

Cobalt(II)-Catalyzed Reaction of Enolizable Aldehydes with Alkenes in the Presence of Dioxygen: The Role of Acyl Radical

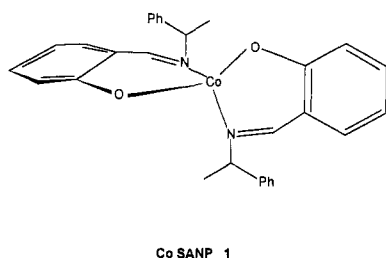
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Complex [bis(salicylidene-*N*-phenethyl)]cobalt(II) (1) catalyzes the reaction of enolizable aliphatic aldehydes and dioxygen with an electron-deficient alkene to afford the adducts 4 and 5, whereas the reaction with unactivated alkenes leads to the corresponding epoxides 6. These reactions are proposed to proceed via a common pathway involving acyl radicals.

The oxidation of aldehydes by transition-metal complexes is a useful method for the generation¹ of acyl radicals, and it is known that cobalt(II) acetate catalyzes the radical² chain addition of aldehydes to 1-alkenes in the presence of air to give ketones in moderate yields. The use of acyl radicals has gained prominence lately in organic synthesis as evidenced from the work of Pattenden,^{3a,b} Boger,^{3c,d} Crich,^{3e} Zard,^{3f} and their co-workers. However, the generation of acyl radicals by these methods involves stoichiometric amounts of acyl radical precursor (e.g., acyl cobalt, selenoesters, and xanthone, etc.) which limits the scope of the reactions. In view of the above limitations, we have explored the possibility of generating the acyl radicals in a catalytic manner using a cobalt(II) complex. We have observed that the acyl radicals can be generated from enolizable aldehydes in the presence of [bis(salicylidene-*N*-phenethyl)]cobalt(II), abbreviated CoSANP (1), and dioxygen. Subsequently, these radicals may be



trapped with acrylates, and the resulting product radical is terminated by incorporation of dioxygen to give 2-hydroxy-4-oxo esters 4 (path a, Scheme 1). On the other hand, the reaction with unactivated alkenes leads to the formation of epoxides 6 which are presumably derived as a result of oxygen capture by the acyl radical (path b, Scheme 1). We report here results of the catalytic oxidation of alkenes in the presence of aldehydes and CoSANP (1).

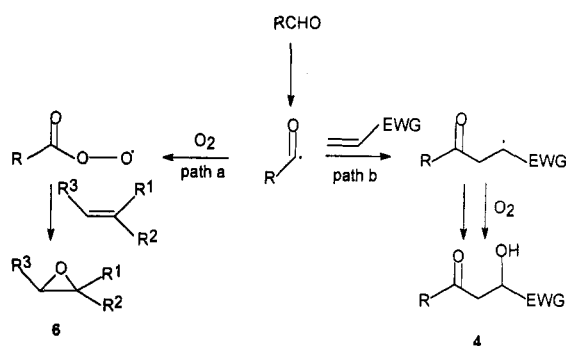
* Abstract published in *Advance ACS Abstracts*, January 1, 1994.

(1) (a) Lee, D. G. In *Oxidation*; Augustine, R. L., Ed.; Dekker: New York, 1959; Vol. 1, p 81. (b) Kochi, J. K. *Organometallic Mechanisms and Catalysis*; Academic Press: New York, 1978; Chapter 5 and references cited therein. (c) Sheldon, R. A.; Kochi, J. K. *Metal Catalyzed Oxidation of Organic Compounds*; Academic Press: New York, 1981; and references cited therein.

(2) Nikishin, G. I.; Vinogradov, M. G.; Verenchikov, S. P. *Bull. Acad. Sci., USSR* 1969, 1698.

