Preparation of *trans,trans,trans*- and *cis,cis,trans*-Perhydrophenalen-9-ols by Application of the Three-migration Cyanoborate Process to Isomeric Perhydro-9b-boraphenalenes: Differences between the Cyanoborate and Carbonylation Reactions

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Summary Application of the three-migration cyanoborate process to *cis,cis*-perhydro-9b-boraphenalene gives *trans,trans,trans*-perhydrophenalen-9-ol, in contrast to carbonylation which gives the *cis,cis,cis*-isomer; *cis-trans*-perhydro-9b-boraphenalene gives *cis,cis,trans*-perhydrophenalen-9-ol by either process.

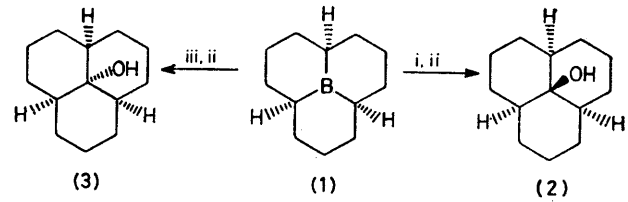
THE ability to replace the boron atom of an organoborane by a functionalised carbon atom [equation (1)][1–3] is one of the most important consequences of recent developments in the use of organoboranes as synthetic reagents.

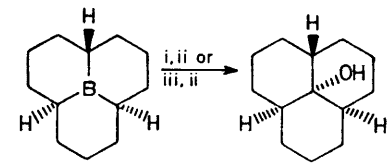
$$R_3B \rightarrow R_3C\text{–}B< \xrightarrow{[O]} R_3C\cdot OH \qquad (1)$$

Three methods are available for carrying out the rearrangements represented by equation (1). These are the cyanoborate process,[1] the carbonylation of organoboranes[2] and the reaction of organoboranes with the anion derived from dichloromethyl methyl ether.[3] Until now it has been assumed that application of each method would lead to the same tertiary alcohol and that in any specific case the choice of reaction would be governed solely by convenience and the tolerance of the organoborane to the reaction conditions. We now show that this assumption is invalid and that different tertiary alcohols may be obtained from the same organoborane depending on the method used.

Perhydro-9b-boraphenalenes are readily available.[4–6] Reaction of the *cis,cis*-isomer (**1**) with potassium cyanide and then trifluoroacetic anhydride, (TFAA), followed by oxidation, gives *trans,trans,trans*-perhydrophenalen-9-ol (**2**) in 41% yield as the only isolable tertiary alcohol. Carbonylation–oxidation of (**1**) has been previously shown to give the *cis,cis,cis*-isomer (**3**) (Scheme).[7] However, application of the three-migration cyanoborate process to *cis,trans*-perhydro-9b-boraphenalene (**4**) gives *cis,cis,trans*-perhydrophenalen-9-ol (**5**) (75% yield), the same product as previously obtained *via* the carbonylation–oxidation of (**4**)[6] (Scheme). Our stereochemical assignments are based on comparison with authentic samples† and on lanthanide-induced shift ^{1}H n.m.r. studies which independently confirm previous assignments.‡

One explanation of the production of (**5**) requires that the reactions proceed *via* the thermodynamically and kinetically favoured *cis,cis,trans* adducts (**6a**) and (**6b**).[6] This requires that all three migrations proceed with retention of configuration of the migrating groups, as is known

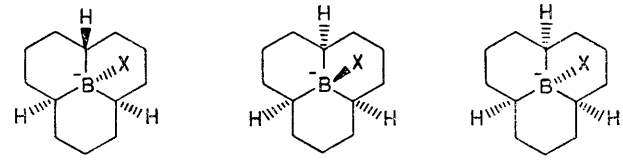




SCHEME. Reagents: i, KCN then $(CF_3CO)_2O$, 40 °C; ii, H_2O_2–OH^-; iii, CO, $(CH_2OH)_2$, 150 °C, 70 atmos pressure.

for all three migrations of the cyanoborate process[8] and for the first migration of the carbonylation reaction.[9] In addition there must be inversion of configuration at the migration terminus of the third migration, the only one for which there are alternative stereochemical consequences. Such inversions have many analogies in organoborane reactions.[10]

The same restrictions applied to the reactions of (**1**) imply that the cyanoborate reaction proceeds through the more stable adduct (**7a**) whilst the carbonylation reaction is channelled through the less stable adduct (**8b**). The conclusions about the stability of the adducts are based on examinations of space filling molecular models and conformational analysis.[7] Examination of molecular models also suggests that there is less hindrance to approach from the *cis*-side of the molecule, so that (**8a**) and (**8b**) would be the kinetically favoured adducts.



a; X = C≡N
b; X = C≡O

† We thank Professor H. C. Brown for samples of isomeric perhydrophenalenols.

‡ The ^{1}H n.m.r. spectrum of (**2**) shifts very little on addition of Eu(fod)$_3$, indicative of only weak complexation. This is expected, as the HO-group of (**2**) is effectively shielded by a ring of six axial protons. The alcohol (**3**) exhibits large shifts, with the signals due to the group of three β-hydrogen atoms being shifted most. Compound (**5**) shows the six most-shifted protons moving in three groups of two, as expected based on their proximity to the hydroxy group in space filling models. The alternative *cis,trans,trans*-isomer should show the six most-shifted proton signals moving in two groups of three.

The intermediacy of (**8b**) in the carbonylation reaction leading to (**3**) has been rationalised[7] by suggesting that whilst both (**7b**) and (**8b**) are present in the reaction mixture, (**8b**) is the more reactive in the first rearrangement step, assumed to be slower than adduct formation or equilibration. An alternative explanation is that adduct formation is slower than the first rearrangement, which thus proceeds *via* the kinetic adduct (**8b**). However, cyanoborates show no tendency to migrate until an electrophile is added and hence equilibration of (**8a**) to (**7a**) can occur prior to migration. The first migration proceeds rapidly at low temperatures and the product (**2**) reflects the preponderance of (**7a**) in solution prior to addition of TFAA.

Although the belief that (**7a**) would be the intermediate in the cyanoborate process governed our design of the experiments, unfortunately we have been unable to obtain *X*-ray evidence to confirm the stereochemistry of the cyanoborate (**7a**) or its (isolated) double migration product.

For the first time, it has been demonstrated that carbonylation of organoboranes and the cyanoborate process can yield different tertiary alcohols from the same organoborane. There may be other cases in which a sagacious choice of reaction will allow the production of one or other of alternative stereoisomers.

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