

SOME EXCHANGE REACTIONS INVOLVING PHENYLTIN HYDRIDES AND ORGANOTIN HALIDES

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Summary

Reaction of diphenyltin dihydride with diphenyltin dichloride or diphenyltin dibromide in a 1 : 1 mole ratio gives good conversion to diphenyltin chloride hydride and diphenyltin bromide hydride, respectively. Triphenyltin hydride with diphenyltin dichloride or diphenyltin dibromide in a 1 : 1 mole ratio gives fair conversion to the corresponding halide hydrides but less than in the case of diphenyltin dihydride. Diphenyltin dihydride reacts with dialkyltin dichloride in a 1 : 1 mole ratio to give a preponderance of organotin chloride hydride along with diphenyltin dihydride but no dialkyltin dihydride. However, triphenyltin hydride did not appear to react with dialkyltin dihalides in a 1 : 1 mole ratio to yield either the dialkyltin halide hydride or the dialkyltin dihydride. Reactions attempted between triphenyltin hydride and several trialkyltin chlorides confirm the tendency of the hydride hydrogen to become attached to the triphenyltin moiety rather than the trialkyltin or the dialkylchlorotin moieties.

Introduction

Considerable work has been done on halide-hydride exchanges involving alkyltin hydrides and in particular butyltin hydrides [1-7]. Very little has been reported on comparable exchanges involving phenyltin hydrides. This paper concerns the results of exchanges we have carried out between phenyltin hydrides and organotin halides [8].

Results and discussion

Reactions of diphenyltin dihydride with diphenyltin dihalides

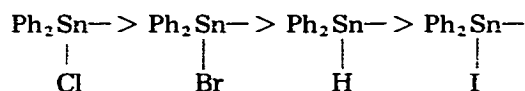
Reactions were carried out between diphenyltin dihydride and diphenyltin dihalides in a 1 : 1 mole ratio according to eq 1

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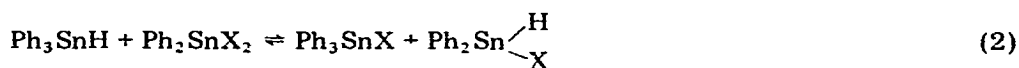
(X = Cl, Br, and I)

Good conversion to diphenyltin chloride hydride (93%) and diphenyltin bromide hydride (90%) was obtained. No evidence, however, was found for diphenyltin iodide hydride. It appears from these experiments that the order of preference for the hydride hydrogen to be attached to tin in the organotin moiety is as follows



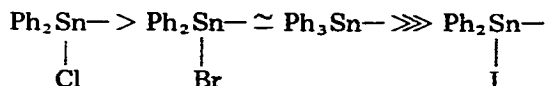
Reactions of triphenyltin hydride with diphenyltin dihalides

Reactions were also carried out between triphenyltin hydride and diphenyltin dihalides in a 1:1 mole ratio according to eq. 2



(X = Cl, Br, and I)

It can be seen in Table 1 that the percentage of halide hydride formed decreases significantly as the halide is changed from chloride to bromide to iodide. Comparable reactions carried out between tri-n-butyltin hydride and di-n-butyltin dihalides showed almost complete conversion to the halide hydride in each case [4] and lead to the conclusion that hydrogen tends to remain on the triphenyltin as opposed to the tri-n-butyltin moiety. Likewise, it appears that the above exchanges show the following order of preference of hydrogen to become attached to tin in the moieties listed below:



It was of some concern that we did not find any evidence for the formation of

TABLE I
REACTIONS OF TRIPHENYLTIN HYDRIDE WITH DIPHENYLTIN DIHALIDES

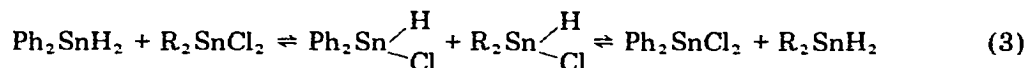
Dihalide	$\text{Ph}_2\text{Sn} \begin{array}{l} \text{H} \\ \diagdown \\ \text{X} \end{array}$ (%)	Ph_3SnH (%)	Total NMR hydride peak area (%) ^a	$\delta(\text{Sn}-\text{H})$ for $\text{Ph}_2\text{Sn} \begin{array}{l} \text{H} \\ \diagdown \\ \text{X} \end{array}$ (ppm)
Ph_2SnCl_2	73	27	100	8.15
Ph_2SnBr_2	54	46	97	8.03
Ph_2SnI_2	0	100	96	

