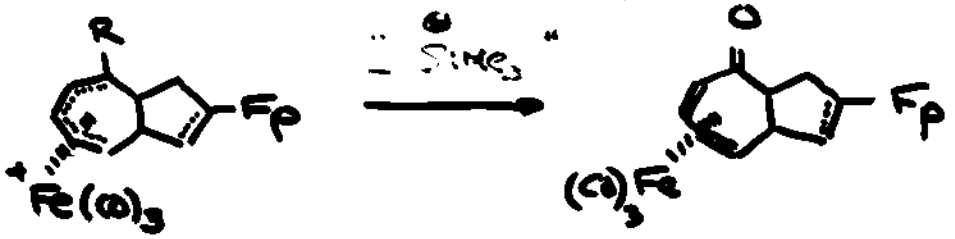
IF R = o-SiMe$_3$

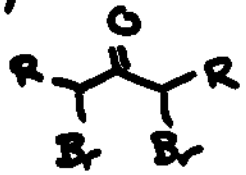


FUNCTIONALIZED HYDROAZULENE RING SYSTEM

ROSENBLUM, M. J. AM. CHEM. SOC. 1990 112 6316 + REFS THEREIN.

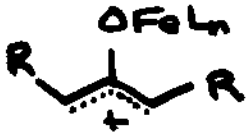
Mo, Ru, Ir ALLYLS - REF. SOURCE - TAKEUCHI, R.; KASHIO, M. JACS 1998, 120, 8647.

η^3(?), η^4(?) COMPLEXES .... IRON OXYALLYLS



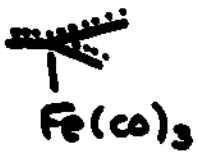
$Fe_2(CO)_9$ → SOME MAGICAL SPECIES WHICH HAS NEVER BEEN ISOLATED

NOYORI HAS PROPOSED

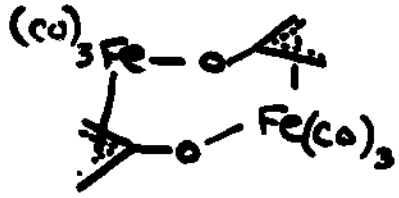


NOYORI, R.; ACC. CHEM RES. 1979 12 61
ORG. REACT. 1983 29 163.

BUT.... THE FOLLOWING HAVE ALL BEEN ISOLATED



SEE ABOVE



FREY, M.; JENNY
ORGANOMETALLICS
1990 9 1806.

X = Br, Cl
R = H, SiMe$_3$

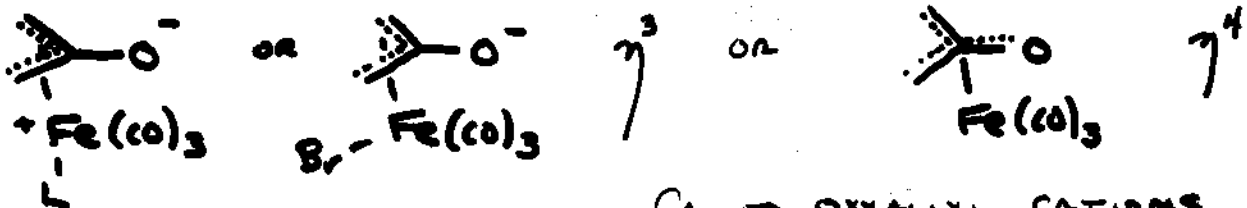
J. ORGANOMET. CHEM
1991 421 257.

ANDO W
J. AM. CHEM. SOC.
1990 112 4574.

M = Pd, Pt

ALBRIGHT, T.A. ET AL ORGANOMETALLICS 1989 8 199
EMERSON, G.F. J. AM. CHEM. SOC. 1966 88 3172.

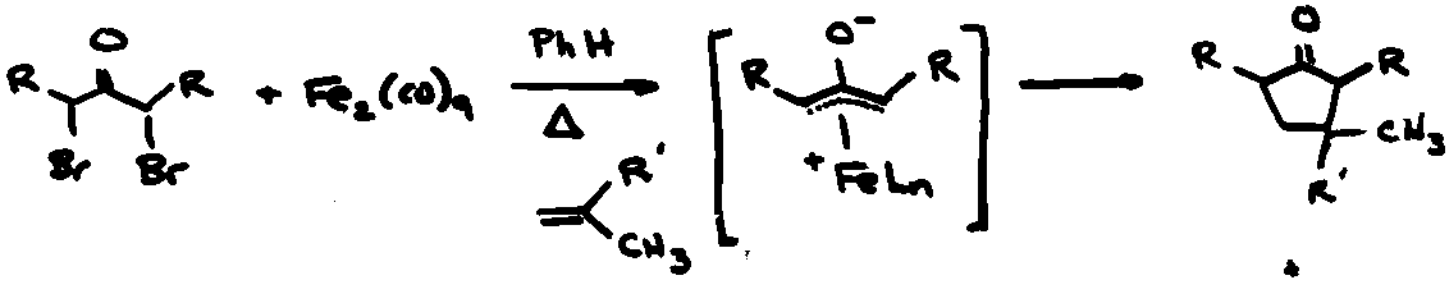
∴ MOST LIKELY STRUCTURES FOR IRON OXYALLYLS ARE...



