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Preliminary communication

Stereochemistry of the photochemical and thermal insertion of oxygen into the carbon–cobalt bond of alkyl(pyridine)cobaloximes

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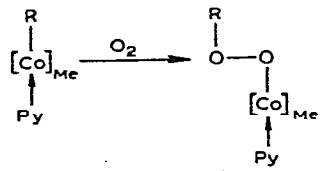
SUMMARY

The insertion of molecular oxygen into the carbon–cobalt bond of optically active alkyl(pyridine)cobaloximes proceeds with complete loss of configuration at the asymmetric carbon center.

Oxygen has been shown to insert into the carbon–cobalt bond of alkyl(pyridine)-cobaloximes to yield stable 1/1 dioxy adducts[1].



The insertion of oxygen proceeds either thermally in the dark or photochemically with benzylic or allylic derivatives[2], but alkyl compounds do not react at moderate temperatures except when irradiated[3].

In two systems, the insertion of oxygen has been reported to proceed stereospecifically at the carbon center. With *trans*-2-hydroxy-1-indanyl(pyridine)cobaloxime, retention of configuration was observed but results with the *cis* isomer were not included[4]. Optically active 2-hydroxy-1-phenethyl(pyridine)cobaloxime was reported to react with oxygen to form optically active 2-hydroxy-1-phenethyldioxy(pyridine)cobaloxime[1]. If this insertion of oxygen were confirmed to be a stereospecific reaction, it would be very interesting and have important implications. However, we were unable to detect any optical activity in the products from two distinctly different optically active complexes; 2-butyl-

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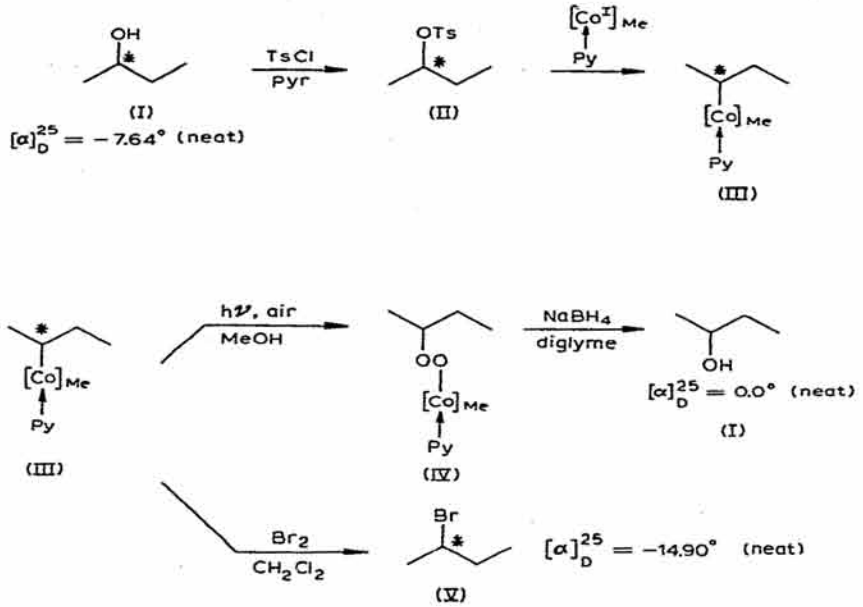
(pyridine)cobaloxime, a simple alkylcobaloxime, and 2-hydroxy-1-phenethyl(pyridine)-cobaloxime, possessing α-phenyl and β-hydroxy functionalities. Both compounds were reacted in the presence of light*, and the latter was also reacted thermally in the dark.

Four mmoles of optically active 2-butyl(pyridine)cobaloxime[6] III in 500 ml of methanol with air passing through the solution was photolyzed at −3° for 21 h. Isolation by column chromatography (silica gel, elution with chloroform/methanol/ethyl acetate 1/1/1) gave 3 mmoles of pure dioxy product IV. Compound IV was cleaved with excess sodium borohydride[2] to give racemic 2-butanol in 61% yield. It was determined that loss of stereochemistry did not occur during reduction by adding optically active 2-butanol to the reaction mixture and recovering active 2-butanol after reduction. The 2-butyl(pyridine)-cobaloxime was shown to be optically active by bromodemetallation (see below)[6]. The full sequence of reactions is as given in Scheme 1.



Scheme 1

Optically active 2-hydroxy-1-phenethylcobaloxime[1] (1.63 mmoles) was photolyzed for 4 h at −5° in 250 ml of chloroform with air passing through the solution (only a negligible extent of reaction occurs in this time without light). The yield of dioxy product was quantitative. Reduction with excess lithium aluminum hydride in THF (sodium borohydride gave little or no yield of phenyl-1,2-ethanediol) gave racemic phenyl-1,2-ethanediol in 30% yield. As before, addition of optically active phenyl-1,2-ethanediol to the reduction mixture yielded active diol. The starting 2-hydroxy-1-phenethyl(pyridine)-cobaloxime was demonstrated to be optically active by measuring its rotation on a Bendix 143-A (Faraday effect) polarimeter. Samples with 46% transmittance gave definite

*775 Watts visible light filtered through $CuSO_4$ as described in ref. 5.

rotations, but the values were not highly reproducible*. Efforts are underway to obtain a reliable value and the reporting of a rotation will be deferred. The rotation of the dioxy product was found to be zero.

For the stereochemical study of the thermal (dark) insertion of oxygen, 1.84 mmoles of optically active 2-hydroxy-1-phenethyl(pyridine)cobaloxime in 85 ml methylene chloride was treated under a positive pressure of oxygen. It was allowed to proceed for seven hours in the dark at 20°. Isolation of the dioxy product, followed by reduction, produced racemic phenyl-1,2-ethanediol.

The above results are consistent with a mechanism involving generation of an alkyl radical at some point during the insertion process. These radicals, being achiral, would account for the observed loss of stereochemistry during the reactions.

There have been four reports, including the current one, concerning rotations of optically active cobaloximes. No rotation was observed for 2-butyl(pyridine)cobaloxime, known to be optically active by independent means[6]. With a closely related compound, 2-octyl(pyridine)cobaloxime, Dodd and Johnson[7] routinely reported a rotation. Gaudemer *et al.*[2] reported observing rotations with both 2-hydroxy-1-phenethyl(pyridine)cobaloxime and the corresponding dioxy product. However, the solutions of both compounds were concentrated and, at least in the latter case, essentially opaque to light. This would give false or "ghost" rotations. Future work in this area will hopefully resolve these differences.

ACKNOWLEDGMENT

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*The instrument manual specifies that meaningful rotation can be obtained with as little as 10% transmittance at 589 nm. Racemic 2-hydroxy-1-phenethyl(pyridine)cobaloxime gave no rotation at the same concentration so the rotation seen with the optically active compound is real.