^a Based on the total hydride peak area for the case of Ph_2SnCl_2 being 100%

diphenyltin iodide hydride in either this or the previous reaction between diphenyltin dihydride and diphenyltin diiodide. Therefore, we did carry out the reactions of triphenyltin hydride with the diphenyltin dihalides using the same quantity of triphenyltin hydride in each case and compared the total product hydride NMR peak absorptions for the three experiments. As can be seen, the sum of the hydride peak areas for the product hydrides was the same within experimental error for all three cases and supports the conclusion that all of the hydride has been accounted for in both the diphenyltin dibromide and the diphenyltin diiodide reactions.

Reactions of diphenyltin dihydride with dialkyltin dichlorides

Reactions of diphenyltin dihydride with dialkyltin dihalides have been carried out in a 1 : 1 mole ratio as indicated in eq. 3



(R = n-butyl, isobutyl, and n-octyl)

Whereas in reactions of R_2SnH_2 (R = n-butyl, isobutyl, and n-octyl) with $\text{R}'_2\text{SnCl}_2$ (R' = methyl, ethyl, n-propyl, n-butyl, isobutyl, n-octyl, and cyclohexyl) there was found to be a preponderance of organotin chloride hydrides at equilibrium as shown by PMR spectral data, in the case of diphenyltin dihydride with the same dialkyltin dichlorides a smaller quantity of organotin chloride hydrides was found and the only dihydride found was diphenyltin dihydride [7]. The reverse reactions were carried out, i.e., of R_2SnH_2 (R = n-butyl, isobutyl, and n-octyl) with Ph_2SnCl_2 in a 1 : 1 mole ratio, with reasonably good agreement between the final results for both the forward and the reverse reactions. These results involving phenyltin hydrides are summarized in Tables 2 and 3. These data indicate that there is a much stronger tendency for hydrogen to become attached to tin in the diphenyl (hydrido) tin species [$\text{Ph}_2\text{Sn}-$] than in the dialkyl (hydrido) tin species [$\text{R}_2\text{Sn}-$]



TABLE 2
PERCENTAGES OF PRODUCTS IN REACTIONS OF Ph_2SnH_2 WITH R_2SnCl_2

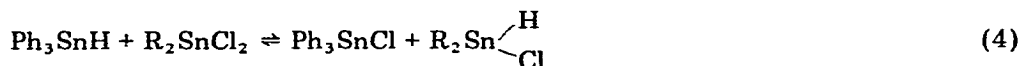
R	R_2SnH_2 (%)	$\text{R}_2\text{Sn} \begin{array}{l} \text{H} \\ \diagup \\ \text{Cl} \end{array} + \text{Ph}_2\text{Sn} \begin{array}{l} \text{H} \\ \diagup \\ \text{Cl} \end{array}$ (combined %)	Ph_2SnH_2 (%)
Methyl	0	53	47
Ethyl	0	71	29
n-Propyl	0	46	54
n-Butyl	0	72	28
iso-Butyl	0	70	30
n-Octyl	0	61	39
Cyclohexyl	0	44	56

TABLE 3
PERCENTAGES OF PRODUCTS IN REACTIONS OF Ph_2SnCl_2 WITH R_2SnH_2

R	R_2SnH_2 (%)	$\text{R}_2\text{Sn} \begin{matrix} \text{H} \\ \diagup \\ \text{Cl} \end{matrix} + \text{Ph}_2\text{Sn} \begin{matrix} \text{H} \\ \diagup \\ \text{Cl} \end{matrix}$ (combined %)	Ph_2SnH_2 (%)
n-Butyl	0	65	35
iso-Butyl	0	70	30
n-Octyl	0	56	44

Reactions of triphenyltin hydride with dialkyltin dihalides

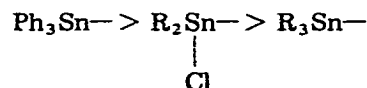
Several reactions were next carried out between triphenyltin hydride and dialkyltin dihalides in a 1 : 1 mole ratio as indicated in eq 4



