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Reaction of cobalt porphyrins with aldehydes in the presence of *t*-butyl hydroperoxide

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Abstract

Co^{II} porphyrin reacted with propanal in the presence of $NaBH_4$ under air to give a mixture of σ-(1-formylethyl)Co^{III} porphyrin and σ-(propanoyl)Co^{III} porphyrin. The latter was formed exclusively by using *t*-butyl hydroperoxide instead of $NaBH_4$ and air. Thus, various σ-(acyl)Co^{III} porphyrins were produced in good yields by way of generation of a *t*-butoxyl radical, hydrogen abstraction from aldehyde, and coupling of an acyl radical and Co^{II} porphyrin. This reaction was applied to acyl radical cyclization of 2-allyloxy-1-naphthaldehyde, 2-allyloxybenzaldehyde, 2-allylbenzaldehyde, and *N*-allylpyrrole-2-carboxaldehyde to give (organo)Co^{III} porphyrins with a cyclized axial alkyl ligand.

Keywords: Cobalt porphyrins; *t*-Butyl hydroperoxide; Aldehydes

1. Introduction

Recent studies on cobalt-mediated radical reactions by Johnson [1], Pattenden [2], Branchaud [3], and Baldwin [4] have established the synthetic methodology which consists of the homolytic CoC bond cleavage of a variety of alkyl and acyl cobalt reagents and the addition of the resulting carbon-centered radical to carbon-carbon multiple bonds. These organocobalt reagents have been synthesized by the reaction of a nucleophilic Co^{I} reagent with alkyl or acyl halides. Pattenden and co-workers have elegantly taken advantage of the weakness of Co-C bonds of a variety of organocobalt compounds using salen (*N*,*N*′-disalicylidene-1,2-diaminoethane) and salophen (*N*,*N*′-disalicylidene-1,2-diaminobenzene) ligands to generate a carbon centered radical [2]. They showed that irradiation of deaerated refluxing CH_2Cl_2 solutions of the σ-(acyl)Co^{III} salophens in the presence of non-activated alkenes led to good yields of the highly functionalized alkene products.

In this context, it is of great importance to establish convenient methods for cobalt-carbon bond formation. There are three ways to synthesize (organo)Co^{III} complexes; (i) reaction of Co^{III} complexes with Grignard reagents [5], (ii) reaction of Co^{II} complexes with organic radicals [6], and (iii) reaction of Co^{I} complexes with alkyl halides [7]. We have paid attention to the second method because Co^{II} complexes are readily prepared. Although the coupling reaction of organic radicals and Co^{II} complexes occurs readily, and is a process occurring in coenzyme B_{12}-dependent biochemical reactions [8], the direct alkylation of Co^{II} is not widely applicable owing to the limitation on the reaction conditions required to generate organic radicals. We have reported that σ-(alkyl)Co^{III} porphyrins are produced in good yields by the reaction of Co^{II} porphyrin with alkene, alkyne [9], and ether [10] in the coexistence of $NaBH_4$ and *t*-BuOOH or O_2. A Co–C bond is formed through the hydrometallation of alkene and alkyne with a hypothetical (hydrido)Co^{III} porphyrin (Scheme 1). This hydrometallation step is explained in terms of the addition

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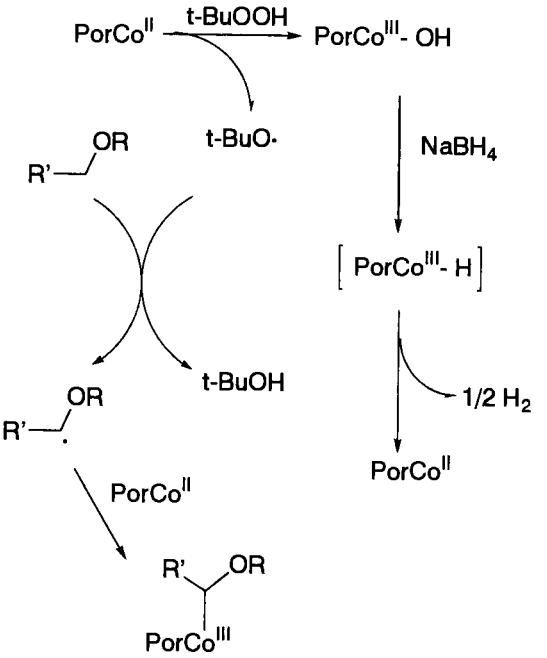
of a hydrogen radical to alkene and the capture of the resulting alkyl radical by Co^{II} porphyrin on the basis of the high regioselectivity corresponding to the formation of the most stable organic radical. On the other hand, a Co–C bond is formed through the reaction of Co^{II} porphyrin with an ether radical caused by hydrogen abstraction with a *t*-butoxyl radical or a hydrogen radical from the α-position of ether (Scheme 2). Thus, our redox system consisting of Co^{II} porphyrin, $NaBH_4$, and an oxidizing agent may be used for generating various organic radicals.

In view of the synthetic utility of σ-(acyl)Co^{III} complexes for functionalization of alkenes, we have investigated the reaction of aldehydes with our radical-generating system [11]. In this paper, we describe the scope and mechanism for the formation of a variety of σ-(acyl)Co^{III} porphyrins including some examples where an acyl radical undergoes cyclization before the coupling with Co^{II} porphyrin.

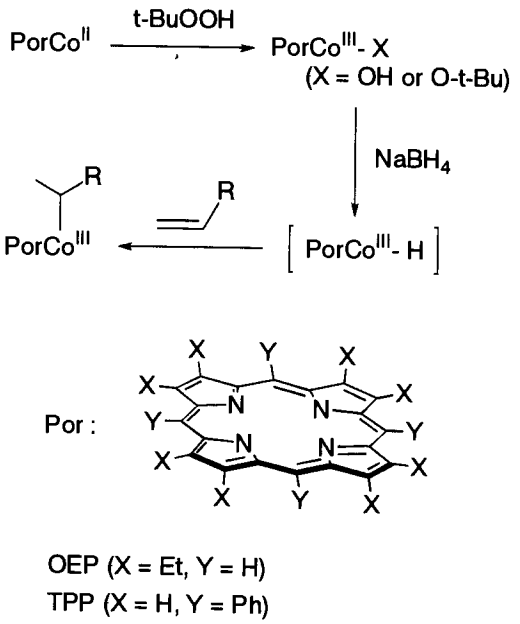


Scheme 2.

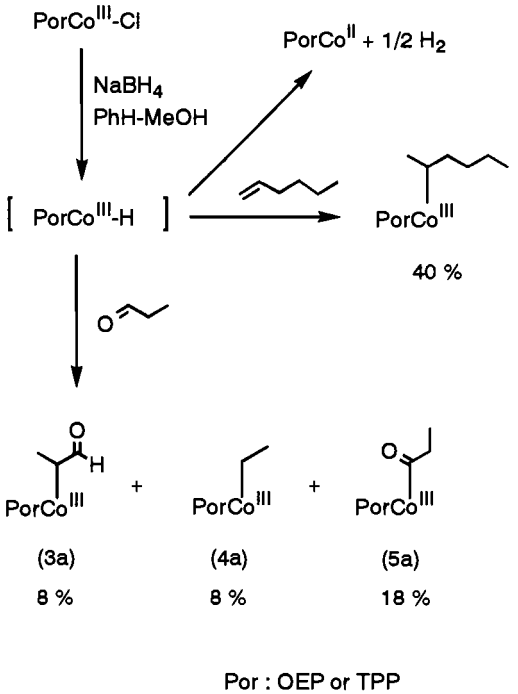
2. Results and discussion

2.1. Reaction of (halogeno)Co^{III} porphyrin with aldehyde in the presence of $NaBH_4$

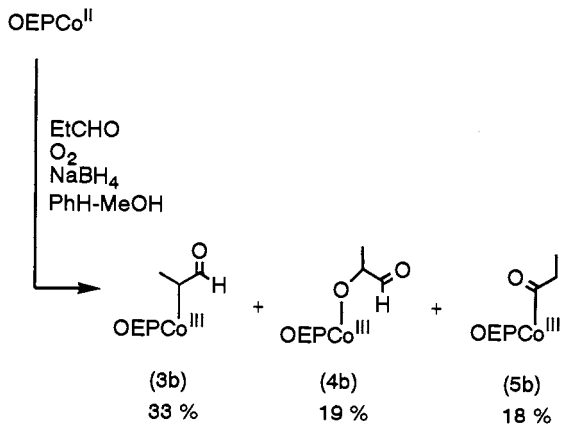
It has been reported that (hydrido)Rh^{III} octaethylporphyrin (OEPRh^{III}-H) is converted quantitatively into σ-(α-hydroxyalkyl)Rh^{III} complexes by the hydrometallation of aldehydes in the presence of an excess amounts of molecular hydrogen [12]. The latter is needed to suppress equilibrium loss of OEPRh^{III}-H leading to OEPRh^{II} and molecular hydrogen. On the other hand, (hydrido)Co^{III} porphyrin has never been known so far, probably due to its rapid decomposition to Co^{II} porphyrin and H_2. $NaBH_4$ readily reduces (halogeno)Co^{III} porphyrin to Co^{II} porphyrin with evolving hydrogen gas probably via a (hydrido)Co^{III} intermediate. This (hydrido)Co^{III} species should be responsible for the formation of σ-(2-hexyl)Co^{III}OEP in a 40% yield, when OEPCo^{III}–Cl was reacted with 1-hex-



Scheme 1.



