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Preliminary communication

A NON-CHAIN FREE RADICAL MECHANISM FOR THE INSERTION OF SULPHUR DIOXIDE INTO CARBON—METAL BONDS

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Summary

1-Phenyl-2[*R*]-propylcobaloxime(III) containing a large excess of one diastereoisomer reacts rapidly with sulphur dioxide to give an equimolar mixture of the two diastereoisomers of the insertion product. 6-Methylhept-5-en-2-ylcobaloxime(III) reacts with sulphur dioxide to give 1,1-dioxathiacyclohex-3-anesulphonylcobaloxime in which two molecules of sulphur dioxide have become incorporated. Each of these products is believed to result from an initial homolysis of the carbon—cobalt bond, followed by a series of non-chain free radical reactions.

Sulphur dioxide insertion into carbon—metal bonds is a reaction which takes place with a remarkably wide range of organometallic compounds. The metal may be one of many transition or main-group elements and the carbon may be of a wide variety of organic ligands. A great deal of effort has been expended invetigating the mechanism of such reactions and attempts have been made to draw together results obtained with several different metals and even more numerous organic ligands [1]. That no unified mechanism has emerged is not surprising, since the very ubiquity of the reaction almost certainly demands a range of different mechanisms appropriate to each metal and even, for a particular metal, to each type of organic ligand.

We had previously presented evidence that the insertion of sulphur dioxide into benzylcobaloximes was a free radical chain reaction in which cobaloxime(II) and the product of its capture by sulphur dioxide were chain-propagating radicals (eq. 1 and 2) [2]. However, the benzyl ligand, unlike simple primary and secondary alkyl ligands of organocobaloximes, is particularly susceptible to attack at the α-carbon by sulphonyl radicals, and thus step 1 of the chain reaction is less likely in the case of alkylcobaloximes [3].

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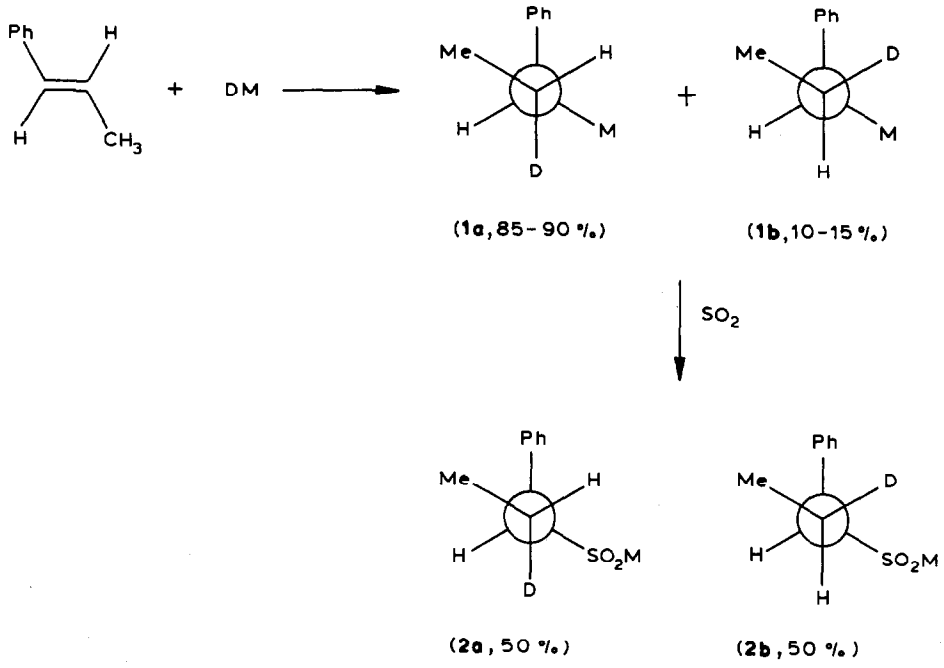
$$\dot{C}o(dmgH)_2py + SO_2 \longrightarrow O_2\dot{S}—Co(dmgH)_2py \quad (1)$$

$$O_2\dot{S}—Co(dmgH)_2py + PhCH_2Co(dmgH)_2py \longrightarrow PhCH_2SO_2Co(dmgH)_2py + \dot{C}o(dmgH)_2py \quad (2)$$

