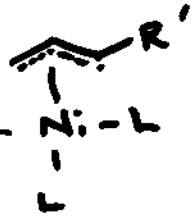
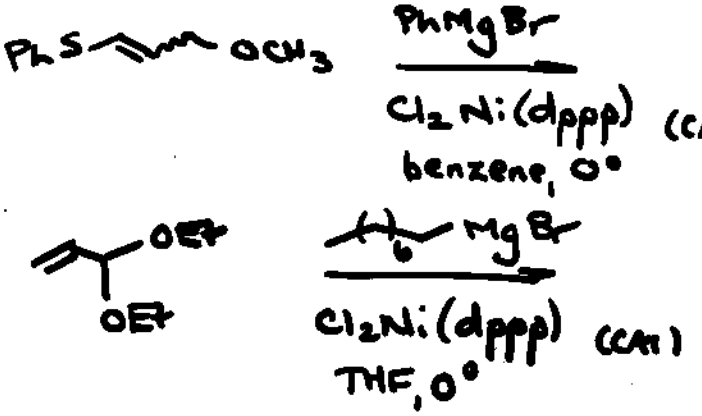
APPARENTLY, INTERMEDIATE IS 

β-ELIMINATION STEP OF R=ALKYL IS SLOW ENOUGH THAN ONE CAN GET REASONABLE AMOUNTS OF C-C BOND FORMATION



SUGIMURA, H.; TAKEI, H. CHEM. LETT. 1984 1501; 1985 351.

OVERALL REVIEW BILLINGTON, D.C. CHEM. SOC. REV. 1985 14 93.

FOR WORK WITH CHIRAL PHOSPHINE CATALYSTS

HAYASHI, T. ET AL J. ORGANOMET. CHEM. 1985 285 359.

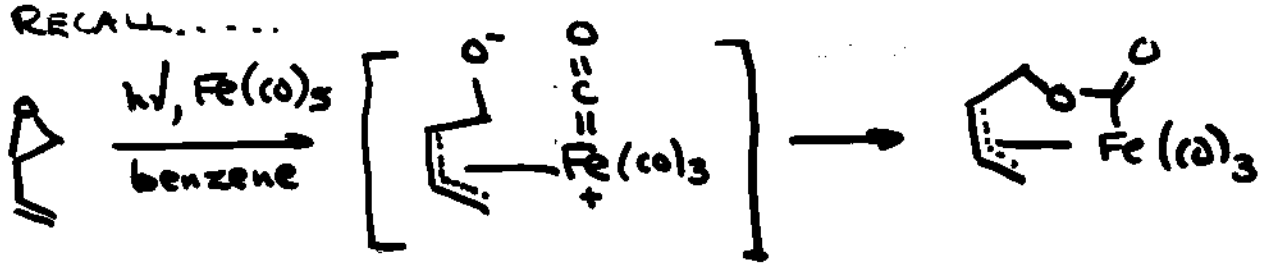
CONSIGLIO, G. ET AL TETRAHEDRON 1986 42 2043

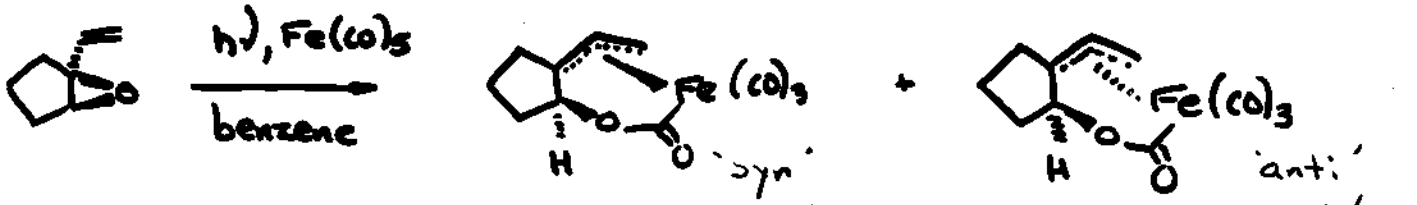
WORK IN THIS AREA HAS REALLY SLOWED SINCE THE MID 1980's.

π-ALLYLIRON TRICARBONYL LACTONE COMPLEXES.

- ALMOST ENTIRELY WORK OF S.Y. LEY

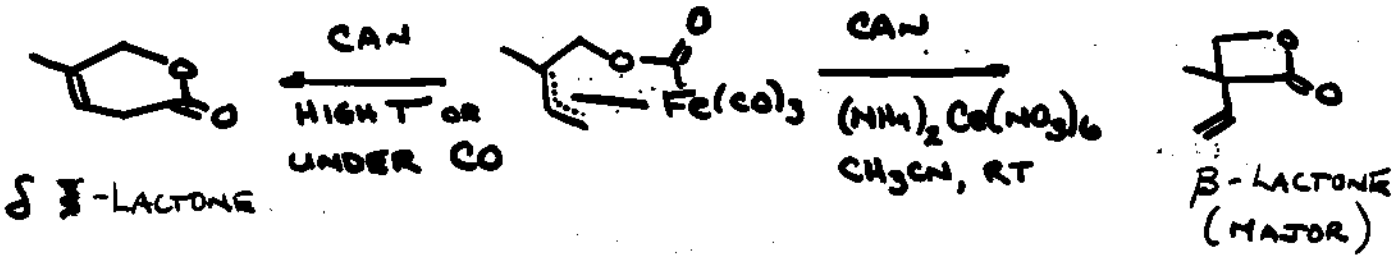
- RECALL.....





