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VL_Reaktionsmechanismen

WS 2010/2011

Lecture notes

from
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Reaktivität : · Ladung (ionische Verb.) / MO - (S_N2-Reaktion)
· sterische Effekte
· stereoelektronische Effekte

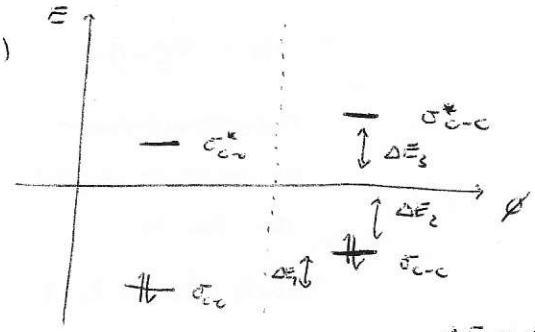
S_N2-Reaktion

A) TMS—≡—H $\xrightarrow[\text{oder BuLi}]{\text{LDA}}$ TMS—≡$^{\ominus}$ (+ OTs) $\xrightarrow{-78\,^\circ C}$ TMS

B) MeO, OMe, $Nu^{\ominus}$ $\xrightarrow[\text{DMSO, DMF}]{\Delta}$ MeO, OMe

• TBSO $\xrightarrow{Me_2CuLi}$ TBSO, Me (→ sterische Effekte)

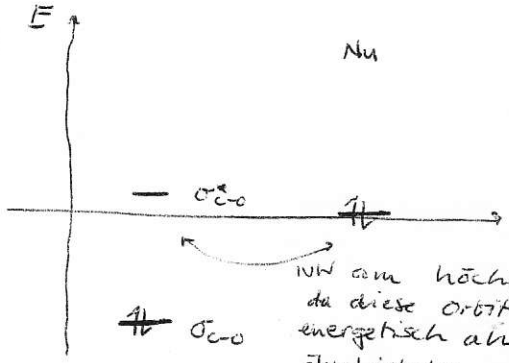
(i)



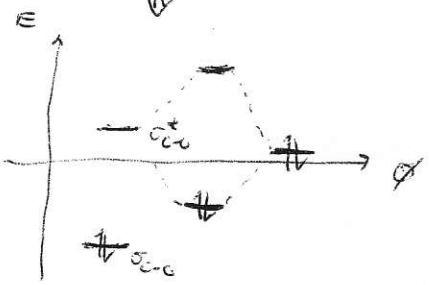
$\Delta E_2 = \Delta E_s$, da homonuklear

S_N2-Reaktion

(ii)



NW am höchsten, da diese Orbitale energetisch am ähnlichsten ⇒ Grund, warum C-O angegriffen werden kann, C-C nicht

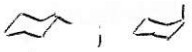


• Stereoelektronische Effekte

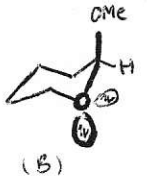
(i) → Anomerer Effekt

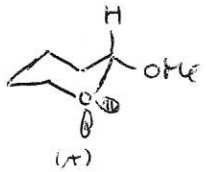
(ii) → α-Effekt

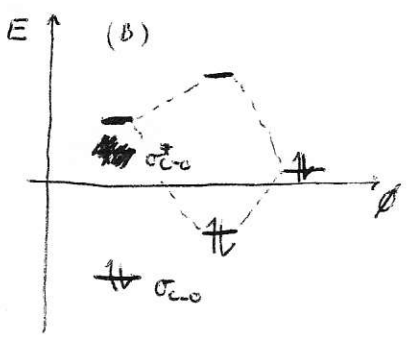
(1) H (ax), OMe (eq) $\xrightarrow[\text{RT}]{\text{MeOH, pTSOH}}$ OMe (eq), H (eq)

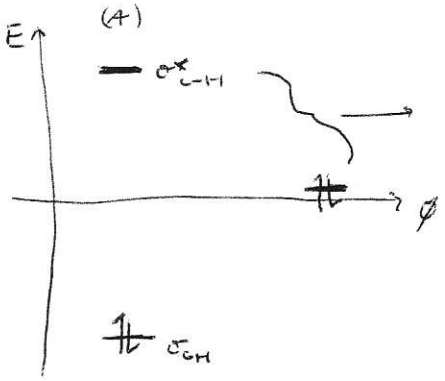
normal:  A stabiler als B ($\Delta E \approx 3$ kcal)

A B



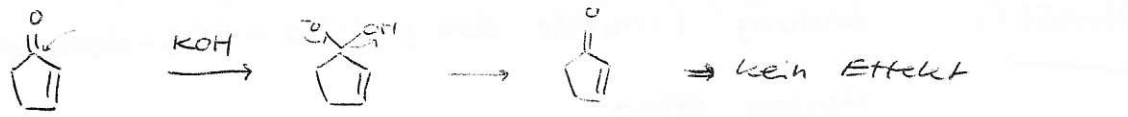




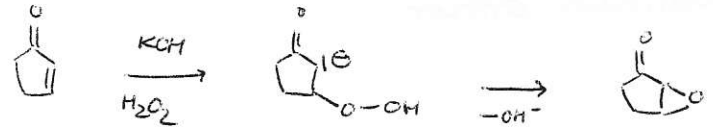


NO weiter entfernt → (A) ist instabiler

α-Effekt:



⇒ kein Effekt



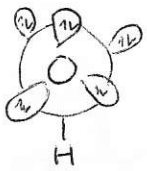
(Scheffer-Weitz-Reaktion)

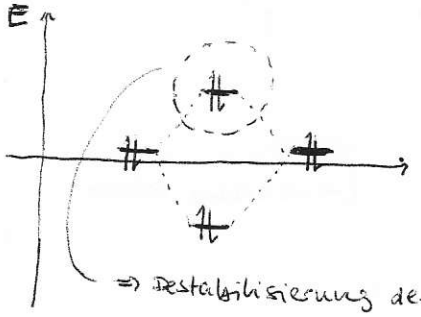
⇒ Warum geht es mit H_2O_2 und nur mit KOH nicht? → α-Effekt

- Nu: $^{\ominus}\bar{O}-\bar{O}H$
- Hydroperoxid-Anion ist weicher → geht an Pos. 4
- harte Nu an Px 1

(⇒ HSAB-Konzept)

Newman:





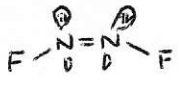
⇒ Destabilisierung des Systems

⇒ nur mit KOH nicht vorhanden, nur bei Hydroperoxid-Anion

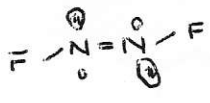
⇒ „α-Effekt"

- Vgl. anomerer Effekt: nur zwei Elektronen müssen verteilt werden → stabilisierung, vier Elektronen → Destabilisierung

- stereochemische Effekte

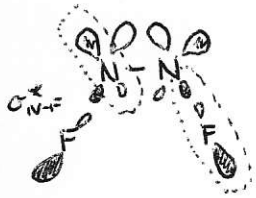


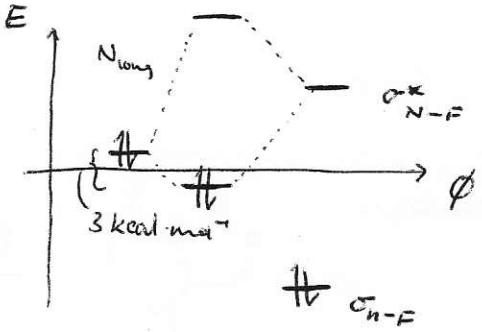
(Z)



(E)

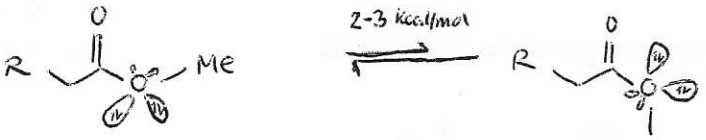
3 kcal/mol stabiler





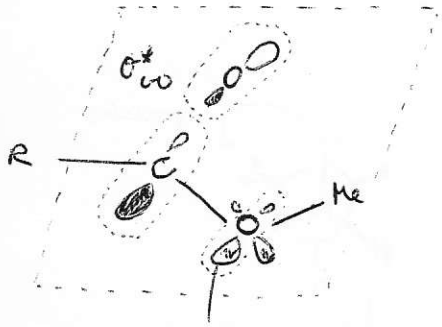
Orbitale stehen parallel → günstig

- Esterkonformation



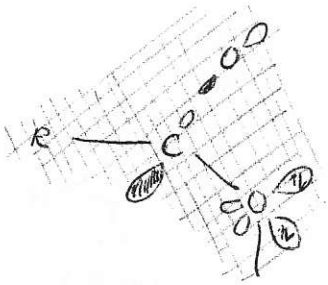
(Z-Konf.)

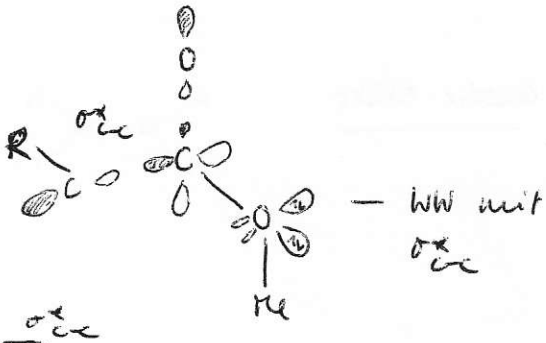
(E-Konf)



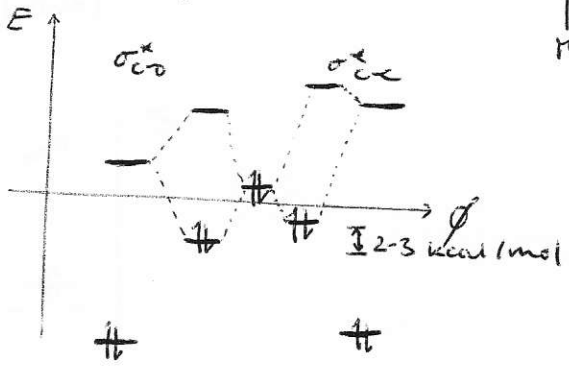
= alle in einer Ebene parallel

Long-Pair liegt in der Ebene, WW mit $\sigma^*_{C=O}$





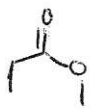
— WW mit σ^*_{C-C}



- Vergleich:

pKa ~25

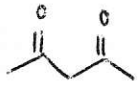
⇔



~30

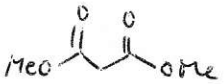
γ-Lacton deutlich nucleophiler

-

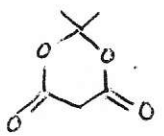


pKa ~13 ;

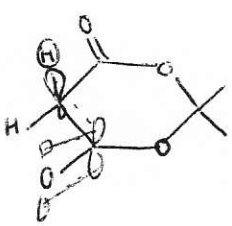
~14 ;



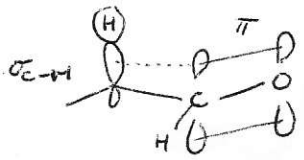
~16 ;



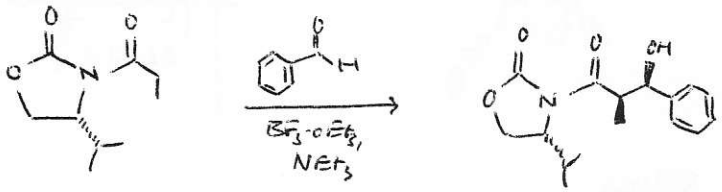
~7 →



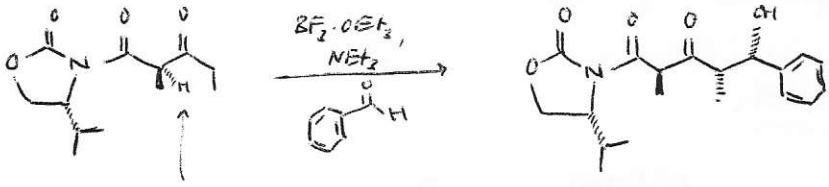
- Deprotonierungen:



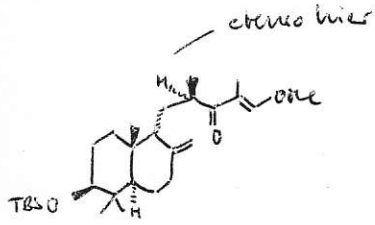
- Evan's Auxiliar:

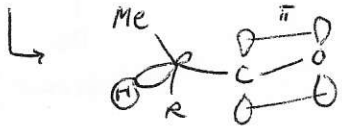


- Extended Evans:

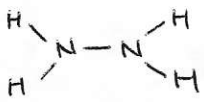


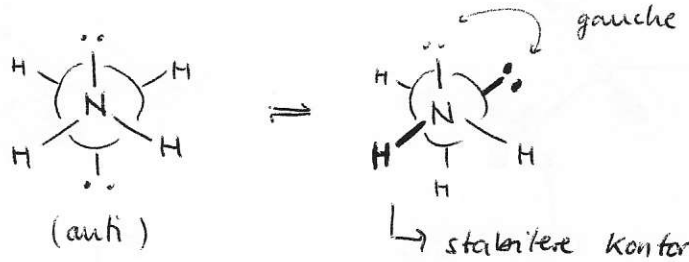
H-Atom kann nicht aufgrund der Stereochemie deprotoniert werden





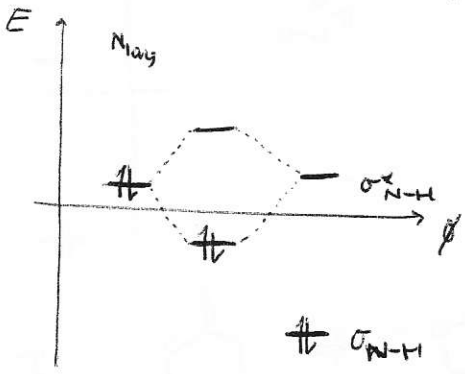
- Gauche-Effekt:





↳ stabilitere Konformation

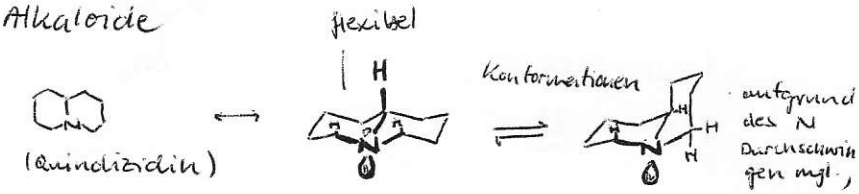
- Effekt nicht groß, reicht aber aus, um Coulomb'sche Kraft zu übertreffen



• Bohlmann Banden.

· Alkaloidchemie → Quinolizidin Alkaloide

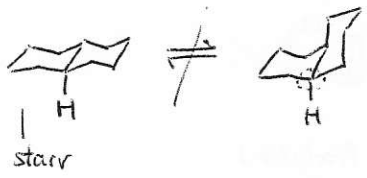
· entscheidendes Strukturelement:



· manche Quinolizidin-Derivate bevorzugen trans-Form, andere cis-Form

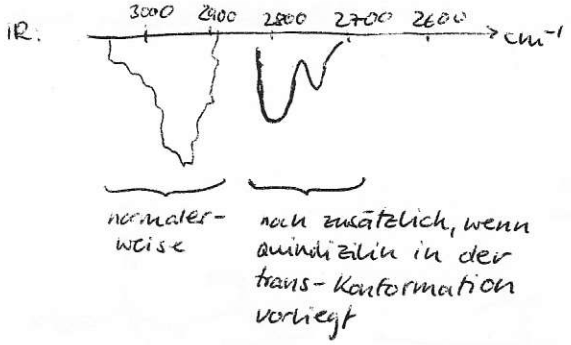
→ mit IR leicht unterscheidbar

bei Decalin:



→ Flexibilität hat Auswirkungen auf Reaktivität

· mit Bohlmann-Banden lässt sich beschreiben, in welcher Konformation Quinolizidin vorliegt



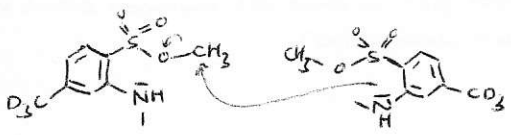
· trans: drei Effekte, cis: nur noch ein Effekt

↳ Bohlmann-Bande kaum sichtbar

• S_N2-Reaktion

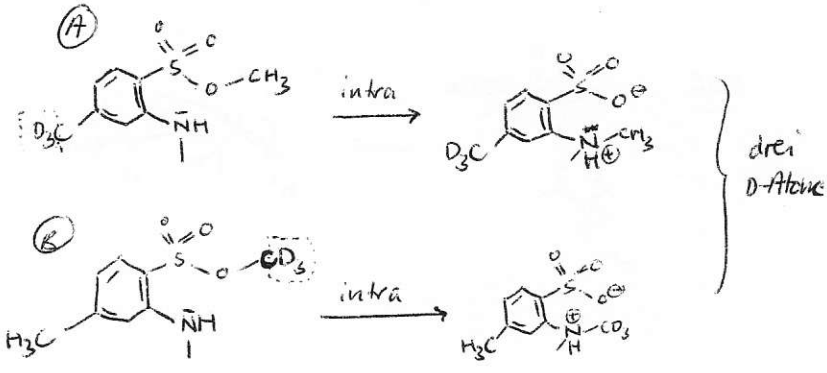
· Wie wichtig 180° ∡ für Reaktion?

→ Experiment von Albert Eschenmoser:

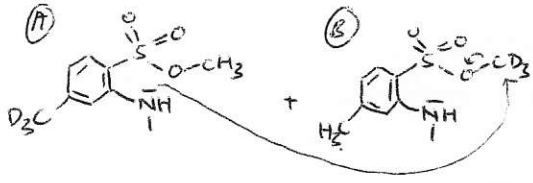


· intermolekular

→ nimmt man nur Ⓐ oder nur Ⓑ, so lässt sich nicht feststellen, ob Reaktion inter- oder intramolekular verläuft, esst, wenn man 1:1-Gemisch von Ⓐ und Ⓑ nimmt



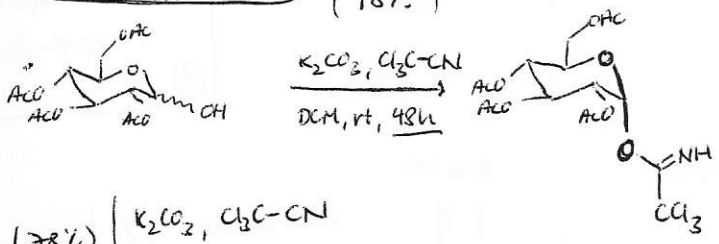
·



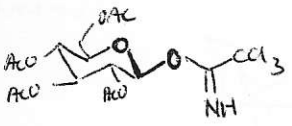
⇒ Ergebnis: Produkt enthält sechs Deuteriumatome

⇒ Reaktion verläuft intermolekular

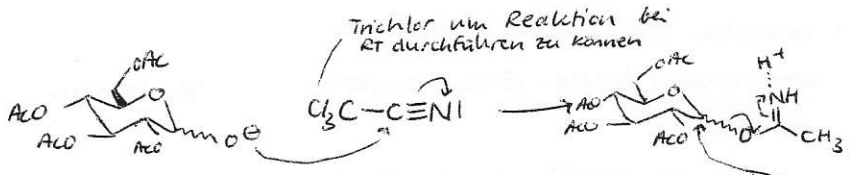
• Trichloracetimidat-Methode (98%) (Bundles Reagenz)

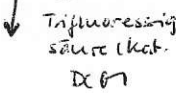


(78%) K_2CO_3, Cl_3C-CN, DCM, rt, 2h

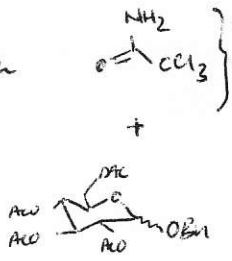


(kinetisches Produkt)

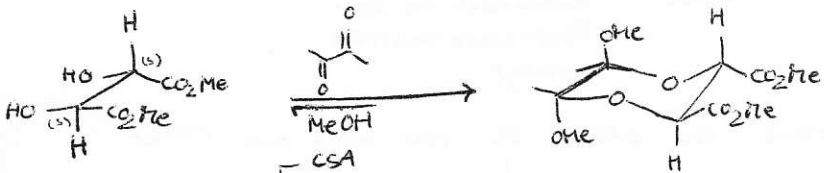




⇒ Einführen einer Benzylgruppe mgl. (als Schutzgruppe), Einsatz von Benzylbromid auf Ausgangsprodukt würde bei vorherrschenden basischen Bedingungen Ac-Schutzgruppen auch angreifen

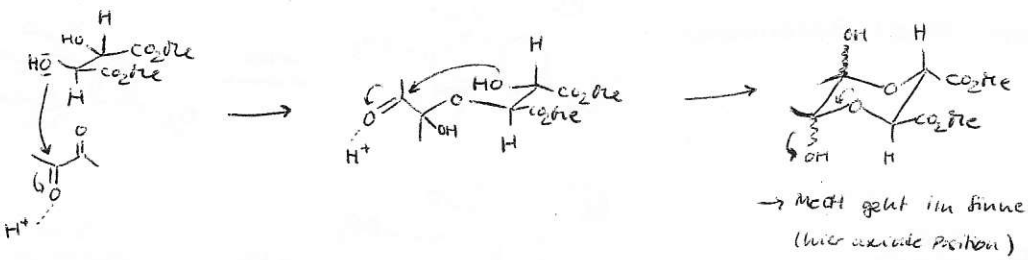


• Ley-Schutzgruppe



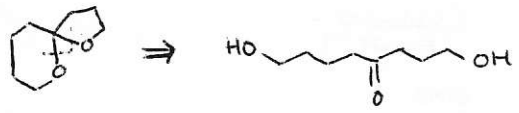
Camphersulfonsäure

Mech.

