Course 343 | Instructor Hackenberger
Day ~~[illegible]~~ Mon | Date 11/25/2013
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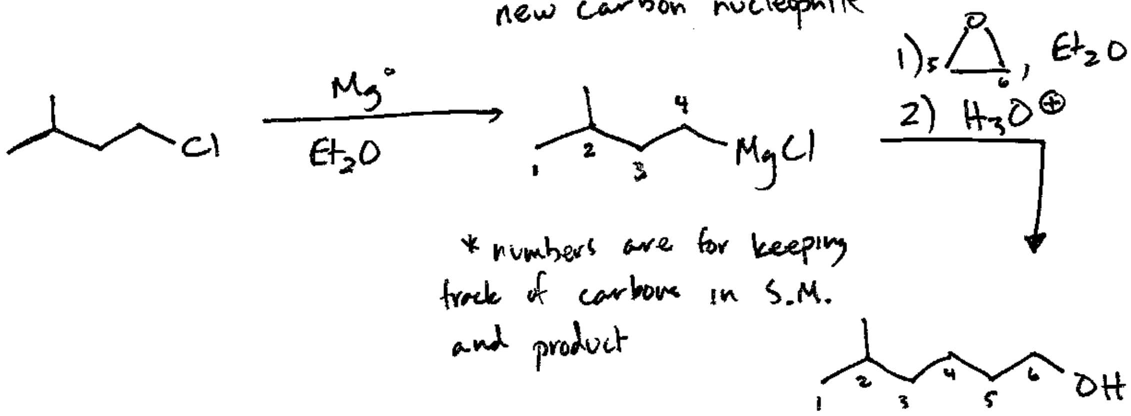
PLEASE COMPLETE NOTES IN INK AND DO NOT STAPLE.

- Last lecture: synthesis of epoxides
  - a) alkene + peracid
  - b) cyclization of halohydrin
  - c) asymmetric synthesis (Sharpless)
- Reactions of epoxides:
  - acid catalyzed reactions with nucleophiles
  - reactions w/ $:\ddot{O}R^{\ominus}$

<u>Today</u>: Epoxides and organometallics

new carbon nucleophile



* numbers are for keeping track of carbons in S.M. and product

new C–C bond

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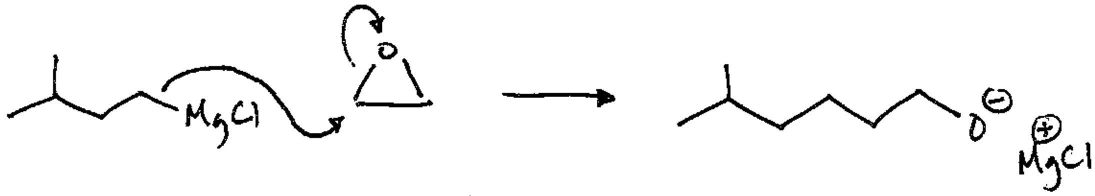
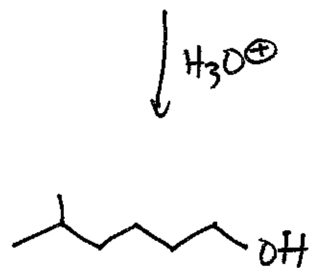
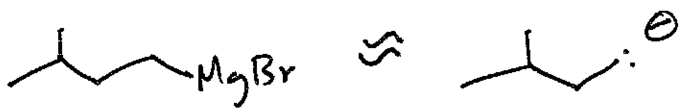
Mechanism:



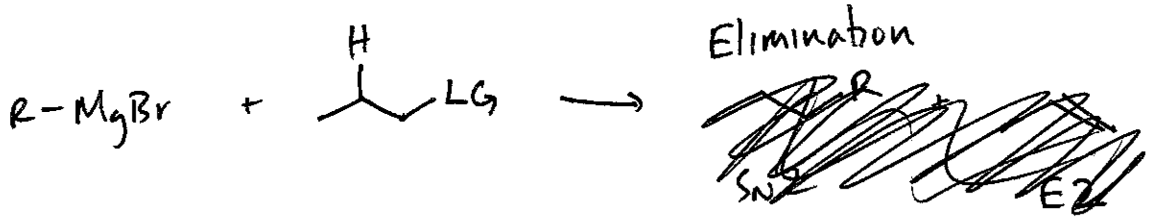
This reaction goes very well because the epoxide can coordinate to Mg^{2+} (a good Lewis acid). This makes it more reactive to ring-opening.



• You can think of Grignard reagents as carbanions:



* Important: Grignard reagents are strong bases as well, so elimination can occur with sp^3-hybridized electrophiles.



