*Journal of Organometallic Chemistry*, 214 (1981) 191—195
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

# ORGANOMETALLIC COMPOUNDS

# LXXI *. SYNTHESIS AND PROPERTIES OF ALDEHYDIC AND KETONIC TETRAORGANOTIN COMPOUNDS

M. GIELEN

*Vrije Universiteit Brussel, T.W., A.O. SC.,Pleinlaan 2, B-1050 Brussel (Belgium)*

S. SIMON and M. VAN DE STEEN

*Université Libre de Bruxelles, Faculté des Sciences, Collectif de Chimie Organique Physique, Avenue F.D. Roosevelt, 50, B-1050 Bruxelles (Belgium)*

(Received January 22nd, 1981)

## Summary

The syntheses of $MeCO(CH_2)_3SnPh_2Me$ and of ($p$-XCOPh)SnMeRR′ (X = Me, R = Ph, R′ = Ph, Cl, $CH_2I$; X = H, R = R′ = Ph; X = Me, R = cyclohexyl, R′ = 1-naphthyl) are described. Some physical chemical properties of these new compounds are described and discussed.

## Introduction

A recent paper on the synthesis of a chiral $p$-(methylphenyl-i-propyl)-stannylbenzaldehyde [2] prompts us to describe some results on a related topic.

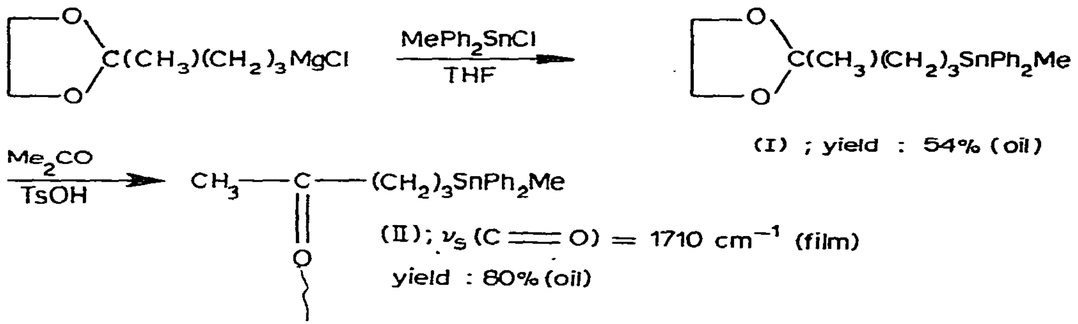
## Results and discussion

### Synthesis of ketonic tetraorganotin compounds

Poller's method [3] was used to synthesize 5-(methyldiphenylstannyl)-2-pentanone (II).

---

* For part LXX see ref. 1.



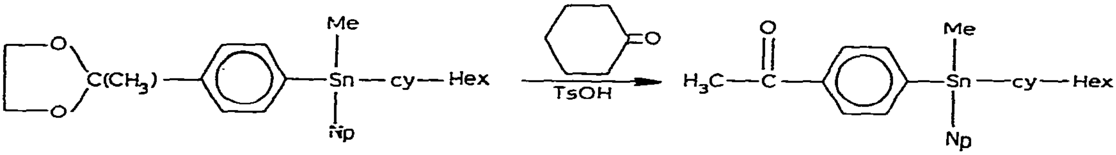
(I) ; yield : 54% (oil)

(II); $\nu_s$(C=O) = 1710 cm$^{-1}$ (film)
yield : 80% (oil)

The 70 eV mono-isotopic mass spectrum of II ($Ph_2MeSnR$) contains the expected [4] fragment ions: $m/e$ = 359 ($Ph_2RSn^+$, 15%); 331 ($Ph_2SnOC(CH_3){=}CH_2^+$, 30%); 297 ($PhMeRSn^+$, 35%); 289 ($Ph_2MeSn^+$, 38%); 227 ($PhMe_2Sn^+$, 43%); 197 ($PhSn^+$, 100%); 135 ($MeSn^+$, 27%) and 120 ($Sn^+$, 95%).

*p*-(Diphenylmethylstannyl)acetophenone (IV) was prepared analogously. Thus 2-[*p*-(diphenylmethylstannyl)phenyl]-2-methyl-1,3-dioxolane (III) (obtained in 77% yield) reacted with cyclohexanone (it does not react with acetone) in the presence of *p*-toluenesulfonic acid (TsOH) to give IV in 95% yield ($\nu_s$(C=O) = 1678 cm$^{-1}$ in KBr).

