(d, 4 H, J = 6 Hz), 5.59 (t, 2 H, J = 6 Hz); MS, m/z 188 (M^+, 100), 173, 145, 115, 91.

Preparation of 5-Methylene-3′,4′,5′,6′-tetrahydro-1,2-benzo-1,3-cycloheptadiene (16). A solution of compound **12e** in EtOAc (20% by weight) was injected on a GC (injection temperature 220 °C, oven temperature 180 °C, detector temperature 250 °C) with a Carbowax 20M (3-m) column. The chromatogram showed the existence of only one component **16**, which was collected with a dry ice trap: colorless oil; IR (neat) 1611, 1448, 879, 792 cm^{-1}; NMR (80 MHz) δ 1.55 (br s, 4 H), 2.08 (br s, 4 H), 2.14 (d, 2 H, J = 10 Hz), 2.47 (d, 2 H, J = 10 Hz), 4.74 (s, 1 H), 4.85 (s, 1 H), 5.56 (d, 1 H, J = 13 Hz), 6.10 (d, 1 H, J = 13 Hz); MS, m/z 160 (M^+, 100), 145, 131, 117, 91, 77. Anal. Calcd for $C_{12}H_{16}$: C, 89.93; H, 10.07. Found: C, 89.76; H, 10.24.

Acknowledgment. We thank the National Science Council of the Republic of China for financial support (Grant NSC76-0208-M001-21).

Registry No. **5a**, 77-79-2; **5b**, 1193-10-8; **5c**, 18214-56-7; **5d**, 7311-87-7; **5e**, 55370-42-8; **10**, 17616-43-2; **11**, 26430-96-6; **12a**, 110417-28-2; **12b**, 110417-29-3; **12c**, 110417-31-7; **12d**, 110417-31-7; **12e**, 110417-32-8; **13a**, 110417-33-9; **13b**, 110417-34-0; **13c**, 110417-35-1; **13d**, 110417-36-2; **13e**, 110417-37-3; **14a**, 110417-38-4; **14b**, 110417-39-5; **14c**, 110417-40-8; **15a**, 110417-41-9; **15b**, 110417-42-0; **15c**, 110417-43-1; **15d**, 110417-44-2; **16**, 110417-45-3.

Allylic Hydroperoxide Rearrangement: β-Scission or Concerted Pathway?

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The rearrangements of the allylic hydroperoxides derived from oleic acid have been studied. Two hydroperoxides are formed by singlet-oxygen oxidation of oleic acid *trans*-9-hydroperoxyoctadec-10-enoic acid (**5**) and *trans*-10-hydroperoxyoctadec-8-enoic acid (**6**). These hydroperoxides can be separated by reverse-phase chromatography. Rearrangement of ^{18}O-labeled hydroperoxides (**5** or **6**) under a $^{32}O_2$ atmosphere led to no incorporation of ^{16}O into the rearrangement products. Similarly, rearrangement of ^{16}O-labeled hydroperoxides (**5** or **6**) under a $^{36}O_2$ atmosphere led to no incorporation of ^{18}O into the rearrangement products. The hydroperoxide **5** rearranges to a mixture of **5** and *trans*-11-hydroperoxyoctadec-9-enoic acid and alcohols and ketones resulting from Russell termination steps. The results are discussed in terms of a concerted rearrangement of allylic peroxyl radicals proceeding through a five-membered-ring transition state.

Allylic hydroperoxides undergo structural rearrangement. This rearrangement has been known since 1957, when Schenck reported that the tertiary C-5 α-hydroperoxide of cholesterol rearranges to its α-allylic isomer.[1-6] At least three mechanisms for the allylic hydroperoxide rearrangement have been proposed.[7-9] These three mechanisms are outlined in Figure 1 and involve the following. (1) Formation of a cyclic five-membered-ring peroxide with a free radical at position 4 of the ring (see structure **1** of Figure 1). This mechanism amounts to a stepwise reaction pathway with **1** being a true intermediate in the rearrangement. (2) Formation of a cyclic five-membered-ring transition state, **2**, that links the two allylic hydroperoxyl radicals. This mechanism is a concerted mechanism in which **2** is not an authentic reaction intermediate, but rather is a transition state. (3) β-Fragmentation of an allylic peroxyl radical to form molecular oxygen and an allyl carbon radical, **3**, which can recombine with oxygen at either end of the radical to give the starting and rearranged peroxyl radicals. Each of these mechanisms involves intermediate peroxyls, and consistent with this is the fact that free-radical initiators facilitate the reaction and phenolic inhibitors stop the rearrangement.[7,8]

