THE REACTIONS OF DIBORANE WITH ARYL-ORGANOTIN COMPOUNDS *

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(Received July 28th, 1983)

Summary

A number of tetraaryltin compounds, Ar_4Sn (where Ar = phenyl, o- and p-tolyl, and p-chlorophenyl) and triphenyltin compounds, Ph_3SnX (where X = Cl, H, OH, $OCOCH_3$, and $OCOCF_3$) have been treated with diborane in tetrahydrofuran. Transmetallation occurs in which one or more aryl groups are transferred to boron. The organoboron intermediates give phenols upon oxidation and boronic and borinic acids upon hydrolysis. Pyridine complexes of organoboranes have also been isolated.

Introduction

The synthetic value of organoboron compounds has prompted attempts to prepare them by reactions other than the hydroboration of alkenes. Recent studies have shown that a number of aryl-organometallic compounds react with diborane in tetrahydrofuran (THF) solution to give intermediates which give phenols upon oxidation, and arylboronic acids upon hydrolysis. Although the intermediates were not isolated, this suggests that transmetallation occurs, resulting in the transfer of at least one organic group from the metal to boron. The first organometallic compounds to be studied were those of mercury [2,3], and later organic compounds of thallium [4], lithium [5], and lithium diarylcuprates [6] were examined. The preparation of phenols from the reaction of Grignard reagents [7] and sodium and potassium compounds [5] has also been reported.

It was observed that for certain of the above systems, transmetallation is

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accompanied by reduction, and often good yields of transmetallation products are obtained only if a large excess of diborane is present. In general only one organic group is transferred to the boron, although indirect evidence suggests that triarylboron compounds may be formed from lithium diaryl cuprates (and a complex of triphenylboron was actually isolated using lithium diphenyl cuprate).

Reactions between diborane and organotin or organolead compounds have received little attention. Amberger [8] observed that trialkyltin hydrides (and trialkyllead hydrides) were formed when diborane was treated with trialkyl-tin (or -lead) alkoxides; interestingly the carbon−metal bond was not cleaved. Holliday [9] however, reported the formation of trimethylboron from the reaction of excess tetramethyllead with diborane in 1,2-dimethoxyethane, although little reaction occurred using THF as solvent.

In the present work we report studies of the transmetallations observed when diborane is treated with a series of aryltin compounds.

Results and discussion

A number of organotin compounds were treated with diborane in dry THF solution. The tin compounds included triphenyltin compounds of type Ph_3SnX (where X = chloride, acetate, trifluoroacetate, hydroxide, and hydride) and five tetraaryltin compounds; one diaryl compound (diphenyltin dichloride) was also used. In general the intermediates formed in the reaction were either oxidised or hydrolysed, but for a limited number of systems pyridine was added and attempts made to isolate pyridine complexes of the organoboranes thought to be present.

Oxidation of intermediates

Diborane solution was added to the organotin compound (in THF) and the reaction mixture oxidised using alkaline hydrogen peroxide. The results are shown in Table 1, for various reaction conditions. It can be seen that phenols are formed in high yields in most of the systems examined. This demonstrates that a transmetallation occurs resulting in the transfer of at least one organic group from tin to boron. However, there are some exceptions to this general picture. For example, when tetrakis(*p*-dimethylaminophenyl)tin was used, no reaction occurred at low relative concentrations of diborane (unreacted starting material was recovered), while at higher diborane concentrations dimethylaniline was formed, i.e. reduction had taken place. For other tin compounds, poor yields of phenols were obtained when the boron/tin ratio was low (e.g. 1/1). Under these conditions both tetra-*p*-tolyltin and triphenyltin hydroxide gave significant amounts of triphenyltin hydride. Triphenyltin hydride itself, when treated with an equivalent amount of diborane (i.e. a diborane/tin compound ratio of 0.5/1 or a boron/tin ratio of 1/1) gave a small quantity (about 20% yield) of hexaphenylditin. However, with the exception of tetrakis(*p*-dimethylaminophenyl)tin, good yields of phenols were obtained when these compounds were treated with an excess of diborane.

