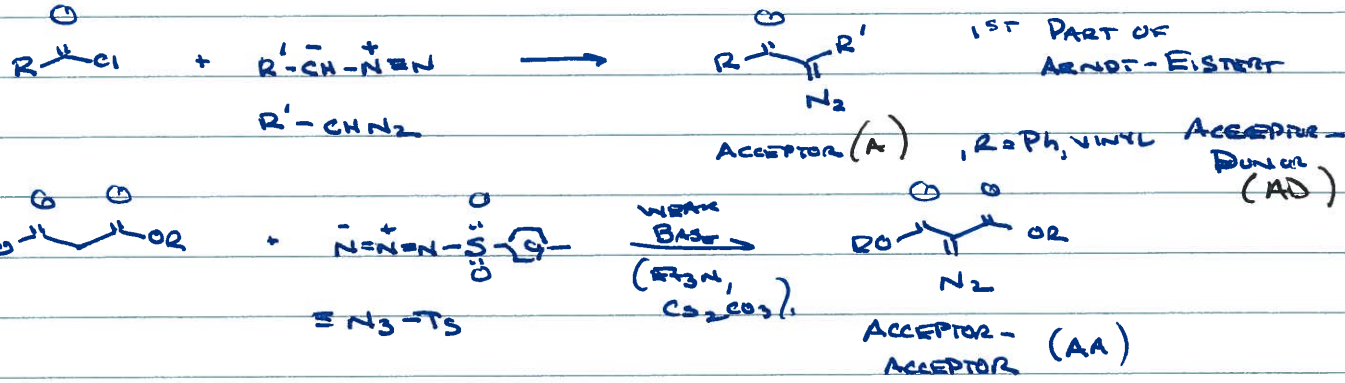
Rh(II) Carbenes

- Cyclopropanation and C–H Insertion

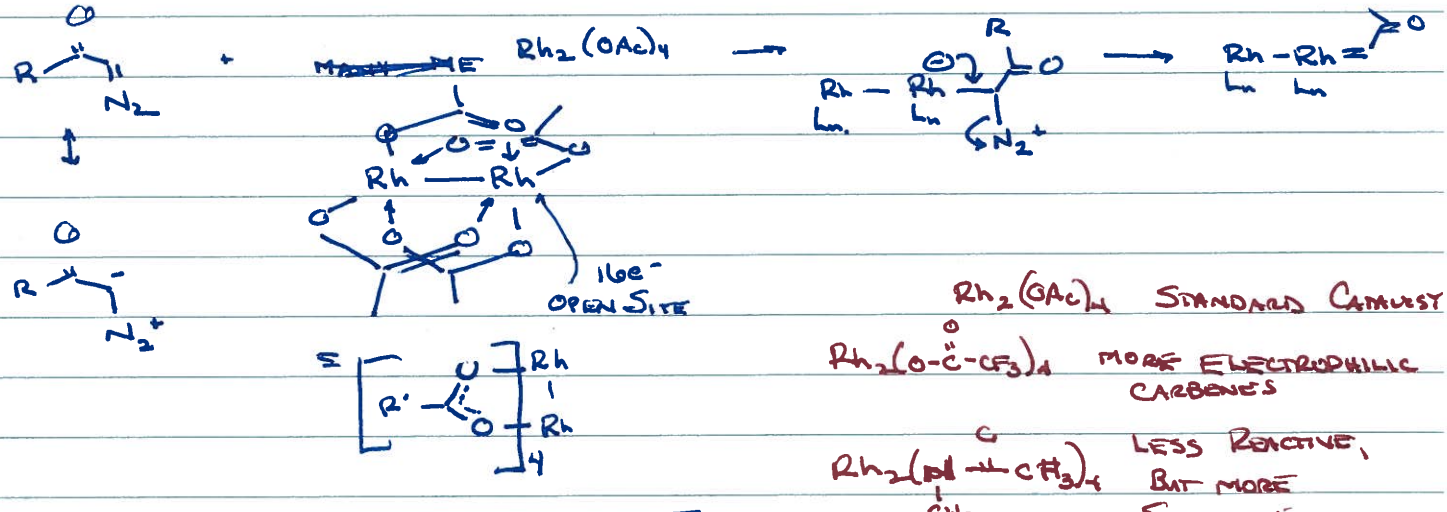
- Other organic synthetic use of carbenes starts with diazo cpds