Scheme 3.



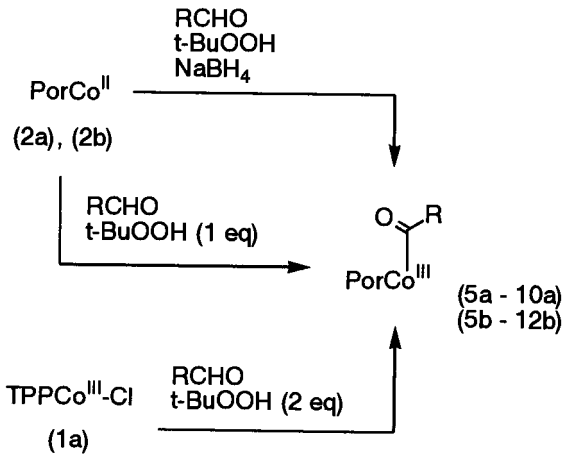
Scheme 4.

ene in the presence of $NaBH_4$ at room temperature under an argon atmosphere (Scheme 3). These reaction conditions were applied to examine reaction behavior of a hypothetical (hydrido)Co^{III} complex toward aldehyde. When TPPCo^{III}–Cl (**1a**) (TPP, *meso*-tetraphenylporphyrin dianion) was allowed to react with propanal and $NaBH_4$ under argon, TPPCo^{III}–CH(Me)CHO (**3a**) [13] (8%), TPPCo^{III}–Et (**4a**) [14] (8%), and TPPCo^{III}–C(O)Et (**5a**) (18%) besides TPPCo^{II} (**2a**) have been detected as a product mixture by ^{1}H-NMR spectroscopy (Scheme 3). A similar reaction of OEPCo^{III}–Cl (**1b**) with propanal and $NaBH_4$ resulted in much lower yields of (organo)Co^{III} porphyrins. Since it has been known that an acyl radical decomposes to an alkyl radical and carbon monoxide [2b], formation of **4a** in the above reaction provides strong evidence in support of generation of a free acyl radical. Thus, it is presumed that a hydrogen radical derived from homolysis of a Co^{III}–H bond abstracts a hydrogen from the CHO group of propanal, giving rise to **5a**. Hydrogen atom abstraction occurred also from the α-CH_2 group of propanal in this reaction, leading to **3a** via an enolate radical.

2.2. Reaction of Co^{II} porphyrin with aldehyde in the presence of $NaBH_4$ and molecular oxygen

Whereas Co^{II} porphyrin is a main product in the above reaction under argon, it can be oxidized to Co^{III} and then converted into (organo)Co^{III} porphyrin. For example, we have shown that hydrometallation of alkenes by using Co^{II} porphyrin and $NaBH_4$ is promoted by molecular oxygen as well as *t*-BuOOH [9]. When OEPCo^{II} (**2b**) was allowed to react with propanal in the presence of $NaBH_4$ and molecular oxygen at room temperature, three Co^{III} porphyrin complexes, OEPCo^{III}–CH(Me)CHO (**3b**) (33%), OEPCo^{III}–OCH(Me)CHO (**4b**) (19%) and OEPCo^{III}–C(O)Et (**5b**) (18%) besides **2b** have been detected as a product mixture by ^{1}H-NMR spectroscopy (Scheme 4). These products could not be separated because they decomposed during column chromatography on silica gel. The compounds, **3b** and **5b**, were identified on the basis of the similarity of their ^{1}H-NMR spectra to those of **3a** and **5a**. Substantially the same splitting pattern of the signals due to the axial ligand of **4b** as that of **3b** with very different ring current effects between **3b** and **4b** is consistent with σ-(1-formylethoxy)Co^{III} structure for **4b**. Although it is well known that insertion of dioxygen into a M^{III}–C bond generates σ-(alkylperoxo)M^{III} complexes especially in the cases of secondary and tertiary σ-alkyl groups [15], σ-(1-formylethylperoxo)Co^{III} structure is not consistent with the ^{1}H-NMR data observed for **4b**. It was reported that the axial CH_2 proton signal shifts from -2.67 to -0.45 ppm upon going from OEPCo^{III}–CH_2Ph to OEPCo^{III}–$OOCH_2$Ph [16]. Therefore, the observed chemical shift (-3.98 ppm) due to the methine proton of **4b** is not consistent with the Co^{III}–OOCH(Me)CHO structure but with the Co^{III}–OCH(Me)CHO structure taking into account the chemical shift (-3.57 ppm) of the methine proton of **3b**. As for the chemical shift of the methine proton of **4b** in comparison with that of **3b**, the stronger shielding effect due to the porphyrin ring current on the axial β-carbon position than on the axial α-carbon position can cancel out the deshielding effect of the oxygen atom inserted into the Co^{III}–C bond. Furthermore, the chemical shifts of the formyl proton and the methyl protons due to the axial ligand are shifted from 2.53 to 6.33 ppm and from -5.93 to -1.20 ppm, respectively, upon going from **3b** to **4b**. These chemical shift changes (ca. 4 ppm) are just in the range expected for the differences in the ring current effect between the protons attached at the β-carbon position and at the γ-carbon position relative to Co [17].

The carbonyl stretching mode of **3b** was observed at 1664 cm^{-1} in the IR spectrum. This much lower frequency than the ordinary ν(C=O) values is characteristic of σ-(alkyl)metal(III) complexes with a carbonyl group at the β-position with respect to the metal and is indicative of the overlap between the filled metal d-orbital and the C=O anti-bonding orbital [18]. The σ-(1-formylethyl)Co^{III} structure of **3b** was confirmed by alternative synthesis from OEPCo^{III}–Cl, Bu_3SnH, and acrolein, according to the method of Fukuzumi [13]. We have found **4b** as a byproduct in this alternative synthesis of **3b**. We have recently shown that oxygenation of σ-(alkyl)Co^{III} porphyrins with a secondary alkyl ligand is promoted under aerobic conditions in the light and an oxygen atom is inserted into the Co–C bond [18a]. Since **4b** is derived from **3b**, hydrogen atom was abstracted preferentially from the α-CH_2 group of propanal and the total yield of (organo)Co^{III} porphyrins was improved under the present reaction conditions. Non-selective hydrogen atom abstraction from



Scheme 5.

aldehyde occurred by using Co^{II} and $NaBH_4$ in the presence of oxygen as well as by using Co^{III} and $NaBH_4$ in the absence of oxygen.

2.3. Reaction of Co^{II} porphyrin with aldehyde in the presence of $NaBH_4$ and t-BuOOH

Reaction of **2a** with propanal (86 equivalents) in the presence of $NaBH_4$ (30 equivalents) and *t*-BuOOH (three equivalents) in a mixture of benzene–methanol gave **5a** in a 99% yield (Scheme 5). The σ-(propanoyl)Co^{III} structure of **5a** is consistent with a carbonyl stretching vibration at 1762 cm^{-1} in the IR spectrum and high-field A_2B_3 multiplets at δ −2.29 (q) and −1.48 (t). Ethanal, butanal, heptanal, benzaldehyde, and 1-naphthaldehyde similarly afforded corresponding σ-(acyl)Co^{III} porphyrins, TPPCo^{III}–C(O)R (**6a**–**10a**) (Table 1, runs 2–6). The complex **2b** also afforded OEPCo^{III}–C(O)R (**5b**–**10b**) in good yields (Table 1, runs 7, 12, 14, 16, 18, 20). These acyl complexes were sufficiently stable so that they could be purified by column chromatography on silica gel with benzene as an eluent. The carbonyl stretching modes of **5b**–**10b** appear at lower frequency by 2–10 cm^{-1} than those of **5a**–**10a** and these CO stretching frequencies of the σ-(acyl)Co^{III} porphyrins are higher by 10–40 cm^{-1} than those of the corresponding σ-(acyl)Rh^{III} porphyrins [19]. These observations are explained in terms of the more electron-withdrawing effects of Co than Rh and also of a TPP ligand than an OEP ligand. Although paraformaldehyde under the present redox conditions caused immediate dissolution of **2a**, which is indicative of the occurrence of a reaction, the corresponding σ-(formyl)Co^{III} porphyrin could not be obtained. In the case of rhodium porphyrin, insertion of carbon monoxide into a Rh^{III}–H bond was demonstrated, and the resulting σ-(formyl)Rh^{III} porphyrin, OEPRh^{III}–CHO, was reported to decompose in 24 h in degassed benzene [20]. Rapid decomposition of a cobalt analogue, even if it is formed, would take place due to a smaller bonding energy of a Co–C bond than a Rh–C bond [21].