Hydrolysis of intermediates

In a second series of experiments the organotin compounds were again treated with diborane solutions, but the intermediates simply decomposed with water. After suitable work up, boronic acids ($ArB(OH)_2$) were isolated, and borinic acids

TABLE 1

YIELDS OF PHENOLS OBTAINED BY OXIDISING INTERMEDIATES FROM REACTION OF DIBORANE WITH ORGANOTIN COMPOUNDS [a]

Substrate	BH_3/substrate (mol/mol)	Substrate (mmol)	ArOH (mmol)	Yield (%)
$(C_6H_5)_4Sn$	1	2.0	2.9	48
	1	4.7	9.4	66 [b]
	2	4.7	14.0	75 [b]
	3	4.7	17.0	92 [b]
	4	4.7	17.0	93 [b]
$(p\text{-}Me_2NC_6H_4)_4Sn$	1	1.0	0	0 [d]
	8	1.0	0	0 [e]
$(p\text{-}CH_3C_6H_4)_4Sn$	1	0.42	0	0
	2	0.42	0.93	55
	3	0.42	1.50	88
	3	2.0	7.9	95 [b]
	4	2.0	8.1	98 [b]
$(o\text{-}CH_3C_6H_4)_4Sn$	1	0.5	0	0
	2	0.5	0	0
	8	0.5	0.11	7
	8	0.5	0.32	22 [c]
$(p\text{-}ClC_6H_4)_4Sn$	1	1.0	1.4	47
	2	1.0	2.2	55
	3	1.0	2.7	69
	4	1.0	3.3	82
$(C_6H_5)_3SnCl$	1	2.0	4.5	75
	2	3.9	10.9	93 [b]
	4	3.9	10.9	93 [b]
$(C_6H_5)_3SnOAc$	1	2.0	0	0
	2	1.3	2.5	67
	3	1.3	3.8	97
$(C_6H_5)_3SnOCOCF_3$	1	1.2	0	0
	2	1.3	0.8	22
	3	1.3	1.1	29
	8	1.3	1.7	44
	8	1.3	2.0	51 [b]
$(C_6H_5)_3SnOH$	1	1.1	1.2	36
	2	1.1	2.6	75
	3	1.1	2.9	84
	4	1.1	3.4	99
$(C_6H_5)_3SnH$	1	0.7	0.6	29
	2	0.85	2.2	87
	3	1.2	3.6	97
	4	1.2	3.6	97
$(C_6H_5)_2SnCl_2$	8	1.9	2.5	65
	8	1.9	3.6	96 [b]

[a] Reactants were stirred for 1 h at room temperature and then heated under reflux for 1 h before oxidation. [b] Reactants were heated under reflux for 2 h. [c] Reactants were heated under reflux for 4 h. [d] Unreacted starting material recovered. [e] Dimethylaniline was obtained (81% yield).

(Ar$_2$BOH) were also obtained (as their ethanolamine complexes) under certain conditions. These results are shown in Table 2.

The isolation of borinic acids suggested the possibility of forming mixed organoboranes (Ar$_2$BR). Two experiments were carried out. Firstly tetraphenyltin

TABLE 2

YIELDS OF ARYLBORONIC AND DIARYLBORINIC ACIDS OBTAINED BY HYDROLYSING INTERMEDIATES FROM REACTION OF DIBORANE WITH ORGANOTIN COMPOUNDS [a]

