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PREPARATION OF ORGANOBORANES
RELATIVE REACTIVITIES OF COMPETING >B–Y SITES TOWARDS ORGANOLITHIUM AND -MAGNESIUM COMPOUNDS

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INTRODUCTION

The transfer of alkyl, alkenyl, alkynyl, or aryl groups from one metal to another provides the most general procedure for the synthesis of organometallic compounds, and organoboron compounds are no exception (*cf.* ref. 1). In this context, the reaction type in question is that between an organometallic compound and a suitable boron substrate, as a consequence of which the organic group is transferred from metal to boron. Among the most important organometallic reagents for this purpose, mainly from the standpoint of availability or easy preparation, are Grignard reagents and organo derivatives of Li, Hg, Al, and Sn. The reaction seems to be most facile with derivatives of the more electropositive elements. The case of the organometallic compound being an organoborane – the redistribution reaction – is also well-known.

The boron substrate may be chosen from a wide range of compounds. The most common are $BF_3{\cdot}O(C_2H_5)_2$, $(CH_3OBO)_3$, $B(OC_4H_9\text{-}n)_3$, or BCl_3 (which preferably should not be used in ether solvents, because these react with BCl_3; *cf.* ref. 2).

The common procedure is to mix the reagents, usually well-diluted in hydrocarbon or ether solvents, often under nitrogen and with cooling, in a Grignard-type apparatus. The work-up is either by direct distillation or, very frequently, by hydrolysis (dilute acid or NH_4Cl) (the B–C bond, unlike Al–C or Ga–C, is reasonably stable towards water), with optional conversion into an easily isolable derivative, such as a water-insoluble ethanolamine ester[3].

Important examples of such reactions are illustrated in the following equations.

$$B(OR)_3 + R'MgBr \rightarrow R'B(OR)_2 + MgBr(OR) \qquad \text{(ref. 4–6)}$$

$$B(OC_4H_9\text{-}n)_3 + LiC_4H_9\text{-}n \rightarrow n\text{-}C_4H_9B(OC_4H_9\text{-}n)_2 + LiOC_4H_9\text{-}n \qquad \text{(ref. 7)}$$

$$BX_3 + HgAr_2 \rightarrow ArBX_2 + ArHgX \quad (X=Cl \text{ or } Br) \qquad \text{(ref. 8, 9)}$$

$$3\,BCl_3 + SnR_4 \rightarrow 3\,RBCl_2 + RSnCl_3 \qquad \text{(ref. 10–12)}$$

$$(CH_3OBO)_3 \xrightarrow[(3)\quad H_2NCH_2CH_2OH]{(1)\ 9\ ArMgBr,\ (2)\ dil.HCl.} Ar_2BOCH_2CH_2NH_2 \qquad \text{(ref. 13)}$$

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$(iso\text{-}C_4H_9OBO)_3 \xrightarrow{(1)\ ArMgBr;\ (2)\ d.HCl} (ArBO)_3 \text{ or } (Ar_2B)_2O$ (ref. 14)

$BF_3 \cdot O(C_2H_5)_2 \xrightarrow{(1)\ RMgBr;\ (2)\ d.HCl} [(n\text{-}C_4H_9)_2B]_2O$ (ref. 15)

$BF_3 \cdot O(C_2H_5)_2 + 3\ RMgBr \rightarrow BR_3 + 3\ MgBrF$ (ref. 16, 17)

$BF_3 + AlR_3 \rightarrow BR_3 + AlF_3$ (ref. 18–20)

$B(OR')_3 + AlR_3 \rightarrow BR_3 + Al(OR')_3$ (ref. 21)

$BPh_3 + LiPh \rightarrow Li[BPh_4]$ (ref. 22)