- All electrophilic at C but selectivity reversed

AA > A > AD.
AD > A > AA

- Also true for reactivity



$Rh_2(OAc)_4$ Standard Catalyst

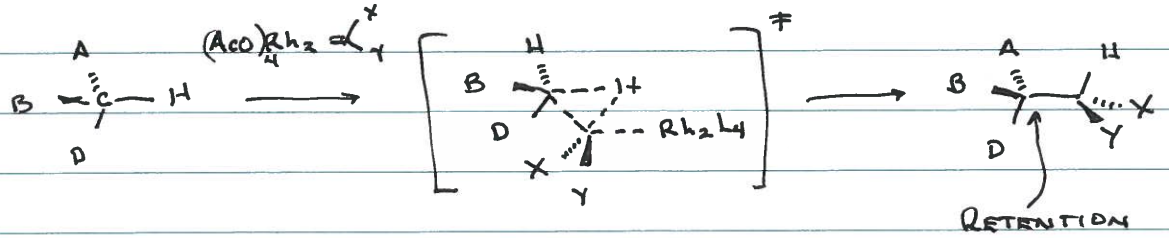
$Rh_2(O\text{-}\overset{O}{\overset{\|}{C}}\text{-}CF_3)_4$ More electrophilic carbenes

$Rh_2(Pd\text{-}\overset{C}{\overset{\|}{C}}H\text{-}CH_3)_4$ (CH_3) Less reactive, but more selective

- Also done by Cu^{I} and Pd^{II}

Main Rxns

C–H insertion Rxns.



+ Rh_2L_4 ∴ Catalyst

High turnovers as many as 600.

TL/73/24/2233.

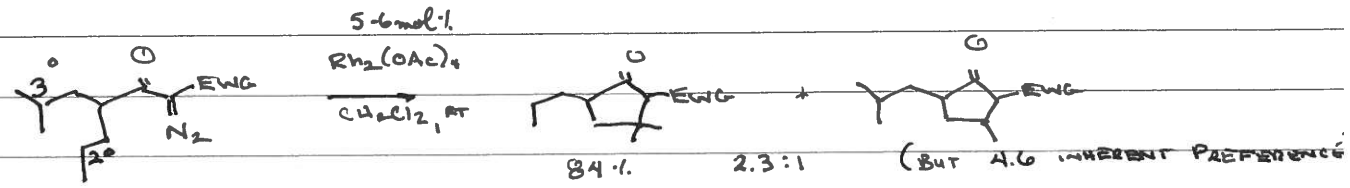
- Selectivity 3° C > 2° C > 1° C

But selectivity not great in intermol. cases.

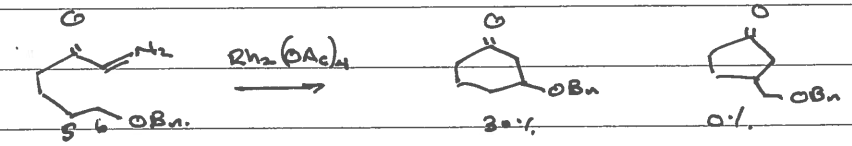
INTRAMOLECULAR RXNS MUCH MORE COMMON SYNTHETICALLY

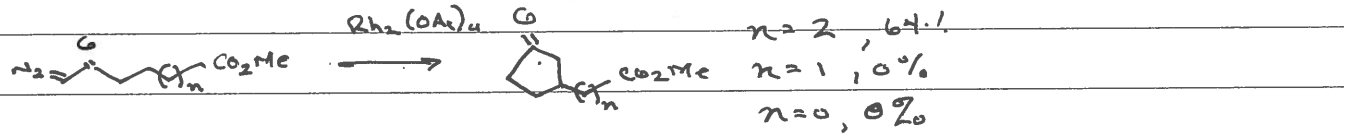
- NORMALLY 5-MEMBERED RINGS > 6-MEMBERED RINGS > OTHERS (i.e. 4-)

UNLESS THERE'S SOME REASON TO BIAS TOWARDS 6-

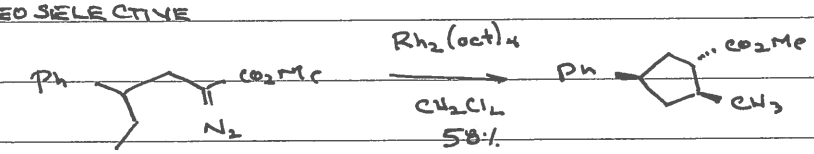
i.e. 

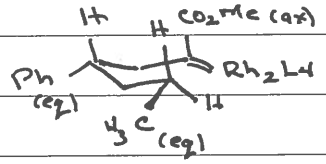
- RXN SPED UP BY EDG'S ON C-H ; SLOWED BY EWG'S.



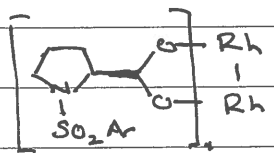


DIASTEREOSELECTIVE



PREDICTED BY PSEUDO-CHAIR 

ENANTIOSELECTIVITY - LOTS OF ROOM FOR THIS BY ALTERING THE CARBOXYLATE

i.e. DAVIES, H. M. 

