NMR δ 7.30–7.14 (m, 5H), 4.16 (q, J = 7.15 Hz, 2H), *3.3* (dq, J = 5.5 Hz, 1H), 2.91–2.64 (m, 2H), 2.57–1.71 (m, 2H), 1.31 (d, J = 5.5 Hz, 3H), 1.26 (t, J = 7.15 Hz, 3H); ^{13}C NMR δ *170.9*, 169.5, *141.3*, *128.5*, *126.1*, *61.5*, 61.4, *60.6*, 59.0, *58.6*, 35.3, *31.6*, 31.1, *29.8*, 14.3, *14.2*, 13.7, *13.6*. Anal. Calcd for $C_{14}H_{18}O_3$: C, 71.77; H, 7.74. Found: C, 71.86; H, 7.56.

Methyl 3,4-epoxy-3-(ethoxycarbonyl)pentanoate (3m): ^{1}H NMR δ 4.02 (q, J = 7.2 Hz, 2H), 3.5 (m, 3H), *3.21* and 3.00 (dq, J = 5.4 Hz, 1H), 2.67 (AB system, J = 17.2 Hz, 2H), 1.2 (dd, J = 5.4 Hz, 3H), 1.07 (t, J = 7.2 Hz, 3H); ^{13}C NMR δ *169.9*, *169.8*, 61.6, *61.4*, 58.6, *57.6*, 58.8, *57.3*, 52.5, *51.8*, 35.7, *33.6*, 14.0, *13.8*, 13.6, *13.5*. Anal. Calcd for $C_9H_{14}O_5$: C, 53.46; H, 6.98. Found: C, 53.51; H, 7.05.

Methyl 2-butyl-4,5-epoxy-4-(ethoxycarbonyl)hexanoate (3n): ^{1}H NMR δ 4.15 (dq, J = 7.1 Hz, 2H), 3.60 (s, 3H), 3.14 (q, J = 5.5 Hz, 1H), 2.6–1.3 (m, 9H), 1.26 (dd, J = 5.5 Hz, 3H), 1.22 (t, J = 7.1 Hz, 3H), 0.80 (dt, J = 6.8 Hz, 3H); ^{13}C NMR δ 175.9, 175.7, 170.6, 169.0, 61.4, 59.5, 58.2, 58.1, 51.5, 51.3, 42.0, 41.8, 32.4, 31.9, 29.7, 29.2, 22.4, 14.0, 13.7, 13.5, 13.4. Anal. Calcd for $C_{14}H_{24}O_5$: C, 61.74; H, 8.88. Found: C, 61.82; H, 8.98.

Methyl 7,8-epoxy-7-(ethoxycarbonyl)nonanoate (5a): ^{1}H NMR δ 4.12–3.91 (m, 2H), 3.48 (s, 3H), *3.07* and 2.87 (q, J = 5.5 Hz, 1H), 2.13 (t, J = 7.4 Hz, 2H), 2.09–1.20 (m, 8H), 1.17 (d, J = 5.5 Hz, 3H), 1.10 (t, J = 7.1 Hz, 3H); ^{13}C NMR δ *173.7*, *170.8*, 169.4, *61.2*, 61.1, 63.1, *60.7*, 58.2, *57.9*, *51.2*, *33.6*, *32.7*, *28.9*, *28.7*, *27.1*, *24.7*, *24.5*, 24.3, 14.1, *13.9*, 13.6, *13.4*. Anal. Calcd for $C_{13}H_{22}O_5$: C, 60.45; H, 8.58. Found: C, 60.29; H, 8.66.

Ethyl 2,3-epoxy-2-[[3-[(methoxycarbonyl)methyl]cyclopentyl]methyl]butanoate (5b): ^{1}H NMR δ 4.2–4.05 (m, 2H), 3.6 (ds, 3H), 3.15–2.95 (m, 1H), 2.3–1.3 (m, 12 H), 1.2 (d, J = 5.5 Hz, 3H), 1.1 (t, J = 7.1 Hz, 3H); ^{13}C NMR δ 176.7, 173.3, 171.1, 170.2, 63.0, 60.7, 60.6, 61.3, 61.2, 61.1, 57.9, 57.6, 57.5, 57.4, 51.4, 51.2, 40.5, 40.3, 40.2, 40.1, 36.9, 36.0, 35.8, 35.6, 34.8, 34.7, 34.6, 38.3, 37.9, 36.7, 36.5, 33.0, 30.7, 14.0, 13.7, 13.5. Anal. Calcd for $C_{15}H_{24}O_5$: C, 63.36; H, 8.51. Found: C, 63.61; H, 8.65.