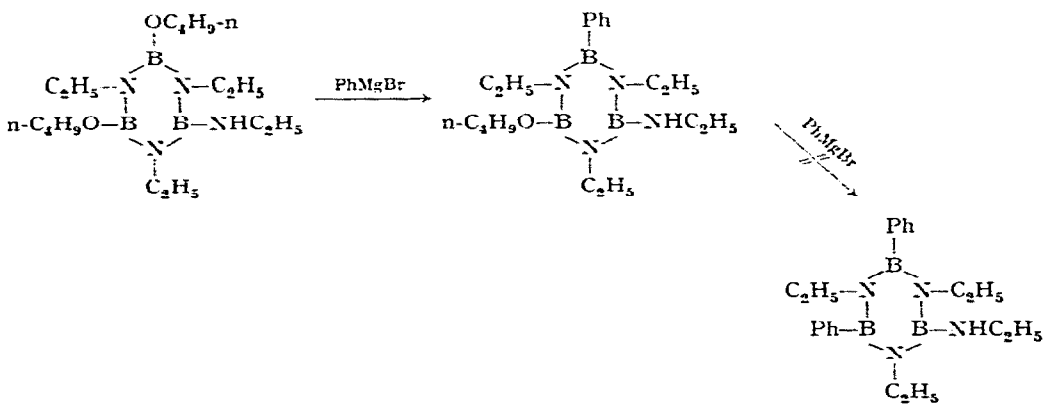
The relative reactivity order of a number of organometallic reagents with respect to tri-n-butoxyborane, $B(OC_4H_9\text{-}n)_3$, has been shown to decrease in the series $ArMgBr > CdAr_2 > ZnAr_2 > HgAr_2$[23]. The converse feature of relative reactivities of various boron substrates has not previously been considered. Accordingly, it is the object of the present paper to collect together random examples of published experiments on preparative organoboron chemistry which throw light on this problem, to present new data, and finally to deduce reactivity orders.

RESULTS

Results on reactions between Grignard reagents and boron substrates which have more than one potential site for substitution are presented. We were especially concerned to determine whether a $>B\text{–}OR$ bond was cleaved more or less readily than a $>B\text{–}NR_2$. The order $>B\text{–}OR > >B\text{–}NR_2$ was established by the following reaction.

$$Ph\text{–}B\begin{matrix}OC_2H_5\\N(C_2H_5)_2\end{matrix} + PhMgBr \rightarrow Ph_2B\text{–}N(C_2H_5)_2 + Mg(OC_2H_5)Br$$

It was further shown that the $>B\text{–}OR$ bond was cleaved more readily than the $>B\text{–}NHR$, or the NH in $>B\text{–}NHR$.



It is interesting to note that the reaction of a second mole of the Grignard reagent caused no further substitution, and this may be due to a steric effect.

Related experiments, which, however, have no bearing on the problem of competing sites, concern observations on $[(iso\text{-}C_3H_7)_2N]_2BCl$. It had earlier been shown[24]

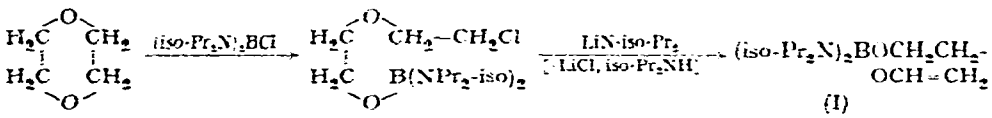
that whereas interaction of trichloroborane and excess of a secondary amine normally affords the trisaminoborane, with diisopropylamine substitution went no further than $[(iso\text{-}C_3H_7)_2N]_2BCl$. Accordingly, an attempt was made to prepare $B[N(C_3H_7\text{-}iso)_2]_3$ by the following route.

$$[(iso\text{-}C_3H_7)_2N]_2BCl + LiN(C_3H_7\text{-}iso)_2 \rightarrow B[N(C_3H_7\text{-}iso)_2]_3 + LiCl$$

When the reaction was carried using a higher boiling petroleum fraction as solvent and with prolonged heating under reflux, the bulk of the chlorobis(diisopropylamino)-borane was recovered, although some crude tris compound was also obtained.

