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Synthesis of Cyclic Peroxides by Chemo- and Regioselective Peroxidation of Dienes with Co(II)/O_2/Et_3SiH

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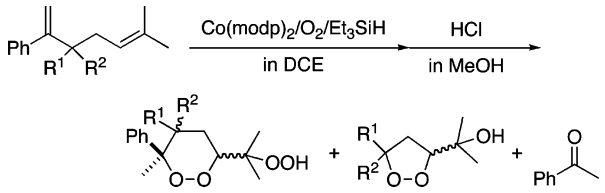

In the competitive peroxidation of mixtures of two alkenes with Co(II)/O_2/Et_3SiH, it was found that the relative reactivities of the alkene substrates are influenced by three major factors:. (1) relative stability of the intermediate carbon-centered radical formed by the reaction of the alkene with HCo(III) complex, (2) steric effects around the C=C double bond, and (3) electronic factors associated with the C=C double bond. Consistent with results from simple alkenes, the chemo- and regioselective peroxidation of dienes was also realized. Depending on the diene structure, the product included not only the expected acyclic unsaturated triethylsilyl peroxides but also 1,2-dioxolane and 1,2-dioxane derivatives via intramolecular cyclization of the unsaturated peroxy radical intermediates.

Introduction

Malaria is recognized as one of the most infective tropical diseases. Since malaria parasites are rapidly developing resistance to the most commonly used chemotherapeutic alkaloidal drugs, there is an urgent need to develop new antimalarial drugs. In this respect, the antimalarial properties of cyclic peroxides such as artemisinin, yingzhaosu A, and their analogues have attracted considerable attention (Figure 1).[1] Although a variety of cyclic peroxides have been synthesized so far, effective methods for the preparation of cyclic peroxides are still limited.[2]

The Co(II)-catalyzed peroxidation of alkenes with molecular oxygen in the presence of triethylsilane affords the corresponding triethylsilyl peroxides with predictable regioselectivity.[3] Thus, allylic alcohols can be conveniently transformed into a variety of cyclic peroxide systems via the corresponding hydroxy-peroxide intermediates.[4] As a logical extension of this methodology, we undertook the peroxidation of dienes such as limonene under similar conditions and obtained the corresponding

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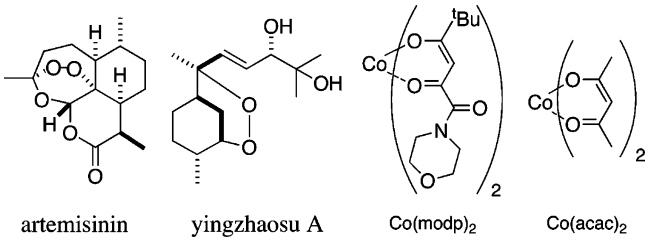


FIGURE 1. Structures of artemisinin, yingzhaosu A, and Co(II) complexes.

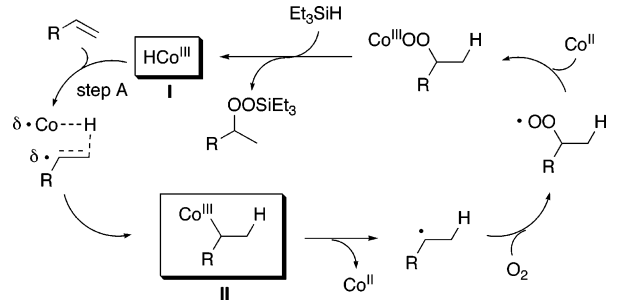
2,3-dioxabicyclo[3.3.1]nonane derivatives,[5] containing the molecular skeleton of yingzhaosu A, via regioselective peroxidation of one of C=C double bonds followed by intramolecular cyclization of the resulting unsaturated peroxy radical intermediates.[1c,6,7]

To explore the scope of this attractive method for the direct synthesis of cyclic peroxides from dienes, the relative reactivities of alkenes, important in accomplishing the chemo- and regioselective peroxidation of dienes, were initially investigated. Subsequently, the peroxidation of a series dienes, designed by taking account of the relative reactivities of alkenes, was examined to obtain information about the influence of diene structure, particularly chain length, on the efficiency of cyclic peroxide formation.

Results and Discussion

Factors Affecting the Relative Reactivities of Alkenes. A tentative mechanism for the Co(II)-catalyzed peroxidation of alkenes in the presence of Et_3SiH and O_2 is outlined in Scheme 1.[8] The reaction of the HCo(III) complex **I** with the alkene substrate (step A) is expected to be sensitive to the relative reactivities of alkenes. In analogous reactions, it has been suggested that the formation of the C−H bond occurs prior to that of C−Co bond.[9] Consequently, these reactions should take place via transition states in which one of the carbon centers has partial radical character.[10] Thus, the stability of the intermediate carbon-centered radical, where the triethylsilylperoxy group will ultimately be located, should correlate with the relative reactivities of the alkene substrates.[11]

SCHEME 1. Reaction Mechanism for Peroxidation of Alkene



To judge the relative reactivity of alkenes, however, it is important to determine whether or not the addition of the HCo(III) complex to the C=C double bond is reversible. Although there is precedent for the reversible formation of alkene via β-elimination from alkylcobalt(III) glyoximate or phorphyrin complexes analogous to **II**,[12] the following results demonstrate that the addition is irreversible in the case of the relatively less stable HCo(III) diketonate complexes generated under Mukaiyama−Isayama reaction conditions.

When the reaction of **1** with O_2 and Et_3SiD was undertaken in DCE (5 mL) in the presence of bis(1-morpholinocarbamoyl-4,4-dimethyl-1,3-pentanedionato)-cobalt(II) [$Co(modp)_2$, 5 mol %] at room temperature for 5 h, a mixture of unchanged alkene **1** and triethylsilyl peroxide **2**-*d* was obtained. Separation of the peroxidic product from starting material was facilitated by desilylation of **2**-*d* to give the corresponding hydroperoxide **4**-*d* (Scheme 2). The ^1H NMR spectrum of the recovered alkene **1** demonstrated that there had been no incorporation of deuterium into the alkene **1**.[13]

Reaction of alkene *cis*-**5** also gave a similar result. Quenching the reaction after 8 h gave only the starting alkene *cis*-**5** in addition to the formation of expected hydroperoxide esters **6** and **7**; isomerization of alkene *cis*-**5** to either the *trans*-isomer or other positional isomers was not observed (Scheme 3). These results suggest that reversible formation of HCo(III) **I** from Co(III)−alkyl complex **II** is not involved. Thus, the relative reactivity seems to be dependent on the ease of the reaction of HCo(III) **I** with the alkene.

To determine if the stabilities of the carbon-centered radicals correlate with the alkene reactivities, a series of competitive reactions were conducted with 1:1 mix-

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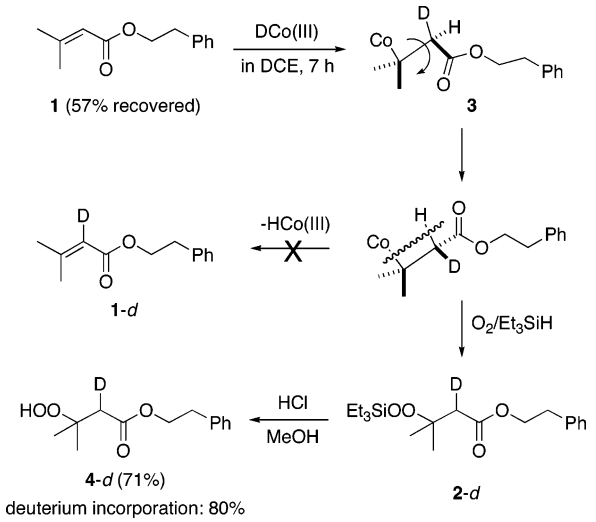
(11) Regioselectivity should be controlled by stability of the intermediate carbon-centered radical. Thus, the triethylsilylyldioxy group tends to be introduced into the more substituted carbon of the C=C double bond.

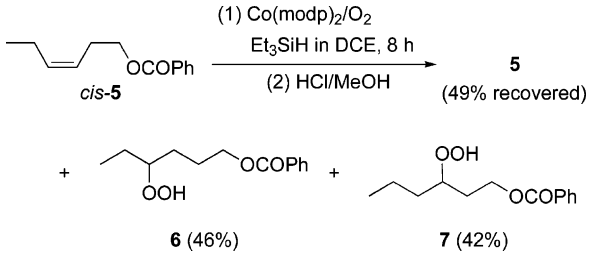
(12) (a) Gridnev, A. A.; Ittel, S. D.; Fryd, M.; Wayland, B. B. *Organometallics* **1996**, *15*, 222. (b) Ohgo, Y.; Takeuchi, S. *J. Chem. Soc., Chem. Commun*. **1985**, 21. (c) Schrauzer, G. N. *Angew. Chem., Int. Ed. Engl*. **1976**, *15*, 417.

(13) It was confirmed from analysis of the ^1H NMR spectrum that deuterium atom transfer to the alkene **1** produced exclusively the triethylsilyl peroxide **2**-*d*. Therefore, the lower deuterium incorporation into **4**-*d* is attributed to the acid-promoted H−D exchange in desilylation step of **2**-*d*.

