Reaktionsmechanismen

in der

für Fortgeschrittene

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Literatur

M.B. Smith, J. March: March‘s Advanced Organic Chemistry, Reactions Mechanisms and Structure,
5.Auflage, Wiley, 2001 (168 DM)

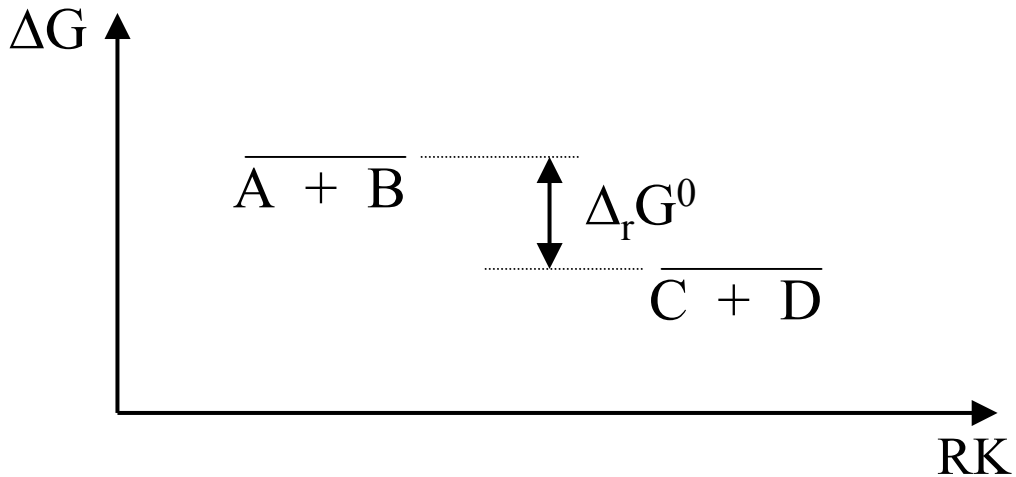
R.Brückner: Reaktionsmechanismen, Stereochemie, moderne Synthesemethoden,
Spektrum Akad. Verlag, 1996 (79.90 DM)

P.Sykes: Reaktionsmechanismen der Organischen Chemie,
Wiley-VCH, 1988 (68.26 DM)

1. Aufklärung von Reaktionsmechanismen

1.1 Thermodynamische Aspekte

$$\Delta_r G^0 = \Delta_r H^0 - T \cdot \Delta_r S^0 \qquad < 0$$



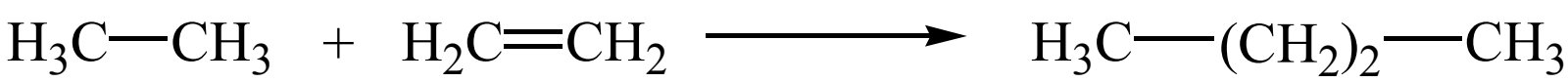
$$\Delta_r H^0 = \sum \Delta_f H^0_{(\text{Produkte})} - \sum \Delta_f H^0_{(\text{Edukte})}$$

$$\approx \sum \text{BDE (gebrochene Bindungen)}$$

$$- \sum \text{BDE (gebildete Bindungen)}$$

BDE = Bindungsdissoziationsenergie

Thermodynamische Aspekte: Beispiel



$\Delta_f H^0$	- 86.6	52.3	- 126.4	[kJ/mol]
S^0	230	219	310	[J/mol K]

$\Delta_r H^0 = -92.1$ kJ/mol

$\Delta_r S^0 = -139$ J/mol K

$\Delta_r G^0_{300} = -50.4$ kJ/mol

BDE	$C\overset{\pi}{=}C$	$C\overset{\sigma}{-}C$	
	248	343	[kJ/mol]

$\Delta_r H^0 \approx -95$ kJ/mol

1.2 Kinetische Untersuchungen

S_N1-Reaktion:

$$R-X \quad + \quad Y^- \quad \rightarrow \quad R-Y \quad + \quad X^-$$

$$-\frac{d[RX]}{dt} = k_{exp} \cdot [RX] \qquad \text{zu Beginn}$$

$$-\frac{d[RX]}{dt} = k'_{exp} \frac{[RX] \cdot [Y^-]}{[X^-]} \qquad \text{im Verlauf}$$

S_N1-Reaktion

$$R{-}X \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} R^+ + X^- \qquad \text{langsam}$$

$$R^+ + Y^- \xrightarrow{k_2} R{-}Y \qquad \text{schnell} \quad k_2 >> k_1$$

$$\frac{d[RY]}{dt} = k_2[R^+][Y^-] \qquad (1)$$

$$\frac{d[R^+]}{dt} = k_1[RX] - k_{-1}[R^+][X^-] - k_2[R^+][Y^-] = 0 \qquad (2)$$

Quasistationaritätsbedingung (Bodenstein)

$$[R^+] = \frac{k_1[RX]}{k_{-1}[X^-] + k_2[Y^-]} \qquad \text{Konkurrenzreaktion} \qquad (2a)$$

$$\frac{d[RY]}{dt} = -\frac{d[RX]}{dt} = \frac{k_1 k_2[RX][Y^-]}{k_{-1}[X^-] + k_2[Y^-]} \qquad (2a) \text{ in } (1)$$

S_N1-Reaktion

Zwei Extremfälle:

a) $k_{-1}[X^-] \ll k_2[Y^-]$ zu Beginn

$$\frac{d[RY]}{dt} = -\frac{d[RX]}{dt} = k_1[RX] \quad \Rightarrow \quad k_1 = k_{exp}$$

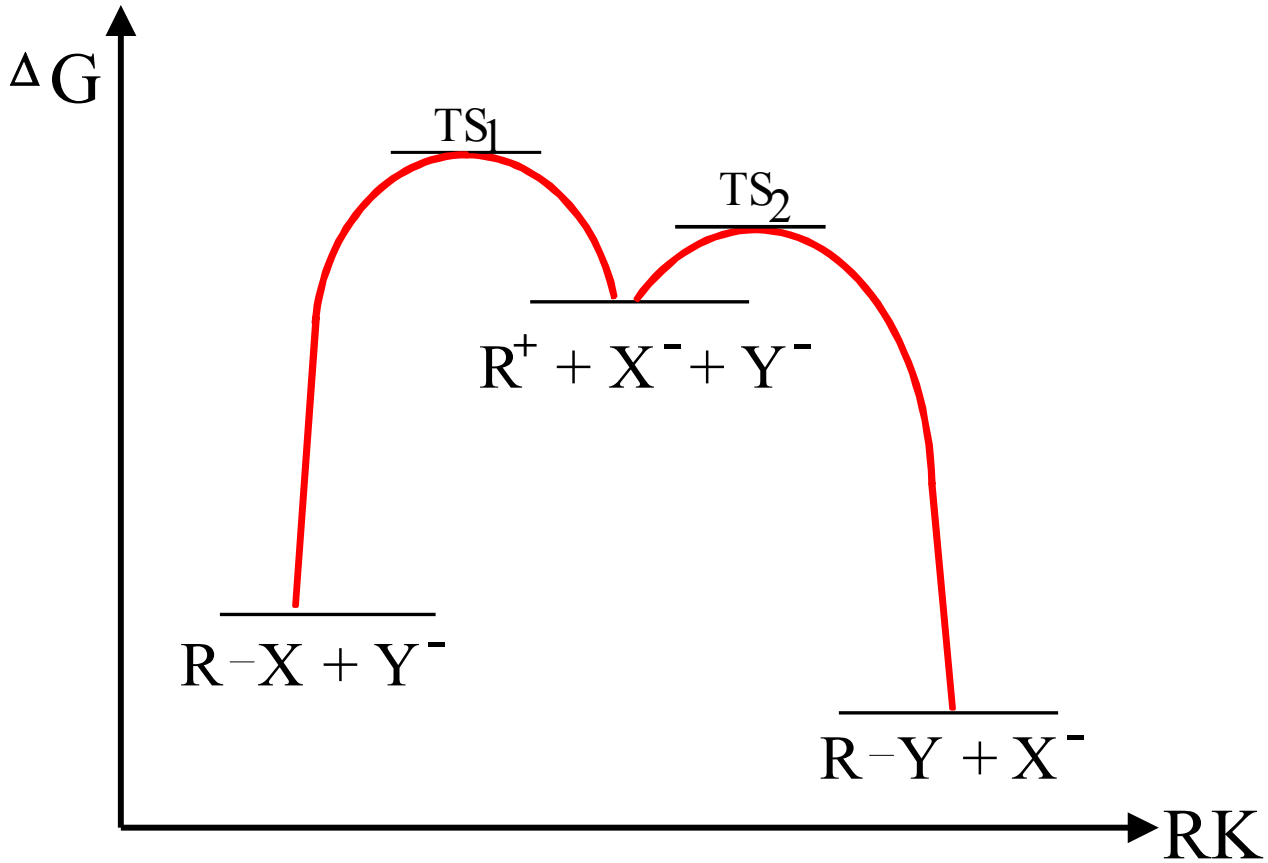
b) $k_{-1}[X^-] \gg k_2[Y^-]$ gegen Ende

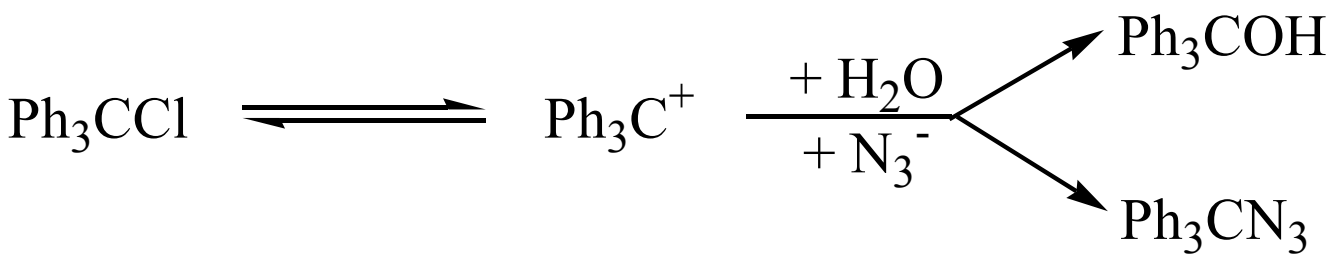
$$\frac{d[RY]}{dt} = -\frac{d[RX]}{dt} = \frac{k_1 \cdot k_2[RX][Y^-]}{k_{-1}[X^-]} \quad \Rightarrow \frac{k_1 \cdot k_2}{k_{-1}} = k'_{exp}$$

Überstöchiometrischer Zusatz von Y^- : Fall a)

Zusatz von X^- : Fall b)

Reaktionsdiagramm





Konkurrenzreaktion

$$\frac{d[RX]}{dt} = k_x[R^+][X^-]$$

$$\frac{d[RY]}{dt} = k_y[R^+][Y^-]$$

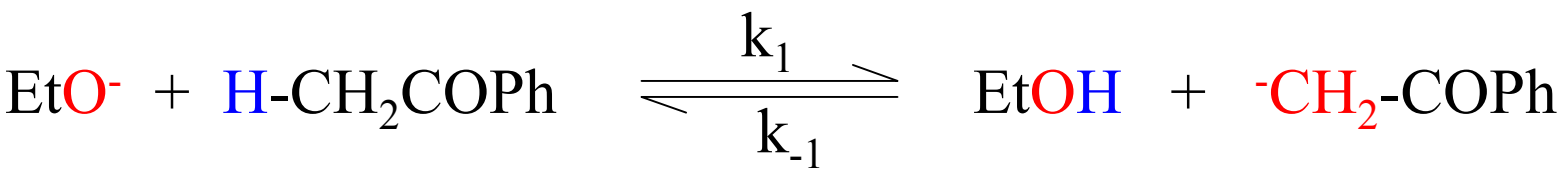
$$\frac{d[R_x]}{d[R_y]} = \frac{k_x[X^-]}{k_y[Y^-]}$$

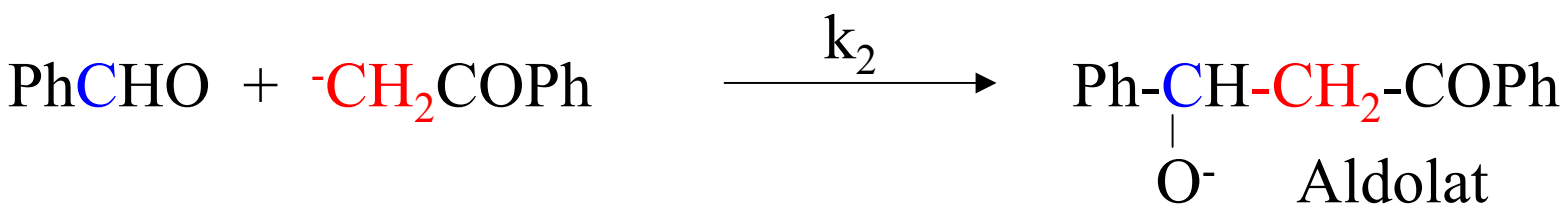
$$\frac{k_x}{k_y} \equiv \text{Konkurrenzkonstante}$$

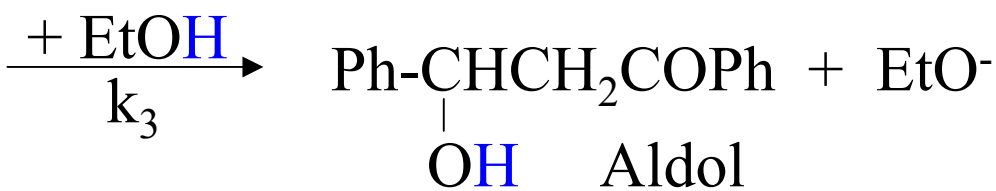
$$S \equiv \log\left(\frac{k_x}{k_y}\right) \qquad \text{Selektivität}$$

Aldoladdition

$$\frac{d[\text{Aldol}]}{dt} = k_{exp}\,[\text{PhCHO}][\text{PhCOMe}][\text{EtO}^-]$$







Aldoladdition

$$\frac{d[Aldol]}{dt} = k_3[Aldol^-][EtOH] \quad (1)$$

$$\frac{d[Aldol^-]}{dt} = k_2[PhCHO][^-CH_2COPh] - k_3[Aldol^-][EtOH] = 0 \quad (2)$$

$$[Aldol^-] = \frac{k_2[PhCHO][^-CH_2COPh]}{k_3[EtOH]} \quad (2a)$$

$$\frac{d[^-CH_2COPh]}{dt} = k_1[EtO^-][MeCOPh] - k_{-1}[EtOH][^-CH_2COPh]$$

$$- k_2[PhCHO][^-CH_2COPh] = 0 \quad (3)$$

$$[^-CH_2COPh] = \frac{k_1[EtO^-][MeCOPh]}{k_{-1}[EtOH] + k_2[PhCHO]} \quad (3a)$$

Aldoladdition

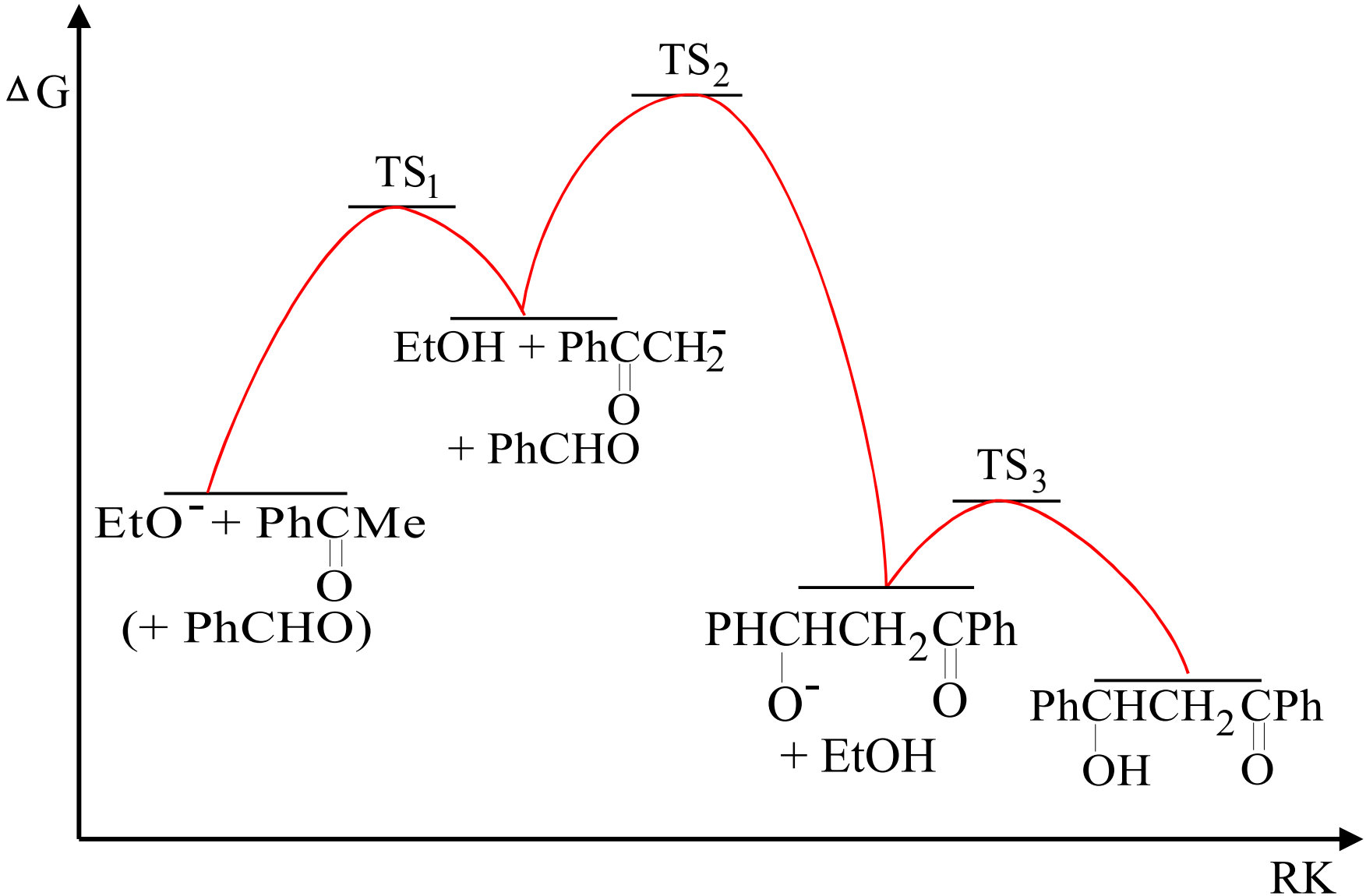
$$[\text{Aldol}^-] = \frac{k_2[\text{PhCHO}] \cdot k_1[\text{PhCOMe}][\text{EtO}^-]}{k_3[EtOH](k_{-1}[\text{EtOH}] + k_2[\text{PhCHO}])} \qquad \text{(3a) in (2a)}$$

$$\frac{d[\text{Aldol}]}{dt} = \frac{k_1 \cdot k_2 \cdot \cancel{k_3}[\text{PhCHO}][\text{PhCOMe}][\text{EtO}^-]\cancel{[\text{EtOH}]}}{\cancel{k_3[\text{EtOH}]}(k_{-1}[\text{EtOH}] + k_2[\text{PhCHO}])} \qquad (4)$$

$$k_{-1}[\text{EtOH}] \quad >> \quad k_2[\text{PhCHO}]$$

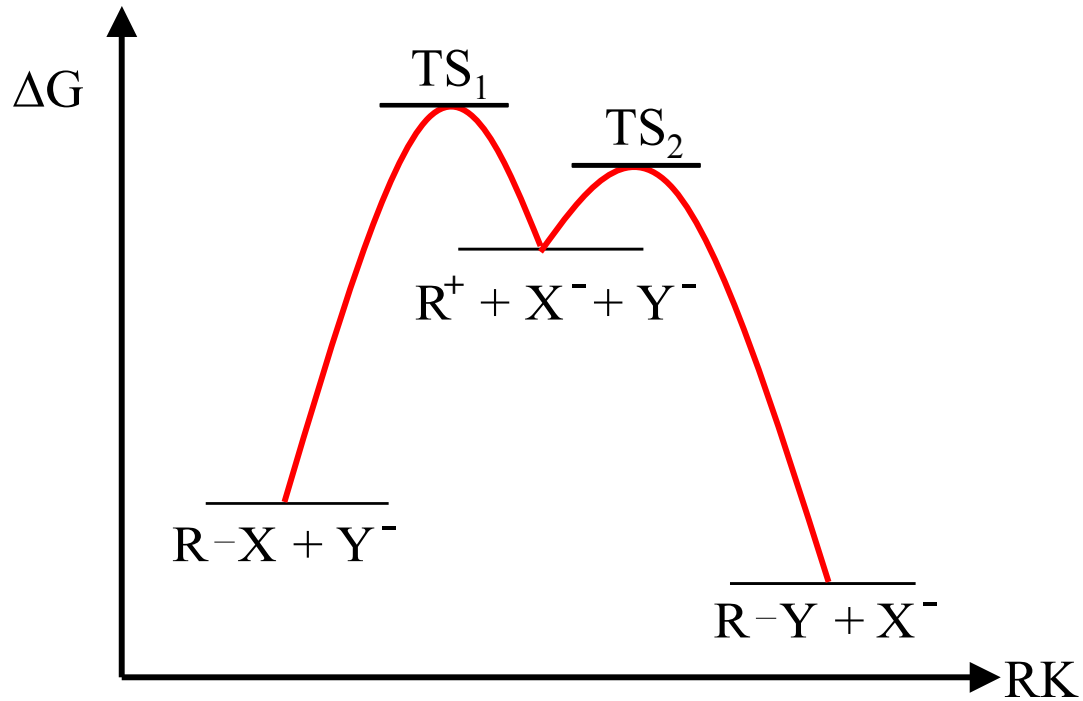
$$k_{exp} = \frac{k_1 \cdot k_2}{k_{-1}[\text{EtOH}]}$$

Reaktionsdiagramm der Aldoladdition



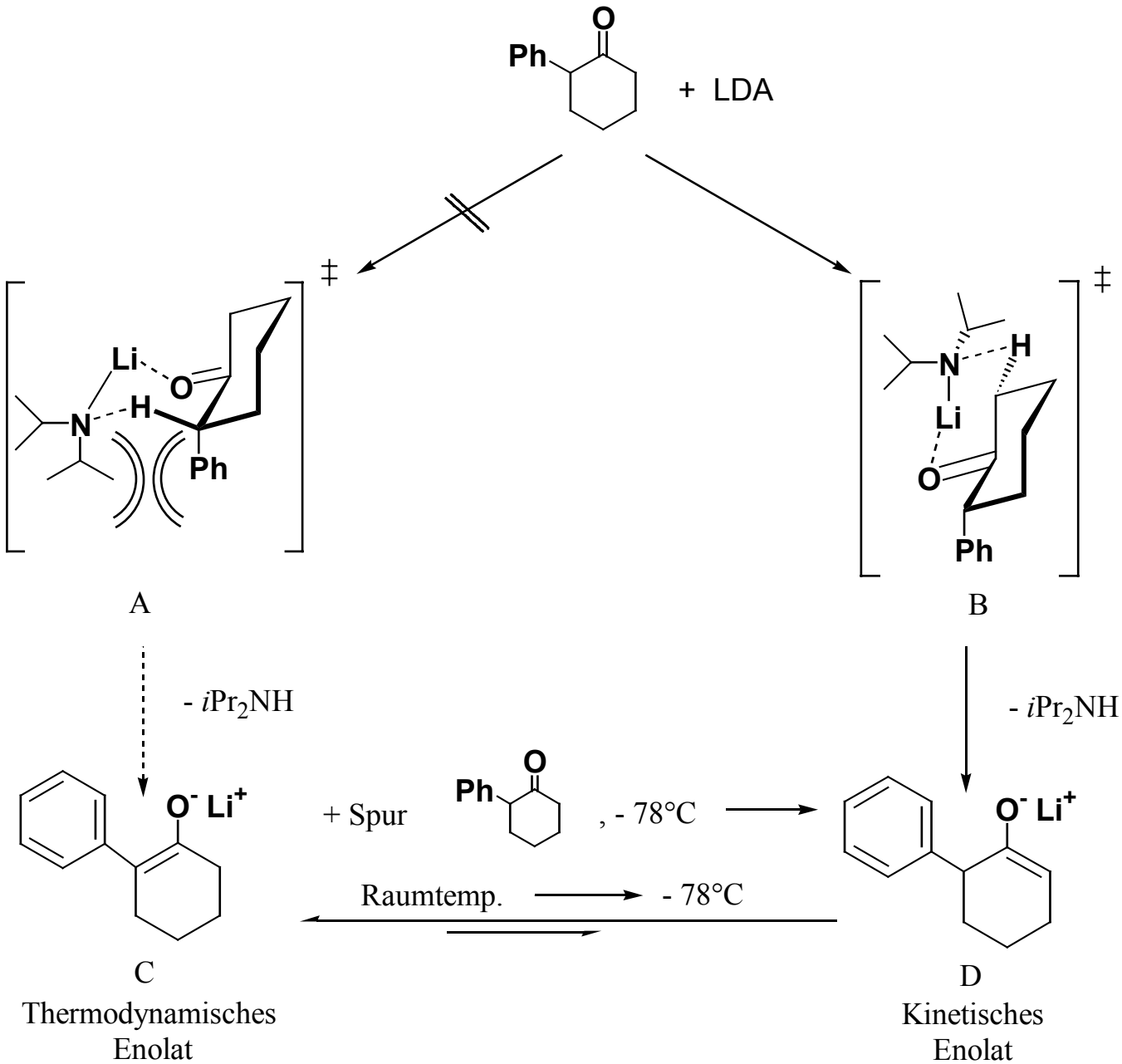
Prinzip der mikroskopischen Reversibilität

Bei einer reversiblen Reaktion verlaufen Hin- und Rückreaktion auf demselben Reaktionsweg, d.h. nach demselben Mechanismus.

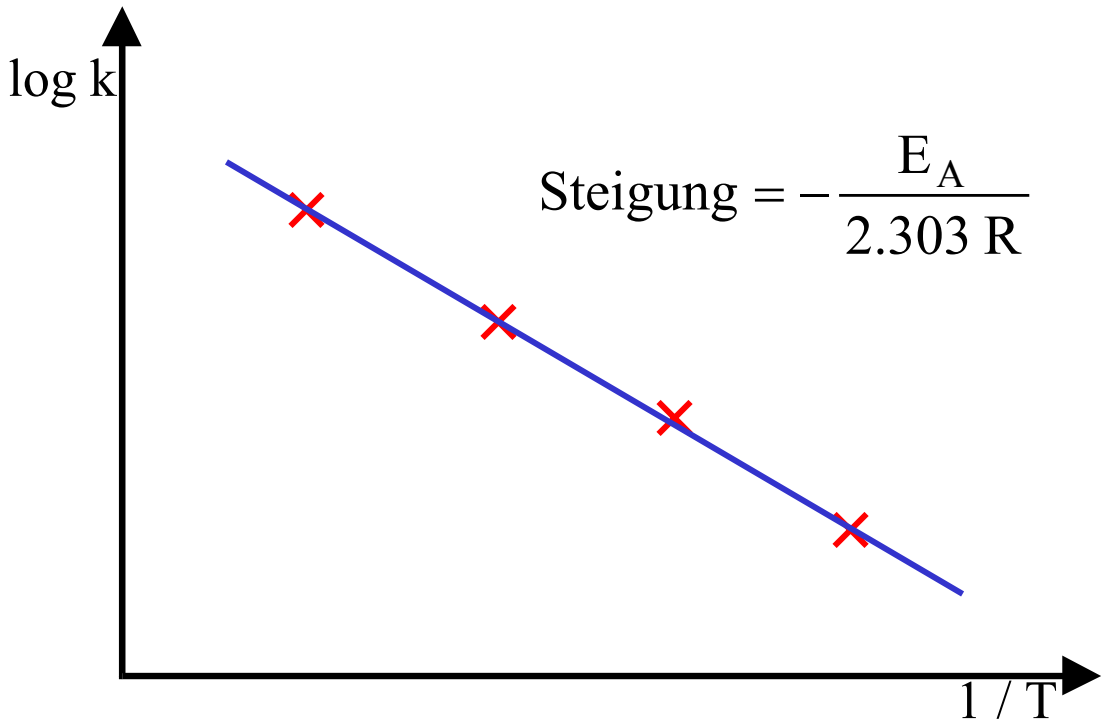


Hammond-Postulat

Die Geometrie des Übergangszustandes ähnelt mehr der Seite der Reaktion (Edukt bzw. Produkt), der er bezüglich der Freien Enthalpie näher ist.


Ph
O
+ LDA
‡
Li
O
N
H
Ph
A
‡
N
H
Li
O
Ph
B
- iPr$_2$NH
- iPr$_2$NH
O$^-$ Li$^+$
+ Spur
Ph
O
, - 78°C
O$^-$ Li$^+$
Raumtemp.
- 78°C
C
Thermodynamisches
Enolat
D
Kinetisches
Enolat

1.2 Kinetische Untersuchungen: Temperaturabhängigkeit von k



Arrhenius-Gleichung (1889) (Svante Arrhenius 1859 - 1927)

$$\log k = \log A - \frac{E_A}{2.303\ RT}$$

$$k = A \cdot e^{-E_A/RT}$$

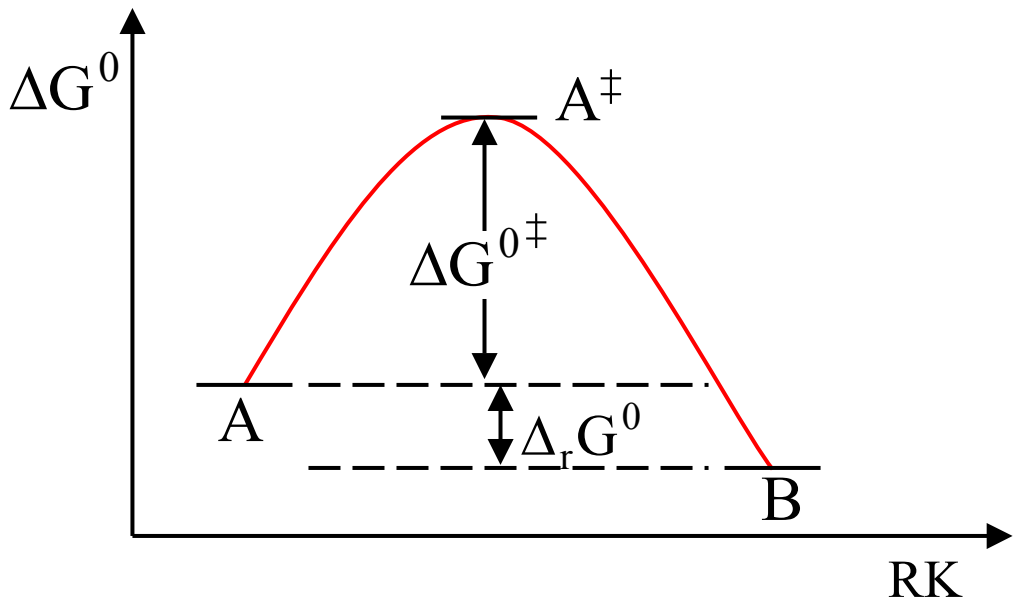
E_A Aktivierungsenergie

A präexponentieller Faktor, A-Faktor

Theorie des Übergangszustandes (1940)

(Henry Eyring, 1901 – 1981)

$$A \rightleftharpoons A^{\ddagger} \rightleftharpoons B$$



$$\log k = \log \frac{k_B}{h} + \log T - \frac{\Delta G^{0\ddagger}}{2.303\,RT}$$

Eyring-Gleichung – nur für Elementarreaktionen gültig!