Table 1
The reaction of Co^{II} porphyrin (**2a** and **2b**) with aldehyde (RCHO) in the presence of *t*-BuOOH[a]

Run	Co^{II} porphyrin	Aldehyde	Conditions	Product	Yield (%)
1	**2a**	Propanal	$NaBH_4/C_6H_6$–MeOH/Ar	**5a**	99
2	**2a**	Ethanal	$NaBH_4/C_6H_6$–MeOH/Ar	**6a**	56
3	**2a**	Butanal	$NaBH_4/C_6H_6$–MeOH/Ar	**7a**	96
4	**2a**	Heptanal	$NaBH_4/C_6H_6$–MeOH/Ar	**8a**	92
5	**2a**	Benzaldehyde	$NaBH_4/C_6H_6$–MeOH/Ar	**9a**	90
6	**2a**	1-Naphthaldehyde	$NaBH_4/C_6H_6$–MeOH/Ar	**10a**	98
7	**2b**	Propanal	$NaBH_4/C_6H_6$–MeOH/Ar	**5b**	95
8	**2b**	Propanal	Methylhydroquinone/C_6H_6/Ar	–	0
9	**2b**	Propanal	C_6H_6/Ar	**5b**	76
10	**2b**	Propanal	CH_2Cl_2/Ar	**5b**	84
11	**2b**	Propanal	CH_2Cl_2/Air	**5b**	42
12	**2b**	Ethanal	$NaBH_4/C_6H_6$–MeOH/Ar	**6b**	65
13	**2b**	Ethanal	CH_2Cl_2/Air	**6b**	61
14	**2b**	Butanal	$NaBH_4/C_6H_6$–MeOH/Ar	**7b**	89
15	**2b**	Butanal	C_6H_6/Ar	**7b**	66
16	**2b**	Heptanal	$NaBH_4/C_6H_6$–MeOH/Ar	**8b**	83
17	**2b**	Heptanal	C_6H_6/Ar	**8b**	45
18	**2b**	Benzaldehyde	$NaBH_4/C_6H_6$–MeOH/Ar	**9b**	78
19	**2b**	Benzaldehyde	C_6H_6/Ar	**9b**	60
20	**2b**	1-Naphthaldehyde	$NaBH_4/C_6H_6$–MeOH/Ar	**10b**	98
21	**2b**	Acrolein	C_6H_6/Ar	**11b**	82
22	**2b**	Citronellal	C_6H_6/Ar	**12b**	72

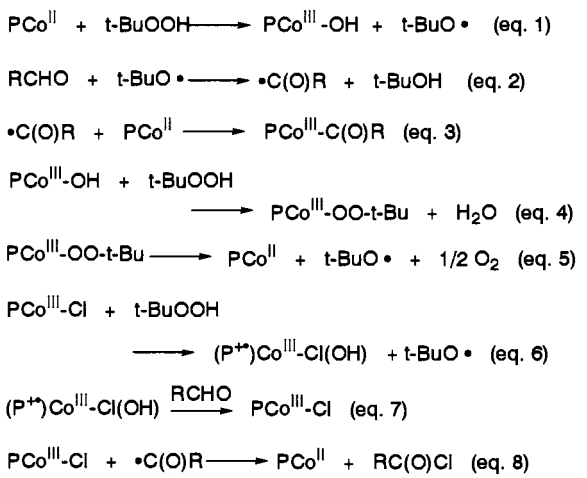
[a] $PorCo^{II}$/RCHO/*t*-BuOOH/$NaBH_4$ = 0.08/2.4/0.24/2.3 mmol in 15.5 ml of C_6H_6–MeOH (30:1) or $PorCo^{II}$/RCHO/*t*-BuOOH = 0.08/2.4/0.24 mmol in 15 ml of solvent.

We have shown that metallation of tetrahydrofuran (THF) with Co^{II} porphyrin proceeds through the abstraction of a hydrogen radical from the α-carbon of THF probably by the action of a hydroxyl radical or a *t*-butoxyl radical generated under the same reaction conditions as the present case [10]. Since it is well known that acyl radicals are readily produced from aldehydes by the peroxide-induced hydrogen atom abstraction [22], the clean formation of σ-(acyl)Co^{III} complexes suggests that a (hydrido)Co^{III} intermediate does not play a key role in the presence of *t*-BuOOH.

2.4. Reaction of Co^{II} porphyrin with aldehyde and *t*-BuOOH

According to the Wayland's paper that OEPRh^{III}–H reacts with aldehyde to generate σ-(hydroxyalkyl)Rh^{III} porphyrin [12], there is a possibility that a transient (hydrido)Co^{III} complex (OEPCo^{III}–H) reacts with aldehyde to generate σ-(hydroxyalkyl)Co^{III} porphyrin and it is then oxidized by *t*-BuOOH to give σ-(acyl)Co^{III} porphyrin. When **2b** was reacted with propanal and *t*-BuOOH under argon, **5b** was obtained in a 76% yield in benzene and in an 84% yield in dichloromethane (Table 1, runs 9 and 10). The yield of **5b** decreased to 42% when the reaction was carried out under air (Table 1, run 11). Similarly, ethanal, butanal, heptanal, benzaldehyde, acrolein, and citronellal afforded the corresponding σ-(acyl)Co^{III} complexes in moderate yields even in the absence of $NaBH_4$ (Table 1, runs 13, 15, 17, 19, 21, 22). Therefore, (hydrido)Co^{III} porphyrin does not take part in the formation of σ-(acyl)Co^{III} porphyrins under the reaction conditions which contain $NaBH_4$ and *t*-BuOOH. It has been shown that acrolein is hydrometallated at the C=C bond under the reaction conditions where TPPCo^{III}–H seems to be generated by the combination of TPPCo^{III}–Cl and Bu_3SnH [13]. This σ-(1-formylethyl)Co^{III} porphyrin **3b** was not detected, but σ-(acyl)Co^{III} porphyrin **11b** was isolated in an 82% yield (Table 1, run 21). This means that a hydridocobalt species does not take place in the formation of σ-(acyl)Co^{III} porphyrins irrespective of whether $NaBH_4$ is present or not. Since methylhydroquinone which is a radical scavenger has completely inhibited the generation of **5b** (Table 1, run 8), a radical species should be a key intermediate in the formation of σ-(acyl)Co^{III} porphyrins. Thus, Co^{II} porphyrin plays a key role as an acyl radical trapping agent.

These experimental facts suggest the following reaction sequence. It is considered that a *t*-butoxyl radical and PorCo^{III}–OH are generated through the one-electron redox reaction between PorCo^{II} and *t*-BuOOH (Scheme 6, Eq. (1)). Then, a *t*-butoxyl radical would attack on aldehyde to give *t*-butanol and an acyl radical (Scheme 6, Eq. (2)). The latter immediately undergoes radical coupling with PorCo^{II} leading to



Scheme 6.

PorCo^{III}–C(O)R (Scheme 6, Eq. (3)). Since GLC analysis indicated that aldehyde was not oxidized by *t*-BuOOH in the absence of PorCo^{II}, PorCo^{II} catalyzes the redox reaction between aldehyde and *t*-BuOOH. This results in effective generation of an acyl radical followed by the combination of PorCo^{II} with an acyl radical. Using 1,4-cyclohexadiene as a substitute for aldehyde in the absence of $NaBH_4$ did not afford the corresponding (organo)Co^{III} porphyrin in spite of rather weaker C–H bonds of the allylic substrates (bond dissociation energies: 87.3 kcal mol^{-1} for acetaldehyde, 73.0 kcal mol^{-1} for 1,4-cyclohexadiene [23]). The difference in the reactivity between allylic compounds and aldehydes towards dehydrometallation with cobalt porphyrin can be explained by the presumption that σ-(acetyl)Co^{III} porphyrins are much more stable than σ-(cyclohexa-2,5-dienyl)Co^{III} porphyrins.

This reaction sequence from Eqs. (1)–(3) means that two equivalents of PorCo^{II} are converted into one equivalent each of PorCo^{III}–OH and PorCo^{III}–C(O)R by the action of one equivalent of *t*-BuOOH. Therefore, $NaBH_4$ helps improve the yield of σ-(acyl)Co^{III} porphyrins by reducing PorCo^{III}–OH to PorCo^{II}, although ca. 70% of benzaldehyde, for example, was converted to benzyl alcohol by $NaBH_4$ under these reaction conditions. Since σ-(acyl)Co^{III} porphyrins were formed in the yields greater than 50% even in the absence of $NaBH_4$, there must be another mechanism by which PorCo^{III}–OH is converted to PorCo^{II}. This is explained in terms of the generation of a (alkylperoxy)Co^{III} complex (Scheme 6, Eq. (4)) and its decomposition to PorCo^{II}, *t*-butoxyl radical and molecular oxygen (Scheme 6, Eq. (5)), as is shown for the reaction of (salen)Co^{III}–OH with *t*-BuOOH [24]. Thus, the 1:1 reaction of PorCo^{III}–OH and *t*-BuOOH leads to σ-(acyl)Co^{III} porphyrin by way of acyl radical which is generated by the reaction of *t*-butoxyl radical and

aldehyde (Scheme 6, Eq. (2)). The total stoichiometry of the reaction of $PorCo^{II}$ and *t*-BuOOH in the presence of excess aldehyde according to the above mechanism is consistent with the observation that one equivalent of *t*-BuOOH was sufficient to get a good yield (82%) of **5a** starting from **2a**, as shown in Table 2.

