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PRELIMINARY COMMUNICATION

EQUILIBRIUM OF β-STANNYL KETONES WITH *O*-STANNYLATED ENOLS

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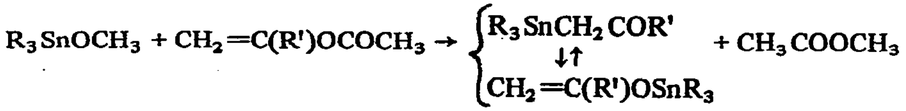
Recently we studied the relative stabilities of isomeric keto-enols containing *O*- or *C*-silicon or -germanium groups[1-3]. It was found that β-silyl ketones when heated up to 160–180° completely isomerize to the *O*-silyl-substituted enols[2], whereas the trimethylgermylacetone–trimethylisopropenyloxygermane system slowly reaches its equilibrium at a temperature as low as 20°[3]. These isomerizations are characteristic in that they are significantly accelerated by catalytical amounts of trialkylhalosilanes or -germanes.

This paper presents NMR data concerning a fast intermolecular exchange in the compounds R_3SnCH_2COR', and a very fast one between the *O*- and *C*-organotin isomers, the mean lifetime of the exchange being 10^{-1} to 10^{-3} sec, in the presence of trialkylhalostannanes.

The organotin derivatives of acetone or acetophenone were obtained by means of a known procedure, *i.e.* via the reaction of trialkylmethoxystannanes with their enol acetates[4]. The starting methoxystannanes obtained from trialkylchlorostannanes and sodium methoxide were twice distilled over fresh portions of the latter to eliminate traces of the chlorostannanes.



$$R_3SnOCH_3 + CH_2{=}C(R')OCOCH_3 \rightarrow \left\{\begin{matrix} R_3SnCH_2COR' \\ \downarrow\uparrow \\ CH_2{=}C(R')OSnR_3 \end{matrix}\right. + CH_3COOCH_3$$

$(R = C_2H_5, C_3H_7, C_4H_9; R' = CH_3, C_6H_5)$

The compounds above are shown by ^1H NMR* spectra to be mixtures of the *C*- and *O*-derivatives, the former prevailing. Phenacylstannanes contain about 25% of the *O*-isomer in the mixture, which fits the data[5,6] well, whereas acetonylstannanes, which were earlier claimed[4-6] to be pure *C*-isomers are shown to contain 6, 9 or 11% of the *O*-isomer in the tributyl-, tripropyl- or triethyltin derivatives, respectively. We believe that the reported[5,6] absence of the *O*-isomers resulted from trialkylhalostannane admixtures whereby the NMR spectra were actually taken under the "fast exchange" condition.

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*In 50% benzene solution at 20° on the RS-60 spectrometer (60 Mc); internal reference hexamethyldisiloxane.