2-[*p*-(cyclohexylmethyl-1-naphthyl)stannyl]-2-methyl-1,3-dioxolane (V) was synthesized by the same method in 72% yield, and *p*-(cyclohexylmethyl-1-naphthylstannyl)acetophenone (VI) was obtained by treatment of V with cyclohexanone in the presence of *p*-toluenesulfonic acid (see above).



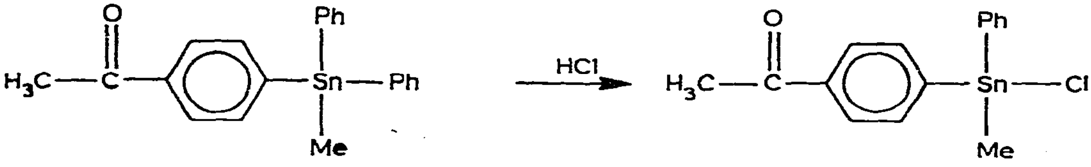
(V) (oil)

(VI) ,$\nu_s$ (C=O) = 1690 cm$^{-1}$ (film)
yield : 64% (oil)

The 70 eV monoisotopic mass spectrum of VI contains the following fragment ions: 464 (cy-HexMeNpSnPhCOMe$^{\cdot+}$, 2%); 449 (cy-HexNpSnPhCOMe$^+$, 2%); 381 (MeNpSnPhCOMe$^+$, 100%); 366 (NpSnPhCOMe$^{\cdot+}$, 12%); 337 (cy-HexMeSnPhCOMe$^+$, 1%); 323 (cy-HexMeCOPhSnH$^+$, 3%); 254 (MeMeCOPhSnH$^+$, 4%); 247 (NpSn$^+$, 5%); 239 (MeCOPhSn$^+$, 2%); 135 (MeSn$^+$, 1%); 121 (SnH$^+$, 4%); 120 (Sn$^{\cdot+}$, 4%).

### *Reactions of the ketonic tetraorganotin compounds*

Ketone IV reacts with HCl in MeOH/PhH to yield methyl(*p*-acetylphenyl)phenyltin chloride (VII) (yield: 80%).



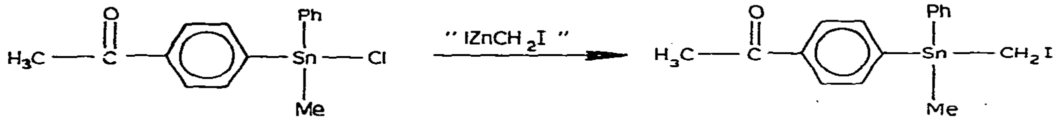
(IV)

$\nu_s$(C=O) = 1768 cm$^{-1}$(KBr)

(VII)

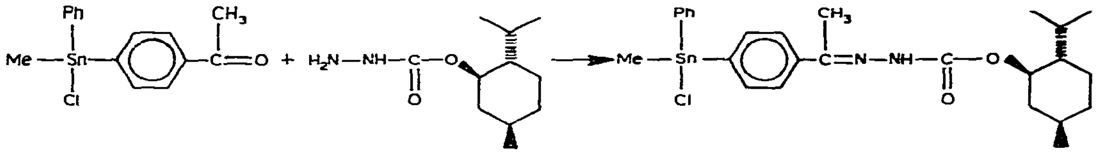
$\nu_s$ (C=O) = 1650 cm$^{-1}$ (KBr)

Ketone VII reacts with the Simmons-Smith reagent to give (iodomethyl)-methyl(*p*-acetylphenyl)phenyltin VIII.



(VII) (VIII)

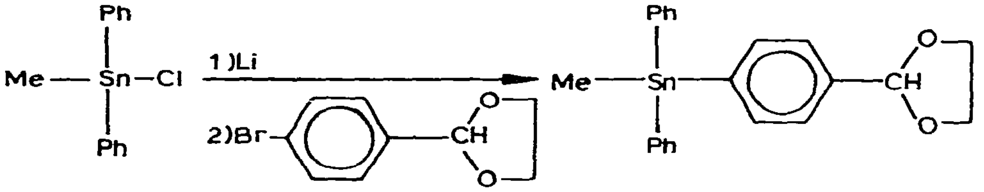
Ketone VII reacts with 1-menthylcarbazate (V) to give the corresponding menthydrazone IX [2,6].