- PHOTOCHEMICAL CONDS USUALLY GIVE RETENTION (COMPLETELY)
  CAN ACTUALLY SEPARATE CHROMATOGRAPHICALLY

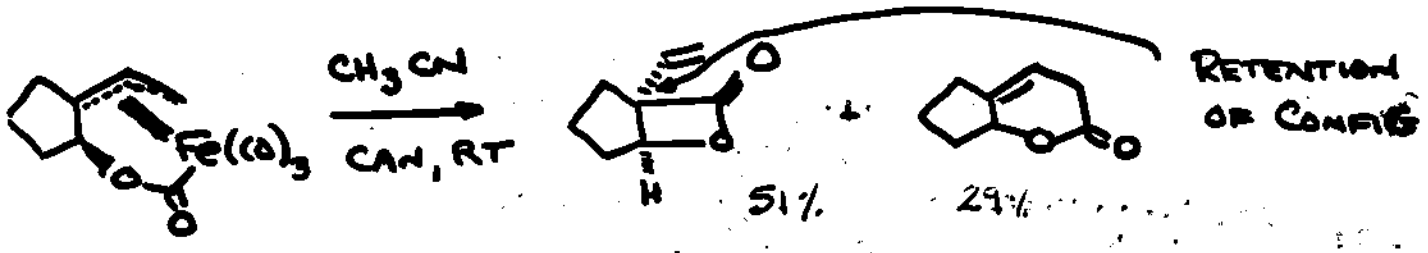
- WHEN ONE ATTEMPTS TYPICAL OXIDATIVE DEMETALLATION IT OCCURS WITH REDUCTIVE ELIMINATION AND C-C BOND FORMATION



δ-LACTONE

β-LACTONE (MAJOR)

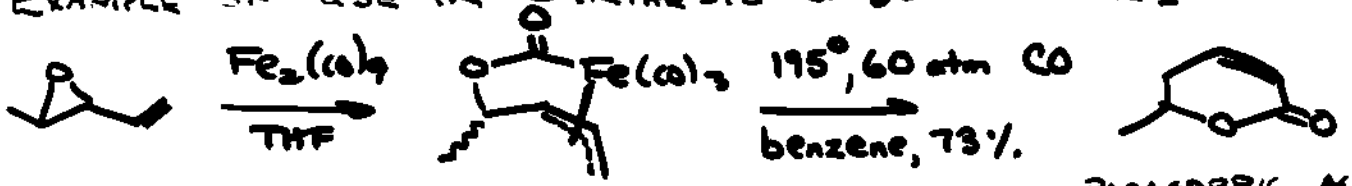
NOTE: STEREOCHEMICAL CONSIDERATIONS ON REDUCTIVE ELIM. STEP



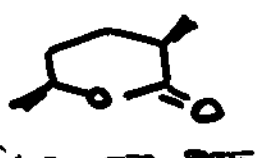
AND

BECAUSE trans FUSED β-LACTONE WOULD BE IMPOSSIBLY STRAINED

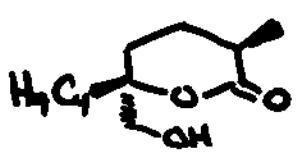
EXAMPLE OF USE IN SYNTHESIS OF δ-LACTONES