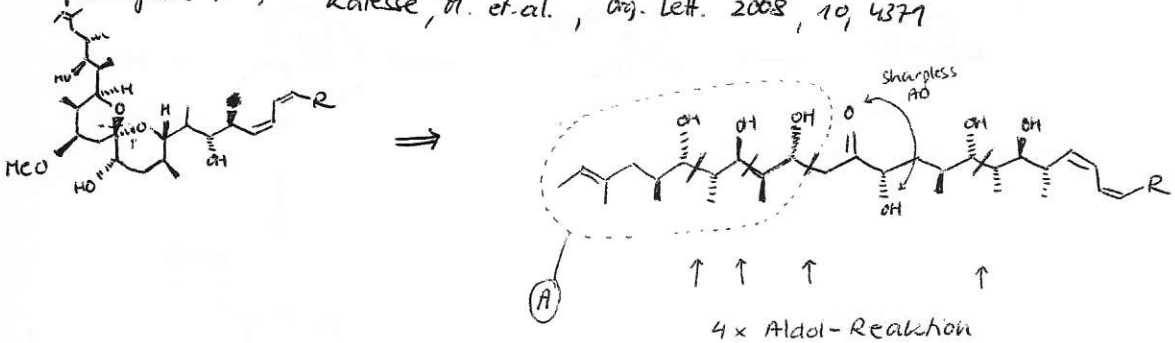


→ MeOH geht im Sinne des anomeren Effekts dran (hier axiale Position)

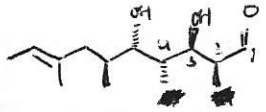
- Naturstoffe mit spiro-Acetal-Motiv

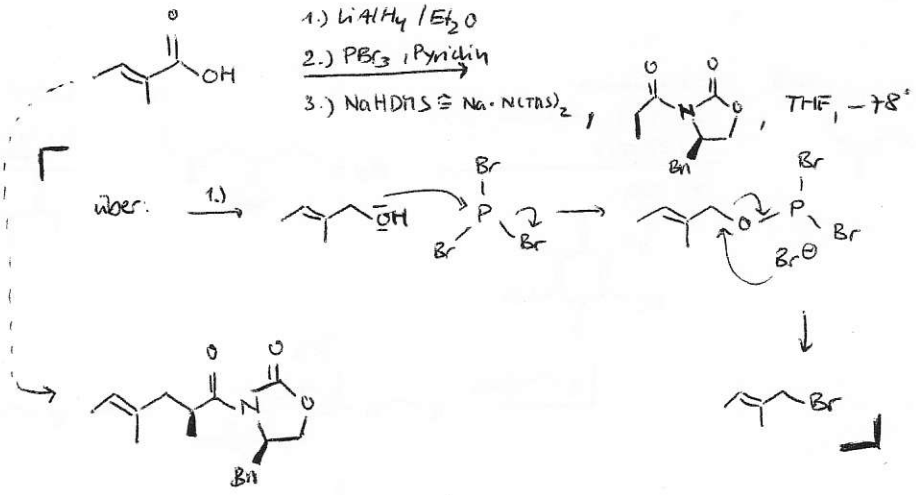


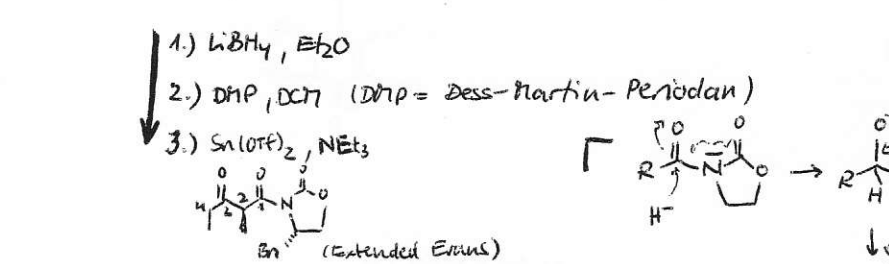
Spirangien A ; Kalesse, M. et.al., Org. Lett. 2008, 10, 4371

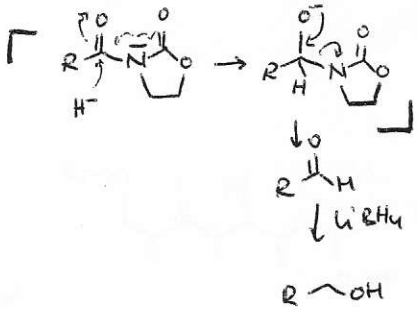


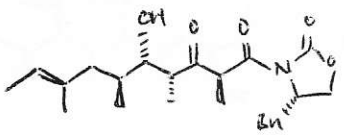
(1):



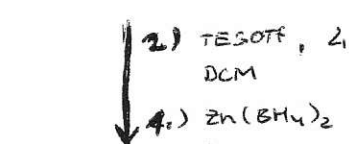


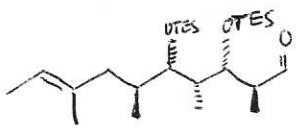




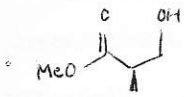


Basizität von Pyridin + sterische Hinderung





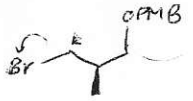
RM
08-11-2010
(1)

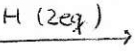


Roche-Ester, kein Naturstoff, enzymatische Gewinnung

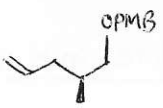
1.) PMB-Bundles
2.) DIBAL-H (2eq)
3.) CBr_4, PPh_3

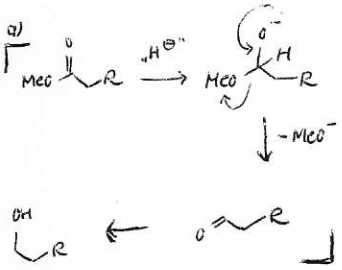
("Appel-Reaktion")



1.) CuI

Et_2O

("Schlosser-Fouquet")



a)


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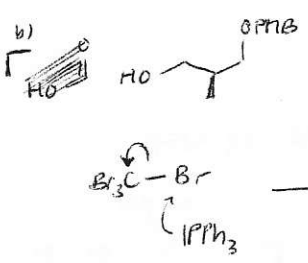
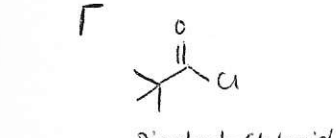
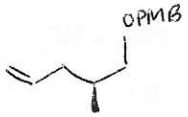
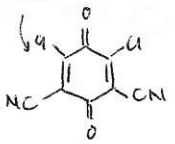


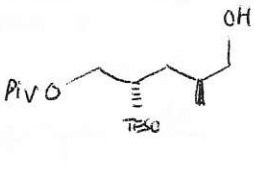


Pivaloyl-Chlorid

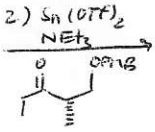


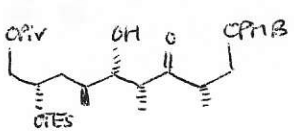
1.) ADmix
2.) PivCl, Pyridin, DCM
3.) TESOTf
4.) DDQ

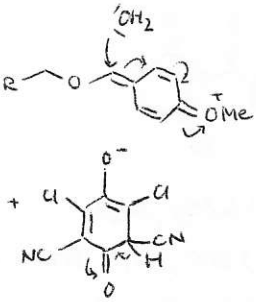


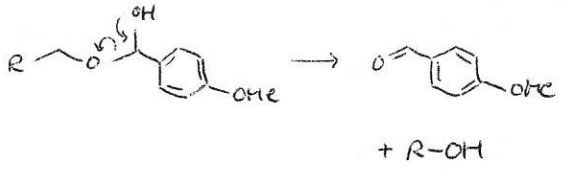


1.) DMP
2.) $Sn(OTf)_2$
NEt_3



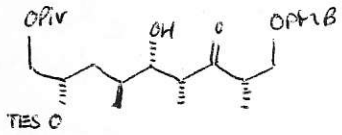




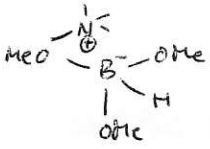


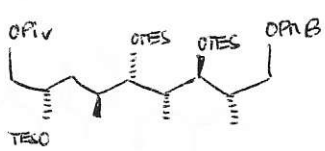
+ R-OH

⇒ DDQ zum Entfernen der PMB-Schutzgruppe

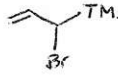


1.) $Me_4NB(OAc)_3H$
2.) 2 eq. TESOTf
2,6-Lutidine

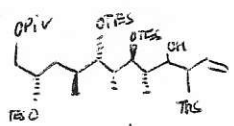




1.) DDQ, H_2O, DCM
2.) DMP, DCM
3.) $CrCl_2$, THF

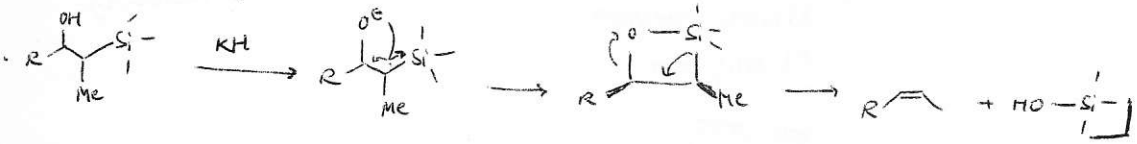


Nozaki-Hijama-Kishi

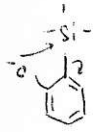


1. KH
(Peterson-Olefinierung)

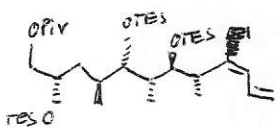
Peterson-Olefinierung:

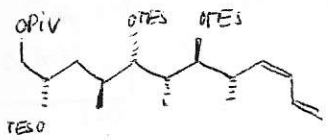


in sauren Bedingungen entsteht „trans"

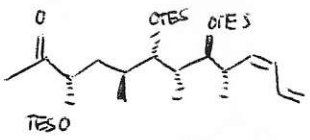


„Brook-rearrangement"

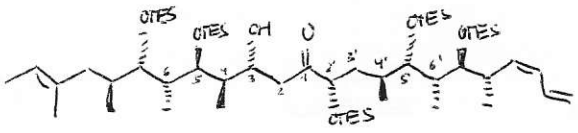




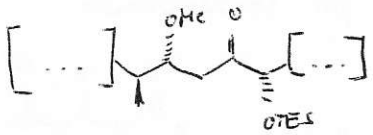
1.) DIBAL-H
2.) DMP
3.) MeMgBr
4.) DMP



1.) LiHMDS,
Verbindung (A)



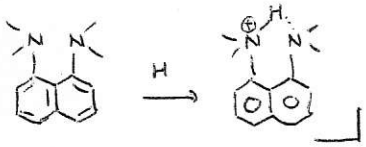
↓ "proton sponge"
DCM, Meerwein-Salz



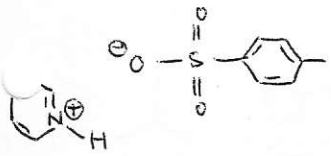
↓ PPTS,
MeOH

Spirangien A

Proton-Sponge:

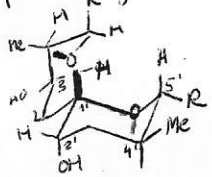


PPTS:



- schwach sauer
- milde Methode

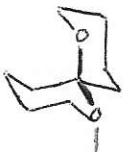
- Spiro-System:



2x anomerer Effekt

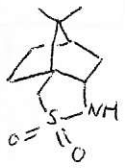
1x

kein anomerer Effekt

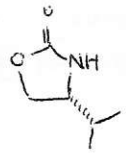


1x

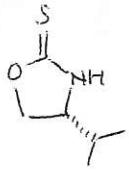
- Auxiliar gesteuerte Aldolreaktion



Oppolzer Auxiliar



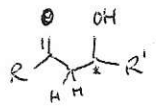
Evans Auxiliar



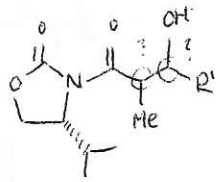
⇒ „Acetal" - tauglich

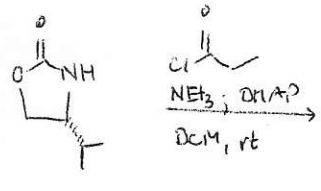
↓

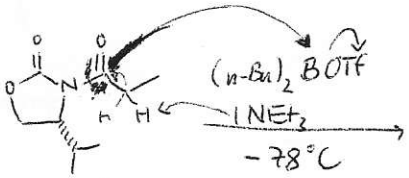
- einige Vorteile ggn. Evans
- wird eingesetzt für 1,4-Reduktionen

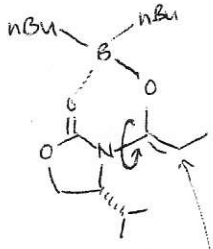


Produkt:









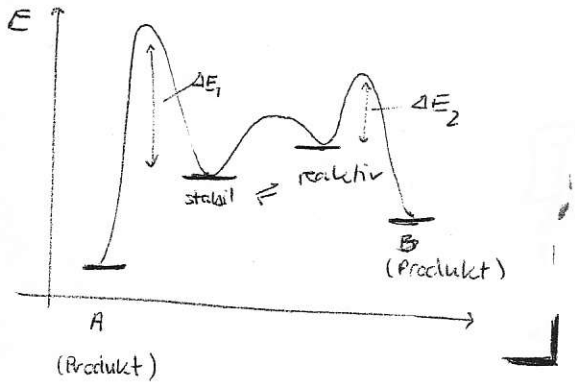
(stabil)

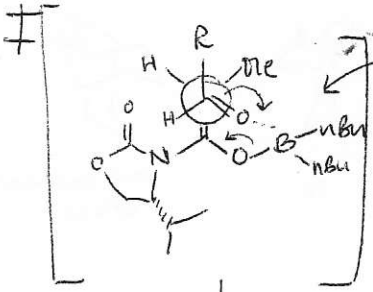
(reaktiv)

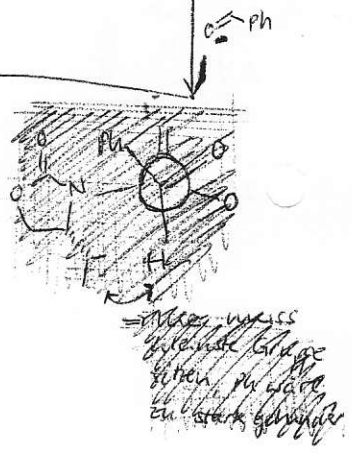
mit BOTf entsteht immer (Z)

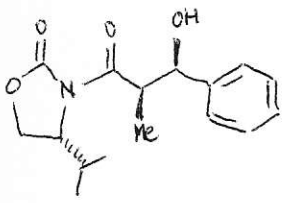
vor der Drehung Angriff hier, von oben; nach Drehung an selber Position

Curtin-Hammet-Situation

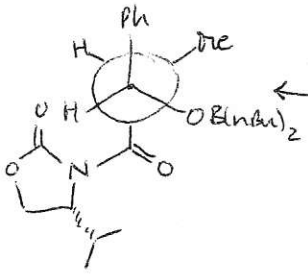








≙

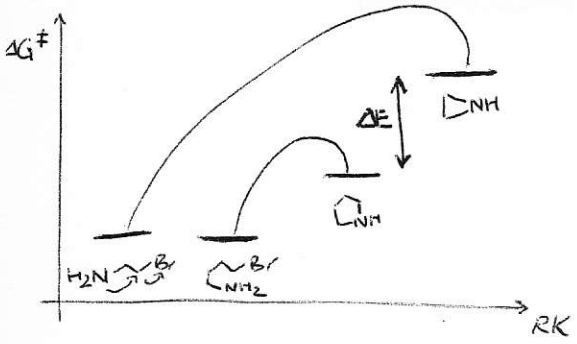


Baldwin-Regeln

RM
15-11-2016

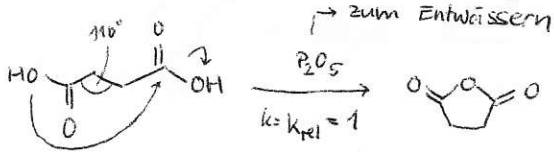
(1)

Ringschlussreaktionen: 5 > 6 > 3 > 7 > 4

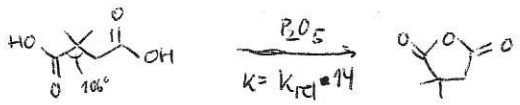


- je länger die Kette, umso weniger entropiebegünstigt der Ringschluss, bei kleineren Ringen ist noch Ringspannung zu berücksichtigen; 4-Ring am ungünstigsten, da hohe Ringspannung + ungünstige Entropie
- 5-Ring kinetisch am schnellsten, thermodynamisch jedoch 6-Ring

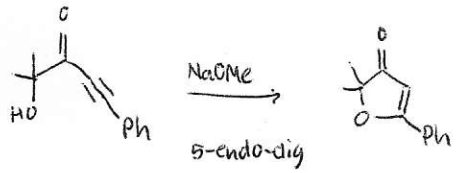
- Thorpe-Ingold-Effekt:



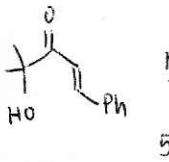
↳ zum Entwässern

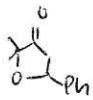


↳ Einschränkung einiger Konformation
→ weniger Konformationen zur Reaktion vorhanden → schneller

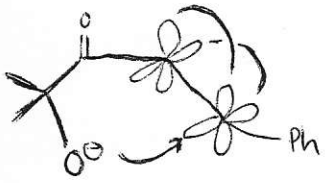


5-endo-dig — diagonal: Hybridisierungszustand
- entstehender Ring
- Bindung vom Angriff am Ende im Ring