(3) (a) Covney, D. J.; Patel, V. F.; Pattenden, G. *Tetrahedron Lett.* 1987, 28, 5949. (b) Pattenden, G.; Reynolds, S. J. *Tetrahedron Lett.* 1991, 32, 259. (c) Boger, D. L.; Mathvink, R. J. *J. Org. Chem.* 1989, 54, 1777. (d) Boger, D. L.; Mathvink, R. J. *J. Am. Chem. Soc.* 1990, 112, 4003. (e) Batty, D.; Crich, D.; Fortt, S. M. *J. Chem. Soc., Chem. Commun.* 1989, 1366. (f) Delduc, P.; Tailhan, C.; Zard, S. Z. *J. Chem. Soc., Chem. Commun.* 1988, 308.



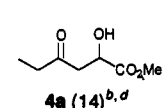
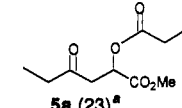

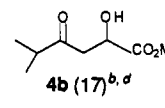
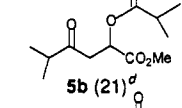

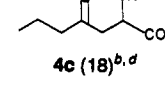
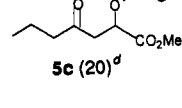

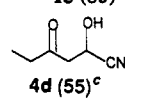
Scheme 1



The cobalt(II)-catalyzed reaction of aldehydes 2a-c with methyl acrylate affords a mixture of 2-hydroxy- and 2-(acyloxy)-4-oxo esters 4a-c and 5a-c in good yields (Table 1, entries 1-3). These reactions can also be performed in the presence of excess acetic anhydride to give the corresponding 2-hydroxy compounds 4a-c in high yields, and it is noteworthy that no 2-(acyloxy) compound 5 is obtained under these conditions (Table 1, entries 4-6). A similar treatment of aldehyde 2a with excess acrylonitrile gave 2-hydroxy-4-oxonitriles 4d in moderate yield (Table 1, entry 7). These reactions are always accompanied by 40-50% of the carboxylic acid and anhydride derived from the corresponding aldehyde; however, an exact quantification of the product was obscured by its loss during the workup. Careful analysis of the reaction mixture revealed the absence of any unchanged aldehyde; however, some unreacted methylacrylate or acrylonitrile was observed. The mass balance of these reactions clearly reveals that approximately 40% of the aldehyde is converted into the addition product(s) 4 and 5, whereas the remaining aldehyde is transformed to a mixture of the corresponding carboxylic acid and anhydride. Interestingly, the reaction with unactivated alkenes favors the formation of the epoxides 6 exclusively (Table 2, entries 1-6). Thus, styrene and 1-dodecene afforded the corresponding epoxides in excellent yields. Similarly, the disubstituted olefins like (*E*)-stilbene and (*Z*)-2-octene gave the corresponding trans and cis epoxides, respectively, in high yields (Table 2, entries 3 and 4). The selective monoepoxidation of dienes can be achieved as indicated by the formation of monoepoxide from linalyl acetate and geranyl acetate, respectively (Table 2, entries 5 and 6). The epoxidation can be carried⁴ out by using propanal (2a) or 2-methylpropanal













(4) For Nickel(II)-catalyzed epoxidation using aldehyde, see: (a) Yamada, T.; Taki, T.; Rhode, O.; Mukaiyama, T. *Chem. Lett.* 1991, 1. (b) Irie, R.; Ito, Y.; Katsuki, T. *Tetrahedron Lett.* 1991, 32, 6891.

Table 1. CoSANP (1)-Catalyzed Oxidative Addition of Aldehydes to Electron-Deficient Alkenes in the presence of Dioxygen

entry	aldehyde	alkene	products (yield, %) ^a	
1				
	2a	3a	4a (14) ^{b,d}	5a (23) ^a
2				
	2b		4b (17) ^{b,d}	5b (21) ^d
3				
	2c		4c (18) ^{b,d}	5c (20) ^d
4	2a		4a (51) ^c	
5	2b		4b (58) ^c	
6	2c		4c (59) ^c	
7	2a			
		3b	4d (55) ^c	

^a Yield of the isolated products. ^b These reactions are performed in the presence of acetic anhydride. ^c These reactions are performed in the presence of excess (~3 equiv with respect to aldehyde) acetic anhydride. ^d In addition to this product a mixture of (40–50%) carboxylic acid (derived from the corresponding aldehyde) and its anhydride is also obtained.