Theorie des Übergangszustandes (1940)

Für Elementarreaktionen gilt:

$$E_A = \Delta H^{0\ddagger} + RT$$

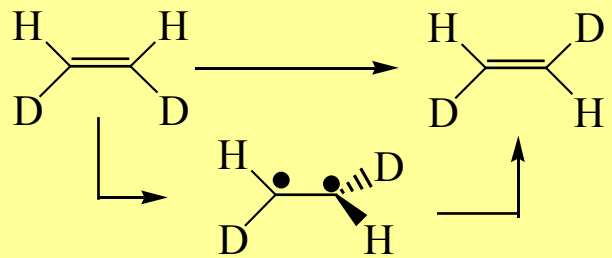
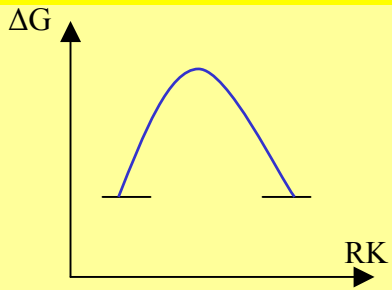
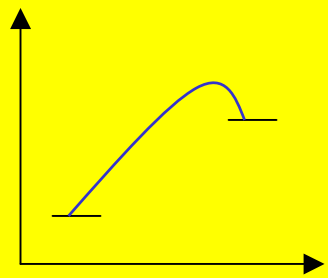
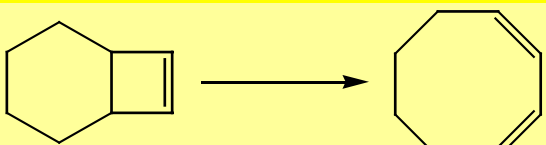
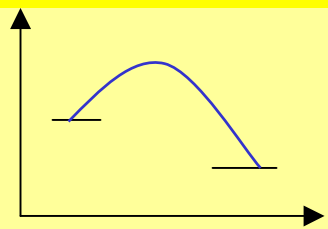
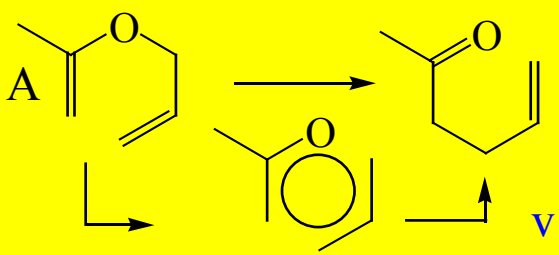
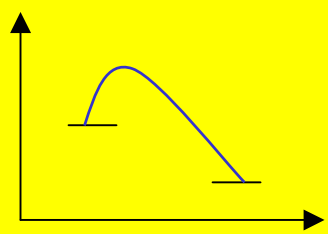
$$\log A = \frac{\Delta S^{0\ddagger}}{2.303\,R} + \log T + \log \frac{k_B}{h} \qquad \text{(monomolekular)}$$

Orientierung für logA

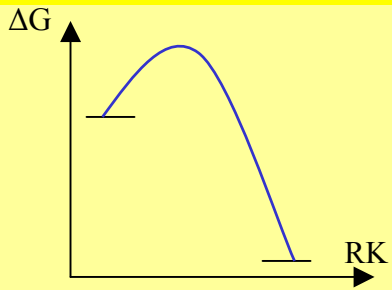
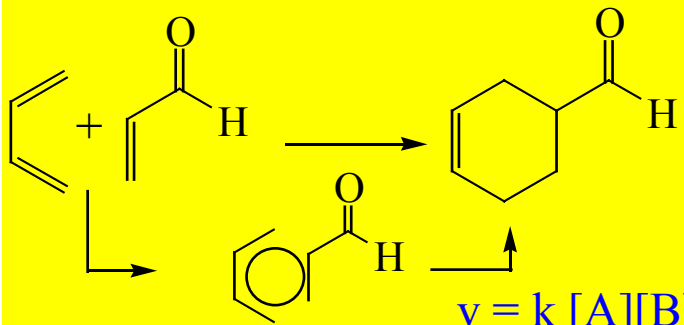
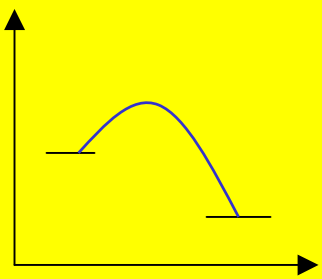
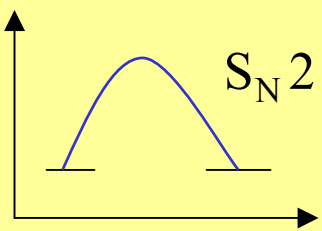
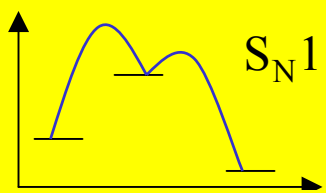
$\Delta S^{0\ddagger}$	≈ 0	> 0	< 0
$\log A$	13	> 13	< 13

$$\log \frac{K_B}{h} = 10.76 \qquad \log 300 = 2.48 \quad (T = 300K)$$

Aktivierungsparameter typischer monomolekularer Reaktionen

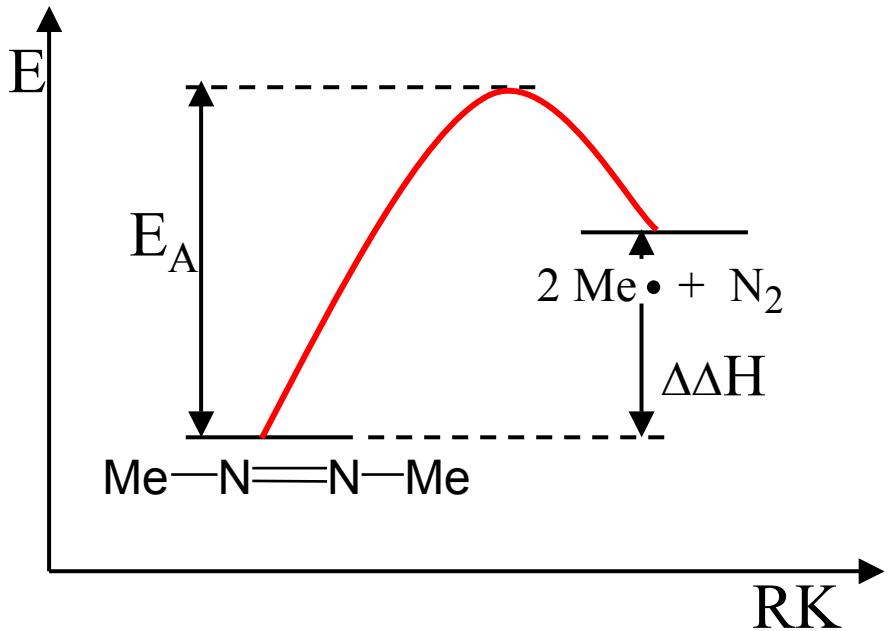
			logA [l mol^{-1} s^{-1}]	E_A [kJ mol^{-1}]
 v = k [HDC=CHD]			13	272
$H_3C—CH_3$ ⟶ $H_3C\bullet + \bullet CH_3$ $H_3C\cdots\cdots CH_3$ v = k [C_2H_6]			16.7	368
 A v = k [A]			14.1	180
 v = k [A]			11.7	123

Aktivierungsparameter typischer bimolekularer Reaktionen

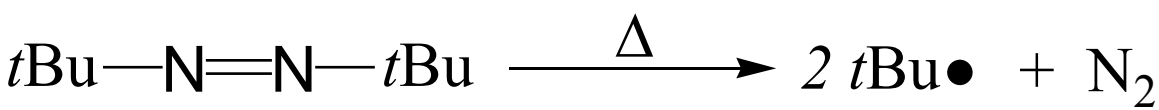
		logA [l mol^{-1} s^{-1}]	E_A [kJ mol^{-1}]
$H_3C\bullet + \bullet CH_3 \longrightarrow H_3C{-}CH_3$ $H_3C\cdots\cdots CH_3$ $v = 2k\,[CH_3\bullet]^2$		10.5	≈ 0
 $v = k\,[A][B]$		5.8	79
$EtBr + Cl^- \longrightarrow EtCl + Br^-$ $v = k\,[EtBr][Cl^-]$		8.9	74
$tBuCl + H_2O \longrightarrow tBuOH + HCl$ $v = k\,[tBuCl]$		16.3	102

Substituenteneffekte

Einfluß auf Aktivierungsenergie

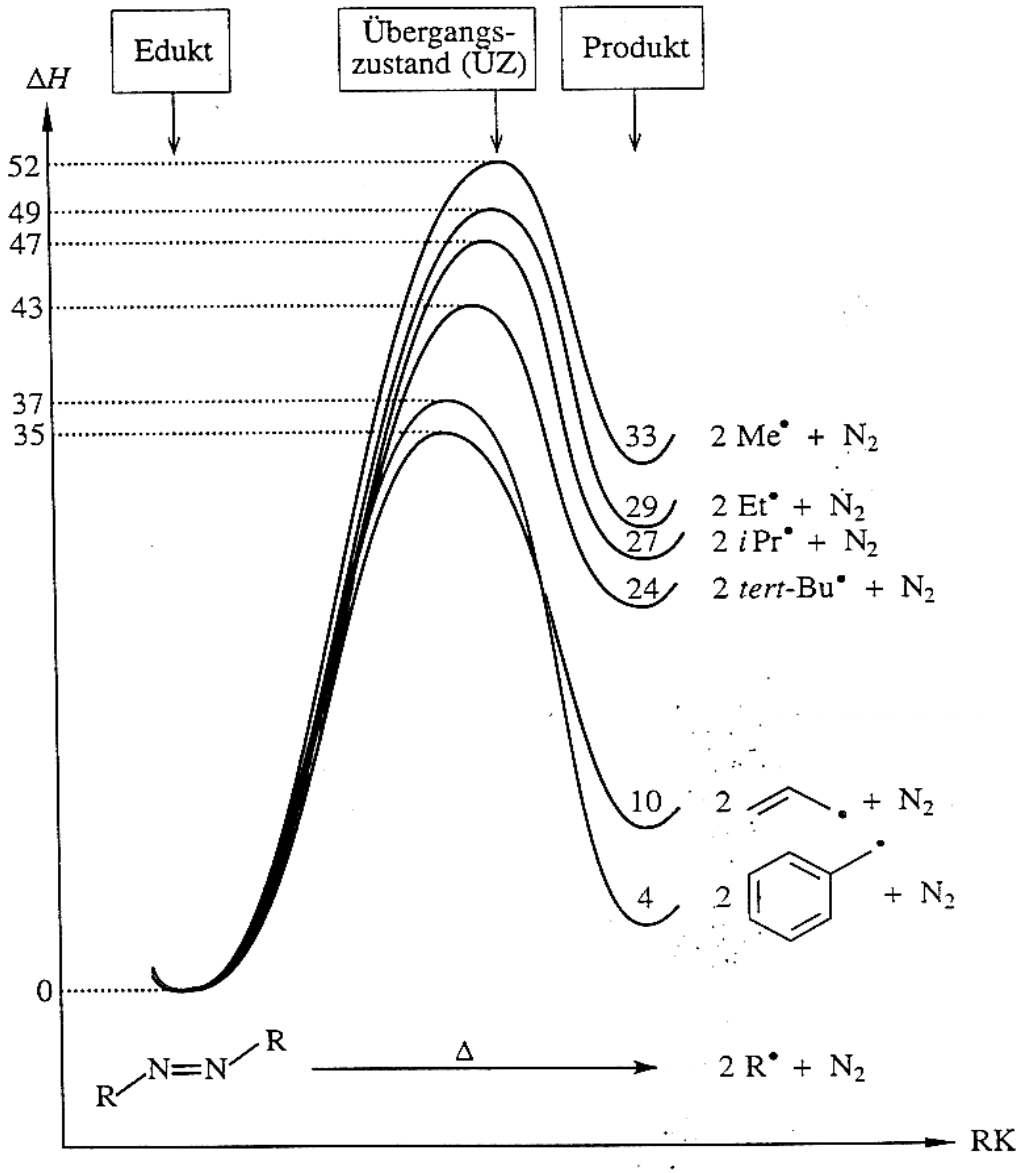


$E_A = 52$ kcal/mol; $\Delta\Delta H = 33$ kcal/mol



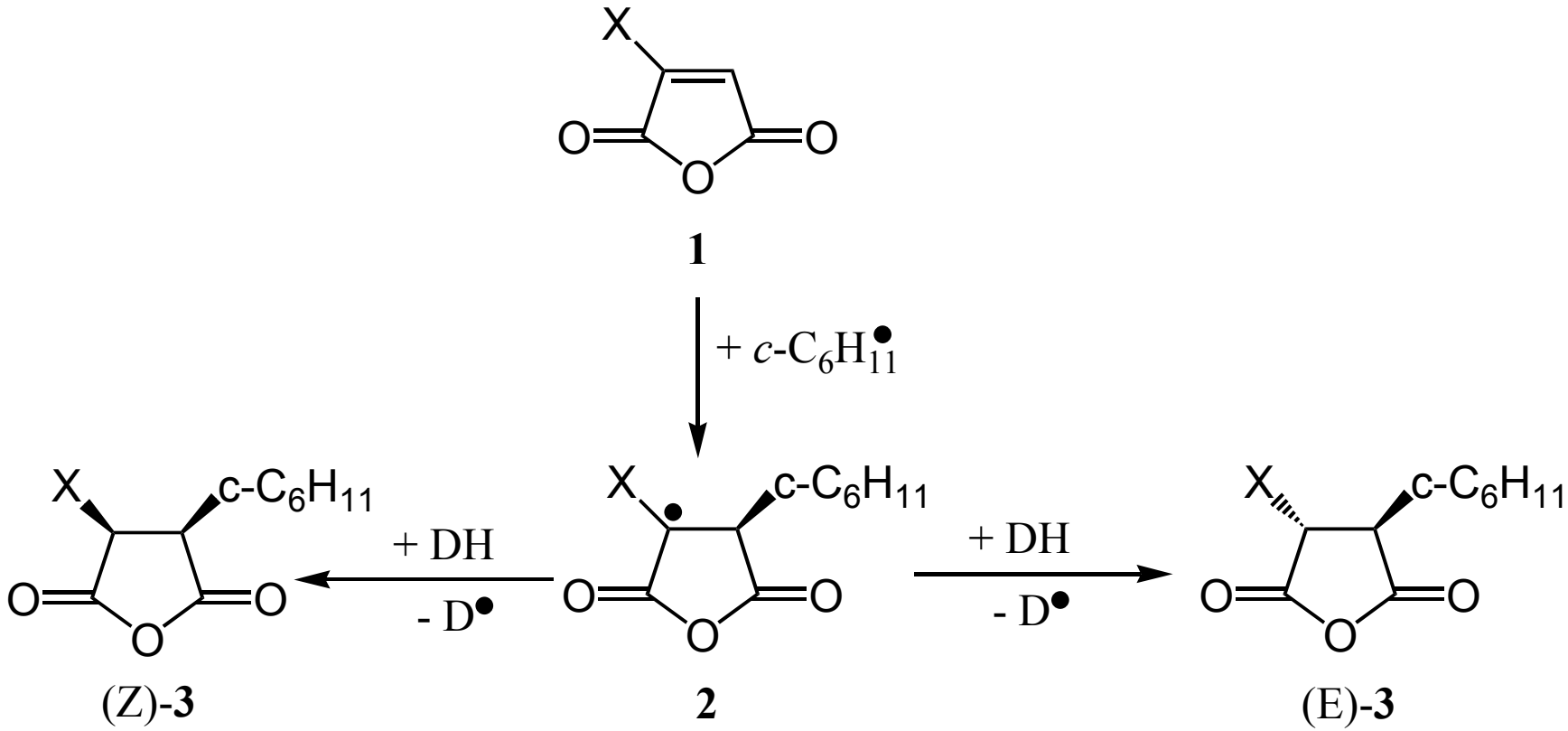
$E_A = 43$ kcal/mol; $\Delta\Delta H = 24$ kcal/mol

Bell-Evans-Polanyi-Beziehung



$$E_A = k + k' \cdot \Delta_r H$$

Stereoselektivität

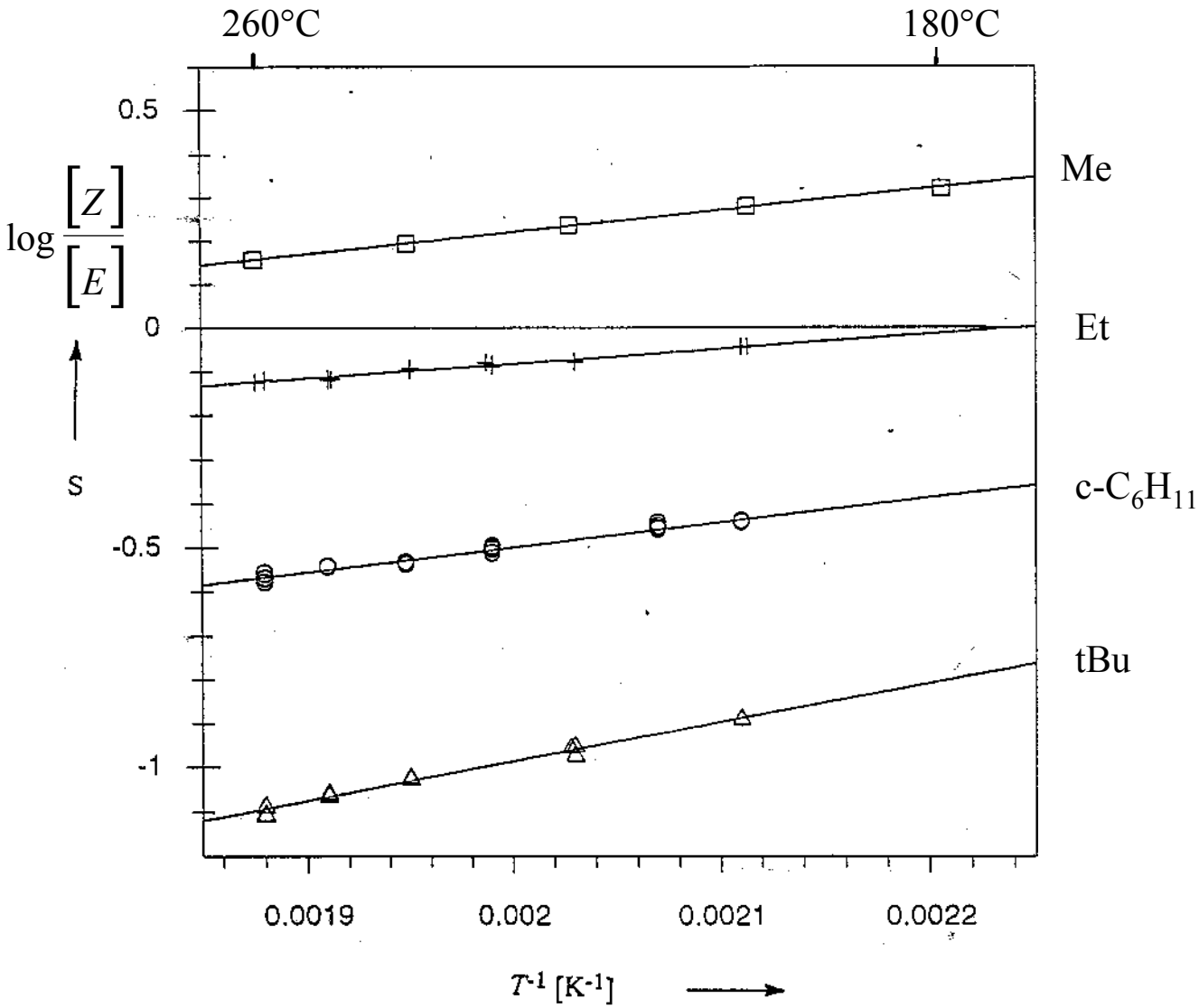


2	a	b	c	d	e	f	G
X	Me	Et	c-C_6H_{11}	t-Bu	CF_3	Ph	F

DH = c-C_6H_{12}, c-$C_6H_{11}HgH$

Chem.Ber. **1994**, *127*, 1069-1073

Konkurrenzreaktionen



Konkurrenzreaktion

$$\frac{d[Z]}{dt} = k_Z[R\bullet][DH] \quad (1)$$

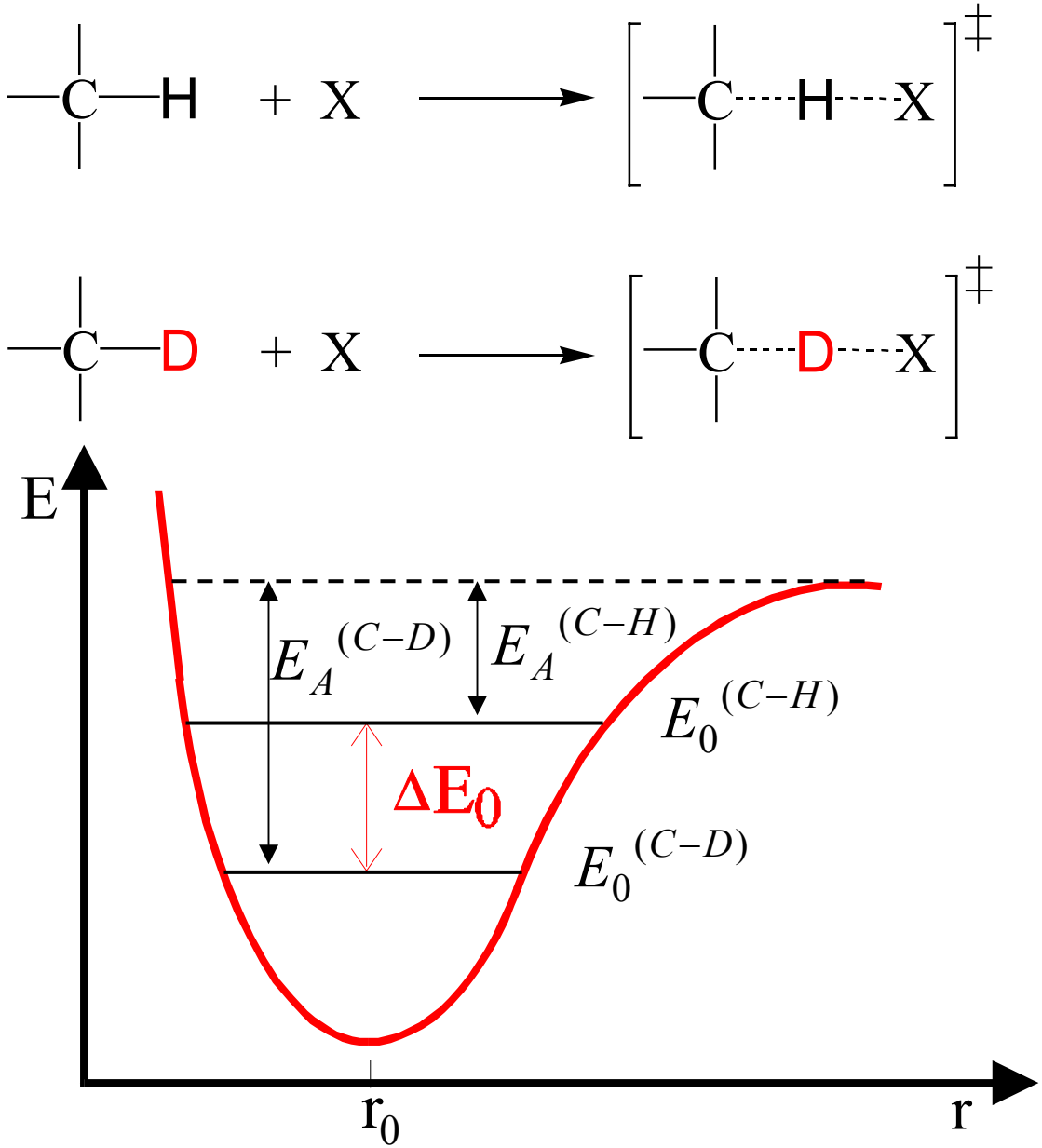
$$\frac{d[E]}{dt} = k_E[R\bullet][DH] \quad (2)$$

$$\left.\begin{matrix}(1)\\(2)\end{matrix}\right\} \Rightarrow \frac{[Z]}{[E]} = \frac{k_Z}{k_E}$$

$$\log\left(\frac{k_Z}{k_E}\right) = \log\left(\frac{A_Z}{A_E}\right) - \frac{\left(E_{A,Z} - E_{A,E}\right)}{2.303\,RT}$$

X	$E_{A,Z} - E_{A,E}$ (kJ/mol)	$\log A_Z - \log A_E$
Me	- 9.7	- 0.79
tBu	- 16.8	- 2.76

1.3 Primärer kinetischer Isotopeneffekt



Primärer kinetischer Isotopeneffekt

$$(1) \quad E_0 = \frac{1}{2} h\nu_S = \frac{1}{2} hc\tilde{\nu}$$

$$(2) \quad \nu_S = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$$

$$(2)\,\text{in}\,(1) \quad E_0 = \frac{h}{4\pi}\sqrt{\frac{k(m_1+m_2)}{m_1 \cdot m_2}}$$

ν_S = Frequenz der Valenzschw. der Bindung

k = Kraftkonstante der Schwingung

$\mu = \dfrac{m_1 \cdot m_2}{m_1 + m_2}$ reduzierte Masse

$$E_0^{(C-H)} > E_0^{(C-D)}$$

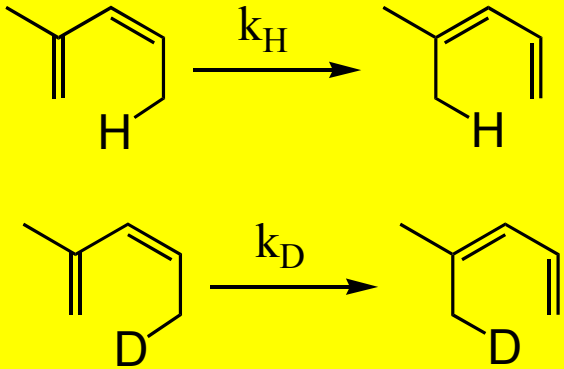
$$\Delta E_0 = \frac{hc}{2}\left(\underbrace{\tilde{\nu}^{(C-H)}}_{\approx 3000\,cm^{-1}} - \underbrace{\tilde{\nu}^{(C-D)}}_{\approx 2100\,cm^{-1}} \right) \approx 4.8\,kJ/mol$$

$$\Delta E_0 = E_A^{(C-D)} - E_A^{(C-H)}$$

$$\frac{\tilde{\nu}_H}{\tilde{\nu}_D} \approx 1.35 \qquad \frac{k_H}{k_D} \approx 7 \quad (300K)$$

Kinetischer Isotopeneffekt - Beispiele

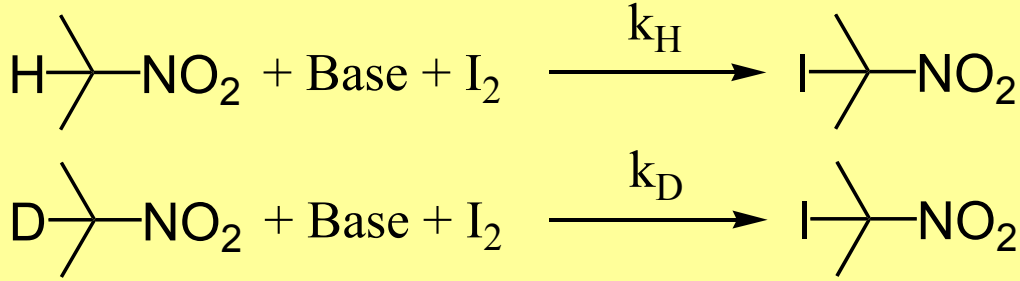
a)

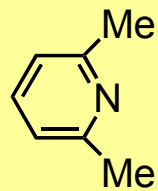


1.5-sigmatrope Umlagerung

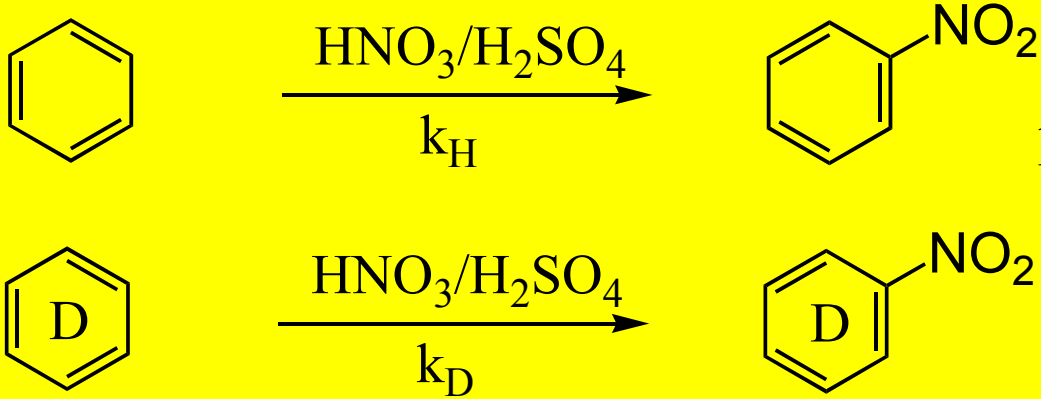
k_H/k_D ~ 12 (25°C)
~ 5 (200°C)

b)



Base	k_H/k_D (25°C)
Pyridin	10
	24

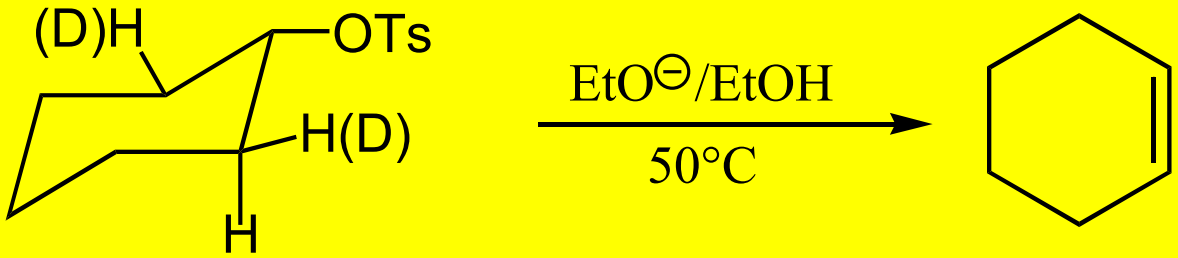
c)



k_H/k_D = 1 (25°C)