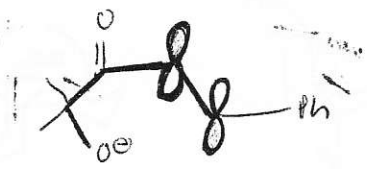


keine Reaktion (nicht  !) ⇒ Baldwin-Regeln

5-endo-dig:



5-endo-trig:



↳ aufgrund von Geometrie kein Ringschluss mgl., π/π*-Orbitale stehen senkrecht zur Ebene

- Baldwin-Regeln sind geometrische Regeln → durchaus Ausnahmen mgl.
- gelten für Ringgrößen 3–7 und für nucleophile Angriffe
- alle exo-tet → erlaubt
- alle exo-trig → erlaubt
- alle endo-dig → erlaubt
- 5,6,7-exo-dig → erlaubt
- 6,7-endo-trig → erlaubt

verboten:
- 5,6-endo-tet
- 3,4,5-endo-trig
- 3,4-exo-dig

• Fragmentierungs-Reaktionen

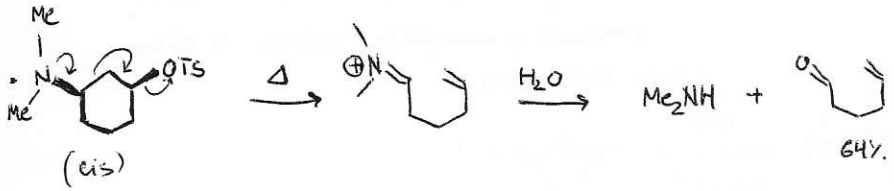
· allg:

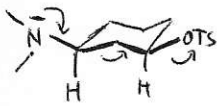
· entropiebegünstigt

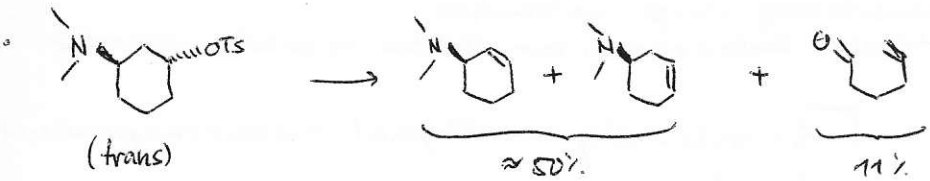
· analog E_2-Reaktion

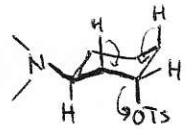
„zig-zag"-Anordnung

Ω-Anordnung

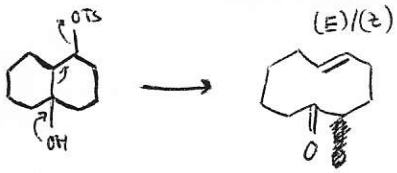


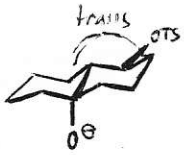




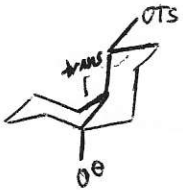
⇒ 

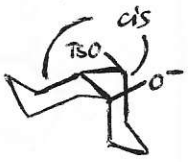
→ Eliminierung bevorzugt





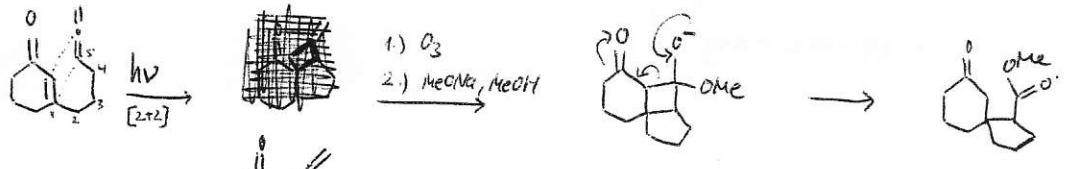
trans-Decalin



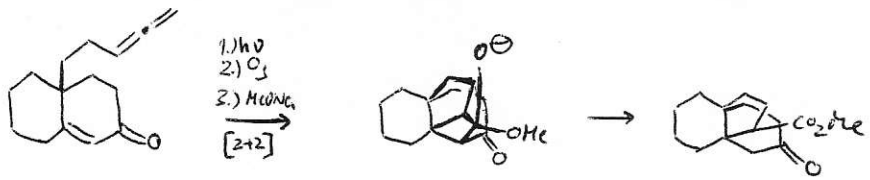


· Beispiele:

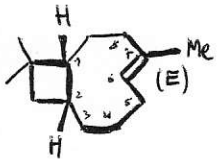
(i) 

(ii) 

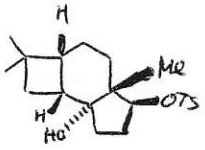
=) Spiro-Verb über Fragmentierung

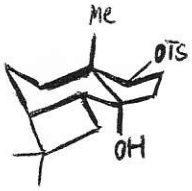


(Propellan)

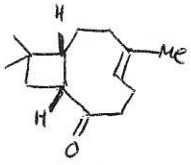


β-Caryophyllene





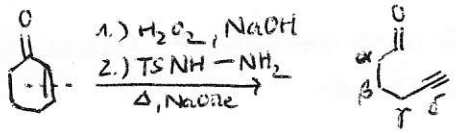
KO tBu



Carbonyl-gruppe entfernen

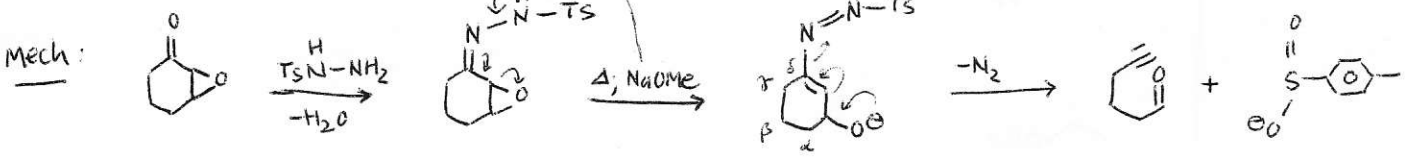
β-Caryophyllene

Eschenmoser - Tanabe - Reaktion



- funktioniert nur mit 6-Ringen

Mech:

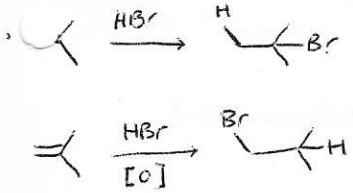


(Kondensation)

- Triebkraft: N_2-Bildung, Ts-Abgangsgruppe

- Beckmann-Fragmentierung (-Umlagerung) : bereits bekannt

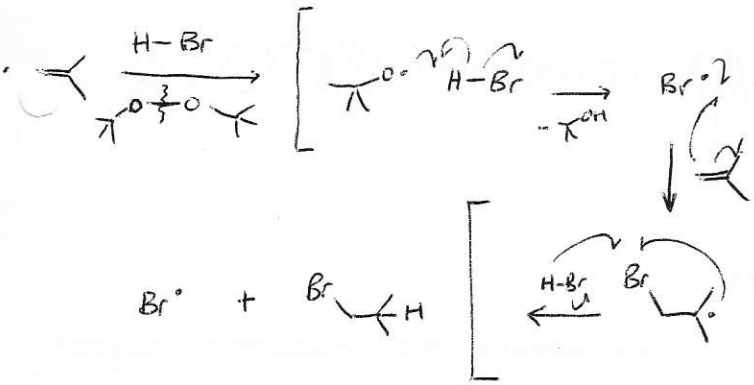
RADIKAL-REAKTIONEN



- Grundlage von Radikal-Reaktionen: Homolyse H—Br
- In der Lösung: H—Br → H^+ / Br^-, exothermer Prozess, aufgrund von Solvation begünstigt
- In Gasphase: H· + Br·

- ionischer Mech: Elektronenpfeile „in eine Richtung" ablaufend, nicht gegeneinander

- radikalischer Mech.: umgekehrt, da homolytische Spaltung

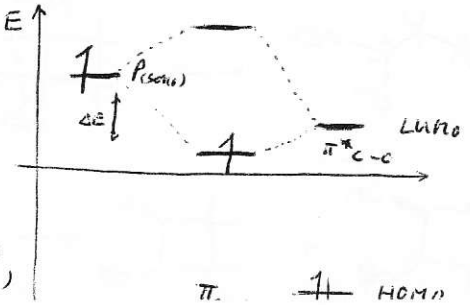


1.) Initiation
2.) Propagierung

- Stabilität: - analog zu Carbokationen (bzgl. prim./sek./tert.)

- Me° < prim. C° < sek. C° < tert. C° < <  < (R= OMe, H, Alkyl) (a)

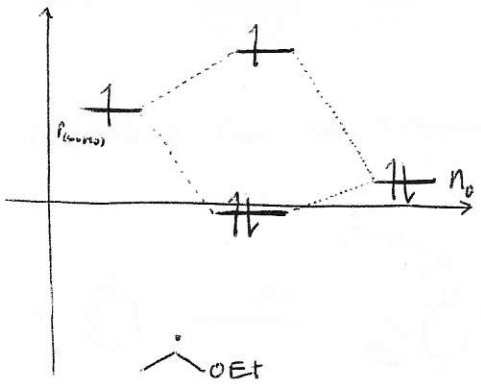
- Warum so stabil?



- (b)
-  (c)

⇐ für Fall a)

für Fall c):

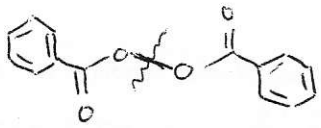


Energiegewinn, da zwei Elektronen energetisch abgesenkt werden
- ganzes Molekül wird stabilisiert, Radikalorbital liegt nun aber höher

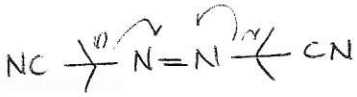
nucleophiles Radikal

- EWG:  → elektrophiles Radikal
- EDG: → nucleophiles —"—

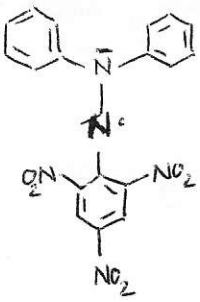
- Radikalstarter:



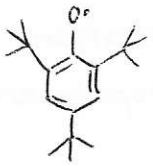
Dibenzoylperoxid

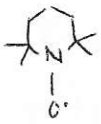


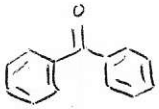
AIBN Azoisobutyronitril

- stabile Radikale: (i) 

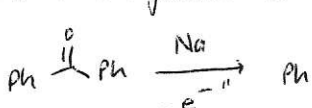
- DPPH (Diphenylpikrylhydrazin)
- Radikal: lila
- während Reaktion: Entfärbung

(ii) 

(iii)  (TEMPO)

(iv) 

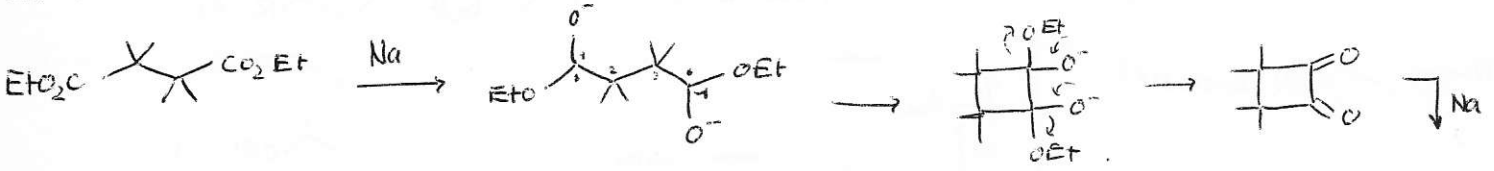
- (iv) wird eingesetzt bei Absolutierung von THF



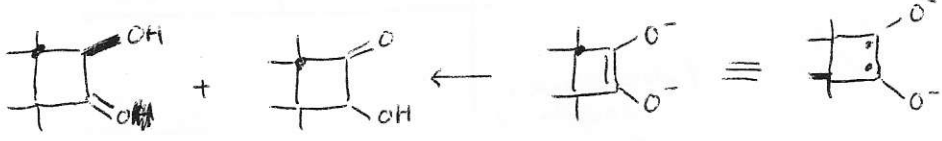
Ketyl-Radikal (violett-blau)

→ solange H_2O vorhanden reagiert Na mit H_2O, erst danach mit Benzophenon

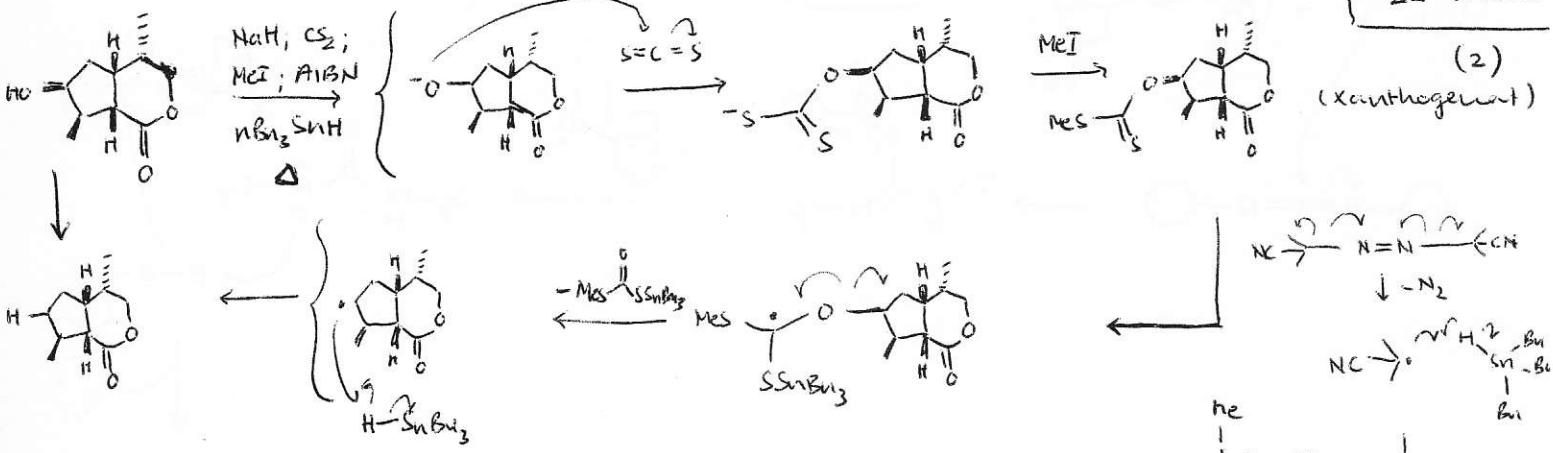
- Acyloin-Kondensation

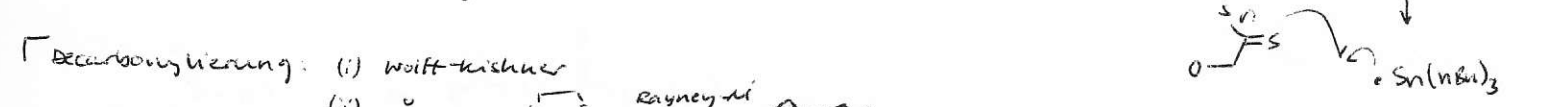


* = ^{13}C-markiert



• Barton-McCombie-Reaktion



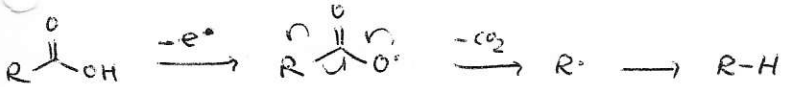


⇒ Sn hat hohe Affinität zu Schwefel

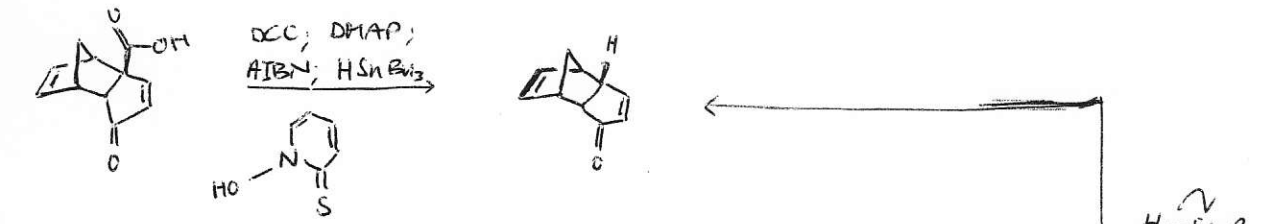
⌜Decarboxylierung: (i) Wolff-Kishner

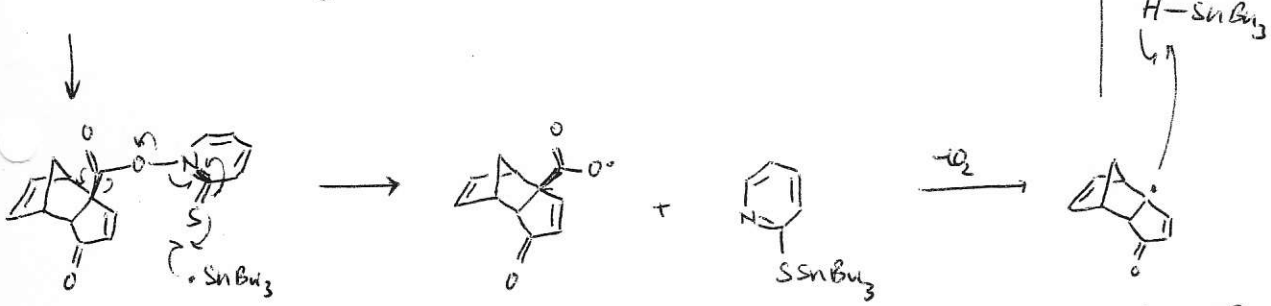
⌟

• Kolbe-Reaktion (zur Decarboxylierung)

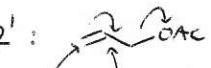


• Barton-Decarboxylierung



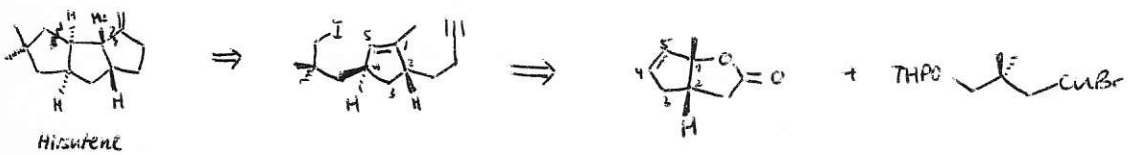


⌜S_N2':



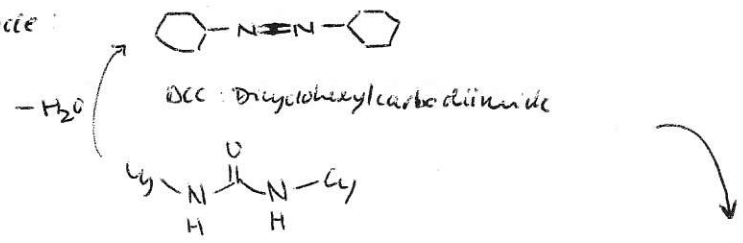
R-CuBr (weiches Nu) | LiR MgBrR } S_N2, hartes Nu ⌟