Several experiments have been carried out to determine the mechanism of the allylic hydroperoxide rearrangement. For example, Brill has attempted to trap the proposed radical intermediate, **1** by carrying out the rearrangement under high pressures of O_2 or with allylic systems designed to undergo further molecular rearrangements at the intermediate radical stage.[8] No oxygen entrapment or other evidence for radical intermediate **1** could be presented to support the stepwise mechanism involving a cyclic peroxide radical. Furthermore, when authentic radicals like **1** are generated, they are found to react by addition of molecular oxygen and cyclic peroxide hydroperoxides (OOH at C-4) can be isolated.[9] It thus seems reasonable to rule out further consideration of the stepwise rearrangement mechanism involving intermediate **1**.

The remaining mechanisms could be distinguished by an appropriate experiment involving the use of isotopically labeled oxygen to determine if fragmentation of the peroxyl radical intermediate occurs. Thus, if a β-scission pathway is followed, a rearrangement carried out under $^{36}O_2$ should show incorporation of $^{36}O_2$ into the hydroperoxide products. We report here the results of such a study of the allylic hydroperoxides formed from singlet-oxygen oxidation of oleic acid.

Results

Synthesis and Purification of Allylic Hydroperoxides. Singlet-oxygen oxidation of oleic acid **4** yields only two allylic hydroperoxides. Thus, photolysis of methylene blue photosensitizer and oleic acid in methanol under $^{32}O_2$ gave two hydroperoxide products[10-12] (Figure 2). These

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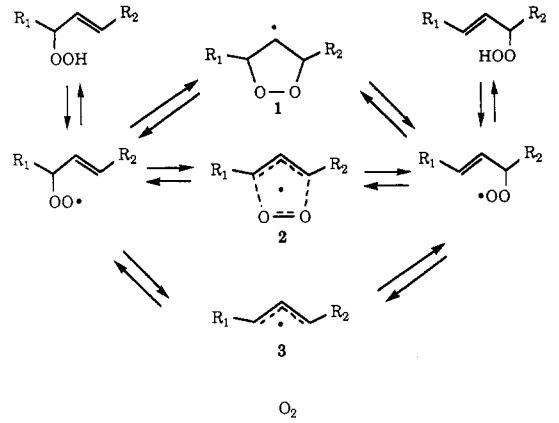

Figure 1.

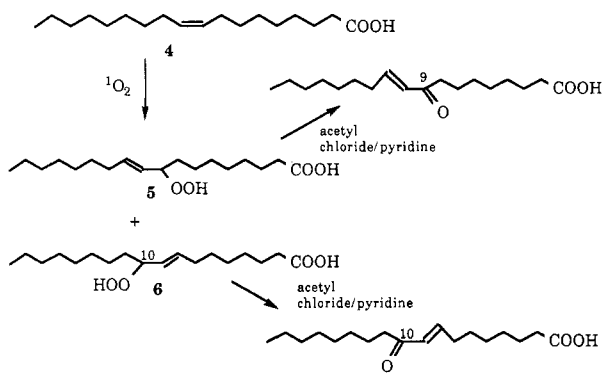

Figure 2.

products, *trans*-9-hydroperoxyoctadec-10-enoic acid (**5**) and *trans*-10-hydroperoxyoctadec-8-enoic acid (**6**) can be separated by reverse-phase chromatography. The structures of **5** and **6** were determined by ^1H and ^{13}C NMR spectroscopy and by conversion of the hydroperoxides to the corresponding ketones (by reaction with acetyl chloride/pyridine), followed by mass spectral analysis of the ketones.[13] NMR and mass spectral fragmentation data are given in the Experimental Section.

Singlet-oxygen oxidation of **4** could also be achieved under a $^{36}O_2$ atmosphere. Thus, a methanol solution of oleic acid and methylene blue was sealed under $^{36}O_2$, and the tube was photolyzed for 3 days with a medium-pressure mercury lamp. The hydroperoxides **5** and **6** were isolated by liquid chromatography and were shown by mass spectrometry to have incorporated up to 90% ^{18}O in the ketones formed, after dehydration of the hydroperoxides with acetyl chloride/pyridine.