SCHEME 2. Peroxidation of Alkene 1 in the Presence of Et_3SiD



SCHEME 3. Peroxidation of Alkene *cis*-5



tures of alkenes.[14] The relative reactivities were evaluated by comparison of the conversions of each substrate as determined by either ^{1}H NMR spectral or GC analysis (Chart 1; an asterisk (*) indicates the location at which triethylsilyldioxy group is introduced). Consistent with our expectation, the relative reactivities of alkenes **8**−**13** followed the sequence of the stability of the corresponding carbon-centered radicals.[15] However, differences in relative reactivities such as **14** vs **15** vs **9** and **1** vs **15** indicate that the stability of the carbon-centered radical is not the sole factor that determines relative reactivities (for example, the stability of the carbon-centered radical derived from **14** should be very similar to those from **15** and **9**).

The second factor seems to be the steric congestion around the C=C double bond. The observed differences in reactivities between alkenes **9**, **14**, and **15** are consistent with the notion that the approach of the bulky HCo(III) complex would be less hindered with less highly substituted substrates. A similar explanation could be advanced to account for the relative reactivities of alkenes **11**, **16**, and **17**.[16−20]

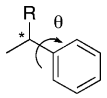
The remarkable difference in reactivity between alkenes **1** and **15** may be attributed to the electronic factors associated with the C=C double bond, in particular the electron-donating ability of the attached substituent. The difference in relative reactivity between the alkenes **9** and **10** may be rationalized on a similar basis. In the case of unsaturated ester **10**, the increase in radical-stabilizing ability arising from conjugation to the ester group is almost completely compensated by a decrease in electron density in the C=C double bond. This would imply that the H−Co(III) complex is intrinsically electrophilic.[21] However, the acidity of $HCo(acac)_2$ does not seem to be high enough to participate in H−D exchange, as the peroxidation of alkene **8** with Et_3SiD in EtOH demonstrates (Scheme 4).

Regioselective Peroxidation of Dienes and Intramolecular Cyclization of the Derived Unsaturated Peroxy Radical Intermediate. Since the relative reactivities of alkenes **11** and **15** suggest that the phenyl-substituted C=C double bond should be more reactive by a factor of >20, the 1,5-diene **19a** was expected to be an appropriate candidate for chemo- and regioselective formation of the peroxy radical analogous to **27c** (Scheme 5), which in turn would provide either the unsaturated triethylsilyl peroxide **20a** or the cyclic peroxide **21a**. Consistent with this expectation, the phenyl-substituted C=C double bond was selectively oxidized to give a mixture of 1,2-dioxane **21a** and unsaturated peroxide **20a**, together with acetophenone **22** (4%) (Table 1, entry

(14) Alkene peroxidation procedure requires an induction period, the length of which depends slightly on the structure of alkene. Therefore, comparisons of the alkene conversions as determined from separate reactions are not meaningful.

(15) Regioselectivities observed for Co(II)−phorphyrin complex-catalyzed peroxidation of dienes can be interpreted by this notion: Sugamoto, K.; Matsushita, Y.; Matsui, T. *J. Chem. Soc., Perkin Trans. 1* **1998**, 3989.

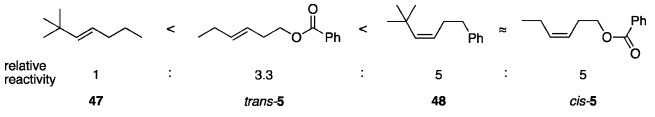
(16) A decrease in reactivities of alkenes **11**, **16**, and **17** would be attributed not only to the steric effects but also differences in stability of the intermediate radicals. Because of the presence of the bulky substituent, the radical intermediates would not be able to adopt conformations in which the phenyl ring is orthogonal to the p-orbital containing the odd electron. The dihedral angles θ for methyl- and *tert*-butyl-substituted radicals, calculated on the UB3LYP/6-31G(d) level of theory[17] with the Gaussian 98 package,[18] were estimated to be 0 and 27°, respectively.



(17) (a) Hariharan, P. C.; Pople, J. A. *Theo. Chim. Acta*. **1973**, *28*, 213. (b) Ditchfield, R.; Hehre, W. J.; Pople, J. A. *J. Chem. Phys*. **1971**, *54*, 724.

(18) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.11; Gaussian, Inc.: Pittsburgh, PA, 1998.

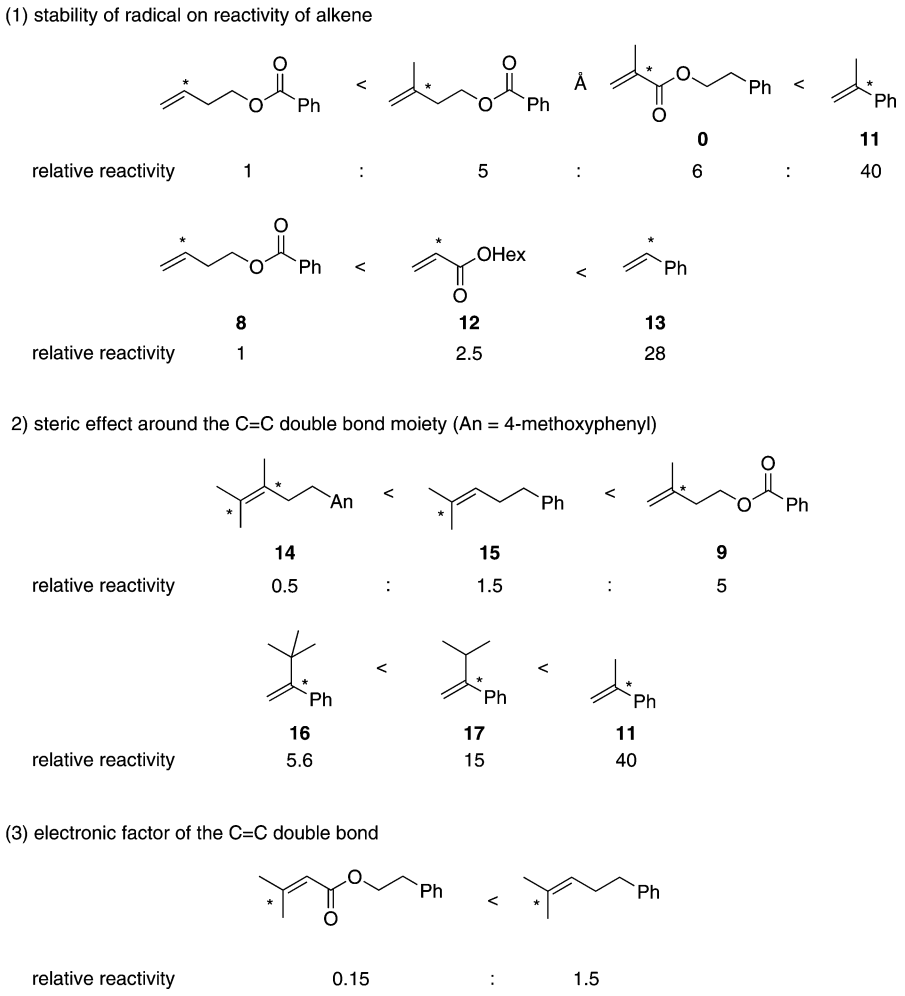
(19) Relative reactivities of alkenes shown below are compatible with this notion. By analogy with the epoxidation reactions of alkenes with transition metal catalysts,[20] *cis*-alkenes are more reactive than *trans*-alkenes. Moreover, substitution with a *tert*-butyl group decreases the reactivity of *trans*-alkene more markedly than the *cis*-alkene. More remarkable steric effects can be seen in a series of styrene derivatives.



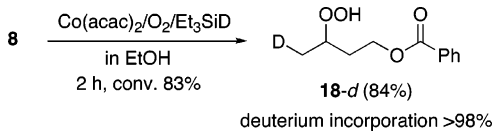
(20) Katsuki, T. *Synlett* **2003**, 281.

(21) Several HCo(III) complexes are known to be acidic: (a) Nishinaga, A.; Yamada, T.; Fujisawa, H.; Ishizaki, K.; Ihara, H.; Matuura, T. *J. Mol. Catal*. **1988**, *48*, 249. (b) Chao, T.-H.; Espenson, J. H. *J. Am. Chem. Soc*. **1978**, *100*, 129. See also ref 12c.

CHART 1. List of Relative Reactivities of Alkenes



SCHEME 4. Reaction of 8 with Et_3SiD in EtOH



1). Subsequent desilylation of the peroxide product mixture afforded, after chromatographic separation on silica gel, the cyclic peroxide **25a** (31% based on consumed diene, a 2:1 mixture of diastereoisomers) and the unsaturated hydroperoxide **24a**.

Expecting the desired 1,2-dioxane **25** to be formed in improved yield as a consequence of the *gem*-dimethyl effect,[22] the reaction of 1,5-diene **19d** was examined. Conversely, the yield of cyclic peroxide **25d** was not improved and instead epoxide **23d** was obtained as an additional product (Table 1, entry 5). Since epoxide **23d** could not be separated from a trace amount of impurities, desilylation using HCl in MeOH was undertaken. However, desilylation was apparently followed by epoxide ring-opening to produce the 1,2-dioxolane **26d** in 28% yield (based on consumed diene **19d**).[23] Similar reactions were observed for **19b**. In the case of **19c**, however, the pure epoxide **23c** could be readily isolated.

