THE DERIVATIVES OF DI-n-BUTYLBORONOUS ACID

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by

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ABSTRACT

Di-n-butylboronous anhydride, $(Bu^n_2 B)_2O$, was prepared by the reaction of n-butylmagnesium bromide with ether-boron trifluoride and subsequent hydrolysis. Its reactions with alcohols (except tert.-butanol), water boron halides, and phosphorus pentachloride resulted in boron-oxygen fission. Thus, with alcohols it yielded the appropriate boronites, $Bu^n_2 BOR$; with water the acid, $Bu^n_2 BOH$; and the boron and phosphorus halides di-n-butylboron halides, $Bu^n_2 BX$. With acetic acid and trifluoroacetic acid carbon-boron fission took place to produce novel compounds of the type $(Bu^n BOCOR)_2O$.

Di-n-butylboron chloride reacted with numerous hydroxy compounds, including alcohols (including tert.-butanol), carboxylic acids, water, and ethyl acetoacetate, in each case eliminating hydrogen chloride.

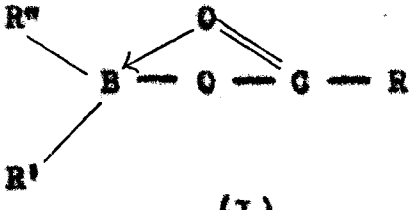
n-Butylboron dichloride was prepared by the reaction of boron trichloride with n-butylboronic anhydride. With water and alcohols it reacted similarly to di-n-butylboron dichloride but with pyridine it formed a 1:1 complex whereas di-n-butylboron chloride formed a 2:1 complex.

Di-n-butylboronous esters were readily hydrolysed and their alcoholysis to form esters of higher molecular weights was also studied. The tendency for complex

formation between certain nitrogen bases ($EtNH_2$, Et_2NH, Et_3N, C_5H_5N) and n-butylboronates, and di-n-butylboronites was also studied as part of a programme to determine factors influencing boron-nitrogen coordination.

The reaction of acetic acid and trifluoroacetic acid with phenylboron and n-butoxyboron chlorides proceeded by the elimination of hydrogen chloride. n-Butoxyboron acetates were not isolated but the diborates, $[(RCOO)_2B]_2O$, n-butyl borate, and acetic anhydride were obtained. The phenylboron chlorides gave benzene with trifluoroacetic acid and the corresponding carboxylates, $CF_3COOBPh_2$ and $(CF_3COO)_2BPh$ were therefore prepared not from the free acid, but from its sodium salt.

The infra-red spectra of the above-mentioned acetates and trifluoroacetates gave valuable information concerning their structures and particularly it has been demonstrated that chelation of the type (I) is evident.



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