

Preliminary communication

STEREOCHEMISTRY AT TITANIUM IN THE SULFUR DIOXIDE INSERTION REACTION OF TITANOCENE COMPOUNDS

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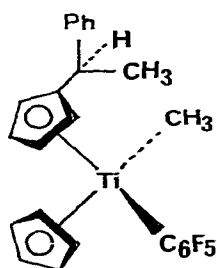
Summary

The insertion reaction of SO₂ has been studied for the two diastereoisomeric forms of $\eta^5\text{-C}_5\text{H}_5\text{-}\eta^5\text{-C}_5\text{H}_4\text{CHMePhTi(C}_6\text{F}_5\text{)CH}_3$. The reaction is regioselective and stereospecific. Arguments that it involves a retention at the titanium atom are given.

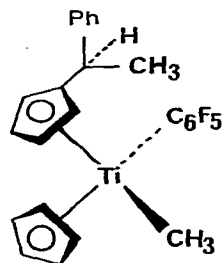
Insertion is now a well-established reaction in organometallic chemistry. The mechanisms of SO₂ and CO insertion are known to be very different [1]. The most striking dissimilarity is that insertion of SO₂ into the Fe—C bond proceeds with inversion of configuration at carbon, while insertion of CO proceeds with retention [2]. But for a detailed mechanistic understanding a knowledge of the stereochemistry at both the metal and the carbon atoms is necessary. It has been found that SO₂ insertion into the iron—carbon bond proceeds with high stereospecificity, and empirical arguments based on circular dichroism spectra [3] suggested that the reaction, unlike the CO insertion, proceeds with retention of configuration at iron. This suggestion has recently been definitely confirmed by a crystallographic determination [4].

We have found that organometallic titanocene derivatives with a chiral center at the metal atom are stereostable; we resolved racemic compounds of this type [5], and established the stereospecificity of some ligand substitution reactions [6]. We now report that the insertion of sulfur dioxide into the titanium—carbon bond is a stereospecific process.

The starting substrates are the two diastereoisomeric forms, Ia and Ib, of a methyl pentafluorophenyltitanocene complex bearing a chiral group on a cyclopentadienyl ring [7]. The complex (Ia or Ib) is placed in a cold trap immersed in a dry ice/acetone bath. Dry sulfur dioxide is then condensed into the trap and dissolves the titanium compound. As soon as all the solid has dissolved the addition of SO₂ is discontinued and the liquid is removed by allowing the trap to warm up to room temperature. The residual SO₂ is



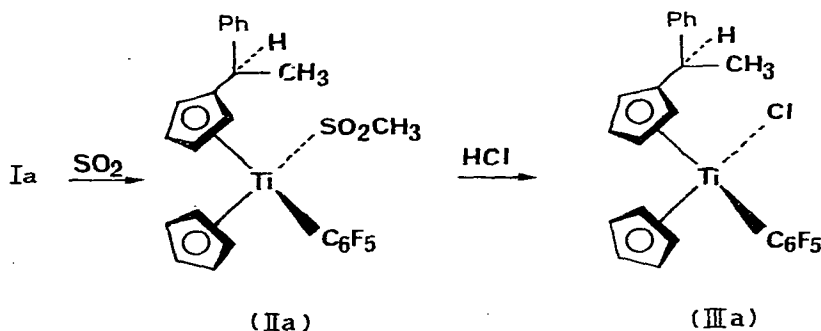
(Ia)



(Ib)

pumped off and the solid residue is chromatographed on silica gel and crystallized from hexane.

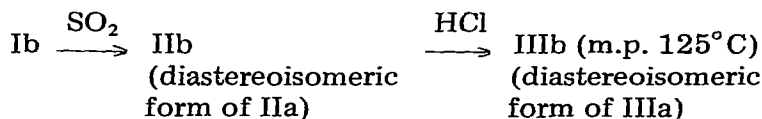
Under these conditions Ia gives exclusively one diastereoisomeric form of the insertion product IIa. This form (m.p. 134°C) reacts with anhydrous HCl in benzene solution to give only one diastereoisomeric form (m.p. 163°C) of the chloro complex IIIa.



(IIa)

(IIIa)

The insertion of sulfur dioxide into Ib gives under the same conditions the other diastereoisomeric form of II (oil), which can be transformed into IIIb by the action of HCl:



The regioselectivity of the insertion into the titanium–methyl bond has been established by spectroscopic analysis (position of the signal of the methyl group in NMR; fragment $[M - \text{SO}_2\text{CH}_3]^+$ in the mass spectra). It is consistent with the lack of reactivity of the titanium– C_6F_5 bond in the insertion reaction.

The compounds IIa and IIb have the characteristics of *O*-sulfinates: the IR spectrum of these compounds in the SO_2 absorption region is characteristic of the *O*-sulfinato moiety (respectively: 1105, 1058 and 860 cm^{-1} for IIa; 1105, 1055 and 850 cm^{-1} for IIb); the fragment $[M - \text{SO}_2]^+$ is present in the mass spectra of the two forms; the NMR signals of the unsubstituted cyclopentadienyl ring and of the S-bonded methyl group are split at room temper-

ature and coalesce on warming. This splitting is due to the asymmetric sulfur atom of the *O*-sulfinato compound, and would not occur for the *S*-sulfinato or *O,O*-sulfinato forms.

These results establish the stereospecificity of the insertion and of the cleavage of the titanium—oxygen bond by HCl. We put forward arguments as follows that the insertion reaction at titanium involves retention:

1. There is a systematic relation between the relative positions of the different NMR signals (C_6H_5 , C_5H_5 , CH_3) for the two forms of the three types of complexes I, II and III.

2. This correlation shows that the sequence Ia \rightarrow IIa \rightarrow IIIa (or Ib \rightarrow IIb \rightarrow IIIb) involves overall retention.

3. The cleavage of the titanium—oxygen bond for the *O*-sulfinato (II) should be retention based on the retention which occurs in cleavage of the Ti—OR bond [7].

4. The first step of the sequence I \rightarrow II \rightarrow III that must also involve retention.

5. The relative positions of the NMR signals of Ia and IIa (or Ib and IIb) agree with this retention.

The NMR data for compound IIa and IIb are given in Table 1.

The relative configurations which are assigned in this note for the different forms are based on comparison with $\eta^5-C_5H_5-\eta^5-C_5H_4CHMePhTiCl-(OC_6H_4CH_3-o)$ [7], the structure of which has been determined by crystallographic analysis [8]. Details about these comparisons and of the stereochemistry at the sulfur atom will be given in the complete account.

TABLE 1

¹H NMR SPECTRA OF IIa AND IIb (SOLVENT) CDCl₃, TMS AS INTERNAL REFERENCE)

	$C_5H_5^a$	CH_3^b	CCH_3^c
IIa	$\left\{ \begin{array}{l} 6.33 (s)^d \\ 6.28 (s) \end{array} \right. [5]^e$	$\left\{ \begin{array}{l} 2.50 (t)^d \\ 2.57 (t) \end{array} \right. [3]$	$1.35 (d)^d [3]$
IIb	$\left\{ \begin{array}{l} 6.42 (s) \\ 6.41 (s) \end{array} \right.$	$2.56 (t) [3]$	$1.53 (d) [3]$

^aUnsubstituted cyclopentadienyl ring. ^bMethyl group in $TiSO_2CH_3$. ^cMethyl group at the chiral carbon atom. ^ds, singlet; d, doublet; t, triplet (due to the coupling with the two *ortho*-fluorine atoms of the C_6F_5 group). ^eRelative intensities of the signal.

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