On the other hand, two equivalents of *t*-BuOOH are required to reach the maximum yield (68%) of **5a** if starting from **1a**. Bruce and co-workers showed that $PorCo^{III}$–Cl is oxidized by *t*-BuOOH to give rise to $Por^{+\bullet}Co^{III}$–Cl(OH) and a *t*-butoxyl radical (Scheme 6, Eq. (6)) [25]. The monitoring UV–vis spectral change indicated that $OEP^{+\bullet}Co^{III}(ClO_4)_2$ (397 nm) was reduced immediately by aldehyde to give $OEPCo^{III}(ClO_4)$ (409 nm). Therefore, $Por^{+\bullet}Co^{III}$–Cl(OH) would be reduced by an excess of aldehyde to regenerate $PorCo^{III}$–Cl (Scheme 6, Eq. (7)). On the other hand, a *t*-butoxyl radical would attack aldehyde to give *t*-butanol and an acyl radical (Scheme 6, Eq. (2)). This acyl radical would not only undergo radical coupling with $PorCo^{II}$ (Scheme 6, Eq. (3)) but also reduce $PorCo^{III}$–Cl to give $PorCo^{II}$ and acyl chloride (Scheme 6, Eq. (8)). In fact, carboxylic acid derived from the corresponding acyl chloride was detected by ^{1}H-NMR analysis of the reaction mixture started from $PorCo^{III}$–Cl [26], whereas it was not detected in the reaction mixture started from $PorCo^{II}$. This reaction sequence (Scheme 6, Eqs. (2), (6)–(8)) means that $PorCo^{III}$–Cl is converted into $PorCo^{II}$ by the action of one equivalent of *t*-BuOOH if excess aldehyde is present. This is consistent with the observation that two equivalents of *t*-BuOOH are required to reach the maximum yield of **5a** from **1a**.

On the other hand, a hydridocobalt species should be responsible for the formation of the product **3a** or **3b** derived from hydrogen abstraction from the α-CH_2 group of aldehyde. That is, hydrogen radical produced by the homolysis of a Co^{III}–H bond may cause non-selective hydrogen abstraction from aldehyde to generate both an acyl radical and an enolate radical.

Table 2
Effect of the amount of *t*-BuOOH in the reaction of Co porphyrin with propanal[a]

Co porphyrin	*t*-BuOOH (equivalents)	Yield (%) of **5a**
$TPPCo^{II}$–Cl	0.5	19
	1	25
	2	68
	3	66
$TPPCo^{II}$	0.5	36
	1	82
	2	80
	3	81

[a] TPPCo/RCHO = 0.08/2.4 mmol in 15 ml of C_6H_6.

2.5. Intramolecular cyclization of aldehyde with a C–C multiple bond by combination of Co^{II} porphyrin and *t*-BuOOH

When three equivalents of *t*-BuOOH were added to a mixture of **2a** and 2-allyloxy-1-naphthaldehyde in benzene under argon at ambient temperature, the conversion of **2a** into (organo)Co^{III} porphyrin was clearly indicated by the dissolution of **2a** upon addition of *t*-BuOOH. The (organo)Co^{III} porphyrin **13a** with a 3-(4-oxo-5,6-benzochromanyl)methyl group as an axial ligand was obtained in an 81% yield. The structure of the axial organo group of **13a** was determined on the basis of the AA′BCC′ coupling pattern for the signals (δ −4.43, −3.97, −3.30, −0.34, 1.25) due to the $-CH_2CHCH_2-$ unit bonded to Co^{III} in the ^{1}H-NMR (Fig. 1) and ^{1}H-^{1}H-COSY (Fig. 2) spectrum. The signal at δ −4.43 is assigned to the methine proton because it is coupled to the other four signals. Since the porphyrin ring current effect on the ^{1}H-chemical shift of the β-carbon position relative to Co^{III} is generally the highest [9,10], this methine proton is thought to be at the β-carbon position. The two signals at δ −3.97 and −3.30 are assigned to the protons of the axial α-carbon position, and the two signals at much lower magnetic fields (δ −0.34 and 1.25) are assigned to those of the axial γ-carbon position according to the strength of the ring current effect of porphyrin [9,10]. These data indicate that Co^{III} is bonded not to the methine carbon but to the methylene carbon in the $-CH_2CHCH_2-$ moiety. The carbonyl stretching mode of **13a** was observed at 1666 cm^{-1} in the IR spectrum. This frequency is similar to that of 4-oxo-5,6-benzochroman (1672 cm^{-1}) [27].

The structure of **13a** is consistent with the following reaction sequence. The acyl radical center is generated and then adds across a C–C double bond intramolecularly to give a six-membered ring. The resulting primary alkyl radical is trapped by Co^{II} porphyrin (Scheme 7). Although σ-(acyl)Co^{III} porphyrins are given in good yields in dichloromethane as well as in benzene (see Table 1, runs 9 and 10), the yield of **13a** decreased to 31% in dichloromethane (Table 3). This is probably because a generated primary alkyl radical is not only trapped by Co^{II} porphyrin but is reactive enough to abstract chlorine or hydrogen from dichloromethane. Reaction of **2b** with 2-allyloxy-1-naphthaldehyde also afforded (organo)Co^{III} porphyrin **13b** in a 71% yield. When 2-allyloxybenzaldehyde, 2-allylbenzaldehyde, and *N*-allylpyrrole-2-carboxaldehyde were used in the same fashion, the corresponding (organo)Co^{III} porphyrins

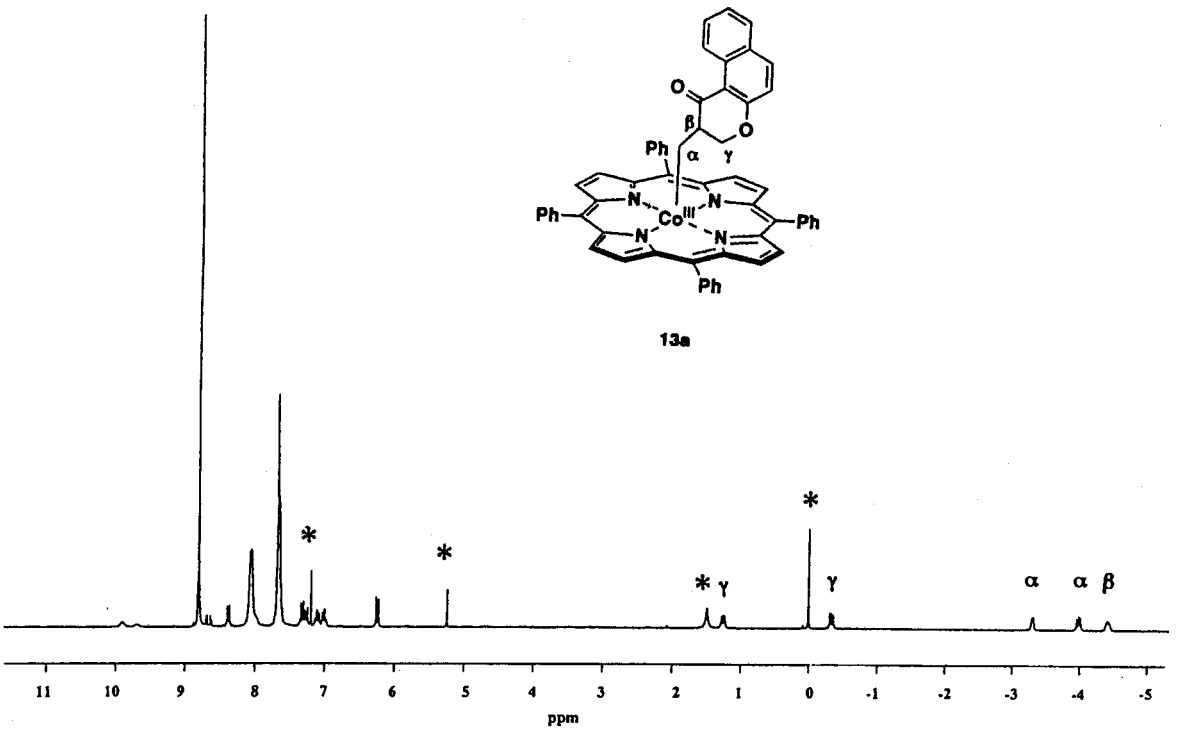


Fig. 1. ^{1}H-NMR spectrum of **13a** in $CDCl_3$. Signals due to TMS, H_2O, CH_2Cl_2, $CHCl_3$ are indicated by asterisks. Some impurities such as **2a** are observed at 8.7, 9.7, and 9.9 ppm.

with a cyclized axial alkyl ligand, **14b**, **15b**, and **16b**, were formed in 59, 59, and 90% yield, respectively, without generation of σ-(acyl)Co^{III} porphyrins (Schemes 7–9). The ^{1}H-NMR signals due to the axial organo group of **13b**–**16b** were assigned according to the ^{1}H-^{1}H-COSY experiment. These ^{1}H-NMR data are consistent with the Co^{III}–CH_2–CHX–CH_2Y connectivity which results from acyl radical cyclization. The acyl radical cyclization of 2-allylbenzaldehyde and *N*-allylpyrrole-2-carboxaldehyde did not lead to a six-membered ring with the Co^{III}–$CH(CH_2X)$–CH_2Y connectivity such as in **15b**′ (Scheme 8). To the contrary, Branchaud reported that acid catalyzed cycliza-