X-ray crystallographic analysis of a single crystal of **25d** shows that the 1,2-dioxane ring adopts the classical chair conformation. As expected from discussions on the stereoselectivity of radical cyclization reactions above,[7g,24] both the hydroperoxy alkyl group at C(1) and the phenyl group at C(4), which is more bulky than the adjacent geminal methyl group, occupy equatorial positions (Figure 2). By NMR experiments, including HMQC, HMBC, and NOE enhancement, similar stereochemical assignments could also be made for the major isomer of 1,2-dioxane **25c**. The phenyl group at C(3) in **25c** was also found to occupy an equatorial position (Figure 3).

As illustrated in Scheme 5, both acetophenone (**22**) and epoxide **23c** may be derived from the carbon-centered radical **28c** by an intramolecular homolytic substitution process.[25] The resulting alkoxy radical **29c** undergoes β-scission to give acetophenone (**22**) and carbon-centered radical **30c**, the latter being efficiently entrapped by molecular oxygen. The recombination of the derived

(22) Eliel, E. L.; Wilen, S. H. *Stereochemistry of Organic Compounds*; Wiley-Interscience: 1994.

(23) Contrary to the general trend on acid-promoted ring-opening reaction of epoxides, intermolecular attack of hydroperoxy group on epoxide moiety occurred at the less substituted carbon of the epoxide ring. However, the ring-opening cyclizations of analogous epoxides were previously examined by Porter and co-workers who observed the competitive formation of 1,2-dioxolane with 1,2-dioxane: Porter, N. A.; Funk, M. O.; Gilmore, D.; Isaac, R.; Nixon, J. *J. Am. Chem. Soc.* **1976**, *98*, 6000.

(24) Roe, A. N.; McPhail, A. T.; Porter, N. A. *J. Am. Chem. Soc.* **1983**, *105*, 1199.

SCHEME 5. Probable Reaction Mechanism for Formation of 1,2-Dioxane 21c and Acetophenone 22

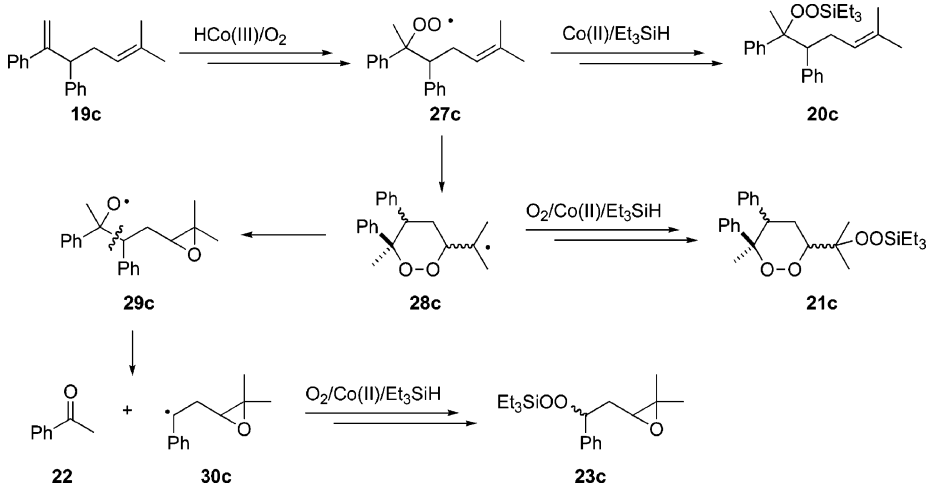
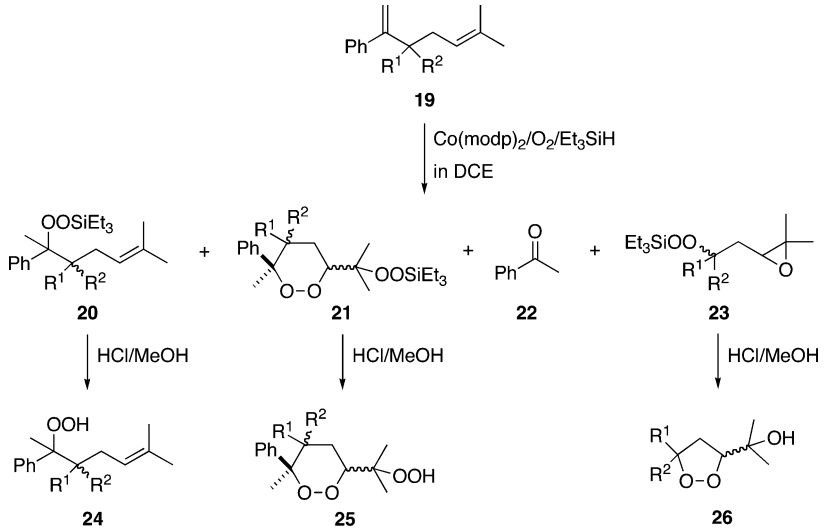


TABLE 1. Competitive Formation of 1,2-Dioxanes with Unsaturated Triethylsilyl Peroxides[a]



entry	diene	R^1	R^2	reaction time (h)	conversion (%)	yields (%)[b] 22	23	24	25	26
1	**19a**	H	H	6	82	4		13	31	
2[c]	**19a**	H	H	6	61			18	45	
3	**19b**	H	Me	2.5	83	36		12	13	33
4	**19c**	H	Ph	3.5	75	57	38	7[d]	27	
5	**19d**	Me	Me	3	84	51			31	26
6[c]	**19d**	Me	Me	3	62	7			64	8

[a] Unless otherwise noted, reaction of dienes (2 mmol) were conducted in the presence of Co(II) (0.10 mmol) and Et_3SiH (4 mmol) in DCE (5.0 mL) under slightly positive oxygen atmosphere (about 1.2 atmosphere). [b] Yields are based on the consumed dienes. [c] Reaction was conducted at 4 atm of oxygen pressure. [d] Hydroperoxide **25c** could not be isolated in pure form. Treatment with excess PPh_3, followed by purification with column chromatography on silica gel, gave the corresponding alcohol in pure form. The described yield is calculated from the amount of the isolated alcohol based on the consumed diene **19c**.

peroxy radical with Co(II) complex, followed by transmetalation with Et_3SiH, finally affords the epoxide **23c**.

The mechanism proposed in Scheme 5 suggests that capture of the intermediate radical **28** by molecular oxygen should occur more effectively at higher oxygen pressure, thereby providing the desired 1,2-dioxane **21** in improved yield. Consistent with this expectation, the reaction of the diene **19a** under 4 atm oxygen pressure proceeded more cleanly to give unsaturated peroxide **24a** and 1,2-dioxane **25a** in 18 and 45% yields, respectively, after desilylation (Table 1, entry 2). Under similar conditions (O_2 at 4 atm), diene **19d** was transformed into the corresponding 1,2-dioxane derivative **25d** in substantially improved yield (Table 1, entry 6).

(25) (a) Wijaya, C. D.; Sumathi, R.; Green, W. H., Jr. *J. Phys. Chem. A* **2003**, *107*, 4908. (b) Degueil-Castaing, M.; Moutet, L.; Maillard, B. *J. Org. Chem*. **2000**, *65*, 3961. (c) Bloodworth, A. J.; Courtneidge, J. L.; Davies, A. G. *J. Chem. Soc., Perkin Trans. 2* **1984**, 523. (d) Porter, N. A.; Cudd, M. A.; Miller, R. W.; McPhail, A. T. *J. Am. Chem. Soc*. **1980**, *102*, 414. (e) Porter, N. A.; Nixon, J. R. *J. Am. Chem. Soc*. **1978**, *100*, 7116. (f) Bloodworth, A. J.; Davies, A. G.; Griffin, I. M.; Muggleton, B.; Roberts, B. P. *J. Am. Chem. Soc*. **1974**, *96*, 7599.

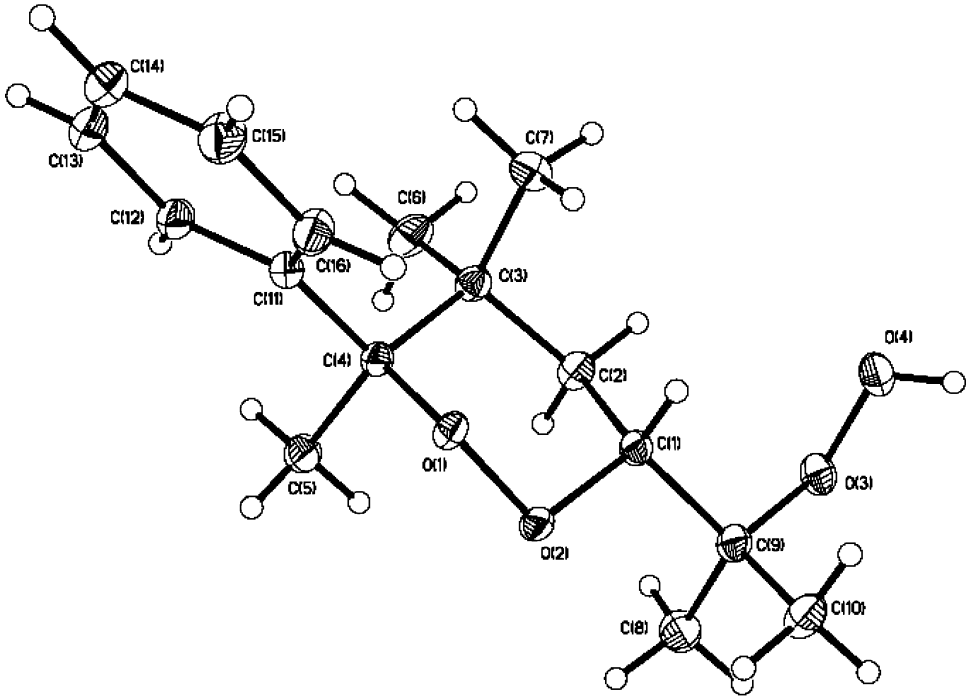


FIGURE 2. Crystal structure of 1,2-dioxane **25d**.

