Organoboron and organosilicon chemistry

Reading Lecture course: *Heteroatoms in Organic Synthesis*, Prof. D. M. Hodgson
S. E. Thomas, *Organic Synthesis – the Roles of Boron and Silicon*, Primer #1
J. Robertson, *Protecting Group Chemistry*, Primer #95 (Chapter 4)

Topics for notes

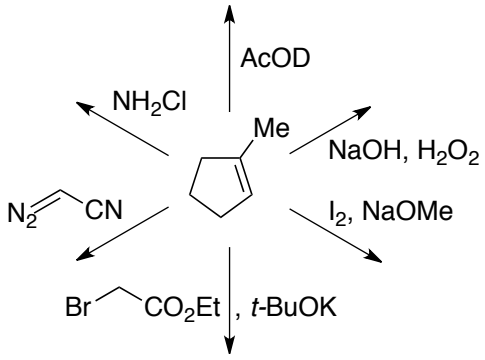
Boron
Structure and Lewis acidity of trivalent B; 6–8–6 valence electron reactivity patterns
Preparation via alkene and alkyne hydroboration; key reagents
Reactions: protonation, oxidation, amination, addition of carbon nucleophiles, carbonylation
Stereoselective alkene synthesis
Allyl boranes and boron enolates

Silicon
Length and polarisation of C–Si bond; strength of Si–O and Si–F bond; O→O and C→O migrations
S_N at and α- to Si
Use in alkoxide-trapping and protecting group chemistry; Si-centred reagents
Olefination reactions
Preparation and reactions of silyl enol ethers
Stabilisation of α-negative and β-positive charge
Reactivity of vinyl, aryl, and allyl/propargyl/allenyl silanes

Tutorial Problems
Provide mechanisms and full explanations for the following, identifying structures for products where not shown, and commenting on aspects of regio- and stereoselectivity where relevant. The final section – *Further questions* – will be covered during the tutorial if time permits.

Boron

(1) BH_3·THF then the reagent shown.



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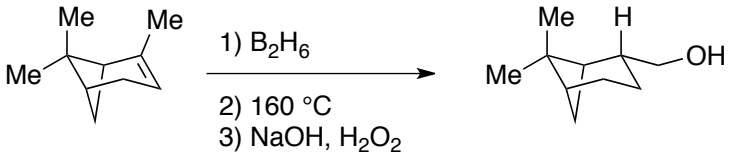

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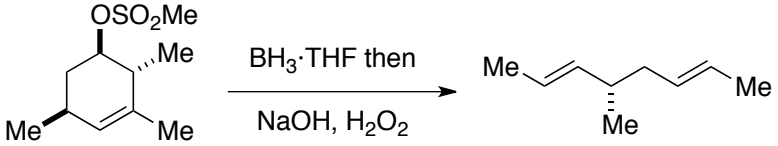

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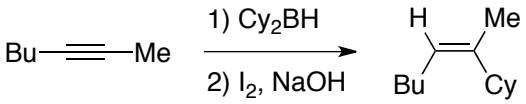

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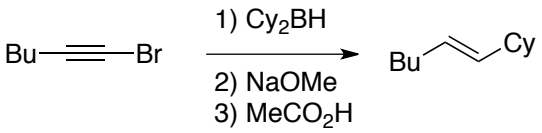

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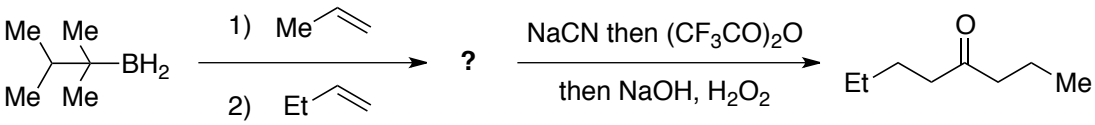

