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Preliminary communication

REACTIONS OF DIBORANE WITH ORGANIC DERIVATIVES OF TIN AND LEAD

F.G. THORPE, S.W. BREUER, G.M. PICKLES and T. SPENCER
Chemistry Department, University of Lancaster, Lancaster, LA1 4YA (Great Britain)
and J.C. PODESTA
Departamento de Quimica e Ing. Qca, Universidad Nacional del Sur, Bahia Blanca (Argentina)

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Summary

Diborane reacts with aryltin and aryllead compounds to give intermediates which on hydrolysis give arylboronic and arylborinic acids, and on oxidation give phenols.

As part of a series of studies of reactions of borane with organometallic compounds, we have investigated the reactions of borane with organic derivatives of tin and lead. The reactions of borane with organic compounds of the alkali metals [1], mercury [2], thallium [3] and magnesium [4] have been previously reported, but very little work has been published using tin or lead compounds. Holliday [5] reported the formation of trimethylboron from the reaction of excess tetramethyllead with borane in 1,2-dimethoxyethane as solvent (although little reaction occurred using tetrahydrofuran as solvent), and a similar process was observed using tetravinyllead. Amberger [6] observed the formation of alkoxydiboranes when borane was treated with trialkyllead and trialkyltin alkoxides, but the carbon—metal bond was not cleaved in these reactions. Trialkyltin hydrides and trialkyllead borohydride were observed to be products.

We report below some preliminary studies of the reaction between aryltin and aryllead compounds and borane. The general procedure was to add the borane solution in THF to the organometallic compound in the same solvent under dry nitrogen. The solution was stirred at room temperature for one hour, and then heated under reflux for another hour. The boron hydrides were decomposed with water, and the products isolated either as the arylboronic and/or borinic acids, or as phenols following oxidation with alkaline hydrogen peroxide [7]. The boronic and borinic acids were extracted from the (unoxidised) aqueous solution with ether. After removal of the ether, the solid residue was extracted with pentane, in which the boronic acid was almost insoluble, and the borinic acid was isolated from the pentane solution as the ethanolamine complex. The phenols were separated from the oxidised reaction product by acidification followed by ether extraction; when the products were obtained as phenols, the yields were determined by UV spectroscopy or by GLC.

Table 1 summarises experiments in which phenols were produced. Since the phenols were formed by a process known to proceed almost quantitatively [7], the results serve as a fairly accurate guide to the extent of transfer of aryl groups to boron. With the single exception of triphenyltin acetate as substrate, phenols were obtained in high yield, and a large excess of diborane was not required. For the tetraaryltin compounds, the general order of reactivity of the aryl groups appears to parallel that in electrophilic aromatic substitution (*p*-tolyl > phenyl > *p*-chlorophenyl) and for the triphenyltin salts, the chloride gives higher yields than the acetate.

TABLE 1

YIELDS OF PHENOLS OBTAINED BY OXIDISING INTERMEDIATES FROM REACTION OF BORANE WITH ORGANIC COMPOUNDS OF TIN AND LEAD

Substrate	BH_3/substrate (mol/mol)	Substrate (mmol)	BH_3 (mmol)	ArOH (mmol)	Yield (%)
$(C_6H_5)_4Sn$	1	4.7	4.7	9.4	66
$(C_6H_5)_4Sn$	2	4.7	9.4	14.2	81
$(C_6H_5)_4Sn$	3	4.7	14.1	17.3	92
$(p\text{-}CH_3C_6H_4)_4Sn$	1	2.1	2.1	5.5	89
$(p\text{-}CH_3C_6H_4)_4Sn$	2	2.1	4.1	7.5	90
$(p\text{-}ClC_6H_4)_4Sn$	1	1.8	1.8	1.5	30
$(p\text{-}ClC_6H_4)_4Sn$	2	1.8	3.5	3.6	51
$(p\text{-}ClC_6H_4)_4Sn$	3	1.8	5.3	5.0	71
$(C_6H_5)_3SnCl$	1	3.9	3.9	9.2	79
$(C_6H_5)_3SnCl$	2	3.9	7.8	10.8	93
$(C_6H_5)_3SnOAc$	1	2.4	2.4	0	0
$(C_6H_5)_3SnOAc$	2	2.4	4.9	2.1	28
$(C_6H_5)_4Pb$	1	1.9	1.9	4.8	84
$(C_6H_5)_4Pb$	2	1.9	3.9	6.6	86
$(p\text{-}CH_3C_6H_4)_4Pb$	1	1.7	1.7	3.7	69
$(p\text{-}CH_3C_6H_4)_4Pb$	2	1.7	3.5	5.4	77

Similar conclusions can be drawn from the results of separate experiments in which boronic and borinic acids were isolated as products (Table 2), except that the triphenyltin chloride gave a lower yield than the acetate.