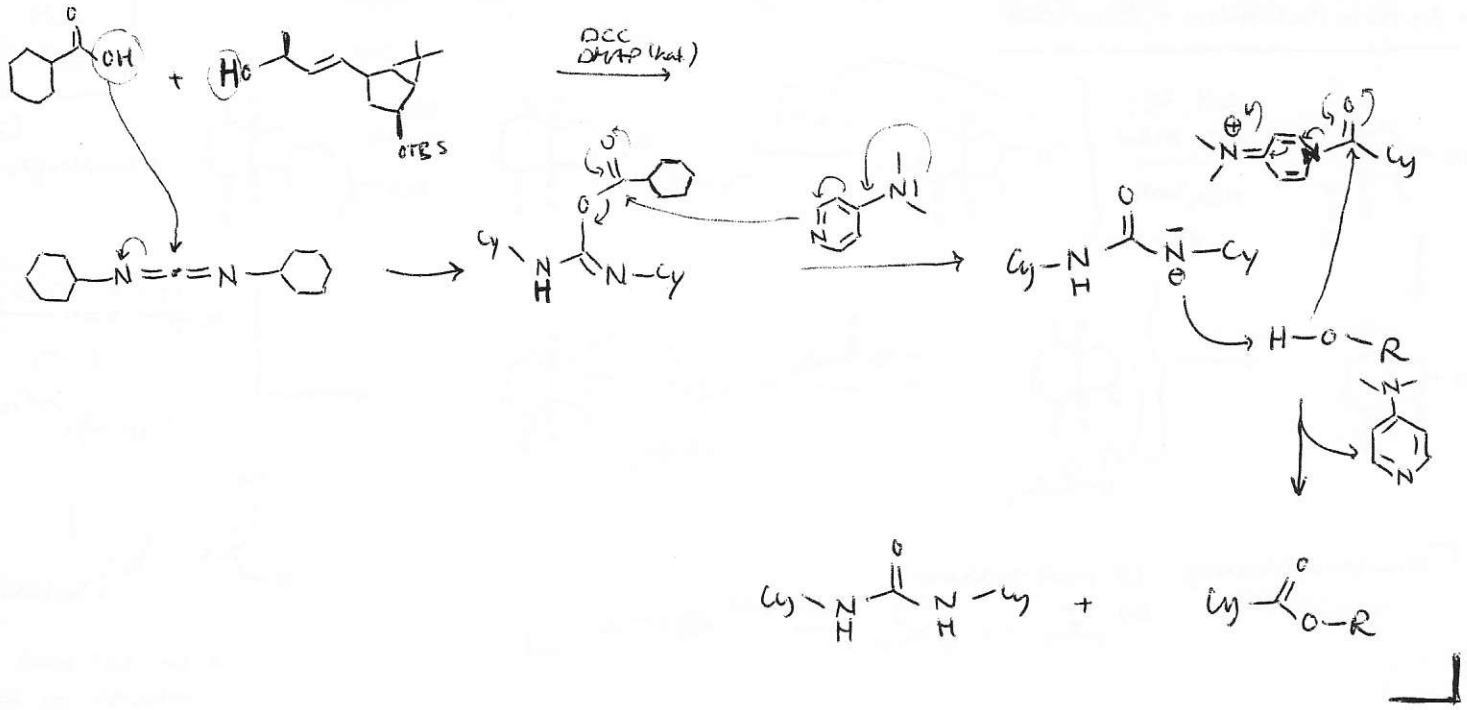
• Dennis-Curran-Reaktion (Totalsynthese von Hirsutene)

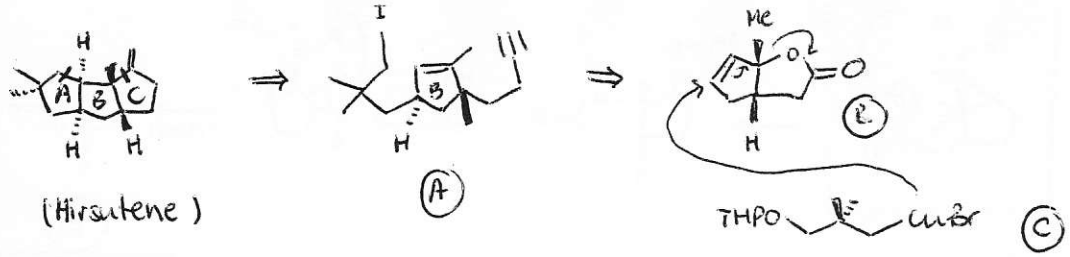


Hirsutene
→ keine funkt. Gr.

⌜DCC/DMAP-Methode:

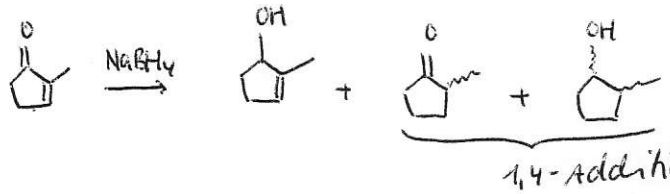



DCC
DMAP (kat.)
OTBS
Cy
R

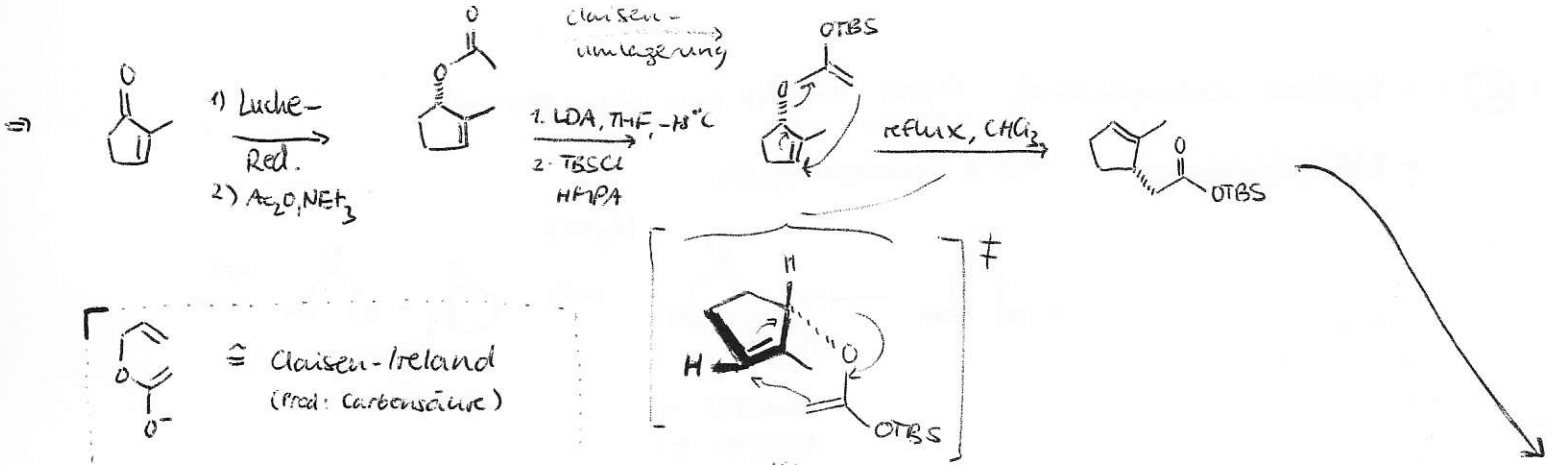


Ⓑ: 1.) $NaBH_4$, $CeCl_3 \cdot 7H_2O$ } „Luche-Reduktion"
2.) Ac_2O, NEt_3

Nur $NaBH_4$:



⇒ Vermeidung, indem das Carbonylsauerstoffatom mehr Elektrophiler gemacht wird
→ Einsatz von Lewis-Säuren: $CeCl_3 \cdot 7H_2O$



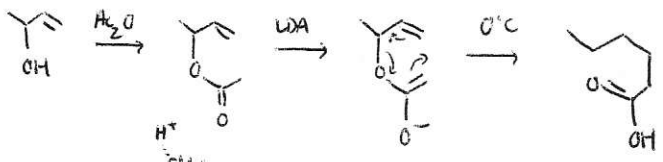
Angriff nur von unten möglich, Proton geht nach oben

≙ Claisen-Ireland (Prod: Carbonsäure)

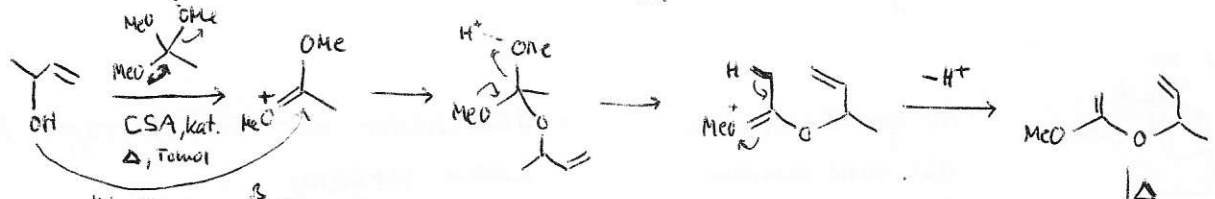
≙ Claisen-Johnson (Ester)

≙ Claisen-Eschenmoser (Amide)

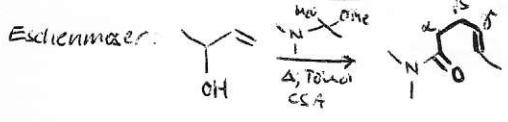
Ireland:



Johnson:

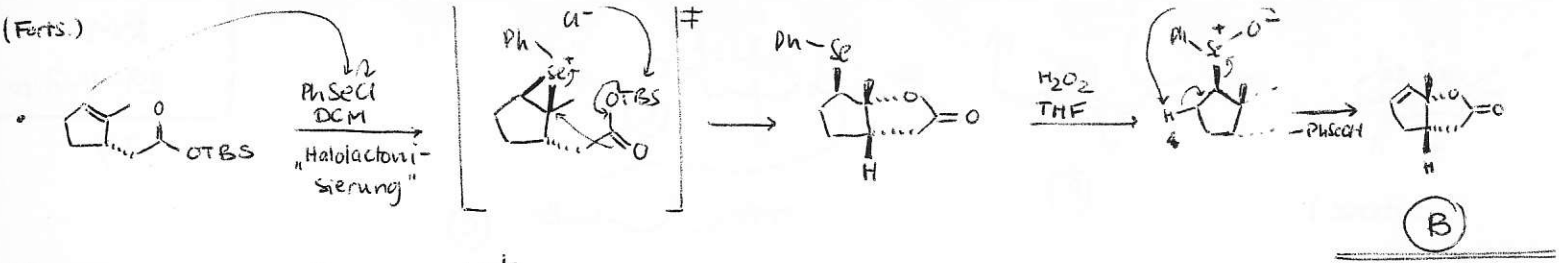


Eschenmoser:



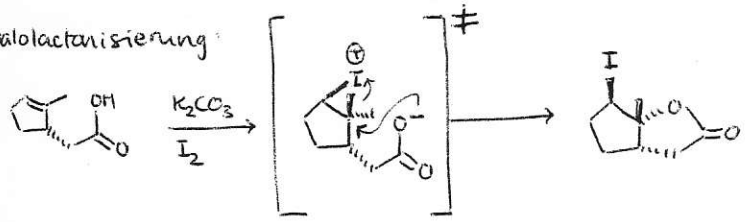
- Doppelbindung an γ-Position
→ Voraussetzungen für Claisen-Umlagerung

(Forts.)



(B)

Halolactonisierung:



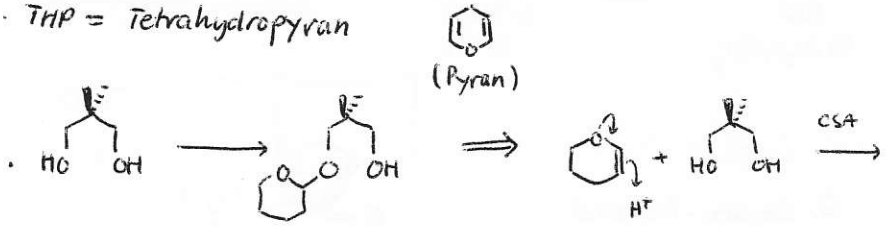
⇒ Vorhandensein von Iod erleichtert Eliminierung (→ (R)), diese kann hier selektiv verlaufen, da neben an ein $C^{(IV)}$ existiert

Andere Reagenzien: Br_2, NBS, NIS

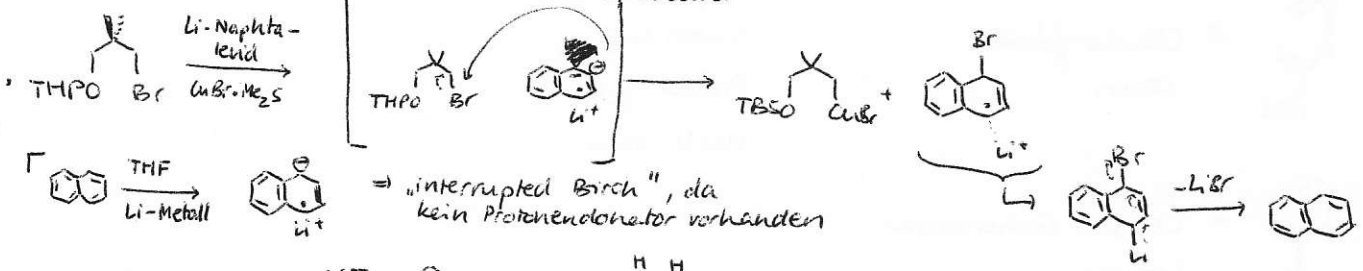
PhSeCl: reagiert sehr leicht mit DB, schon bereits bei geringen Temp. (−78°)

⇒ Vorteil hier: bessere Stereoselektivität bei geringen Temp.

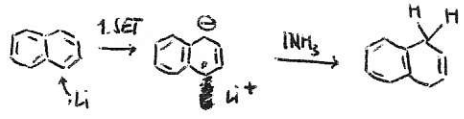
- (C): - Synthese einleuchtend, Cuprat entsteht aus dem Bromid
  - THP-Schutzgruppe: · THP = Tetrahydropyran (Pyran)

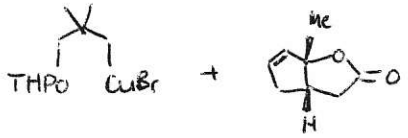


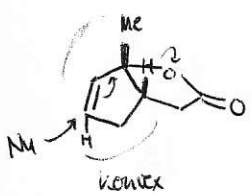
⇒ Alkohlfkt. ist acetalisch geschützt



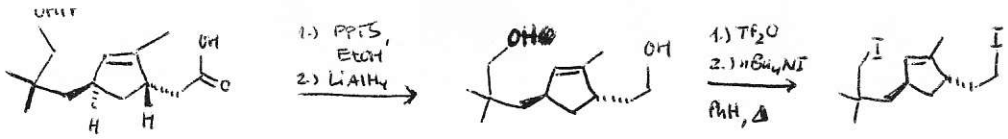
normalerweise:



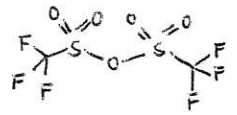


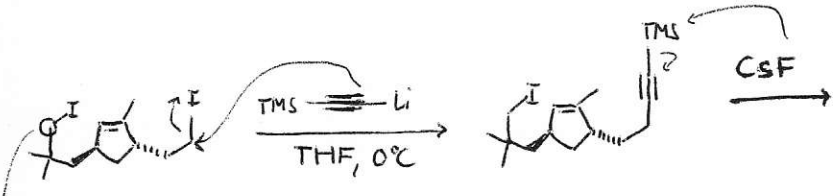


- Nu greift von oben an und schiebt das Proton nach unten
- Stereochemie der Methylgruppe bestimmt diesen Vorgang
- „open-book-effect"



Tf_2O =

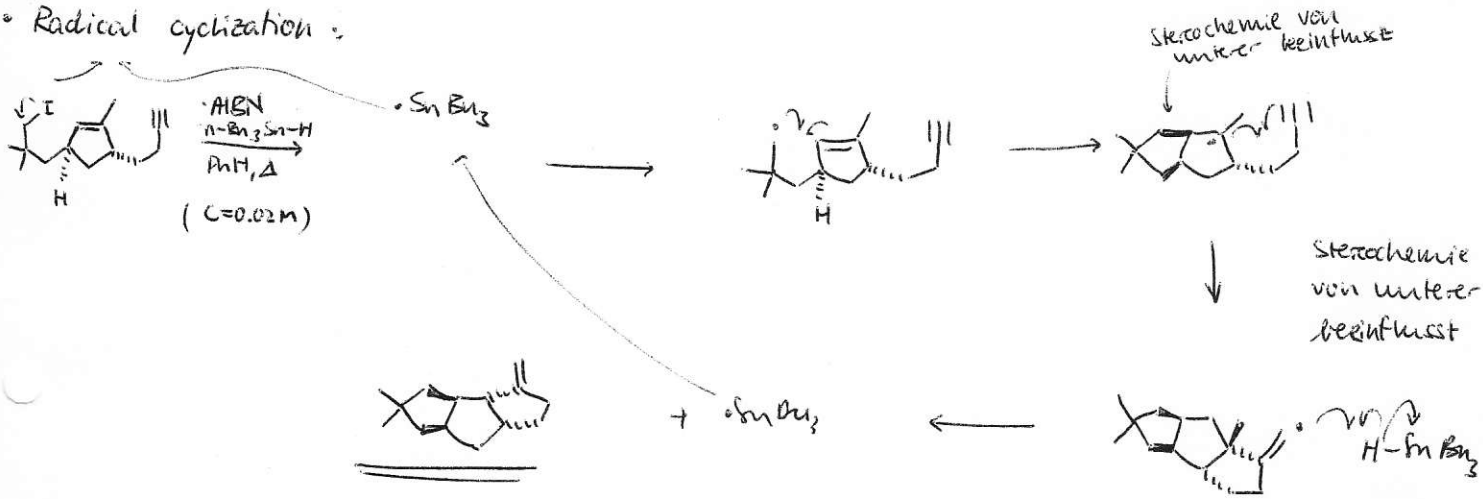




neo-Pentylposition,
→ S_N2-Reaktion kann nicht ablaufen!
→ nur eine Seite wird angegriffen

warum nicht H—≡—Li ?
⇒ H-Atom der Dreifachbindung muss geschützt werden, da H-C-Bindungs-s-Anteil bei Dreifachbindung erhöht ist → leichterer Angriff

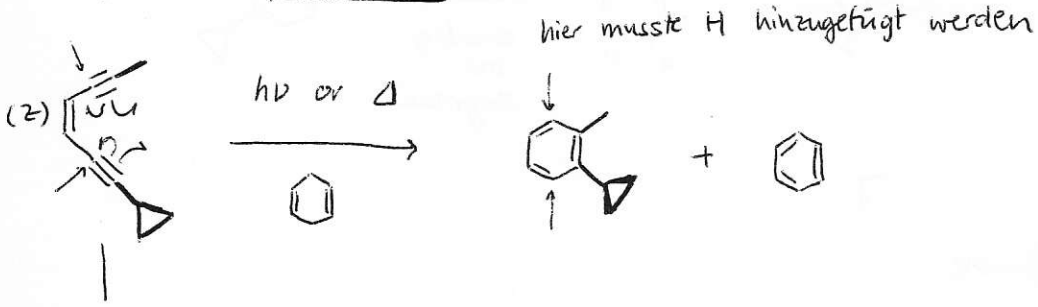
• Radical cyclization:



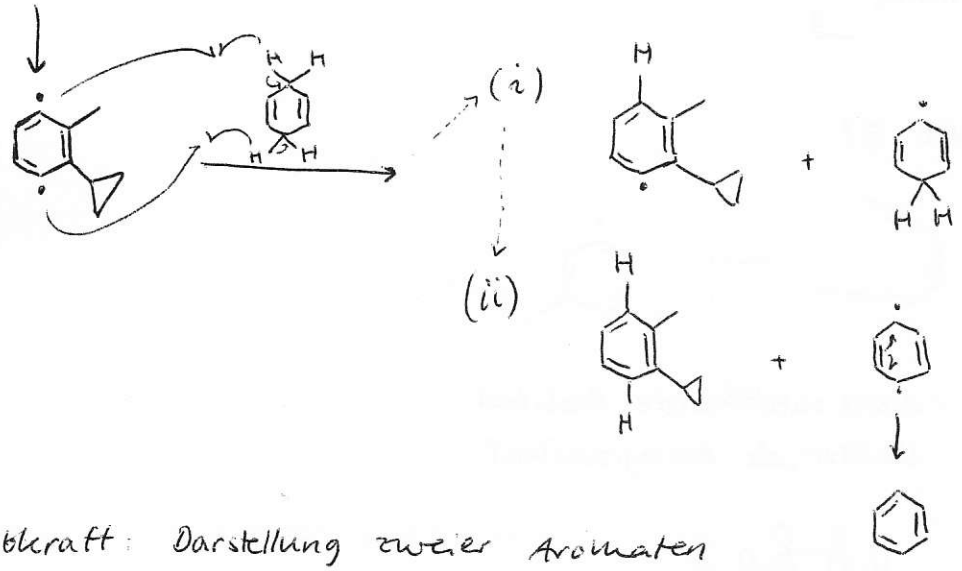
RM
06-12-2010

- Radical reactions

- Bergmann-cyclization

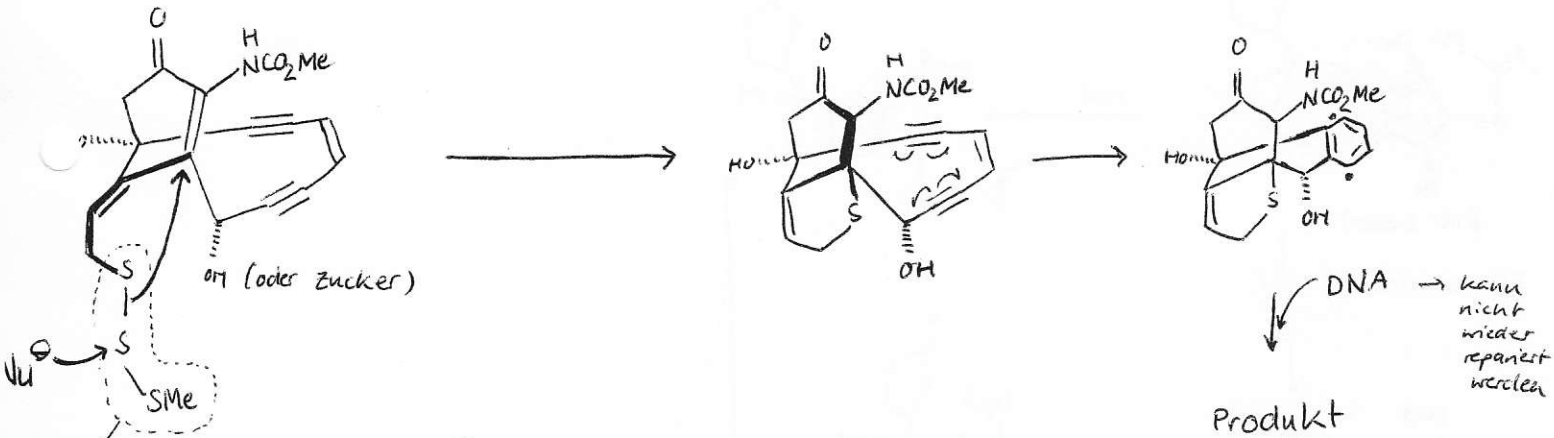


→ Mechanismus:



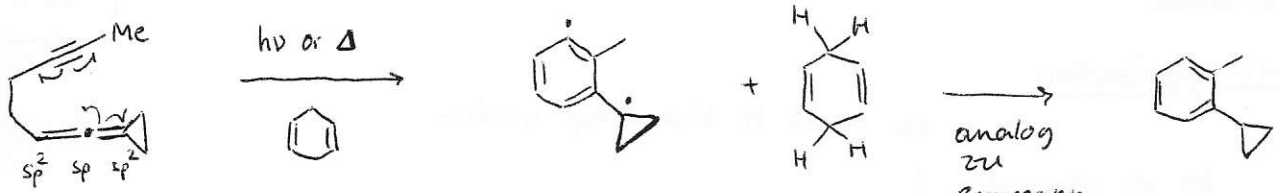
- Triebkraft: Darstellung zweier Aromaten

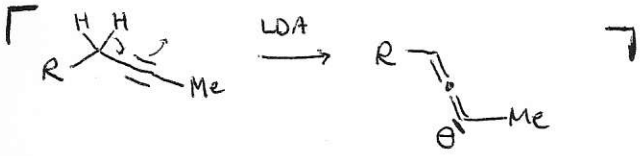
→ En-Diyne-Natural products: bspw. Calicheamycin



- Angriff des $Nu^{\ominus}$ an diese Pos. aufgrund von α-Effekt, dann 1,4-Addition (Michael)

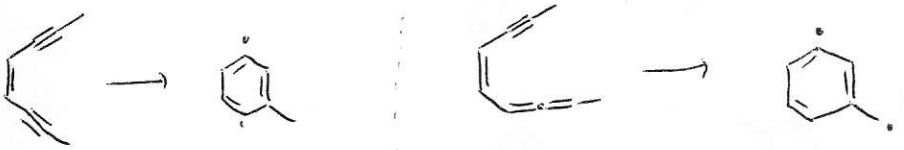
· Myers – Saïto – Cyclization



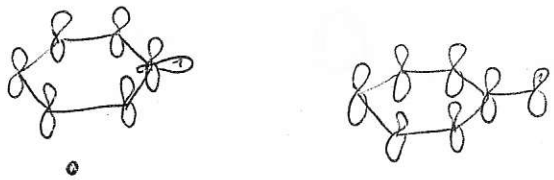


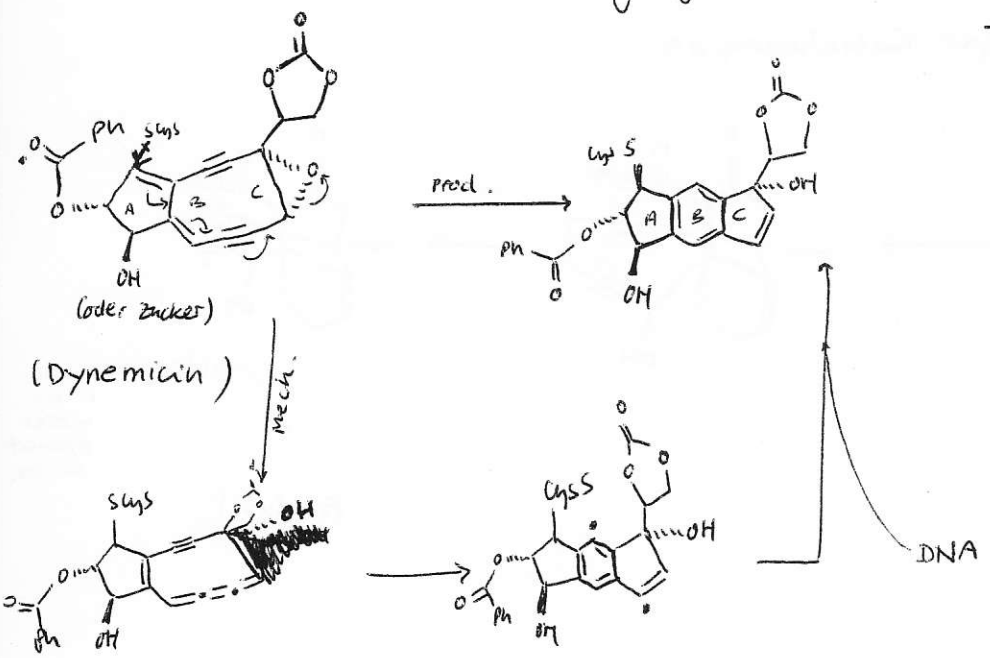
· quasi Tautomerie eines Alkins

Welche Reaktion hat geringere E_a?



· dieses entstehende Radikal stabiler, da Benzyradikal

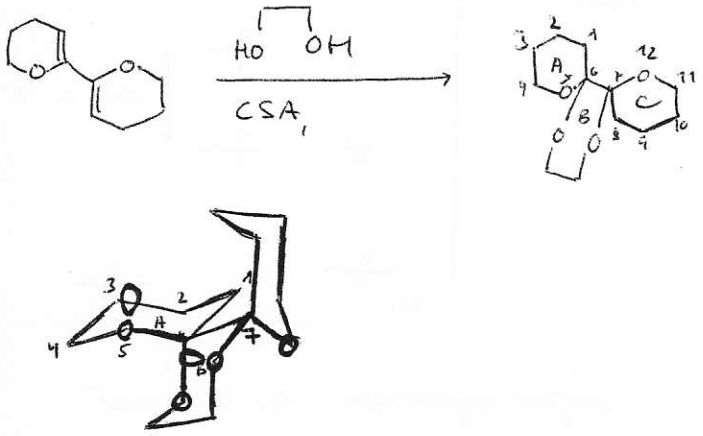




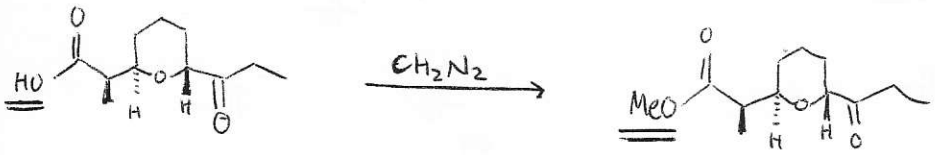
Übungsblatt : Afg. 6

RM
13-12-2010

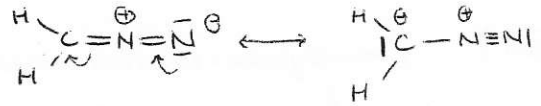
(1)

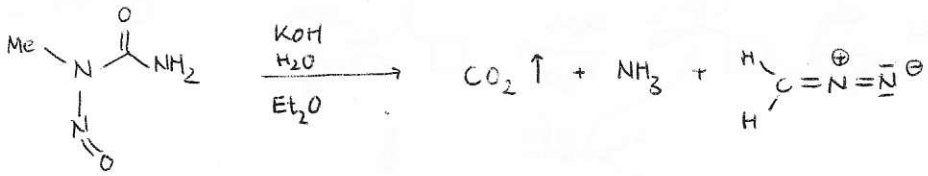


CARBENE

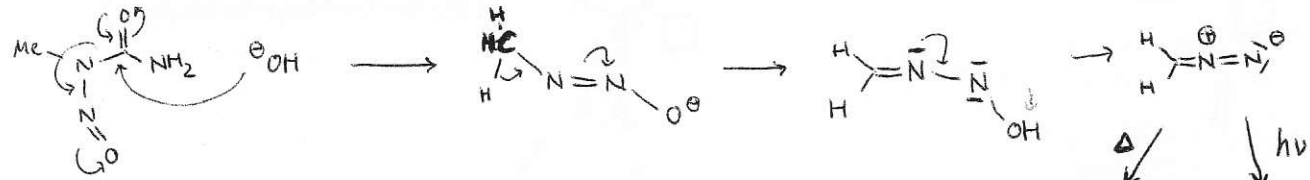


CH_2N_2 für Methylierung zum Methylester.

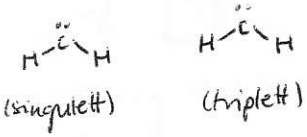
CH_2N_2 :  (Gas ; bp = -24 °C ; explosive)

wird hergestellt aus. 

(N-Me-Nitroso-urea)

Mech. 

Singulett-Carben :  Triplett 



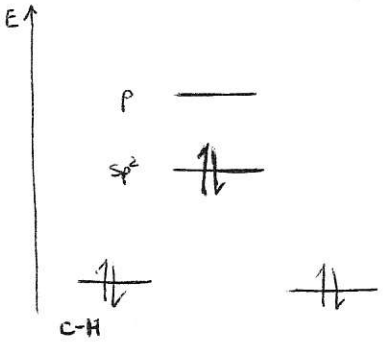
(singulett) (triplett)

e⁻ - sextett	e⁻ - sextett
charged	uncharged
no e⁻ available	e⁻ - available
electrophilic	electrophilic

- Triplett-Carben ist detektierbar (mit ESR), singulett-Carben ist nicht detektierbar

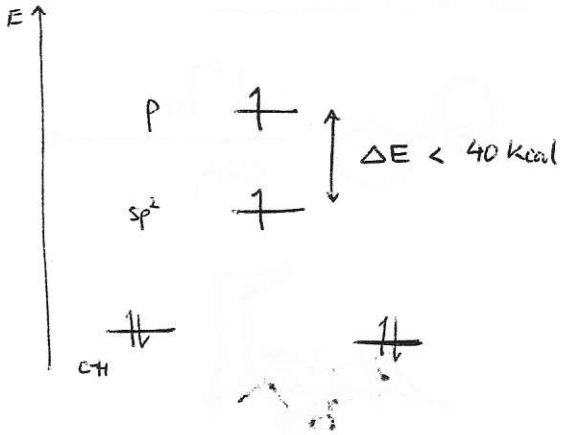
- MO-schemata:

(i) Singulett



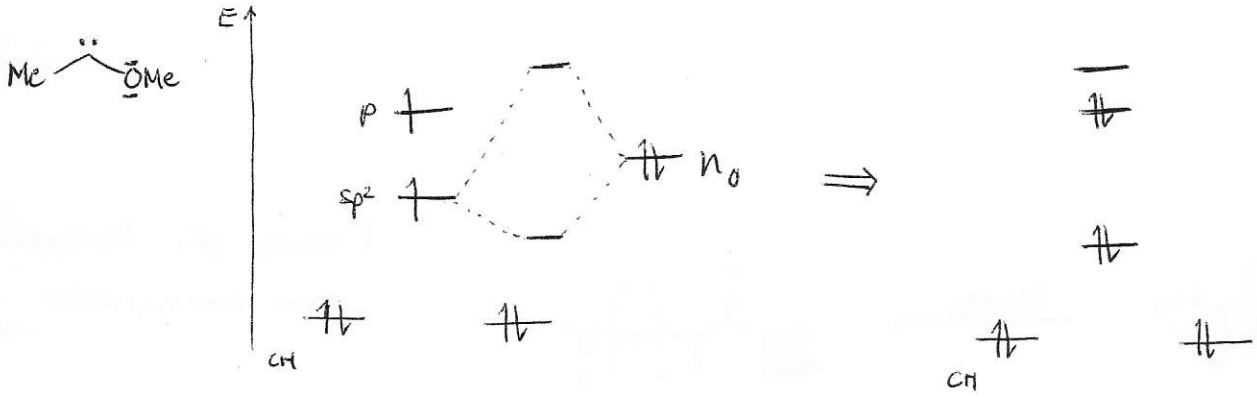
→ da sp^2 → nicht linear

ii) Triplett



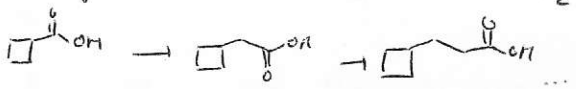
- Spinpaarungsenergie: 40 kcal · mol^{-1}

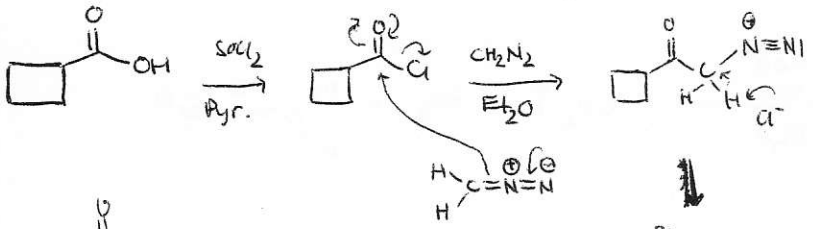
-

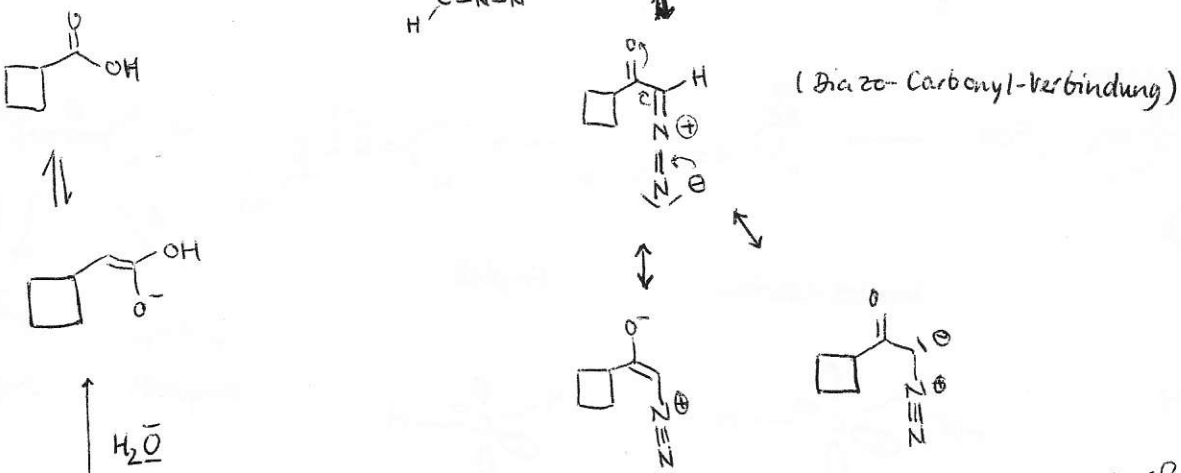


- Arndt-Eistert-Reaction („Homologation-Reaction")

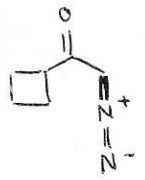
Homologation-Reaction: Einführen von CH_2



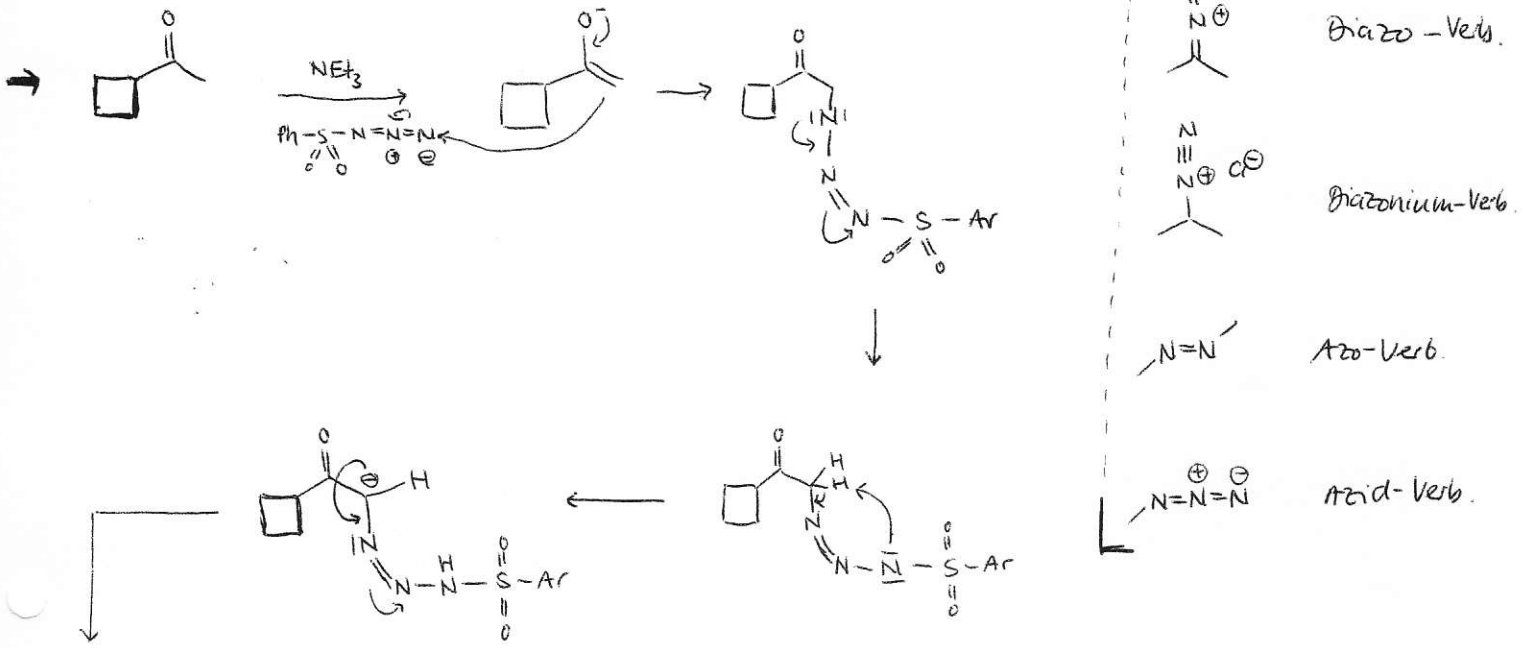


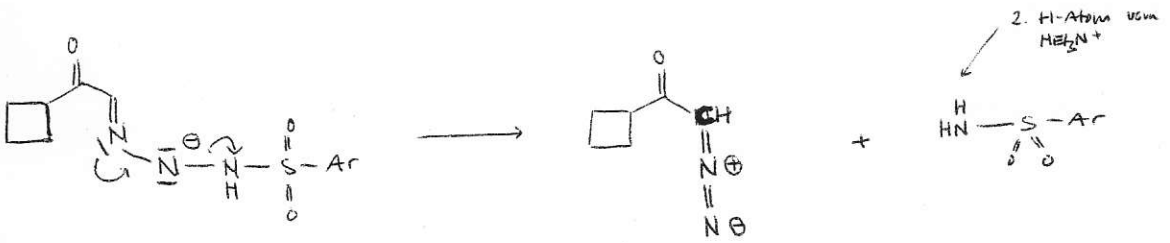


(Diazo-Carbonyl-Verbindung)