Table 2. CoSANP (1)-Catalyzed Epoxidation of Alkenes in the Presence of 2-Methylpropanal and Dioxygen

entry	alkene	products (yield, %) ^a
1		
	3c	6a (88)
2		
	3d	6b (62)
3		
	3e	6c (90)
4		
	3f	6d (45) ^b
5		
	3g	6e (73) ^c
6		
	3h	6f (67)

^a Yield of the isolated products. ^b This is contaminated with the corresponding trans isomer (~5%). ^c Obtained as a mixture of diastereomers.

(2b); however, the latter is more efficient than the former in affecting this transformation. It is also noteworthy that no addition of aldehydes to the unactivated alkenes is observed under these conditions. The 2-(acyloxy) compounds 5a–c may be a result of the acylation of the hydroxy compounds 4a–c, respectively, by the anhydrides derived from the corresponding aldehydes. We have already shown that aliphatic aldehydes are converted to the corresponding^{5a} anhydrides in the presence of cobalt(II) and

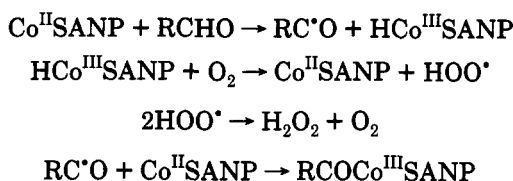
dioxygen. The reaction with methyl acrylate can be performed in the presence of an excess of acetic anhydride to give 2-hydroxy esters 4 exclusively in good yield. Interestingly, no 2-(acyloxy) esters 5 are observed in this reaction, and the yield of 4 is considerably higher than as compared with similar transformations in the absence of acetic anhydride. Also, no significant quantity of the carboxylic acid derived from the corresponding aldehyde was observed in reactions with acetic anhydride. Acetic acid and unchanged acetic anhydride were also obtained in this reaction; however, no quantification of the products could be done as significant losses of these were observed during the workup process. Formation of isobutyric acid was also observed during the epoxidation; however, no attempt was made to isolate it. Its presence is also indicated by isolating the vicinal hydroxy butyrate which are obtained on prolonging (24 h) the length of the epoxidation reaction. It is interesting to note that no epoxidation is observed when *trans*-stilbene, 2-methylpropanal, and CoSANP (1) are reacted in the presence of excess acetic anhydride, and an analysis of the reaction product showed unchanged *trans*-stilbene along with a small amount of isobutyric acid. Thus, it is evident that acetic anhydride plays a dominant role on the reactivity of aliphatic aldehydes.

The dichotomous nature of these reactions suggests that a common intermediate may be involved whose reactivity is dependent upon the nature of the alkene. The catalytic nature of this reaction may be explained by an initial redox reaction^{1b} of aldehyde with CoSANP (1) to give a hydrido-cobalt species and an acyl radical (Scheme 2). Mimoun has proposed⁶ a hydridocobalt species from the reaction of CoSMPDT with alcohol. The reaction of dioxygen with hydrido species may regenerate the catalyst 1 and hydroperoxy radical, which is likely to fragment at a diffusion-controlled rate to hydrogen peroxide and dioxygen (Scheme 2). The acyl radical may exist as an acyl-cobalt(III)

(5) (a) Bhatia, B.; Punniyamurthy, T.; Iqbal, J. *J. Org. Chem.* 1993, 58, 5518. (b) Ahmad, S.; Iqbal, J. *J. Chem. Soc., Chem. Commun.* 1987, 692.

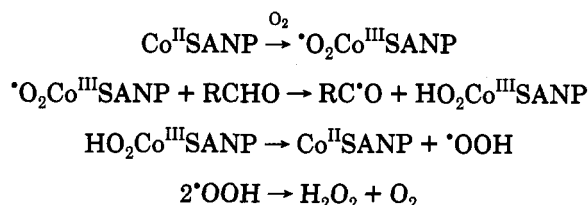
(6) Mimoun, H. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, 1985.

