Stereochemistry and Order of the Three Alkyl Migrations in the Cyanoborate† Process

By Andrew Pelter,* Michael G. Hutchings, and Keith Smith

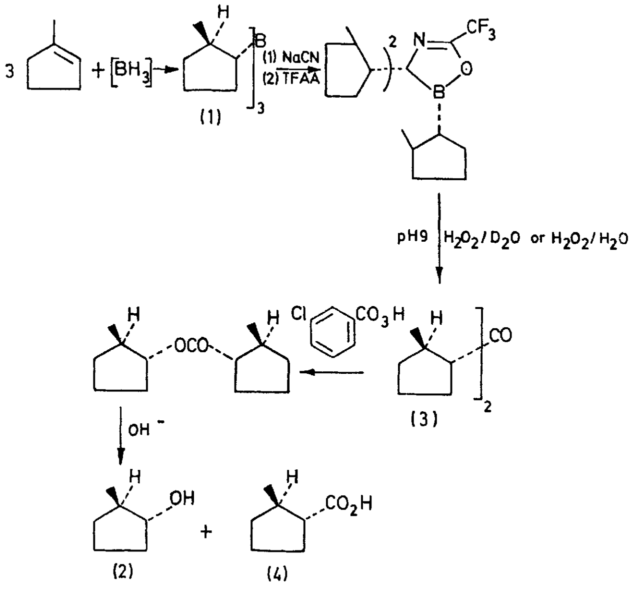
(*Department of Chemistry, University College of Swansea, Singleton Park, Swansea SA2 8PP, and The University, Manchester M13 9PL)

Summary All three possible migrations from boron to carbon in the cyanoborate process proceed with retention of configuration of the migrating group and the ease of migration of alkyl groups is in the order primary > secondary > tertiary for each of the migrations.

We have previously reported that acylating agents react with trialkylcyanoborate salts to induce either two[1,2] or three migrations,[3] suitable work up then giving ketones, trialkyl carbinols,[3] and amides[4] in high yields. The value of the process would be strongly enhanced if the stereochemistry of each separate migration were known as well as the migratory aptitudes of the different classes of alkyl groups. We here report studies which settle these points.

2-Methylcyclopentene was treated with diborane to yield tris-(*trans*-2-methylcyclopentyl)borane (**1**),[5] which on oxidation gave only *trans*-2-methylcyclopentanol (**2**). Addition of sodium cyanide to a solution of (**1**), followed by treatment with trifluoroacetic anhydride (TFAA)[1,2] and then by oxidation with aqueous hydrogen peroxide at pH 9 gave ketone (**3**) (82%).‡ A parallel oxidation in D_2O gave no deuterium incorporation. Baeyer–Villiger oxidation of (**3**) in conditions such that migration from carbon to oxygen proceeds with retention[6] was followed by hydrolysis to give (**2**) and (**4**) only. (Scheme 1). Compounds (**2**) and (**4**) were characterised by spectroscopic and chromatographic comparison with authentic samples of the *cis*- and *trans*-compounds and derivatives. Thus the first and second migrations proceed with retention.

Our reported procedure[3] for inducing the third migration was suitable only for primary alkyl groups. We have since found that the use of pyridine or DMF as solvent allows the migration of three bulky groups under mild conditions.[4] The borane (**1**) was submitted to the new procedure followed by oxidation to give carbinol (**5**). (Scheme 2). Acid catalysed dehydration gave an olefin which on ozonolysis followed by degradation as before gave (**2**) and (**4**) only. Hence the third group also migrates with retention. The conclusion that all three groups migrate with retention was also reached by a parallel study of tris-(*exo*-norbornyl)borane which will be reported in our full paper.



Scheme 1

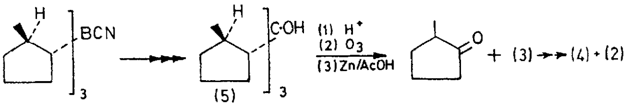
We have previously shown[2] that for the first two migrations tertiary alkyl groups migrate after primary and second groups. It proved simple to carry this further by use of mixed organoboranes produced *via* dialkylthioalkylboranes.[7] The cyanoborate process was applied to diethylcyclohexylborane to yield diethyl ketone as the only ketonic product. A g.l.c. analysis showed the absence of

---

† The term "cyanoborate process" is used to cover all those reactions in which there is migration from boron to carbon and which involve cyanoborate salts.

‡ All new compounds have been fully characterised.

cyclohexyl ethyl ketone, an authentic sample of which was made from dicyclohexylethylborane by the same procedure. Similarly dibutylcyclohexylborane gave only dibutyl ketone. Hence the order of ease of migration for the first two migrations is primary > secondary > tertiary.



Scheme 2

The evidence for the third migration must of necessity involve comparative rates rather than intramolecular competition experiments. However since the mild conditions used to induce the third migration of primary alkyl group failed for secondary alkyl groups and we have not been able to effect the third migration of a tertiary group, the same order must be inferred as for the first two migrations.

Previous stereochemical investigations have been confined to once migrated product.[5] The present study would support the view that retention of configuration of the migrating group is general for all migrations from boron to carbon that involve ionic processes. The migratory aptitudes found for these processes agree well with other findings,[8] and may also be general. They are in complete contrast to the migratory aptitudes found for the isoelectronic Wagner–Meerwein shifts.

We thank Dr. D. N. Sharrocks and Mr. D. Williams for help with the mixed boranes, Mr. G. W. Bates for valuable technical assistance, and the S.R.C. for financial support (for M. H. and K. S.).

(*Received*, 9*th January* **1973**; *Com.* 032.)

---

[1] A. Pelter, M. G. Hutchings, and K. Smith, *Chem. Comm.*, 1970, 1529.
[2] A. Pelter, M. G. Hutchings, and K. Smith, *Chem. Comm.*, 1971, 1048.
[3] A. Pelter, M. G. Hutchings, and K. Smith, *Chem. Comm.*, 1971, 1048.
[4] M. G. Hutchings, Ph.D. thesis, Manchester University, 1972.
[5] H. C. Brown, M. M. Rogic, M. W. Rathke, and G. W. Kabalka, *J. Amer. Chem. Soc.*, 1969, **91**, 2150.
[6] R. A. Smith, in 'Molecular Rearrangements, Part I,' ed., P. de Mayo, Interscience, 1964, p. 579.
[7] A. Pelter and D. N. Sharrocks, *J.C.S. Chem. Comm.*, 1972, 566.
[8] H. C. Brown, *Accounts Chem. Res.*, 1969, **2**, 65.