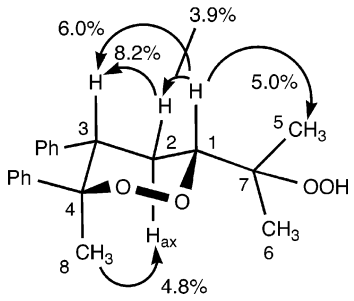
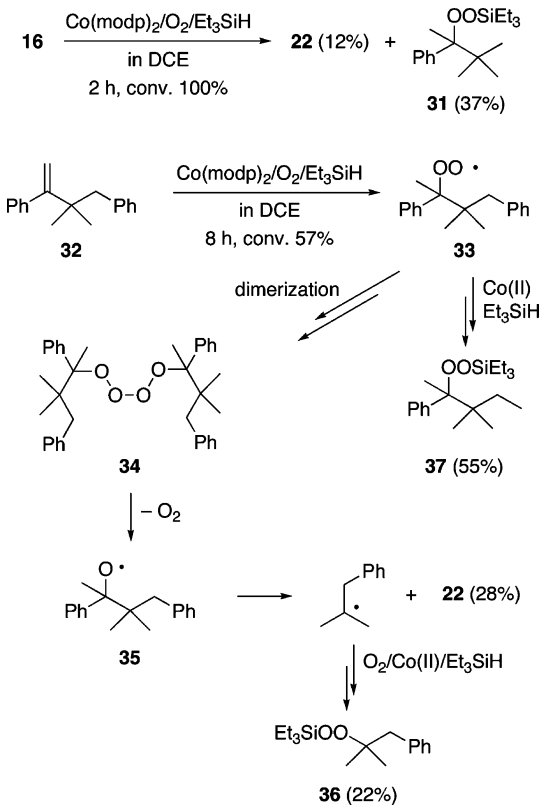


FIGURE 3. Determination of structure of the major isomer of 1,2-dioxane **25c**.

Acetophenone (**22**) was isolated as a significant product not only from dienes **19** but also from several sterically crowded monoenes. Thus, peroxidation of α-*tert*-butylstyrene (**16**) gave triethylsilyl peroxide **31** (37%; this yield is that of the corresponding hydroperoxide after desilylation) and acetophenone (**22**) (12%).[26] From alkene **32**, acetophenone (**22**) (10%), together with the triethylsilyl peroxide **36** and the expected triethylsilyl peroxide **37**, was obtained; the latter peroxidic products were isolated in 22 and 55% yields, respectively, after desilylation (Scheme 6).[27] These results suggest that a process different from that shown in Scheme 5 is operating for the formation of **22** from bulky alkenes.

SCHEME 6. Dimerization of Peroxy Radical Intermediate

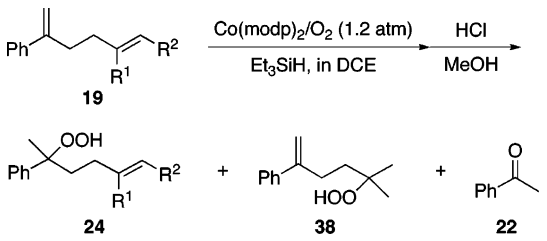


That is, in the case of the bulky peroxyl radical **33**, recombination with a sterically crowded Co(II) complex is significantly retarded, and as a result, dimerization of **33** occurs competitively to give the corresponding tetroxide intermediate **34**, which in turn undergoes ejection of an oxygen molecule to give the alkoxyl

(26) Since monitoring the course of the peroxidation reaction by ^{1}H NMR spectroscopy indicated the formation of acetophenone (**22**) from the beginning of the reaction, the acid-mediated decomposition of the peroxide **31** to acetophenone (**22**) during workup, i.e., heterolytic cleavage of O−O bond (Hock-type cleavage) followed by migration of *tert*-butyl group can be ruled out in this case.[7j]

(27) After treatment of a mixture of triethylsilyl peroxides **36** and **37** with HCl in MeOH, 2-methyl-1-phenylpropan-2-ol was obtained as an additional product. Moreover, ^{1}H NMR spectroscopic analysis indicated an increase in the yield of acetophenone as compared to the crude reaction mixture. Possibly, these products are formed by acid-promoted decomposition (Hock-type cleavage of O−O bond) of triethylsilyl peroxide **36**.[7j]

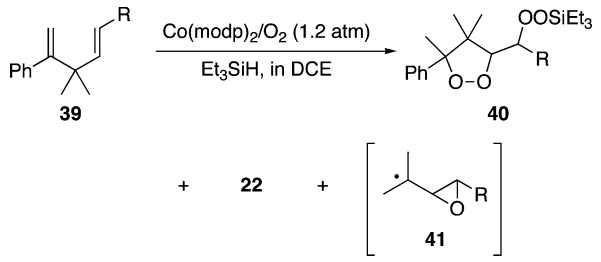
TABLE 2. Substituent Effects on Peroxidation of Dienes 19e,f



entry	diene	R^1	R^2	reaction time (h)	conversion (%)	yields (%) **24**	**38**[a]	**22**
1	**19e**	Me	H	8	29	39	8	37
2	**19f**	H	CO_2Et	24	95	33		

[a] This compound was obtained as an admixture with 83% of **24e**.

TABLE 3. Synthesis of 1,2-Dioxane 40[a]



entry	diene	R	reaction time (h)	conversion (%)	yields (%) **40**	**22**
1	**39a**	H	4.5	47	27	49
2	**39b**	CO_2Et	2	44	56	22

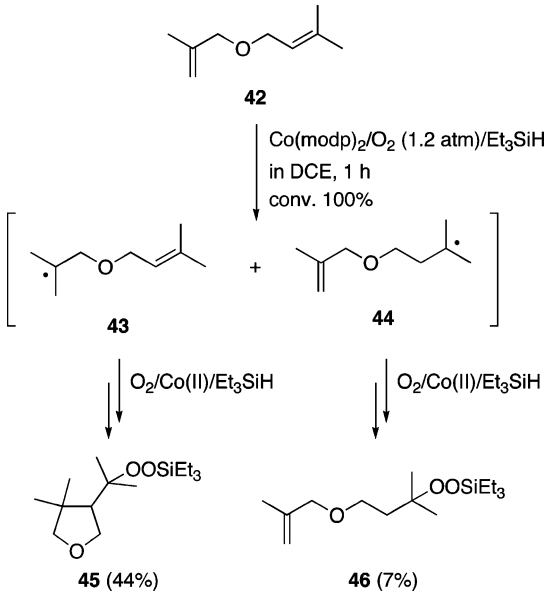
radical **35** (Russell termination).[7j] Subsequent β-scission results in the production of **22** and the triethylsilyl peroxide **36**.

To obtain information about the effect of the diene substituents on the efficiency of 1,2-dioxane production, the peroxidation reactions of 1,5-dienes **19e**,**f** were examined. Unfortunately, peroxidation of diene **19e** gave a mixture of the acyclic unsaturated hydroperoxides **24** and **38** rather than the corresponding 1,2-dioxane. This is consistent with the observation of Beckwith and co-workers that the rate of 5-exo cyclization of the 5-methyl-5-hexenyl radical is ca. 43 times slower than that of the 5-hexenyl radical.[28] The reaction of diene **19f** gave only the unsaturated hydroperoxide **24f** (Table 2). These results imply that presence of a 4-methyl-3-pentenyl moiety could be an important factor for the efficient production of the 1,2-dioxanes from 1,5-dienes. In such cases, the resulting intermediate peroxyl radical rapidly cyclizes onto the less congested alkenyl carbon, thereby providing a stable *tert*-alkyl radical.

The applicability of this method to the synthesis of cyclic peroxides having a range of different ring sizes was examined. Peroxidation of the 1,4-dienes **39a**,**b** gave the corresponding 1,2-dioxolanes **40a**,**b** in 27 and 56% yields, respectively, together with acetophenone (**22**) (Table 3; the yields of **40a**,**b** are those of the corresponding hydroperoxides after desilylation). When compared to the

(28) Beckwith, A. L. J.; Schiesser, C. H. *Tetrahedron* **1985**, *41*, 3925.

SCHEME 7. Peroxidation of Diene 42



results from dienes **19e**,**f**, (Table 2), the ready formation of 1,2-dioxolanes from **39a**,**b** is entirely consistent with an estimate of the rate of 6-exo cyclization of peroxy radical being about 2 orders of magnitude lower than that of 5-exo cyclization.[29] Although isolation of acetophenone (**22**) implies concomitant formation of the carbon-centered radical **41**, no products derived from this intermediate were identified.

