BH_2I Etherate, $BH_2(OEt_2)_2{}^+I^-$, and the Corresponding Tri-iodide Derivatives as Long-lived Intermediates in the Reaction of Iodine with Diborane and Diethyl Ether

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ALTHOUGH the compound BH_2I has not been isolated, complexes of the type BH_2I,amine and $BH_2(amine)_2{}^+I^-$ have been reported for aliphatic and heteroaromatic amines.[1–5] Generally, the BH_2I,amine compounds may be prepared by reaction of iodine with amine boranes, while in the presence of excess amine the boronium compounds are obtained. It has recently been reported that iodine, diborane, and diethyl ether react together rapidly at ambient temperature, forming iodoethane, hydrogen, and unidentified products.[6] During the reaction, it became evident that long-lived iodinated intermediates are formed, which appear to be respectively, the less stable and hitherto unknown diethyl ether analogues of the above amine complexes, and the corresponding tri-iodide compounds. No ether complex of BH_2I has been reported previously although stable $Ph_2B(OEt_2)_2{}^+$ compounds are known.[7]

Thus a reaction mixture containing I_2, B_2H_6, and Et_2O was frozen into an evacuated grease-free vessel and allowed to warm up rapidly from −196° to 25°. Within seconds of the melting of the ether, the mixture was observed to separate into two distinct liquid phases: a heavy, viscous, dark-brown lower phase and a very pale ethereal phase, constituting the bulk of the reaction mixture. The mixture was immediately cooled to −196°, when it was observed to have evolved slightly more than one third of a mole of H_2 per mole of I_2 in the reaction mixture. On distillation at −45° only unchanged Et_2O and B_2H_6 distilled, while the residue, consisting of the ether-insoluble phase, was a dark-brown viscous material, which evidently contained a little mechanically trapped Et_2O. This could not be removed, because, on warming up, the residue decomposed rapidly, liberating more H_2, to form a mixture consisting of EtI and products containing B–H and B–OEt bonds, as indicated by the H_3BO_3, EtOH, and further hydrogen obtained on treatment with water. By quantitative analysis of these products, the original composition of the lower phase was established as BH_2I_3,xEt_2O. The exact number of ether molecules in the intermediate could not be definitely established because of the trapped Et_2O, but experimentally was approximately 2. It is therefore best represented as $[BH_2(OEt_2)_2]^+I_3{}^-$, or, in view of its liquid form, as a mixture of the formally covalent $BH_2(I_3),Et_2O$ and electrovalent $BH_2(OEt_2)_2{}^+I_3{}^-$ in equilibrium:

$$BH_2(I_3),OEt_2 + Et_2O \rightleftharpoons BH_2(OEt_2)_2{}^+I_3{}^-$$

Although the ether-insoluble phase is too opaque and too unstable at room temperature for its absorption maxima to be measured, the presence of tri-iodide species is indicated by the very dark brown colour, while their formation can be represented quantitatively by the following equations:

$$B_2H_6 + 3I_2 + 2Et_2O = 2BH_2(I_3),OEt_2 + H_2$$

$$B_2H_6 + 3I_2 + 4Et_2O = 2BH_2(OEt_2)_2{}^+I_3{}^- + H_2$$

Similar experiments with different reaction times were conducted to establish a full reaction profile. In the undisturbed system, the lower phase does not decompose rapidly, but disappears slowly over a period of 1 hr. at 25°. The iodine bound up in the tri-iodide compounds appears to react slowly with the excess B_2H_6 and Et_2O, forming the analogous BH_2I compounds. By the time the lower phase has disappeared, over 90% of the iodine has been converted to EtI, but a virtually quantitative yield is not observed until some time later, suggesting the presence of a colourless, soluble intermediate. This would appear to be BH_2I,OEt_2, since at this stage it has been established that the mole ratio

$$I_2(\text{total}) : H_2(\text{evolved}) : \text{EtI} : \text{B–OEt} = 1:1:2:2,$$

while the boron products still contain much hydridic hydrogen, the analytical data here being consistent with BH_2OEt, which, since it normally disproportionates, is apparently stabilised by co-ordination with ether.

Thus, under these conditions, $BH_2(OEt_2)_2{}^+I_3{}^-$ and $BH_2(I_3),OEt_2$, and, less prominently, $BH_2(OEt_2)_2{}^+I^-$ and BH_2I,OEt_2, appear to function as intermediates in the overall reaction:

$$B_2H_6 + I_2 + 4Et_2O = H_2 + 2EtI + 2BH_2OEt,OEt_2$$

However, the boron product was not positively identified and indeed is itself of limited stability, since in the undisturbed system it appears to react further, liberating more hydrogen and forming more B–OEt groups.

The same intermediates are believed to be involved when similar reagent mixtures are allowed to react in a hydrocarbon or CCl_4 as solvent. A short-lived buff-to-brown suspension is first observed, showing characteristic bands (λ_{max} at 290 and 360 mμ) of the intensely absorbing $I_3{}^-$ ion in the u.v. spectrum, the absorption extending into the visible region. This suspension is however mainly the monoiodide $BH_2(OEt_2)_2{}^+I^-$ containing traces of $I_3{}^-$, in accordance with its light colour. It disappears after a few minutes in the undisturbed system, but also decomposes rapidly if separated. If allowed to disappear as a suspension, a colourless solution is formed, in which the concentration of EtI slowly increases from a trace to a virtually quantitative yield after a few days' reaction at ambient temperature. The colourless soluble intermediate absorbs very strongly below 200 mμ, the tail of this absorption extending typically beyond 260 mμ. ^{1}H n.m.r. spectra of these solutions indicated an Et_2O-co-ordinated intermediate with one molecule of Et_2O per iodine atom. Neglecting the possibility of an intermediate containing B–Et bonds, this result is again in accord with the formulation BH_2I,OEt_2, as is, once again, the formation of boron products containing hydridic hydrogen. At diethyl ether concentrations above 2M, a more permanent white precipitate is observed to be formed from the buff suspension. The white colour suggests that it is now pure $BH_2(OEt_2)_2{}^+I^-$, this being stabilised by the larger excess of Et_2O.

The interesting long-lived intermediates observed in the above reactions of this very complex system are an indication of the striking increase of Lewis acidity through the substitution of one of the hydrogen atoms in BH_3, as the compound BH_3,OEt_2 is very unstable and only observable at really low temperatures.

(*Received, October 23rd*, 1967; *Com.* 1140.)

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