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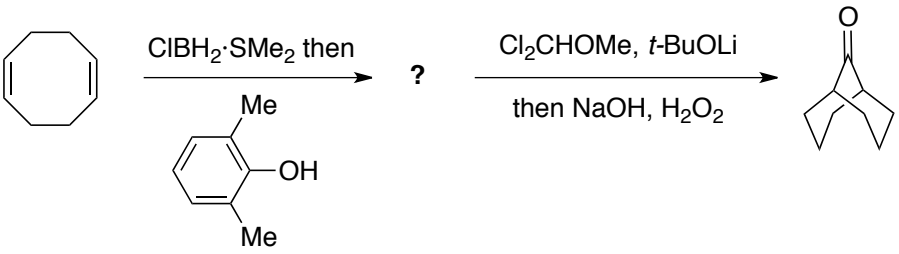

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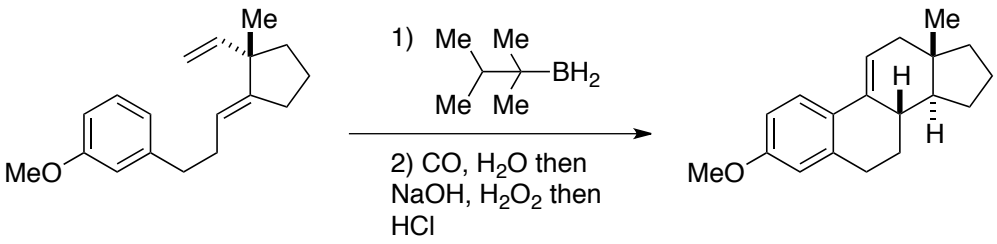

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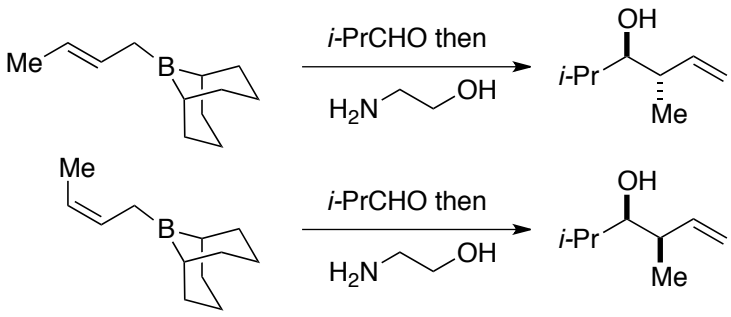
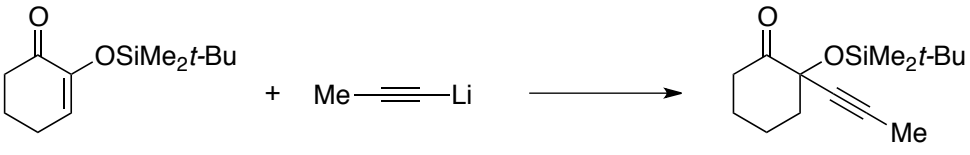


Silicon

(1)



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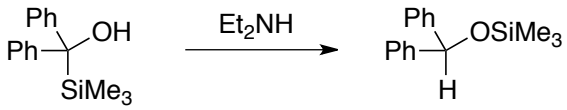

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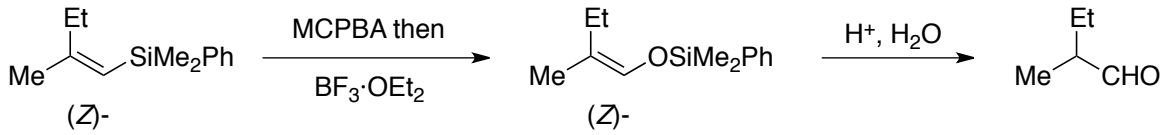
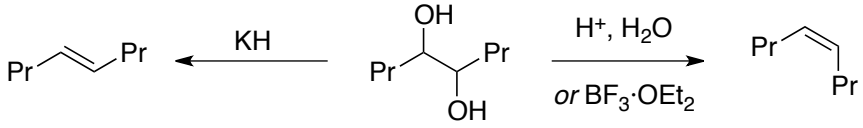


(4) Identify the diol diastereomer giving rise to *E*- or *Z*-oct-4-ene under the conditions shown.