Scheme 2



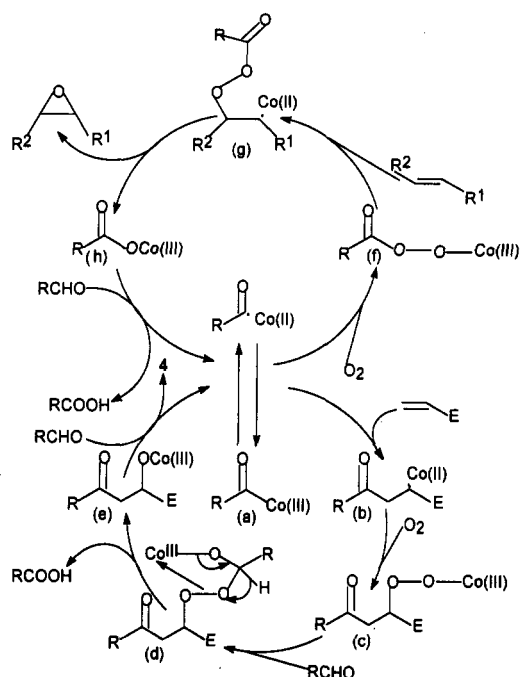
complex; however, in the presence of oxygen it may just be a transient species. Alternatively, acyl radical formation can also be initiated by interaction of an oxygen complex of 1 with aldehyde, and the hydroperoxy cobalt complex⁷ thus formed may spontaneously⁸ disproportionate to hydrogen peroxide and oxygen (Scheme 3). The acyl

Scheme 3

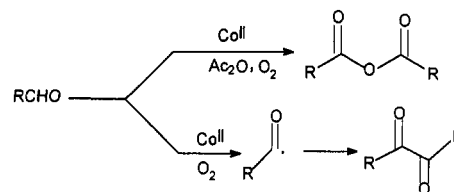


radical may then interact with CoSANP (1) to provide a acylcobalt(III) species. The acyl radical will react with electron-deficient alkene to give an adduct radical b which may readily undergo insertion⁹ of dioxygen to yield a peroxycobalt intermediate c (Scheme 4). The reaction of c with aldehyde may provide a labile intermediate d which will fragment readily to afford the alkoxycobalt complex e and the corresponding carboxylic acid. A redox reaction between another molecule of aldehyde and the complex e may provide the 2-hydroxy-4-oxo esters 4 or nitriles, and the acyl radical or acylcobalt complex a will be regenerated to complete the cycle. The acyl radical generated from acylcobalt complex is known to undergo 1,4-addition to electron-deficient alkenes under thermal or photochemical conditions. The cobalt-carbon bond may not survive in the presence of dioxygen, and therefore, the adduct b is likely to be a free radical. However, the reduction of the peroxy species c with aldehyde via the intermediate d will probably be mediated by the cobalt complex as the fragmentation of d to give e, and carboxylic acid may not be favored by a free-radical process. The improved yield of 2-hydroxy esters and the absence of any 2-(acyloxy) ester in the presence of excess acetic anhydride is surprising; however, it is conceivable that the latter,¹⁰ instead of the aldehyde, may act as a reducer of c to give e. Thus, more aldehyde will be available for the generation of acyl radical as this pathway would circumvent the sacrificial role of aldehyde during the reduction of c. Alternatively, in the presence of unactivated alkenes the acyl radical or acylcobalt complex a will undergo the insertion of dioxygen, instead of addition to the alkene,

Scheme 4



Scheme 5



to yield a peroxyacylcobalt species f which may react with the alkene (Scheme 4) to give a peroxyacyl organocobalt intermediate g. A homolytic fragmentation of the latter will afford the corresponding epoxide and the cobalt carboxylate h, and the latter may interact with aldehyde via a redox process to regenerate the acyl radical or acylcobalt complex a. The cobalt(II)-catalyzed epoxidation of the alkenes with dioxygen is also known to occur via a β -peroxy radical which resembles the proposed¹¹ intermediate g. The nonobservance of epoxide in the presence of acetic anhydride is not surprising, as our earlier studies have shown that its presence favors the formation^{5b} of 1,2-diones from aldehydes, whereas its absence leads to the corresponding carboxylic acid and anhydride. This implies that the acyl radical is not very efficient in capturing the dioxygen in the presence of excess acetic anhydride, and thus, addition of this radical to an electron-deficient alkene or its self-coupling become favored pathways (Scheme 5). Further evidence in support of this mechanism is also reflected in the observation that for each equivalent of 4 or 6 which is being formed approximately 1 equiv of the corresponding carboxylic acid is also obtained.