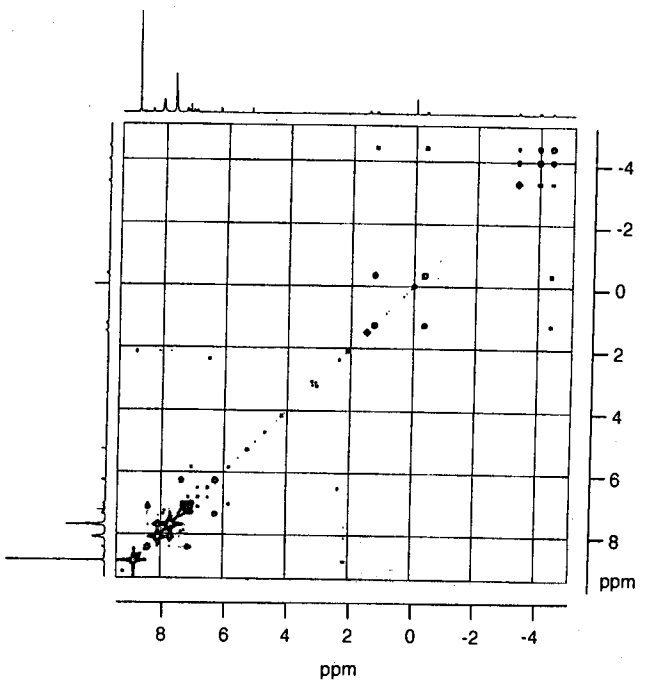
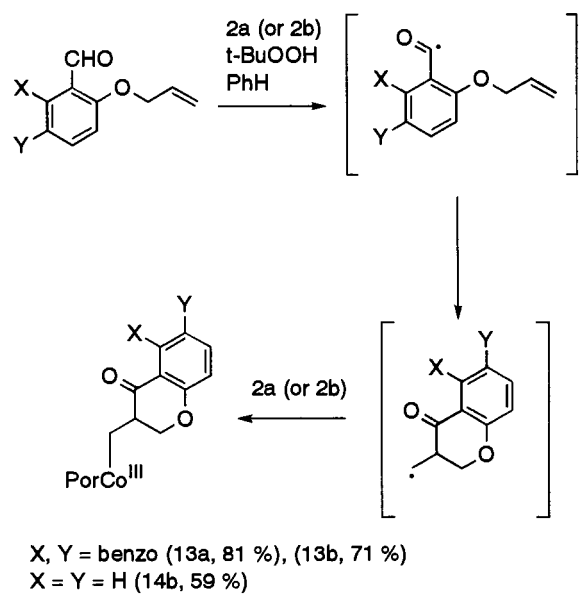


Fig. 2. ^{1}H-^{1}H-COSY spectrum of **13a** in $CDCl_3$.



Scheme 7.

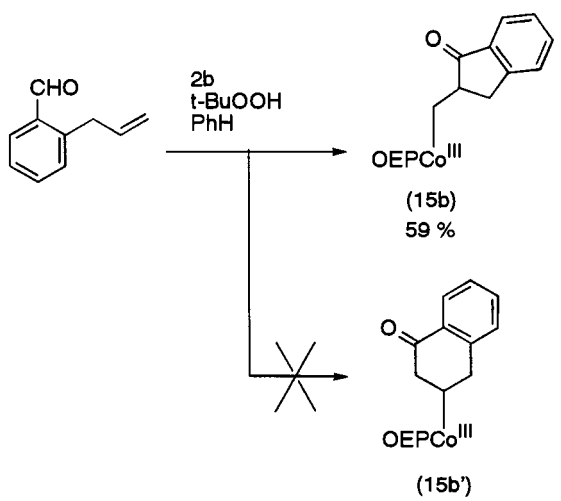
Table 3
Yield of **13a** in the reaction of **2a** with 2-allyloxy-1-naphthaldehyde[a]

Solvent	Atmosphere	Yield (%) of **13a**
C_6H_6	Argon	81
CH_2Cl_2	Argon	31
C_6H_6	Air	46
CH_2Cl_2	Air	19

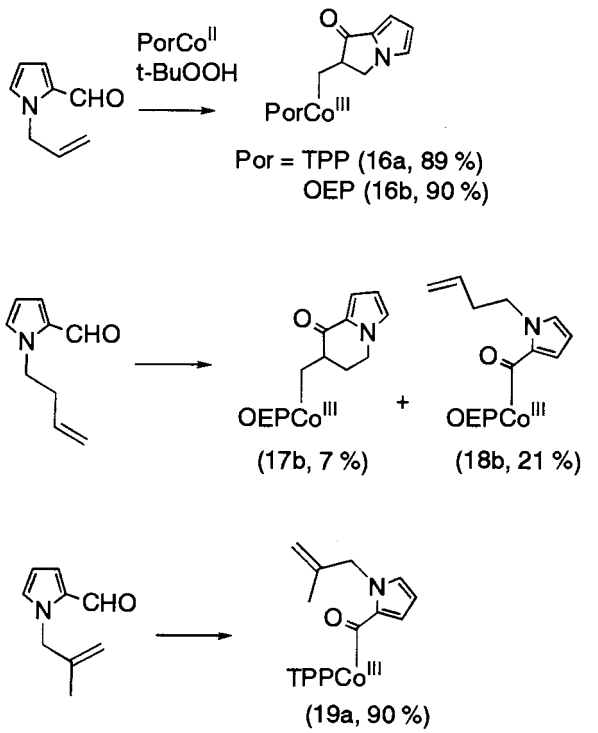
[a] **2a**/2-allyloxy-1-naphthaldehyde/*t*-BuOOH = 0.08/2.4/0.24 mmol in 15 ml of solvent.

tion of (2-hydroxy-4-*N*-pyrrolylbutyl)cobaloxime led to a six-membered ring with the Co^{III}–$CH(CH_2X)$–CH_2Y connectivity [28]. While a strained 5-membered ring transition state is not preferred in the intramolecular electrophilic substitution of the pyrrole ring, the regioselectivity in the present acyl radical cyclization is governed by a probability factor favoring 5-membered ring formation.

Similar acyl radical cyclization occurred in the case of *N*-(3-butenyl)pyrrole-2-carboxaldehyde to give (organo)Co^{III} porphyrins **17b** in a 7% yield. The ^{1}H-NMR signals (δ −5.01, −4.67, −3.90, −3.05, −1.81, 1.18, 2.00) due to the axial organo group of **17b** are consistent with a six-membered ring which consists of Co^{III}–CH_2–CHX–CH_2CH_2Y connectivity. Because, the methine proton is assigned to the signal at the highest magnetic field (δ −5.01) characteristic of the β-carbon position with respect to Co. However, this reaction was accompanied by the formation of the corresponding σ-(acyl)Co^{III} porphyrin **18b** in a 21% yield (Scheme 9). Since these products could not be separated because they decomposed during column chromatography on silica gel, the yields were determined by ^{1}H-NMR spectrum of the mixture. On the other hand, *N*-methallylpyrrole-2-carboxaldehyde gave σ-(acyl)Co^{III} porphyrin **19a** in a 90% yield as a single



Scheme 8.



Scheme 9.

product (Scheme 9). Whereas the ^{1}H-NMR signals due to the β-pyrrole protons of the axial ligand of **16a**, **16b**, and **17b** appear at 5.5–6.2 ppm, one of those signals in **18b** and **19a** is shifted to a higher magnetic field (0.47 ppm in **18b**; 1.06 ppm in **19a**) due to the porphyrin ring current effect. This indicates that the β-pyrrole proton is forced to come close to the porphyrin plane owing to the steric repulsion between the pyrrole *N*-substituent and the porphyrin plane.

Photolysis of **13b** by a xenon lamp afforded 3-methyl-4-oxo-5,6-benzochrom-2-en (**20**) in an 87% yield (Scheme 10). The methyl and the olefin protons of **20** appear at δ 2.13 and 7.86, respectively, in the ^{1}H-NMR. The carbonyl stretching mode of **20** at 1644 cm^{-1} in the IR spectrum is shifted to the lower frequency by 20–30 cm^{-1} than that of 4-oxo-5,6-benzochroman or **13b**. These data are consistent with the enone structure of **20**. It is considered that β-elimination of Co^{III}–H species from **13b** gives **2b** and an enone intermediate (**A**) and the latter rearranges to **20** because of its relative thermodynamic stability.

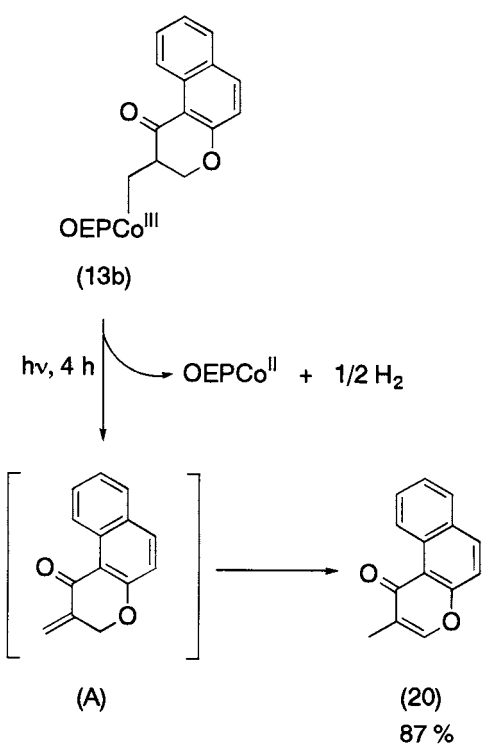
In conclusion, acyl radicals are readily produced from aldehydes through the reaction with Co porphyrin and *t*-BuOOH. The generated acyl radicals were directly captured by Co^{II} porphyrin or underwent radical cyclization before the coupling with Co^{II} porphyrin. The yields and the reaction pathway in the formation of σ-(acyl)Co^{III} porphyrins are dependent on the oxidation state of the starting Co porphyrin and the amount of *t*-BuOOH.