Substrate	BH$_3$/Substrate (mol/mol)	Substrate (mmol)	ArB(OH)$_2$ mmol (A)	Ar$_2$BOH [g] mmol (B)	Total yield (%) (A + B)
(C$_6$H$_5$)$_4$Sn	1	4.7	0	2.24	48 [b]
	2	4.7	0	4.0	42 [b]
	3	4.7	2.6	3.8	54 [b]
	4	2.3	3.3	1.1	58 [b]
(p-CH$_3$C$_6$H$_4$)$_4$Sn	1	0.85	0	0	0 [d]
	2	0.85	0.31	0.46	45
	4	0.85	1.2	0.76	80
(o-CH$_3$C$_6$H$_4$)$_4$Sn	8	1.0	0.24	0	6
	8	1.0	1	0	25 [c]
(p-ClC$_6$H$_4$)$_4$Sn	1	1	0	0.36	36
	2	1	0.63	0.38	51
	3	1	1.1	0.52	54
	4	1	2.2	0.41	76
(C$_6$H$_5$)$_3$SnCl	1	1.9	0	0	0 [e]
	2	2.6	1.4	0.59	39 [b]
	4	2.6	3.9	0	50 [b]
(C$_6$H$_5$)$_3$SnOAc	1	1.8	0	0	0
	2	1.8	0	1.44	54
	3	1.8	1.7	0.52	50
(C$_6$H$_5$)$_3$SnOCOCF$_3$	1	1	0	0	0
	2	1	0.13	0.15	14
	3	1	0.78	0	26
	8	1	1.1	0	36
(C$_6$H$_5$)$_3$SnOH	1	1.14	0	0.28	25 [d]
	2	1.14	0.42	0.89	64
	3	1.14	0.75	0.83	71
	4	1.14	2.4	0.35	91
(C$_6$H$_5$)$_3$SnH	1	2.5	0	0	0 [f]
	2	1.1	0	0	0
	3	1.66	1.1	1.1	66
	4	1.34	2.31	0.39	77
(C$_6$H$_5$)$_2$SnCl$_2$	8	1.9	2.6	0	69 [b]

[a] Reactants stirred for 1 h at room temperature and then heated under reflux for 1 h. [b] Reactants heated under reflux for 2 h. [c] Reactants heated under reflux for 4 h. [d] Some triaryltin hydrides detected as products. [e] (C$_6$H$_5$)$_3$B isolated (as the pyridine complex) in 70% yield. [f] (C$_6$H$_5$)$_6$Sn$_2$ isolated in 20% yield. [g] Isolated as ethanolamine complexes.

was treated with diborane (using a boron/tin ratio of 1/1), and then one equivalent of tetra-*p*-tolyltin was added. Secondly, one equivalent of 2-octene was added in place of the tetra-*p*-tolyltin. In both systems the reaction conditions were selected so as to consume all the diborane added in the first step, and so prevent reaction between excess diborane and the reagent added in the second stage. The intermediates formed were then oxidised. From the reaction using the alkene, both phenol and 2-octanol were obtained in a ratio 2/1. However, for the reaction using tetra-*p*-tolyltin in the second stage, only phenol could be detected as a product.

Complex formation

In a third series of experiments, the effect of adding pyridine to the intermediates formed by treatment of diborane with tetraphenyltin, tetrakis(*p*-chlorophenyl)tin, or triphenyltin chloride was examined. Using tetraphenyltin, and a boron/tin ratio of 4/1 and 3/1, a solid was obtained (in 37 and 12% yield) which was characterized as the pyridine complex of phenylboron dihydride. No solid could be isolated from the reaction with tetrakis(*p*-chlorophenyl)tin (although spectroscopic evidence suggested that a similar complex may have been present in solution). The pyridine complex of triphenylboron was obtained (in 70% yield) from the reaction using triphenyltin chloride. Attempts were made to isolate other triarylboron complexes, but none were successful.

Conclusions

The high yields of phenols obtained upon oxidation of the intermediates formed when aryltin compounds are treated with excess diborane demonstrate that transmetallation occurs readily. A large excess of diborane is not required, as is the case with organomercury compounds. Since the oxidation is known to proceed almost quantitatively [10], the results serve as a fairly accurate guide to the extent of transfer of an organic group from tin to boron. However, the phenols could derive from mono-, di-, or tri-arylboron compounds. The formation of boronic acids as the major hydrolysis products when an excess of diborane was used suggests that a monoarylboron dihydride ($ArBH_2$) is the main intermediate in these conditions. The formation of borinic acids as hydrolysis products using lower relative concentrations of diborane shows that diarylboranes can also be formed, and the presence of phenylborane was also demonstrated by isolating it as the pyridine complex.
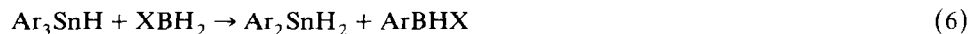
The transfer of the organic group is likely to occur step by step, and the probable sequence for the tetraaryltins are shown in reactions 1, 2, and 3.

