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Reaction products of dichlorodiorganostannanes with sodium in liquid ammonia: *In-situ* investigations with ^{119}Sn NMR spectroscopy and usage as intermediates for the synthesis of tetraorganostannanes

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ABSTRACT

Dichlorodibutylstannane, dichlorodioctylstannane and dichlorodiphenylstannane were reacted with different amounts of sodium in liquid ammonia. At a molar ratio of R_2SnCl_2/Na of 1:2, polystannanes precipitated, in some cases accompanied by cyclic oligostannanes. The products resulting from mixtures with R_2SnCl_2/Na ratios of 1:3 to 1:10 were soluble and, hence, could be studied *in-situ* in liquid ammonia with ^{119}Sn NMR spectroscopy. The compounds obtained, tin hydrides of the type R_2SnH^- and in certain cases distannides of the composition $R_4Sn_2^{2-}$, formed essentially independent of the R_2SnCl_2/Na ratio; this, in contrast to views expressed in the literature. Our experiments showed that the chemical structure of the *in-situ* generated species did not permit to draw conclusions about the composition of the reaction products with bromoethane and *vice versa* – a practice commonly described. Furthermore, we observed migration of the butyl groups both *in-situ* during the reaction of dichlorodibutylstannane with sodium in liquid ammonia, as well as in the final reaction product. By contrast in the case of the phenyl substituent, migration was detected not during the chemical event in liquid ammonia, but only in the compounds formed. These observations imply a different mechanism for butyl and phenyl group migration.

1. Introduction

The reaction of haloorganostannanes with sodium in liquid ammonia has attracted attention since the early part of the past century [1–11]. The resulting products have been used *in-situ* as intermediates for the preparation of organotin compounds (organostannanes). In particular, conversion of such intermediates with haloalkanes and haloarenes yielded tetraorganostannanes [12–25]. In this context, also dihalodiorganostannanes, R_2SnCl_2, have been exposed to sodium, and were regarded to yield diorganotin dianions (Fig. 1, diorganostannide dianions, R_2Sn^{2-}), which can subsequently act as reaction intermediates for the synthesis of tetraorganostannanes, with the respective sodium halides as reaction byproducts [18,26–30]. However, surprisingly, recent studies performed *in-situ* with ^{119}Sn NMR spectroscopy experiments indicated that diorganostannide dianions were not formed when stoichiometric ratios of dichlorodiorganostannanes and sodium are present in liquid ammonia (i.e. 4 molar equivalents of sodium per mol stannane) [31].

Further, it has been suggested (but not spectroscopically verified) [5,26] that the composition of the reaction intermediates changes upon variation of the diorganostannane/sodium ratio. In addition, it has been claimed that treatment of dihalodiorganostannanes with less than 4 molar equivalents of sodium (preferentially two equivalents) gives rise to the formation of oligostannanes or polystannanes (Fig. 1) [1,4,5]; however the resulting products were not thoroughly characterized. Polystannanes are a unique class of polymers as their backbone consists of covalently bound metal atoms; they were first prepared by Löwig [32] and then mainly during the last two decades in various laboratories by different methods [33–52].

In order to resolve the various discrepancies alluded above, we carried out *in-situ* investigations of the species arising from reactions of dichlorodiorganostannanes and sodium at different molar ratios in liquid ammonia and explored their applicability as reaction intermediates for the synthesis of tetraorganostannanes by conversion with bromoethane.

2. Results

For the experiments, dichlorodibutylstannane and dichlorodioctylstannane were employed as representatives for alkyl

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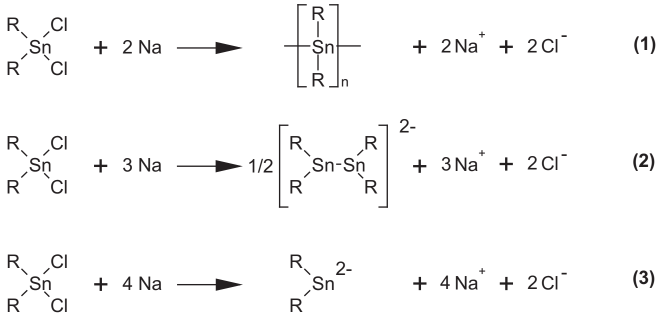

Fig. 1. Previously advanced reactions of dihalodiorganostannanes with sodium.

stannanes and dichlorodiphenylstannane as the most convenient arylstannane. All those compounds were exposed to 2, 3, 4 and 10 equivalents of sodium, respectively. A summary of the resulting products is presented in Table 1.

2.1. Dihalodiorganostannane/sodium 1:2

A general feature of reactions with a dichlorodiorganostannane/sodium ratio of 1:2 was formation of polymers (cf. Table 1). Below, the results obtained for the individual systems are described in more detail.

2.1.1. Dichlorodibutylstannane

Exposure of dichlorodibutylstannane to 2 molar equivalents of sodium in liquid ammonia caused immediate precipitation of a yellow product, which is typical for poly(dibutylstannane). The GPC diagrams revealed the presence of polymer with a molar mass of 8 kg/mol. In addition, products in a mass range of cyclic byproducts (cyclopentastannane and cyclohexastannane) were detected. ^{119}Sn NMR spectra showed a broad signal at −190 ppm characteristic for poly(dibutylstannane) and signals at −202 ppm and −203 ppm, which are typical for cyclic byproducts [50]. The elemental composition of the isolated yellow product was consistent with products of the composition $(SnBu_2)_n$, which is in agreement both with the composition of linear polymers and cyclic oligomers.

