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A NEW ORGANOCOBALOXIME WITH AN ACETOXY SUBSTITUTED TERTIARY CARBON TO COBALT BOND, DERIVED FROM ENOLPYRUVIC ACID *

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Summary

The reaction of pyridinecobaloxime(II) with methyl 2-acetoxyacrylate under H_2 atmosphere leads to a novel organocobaloxime containing an acetoxy substituted tertiary α-carbon. The reaction occurs via addition of the hydridocobaloxime across the double bond.

Introduction

The synthesis, properties and reactions of organocobaloximes, $RCo(Hdmg)_2B$, where $Hdmg^-$ is the monoanion of dimethylglyoxime, B is a base (e.g. pyridine, t-phosphine) and R is an alkyl, aryl or substituted alkyl or aryl group, have been extensively studied and documented [1–10]. The major synthetic routes include (**A**) the reaction of alkyl halides with cobaloxime(I) supernucleophiles [1], (**B**) of olefins with cobaloxime(II) derivatives in H_2 atmosphere [1,2], and (**C**) of alkyl halides with cobaloxime(II) derivatives in an inert atmosphere [3].

In the wide variety of known organocobaloximes the carbon atom bonded to cobalt is either primary or secondary. Compounds with t-carbon to cobalt bonds are rare among cobaloxime derivatives. The known examples are summarized in Table 1. As can be seen, synthetic route **A** or **C** was used in most cases, however, route **B** is feasible too with the 2-cyanoisopropyl derivative [2].

We now report the synthesis of a new organocobaloxime, derived from enolpyruvic acid, with a t-carbon to cobalt bond, via what is apparently the hydride route **B**.

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* Dedicated to Professor Jack Halpern on the occasion of his 60th birthday.

TABLE 1

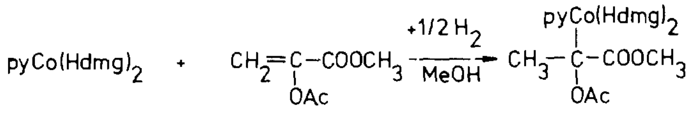
THE KNOWN EXAMPLES OF ORGANOCOBALOXIMES WITH TERTIARY α-CARBON ATOMS [a]

R	Method of synthesis	Ref.
$(CH_3)_2CCN$	**A,B**	1,2
1-Methyl-2,2-diphenylcyclopropyl	**A**	11
t-Adamantyl	**A**	12
t-Norbornyl	**A**	12
$CH_3C(CH_3)CH{=}CH_2$	**A**	13
$CH_3C(C_2H_5)C{\equiv}CH$	**A**	13
$Cl_2CC(O)OCH_3$	**C**	14
Cl_2CCN	**C**	14
Cl_3C	**C**	14,15
Br_2CPh [b]	–	16

[a] Cobaloximes containing $Co{-}C{=}CH_2$ units are not included. [b] Suggested intermediate in the reaction of organocobaloximes.

Results and discussion

Olefincarboxylic acids and their esters are known to undergo hydrogenation in the presence of cobaloxime derivatives [2], but no organocobaloxime could be isolated from the reaction mixture, although their hydrogenation should necessarily involve an organocobaloxime intermediate. We have now found that the enol ester of methyl pyruvate (I) forms a relatively stable organocobaloxime when it is treated with H_2 in the presence of pyridinecobaloxime(II) under neutral conditions:



$$\mathrm{pyCo(Hdmg)_2} + \mathrm{CH_2{=}}\underset{\mathrm{OAc}}{\mathrm{C}}\mathrm{{-}COOCH_3} \xrightarrow[\mathrm{MeOH}]{+1/2\,\mathrm{H_2}} \mathrm{CH_3{-}}\overset{\mathrm{pyCo(Hdmg)_2}}{\underset{\mathrm{OAc}}{\mathrm{C}}}\mathrm{{-}COOCH_3} \qquad (1)$$

(I) (II)

The structure of II has been fully confirmed by ^1H NMR spectroscopy and elemental analysis (cf. Experimental). II is believed to be the first organocobaloxime with an acetoxy-substituted tertiary α-carbon. ^1H NMR investigations have revealed that II is slowly decomposed in solution via hydridocobaloxime elimination, thus regenerating the starting materials. This behavior is well known among organocobaloxime derivatives. It should be noted that the attempted synthesis of analogous organocobaloximes from acetylacetone and ethyl acetoacetate has met with failure. Stabilization of the enol form seems to be a necessary requirement for the formation of stable organocobaloximes from similar compounds.

The cobaloxime(I) route **A**, involving the reaction of I with $pyCo(Hdmg)_2$ in an alkaline $NaBH_4$ solution leads to a so far unidentified product, which, however, is different from II.

Experimental

All experiments were carried out in dim light; the reaction flasks and NMR tubes were covered with aluminium foil whenever possible. Commercially available materials were used throughout, except for methyl 2-acetoxyacrylate, which was a gift from Richter Chemical Works, Ltd., Budapest.

Methylacetoxycarbomethoxymethyl(pyridine)cobaloxime (II)

To a stirred mixture of 5.8 g (0.05 mol) dimethylglyoxime, 2.0 g (0.05 mol) finely powdered NaOH and 2.5 ml (0.03 mol) pyridine in 100 ml MeOH, was added under H_2 atmosphere 9.15 g (0.025 mol) $Co(ClO_4)_2 \cdot 6H_2O$ dissolved in 20 ml MeOH. After about 2 min stirring, 4.3 g (0.03 mol) methyl 2-acetoxyacrylate (I) was added, and the solution was stirred until the H_2-uptake ceased (ca. 230 ml hydrogen was consumed). The mixture was then cooled in ice, diluted with 200 ml water, stirred for 30 min, filtered off and washed with water. Recrystallization from methanol/water containing 1 ml pyridine. Yield: 6.0 g, 46.7%. (A second crop of organocobaloxime can be obtained by concentrating the filtrate in vacuum.) Anal. Found: C, 43.95; H, 5.50; N, 13.90. $C_{19}H_{28}N_5O_8Co$ (513.39) calcd.: C, 44.45; H, 5.50, N, 13.64%.

^1H NMR ($CDCl_3$, δ): 1.0 ppm (s, 3H, CH_3), 1.88 ppm (s, 3H, OAc), 2.23 ppm (s, 12H, $4CH_3$), 3.55 ppm (s, 3H, $COOCH_3$), 7.2–8.7 ppm (m, 5H, pyridine), 17.7 ppm (broad s, 2H, OH...O).

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