Since cyclic peroxides with ring-sizes ≥ 7 are of interest,[7c,h] peroxidation of the 1,6-diene **42** was also investigated. The formation of the tetrahydrofuran derivative **45** clearly demonstrates that the resulting carbon-centered radical **43** underwent rapid 5-exo cyclization before entrapment with molecular oxygen followed by complexation and silylation, thereby providing **45** in a moderate yield of 44% (Scheme 7).[30] On the other hand, the alternative carbon-centered radical **44**, generated by reaction of trisubstituted C=C double bond of **42** with HCo(III), was entrapped by molecular oxygen before 6-exo cyclization to give the acyclic unsaturated peroxide **46** in 7% yield (the yields of **45** and **46** show those of the corresponding hydroperoxides after desilylation).

Conclusion

It has been found that the relative reactivity of alkenes in the $Co(II)/O_2/Et_3SiH$ peroxidation is affected by the following three majors factors: (1) relative stability of the intermediate carbon-centered radical formed by reaction of the alkene with the HCo(III) complex, (2) steric effects around the C=C double bond, and (3) the electron density in the C=C double bond. Consistent with the

(29) Courtneidge, J. L. *J. Chem. Soc., Chem. Commun*. **1992**, 1270.

(30) In contrast to our result, Okamoto and Oka did not observe cyclization of the 1-phenyl-5-hexenyl radical derived from the corresponding 1-phenyl-5-hexenyl cobalt(III) complex during the similar peroxidation reaction with BH_4^- rather than Et_3SiH as the hydrogen donor.[31] However, our observation is compatible with the result reported by Jensen and co-workers who observed cyclization of the intermediate 5-hexenyl radical on thermal decomposition of the 5-hexenylcobalt(III) complex.[32]

observed relative reactivities of alkenes, chemo- and regioselective monoperoxidation of appropriate dienes gave the expected unsaturated triethylsilyl peroxides. In favorable cases, the corresponding 1,2-dioxanes and 1,2-dioxolanes were obtained via intramolecular cyclization of the putative unsaturated peroxy radical intermediates. As expected, reactions carried out at higher oxygen pressure gave the cyclic peroxides in higher yields. Contrary to conventional methods in which unsaturated hydroperoxides have been employed as precursors, this method provides an alternative synthetic route to cyclic peroxides directly from dienes.

Experimental Section

The synthetic methods and the physical properties of alkenes **1**, **5**, **8**−**10**, **14**, **15**, **32**, and **48** and dienes **19**, **39**, and **42** are described in Supporting Information. Alkenes **16** and **17** were prepared by literature procedures.[33] The product study on peroxidation of the series of alkenes **5**, **8**, **10**−**12**, and **14**−**17** is detailed in Supporting Information. Peroxidation of the alkene **9** and the physical data for the derived products have been already reported.[8]

Since triethylsilyl peroxides, **2**-*d*, **18**-*d*, **20**, **21**, **23d**, **31**, **36**, **37**, **40**, and **45**−**46** were difficult to isolate in pure form, they were transformed into the corresponding hydroperoxides. To determine the purity of labile unsaturated hydroperoxide **24a**, it was converted into the corresponding alcohol. To identify the product **24c**, which could not be separated from a small amount of impurities, this hydroperoxide was also converted into the corresponding alcohol. The structures of 2-(3-methyl-3,4-diphenyl-1,2-dioxan-3-yl)propan-2-yl hydroperoxide obtained by desilylation of 1,2-dioxane **21c** was determined by NOE difference.

The catalyst $Co(modp)_2$ was prepared by the literature method.[3a] 1,2-Dichloroethane and ethanol were purified by distillation over CaH_2 and CaO, respectively. α-Methylstyrene (**11**), *n*-hexyl acrylate (**12**), styrene (**13**), *trans*-2,2-dimethyl-3-heptene (**47**), and $Co(acac)_2$ were commercially available reagents and used as received.

Caution. Since organic peroxides are potentially hazardous compounds, they must be handled with due care; avoiding exposure to strong heat or light, mechanical shock, oxidizable organic materials, or transition metal ions. No particular difficulties were experienced in handling any of the new peroxides synthesized in this work using the reaction scales and procedures described below together with the safeguards mentioned above.

General Procedure for Peroxidation of Alkenes 5, 16, and 32. Peroxidation of alkene **32** is representative. Into a two-neck, 50 mL flask charged with dioxygen were added alkene **32** (460 mg, 1.9 mmol), bis(1-morpholinocarbamoyl-4,4-dimethyl-1,3-pentanedionato)cobalt(II) ($Co(modp)_2$) (53 mg, 0.098 mmol), and DCE (5.0 mL), and then the flask was again charged with dioxygen. Triethylsilane (490 mg, 4.2 mmol) was added via a 1.0 mL gastight syringe, and the reaction mixture was stirred vigorously under an oxygen atmosphere at room temperature. After the mixture was stirred for 8 h, the solvent was evaporated under reduced pressure. Hexane (10 mL) was added to the residue, and then the precipitated solid materials were removed by filtration over Celite. After concentration of the filtrate, the components of the residue were separated by column chromatography on silica gel. Elution with diethyl ether−hexane (2:98) gave a mixture of the alkene **32** and the triethylsilyl peroxides **36** and **37** (600 mg). Subsequent elution with diethyl ether−hexane (8:92) gave acetophenone (**22**) (13 mg, 10%).

A mixture of alkene **32** and the triethylsilyl peroxides **36** and **37** was dissolved in MeOH (1.0 mL) and treated with one portion of concentrated HCl. After the mixture was stirred for 30 s, solid $NaHCO_3$ and then $MgSO_4$ were added. The reaction mixture was stirred for an additional 5 min, and solid materials were removed by filtration over Celite. After concentration of filtrate under reduced pressure, products were separated by column chromatography on silica gel. The alkene **32** (200 mg) was recovered by elution with diethyl ether−hexane (3:97) (conversion = 57%). Elution with diethyl ether−hexane (4:96) gave acetophenone (**22**) (23 mg, 18%). Subsequent elution with diethyl ether−hexane (5:95) gave 3,3-dimethyl-2,4-diphenylbutan-2-yl hydroperoxide (170 mg, 55%), and then 2-methyl-1-phenylpropan-2-yl hydroperoxide (37 mg, 22%) was obtained by elution with diethyl ether−hexane (6:94).

2-Methyl-1-phenylpropan-2-yl Hydroperoxide (Corresponding OOH Form of Compound 36): colorless solid, mp 37−40 °C (from hexane); ^{1}H NMR δ 1.21 (s, 6 H), 2.89 (s, 2 H), 7.20−7.35 (m, 5 H), 7.49 (s, 1 H); ^{13}C NMR δ 24.0 (CH_3, 2 C), 44.4 (CH_2), 83.0 (C), 126.2 (CH), 127.9 (CH, 2 C), 130.4 (CH, 2 C), 137.5 (C). Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 72.30; H, 8.55.

2-Methyl-1-phenylpropan-2-ol:[34] oil; ^{1}H NMR δ 1.22 (s, 6 H), 1.42 (s, 1 H), 2.77 (s, 2 H), 7.20−7.31 (m, 5 H); ^{13}C NMR δ 29.2, 49.7, 70.7, 126.4, 128.1 (2 C), 130.3 (2 C), 137.6.

3,3-Dimethyl-2,4-diphenylbutan-2-yl Hydroperoxide (Corresponding OOH Form of Compound 37): colorless solid, mp 126−127 °C (from ether−hexane); ^{1}H NMR δ 0.78 (s, 3 H), 0.82 (s, 3 H), 1.85 (s, 3 H), 2.67 (s, 2 H), 7.02−7.05 (m, 2 H), 7.10−7.42 (m, 8 H); ^{13}C NMR δ 20.0, 21.8, 21.9, 41.7, 42.2, 91.3, 125.7, 126.9, 127.4 (2 C), 127.7 (2 C), 127.8 (2 C), 131.2 (2 C), 138.5, 141.6. Anal. Calcd for $C_{18}H_{22}O_2$: C, 79.96; H, 8.20. Found: C, 79.77; H, 8.13.

3,3-Dimethyl-2-phenylbutan-2-yl Hydroperoxide (Corresponding OOH Form of Compound 31): oil; ^{1}H NMR δ 0.91 (s, 9 H), 1.74 (s, 3 H), 7.30−7.40 (m, 6 H); ^{13}C NMR δ 19.6, 25.9 (3 C), 38.0, 90.7, 126.8, 127.4 (2 C), 127.5 (2 C), 141.8. Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 73.94; H, 9.23.

Peroxidation of 2-Phenylethyl 3-Methyl-2-butenoate 1 with $Co(modp)_2$ and Et_3SiD. Reaction of 2-phenylethyl 3-methyl-2-butenoate (**1**, 300 mg, 1.5 mmol) with $Co(modp)_2$ (40 mg, 0.074 mmol) and Et_3SiD (360 mg, 3.1 mmol) in DCE (3.7 mL) was conducted according to the general procedure, and the reaction mixture was stirred for 7 h. The conventional workup afforded a mixture of alkene **1** and the corresponding triethylsilyl peroxide **2**-*d*, which was eluted with diethyl ether−hexane (5:95). After treatment of this mixture with a drop of concentrated HCl, followed by the similar workup as described in general procedure, products were separated by column chromatography on silica gel. 2-Phenylethyl 3-methyl-2-butenoate (**1**, 170 mg), which did not contain any deuterium, was recovered by elution with diethyl ether−hexane (5:95) (conversion = 43%). Subsequent elution with diethyl ether−hexane (15:85) gave the hydroperoxide **4**-*d* as an admixture with 20% yield of **4** (110 mg, 71%).