Free-Radical Rearrangement of Hydroperoxides 5 and 6. Compounds **5** and **6** (with or without ^{18}O incorporated) were rearranged under $^{32}O_2$ and $^{36}O_2$ atmospheres. The rearrangement of **5** is illustrative and indicates the procedures involved in the rearrangement experiment. A hexane solution (5 mL) of 30 mg of hydroperoxide **5** and 4 mg of the free-radical initiator di-*tert*-butyl hyponitrite (DTBN)[14,15] was heated for 5 h at 40 °C. The crude reaction mixture was then analyzed by ^1H NMR and was shown to consist of a 67:17:16 mixture of allylic hydroperoxide, allylic alcohol, and α,β-unsaturated ketone. The characteristic NMR resonances used to determine the product ratio for the hydroperoxide are as follows: the proton on the carbon bearing OOH (a quartet at δ 4.2); for the alcohol, the analogous proton (a quartet at δ 4.0); and for the α,β-unsaturated ketone, the vinyl proton α to the ketone (a doublet at δ 6.1). For **5**, the product mixture consisted of hydroperoxides, alcohols, and ketones substituted at the 9-position with a 10–11 trans double bond (no rearrangement) and compounds substituted at the 11-position with a 9–10 trans double bond (allylic rearrangement). After 5 h at 40 °C, the 9 and 11 substituted compounds were present in approximately equal amounts. The allylic alcohols and α,β-unsaturated ketones are presumably formed by termination reactions, as described in the Discussion. The products formed in the rearrangement of **5** are presented in Figure 3.

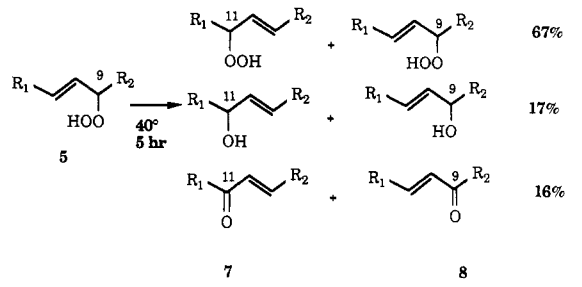

Figure 3.

Table I. Rearrangement of ^{18}O-Labeled Hydroperoxide 5 under a $^{32}O_2$ Atmosphere

run no.	% ^{18}O in 8 before rearrangement[a]	% ^{18}O in 8 after rearrangement[a]	% ^{18}O in 7 after rearrangement[a]
1	89 ± 1	87 ± 1	86 ± 1
2	63 ± 2	70 ± 4	64 ± 2
3	48 ± 7	48 ± 3	50 ± 3

[a] Determined from the ratio of M and M + 2 ions.

Table II. Rearrangement of ^{18}O-Labeled Hydroperoxide 6 under a $^{32}O_2$ Atmosphere

run no.	% ^{18}O in 10 before rearrangement[a]	% ^{18}O in 10 after rearrangement[a]	% ^{18}O in 9 after rearrangement[a]
1	89 ± 1	88 ± 1	86 ± 1
2	47 ± 3	52 ± 4	50 ± 4

[a] Determined from the ratio of M and M + 2 ions.

After rearrangement was complete, the crude product mixture was treated with acetyl chloride/pyridine. This treatment converted all allylic hydroperoxides present into the α,β-unsaturated ketones **7** and **8**, while allylic alcohols were converted to acetates. The ketone products **7** and **8**, were separated by reverse-phase HPLC. These purified ketones were then analyzed by mass spectrometry. The incorporation of atmospheric oxygen into the hydroperoxide during rearrangement can be ascertained by analysis of the molecular ion of the ketones and by comparison of the M and M + 2 (^{18}O) ions. A similar analysis was carried out for rearrangement of the 10-substituted hydroperoxide **6**. The hydroperoxide **6** rearranges to a mixture of 10- and

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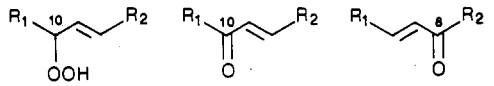
8-substituted hydroperoxides, alcohols, and ketones analogous to those formed from **5**.