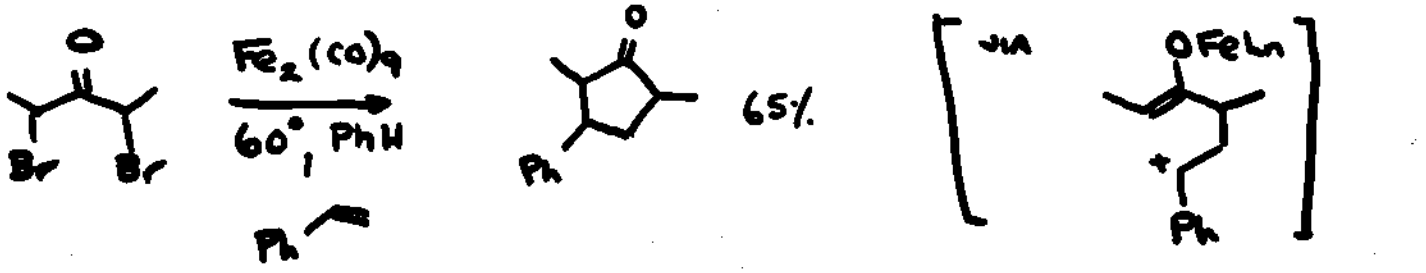
– CALLED OXYALLYL CATIONS.

- THESE REACT WITH SIMPLE ALKENES TO GIVE EITHER

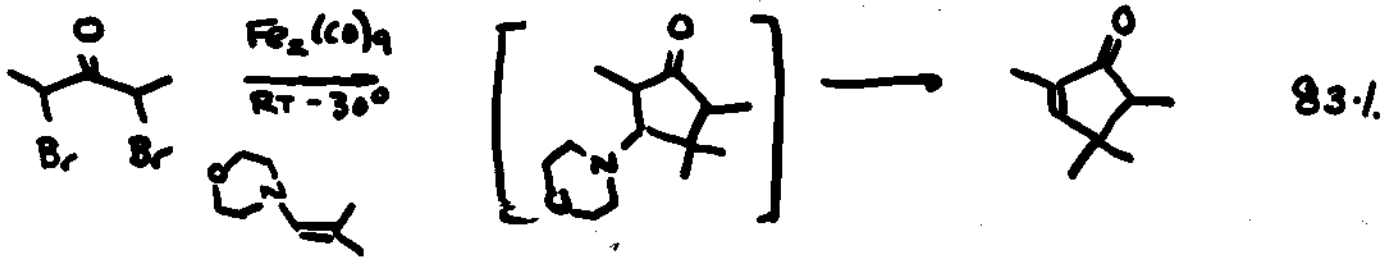
[3+2] CYCLOADDITIONS OR ENE REACTION PRODUCTS



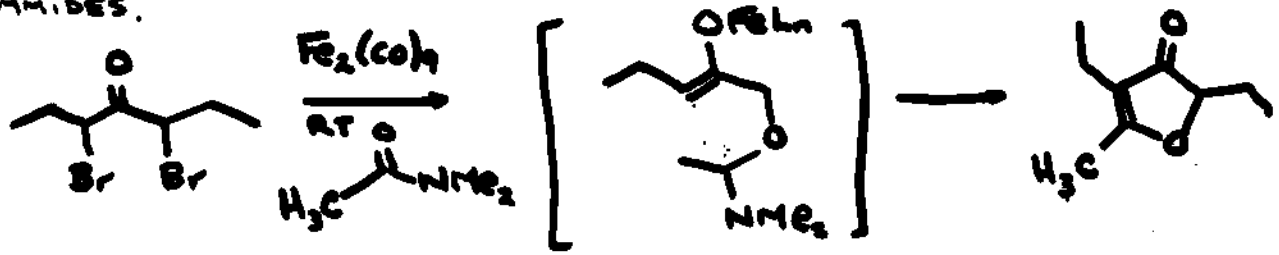
- [3+2] CYCLOADDITIONS WORK BEST WHEN THE ALKENE HAS SOME CARBOCATION STABILIZING FUNCTIONAL GROUPS



ENAMINES.



AMIDES.



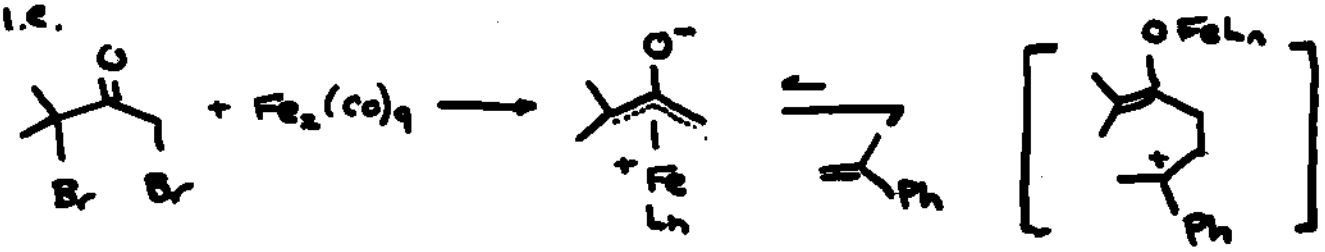
NITRILES ALSO (IN A FEW CASES) REACT.

