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TAUTOMERY OF ORGANOTIN CARBONYL DERIVATIVES*

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SUMMARY

Metallotropic equilibria in keto–enol systems exemplified by organotin derivatives of acetaldehyde, acetone, or acetophenone are reported. The rate characterizing the exchange between the *O*- and *C*-isomeric organotin derivatives has been studied qualitatively as a function of various additives and the ratio of isomers has been studied as a function of temperature and solvent.

INTRODUCTION

As a rule, the problems of tautomery were limited to the prototropic transformations whereas the structure of metallic or organoelement species belonging to tautomeric or virtually tautomeric systems remained in the shadow. The dual reactivity of metallic derivatives of keto–enols was for a long time believed, but never proved, to be explained by the tautomery. Some twenty years ago, however, Nesmeyanov and one of the present authors studied α-mercurated aldehydes and ketones with an absolutely reliable *C*-structure and showed that the dual reactivity could be observed with no tautomeric equilibrium occurring in the system and should be explained by the transfer of the reaction centre of an initial compound.

Recently a non-prototropic tautomerism becomes more and more attractive, partially owing to newer spectral procedures which allow to follow the course of rather fast tautomeric equilibria where isolation of the isomers is not possible *e.g.*, metallic (Hg, Sn, Pb) derivatives of nitrosophenols[3,4], silylated derivatives of hydrocyanic acid[5–7], substituted amides[8,9], ureas[10], or reversible and irreversible isomerizations of substituted organo-element amines and imines[11]. As for keto–enols, where the behaviour of the unsubstituted compounds makes isolation of the pure isomers most probable, there must be noted the papers concerning the structure of the Reformatsky reagent[12], and the structure of magnesium derivatives of acetoacetic ester[13,14] or of its phosphorus analogue, (diethylphosphono)acetone[15,16]. The Bulgarian chemists who recorded IR spectra of the two latter compounds, discussed possible equilibria between the *C*-, *O*-, and chelate isomers present in the solution. Nevertheless, the problem as to whether metallic or organoelement keto–enol

* Preliminary communication see ref. 1.

derivatives can be equilibrated through their isomerization remains far from having been resolved*.

Recently relative stability of *O*- and *C*-isomeric silicon- or germanium-containing monocarbonyl derivatives has been studied in detail[19,20], and α-silylated ketones when heated up to 160 to 200° were observed to isomerize irreversibly and produce the *O*-silylated enols retaining the configuration at the silicon atom[21,22]:

$$R_3SiCH_2COR' \rightarrow R_3SiOC(R')=CH_2 \quad (1)$$

(R and R′ are alkyls or aryls)

Trialkylhalosilanes or mercury halides used in catalytic amounts make the isomerization to proceed under much milder conditions and to take the intermolecular course[22].

The isomers obtained by us with similar compounds of germanium[23] were slowly equilibrated at room temperature:

$$R_3GeCH_2COR' \leftrightarrows R_3GeOC(R')=CH_2 \quad (2)$$

The equilibrium was reached much faster at elevated temperatures and, especially, in the presence of small amounts of trialkylgermyl halides.

When silicon is replaced by germanium in the organoelement ketone derivatives, we obtain a much more active system, thus analogous compounds of tin may be supposed to isomerize even faster.

This agrees with the fact that reactions leading to the organotin ketone derivatives are thermodynamically controlled, in other words the same mixture of isomers possible for a given derivative is obtained whatever be the procedure or the conditions[24,25]:

$$\begin{array}{l} CH_3CH_2CH{=}C(OCOCH_3)CH_3 + Bu_3SnOMe \xrightarrow{(a)} \\ \quad (cis \text{ or } trans) \\ CH_3CH{=}CHCOCH_3 + Bu_3SnH \xrightarrow{(b)} \end{array} \begin{cases} CH_3CH_2CH(SnBu_3)COCH_3 \\ (25\%) \\ CH_3CH_2CH{=}C(OSnBu_3)CH_3 \\ (75\%, \text{a mixture of } 10\% \textit{ cis} \text{ and} \\ 90\% \textit{ trans}) \end{cases} \quad (3)$$

$$\begin{array}{l} Me_3CC(OCOCH_3){=}CH_2 + Bu_3SnOMe \xrightarrow{(a)} \\ CH_3COCMe_3 + Bu_3SnNEt_2 \xrightarrow{(b)} \end{array} \begin{cases} Bu_3SnCH_2COCMe_3 \ (66\%) \\ CH_2{=}C(OSnBu_3)CMe_3 \ (33\%) \end{cases} \quad (4)$$

Again, if an excess of enolacetate with a definite structure (*cis* and *trans*), was taken in reaction (3a) the recovered enolacetate was isomerized to some extent[24].