2.1.2. Dichlorodioctylstannane

Conversion of dichlorodioctylstannane with 2 molar equivalents of sodium was performed in the same manner as the above described reaction of dichlorodibutylstannane, resulting in precipitation of a yellow, pasty material. Analogously, GPC analysis indicated the generation of poly(dioctylstannane) (M_p around 6 kg/mol), together with cyclic pentamers and hexamers. The elemental composition of the isolated product was in agreement with that of $(Oct_2Sn)_n$, and ^{119}Sn NMR spectroscopy in deuterated dichloromethane revealed a broad signal at −192 ppm which corresponds to the value of poly(dioctylstannane), and signals at −203 ppm and −205 ppm for the cyclic byproducts [50].

Table 1
Overview of the detected products that emerged from reaction of dichlorodiorganostannanes, R_2SnCl_2, with different ratios of sodium in liquid ammonia.

R_2SnCl_2: Na ratio	R = butyl	R = octyl	R = phenyl
1:2	$(SnBu_2)_n$ polymer and cyclic oligomers	$(SnOct_2)_n$ polymer and cyclic oligomers	$(SnPh_2)_n$ polymer
1:3	Bu_2SnH^-, $(Bu_4Sn_2)^{2-}$, Bu_3Sn^-, one unidentified product	Oct_2SnH^-	Ph_2SnH^-, $(Ph_4Sn_2)^{2-}$ [a]
1:4	Bu_2SnH^-, $(Bu_4Sn_2)^{2-}$, Bu_3Sn^-, one unidentified product	Oct_2SnH^-	Ph_2SnH^-, $(Ph_4Sn_2)^{2-}$
1:10	Bu_2SnH^-, $(Bu_4Sn_2)^{2-}$, Bu_3Sn^-, one unidentified product	Oct_2SnH^-	Ph_2SnH^-, $(Ph_4Sn_2)^{2-}$

[a] Additional signals are attributed to degradation products formed during transfer of the reaction solutions to the NMR tubes that could not be avoided. Thus, the signal of the distannide was not always present in the spectra.

2.1.3. Dichlorodiphenylstannane

Also treatment of dichlorodiphenylstannane with 2 molar equivalents of sodium resulted in immediate precipitation of a yellow, shiny product. The material obtained was insoluble in all tested organic solvents at room temperature and as well at elevated temperatures (close to the boiling point of the solvents). Therefore, it was not possible to determine its molar mass. The product was washed with a water/ethanol mixture (9:1) to remove sodium chloride and, thereafter, extracted with hot dichloromethane to dissolve potential byproducts, in particular cyclic oligo(diphenylstannane)s. ^{119}Sn NMR analysis of the concentrated extracts indicated that no significant amounts of cyclic byproducts were formed. Elemental analysis of the material was consistent with that of $(Ph_2Sn)_n$.

2.2. Dichlorodiorganostannane/sodium 1:3, 1:4 and 1:10

Recently, we reported [31] that in contrast to general views (Fig. 1), dichlorodibutylstannane and dichlorodiphenylstannane do not react with four equivalents of sodium to yield the respective diorganostannide dianions. Instead, the anions $HSnR_2^-$ and $(R_2Sn{-}SnR_2)^{2-}$ formed in quantities of similar order of magnitude, and in the case of dichlorodibutylstannane additionally R_3Sn^- and a fourth unidentified product (e.g. H_2RSn^- or $(HRSn{-}SnHR)^{2-}$) arose by alkyl group migration. Considering that Na in fact is present in liquid ammonia as Na^+ and solvated electrons, the latter providing the typical blue color of the corresponding solutions [53], the existence of $(R_2Sn{-}SnR_2)^{2-}$ may be somewhat surprising, as two of the highly reactive solvated electrons per dianion may remain under a dichlorodiorganostannane/sodium ratio of 1:4. In order to investigate if larger quantities of sodium would ultimately lead to cleavage of Sn–Sn bonds in the dianions and if lower amounts influence the ratio between the aforementioned stannides, dichlorodiorganostannanes were exposed to 3, 4 and 10 molar equivalents of Na. According to the literature [5,26] substantial differences in the *in-situ* formed reaction products are expected at these different ratios.

Since the solvated electrons produced upon dissolution of metallic sodium are consumed when dichlorodiorganostannanes react - due to the generation of stannides and chloride ions - the electric conductivity of the reaction mixture is expected to decrease during the reaction of dichlorodiorganostannanes with sodium because highly mobile electrons are removed from the system. Thus, we employed *in-situ* measurements of the electric conductivity in liquid ammonia to qualitatively follow the course of the reaction.

An overview of the soluble products detected by *in-situ* ^{119}Sn NMR spectroscopy in liquid ammonia obtained with the different compounds is displayed in Table 2; the results are described in more detail in the following sections.

2.2.1. Dichlorodibutylstannane

The electric conductivity of mixtures of dichlorodibutylstannane/sodium 1:4 versus reaction time is presented in Fig. 2a. The data show that the conductivity reached a constant value after 30 min, indicating that the reaction was terminated within this period (Fig. 2a). Accordingly, *in-situ* NMR measurements in liquid ammonia were performed after a reaction time of 30 min. Remarkably, regardless of the dichlorodibutylstannane/sodium molar ratio in the range of 1:3 up to 1:10, not only the same