$$Ar_4Sn + BH_3 \rightarrow ArBH_2 + Ar_3SnH \tag{1}$$

$$Ar_3SnH + BH_3 \rightarrow ArBH_2 + Ar_2SnH_2 \tag{2}$$

$$Ar_4Sn + ArBH_2 \rightarrow Ar_2BH + Ar_3SnH \tag{3}$$

This scheme explains the formation of the boronic acid (from hydrolysis of the arylboron dihydride) in the presence of excess diborane (reactions 1 and 2), and the formation of the borinic acid (from diarylborane) at lower relative diborane concentrations (reaction 3). There is no evidence for the formation of triarylboranes from the tetraaryltin systems. This suggests that the third transfer of an aryl group,

i.e. from the aryltin to a diarylborane, is slow. This is supported by the experiment in which tetraphenyltin and tetra-*p*-tolyltin were treated with diborane in a stepwise manner, when there was no evidence indicating transfer of the tolyl group to diphenylborane. In contrast the formation of phenol and octanol (in a ratio of 2/1) in the stepwise reaction using 2-octene as the second reactant in place of the tolyltin compound indicates that the diphenylborane does react further with an alkene in a hydroboration process.

For the reactions of triaryltin compounds with diborane, the situation will depend on the nature of X. The first step could be the formation of Ar_3SnH and H_2BX, or Ar_2SnXH and H_2BAr. The isolation of Ar_3SnH in at least one system makes the first possibility more likely. The steps are shown in reactions 4, 5, and 6.

$$Ar_3SnX + BH_3 \rightarrow Ar_3SnH + XBH_2 \tag{4}$$

$$Ar_3SnH + BH_3 \rightarrow Ar_2SnH_2 + ArBH_2 \tag{5}$$

$$Ar_3SnH + XBH_2 \rightarrow Ar_2SnH_2 + ArBHX \tag{6}$$

Reaction 5 explains the formation of monoarylboron species in the presence of excess diborane. In the absence of excess diborane, reaction 6 becomes important, and this will depend on the reactivity of XBH_2, i.e. on the nature of X. For example, for similar conditions using a low relative concentration of diborane, triphenyltin acetate gave no detectable yield of phenol (or organoboron compounds), whereas triphenyltin chloride gave a 75% yield of phenol (and a 70% yield of organoboron compound). This suggests that the boron-oxygen species is less reactive than the boron-chlorine species in the exchange reaction (eq. 6).

No information is available on the relative rates of any of the above reactions, so the detailed mechanisms of the transmetallations are not known. The exchange most probably occurs by a four centre process or via a type of Wheland intermediate (I).
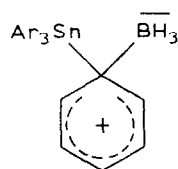
(I)

A six-centre mechanism (which has been postulated [11] for some organometal exchange reactions) involving simultaneous transfer of two aryl groups is unlikely, as it would not easily explain the formation of monoarylboron species from tetraaryltin compounds.

Experimental

Starting materials

Tetrahydrofuran was dried by heating under reflux with calcium hydride and stored over a molecular sieve. The method reported by Brown [10] was used to prepare solutions of diborane; the solution was usually about 0.6 M in diborane. The organotin compounds were either commercial materials or were prepared by standard procedures [12].

Reactions of organotin compounds with diborane

The organotin compound (typically 0.002 mol) was placed in a 100 ml 3-necked flask, dry THF was added (15 ml) and the solution was stirred magnetically under a slow stream of dry nitrogen. Diborane solution (various amounts) was added rapidly via a septum cap using a syringe (usually a grey precipitate formed at this stage). The mixture was then stirred at room temperature for one hour and then heated under reflux for a further hour (see Tables for details of other reaction times and temperatures), and then cooled to room temperature. Distilled water (5–10 ml) was added to decompose the excess of diborane and to hydrolyse the reaction products. Different work-up procedures were then used, depending on the desired products.

Preparation of phenols (by oxidation)

A mixture of a 3 *M* sodium hydroxide solution (3 ml) and 30% hydrogen peroxide (5 ml) was added slowly to the above solution and the resulting mixture stirred for 30 minutes. Ether (30 ml) was added, and the mixture extracted with a 3 *M* sodium hydroxide solution (3 × 10 ml). The combined aqueous extracts were acidified with dilute hydrochloric acid and extracted with ether (3 × 20 ml). The ether extracts were combined, made up to a known volume with ether, and the yield of phenol determined quantitatively by UV spectroscopy, using standard calibration curves prepared for each phenol.