In conclusion, the CoSANP (1)-catalyzed reaction of enolizable aliphatic aldehyde with an electron-deficient alkene leads to the formation of 4, whereas reaction with unactivated alkene affords the corresponding epoxides 6 in good yields. This process seems to be proceeding via a common pathway involving an acyl radical which reacts preferentially with electron-deficient alkenes to give an

(7) For a similar reaction of dioxygen with cobalt(II) complex see: Hamilton, D. E.; Drago, R. S.; Zombeck, A. *J. Am. Chem. Soc.* 1987, 109, 374.

(8) The hydroperoxy cobalt complex is formed only during the initiation step; hence, no ketones or alcohols due to its reaction with alkenes are observed as shown earlier by Drago and co-workers.⁷

(9) For the insertion of dioxygen in a cobalt-carbon bond, see: (a) Bhandal, H.; Patel, V. F.; Pattenden, G.; Russell, J. J. *J. Chem. Soc., Perkin Trans. 1* 1990, 2691 and references cited therein. (b) Inoki, S.; Mukaiyama, T. *Chemistry Lett.* 1990, 67.

(10) The peroxycobalt complex (c) may react with acetic anhydride to form acyl carbonate; however, we have not been able to isolate it as it might undergo hydrolysis during the workup process.

(11) Budnik, R. A.; Kochi, J. K. *J. Org. Chem.* 1976, 41, 1384.

adduct radical, and the later terminates by incorporation of dioxygen followed by reduction to afford 4. On the other hand unactivated alkenes do not undergo addition of acyl radical as the later preferentially reacts with dioxygen to give a peroxy carbonyl species which readily affords the epoxides 6 on interaction with carbon-carbon double bond.

Experimental Section

Materials and Methods. Acetonitrile and acetic anhydride were purified by the standard procedures.¹² CoCl₂ was purchased from LOBA India Ltd., Bombay, and dried at 110 °C for 2–3 h prior to use. Flash chromatography was performed by using ACME TLC silica gel or neutral aluminum oxide. Aldehydes and alkenes were purchased commercially and purified prior to use. ¹H NMR spectra were recorded at 60 and 80 MHz in CCl₄ or CDCl₃. The UV-vis spectrum was recorded on a Perkin-Elmer Lambda-2 spectrophotometer. Magnetic moment (μ_{eff}) was calculated by the Evans method.¹³ Conductivity was recorded on a conductivity bridge, type CM 82T. Mass spectra were recorded on a JEOL SX 102/DA-6000. Elemental analyses were conducted using a Coleman automatic C, H, and N analyzer. All the known compounds were characterized by comparison with the data from the literature.

Preparation of CoSANP (1). The Schiff's base ligand was prepared by the reaction of salicylaldehyde (0.61 g, 5 mmol) with (*α*)-(S)-methylbenzylamine (0.60 g, 5 mmol) in absolute ethyl alcohol (5 mL) at 25 °C for 5 h: ¹H NMR (CDCl₃) δ 1.55 (d, 3H, *J* = 7.0 Hz), 4.2 (q, 1H, *J* = 6.0 Hz), 6.5–7.0 (m, 5H), 7.1 (m, 5H), 8.2 (s, 1H); mp 66–67 °C. Anal. Calcd for C₁₅H₁₅ON: C, 80.00; H, 6.67. Found: C, 79.99; H, 6.69.