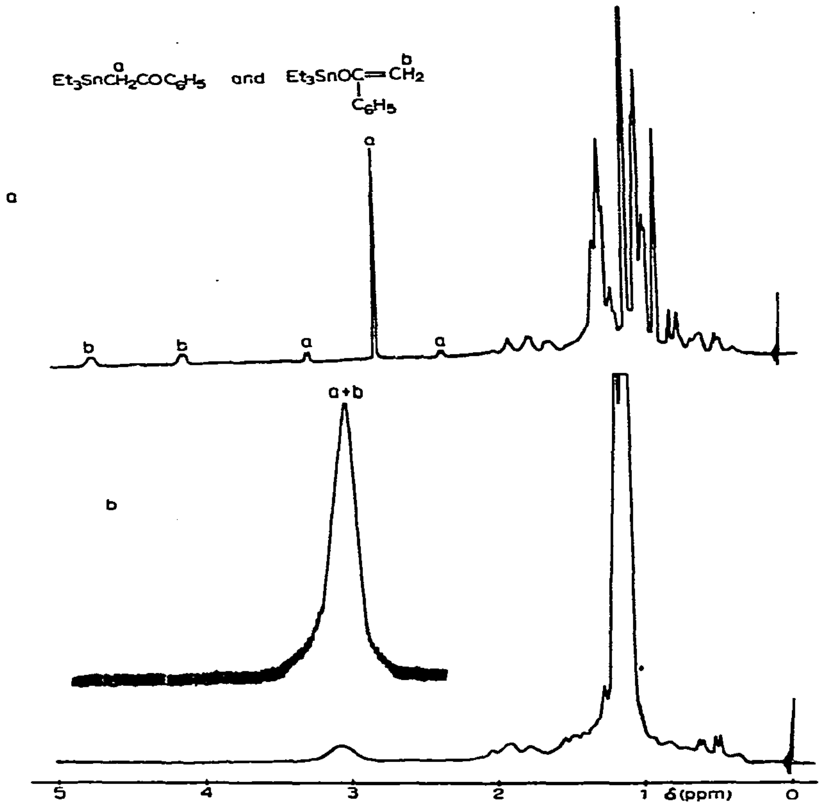

Fig.1. ^1H NMR spectra of a mixture of phenacyl derivatives of triethyltin: (a) pure sample; (b) contaminated with 20 mol.% of Et_3SnBr.

Figures 1 and 2 show ^1H NMR spectra of pure acetonyl or phenacyl derivatives of triethyltin, the derivatives being mixtures of the *C*- and *O*-isomers, and the spectra of the compounds contaminated with Et_3SnBr. Triethylbromostannane causes a coalescence of CH_2 proton signals of the *O*- and *C*-isomers, at the same time the $^{117/119}Sn{-}CH_2$ satellite lines and the coupling through the carbonyl of triethylacetonylstannane disappear, which demonstrates the very fast exchange between the isomers. The tributyl- or tripropyltin derivatives behave similarly. Trialkylchlorostannanes accelerate the exchange somewhat less, acetoxystannane significantly less, whereas trialkylmethoxystannanes as well as the carbonyl compounds do not affect the rate of the exchange.

The ^1H NMR spectrum of a mixture of tributylacetonylstannane with triethylphenacylstannane recorded at 1.5 to 3.5 ppm immediately after the compounds were put together. Fig.3 shows two signals of the phenacyl CH_2-group, two somewhat overlapped triplets of the methyls, and two somewhat overlapped quadruplets belonging to the methylene groups of the acetonyl, which demonstrates that the four *C*-isomers are actually present.