Methyl 8,9-epoxy-8-(ethoxycarbonyl)decanoate (5c): ^{1}H NMR δ 4.05 (q, J = 7.1 Hz, 2H), 3.50 (s, 3H), *3.09* and 2.90 (q, J = 5.5 Hz, 1H), 2.15 (t, J = 7.4 Hz, 2H), 1.50–1.27 (m, 10H), 1.20 (d, J = 5.5 Hz, 3H), 1.13 (t, J = 7.1 Hz, 3H); ^{13}C NMR δ *173.9*, *170.9*, 169.5, *61.2*, 61.1, 63.2, *60.8*, 58.3, *57.9*, *51.2*, *33.8*, 32.9, *29.1*, 28.9, *28.7*, *27.2*, *24.8*, *24.6*, 24.5, 14.2, *14.0*, 13.6, *13.5*. Anal. Calcd for $C_{14}H_{24}O_5$: C, 61.74; H, 8.88. Found: C, 61.83; H, 9.00.

***tert*-Butyl 8,9-epoxy-8-(ethoxycarbonyl)perdecanoate (5d)**: ^{1}H NMR δ 4.04 (q, J = 7.2 Hz, 2H), *3.08* (q, J = 5.5 Hz, 1H) 2.15 (t, J = 7.4 Hz, 2H), 1.97–1.24 (m, 10H), 1.19 (d, J = 5.5 Hz, 3H), 1.16 (s, 9H), 1.12 (t, J = 7.2 Hz, 3H); ^{13}C NMR δ 170.8, 170.7, 82.9, 61.2, 61.1, 60.7, 58.2, 57.9, 30.9, 30.6, 29.3, 29.0, 28.6, 27.1, 26.0, 24.8, 24.6, 24.5, 14.2, 14.0, 13.6,

13.5. Anal. Calcd for $C_{17}H_{30}O_6$: C, 61.80; H, 9.15. Found: C, 61.84; H, 9.07.

2,3:11,12-diepoxy-3,11-bis(ethoxycarbonyl)tridecane (5e): ^{1}H NMR δ 4.13–3.52 (m, 4H), 3.11–3.03 (m, 1H), 2.15–1.07 (m, 26 H); ^{13}C NMR δ *171.9*, 169.6, 63.3, *60.7*, 61.2, *61.1*, 58.3, *57.9*, 32.9, *29.3*, *29.1*, 29.0, 28.7, *27.3*, *24.9*, 24.6, 14.2, *14.0*, 13.6, *13.5*. Anal. Calcd for $C_{19}H_{32}O_6$: C, 64.02; H, 9.05. Found: C, 64.21; H, 9.06.

Methyl 8,9-epoxy-8-(ethoxycarbonyl)dec-4-enoate (5f): ^{1}H NMR δ 5.78–5.18 (m, 2H), 4.05–3.86 (m, 2H), 3.40 (ds, 3H), 3.0 (dq, J = 5.4 Hz, 1H), 2.35–1.22 (m, 8H), 1.11 (dd, J = 5.4 Hz, 3H), 1.05 (dt, J = 7.1 Hz, 3H); ^{13}C NMR δ 173.7, 173.1, 170.8, 170.3, 133.5, 132.2, 130.7, 130.0, 129.7, 128.9, 122.2, 121.5, 61.1, 61.0, 60.7, 60.6, 60.3, 58.0, 57.9, 57.8, 51.4, 51.1, 33.7, 33.6, 29.0, 28.6, 28.0, 27.6, 27.5, 27.2, 27.0, 26.6, 24.7, 24.6, 24.5, 24.4, 14.1, 13.9, 13.5, 13.4. Anal. Calcd for $C_{14}H_{22}O_5$: C, 62.20; H, 8.20. Found: C, 62.09; H, 8.25.

Compound **5f'** was not isolated. Its presence was identified by ^{1}H NMR chemical shifts of the fragment H_2C=CH (4.80–4.75 ppm) and from ^{13}C NMR chemical shifts of the corresponding sp^2 carbons (115.2 and 141.4 ppm).

Ethyl 2,3-epoxy-2-[4-(formyloxy)butyl]butanoate (7a): ^{1}H NMR δ 7.87 (s, 1H), 4.08–3.94 (m, 4H), *3.07* and 2.90 (q, J = 5.5 Hz, 1H), 1.93–1.27 (m, 6H), 1.17 (d, J = 5.5 Hz, 3H), 1.09 (t, J = 7.1 Hz, 3H); ^{13}C NMR δ *170.7*, 169.3, *160.9*, *63.3*, *61.3*, 61.2, *60.5*, 58.2, *57.9*, 32.4, *28.3*, 28.0, *26.8*, *21.5*, 21.1, 14.1, *13.9*, 13.5, *13.4*. Anal. Calcd for $C_{11}H_{18}O_5$: C, 57.38; H, 7.88. Found: C, 57.28; H, 7.74.

