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**Preliminary communication**

# ORGANOMETALLIC COMPOUNDS

## L[*]. THE RACEMISATION OF TRIORGANOTIN HALIDES: A THIRD-ORDER PROCESS AS SHOWN BY COALESCENCE AT 60, 100 AND 270 MHz[**]

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### Summary

Determination of the concentrations of pyridine required to cause coalescence of the neophylic methyl group resonances at 60, 100 and 270 MHz has shown that the racemisation of methylneophyl-t-butyltin chloride or bromide in benzene is of second order in the nucleophile.

Corriu has observed that the racemisation of halosilanes is a second-order process with respect to nucleophiles [2,6]. We describe below a NMR method used to determine the order with respect to the nucleophile pyridine in inducing the racemisation of triorganotin halides in $C_6D_6$. To our knowledge this is the first time that the study of the effect of the concentration of a reagent causing the coalescence of diastereotopic groups at different field strengths, $H_0$, has been used to determine a reaction order. The use of different field strengths has, however, been used recently to get a rough estimate of the activation parameters [3].

The rate at which diastereotopic groups are permuted in methylneophyl-t-butyltin bromide (I) or in methylneophylphenyltin chloride (II)[***] as a consequence of a change of the absolute configuration of the tin atom, is a function of the presence of nucleophiles and of their activity towards tin [4].

The rate $v$ of the coalescence of the two neophylic methyl groups[☆] of

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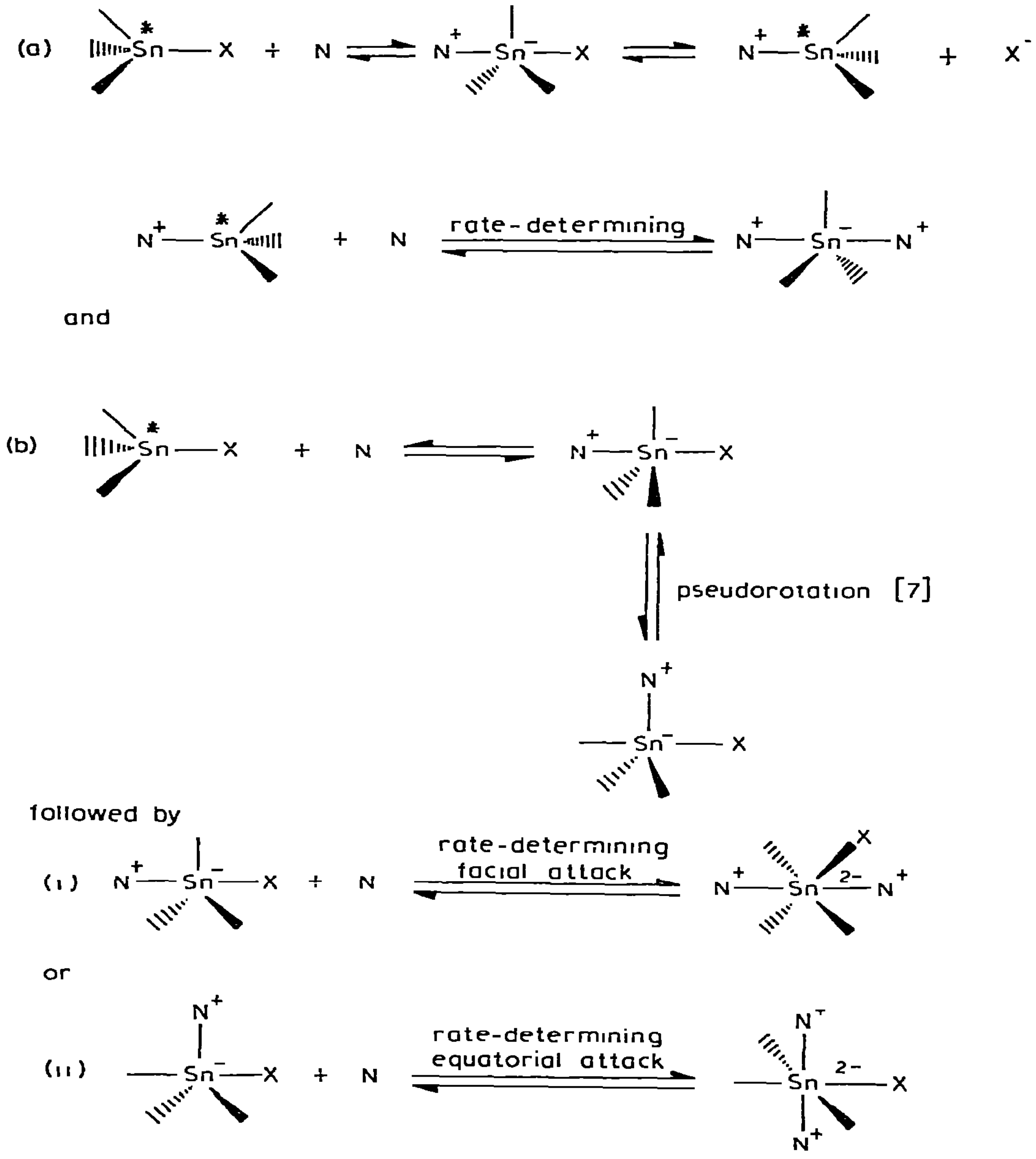
[*] For Part IL see ref. 1.

