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AMINOBOROXINES

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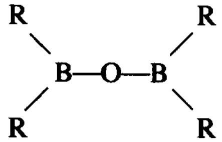
Abstract—Aminoboroxines have been prepared from the reaction of chlorobis(dialkylamino)boranes with mercuric oxide. Chlorobis(di-*i*-propylamino)borane failed to react and the isolation of bis(*n*-butoxyphenylboryl)oxide from the reaction of *n*-butoxychlorophenylborane and mercuric oxide was not successful.

INTRODUCTION

COMPOUNDS of the type (*A*) are known e.g. $(Ph_2B)_2O$[1] but are very limited in number and type.



(*A*)

It was the intention to extend this class of compounds, for example by reacting *n*-butoxychlorophenylborane with mercuric oxide, but in our experiments the bis(boryl)oxide was never isolated and the corresponding boroxine and alkoxyborane were obtained as products. This type of reaction was utilized in the synthesis of aminoboroxines and it can be appreciated that its use could be further extended to the preparation of substituted boroxines providing the requisite starting material is available.

EXPERIMENTAL

General procedures. Chlorobis(diethylamino)borane[2], chlorobis(di-*n*-propylamino)borane[3], and chlorobis(di-*i*-propylamino)borane[4] were prepared by methods reported in the literature. Mercuric oxide was dried at 100° before use. Benzene and light petroleum were stored over sodium wire and distilled before use. All necessary precautions were taken for air sensitive materials. Infra-red spectra were recorded on a Perkin–Elmer model 21(2–15μ) instrument equipped with sodium chloride optics.

*Attempted preparation of bis(*n*-butoxyphenylboryl)oxide.* A suspension of mercuric oxide (5·1 g) in light petroleum (b.p. 30–40°) was cooled at −78°, *n*-butoxychlorophenylborane (9·28 g) was added slowly and the mixture was allowed to attain room temperature. The solid (originally, mercuric oxide) gradually became white showing that reaction had occurred. The product was filtered and the solvent removed at 10 mm pressure. A solid gradually settled out from the liquid, which subsequently gave di-*n*-butoxyphenylborane (5·45 g, 96%), b.p. 92–96°/0·08 mm n_D^{20} 1·4743 (Found: B, 4·5. Calc. for $C_{14}H_{23}BO_2$: B, 4·6%). The solid on the filter was extracted with benzene and a residue of mercuric chloride (6·40 g, 100%) and a solution of phenylboroxine (2·45 g, 96%) m.p. 212–214° (Found: B, 10·3.

1. E. W. Abel, W. Gerrard and M. F. Lappert, *J. chem. Soc.* 5051 (1957).
2. W. Gerrard, M. F. Lappert and C. A. Pearce, *J. chem. Soc.* 381 (1957).
3. H. H. Anderson, *J. Am. chem. Soc.* 74, 1421 (1952).
4. D. W. Aubrey, M. F. Lappert and M. K. Majumdar, *J. chem. Soc.* 4088 (1962).

Calc. for C_6H_5BO: 10·4%) were obtained. The yield of phenylboroxine was the total compound obtained from the benzene extraction and that which precipitated out of the reaction product.

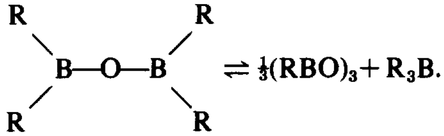
Preparation of diethylaminoboroxine. Mercuric oxide (3·22 g), and chlorobis(diethylamino)-borane (5·65 g) were refluxed in benzene (15 ml) for 3 hr. As there appeared to be no reaction, the solvent was removed, at 10 mm pressure, to allow a higher reflux temperature to be employed. The solid (originally mercuric oxide) gradually became white, showing that reaction had occurred. After half an hour the mercuric chloride (4·32 g, 100%) was filtered off and on distillation of the residue tris(diethylamino)borane (2·85 g, 86%) b.p. 50–52°/0·5 mm and diethylaminoboroxine (1·3 g, 90%), b.p. 90–91°/0·2 mm, n_D^{20} 1·4338. (Found: C, 47·9; H, 9·9; N, 14·2; B, 10·7%; M, 305·3. $C_{12}H_{30}N_3B_3O_3$ requires C, 48·4; H, 10·15; N, 14·1; B, 10·9%, M, 296·4) were obtained.

Preparation of di-n-propylaminoboroxine. Mercuric oxide (5·6 g) and chlorobis(di-*n*-propylamino)-borane (17·2 g) were refluxed for three hours in the absence of a solvent. Mercuric chloride (6·9 g, 98%) was filtered off, leaving a liquid residue which on distillation gave tris(di-*n*-propylamino)borane (14·1 g, 87%) b.p. 97°/0·13 mm, and di-*n*-propylaminoboroxine (5·9 g, 90%) b.p. 105°/0·02 mm n_D^{20} 1·4703 (Found: C, 56·6; H, 11·1; N, 10·9; B, 8·4% $C_{18}H_{42}N_3O_3B_3$ requires C, 56·2; H, 11·0; N, 11·0; B, 8·5%).

Attempted preparation of di-i-propylaminoboroxine. Mercuric oxide (5·2 g) and chlorobis(di-*i*-propylamino)borane (11·8 g) were refluxed for three hours. The solid mercuric oxide (5·1 g) was filtered off, leaving a liquid residue (11·6 g) which was identified, by i.r. spectroscopy, as chlorobis(di-*i*-propylamino)borane.