Rearrangement of ^{18}O-labeled hydroperoxides was carried out in a vessel open to the atmosphere or in a closed system under a $^{32}O_2$ atmosphere. In the closed-system experiment, the incorporation of $^{32}O_2$ into the hydroperoxide could be determined by mass spectral analysis of the corresponding ketones, and the residual atmospheric oxygen could be monitored for evolution of $^{36}O_2$ from the hydroperoxide. Data for isotopic incorporation for the rearrangement of ^{18}O-labeled **5** are presented in Table I. The recovered atmospheric oxygen showed no detectable $^{36}O_2$ above background levels. Table II presents similar data for the rearrangement of ^{18}O-labeled **6** under a $^{32}O_2$ atmosphere. The structures of the ketones (**9** and **10**) formed in the rearrangemnt of **6** are shown below. These ketones were purified by HPLC after the crude reaction mixture was treated with acetyl chloride/pyridine to convert hydroperoxides to ketones. Recovered atmospheric oxygen showed no detectable $^{36}O_2$ above background levels in the experiments with **6**. No scrambling of isotopic oxygen (outside experimental error) was observed for any of the rearrangements of ^{18}O-labeled **5** or **6** under a $^{32}O_2$ atmosphere.



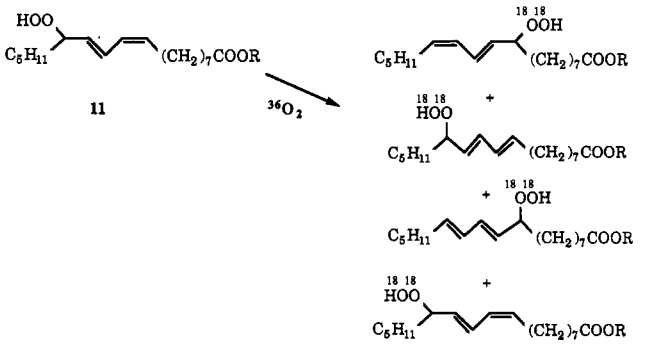
6 **10** **9**

Parallel experiments were carried out with rearrangement of ^{16}O-labeled hydroperoxides and a 98% $^{36}O_2$ atmosphere. The results from these experiments are similar in every respect to the data presented in Tables I and II; that is, no incorporation of atmospheric oxygen into the rearrangement products is detected under any of the conditions of rearrangement. This conclusion was reached after seven separate experiments involving both hydroperoxides **5** and **6**, labeled or unlabeled, under a $^{32}O_2$ or $^{36}O_2$ atmosphere.

Discussion

The allylic rearrangement of hydroperoxides is catalyzed by UV light and free-radical initiators and is inhibited by 2,6-di-*tert*-butyl-4-methylphenol.[7,8] One step in chain propagation presumably involves generation of an allylic peroxyl radical from the corresponding hydroperoxide by H-atom transfer. The H-atom-abstracting agent may be the initiator radical or another peroxyl radical present in solution. The ROO–H bond is known to be weak, and transfer of a hydroperoxyl H to alkoxyl radicals or other peroxyls is a facile process.[16-21] Once formed, the allylic peroxyl radicals rearrange by an allylic shift. The mechanism of this rearrangement has been the subject of much debate.

Previous studies have ruled out a cyclic intermediate radical, such as **1** (Figure 1), from consideration as a reactive intermediate in the rearrangement.[8,9] The stepwise pathway involving **1** was first proposed for the cholesterol rearrangements and later for rearrangements of acyclic



11

Figure 4.

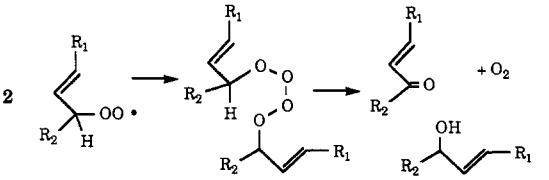


Figure 5.

allylic hydroperoxides.[7] Two other mechanisms are left for consideration. One mechanism involving a cyclic transition state **2** (Figure 1) was proposed by Brill[8] after the radical **1** was ruled out as a possible intermediate. Another mechanistic possibility has good precedent in the rearrangements of the dienyl hydroperoxides derived from homoconjugated diene systems, such as linoleic acid. This mechanism, β-scission–recombination involving the allylic radical **3** (Figure 1) is the accepted mechanism for linoleate hydroperoxide rearrangements such as the rearrangement of the 13-linoleate hydroperoxide **11** (Figure 4).[22-24]