Ethyl 2,3-epoxy-2-[4-(ethanoyloxy)butyl]butanoate (7b): ^{1}H NMR δ 4.05 (q, J = 7 Hz, 2H), 3.91 (t, J = 6.2 Hz, 2H), *3.10* and 2.91 (q, J = 5.5 Hz, 1H), 1.87 (s, 3H), 1.58–1.27 (m, 6H), 1.20 (d, J = 5.5 Hz, 3H), 1.12 (t, J = 7 Hz, 3H); ^{13}C NMR δ *170.8*, 169.4, *170.7*, *63.9*, *61.3*, 61.2, *60.6*, 58.3, *58.0*, 32.5, *28.4*, 28.2, *26.9*, *21.6*, 21.2, *20.7*, 14.2, *14.0*, 13.6, *13.5*. Anal. Calcd for $C_{11}H_{18}O_5$: C, 57.38; H, 7.88. Found: C, 57.45; H, 8.01.

Ethyl 2,3-epoxy-2-[4-(formyloxy)-4-methoxybutyl]butanoate (7c): ^{1}H NMR δ 7.96 (s, 1H), 5.64 (br t, 1H), 4.0 (dq, J = 7.3 Hz, 2H), 3.20 (s, 3H), *3.04* and 2.86 (q, J = 5.4 Hz, 1H), 2.05–1.18 (m, 6H), 1.14 (d, J = 5.4 Hz, 3H), 1.07 (t, J = 7.3 Hz, 3H); ^{13}C NMR δ *170.6*, 169.2, *160.6*, *99.0*, 62.8, *60.4*, *61.2*, 61.1, 58.2, *57.9*, *56.4*, *33.6*, 33.4, *27.1*, 26.8, 19.5, *19.1*, 14.1, *13.9*, 13.5, *13.4*. Anal. Calcd for $C_{12}H_{20}O_6$: C, 55.37; H, 7.75. Found: C, 55.29; H, 7.80.

Ethyl 2,3-epoxy-2-[5-(formyloxy)pentyl]butanoate (7d): ^{1}H NMR δ 7.97 (s, 1H), 5.79–4.05 (m, 4H), 3.2–2.94 (m, 1H), 2.2–1 (m, 14H); ^{13}C NMR δ *171.0*, 169.5, *161.0*, 63.7, *63.2*, 61.4, *61.3*, *60.8*, 58.4, *58.1*, *32.9*, 28.2, *27.2*, *25.8*, 25.6, 24.7, *24.4*, 14.2, *14.0*, 13.7, *13.5*. Anal. Calcd for $C_{12}H_{20}O_5$: C, 59.00; H, 8.25. Found: C, 58.93; H, 8.31.

Ethyl 2,3-epoxy-2-[5-ethoxy-5-(formyloxy)pentyl]butanoate (7e): ^{1}H NMR δ 7.97 (s, 1H), 5.74 (br t, 1H), 4.0 (dq, J = 7.1 Hz, 2H), 3.7–3.2 (m, 2H), *3.06* and 2.87 (q, J = 5.5 Hz, 1H), 2.1–1.2 (m, 8H), 1.18 (dd, J = 5.5 Hz, 3H), 1.1 (t, J = 7.1 Hz, 3H), 1.01 (t, J = 7 Hz, 3H); ^{13}C NMR δ 170.8, 169.4, 160.6, 103.0, 102.7, 61.3, 61.2, 61.1, 60.9, 60.8, 58.2, 57.9, 34.0, 33.3, 27.2, 27.1, 24.7, 24.6, 21.8, 15.2, 14.7, 14.1, 13.9, 13.6, 13.4. Anal. Calcd for $C_{14}H_{24}O_6$: C, 58.32; H, 8.39. Found: C, 58.27; H, 8.44.

Thermolysis of Ethyl 2-[1-[(1-Methoxy-2,2-dimethylpropyl)peroxy]ethyl]propenoate (1e). A solution of **1e** (0.78 g, 3 mmol) in benzene (5.8 mL) was heated to 80 °C for 12 h. Liberated gas (65 mL at 20 °C) was isolated and analyzed by GC as essentially only dihydrogen. The volatiles were then removed under reduced pressure and the polymeric residue was analyzed by spectroscopic methods: ^{1}H NMR δ 4.3–4.0, 2.4–2.1, 2.1–1.9, 1.3–0.7; ^{13}C NMR δ 201, 167, 66–59, 29–27, 24–14.

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Supplementary Material Available: A listing of 250-MHz ^{1}H NMR spectra and 62.9-MHz ^{13}C NMR spectra of all the compounds, complete with assignments (17 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.