Direct hydroperoxygenation of conjugated olefins catalyzed by cobalt(II) porphyrin

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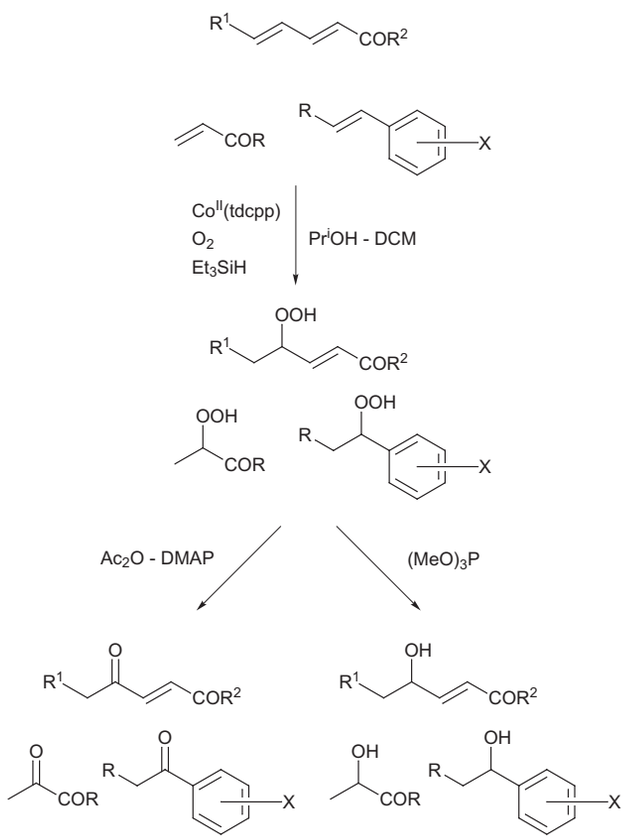
A novel and direct synthesis of hydroperoxy compounds from various types of conjugated olefins was established *via* cobalt(II) porphyrin-catalyzed hydroperoxygenation. The reaction of α,β,γ,δ-unsaturated carbonyl compounds, acrylic esters, α-substituted acrylic esters and styrene derivatives with molecular oxygen and triethylsilane in the presence of a catalytic amount of cobalt(II) porphyrin proceeded rapidly to give the corresponding hydroperoxygenated compounds in high or moderate yields.

Introduction

Due to the importance of alkyl hydroperoxides in biology and chemistry, various methods for their preparation have been developed.[1] For example, the autooxidation of alkanes, the singlet oxygenation of olefins,[2] the acidic addition of hydrogen peroxide to olefins[3] and the alkylation of hydrogen peroxide under basic conditions[4] are well known, however the yields of the alkyl hydroperoxides are sometimes unsatisfactory due to their lability. Recently, Bloodworth *et al.* reported a four-step synthesis of alkyl hydroperoxides *via* hydroperoxymercuriation of alkenes followed by protection with 2-methoxypropene, reductive demercuriation, and deprotection.[5] Dussault *et al.* reported an efficient method for the preparation of alkenyl hydroperoxides *via* Wittig or Horner–Emmons olefination of peroxy-substituted aldehydes which are obtained by photochemical oxygenation of dec-5-ene or lipoxygenase-catalyzed aerobic oxygenation of linoleic acid followed by acetal protection and ozonolysis.[6] Although these methods needed multi-step procedures, the hydroperoxides were produced in good yields. A direct hydroperoxygenation of aralkanes with *tert*-butyl hydroperoxide using calcined $ZnCrCO_3$–HTlc,† a homogeneously dispersed bimetallic oxide as a hydrocarbon activator, was described by Choudary *et al.*, but the yields of the alkyl hydroperoxides were low and the substrates are limited to aralkanes.[7] Mukaiyama *et al.* found a novel method for preparation of alkyl triethylsilyl peroxides with molecular oxygen and triethylsilane in the presence of bis(1,3-diketonato)-cobalt(II) as a catalyst. The reaction took place in aprotic solvents such as 1,2-dichloroethane and benzene, although not in alcohols such as propan-1-ol, and had a tendency to be more active for non-conjugated olefins such as 4-phenylbut-1-ene than for styrene.[8]

In our previous communication, we preliminarily reported that cobalt(II) porphyrin-catalyzed hydroperoxygenation of conjugated olefins with molecular oxygen and triethylsilane in propan-2-ol–DCM gave the corresponding hydroperoxides in good yields.[9] In addition, appropriate treatment of the intermediary hydroperoxides after the hydroperoxygenation was found to afford ketones and alcohols in one pot (Scheme 1).[10–12] Although γ-hydroxy- or γ-oxo-α,β-unsaturated carbonyl compounds have been synthesized by various methods,[13] our method *via* the hydroperoxygenation provides a novel and versatile route to γ-hydroxy- or γ-oxo-α,β-unsaturated carbonyl compounds and is easily applicable to the syntheses of several natural products.[14–16] We describe herein the scope and features of our cobalt(II) porphyrin-catalyzed hydroperoxygenation in detail.



Scheme 1

Results and discussion

Effects of catalysts and substituted silanes

Since the hydroperoxygenation of conjugated olefins catalyzed by cobalt(II) porphyrin was found to proceed in a mixture of alcohol and DCM but not in DCM from our previous work,[10] we chose a 1:1 mixture of propan-2-ol and DCM as the solvent. The effect of catalysts on the hydroperoxygenation was

† HTlc: Hydrotalcite-like compound.

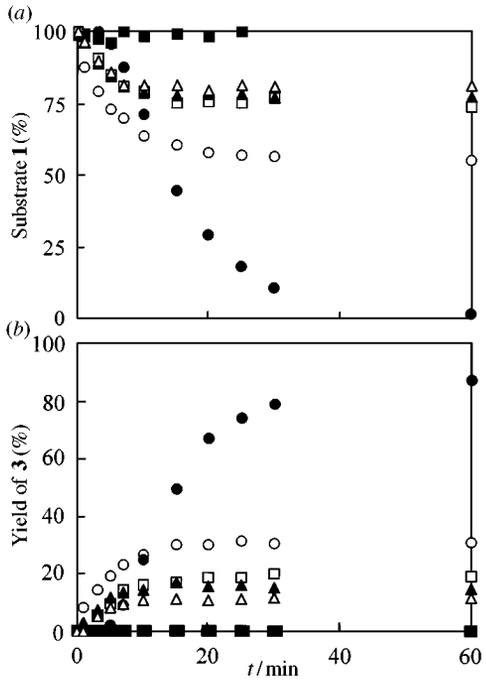
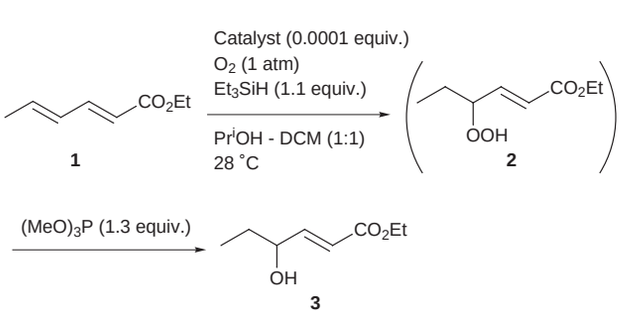


Fig. 1 Time course of the reaction of ethyl (2*E*,4*E*)-hexa-2,4-dienoate **1** (1 mmol) with 1 atm of oxygen and Et_3SiH (1.1 mmol) catalyzed by cobalt(II) porphyrins (0.0001 mmol) at 28 °C in Pr^iOH–DCM (5 cm^3, 1:1): (*a*) consumption of **1** and (*b*) production of **3**. (■) [Co^{II}(tpfpp)], (□) [Co^{II}(tmcpp)], (●) [Co^{II}(tdcpp)], (○) [Co^{II}(tpp)], (▲) [Co^{II}(tmpp)] and (△) [Co^{II}(ttmpp)]. Abbreviations: tpfpp = 5,10,15,20-tetrakis-(pentafluorophenyl)porphine; tmcpp = 5,10,15,20-tetrakis(4-methoxycarbonylphenyl)porphine; tdcpp = 5,10,15,20-tetrakis(2,6-dichlorophenyl)porphine; tpp = 5,10,15,20-tetraphenylporphine; tpm = 5,10,15,20-tetramesitylporphine; ttmpp = [5,10,15,20-tetrakis(3,4,5-trimethoxyphenyl)porphine.

first examined. In propan-2-ol–DCM (1:1) as solvent, ethyl (2*E*,4*E*)-hexa-2,4-dienoate **1** was allowed to react under 1 atm of oxygen with 1.1 equiv. of triethylsilane at 28 °C in the presence of 0.0001 equiv. of metal complexes, and then the reaction mixture was treated with trimethyl phosphite in order to convert the intermediary hydroperoxide **2** into the corresponding alcohol **3** (Scheme 2). The reaction's progress was followed by