The hydroperoxide **11** is suggested to rearrange via the corresponding peroxyl radical by β-scission to the stabilized pentadienyl radical. This β-scission–recombination mechanism has been supported by rearrangement of **11** under a $^{36}O_2$ atmosphere. Product hydroperoxides formed by rearrangement in this system have incorporated ^{18}O from the atmosphere in agreement with the fragmentation mechanism.[22] β-Scission of peroxyl radicals has also been substantiated by ESR experiments[26] and benzylic, cumyl, benzhydryl, and trityl peroxyls undergo fragmentation.[18-21] It should be noted, however, that the peroxyl radical derived from **11** would have a significantly larger driving force for fragmentation than a simple allylic peroxyl (e.g., as shown in Figure 1). Pentadienyl radicals are stabilized by 24–28 kcal/mol, while the allyl radical is stabilized by only 13–14 kcal/mol.[27] Furthermore, concerted rearrangement of dienyl peroxyls would require disruption of diene conjugation, whereas this would not be the case for a simple allyl system. It thus seems likely that the simple allyl systems would be more likely to undergo the concerted radical rearrangement than would dienyl peroxyls.

We have chosen the simple allylic hydroperoxides derived from oleic acid for study because of the importance of these hydroperoxides as primary products in lipid peroxidation and since these acyclic hydroperoxides are prepared by straightforward means. Singlet-oxygen oxi-

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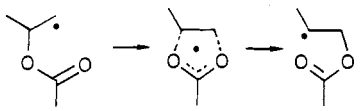
dation of oleic acid is known to produce only two hydroperoxides, and we find that these hydroperoxides (5 and 6) can be readily separated by reverse-phase chromatography. Furthermore, rearrangement of the hydroperoxides readily occurs in organic solvent at 40 °C when initiated by DTBN, and the product mixture formed is relatively clean. Only allylic hydroperoxides, allylic alcohols, and α,β-unsaturated ketones are present in the rearrangement product mixture. The presence of allylic alcohols and the α,β-unsaturated ketones can be accounted for by Russell termination, as indicated in Figure 5.[17] Furthermore, the rearrangement product mixture can be simplified by conversion of the hydroperoxides to ketones by treatment with acetyl chloride/pyridine.

The results of our rearrangement studies support the concerted radical rearrangement pathway via a five-membered-ring transition state 2. Under no circumstance was any significant atmospheric oxygen incorporated into the rearrangement products, nor was atmospheric oxygen detected in the recovered starting hydroperoxide. We conclude that the dienyl peroxyl rearrangements previously investigated[22-24] differ mechanistically from the rearrangement of simply allyl peroxyls. The dienyl peroxyls rearrange by a β-scission pathway, while the simple allyl peroxyls rearrange by a concerted 3,2-pathway. One might suggest that a caged allyl radical/dioxygen species was responsible for the lack of O_2 incorporation in the allyl peroxyls. If one assumes a 1% uncertainty in the oxygen incorporation data, then the lifetime of the cage radical/O_2 species could be on the order of 10^{13} s, and it would be indistinguishable from the activated complex proposed here.[25]

Other examples of concerted 3,2-radical rearrangements have been reported in the literature. For example, β-acetoxyl radicals undergo a rearrangement, as described below, and the evidence presented suggests that this rearrangement proceeds via a concerted free radical pathway.[26-30] It seems likely that this mechanistic option is



a general one, and a search for other examples of this radical rearrangement seems warranted. Unlike the acetoxyl rearrangement, we note that stereochemical information would be transferred from one end of the allyl peroxyl to the other end of the system in a concerted rearrangement, and we are currently exploring the stereochemical implications of the concerted 3,2-allylperoxyl shift.

Experimental Section

Oleic acid (*cis*-9-octadecenoic acid) was obtained from Aldrich Chemical Co. (Milwaukee, WI) and purified by using flash silica gel chromatography (hexane/2-propanol/acetic acid, 229:20:1).

Isotopically enriched "Oxygen 18 (gas, 98 atom %, ^{18}O)" was obtained from MSD Isotopes (St. Louis, MO) and Cambridge Isotope Laboratory (Woburn, MA).

pH 9.0 borate buffer (Borax) was obtained by diluting borate buffer concentrate (Fisher Scientific Co., Fair Lawn, NJ), 1 volume with 9 volumes of water.