PARASORBIC ACID LACTONE (RACEMIC) - NATURALLY OCCURRING LACTONE FROM SORBUS ACUCUPARIA



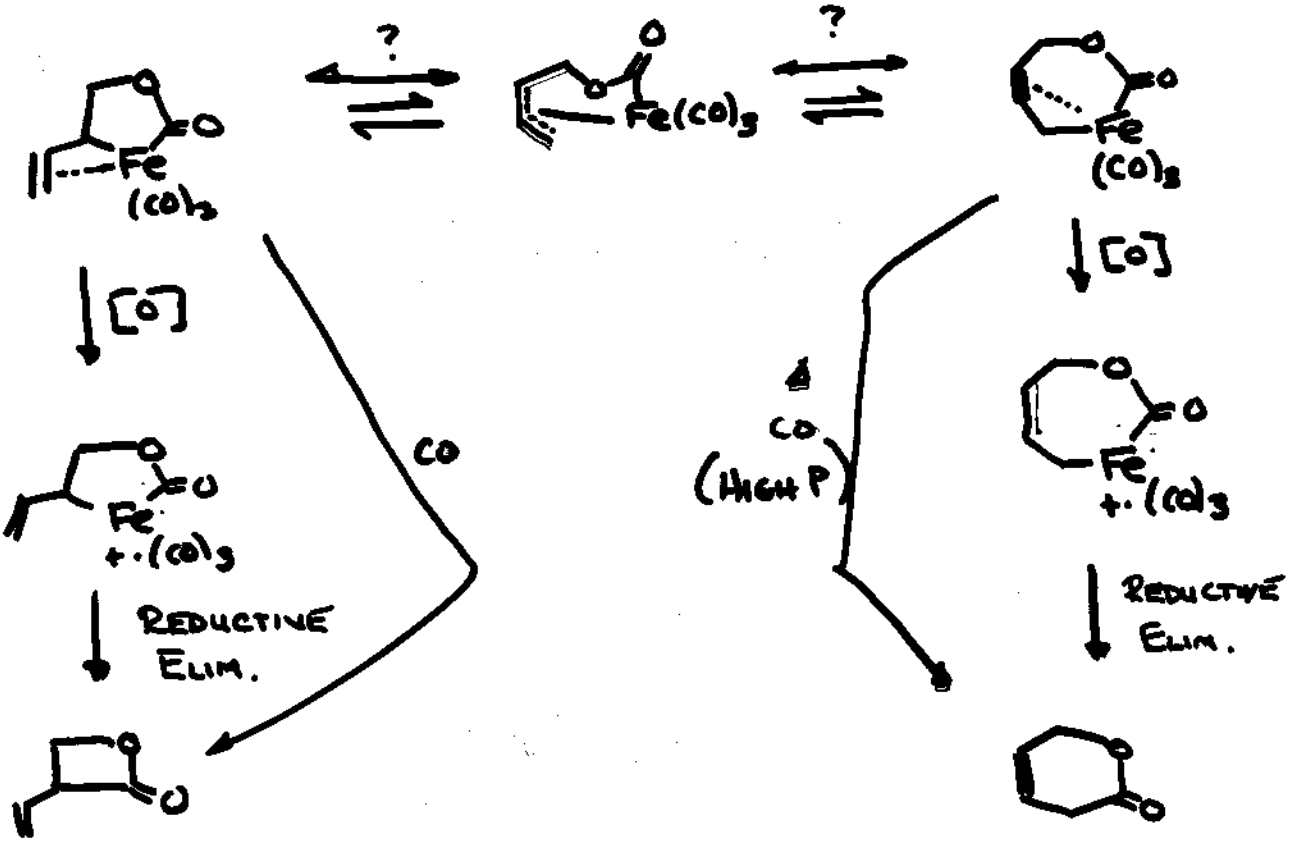
CARPENTER BEE PHEROMONE



MALYNGOLIDE - MADE SIMILARLY

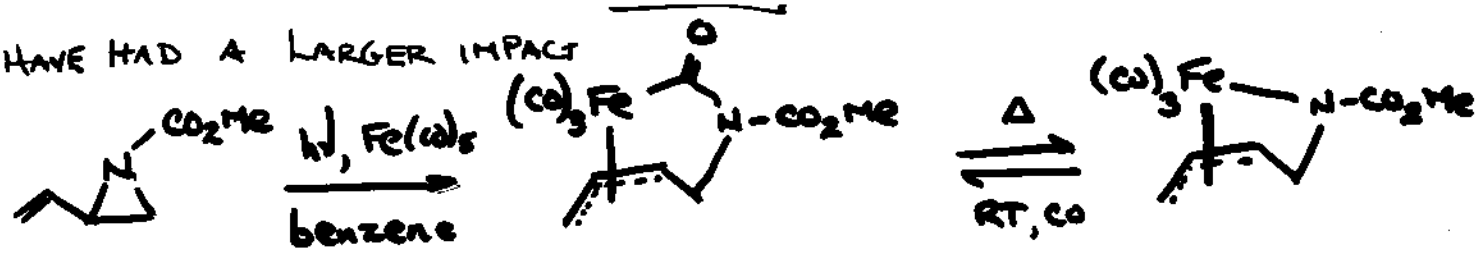
LEY, S.V. ET AL. J. ORGANOMET. CHEM. 1985 285, C17.

TWO ROUTES OF C-C FORMATION



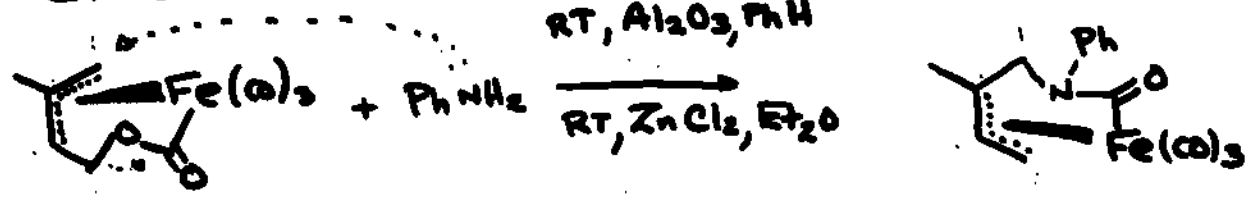
π-ALLYLIRON TRICARBONYL LACTAM COMPLEXES

- HAVE HAD A LARGER IMPACT



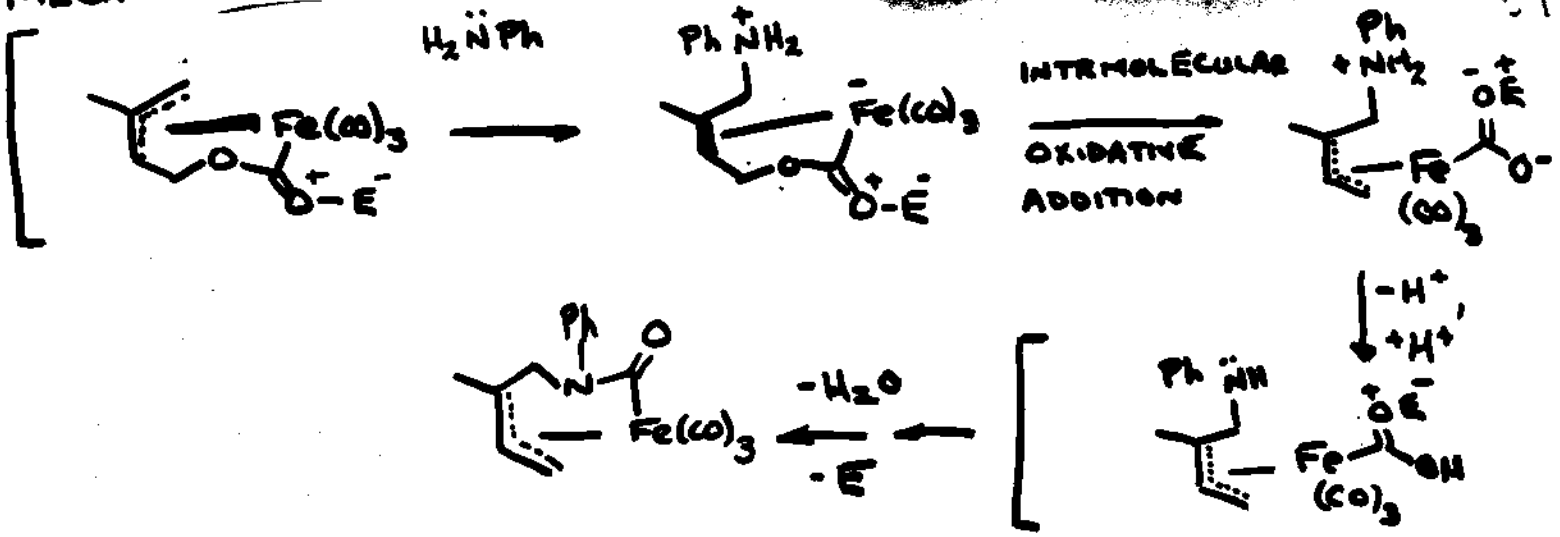
↳ THESE, HOWEVER AREN'T THE MOST EASILY ACCESSIBLE COMPOUNDS

- CAN BE MADE READILY FROM THE LACTONE COMPLEXES, THOUGH

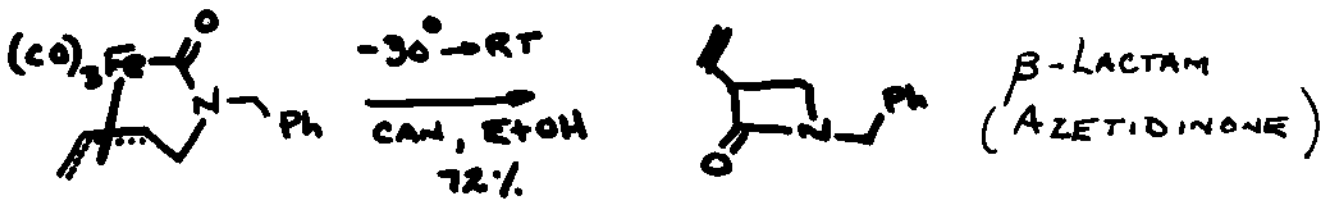


THIS GOES WITH TRANSPOSITION OF THE ALLYLIC FRAGMENT VIA THE FOLLOWING MECHANISM (NOTE: "E" = LEWIS ACID)