Scheme 2

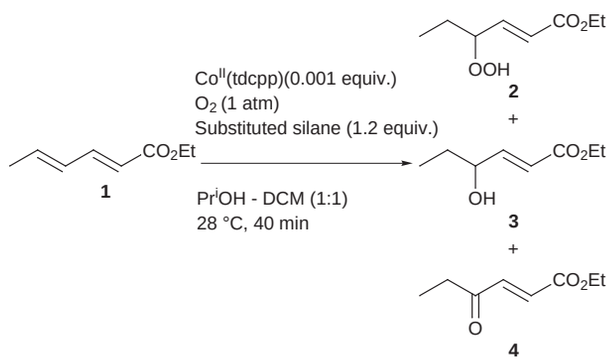
measurement of the consumption of **1** and the production of **3** by gas chromatography (Fig. 1). Under these reaction conditions, neither bis(acetylacetonato)cobalt(II) [$Co^{II}(acac)_2$] nor (*N*,*N*′-disalicylideneethylenediaminato)cobalt(II) [Co^{II}(salen)] had catalytic activity, although they were reported to catalyze the peroxygenation of alkenes with oxygen and triethylsilane[8] or the hydroxylation of alkenes with oxygen and $NaBH_4$.[17] Fe^{III}, Mn^{III} and Ni^{II} complexes of 5,10,15,20-tetrakis(2,6-dichlorophenyl)porphine [Fe^{III}(tdcpp)Cl, Mn^{III}(tdcpp)Cl and Ni^{II}(tdcpp)] did not act as catalysts. As shown in Fig. 1, the reaction proceeded in the presence of all cobalt(II) porphyrins except for Co^{II}(tpfpp). Co^{II}(tdcpp) was the most suitable catalyst for the hydroperoxygenation among the metal complexes used; the reaction of **1** was completed in 60 min in the presence of 0.0001 equiv. of Co^{II}(tdcpp). However, we primarily used 0.001 equiv. of Co^{II}(tdcpp) in subsequent experiments, considering that the reaction is applied to various substrates, which may include less reactive ones than **1**.

Table 1 Reversible half-wave potentials for the oxidation of cobalt^{II} porphyrins[a]

Entry	Cobalt porphyrin	$E_{\frac{1}{2}}$/V *vs.* Ag/AgCl $Co^{II} \longleftrightarrow Co^{III}$
1	Co^{II}(tpfpp)	0.475
2	Co^{II}(tmcpp)	0.380
3	Co^{II}(tdcpp)	0.355
4	Co^{II}(tpp)	0.325
5	Co^{II}(tmpp)	0.295
6	Co^{II}(ttmpp)	0.265

[a] Conditions: cobalt^{II} porphyrin (1 mmol dm^{-3}), electrode Pt–Pt, Et_4NClO_4 (0.1 mol dm^{-3}) in DMF under Ar.

Table 2 Effect of substituted silanes on the hydroperoxygenation of ethyl (2*E*,4*E*)-hexa-2,4-dienoate

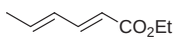
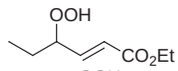
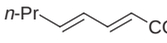
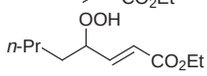
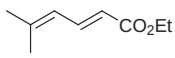
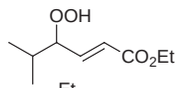
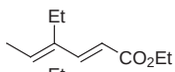
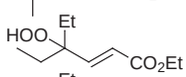
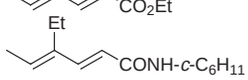
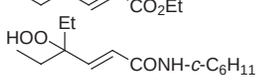
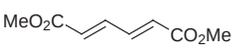
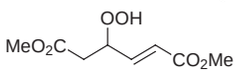
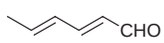
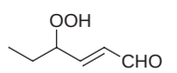
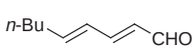
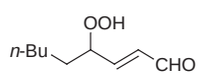
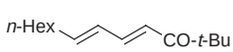
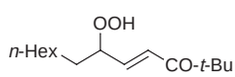
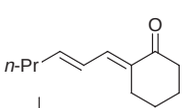
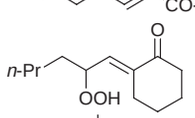
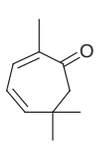
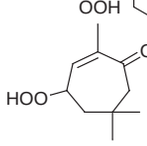
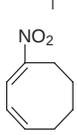
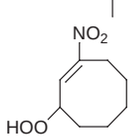
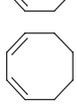
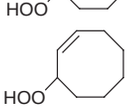
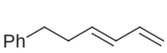


Entry	Substituted silane	Isolated yield (%) **2**	**3**	**4**
1	Et_3SiH	77	0	Trace
2	$Me_2(EtO)SiH$	56	0	22
3	$MePhSiH_2$	69	0	7
4	$C_6H_{13}SiH_3$	65	0	20
5	$PhSiH_3$	14	35	22
6	$(EtO)_3SiH$	No reaction		
7	Ph_3SiH	No reaction		

The redox potential ($E_{1/2}$) between Co^{II} and Co^{III} was measured in DMF containing 0.1 mol dm^{-3} of Et_4NClO_4. The cobalt porphyrins having redox potentials in the range from 0.27 to 0.38 V are reactive as catalysts, but Co^{II}(tpfpp), having a potential >0.45 V is not (Table 1). The consumption of the substrate in the reaction decreases remarkably with decreasing the redox potentials of the catalysts. It is assumed that active oxygen species, produced during the reaction, easily decompose the porphyrin ring of the catalysts owing to their high electron density and/or their low steric hindrance; a similar relationship between the catalytic activity and the redox potentials of bis(1,3-diketonato)cobalt(II) complexes was reported for the oxidation–reduction–hydration of olefins with oxygen and propan-2-ol as a reductant.[18]

Second, the effect of substituted silanes on the hydroperoxygenation was examined and the results are depicted in Table 2. The hydroperoxygenation of **1** using triethylsilane, ethoxydimethylsilane, methylphenylsilane and *n*-hexylsilane proceeded smoothly to give the hydroperoxide **2** as a major product along with ketone **4**: since the ketone **4** was formed from the hydroperoxide **2** by cobalt porphyrin-mediated degradation *via* a redox cycle, the reaction mixture had to be post-treated and

Table 3 The hydroperoxygenation of conjugated dienes[a]

Entry	Substrate	*t*/h	Product	Yield (%)[b]
1		0.67		77
2		1		68
3		1		70
4		2		74
5		2		90
6[c]		3		65
7		1.5		49
8		1.5		54
9		1		55
10		1		61
11		0.5		67
12		1		50
13		1		92
14		2	Unseparable mixture	

[a] Conditions: substrate (1 mmol), [Co^{II}(tdcpp)] (0.001 equiv.), O_2 (1 atm), Et_3SiH (1.1 equiv.), Pr^iOH–DCM (5 cm^3, 1 : 1) at 28 °C. [b] Isolated yield. [c] 0.005 equiv. of Co^{II}(tdcpp) was used.

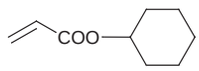
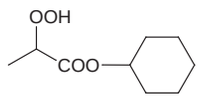
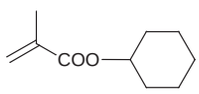
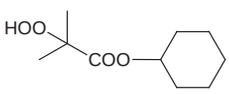
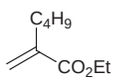
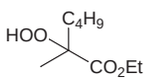
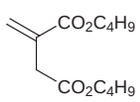
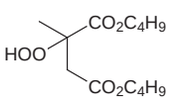
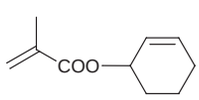
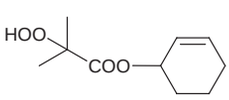
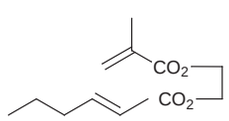
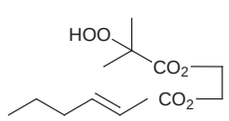
separated by flash column chromatography as rapidly as possible after the completion of the reaction. On the other hand, overreduction of **2** into the alcohol **3** was observed for phenylsilane. When triethoxysilane and triphenylsilane were used, no reaction took place due to their weak reducibility. Triethylsilane was found to be the most effective reductant among the silanes used for the formation of the hydroperoxide **2**.