2-Phenylethyl 3-Hydroperoxy-3-methylbutanoate (4): oil; ^{1}H NMR δ 1.26 (s, 6 H), 2.62 (s, 2 H), 2.95 (t, J = 6.9 Hz, 2 H), 4.34 (t, J = 6.9 Hz, 2 H), 7.20−7.29 (m, 5 H), 8.70 (s, 1 H); ^{13}C NMR δ 24.5 (CH_3, 2 C), 34.9 (CH_2), 43.3 (CH_2), 65.2 (CH_2), 81.0 (C), 126.5 (CH), 128.4 (CH, 2 C), 128.6 (CH, 2 C), 137.3 (C), 171.3 (C). Anal. Calcd for $C_{13}H_{18}O_4$: C, 65.53; H, 7.61. Found: C, 65.27; H, 7.54.

2-Phenylethyl 2-Deuterio-3-hydroperoxy-3-methylbutanoate (4-*d*): oil; ^{1}H NMR δ 1.25 (s, 6 H), 2.60 (br s, 1 H),

(31) Okamoto, T.; Oka, S. *J. Org. Chem*. **1984**, *49*, 1589.

(32) Jensen, F. R.; Kiskis, R. C. *J. Am. Chem. Soc*. **1975**, *97*, 5825; see also (a) Bhandal, H.; Patel, V. F.; Pattenden, G.; Russell, J. J. *J. Chem. Soc., Perkin Trans. 1* **1990**, 2691. (b) Bamhaoud, T.; Prandi, J. *Chem. Commun*. **1996**, 1229.

(33) Baciocchi, E. J.; Ruzziconi, R. *J. Org. Chem*. **1991**, *56*, 4772.

(34) Alexakis, A.; Jachiet, D.; Normant, J. F. *Tetrahedron* **1986**, *42*, 5607.

2.96 (t, J = 7.0 Hz, 2 H), 4.35 (t, J = 7.0 Hz, 2 H), 7.20−7.29 (m, 5 H), 8.64 (s, 1 H); ^{13}C NMR δ 24.5 (2 C), 34.9, 43.1 (t, J = 19.3 Hz), 65.3, 81.0, 126.5, 128.4 (2 C), 128.6 (2 C), 137.3, 171.3.

Peroxidation of Alkene 8 with Co(acac)$_2$ and Et$_3$SiD in EtOH. Reaction of 3-butenyl benzoate (**8**, 360 mg, 2.0 mmol) with Co(acac)$_2$ (27 mg, 0.10 mmol) and triethylsilane-*d* (480 mg, 4.1 mmol) in 5 mL of EtOH was conducted according to general procedure, and the reaction mixture was stirred for 2 h. The conventional workup afforded a mixture of alkene **8** and the corresponding triethylsilyl peroxide **18**-*d*, which was eluted with diethyl ether−hexane (3:97). After treatment of this mixture with a drop of concentrated HCl, followed by workup similar to that described in the general procedure, products were separated by column chromatography on silica gel. 3-Butenyl benzoate (**8**, 60 mg) was recovered by elution with diethyl ether−hexane (3:97) (conversion = 83%). Subsequent elution with diethyl ether−hexane (15:85) gave 4-deuterio-3-hydroperoxybutyl benzoate (300 mg, 84%).

4-Deuterio-3-hydroperoxybutyl Benzoate (18-*d*): oil; ^{1}H NMR δ 1.30 (dt, J = 6.2 and 1.8 Hz, 2 H), 1.89−2.18 (m, 2 H), 4.28 (quintet, J = 6.2 Hz, 1 H), 4.42−4.47 (m, 2 H), 7.39−7.44 (m, 2 H), 7.51−7.57 (m, 1H), 8.00−8.04 (m, 2 H), 9.10−9.12 (m, 1 H); ^{13}C NMR δ 18.1 (t, J = 19.3 Hz), 31.1, 61.9, 78.3, 128.2 (2 C), 129.3 (2 C), 129.8, 132.9, 166.8.

General Procedure for Peroxidation of Dienes with Co(modp)$_2$. Reaction of 3,3,6-trimethyl-2-phenyl-1,5-heptadiene (**19d**) is representative. Into a two-neck, 50 mL flask charged with dioxygen were added the diene **19d** (428 mg, 2.0 mmol), Co(modp)$_2$ (53 mg, 0.098 mmol), and DCE (5.0 mL), and then the flask was again charged with dioxygen. Triethylsilane (460 mg, 4.0 mmol) was added via 1.0 mL gastight syringe, and the reaction mixture was stirred vigorously under an oxygen atmosphere at room temperature. After the mixture was stirred for 3 h, the solvent was evaporated under reduced pressure. Hexane (10 mL) was added to the residue, and then the precipitated solid materials were removed by filtration over Celite. After concentration of the filtrate, the components of the residue were separated by column chromatography on silica gel. Elution with diethyl ether−hexane (5:95) gave a mixture of diene **19d** and the triethylsilyl peroxide **21d** (320 mg). Subsequent elution with diethyl ether−hexane (7:93) gave epoxide **23d** (240 mg), which was contaminated with small amount of impurities. Acetophenone **22** (103 mg, 51%) was obtained by elution with diethyl ether−hexane (10:90).

The first fraction, a mixture of diene **19d** and the triethylsilyl peroxide **21d**, was dissolved in MeOH (1.0 mL) and treated with one portion of concentrated HCl. After the mixture was stirred for 1 min, solid $NaHCO_3$ and $MgSO_4$ were added. The reaction mixture was stirred for an additional 5 min, and solid materials were removed by filtration over Celite. After concentration of the filtrate under reduced pressure, products were separated by column chromatography on silica gel. The diene **19d** (70 mg) was recovered by elution with diethyl ether−hexane (5:95) (conversion = 84%). Elution with diethyl ether−hexane (15:85) gave 2-(5,5,6-trimethyl-6-phenyl-1,2-dioxan-3-yl)propan-2-yl hydroperoxide (**25d**, 146 mg, 31%).

Desilylation of epoxide **23**, eluted by diethyl ether−hexane (7:93), was conducted in the same way as described for the treatment of the first fraction. Product was isolated by column chromatography on silica gel. Elution with diethyl ether−hexane (40:60) gave 2-(5,5-dimethyl-1,2-dioxolan-3-yl)propan-2-ol (**26d**, 69 mg, 26%).

[2-Methyl-1-(3,3-dimethyloxiran-2-yl)propan-2-yl]triethylsilane (23d): oil; ^{1}H NMR δ 0.69 (q, J = 7.9 Hz, 6 H), 0.98 (t, J = 7.9 Hz, 9 H), 1.27 (s, 3 H), 1.28 (s, 3 H), 1.29 (s, 3 H), 1.33 (s, 3 H), 1.70 (dd, J = 14.6, 5.7 Hz, 1 H), 1.93 (dd, J = 14.6, 5.7 Hz, 1 H), 2.90 (t, J = 5.7 Hz, 1 H); ^{13}C NMR δ 3.9 (CH_2, 3 C), 6.9 (CH_3, 3 C), 19.1 (CH_3), 24.2 (CH_3), 24.9 (CH_3), 25.2 (CH_3), 37.8 (CH_2), 57.7 (C), 61.0 (CH), 81.6 (C).

2-(5,5,6-Trimethyl-6-phenyl-1,2-dioxan-3-yl)propan-2-yl Hydroperoxide (25d): colorless solid, mp 115−116 °C (from ether−hexane); ^{1}H NMR δ 0.81 (s, 3 H), 1.05 (s, 3 H), 1.28 (s, 3 H), 1.33 (s, 3 H), 1.35 (dd, J = 13.1, 2.4 Hz, 1 H), 1.76 (s, 3H), 2.03 (t, J = 13.1 Hz, 1 H), 4.62 (dd, J = 13.1, 2.4 Hz, 1 H), 7.2−7.3 (m, 5 H), 7.90 (s, 1 H); ^{13}C NMR δ 20.2 (CH_3), 20.8 (CH_3), 20.9 (CH_3), 24.2 (CH_3), 26.3 (CH_3), 35.7 (C), 35.8 (CH_2), 81.6 (CH), 83.3 (C), 86.7 (C), 126.0 (CH, 2 C), 126.8 (CH), 127.4 (CH, 2 C), 141.6 (C). Anal. Calcd for $C_{16}H_{24}O_4$: C, 68.54; H, 8.63. Found: C, 68.32; H, 8.43.

2-(5,5-Dimethyl-1,2-dioxolan-3-yl)propan-2-ol (26d): oil; ^{1}H NMR δ 1.14 (s, 3 H), 1.27 (s, 3 H), 1.34 (s, 6 H), 2.08 (s, 1 H; H−D exchange in D_2O), 2.33 (dd, J = 12.0 and 7.6 Hz, 1 H), 2.40 (dd, J = 12.0, 7.6 Hz, 1 H) 4.13 (t, J = 7.6 Hz, 1 H); ^{13}C NMR δ 24.4, 25.0, 26.0, 27.2, 46.8, 71.8, 83.8, 87.1.

