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Cobalt−Salen Complex-Catalyzed Oxidative Generation of Alkyl Radicals from Aldehydes for the Preparation of Hydroperoxides

Eiichi Watanabe, Atsushi Kaiho, Hiroyuki Kusama, and Nobuharu Iwasawa*

Department of Chemistry, Tokyo Institute of Technology, O-okayama, Meguro-ku, Tokyo 152-8551, Japan

Supporting Information

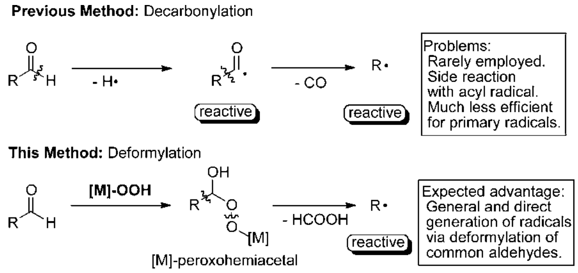
ABSTRACT: Catalytic generation of alkyl radicals from aldehydes via oxidative deformylation was realized using a cobalt-salen complex with H_2O_2. The deformylation was thought to proceed through homolytic cleavage of peroxohemiacetal intermediates to provide even primary alkyl radicals under mild conditions. Variously substituted and functionalized hydroperoxides were obtained from corresponding aldehydes in good yield.

Exploitation of a new methodology for the generation of alkyl radicals is of great importance in organic chemistry. Various methods have already been developed, but most suffer from several disadvantages such as the use of highly toxic tin compounds, instability of the substrates, the use of stoichiometric amounts of metallic oxidants or reductants, and harsh reaction conditions.[1]

Aldehydes are readily available compounds that have been utilized as precursors of acyl radicals, although methods for abstracting the aldehydic H atom have been limited.[2] Decarbonylation of acyl radicals could afford alkyl radicals, but the use of this method is restricted because decarbonylation usually requires high temperature, particularly with primary aldehydes, and it is difficult to realize selective reactions of alkyl radicals while suppressing the reactions of intermediate acyl radicals.[3,4] Therefore, an efficient method to generate alkyl radicals from aldehydes without forming acyl radicals would be highly desirable to enable the use of aldehydes as alkyl radical precursors.

To realize such a reaction, we thought of utilizing the deformylation of aldehydes by cytochrome P450. It was reported that treatment of cyclohexanecarboxaldehyde with P450 in the presence of H_2O_2 gave cyclohexene, although the catalytic efficiency was low.[5] As a model of this reaction, oxidative deformylation of aldehydes using a stoichiometric amount of metal−peroxo complexes was also reported.[6] Among several plausible mechanisms for these reactions, the generation of alkyl radicals from the peroxohemiacetal intermediates produced by nucleophilic addition of the peroxo complex to the aldehyde carbonyl group was proposed,[7] although there was no direct evidence of the formation of alkyl radicals.[8] There is a single report of catalytic deformylation using a designed mononuclear non-heme ferric−peroxo complex, but only the conversion of 2-phenylpropionaldehyde to acetophenone was reported, and the reaction efficiency was low (ca. 20% yield based on the aldehyde).[9] If radical species were really involved in these reactions and could be utilized in synthesis, the reaction would become a highly useful method for the catalytic generation of alkyl radicals from aldehydes without the formation of acyl radicals (Scheme 1). Herein we report a general method for oxidative generation of alkyl radicals from aldehydes using a catalytic amount of a Co−salen complex with H_2O_2 as a stoichiometric oxidant to give hydroperoxides in good yields with wide generality.[10]