MECH

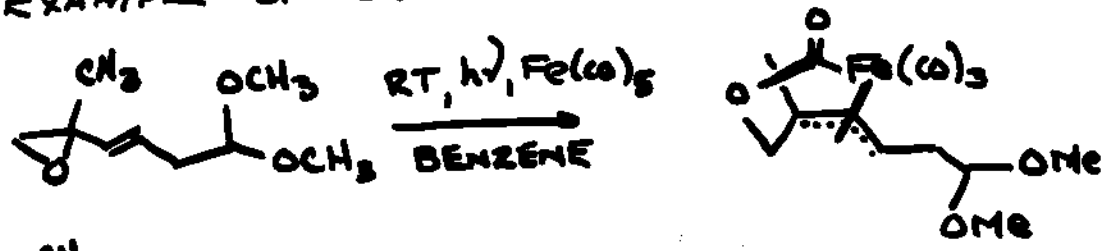


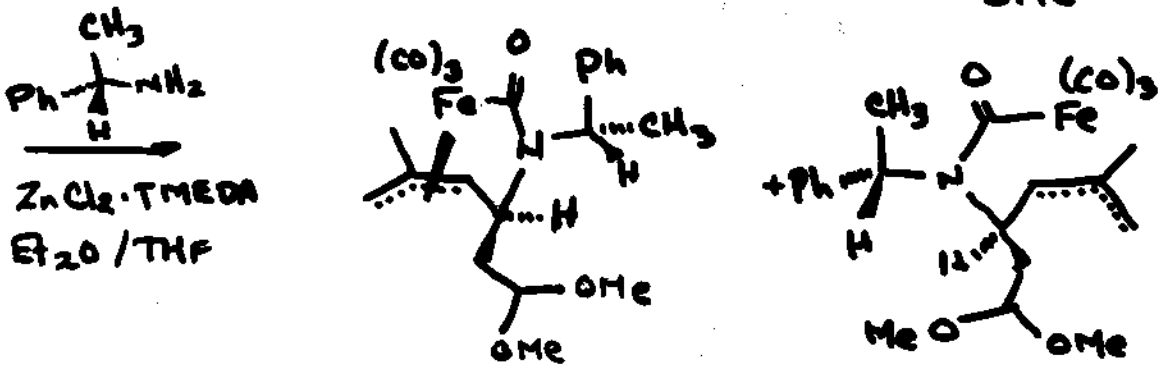
- WHEN THESE COMPOUNDS ARE OXIDIZED, THE REDUCTIVE ELIMINATION TAKES A MORE HIGHLY SELECTIVE PATHWAY



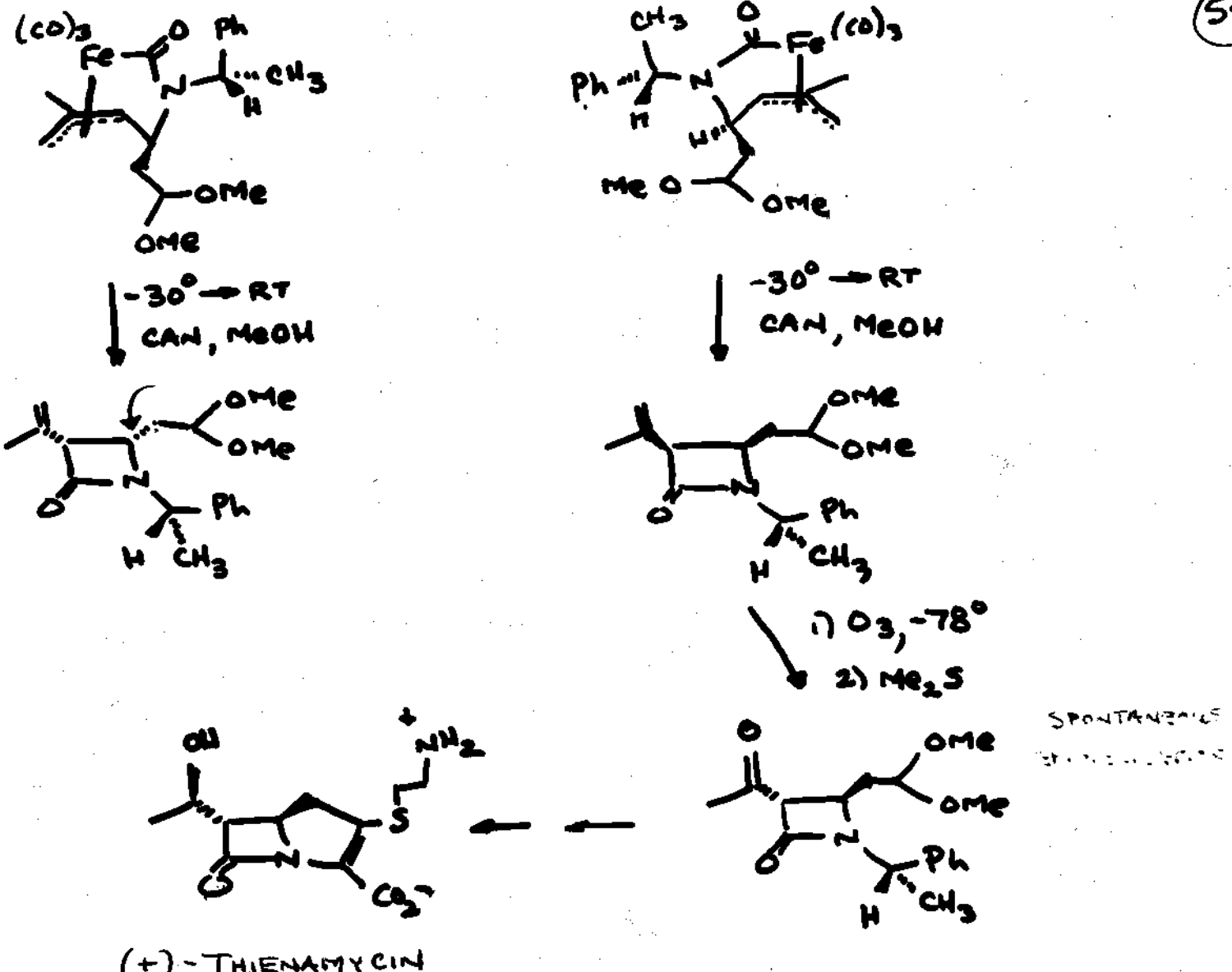
THESE 3-ALKENYL-2-AZETIDINONE ARE NOT SO READILY ACCESSIBLE BY OTHER METHODS

- EXAMPLE OF SYNTHETIC USE (+)-THIENAMYCIN





CAN SEPARATE CHROMATOGRAPHICALLY



(+)-THIENAMYCIN

LEY, S.V. TETRAHEDRON 1985 41 5871

LEY, S.V.; COX L.R. MEEK G. CHEM REV. 1996 96 423.