The French authors, however, do not believe that any stannotropic equilibrium is possible because they found that the *O*- to *C*-isomer ratio determined for tributylstannylated pinacolinos did not depend on temperature[24,**].

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* *Cf., e.g.*, diphenylstibinated acetylacetone the tautomeric equilibrium of which was stated in ref. 17 was disproved in ref. 18.

** The cited authors suggest that reactions (3a) and (3b) involve the same intermediate, a mesomeric anion stabilized via three possible routes. But if this is so then any if the resulting compounds may form this anion as well.

DISCUSSION

This paper describes equilibria between the *O*- and *C*-organotin derivatives of acetaldehyde, acetone, or acetophenone.

For the most part, the compounds have been synthesized according to a procedure described earlier (by the interaction of trialkylmethoxytin compounds with enol acetates[26]). As trimethylmethoxytin is difficult to prepare, the trimethyltin derivatives have been obtained via the "sulphide method"[27]:

$$R_3SnOMe + CH_2{=}C(R')OCOMe \rightarrow R_3SnCH_2COR' + CH_2{=}C(R')OSnR_3 + MeCOOMe \quad (5)$$

$$(Me_3Sn)_2S + Hg(CH_2COR')_2 \rightarrow Me_3SnCH_2COR' + CH_2{=}C(R')OSnMe_3 + HgS \quad (6)$$

Each of the organotin derivatives obtained, (Table 1) is a mixture of the *O*- and *C*-isomers (IR and NMR data). The ratio of isomers has been determined from the PMR spectra (summarized in Table 2).

TABLE 1

ORGANOTIN DERIVATIVES OF ACETALDEHYDE, ACETONE, OR ACETOPHENONE: R_3SnCH_2COR' AND $R_3SnOC(R')=CH_2$

A. NEW DATA

R	R'	Technique[a]	Yield (%)	B.p. [°C (mm)]	Composition	
					O-isomer (%)	*C*-isomer (%)
CH_3	CH_3	A	83	84–86(25)	[b]	[b]
C_2H_5	CH_3	B	95	98–99(5)	10 ±1	90 ±1
C_3H_7	CH_3	B	88	105–106(2)	8.5±1	91.5±1
C_4H_9	CH_3	B	90	130–132(2)	6 ±1.5	94 ±1.5
CH_3	C_6H_5	A	83	89– 89.5(1.5)	22.3±0.3	77.7±0.3
C_2H_5	C_6H_5	B	81	138–139(3)	23 ±1	77 ±1
C_3H_7	H	B	70		20 ±2	80 ±2

B. EARLIER DATA

R	R'	Yield (%)	B.p. [°C (mm)]	*O*-isomer (%)	Ref.
CH_3	CH_3	15	54–60(7)		29
C_2H_5	CH_3	95	100–101(6)		26
C_3H_7	CH_3	78	98–100(17)		26
C_4H_9	CH_3	85	130–132(2)		26
C_2H_5	C_6H_5	40	110–112(0.5)	20	31

[a] A, from bis(trimethyltin) sulphide and α-mercurated ketones; B, from enol acetates and trialkyl methoxystannanes. [b] Not determined because the signals in PMR spectrum were broadened through fast exchange.