Scheme 1. Generation of Alkyl Radicals from Aldehydes



It was found that when aldehyde **1** was treated with with 4 equiv of 35% aqueous H_2O_2 as an oxidant in the presence of a catalytic amount (5 mol %) of the Co complex with salen ligand **L1** in EtOH at −20 °C, hydroperoxide **2** was obtained in 22% yield along with recovery of the starting material (Table 1, entry 1). Trace amounts of carboxylic acid (6%) and 4-(2-naphthyl)-butan-2-one (**3b**) (3%) were also obtained. The carboxylic acid was obtained by oxidation of **1**, and **3b** was thought to result from decomposition of **2**. As the expected catalytic deformylation reaction really proceeded, and more interestingly, a hydroperoxide (which has never been isolated in related reactions[11]) was obtained as a major product, we decided to examine this reaction in more detail. Acetonitrile was found to be the best solvent, and concerning the substituents of the salen ligand, use of 3,3′-Me_2-substituted **L4** dramatically accelerated the reaction and improved the yield.[12] Although the effect of 5,5′-substitution was small, 5,5′-$(MeO)_2$-substituted **L2** gave a slightly better result than **L1**. Furthermore, the reaction using 3,3′-Me_2-5,5′-$(MeO)_2$-substituted **L5** afforded the best results giving hydroperoxide **2** in 74% isolated yield. The catalyst loading could be reduced to 2.5 mol % without problems. It was possible to obtain alcohol **3a** in good yield in one pot by reduction of **2** (Scheme 2).[13]

As the novel Co(salen)-catalyzed deformylation reaction of an aldehyde to form a hydroperoxide was found to proceed under

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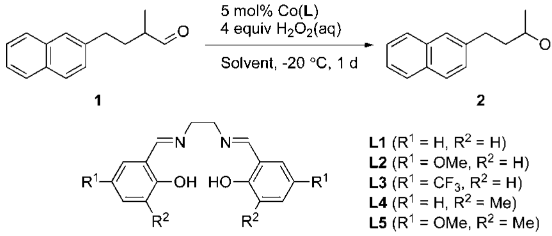
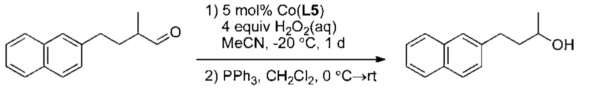
Table 1. Investigation of Reaction Conditions



entry	solvent	L	2 (%)[a]	recovery of 1 (%)[a]
1	EtOH	L1	22	25
2	*i*-PrOH	L1	19	26
3	DMF	L1	3	26
4	MeCN	L1	32	23
5	MeCN	L2	32	31
6	MeCN	L3	17	54
7	MeCN	L4	75	1
8	MeCN	L5	77 (74[b])	1
9[c]	MeCN	L5	80 (77[b])	2

[a]Determined by ^{1}H NMR analysis of the crude products using 1,1,2,2-tetrachloroethane as an internal standard. [b]Isolated yield. [c]2.5 mol % catalyst was used.

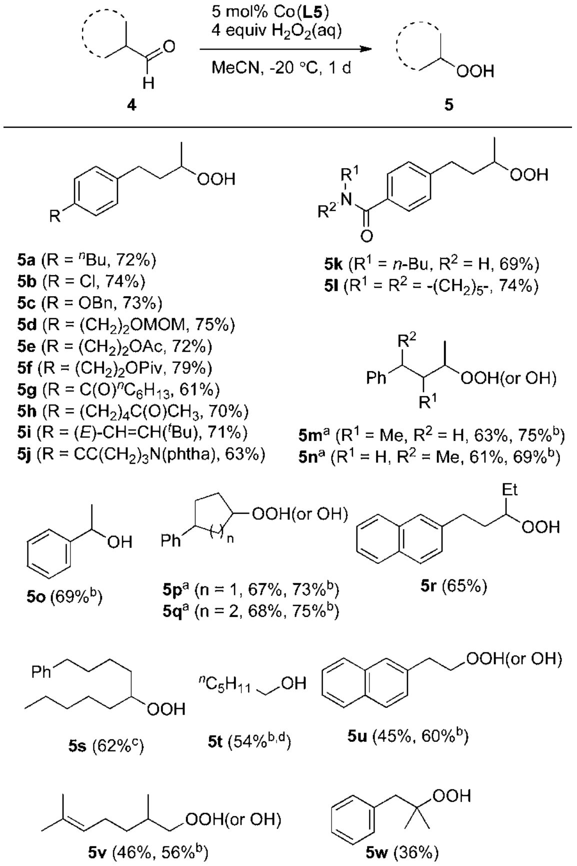
Scheme 2. One-Pot Reaction for the Preparation of Alcohol



1

3a (78%)