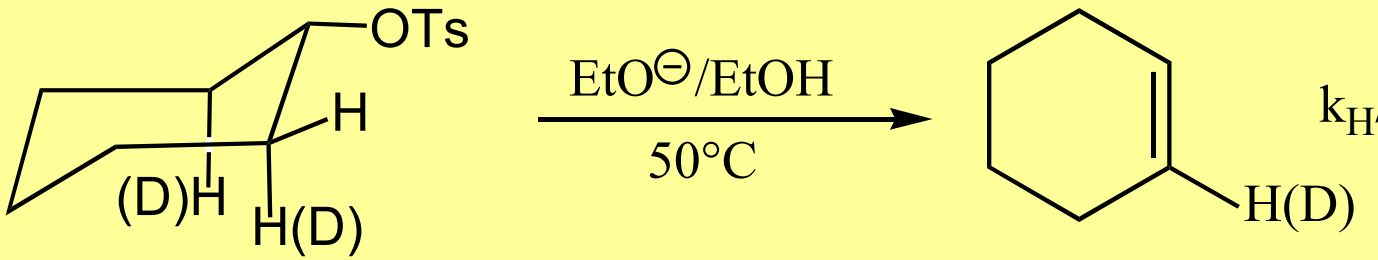
Kinetischer Isotopeneffekt - Beispiele

d)



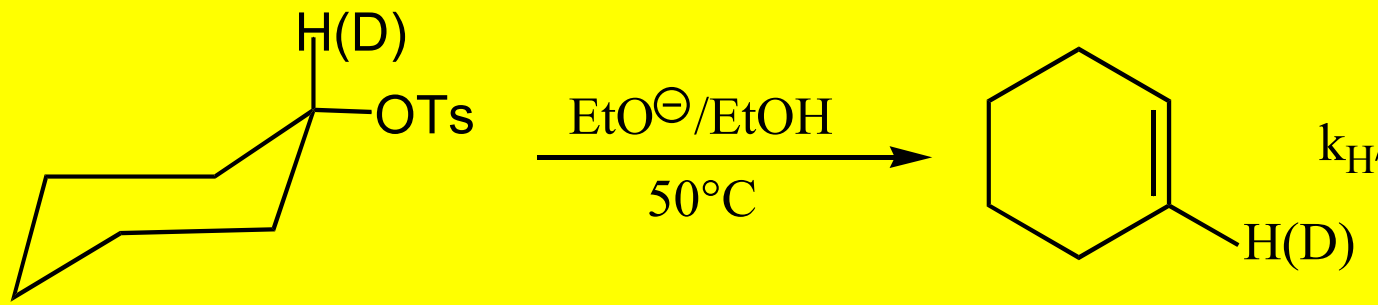
$k_H/k_D = 4.47$

e)



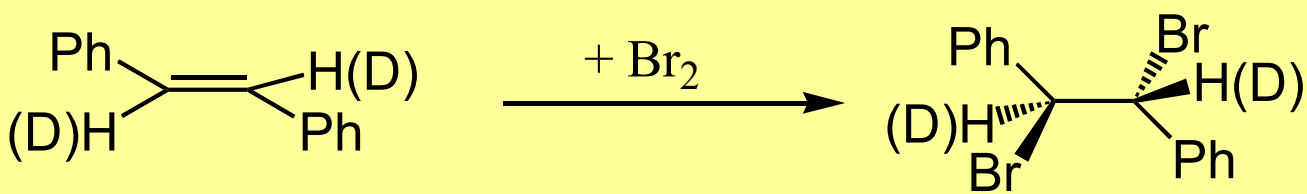
$k_H/k_D = 1.36$

f)



$k_H/k_D = 1.14$

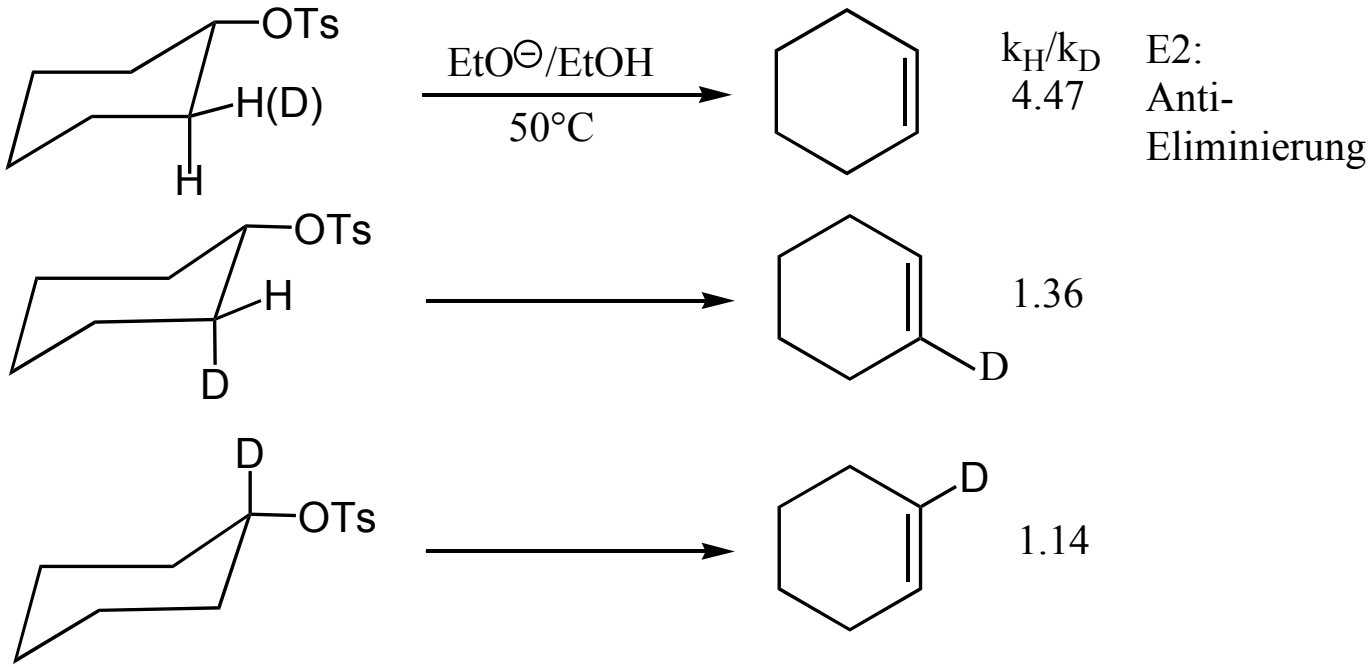
g)



meso

$k_H/k_D = 0.91$ (25°C)

Sekundärer kinetischer Isotopeneffekt - Beispiele



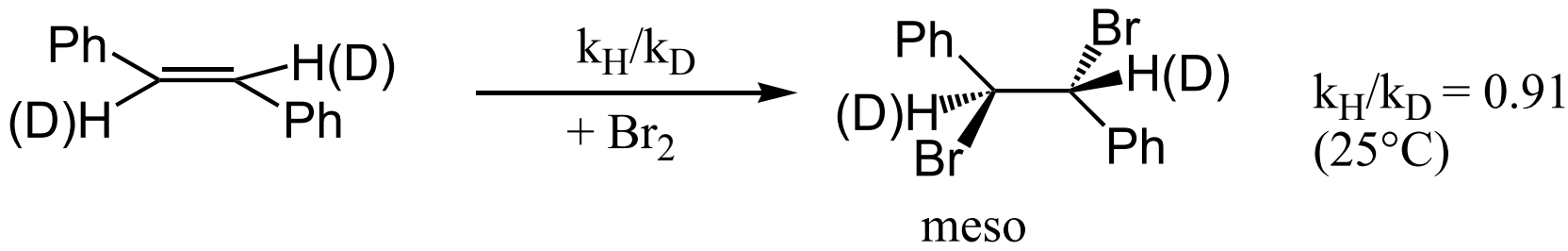
Ursache für sekundären Isotopeneffekt k_H/k_D:

Umhybridisierung im TS:

C sp^3 ⟶ sp^2 $\quad k_H/k_D > 1$

sp^2 ⟶ sp^3 $\quad k_H/k_D < 1$

Sekundärer kinetischer Isotopeneffekt - Beispiele



Hyperkonjugation:

1.4 Substituenteneffekte:

Lineare Freie Enthalpie-Beziehungen

Acidität:

$CH_3COOH < ClCH_2COOH < Cl_2CHCOOH < Cl_3CCOOH$

Verseifungsgeschwindigkeit:

$$X\text{-}COOEt \xrightarrow[k_x]{+\ OH^{\ominus},\ H_2O} X\text{-}COO^{\ominus} + EtOH$$

k_x : X = H > Me > Et > iPr > tBu

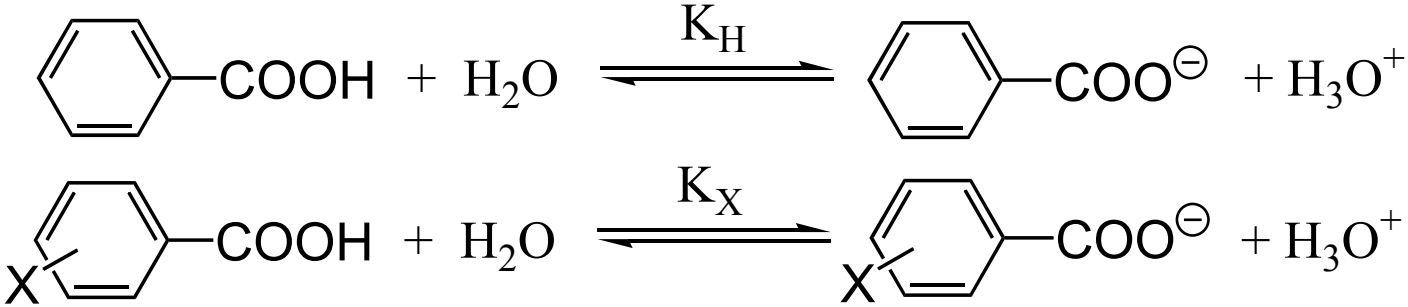
➡ Man unterscheidet: - polare

- sterische

- stereoelektronische Substituenteneffekte.

Polare Substituenteneffekte

L. P. Hammett (1935):



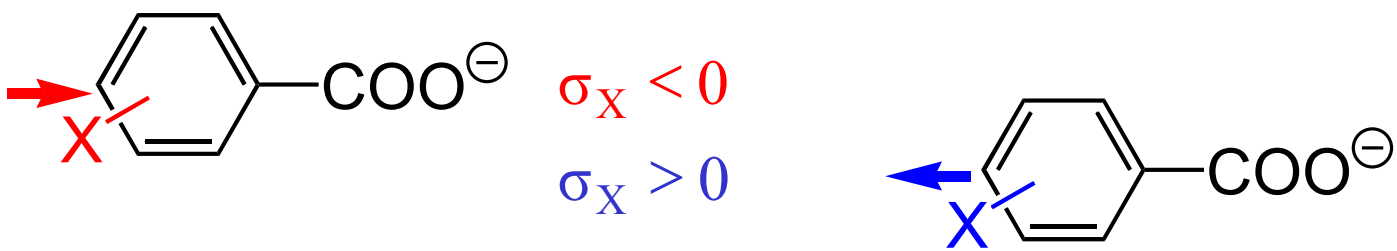
para = ∑induktive–, Feld–, mesomere Effekte

meta = ∑induktive–, Feldeffekte

ortho = Störung durch sterische Effekte

$$\log \frac{K_X}{K_H} \equiv \sigma_X \quad \text{(in } H_2O\text{, 25°C)}$$

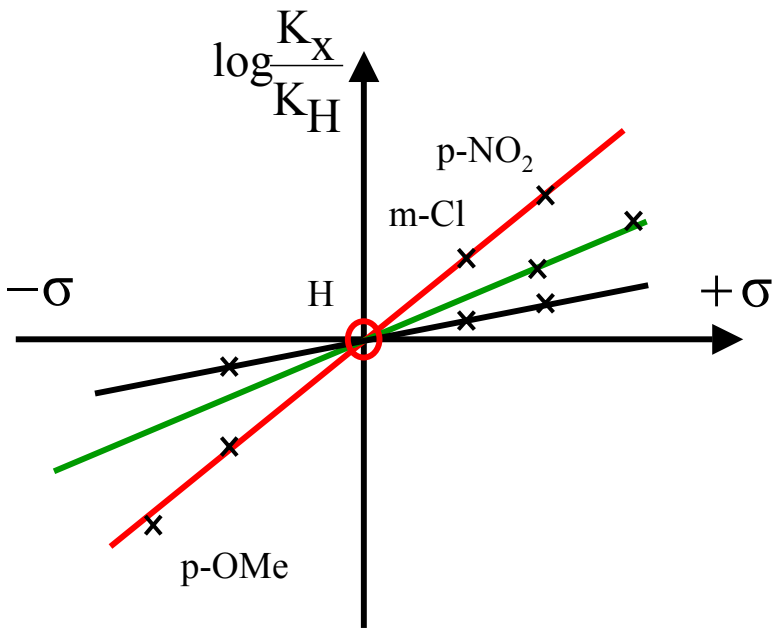
σ_X = Substituentenkonstante
polarer Effekt von X

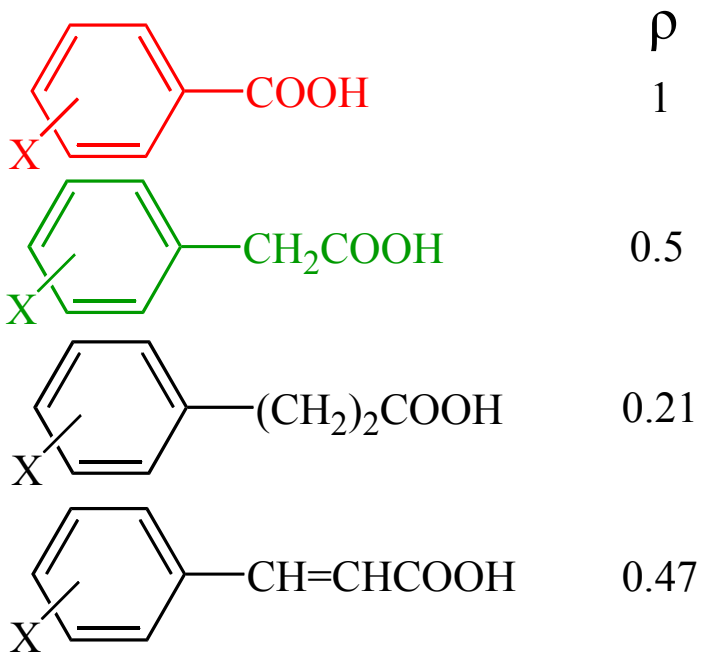


Substituentenkonstanten

Nr.	Substituent	σ_m	σ_p
1	$N(CH_3)_2$	-0,21	-0,83
2	NH_2	-0,16	-0,66
3	OH	0,12	-0,37
4	OCH_3	0,12	-0,27
5	CH_3	-0,07	-0,17
6	$C(CH_3)_3$	-0,10	-0,20
7	C_6H_5	0,06	-0,01
8	H	0	0
9	F	0,34	0,06
10	Cl	0,37	0,23
11	Br	0,39	0,23
12	I	0,35	0,18
13	$COOC_2H_5$	0,37	0,45
14	$COCH_3$	0,38	0,50
15	CN	0,56	0,66
16	SO_2CH_3	0,60	0,72
17	NO_2	0,71	0,78
18	$N(CH_3)_3^+$	0,88	0,82

Hammett - Gleichung





$$\log\frac{K_x}{K_H} = \rho\cdot\sigma_x = -\frac{\left(\Delta\Delta G^0_x - \Delta\Delta G^0_H\right)}{2.3\,RT}$$

Hammett – Gleichung

"lineare freie Enthalpiebeziehung"

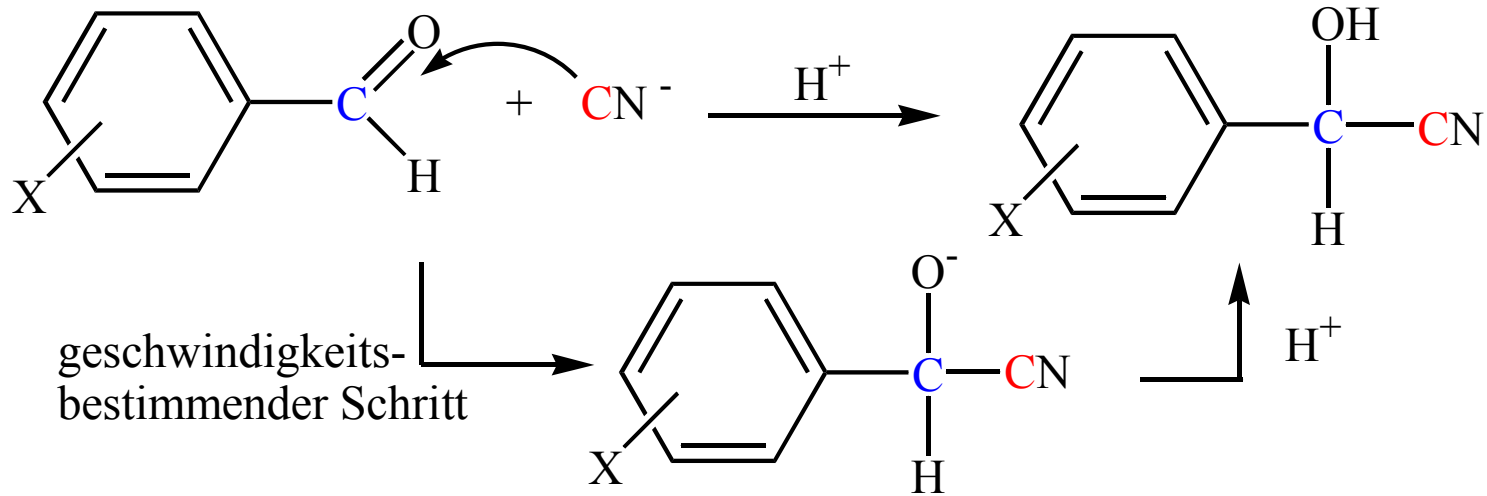
$$\log\frac{k_x}{k_H} = \rho\cdot\sigma_x$$

ρ Reaktionskonstante

für ρ >1: Substituenten beeinflussen die Reaktion stärker als die Dissoziation von Benzoesäure.

Beispiel: Nucleophile Addition

1.



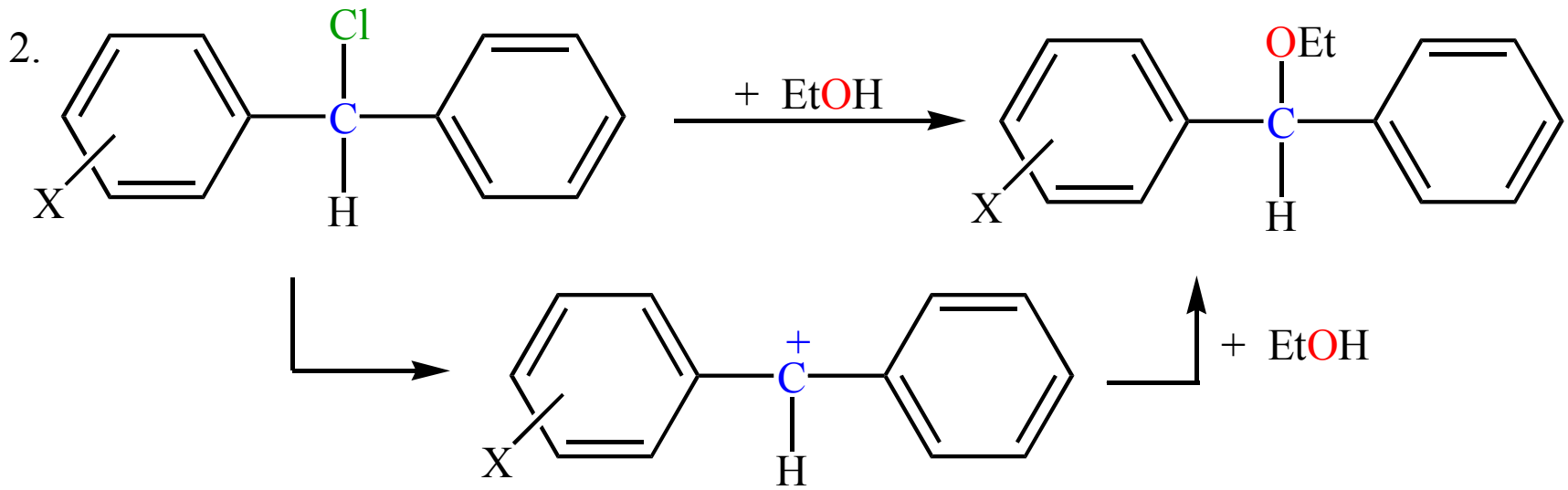
$\rho = 2.3 \quad (20°C)$

$\rho > 0$ -M, -I-Substituenten beschleunigen Reaktionen, bei der eine Erhöhung der Elektronendichte am Reaktionszentrum erfolgt.

- nucleophiler Angriff

- Ausbildung einer negativen Ladung

Beispiel: Nucleophile Substitution (S_N1)



$\rho = -5.1$

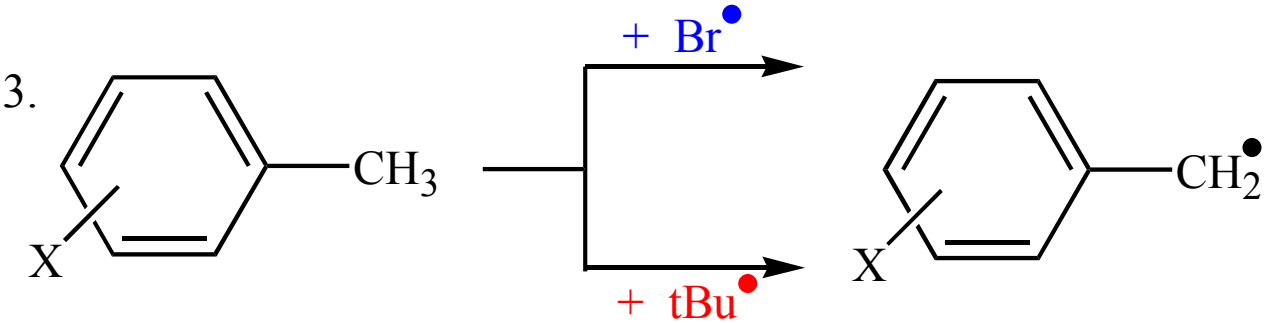
$\rho < 0$ +M, +I-Substituenten beschleunigen Reaktionen, bei der eine Erniedrigung der Elektronendichte am Reaktionszentrum erfolgt.

- elektrophiler Angriff

- Ausbildung einer positiven Ladung

Beispiel: Radikalische Substitution

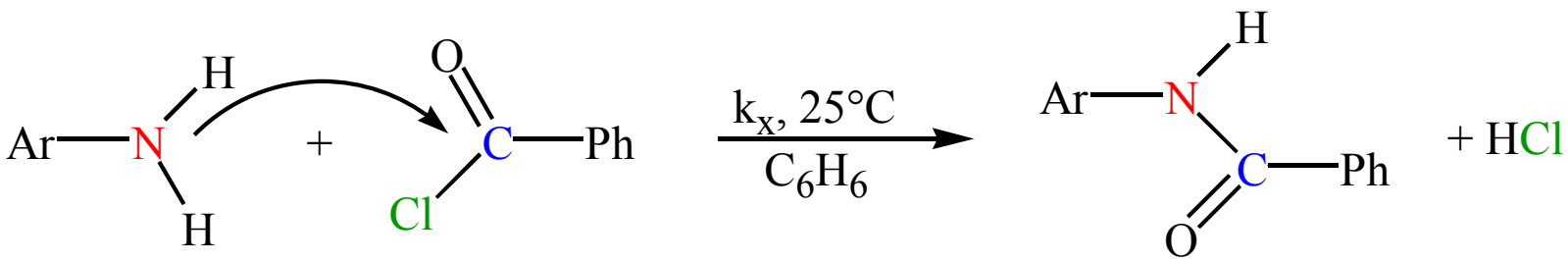
3.



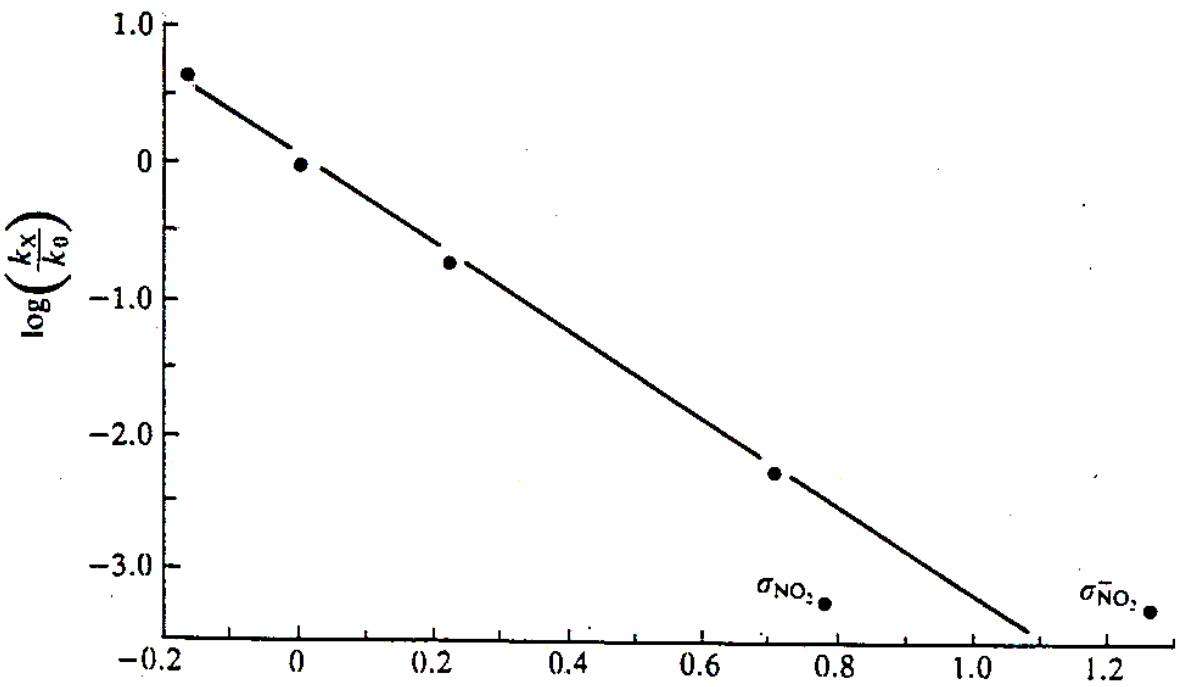
+ HBr $\rho = -1.7$

+ tBuH $\rho = +0.99$

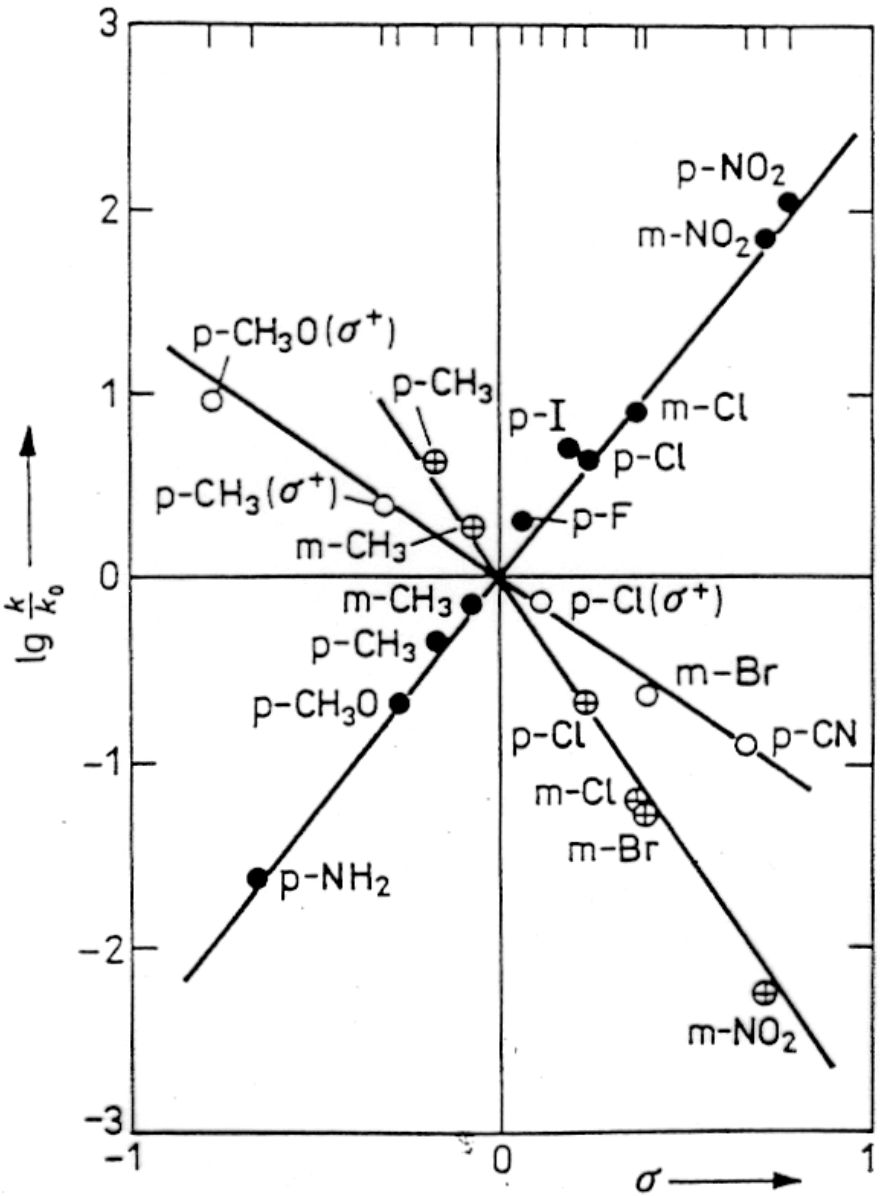
Hammett-Korrelation: Elektrophiler Angriff