In an attempt to facilitate reaction, dioxane was employed in another experiment in place of a petroleum fraction; the compound obtained, on the basis of elemental analysis, molecular weight determination, and infrared spectral data, is thought to have structure (I). Absorption bands at 1610 (s) and 1630 (m) cm^{-1} are characteristic for vinyl groups. The stronger band is assigned to C=C stretching frequency, and the other to the overtone of a CH out-of-plane deformation frequency arising from the $=CH_2$ group.

Compound (I) was obtained presumably through cleavage of dioxane. It is proposed that the initial product, formed as a result of ring cleavage, is dehydrochlorinated through the agency of the lithioamine.



(I)

Another method of preparation of tris(diisopropylamino)borane, $B(N\text{-}iso\text{-}Pr_2)_3$, using a Grignard reagent was explored. Trifluoroborane etherate reacted vigorously with diisopropylamine and ethylmagnesium bromide. However, the product was found to be only partially-substituted, and a wide range of boiling point, as well as elemental analysis, indicated that it was probably a mixture of bis(diisopropylamino)-fluoroborane, $(iso\text{-}Pr_2N)_2BF$, and (diisopropylamino)difluoroborane, $iso\text{-}Pr_2NBF_2$.

DISCUSSION

The approach which has been used is to examine the product(s) obtained from interaction of an organometallic compound and a boron substrate of type $-BYY'$. When the $>B-Y$ bond is more readily cleaved than $>B-Y'$, the principal reaction path is as follows. Data are summarised in Table 1.

$$-B\langle^{Y}_{Y'} + R^- \rightleftharpoons \left[R\rangle B\langle^{Y}_{Y'}\right]^- \rightleftharpoons -B\langle^{R}_{Y'} + Y^-$$

The overall picture, with regard to reactivity orders, which emerges from the above data may be summarised as follows: (*i*) B–Cl > B–OR > $B–NR_2$, (*ii*) B–Cl or B–Br or B–OR or B–SR each > N–H in B–NH–, (*iii*) B–H > N–H in $(HBNH)_3$, (*iv*) B–C > B–OR with respect to AlkMgX but B–C < B–OR with respect to ArMgX, and (*v*) the borazine ring is rather resistant to organometallic attack. It is appreciated that, strictly, all the information of Table 1 should ideally refer to the

TABLE 1

RELATIVE REACTIVITIES OF COMPETING > B–Y SITES WITH RESPECT TO ORGANOLITHIUM AND MAGNESIUM COMPOUNDS[a]

No.	*Reactants*	*Organoboron product*	*Reference*
1	$PhB(OC_4H_9\text{-iso})Cl/o\text{-}CH_3C_6H_4MgBr$	$PhB(OC_4H_9\text{-iso})C_6H_4CH_3\text{-}o$	25
2	$(CH_2)_3O_2BCl/LiC_4H_9\text{-}n$	$(CH_2)_3O_2BC_4H_9\text{-}n$	26
3	$PhB(OC_2H_5)N(C_2H_5)_2/PhMgBr$	$Ph_2BN(C_2H_5)_2$	This work
4	$PhNHBCl_2/PhMgBr$	$PhNHBPh_2$	27
5	$R_2NBCl_2/R'MgX$	R_2NBR_2'	28–30
6	$R_2NB(R')X/LiR''$ or $R''MgX$	$R_2NB(R')R''$	31, 32
7	$(Me_2N)_2BCl/LiR$	$(Me_2N)_2BR$	33
8	$(XBNR)_3/R'MgBr$	$(R'BNR)_3$, $R_2'XB_3N_3R_3$, or $R'X_2B_3N_3R_3$	34–37
9	$(XBNH)_3/RMgBr$	$(RBNH)_3$	38–40
10	$(n\text{-}C_4H_9SBNH)_3/n\text{-}C_4H_9MgCl$	$n\text{-}C_4H_9(n\text{-}C_4H_9S)_2B_3N_3H_3$	41
11	$(HBNH)_3/PhMgBr$	$PhH_2B_3N_3H_3$	42
12	$(HBNR)_3/LiR'$ or $R'MgX$	$(R'BNR)_3$, $R_2'HB_3N_3R_3$, or $R'H_2B_3N_3H_3$	43, 44
13	$[Br(CH_2)_3BNPh]_3/RMgBr$	$(RBNPh)_3$	45
14	$RB(OC_4H_9\text{-}n)_2/R'MgBr$	$RB(OC_4H_9\text{-}n)_2$	46–48
15	$HC{\equiv}CB(OC_4H_9\text{-}n)_2/ArMgBr$	$HC{\equiv}CB(OC_4H_9\text{-}n)Ar$	47
16	$(n\text{-}C_4H_9O)_2(C_2H_5NH)B_3N_3(C_2H_5)_3/PhMgBr$	$(n\text{-}C_4H_9O)(C_2H_5NH)PhB_3N_3(C_2H_5)_3$	This work