The ligand (1.125 g, 5 mmol) was dissolved in anhydrous acetonitrile (10 mL) and reacted with cobalt(II) chloride (0.33 g, 2.5 mmol) under nitrogen atmosphere for 15 h at ambient temperature. Addition of a mixture of dry diethyl ether and petroleum ether (1:5) to this solution resulted in the formation of a green complex. The complex was separated by filtration and dried under vacuo at 25 °C for 20 h. CoSANP (1) was obtained as crystals (1.0 g, 80%). The geometry of this complex was found to be tetrahedral based on UV-vis data and magnetic moment^{13,14} studies: UV-vis (ClCH₂CH₂Cl) λ_{max} 630, 666, 693 nm; μ_{eff} 4.50 μ_{B} (lit.¹⁴ μ_{eff} 4.59–4.77 μ_{B}); conductivity (CH₃CN) 25 m Ω cm² mol⁻¹; MS (*m/e*) 508 (M + 1), 507 (M⁺), 283, 105 (100), 77, 51. Anal. Calcd for C₃₀H₂₈N₂O₂Co: C, 71.00; H, 5.52. Found: C, 70.94; H, 5.48.

General Procedure for the Synthesis of 2-Hydroxy or 2-(Acyloxy)-4-oxo Esters. Aldehyde (10 mmol) and electron-deficient alkene (30 mmol) were added to a stirred solution of CoSANP (1) (5 mol %) in anhydrous acetonitrile (60 mL). The mixture was stirred at ambient temperature (25 °C) for 20–24 h. The solvent was evaporated in vacuo, and the residue was dissolved in ether. The ether layer was washed successively with saturated NaHCO₃ solution (3 × 15 mL), brine solution (2 × 20 mL), and water (2 × 20 mL). Drying (MgSO₄) and evaporation yielded a residue which was subjected to column chromatography to afford the pure compound.

General Procedure for the Synthesis of Epoxides. Aldehyde (10 mmol) and unactivated alkene (5 mmol) were added to

a stirred solution of CoSANP (1) (5 mol %) in anhydrous acetonitrile (30 mL). The mixture was stirred at ambient temperature (25 °C) under dioxygen balloon for 20–24 h. The solvent was evaporated in vacuo, and the residue was dissolved in ether. The ether layer was washed with saturated NaHCO₃ solution (3 × 15 mL), brine solution (2 × 20 mL), and water (2 × 20 mL). Drying (MgSO₄) and evaporation yielded a residue which was purified by flash column chromatography.

Methyl 2-Hydroxy-4-oxohexanoate (4a). Propionaldehyde (2a) (0.58 g, 10 mmol), methyl acrylate (2.58 g, 30 mmol), and CoSANP (1) (~5 mol %) were subjected to the reaction conditions according to the general procedure. The usual workup followed by column chromatography on silica gel (60–120 mesh, 15:85 EtOAc/petroleum ether, 60–80 °C) afforded 4a (0.23 g, 14%) as a liquid: ¹H NMR (CCl₄) δ 1.1 (t, 3H, *J* = 6.0 Hz), 2.4 (q, 2H, *J* = 6.0 Hz), 2.8 (d, 2H, *J* = 6.0 Hz), 3.8 (s, 3H), 4.5 (t, 1H, *J* = 6.0 Hz); IR (thin film) 3450, 1750, 1720 cm⁻¹. Anal. Calcd for C₇H₁₂O₄: C, 52.49; H, 7.45. Found: C, 52.50; H, 7.47.

Methyl 2-Hydroxy-5-methyl-4-oxohexanoate (4b). Isobutyraldehyde (2b) (0.72 g, 10 mmol), methyl acrylate (2.58 g, 30 mmol), acetic anhydride (3.06 g, 30 mmol), and CoSANP (1) (~20 mg) were subjected to the reaction conditions as described above. The usual workup followed by column chromatography on silica gel (1:10 EtOAc/petroleum ether) afforded compound 4b (1.0 g, 58%): ¹H NMR (CCl₄) δ 1.0 (d, 6H, *J* = 7.0 Hz), 2.1–2.7 (m, 1H), 2.8 (d, 2H, *J* = 7.0 Hz), 3.8 (s, 3H), 4.2 (t, 1H, *J* = 6.0 Hz); IR (neat) 3450, 1755, 1720 cm⁻¹. Anal. Calcd for C₈H₁₄O₄: C, 55.15; H, 7.40. Found: C, 55.19; H, 7.34.