$\rho = -3.21$



Abhängigkeit der Reaktionsgeschwindigkeit von σ



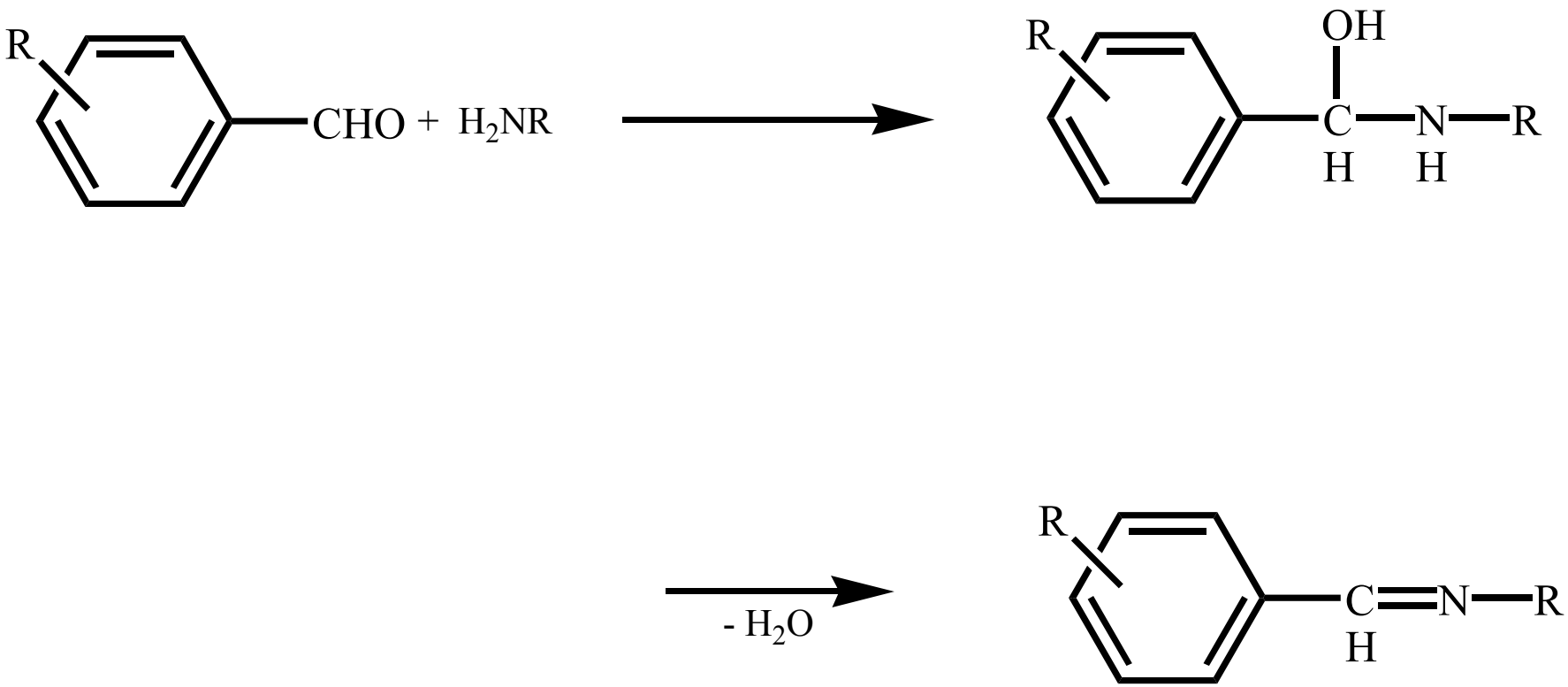
Abhängigkeit der Reaktionsgeschwindigkeiten von den Hammettschen σ-Werten

●—● Alkalische Hydrolyse von Benzoesäureethylestern; 25°C, $\varrho = +2{,}54$

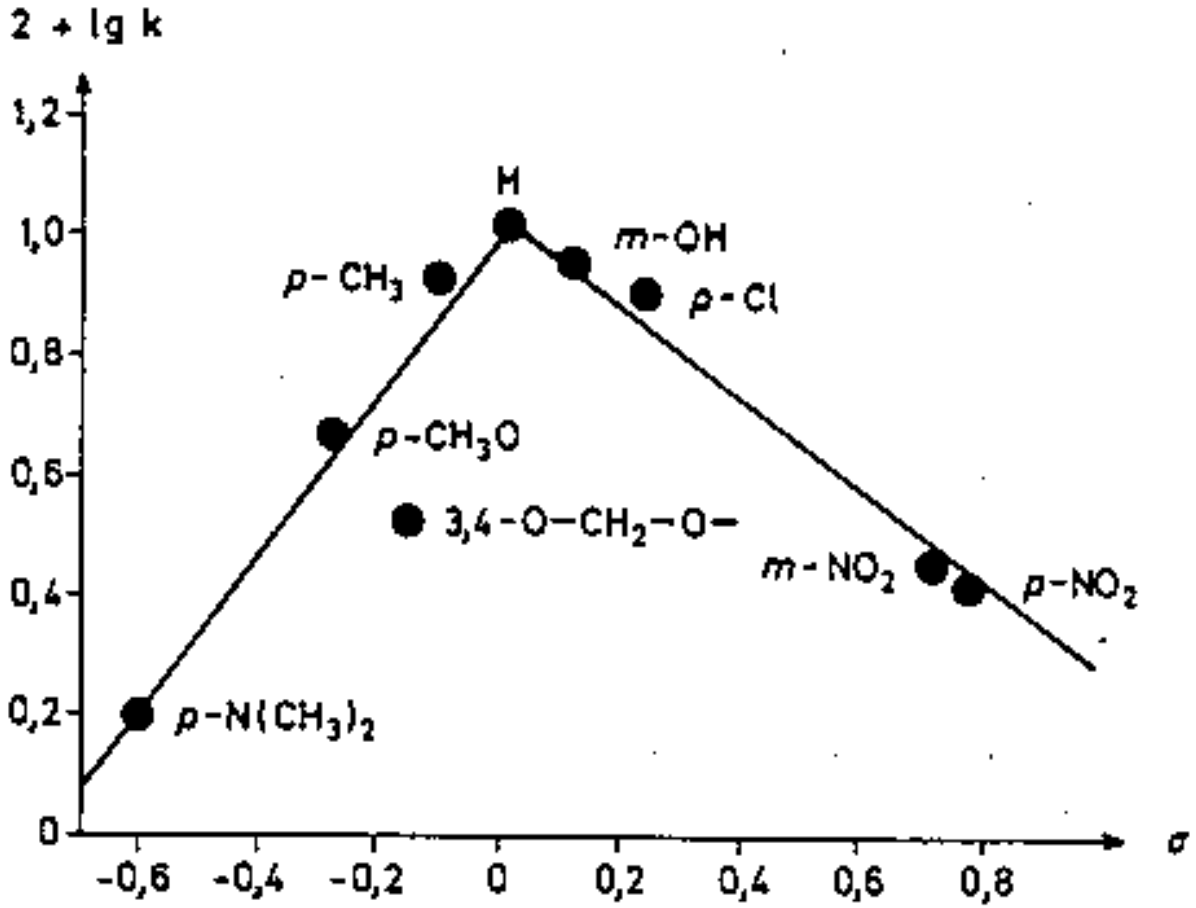
⊕—⊕ Reaktion von substituierten Anilinen mit Benzoylchlorid; 25°C, $\varrho = -2{,}78$

○—○ Bromierung von substituierten Toluenen; 80°C, $\varrho = -1{,}39$ (mit σ^+-Werten, s. unten)

Bildung Schiff‘scher Basen

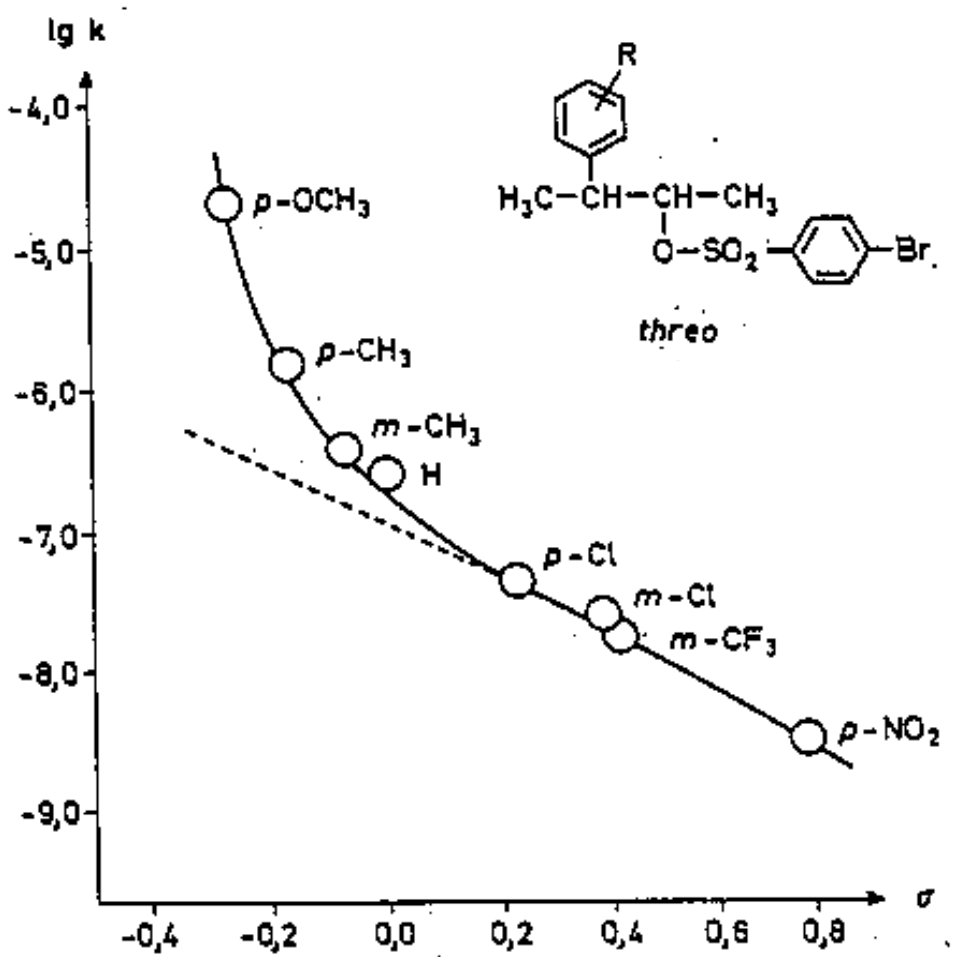


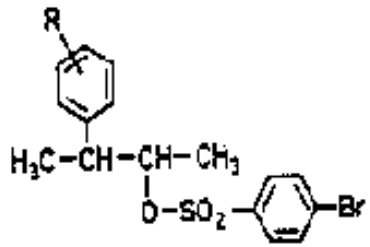
Hammett-Korrelation: Schiff´sche Basen

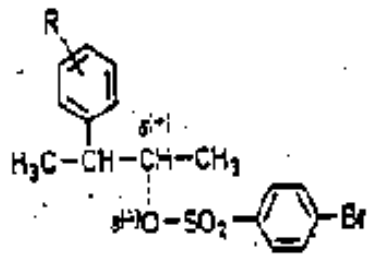


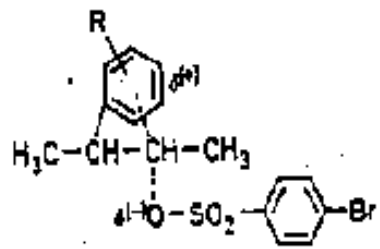
Hammett-Diagramm für die Bildung Schiff‘scher Basen aus substituierten Benzaldehyden (J.Chem.Educ. 48, 104 (1971))

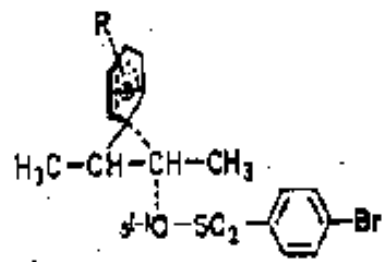
Hammett-Korrelation: Acetolyse





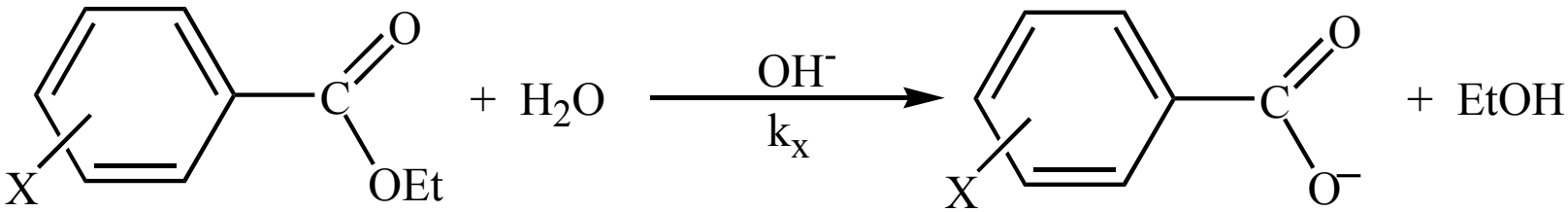






Acetolysegeschwindigkeit substituierter *threo*-3-Aryl-2-butyl-4'-brom benzolsulfonate in Abhängigkeit von σ [J. Amer. Chem. Soc. 91, 4290 (1969)]

Hammett-Korrelation: Basenkatalysierte Verseifung



$\rho = 2.23$

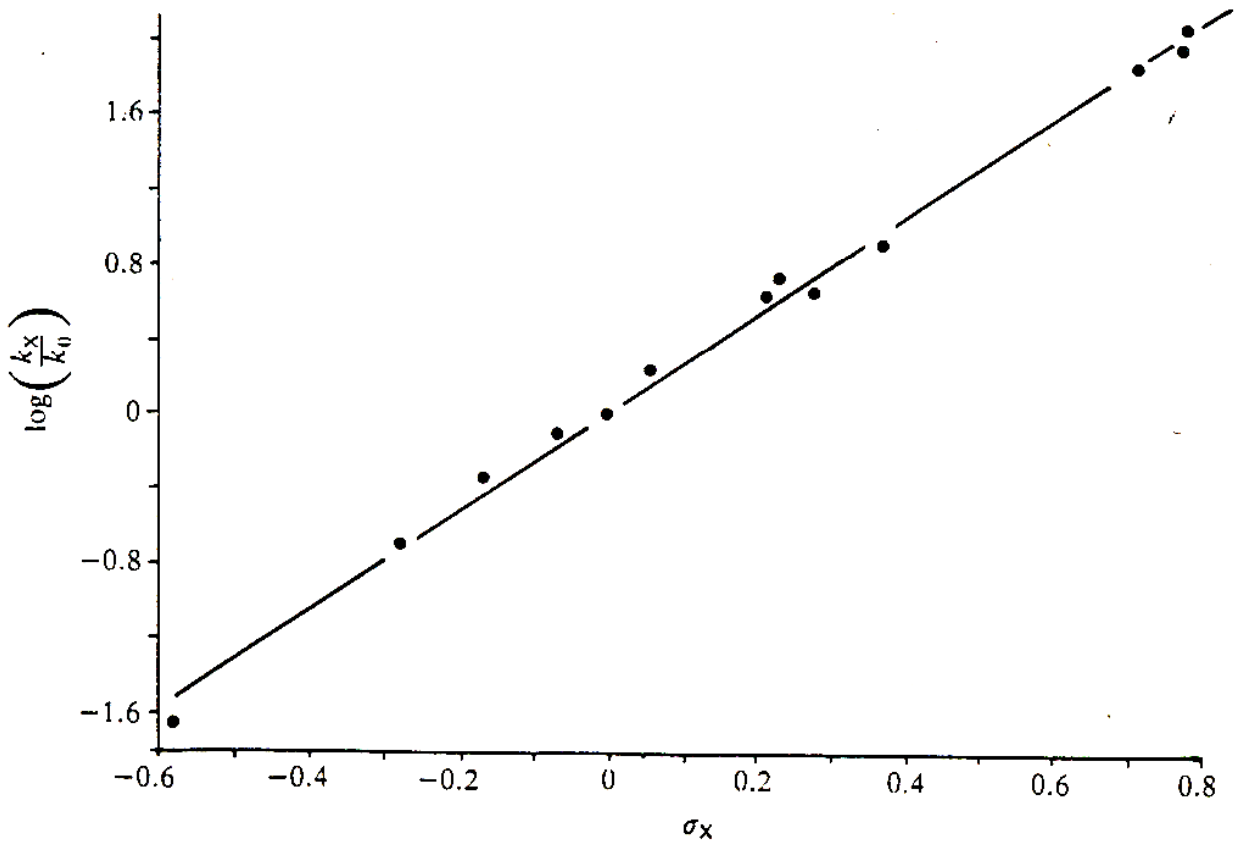
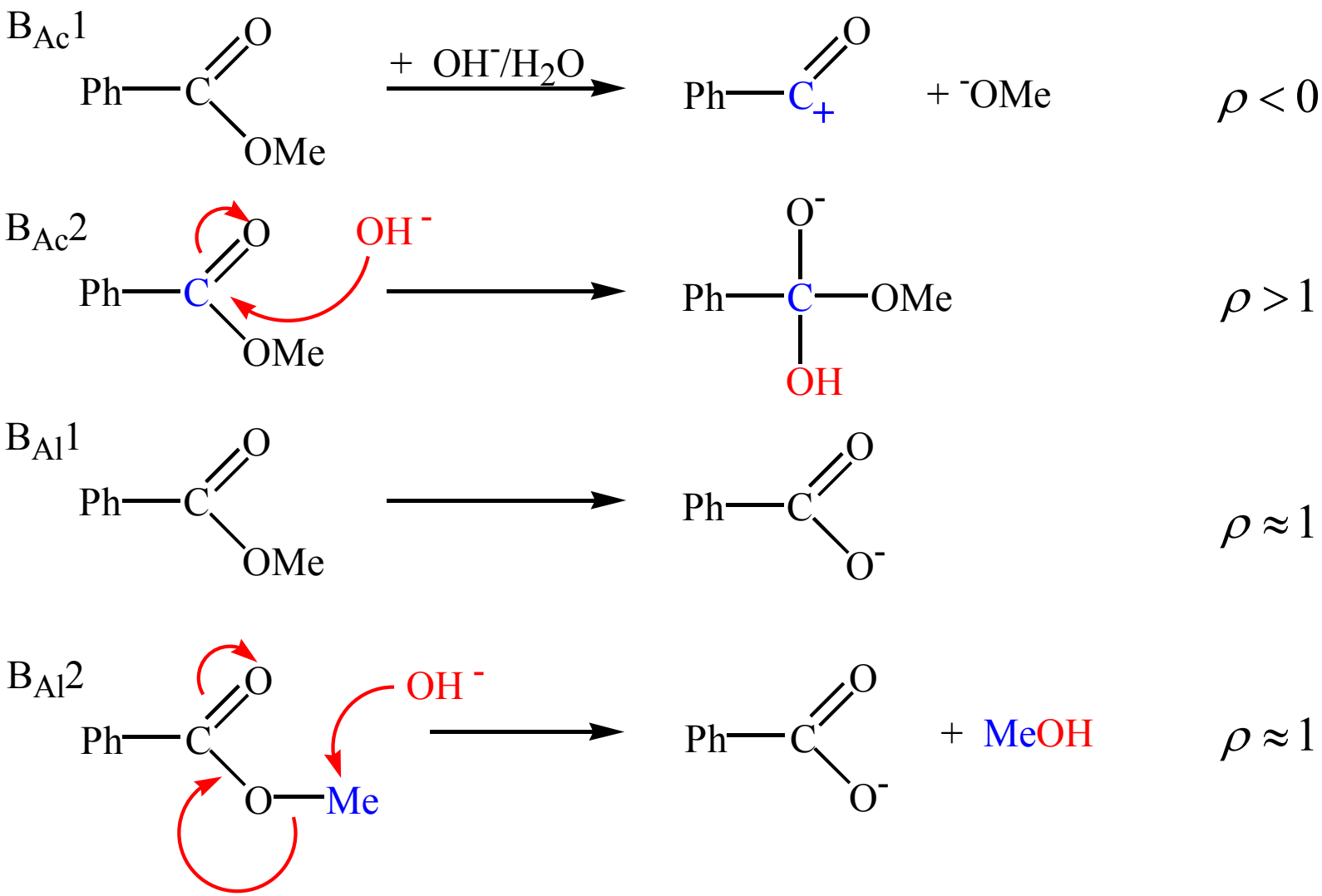


Fig. 10.17. Hammett plot for second-order rate constants of the base-induced hydrolysis of ethyl bezoates, 85 per cent aqueous ethanol, 25 °C.[21]

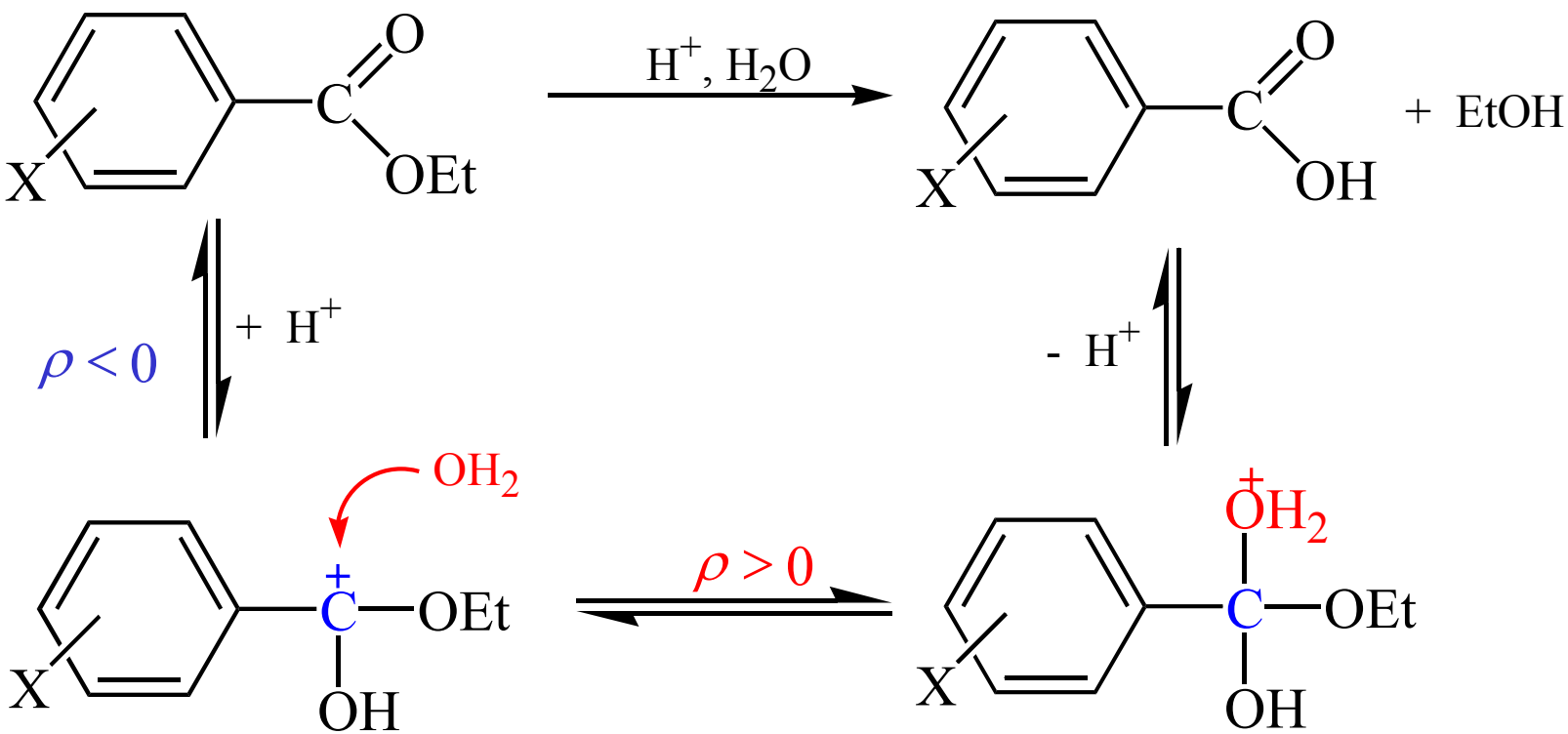
Alkalische Esterhydrolyse $\rho = 2.23$

Mechanistische Möglichkeiten der alkalischen Esterhydrolyse



Saure Esterhydrolyse $\rho = 0.106$

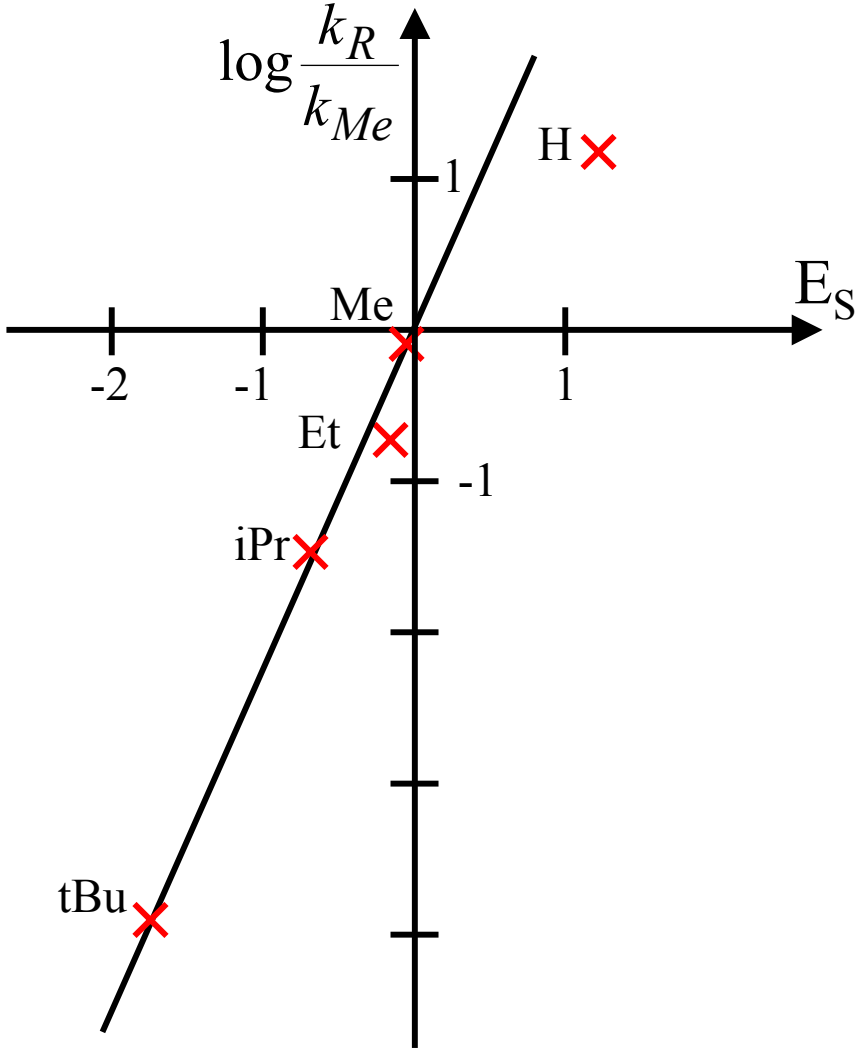
$A_{Ac}2$-Mechanismus

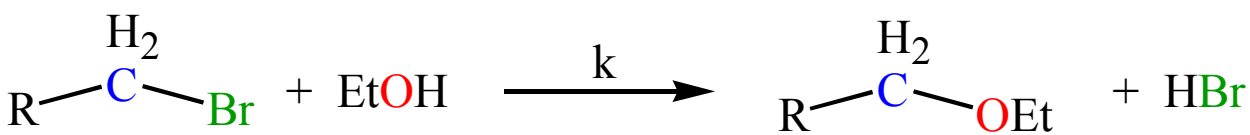


Sterische Substituenteneffekte nach R.W.Taft (1952)

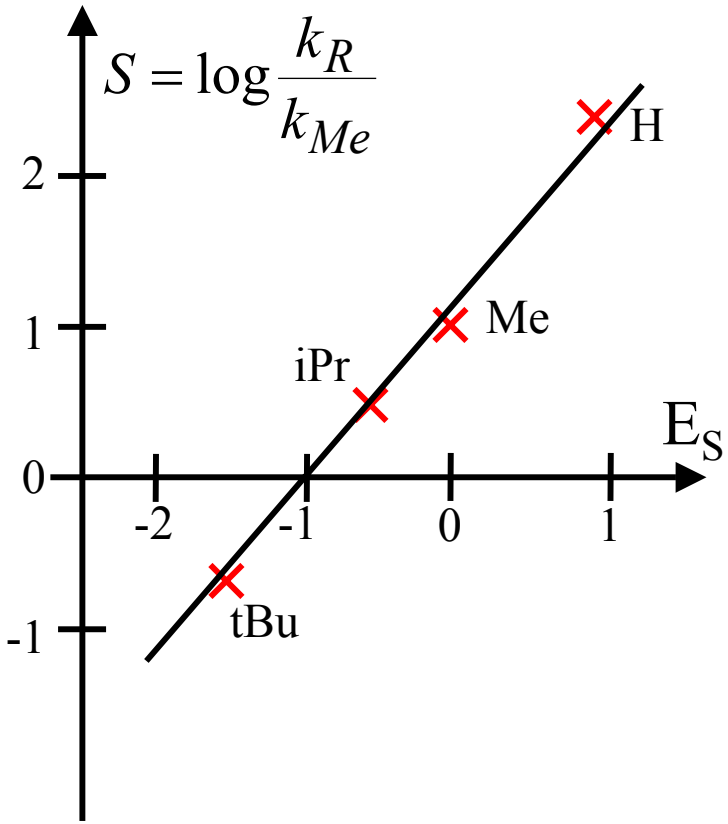
R in RCOOH	E_S
H	+1,24
Me	0
Et	-0,07
$ClCH_2$	-0,24
ICH_2	-0,37
$PhCH_2$	-0,38
$Me(CH_2)_3$	-0,39
Me_2CHCH_2	-1,13
Me_3C	-1,54
Me_3CCH_2	-1,74
Ph_2CH	-1,76
Et_3C	-3,81

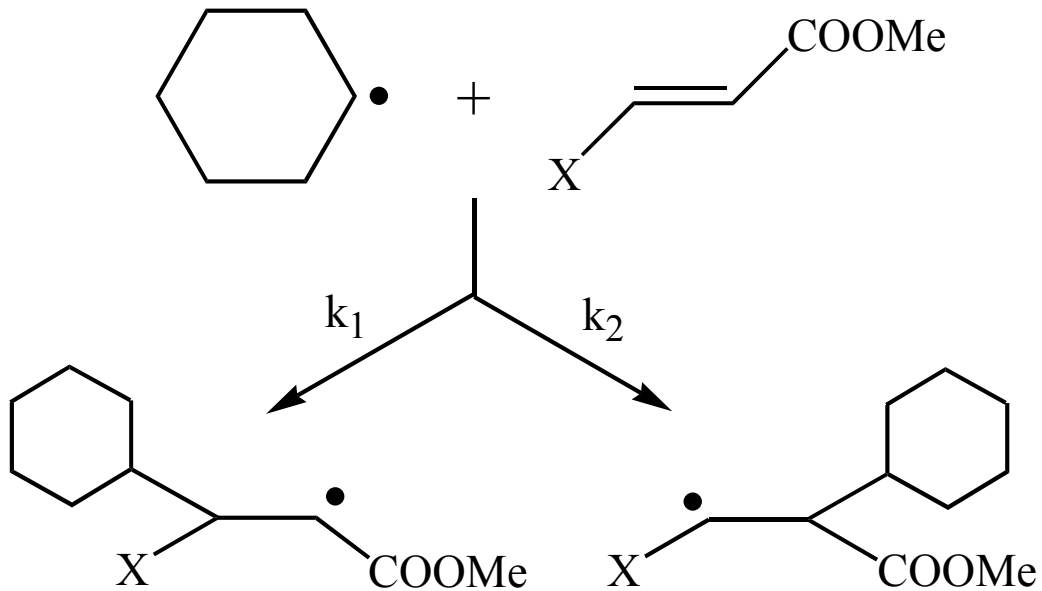
Korrelation der rel. Reaktionsgeschwindigkeit mit E_S