All inorganic acids and bases were obtained from EM Scientific (Gibbstown, NJ) and used without further purification.

All HPLC solvents were OmniSolv brand obtained from EM Scientific and filtered prior to use.

Synthesis of *trans*-9-Hydroperoxyoctadec-10-enoic Acid (5) and *trans*-10-Hydroperoxyoctadec-8-enoic Acid (6). ***trans*-9-Hydroperoxyoctadec-10-enoic acid (5)**: ^1H NMR (300 MHz, $CDCl_3$) δ 5.76 (dt, 1 H, H-11), 5.35 (dd, 1 H, H-10), 4.25 (dt, 1 H, H-9), 2.34 (t, 2 H, H-2), 2.07 (dt, 2 H, H-8), 1.62 (br t, 2 H, H-12), 1.30 (br m, 18 H), 0.88 (t, 3 H, H-1); ^{13}C NMR (300 MHz, $CDCl_3$) δ 179.9 (COOH), 137,2 (C-11), 128.4 (C-10), 87.1 (C-9), 33.9, 32.4, 32.3, 32.2, 31.8, 31.7, 29.3, 29.1, 29.0, 28.9, 25.2, 24.6, 22.7, 14.1 (CH_3); TLC R_f 0.27 eluted on silica gel with hexane/2-propanol/acetic acid, 229:20:1. Anal. Calcd: C, 68.75; H, 10.898. Obsvd: C, 68.46; H, 11.53.

***trans*-10-Hydroperoxyoctadec-8-enoic acid (6)**: ^1H NMR (300 MHz, $CDCl_3$) δ 5.76 (dt, 1 H, H-8), 5.35 (dd, 1 H, H-9), 4.25 (dt, 1 H, H-10), 2.34 (t, 2 H, H-2), 2.07 (dt, 2 H, H-11), 1.62 (br t, 2 H, H-7) 1.30 (br m, 18 H), 0.88 (t, 3 H, H-18); ^{13}C NMR (300 MHz, $CDCl_3$) δ 179.5 (COOH), 136.7 (C-8), 128.8 (C-9), 87.1 (C-10), 33.8, 32.4, 32.1, 31.8, 29.5, 29.4, 29.2, 28.7, 28.5, 25.3, 24.5, 22.6, 14.1 (CH_3); TLC R_f 0.27 eluted on silica gel with hexane/2-propanol/acetic acid, 229:20:1. Anal. Calcd: C, 68.75; H, 10.898. Obsvd: C, 67.94; H, 10.48.

Oleic acid (3 g, 0.01 mol) and methylene blue (50 mg, 1.3×10^{-4} mol) were dissolved in 30 mL of methanol. This solution was placed in a Pyrex photolysis vessel equippled with a ground-glass dispersion tube. Oxygen was bubbled through the dispersion tube into the oleic acid solution throughout the reaction. (If the reaction was run under $^{36}O_2$, the vessel was sealed.) This solution was irradiated at room temperature with a 450-W Hg lamp jacketed in flowing cold water while stirring for 72 h. The methanol was then removed in vacuo, and the hydroperoxy acids were purified via flash column chromatography (hexane/2-propanol/acetic acid, 229:20:1). The two hydroperoxides were then separated by semipreparative RP-HPLC (acetonitrile/water/acetic acid, 780:220:1). These analyses were performed on a Rainin Dynamax C18 semipreparative column with a flow rate of 9.0 mL/min. The HPLC fractions were extracted with 5 × 50 mL of chloroform and 1 × 50 mL of ethyl acetate and dried (Na_2SO_4), and the solvent was removed in vacuo. The hydroperoxides were obtained in a total recovered yield ranging from 6.6 to 18.9%.

In order to determine the natural ^{18}O incorporation level, each hydroperoxide was derivatized. The hydroperoxide (10 mg, 2.9 × 10^{-5} mol) was dissolved in 0.5 mL of pyridine and cooled to 0 °C. Acetyl chloride (250 μL) was added dropwise to the stirring solution. After 15 min, the reaction was quenched by the addition of water, and the reaction mixture was extracted with 5 × 50 mL of diethyl ether. The ether layer was washed with saturated $CuSO_4$ until no color change was observed and dried (Na_2SO_4), and the solvent was removed in vacuo. The resulting oxooctadecenoic acid was purified by preparative thin-layer chromatography (hexane/2-propanol/acetic acid, 229:20:1). The R_f for the oxooctadecenoic acid formed from 5 and 6 was 0.33 when eluted on silica gel. The ^{18}O-incorporation level was determined by low-resolution direct-probe mass spectroscopy by which the molecular ion peak intensities for the ^{16}O-containing compound (M + 2 = 296) and the ^{18}O-containing compound (M^+ = 298) were obtained.