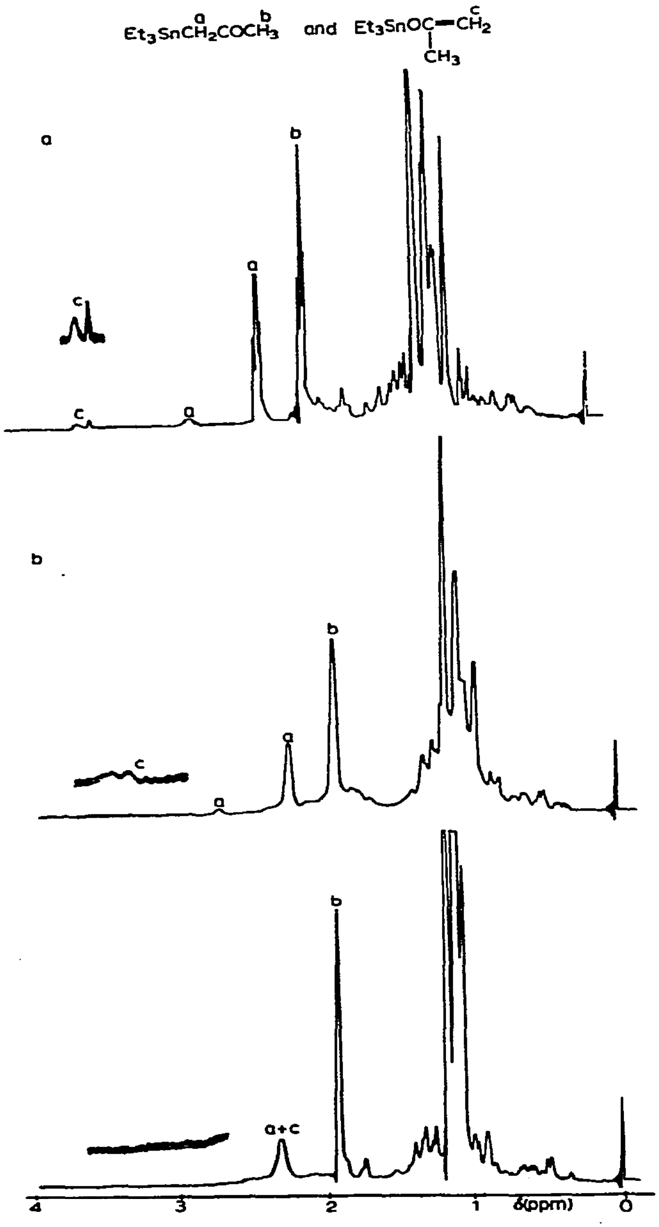

Fig.2. ^{1}H NMR spectra of a mixture of acetonyl derivatives of triethyltin: (a) pure sample; (b) contaminated with 2 mol.% of Et_3SnBr; (c) contaminated with 20 mol.% of Et_3SnBr.

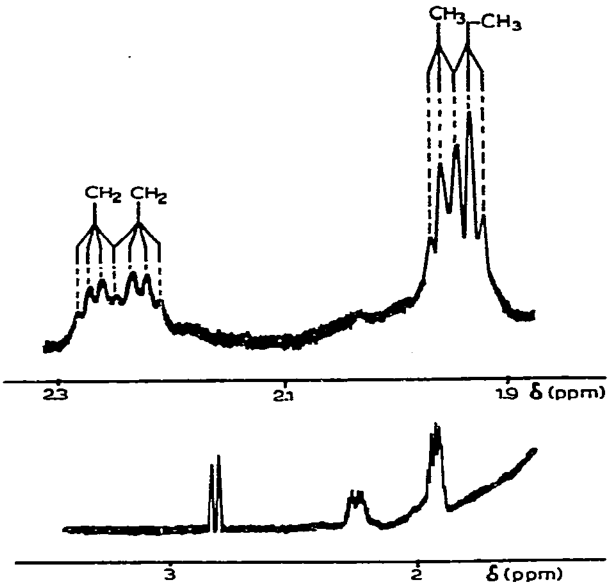

Fig.3. ^{1}H NMR spectrum of a mixture of phenacyl derivatives of triethyltin and acetonyl derivatives of tributyltin.

Thus, our data exhibit the fast exchange proceeding in the *O*- and *C*-organotin keto-enol derivatives. These facts must be taken into account when trying to separate the desmotropic forms from such tautomeric systems or when discussing their reactivity or spectra.

At present we are investigating the temperature dependence of the exchanges reported here and an equilibrium in the functionally substituted organolead derivatives.

REFERENCES

1 I.F. Lutsenko, Yu.I. Baukov, G.S. Burlachenko and B.N. Khasapov, *J. Organometal. Chem.*, 5 (1966) 20
2 I.F. Lutsenko, Yu.I. Baukov, O.V. Dudukina and E.N. Kramarova, *J. Organometal. Chem.*, 11 (1968) 35.
3 I.F. Lutsenko, Yu.I. Baukov, I.Yu. Belavin and A.N. Tvorogov, *J. Organometal. Chem.*, 14 (1968) 229.
4 A.N. Nesmeyanov, I.F. Lutsenko and S.V. Ponomarev, *Doklady Akad. Nauk SSSR*, 135 (1959) 1073.
5 M. Pereyre, B. Bellegarde, J. Mendelsohn and J. Valade, *J. Organometal. Chem.*, 11 (1968) 97.
6 L.P. Petrovskaya, *Dissertation*, Moscow, 1967.