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A SEARCH FOR REDISTRIBUTION REACTIONS OF CARBONIUM IONS WITH BORANES AND ALANES

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The isoelectronic relationship between R_3B and R_3C^+ is frequently alluded to, although structural similarities are rare. The conjugative and hyperconjugative interactions which clearly play an important part in the structures of carbonium (carbenium)[1] ions are of little consequence in organoboron structures (charge separation is involved in the contributing valence bond structures). However CH_5^+[2] and BH_5[3] are probably isostructural. One may also note that the transition state in the hydroboration reaction probably resembles either edge- or corner-protonated cyclopropane. Very recently Hogeveen and Kwant[4] have suggested a C_{5v} structure for a $(CH_3C)_6^{++}$ ion (obtained from hexamethyldewarbenzene epoxide in HSO_3F-SbF_5) which is analogous to the known $(C_2H_5)C_4B_2$ carborane.[5] It seemed worthwhile to enquire if dimeric electron-deficient structures, well-known for R_3B and $R_3A\ell$, could play any part in R_3C^+ chemistry. It appeared more profitable to look for mixed species $[R_3B,R_3C]^+$ and $[R_3A\ell,R_3C]^+$ than for doubly-charged $[R_6C_2]^{++}$ ions and initially to search for such structures as unstable species or transition states in redistribution reactions[6] rather than to expect to find stable ions with these structures. We describe here our initial attempts to observe redistribution reactions of the type:-

$$R_2R'C^+ + R_3B \rightleftharpoons R_3C^+ + R_2R'B$$

which might occur via the mixed species $[R_3BR_2R'C]^+$.

The choice of R and R' for a practical experiment is severely limited by the thermal instability of most carbonium ions, and the need to produce many of them in strongly acidic solutions. Also many carbonium ions are likely themselves to be powerful protic acids, capable of causing protolysis of C-B and C-Aℓ bonds. We therefore used R = phenyl and R' = p-tolyl. Although phenyl is known to be an excellent bridging group in alane structures,[7] it is probable that the extensive stabilisation of Ph_3C^+ by conjugation outweighs this favourable factor, so that our example is perhaps a rather poor case.

A dry acetonitrile solution of triphenylboron[8] (0.055M) and p-methylphenyldiphenylcarbonium tetrafluoroborate (0.055 M) was refluxed under nitrogen for 20 hours. The products were oxidised with alkaline hydrogen peroxide and the phenolic products from the organoboranes were silylated and examined by g.l.c. The trimethylsilyl ether of phenol was observed as expected but no derivative of p-cresol was detected. We estimate that as little as 0.015% reaction could have been detected. A solution of freshly-prepared triphenylalane[9] (0.025 M) and p-methylphenyldiphenylcarbonium tetrafluoroborate (0.025 M) in dry o-dichlorobenzene was refluxed (180°) for 20 hours under nitrogen. Addition of water caused protolysis of the alanes present and the hydrocarbon products were analysed by g.l.c. Benzene, but not toluene, was observed; as little as 0.03% reaction could have been detected.

Our experiments indicate that if the sought for redistributions can occur, they must have free energies of activation of >33 $Kcal.mole^{-1}$ in the boron case and >41 $Kcal.mole^{-1}$ in the case of the triphenylalane. We emphasise that our example is probably far from ideal, but it seems unlikely that bridged $[R_3B,R_3C]^+$ and similar species will be readily formed in any simple case. Perhaps the best opportunities for mixed Group III/Group IV ions of this type lie with heavier elements, e.g. $[SiCl_3,AlCl_3]^+$.

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