Exchange between O- and C-isomers

No additives used. IR spectrum of trimethylstannylated acetone (Fig. 1) con-

TABLE 2

PMR DATA OF $(C_nH^a_{2n+1})_3SnCH^b_2C(O)R^c$ AND $(C_nH^a_{2n+1})SnOC(R^c)=CH^b_2$

Compound	Chemical shifts (ppm)			Coupling constants (Hz)		
	δH_a	δH_b	δH_c	$J(Sn-H_a)^a$	$J(Sn-H_b)^a$	$J(H_b-H_c)$
$(CH_3)_3SnCH_2COCH_3$						
$(CH_3)_3SnOC(CH_3)=CH_2$						
Fast exchange	0.2	2.42	1.93	58		
$(C_2H_5)_3SnCH_2COCH_3$		2.22	1.93		57	1
$(C_2H_5)_3SnOC(CH_3)=CH_2$		3.40, 3.48				
Fast exchange		2.34	1.91			
$(C_3H_7)_3SnCH_2COCH_3$		2.19	1.89		57	1
$(C_3H_7)SnOC(CH_3)=CH_2$		3.38, 3.48				
Fast exchange		2.27	1.89			
$(C_4H_9)_3SnCH_2COCH_3$		2.12	1.88			
$(C_4H_9)_3SnOC(CH_3)=CH_2$		3.33, 3.46				
Fast exchange		2.22	1.88			
$(CH_3)_3SnCH_2COC_6H_5$	0.23	3.1	7.5–8.4	57	66[b]	
$(CH_3)_3SnOC(C_6H_5)=CH_2$	0.7	4.3, 4.95	7.5–8.4	62		
Fast exchange	0.4	3.36	7.5–8.4	59		
$(C_2H_5)_3SnCH_2COC_6H_5$		2.49				
$(C_2H_5)_3SnOC(C_6H_5)=CH_2$		4.08, 4.7				
Fast exchange		3.1				
$(C_3H_7)_3SnCH_2CHO$		2.34	9.60			5
$(C_3H_7)_3SnOCH=CH_2$		3.67, 3.82	6.7			5.5, 13
Fast exchange		3.12	8.2			8

[a] Coupling with ^{117}Sn and ^{119}Sn isotopes. [b] This compound may display intramolecular coordination which would explain the fact that the J-value is higher than that of other C-isomers and does not decrease when the sample is diluted by a non-polar solvent (*cf.* the data from Table 6).

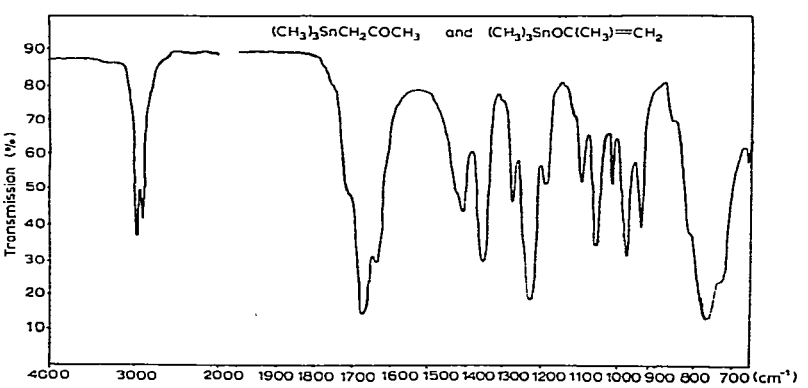

Fig. 1. IR spectrum of trimethylstannylacetone.

tains the band at 1690 cm^{-1} [ν(C=O) of the *C*-isomer[26]] together with a medium intensity band at 1640 cm^{-1} which may be assigned to ν(C=C) of the *O*-isomer[23]. However, the PMR spectrum of the compound (Fig. 2) shows a system of broad