REGIOCHEMISTRY

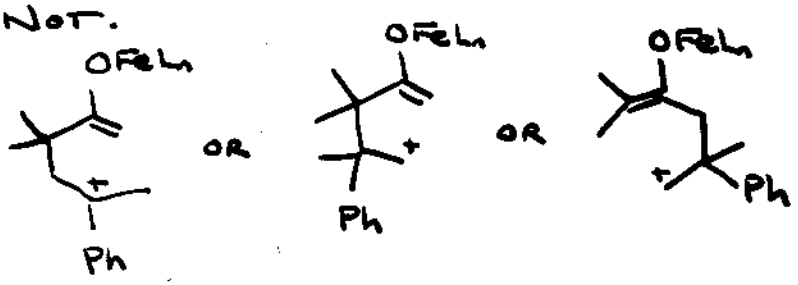
- ON OXYALLYL - MAJOR PRODUCT RESULTS FROM INITIAL REACTION AT THE LEAST SUBSTITUTED END (GIVES MOST SUBST. Fe ENOLATE)

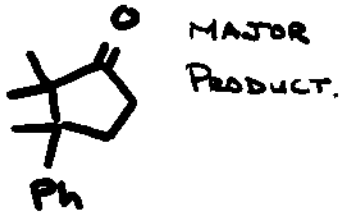
- ON ALKENE - MAJOR PRODUCT IS ONE THAT GOES THROUGH MOST STABLE CARBOCATIONIC INTERMEDIATE

I.E.



NOT.

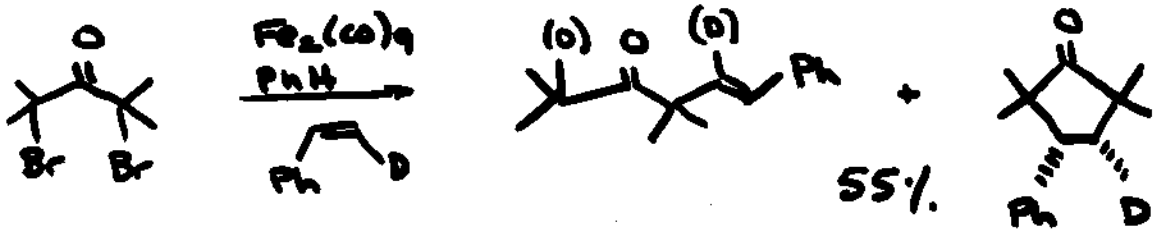




MAJOR PRODUCT.

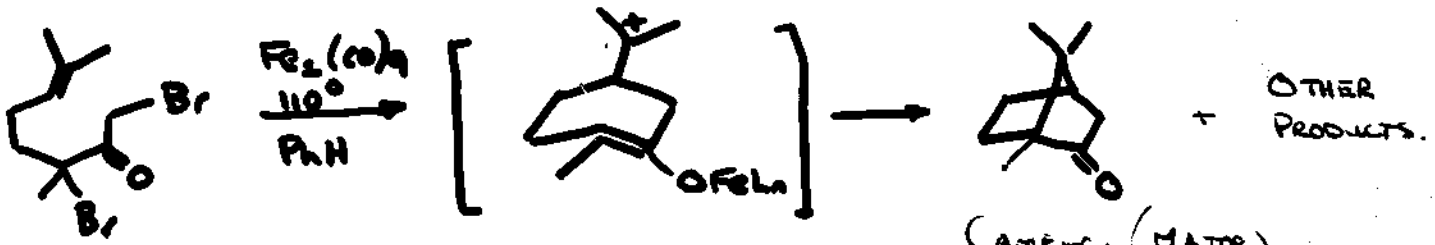
STEREOCHEMISTRY - NORMALLY, GET RETENTION OF STEREOCHEMISTRY ABOUT ALKENE

- APPARENTLY, INTERMEDIATE CARBOCATION IS (VERY) SHORT-LIVED
  - NOT ENOUGH TIME FOR BOND ROTATION



55%

- INTRAMOLECULAR CASES - ?! - SURE!

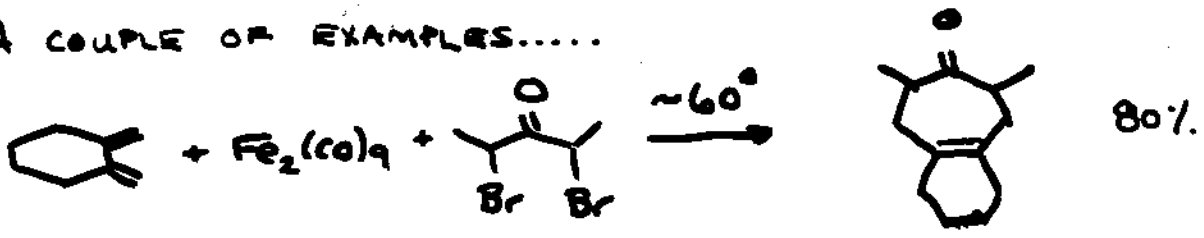


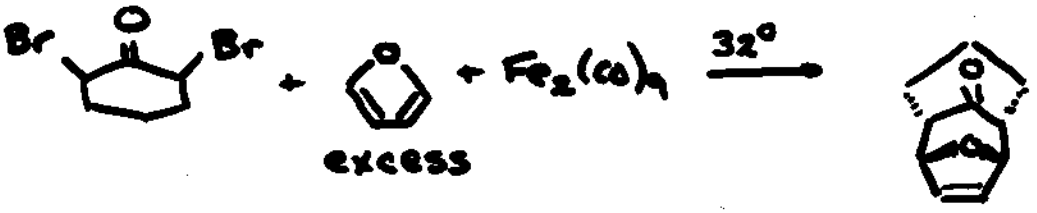
CAMPHOR - (MAJOR)