Reactivity and selectivity in the hydroperoxygenation

The procedure of the hydroperoxygenation using both 0.001 equiv. Co^{II}(tdcpp) as the catalyst and 1.1 equiv. of triethylsilane as the reductant was applied to conjugated dienes (Table 3). The hydroperoxygenation of dienes conjugated with electron-withdrawing groups predominantly gave the corresponding γ-hydroperoxy-α,β-unsaturated compounds along with a small amount of γ-oxo-α,β-unsaturated compounds, as shown in entries 1–12. No other isomer hydroperoxygenated at a different position was observed in all cases. From alkadienoic esters, alkadienamide, alkadienals and alkadienones, the corresponding γ-hydroperoxy compounds were produced in good or moderate yields, independent of the alkyl substituents in the substrates. For entry 6, an increased amount of Co^{II}(tdcpp) was required in order to accelerate the reaction. In addition, the reaction of 1-nitrocycloocta-1,3-diene was found to afford 3-hydroperoxy-1-nitrocyclooct-2-ene. It is interesting to point out that the present reaction conditions are mild enough to permit the presence of reduction- and/or oxidation-labile groups such as aldehyde, ketone and nitro groups on the substrates. It is particularly noteworthy that 4-hydroperoxyalk-2-enals such as (*E*)-4-hydroperoxyhex-2-enal and (*E*)-4-hydroperoxynon-2-enal, remarkably cytotoxic and genotoxic compounds produced during lipid peroxidation in biological systems,[19] can be synthesized in one step from commercially available (2*E*,4*E*)-alka-2,4-dienals.‡ On the other hand, the reaction of cycloocta-1,3-diene gave the allyl hydroperoxide in high yield (entry 13), while that of 6-phenylhexa-1,3-diene resulted in an inseparable mixture of regioisomeric hydroperoxides (entry 14). These results suggest that the substitution of the electron-withdrawing group on the diene is important for regioselective hydroperoxygenation. To the best of our

‡ (2*E*,4*E*)-2,4-alkadienals: (2*E*,4*E*)-2,4-Hexadienal and (2*E*,4*E*)-2,4-nonadienal were purchased from Tokyo Kasei Kogyo Co., Ltd. and freshly distilled under reduced pressure.

Table 4 The hydroperoxygenation of acrylic esters[a]

Entry	Substrate	*t*/h	Product	Yield (%)[b]
1		4		72
2		2		80
3		0.5		78
4		1		81
5		2		89
6		1.5		86

[a] Conditions: substrate (1 mmol), [Co^{II}(tdcpp)] (0.001 equiv.), O_2 (1 atm), Et_3SiH (1.1 equiv.), Pr^iOH–DCM (5 cm^3, 1 : 1) at 28 °C. [b] Isolated yield.

knowledge, the present method is the first to enable direct synthesis of γ-hydroperoxy-α,β-unsaturated carbonyl and nitro compounds.

Acrylic ester derivatives were found to be converted into α-hydroperoxy compounds (Table 4). We previously found that non-conjugated olefins such as dodec-1-ene and 3-(4-methoxyphenyl)prop-1-ene were unreactive and alk-2-enoic esters less reactive under similar reaction conditions.[12] According to the different reactivities for olefins on the reaction, the chemoselective hydroperoxygenation of the acrylic moiety became feasible, as shown in entries 5 and 6.

It has already been described by us that styrene derivatives were directly converted into acetophenone derivatives in many cases when 0.001 equiv. of Co^{II}(tdcpp) was used as the catalyst.[12] Since rapid degradation of the corresponding hydroperoxides mediated by Co^{II}(tdcpp) was the reason for producing the acetophenones as the major product, a decrease in the amount of Co^{II}(tdcpp) was attempted for the preparation of the hydroperoxides as the major product (Table 5). When 0.0001 equiv. of Co^{II}(tdcpp) was used in the reaction of styrene, the yield of α-phenethyl hydroperoxide increased dramatically (entries 1 and 2). Under similar conditions to those shown in entry 2, the reaction of the other styrene derivatives also gave the corresponding hydroperoxides in good yields (entries 3–7).

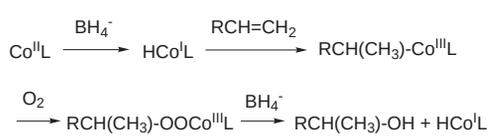
All hydroperoxides were identified by ^1H NMR, ^{13}C NMR, IR and MS analysis, although not by elemental analysis because of their lability. The hydroperoxide content of the products was analyzed by iodometric titration,[20] and their peroxide values were over 96% in all cases.

Thus, our hydroperoxygenation of conjugated olefins was observed to take place rapidly, chemoselectively and regioselectively. Mukaiyama *et al.* reported that the peroxygenation reaction of non-conjugated olefins proceeded over 5 h with $Co^{II}(acac)_2$ as the catalyst, however, the combined use of $Co^{II}(acac)_2$ and *tert*-butyl hydroperoxide or the use of the other cobalt complexes such as Co^{II}(modh)§ instead of $Co^{II}(acac)_2$ was necessary for the smooth conversion of styrenes and alk-2-enoic esters into the corresponding peroxides.[8] On the contrary, no reaction using our hydroperoxygenation conditions was observed for non-conjugated olefins. On the basis of these differences, Mukaiyama's method and our method are considered to be complementary to each other for the direct preparation of (hydro)peroxy compounds from olefins.

§ Co^{II}(modh): bis(1-morpholino-5,5′-dimethyl-1,2,4-hexanetrionato)-cobalt(II).

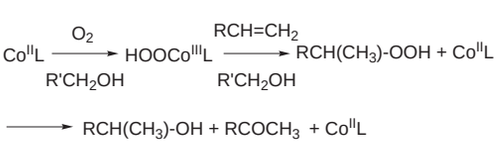
Mechanism

Two types of mechanism of cobalt(II) complex-catalyzed reduction–oxygenation of olefins have been proposed previously. Okamoto *et al.* reported that the reaction of styrene with oxygen and $NaBH_4$ proceeded *via* the σ-alkylcobalt (Scheme 3).[17] On the other hand, Drago *et al.* proposed that cobalt(III)



Scheme 3

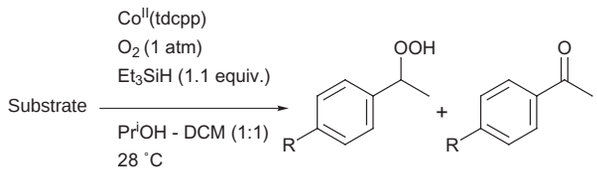
hydroperoxide produced with oxygen from a cobalt(II) Schiff-base complex was the reactive intermediate in the reaction of olefins (Scheme 4).[21] To study the mechanism of the present hydroperoxygenation, we performed the following experiments.

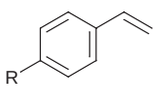
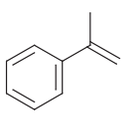
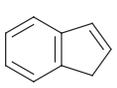


Scheme 4

Deuterium incorporation during the course of the hydroperoxygenation of ethyl (2*E*,4*E*)-5-methylhexa-2,4-dienoate was examined by use of triethyldeuterosilane instead of triethylsilane in propan-2-ol or [*O*-^{2}H]propan-2-ol. After the hydroperoxides had been reduced with trimethyl phosphite, the distribution of deuterium in the corresponding alcohols was determined on the basis of their ^1H NMR spectra (Table 6).

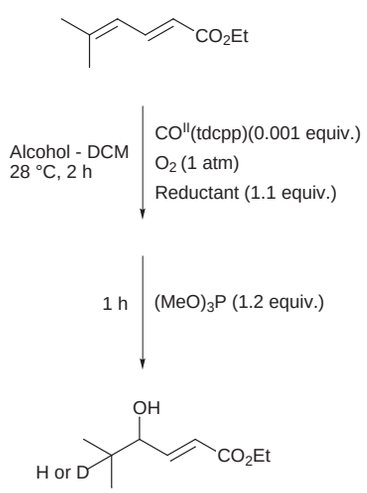
Table 5 The hydroperoxygenation of styrene derivatives[a]



Entry	Substrate		Co^{II}(tdcpp)/ equiv.	*t*/h	Yield (%)[b] Hydro-peroxide	Ketone
1		R = H	0.001	3	13	76
2		R = H	0.0001	1	80	trace
3		R = OMe	0.0001	1	72	22
4		R = Me	0.0001	0.5	87	trace
5		R = Cl	0.0001	2	78	19
6			0.0001	1	72	-
7			0.0001	1.5	60	trace

[a] Conditions: substrate (1 mmol), [Co^{II}(tdcpp)] (0.0001 equiv. or 0.001 equiv.), O_2 (1 atm), Et_3SiH (1.1 equiv.), Pr^{i}OH–DCM (5 cm^3, 1 : 1) at 28 °C. [b] Isolated yield.

Table 6 Deuterium distribution in the product on the hydroperoxygenation of ethyl (2*E*,4*E*)-5-methylhexa-2,4-dienoate



Entry	Reductant	Alcohol	Yield (%)[a]	Deuterium distribution (%)[b]
1	Et_3SiH	Pr^{i}OH	81	0
2	Et_3SiH	Pr^{i}OD	78	0
3	Et_3SiD	Pr^{i}OH	74	66
4	Et_3SiD	Pr^{i}OD	74	100

[a] Isolated yield. [b] Analyzed by ^{1}H NMR spectroscopy.