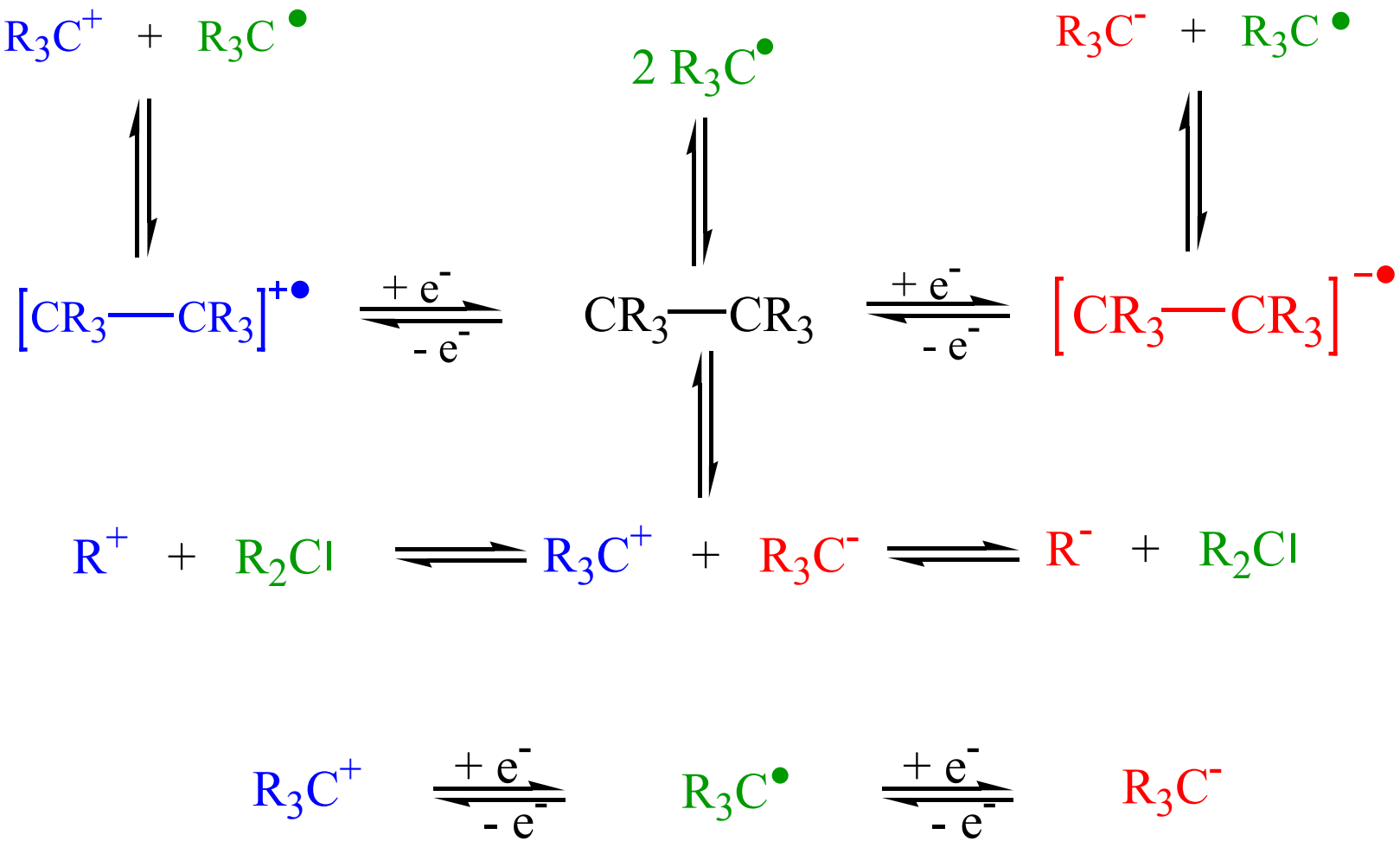
Regioselektivität S und E_S





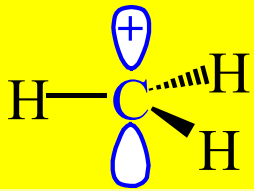
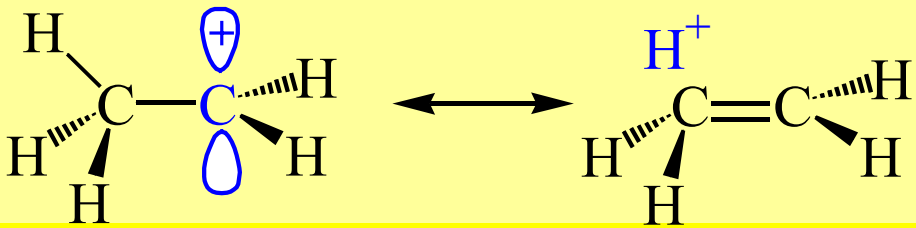
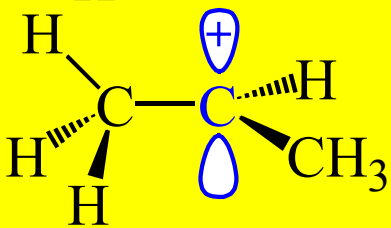
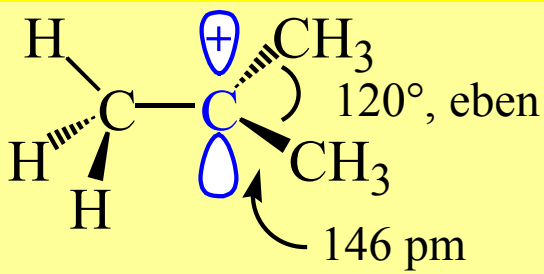
2. Reaktive Zwischenstufen

Reaktive Zwischenstufen



2.1 Carbokationen

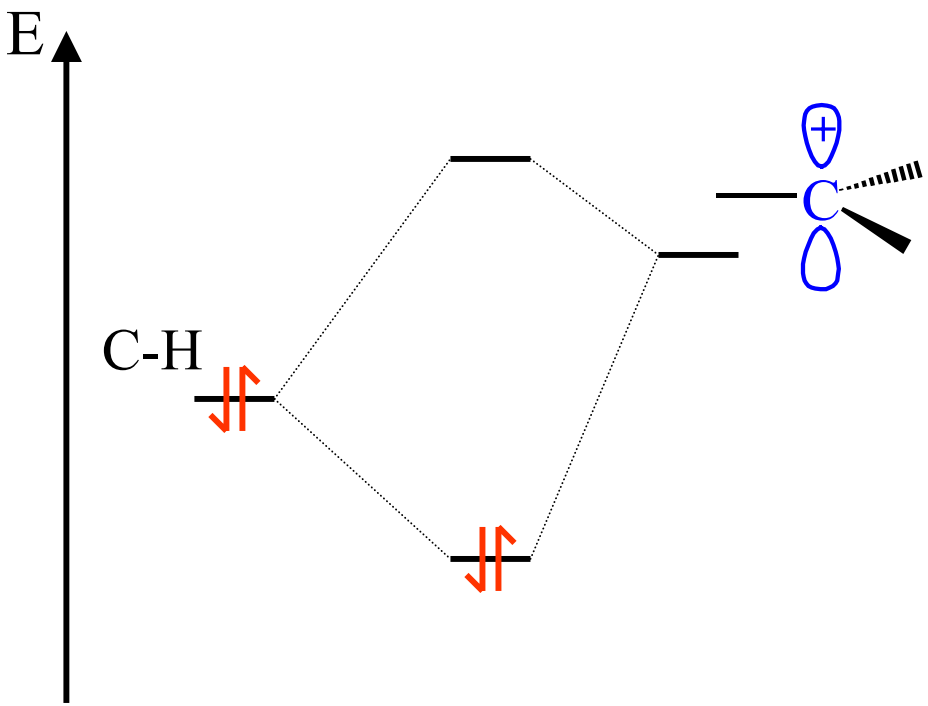
$$RH \longrightarrow R^+ + H^-$$

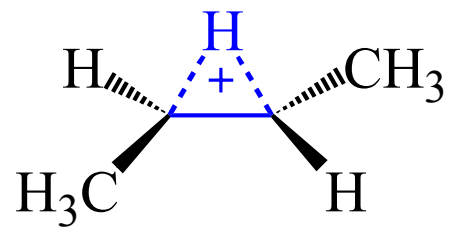
R		$D(R^+ H^-)$ [kJ/mol]
Me		1316
Et		1158
iPr		1043
tBu		970

$Me_3C^+ SbF_6^-$ stabil < -20°C

Stabilisierung durch Hyperkonjugation

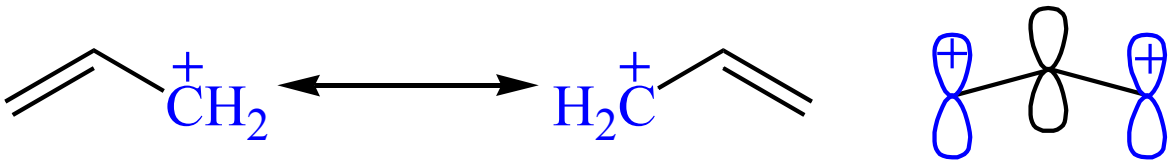
Hyperkonjugation: auch induktiver Effekt, Feldeffekt





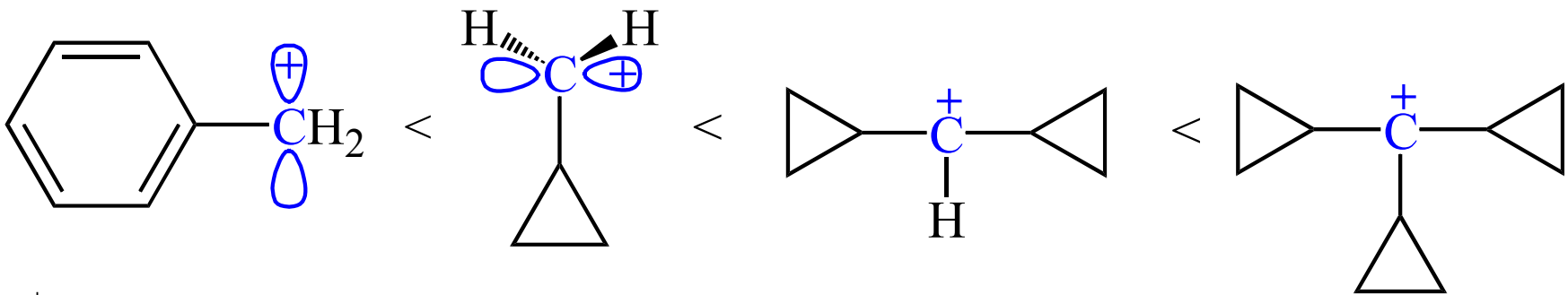
2-Butylkation
2e - 3Zentrenbindung

Stabilisierung durch Konjugation



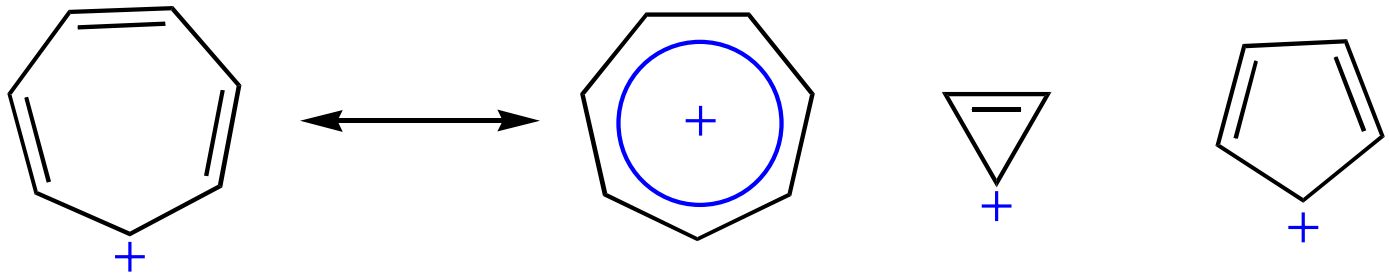
$D(R^+H^-)$ 1070

Stabilität:

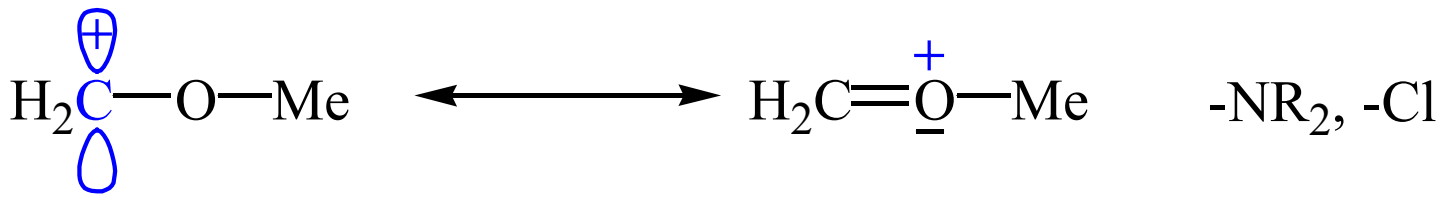


$D(R^+H^-)$ 996

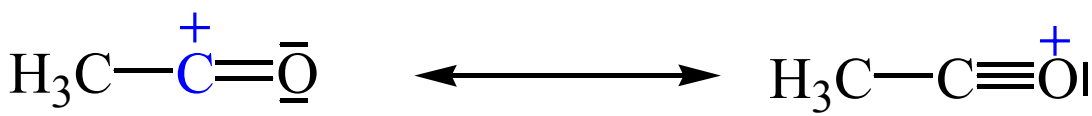
Stabilisierung durch Konjugation



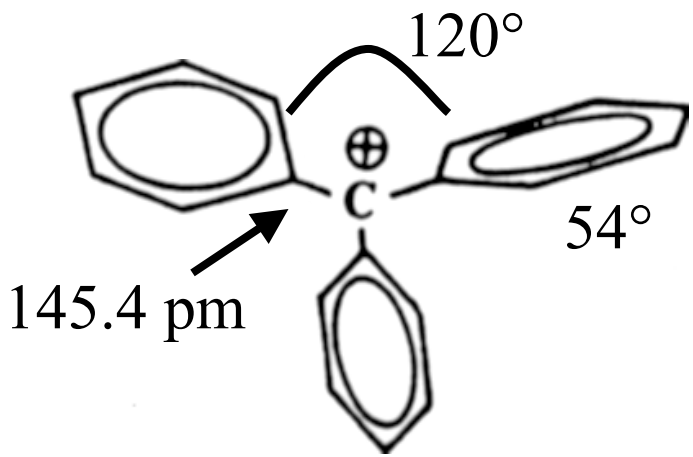
$D(R^+H^-)$ 840 940 1154 destabilisiert

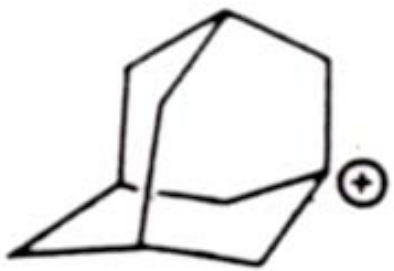


$D(R^+H^-)$ 1010

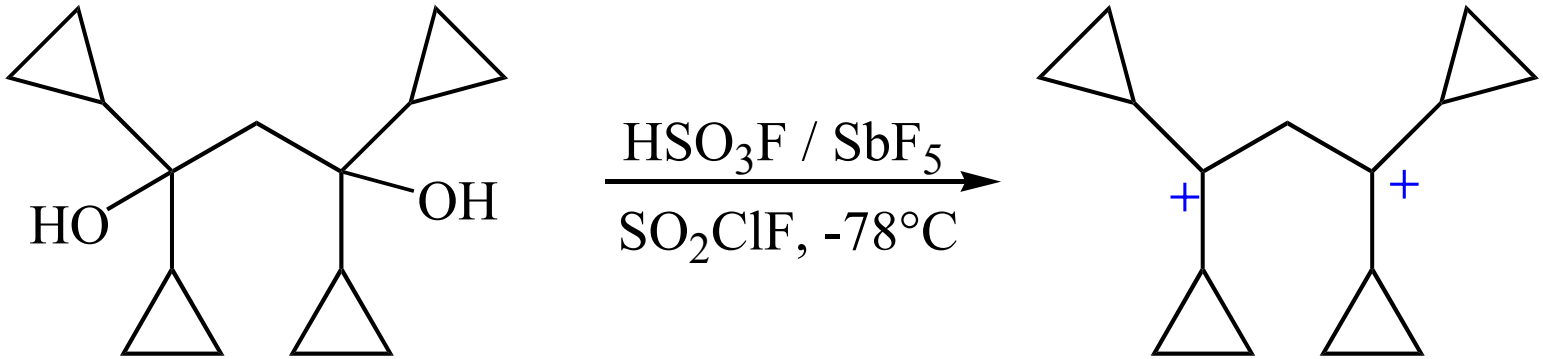


Triphenylmethyl- und polycyclische Kationen

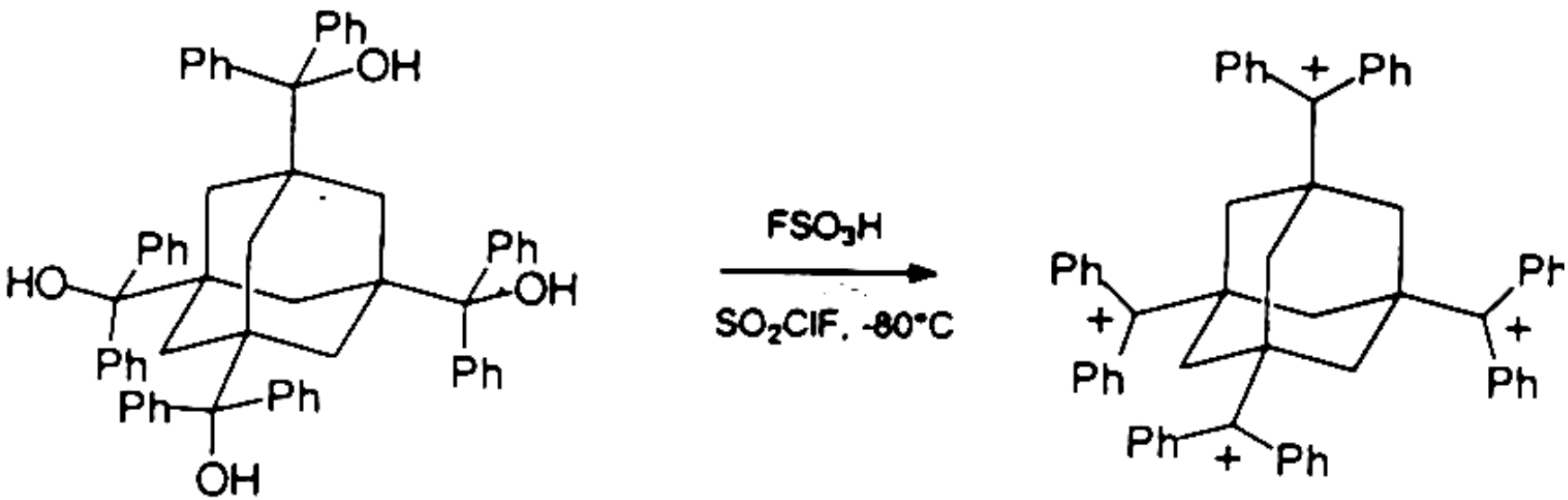




Di- und Tetracarbokationen



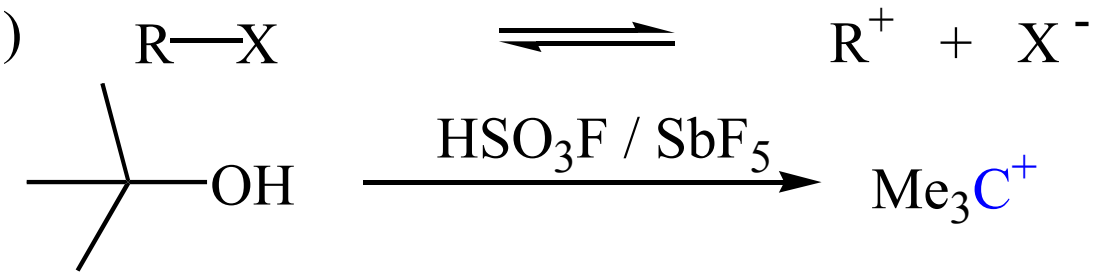
S.A. Olah et al., *J. Am. Chem. Soc.* **1999**, *121*, 9994-9998



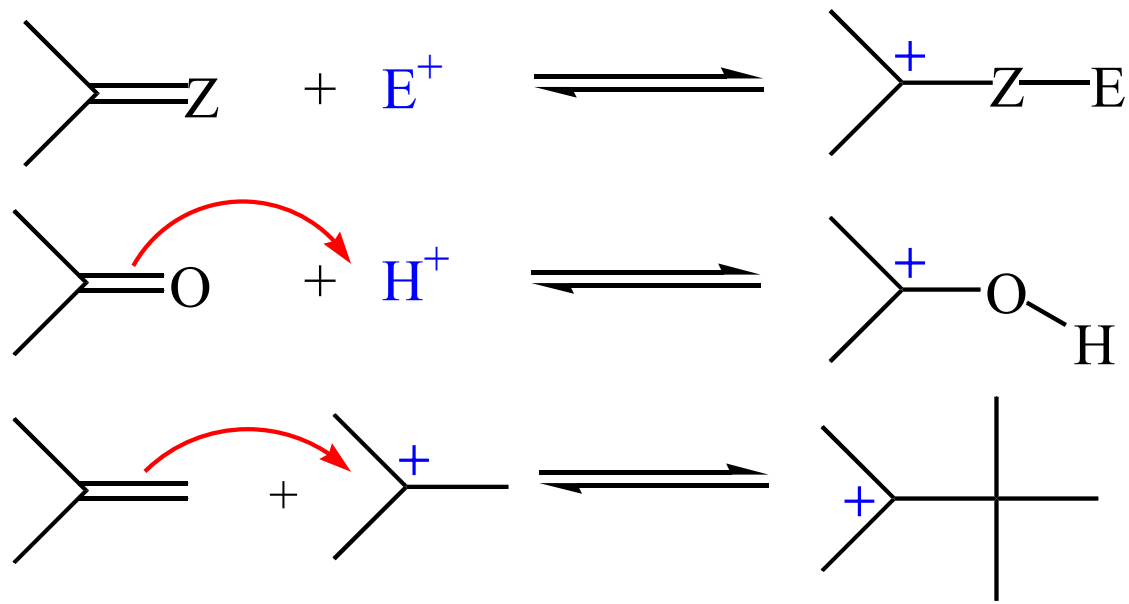
1 **2**

Darstellung und Reaktionen

1)



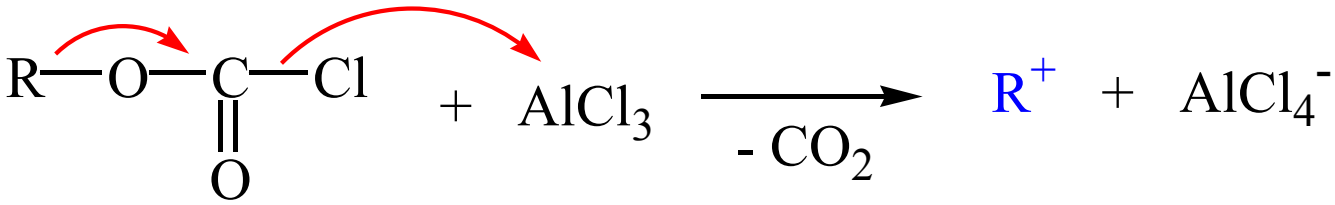
2)



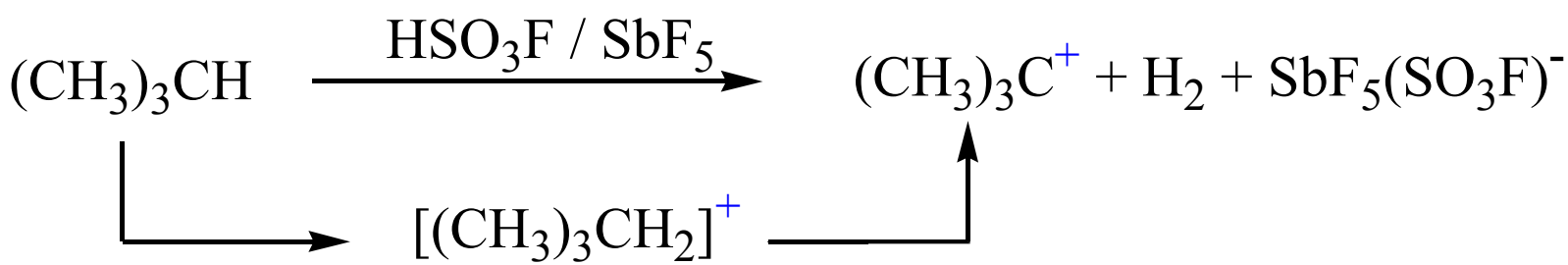
3)

Darstellung und Reaktionen

4) $R{-}NH_2 \xrightarrow[-\,N_2]{HNO_3} R^+$

5) 

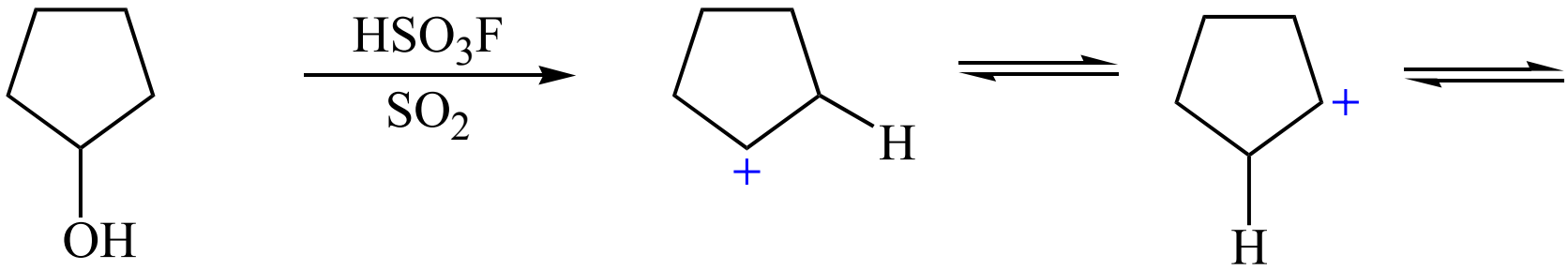
6) $RCO_2^- \xrightarrow[-\,e^-\ -\,CO_2]{} R \xrightarrow[-\,e^-]{} R^+$ (Anode)

7) 

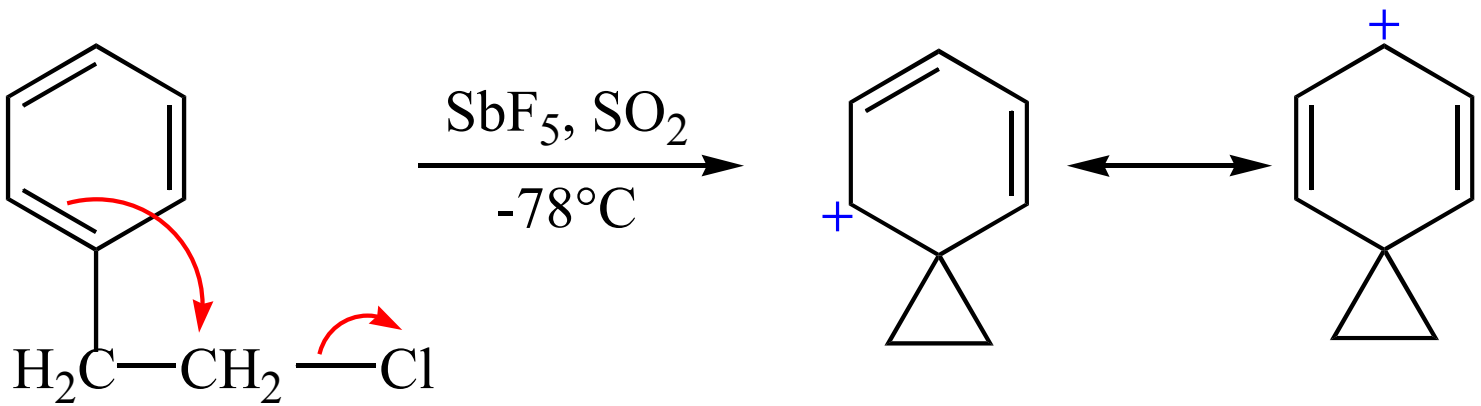
stabile Lösungen von tBu^+ in „magischer Säure“;

$SbF_5(SO_3F)^-$ in SO_2 (fl): sehr schwaches Nucleophil. (NMR bis –150°C)