4+3 CYCLOADDITIONS

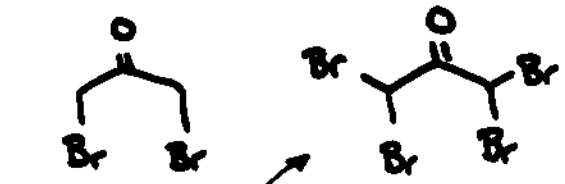
- MORE IMPORTANTLY THAN THE [3+2]'S, THESE OXYALLYL CATIONS REACT WITH DIENES TO GIVE 7 MEMBERED RINGS

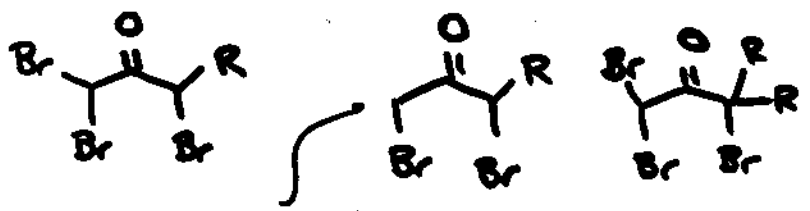
A COUPLE OF EXAMPLES.....

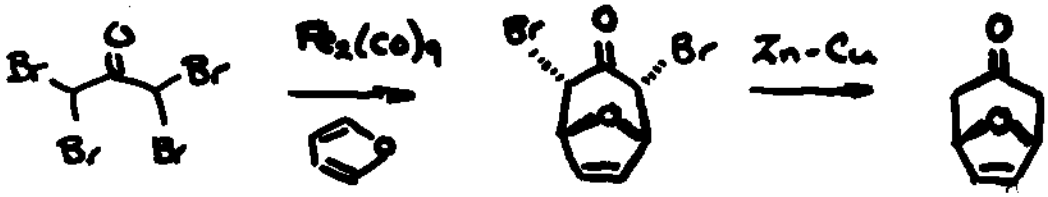




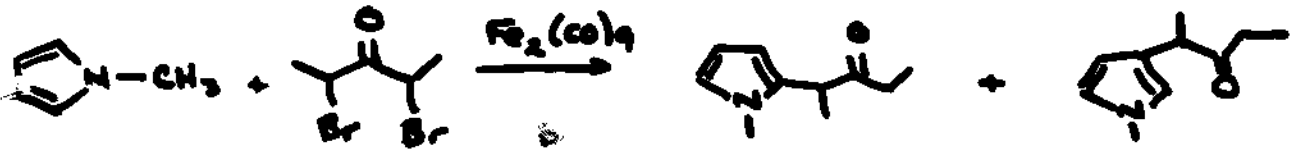
LIMITATIONS - ON DIBROMOKETONE.







- IN CASES WITH N-ALKYL PYRROLES, GET ELECTROPHILIC AROMATIC SUBSTITUTION



MECHANISM

ALLYL CATION FRAGMENT IS A 3C, $2\pi e^-$ SYSTEM

DIENE IS 4π e⁻ SYSTEM

- COULD THIS BE A CONCERTED $[4\pi + 2\pi]$ CYCLOADDITION?
- NOYORI THINKS YES
- HOFFMANN THINKS ONLY SOMETIMES, BUT MOSTLY NO
  (ANGEW. CHEM. INT. ED. ENGL. 1984, 23, 1.)

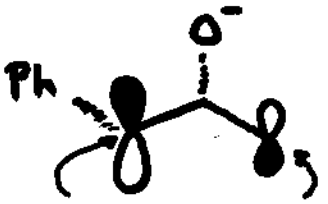
REGIOCHEMISTRY

- BEHAVES AS IF IT IS A CONCERTED REACTION

∴ CONTROLLED BY HOMO - LUMO INTERACTIONS.

CONSIDER.

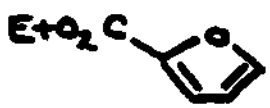
+ FORGET THE IRON

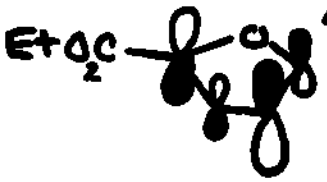


LUMO

LARGER SMALLER } ORBITAL COEFFICIENTS

AND.

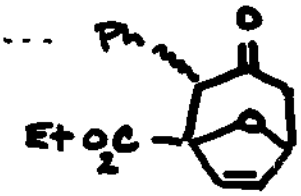




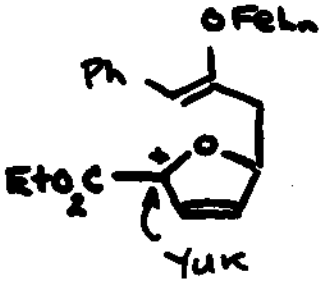
HOMO

- FRONTEIR M.O. ARGUMENTS REQUIRE THAT ATOMS WITH LARGER COEFFICIENTS INTERACT WITH LARGER, AND SMALLER WITH SMALLER.

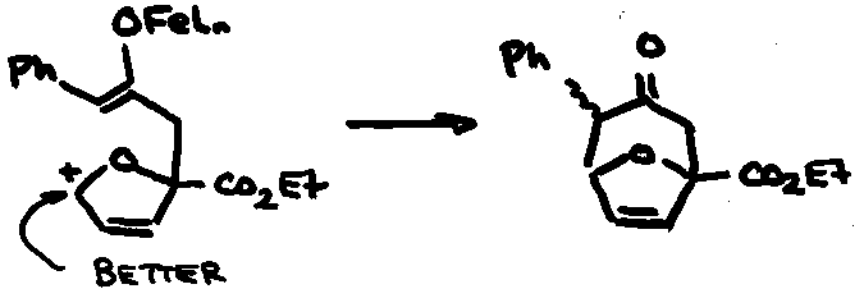
∴ FMO ARGUMENTS WOULD PREDICT....