[a] R, R', and R'' may be alkyl, alkenyl, or aryl groups, and X is Cl or Br.

same organometallic reagent, *e.g.* $n\text{-}C_4H_9MgBr$, and that therefore the propositions (*i*)–(*v*) may not be completely general.

Attempt at detailed interpretation is not practicable, as there are too many variable parameters in these systems. They include bond strengths and solvation energies, and steric and electronic effects. It would be helpful if kinetic results were available also.

Results of the type presented here for boron compounds are available, but not in such detail, for derivatives of other elements. For example, the $Si\text{–}OC_2H_5$ bond is less readily cleaved than the Si–Cl (*cf.* ref. 49), and likewise the relative reactivities of three $P^{III}\text{–}X$ bonds towards cleavage by carbanions decrease in the series (*i*) P–Cl > P–OR[50] and (*ii*) P–Cl > $P\text{–}NR_2$[51].

EXPERIMENTAL

Preparation of (diethylamino)ethoxyphenylborane

Ethanol (2.38 g, 1 mol.) was added dropwise to bis(diethylamino)phenylborane (12.17 g, 1 mol.) at −78°. The reaction mixture was allowed to warm to 20° during 1 h. Diethylamine (3.65 g, 96 %), n_D^{20} 1.3862 was eliminated and was trapped at −78°/20 mm. The residue was distilled, affording diethylaminoethoxyphenylborane (9.78 g, 91 %), b.p. 102–4°/10 mm, n_D^{20} 1.4835. (Found: C, 69.9; H, 9.7; N, 6.5. $C_{12}N_{20}BNO$ calcd.: C, 70.0; H, 9.8; N, 6.8 %.)

Interaction of (diethylamino)ethoxyphenylborane and phenylmagnesium bromide

The Grignard reagent was prepared from bromobenzene (7.7 g) and magnesium (1.16 g) in ether (200 ml). The reagent was filtered and analysis (hydrolysis followed by titration with standard acid) showed it to be 0.5 *M*.

The phenylmagnesium bromide solution (50 ml, 1 mol.) was added to the borane (5.47 g, 1 mol.). The reaction mixture, which was dark-brown, was refluxed for 30 min. Solvent was removed under reduced pressure and fractionation afforded: (*i*) (diethylamino)ethoxyphenylborane (1.18 g, 21.5 %), b.p. 78–98°/0.8 mm, n_D^{20} 1.5062 (authentic infrared spectrum); and (*ii*) (diethylamino)diphenylborane[52] (4.21 g, 67 %), b.p. 104°/0.1 mm, m.p. 32°, n_D^{20} 1.5606. (Found: C, 81.0; H, 8.4; N, 5.96. $C_{16}H_{20}BN$ calcd.: C, 81.0; H, 8.4; N, 5.90 %.)