Umlagerungen



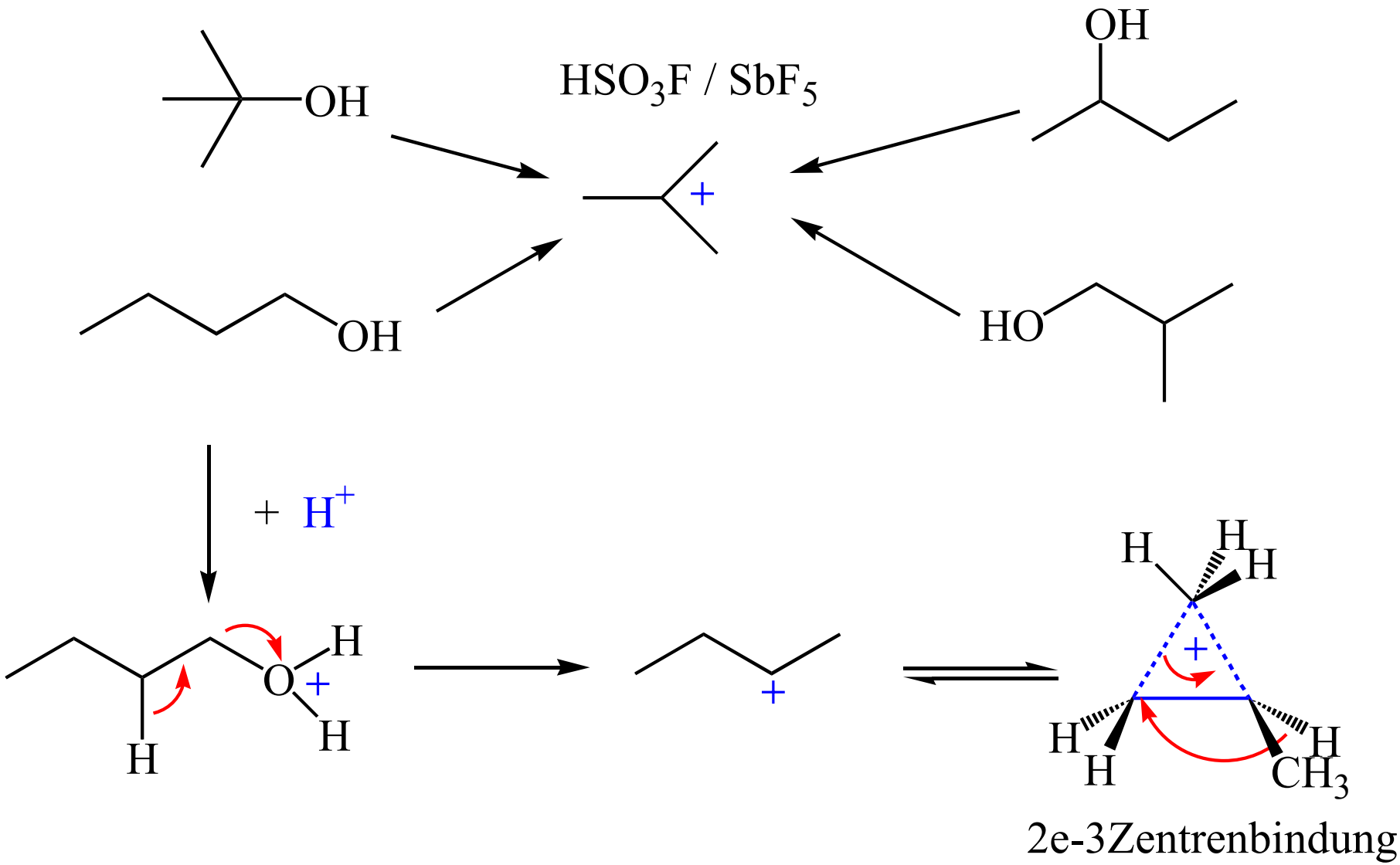
bis -140°C ein Signal im ^{1}H-NMR: sehr schnelle Wagner-Meerwein Umlagerung



Nachbargruppeneffekt des Phenylrestes

Phenoniumion

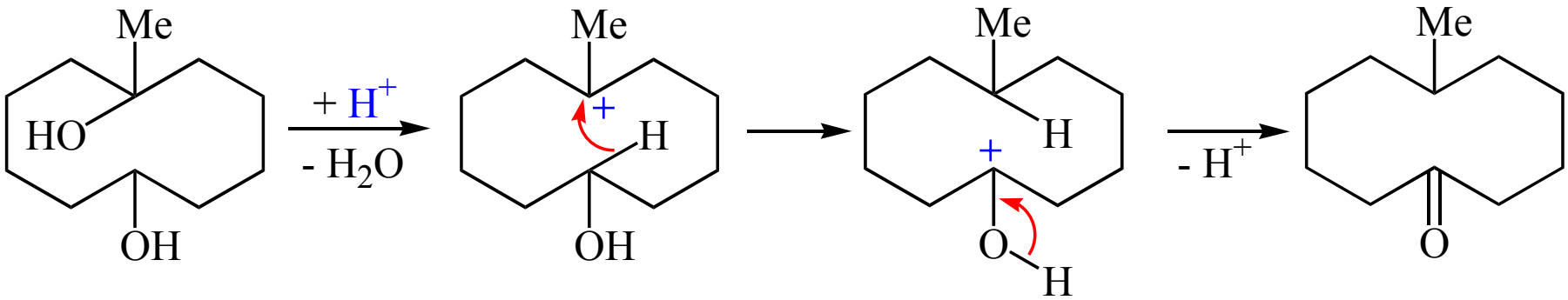
Umlagerungen



2e-3Zentrenbindung

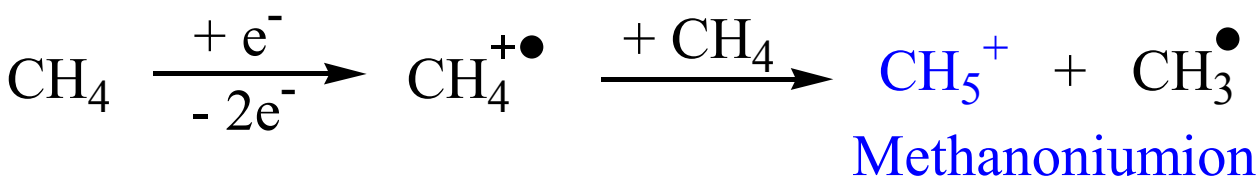
Umlagerungen

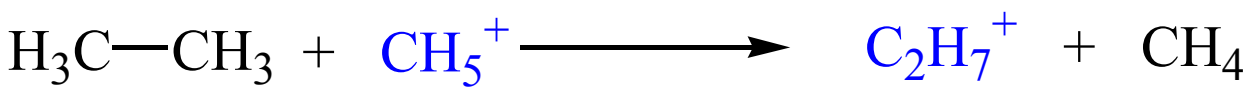
transansannulare Umlagerung:



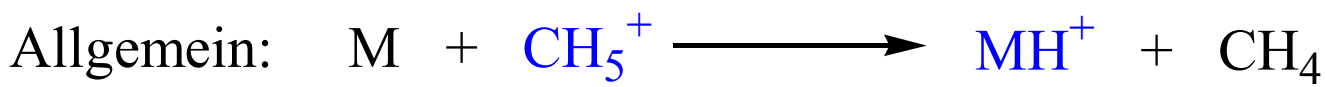
Carboniumionen

1. Gasphase



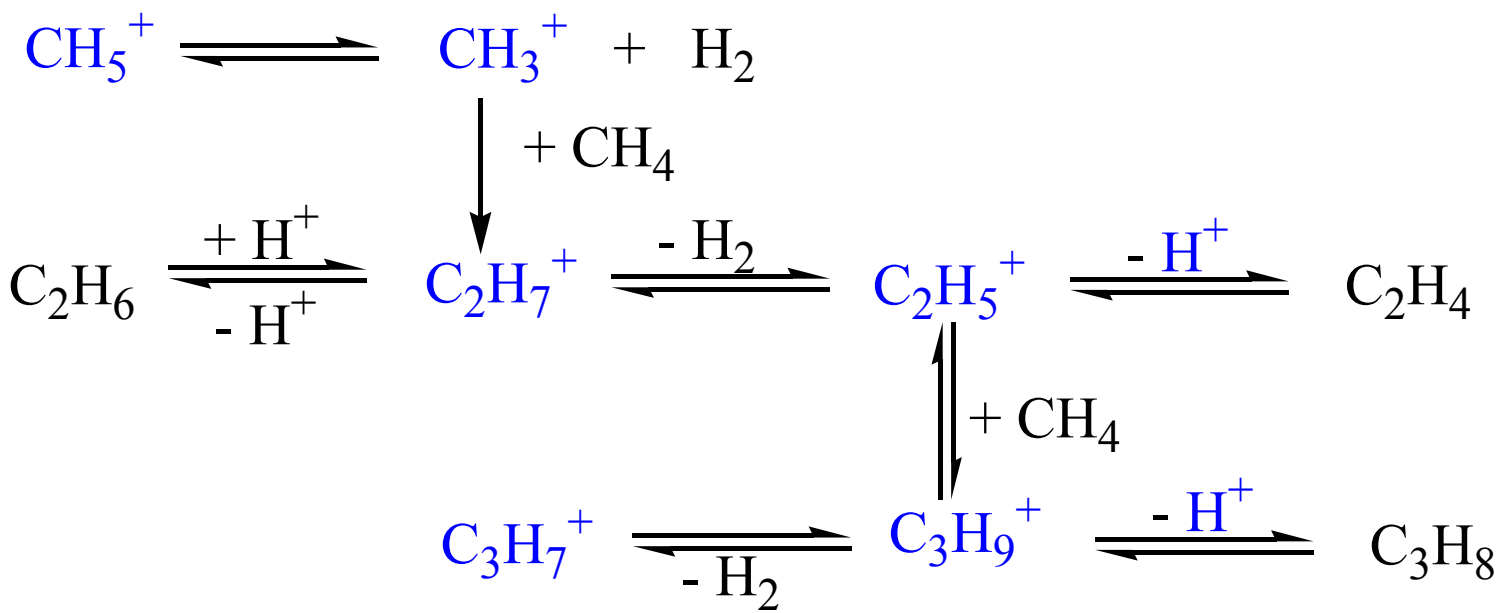


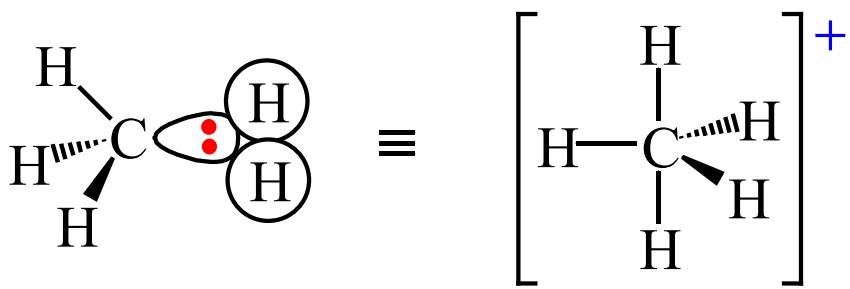
Chemische Ionisation



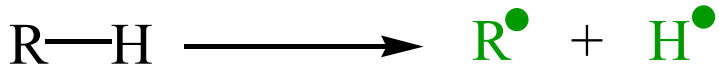
Carboniumionen

2. Lösung $CH_4 \xrightleftharpoons{DSO_3F / SbF_5} [CH_4D]^+ \xrightleftharpoons{-H^+} CH_3D$



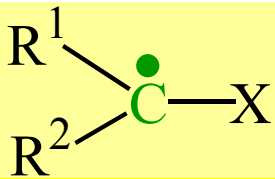


2.2 Radikale

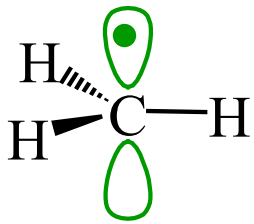


R:	Me	Et	iPr	tBu
BDE [kJ/mol]	440	410	396	389

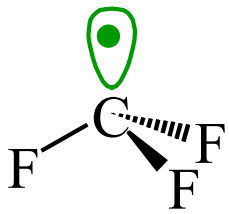
Stabilität R• ⟶

	Stabilisierung [kJ/mol]
Me	0
Ph < $HC{=}CH_2$ ≈ $C{\equiv}CH$	45 - 50
COOR < $C{\equiv}N$ < $CR'{=}O$ ≈ NO_2	25 - 40
Cl < OR' < NR'_2 < SR'	10 - 40
CF_3	- 5
NH_3^+	- 16

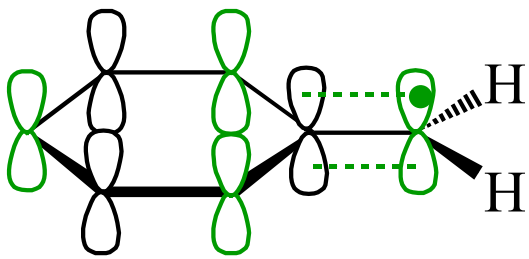
Struktur von Radikalen



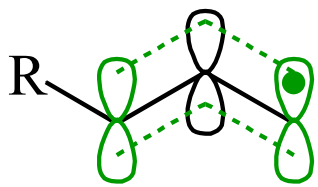
sp^2



sp^3



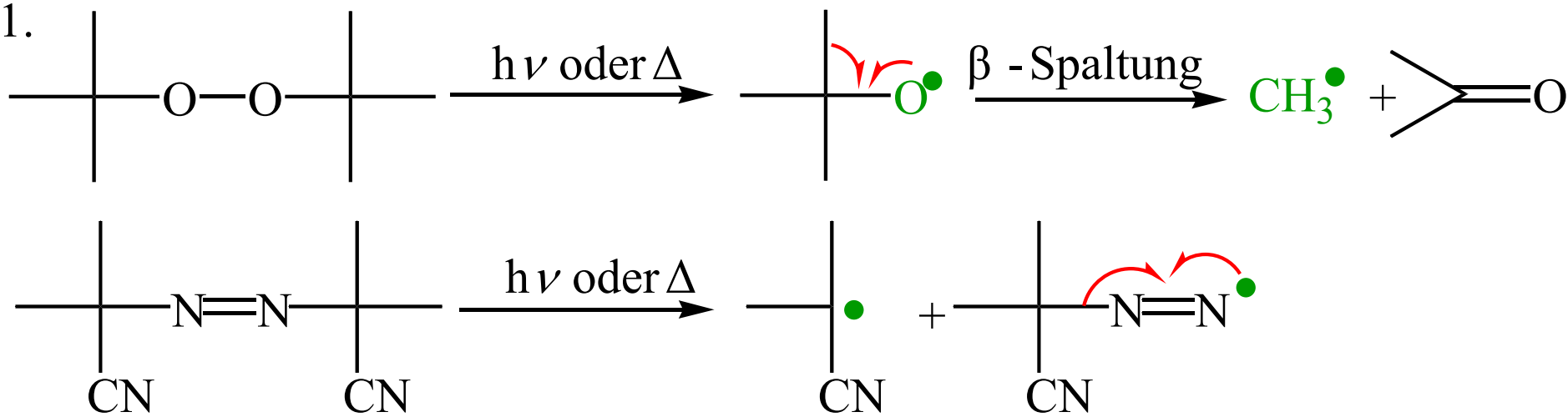
sp^2



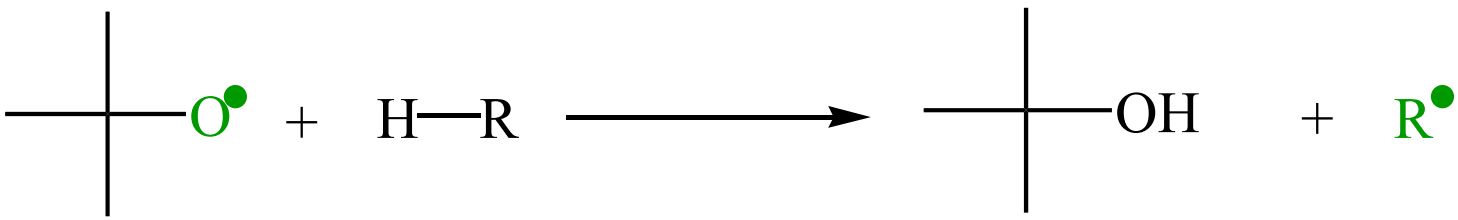
sp^2

Erzeugung und Reaktion von Radikalen

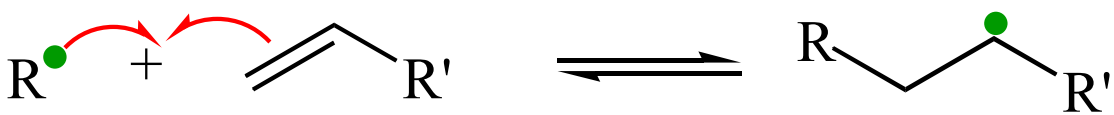
1.



2. Atomabstraktion

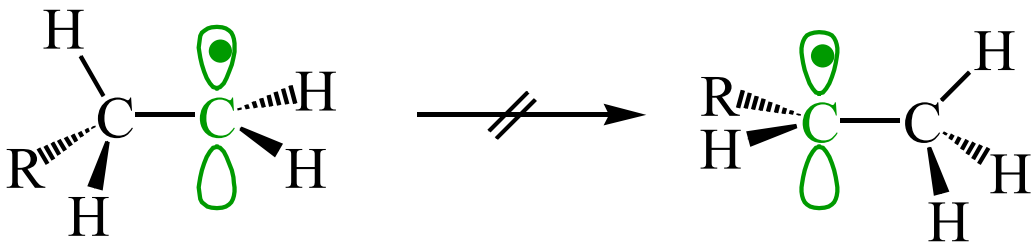


3. Addition ⇌ β - Spaltung

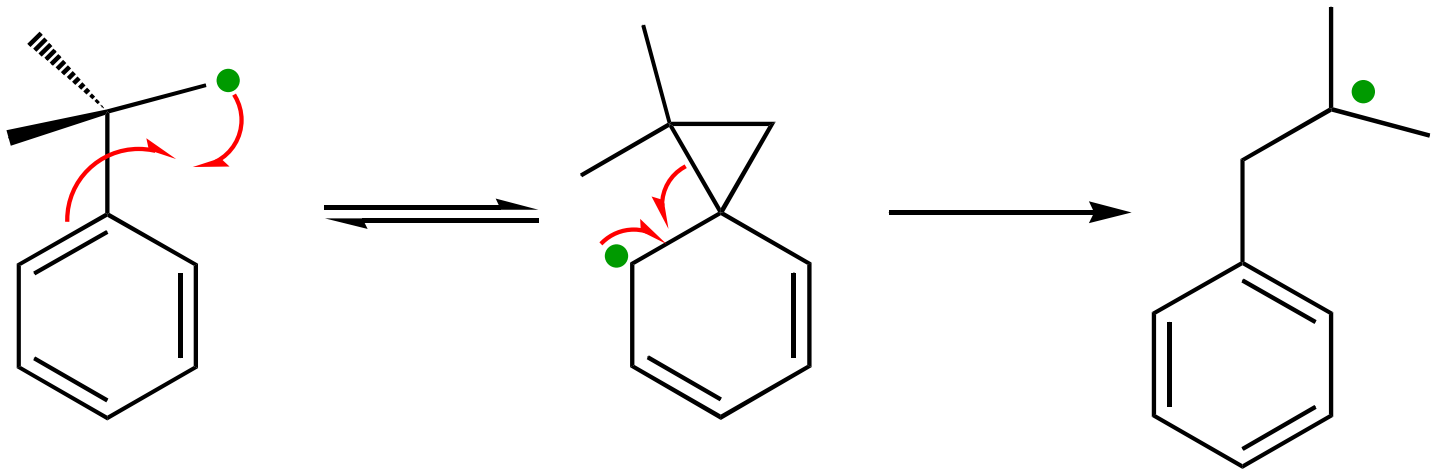


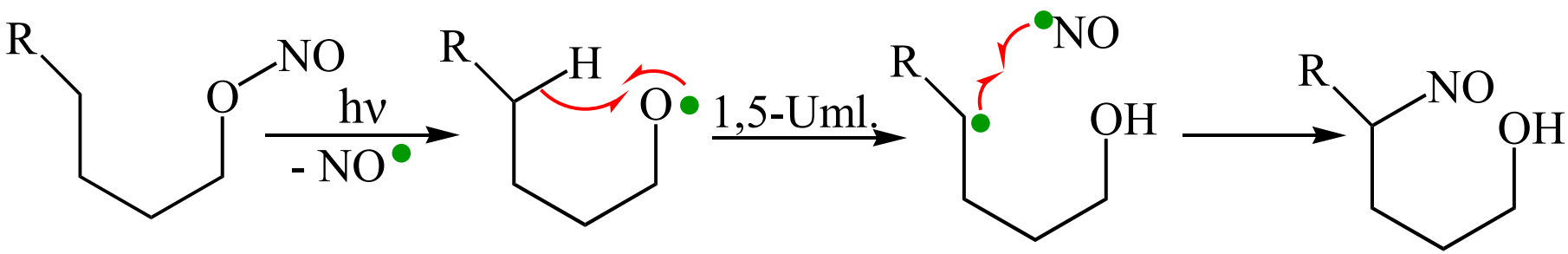
Erzeugung und Reaktionen von Radikalen

4. Umlagerungen



1,2 Umlagerung (R,H) geht nicht.



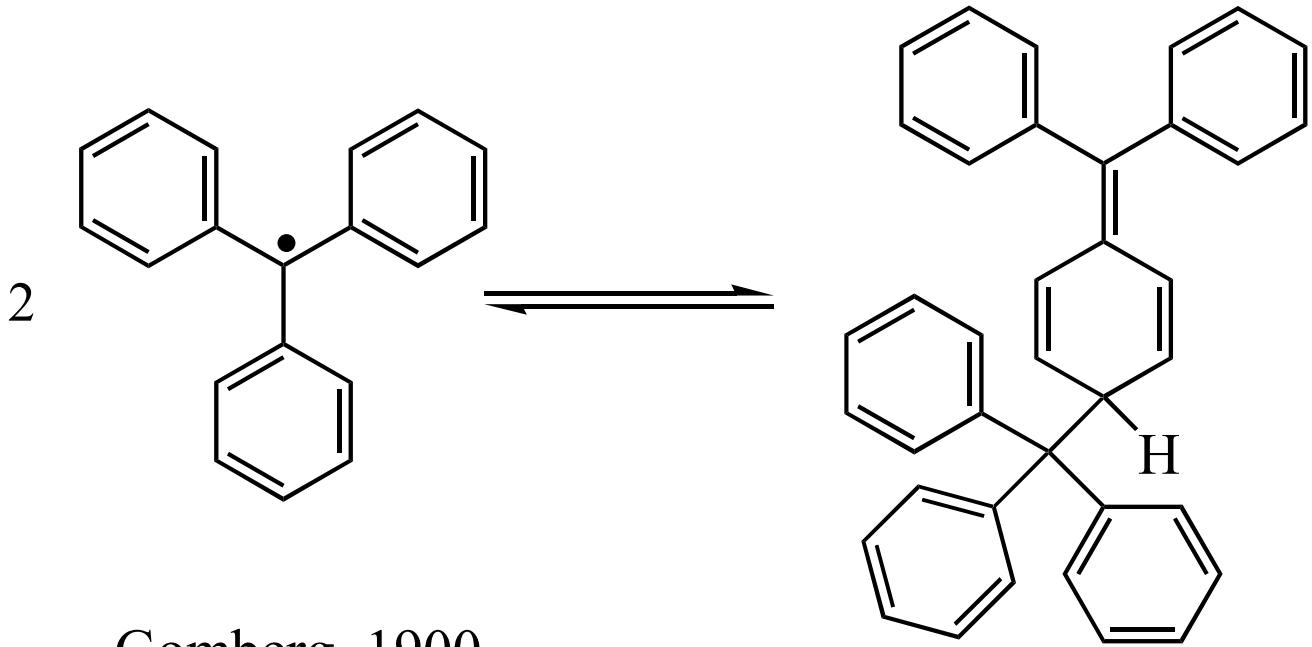


Erzeugung und Reaktionen von Radikalen

5. Radikal-Radikalreaktionen: Rekombination
Disproportionierung

6. Radikalkettenreaktionen

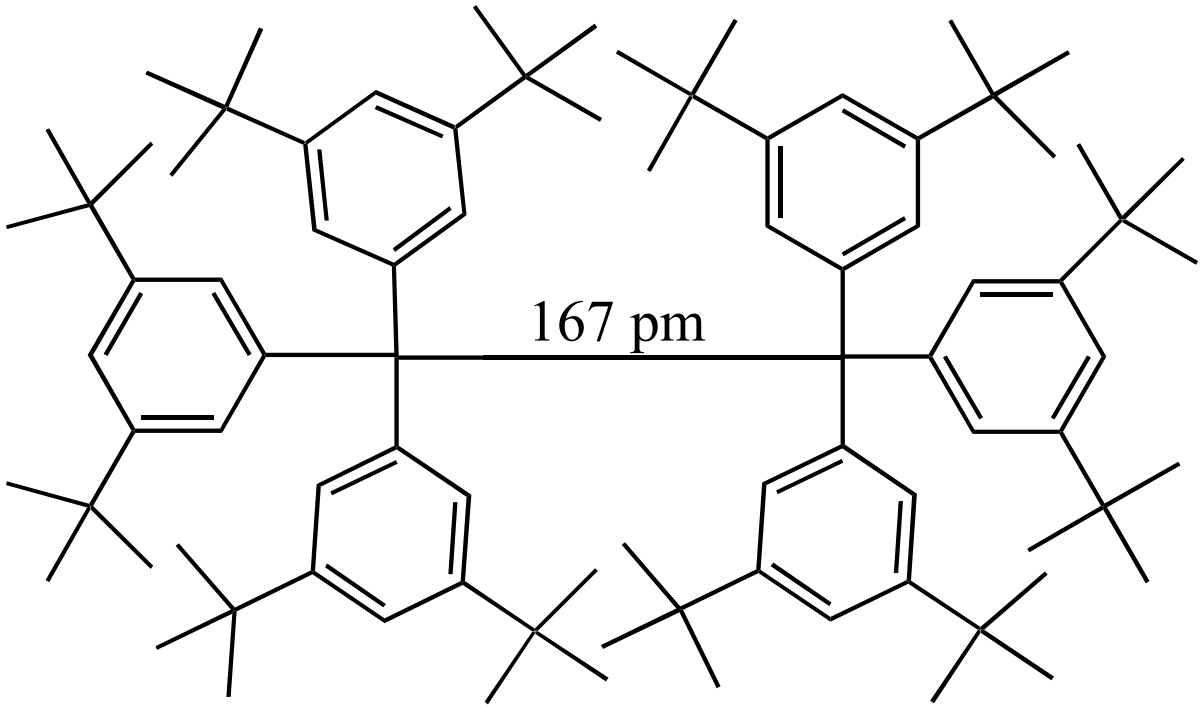
Stabile Radikale



Gomberg, 1900

1-Diphenylmethylen-4-trityl-
2,5-cyclohexadien

http://www.cpes.sussex.ac.uk/motm/index.html



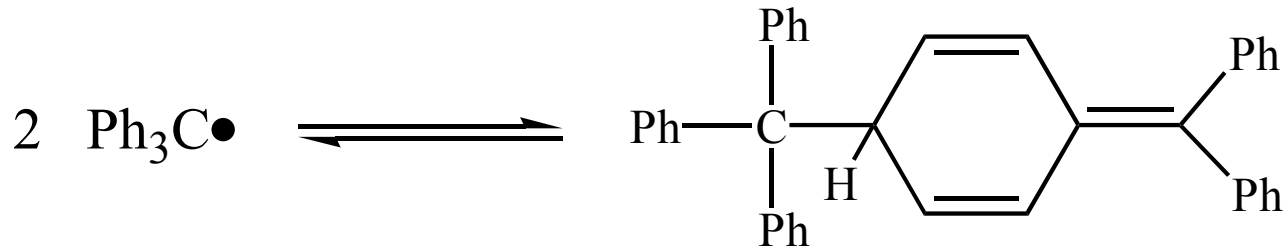
Mislow, 1986

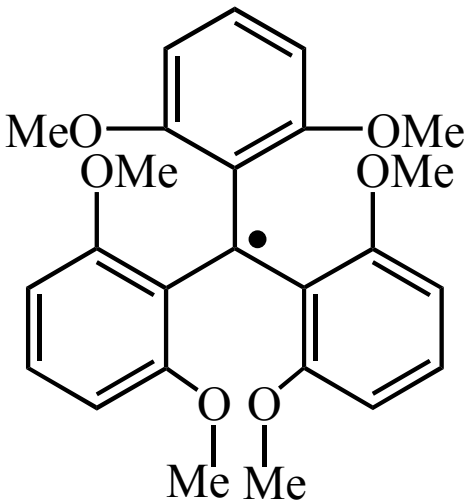
154 pm

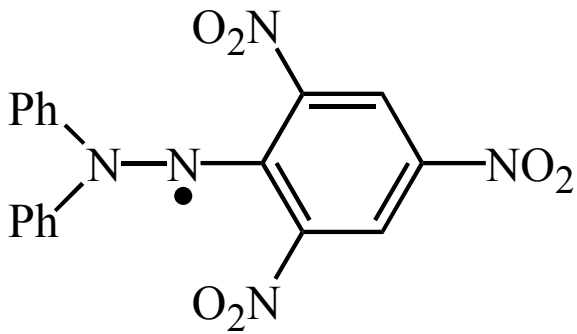
$H_3C—CH_3 \rightleftharpoons 2\ {}^{\bullet}CH_3$