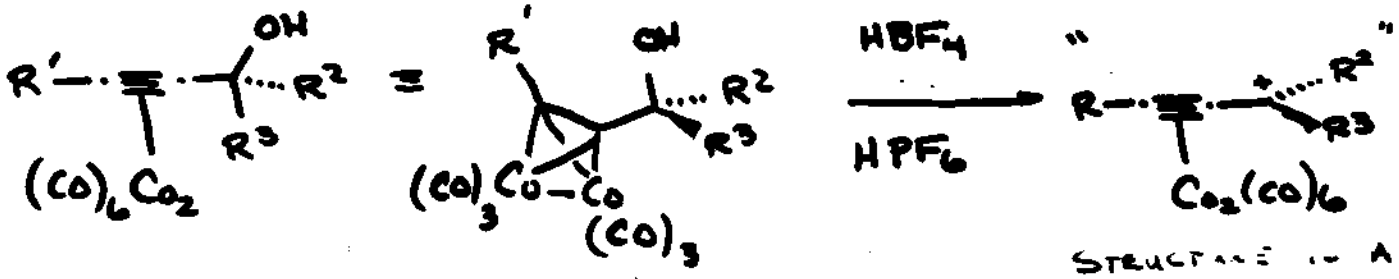
COX L.R.; LEY, S.V. CHEM SOC. REV. 1998 27 301.

PROPARGYL CATION - DICOBALT HEXACARBONYL COMPLEXES

R: NICHOLAS, K.M. ACC CHEM. RES. 1987 20 208.

CAFFYN, A.J.M.; NICHOLAS, K.M. IN COMPREHENSIVE ORGANOMETALLIC CHEMISTRY II 1995 VOL 12, CH. 7.1.

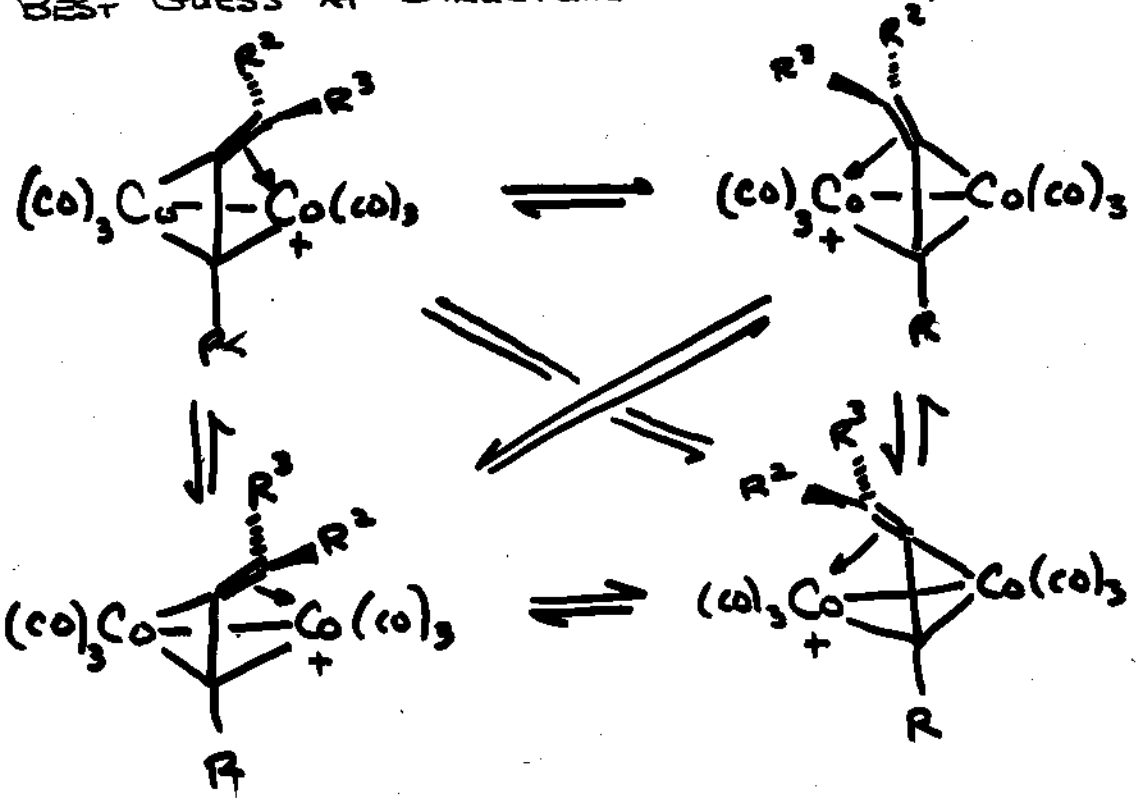
R GREEN, J.R. CURR. ORG. CHEM. 2001, 5, 809.



THERMALLY STABLE, DARK RED/BEET SOLIDS

STRUCTURE IS A LIE.

BEST GUESS AT STRUCTURE - SCHREIBER S.L.; ET AL J.AM.CHEM.SOC. 1987, 109, 5749.



- PROCESS OF THIS EXCHANGE IS FAIRLY COMPLICATED

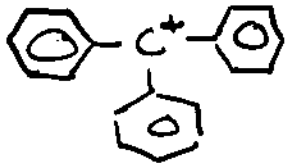
RECENT X-TAL STRUCTURE! MELIKYAN, G.G. ET AL ANGEW. CHEM. INT. ED. ENGL. 1998, 37, K1; ANGEW. CHEM. 1998, 110, 170.