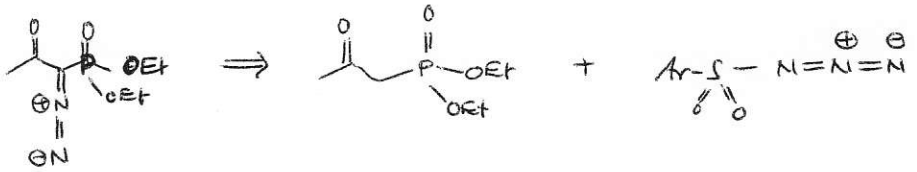
- Direkte Einführung einer Diazo-Gruppe in Carbonyle
- Diazo-Transfer



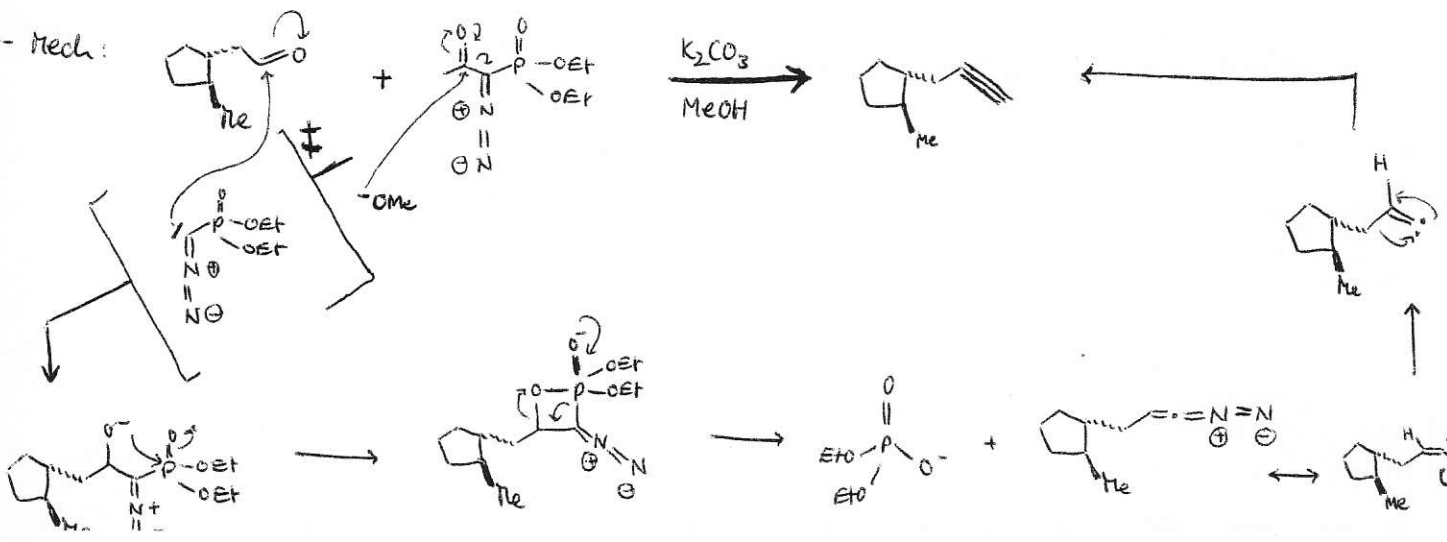


- Corey-Fuchs
- Ohira-Bestman

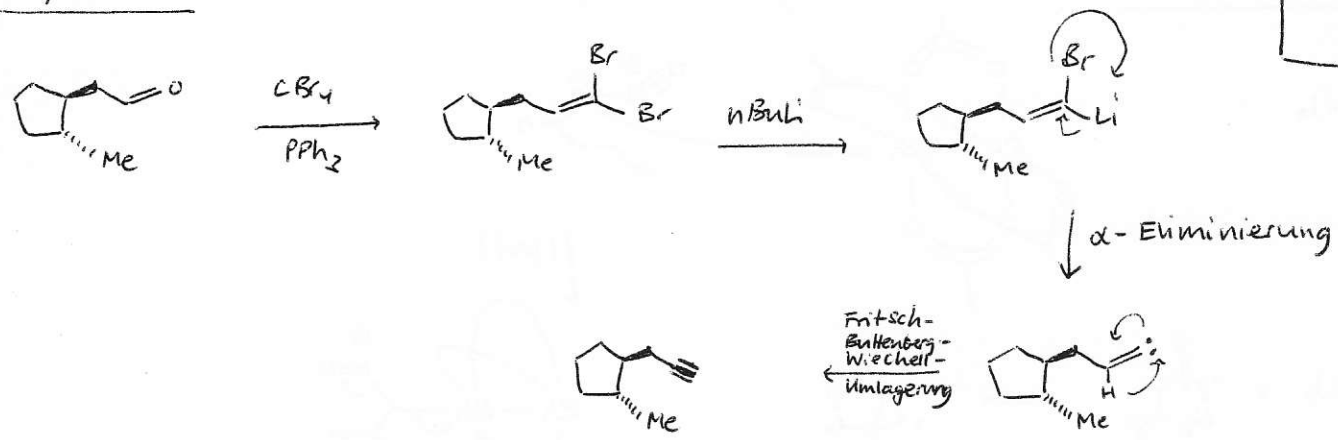
- Ohira-Bestman-Reagenz:



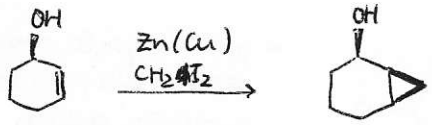
- Mech:



- Corey-Fuchs:

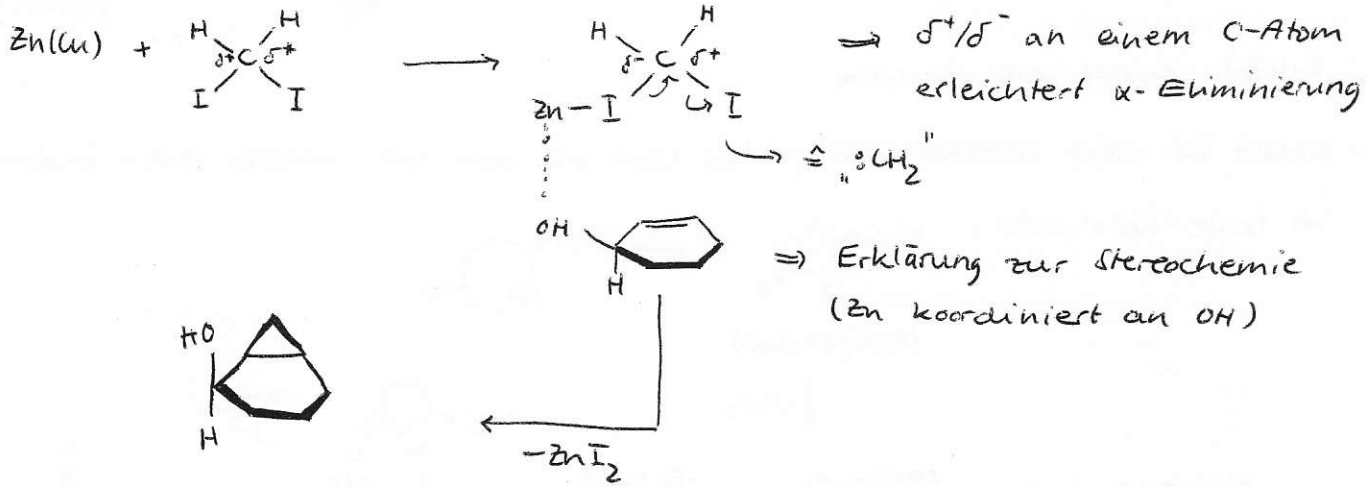


- Simmons-Smith-Reaktion



- Cyclopropylrest hat selbe Stereochemie, wie der Alkohol

Mech:



⇒ δ^+/δ^- an einem C-Atom erleichtert α-Eliminierung

⇒ Erklärung zur Stereochemie (Zn koordiniert an OH)

- Übergangsmetallkomplexe (Carbenoide)

(carben)

→ Ausbildung einer Metall-Kohlenstoffbindung (doppel): $L_nM=$ ← carbenoides C-Atom

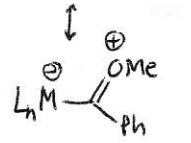
↓ Liganden am Metall

- Fischer-Carbene:

- elektrophil

- 

↕

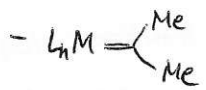


⇒ Resonanzstabilisierung mgl.

- niedrige Ox-Stufe des Metalls

Schrock-Carbene:

- nucleophil

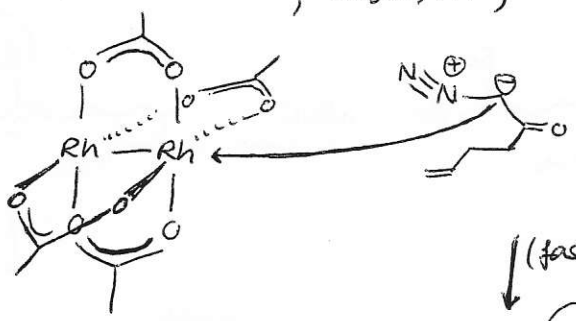
- 

⇒ keine Resonanzstabilisierung mgl., vollkommen andere Reaktivität

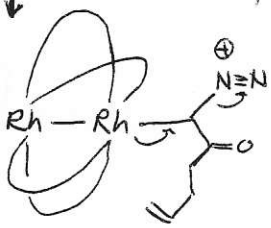
- hohe Ox-Stufe des Metalls

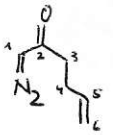
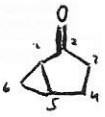
- **Rhodium – Carbenoide** (~1975 ↗, Doyle, M.)

- $Rh_2(OAc)_4$:

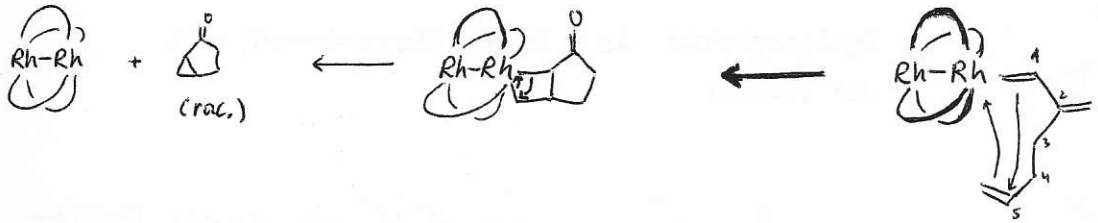


(fast)



- $Rh_2(OAc)_4$ [kat.] +  → 

$\downarrow -N_2$



⇒ gute Ringgröße muss gegeben sein; es herrscht kinetische Reaktion !.
(↳ 5-Ring wird gegenüber größeren Ringen bevorzugt)

- Cu(OTf) liefert selbe Reaktion

- Produkt ist nicht stereokontrolliert, dieses lässt sich aber mit chiralen Resten ändern

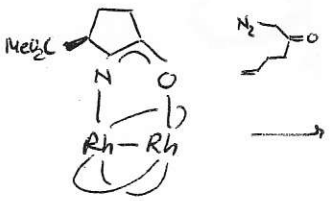
⇒ Doyle-katalysator:

(Pyroglutamat)

$\downarrow CH_2N_2$

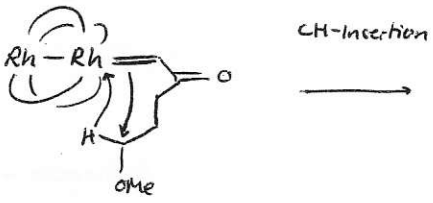
Blockierung d. ⇐ Carbonsäure, koordinierung an Cyclus nur noch über den Ring mgl.

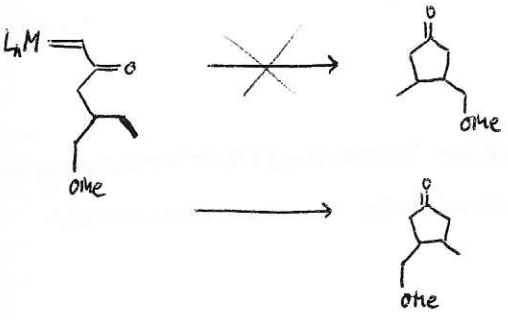
$\xrightarrow{Rh_2(OAc)_4}$



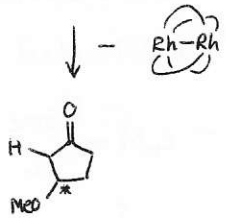
(>90% ee.)

- wenn keine DB im System vorhanden:

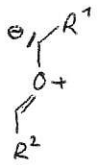


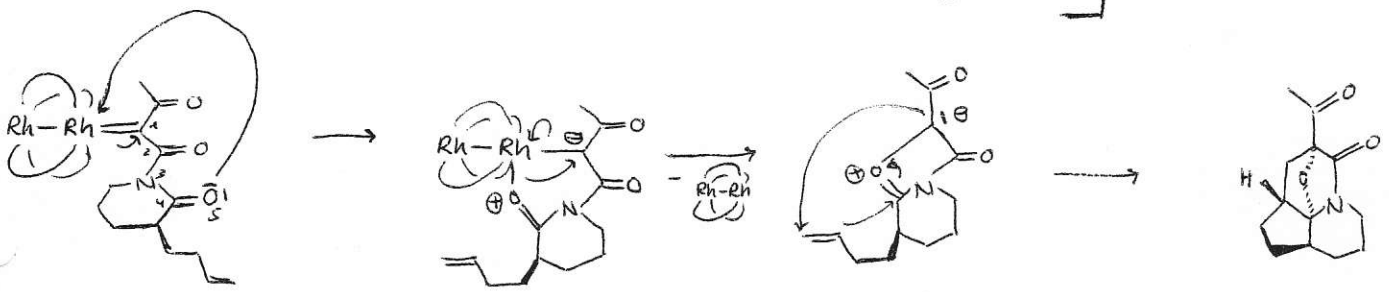


- Insertion erfolgt:
  - möglichst 5-Ring
  - selektiv an dem C-Atom, das das stabilere Carbenium-ion bilden würde.

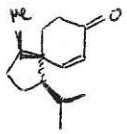


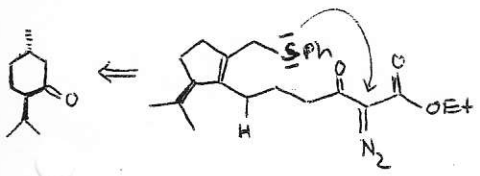
- Ylide: – P-Ylide (Wittig)
  – S-Ylide (Pummer-Reak.; Corey-Chaikowsky) + Stevens-Umlagerung
  – N-Ylide (Cope-Eliminierung) + Sommelet-Hauser
  – O-Ylide (Carbonyloxid; Carbonylylid; Ozonolyse; 1,3-dipolare Cycloaddition)

Carbonyloxid:  ; Carbonylylid: 



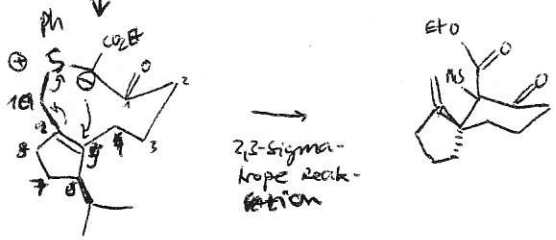
- Stevens-Umlagerung

Ziel:  (Acorenon B)



- Möglichkeiten: · CH-Insertion an 1,5
  · Cyclopropanierung an 1,6
  · Angriff des Schwefels → bevorzugt, hier ungl., da S d-Elektronen vorhanden (obwohl ungünstige Ringgröße)

$Rh_2(OAc)_4$



„Stevens-Rearrangement"

Klausur: 28.03. – 31.03.