Table 2. Generality of Substrates



5a (R = ^{n}Bu, 72%)
5b (R = Cl, 74%)
5c (R = OBn, 73%)
5d (R = $(CH_2)_2$OMOM, 75%)
5e (R = $(CH_2)_2$OAc, 72%)
5f (R = $(CH_2)_2$OPiv, 79%)
5g (R = C(O)$^n C_6H_{13}$, 61%)
5h (R = $(CH_2)_4C(O)CH_3$, 70%)
5i (R = (*E*)-CH=CH(^{t}Bu), 71%)
5j (R = $CC(CH_2)_3$N(phtha), 63%)
5k (R^1 = *n*-Bu, R^2 = H, 69%)
5l (R^1 = R^2 = -$(CH_2)_5$-, 74%)
5m[a] (R^1 = Me, R^2 = H, 63%, 75%[b])
5n[a] (R^1 = H, R^2 = Me, 61%, 69%[b])
5o (69%[b])
5p[a] (n = 1, 67%, 73%[b])
5q[a] (n = 2, 68%, 75%[b])
5r (65%)
5s (62%[c])
5t (54%[b,d])
5u (45%, 60%[b])
5v (46%, 56%[b])
5w (36%)

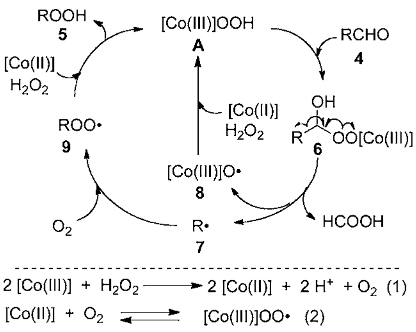
[a]Diastereomeric mixture. [b]Isolated as an alcohol by reduction using PPh_3. [c]7.5 mol % catalyst was used, and the reaction was conducted with [M] = 0.1 mol/L. [d]GC yield.

very mild reaction conditions, the generality of this reaction was examined next (Table 2). Substrates **4b−d** containing a halide or alkoxy group afforded the corresponding products in good yields. Aldehydes **4e−h**, **4k**, and **4l** with ketone, ester, and amide functionalities gave corresponding hydroperoxides in reasonable yields without affecting these carbonyl moieties. When alkenyl- and alkynyl-substituted aldehydes **4i** and **4j** were used, the products were obtained in good yields without oxidation of the alkene and alkyne moieties. Acyclic aldehydes **4m** and **4n** and benzylic aldehyde **4o** also provided corresponding hydroperoxides in a similar manner. Cyclic aldehydes **4p** and **4q** containing a five- and six-membered rings also afforded the hydroperoxides. Some aldehydes gave higher yields of the deformylation products upon their isolation as alcohols by PPh_3 reduction because of difficulty in isolation or slight instability of the hydroperoxides, as observed with branched and cyclic hydroperoxides. α-Alkyl-substituted aldehydes **4r** and **4s** could also be employed, although the reactivity slightly decreased because of steric hindrance. All of these reactions were accompanied by formation of the carboxylic acid in ca. 15% yield via substrate oxidation. Peroxides are usually synthesized by S_N2 reaction of alkyl halides/pseudohalides with H_2O_2 (or hydroperoxide derivatives), and the yields of secondary hydroperoxides are usually moderate. Thus, the present reaction would be very useful for the preparation of secondary hydroperoxides.

We next examined the reaction of primary alkyl aldehydes. Under the same reaction conditions, *n*-heptanal (**4t**) afforded *n*-hexanol (**5t**) in 54% GC yield after reduction of the intermediate hydroperoxide with PPh_3.[14] The yield of this reaction was somewhat lower than those of secondary aldehydes, partly due to the instability of the primary hydroperoxide[12,15,16] and the formation of the undesired oxidation product *n*-heptanoic acid (28% yield). The reactions of 3-(2-naphthyl)propanal (**4u**) and citronellal (**4v**) also proceeded in a similar manner. Although the yield was moderate, even tertiary aldehyde **4w** could be converted to the corresponding hydroperoxide **5w**. This reaction would be useful not only as a method for the preparation of hydroperoxides but also as a one-carbon elimination reaction of aldehydes under mild conditions.