BUT IF STEPWISE, WOULD PREDICT.....



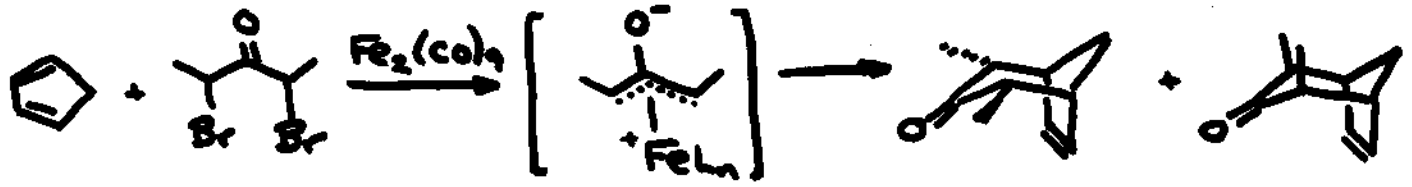
VS.



THE RESULT?

90 : 10

STEREOCHEMICAL CONSIDERATIONS



PRESUMED CONFIGURATION

USUALLY MAJOR (ENDO)

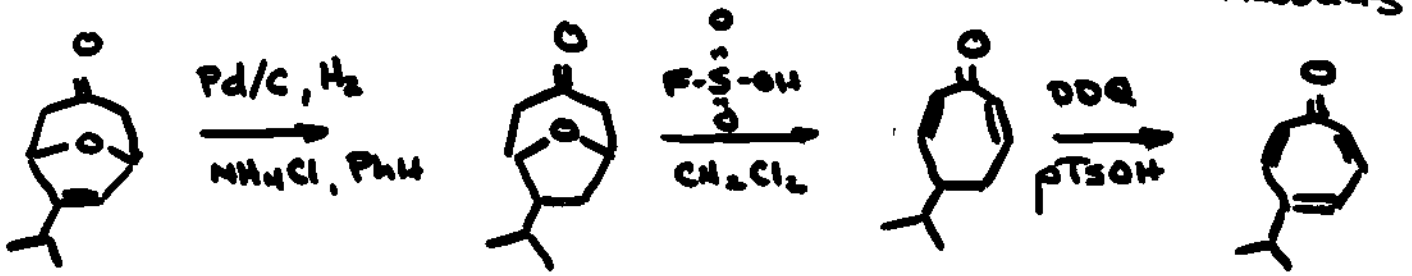
USUALLY MINOR (EXO)

PRETTY MUCH RANDOM MIXTURE

- IT IS THE PRESENCE OF THESE TYPES OF PRODUCTS THAT MAKES HOFFMANN THINK THAT THE RXN. ISN'T CONCERTED

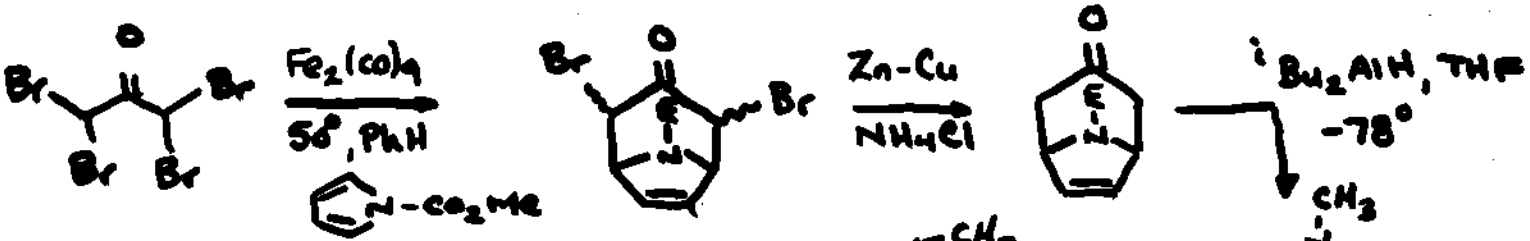
- USE - PRETTY GOOD WAY OF MAKING 7-MEMB. RING NATURAL PRODUCTS

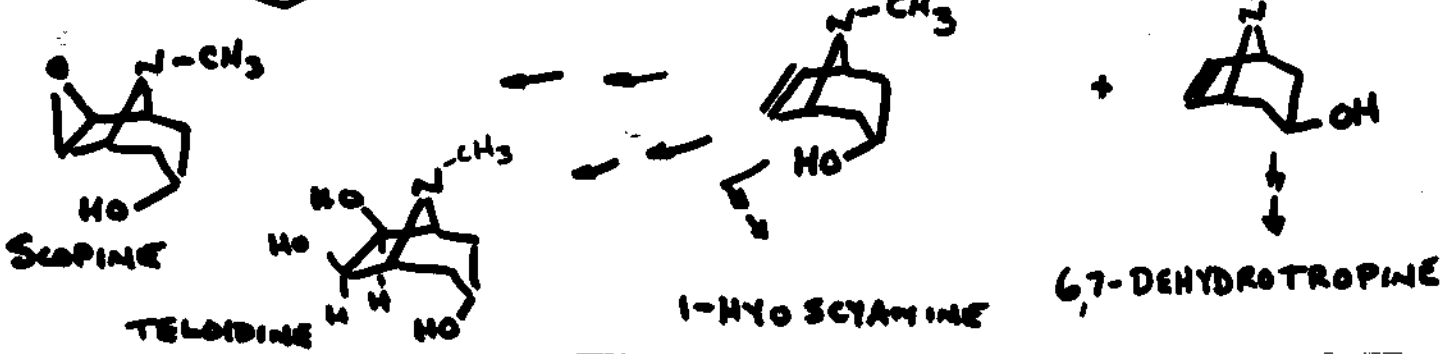
i.e.