(VII) (IX)

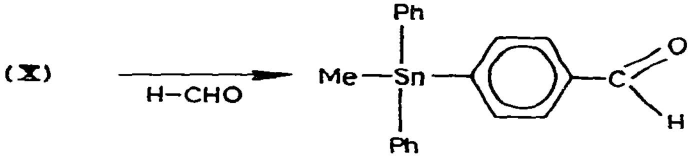
*Synthesis of an aldehydic tetraorganotin compound*

The synthesis of 2-[*p*-(methyldiphenylstannyl)phenyl]-1,3-dioxolane (X) was achieved by treating methyldiphenylstannyllithium (prepared from methyldiphenyltin chloride and lithium) with 2-[*p*-bromophenyl]-1,3-dioxolane.



(X)

Compound X was then transformed into the corresponding aldehyde (XI).



(XI)

## Experimental

*Synthesis of 2-triorganostannylpropyl- or 2-(p-triorganostannylphenyl)-2-methyl-1,3-dioxolanes I, III and V*

A solution of 5.89 g (35.8 mmol) of 2-(3-chloropropyl)-2-methyl-1,3-dioxolane in 40 ml THF was added to 0.96 g Mg in 10 ml THF at 70° C. After 12 hours, of reflux, 5.81 g (17.9 mmol) methyldiphenyltin chloride in THF were added slowly. After 24 hours, reflux, the mixture was poured onto ice. Elution through $SiO_2$ with benzene yielded 4.02 g of I.

Compound III (mp. 84—84.5° C) was made analogously; Found: C, 61.22; H,

TABLE 1

NMR SPECTRA OF ORGANOTIN COMPOUNDS OF THE TYPE RR'R"SnY

| Compound | Solvent | $\delta(SnCH_3)$ [b] (ppm) | $J(^{117}SnCH_3)$ (Hz) | $\delta(C—CH_3)$ [b] (ppm) | $\delta(SnCH_2I)$ [b] (ppm) | $\delta(C(2)H)$ [b] (ppm) |
|---|---|---|---|---|---|---|
| I | $CCl_4$ | 0.48 | 51.2 | 1.17 | | |
| II | $CCl_4$ | 0.48 | 52.4 | 1.92 | | |
| III | $C_6D_6$ | 0.49 | 53.0 | | | |
| IV | $C_6D_6$ | 0.57 | 54.8 | 2.14 | | |
| V | $CCl_4$ | 0.57 | 48.8 | 1.57 | | |
| VI | $CCl_4$ | 0.68 | 48.8 | 2.43 | | |
| VII | $C_6D_6$ | 0.44 | 59.6 | 1.87 | | |
| VIII | $C_6D_6$ | 0.47 | 55.2 | 2.07 | 1.89 | |
| IX [a] | $C_6D_6$ | 0.57 | 57.6 | | | |
| X | $C_6D_6$ | 0.545 | 53.5 | | | 5.76 |
| XI | | 0.51 | 54 | | | 9.66 |

[a] The menthyl methyl group shows up as a doublet at 0.87 and 0.92 ppm; the methyl groups of the menthyl isopropyl residue appear at 0.98 and 1.03 ppm. [b] $\delta(TMS) = 0$ ppm except for VIII, for which $\delta(SnCH_3) = 0$ ppm.

5.34 $C_{23}H_{24}O_2Sn$ calcd.: C, 61.24; H, 5.36%.

Compound V was made by the same method Found: C, 64.75; H, 6.46. $C_{27}H_{32}O_2Sn$ calcd.: C, 63.84; H, 6.50%.

The $^1H$ NMR spectral characteristics of I, III and V are listed in Table 1.

### *Synthesis of ketonic tetraorganotin compounds II, IV and VI*

Compound II was prepared as described by Poller [11].

Compounds IV and VI were synthesized as follows. 10 mmol of the ketal III or V were dissolved in 100 ml cyclohexanone containing 5 ml water and 250 mg *p*-toluenesulfonic acid. After 1 hour at 140°C, 100 ml water were added. The mixture was then extracted with ether, and the organic layer was washed with a 10% $NaHCO_3$ solution and dried over $K_2CO_3$. The yellow oil obtained after evaporation of the ether and of the cyclohexanone was chromatographed on $SiO_2$ (elution with benzene).

Compound IV was recrystallized from methanol; m.p. 84—85°C. Found: C, 61.80; H, 5.01, $C_{21}H_{20}OSn$ calcd.: C, 61.96; H, 4.95%.