6-Methyl-2-phenyl-5-hepten-2-yl Hydroperoxide (24a): oil; ^{1}H NMR δ 1.53 (s, 3 H), 1.66 (s, 6 H), 1.79−1.97 (m, 4 H), 5.06−5.09 (m, 1 H), 7.26−7.45 (m, 5 H); ^{13}C NMR δ 17.7, 22.6, 22.8, 25.7, 39.5, 86.2, 123.8, 125.5 (2 C), 127.2, 128.4 (2 C), 132.1, 143.8.

6-Methyl-2-phenyl-5-hepten-2-ol:[35] oil; ^{1}H NMR δ 1.47 (s, 3 H), 1.54 (s, 3 H), 1.63 (s, 3 H), 1.81−1.97 (m, 5 H), 5.04−5.10 (m, 1H), 7.20−7.44 (m, 5 H); ^{13}C NMR δ 17.7, 23.0 (2 C), 25.8, 30.6, 75.0, 124.0, 124.7 (2 C), 126.3, 128.0 (2 C), 132.1, 147.7.

2-(6-Methyl-6-phenyl-1,2-dioxan-3-yl)propan-2-yl Hydroperoxide (25a): oil (ca. 2:1 mixture of two stereoisomers); ^{1}H NMR δ 1.04 (s, 1 H), 1.12 (s, 1 H), 1.30 (s, 2 H, major), 1.32 (s, 2 H, major), 1.36 (s, 1 H), 1.63 (s, 2 H, major), 1.70−2.20 (m, 3.67 H), 2.58 (dt, J = 13.9, 3.5 Hz, 0.33 H), 4.24 (dd, J = 9.8, 4.0 Hz, 0.67 H, major), 4.32 (dd, J = 9.8, 4.0 Hz, 0.33 H), 7.24−7.47 (m, 5 H), 7.60 (s, 0.33 H), 8.08 (s, 0.67 H); ^{13}C NMR δ 20.4 (CH_2, major), 20.8 (CH_3), 20.9 (CH_3), 21.0 (CH_3), 23.8 (CH_3), 30.0 (CH_3), 33.0 (CH_2), 33.4 (CH_2, major), 81.6 (C, major), 82.7 (C), 83.1 (C), 83.3 (C, major), 84.5 (CH, major), 84.6 (CH), 124.5 (CH), 125.7 (CH), 126.8 (CH), 127.4 (CH), 128.3 (CH), 143.3 (C), 145.2 (C). Anal. Calcd for $C_{14}H_{20}O_4$: C, 66.65; H, 7.99. Found: C, 66.48; H, 8.03.

3,6-Dimethyl-2-phenyl-5-hepten-2-yl Hydroperoxide (24b): oil (3:1 mixture of two stereoisomers); ^{1}H NMR δ 0.64 (d, J = 6.6 Hz, 0.75 H), 0.94 (d, J = 7.3 Hz, 2.25 H, major), 1.39 (s, 2.25 H, major), 1.58 (s, 1.5 H), 1.61 (s, 2.25 H, major), 1.67 (s, 2.25 H, major), 1.68 (s, 0.75 H), 1.40−1.90 (m, 2.75 H), 2.30−2.40 (m, 0.25 H), 4.91−4.97 (m, 0.75 H, major), 5.00−5.10 (m, 0.25 H), 7.09−7.46 (m, 6 H); ^{13}C NMR δ 14.1 (major), 14.8, 17.5, 17.6 (major), 17.7 (major), 17.9, 25.8 (major), 25.9, 29.7, 30.4 (major), 43.0 (major), 43.2, 89.0 (major), 89.2, 122.8 (major), 123.2, 126.1, 126.3 (major), 127.2, 127.3 (major), 128.3 (major), 132.5 (major), 143.2 (major). Anal. Calcd for $C_{15}H_{22}O_2$: C, 76.88; H, 9.46. Found: C, 76.59; H, 9.48.

1-(5,6-Dimethyl-6-phenyl-1,2-dioxan-3-yl)propan-2-yl Hydroperoxide (25b): oil (1:1 mixture of two stereoisomers); ^{1}H NMR δ 0.83 (d, J = 6.9 Hz, 1.5 H), 0.99 (br d, J = 7.7 Hz, 1.5 H), 1.10−1.80 (m, 2 H), 1.23 (s, 1.5 H), 1.27 (s, 1.5 H), 1.30 (s, 1.5 H), 1.36 (s, 1.5 H), 1.58 (s, 1.5 H), 1.66 (s, 1.5 H), 2.10−2.35 (m, 1 H), 4.38 (t, J = 7.4 Hz, 0.5 H), 4.49−4.55 (m, 0.5 H), 7.23−7.57 (m, 5 H), 7.91 (br s, 0.5 H), 8.03 (br s, 0.5 H); ^{13}C NMR δ 20.9, 21.0, 21.1 (2 C), 29.5, 38.8, 83.3, 85.3, 85.7, 126.1, 127.0, 127.7, 128.0. Anal. Calcd for $C_{15}H_{22}O_4$: C, 67.64; H, 8.33. Found: C, 67.51; H, 8.54.

1-(5-Methyl-1,2-dioxolan-3-yl)propan-2-ol (26b): oil (ca. 1:1 mixture of two mixtures); ^{1}H NMR δ 1.16−1.32 (m, 9 H), 2.06 (s, 0.5 H), 2.13 (s, 0.5 H), 2.16−2.29 (m, 1 H), 2.62−2.78 (m, 1 H), 4.10−4.18 (m, 1 H), 4.34−4.46 (m, 1 H); ^{13}C NMR δ 16.4 (CH_3), 18.5 (CH_3), 24.7 (CH_3), 25.3 (CH_3), 26.9 (CH_3), 27.0 (CH_3), 42.2 (CH_2), 42.3 (CH_2), 70.9 (C), 71.4 (C), 77.7 (CH), 77.9 (CH), 86.5 (CH) 87.1 (CH). Anal. Calcd for $C_7H_{14}O_3$: C, 57.51; H, 9.65. Found: C, 57.83; H, 9.50.

[2-(3,3-Dimethyloxiran-2-yl)-1-phenylethylperoxy]triethylsilane (23c): oil (1:1 mixture of two stereoisomers); ^{1}H NMR δ 0.63−0.70 (m, 6 H), 0.91−0.97 (m, 9 H), 1.09 (s, 1.5

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H), 1.16 (s, 1.5 H), 1.19 (s, 1.5 H), 1.27 (s, 1.5 H), 1.80−1.90 (m, 0.5 H), 1.95−2.06 (m, 1 H), 2.29 (dt, J = 14.0, 6.0 Hz, 0.5 H), 2.68 (t, J = 6.4 Hz, 0.5 H), 2.88 (t, J = 6.1 Hz, 0.5 H), 4.98 (dd, J = 8.1, 6.2 Hz, 0.5 H), 5.03 (dd, J = 8.1, 5.2 Hz, 0.5 H), 7.29−7.32 (m, 5 H); ^{13}C NMR δ 3.5 (CH_2), 3.6 (CH_2), 6.5 (CH_3), 6.6 (CH_3), 18.6 (CH_3), 24.5 (CH_3), 24.6 (CH_3), 34.2 (CH_2), 34.8 (CH_2), 58.2 (C), 58.5 (C), 60.8 (CH), 61.2 (CH), 85.0 (CH), 85.5 (CH), 126.7 (CH), 126.8 (CH), 127.9 (CH), 128.0 (CH), 128.1 (CH), 128.2 (CH), 139.9 (C), 140.4 (C). Anal. Calcd for $C_{18}H_{30}O_3Si$: C, 67.03; H, 9.38. Found: C, 66.74; H, 9.48.

6-Methyl-2,3-diphenyl-5-hepten-2-ol (Corresponding OH Form of Compound 24c): oil (a 3:2 mixture of two stereoisomers); ^{1}H NMR δ 1.29 (s, 1.8 H), 1.32 (s, 1.8 H), 1.43 (s, 3 H), 1.47 (s, 1.2 H), 1.55 (s, 1.2 H), 1.79 (s, 0.6 H; H−D exchange in D_2O), 1.87 (s, 0.4 H; H−D exchange in D_2O), 2.07−2.52 (m, 2 H), 2.89−2.99 (m, 1 H), 4.68−4.79 (m, 1 H), 7.00−7.44 (m, 10 H); ^{13}C NMR δ 17.6, 17.8, 25.7, 26.0, 27.9, 28.2, 30.2, 57.3, 58.0, 76.3, 76.5, 122.7, 122.8, 124.9, 125.8, 126.2, 126.4, 126.5, 127.5, 127.6, 127.8, 127.9, 129.7, 130.0, 131.6, 131.8, 139.8, 140.7, 146.4, 147.4. Anal. Calcd for $C_{20}H_{24}O$: C, 85.67; H, 8.63. Found: C, 85.41; H, 8.71.