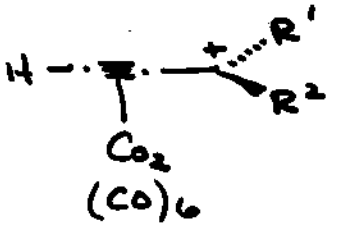
- AS CARBOCATIONS GO, THESE ARE VERY STABLE

- CONSIDER $R^+ + 2H_2O \overset{K_{R^+}}{\rightleftharpoons} ROH + H_3O^+$

$$-\log K_{R^+} = pK_{R^+}$$

∴ THE LESS NEGATIVE (MORE POSITIVE) THE NUMBER, THE MORE STABLE

CONSIDER Ph_3C^+ =  $pK_{R^+} = -6.6$

 = −6.8 TO −7.4 OR −5.50 DEPENDING ON REFERENCE.

- THEY ARE ELECTROPHILIC ENOUGH TO REACT WITH SEVERAL NUCLEOPHILES

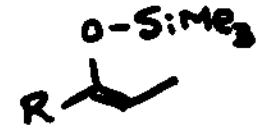
 ELECTRON RICH AROMATICS

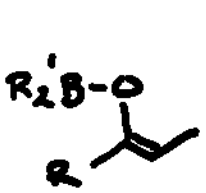
- ARENE NEEDS ONE OR MORE ACTIVATING GROUPS

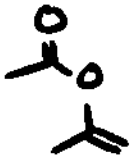
$-OCH_3$, $-OH$, $-NMe_2$, 

- KEEP IN MIND o,p- RULE

 β-KETO-ESTERS

 SILYL ENOL ETHERS

 ENOL BORINATES

 ENOL ACETATES

 ALLYLSILANES OR TINS

R_3Al, $RCu(CN)ZnI$??

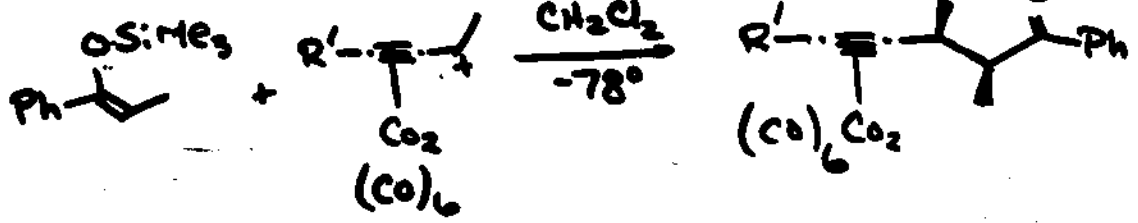
ALKYLATION – ALKYL ALUMINUMS
– ZINC CYANOCUPRATES

Et_2AlCN CYANATION

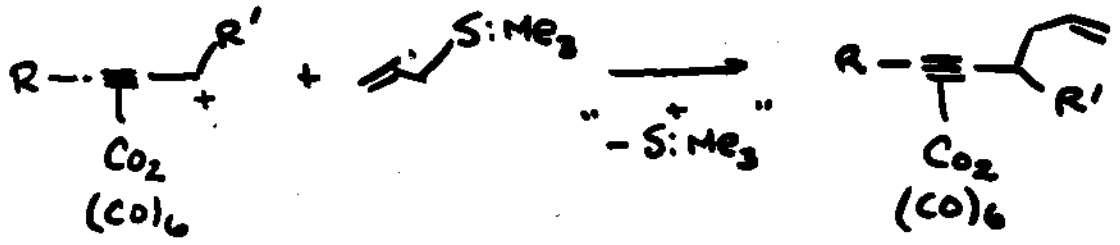
$NaBH_4$ / Et_3SiH + CF_3COOH REDUCTION

R_2NH AMINES

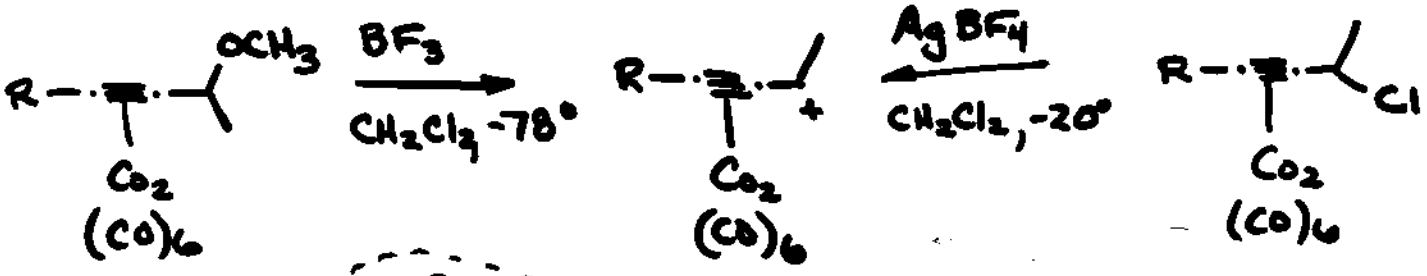
A COUPLE OF EXAMPLES

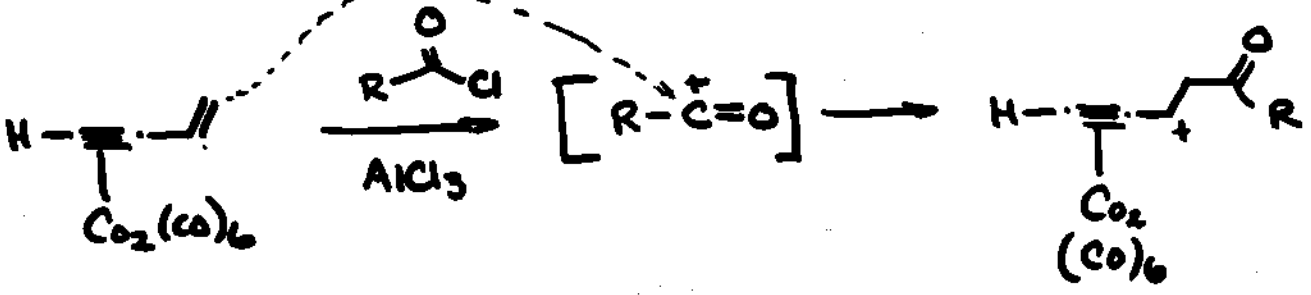


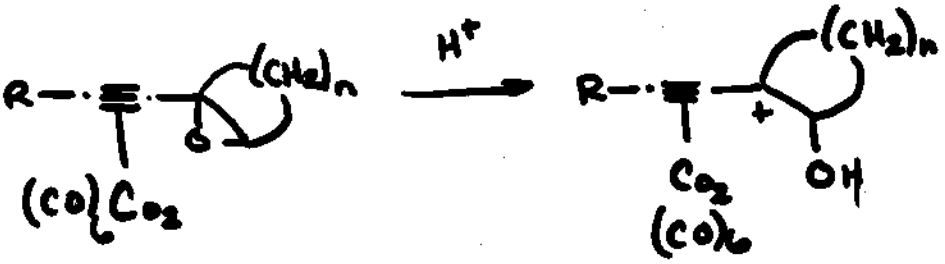
NOTE: HIGH SYN DIASTEREOSELECTION



- CAN GENERATE THESE CATIONS IN SEVERAL RELATED WAYS, I.E., FROM ETHERS, HALIDES, ALKENES, EPOXIDES, ETC.

