

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

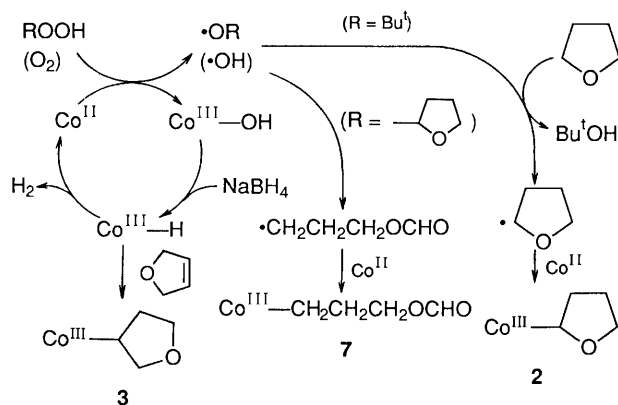
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Treatment of cobalt(II) porphyrins with hydroperoxides and an excess of NaBH<sub>4</sub> effectively gave  $\sigma$ -alkylcobalt(III) porphyrins, the  $\sigma$ -alkyl groups of which were derived from ethers used as solvents.

Three methods for the formation of a Co<sup>III</sup>-C bond utilizing Co<sup>III</sup>, Co<sup>II</sup> and Co<sup>I</sup> complexes as starting materials are known for a number of macrocyclic cobalt complexes<sup>1</sup> including cobalt porphyrins.<sup>2</sup> Although the combination of organic radicals and Co<sup>II</sup> complexes occurs readily, and is the process occurring in coenzyme B<sub>12</sub>-dependent biochemical reactions,<sup>3</sup>



Scheme 1

the direct alkylation of Co<sup>II</sup> is not widely applicable owing to the limitation on the reaction conditions required to generate organic radicals.<sup>4</sup> Here, we report that ethers are regioselectively metallated at the  $\alpha$ -position through a quite convenient procedure using Co<sup>II</sup> porphyrin, NaBH<sub>4</sub> and hydroperoxide (or O<sub>2</sub>).

When a mixture of (oep)Co<sup>II</sup> (oep = octaethylporphyrin dianion) **1** and NaBH<sub>4</sub> (ca. 30–50 equiv.) was stirred in purified tetrahydrofuran (THF) at room temperature under argon containing a limited amount of air, the  $\alpha$ -methylene position of THF was metallated in 14 h to give  $\sigma$ -(tetrahydrofuran-2-yl)Co<sup>III</sup> (oep) **2**<sup>†</sup> in 70% yield after recrystallization

<sup>†</sup> Selected <sup>1</sup>H NMR data (CDCl<sub>3</sub>;  $\alpha, \beta, \gamma, \delta$  are positions relative to cobalt): **2**,  $\delta$  10.00 (porph. *meso*-H), 4.00 (porph. CH<sub>2</sub>Me), 1.85 (porph. CH<sub>2</sub>Me); -1.99 (br, 1H,  $\alpha$ -H), -4.95 (m, 1H,  $\beta$ -H), -3.97 (m, 1H,  $\beta$ -H), -2.83 (m, 1H,  $\gamma$ -H), -0.78 (m, 1H,  $\gamma$ -H), -0.79 (m, 1H,  $\gamma$ -H) and 0.85 (m, 1H,  $\gamma$ -H).

**3**,  $\delta$  10.12 (porph. *meso*-H), 4.02 (porph. CH<sub>2</sub>Me), 1.87 (porph. CH<sub>2</sub>Me); -4.13 (br, 1H,  $\alpha$ -H), -5.80 (m, 1H,  $\beta$ -H), -3.60 (m, 1H,  $\beta$ -H), -3.78 (t, 1H,  $\beta$ -H), and -1.81 (dd, 1H,  $\beta$ -H).

**7**,  $\delta$  10.06 (porph. *meso*-H), 4.01 (porph. CH<sub>2</sub>Me), 1.87 (porph. CH<sub>2</sub>Me); -4.37 (br, 2H,  $\alpha$ -H), -4.93 (quint., 2H,  $\beta$ -H), 0.91 (t, 2H,  $\gamma$ -H), and 6.85 (s, 1H,  $\delta$ -H).