Ar =

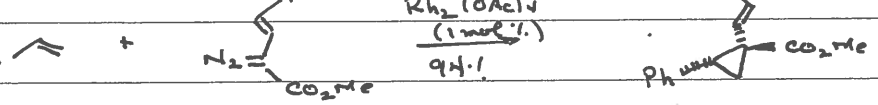
≈ $Rh_2(S\text{-}DOSP)_4$

J. AM. CHEM. SOC. 1997, 119, 9075.

MODEL

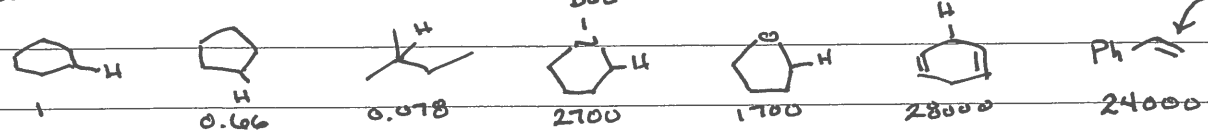
J. ORG. CHEM. 2009, 74, 6555.

OTHER MAJOR REACTION PATHWAY - CYCLOPROPANATION OF ALKENES

i.e. Ph 

REACTIVITY INHERENTLY GREATER THAN C-H INSERTION

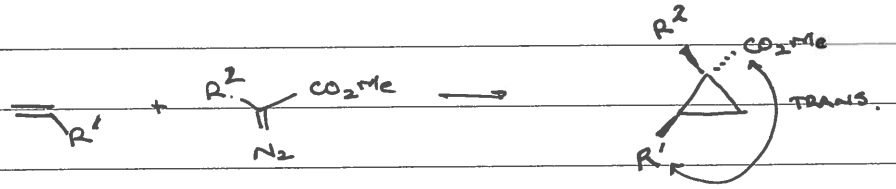
REL. RATE



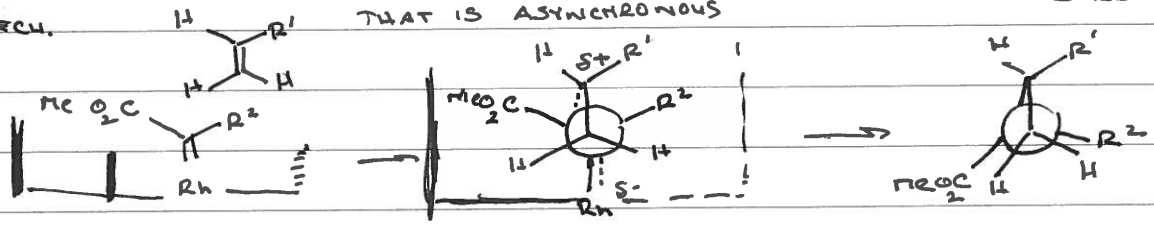
ELECTRON RICH ALKENES > ELECTRON POOR

INTERMOLECULAR CASES ARE USUALLY DONE ON MONO SUBSTST. ALKENES, BUT DISUBST. OR MORE HEAVILY SUBST. ARE POSSIBLE

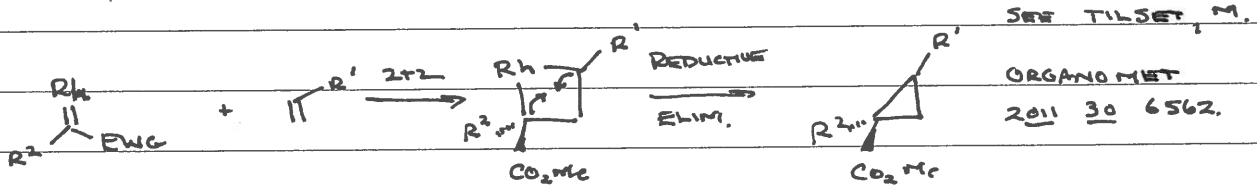
- STEREOCHEM ENDS UP WITH PREDOMINANT E TRANS R TO ESTER



- MECHANISTIC STUDIES - ARE ACTUALLY FAIRLY LIMITED - DAVIES LIKES A CONCERTED THAT IS ASYNCHRONOUS JACS 2003, 125, 15902.