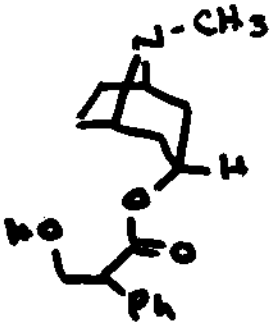


NEZUKONE

- ALSO - TROPANE ALKALOID SYNTHESIS.







l-HYOSCYAMINE

MANY OTHER NATURAL PRODUCT SYNTHESIS

FOR REVIEWS, SEE NOYORI, R. ACC. CHEM. RES. 1979 12, 61 (R)

ORG. REACT. 1983 29 163 (R)

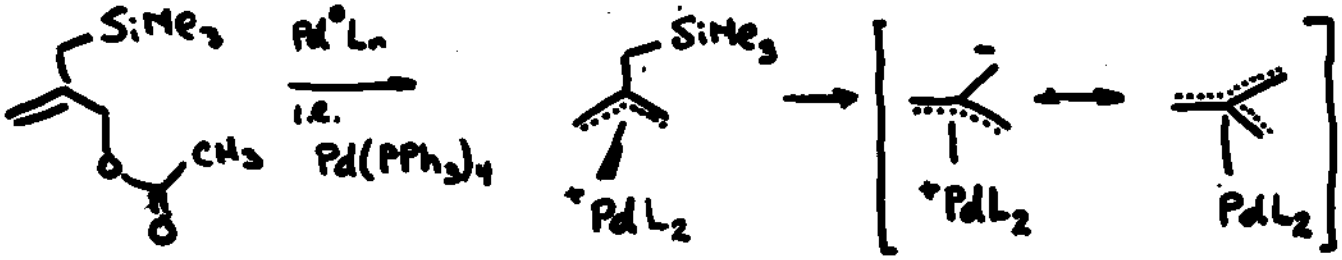
MANN, J. TETRAHEDRON 1986 42, 4611. (R)

PART OF RIGBY, J.H., PIGGE F.C. ORG. REACT. 1997 51 351

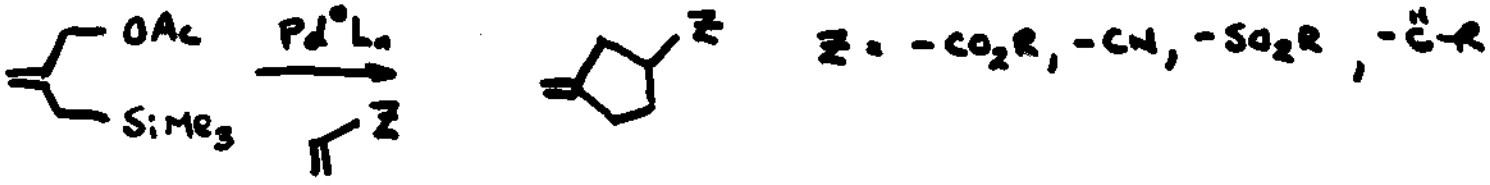
η^4 - COMPLEXES

η^4 - TRIMETHYLENEMETHANE COMPLEXES

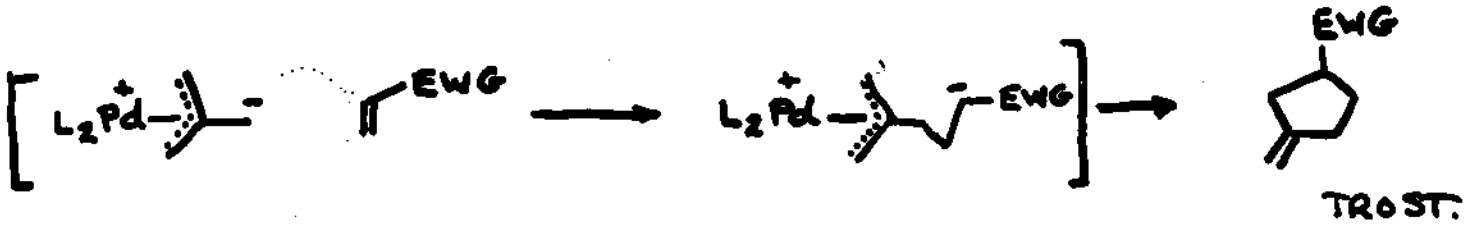
- PREDOMINANTLY USED WITH PALLADIUM
- THE FOLLOWING LOOKS LIKE A DECENT PRECURSOR TO AN π^3-ALLYL Pd



- IN THESE CASES, Pd IS COORDINATED TO ALL 4 C ATOMS
- TRIMETHYLENEMETHANE COMPLEX
- EXCELLENT AT [3+2] CYCLOADDITION REACTIONS