Spectral Data for the α,β-Unsaturated Ketones 7–10. ***trans*-11-Oxooctadec-9-enoic acid (7)**: ^1H NMR (300 MHz, $CDCl_3$) δ 6.8 (dt, 1 H, H-9), 6.1 (dd, 1 H, H-10), 2.5 (t, 2 H, H-12), 2.3 (t, 2 H, H-2), 2.2 (dt, 2 H, H-8), 1.6 (br m, 2 H), 1.4 (br m, 2 H), 1.3 (br m, 16 H), 0.8 (t, 3 H, H-18); MS, m/z 296 (M^+, $C_{18}H_{32}O_3$), 197 ($COCHCH(CH_2)_7COOH$), 169 ($CHCH(CH_2)_7CO-OH$), 153 ($CHCHCO(CH_2)_6CH_3$), 127 ($CO(CH_2)_6CH_3$).

***trans*-9-Oxooctadec-10-enoic acid (8)**: ^1H NMR (300 MHz, $CDCl_3$) δ 6.8 (dt, 1 H, H-11), 6.1 (dd, 1 H, H-10), 2.5 (t, 2 H, H-8), 2.3 (t, 2 H, H-2), 2.2 (dt, 2 H, H-12), 1.6 (br m, 2 H), 1.4 (br m, 2 H), 1.3 (br m, 16 H), 0.8 (t, 3 H, H-18); ^{13}C NMR (300 MHz, $CDCl_3$) δ 200.8 (C-9), 178.3 (COOH), 147.4 (C-11), 130.2 (C-17), 40.0, 33.8, 32.5, 31.8, 29.2, 29.1, 29.04, 29.00, 28.9, 28.2, 24.7, 24.3, 22.7, 14.2 (CH3); UV γ_{max} 233 and 276 nm; MS, m/z 296 (M^+, $C_{18}H_{32}O_3$), 197 ($CHCHCO(CH_2)_7COOH$), 171 ($CO(CH_2)_7COOH$), 153 ($COCHCH(CH_2)_6CH_3$), 125 ($CHCH(CH_2)_6CH_3$).

***trans*-8-Oxooctadec-9-enoic acid (9)**: ^1H NMR (300 MHz, $CDCl_3$) δ 6.8 (dt, 1 H, H-10), 6.1 (dd, 1 H, H-9), 2.5 (t, 2 H, H-7), 2.3 (t, 2 H, H-2), 2.2 (dt, 2 H, H-11), 1.6 (br m, 2 H), 1.4 (br m,

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2 H), 1.3 (br m, 16 H), 0.8 (t, 3 H, H-18); MS, m/z 296 (M^+ $C_{18}H_{32}O_3$), 183 ($CHCHCO(CH_2)_6COOH$), 167 ($COCHCH(CH_2)_7CH_3$), 157 ($CO(CH_2)_6COOH$), 139 ($CHCH(CH_2)_7CH_3$).

***trans*-10-Oxooctadec-8-enoic acid (10)**: ^1H NMR (300 MHz, $CDCl_3$) δ 6.8 (dt, 1 H, H-8), 6.1 (dd, 1 H, H-9), 2.5 (t, 2 H, H-11), 2.3 (t, 2 H, H-2), 2.2 (dt, 2 H, H-7), 1.6 (br m, 2 H), 1.4 (br m, 2 H), 1.3 (br m, 16 H), 0.8 (t, 3 H, H-18); ^{13}C NMR (300 MHz, $CDCl_3$) δ 200.8 (C-10), 178.3 (COOH), 146.9 (C-8), 130.3 (C-9), 40.2, 33.8, 32.4, 31.9, 29.5, 29.4, 29.2, 29.1, 28.8, 27.9, 24.6, 24.4, 22.7, 14.2 (CH_3); UV δ_{max} 223 and 276 nm; MS, m/z 296 (M^+, $C_{18}H_{32}O_3$), 183 ($COCHCH(CH_2)_6CH_3$), 167 ($CHCHCO(CH_2)_7CH_3$), 155 ($CHCH(CH_2)_6COOH$), 141 ($CO(CH_2)_7CH_3$).