10°° Uhr (2h)

(10 Fragen)

RM
10-01-2011
(1) EN

Übergangsmetallkatalysierte Reaktionen

- Rhodium: - Metallcarbenes (Cyclopropanations; C-H-insertions; Carbonylylids → 1,3-dipolar CA)
  - Asymmetric Hydrogenation of Alkens
  - Hydroformylation reaction

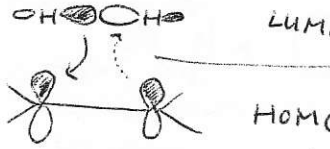
(1) Asymmetic Hydrogenation:

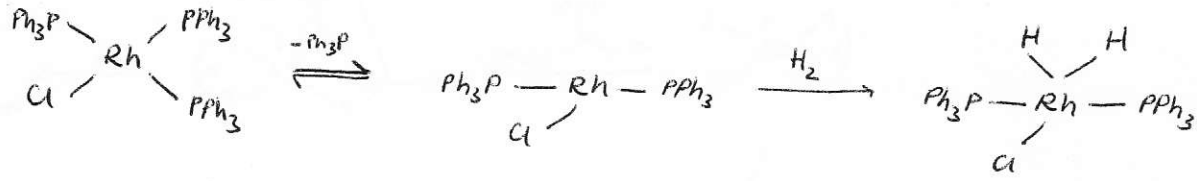
- Wilkinson: $(PPh_3)_3RhCl$

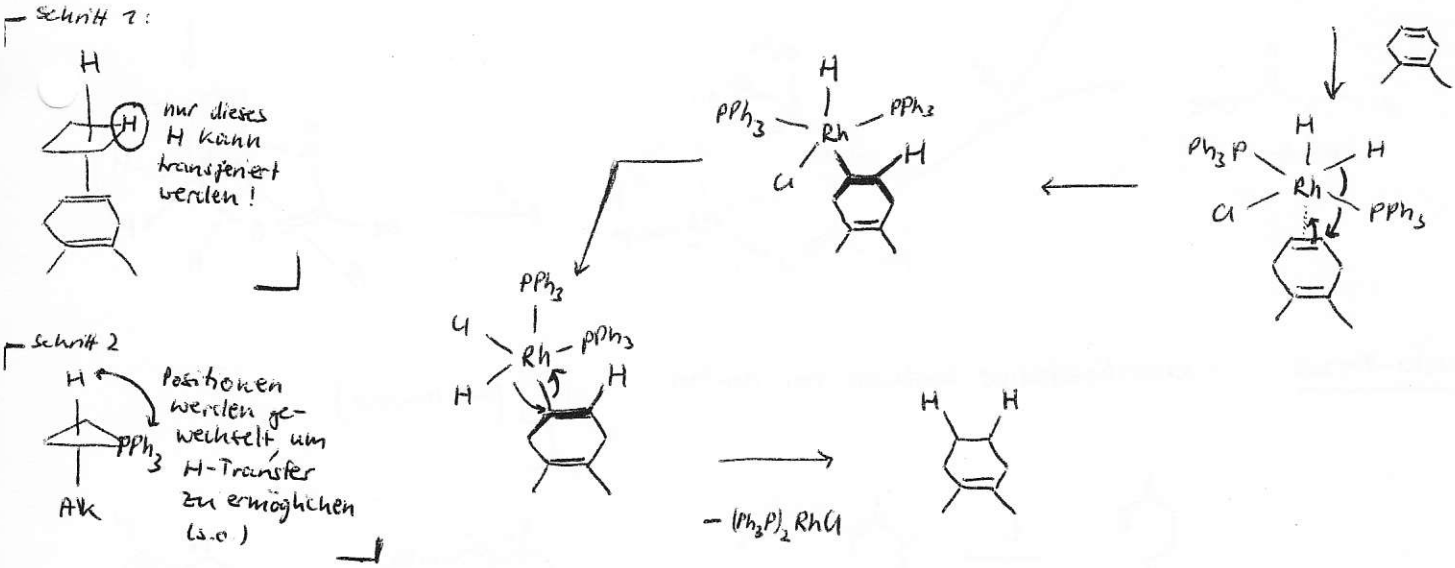
→ less substitued is hydrogenated

- Conditions: 25 °C; 1 bar H_2

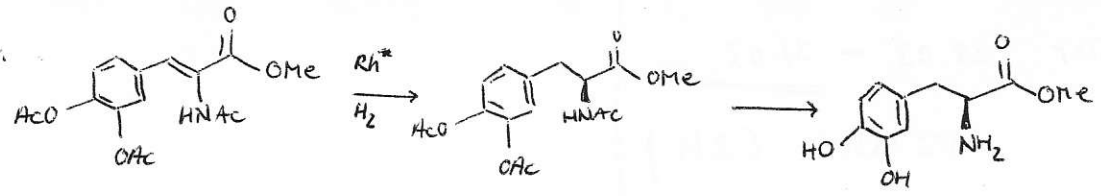
→ Warum Kat. nötig?







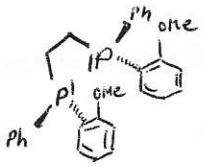
- **Monsanto-Prozess**

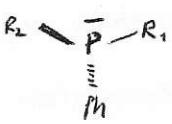


- 1. Schritt der Reaktion ähnlich zur Wilkinson-Reak. (L-Dopa)
- genutzter Kat.: $[Rh(DiPAMP)COD]\,BF_4$

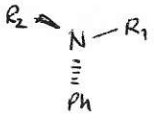
COD = Cyclooctadien

DiPAMP =

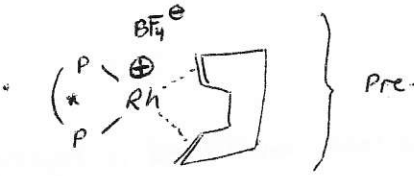




konfigurationsstabil



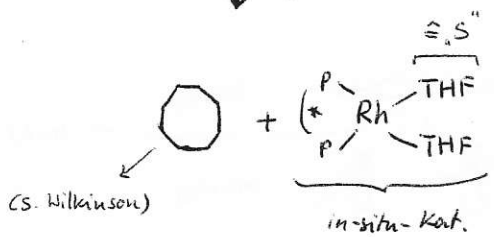
nicht konfigurationsstabil!



Pre-Kat.

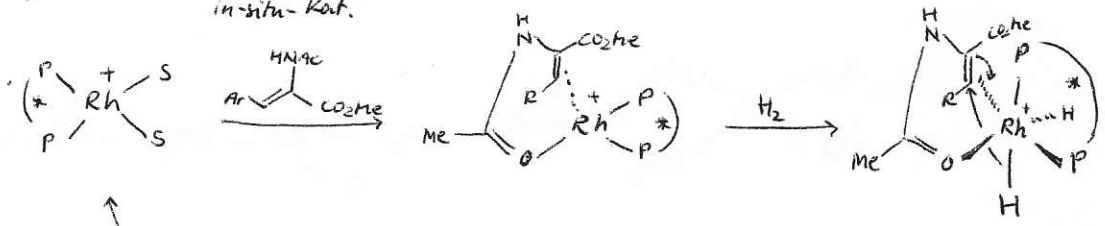
H_2, THF

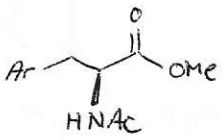
auch konfigurationsstabil

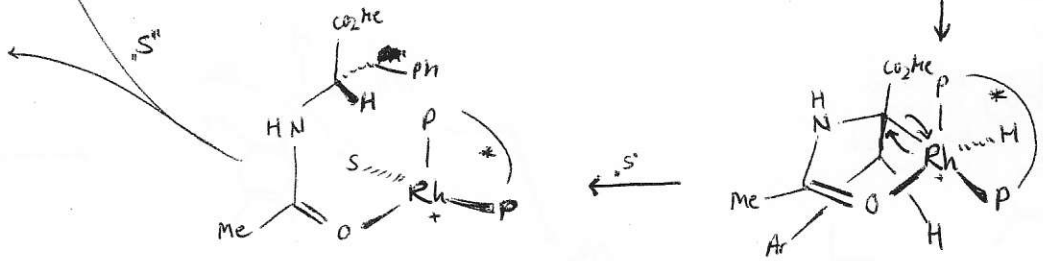


(s. Wilkinson)

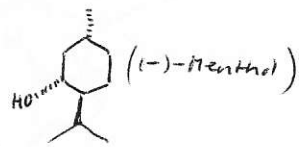
in-situ-Kat.



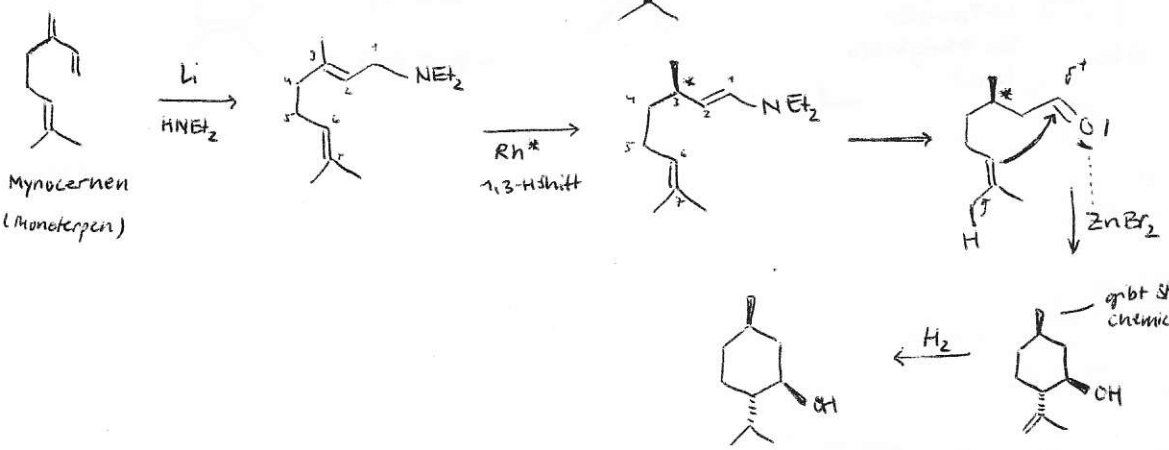




- **Tagasako-Prozess**: • enantioselektive Synthese von Menthol

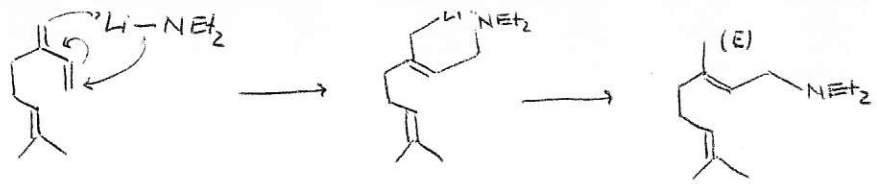


(-)-Menthol



Myrcennen (Monoterpen)

(Forts.) • Mech.:



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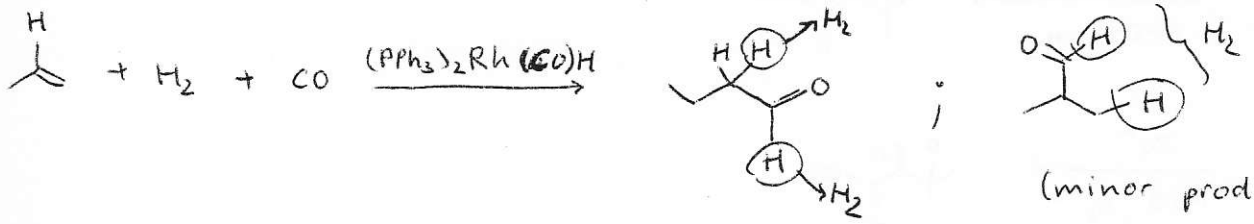
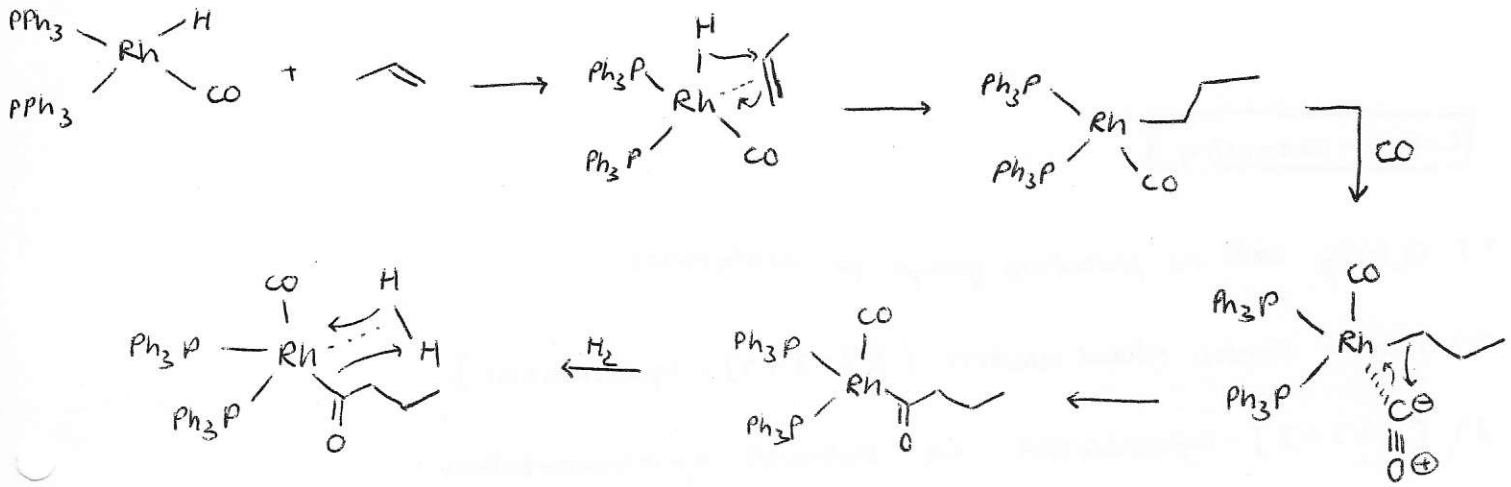
(2)

• Mech. Hydrogenierung: selber Kat. wie im Monsanto-Prozess



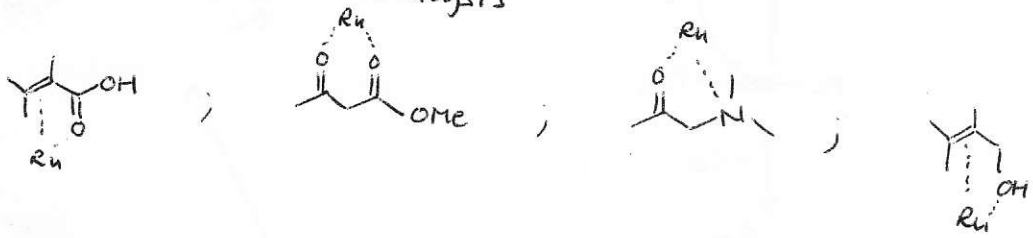
(minor product)



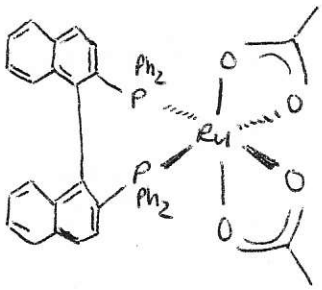
Noyori - Transfer Hydrogenation

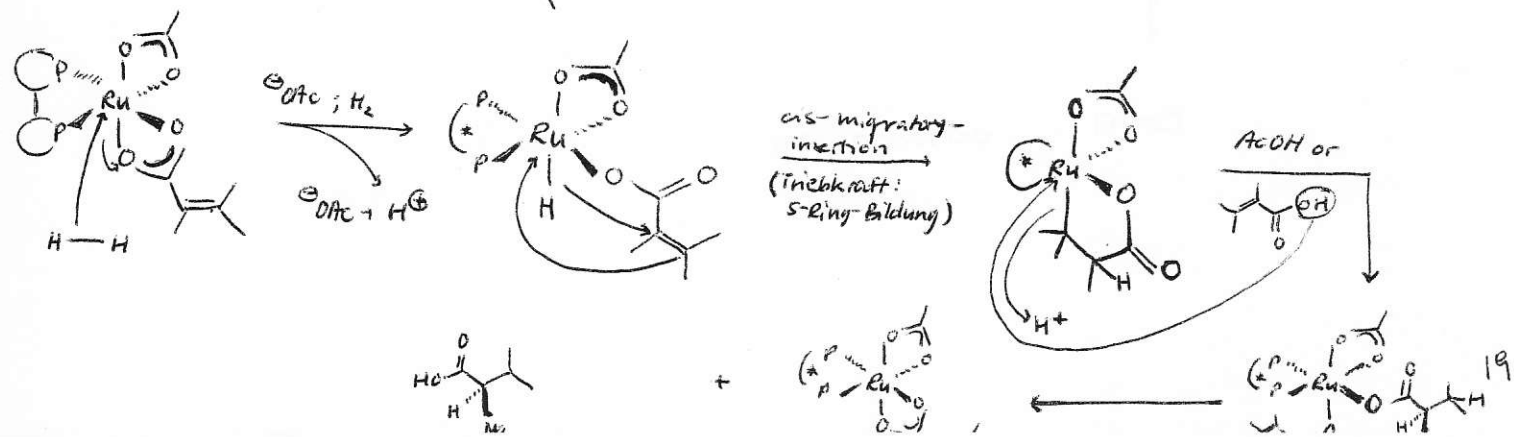
1.) Ru; H_2; chiral ligands

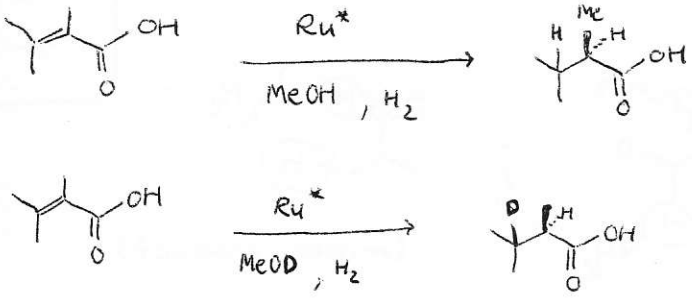
2.) Substrate chelats to catalysts



- last common: [(R)-BINAP-Ru(OAc)$_2$]







Cobalt-Chemistry

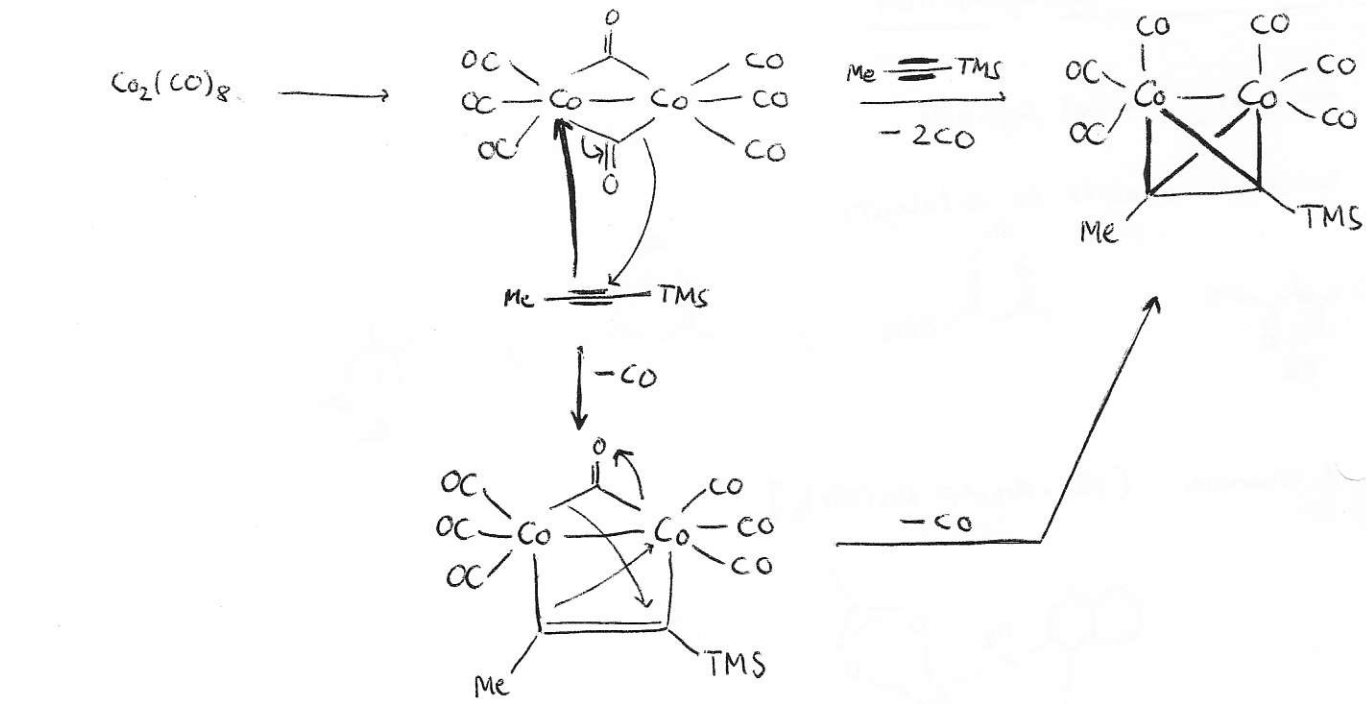
1.) $Co_2(CO)_8$ acts as protecting group for acetylenes

2.) PKR = Pauson Khand reaction ([2+2+1] - cycloaddition)

3.) [2+2+2] - cycloaddition → Vollhardt cyclotrimerization

4.) Nickolas-Reaction

zu 1.)