Preparation of boronic and borinic acids (by hydrolysis)

After completion of the reaction between the tin compound and the diborane (see above), more distilled water (30 ml) was added, the mixture was stirred for 30 minutes at room temperature, and then extracted with ether (3 × 15 ml). The combined ether extracts were dried over magnesium sulphate, and the solvent was then removed under reduced pressure. A white solid remained. This solid was heated with pentane (40 ml), and the mixture was then filtered. The residue was recrystallised from water and identified as the boronic acid by m.p., IR, and PMR spectra. The ethanolamine complexes of borinic acids were obtained from the pentane filtrate as follows. The pentane was removed under reduced pressure and the residue was rapidly dissolved in ether. Ethanolamine (0.6 ml) in ethanol (6 ml) was added and the mixture heated under reflux for 30 minutes and then filtered while hot. For those systems in which borinic acids were present, the ethanolamine complex precipitated from the cooled filtrate and was identified by m.p, IR, and PMR. (It was found that the yields of these complexes could be improved by reducing the volume of the filtrate by about half and then adding aq. ethanol dropwise until no further precipitation occurred).

Preparation of organoborane complexes

Tetraphenyltin (0.002 mol) was treated with diborane (0.004 mol) as described above. After completion of the reaction the mixture was cooled to 0°C and then an excess of dry pyridine (15 ml) was added. The flask was allowed to warm slowly to room temperature (30 min), and then it was cooled again to 0°C and aq. pyridine (50%, 15 ml) was added. The mixture was stirred for a further 30 minutes and then extracted with ether (3 × 20 ml). The ether solution was dried (magnesium sulphate) and the solvent removed under reduced pressure. A thick oil remained. This oil was dissolved in a small volume of an ether/pentane mixture (50%); a white solid was

formed when this solution was cooled to 0°C. The product was identified as the pyridine complex of phenylborane. The IR showed strong absorption at 2320 cm^{-1} (B–H stretch) but no absorption in the region 1300–1400 cm^{-1}, characteristic of boron oxygen compounds; PMR (CDCl$_3$): δ7.0 to 8.0 (8-H, phenyl protons and β- and γ-protons of pyridine) and 8.7 ppm (2-H, α-protons of pyridine); observed m.p. 81–83°C (lit. [13] m.p. 80–83°C); yield 37%. The same complex was obtained when a smaller quantity of diborane was used (0.0015 mol in place of 0.002 mol), yield 12%.

The pyridine complex of triphenylborane was isolated from only one reaction, that between triphenyltin chloride and (0.002 mol) and diborane (0.001 mol). A preliminary experiment had shown that no borinic acid was present under these reaction conditions. A second experiment was carried out using the procedure described above for the preparations of borinic acids. After elimination of the pentane solvent ether was added, followed by the calculated quantity of distilled pyridine. A precipitate formed immediately, m.p. 170–172°C (the m.p. of a pyridine complex prepared in an analogous way from a commercial sample of triphenylborane was found to be 169–173°C). The IR spectrum showed no absorption in the region 1300–1400 cm^{-1}. Yield 70%.

Formation of (2-octyl)diphenylborane in solution

Tetraphenyltin (0.0047 mol) in dry THF (15 ml) was treated with diborane (0.0024 mol) as described above. After completion of the reaction the flask was cooled to 0°C and then *cis*-2-octene (0.0047 mol) in dry THF (10 ml) was added dropwise with continuous stirring. The mixture was then stirred for one hour at room temperature. After cooling to 0°C distilled water (5 ml) was added, followed by a mixture of a 3 *M* sodium hydroxide solution (4 ml) and 30% hydrogen peroxide (5 ml). The mixture was filtered and the filtrate was extracted with ether (3 × 20 ml). The amount of phenol present in the aqueous layer was determined as described above. The ether layer was dried (magnesium sulphate), and the solvent removed. A waxy solid remained, which was extracted with pentane. After filtration and removal of the pentane, a clear liquid remained. The amount of 2-octanol present was determined by GLC (using reference octanol prepared from 2-octene and diborane).

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