3. Experimental section

^{1}H-NMR (250 MHz) spectra were recorded on a Bruker AC-250 spectrometer in $CDCl_3$, and chemical shifts were referenced with respect to tetramethylsilane as an internal standard. UV–visible spectra were measured on a Shimadzu UV-240 spectrophotometer. IR spectra were obtained in a KBr disk on a Hitachi I-2000 spectrophotometer. Elemental analyses were performed by a Yanagimoto Model Mt-3 CHN analyzer. Low-resolution mass spectra were measured on a Shimadzu GCMS-QP2000A spectrometer with a direct-inlet method. Gel permeation chromatography was performed by a JAI LC-908 system. Benzene and dichloromethane were distilled from CaH_2 and methanol was distilled simply before use. Aldehydes were obtained from commercial suppliers and used as received. $TPPCo^{II}$ [29], $OEPCo^{II}$ [30], $TPPCo^{III}$–Cl [31], $OEPCo^{III}$–Cl [31] were synthesized according to the literature methods.

3.1. Reaction of Co^{III} porphyrin with propanal in the presence of $NaBH_4$ under an argon atmosphere

In a two necked round-bottomed 50-ml flask equipped with a septum and a two-way cock connected to an argon line, **1a** (23.2 mg, 0.033 mmol), $NaBH_4$ (44.4 mg, 1.2 mmol) and a magnetic stirrer were placed under an argon atmosphere. To the flask, benzene (15 ml) and methanol (0.5 ml), propanal (0.5 ml) were added through a syringe. Then, the reaction mixture was stirred for 10 min. The resulting mixture was filtered to remove the remaining $NaBH_4$ and **2a**. The filtrate was evaporated with a rotary evaporator, and washed with methanol. Yields of σ-(alkyl)Co^{III} complexes were determined on the basis of their signal intensities in the ^{1}H-NMR: **3a** = 8%, **4a** = 8%, **5a** = 18%.



Scheme 10.

3.2. Reaction of Co^{II} porphyrin with propanal in the coexistent system of O_2 and $NaBH_4$

In a 50-ml Erlenmeyer flask, **2b** (23.8 mg, 0.040 mmol), $NaBH_4$ (45.3 mg, 1.3 mmol) and a magnetic stirrer were placed. To the flask, benzene (15 ml), methanol (0.5 ml) and propanal (0.5 ml) were added and this reaction mixture were stirred for 1 h. The mixture was filtered to remove the remaining $NaBH_4$ and **2b**. The filtrate was evaporated with a rotary evaporator, and the residue was washed with methanol to give a product mixture (21.2 mg). Yields of **3b**, **4b** and **5b** were determined on the basis of their signal intensities in the ^{1}H-NMR. **3b** = 33%, **4b** = 19%, **5b** = 18%, and **2b** was recovered.

3b: ^{1}H-NMR ($CDCl_3$): δ −5.93 (d, 3H, CH(*Me*)CHO), −3.57 (dq, 1H, *CH*(Me)CHO), 2.53 (d, 1H, CH(Me)*CHO*), 1.87 (t, 24H, CH_2CH_3), 4.12 (m, 16H, CH_2CH_3), 10.21 (s, 4H, *meso*-H).

4b: ^{1}H–NMR ($CDCl_3$): δ −3.98 (dq, 1H, O*CH*(Me)CHO), −1.20 (d, 3H, OCH(*Me*)CHO), 6.33 (d, 1H, OCH(Me)*CHO*), 1.85 (t, 24H, CH_2CH_3), 3.96 (m, 16H, CH_2CH_3), 10.64 (s, 4H, *meso*-H).

Spectroscopic and analytical data of **5b** are described later.

3.3. Reaction of Co^{II} porphyrin with aldehydes in the coexistent system of t-BuOOH and $NaBH_4$

3.3.1. General procedure

In a two necked round-bottomed 50-ml flask equipped with a septum and a two-way cock connected to an argon line, **2a** (ca. 0.08 mmol), $NaBH_4$ (ca. 2.3 mmol), and a magnetic stirrer were placed under an argon atmosphere. To the flask, benzene (15 ml), methanol (0.5 ml) and aldehyde (0.5 ml) were added through a syringe. Then, *t*-BuOOH (10 μl) was added through a micro syringe every 5 min (three times). The mixture was filtered to remove the remaining $NaBH_4$ and **2a**. The filtrate was evaporated under vacuum, and the residue was washed with methanol. The crude product was purified by column chromatography on silica gel with benzene as an eluent and recrystallized from dichloromethane-methanol.

5a: ^{1}H-NMR ($CDCl_3$): δ −2.29 (q, 2H, $COCH_2CH_3$), −1.48 (t, 3H, $COCH_2CH_3$), 7.74 (m, 12H, m and *p*-Ph–H), 8.11 (br, 8H, *o*-Ph–H), 8.93 (s,

8H, β-Py–H). IR (KBr), cm^{-1}: 1762 [ν(C=O)]. UV–vis (CH_2Cl_2), nm: 408.0, 530.0. Anal. Calc. for $C_{47}H_{33}N_4OCo$: C, 77.46; H, 4.56; N, 7.69. Found: C, 76.78; H, 4.62; N, 7.62.

6a: ^{1}H-NMR ($CDCl_3$): δ −2.20 (s, 3H, COCH_3), 7.70–7.72 (m, 12H, m and *p*-Ph–H), 8.10 (br, 8H, *o*-Ph–H), 8.84 (s, 8H, β-Py–H). IR (KBr), cm^{-1}: 1732 [ν(C=O)]. UV–vis (CH_2Cl_2), nm: 408.0, 530.0. Anal. Calc. for $C_{46}H_{31}N_4OCo$: C, 77.30; H, 4.37; N, 7.84. Found: C, 77.43; H, 4.59; N, 7.87.

7a: ^{1}H-NMR ($CDCl_3$): δ −2.32 (t, 2H, CO$CH_2$$CH_2CH_3$), −1.10 (m, 2H, CO$CH_2CH_2$$CH_3$), −1.06 (t, 3H, CO$CH_2CH_2CH_3$), 7.72 (m, 12H, m and *p*-Ph–H), 8.10 (br, 8H, *o*-Ph–H), 8.83 (s, 8H, β-Py–H). IR (KBr), cm^{-1}: 1742 [ν(C=O)]. UV–vis (CH_2Cl_2), nm: 408.0, 530.0. Anal. Calc. for $C_{48}H_{35}N_4OCo{\cdot}0.5H_2O$: C, 76.69; H, 4.83; N, 7.45. Found: C, 76.72; H, 4.78; N, 7.18.

8a: ^{1}H-NMR ($CDCl_3$): δ −2.32 (t, 2H, CO$CH_2$$CH_2CH_2CH_2CH_3$), −1.16 (m, 2H, CO$CH_2CH_2$$CH_2CH_2CH_3$), −0.77 (m, 2H, CO$CH_2CH_2CH_2$$CH_2CH_2CH_3$), 0.00 (m, 2H, CO$CH_2CH_2CH_2CH_2$$CH_2CH_3$), 0.45–0.60 (m, 5H, CO$CH_2CH_2CH_2CH_2$$CH_2CH_3$), 7.67–7.77 (m, 12H, *m*- and *p*-Ph–H), 8.10 (br, 8H, *o*-Ph–H), 8.83 (s, 8H, β-Py–H). IR (KBr), cm^{-1}: 1734 [ν(C=O)]. UV–vis (CH_2Cl_2), nm: 408.0, 530.0. Anal. Calc. for $C_{51}H_{41}N_4OCo{\cdot}0.5H_2O$: C, 77.16; H, 5.33; N, 7.06. Found: C, 77.24; H, 5.51; N, 6.96.

9a: ^{1}H-NMR ($CDCl_3$): δ 2.61 (d, 2H, COPh, *o*-H), 6.03 (t, 2H, COPh, *m*-H), 6.50 (t, 1H, COPh, *p*-H), 7.67–7.73 (m, 12H, *m*- and *p*-Ph–H), 8.06 (br, 8H, *o*-Ph–H), 8.79 (s, 8H, β-Py–H). IR (KBr), cm^{-1}: 1728 [ν(C=O)]. UV–vis (CH_2Cl_2), nm: 408.0, 528.0. Anal. Calc. for $C_{51}H_{33}N_4OCo{\cdot}0.5H_2O$: C, 77.95; H, 4.36; N, 7.13. Found: C, 77.82; H, 4..74; N, 7.12.

10a: ^{1}H-NMR ($CDCl_3$): δ 2.04 (d, 1H, 2-Nap–H), 3.14 (d, 1H, 8-Nap–H), 6.13 (t, 1H, 3-Nap–H), 6.52 (t, 1H, 7-Nap–H), 6.94 (t, 1H, 6-Nap–H), 7.00 (d, 1H, 4-Nap–H), 7.19 (d, 1H, 5-Nap–H), 7.71 (m, 12H, *m*- and *p*-Ph–H), 8.00 (br, 8H, *o*-Ph–H), 8.79 (s, 8H, β-Py–H). IR (KBr), cm^{-1}: 1714 [ν(C=O)]. UV–vis (CH_2Cl_2), nm: 408.0, 528.0. Anal. Calc. for $C_{55}H_{35}N_4OCo{\cdot}2.5H_2O$: C, 75.76; H, 4.62; N, 6.43. Found: C, 75.64; H, 4.67; N, 6.44.