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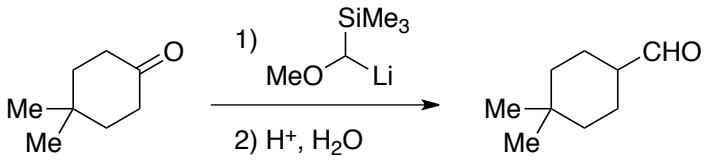

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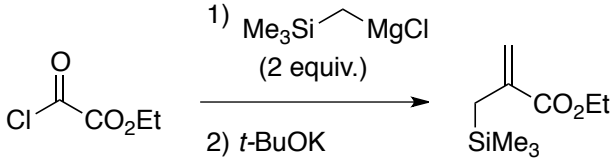

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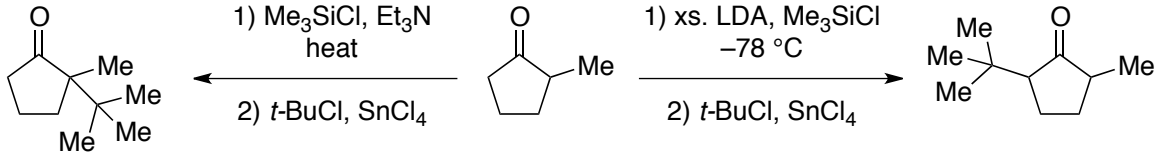

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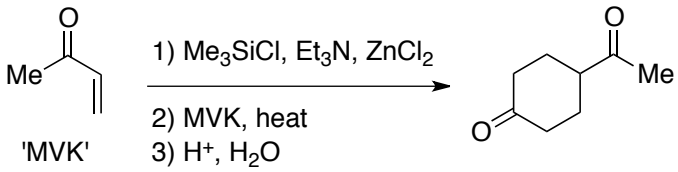

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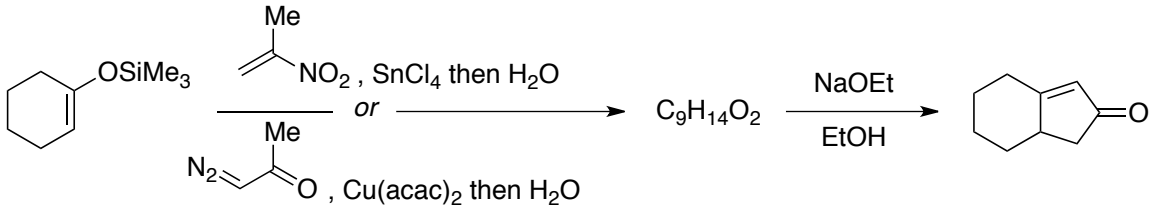

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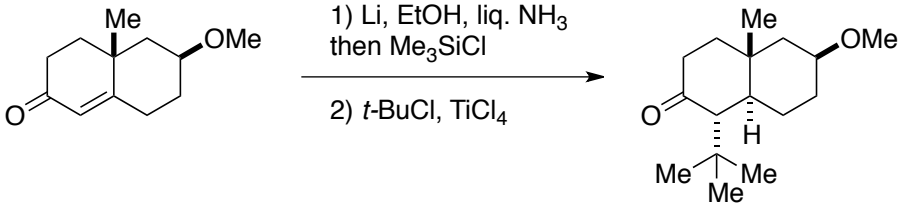

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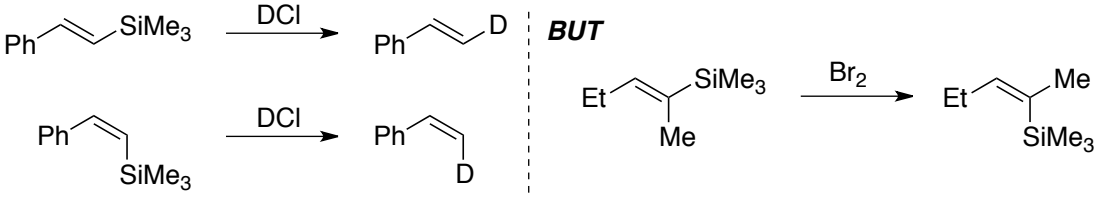

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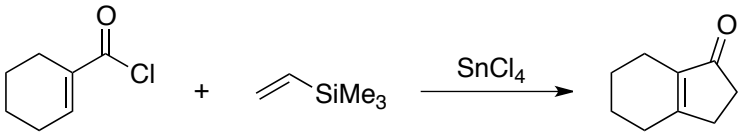

