Metallation of Ethers with Cobalt(II) Porphyrins Induced by Reductive Decomposition of Hydroperoxides

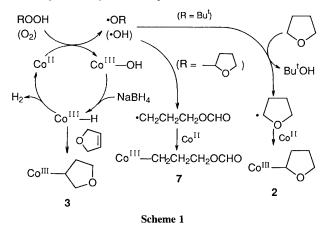
Jun-ichiro Setsune,* a Yoshihiro Ishimaru, a Tohru Moriyama and Teijiro Kitao b

^a Department of Chemistry, Faculty of Science, Kobe University, Nada, Kobe 657, Japan

^b Department of Applied Chemistry, College of Engineering, University of Osaka Prefecture, Sakai, Osaka 591, Japan

Treatment of cobalt(II) porphyrins with hydroperoxides and an excess of NaBH₄ effectively gave σ -alkylcobalt(III) porphyrins, the σ -alkyl groups of which were derived from ethers used as solvents.

Three methods for the formation of a Co^{III}–C bond utilizing Co^{III}, Co^{II} and Co^I complexes as starting materials are known for a number of macrocyclic cobalt complexes¹ including cobalt porphyrins.² Although the combination of organic radicals and Co^{II} complexes occurs readily, and is the process occurring in coenzyme B₁₂-dependent biochemical reactions,³



the direct alkylation of Co^{II} is not widely applicable owing to the limitation on the reaction conditions required to generate organic radicals.⁴ Here, we report that ethers are regioselectively metallated at the α -position through a quite convenient procedure using Co^{II} porphyrin, NaBH₄ and hydroperoxide (or O₂).

When a mixture of (oep)Co^{II} (oep = octaethylporphyrin dianion) **1** and NaBH₄ (*ca.* 30–50 equiv.) was stirred in purified tetrahydrofuran (THF) at room temperature under argon containing a limited amount of air, the α -methylene position of THF was metallated in 14 h to give σ -(tetrahydrofuran-2-yl)Co^{III} (oep) **2**[†] in 70% yield after recrvstallization

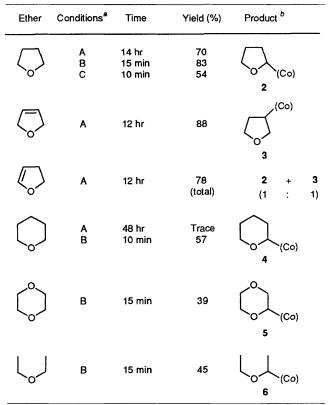
[†] Selected ¹H NMR data (CDCl₃; α , β , γ , δ are positions relative to cobalt): **2**, δ 10.00 (porph. *meso*-H), 4.00 (porph. CH₂Me), 1.85 (porph. CH₂Me); -1.99 (br, 1H, α -H), -4.95 (m, 1H, β -H), -3.97 (m, 1H, β -H), -2.83 (m, 1H, γ -H), -0.78 (m, 1H, γ -H), -0.79 (m, 1H, γ -H) and 0.85 (m, 1H, γ -H).

3, δ 10.12 (porph. *meso*-H), 4.02 (porph. CH₂Me), 1.87 (porph. CH₂Me); -4.13 (br, 1H, α -H), -5.80 (m, 1H, β -H), -3.60 (m, 1H, β -H), -3.78 (t, 1H, β -H), and -1.81 (dd, 1H, β -H).

β-H), -3.78 (t, 1H, β-H), and -1.81 (dd, 1H, β-H). 7, δ 10.06 (porph. *meso*-H), 4.01 (porph. *CH*₂Me), 1.87 (porph CH₂Me); -4.37 (br, 2H, α-H), -4.93 (quint., 2H, β-H), 0.91 (t, 2H, γ-H), and 6.85 (s, 1H, δ-H).

