Journal of Organometallic Chemistry, 129 (1977) 325—330

ORGANOMETALLIC COMPOUNDS

LIV *. ON THE MECHANISM EXPLAINING THE CONFIGURATIONAL INSTABILITY OF TRIORGANOTIN HALIDES

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(Received October 6th, 1976)

Summary

The configurational instability of triorganotin halides RR'R''SnX, which is a second order process with respect to added nucleophiles (S) such as pyridine, can be rationalized in terms of a two-step process involving an attack by S at tin to displace X, followed by a rate-determining attack of the second S molecule at the metal atom to give an achiral pentacoordinate-complex. This conclusion follows the estimation of the equilibrium constant of the first step, by measurement of the rate of the second step and by study of the intermolecular halogen exchange which occurs simultaneously with the coalescence of diastereotopic signals showing that the intermolecular exchange and the configurational instability are not independent processes.

Introduction

Corriu [1] and Cartledge [2] have shown that the racemization of triorganosilicon halides RR'R"SiX is a third-order process, first order with respect to RR'R"SiX and second order with respect to added nucleophiles which cause the racemization (HMPT, DMF, DMSO ≡ S).

$$\text{rate of racemization} = k^{\text{exp}}_{\text{RR'R''SiX}}[\text{RR'R''SiX}][\text{S}]^2$$

The strongly negative activation entropy suggests a very organized transition state.

Two intermediates might be responsible for this racemization: a six-coordinate one, with two solvent molecules in *trans*-position or a five-coordinate one, with

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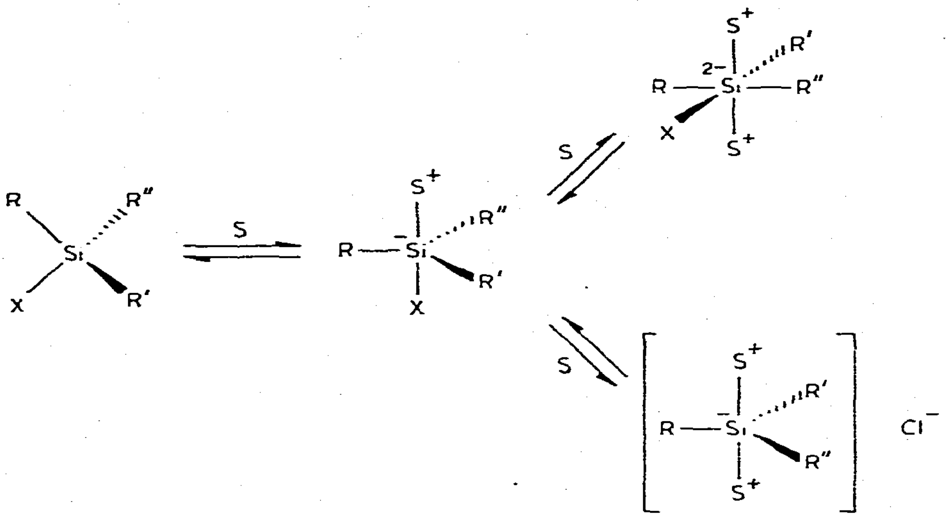
* For part LIII see ref. 15.

two apical solvent molecules, both belonging to the C_S symmetry point group.



These mechanisms, with an extension of the coordination number of the metal atom, are consistent with the decrease in the racemization rate for a series of compounds of the type RPhNpSiCl: Me > Et > Pr > i-Pr >> t-Bu [3]. Cartledge has provided some evidence for the mechanism involving an ionic pentacoordinate complex [2].

We have shown [4] that the behaviour of triorganotin halides is very similar. The rate v at which diastereotopic groups are permuted in methylneophyl-t-butyltin bromide or methylneophylphenyltin chloride in the presence of pyridine (S) as a consequence of a change of the absolute configuration of the tin atom, is given by:

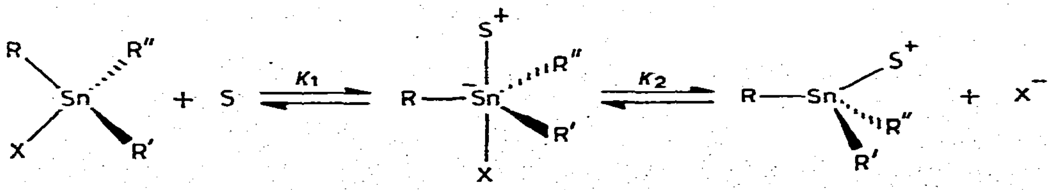
$$v = k^{\text{exp}}_{\text{RR'R''SnX}}[\text{RR'R''SnX}][\text{S}]^2$$