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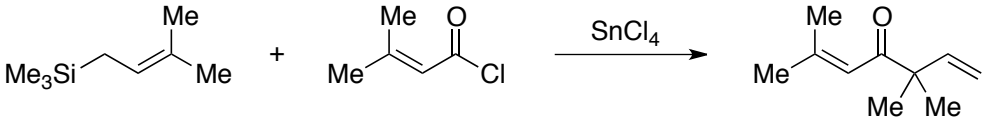

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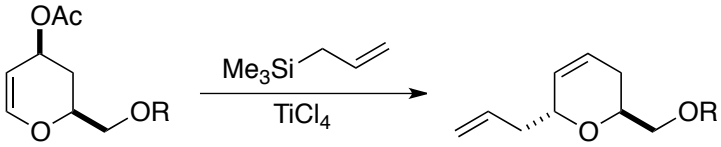

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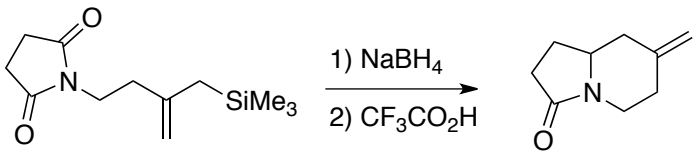
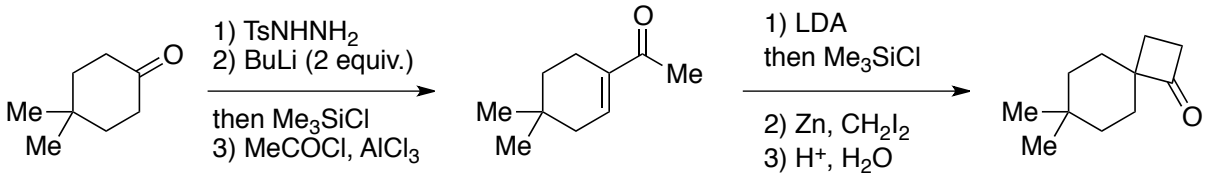
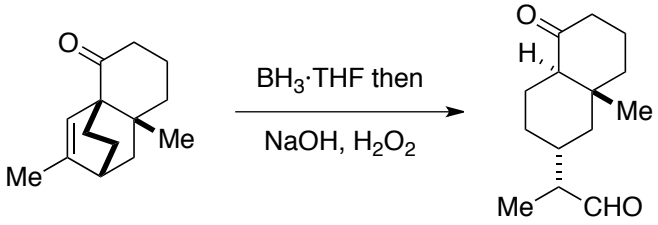


(17) How could the overall transformation be achieved in less steps? [Hint: organosulfur chemistry]



Further questions

(B1)



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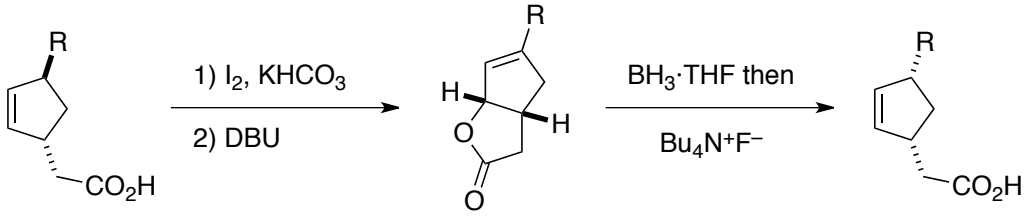