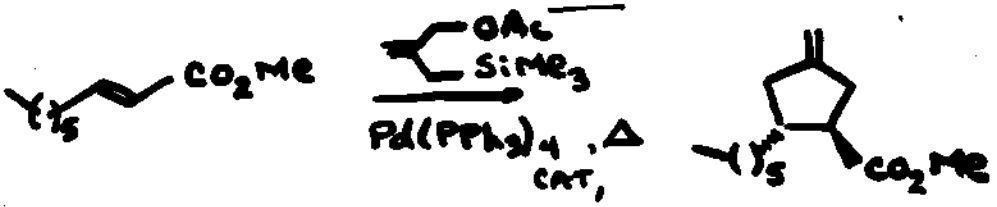
- MECHANISM

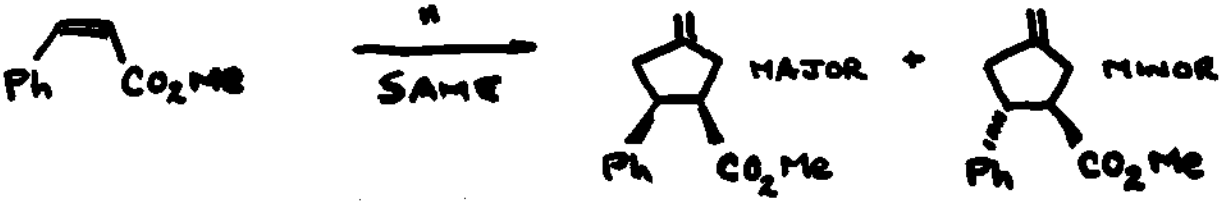


TROST.

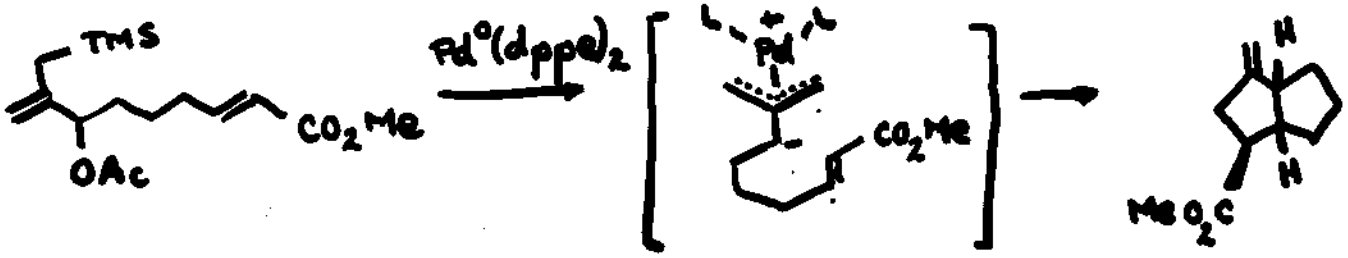
- STEREOCHEMICAL CONSIDERATIONS

- ABOUT ALKENE - GET MOSTLY RETENTION OF CONFIGURATION, BUT NOT PERFECTLY SO



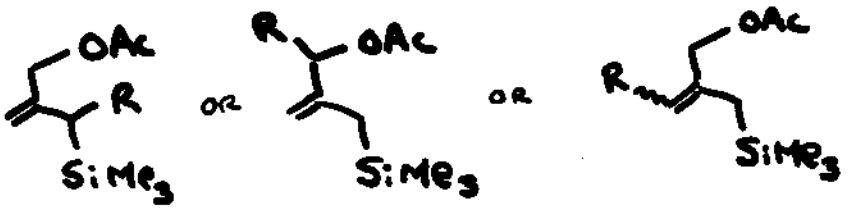


INTRAMOLECULAR REACTIONS ALSO WORK WELL



- OTHER ASPECTS OF STEREOCHEMISTRY (i.e. DIASTEREOSELECTIVITY) HAVE BEEN WELL ESTABLISHED, BUT ARE BEYOND THE COURSE'S SCOPE

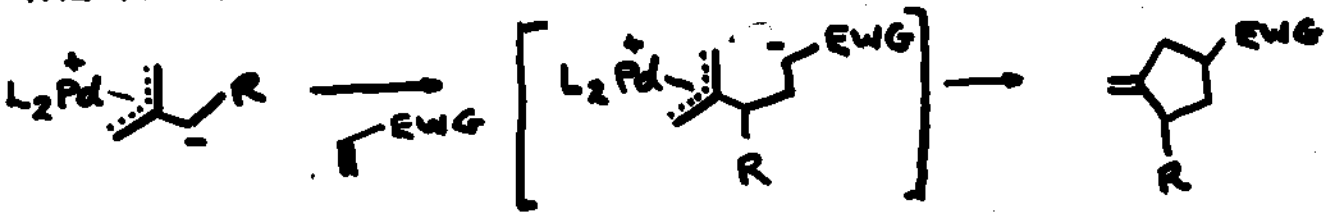
REGIOCHEMISTRY



R = ALKYL
ELECTRON DONATING
ELECTRON WITHDRAWING

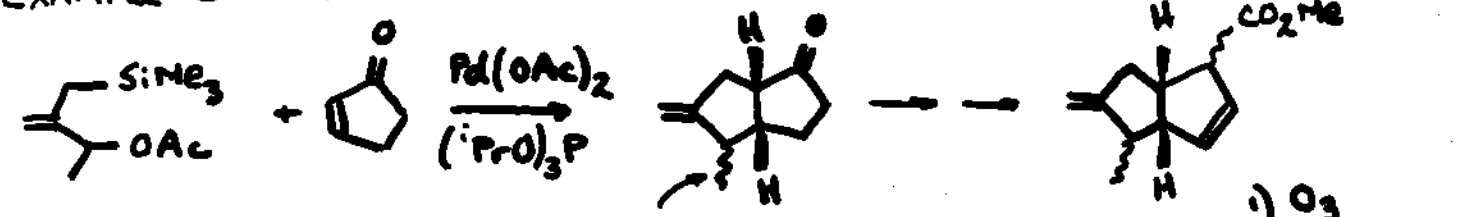
- DOESN'T MATTER (MUCH)

