Journal of Organometallic Chemistry, 67 (1974) C13—C15

Preliminary communication

OXIDATIVE ADDITION REACTIONS OF SOME ORGANOTIN(II) AND ORGANIC TIN(II) COMPOUNDS [1]

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(Received December 21st, 1973)

Summary

Dicyclopentadienyltin, tin dimethoxide and tin bis(acetylacetonate) undergo oxidative addition reactions with diphenyl disulphide, diethyl acetylenedicarboxylate and with organic halides, while dicyclopentadienyltin reacts with organotin(IV) halides to give mixed alkylcyclopentadienyltin(IV) halides.

Little is known about reactions of organotin(II) and organic tin(II) compounds (cf. ref. 2—4). As part of a study of tin(II) chemistry we have investigated some oxidative addition reactions of dicyclopentadienyltin, $(C_5H_5)_2Sn$, tin dimethoxide, $Sn(OMe)_2$, and tin bis(acetylacetonate), $Sn(acac)_2$ [5].

Tin(II) compounds react smoothly at room temperature with diphenyl disulphide to give the corresponding tin(IV) products:

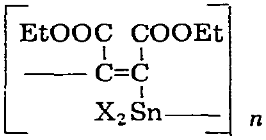
$$SnX_2 + PhSSPh \rightarrow SnX_2(SPh)_2 \rightleftarrows SnX_3(SPh) + SnX(SPh)_3$$

X = e.g. C_5H_5, OMe, SPh

Reaction of $Sn(acac)_2$ with chlorine affords *cis*-dichlorobis(acetylacetonato)-tin(IV) which has been previously prepared from $SnCl_4$ and acetylacetone [6]. Very recently the carbenoid insertion reaction of $(C_5H_5)_2Sn$ with halogens leading to $(C_5H_5)_2SnHal_2$ has been reported [7]. However, this reaction is more complicated, as we have demonstrated the transient formation of $(C_5H_5)_3SnI$, C_5H_5SnI and $C_5H_5SnI_3$ upon addition of I_2 to a $(C_5H_5)_2Sn$ solution at room temperature:

$$\begin{tikzcd}
(C_5H_5)_2Sn \arrow[r, "I_2"] & (C_5H_5)_2SnI_2 \arrow[r, "(C_5H_5)_2Sn"] & (C_5H_5)_3SnI + C_5H_5SnI \arrow[d, "I_2"] \\
 & & C_5H_5SnI_3 \arrow[ul, "(C_5H_5)_3SnI"]
\end{tikzcd}$$

Divalent germanium species react readily with unsaturated compounds, such as 2,3-dimethyl-1,3-butadiene [8]. Although $(C_5H_5)_2Sn$ and $Sn(OMe)_2$ fail to react with 2,3-dimethyl-1,3-butadiene or with *cis,cis*-1,3,5-hexatriene, these compounds and $Sn(acac)_2$ react readily with diethyl azodicarboxylate and diethyl acetylenedicarboxylate:



$$SnX_2 + EtOOC{-}C{\equiv}C{-}COOEt \rightarrow \left[\begin{array}{c} EtOOC\quad COOEt \\ \quad | \qquad | \\ —\!\!—\ C{=}C \\ \qquad\ \ | \\ \qquad X_2Sn—\!\!— \end{array}\right]_n$$

$X = C_5H_5$, OMe, acac

The molecular weights of these products, which are soluble in benzene, point to the presence of six-, nine-, and higher-membered rings. Recently, the reaction of $SnCl_2$ with diethyl acetylenedicarboxylate has been reported to give a six-membered ring structure, but molecular weight data were not given [9].

$Sn(acac)_2$ and $(C_5H_5)_2Sn$ react at room temperature with reactive organic halides, such as methyl iodide, allyl bromide and benzyl bromide, with the formation of the corresponding tin(IV) products:

$$Sn(acac)_2 + RX \rightarrow RSn(acac)_2X$$

R = Me, allyl, benzyl

The reaction of $(C_5H_5)_2Sn$ with methyl iodide in benzene solution at room temperature in daylight initially gives rise to the formation of a precipitate of C_5H_5SnI. Upon completion only $Me(C_5H_5)_2SnI$ (> 90%) is present, suggesting the following reaction scheme (cf. ref. 7):

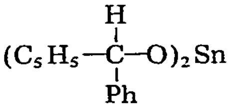
$$\begin{tikzcd}
(C_5H_5)_2Sn + MeI \arrow[r] & Me(C_5H_5)_2SnI \arrow[r, shift left, "(C_5H_5)_2Sn"] & Me(C_5H_5)_3Sn + C_5H_5SnI\downarrow \arrow[l, shift left] \arrow[d, "MeI"] \\
 & & Me(C_5H_5)SnI_2 \arrow[lu, "Me(C_5H_5)_3Sn"]
\end{tikzcd}$$

$(C_5H_5)_2Sn$ readily undergoes exchange reactions with alkyltin(IV) halides leading to alkylcyclopentadienyltin(IV) halides and cyclopentadienyltin(II) chloride [4] or $SnCl_2$, e.g.:

$$(C_5H_5)_2Sn + Me_2SnCl_2 \rightarrow Me_2(C_5H_5)SnCl + C_5H_5SnCl\downarrow$$

$$(C_5H_5)_2Sn + 2\ MeSnCl_3 \rightarrow 2\ Me(C_5H_5)SnCl_2 + SnCl_2\downarrow$$

Reaction of $(C_5H_5)_2Sn$ with reactive carbonyl compounds does not involve oxidative addition. Instead, addition of the tin—carbon bond to the carbon—oxygen double bond takes place with formation of a tin(II) alkoxide:



$$(C_5H_5)_2Sn + 2\ PhCHO \rightarrow (C_5H_5{-}\overset{\displaystyle H}{\underset{\displaystyle Ph}{C}}{-}O)_2Sn$$

TABLE 1

PMR-DATA [a] OF SOME CYCLOPENTADIENYLTIN(IV) COMPOUNDS

	δ [b] (C_5H_5) $n = 1$	J [c] $n = 1$	δ [b] (C_5H_5) $n = 2$	J [c] $n = 2$	δ [b] (C_5H_5) $n = 3$	J [c] $n = 3$
$(C_5H_5)_nSn(SPh)_{4-n}$	5.87	33.8/35.4	5.90	31.0/32.5	5.92	28.8/30.0
$(C_5H_5)_nSnI_{4-n}$	6.32	44.5/46.5	6.17	35.5/37.1	6.06	30.2/31.5
$Me(C_5H_5)SnI_2$	6.26	37.7/39.4				
$Me(C_5H_5)_2SnI$			6.15	29.9/31.2		
$Me(C_5H_5)SnCl_2$	6.36	41.9/43.8				
$Me_2(C_5H_5)SnCl$	6.02 [d]	29 [d]				
$Me(C_5H_5)_2SnCl$			6.13	31.2/32.6		

[a] $CDCl_3$ solution. [b] Downfield from TMS. [c] $J(^{117}Sn—C_5H_5)$ and $J(^{119}Sn—C_5H_5)$, respectively. [d] C_6H_6 solution.

In this respect $(C_5H_5)_2Sn$ resembles allyltin(IV) [10] and α-functionally substituted organotin compounds [11], which, likewise, readily add to the carbonyl function.

PMR data of some of the new compounds reported are given in Table 1.

A detailed account of this work including Mössbauer and PMR data will be published shortly.

Acknowledgement

Financial support by the International Tin Research Council, London, is gratefully acknowledged.

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