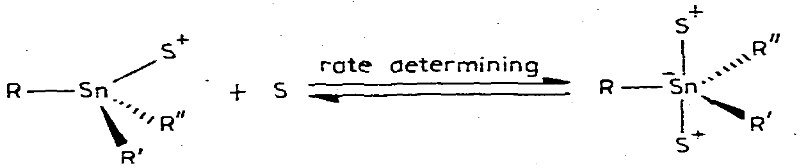
Here also, the presence of very bulky ligands around the tin atom, like a trityl group for instance, very strongly increases the configurational stability of triorganotin halides [5].

Discussion

The mechanisms depicted by Corriu for organosilicon compounds [1] and thus applicable to organotin chemistry, are somewhat complex [6].

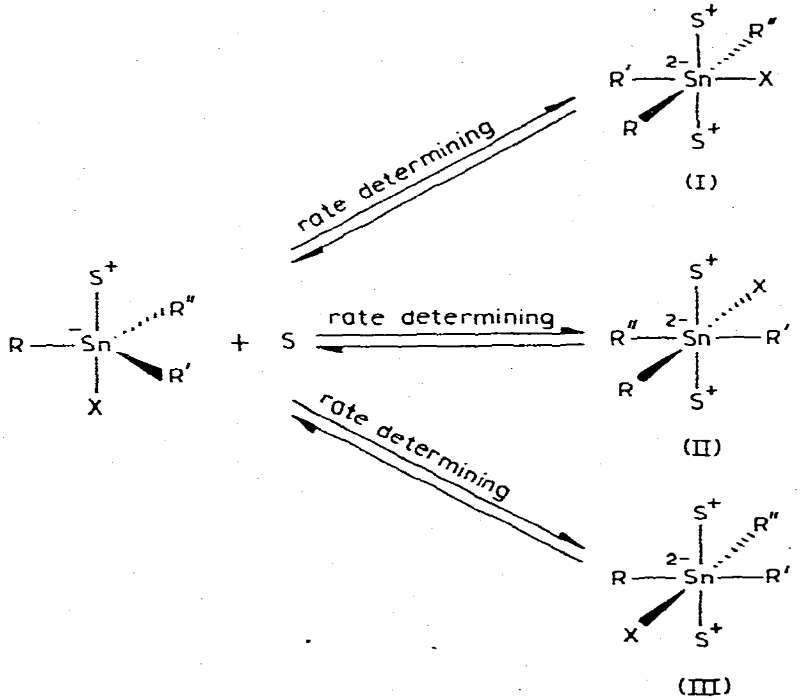
One of them (A) involves an ion pair in which the metal atom is bipyramidal. The various steps leading to this achiral intermediate complex may be visualized as follows:



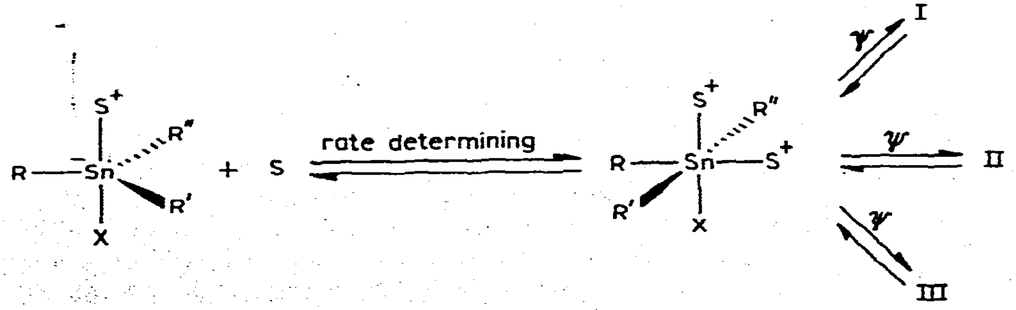


(A)

The other process B goes to an achiral six-coordinate intermediate complex which can be reached by three different routes:
(a) By a facial attack of S at RR'R''SnSX yielding the *trans* product in one step:

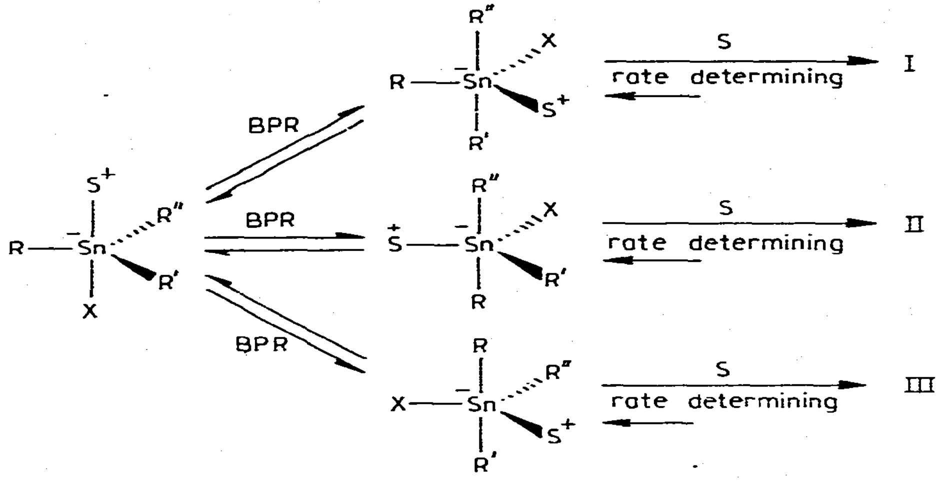


However a facial attack at a bipyramid has not yet been reported.
(b) by equatorial addition of S at RR'R''SnSX yielding a still chiral octahedral complex, followed by at least one pseudo-rotation Ψ (for instance, belonging to mode *P6* [7], like a Bailar trigonal twist [8] or a Ray—Dutt rhombic twist [9]) transforming it into an achiral *trans* compound:



However, pseudorotations of octahedral complexes seem to be much less frequent than those of bipyramidal complexes.

(c) By at least one pseudorotation (for instance belonging to mode *P*1 [7], like the Berry pseudorotation [10] (BPR) on RR'R''SnSX followed by the equatorial addition of S at tin:



However, the three diastereoisomers obtained after these three possible BPR are rather unfavorable, according to Bent's rule, since both electronegative ligands are in equatorial position.

The first step of both mechanisms is the same, namely the nucleophilic attack of a solvent molecule at the electrophilic tin atom of the triorganotin halide to give a pentacoordinate complex.

Mechanism A operates if the tin—halogen bond of this trigonal bipyramidal complex is broken. Mechanism B applies if a second solvent molecule is added at the tin atom of this trigonal bipyramidal molecule.

The influence of the halogen atom can be safely predicted if mechanism A is operative. If the equilibrium constant K_1 for the formation of the trigonal bipyramidal complex is not very different for X = Cl and for X = Br, then, since Cl^- is harder [11] than Br^- [12], the cleavage of the Sn—X bond of RR'R''SnSX to give $RR'R''SnS^+$ must be easier for the bromide than for the chloride, thus the rate at which the pentacoordinate ion $(RR'R''SnS_2)^+$ is formed must be greater for the bromide than for the chloride. Thus the racemization of RR'R''SnBr must be faster than that of the analogous chloride.

Results

In order to get information about the value of K_1 (cf. ref. 14) for methylneophylphenyltin halides, we have examined the variation of the *J*(Sn—Me) coupling constant when the concentration of pyridine added to solutions of I and II in benzene is increased. The results are given in Fig. 1, and show that the coupling constants change similarly for the two compounds. In pyridine, a common limiting value is not reached. Even in DMSO there remains a small differ-