THE PRODUCT IS AS IF :



- NO REAL MECHANISTIC EXPLANATION OF THIS RESULT

EXAMPLE OF USE IN SYNTHESIS - LOGANIN



(±)-LOGANIN
(KEY INTERMEDIATE IN ALKALOID BIOSYNTHESIS)

- IS SOME WORK ON REACTING TMM-Pd COMPLEXES WITH C=O AND C=N-EWG IN PRESENCE OF R_3SnX COCATALYSTS

- SEE TROST, BM ET AL J. AM. CHEM. SOC. 1990 112, 408.
J. AM. CHEM. SOC. 1993 115 6636

FOR REVIEWS IN AREA, SEE:

TROST : ANGEW. CHEM. INT. ED. ENGL. 1986 25 1.
PURE APPL. CHEM. 1988 60 1615
'COMPREHENSIVE ORGANIC SYNTHESIS' VOL. 5 p. 271 1991

- IRON TRICARBONYL - TRIMETHYLENEMETHANE COMPLEXES ALSO KNOWN:

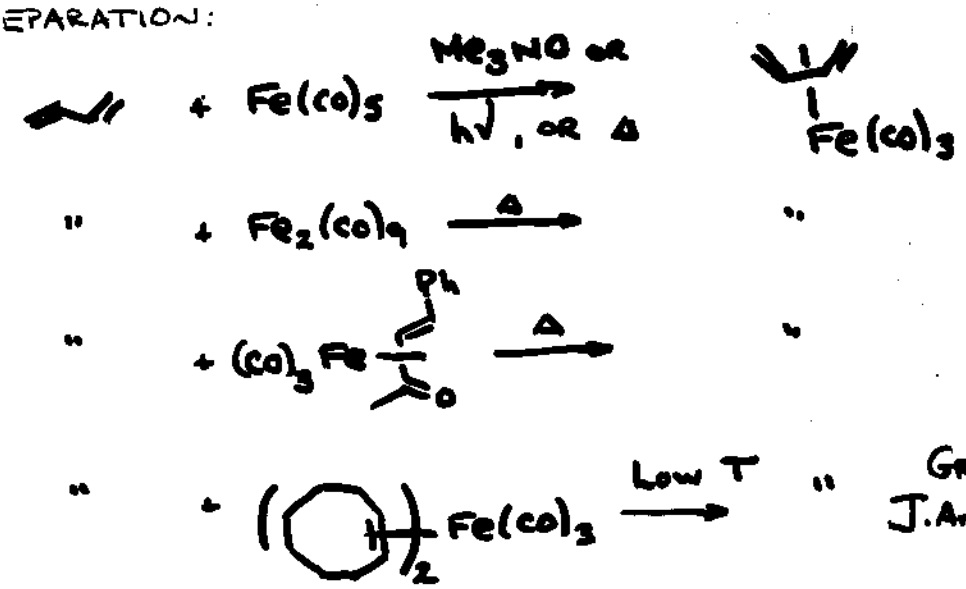
SEE DONALDSON W.A. J. ORG. CHEM. 1995 60 1611
FRANCK-NEUMANN M. TETRAHEDRON : ASYM. 1996 7 3193.

GREEN, J.R. DONALDSON W.A. 'ENCYCLOPEDIA OF INORGANIC CHEMISTRY' VOL 4 1994.

η^4-Diene Complexes.

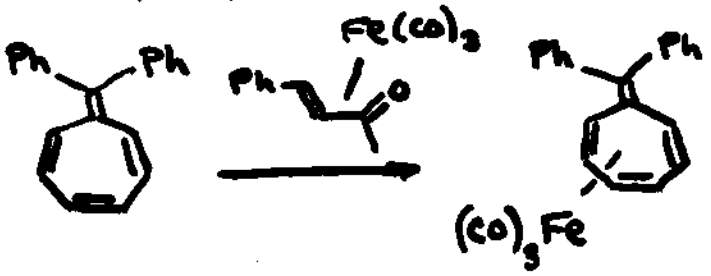
- Absolutely dominated by iron tricarbonyl complexes

Preparation:



Grevels
J. Am. Chem. Soc. 1984 106 2027

- $Fe(CO)_3$ fragment seems unusually stable
  - even in cases where it could lose more CO ligands, it normally does not.

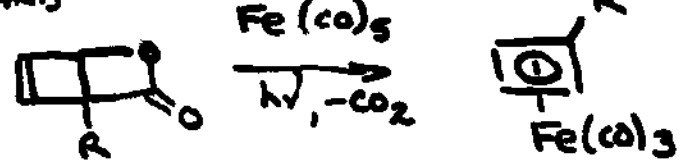


Recall - esters / amides give η^2-$Fe(CO)_4$ complexes

(R) Gree, R.; Lellouche, J.P. Adv. Met.-Org. Chem. 1995, 4. Ch 4.
(R) R.B. King. "The Organic Chemistry of Iron", Vol. 1 1978
(R) Pearson, A.J. "Iron Compounds in Organic Synthesis", 1994, Ch. 4.
Green, J.R.; Donaldson, W.A.. "Encyclopedia of Inorganic Chemistry", 1994, Vol. 4

Me_3NO Shvo, Y.; Hazum, E. J.C.S. Chem. Commun. 1975 829

And



Very stable complex
- Free cyclobutadiene is very unstable

Agar, J.; Kaplan, F.; Roberts, B.W. J. Org. Chem. 1974 39 3451.