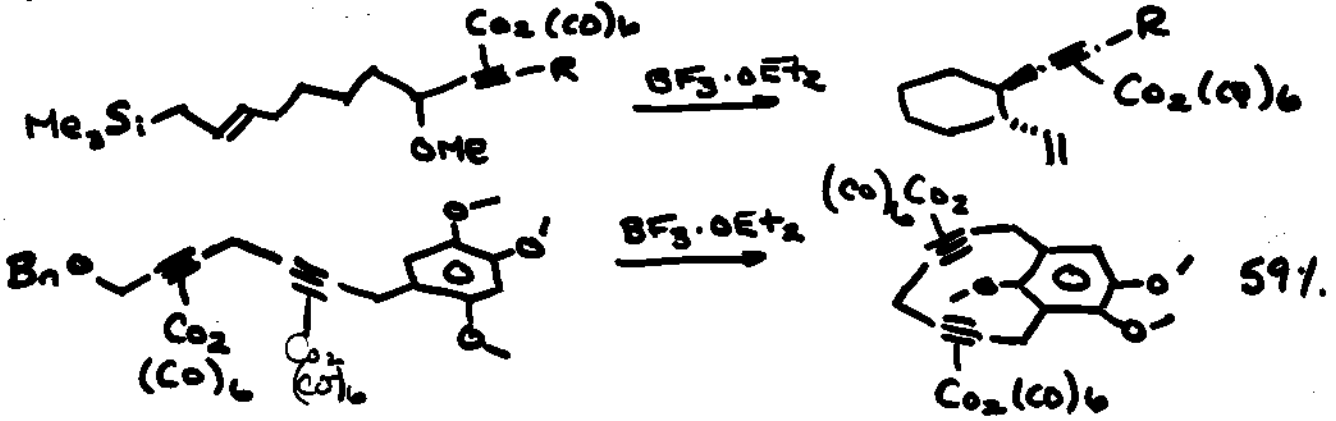




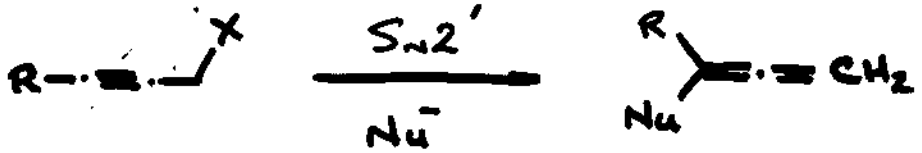


SMIT, W.A.; CAPLE, R.; SMOLIAKOVA, I.P. CHEM. REV. 1994, 94 2359.

I. INTRAMOLECULAR VARIANTS OF THIS REACTION ARE POSSIBLE



IMPORTANCE - IN TRADITIONAL ORGANIC CHEMISTRY, S_N2' REACTIONS ARE A MAJOR PROBLEM IN SUBSTITUTIONS OF PROPARGYL – X

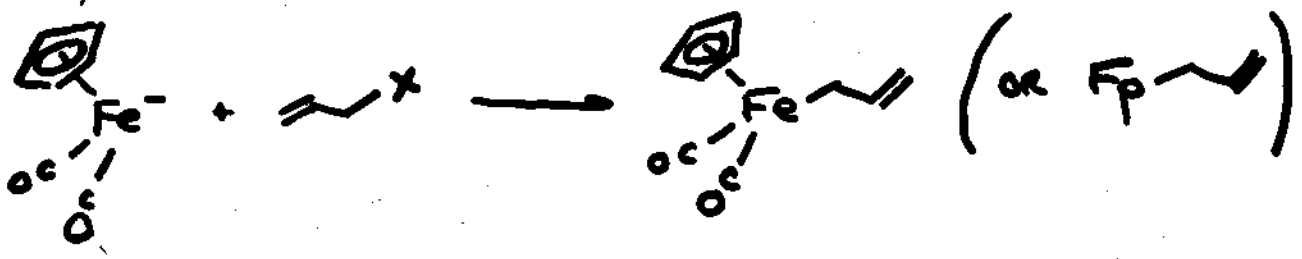
i.e. 

ALLENES

– THIS NEVER, EVER, EVER HAPPENS WITH Co PROPARGYL CATIONS (NICHOLAS REACTION)