When triethyldeuterosilane was used in [*O*-^{2}H]propan-2-ol for the reaction, complete incorporation of deuterium occurred at the δ-position of the product (entry 4). No deuterium incorporation was observed for the combined used of triethylsilane and [*O*-^{2}H]propan-2-ol (entry 2). On the other hand, partial deuterium incorporation (66%) was observed for the combined use of triethyldeuterosilane and propan-2-ol. It is presumed that D–H exchange between triethyldeuterosilane and a large excess of propan-2-ol occurs under the reaction conditions. These results suggest that the origin of hydrogen in the product is from triethylsilane rather than propan-2-ol.

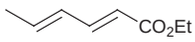
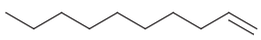
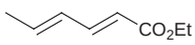
Evidence for the coordination and activation of the conjugated olefins by Co^{II}(tdcpp) was sought using EPR spectroscopy. The EPR spectral data for Co^{II}(tdcpp) in the absence and in the presence of olefins at 77 K *in vacuo* are collected in Table 7. Co^{II}(tdcpp) showed a typical four-coordinated spectrum in DCM, similar to that of Co^{II}(tpp) reported in the literature.[22] In DCM, the spectrum of Co^{II}(tdcpp) in the presence of **1**, one of the reactive substrates on the hydroperoxygenation, indicated the formation of a five-coordinated complex ($g_\perp = 2.292$, $g_\parallel = 2.033$), whereas that in the presence of dec-1-ene, the unreactive substrate, was entirely unchanged. Moreover, in the presence of **1**, Co^{II}(tdcpp) showed the same five-coordinated spectrum in propan-2-ol–DCM (1 : 1) as in DCM. On the other hand, we observed a different type of five-coordinate spectrum ($g_\perp = 2.387$, $g_\parallel = 2.029$) in the absence of **1** in propan-2-ol–DCM, which probably resulted from the coordination of propan-2-ol to Co^{II}(tdcpp). It is considered that the coordination of conjugated olefins to Co^{II}(tdcpp) contributes to the activation and regioselectivity of the hydroperoxygenation of the olefins.

From these results, we deduced the reaction mechanism for the hydroperoxygenation as shown in Scheme 5. The olefin activated by cobalt(II) porphyrin is reduced by triethylsilane to form σ-alkylcobalt complex **A** as a reactive intermediate, which subsequently reacts with oxygen to produce alkylperoxycobalt complex **B**. Finally, the hydroperoxide is produced from the complex **B**, and cobalt(II) porphyrin is regenerated along with triethylsilyl isopropoxide.

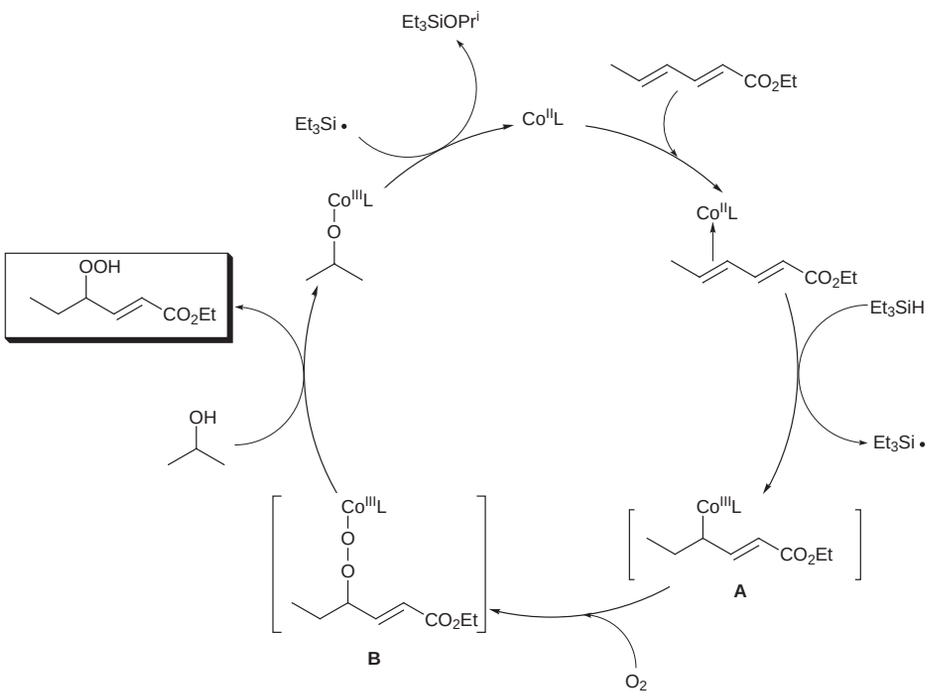
Conclusion

A wide variety of hydroperoxides was prepared using the present hydroperoxygenation of conjugated olefins in good or

Table 7 EPR parameters of Co^{II}(tdcpp) under various conditions[a]

Entry	Solvent	Olefin	$g_\perp$	$g_\parallel$	Coordination No.
1	DCM	none	2.723	2.042	4
2	DCM		2.292	2.033	5
3	DCM		2.723	2.042	4
4	Pr^iOH - DCM	none	2.387	2.029	5
5	Pr^iOH - DCM		2.292	2.033	5

[a] EPR spectra were measured at 77 K *in vacuo* in solvent with 0.0005 mol dm^{-3} of Co^{II}(tdcpp) and 0.5 mol dm^{-3} of olefin.



Scheme 5

moderate yields. The following characteristic features are noted. (i) Conditions: the reaction proceeds rapidly under neutral and mild conditions (at room temperature under 1 atm of O_2). (ii) Reactivity: the reaction of α,β,γ,δ-unsaturated carbonyl compounds, acrylic esters, α-substituted acrylic esters and styrene derivatives proceeds completely, while that of non-conjugated olefins does not. (iii) Selectivity: α,β,γ,δ-unsaturated carbonyl compounds are predominantly converted to γ-hydroperoxy-α,β-unsaturated carbonyl compounds, and acrylic esters, α-substituted acrylic esters and styrene derivatives to α-hydroperoxygenated compounds.

Experimental

General

^1H and ^{13}C NMR spectra were recorded on a Bruker AC-250P spectrometer in $CDCl_3$ solution with TMS (δ 0.00) as an internal standard. IR spectra were measured in $CHCl_3$ solution on a Hitachi IR 270-30 spectrometer. High resolution mass spectrometry (HRMS) was performed on a Hitachi M-2000AM mass spectrometer in electron impact mode at 70 eV, and low resolution mass spectrometry in secondary ionization (SIMS) using 3-nitrobenzyl alcohol as a matrix. EPR spectra were recorded at 77 K on a JEOL RE-1X EPR spectrometer. The solution of Co^{II}(tdcpp) in DCM or in propan-2-ol–DCM (1 : 1) was prepared by the complete removal of dissolved oxygen according to the usual freeze–thaw method. The EPR spectrum of the Co^{II}(tdcpp) solution was measured in the absence and in the presence of ethyl (2*E*,4*E*)-hexa-2,4-dienoate or dec-1-ene. The *g* factors of the spectra were determined by comparison with those of a Mn^{II} marker. Cyclic voltammograms of 0.001 mol dm^{-3} cobalt(II) porphyrins were recorded on a BAS Model CV-27 in DMF solution containing 0.1 mol dm^{-1} tetraethylammonium perchlorate (Tokyo Kasei Kogyo Co., Ltd.) under Ar. Both the working and auxiliary electrodes were platinum and the reference electrode was Ag/AgCl. GC was performed on a Shimadzu GC-8A chromatograph instrument with SE-30-supporting glass column (200 mm × 3.2 mm) and a flame ionization detector (FID). The consumption of the substrate and the yield of the product were calculated from peak areas on a Shimadzu chromatopack C-R3A. N_2 was used as the carrier gas (1.1 kg cm^{-3}). The temperature program used was 1 °C min^{-1} from 70 to 270 °C. The injection port and FID were kept at 270 °C. Silica gel BW-300 purchased from Fuji Silysia Co., Ltd. was used for flash column chromatography. Propan-2-ol and DCM were distilled from calcium hydride. DMF was distilled under reduced pressure from calcium hydride. Substituted silanes and chlorotriethylsilane were purchased from Shin-Etsu Chemical Co. Ltd. and [*O*-^{2}H]-propan-2-ol and lithium aluminium deuteride from Aldrich Chemical Co., Inc. 5,10,15,20-Tetrakis(pentafluorophenyl)porphine (tpfpp), 5,10,15,20-tetrakis(4-methoxycarbonylphenyl)-porphine (tmcpp), 5,10,15,20-tetrakis(2,6-dichlorophenyl)porphine (tdcpp), 5,10,15,20-tetraphenylporphine (tpp), 5,10,15,20-tetramesitylphenylporphine (tmp) and 5,10,15,20-tetrakis-(3,4,5-trimethoxyphenyl)porphine (ttmpp) were prepared

according to the literature methods.[23,24] The insertion of cobalt(II) ion into the porphyrins by Alder's method[25] gave the corresponding cobalt(II) porphyrins. Triethyldeuterosilane was prepared by the reaction of chlorotriethylsilane with lithium aluminium deuteride by the same method as described in the literature.[26]