BDE = 376 kJ mol^{-1}

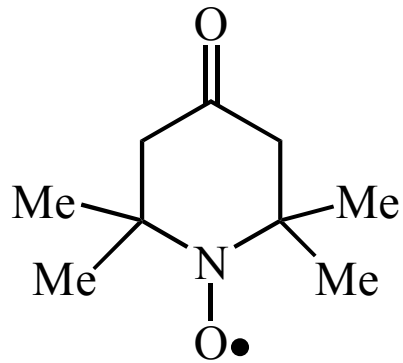
Stabile Radikale



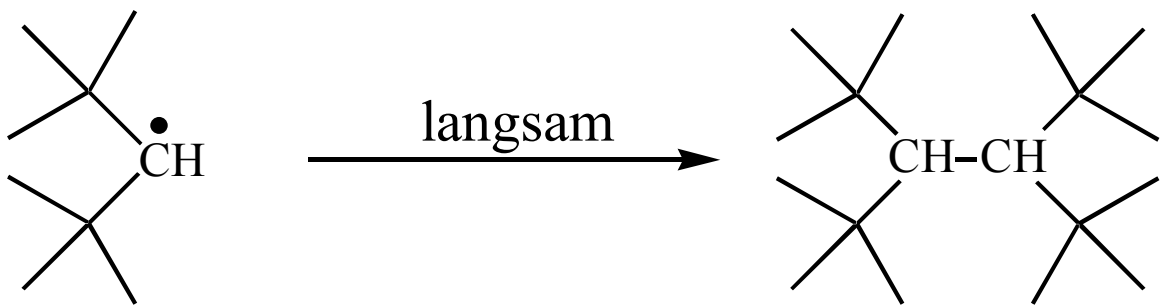




Diphenylpicrylhydrazyl

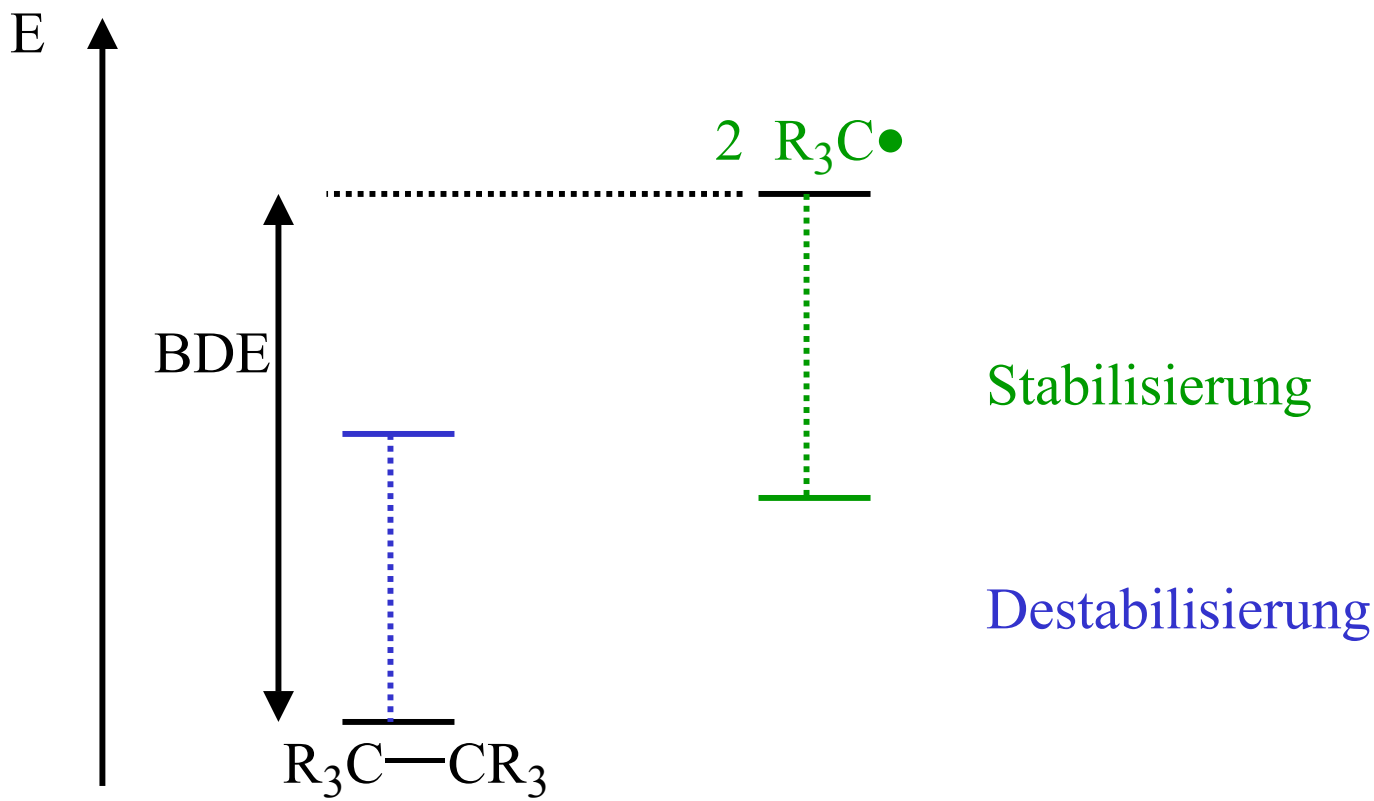


4-Oxo-TEMPO

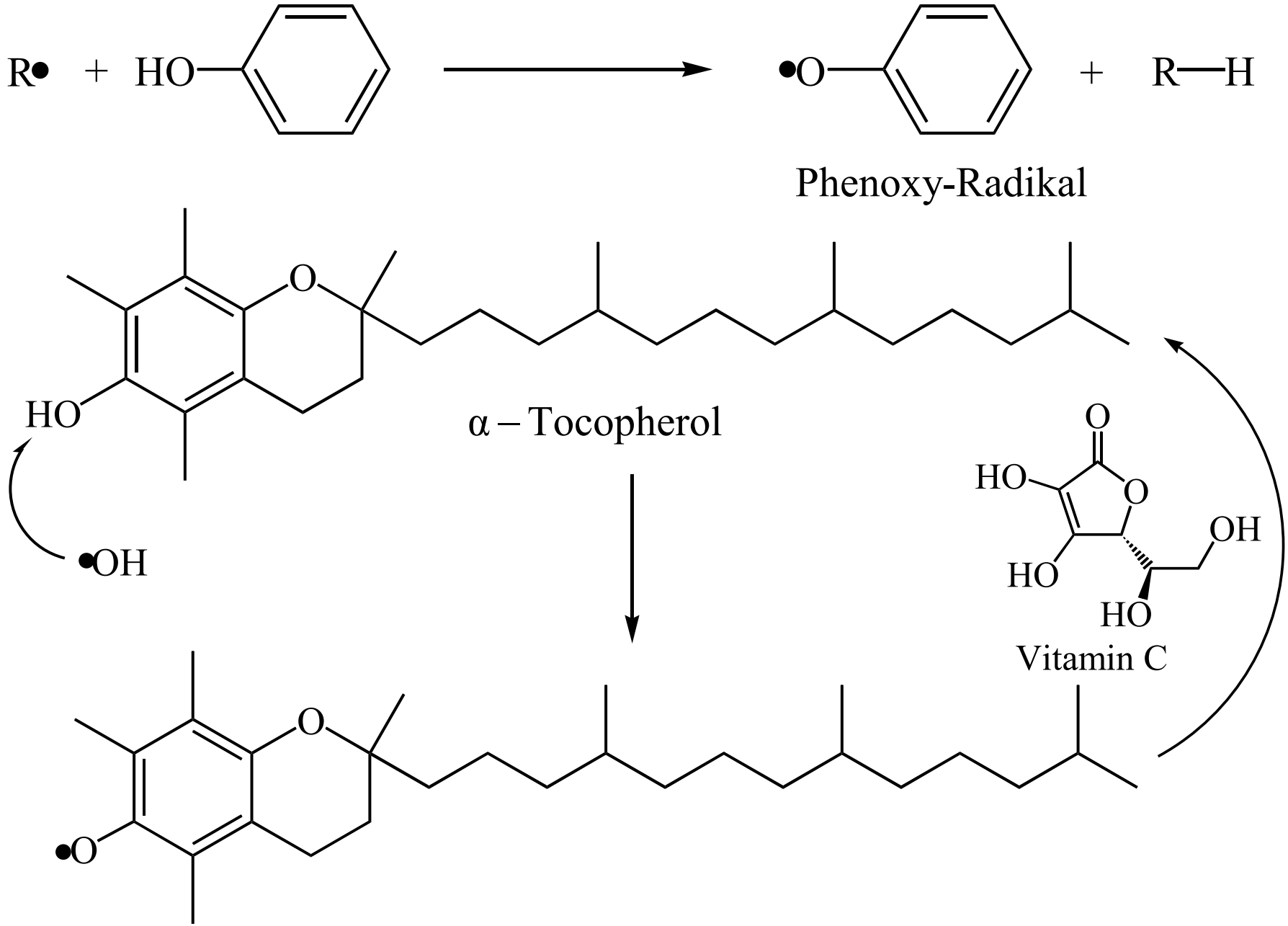


persistentes Radikal

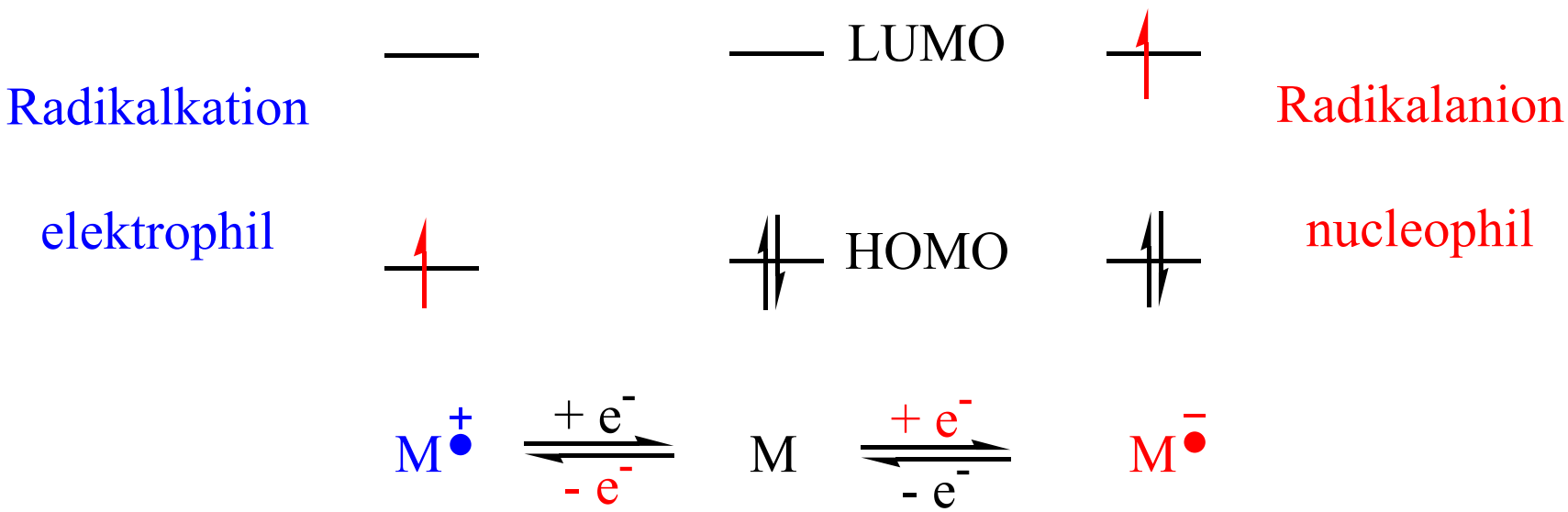
Stabile Radikale



Phenole als Radikalfänger; Tocopherol



2.3 Radikalionen



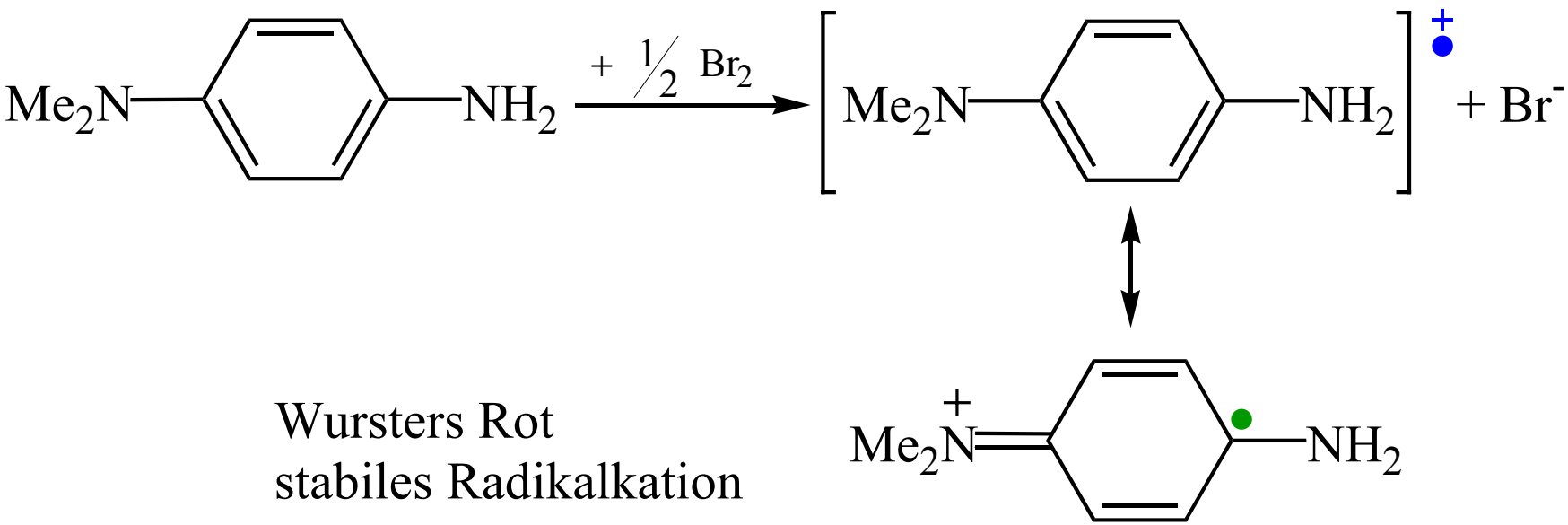
2.3.1 Radikalkationen

1. $M + e^- \longrightarrow M^{+\bullet} + 2\,e^-$ Elektronenstoßionisation
   → Massenspektrometrie

2. In Lösung: $M + Ox \longrightarrow M^{+\bullet} + Red^-$

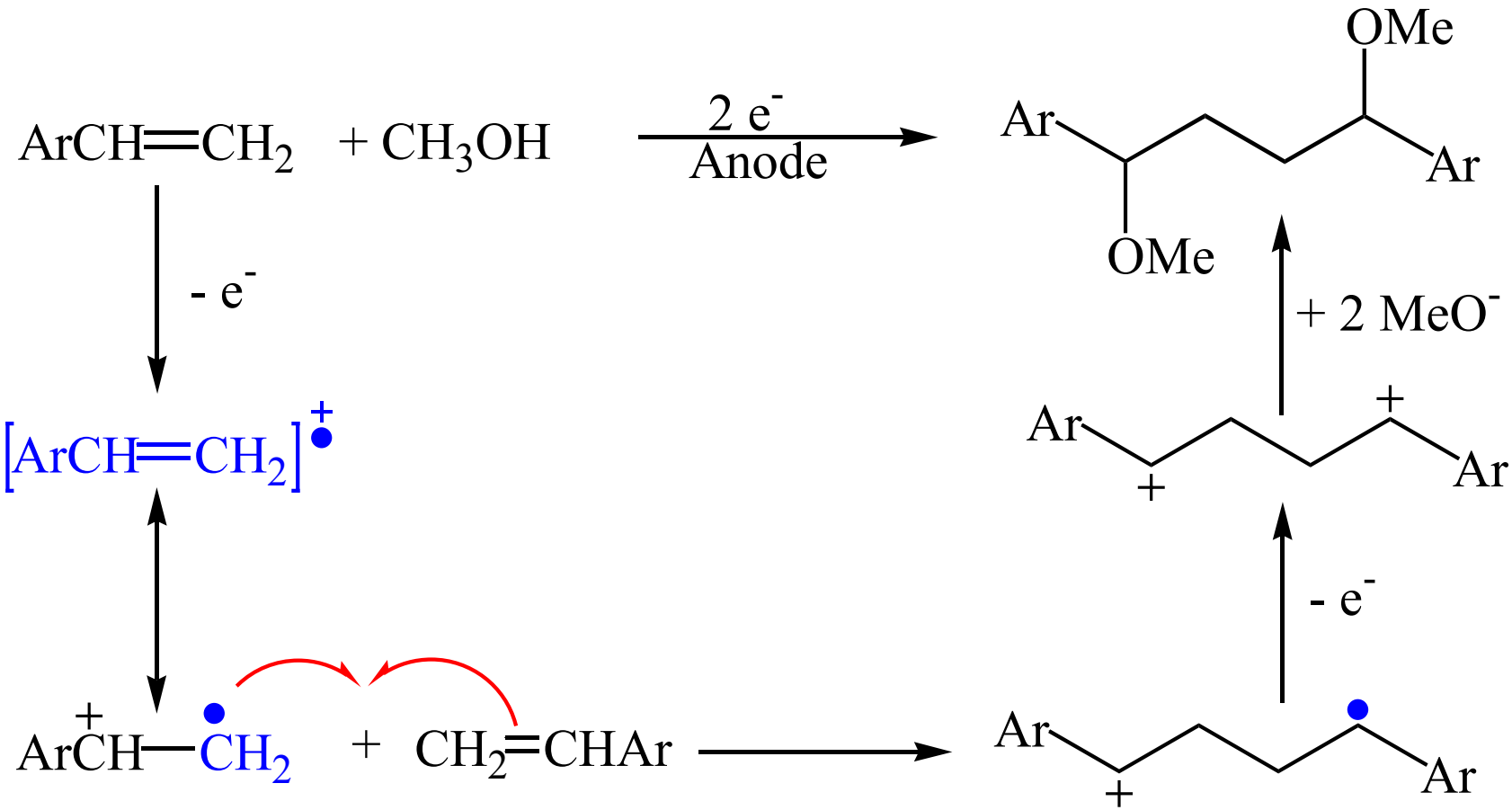
   Ox: Einelektronenoxidationsmittel

   Anode, Co^{3+}, Mn^{3+}, Cu^{2+}, Ce^{4+} u.a.

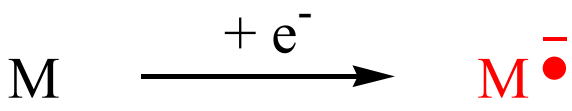


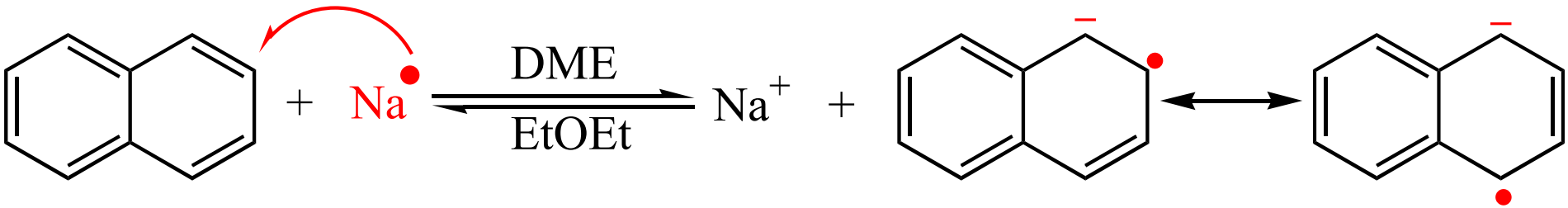
Wursters Rot
stabiles Radikalkation

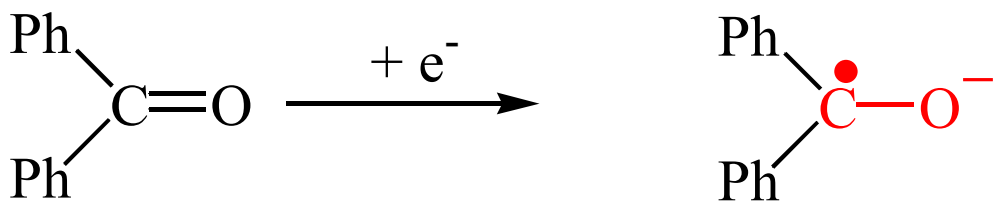
Radikalkationen



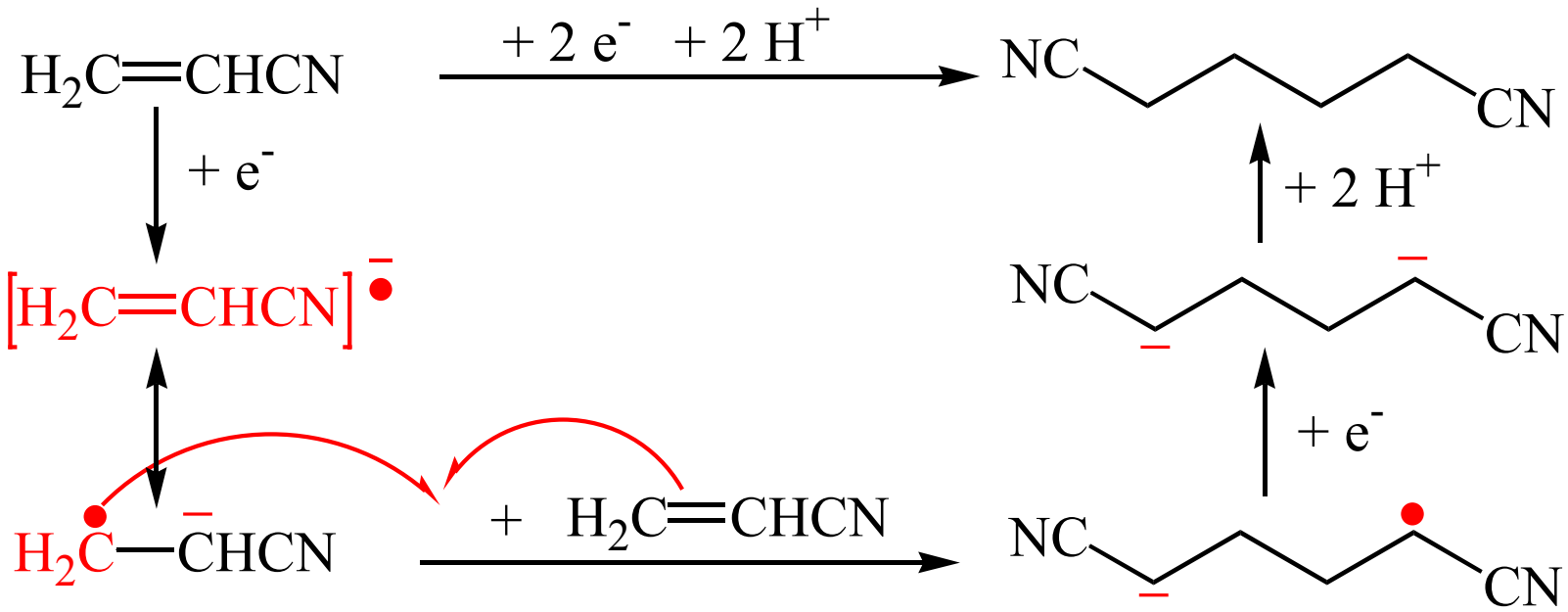
2.3.2 Radikalanionen

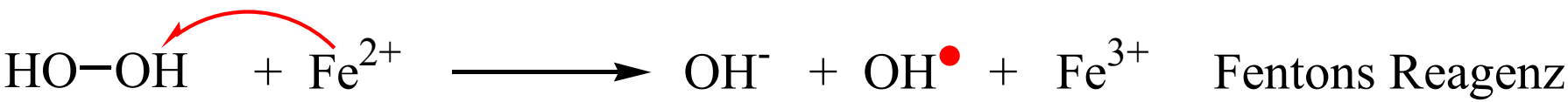


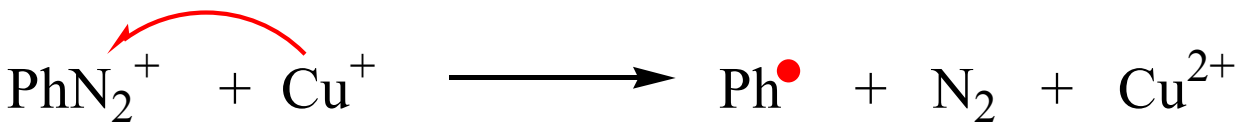


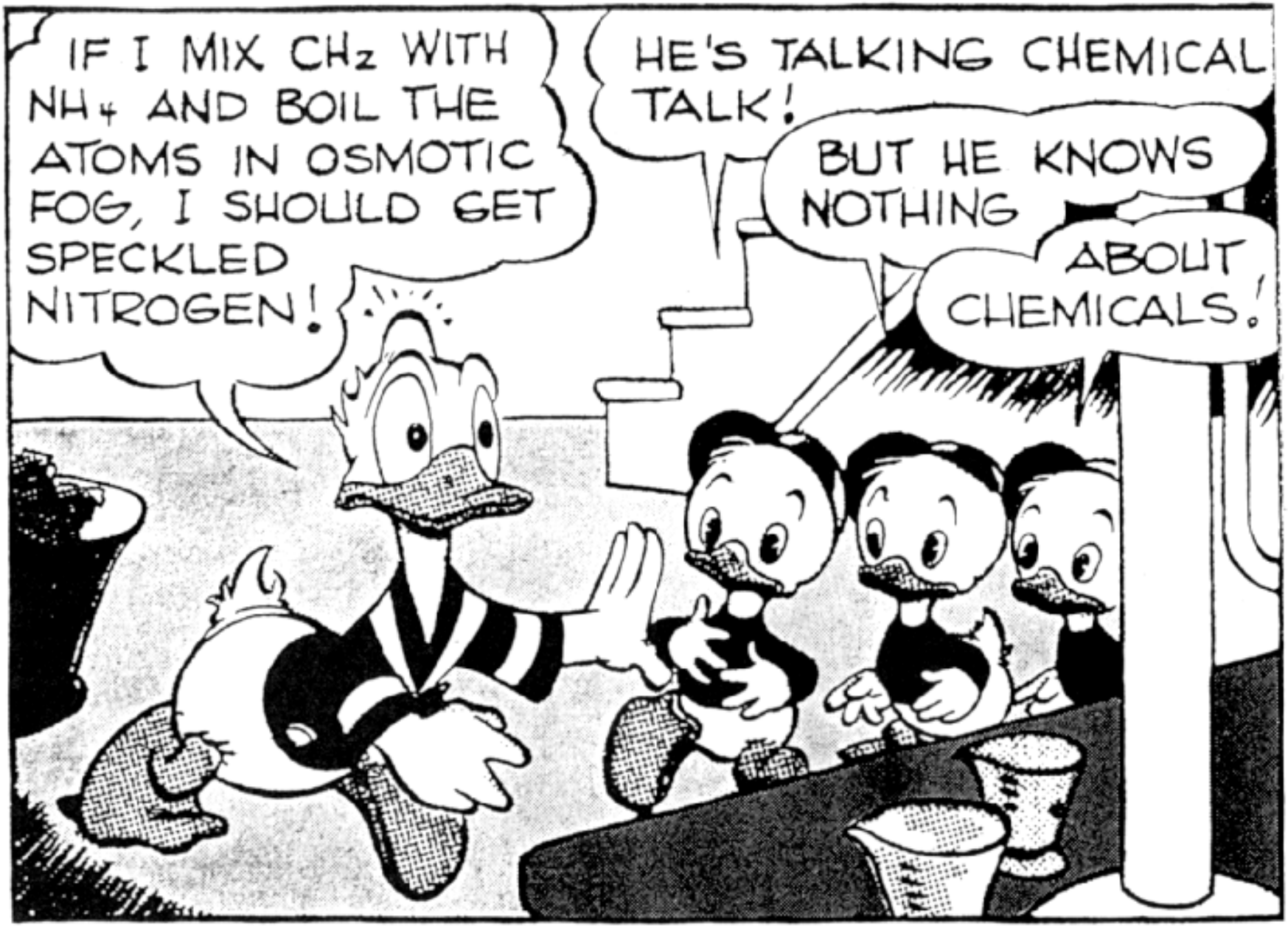


Radikalanionen



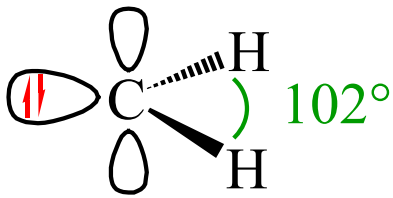


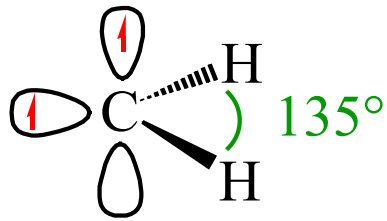




2.4 Carbene

2.4.1 Struktur



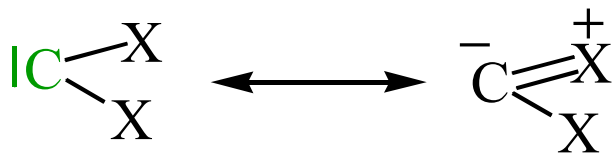


sp^2, gewinkelt
$^1CH_2$

sp^2
$^3CH_2$ (Grundzustand)