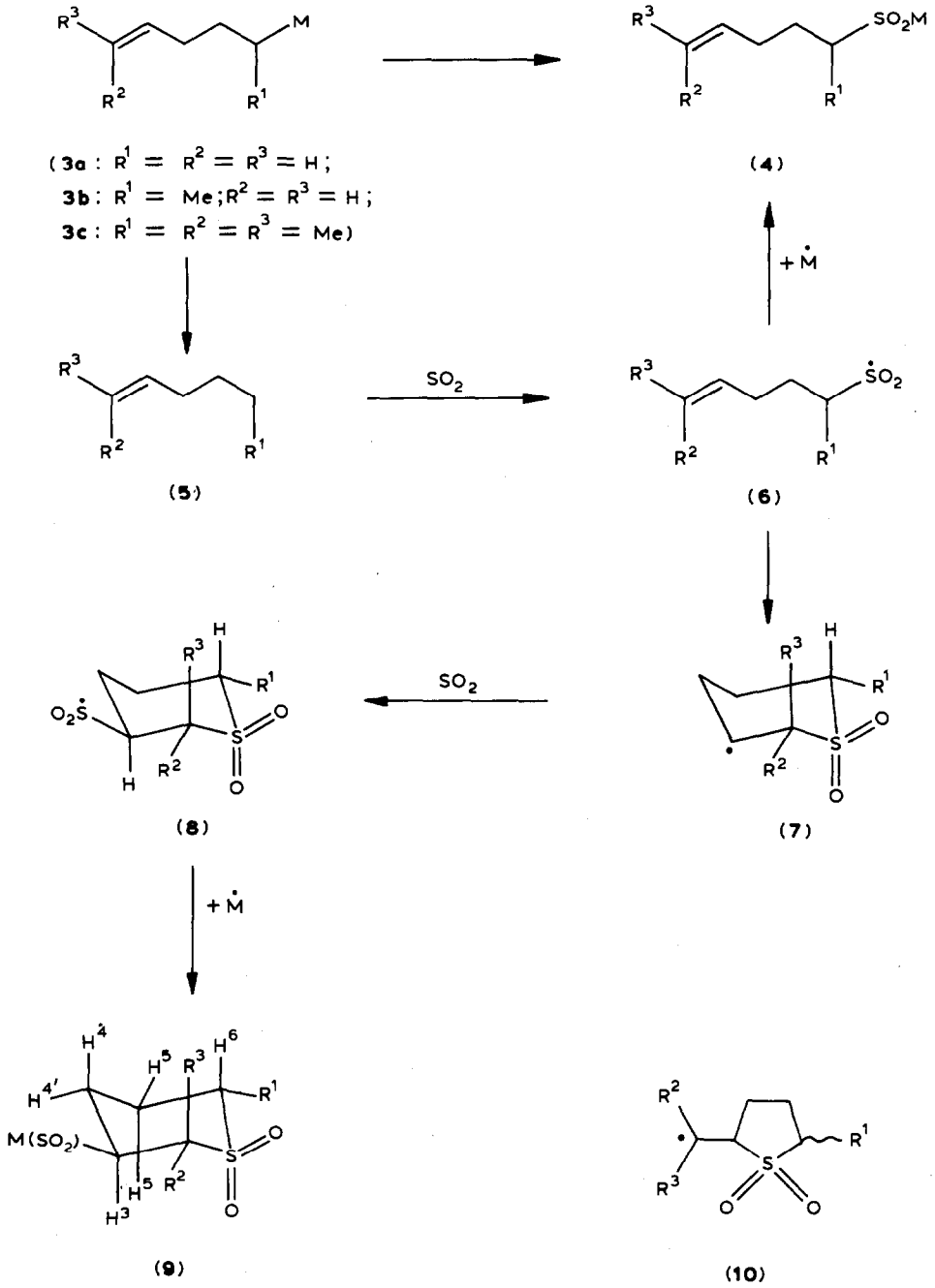
We now present evidence that sulphur dioxide insertion into carbon—cobalt bonds may also take place by a non-chain free radical mechanisms. Thus, the product of addition of $DCo(dmgH)_2py$ to *trans*-1-phenylpropene in MeD/D_2O is 1-phenyl-2-[$^2H^1$]-propylcobaloxime containing a large excess (85—90%) of that distereoisomer **1a** (NMR: H^1 δ 3.38 ppm H^2 δ 1.61 ppm; *J*(HH) 12 Hz) formed by a *syn*-addition, over the other **1b** (NMR: H^1 δ 3.38 ppm, H^2 δ 1.18 ppm; *J*(HH) 6 Hz). Reaction of this mixture with sulphur dioxide at ambient temperature takes place within a few minutes to give an equimolar mixture of the two diastereoisomers **2a** (NMR: H^1 δ 4.08 ppm, *J*(HH) 11.3 Hz) and **2b** (NMR: H^1 δ 4.08 ppm, *J*(HH) 3.2 Hz) of the insertion product (Scheme 1).