Rearrangement of ^{18}O-Labeled 5 and 6 under $^{32}O_2$. The following procedure was used with each hydroperoxyoctadecenoic acid. The purified ^{18}O-labeled hydroperoxyoctadecenoic acids (100 mg, 2.9×10^{-4} mol) and DTBN (5 mg) were dissolved in 10 mL of hexane and placed into a flask fitted with a vacuum-stoppered catch flask with condensing sidearm.

The apparatus was filled with $^{16}O_2$ gas through the upper vacuum stopcock, with the lower stopcock open. The system was closed off, and the reaction flask was immersed in a 40 °C constant temperature oil bath. After 5 h, the gaseous O_2 in the system was condensed into the condensing sidearm (liquid N_2) of the catch flask, and the reaction mixture was allowed to cool to room temperature. The catch flask's vacuum stopcock was closed after 15 min. The hexane was removed in vacuo, and the hydroperoxyoctadecenoic acids were converted to the oxooctadecenoic acids by treatment with pyridine/acetyl chloride. The oxooctadecenoic acids were purified by preparative TLC, separated by semipreparative RP-HPLC, and analyzed for their incorporation level by direct-probe low-resolution mass spectroscopy. The recovered gas samples were analyzed for $^{16}O_2$ vs $^{18}O_2$ via the same mass spectroscopic technique.

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Registry No. 5, 110551-46-7; 5-$^{18}O_2$, 110551-47-8; 6, 96963-17-6; 6-$^{18}O_2$, 110551-48-9; 7, 99640-09-2; 7-ol, 110567-68-5; 7 (peroxide), 110551-49-0; 8, 99640-11-6; 8-ol, 110657-92-6; 9, 99640-10-5; 10, 99640-12-7; oleic acid, 112-80-1; di-*tert*-butyl hyponitrite, 14976-54-6.

Cobalt-Catalyzed Reaction of Nitric Oxide with Aryl-Substituted Olefins in the Presence of Tetrahydroborate Ion

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A new transition-metal-catalyzed reaction of nitric oxide with aryl-substituted olefins in the presence of BH_4^- has been reported, where the oximes of alkyl aryl ketones are the products. The most successful results were obtained by using styrene and its ring-substituted derivatives as the substrate and $Co(DH)_2(py)Cl$ as the catalyst. A process involving the intermediate formation of a metal–alkyl complex and its subsequent decomposition to alkyl radical followed by the reaction of the radical with NO was proposed as the reaction mechanism in relation to the already reported cobalt-catalyzed oxygenation of aryl-substituted olefins.

Catalysis by transition-metal complexes is widely used in organic synthesis.[1] Many of them proceed via catalytic activation of small molecules such as hydrogen, carbon monoxide, carbon dioxide, and even molecular oxygen, but little is known about the activation of nitric oxide (NO) in spite of the abundance in the environment.[2] In the field of coordination chemistry, however, it is known that NO is a versatile ligand which stabilizes both electron-rich and electron-deficient transition-metal complexes by changing its charge distribution and structure.[2a] Some stoichiometric reaction of NO with organo-transition-metal complexes are known affording alkyl- or arylnitrosohydroxylamines as the main products.[3] Recently, insertion of (or ligand migration to) coordinated NO leading to the formation of nitrogen–carbon bond as well as mononitrosation of organic groups to nitroso compounds, oximes, or nitriles have been reported.[4,5]

Nevertheless, no catalytic reaction involving NO has been reported[6] probably because the coordination abilities of insertion products are too high for replacing them by either NO or the organic substrates, a process necessary for ensuring the catalytic cycle.

In this report we describe a new transition-metal-catalyzed reaction of NO with aryl-substituted olefins in the presence of BH_4^- and bis(dimethylglyoximato)cobalt as the catalyst.[6] The products obtained were the oximes of alkyl aryl ketones. Although the isolated yields of oximes based on the used substrates were moderate, this is the first example of transition-metal-catalyzed organic synthesis utilizing NO (eq 1). The cobalt-catalyzed oxygenation[7] of

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