The elemental analysis of VI gives: Found: C, 65.40; H, 6.15. $C_{25}H_{28}OSn$ calcd.: C, 64.83; H, 6.09%.

The $^1H$ NMR spectral characteristics of II, IV and VI are listed in Table 1.

### *Synthesis of methyl(p-acetylphenyl)phenyltin chloride (VII)*

A suspension of 40.7 g of IV in a mixture of 400 ml methanol and 50 ml benzene was treated with 200 ml of a 0.5 *M* HCl in methanol at room temperature; 6 hours were necessary for this addition. The mixture was left at room temperature for 2 days, then the solvents were evaporated at room temperature. 37 g of the residual yellow oil were recrystallized from a hexane/methanol mixture to give VII, m.p. 100.5—110.5°C. Found: C, 49.42; H, 4.36; Cl, 9.86. $C_{15}H_{15}ClOSn$ calcd.: C, 49.30; H, 4.14; Cl, 9.70%.

### *Synthesis of (iodomethyl)methyl(p-acetylphenyl)phenyltin (VIII)*

Following the procedure described by Seyferth [7], compound VII was converted into VIII, which was purified by chromatography on $Al_2O_3$ (elution with a 2/1 benzene/chloroform mixture). Compound VIII is an oil. Found: C, 40.85; H, 3.80; I, 27.05. $C_{16}H_{17}IOSn$ calcd.: C, 40.81; H, 3.64; I, 26.95%.

### *Synthesis of the menthydrazone of methyl(p-acetylphenyl)phenyltin chloride (IX)*

A solution of 0.5 g of compound VII, 293 mg of *l*-menthylcarbazate and 1 mg of *p*-toluenesulfonic acid in 20 ml absolute ethanol was refluxed for 2 hours. The solution was dried on $K_2CO_3$ and the solvent evaporated under reduced pressure. The solid residue was recrystallized from benzene/petroleum ether (b.p. 60—90°C). Pure IX melts at 128—129°C. Found: C, 55.7; H, 6.31. $C_{26}H_{35}ClN_2O_2Sn$ calcd.: C, 55.59; H, 6.08%.

### *Synthesis of 2-[p-(methyldiphenylstannyl)phenyl]-1,3-dioxolane (X)*

A solution of 60 mmol methyldiphenyltin chloride in 70 ml of THF was added under nitrogen to 0.6 mol of lithium shot in 30 ml THF, the temperature being kept below 25°C. The dark green mixture was left for one more hour, then filtered to remove the residual lithium, and was added to a solution of 0.8 mol of 2-(*p*-bromophenyl-1,3-dioxolane in 90 ml THF. The mixture was left overnight, then treated with water. Extraction with benzene and drying of the extract ($K_2CO_3$) and evaporation of the solvent gave 31 g of crude oil, which was kept for 12 hours at 40°C under 0.1 Torr. Recrystallization from methanol gave 20 g 2-[*p*-(diphenylmethylstannyl)phenyl]-1,3-dioxolane, m.p. 59.5—61°C. Found: C, 61.00; H, 5.15. $C_{22}H_{22}O_2Sn$ calcd.: C, 60.45; H, 5.07%.

### *Synthesis of p-(methyldiphenylstannyl)benzaldehyde (XI)*

A suspension of 2 g of compound X in 50 ml aqueous formaldehyde (37%) in the presence of *p*-toluenesulfonic acid was refluxed for 2 h. After evaporation of the solvent under reduced pressure and chromatography on $Al_2O_3$ (elution with benzene), the oil (0.75 g) obtained was recrystallized from methanol. Found: C, 61.21; H, 4.50. $C_{20}H_{18}OSn$ calcd.: C, 61.12; H, 4.62%.

## References

1 M. Gielen and M. Vanden Eynde, Bull. Soc. Chim. Belg., 90 (1981) 101.
2 M. Lequan and S. Queroix, J. Organometal. Chem., 194 (1980) 33.
3 S.Z. Abbas and R.C. Poller, J. Chem. Soc. Dalton, (1974) 1769.
4 H.G. Kuivila, K.H. Tsai and D.G. Kingston, J. Organometal. Chem., 23 (1970) 129.
5 R.B. Woodward, T.D. Kohman and G.C. Harris, J. Amer. Chem. Soc., 63 (1941) 120.
6 M. Gielen and S. Simon, Bull. Soc. Chim. Belg., 86 (1977) 39.
7 D. Seyferth and S.B. Andrews, J. Organometal. Chem., 30 (1971) 151.