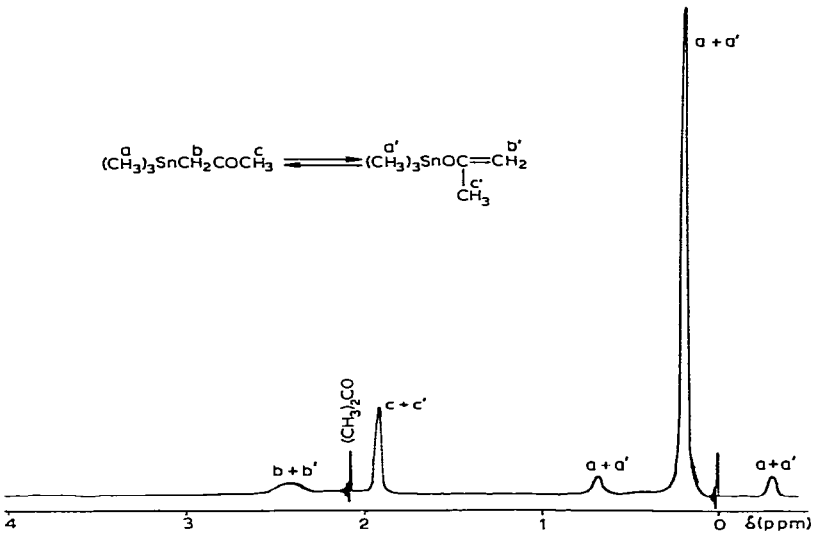

Fig. 2. PMR spectrum of trimethylstannylacetone without a solvent.

signals at as low a temperature as 20°, their positions being close to those of *C*-isomers of similar structure indicating that the *C*-isomer prevails in the mixture equilibrated through the fast exchange which broadens the PMR signals.

Trimethylstannylated acetophenone displays a similar broadening when the sample is heated up to 150°, (Fig. 3). At room temperature, the initial spectrum is recovered.

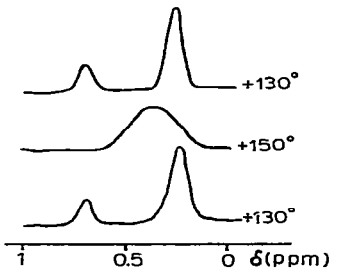

Fig. 3. Part of the PMR spectrum obtained with trimethylphenacyltin at 130, 150, and at 130° again.

Other compounds reveal the broadening only if trialkylsilyl halides are added to them. We believe, however, that the exchange is fast enough even if no additives are added. Actually, the PMR spectrum recorded immediately after two organotin derivatives differing in both their trialkylstannyls and initial ketones have been mixed, demonstrates a fast migration of the organotin groups from one keto–enol system to

the other. The spectrum allows to identify four *C*-derivatives*.

$$\left.\begin{array}{l} Bu_3SnCH_2COMe + Bu_3SnOC(Me)=CH_2 \\ Et_3SnCH_2COPh + Et_3SnOC(Ph)=CH_2 \end{array}\right\} \rightarrow$$

$$\rightarrow \left\{\begin{array}{l} Bu_3SnCH_2COMe + Bu_3SnOC(Me)=CH_2 \\ Bu_3SnCH_2COPh + Bu_3SnOC(Ph)=CH_2 \\ Et_3SnCH_2COMe + Et_3SnOC(Ph)=CH_2 \\ Et_3SnCH_2COPh + Et_3SnOC(Ph)=CH_2 \end{array}\right. \quad (7)$$

Trialkyltin halides added. Trialkyltin halides cause even faster exchange between *O*- and *C*-isomers. If the halide concentration is sufficient, the PMR spectra showed the averaged signals only (mean lifetime of the molecules, 10^{-1} to 10^{-3} sec) and not those which could be assigned to either *O*- or *C*-isomer.

Figs. 4 and 5 contain the PMR spectra of trimethylstannylated acetophenone

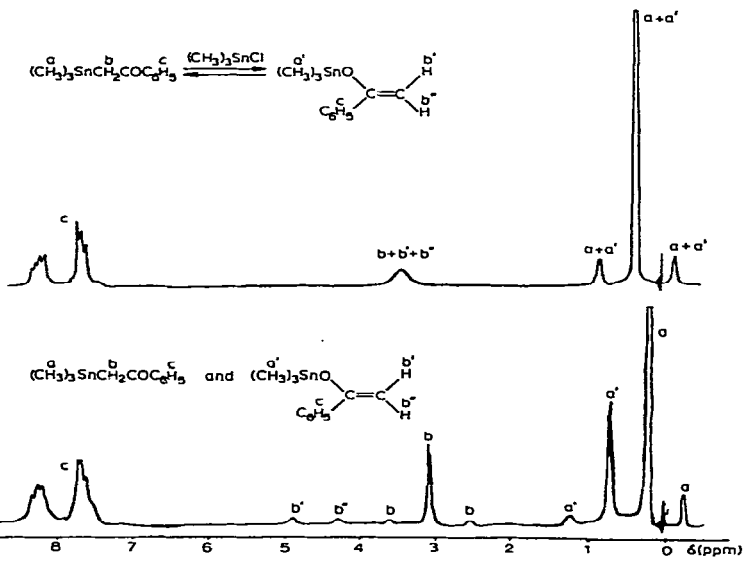

Fig. 4. PMR spectrum of solvent-free trimethylphenacyltin containing no additives (down) or 5% trimethyltin chloride (up).

and tripropylstannylated acetaldehyde to which the catalysts were added gradually or not at all. Our preliminary communication[1] reported similar spectra for stannylated acetone and acetophenone in presence of a triethyltinbromide additive.