In each case no Sn—H signal was obtained for either the dialkyltin halide hydride or the dialkyltin dihydride and the only Sn—H signal found was that for triphenyltin hydride. Excess triphenyltin hydride did not produce a signal for the dialkyltin dihydride in any case and served only to increase the triphenyltin hydride signal. If the initial hydride had been tri-n-butyltin hydride, its use in excess would have resulted in essentially complete conversion to the dialkyltin dihydrides [6]. Therefore, we must conclude that there is a greater tendency of hydrogen to be attached to the Ph_3Sn — moiety than to the Bu_3Sn — moiety. Furthermore, from the lack of reaction above one might also conclude that there is a strong tendency for the hydride hydrogen to remain on the Ph_3Sn — moiety in contrast to the R_2Sn — moiety. Since the preference

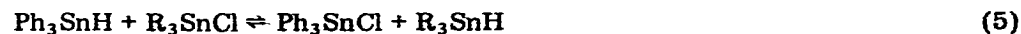
$\text{R}_2\text{Sn} \begin{matrix} \text{H} \\ \diagup \\ \text{Cl} \end{matrix} > \text{R}_3\text{Sn}$ has previously been shown to exist [4,6], the following order

$\text{R}_2\text{Sn} \begin{matrix} \text{H} \\ \diagup \\ \text{Cl} \end{matrix} > \text{R}_3\text{Sn}$
would seem to pertain



Reactions of triphenyltin hydride with trialkyltin chlorides

Reactions were finally carried out between triphenyltin hydride and several trialkyltin chlorides in a 1 : 1 mole ratio



(R = methyl, ethyl, n-propyl, and n-butyl)

As can be seen in Table 4, varying the alkyl group has little effect on the overall result which is that in all cases there is a strong tendency for hydrogen to

TABLE 4
REACTIONS OF TRIPHENYLTIN HYDRIDE WITH TRIALKYLTIN CHLORIDES

R	Ph ₃ SnH (%)	R ₃ SnH (%)
Methyl	94	6
Ethyl	93	7
n-Propyl	91	9
n-Butyl	85	15

become attached to the triphenyltin moiety instead of the trialkyltin moiety. This result was confirmed by running a reaction between tri-n-butyltin hydride and triphenyltin chloride in a 1 : 1 mole ratio to obtain a high yield of triphenyltin hydride (77%). It should also be noted that whereas previously discussed exchanges were rapid and were completed within a few minutes of mixing the reactants (as determined by rerunning spectra and in some cases by testing the reverse reactions) in this system the exchange was much slower. For example, the exchange between tri-n-butyltin hydride and triphenyltin chloride was accomplished over a period of six hours.

Experimental

All reactions involving hydrides were carried out in an atmosphere of pre-purified nitrogen. Triorganotin hydrides and diorganotin dihydrides were prepared by established procedures involving the reduction of triorganotin chlorides and diorganotin dichlorides, respectively, with lithium aluminum hydride in anhydrous ether. Triorganotin halides and diorganotin dihalides were obtained from M and T Chemicals, Inc., except that diethyltin dichloride was obtained from Alpha Inorganics, Inc.

Technique

Proton magnetic resonance spectra were obtained using a Varian Model A-60 NMR spectrometer, using tetramethylsilane as an internal standard. Unless otherwise noted, spectra were run neat. Reference spectral data are found in ref. 6.

Reactions were carried out by thoroughly mixing the appropriate molar ratio of the reactants in a small flask after which a small portion was transferred under nitrogen to a NMR tube and its spectrum was run immediately.

The areas under the hydride peaks were measured by a planimeter and were also usually checked by integration. The percentages of organotin hydrides in the product mixture were determined by comparing the appropriate peak areas in NMR spectra. Where applicable the percentage of total hydride molecules attributable to diorganotin halide hydrides was calculated recognizing that one molecule of organotin dihydride would have twice the effect on the NMR signal as would one molecule of organotin halide hydride.

The results obtained in these reactions are shown in Tables 1-4 in the Results and discussion section.

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