SCHEME 1. M = $Co(dmgH)_2py$.

Secondly, though the slower reaction of pent-4-enylcobaloxime (**3a**) with sulphur dioxide under the same conditions does give substantially the normal insertion product **4** ($R^1 = R^2 = R^3 = H$) [4], the corresponding secondary alkenyl analogues, i.e. the hex-5-en-2-ylcobaloximes such as **3b** and **3c**, give lower yields of the normal insertion product accompanied by substantial amounts of organocobaloximes containing two sulphur dioxide moieties. Indeed, the main product of reaction of 6-methylhept-5-en-2-ylcobaloxime

(3c) with sulphur dioxide is the double insertion product 9 ($R^1 = R^2 = R^3 =$ Me; NMR: δ 1.32 (d, CH_3); 1.47, 1.58 (s, CH_3); 1.6—2.1 (m, 4H); 2.33, 2.36 (s, dmg); 3.02 (q, J 6.8, 11.6 Hz, H^6); 3.49 (q, J 3.1, 11.6 Hz); 7.33, 7.77, 8.37 ppm (all m, py) Scheme 2).



SCHEME 2. M = Co(dmgH)$_2$py.

Each of these products can be rationalised in terms of an initial homolysis of the carbon—cobalt bond. In the former case the planar radical from **1** is captured by sulphur dioxide (or by the sulphur dioxide adduct of cobaloxime(II)) to give, subsequently, the equimolar mixture of **2a** and **2b**. The configurational stability of **1a** in aqueous methanol suggests that this racemisation does not occur prior to reaction with sulphur dioxide [5]. In the case of the cobaloxime **3c**, the initial homolysis gives the radical **5** ($R^1 = R^2 = R^3 = Me$) which is captured by sulphur dioxide and then, rather than recombine with cobaloxime(II) to give the normal product **4** ($R^1 = R^2 = R^3 = Me$), cyclises to give the six-membered cyclic radical **7** ($R^1 = R^2 = R^3 = Me$) [6]. Since **7** is also a carbon radical formed in the presence of sulphur dioxide as solvent, it too is captured to give the sulphonyl radical **8** which recombines with cobaloxime(II) to give the observed product **9** ($R^1 = R^2 = R^3 = Me$).

The formation of six-membered dioxathiacyclohex-3-yl radicals **7** rather than the five-membered sulpholanylmethyl radicals **10** was noted as a side reaction in the treatment of similar pentenylcobaloximes with trichloromethanesulphonyl chloride at elevated temperature [6]. That it is the six-membered product in the case of **7** ($R^1 = R^2 = R^3 = Me$) is even more surprising in view of the steric hindrance of the axial methyl group at position 2 and the fact that the alternative sulpholanylmethyl radical would be a tertiary radical. The identity of the six-membered product **9** is clear from the large *axial/axial* proton coupling characteristics of chair conformations and is inconsistent with those for a five-membered sulpholane ring.

It is also evident (a) that this mechanism requires that the reaction of cobaloxime(II) with sulphur dioxide be either reversible or slow in order that recombination of the organosulphonyl radical and cobaloxime(II) can occur, or, less likely, that the sulphur dioxide adduct of cobaloxime(II) is particularly reactive towards organic radicals even in sulphur dioxide as solvent; and (b) that the homolysis of **3** is faster in sulphur dioxide at ambient temperature than in other atom-donor solvents such as carbon tetrachloride [6]. Some other, possibly reductive, interaction between the parent cobaloxime(III) and sulphur dioxide must therefore assist the primary homolysis.

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