NOTE

TRIPHENYLTINMAGNESIUM BROMIDE. EVIDENCE FOR THE OCCUR-RENCE OF DIPHENYLSTANNENE STABILIZED BY COORDINATION

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Whereas organotin alkali metal derivatives have been widely investigated[1] information on organotin magnesium derivatives is restricted to a brief report on the solution chemistry of $(Ph_3Sn)_2Mg$[2]. Evidence has been presented for the existence in solution of $Ph_3GeMgCl$[3,4] and $Ph_3PbMgBr$[5], but these compounds have not been isolated. The isolation of triphenyltin derivatives of the Group IIB metals Zn and Cd has recently been reported[6].

The hydrostannolysis of reactive metal–carbon bonds offers a particularly useful route to compounds containing metal–tin bonds[6-8]. This reaction has now been applied to a study of the triphenyltin Grignard reagent.

The reaction of triphenyltin hydride with an equimolecular amount of ethylmagnesium bromide–triethylamine complex[9,10] in diethyl ether at $-15-0°$ results in selective hydrostannolysis of the Mg–C bond as evidenced by the quantitative formation of ethane:

$$Ph_3SnH + EtMgBr \cdot NEt_3 \longrightarrow Ph_3SnMgBr \cdot NEt_3 + EtH\uparrow$$
$$(I)$$
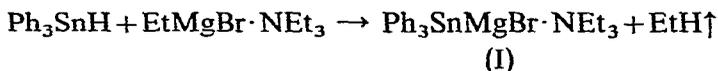
An ether-insoluble oil (I) was isolated which could not be made to crystallize. Hydrolysis of (I) affords Ph_3SnH and a trace of benzene. Reaction with triphenyltin chloride results in the formation of hexaphenylditin (isolated in 40% yield after recrystallization). Reaction with benzyl chloride yields triphenylbenzyltin identified by m.p. and the NMR spectrum. Iodination of (I) and subsequent alkylation with methylmagnesium iodide yielded a mixture of phenylmethyltin compounds consisting for 70% of triphenylmethyltin as determined by NMR spectroscopy. Each of these reactions is as expected for a triphenyltinmagnesium species (I).

(I) upon being kept *in vacuo* (5 h at 50°/0.01 mm) gradually solidifies. The resulting slightly yellow, air-sensitive product (II) analyzes for the unsolvated triphenyltin Grignard reagent $Ph_3SnMgBr$. A mol.wt. determination reveals dimeric association in freezing benzene. A fully identical product was obtained by the reaction of Ph_3SnH with EtMgBr in diethyl ether followed by keeping *in vacuo*.

Hydrolysis of (II) affords benzene and no Ph_3SnH as shown by IR and GLC. Reaction with Ph_3SnCl yields Ph_4Sn isolated in 35% yield after recrystallization. $Ph_3SnSnPh_3$ was not formed as appeared from thin layer chromatography of the crude reaction product. We interpret these results in terms of phenyl-group transfer from tin to magnesium occurring upon transformation of the triethylamine or di-

ethyl ether complex (I) into (II), the phenylmagnesium moiety in (II) being responsible for the formation of benzene and tetraphenyltin, respectively. In the extreme case of phenyl-group transfer (II) is formulated as dimeric phenylmagnesium bromide with bridging bromine atoms and diphenyltin via its free electron pair occupying the fourth coordination position at magnesium (cf. the recently reported X-ray structure of dimeric $EtMgBr \cdot NEt_3$[10]):

$$2\ Ph_3SnMgBr \cdot NEt_3 \xrightarrow{-Et_3N} \underset{(II)}{\begin{array}{c} Ph_2Sn \diagdown \quad \diagup Br \diagdown \quad \diagup Ph \\ Mg \qquad Mg \\ Ph \diagup \quad \diagdown Br \diagup \quad \diagdown SnPh_2 \end{array}}$$

$$(I) \hspace{10em} (II)$$
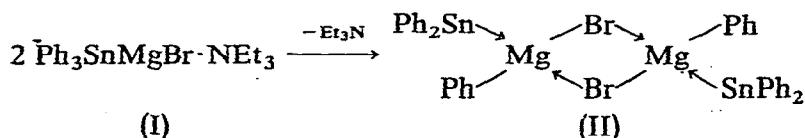
The migration of a phenyl group (which keeps its electron pair) from tin to magnesium (which has become an electrophilic centre upon removal of the coordinated ligand) is fully comparable to the various 1,2-nucleophilic molecular rearrangements in organic chemistry. The high migratory aptitude of the phenyl group in e.g. the Wagner–Meerwein rearrangement is well-documented[11].