[**] The NMR spectra have been recorded on a Varian A60, on a Jeol MH 100 and on a Bruker HDX-270 apparatus.

[***] The synthesis and physicochemical properties of these triorganotin halides are described in ref. 1.

[☆] Even when there is coalescence of the signals of the two neophylic methyl substituents, the methyl resonance of the methyl group bound to tin remains unbroadened. $\Delta\sigma_\infty$ equals 0.083 ppm for I and 0.090 ppm for II.

SCHEME 1



(iii) another rate-determining type of addition to the bipyramidal intermediate complex followed by stereomutations of the formed octahedral complex [8].

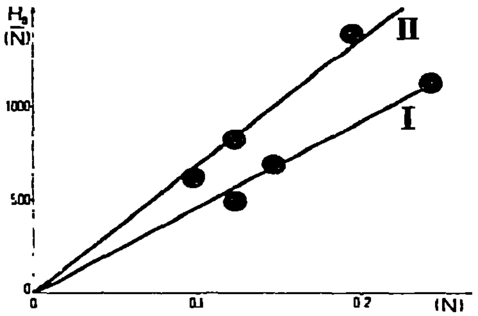


Fig. 1. Determination of the reaction order with respect to pyridine (N) for the racemisation of 0.262 $M$ methylneophyl-t-butyltin bromide (I) and of 0.332 $M$ methylneophylphenyltin chloride (II) at 22 °C.

I or II can thus * be expressed by:

$$v = k_2[\mathrm{RR'R''SnX}][\mathrm{N}] + k_3[\mathrm{RR'R''SnX}][\mathrm{N}]^2$$

$$\text{or } v/[\mathrm{RR'R''SnX}] = k_2[\mathrm{N}] + k_3[\mathrm{N}]^2$$

On the other hand, one has [5] $v/[\mathrm{RR'R''SnX}] = (\pi/\sqrt{2})\Delta\nu_\infty$ (in Herz) = $(\pi/\sqrt{2})\Delta\sigma_\infty$ (in ppm). $H_o$ (in MHz) $\div H_o$ assuming $\Delta\sigma_\infty$ (in ppm) to be practically identical in $C_6D_6$ and in $C_6D_6$ containing small quantities (2-3 %) of pyridine.

At a given temperature and with a constant concentration of RR'R"SnX, one gets

$$H_o \div k_2\,[\mathrm{N}] + k_3\,[\mathrm{N}]^2 \text{ or } H_o/[\mathrm{N}] \div k_2 + k_3\,[\mathrm{N}]$$

where [N] is the concentration of pyridine which causes the coalescence at a given temperature for a given concentration of the RR'R"SnX at a given field strength $H_o$.

The experimental results are summarized in Fig. 1. From these results, it is clear that the racemisation of triorganotin halides is second-order in pyridine. There are several reasonable mechanisms for the racemisation [6] consistent with this observation (see Scheme 1).

This type of NMR study could clearly be widely applicable to the order determinations of many other reactions in which conventional kinetic studies are very difficult or even impossible because the rates are too high.

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* The same method has been used to confirm that this process is of first order with respect to the triorganotin halide in the concentration range used.

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