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NOTE

SOME REACTIONS OF DIORGANOTIN DIHYDRIDES WITH DIORGANOTIN DICHLORIDES*

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Several examples of reactions of diorganotin dihydrides with diorganotin dichlorides have been reported. Almost all of these correspond to the generalized reaction (1) in which the organic groups in the hydride are the same as those in the

$$R_2SnH_2+R_2SnX_2 \rightleftarrows R_2SnXH \quad (1)$$

halide[1-5]. A specific case involving the generalized reaction (2) was reported by

$$R_2SnH_2+R'_2SnX_2 \rightleftarrows R_2SnX_2+R'_2SnH_2 \quad (2)$$

Neumann and Pedain[2] in which dimethyltin dihydride was obtained in 73% yield from the distillation of a reaction mixture of dibutyltin dihydride and dimethyltin dichloride.

We have carried out a number of reactions in which the organic group in the dihydride differs from that in the dihalide. The experimental results may be represented by the generalized reaction (3), since in most cases large proportions of

$$R_2SnH_2+R'_2SnX_2 \rightleftarrows R_2SnXH+R'_2SnXH \rightleftarrows R_2SnX_2+R'_2SnH_2 \quad (3)$$

mixtures of organotin halide hydrides are found in equilibrium with other species, and since the equilibrium has been approached from both sides of the reaction.

The results of reactions of di-n-butyltin dihydride, diisobutyltin dihydride, di-n-octyltin dihydride and diphenyltin dihydride with a number of diorganotin dihalides as analyzed by proton magnetic resonance spectroscopy are shown in Table 1. The organic group in the organotin dihalide was varied including methyl, ethyl, n-propyl, n-butyl, isobutyl, n-octyl, phenyl, and cyclohexyl. The values shown for the percent of organotin halide hydride molecules in the reaction mixture were calculated from the dihydride and halide hydride Sn-H signals. In almost all cases, except those involving methyl, the two halide hydride signals were indistinguishable from each other and appeared as one broad signal. We believe that rapid halogen exchange is responsible for this phenomenon. The remaining percentages in each case are for the mixture of organotin dihydrides. Again, in all cases except phenyl

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TABLE 1

PERCENTAGES OF ORGANOTIN HALIDE HYDRIDES IN THE REACTIONS OF R_2SnH_2 WITH R'_2SnCl_2

R'_2SnCl_2 R'	n-Bu_2SnH_2	iso-Bu_2SnH_2	n-Oct_2SnH_2	Ph_2SnH_2
Methyl	98	80	90	(53)[g]
Ethyl	95	93	95	(71)[g]
n-Propyl	94	87	90	(46)[g]
n-Butyl	93	88[a]	93[b]	(72)[c,g]
iso-Butyl	90[a]	92	86[d]	(70)[e,g]
n-Octyl	90[b]	90[d]	94	(61)[f,g]
Phenyl	(65)[c,g]	(70)[e,g]	(56)[f,g]	92
Cyclohexyl	86	91	86	(44)[g]

[a–f] *a, b, c, d, e,* and *f* occur twice in the Table and call attention to the results of both forward and reverse reactions of eqn. 3. [g] The values in parentheses are for the percentages of halide hydrides discounting the possibility that another halide hydride signal may be buried under the phenyl peaks. These values, then, represent minimum percentages in all cases where phenyl is involved except where R = R' = Ph.

and cyclohexyl, the individual signals were not separated since the δ values for the dialkyltin dihydrides were not resolved. In all cases involving phenyl, however, either in the dihydride or dihalide, only diphenyltin dihydride was found at $\delta = 5.73$, and no evidence was found for dialkyltin dihydrides at about $\delta = 4.5$, or dicyclohexyltin dihydride at about $\delta = 4.85$.

To determine whether or not equilibrium had been established, the results for cases where both forward and reverse reactions were done can be compared. The good agreement between the percent of chloride hydrides for each pair indicates that equilibrium had been established in these redistribution reactions. These comparisons are also indicated in Table 1.