Time course of the reaction of ethyl (2*E*,4*E*)-hexa-2,4-dienoate 1

To a mixture of **1** (140 mg, 1 mmol) and a catalyst (0.095 mg, 0.0001 mmol) in 5 cm^3 of propan-2-ol and DCM (1:1) in a 50 cm^3 kjeldahl flask with a three-way stopcock was added 4-bromotoluene (85 mg, 0.5 mmol) as an internal standard for GC. The atmosphere in the flask was replaced with oxygen by bubbling for 5 min and then an oxygen balloon was attached to the flask through the three-way stopcock. Triethylsilane (0.18 cm^3, 1.1 mmol) was added to the solution at 28 °C and the reaction mixture was stirred. 0.1 cm^3 of the solution was withdrawn at appropriate intervals, followed by immediate treatment with 0.01 cm^3 of trimethyl phosphite. The consumption of **1** and the production of the alcohol **3** were measured by GC.

Typical procedure for synthesis of ethyl (*E*)-4-hydroperoxyhex-2-enoate 2

The dienoate **1** (140 mg, 1 mmol) and Co^{II}(tdcpp) (0.95 mg, 0.001 mmol) were dissolved in 5 cm^3 of propan-2-ol–DCM (1:1) in a 50 cm^3 kjeldahl flask equipped with three-way stopcock. The atmosphere in the flask was replaced with oxygen by bubbling for 5 min, and then an oxygen balloon was attached to the flask through the three-way stopcock. After triethylsilane (0.18 cm^3, 1.1 mmol) had been added to the solution at 28 °C, the reaction was checked by TLC until the substrate was completely consumed. The solvent was removed under reduced pressure, and the residue was purified by flash column chromatography on silica gel with *n*-hexane–ethyl acetate (20:1–10:1 v/v) to afford oily hydroperoxide **2** (133 mg, 77%).

Deuterium incorporation on the reaction of (2*E*,4*E*)-5-methylhexa-2,4-dienoate with triethyldeuterosilane

To a DCM solution (1 cm^3) of ethyl (2*E*,4*E*)-5-methylhexa-2,4-dienoate (77 mg, 0.5 mmol) and Co^{II}(tdcpp) (0.47 mg, 0.0005 mmol) was added 1 cm^3 of [*O*-^{2}H]propan-2-ol. The atmosphere in the flask was replaced with oxygen by bubbling for 5 min and then an oxygen balloon was attached to the flask. Triethyldeuterosilane (0.09 cm^3, 0.55 mmol) was added to the solution and the mixture was stirred at 28 °C for 2 h, followed by treatment with trimethyl phosphite (0.07 cm^3, 0.6 mmol) at 0 °C for 1 h at room temperature. After the solvent had been removed under reduced pressure, the residue was purified by silica gel column chromatography with *n*-hexane–ethyl acetate (20:1–10:1 v/v) to afford oily ethyl (*E*)-4-hydroxy-5-methyl-[5-^{2}H$_1$]hex-2-enoate (64 mg, 74%).

Ethyl (*E*)-4-hydroperoxyhex-2-enoate

R_f (Hexane–EtOAc 4:1) 0.19; ν_{max}($CHCl_3$)/cm^{-1} 3550, 3400, 3050, 3000, 2975, 2900, 1720, 1670, 1470, 1375, 1320, 1300, 1260, 1200, 1140, 1110, 1040 and 990; δ_H(250 MHz, $CDCl_3$) 0.95 (3 H, t, *J* 7.5 Hz, CH_3), 1.30 (3 H, t, *J* 7.2 Hz, OCH_2CH_3), 1.56–1.70 (2 H, m, CH_2), 4.22 (2 H, q, *J* 7.2 Hz, OCH_2), 4.45 (1 H, dd, *J* 6.7 and 6.8 Hz, C*H*OOH), 6.04 (1 H, d, *J* 15.8 Hz, CH=C*H*CO), 6.89 (1 H, dd, *J* 6.8 and 15.8 Hz, C*H*=CHCO) and 9.34 (1 H, br s, OOH); δ_C(63 MHz, $CDCl_3$) 9.33, 14.02, 25.13, 60.69, 85.55 (COOH), 122.99, 146.60 and 175.37; *m*/*z* (HRMS) 175.0922 (MH^+; $C_8H_{15}O_4$ requires *MH*, 175.0970).

Ethyl (*E*)-4-hydroperoxyoct-2-enoate

R_f (Hexane–EtOAc 4:1) 0.25; ν_{max}($CHCl_3$)/cm^{-1} 3550, 3400, 3030, 2960, 2940, 2860, 1720, 1660, 1475, 1375, 1320, 1270, 1180, 1040 and 980; δ_H(250 MHz, $CDCl_3$) 0.90 (3 H, t, *J* 7.2 Hz, CH_3), 1.30 (3 H, t, *J* 7.2 Hz, OCH_2CH_3), 1.30–1.68 (6 H, m, 3 × CH_2), 4.19 (2 H, q, *J* 7.3 Hz, OCH_2), 4.52 (1 H, dd, *J* 6.7 and 6.8 Hz, C*H*OOH), 6.04 (1 H, d, *J* 16.0 Hz, CH=C*H*CO), 6.90 (1 H, dd, *J* 6.8 and 16.0 Hz, C*H*=CHCO) and 8.84 (1 H, s, OOH); δ_C(63 MHz, $CDCl_3$) 13.87, 14.19, 22.56, 27.23, 31.84, 60.79, 84.64 (COOH), 123.14, 146.88 and 166.53; *m*/*z* (HRMS) 203.1280 (MH^+; $C_{10}H_{19}O_4$ requires *MH*, 203.1283).

Ethyl (*E*)-4-hydroperoxy-5-methylhex-2-enoate

R_f (Hexane–EtOAc 4:1) 0.23; ν_{max}($CHCl_3$)/cm^{-1} 3580, 3440, 3070, 3000, 2980, 2950, 2910, 1730, 1680, 1480, 1460, 1420, 1390, 1350, 1320, 1300, 1260, 1200, 1150, 1140, 1120, 1060 and 1000; δ_H(250 MHz, $CDCl_3$) 0.90 (3 H, d, *J* 6.9 Hz, CH_3), 0.98 (3 H, d, *J* 6.8 Hz, CH_3), 1.31 (3 H, t, *J* 7.2 Hz, OCH_2CH_3), 1.82–2.00 (1 H, m), 4.13–4.31 (3 H, m, OCH_2 and C*H*OOH), 6.06 (1 H, d, *J* 15.7 Hz, CH=C*H*CO), 6.90 (1 H, dd, *J* 7.3 and 15.7 Hz, C*H*=CHCO) and 9.14 (1 H, br s, OOH); δ_C(63 MHz, $CDCl_3$) 14.08, 18.02, 18.37, 30.69, 60.71, 89.43 (COOH), 124.02, 145.42 and 166.41; *m*/*z* (HRMS) 189.116 (MH^+; $C_9H_{17}O_4$ requires *MH*, 189.1127).

Ethyl (*E*)-4-hydroperoxyhex-2-enoate

R_f (Hexane–EtOAc 4:1) 0.30; ν_{max}($CHCl_3$)/cm^{-1} 3550, 3400, 3050, 3000, 2975, 2900, 1710, 1660, 1460, 1380, 1320, 1300, 1230, 1200, 1160, 1140, 1110, 1050 and 1000; δ_H(250 MHz, $CDCl_3$) 0.88 (6 H, t, *J* 7.5 Hz, 2 × CH_3), 1.28 (3 H, t, *J* 7.1 Hz, OCH_2CH_3), 1.71 (4 H, q, *J* 7.5 Hz, CH_2), 4.21 (2 H, q, *J* 7.1 Hz, OCH_2), 5.95 (1 H, d, *J* 16.2 Hz, CH=C*H*CO), 6.89 (1 H, d, *J* 16.2 Hz, C*H*=CHCO) and 8.23 (1 H, s, OOH); δ_C(63 MHz, $CDCl_3$) 7.48, 12.31, 26.70, 60.69, 86.67 (COOH), 121.57, 149.82 and 166.77; *m*/*z* (HRMS) 203.1320 (MH^+; $C_{10}H_{19}O_4$ requires *MH*, 203.1283).

