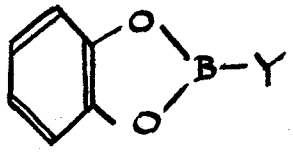
SYNOPSIS OF THESIS.

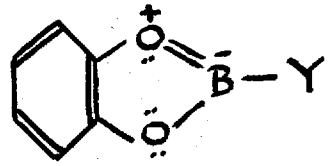
The preparation and stability of certain o-phenylene dioxyboron derivatives I are described. These include



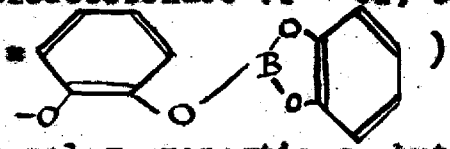
I.

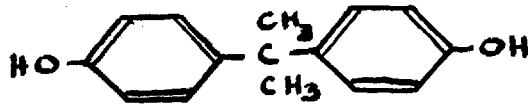
the o-phenylene halogenoboronates (Y = Cl, Br), the phenyl and tert.-butylboronates (Y = Ph, Bu^t), the dialkylamino-boronates (Y = NR_2), the alkyl and phenyl o-phenylene borates (Y = OR, OPh) and the thioalkyl o-phenylene borates (Y = SR). These compounds are, in general, easily hydrolysed. The o-phenylene halogenoboronates have greater thermal stability than the corresponding dialkyl or diphenyl chloro-boronates; the bromo-derivative is the first recorded bromo-boronate. The alkyl and phenyl o-phenylene borates, which form amine complexes, provide an interesting example of stable mixed orthoborate esters analogous to the alkyl and phenyl ethylene borates whilst the thioalkyl o-phenylene borates are the first recorded examples of mixed thio-oxy-orthoborates. The thermal stability of these halogenoboronates and alkyl, or thioalkyl, and phenyl o-phenylene borates must be related to the location of the boron atom in a cyclic system and it is postulated that this stabilisation might be due to the

contribution of canonical structures of the type II, a view supported by infra-red spectroscopic measurements.

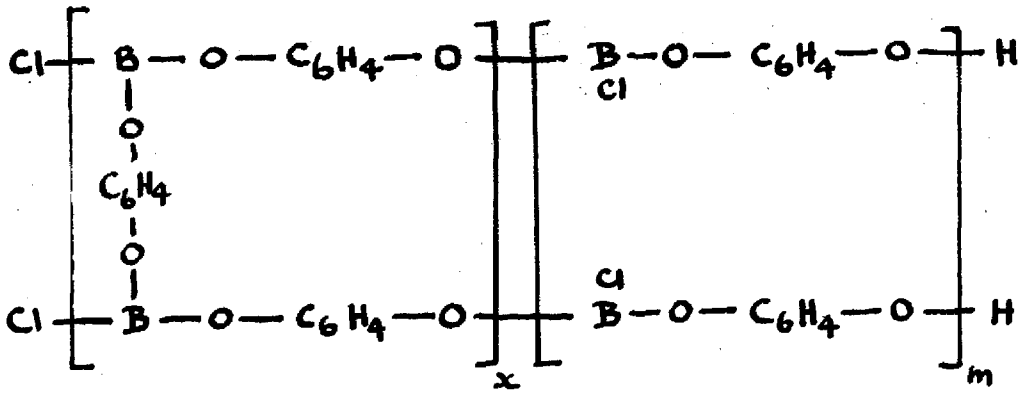


II.

Catechol and boron trichloride readily afford o-phenylene chloroboronate (Y = Cl) or tri-o-phenylene diborate (Y = ) depending on molar proportions, but not the o-phenylene bis-dichloroboronite. However, interaction of the trichloride with non-vicinal dihydric phenols such as quinol, resorcinol and the "bis-phenol A" (III) type of compound, where formation of ring systems by intramolecular reaction is prohibited by steric requirements, results in the formation of polymeric compounds for which structures such as IV are postulated

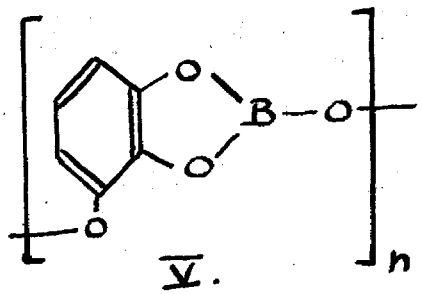


III.



IV.

Boron trichloride and pyrogallol also afford a polymer (V).



V.

The polymeric aryl borates are generally stable to heating (~ 300°) whilst the polymeric chloroesters eliminate boron trichloride by a redistribution reaction tending to form a chlorine free polymer; all are readily hydrolysed.