Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

THE QUESTION OF ISOMERIZATION DURING THE ALKYLATION OF BORON TRIFLUORIDE ETHERATE WITH ALKYLMAGNESIUM HALIDES

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(Received March 29th, 1971)

SUMMARY

It is shown that, contrary to what has been implied, the reaction of n-, s-, or iso-butylmagnesium bromides with boron trifluoride etherate is not accompanied by isomerisation of the alkyl groups.

RESULTS AND DISCUSSION

It is well established that t-butylmagnesium halides react with boron trifluoride etherate to give a partially isomerised product which consists principally of diisobutyl-t-butylborane[1].

A recent paper by El-Fayoumy, Wahab and Roushdy[2] suggests that isomerization may also occur during the reaction of n- or s-butylmagnesium halides. For example, n-butylmagnesium halide (probably bromide) gave a middle fraction of trialkylborane, b.p. 91–95°/8 mm, which was oxidised with alkaline hydrogen peroxide to give a mixture of alcohols of the following composition (volume %, by GLC): t-BuOH 10.05, s-BuOH 3.96, i-BuOH 5.09, n-BuOH 80.45%.

If the alkylation of boron trifluoride etherate is indeed accompanied by isomerization of n- or s-alkyl groups, it would invalidate some of our earlier results. We have therefore checked the composition of samples of tri-n-butyl-, tri-s-butyl-, and triisobutylboranes which had been prepared by the Grignard route.

The boranes were oxidised with alkaline hydrogen peroxide and the alcohols which were formed were analysed by GLC. Each borane gave the corresponding alcohol in at least 99% isomeric purity. We conclude that the alkylation of the boron is not accompanied by any significant amount of isomerization, and we suggest that the composition of the boranes which El-Fayoumy, Wahab, and Roushdy obtained reflects the isomeric purity of their initial butyl halides.

EXPERIMENTAL

The trialkylboranes were prepared by treating boron trifluoride etherate with the appropriate alkylmagnesium bromide[3], and showed the following boiling points: tri-n-butylborane, 95–96°/12 mm, triisobutylborane 75°/15 mm, tri-s-butylborane

82–83°/13 mm. Proton NMR spectroscopy showed the presence of less than 1% of products due to adventitious autoxidation.

Weighed samples of each borane were dissolved in diglyme under nitrogen and cleaved with alkaline hydrogen peroxide[4]. The products were analysed by GLC at 80° using a Perkin–Elmer F11 instrument fitted with a 4m × 3mm Antarox (8%) column and a flame ionisation detector.

ACKNOWLEDGEMENTS

We are grateful to Borax Consolidated Ltd., the Science Research Council and the Turner and Newall Research Fellowships Committee, for support.

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