The proposed reaction pathway is shown in Scheme 3. Hydroperoxocobalt(III) complex **A** is generated from the Co(II) complex and H_2O_2[17] and then reacts with aldehyde **4** to provide peroxohemiacetal intermediate **6**.[18,19] This intermediate undergoes homolytic cleavage to give alkyl radical **7**, cobalt oxyl radical **8**, and formic acid. The peroxide formation step has several

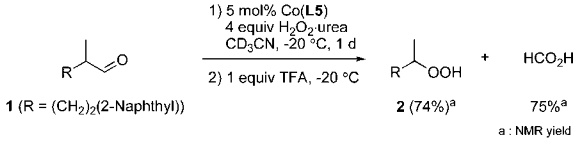
Scheme 3. Proposed Mechanism



possibilities, but O_2 is thought to play an important role on the basis of the $^{18}O_2$ experiment described below; in one possible pathway, shown in Scheme 3, **7** reacts with O_2, which is thought to be generated by the reaction of Co(III) species with H_2O_2 (eq 1),[20,21] to give peroxy radical **9**, which is further reduced by Co(II) to give the product. It is also conceivable that alkyl radical **7** directly couples with a Co(III)OO· species generated from Co(II) and O_2 (eq 2)[22] to give Co(III)OOR. The cobalt oxyl radical **8** is thought to be converted to hydroperoxocobalt(III) complex **A** by reduction with Co(II) followed by ligand exchange with H_2O_2.

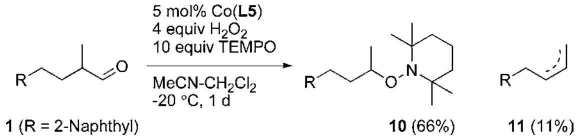
Several experiments were carried out to support the proposed reaction mechanism. First of all, ^{1}H NMR observation of the oxidative deformylation of **1** revealed the formation of 75% of the predicted amount of formic acid and a 74% yield of alkyl hydroperoxide (Scheme 4).[23] This result strongly indicates that the reaction does not proceed via decarbonylation through acyl radicals but instead proceeds via deformylation through peroxohemiacetal intermediates.[24]

Scheme 4. Detection of Formic Acid

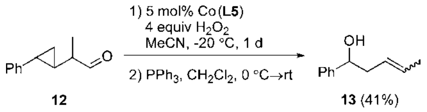


In regard to the decomposition of peroxohemiacetal intermediates, their deformylation by heterolytic cleavage to give carbocations has been proposed by several groups,[5b,25] so we next examined whether alkyl radicals are really generated in this reaction. In a radical trapping experiment, aldehyde **1** was treated under the standard reaction conditions in the presence of 2,2,6,6-tetramethylpiperidine *N*-oxyl (TEMPO), and *N*-alkoxypiperidine **10**, the radical-trapped product, was obtained in good yield along with alkene **11** (Scheme 5). Ring opening of cyclopropylmethyl radical is another important reaction to confirm the generation of radical species, and treatment of aldehyde **12** containing a cyclopropane moiety with H_2O_2 in the presence of a catalytic amount of cobalt complex gave ring-opening product **13**,[26] although the yield was not very good (Scheme 6).[27] Furthermore, this reaction could be used to achieve radical cyclization (Scheme 7). Under the standard reaction conditions, olefinic aldehyde **14** underwent 5-exo cyclization to give cyclopentane derivatives **15** and **16** in a combined yield of ca. 60%. All of these reactions strongly supported the intermediacy of an alkyl radical in this reaction.

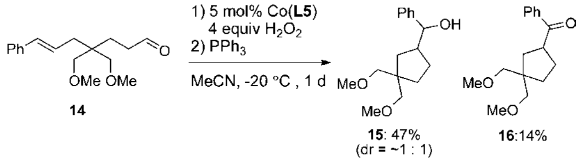
Scheme 5. Trapping of the Alkyl Radical with TEMPO



Scheme 6. Ring-Opening Reaction of Aldehyde 12

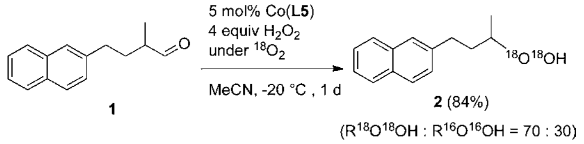


Scheme 7. Cyclization Reaction of Aldehyde 14



The final stage of the reaction was examined by employing $^{18}O_2$ to confirm the source of the O atoms in the hydroperoxide product (Scheme 8). When **1** was reacted with $H_2{}^{16}O_2$ under an $^{18}O_2$ atmosphere with otherwise similar conditions, the product in which both of the peroxy O atoms were labeled with ^{18}O was obtained with about 70% ^{18}O incorporation. This result strongly supports the proposal that O_2 generated by the reaction of Co(III) with H_2O_2, or its cobalt complex Co(III)OO·, traps the alkyl radical generated from peroxohemiacetal intermediate **6** (Scheme 3).[21]