5b: ^{1}H-NMR ($CDCl_3$): δ −2.90 (q, 2H, COCH_2CH_3), −1.78 (t, 3H, COCH_2CH_3), 1.87 (t, 24H, CH_2CH_3), 3.91–4.14 (m, 16H, CH_2CH_3), 10.07 (s, 4H, *meso*-H). IR (KBr), cm^{-1}: 1756 [ν(C=O)]. UV–vis (CH_2Cl_2), nm: 389.5, 518.0, 552.5. Anal. Calc. for $C_{39}H_{49}N_4OCo$: C, 72.20; H, 7.61; N, 8.64. Found: C, 72.45; H, 7.90; N, 8.65.

6b: ^{1}H-NMR ($CDCl_3$): δ −2.75 (s, 3H, COCH_3), 1.87 (t, 24H, CH_2CH_3), 3.92–4.12 (m, 16H, CH_2CH_3), 10.07 (s, 4H, *meso*-H). IR (KBr), cm^{-1}: 1730 [ν(C=O)]. UV–vis (CH_2Cl_2), nm: 389.5, 518.0, 552.5. Anal. Calc. for $C_{38}H_{47}N_4OCo$: C, 71.91; H, 7.46; N, 8.83. Found: C, 72.06; H, 7.67; N, 8.71.

7b: ^{1}H-NMR ($CDCl_3$): δ −2.92 (t, 2H, CO$CH_2CH_2CH_3$), −1.40 (m, 2H, CO$CH_2CH_2CH_3$), −1.30 (t, 3H, CO$CH_2CH_2CH_3$), 1.86 (t, 24H, CH_2CH_3), 3.92–4.12 (m, 16H, CH_2CH_3), 10.06 (s, 4H, *meso*-H). IR (KBr), cm^{-1}: 1738 [ν(C=O)]. UV–vis (CH_2Cl_2), nm: 389.5, 518.0, 552.5. Anal. Calc. for $C_{40}H_{51}N_4OCo{\cdot}0.5H_2O$: C, 71.51; H, 7.80; N, 8.34. Found: C, 71.74; H, 7.64; N,8.37.

8b: ^{1}H-NMR ($CDCl_3$): δ −2.90 (t, 2H, COCH_2CH_2-$CH_2CH_2CH_2CH_3$), −1.48 (m, 2H, CO$CH_2CH_2CH_2$-$CH_2CH_2CH_3$), −1.07 (m, 2H, CO$CH_2CH_2CH_2CH_2$-CH_2CH_3), −0.17 (m, 2H, CO$CH_2CH_2CH_2CH_2CH_2$-CH_3), 0.39–0.49 (m, 5H, CO$CH_2CH_2CH_2CH_2$-CH_2CH_3), 1.86 (t, 24H, CH_2CH_3), 4.02 (m, 16H, CH_2CH_3), 10.06 (s, 4H, *meso*-H). IR (KBr), cm^{-1}: 1730 [ν(C=O)]. UV–vis (CH_2Cl_2), nm: 389.5, 518.0, 552.5. Anal. Calc. for $C_{43}H_{57}N_4OCo{\cdot}0.5H_2O$: C, 72.34; H, 8.19; N, 7.85. Found: C, 72.40; H, 8.44; N,7.76.

9b: ^{1}H-NMR ($CDCl_3$): δ 1.84 (t, 24H, CH_2CH_3), 2.13 (d, 2H, COPh, *o*-H), 3.98 (q, 16H, CH_2CH_3), 5.75 (t, 2H, COPh, *m*-H), 6.23 (t, 1H, COPh, *p*-H), 9.95 (s, 4H, *meso*-H). IR (KBr), cm^{-1}: 1720 [ν(C=O)], UV–vis (CH_2Cl_2), nm: 389.5, 518.0, 552.5. Anal. Calc. for $C_{43}H_{49}N_4OCo{\cdot}0.5H_2O$: C, 73.17; H, 7.14; N, 7.94. Found: C, 73.54; H, 7.25; N, 7.98.

10b: ^{1}H-NMR ($CDCl_3$): δ 1.59 (d, 1H, 2-Nap–H), 1.80 (t, 24H, CH_2CH_3), 2.75 (d, 1H, 8-Nap–H), 3.93 (q, 16H, CH_2CH_3), 5.95 (t, 1H, 3-Nap–H), 6.38 (t, 1H, 7-Nap–H), 6.77 (d, 1H, 4-Nap–H), 6.83(t, 1H, 6-Nap–H), 7.00 (d, 1H, 5-Nap–H), 10.00 (s, 4H, *meso*-H). IR (KBr), cm^{-1}: 1704 [ν(C=O)]. UV–vis (CH_2Cl_2), nm: 391.0, 517.0, 552.5. Anal. Calc. for $C_{47}H_{51}N_4OCo$: C, 75.58; H, 6.88; N, 7.50. Found: C, 75.52; H, 7.08; N, 7.65.

3.4. Reaction of Co^{II} porphyrin with aldehydes in the presence of t-BuOOH

3.4.1. General procedure

In a two necked round-bottomed 50-ml flask equipped with a septum and a two-way cock connected to an argon line, **2a** (ca. 0.08 mmol) and a magnetic stirrer were placed under an argon atmosphere. To the flask, benzene (15 ml), methanol (0.5 ml) and aldehyde (0.5 ml) were added through a syringe. Then, *t*-BuOOH (10 μl) was added through a micro syringe every 5 min (three times). The mixture was filtered to remove the remaining **2a**. The filtrate was evaporated under vacuum, and the residue was washed with methanol. The crude product was purified by column chromatography on silica gel with benzene as an eluent and recrystallized from dichloromethane–methanol.

11a: ^{1}H-NMR ($CDCl_3$): δ 0.66 (dd, 1H, CO*CH*=CH_2) (J_{trans} = 17.0 Hz, J_{cis} = 10.4 Hz), 2.29 (dd, 1H, COCH=*CH_2*, *cis*) (J_{gem} = 1.3 Hz), 2.64 (dd, 1H, COCH=*CH_2*, *trans*), 7.67–7.77 (m, 12H, *m*- and *p*-Ph–H), 8.11 (br, 8H, *o*-Ph–H), 8.84 (s, 8H, β-Py–H). IR (KBr), cm^{-1}: 1714 [ν(C=O)]. UV–vis (CH_2Cl_2), nm: 408.0, 530.0. Anal. Calc. for $C_{47}H_{31}N_4OCo\cdot H_2O$: C, 75.80; H, 4.47; N, 7.53. Found: C, 75.81; H, 4.71; N, 7.51.

11b: ^{1}H-NMR ($CDCl_3$): δ −0.03 (dd, 1H, CO*CH*=CH_2) (J_{trans} = 17.0 Hz, J_{cis} = 10.3 Hz), 1.86 (dd, 1H, COCH=*CH_2*, *cis*) (J_{gem} = 1.6 Hz), 2.24 (dd, 1H, COCH=*CH_2*, *trans*), 1.79 (t, 24H, CH_2*CH_3*), 3.95 (m, 16H, *CH_2*CH_3), 10.00 (s, 4H, *meso*-H). IR (KBr), cm^{-1}: 1708 [ν(C=O)]. UV–vis (CH_2Cl_2), nm: 389.5, 518.0, 552.5. Anal. Calc. for $C_{39}H_{49}N_4OCo\cdot 0.5H_2O$: C, 71.21; H, 7.66; N, 8.52. Found: C, 71.66; H, 7.56; N, 8.69.

12b: ^{1}H-NMR ($CDCl_3$): δ −3.21, −2.84 (dd × 2, 1H × 2, CO*CH_2*–), −1.51 (d, 3H, COCH$_2$CH*CH_3*–), −1.08 (m, 1H, COCH$_2$CH(CH$_3$)*CH_2*–), −0.90 (m, 1H, COCH$_2$*CH*–), 0.51 (m, 2H, COCH$_2$CH(CH$_3$)CH$_2$*CH_2*–), 1.09, 1.37 (s × 2, 3H × 2, COCH$_2$CH(CH$_3$)CH$_2$CH$_2$CH=C(*CH_3*)$_2$), 1.86 (t, 24H, CH_2*CH_3*), 4.02 (m, 16H, *CH_2*CH_3), 4.23 (t, 1H, COCH$_2$CH(CH$_3$)CH$_2$CH$_2$*CH*=C(CH$_3$)$_2$), 10.05 (s, 4H, *meso*-H). IR (KBr), cm^{-1}: 1722 [ν(C=O)]. UV–vis (CH_2Cl_2), nm: 389.5, 518.0, 552.5. Anal. Calc. for $C_{46}H_{61}N_4OCo\cdot 1.5H_2O$: C, 71.57; H, 8.36; N, 7.26. Found: C, 71.79; H, 8.35; N, 7.28.