Our proposal of monomeric diphenyltin functioning as a donor ligand finds a precedent in the isolation of well-documented transition metal–carbene complexes[12]. As appears from a recent review evidence for IVth group organometallic carbene analogs is mainly based on derivative chemistry[13]. (II) may be regarded as complex-stabilized diphenylstannene. A complex in which diphenyltin acts as an acceptor for triphenylphosphine has been proposed as an intermediate in the high-temperature reaction of tetraphenyltin and phosphorus[14].

A related 1,2-phenyl-group migration, attended, however, by loss of the diphenyltin moiety, has recently been observed by Baird[15] who isolated $PhPtCl(PPh_3)_2$ upon heating $Ph_3SnPtCl(PPh_3)_2$ in refluxing acetone. Similarly, the formation of $Ph_3PbPbPh_3$ from Ph_2Pb and of Ph_4Pb from $Ph_3PbPbPh_3$ has been discussed in terms of 1,2-phenyl shifts[16].

The transformation into unsolvated (II) cannot be effected if (I) does contain a strong complexing agent such as tetramethylethylenediamine (TMED).

The phenyl shift can be reversed with complexing ligands such as diethyl ether and TMED. When TMED was added to a benzene solution of (II) and Ph_3SnCl was added to aliquots taken at fixed time intervals, one hour after the addition of TMED $Ph_3SnSnPh_3$ again appeared to be the only product formed. The formation of Ph_3SnLi from $SnCl_2$ and PhLi[17] involves insertion of diphenyltin into the Li–C bond of phenyllithium possibly via the complex $Ph_2Sn \cdot PhLi$.

Further chemical evidence for the presence of a diphenyltin group in (II) has been obtained by heating (II) with methyl iodide in a sealed tube (3 h at 140°). The resulting reaction mixture after removal of volatiles (a.o. toluene and unreacted methyl iodide) was treated with MeMgBr. The formation of toluene and of Ph_3SnMe (60%) and Ph_2SnMe_2 (40%) (yields determined by NMR spectroscopy) can be rationalized as follows (cf. the reaction of "divalent" tin compounds with alkyl halides[18]):

$$Ph_2Sn \cdot PhMgBr + 2\ MeI \xrightarrow{\Delta} \quad Ph_2SnMeI \quad + PhMgBr$$

$$\underset{Ph_2SnMe_2 \quad Ph_3SnMe}{\overset{MeMgBr \diagup \quad \diagdown PhMgBr}{}} \quad \underset{PhMe}{\overset{\big| MeI}{}}$$
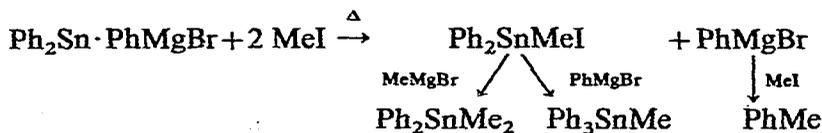
Disproportionation of Ph_2SnMeI is an additional source of Ph_3SnMe[18].

The reaction of (II) with dicobalt octacarbonyl lends further support to the presence of a stannacarbene entity in (II). Bonati *et al.*[19] have recently synthesized bis(tetracarbonylcobalt)diphenyltin by insertion of $SnCl_2$ into the Co–Co bond of $Co_2(CO)_8$ followed by reaction with PhMgBr. Reaction of (II) with $Co_2(CO)_8$ affords after purification by column chromatography a yellow product with carbonyl and skeletal vibrations essentially similar to those reported[19]. Reaction of the crude product with triphenylphosphine in diethyl ether afforded yellow-brown bis[tricarbonyl(triphenylphosphine)cobalt]diphenyltin (m.p.: 140°, dec.) identical (IR, UV, m.p.) with the product formed upon reaction of authentic $Ph_2Sn[Co(CO)_4]_2$[19] with triphenylphosphine:

$$[Ph_2Sn \cdot PhMgBr]_2 + 2\,Co_2(CO)_8 \rightarrow 2\,Ph_2Sn[Co(CO)_4]_2 \xrightarrow{2\,Ph_3P}$$
$$2\,Ph_2Sn[Co(CO)_3PPh_3]_2 + 4\,CO\uparrow$$
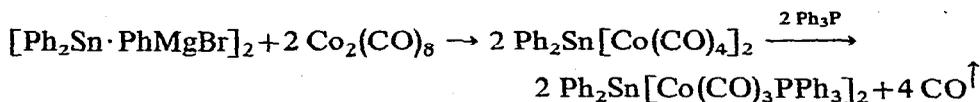
Difficulties were encountered in obtaining satisfactory analytical data for the cobalt carbonyl complexes (*cf.* ref. 20).