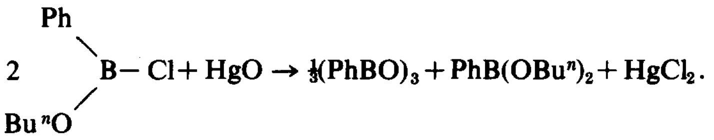
RESULTS AND DISCUSSION

The decomposition of bis(boryl)oxides, $(R_2B)_2O$, to give boranes, R_3B, has an appreciable induction period but once begun is rapid enough to allow conversion to borane and boroxine on distillation[5]. The reaction may be reversed to give an equilibrium mixture containing about 25 per cent of bis(boryl)oxide as shown in the first equation.



$$R_2B{-}O{-}BR_2 \rightleftharpoons \tfrac{1}{3}(RBO)_3 + R_3B. \tag{1}$$

The first approach was the attempted preparation of bis(*n*-butoxyphenylboryl)-oxide. Mercuric oxide was reacted with *n*-butoxychlorophenylborane – the overall reaction is given in the second equation:



$$2\,\mathrm{Ph(Bu^nO)B{-}Cl} + \mathrm{HgO} \rightarrow \tfrac{1}{3}(\mathrm{PhBO})_3 + \mathrm{PhB(OBu^n)_2} + \mathrm{HgCl_2}. \tag{2}$$

The product of the reaction after filtration was initially a colourless liquid (*B*), which slowly gave a solid, phenylboroxine, and di-*n*-butoxyphenylborane. The i.r. spectrum of the liquid product (*B*) showed a doublet at 1205 and 1183 cm^{-1} which was not present in di-*n*-butoxyphenylborane or phenylboroxine, and could be due to the presence of a $>B{-}O{-}B<$ grouping in the compound. It is possible that (*B*) was an unstable intermediate which disproportionated; the equilibrium of the reaction lying very much to the right.

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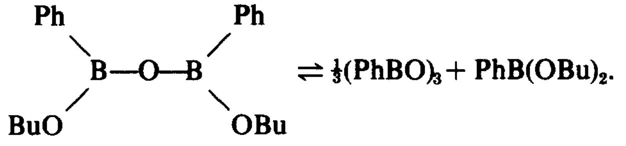
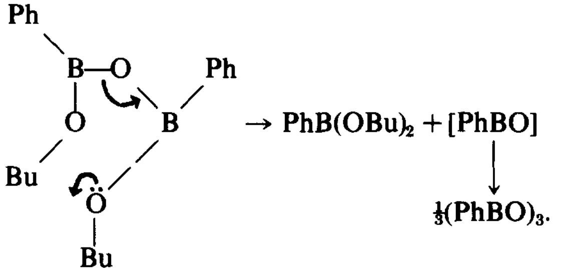
5. G. L. O'Connor, and H. R. Nace, *J. Am. chem. Soc.* **77**, 1578 (1955).



(*B*)

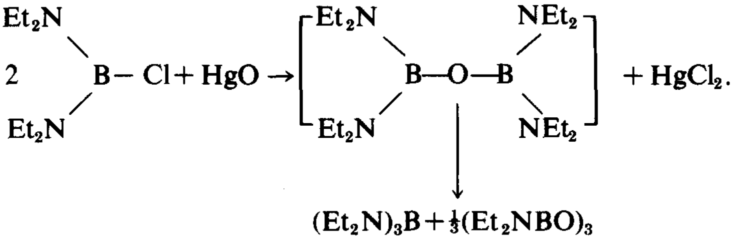
$$\rightleftharpoons \tfrac{1}{3}(PhBO)_3 + PhB(OBu)_2. \quad (3)$$

However, is could be that phenylboroxine, being very stable, is initially formed and precipitates out only when the solution becomes supersaturated, and it is envisaged that the disproportionation of the anhydride would be as represented in the fourth equation:



(4)

It is interesting to note that intramolecular 1,3-nucleophic rearrangements have been postulated in analogous bisborylamine systems[6]. Aminoboroxines have received little attention[7–9]. The above type of reaction was extended to the preparation of aminoboroxines in good yields. Chlorobis(diethylamino)borane was refluxed for six hours with mercuric oxide in benzene. On distillation of the liquid product, tris(diethylamino)borane was removed and the less volatile boroxine remained. The reaction taking place is represented in the fifth equation, the anhydride being postulated as an unstable intermediate.



(5)

The i.r. spectrum showed peaks at 725 and 714 cm^{-1} which are characteristic of the presence of a boroxine ring[10]. Chlorobis(di-*n*-propylamino)borane reacted analogously with mercuric oxide. The i.r. spectrum of the product gave characteristic boroxine peaks at 722 and 712 cm^{-1}. There was no reaction between chlorobis(di-*i*-propylamino)borane and mercuric oxide. Steric hindrance could

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6. M. F. Lappert and M. K. Majumdar, *Adv. Chem. Ser.* **42**, 208 (1964).
7. D. W. Aubrey and M. F. Lappert, *Proc. chem. Soc.* 148 (1960).
8. T. C. Chandhuri, *J. chem. Soc.* 1081 (1920).
9. J. Goubeau and H. Keller, *Z. anorg. allg. Chem.* **267**, 1 (1951).
10. M. F. Lappert, *J. chem. Soc.* 2790 (1958).

be a controlling factor in the reaction. It has not been found possible to place three di-*i*-propylamino groups around one boron atom[4], although recently evidence has been published confirming the preparation of tris(di-*i*-propylamino) borane[11].

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11. M. F. Lappert and M. K. Majumdar, *J. organomet. Chem.* **6**, 316 (1966).