


1) The name of the Zr reagent. What’s the product of the reaction below, explain why?

2) The mechanism?

3) The mechanism? *hint: [3+2+1] cycloaddition.* What’s the name of the homologous [2+2+1] reaction that also involves CO?

4) Name and mechanism of the reaction? What reaction can achieve opposite regioselectivity?

5) Name and mechanism of the reaction?

6) to isomerize one double bond;

7) both are desired products

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1) $\text{Cp}_2\text{ZrHCl}, \text{TMSCl}, \text{CuBrMe}_2\text{S}, \text{BF}_3\text{Et}_2\text{O}$

2) $\text{t-BuOK}, \text{TBAF}$

3) $[\text{Rh(CO)}_2\text{Cl}]_2, \text{CO}$

4) $\text{TIPSOTf}, \text{DBU}$, then $\text{Pd(OAc)}_2$

5) $\text{Mn(dpm)}_3, \text{PhSiH}_3, \text{O}_2$

6) $\text{SOCl}_2, \text{Et}_3\text{N}$

7) $\text{NaBH}_4, -78^\circ\text{C}$

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12-oxo- 9,11-dehydrokaurene

ent-1α-hydroxykauran-12-one
8) TCDI, DMAP, then nBu₃SnH, AIBN
9) NaBH₄, CeCl₃
10) Raney Ni, H₂
11) MnO₂ DCM
12) Li/NH₃, EtOH, -78°C

8) Name and mechanism of the reaction?
10) Rationalize the regio- and stereoselectivity
Key:

1) : Schwartz’s reagent. Hydrometallation of alkene and alkyne, reduction of amide (tertiary).

Schwartz’s reagent

O
OEt
H

DIBAL

O
H
Me₂N
2) the lone pair of the nitrogen can coordinate to Zr
2) the carbonyl group of ester is more electron-deficient

O|--I--|--TMS

O

TBAF

O

active agent, not stable

O

HO

O

HO

1,2-shift

5) Mukaiyama hydration. Alternative selectivity can be achieved from hydroboration-oxidation.
8) Barton-McCombie reaction

![Chemical reaction diagram](image)

10) The author mentioned the directing effect of the OH group (other hydrogenation reaction on the ketone compound gave wrong diastereoisomer). And this is reason that they do the reduction and reoxidation.