Scheme 8. Labeling Experiment Using $^{18}O_2$



In conclusion, we have developed a highly useful and general method for the generation of alkyl radicals from aldehydes via oxidative deformylation using a Co−salen catalyst. This method affords hydroperoxides in good yields with wide generality. Primary alkyl radicals, which are usually difficult to generate from aldehydes through acyl radicals because of the higher activition energy required for decarbonylation, are also provided at even −20 °C. Homolytic radical cleavage of a peroxohemiacetal intermediate to generate the alkyl radical is the key step of this reaction.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Procedures and characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

niwasawa@chem.titech.ac.jp

Notes

The authors declare no competing financial interest.

CAUTION: Although we did not meet with explosion of hydroperoxides during this work, these products are potentially explosive and should be handled with sufficient care behind shielding.

■ ACKNOWLEDGMENTS

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(2) Chatgilialoglu, C.; Crich, D.; Komatsu, M.; Ryu, I. *Chem. Rev.* **1999**, *99*, 1991 and references therein.

(3) Actually the only practical reaction of alkyl radicals generated by H-atom abstraction from aldehydes is reduction to alkanes when the reaction is performed in the presence of a thiol as a radical mediator at high temperature. In this reaction, the decarbonylation products are obtained in good yields because H-atom abstraction by acyl radicals simply regenerates the starting aldehydes. See: (a) Harris, E. F. P.; Waters, W. A. *Nature* **1952**, *170*, 212. (b) Bergman, J. D.; Stanley, J. H.; Sherman, W. V.; Cohen, S. G. *J. Am. Chem. Soc.* **1963**, *85*, 4010.

(4) Few examples of C−C bond formation using alkyl radicals generated from aldehydes by H-atom abstraction have been reported. In these reactions, the product yields and selectivities were not high. See: (a) Tsujimoto, S.; Iwahama, T.; Sakaguchi, S.; Ishii, Y. *Chem. Commun.* **2001**, 2352. (b) Jang, Y.-J.; Yan, M.-C.; Lin, Y.-F.; Yao, C.-F. *J. Org. Chem.* **2004**, *69*, 3961. (c) Espost, E.; Dondi, D.; Fagnoni, M.; Albini, A. *Angew. Chem., Int. Ed.* **2007**, *46*, 2531.

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(12) In some experiments, alcohol **3a** was also obtained (0−4% yield), likely via reduction of the hydroperoxide. See: (a) Richardson, W. H. *J. Am. Chem. Soc.* **1965**, *87*, 247. (b) Richardson, W. H. *J. Am. Chem. Soc.* **1965**, *87*, 1096. (c) Richardson, W. H. *J. Org. Chem.* **1965**, *30*, 2804. (d) Spier, E.; Neuenschwander, U.; Hermans, I. *Angew. Chem., Int. Ed.* **2013**, *52*, 1581.

(13) Ketone **3b** was also obtained from **2** in 98% yield under acylation conditions (see the Supporting Information).

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(21) The possibility that a small amount of O_2 in the reaction medium, particularly in H_2O_2 solution, works as an O_2 source cannot be excluded, although the reaction under an Ar atmosphere using degassed solvent and H_2O_2−urea adduct gave the hydroperoxide product with no decrease in the yield. Similarly, this result does not rule out a pathway in which H_2O_2 is directly introduced into the product without being converted to O_2.

(22) Co(II)−salen complexes and related species are well-known to combine reversibly with O_2 to give Co(III)OO· species. For examples, see: (a) Tiné, M. R. *Coord. Chem. Rev.* **2012**, *256*, 316. (b) Nishinaga, A.; Tomita, H. *J. Mol. Catal.* **1980**, *7*, 179. (c) Smith, T. D.; Pilbrow, J. R. *Coord. Chem. Rev.* **1981**, *39*, 295. (d) Hamilton, D. E.; Drago, R. S.; Zombeck, A. *J. Am. Chem. Soc.* **1987**, *109*, 374. (e) Mukaiyama, T.; Yamada, T. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 17. (f) Schuch, D.; Fries, P.; Dönges, M.; Pérez, B. M.; Hartung, J. *J. Am. Chem. Soc.* **2009**, *131*, 12918.

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(27) Because of the instability of product under these reaction conditions, the yield was not good.