2-(6-Methyl-5,6-diphenyl-1,2-dioxan-3-yl)propan-2-yl Hydroperoxide (25c) (Major Isomer): mp 134−136 °C (from ether−hexane); ^{1}H NMR δ 1.34 (s, 3 H, Me-6), 1.39 (s, 3 H, Me-5), 1.66 (s, 3H, Me-8), 1.90 (ddd, J = 13.4, 3.9, 2.4 Hz, 1 H, H-2eq), 2.47 (br q, J = 12.6 Hz, 1 H, H-2ax), 3.38 (dd, J = 13.0, 4.0 Hz, 1 H, H-3), 4.66 (dd, J = 11.5, 2.5 Hz, 1 H, H-1), 6.75 (d, J = 5.8 Hz, 2 H), 7.11−7.30 (m, 8 H), 8.01 (s, 1 H, OOH); ^{13}C NMR δ 16.3 (CH_3, Me-8), 20.9 (CH_3, Me-6), 21.1 (CH_3, Me-5), 26.7 (CH_2, C-2), 51.7 (CH, C-3), 83.2 (C, C-4), 85.5 (CH, C-1), 85.7 (C, C-7), 126.2 (CH, 2C), 126.9 (CH), 127.7 (CH, 2 C), 127.8 (CH, 2 C), 127.9 (CH), 129.0 (CH, 2 C), 139.4 (C), 142.0 (C). Anal. Calcd for $C_{20}H_{24}O_4$: C, 73.15; H, 7.37. Found: C, 72.90; H, 7.39. The minor isomer was obtained as an admixture with 75% of the major isomer, and the following additional signals were assigned to this isomer: ^{1}H NMR δ 1.26 (s, 3 H), 1.32 (s, 3 H), 1.33 (s, 3 H), 1.77 (dt, J = 12.9, 3.3 Hz, 1 H), 2.16 (br q, J = 11.9 Hz, 1 H), 4.51 (dd, J = 11.1, 3.5 Hz, 1 H), 8.06 (br s, 1 H); ^{13}C NMR δ 20.8 (CH_3), 20.9 (CH_3), 21.1 (CH_3), 26.1 (CH_2), 51.3 (CH), 83.4 (C), 86.0 (CH), 87.2 (C), 127.1 (CH), 127.2 (CH), 127.4 (CH), 127.9 (CH), 129.4 (CH), 139.7 (C), 140.7 (C).

5-Methyl-2-phenyl-5-hexen-2-yl Hydroperoxide (24e): oil; ^{1}H NMR δ 1.66 (s, 3 H), 1.68 (s, 3 H), 1.94−1.98 (m, 4 H), 4.65 (s, 1 H), 4.68 (s, 1 H), 7.31−7.42 (m, 6 H); ^{13}C NMR δ 22.8 (CH_3), 22.8 (CH_3), 31.9 (CH_2), 37.7 (CH_2), 86.1 (C), 109.6 (CH_2), 125.5 (CH, 2 C), 127.3 (CH), 128.4 (CH, 2 C), 143.7 (C), 145.5 (C). Anal. Calcd for $C_{13}H_{18}O_2$: C, 75.69; H, 8.80. Found: C, 75.40; H, 8.84.

2-Methyl-5-phenyl-5-hexen-2-yl Hydroperoxide (38). This compound was obtained as an admixture with 83% of 5-methyl-2-phenyl-5-hexen-2-yl hydroperoxide (**24e**), and the following signals were assigned to this compound: ^{1}H NMR δ 1.25 (s, 6 H), 1.67−1.76 (m, 2 H), 2.54−2.60 (m, 2 H), 5.10 (s, 1 H), 5.29 (s, 1 H); ^{13}C NMR δ 24.0 (CH_3), 29.6 (CH_2), 37.1 (CH_2), 82.6 (C), 112.2 (CH_2), 126.1 (CH), 128.6 (CH), 143.8 (C), 148.6 (C).

Ethyl 6-Hydroperoxy-6-phenyl-2-heptenoate (24f): oil; ^{1}H NMR δ 1.24 (t, J = 7.3 Hz, 3 H), 1.67 (s, 3 H), 1.95−2.02 (m, 2 H), 2.12−2.21 (m, 2 H), 4.12 (q, J = 7.3 Hz, 2 H), 5.74 (dt, J = 14.3, 23.2, 26.7, 37.6, 60.2, 85.6, 121.2, 125.4 (2 C), 127.5, 128.5 (2 C), 143.2, 148.4, 166.4. Anal. Calcd for $C_{15}H_{20}O_4$: C, 68.16; H, 7.63. Found: C, 67.87; H, 7.57.

(4,4,5-Trimethyl-5-phenyl-1,2-dioxolan-3-yl)methyl Hydroperoxide (Corresponding OOH Form of Compound 40a): oil; ^{1}H NMR δ 0.59 (s, 3 H), 1.27 (s, 3 H), 1.65 (s, 3 H), 4.14 (d, J = 5.2 Hz, 2 H), 5.44 (t, J = 5.2 Hz, 1 H), 7.26−7.40 (m, 5 H), 8.82 (br s, 1 H); ^{13}C NMR δ 20.1 (CH_3), 21.2 (CH_3), 23.6 (CH_3), 54.2 (C), 75.8 (CH_2), 85.8 (CH), 89.9 (C), 125.1 (CH, 2 C), 127.2 (CH), 128.1 (CH, 2 C), 140.8 (C). Anal. Calcd for $C_{13}H_{18}O_4$: C, 65.53; H, 7.61. Found: C, 65.75; H, 7.65.

Ethyl 2-(4,4,5-Trimethyl-5-phenyl-1,2-dioxolan-3-yl)-2-hydroperoxyacetate (Corresponding OOH Form of Compound 40b): oil; ^{1}H NMR δ 0.77 (s, 3 H), 1.21 (s, 3 H), 1.34 (t, J = 7.1 Hz, 3 H), 1.64 (s, 3 H), 4.32 (q, J = 7.1 Hz, 2 H), 4.47 (d, J = 6.9 Hz, 1 H), 4.64 (d, J = 6.9 Hz, 1 H), 7.20−7.30 (m, 5 H), 9.66 (s, 1 H); ^{13}C NMR δ 14.0 (CH_3), 20.8 (CH_3), 21.4 (CH_3), 23.1 (CH_3), 54.4 (C), 62.0 (CH_2), 83.3 (CH), 86.1 (CH), 90.4 (C), 125.1 (CH, 2 C), 127.3 (CH), 128.0 (CH, 2 C), 139.8 (C), 168.9 (C). Anal. Calcd for $C_{16}H_{22}O_6$: C, 61.92; H, 7.15. Found: C, 62.05; H, 7.33.

2-(Tetrahydro-4,4-dimethylfuran-3-yl)propan-2-yl Hydroperoxide (Corresponding OOH Form of Compound 45): oil; ^{1}H NMR δ 1.14 (s, 6 H), 1.29 (s, 3 H), 1.33 (s, 3 H), 2.26 (t, J = 8.9 Hz, 1 H), 3.48 (s, 2 H), 3.90 (t, J = 8.9 Hz, 1 H), 4.01 (t, J = 8.9 Hz, 1 H), 8.62 (s, 1 H); ^{13}C NMR δ 22.5 (CH_3), 23.4 (CH_3), 24.1 (CH_3), 27.0 (CH_3), 40.8 (C), 54.7 (CH), 69.7 (CH_2), 82.5 (CH_2), 83.7 (C). Anal. Calcd for $C_9H_{18}O_3$: C, 62.04; H, 10.41. Found: C, 61.97; H, 10.20.

4-(2-Methyl-2-propenyloxy)-2-methylbutan-2-yl Hydroperoxide (Corresponding OOH Form of Compound 46): oil; ^{1}H NMR δ 1.25 (s, 6 H), 1.76 (s, 3 H), 1.88 (t, J = 5.1 Hz, 2 H), 3.54 (t, J = 5.1 Hz, 2 H), 3.96 (s, 2 H), 4.92−4.97 (m, 2 H), 9.49 (s, 1 H); ^{13}C NMR δ 19.4, 24.7 (2 C), 37.9, 65.9, 75.2, 80.9, 112.7, 141.2.

Competitive Reaction. The competitive reaction with a 1:1 mixture of alkenes **8** and **9** is representative. A solution of alkene **8** (370 mg, 2.1 mmol), alkene **9** (380 mg, 2.0 mmol), and 3,5-dimethylanisole (internal standard, 130 mg, 1.0 mol) in DCE (5.0 mL) was prepared in a two-neck, 50 mL flask, and the ratios of alkenes **8** and **9** to the internal standard were evaluated by ^{1}H NMR spectrum or GC. Into the prepared solution were added $Co(modp)_2$ (50 mg, 0.093 mmol) and Et_3SiH (240 mg, 2.1 mmol), and the flask was charged with molecular oxygen. After the mixture was stirred for 1.5 h, 50 μL of reaction solution, removed from the flask, was dissolved in 1.0 mL of $CDCl_3$, and conversions of each substrate were evaluated by ^{1}H NMR spectra or GC.

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Supporting Information Available: Synthetic methods and physical properties of alkenes **1**, **5**, **8**−**10**, **14**, **15**, **32**, and **48** and the dienes **19**, **39**, and **42**, results of peroxidations of alkenes **5**, **8**, **10**−**12**, and **14**−**17**, tabular results of a series of competitive reactions, a CIF file of compound **25d**, and NMR charts of compounds *trans*-**5**, **19f**, **26d**, and **46**. This material is available free of charge via the Internet at http://pubs.acs.org.

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