Although the percent of the total hydride signals attributable to the mixture of halide hydrides varied somewhat from case to case, in all cases except possibly those involving phenyl, a high percentage of halide hydride in the reaction mixture was indicated. Also, there seemed to be no significant difference, outside of possible experimental error, due to varying the alkyl groups. In the cases of diphenyltin dichloride with di-n-butyltin dihydride, diisobutyltin dihydride and di-n-octyltin dihydride respectively, the only dihydride found in the reaction mixture was diphenyltin dihydride. Reverse reactions using diphenyltin dihydride and the dialkyltin dihalides produced the same results which are summarized by eqn. (4):

$$R_2SnH_2 + Ph_2SnCl_2 \rightarrow R_2SnClH + Ph_2SnClH \rightleftharpoons R_2SnCl_2 + Ph_2SnH_2 \quad (4)$$

In comparing the relative tendency of the hydride hydrogen to be found on the organotin moiety, it appears that diphenyl(hydrido)tin [$Ph_2Sn(H)$-] is greater than dialkyl(hydrido)tin [$R_2Sn(H)$-]. The order is that which would be expected from the effects of the electron withdrawing tendency of phenyl and the electron releasing tendency of alkyl groups on the electron densities at the tin atoms.

In previous work, with the same R groups in the dihydride and the dihalide, IR and NMR spectra indicated essentially complete conversion to the halide hydrides in all cases. Along with this work we reran a number of these at high spectrum amplitude in order to get more quantitative information. These results, noted in

TABLE 2

PERCENTAGES OF HALIDE HYDRIDES IN THE REACTIONS OF n-Bu_2SnH_2 WITH n-Bu_2SnX_2

X	Halide hydride (%)
Cl	93
Br	87
I	85

Table 1 for the cases of R=R'=n-butyl (93%), isobutyl (92%), n-octyl (94%), and phenyl (92%), indicate that the nature of the R group does not materially affect the position of equilibrium and that, neat and at room temperature, there is a small amount (about 7%) of dihydride in equilibrium with the halide hydride.

Experiments were also carried out in which the organic groups in the hydride and the halide were the same but in which the halogen was varied. Reactions had previously been carried out between di-n-butyltin dihydride and di-n-butyltin dihalides forming the corresponding di-n-butyltin halide hydrides[4]. Proton magnetic resonance spectra at low spectrum amplitude gave the δ values for the protons on tin in these compounds. We have carried out the reactions again and from spectra taken at high spectrum amplitude have found that there is in each case a small amount of dihydride in equilibrium with the halide hydride. These results are summarized in Table 2.

EXPERIMENTAL

All reactions involving organotin hydrides were carried out in an atmosphere of prepurified nitrogen. The organotin hydrides were prepared by established procedures using lithium aluminum hydride[6-8].

The diorganotin dichlorides were obtained from M & T Chemicals, Inc., except for diethyltin dichloride which was obtained from Alpha Inorganics, Inc.

Proton magnetic resonance spectra were determined with a Varian Model A-60 Nuclear Magnetic Resonance Spectrometer, using tetramethylsilane as an internal standard, except that where R'=methyl it was used as an external standard. Unless otherwise noted spectra were run neat. Reference spectral data for the diorganotin dihydrides and diorganotin halide hydrides are found in ref. 9.

The reactions were carried out by mixing thoroughly equimolar quantities of the dihydrides and the dihalides to obtain a homogeneous mixture, after which spectra were immediately run. The areas under the hydride peaks were determined using a planimeter and were usually checked also by integration. The numbers used do not denote accuracy but are as calculated from the experimental data. The percentage of total hydride molecules in the mixture attributable to diorganotin halide hydride was calculated from the dihydride and the chloride hydride areas recognizing that one molecule of a dihydride would have twice the effect on the NMR signal of one molecule of a chloride hydride. As much as ten percent error may have been present in determining the areas although attempts were made to keep this to a minimum by using the average of a number of determinations. When samples were rerun under the same conditions, the agreement was always within ten percent.

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