Preparation of B,B'-di-n-butoxy-B"-(ethylamino)-N,N',N"-triethylborazine

n-Butanol (6.0 g, 2 mol.) in light petroleum (b.p. 0–40°) (25 ml) was added dropwise during 2 h with continuous stirring to *B,B',B"*-tris(ethylamino)-*N,N',N"*-triethylborazine (11.88 g, 1 mol.) in light petroleum (b.p. 0–40°) (200 ml) at —78°. The solvent, together with ethylamine, was removed under reduced pressure and the residue was fractionated to give: (*i*) n-butoxybis(ethylamino)borane[53] (2.28 g), b.p. 48–58°/0.2 mm, n_D^{20} 1.4259 (found: B, 6.7 %) (authentic infrared spectrum); and (*ii*) *B,B'*-di-n-butoxy-*B"*-(ethylamino)-*N,N',N"*-triethylborazine[54] (8.52 g, 60 %) b.p. 108–112°/0.01 mm, n_D^{20} 1.4645. (Found: B, 9.2; N, 16.3. $C_{16}H_{39}B_3N_4O_2$ calcd.: B, 9.2; N, 15.9 %.)

Interaction of B,B'-di-n-butoxy-B"-(ethylamino)-N,N',N"-triethylborazine and phenylmagnesium bromide

Phenylmagnesium bromide was prepared from magnesium (2.40 g) and bromobenzene (16.0 g, 10.5 ml) in ether. Unreacted magnesium was filtered off and the concentration (1.12 *M*) of the reagent was determined. Phenylmagnesium bromide (6.20 g, 30.5 ml, 2 mol.) was added dropwise to the borazine (6.01 g, 1 mol.). The mixture was then refluxed for 1 h. The solvent was removed under reduced pressure leaving a yellowish residue, which was distilled under reduced pressure to give a liquid (3.40 g), b.p. 128–138°/0.05 mm, n_D^{20} 1.5107, which on redistillation afforded: (*i*) (1.54 g), b.p. 118–120°/0.1 mm, n_D^{20} 1.5017, (found: B, 8.7; N, 16.3 %); and (*ii*) *B*-n-butoxy-*B'*-(ethylamino)-*B"*-phenyl-*N,N',N"*-triethylborazine (0.47 g), b.p. 130–5°/0.005 mm, m.p. 68–70°, n_D^{20} 1.5209. (Found: C, 60.6; H, 9.3; B, 8.8; N, 15.3. $C_{18}H_{35}B_3N_4O$ calcd.: C, 60.9; H, 9.8; B, 9.1; N, 15.8 %.)

Attempted synthesis of tris(diisopropylamino)borane using a lithium reagent

n-Butyllithium solution was prepared by the interaction of lithium (14.0 g, 2 mol.) and 1-chlorobutane (110 ml, 1 mol.) in light petroleum (b.p. 30–40°) (200 ml). The solid precipitate was filtered off and the concentration of the solution was determined by hydrolysis and subsequent titration with acid.

(*a*) *Petroleum (b.p. 100–200°).* Diisopropylamine (10.5 g, 15 ml, 2.5 mol.) was added to n-butyllithium (2.56 g, 14.5 ml of 2.8 *M* solution) and was refluxed for 1 h, until butane evolution ceased. More amine (10 ml) was added, followed by addition of higher-boiling petroleum (b.p. 100–120°) (150 ml). The lower-boiling solvent was then removed and bis(diisopropylamino)chloroborane[24] (10.1 g, 1 mol.) was added. The mixture was refluxed for 7 h. The white precipitate which formed was filtered off and, after removing solvent from the filtrate, the residue was fractionated to give (*i*) bis(diisopropylamino)chloroborane (5.21 g), b.p. 56–60°/0.1 mm, n_D^{20} 1.4528, (found: B, 4.5; Cl, 13.0 %); and (*ii*) (1.34 g), b.p. 65–72°/0.05 mm, n_D^{20} 1.4581 (found: B, 4.38;

Cl, 6.5 %). Fraction (*ii*), on redistillation, afforded crude tris(diisopropylamino)-borane (0.31 g), b.p. 70–72°/0.05 mm, n_D^{20} 1.4585. (Found: C, 68.5; H, 12.3; B, 3.8; Cl, 2.2; N, 12.4. $C_{18}H_{42}BN_3$ calcd.: C, 69.6; H, 13.5; B, 3.5; N, 13.5 %.)

