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

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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

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^H 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 a-(tetrahydrofuran-2-yl)CoIII (oep) **2t** in 70% yield after recrvstallization

 \dagger Selected ¹H NMR data (CDCl₃; $\alpha, \beta, \gamma, \delta$ 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 $(m, 1H, \beta-H), -2.83$ $(m, 1H, \gamma-H), -0.78$ $(m, 1H, \gamma-H), -0.79$ $(m,$ lH, $γ$ -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, $(\beta-H)$, -3.78 (t, 1H, $\beta-H$), and -1.81 (dd, 1H, $\beta-H$).

7, 6 10.06 (porph. meso-H), 4.01 (porph. CH2Me), 1.87 (porph CH₂Me); -4.37 (br, 2H, α -H), -4.93 (quint., 2H, β -H), 0.91 (t, 2H, y-H), and 6.85 **(s,** 1H, 6-H).

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Table 1 Oxidative metallation of ethers with Co porphyrins

a Conditions: A; O_2 , Ar $(0.01-0.1\%)$; B, Ar, Bu^tOOH (1-2 equiv.); C, Air. \mathfrak{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 Bu'OOH (1.2 equiv.) caused metallation within 15 min, to give **a-(tetrahydropyran-2-yl)CoIII(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)CoIII(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 a-(1-ethoxyethyl)CoIII(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(II1) porphyrins. Hydrometallation of alkenes and alkynes takes place under essentially the same conditions.⁵ Although addition of NaBH₄ to a mixture of (oep)-CoIIIBr **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(II1) 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 $Na+[(oep)Co^T]$ 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)Co^{III} 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 CrII 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. Cobaltcatalysed oxidation of organic compounds based on the present system is now being studied in our laboratory.

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