The influence of coordinating ligands on the chemistry of related triphenyltinzinc derivatives will be discussed separately[21].

EXPERIMENTAL*

Thin-layer chromatography experiments were carried out on "Eastman Chromagram sheet type K 301 R2 Silica Gel". A 1 : 1 mixture of carbon tetrachloride and cyclohexane was used as developing solvent. The spots were detected with iodine and a 0.1% solution of pyrocatechol violet in alcohol.

(Triphenyltin)magnesium bromide (I)

To 5.8 g (0.025 mole) of ethylmagnesium bromide–triethylamine complex (prepared from ethyl bromide and magnesium in triethylamine[9]) in 40 ml of ether kept at −70°, 8.75 g (0.025 mole) of triphenyltin hydride were added. The reaction mixture was warmed up slowly and at −15° the evolution of gas started. In the course of 4 h the theoretical amount of gas was collected. A gas chromatogram showed the presence of ethane and a trace of hydrogen. (Triphenyltin)magnesium bromide complex separated as a slightly yellow oil. Yield 94%, calculated on the amount of ethane.

Diphenyltin–phenylmagnesium bromide (II)

The oil obtained was kept in high vacuum (50°/0.01 mm) for 5 h. A slightly yellow solid was obtained. (Found: C, 47.7; H, 4.8; Br, 17.6; mol.wt. cryosc., 949. $C_{18}H_{15}BrMgSn$ calcd.: C, 47.60; H, 3.32; Br, 17.60%; mol.wt. for dimer, 908.) The same product was obtained upon reacting a solution of ethylmagnesium bromide in ether and triphenyltin hydride, followed by keeping *in vacuo* for 5 h. (Found: C, 46.75; H, 4.6; Br, 18.1; Sn, 26.9. $C_{18}H_{15}BrMgSn$ calcd.: C, 47.60; H, 3.32; Br, 17.60; Sn, 26.13%.)

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* With Mr. F. Verbeek.

Reaction of diphenyltin–phenylmagnesium bromide with methyl iodide

In a sealed tube 3.0 g (0.006 mole) of diphenyltin–phenylmagnesium bromide and 3.7 g (0.026 mole) of methyl iodide were heated together for 3 h at 140°. The content of the tube was extracted with ether. The volatiles (ether, toluene and unreacted methyl iodide) were distilled off. The residue (1.7 g) was treated with methylmagnesium iodide. After decomposition of the reaction mixture 1.2 g of a slightly yellow liquid remained. The composition of this mixture was determined by NMR analysis.

Reaction of diphenyltin–phenylmagnesium bromide with dicobalt octacarbonyl

Diphenyltin–phenylmagnesium bromide (1.7 g, 0.003 mole) in benzene was added to a slurry of dicobalt octacarbonyl (1.3 g, 0.003 mole) in benzene. Gas was evolved; the solution became dark red. After 3 days, benzene was removed under vacuum and the dark coloured residue was extracted with pentane. The pentane extract contained 0.8 g of sticky dark-brown mass. This was dissolved in ether and 0.68 g of triphenylphosphine in ether was added. A moderate evolution of gas set in (carbon monoxide). In the course of one night a yellow brown precipitate was formed (0.15 g). The product decomposed at ±140°.

Difficulties were encountered in obtaining satisfactory analytical data for $Ph_2Sn[Co(CO)_3PPh_3]_2$ obtained by the $Ph_2Sn \cdot PhMgBr$-route [Product (A). Found: C, 58.7; H, 4.9. $C_{54}H_{40}Co_2O_6P_2Sn$ calcd.: C, 59.87; H, 3.72%.] and for the product obtained from authentic $Ph_2Sn[Co(CO)_4]_2$[19] [Product (B)]. The IR spectrum in the carbonyl region [(A); $v_{max}(cm^{-1})$: 2006; 1976 (sh); 1951; 1931; 1887. (B): v_{max} (cm^{-1}): 2008; 1980 (sh); 1953; 1927; 1888] and the UV spectrum [(A); v_{max} (nm): 390; 308 (sh); 272; 265. (B); v_{max} (nm): 391; 309 (sh); 272; 265] for (A) and (B) were identical.

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