Cyclohexyl (*E*)-4-ethyl-4-hydroperoxyhex-2-enamide

R_f (Hexane–EtOAc 1:1) 0.35; mp 126.5–127.5 °C (decomp.); ν_{max}($CHCl_3$)/cm^{-1} 3460, 3320, 3030, 2980, 2950, 2860, 1680, 1640, 1520, 1460, 1340, 1160, 1100 and 990; δ_H(250 MHz, $CDCl_3$) 0.86 (6 H, t, *J* 7.4 Hz, CH_3), 1.08–2.41 (14 H, m, 7 × CH_2), 3.80–3.83 (1 H, m, CH), 5.94 (1 H, d, *J* 15.8 Hz, CH=C*H*CO), 6.01 (1 H, br s, NH), 6.74 (1 H, d, *J* 15.8 Hz, C*H*=CHCO) and 9.43 (1 H, br s, OOH); δ_C(63 MHz, $CDCl_3$) 7.56, 24.84, 25.51, 26.66, 33.04, 48.41, 86.61 (COOH), 124.13, 145.43, 164.99 and 165.22; *m*/*z* (HRMS) 255.1812 (M^+; $C_{14}H_{25}O_3$ requires *M*, 255.1834).

Dimethyl (*E*)-4-hydroperoxyhex-2-ene-1,5-dioate

R_f (Hexane–EtOAc 4:1) 0.30; ν_{max}($CHCl_3$)/cm^{-1} 3550, 3400, 3050, 3020, 2980, 2950, 2900, 1740, 1680, 1460, 1430, 1410, 1390, 1320, 1230, 1210, 1150, 1110, 1070 and 1040; δ_H(250 MHz, $CDCl_3$) 2.58–2.83 (2 H, m, CH_2), 3.73 (3 H, s, CH_3), 3.76 (3 H, s, CH_3), 5.00 (1 H, m, C*H*OOH), 6.13 (1 H, d, *J* 15.9 Hz, CH=C*H*CO) and 6.93 (1 H, dd, *J* 6.1 and 15.9 Hz, C*H*=CHCO) and 9.67 (1 H, br s, OOH); δ_C(63 MHz, $CDCl_3$) 37.18, 51.83, 51.96, 80.22 (COOH), 123.35, 144.33, 166.58 and 170.76; *m*/*z* (SIMS) 205 (MH^+).

(*E*)-4-Hydroperoxyhex-2-enal

R_f (Hexane–EtOAc 4:1) 0.12; ν_{max}($CHCl_3$)/cm^{-1} 3550, 3400, 3030, 2980, 2950, 2880, 2830, 1700, 1640, 1465, 1390, 1220, 1120, 1090 and 980; δ_H(250 MHz, $CDCl_3$) 0.99 (3 H, t, *J* 7.5 Hz, CH_3), 1.59–1.78 (2 H, m, CH_2), 4.60 (1 H, q, *J* 6.4 Hz, C*H*OOH), 6.31 (1 H, dd, *J* 7.8 and 16.0 Hz, CH=C*H*CHO), 6.83 (1 H, dd, *J* 6.4 and 16.0 Hz, C*H*=CHCHO), 8.90 (1 H, br s, OOH) and 9.78 (1 H, d, *J* 7.8 Hz, CHO); δ_C(63 MHz, $CDCl_3$) 9.50, 25.23, 85.52 (COOH), 133.09, 155.45 and 193.91; *m*/*z* (HRMS) 131.0702 (MH^+; $C_6H_{11}O_3$ requires *MH*, 131.0708).

(*E*)-4-Hydroperoxynon-2-enal

R_f (Hexane–EtOAc 4:1) 0.15; $\nu_{max}(CHCl_3)/cm^{-1}$ 3550, 3400, 3030, 2970, 2950, 2850, 1700, 1650, 1475, 1390, 1340, 1230, 1140, 1120 and 990; δ_H(250 MHz, $CDCl_3$) 0.89 (3 H, t, *J* 6.5 Hz, CH_3), 1.21–1.73 (8 H, m, 4 × CH_2), 4.66 (1 H, dd, *J* 6.3 and 6.5 Hz, C*H*OOH), 6.32 (1 H, dd, *J* 7.8 and 15.8 Hz, CH=C*H*CHO), 6.82 (1 H, dd, *J* 6.5 and 15.8 Hz, C*H*CHCHO), 8.51 (1 H, br s, OOH) and 9.59 (1 H, d, *J* 7.8 Hz, CHO); δ_C(63 MHz, $CDCl_3$) 15.79, 22.43, 24.79, 31.58, 32.02, 84.48 (COOH), 133.00, 155.51 and 193.72; *m*/*z* (HRMS) 173.1214 (MH^+; $C_9H_{17}O_3$ requires *MH*, 173.1178).

(*E*)-6-Hydroperoxy-2,2-dimethyltridec-4-en-3-one

R_f (Hexane–EtOAc 4:1) 0.34; $\nu_{max}(CHCl_3)/cm^{-1}$ 3550, 3400, 3030, 2980, 2950, 2870, 1700, 1640, 1490, 1480, 1410, 1380, 1330, 1290, 1240, 1150, 1080, 1020 and 990; δ_H(250 MHz, $CDCl_3$) 0.88 (3 H, t, *J* 6.8 Hz, CH_3), 1.17 (9 H, s, 3 × CH_3), 1.26–1.66 (12 H, m, 6 × CH_2), 4.53 (1 H, dt, *J* 6.3 and 6.5 Hz, C*H*OOH), 6.71 (1 H, d, *J* 15.6 Hz, CH=C*H*CO), 6.86 (1 H, dd, *J* 6.5 and 15.6 Hz, C*H*CHCO) and 9.22 (1 H, br s, OOH); δ_C(63 MHz, $CDCl_3$) 14.09, 22.63, 25.16, 26.04, 29.11, 29.44, 31.76, 32.23, 43.16, 85.07 (COOH), 125.57, 145.03 and 205.14; *m*/*z* (HRMS) 257.2136 (MH^+; $C_{15}H_{29}O_3$ requires *MH*, 257.2117).

2-(2′-Hydroperoxyhexylidene)cyclohexanone

R_f (Hexane–EtOAc 4:1) 0.12; $\nu_{max}(CHCl_3)/cm^{-1}$ 3550, 3400, 3030, 2950, 2880, 1690, 1630, 1460, 1440, 1420, 1380, 1310, 1220, 1140, 1075 and 980; δ_H(250 MHz, $CDCl_3$) 0.89 (3 H, t, *J* 5.3 Hz, CH_3), 1.31–1.92 (10 H, m, 5 × CH_2), 2.41–2.76 (4 H, m, 2 × CH_2), 4.71 (1 H, dt, *J* 6.6 and 8.9 Hz, C*H*OOH), 6.45 (1 H, dt, *J* 2.0 and 8.9 Hz, CH=C) and 9.27 (1 H, br s, OOH); δ_C(63 MHz, $CDCl_3$) 13.91, 22.37, 22.66, 23.37, 23.66, 27.28, 27.44, 31.72, 40.46, 81.02 (COOH), 136.92, 139.41 and 212.29; *m*/*z* (HRMS) 213.1441 (MH^+; $C_{12}H_{21}O_3$ requires *MH*, 213.1491).

4-Hydroperoxy-2,6,6-trimethylcyclohept-2-enone

R_f (Hexane–EtOAc 4:1) 0.21; $\nu_{max}(CHCl_3)/cm^{-1}$ 3550, 3400, 3025, 2975, 2940, 2880, 1720, 1670, 1470, 1450, 1380, 1340, 1320, 1220, 1155, 1100, 1080, 1020 and 1005; δ_H(250 MHz, $CDCl_3$) 1.04 (3 H, s, CH_3), 1.15 (3 H, s, CH_3), 1.40–1.63 (2 H, m, CH_2), 1.86 (3 H, s, CH_3), 2.34 and 2.53 (2 H, ABq, *J* 12.0 Hz, CH_2), 4.70–4.75 (1 H, m, C*H*OOH), 6.82 (1 H, br s, CH=C) and 8.69 (1 H, br s, OOH); δ_C(63 MHz, $CDCl_3$) 18.84, 29.72, 29.89, 45.66, 56.09, 80.93 (COOH), 138.04, 144.64 and 201.81; *m*/*z* (HRMS) 185.1159 (MH^+; $C_{10}H_{17}O_3$ requires *MH*, 185.1178).

