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Preliminary communication

STEREOCHEMICAL STUDY OF THE REACTION OF MOLECULAR OXYGEN WITH ALKYLCOBALOXIMES

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Summary

The insertion of molecular oxygen into the cobalt—carbon bond of a secondary alkylcobaloxime takes place with racemisation.

Alkylcobaloximes *a** have been shown [1] to react with molecular oxygen to give the alkyldioxycobaloximes *b* produced by insertion of O_2 into the cobalt—carbon bond of the organocobalt complex (eq. 1):

$$\underset{(a)}{RCo(dmgH)_2Py} + O_2 \rightarrow \underset{(b)}{ROOCo(dmgH)_2Py} \quad (1)$$

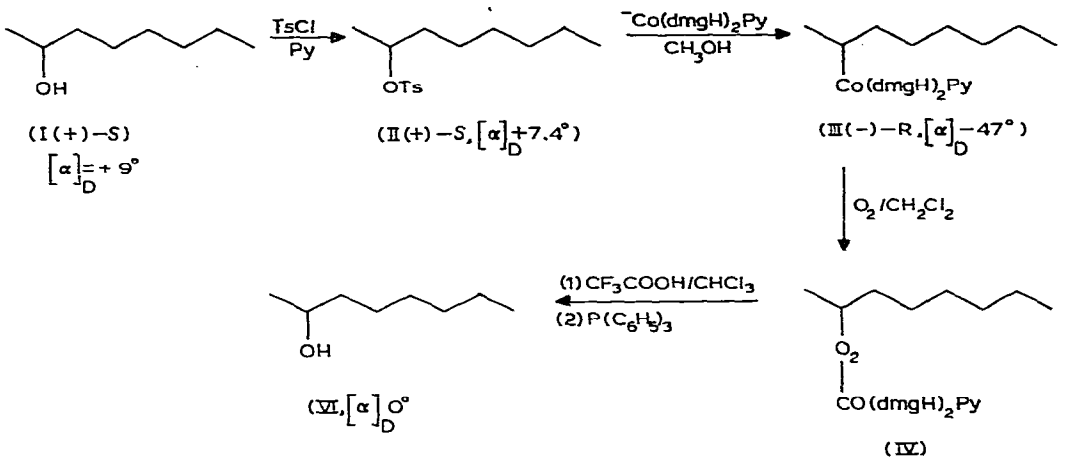
Several ESR [2], kinetic [3] and stereochemical [4,5] studies of the mechanism of this reaction have been reported. In particular there have been two reports [4,5] indicating that the reaction occurs with racemisation at the α-carbon. However, the reaction sequence used to establish the stereochemistry did not give an unambiguous answer because it involved the sodium borohydride reduction of the alkyldioxycobaloxime, a reaction which, as we have shown [6], yields as the main primary product the corresponding aldehyde or ketone, which is subsequently reduced to the alcohol by the excess borohydride.

In this note, we report the results of the stereochemical study of the reaction using a non-equivocal sequence of reactions (Scheme 1).

(−)-*R*-(2-octyl)pyridine cobaloxime (III) $[\alpha]_D^{25}$ −47° (*c* 1, ethanol) was prepared from cobaloxime (I) and (+)-*S*-2-octyl-tosylate (II) $[\alpha]_D^{25}$ +7.4° (Litt.: $[\alpha]_D^{20}$ 7.44°) [7]. A solution of III (20 mmol l^{-1} in CH_2Cl_2) was irradiated for 2 h at −3°C by two 300 W tungsten lamps.

The course of the reaction was followed by TLC and ^1H NMR spectroscopy.

*R = alkyl radical, dmgH = dimethyl glyoximate monoanion, Py = pyridine.



SCHEME 1

The reaction mixture was chromatographed on a silica gel column (CC7; solvent: ethyl acetate) in order to separate (2-octyl)dioxypyridinecobaloxime (IV) from unreacted III. The pure compound IV (0.47 mmol) was dissolved into 2.7 ml of $CHCl_3$ containing 4% (v/v) CF_3COOH [8] (1.45 mmol). 2-Octyl hydroperoxyde (V) was not isolated but treated in situ with 0.95 mmol $P(C_6H_5)_3$. 2-Octanol (VI), which was isolated from the reaction mixture by distillation under vacuum (70°C, 1 mmHg) was characterised by its ^1H NMR spectrum. It showed no optical rotation.

The conditions used for the conversion of IV into the hydroperoxyde V are very mild and cannot produce racemisation at the α-carbon. The next step, reduction of V with $P(C_6H_5)_3$ to 2-octanol-2 (VI) has been shown to occur with complete retention of configuration [9]. Consequently, the fact that racemic 2-octanol is obtained indicates that insertion of O_2 into the Co—C bond of III occurs with racemisation. We have confirmed that III is not partially or totally racemised during the reaction; unreacted III recovered from the reaction mixture showed the same rotation as an authentic sample.

References

1 C. Fontaine, K.N.V. Duong, C. Merienne, A. Gaudemer and C. Giannotti, J. Organometal. Chem., 38 (1972) 167.
2 C. Giannotti, G. Merle and J.R. Bolton, J. Organometal. Chem., 99 (1975) 145.
3 C. Bied-Charreton and A. Gaudemer, J. Organometal. Chem., 124 (1977) 299.
4 F.R. Jensen and R. Kiskis, J. Organometal. Chem., 49 (1973) C46.
5 H. Shinozaki and M. Tada, Chem. Ind., 4 (1975) 178.
6 C. Bied-Charreton and A. Gaudemer, J. Amer. Chem. Soc., 98 (1976) 3997.
7 A. Streitwieser Jr., T.D. Walsh and J.R. Wolfe Jr., J. Amer. Chem. Soc., 87 (1965) 3682.
8 C. Bied-Charreton and A. Gaudemer, Tetrahedron Lett., 46 (1976) 4153.
9 A.G. Davies and R. Feld, J. Chem. Soc., (1956) 665; J. Chem. Soc., (1958) 4637.