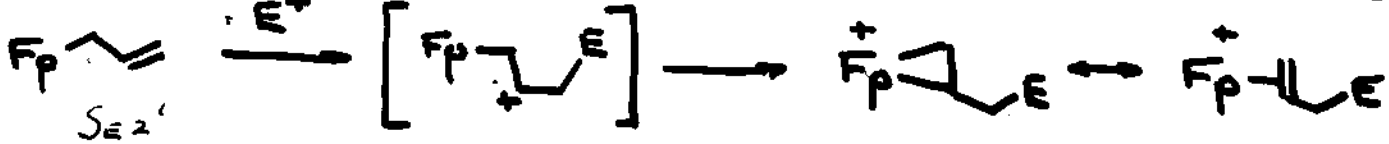
NUCLEOPHILIC ALLYLS

η^1-ALLYL Fp ($Cp Fe(CO)_2$) COMPLEXES



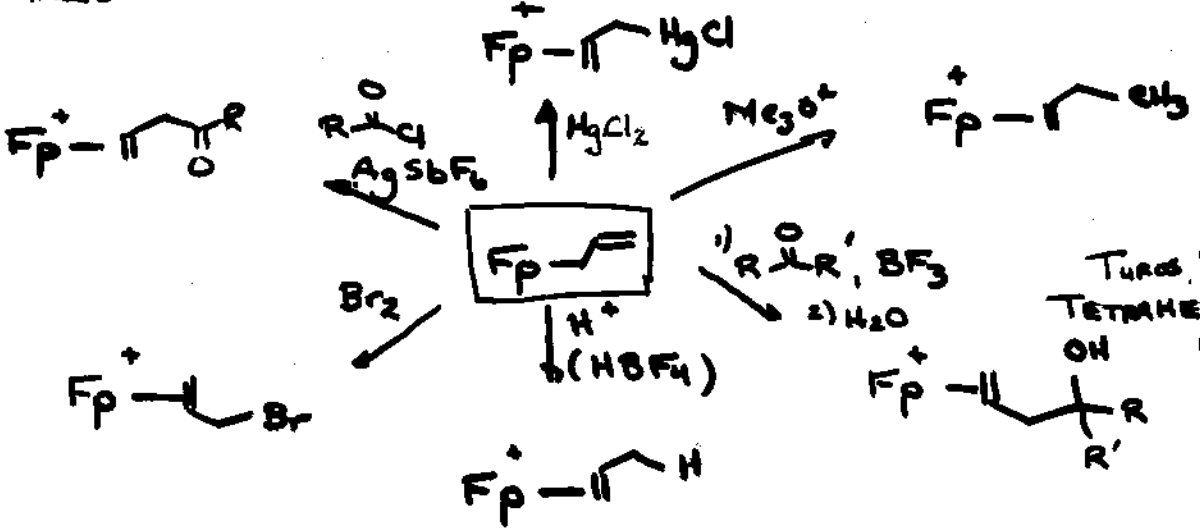
THESE ARE η^1, NOT η^3 ALLYLS

– BEHAVE AS MODESTLY REACTIVE NUCLEOPHILES TO A WIDE RANGE OF E^+



S_E2'

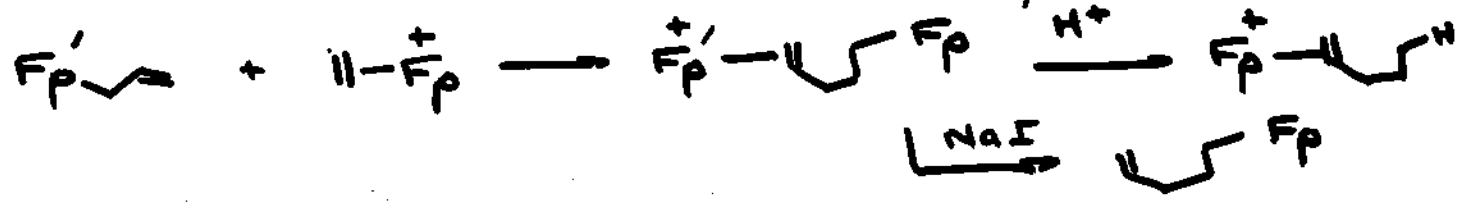
EXAMPLES

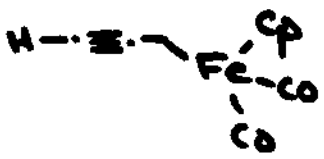


TURÓS E. ET AL TETRAHEDRON LETT. 1991, 32, 3001, 4639.

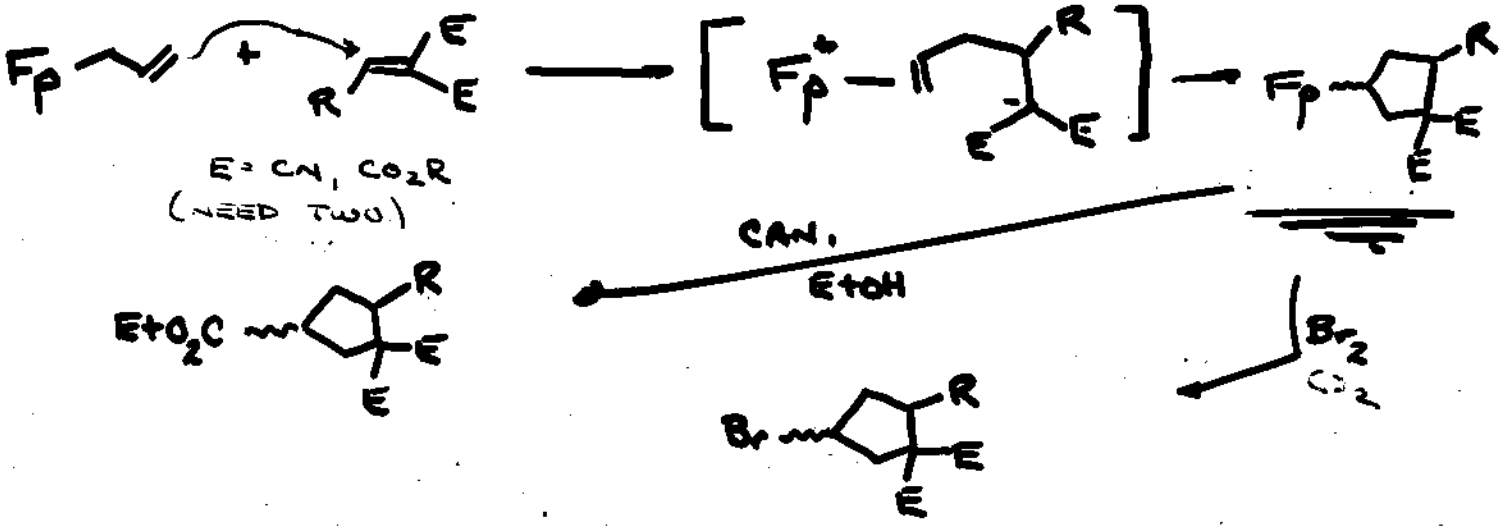
ROSENBLUM, M. J. ORGANOMET. CHEM. 1986, 300, 191

EVEN Fp^+-ALKENE COMPLEXES REACT WITH η^1-Fp ALLYLS



PROPARGYLS, i.e.  DO ANALOGOUS CHEMISTRY

- CAN DO TANDEM NUCLEOPHILIC ATTACK / ELECTROPHILIC ATTACK ON PRODUCT — [3+2] CYCLOADDITION RESULTS.



- ALKENE USUALLY NEEDS TWO ELECTRON WITHDRAWING GROUPS
- ALTHOUGH  WORKS WITH $AlBr_3$ (LEWIS ACID)

- OTHER [3+2] PARTNERS $Ts-N=C=O$, $MeO_2C-N=SO_2$, $CH_2=SO_2$
- AND CYCLOHEPTADIENYL IRON CATIONS!