3-Hydroperoxy-1-nitrocycloct-1-ene

R_f (Hexane–EtOAc 4:1) 0.17; $\nu_{max}(CHCl_3)/cm^{-1}$ 3550, 3450, 3030, 2950, 1700, 1600, 1520, 1450, 1340, 1280, 1220, 1040 and 960; δ_H(250 MHz, $CDCl_3$) 1.49–1.79 (6 H, m, 3 × CH_2), 1.95–2.07 (2 H, m, CH_2), 2.44 [1 H, ddd, *J* 5.5, 11.7 and 14.9, CH=C(NO_2)C(H)*H*], 3.05 [1 H, ddd, *J* 3.9, 4.0 and 14.9 Hz, CH=C(NO_2)-C(*H*)H], 4.87 (1 H, m), 7.34 (1 H, d, *J* 7.1 Hz) and 8.72 (1 H, br s, OOH); δ_C(63 MHz, $CDCl_3$) 23.26, 25.35, 25.63, 27.94, 33.19, 82.95 (COOH), 137.26 and 150.47; *m*/*z* (SIMS) 205 (MH^+).

3-Hydroperoxycyclooct-1-ene

R_f (Hexane–EtOAc 4:1) 0.14; $\nu_{max}(CHCl_3)/cm^{-1}$ 3680, 3550, 3400, 3020, 2950, 2880, 1660, 1600, 1460, 1410, 1330, 1220, 1100, 1070, 1030 and 960; δ_H(250 MHz, $CDCl_3$) 1.07–1.69 (6 H, m, 3 × CH_2), 1.91–1.96 (2 H, m, CH_2), 2.11–2.18 (2 H, m, CH_2), 4.90–4.99 (1 H, m, C*H*OOH), 5.58–5.65 (1 H, m, C*H*=CH), 5.70–5.80 (1 H, m, CH=C*H*) and 8.30 (1 H, br s, OOH); δ_C(63 MHz, $CDCl_3$) 23.38, 26.10, 26.38, 28.76, 32.75, 83.27 (COOH), 130.48 and 131.29; *m*/*z* (HRMS) 142.1005 (M^+; $C_8H_{14}O_2$ requires *M*, 142.0994).

Cyclohexyl 2-hydroperoxypropanoate

R_f (Hexane–EtOAc 4:1) 0.20; $\nu_{max}(CHCl_3)/cm^{-1}$ 3450, 3050, 3000, 2950, 2860, 1730, 1460, 1390, 1360, 1340, 1290, 1220, 1160, 1120, 1090, 1040, 1010 and 995; δ_C(250 MHz, $CDCl_3$) 1.39 (3 H, d, *J* 7.0 Hz, CH_3), 1.45–1.84 (10 H, m, 5 × CH_2), 4.60 (1 H, q, *J* 7.0 Hz, C*H*OOH), 4.88 (1 H, m, CH) and 9.70 (1 H, s, OOH); δ_C(63 MHz, $CDCl_3$) 15.34, 23.58, 25.23, 31.43, 74.02, 79.47 (COOH) and 172.42; *m*/*z* (HRMS) 189.1118 (MH^+; $C_9H_{17}O_4$ requires *MH*, 189.1127).

Cyclohexyl 2-hydroperoxy-2-methylpropanoate

R_f (Hexane–EtOAc 4:1) 0.32; $\nu_{max}(CHCl_3)/cm^{-1}$ 3470, 3030, 3000, 2950, 2860, 1720, 1470, 1450, 1390, 1360, 1290, 1220, 1160, 1120, 1040 and 1010; δ_H(250 MHz, $CDCl_3$) 1.48 (6 H, s, 2 × CH_3), 1.36–1.87 (10 H, m, 5 × CH_2), 4.86 (1 H, m, CH) and 9.37 (1 H, br s, OOH); δ_C(63 MHz, $CDCl_3$) 22.52, 23.37, 25.21, 27.05, 73.72, 83.42 (COOH) and 173.92; *m*/*z* (HRMS) 203.1263 (MH^+; $C_{10}H_{19}O_4$ requires *MH*, 203.1283).

Ethyl 2-hydroperoxy-2-methylhexanoate

R_f (Hexane–EtOAc 4:1) 0.44; $\nu_{max}(CHCl_3)/cm^{-1}$ 3500, 3050, 3000, 2975, 2900, 1740, 1490, 1480, 1390, 1360, 1330, 1290, 1260, 1230, 1150, 1100, 1080 and 1030; δ_H(250 MHz, $CDCl_3$) 0.89 (3 H, t, *J* 7.0 Hz, CH_3), 1.37 (3 H, t, *J* 7.1 Hz, OCH_2CH_3), 1.22–1.93 (6 H, m, 3 × CH_2), 1.49 (3 H, s, CH_3), 4.25 (2 H, q, *J* 7.1 Hz, OCH_2) and 9.22 (1 H, s, OOH); δ_C(63 MHz, $CDCl_3$) 13.90, 14.22, 20.41, 22.83, 25.29, 36.00, 61.46, 86.13 (COOH) and 174.49; *m*/*z* (HRMS) 191.1297 (MH^+; $C_9H_{19}O_4$ requires *MH*, 191.1283).

Dibutyl 2-hydroperoxy-2-methylbutane-1,3-dioate

R_f (Hexane–EtOAc 4:1) 0.28; $\nu_{max}(CHCl_3)/cm^{-1}$ 3480, 3050, 2975, 2950, 2880, 1740, 1730, 1460, 1350, 1300, 1220, 1185, 1120, 1060, 1020, 1000 and 960; δ_H(250 MHz, $CDCl_3$) 0.93 (3 H, t, *J* 7.3 Hz, CH_3), 0.95 (3 H, t, *J* 7.3 Hz, CH_3), 1.33–1.47 (4 H, m, 2 × OCH_2CH_2), 1.53 (3 H, s, CH_3), 1.56–1.71 (4 H, m, 2 × $OCH_2CH_2CH_2$), 2.79 and 3.02 (2 H, ABq, *J* 15 Hz, CH_2CO), 4.10 (2 H, t, *J* 6.7 Hz, OCH_2), 4.22 (2 H, t, *J* 6.6 Hz, OCH_2) and 9.61 (1 H, s, OOH); δ_C(63 MHz, $CDCl_3$) 13.68, 19.07, 21.43, 30.42, 30.47, 41.07, 65.00, 65.75, 83.66 (COOH), 169.93 and 172.28; *m*/*z* (HRMS) 277.1621 (MH^+; $C_{13}H_{25}O_6$ requires *MH*, 277.1651).

Cyclohex-2-en-1-yl 2-hydroperoxypropanoate

R_f (Hexane–EtOAc 4:1) 0.25; $\nu_{max}(CHCl_3)/cm^{-1}$ 3470, 3040, 2990, 2950, 2840, 1720, 1650, 1600, 1470, 1450, 1440, 1380, 1360, 1340, 1280, 1220, 1150, 1040, 1010 and 1000; δ_H(250 MHz, $CDCl_3$) 1.48 (3 H, s, CH_3), 1.49 (3 H, s, CH_3), 1.54–2.08 (6 H, m, 3 × CH_2), 5.33 (1 H, m, CH), 5.71 (1 H, dt, *J* 1.6 and 10.2 Hz, C*H*=CH), 6.00 (1 H, dt, *J* 3.3 and 10.2 Hz, CH=C*H*) and 9.19 (1 H, br s, OOH); δ_C(63 MHz, $CDCl_3$) 18.67, 22.56, 24.80, 28.12, 69.32, 83.57 (COOH), 124.81, 133.51 and 174.21; *m*/*z* (HRMS) 201.1141 (MH^+; $C_{10}H_{17}O_4$ requires *MH*, 201.1127).

2-[(*E*)-Hex-2-enoyloxy]ethyl 2-hydroperoxy-2-methylpropanoate

R_f (Hexane–EtOAc 4:1) 0.18; $\nu_{max}(CHCl_3)/cm^{-1}$ 3450, 3050, 3000, 2970, 2900, 1750, 1740, 1670, 1480, 1470, 1460, 1400, 1380, 1360, 1340, 1300, 1230, 1200, 1170, 1140, 1080 and 1000; δ_H(250 MHz, $CDCl_3$) 0.94 (3 H, t, *J* 7.3 Hz, CH_3), 1.38–1.59 (2 H, m, CH_2CH_3), 1.48 (6 H, s, 2 × CH_3), 2.20 (2 H, dt, *J* 7.0 and 7.1 Hz, CH=CHCH_2), 4.42 (4 H, br s, 2 × OCH_2), 5.83

(1 H, d, *J* 15.6 Hz, CH=C*H*CO), 7.01 (1 H, dt, *J* 7.0 and 15.6 Hz, C*H*=CHCO) and 9.35 (1 H, s, OOH); δ_C(63 MHz, $CDCl_3$) 13.65, 21.20, 22.57, 34.29, 61.70, 63.20, 83.75 (COOH), 120.50, 150.95, 166.64 and 174.01; *m*/*z* (HRMS) 261.1297 (MH^+; $C_{12}H_{21}O_6$ requires *MH*, 261.1338).