The overall yields and product distributions vary considerably. By suitable choice of conditions, either the borinic or boronic acid can be produced as the major product. This suggests a stepwise process:

$$Ar_3MX + BH_3 \rightarrow Ar_3MH + XBH_2$$

$$Ar_3MH + XBH_2 \rightarrow Ar_2MH_2 + ArBHX$$

$$Ar_2BH + BH_3 \rightleftharpoons 2ArBH_2$$

$(X = Ar, Cl, OAc; M = Sn, Pb)$

TABLE 2

YIELDS OF ARYLBORONIC ACIDS AND ARYLBORINIC ACIDS OBTAINED BY HYDROLYSING INTERMEDIATES FROM REACTION OF BORANE WITH ORGANIC COMPOUNDS OF TIN AND LEAD

Substrate	BH_3/substrate (mol/mol)	Substrate (mmol)	BH_3 (mmol)	ArB$(OH)_2$ (mmol)	$Ar_2B(OH)$ (mmol)	Total yield (%) ArB$(OH)_2$+$Ar_2B(OH)$
$(C_6H_5)_4Sn$	1	4.7	4.7	0	2.2	48
	2	4.7	9.4	0	4.0	42
	4	2.3	9.4	3.3	1.1	58
$(p\text{-}CH_3C_6H_4)_4Sn$	1	4.1	4.1	1.2	2.0	76
	2	2.1	4.1	1.7	1.5	75
$(p\text{-}ClC_6H_4)_4Sn$	1	1.8	1.8	0.6	0	33
	2	1.8	3.5	1.0	0	59
$(C_6H_5)_3SnCl$	1	2.6	2.6	0	0	0
	3	2.6	7.8	3.6	0.22	52
$(C_6H_5)_3SnOAc$	1	2.4	2.4	0	0	0
	3	2.4	7.3	2.5	0	34
$(C_6H_5)_4Pb$	1	2.9	2.9	0	0.35	12
	4	1.9	7.7	3.3	0.55	56
$(p\text{-}CH_3C_6H_4)_4Pb$	1	1.7	1.7	0.15	0.70	48
	4	1.7	7.0	2.6	0	37

The presence of $ArBH_2$ as an intermediate was demonstrated by isolating it as the pyridine complex in 37% yield from the reaction of tetraphenyltin with four molar equivalents of borane, and in 12% yield when three molar equivalents were used.

It is significant that the combined yields of arylboronic and borinic acids are always considerably lower than the yields of corresponding phenols. This may be simply the result of losses during the isolation procedures, but it may indicate the formation of triarylboron compounds. Further work is in progress.

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References

1 F.G. Thorpe, G.M. Pickles and J.C. Podesta, J. Organometal. Chem., 128 (1977) 305.

2 S.W. Breuer, M.J. Leatham and F.G. Thorpe, Chem. Commun., (1971) 1475; S.W. Breuer, J.C. Podesta and F.G. Thorpe, Tetrahedron Lett., (1974) 3719.

3 S.W. Breuer, G.M. Pickles, J.C. Podesta and F.G. Thorpe, Chem. Commun., (1975) 36.

4 S.W. Breuer and F.A. Broster, J. Organometal. Chem., 35 (1972) C5, Tetrahedron Lett., (1972) 2194.

5 A.K. Holliday and G.N. Jessop, J. Organometal. Chem., 10 (1967) 291; A.K. Holliday and R.E. Pendlebury, ibid., 10 (1967) 295.

6 E. Amberger and R. Hönigschmid-Grossich, Chem. Ber., 99 (1966) 1673; E. Amberger and M.R. Kula, Chem. Ber., 96 (1963) 2560.

7 G. Zweifel and H.C. Brown, Org React., 13 (1963) 1.