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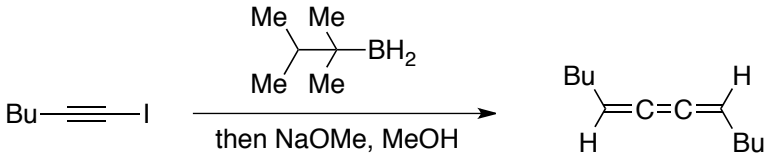
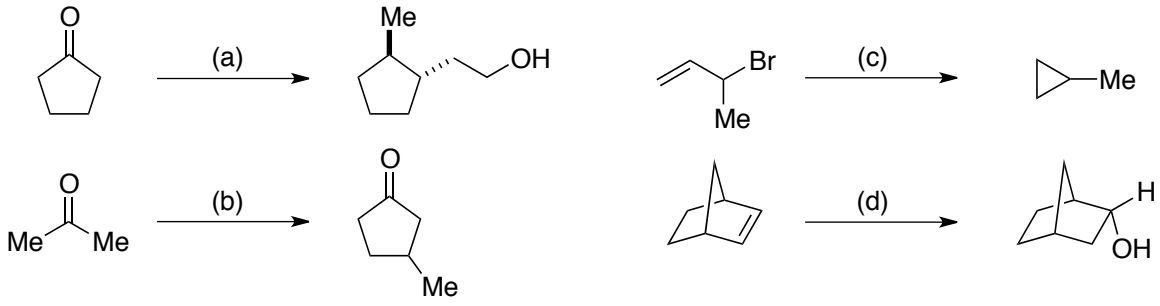
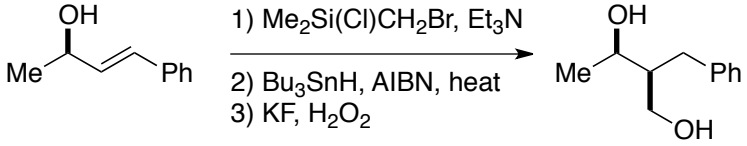


99% (*E*)-

(B4) How would you effect the following conversions using organoboron reagents at some stage in the synthesis. [more than one step will be required in each case]



(Si1)



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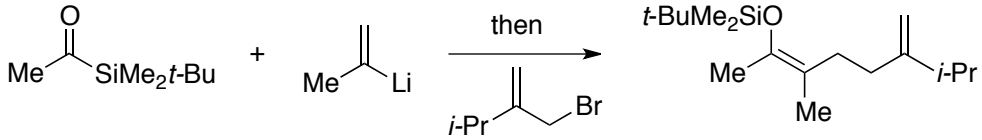
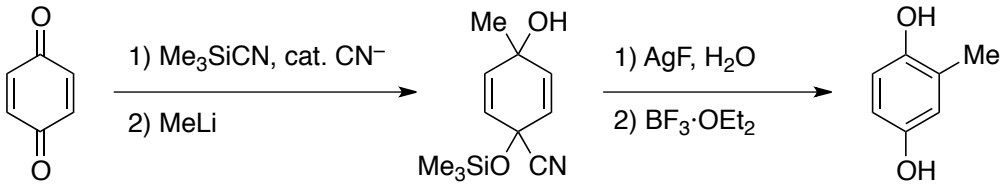
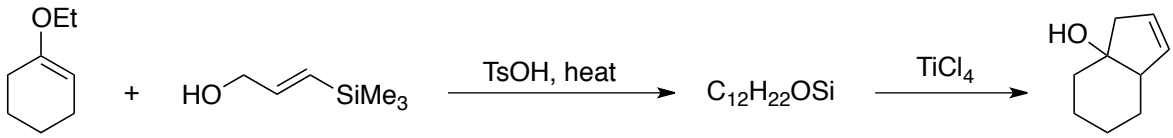


(Si3)

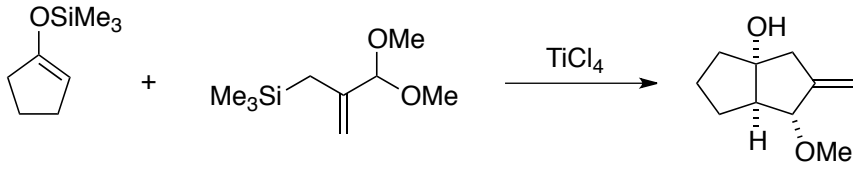
(Si4)



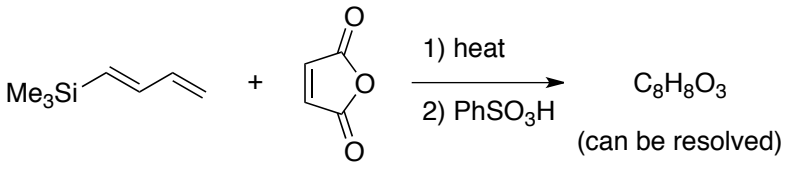
(Si5)



(Si6)



(Si7)



(Si8)