- $^{\ominus}C\equiv O^{\oplus}$ dipolar form

$\updownarrow$

$C=O$ carbenoid form

Cobalt mediated cyclizations

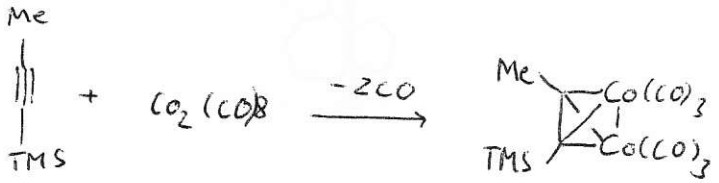
i) Protecting group

ii) Nicholas reaction

iii) Pauson Khanol

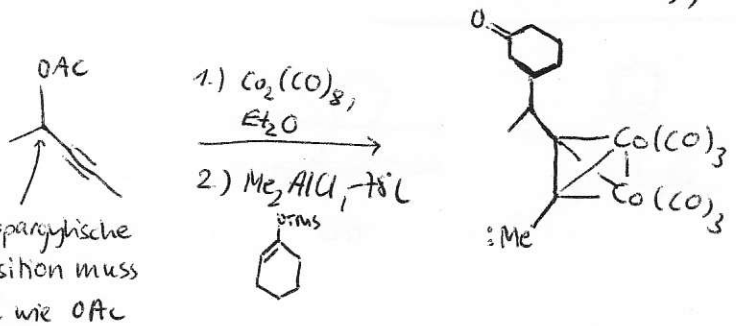
iv) [2+2+2] - Vollhardt cyclo-trimerization

i)



(Freisetzung des Alkins durch oxidative Aufarbeitung)

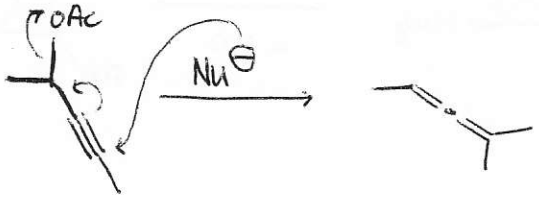
ii) Nicholas Reaction:



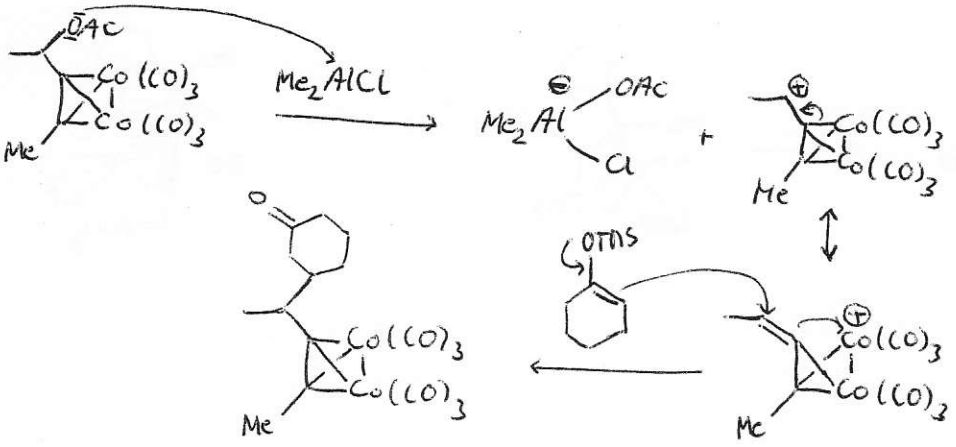
propargylische Position muss Gr. wie OAc vorhanden sein

- „nucleophile Substitution"

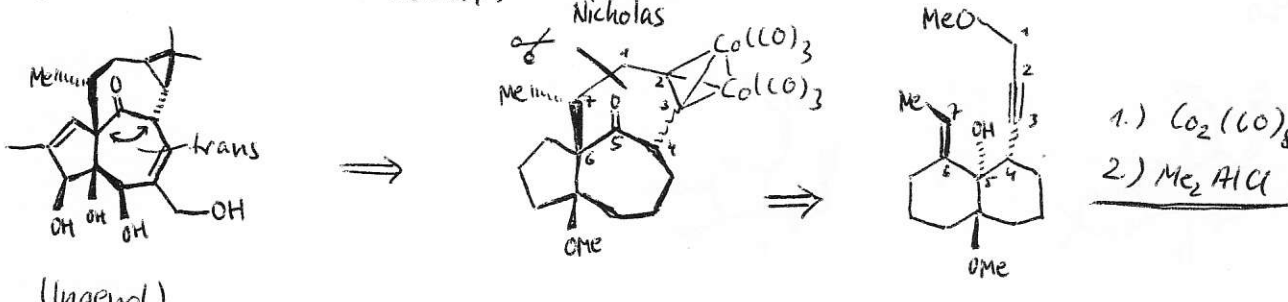
- Konkurrenzreaktion: S_N2'



- Mechanismus:

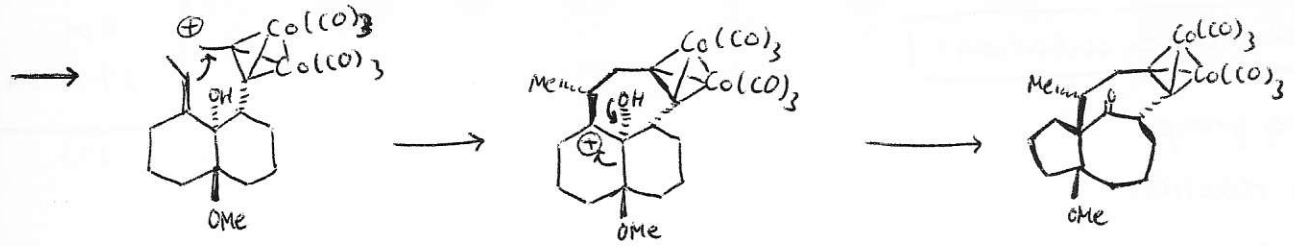


- Ingenol / Nicholas-Reaktion:



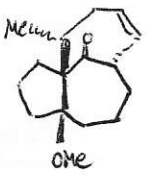
(Ingenol)

20

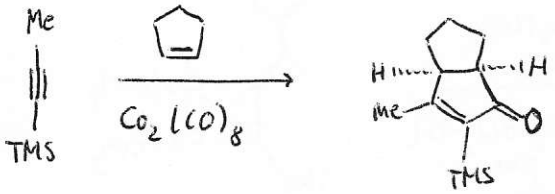


wie Pinakol-Umlagerung

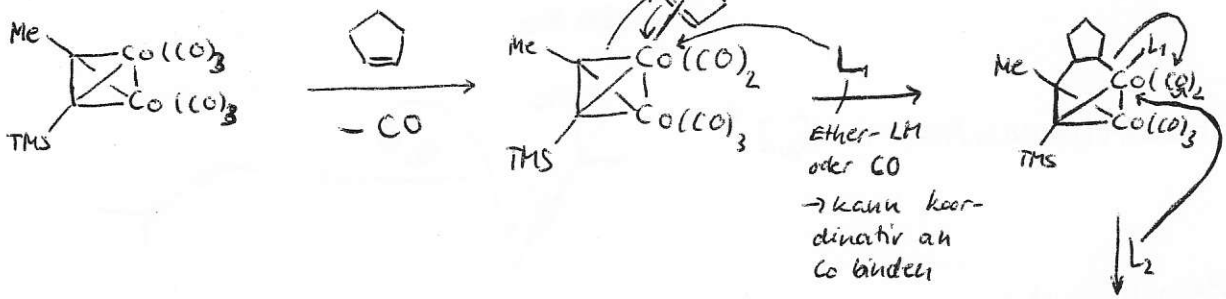
↓ Li, NH_3 (fl.)



iii) Pauson - Khand - Reaktion

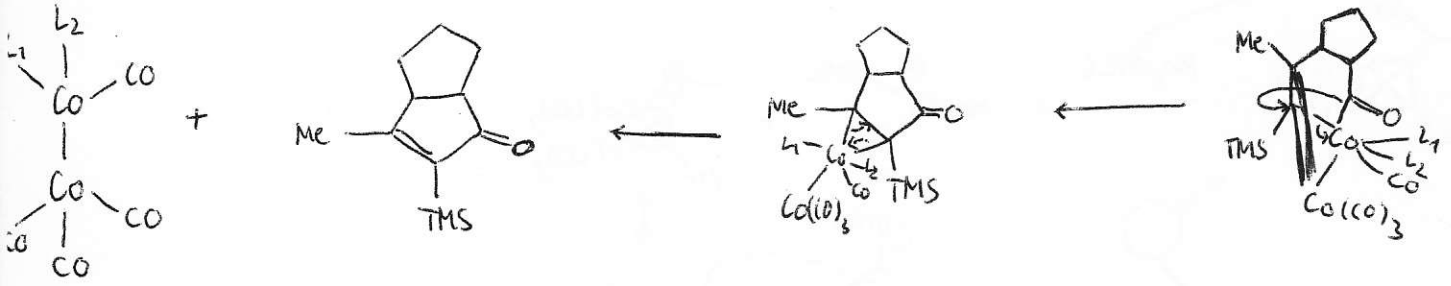


Mech.:

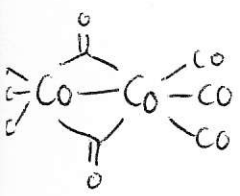


Alkin setzt sich an das CO, welches neben dem kleineren Substr. sitzt

Ether-LM oder CO → kann koordinativ an Co binden

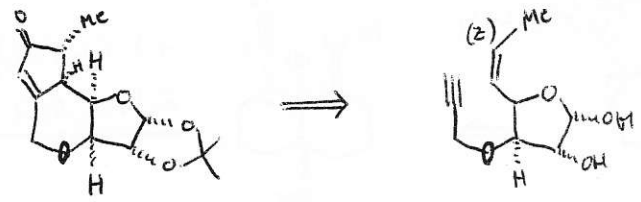


↓ CO-Druck, 70-80°C



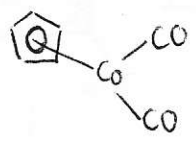
⇒ unter CO-Druck katalytisches Arbeiten mgl.

Bsp.:

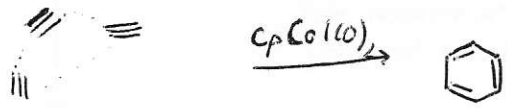


iv) [2+2+2] - Cyclotrimerisation (Vollhardt K.P.C.)

- Komplex:

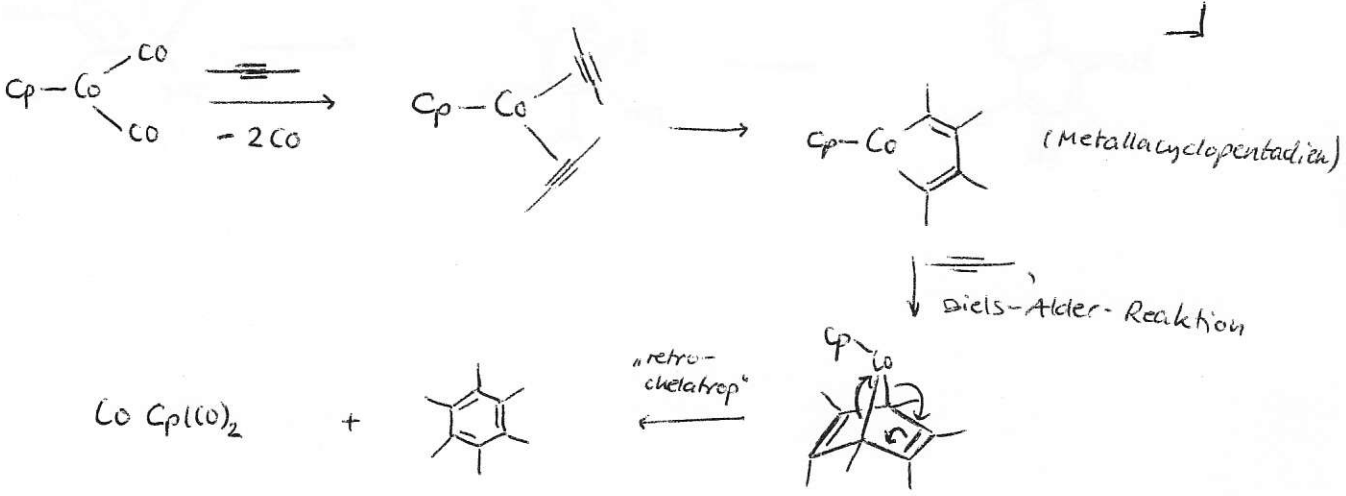


- formal:

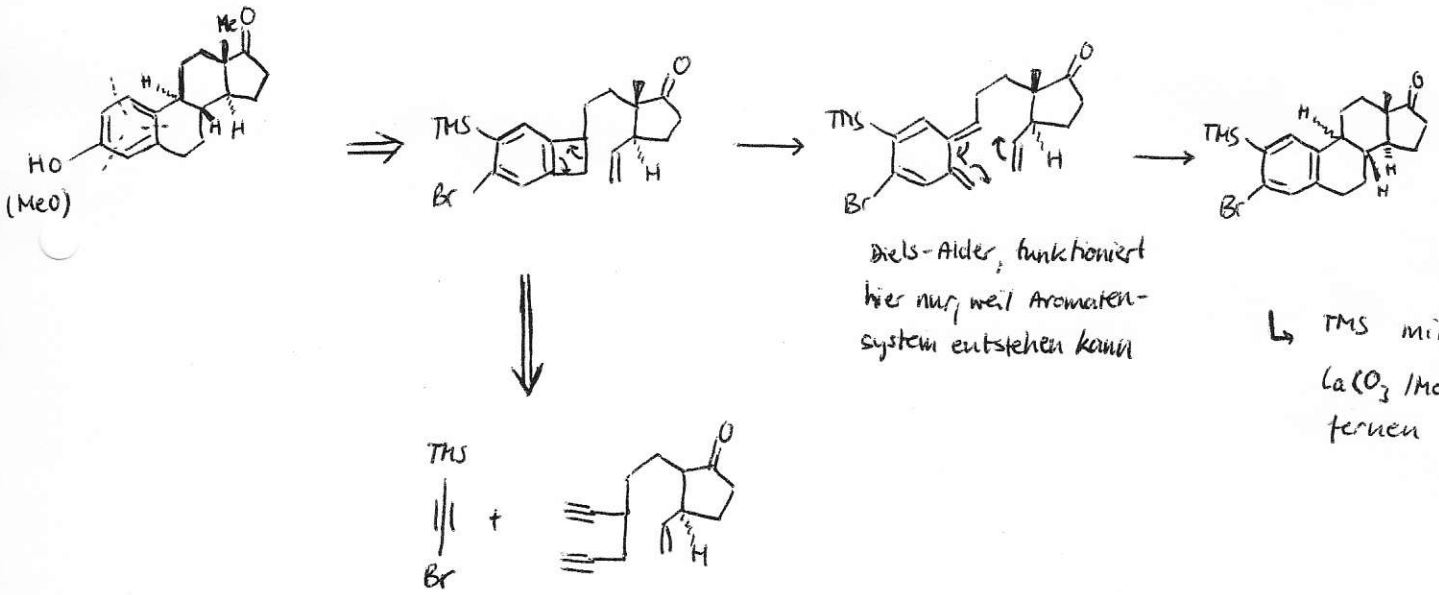


Ähnlichkeit zum Reppe-Prozess

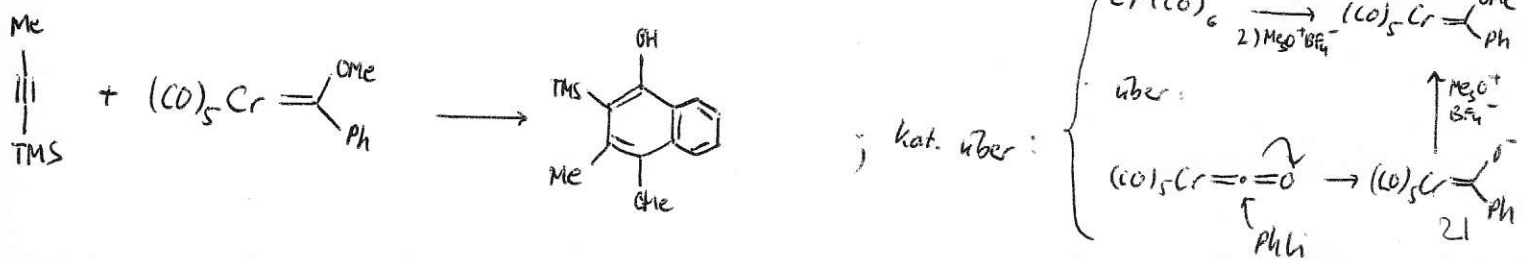
- Mech.:



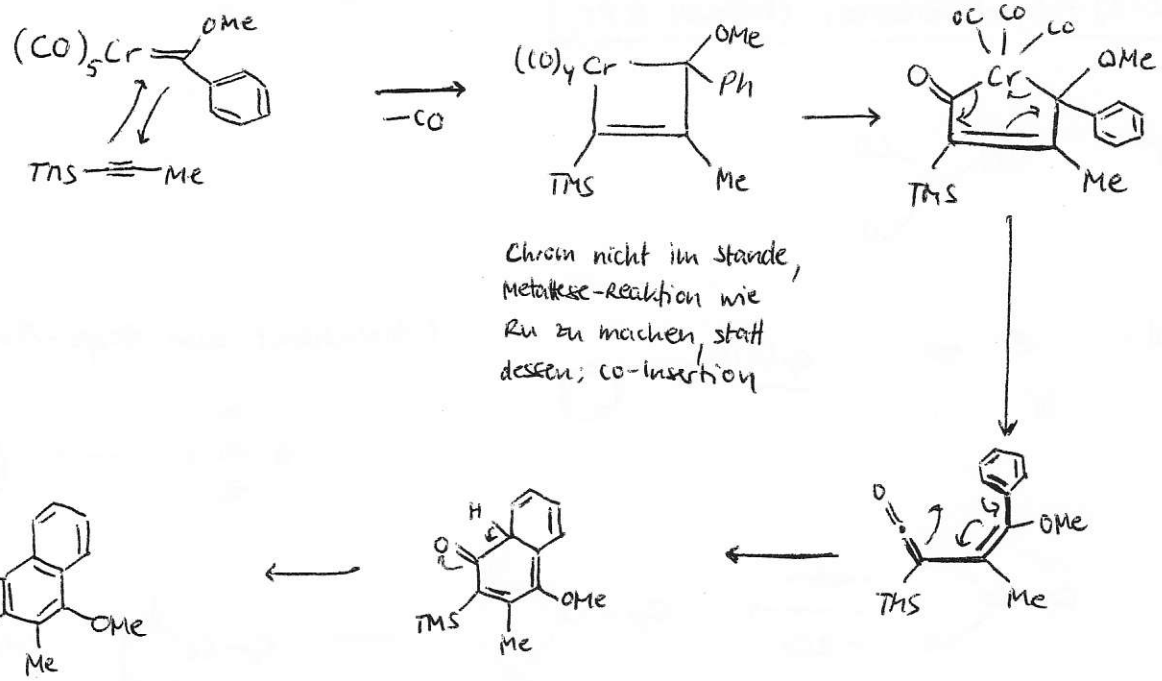
- Ergosteron (mittels [2+2+2])



- Dötz-Reaktion



Mech.:


(CO)5Cr
OMe
TMS
Me
−CO
(CO)4Cr
OMe
Ph
TMS
Me
OC CO CO
Cr
OMe
O
TMS
Me
Chrom nicht im Stande, Metathese-Reaktion wie Ru zu machen, statt dessen; CO-Insertion
O
C
OMe
TMS
Me
H
O
OMe
TMS
Me
HO
OMe
TMS
Me