α-Methylbenzyl hydroperoxide

R_f (Hexane–EtOAc 10:1) 0.24; ν_{max}($CHCl_3$)/cm^{-1} 3675, 3550, 3100, 3075, 3040, 3000, 2960, 2950, 2920, 2900, 1600, 1500, 1460, 1380, 1360, 1330, 1300, 1280, 1220, 1130, 1080, 1040, 1020, 1000 and 995; δ_H(250 MHz, $CDCl_3$) 1.37 (3 H, d, *J* 6.7 Hz, CH_3), 5.09 (1 H, q, *J* 6.7 Hz, C*H*OOH), 7.31–7.41 (5 H, m, ArH) and 7.72 (1 H, s, OOH); δ_C(63 MHz, $CDCl_3$) 20.10, 83.60 (COOH), 126.50, 128.29 and 128.69; *m*/*z* (HRMS) 138.0724 (M^+; $C_8H_{10}O_2$ requires *M*, 138.0681).

4-Methoxy-α-methylbenzyl hydroperoxide

R_f (Hexane–EtOAc 4:1) 0.20; ν_{max}($CHCl_3$)/cm^{-1} 3675, 3550, 3050, 3025, 2995, 2975, 2950, 2920, 2850, 1610, 1580, 1505, 1460, 1440, 1420, 1380, 1360, 1330, 1300, 1290, 1250, 1220, 1180, 1140, 1100, 1080, 1040 and 1000; δ_H(250 MHz, $CDCl_3$) 1.44 (3 H, d, *J* 6.7 Hz, CH_3), 3.78 (3 H, s, OCH_3), 4.99 (1 H, q, *J* 6.7 Hz, C*H*OOH), 6.87–6.90 (2 H, m, ArH), 7.24–7.30 (2 H, m, ArH) and 8.43 (1 H, s, OOH); δ_C(63 MHz, $CDCl_3$) 19.65, 55.16, 83.04 (COOH), 113.79, 129.94, 133.21 and 159.29; *m*/*z* (HRMS) 168.0737 (M^+; $C_9H_{12}O_3$ requires *M*, 168.0786).

4,α-Dimethylbenzyl hydroperoxide

R_f (Hexane–EtOAc 9:1) 0.13; ν_{max}($CHCl_3$)/cm^{-1} 3660, 3530, 3050, 3000, 2950, 1610, 1510, 1470, 1430, 1380, 1340, 1320, 1300, 1230, 1200, 1140, 1120, 1090, 1040 and 1020; δ_H(250 MHz, $CDCl_3$) 1.44 (3 H, d, *J* 6.7 Hz, CH_3), 2.35 (3 H, s, $ArCH_3$), 5.02 (1 H, q, *J* 6.7 Hz, C*H*OOH), 7.16–7.27 (4 H, m, ArH) and 7.99 (1 H, s, OOH); δ_C(63 MHz, $CDCl_3$) 19.70, 21.08, 83.49 (COOH), 126.53, 137.98 and 138.27; *m*/*z* (HRMS) 152.0845 (M^+; $C_9H_{12}O_2$ requires *M*, 152.0837).

4-Chloro-α-methylbenzyl hydroperoxide

R_f (Hexane–EtOAc 4:1) 0.23; ν_{max}($CHCl_3$)/cm^{-1} 3600, 3540, 3050, 3000, 2900, 1900, 1600, 1490, 1460, 1450, 1410, 1380, 1340, 1300, 1280, 1220, 1135, 1300, 1280, 1220, 1135, 1100, 1080, 1020 and 1000; δ_H(250 MHz, $CDCl_3$) 1.41 (3 H, d, *J* 6.5 Hz, CH_3), 4.99 (1 H, q, *J* 6.5 Hz, C*H*OOH), 7.24–7.34 (4 H, m, ArH) and 8.54 (1 H, br s, OOH); δ_C(63 MHz, $CDCl_3$) 19.88, 82.85 (COOH), 127.86, 128.62, 133.72 and 139.87; *m*/*z* (HRMS) 172.0261 (M^+; $C_8H_9ClO_2$ requires *M*, 172.0291).

α,α-Dimethylbenzyl hydroperoxide

R_f (Hexane–EtOAc 9:1) 0.13; ν_{max}($CHCl_3$)/cm^{-1} 3550, 3100, 3075, 3020, 3000, 2950, 2870, 1610, 1500, 1460, 1380, 1370, 1330, 1270, 1220, 1160, 1105, 1080 and 1030; δ_H(250 MHz, $CDCl_3$) 1.60 (6 H, s, 2 × CH_3) and 7.16–7.48 (6 H, m, ArH and OOH); δ_C(63 MHz, $CDCl_3$) 26.03, 83.91 (COOH), 125.30, 127.41, 128.49 and 144.45; *m*/*z* (HRMS) 152.0842 (M^+; $C_9H_{12}O_2$ requires *M*, 152.0837).

1-Hydroperoxyindene

R_f (Hexane–EtOAc 4:1) 0.20; ν_{max}($CHCl_3$)/cm^{-1} 3600, 3550, 3100, 3050, 2975, 2850, 1715, 1610, 1480, 1460, 1350, 1330, 1230, 1170, 1100, 1060, 1050 and 1035; δ_H(250 MHz, $CDCl_3$) 2.23–2.31 (2 H, m, $ArCH_2CH_2$), 2.81 (1 H, dt, *J* 6.2 and 16.0 Hz, $ArCH_2$), 3.07 (1 H, dt, *J* 8.0 and 16.0 Hz, $ArCH_2$), 5.45 (1 H, t, *J* 4.7 Hz, C*H*OOH), 7.16–7.43 (3 H, m, ArH), 7.45 (1 H, d, *J* 7.4 Hz, ArH) and 8.44 (1 H, br s, OOH); δ_C(63 MHz, $CDCl_3$) 29.93, 30.19, 89.14 (COOH), 123.85, 124.91, 125.96, 126.30, 139.69 and 145.40; *m*/*z* (HRMS) 150.0671 (M^+; $C_9H_{10}O_2$ requires *M*, 150.0681).

Ethyl (*E*)-4-hydroxy-5-methylhex-2-enoate

R_f (Hexane–EtOAc 4:1) 0.18; ν_{max}($CHCl_3$)/cm^{-1} 3650, 3550, 3050, 3000, 2980, 2950, 2900, 1720, 1670, 1480, 1460, 1410, 1380, 1320, 1300, 1230, 1200, 1100, 1040 and 1000; δ_H(250 MHz, $CDCl_3$) 0.95 (6 H, d, *J* 7.0 Hz, CH_3), 1.29 (3 H, t, *J* 7.2 Hz, OCH_2CH_3), 1.77–1.90 (1 H, m), 2.37 (1 H, br s, OH), 4.09 (1 H, dd, *J* 4.8 and 7.2 Hz, C*H*OOH), 4.20 (2 H, q, *J* 7.2 Hz, OCH_2), 6.04 (1 H, dd, *J* 1.7 and 15.7 Hz, CH=C*H*CO) and 6.96 (1 H, dd, *J* 4.8 and 15.7 Hz, C*H*=CHCO); δ_C(63 MHz, $CDCl_3$) 14.18, 17.40, 18.19, 33.61, 60.41, 75.88 (COH), 121.09, 148.88 and 166.52; *m*/*z* (HRMS) 172.1071 (M^+; $C_9H_{16}O_3$ requires *M*, 172.1099).

Ethyl (*E*)-4-hydroxy-5-methyl[5-$^2H_1$]hex-2-enoate

R_f (Hexane–EtOAc 4:1) 0.18; ν_{max}($CHCl_3$)/cm^{-1} 3650, 3550, 3050, 3000, 2980, 2950, 2900, 1720, 1670, 1480, 1460, 1410, 1380, 1320, 1300, 1230, 1200, 1100, 1030 and 950; δ_H(250 MHz, $CDCl_3$) 0.94 (6 H, s, CH_3), 1.29 (3 H, t, *J* 7.2 Hz, OCH_2CH_3), 2.34 (1 H, br s, OH), 4.09 (1 H, d, *J* 4.8 Hz, C*H*OOH), 4.20 (2 H, q, *J* 7.2 Hz, OCH_2), 6.04 (1 H, dd, *J* 1.6 and 15.7 Hz, CH=C*H*CO) and 6.95 (1 H, dd, *J* 4.8 and 15.7 Hz, C*H*=CHCO); δ_C(63 MHz, $CDCl_3$) 14.18, 17.27, 18.08, 32.85, 33.16, 33.47, 60.41, 75.84 (COH), 121.12, 148.83 and 166.49; *m*/*z* (HRMS) 173.1152 (M^+; $C_9H_{15}D_1O_3$ requires *M*, 173.1161).

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