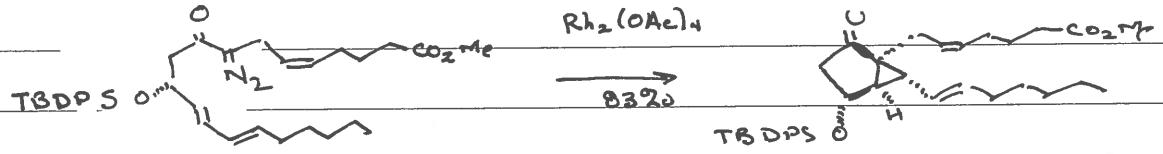
- I WOULDN'T DOUBT IF THEY EVENTUALLY FIND IT TO BE A 2+2 CYCLOADDN, THEN REDUCTIVE ELIMINATION

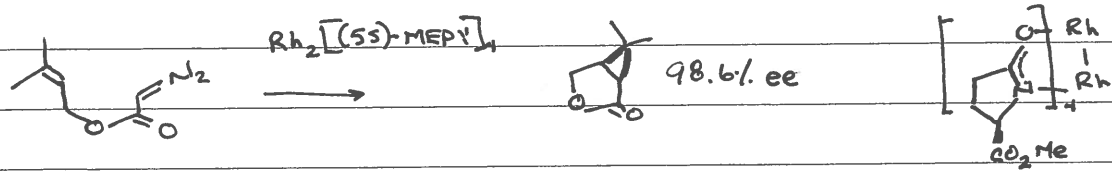


SEE TILSET, M. ORGANOMET 2011, 30, 6562.

- MANY EXAMPLES OF INTRAMOLECULAR CYCLOPROPANATIONS KNOWN

FIVE MEMBERED RINGS PREDOMINATE, BUT 6-MEMBERED & LARGER ARE CERTAINLY POSSIBLE

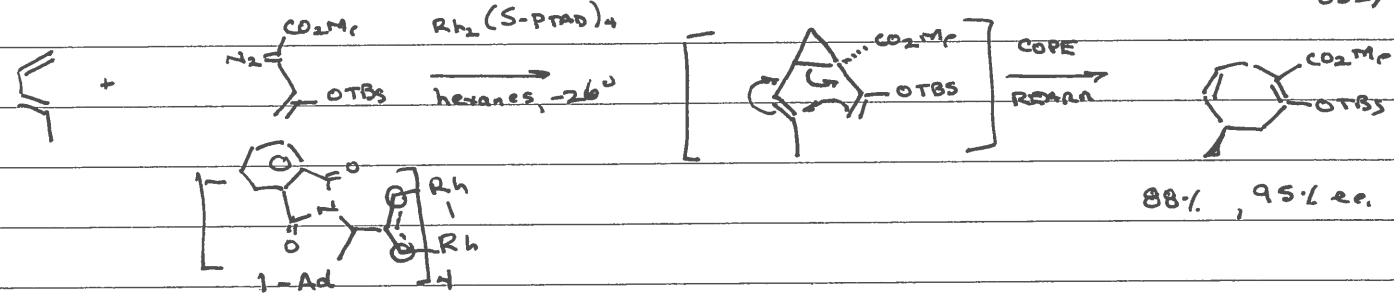


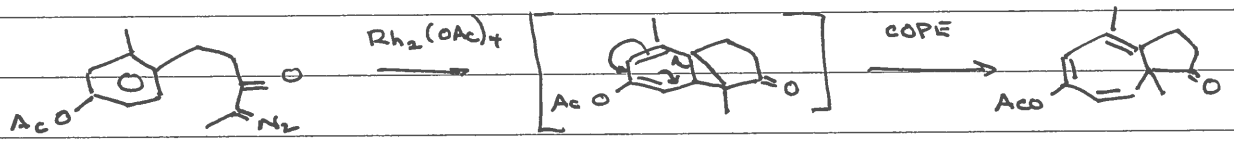


FINALLY, THERE ARE MANY CASCADE PROCESSES. WHERE CYCLOPROPANATION IS JUST THE OPENING PROCESS

1.c.

DANIES, JACS 2009 131 8329



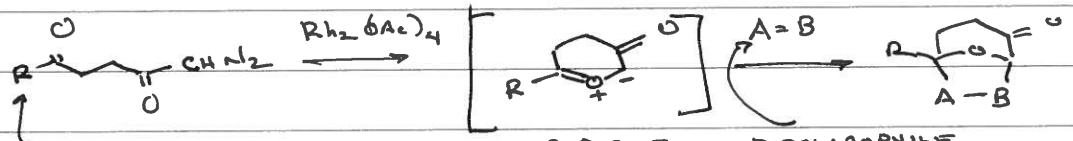


- OTHER NOTES:

ALKYNES CAN ALSO FORM CYCLOPROPENES, BUT USUALLY ENGAGE IN FURTHER RXN.

- PADWA (ESPECIALLY) HAS USED OTHER FUNCTIONAL GROUPS TO I.R. CARBONYLS TO TRAP CARBENE AS A OXONIUM YLIDE, WHICH IS A 1,3-DIPOLE

PADWA, A.
JOC 1996, 61, 2283.



OFTEN AN AMIDE

1,3-DIPOLE

DIPOLAROPHILE.