• Other organometallic reagents: organolithiums

(does not react w/ epoxides)

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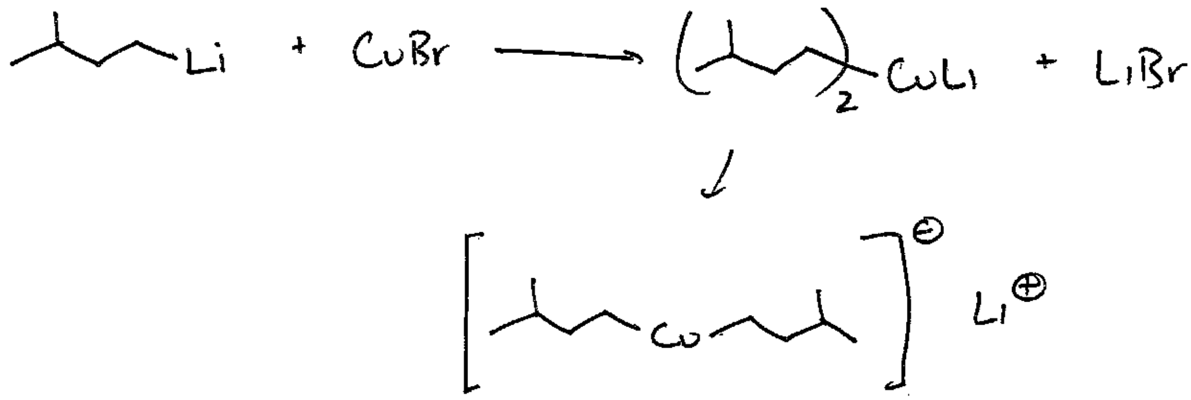
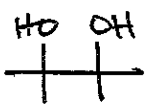
· Organocuprates do work well:

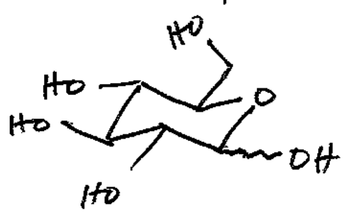


Cuprates react with epoxides in the same way as Grignard reagents.

· 1,2-diols or glycols



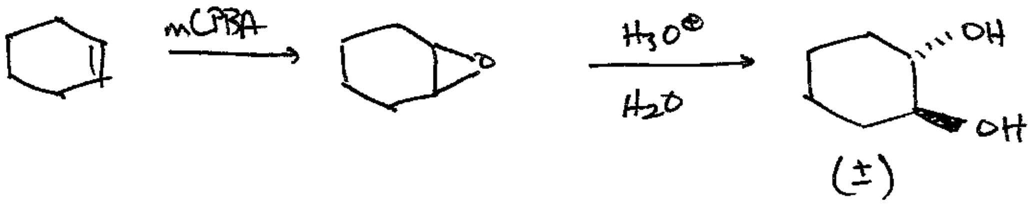
common functional group in carbohydrates



glucose

How to synthesize them?

1)



trans exclusively

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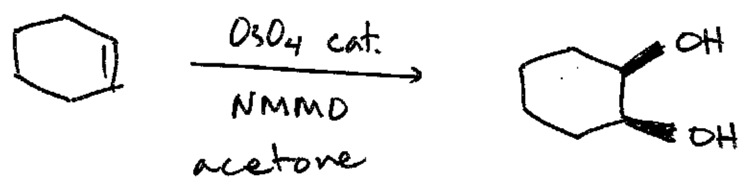
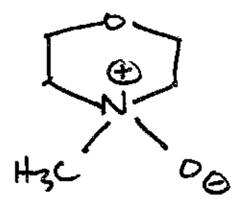
2) 

syn addition (no trans)

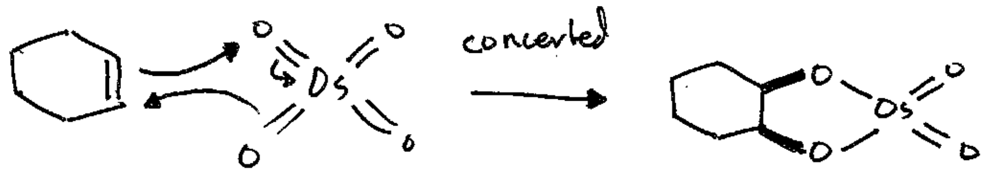
OsO_4 = catalytic oxidant

NMMO = N-methylmorpholine oxide (stoichiometric oxidant)