3.5. Reaction of Co^{III} porphyrin with propanal in the presence of t-BuOOH

In a two necked round-bottomed 50-ml flask equipped with a septum and a two-way cock connected to an argon line, **1a** (42.3 mg, 0.060 mmol) and a magnetic stirrer were placed under an argon atmosphere. To the flask, benzene (15 ml) and propanal (0.5 ml) were added through a syringe. Then, *t*-BuOOH (10 μl) was added through a micro syringe every 5 min (three times). The resulting mixture was evaporated with a rotary evaporator, and the residue was washed with methanol. **5a** was given in a 68% yield.

3.6. Intramolecular cyclization of aldehyde with C–C multiple bond by combination of Co^{II} porphyrin and t-BuOOH

The reactions were performed according to the method of Section 3.4.

13a: ^{1}H-NMR ($CDCl_3$): δ −4.43 (m, 1H, axial β-H), −3.97, −3.30 (dd × 2, 1H × 2, axial α-H), −0.34, 1.25 (dd × 2, 1H × 2, axial γ-H), 6.27 (d, 1H, Naph–H), 7.04 (t, 1H, Naph–H), 7.14 (t, 1H, Naph–H), 7.32 (d, 1H, Naph–H), 7.36 (d, 1H, Naph–H), 7.71 (m, 12H, *m*- and *p*-Ph–H), 8.09 (br, 8H, *o*-Ph–H), 8.41 (d, 1H, Naph–H), 8.84 (s, 8H, β-Py–H). IR (KBr), cm^{-1}: 1666 [ν(C=O)]. UV–vis (CH_2Cl_2), nm: 408.0, 530.0. Anal. Calc. for $C_{58}H_{39}N_4Co\cdot 3H_2O$: C, 76.98; H, 5.01; N, 6.19. Found: C, 76.70; H, 5.04; N, 6.23.

13b: ^{1}H-NMR ($CDCl_3$): −4.95 (m, 1H, axial β-H), −4.54, −4.00 (dd × 2, 1H × 2, axial α-H), −0.70, 0.53 (dd × 2, 1H × 2, axial γ-H), 1.86 (t, 24H, CH_2*CH_3*), 4.01 (m, 16H, *CH_2*CH_3), 6.12 (d, 1H, Naph–H), 7.01 (m, 1H, Naph–H), 7.05 (m, 1H, Naph–H), 7.27 (d, 2H, Naph–H), 8.27 (d, 1H, Naph–H), 10.09 (s, 4H, *meso*-H). IR (KBr), cm^{-1}: 1668 [ν(C=O)]. UV–vis (CH_2Cl_2), nm: 389.5, 518.0, 552.5. Anal. Calc. for $C_{50}H_{55}N_4O_2Co\cdot H_2O$: C, 73.15; H, 7.00; N, 6.83. Found: C, 73.39; H, 6.88; N, 6.97.

14b: ^{1}H-NMR ($CDCl_3$): −5.28 (m, 1H, axial β-H), −4.62 (t, 1H, axial α-H), −4.03 (d, 1H, axial α-H), −0.55, 0.17 (dd × 2, 1H × 2, axial γ-H), 1.85 (t, 24H, CH_2*CH_3*), 4.01 (m, 16H, *CH_2*CH_3), 6.04 (d, 1H, Ph–H), 6.29 (t, 1H, Ph–H), 6.69 (dd, 1H, Ph–H), 6.84 (t, 1H, Ph–H), 10.09 (s, 4H, *meso*-H). IR (KBr), cm^{-1}: 1686 [ν(C=O)]. UV–vis (CH_2Cl_2), nm: 389.5, 518.0, 552.5. Anal. Calc. for $C_{46}H_{53}N_4Co\cdot 2.5H_2O$: C, 72.13; H, 7.63; N, 7.32. Found: C, 72.05; H, 7.50; N, 7.28.

15b: ^{1}H-NMR ($CDCl_3$): −4.78 (m, 1H, axial β-H), −4.59, −3.74 (dd × 2, 1H × 2, axial α-H), −2.68, −0.89 (dd × 2, 1H × 2, axial γ-H), 1.89 (m, 24H, CH_2*CH_3*), 4.01 (m, 16H, *CH_2*CH_3), 6.38 (d, 1H, Ph–H), 6.60 (m, 2H, Ph–H), 6.92 (m, 1H, Ph–H), 10.09 (s, 4H, *meso*-H). IR (KBr), cm^{-1}: 1708 [ν(C=O)]. UV–vis (CH_2Cl_2), nm: 389.5, 518.0, 552.5. Anal.Calc. for $C_{46}H_{53}N_4OCo\cdot H_2O$: C, 73.19; H, 7.34; N, 7.42. Found: C, 72.63; H, 7.32; N, 7.28.

16a: ^{1}H-NMR ($CDCl_3$): −4.04, −3.03 (dd × 2, 1H × 2, axial α-H), −3.53 (m, 1H, axial β-H), −1.22 (dd, 1H, axial γ-H), 0.45 (t, 1H, axial γ-H), 5.86 (d, 1H, Py–H), 5.92 (m, 1H, Py–H), 6.13 (m, 1H, Py–H), 7.73 (m, 12H, m, *p*-Ph–H), 8.09 (br, 8H, *o*-Ph–H), 8.85 (m, 8H, β-Py–H). IR (KBr), cm^{-1}: 1686 [ν(C=O)]. UV–vis (CH_2Cl_2), nm: 408.0, 530.0. Anal. Calc. for $C_{52}H_{36}N_5OCo\cdot 0.2H_2O$: C, 77.16; H, 4.53; N, 8.65. Found: C, 77.23; H, 4.35; N, 8.54.

16b: ^{1}H-NMR ($CDCl_3$): −4.58, −3.77 (dd × 2, 1H × 2, axial α-H), −4.13 (m, 1H, axial β-H), −1.76 (dd, 1H, axial γ-H), 0.07 (t, 1H, axial γ-H), 1.88 (m, 24H, CH_2*CH_3*), 4.02 (m, 16H, *CH_2*CH_3), 5.69 (m, 1H, Py–H), 5.76 (m, 1H, Py–H), 5.93 (m, 1H, Py–H), 10.10 (s, 4H, *meso*-H). IR (KBr), cm^{-1}: 1698 [ν(C=O)]. UV–vis (CH_2Cl_2), nm: 389.5, 518.0, 552.5. Anal. Calc. for $C_{44}H_{52}N_5OCo\cdot H_2O$: C, 71.04; H, 7.32; N, 9.42. Found: C, 70.79; H, 7.55; N, 9.13.

17b: ^{1}H-NMR ($CDCl_3$): δ −5.01 (m, 1H, axial β-H), −4.67, −3.90 (dd × 2, 1H × 2, axial α-H), −3.05, −1.81 (m × 2, 1H × 2, axial γ-H), 1.18, 2.00 (m × 2, 1H × 2, axial δ-H), 1.88 (m, 24H, CH_2*CH_3*), 4.00 (m, 16H, *CH_2*CH_3), 5.53 (m, 1H, Py–H), 5.90 (m, 2H, Py–H), 10.04 (s, 4H, *meso*-H).

18b: ^{1}H-NMR ($CDCl_3$): δ 0.47 (dd, 1H, Py–H), 1.73 (t, 2H, N–CH_2), 1.85 (t, 24H, CH_2CH_3), 3.99 (m, 16H, CH_2CH_3), 4.2–4.7 (m, 6H, N–$CH_2CH_2CH{=}CH_2$ and Py–H), 5.01 (t, 1H, Py–H), 9.97 (s, 4H, *meso*-H).

19a: ^{1}H-NMR ($CDCl_3$): δ 0.51 (s, 3H, N–$CH_2C(Me){=}CH_2$), 1.06 (dd, 1H, Py–H), 2.30 (s, N–$CH_2C(Me){=}CH_2$), 3.03, 3.94 (s × 2, 1H × 2, N–$CH_2C(Me){=}CH_2$), 4.90 (dd, 1H, Py–H), 5.32 (t, 1H, Py–H), 7.70 (m, 12H, *m*-, *p*-Ph–H), 8.07 (m, 8H, *o*-Ph–H), 8.79 (m, 8H, β-Py–H). IR (KBr), cm^{-1}: 1682 [ν(C=O)]. UV–vis (CH_2Cl_2), nm: 408.0, 530.0. Anal.Calc. for $C_{53}H_{38}N_5OCo$: C, 77.64; H, 4.67; N, 8.54. Found: C, 77.79; H, 4.74; N, 8.75.

3.7. Photolysis of **13b** by a xenon lamp

A solution of **13b** (97.0 mg) in deoxygenated benzene (20 ml) was irradiated using a xenon lamp for 4 h under argon. The solution was filtered to remove the generated $OEPCo^{II}$. The filtrate was evaporated under vacuum, and the residue was separated by gel permeation chromatography to give **20** (22.0 mg, 87%).

20: ^{1}H-NMR ($CDCl_3$): δ 2.12 (s, 3H, CH_3), 7.47 (d, 1H, Naph–H), 7.62 (t, 1H, Naph–H), 7.77 (t, 1H, Naph–H), 7.86 (s, 1H, O–CH=), 7.89 (d, 1H, Naph–H), 8.05 (d, 1H, Naph–H), 10.10 (d, 1H, Naph–H). IR (KBr), cm^{-1}: 1644 [ν(C=O)]. Anal. Calc. for $C_{14}H_{10}O_2$: C, 79.98; H, 4.79. Found: C, 79.68; H, 4.78. Mass (EI), m/z: 210 (M^+).

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