J. CHEM. SOC., CHEM. COMMUN., 1991

Table 1 Oxidative metallation of ethers with Co porphyrins



^a Conditions: A; O₂, Ar (0.01–0.1%); B, Ar, Bu^tOOH (1–2 equiv.); C, Air. ^b (Co) = (oep)Co.

from benzene-methanol. This reaction was greatly accelerated, reaching completion within 15 min, by the addition of tert-butyl hydroperoxide (1.2 equiv.) or under air, resulting in 83 or 54% yields of 2, respectively. While a similar reaction in tetrahydropyran under argon containing a limited amount of air (0.01-0.1%) did not take place at all even after 48 h, addition of ButOOH (1.2 equiv.) caused metallation within 15 min, to give σ -(tetrahydropyran-2-yl)Co^{III}(oep) 4 in 57% yield. 2,5-Dihydrofuran did not undergo this oxidative metallation at the α -position under the standard reaction conditions. Instead, facile hydrometallation⁵ across the carboncarbon double bond occurred to afford σ-(tetrahydrofuran-3yl)Co^{III}(oep) 3 in 88% yield. Furthermore, a similar reaction of 1 with 2,3-dihydrofuran gave rise to a 1:1 mixture of 2 and 3 in 78% total yield. The fact that complex 2 was not formed from 2,5-dihydrofuran but was from 2,3-dihydrofuran by hydrometallation provides strong evidence in support of the tetrahydrofuran-2-yl structure for complex 2. The ButOOHpromoted reaction in 1,4-dioxane and diethyl ether took place smoothly to produce σ -(1,4-dioxan-2-yl)Co¹¹¹(oep) 5 and σ -(1-ethoxyethyl)Co^{III}(oep) 6 in 39 and 45% yield, respectively. The relatively low yields of 5 and 6 are mainly due to their thermal instability.

Espenson showed that a *tert*-butoxyl radical which is generated by the reductive decomposition of Bu^tOOH by Co^{II} complexes undergoes β -scission and then the resulting methyl radical is trapped by Co^{II} complexes.^{4c} As shown in Scheme 1, the *tert*-butoxyl radical may be responsible for hydrogen abstraction from the α -position of ethers under the present reaction conditions, which also allow efficient regeneration of Co^{II} from (oep)Co^{III}–OH, thus leading to excellent yields of organocobalt(III) porphyrins. Hydrometallation of alkenes and alkynes takes place under essentially the same conditions.⁵ Although addition of NaBH₄ to a mixture of (oep)-Co^{III}Br **9** and an alkene did result in hydrocobaltation in competition with simple reduction,⁵ addition of NaBH₄ to **9** in THF only led to quantitative generation of **1**. This fact precludes the possibility that the hydrogen radical formed from a hydridocobalt(III) porphyrin intermediate is responsible for the hydrogen abstraction from the ethers, whereas hydrometallation would be initiated by the homolytic cleavage of the Co^{III} -H bond.

In accord with this mechanism, when the complex 1 and an excess of NaBH₄ were added to aged THF and 2-methyltetrahydrofuran containing 2-hydroperoxy derivatives under argon, the 2-hydroperoxy derivatives were similarly decomposed to generate alkoxyl radicals, which underwent β scission and then combined with 1 to give σ -(3-acyloxypropyl)Co^{III}(oep) 7 and σ -(3-acetoxypropyl)Co^{III}(oep) 8 in 89 and 47% yields, respectively (see Scheme 1). The spectral properties of 8 were identical with those of the material obtained from the reaction of Na⁺[(oep)Co^I]⁻ with 3bromopropyl acetate. It was claimed that nucleophilic ring opening of tetrahydrofuran as well as of ethylene oxide occurred on reaction with vitamin B_{12s} to yield a σ -(4hydroxybutyl)CoIII complex on the basis of UV-VIS evidence.⁶ While ethylene oxide was successfully cleaved also by Co^I model complexes,¹ the cleavage of tetrahydrofuran has never been reproduced by B_{12s} and synthetic model complexes. The present result suggests that the previously reported reaction of vitamin B_{12s} is not with tetrahydrofuran itself but with 2-hydroperoxytetrahydrofuran.

Mechanistically analogous direct metallation of α -carbon atoms of alcohols and ethers is known to proceed by the combination of a Cr^{II} ion and hydrogen peroxide in aqueous solution.⁷ Although Schrauzer reported that alcohols and ethers as well as alkanes and carbonyl compounds were metallated with vitamin B_{12r} in the presence of vanadium(*III*) salts and oxidizing agents,⁸ their α -positions were not metallated in contrast to the regioselective α -metallation observed here.

In conclusion, this work shows that organic radicals generated by Fenton-type oxidation of ethers may be utilized to prepare σ -(1-alkoxyalkyl)Co^{III} porphyrins. Cobalt-catalysed oxidation of organic compounds based on the present system is now being studied in our laboratory.

This work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, and Culture, Japan and a grant from Nagase Science and Technology Foundation, Japan.

Received, 10th January 1991; Com. 1/00128K

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