(*b*) *Dioxane.* The solvent was purified by refluxing over sodium, and the fraction b.p. 100–102°/760 mm was collected. Experimental procedure was exactly as in (*a*). Diisopropylamine (10.4 g, 15 ml 2 mol.) was refluxed with n-butyllithium (1 mol., 23 ml, of 2.45 *M* solution). Dioxane (100 ml) was added and lower-boiling solvent was removed. Bis(diisopropylamino)chloroborane (13.7 g, 1 mol.) was added and the mixture was refluxed for 5 h. The white precipitate (2.0 g, 85 %) was filtered off. Solvent was removed from the filtrate and the residue was distilled into: (*i*) a liquid (2.48 g), b.p. 42–60°/0.2 mm, n_D^{20} 1.4532, (*found*: Cl, 8.4 %); and (*ii*) (8.11 g), b.p. 100–102°/1.0 mm, n_D^{20} 1.4532, d_4^{20} 0.8880. (Found: C, 65.3; H, 11.6; B, 3.9; Cl, 0.0; N, 9.3; mol. wt., 324. $C_{16}H_{35}BN_2O_2$ calcd.: C, 65.0; H, 11.8; B, 3.7; N, 9.5 %; mol. wt., 298.) Presence of a double bond was confirmed by decolourisation of bromine water in carbon tetrachloride solution.

Attempted preparation of tris(diisopropylamino)borane using a Grignard reagent

Ethylmagnesium bromide was prepared from magnesium (4.8 g) and bromo-ethane (21.8 g) in diethyl ether.

Trifluoroborane etherate (9.40 g, 1 mol.) was added with continuous stirring to diisopropylamine (20.5 g, 3 mol.) in benzene (50 ml). An ethereal solution of ethyl-magnesium bromide (3 mol.) was added dropwise to the reaction mixture. The re-action was exothermic and the mixture was set aside for 12 h. Solvent was removed under reduced pressure and the residue was distilled, affording a mixture probably of bis(diisopropylamino)fluoroborane and (diisopropylamino)difluoroborane (8.02 g), b.p. 60–78°/8 mm, n_D^{20} 1.4258. (Found: B, 5.4; F, 11.6; N, 10.7. $C_{12}H_{28}BFN_2$ calcd.: B, 4.7; F, 8.3; N, 12.1; $C_6H_{14}BF_2N$ calcd.: B, 7.3; F, 25.5; N, 9.4 %.)

SUMMARY

Some new results are presented on systems involving interaction of a deficiency of an organometallic compound and a boron substrate which has more than one potential site for substitution. Earlier literature data on such reactions are collated. The overall conclusions with regard to reactivity orders with respect to carbanion substitution are: (*i*) B–Cl > B–OR > B–NR_2, (*ii*) B–Cl or B–Br or B–OR or B–SR each > N–H in B–NHR, (*iii*) B–H > N–H in $(HBNH)_3$, (*iv*) B–C > or < B–OR depending on structural features, and (*v*) the borazine ring is rather stable.

In addition, it is shown that $[(iso\text{-}C_3H_7)_2N]_2BCl$ and $LiN(C_3H_7)_2$ afford some of the sterically-hindered $B[N(C_3H_7\text{-}iso)_2]_3$ in high-boiling petroleum, whilst in dioxane the major product is $[(iso\text{-}C_3H_7)_2N]_2BOCH_2CH_2OCH{=}CH_2$.

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