Fig. 6 shows the CH_2 averaged signals obtained for triethylphenacyltin containing 15 molar per cent of a triethyltin halide. Fig. 6 demonstrates that the accelerating ability of the organotin halides follows the order:

$$R_3SnI > R_3SnBr > R_3SnCl > R_3SnF .$$

* For the PMR pattern, see ref. 1.

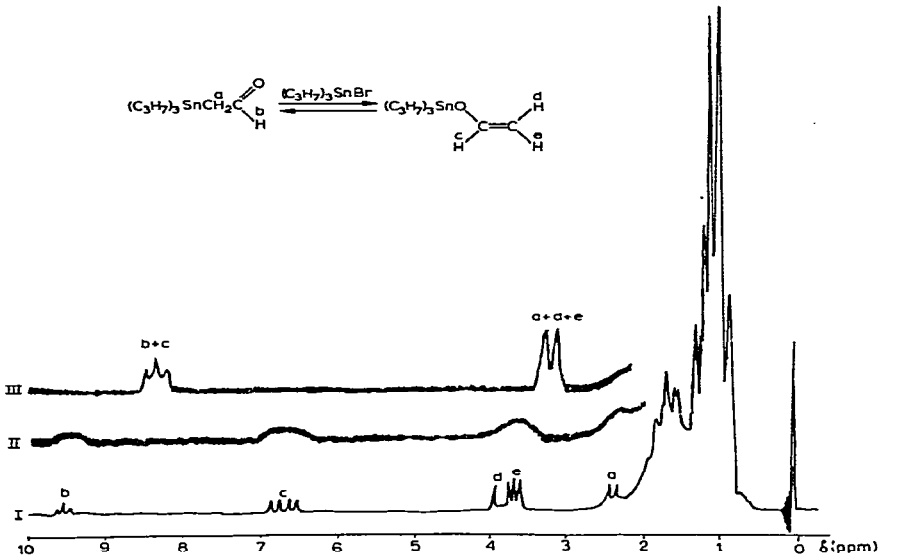

Fig. 5. PMR spectrum of tripropylstannylated acetaldehyde: I, pure compound (liquid); II, 20% tripropyltin bromide added: III, 20% solution in tripropyltin bromide.

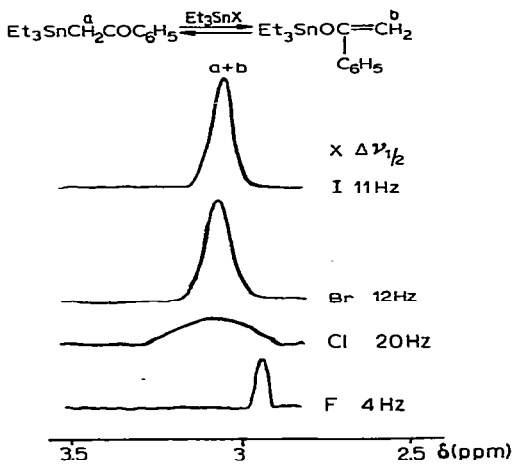

Fig. 6. CH_2–PMR signals obtained with triethylphenacyltin containing various triethyltin halides (15%).

Further, trialkyltin acetates also accelerate the exchange to some extent while either alkoxytin compounds or non-metallated carbonyl compounds are apparently inactive.

Effect of temperature

The ratio of isomers obtained with trimethylstannylated acetophenone does not depend on temperature, Table 3, which agrees with the data reported by Valade *et al.* for the pinacolone derivatives[24]. Thus, the isomers differ in their energies insignificantly.