2-Hydroxy-4-oxohexanenitrile (4d). Propionaldehyde (2a) (0.58 g, 10 mmol), acrylonitrile (1.59 g, 30 mmol), acetic anhydride (3.06 g, 30 mmol), and CoSANP (1) (~20 mg) were subjected to the reaction conditions mentioned above to afford 4d (0.70 g, 55%) as an oil: ¹H NMR (CCl₄) δ 1.1 (t, 3H, *J* = 6.0 Hz), 2.4 (q, 2H, *J* = 6.0 Hz), 2.8 (d, 2H, *J* = 6.0 Hz), 4.7 (t, 1H, *J* = 6.0 Hz); IR (neat) 3500, 2260, 1710 cm⁻¹. Anal. Calcd for C₆H₉O₂N: C, 56.69; H, 7.08. Found: C, 56.59; H, 7.11.

Methyl 2-(propionyloxy)-4-oxohexanoate (5a). This compound was isolated by column chromatography on silica gel (1:19 EtOAc/petroleum ether) according to the above procedure to afford liquid 5a (0.50 g, 23%): ¹H NMR (CCl₄) δ 0.95 (t, 3H, *J* = 6.0 Hz), 1.1 (t, 3H, *J* = 6.0 Hz), 2.1 (q, 2H, *J* = 6.0 Hz), 2.3 (q, 2H, *J* = 6.0 Hz), 2.75 (d, 2H, *J* = 6.0 Hz), 3.6 (s, 3H), 5.1 (t, 1H, *J* = 6.0 Hz); IR (thin film) 1750, 1720 cm⁻¹; MS (*m/e*) 217 (M + 1), 216 (M⁺), 153, 143, 73, 57 (100), 29, 15. Anal. Calcd for C₁₀H₁₆O₅: C, 55.55; H, 7.40. Found: C, 55.59; H, 7.38.

Methyl 2-(isobutyryloxy)-5-methyl-4-oxohexanoate (5b). Isobutyraldehyde (2b) (0.72 g, 10 mmol), methyl acrylate (2.58 g, 30 mmol), and CoSANP (1) (~20 mg) were subjected to the reaction conditions as described in the general procedure. Usual workup followed by column chromatography on silica gel (60–120 mesh, 1:19 EtOAc/petroleum ether) yielded 5b (0.51 g, 21%): ¹H NMR (CCl₄) δ 0.9 (d, 6H, *J* = 7.0 Hz), 1.0 (d, 6H, *J* = 7.0 Hz), 2.1–2.8 (m, 2H), 2.9 (d, 2H, *J* = 6.0 Hz), 3.8 (s, 3H), 5.6 (t, 1H, *J* = 6.0 Hz); IR (thin film) 1755, 1720 cm⁻¹. Anal. Calcd for C₁₂H₂₀O₅: C, 59.01; H, 8.20. Found: C, 59.93; H, 8.31.

3-Acetoxy-3,7-dimethyl-6,7-epoxy-1-octene (6e). 3-Acetoxy-3,7-dimethyl 1,6-octadiene (3g) (0.98 g, 5 mmol), isobutyraldehyde (0.72 g, 10 mmol), and CoSANP (1) (~20 mg) were subjected to the reaction conditions as described in the general procedure. Usual workup followed by flash chromatography on silica gel (1:19 EtOAc/petroleum ether) gave 6e (0.77 g, 73%): ¹H NMR (CDCl₃) δ 1.1 (s, 3H), 1.2 (s, 3H), 1.45 (s, 3H), 1.6 (m, 4H), 1.85 (s, 3H), 2.4 (t, 1H, *J* = 6.0 Hz), 4.8–5.2 (m, 2H), 5.45–6.0 (m, 1H); IR (thin film) 1360, 1240 cm⁻¹. Anal. Calcd for C₁₂H₂₀O₃: C, 67.92; H, 9.43. Found: C, 67.87; H, 9.44.

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