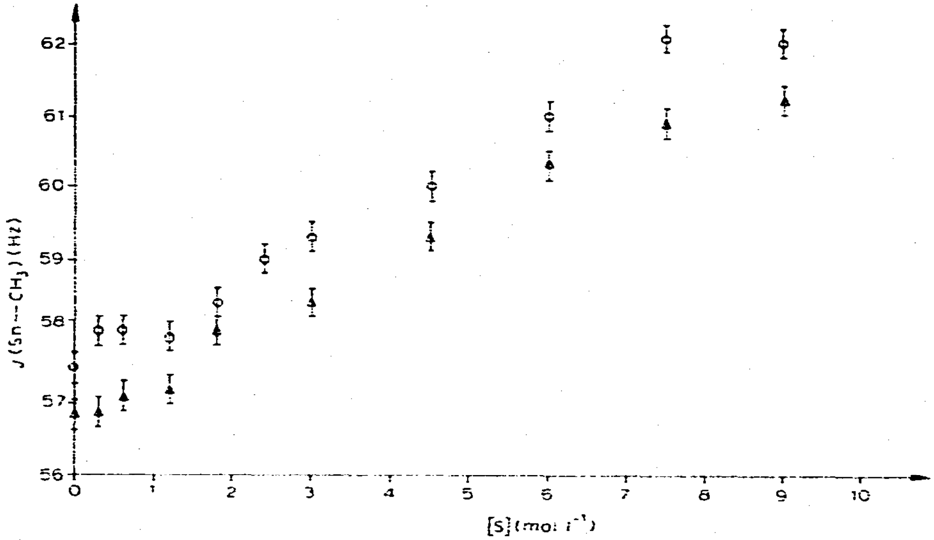


Fig. 1. Variation of $J(^{119}Sn—CH_3)$ as a function of the concentration of pyridine [S] for methylneophylphenyltin halides ○ for X = Cl (II) ▲ for X = Br (I) (cf. ref. 14).

ence ($J(^{119}Sn—Me)$ 69.0 Hz for II and 68.6 Hz for I). This shows that the equilibrium constant K_t is of the same order of magnitude for I and for II.

On the other hand, it is easy to show that methylneophylphenyltin bromide (I) racemizes more easily than the analogous chloride (II). For the latter, the diastereotopic signals coalesce when the concentration of pyridine reaches about 0.1 *M* for a 0.3 *M* solution of II [4]; in contrast the two signals observed for the diastereotopic neophilic groups of I coalesce to a fine single line when only 0.05 *M* of pyridine is added.

These experimental facts are thus compatible with mechanism A. If mechanism A is operative, an intermolecular exchange of halogen * is expected for a mixture of I and II (because the same $RR'R''SnS^+$ intermediate complex is reached from I and from II) and must be correlated with their configurational instability. The NMR spectrum of an equimolecular (0.3 *M*) mixture of I and II in C_6D_6 shows the superposition of the spectra of both components to be almost unchanged (see Table 1).

It can be seen that the separation of the MeSn and of the CH_2Sn peaks between I and II is about 0.08 ppm. In contrast, the diastereotopic methyl signals are also separated by about 0.09 ppm but coincide for I and II.

When pyridine is added to give a 0.07 *M* solution in this nucleophile, two important changes are visible: (a) only one mean peak at 12.6 Hz is obtained for SnMe, showing that an intermolecular exchange takes place and (b) the peaks of the neophylic methyl groups coalesce.

The evidence favours mechanism A involving an ionic five-coordinate trigonal bipyramidal complex while our results do not completely rule out mechanism

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* Intermolecular exchange between two triorganotin halides has been reported [13].

TABLE 1

60 MHz NMR PARAMETERS OF METHYLNEOPHYLPHENYLTIN CHLORIDE AND BROMIDE AND OF THEIR EQUIMOLAR MIXTURE. INTERNAL STANDARD TMS

	δ(Me—Sn) (Hz)	$\delta(CH_2)$ [a] (Hz)	$\delta(CMe_2)$ (Hz)
PhMeNeophSnCl (II)	10.3	112.7	69.2, 74.7
PhMeNeophSnBr (I)	15.0	117.7	69.2, 74.7
I + II	9.2 and 14.3	112.5 and 117.5	69.2, 74.3

[a] At 60 MHz, the resolution is not sufficient to see the AB pattern for these diastereotopic protons.

B, they are exactly what would be predicted on the basis of mechanism A, and cannot easily be reconciled with mechanism B.

Acknowledgements

The authors are indebted to Prof. J. Nasielski for stimulating discussions. They thank Mr. F. Resseler and Mr. R. Polain for recording the NMR spectra and the "Fonds voor Kollektief Fundamenteel Onderzoek" (F.K.F.O.) and the "Nationale Raad voor Wetenschapsbeleid" for a grant.

Financial help from the A.G.C.D. is gratefully acknowledged (H.M.J.).

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