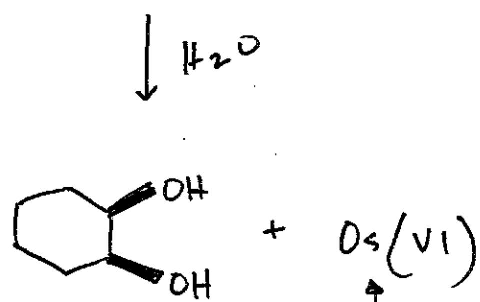
NMMO



Mechanism: Os^{VIII} → Os^{VI}



similar to ozonolysis



syn

oxidized back to active oxidant by NMMO

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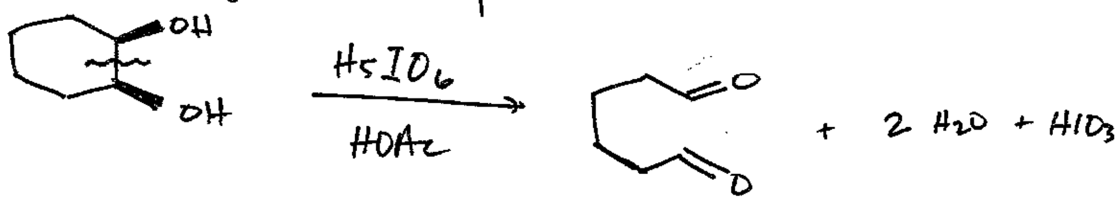
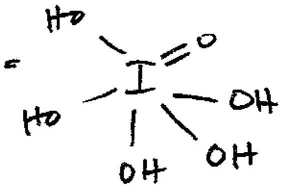
glycol cleavage with periodic acid:

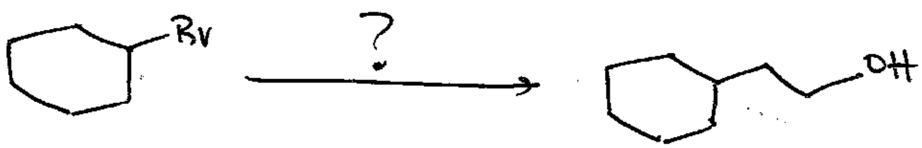


H_5IO_6 =



Mechanism: cycloaddition
(see p. 506)

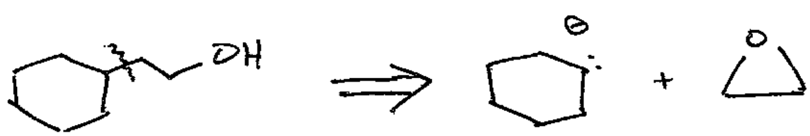
Examples of multistep transformations:



Solution:
1) Mg°, Et_2O
2) 
3) $H_3O^{\oplus}$

term: retrosynthesis

One strategy for these problems: think backwards from the product



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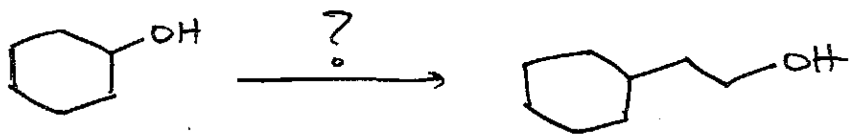
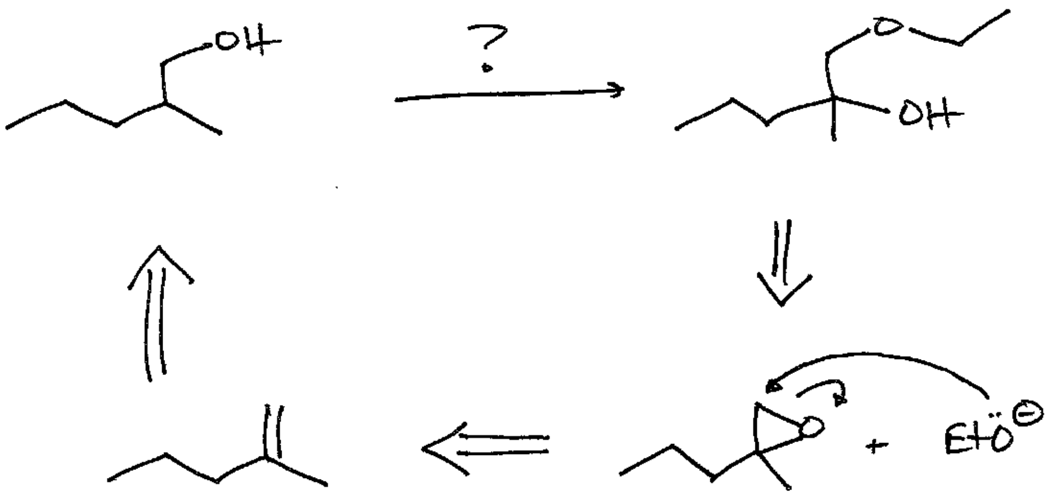


1) PBr_3
2) Mg°, Et_2O
3) 
4) $H_3O^{\oplus}$



Answer:
1) H_2SO_4, H_2O
2) mCPBA
3) NaOEt, EtOH

or, instead of step 1:
1) PBr_3
2) KOtBu

(different ways to make alkene)