Trimethylstannylated acetone, however, displays the shift of its broadened

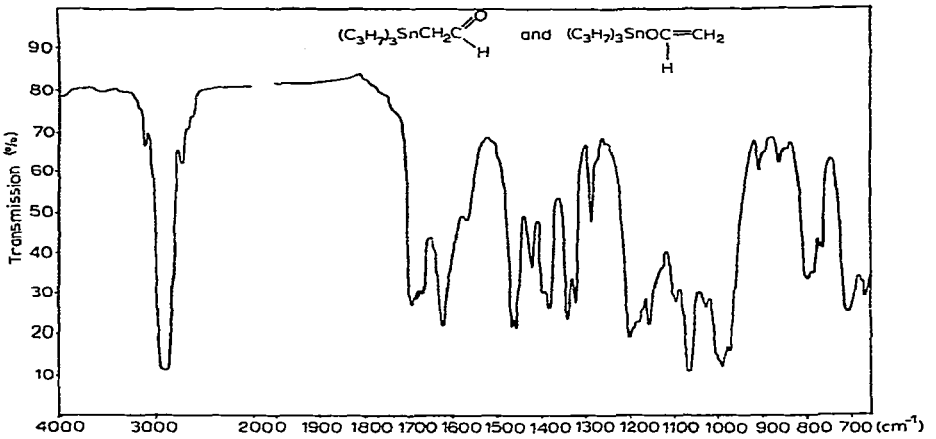

Fig. 7. IR spectrum of tripropylstannylated acetaldehyde.

Trimethylchlorosilane was added to this mixture (4.1 g, 0.015 mole), which resulted in an exothermic reaction, distillation gave trimethyl(vinyloxy)silane, 1.2 g (70%), b.p. 74°, n_D^{20} 1.3900 (lit.[30]: b.p. 74–76°, n_D^{20} 1.3885).

2. (*Trimethylphenacyl*)*tin*

Bis(trimethyltin) sulphide (10 g, 0.03 mole) was added dropwise at 70° to diphenacylmercury (15 g, 0.033 mole) suspended in 60 ml of absolute benzene, a black precipitate of mercury sulphide was filtered off, the solvent was removed from the

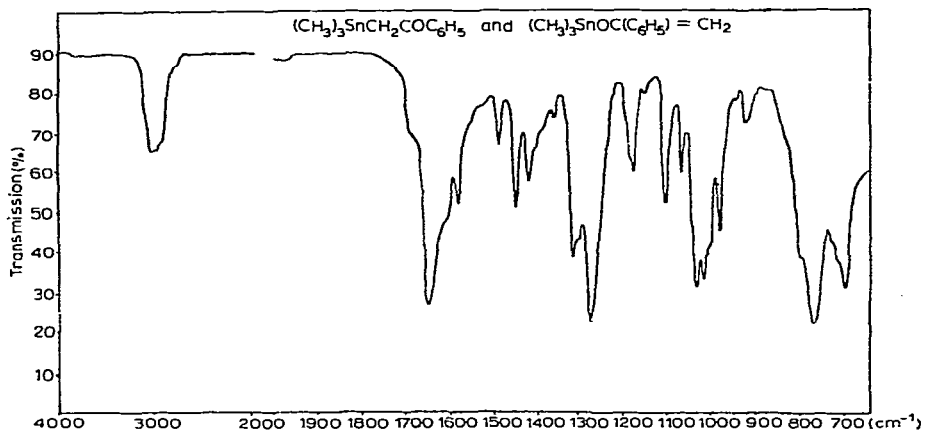

Fig. 8. IR spectrum of trimethylphenacyltin.

filtrate, the residue was distilled under reduced pressure. There was obtained 14 g (83% theoretical) of trimethylphenacyltin, b.p. 108–110° (1 mm), n_D^{20} 1.5620, d_4^{20} 1.3684; MR_D: found 66.21, calcd. 66.57 (*C*-isomer), 66.28 (*O*-isomer). (Found: C, 47.30, 46.98; H, 5.83, 5.61; Sn, 41.26, 41.49. $C_{11}H_{16}OSn$ calcd.: C, 46.70; H, 5.70; Sn, 41.85%.) IR spectrum: see Fig. 8.

Trimethylacetonyltin was obtained in a similar manner.

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