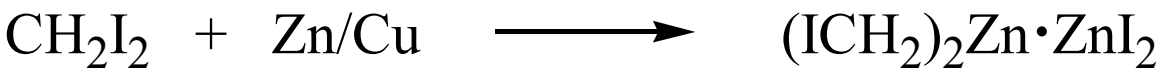
$$^1E_0 - {}^3E_0 \approx 35\ kJ/mol$$

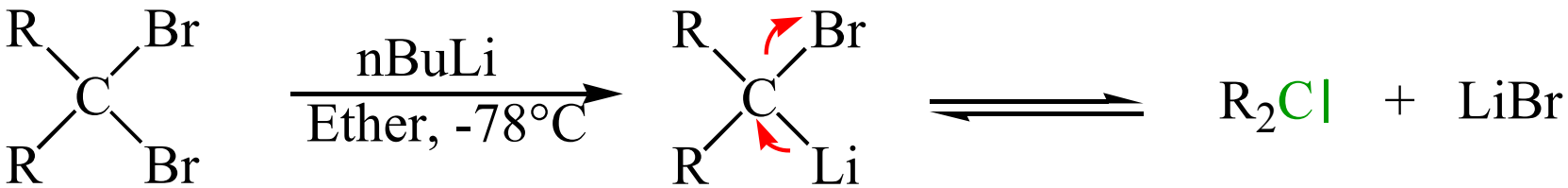
$^1CCl_2$, $^1CBr_2$, $^1CI_2$



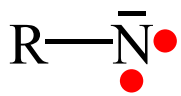
Arylcarbene ^3HCAr

Carbenoide

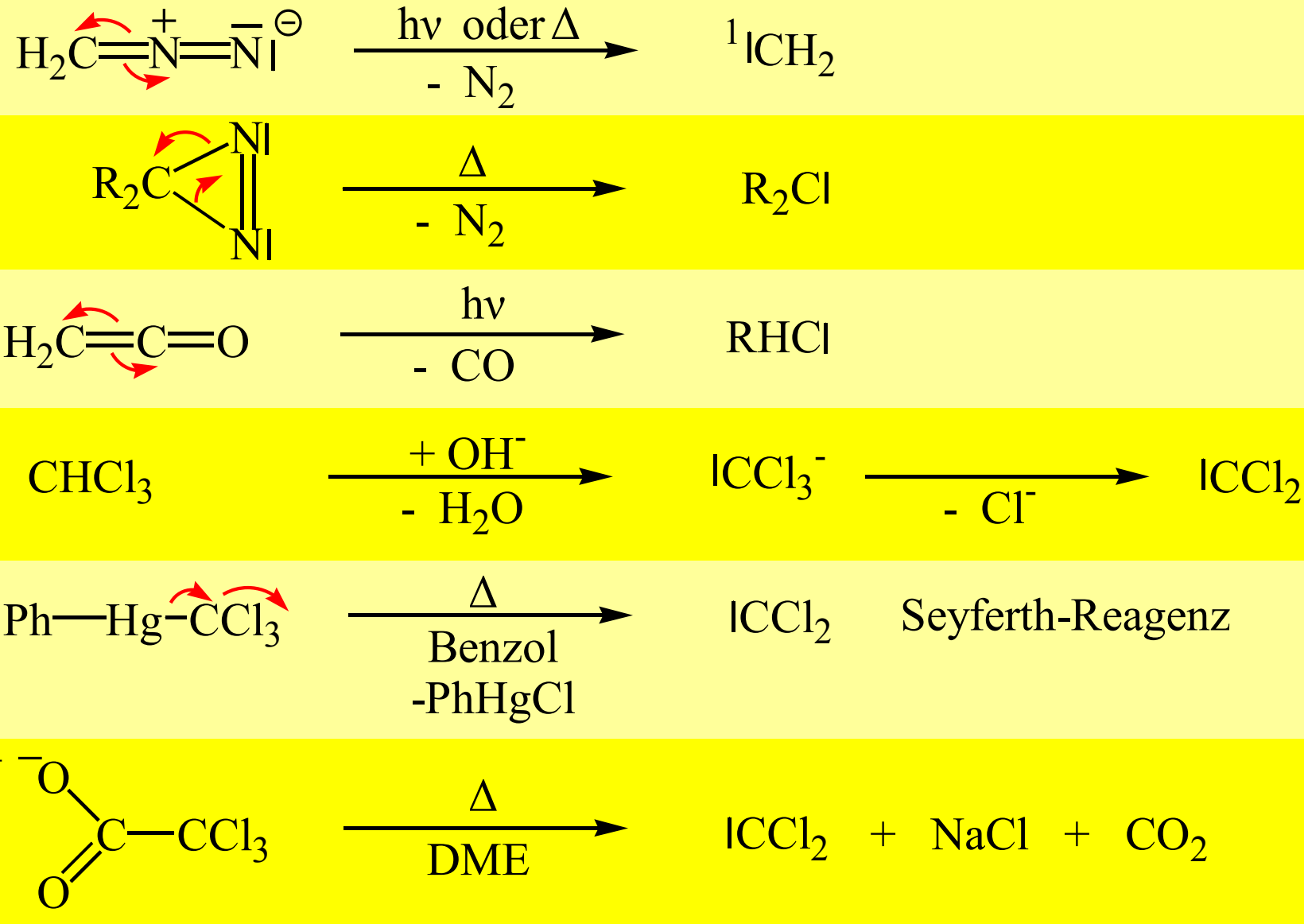




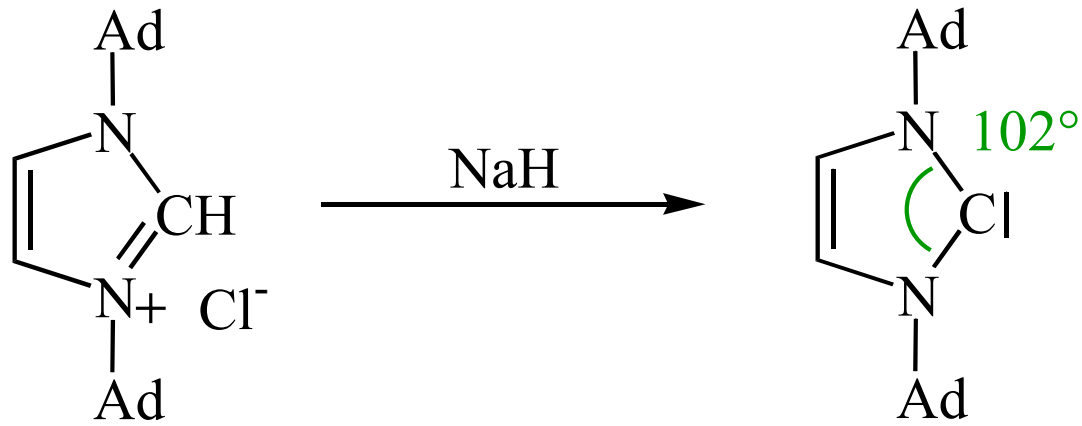
Nitrene



2.4.2 Erzeugung



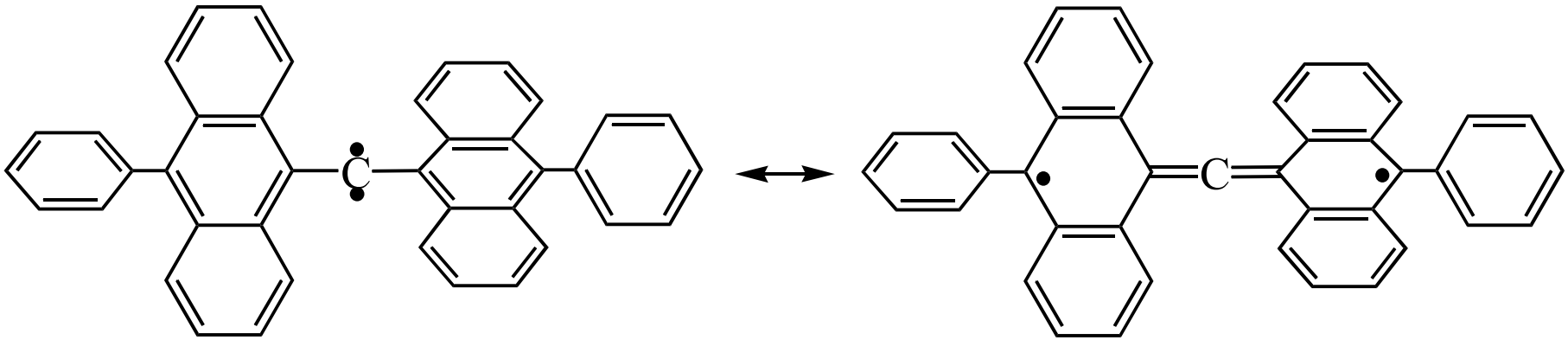
Stabile Carbene



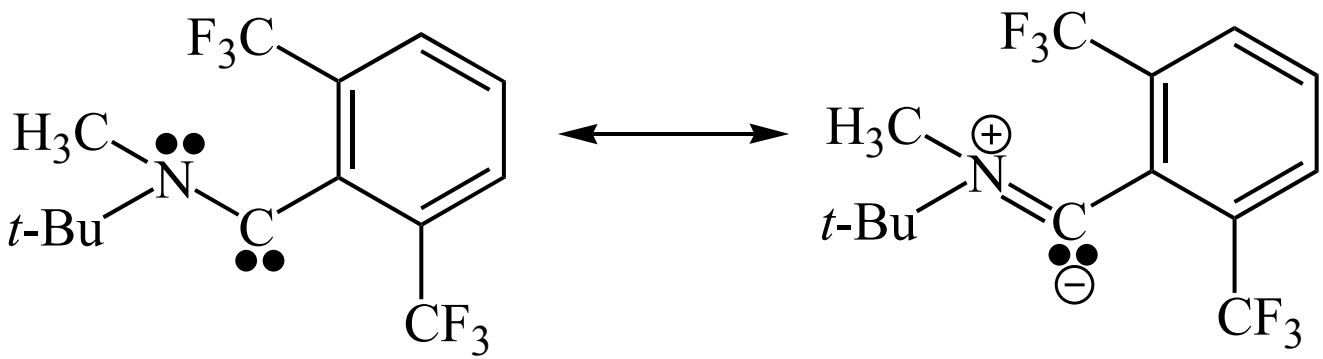
1,3-Di-1-adamantyl-imidazol-2-yliden-imidazoliumchlorid

A.J. Arduengo, III und R. Krafczyk, *ChiuZ* **1998**, *32*, 6

Stabile Carbene

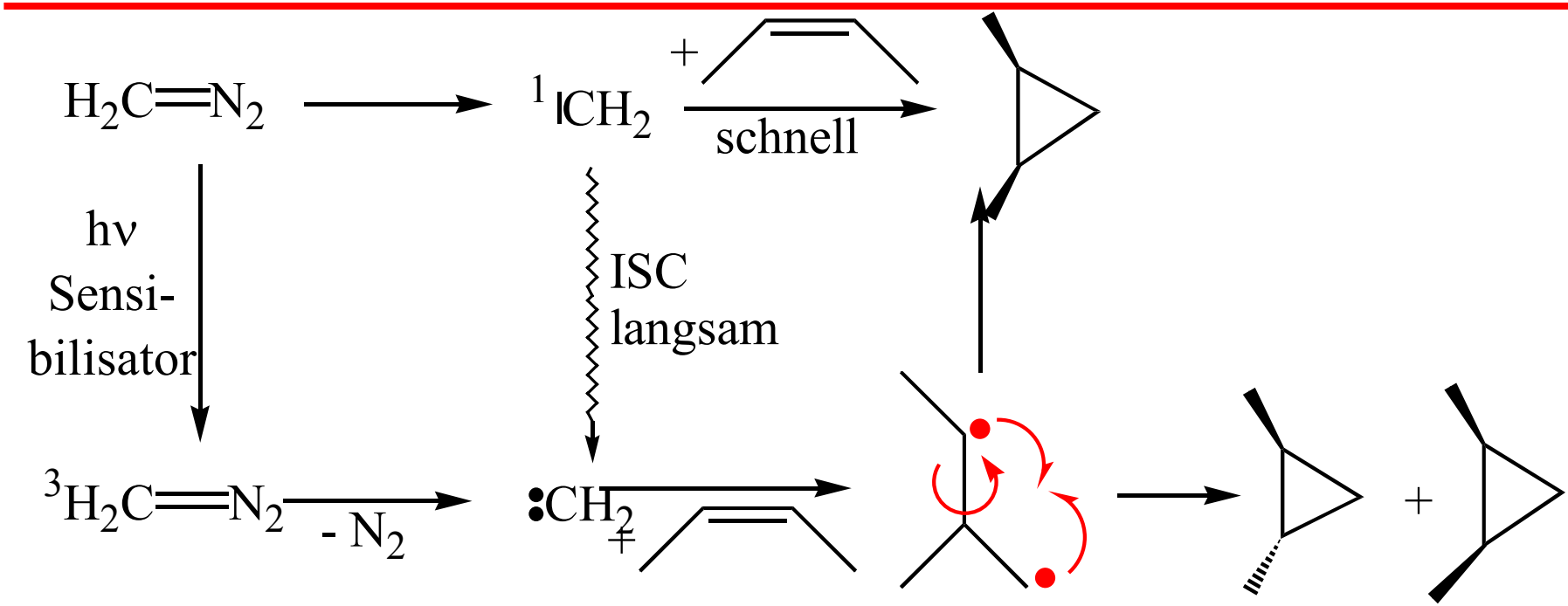


Hideo Tomioka et al., *Nature* **2001**, *412*, 626

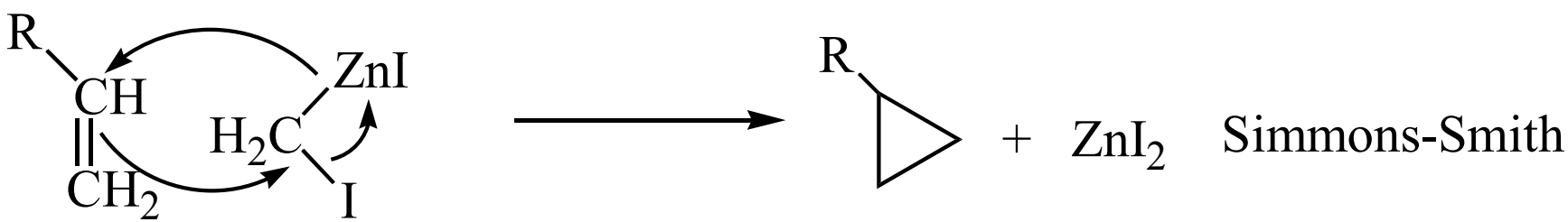


Guy Bertrand et al., *Science* **2001**, *292*, 1901 - 1903

2.4.3 Reaktionen



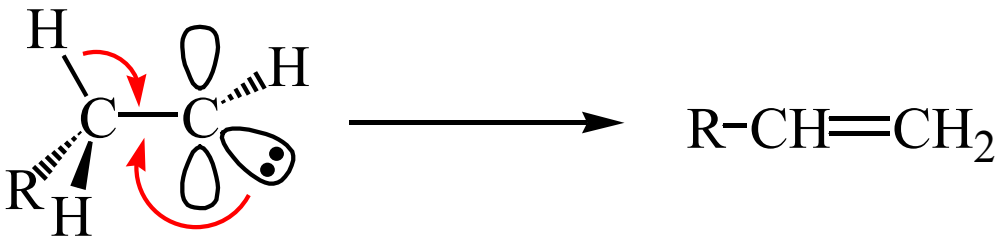
Reaktivität: $^1|CH_2 > {}^1|CHCl > {}^1|CCl_2 > {}^1|CBr_2 > {}^1|CI_2 >$ Carbenoide



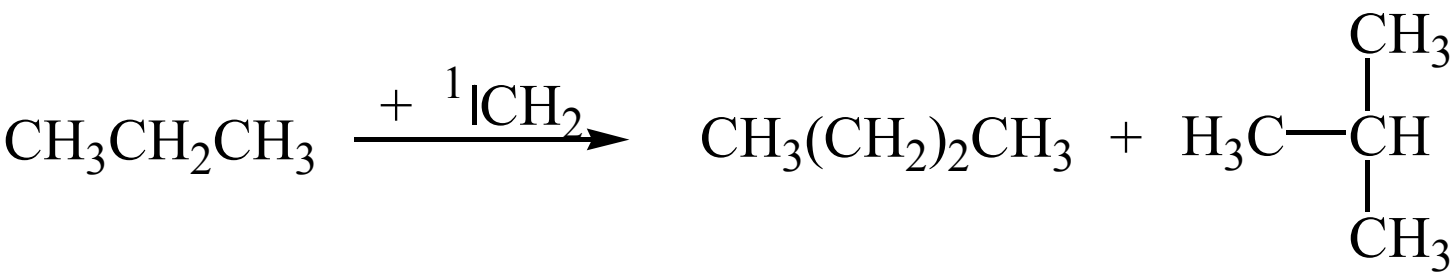
analog: $RCHI_2$, $ArCHI_2$

Reaktionen

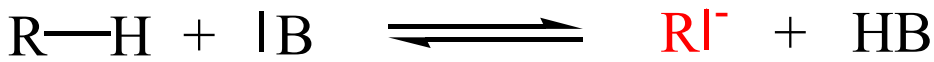
Umlagerung: schneller 1,2 Shift



Insertion in C-H-Bindungen



2.5 Carbanionen

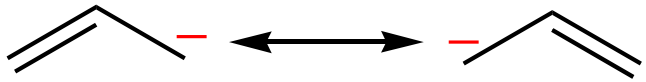


	Me^-	Et^-	iPr^-	tBu^-
pK_S	48	50	51	> 51

Stabilität ← (in Lösung)

2.5.1 Stabilisierung von Carbanionen

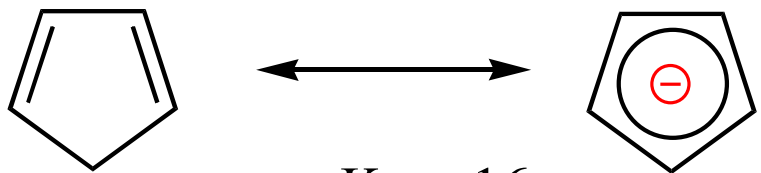
1. Konjugation



$PhCH_2^-$ Ph_2CH^- Ph_3C^-

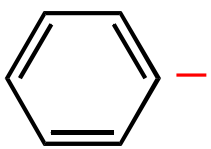
pK_S	43	40	33	31
	$R\bar{C}HCN$	$R\bar{C}HCOOR'$	$^-CH_2NO_2$	$R\bar{C}HC(=O)R'$
	25	24.5	10.6	20

2. Aromatisierung



$pK_S = 16$

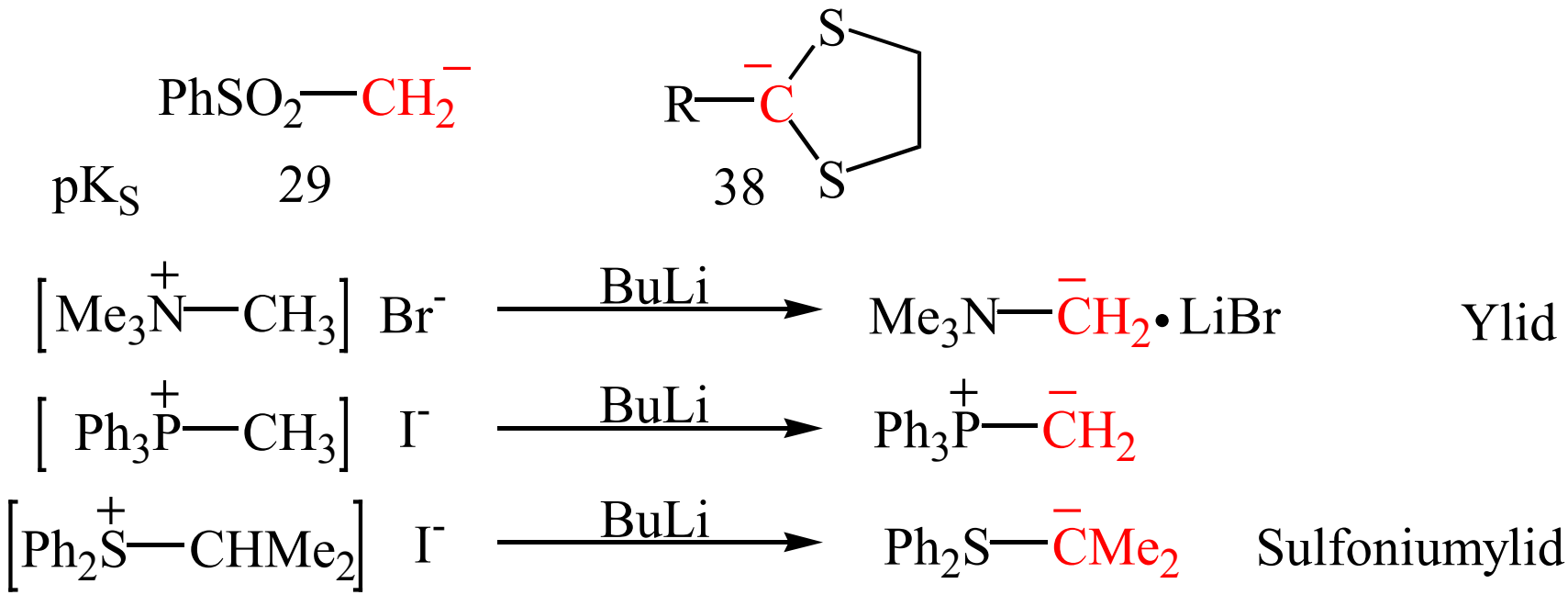
3. Hybridisierung

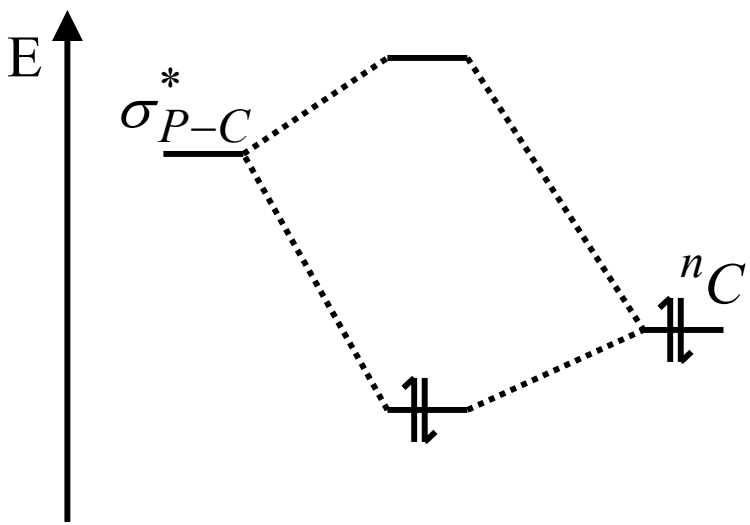


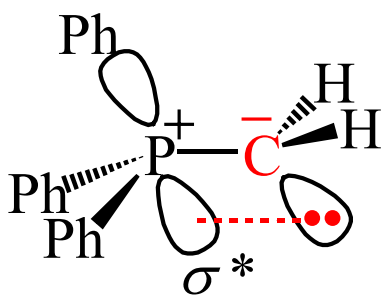
	$R_3C-CH_2^-$	$R_2C=CH^-$		$R-C\equiv C^-$
	sp^3	sp^2	sp^2	sp
pK_S	50	43	43	25

Stabilität →

4. Stabilisierung durch S, P, Si in α-Position



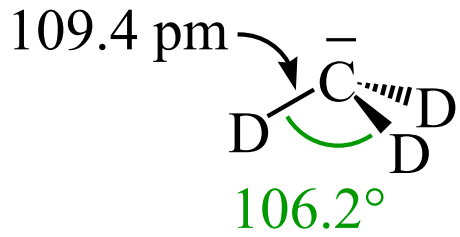




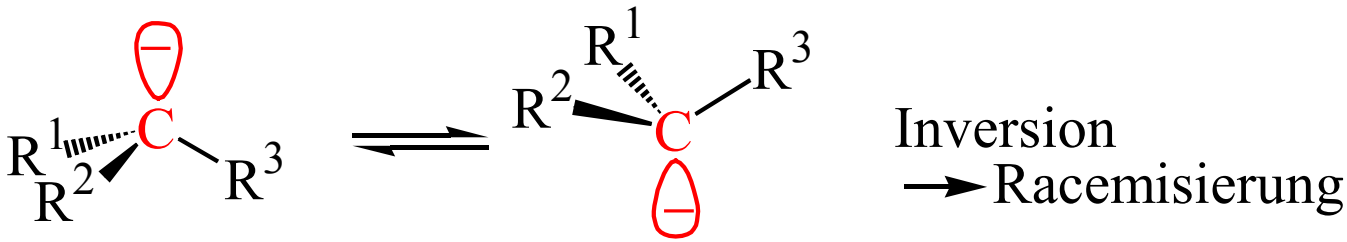
"anomerer Effekt"

2.5.2 Struktur

$(NaCD_3)_4$

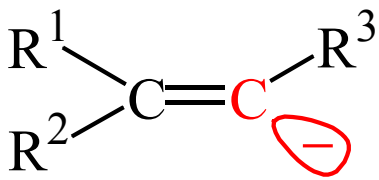


sp^3

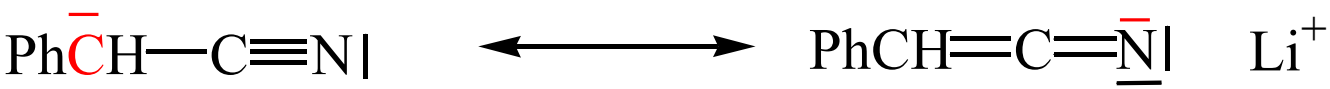


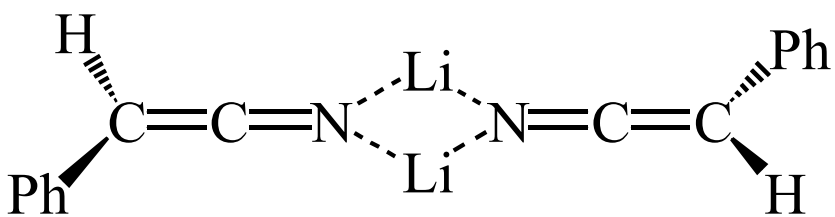
Inversion
→ Racemisierung

sp^2



Retention

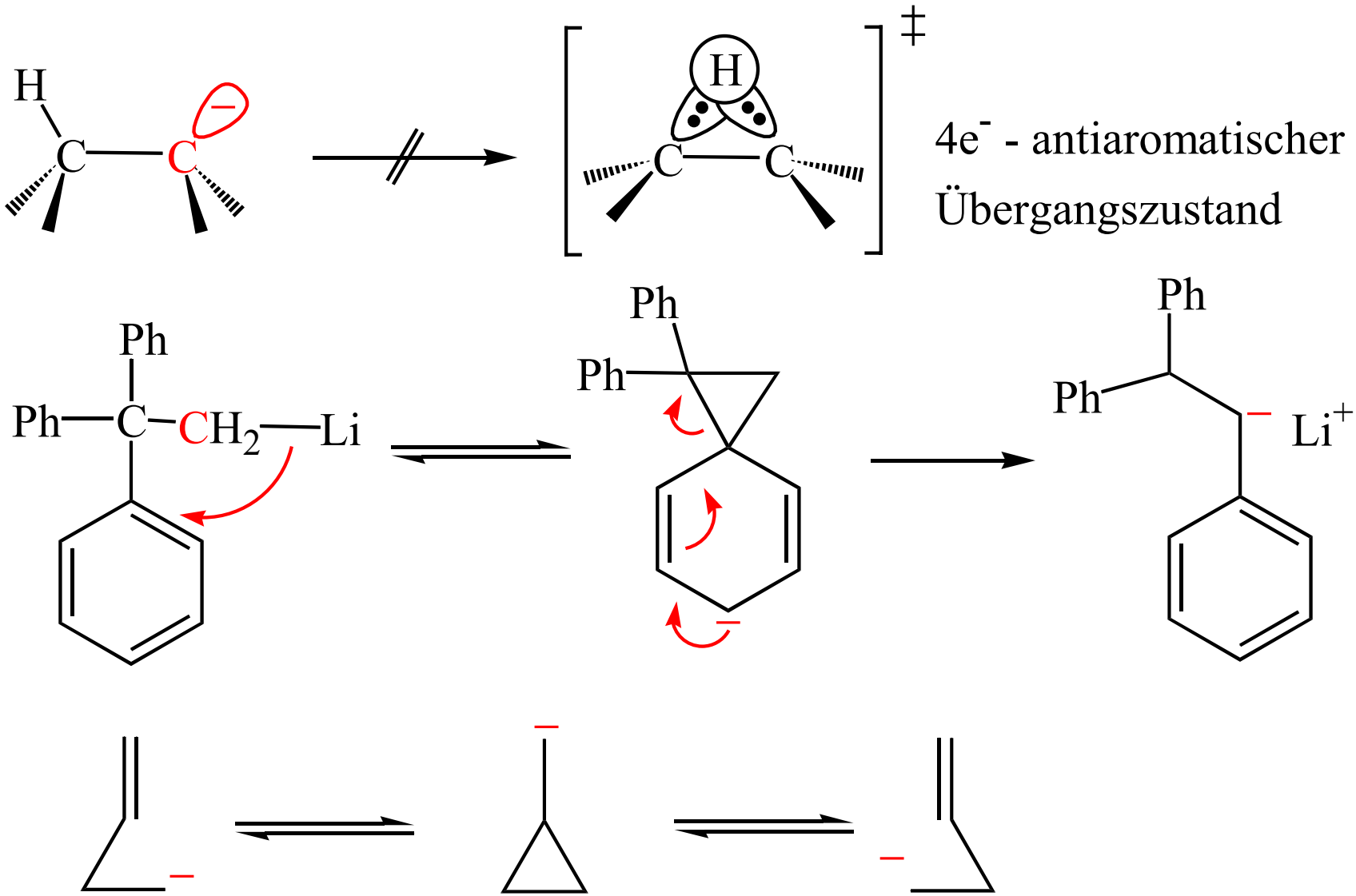




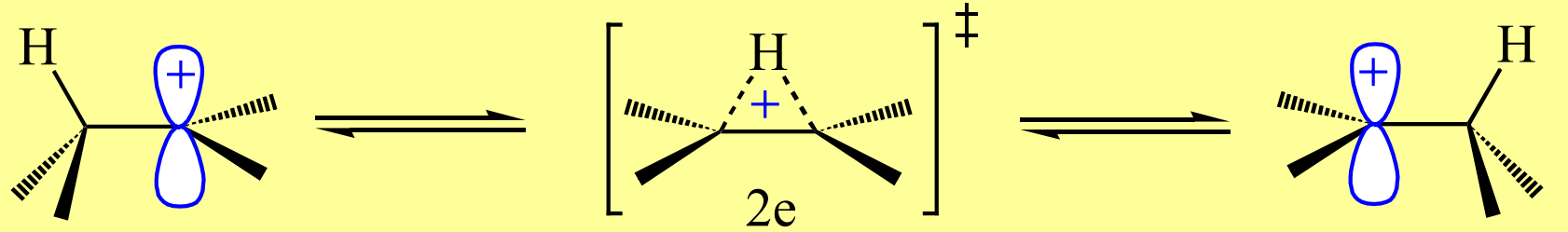
planar

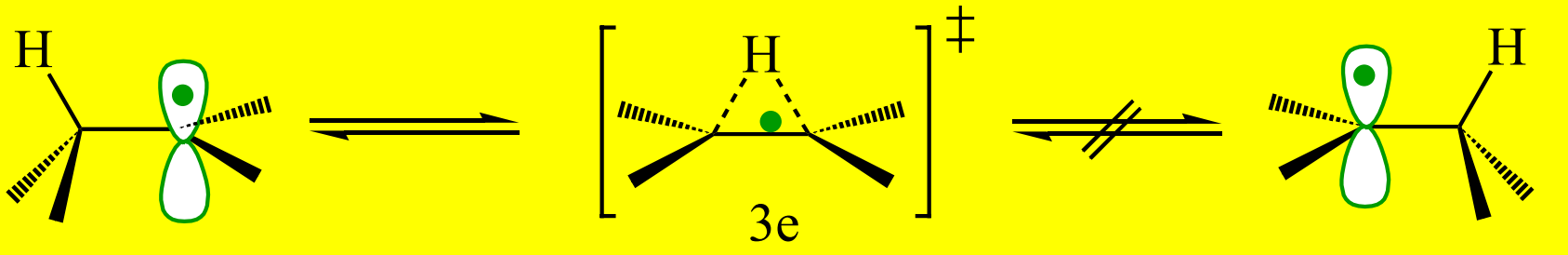
2.5.3 Reaktionen

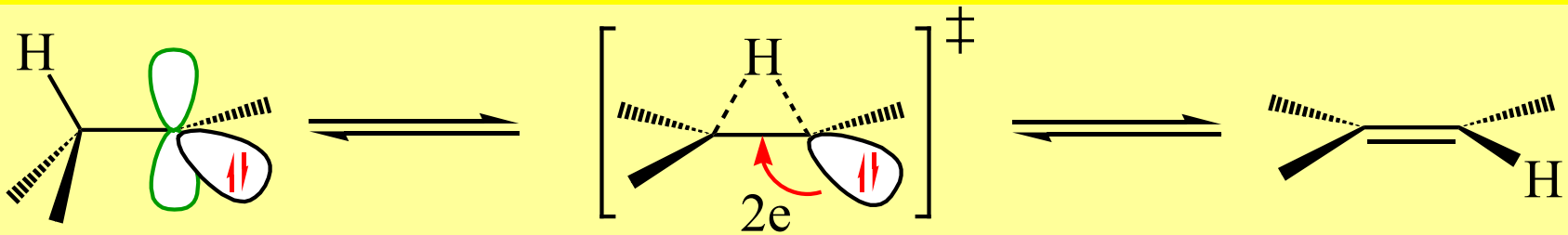
Umlagerungen

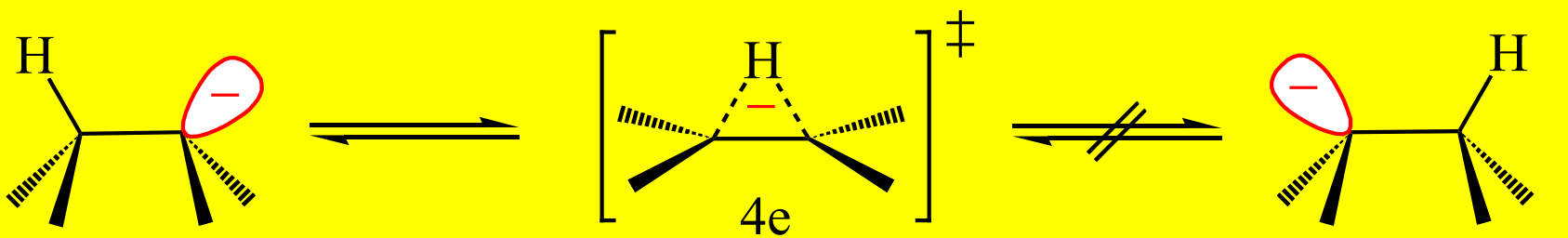


1.2-Umlagerungen der reaktiven Zwischenstufen



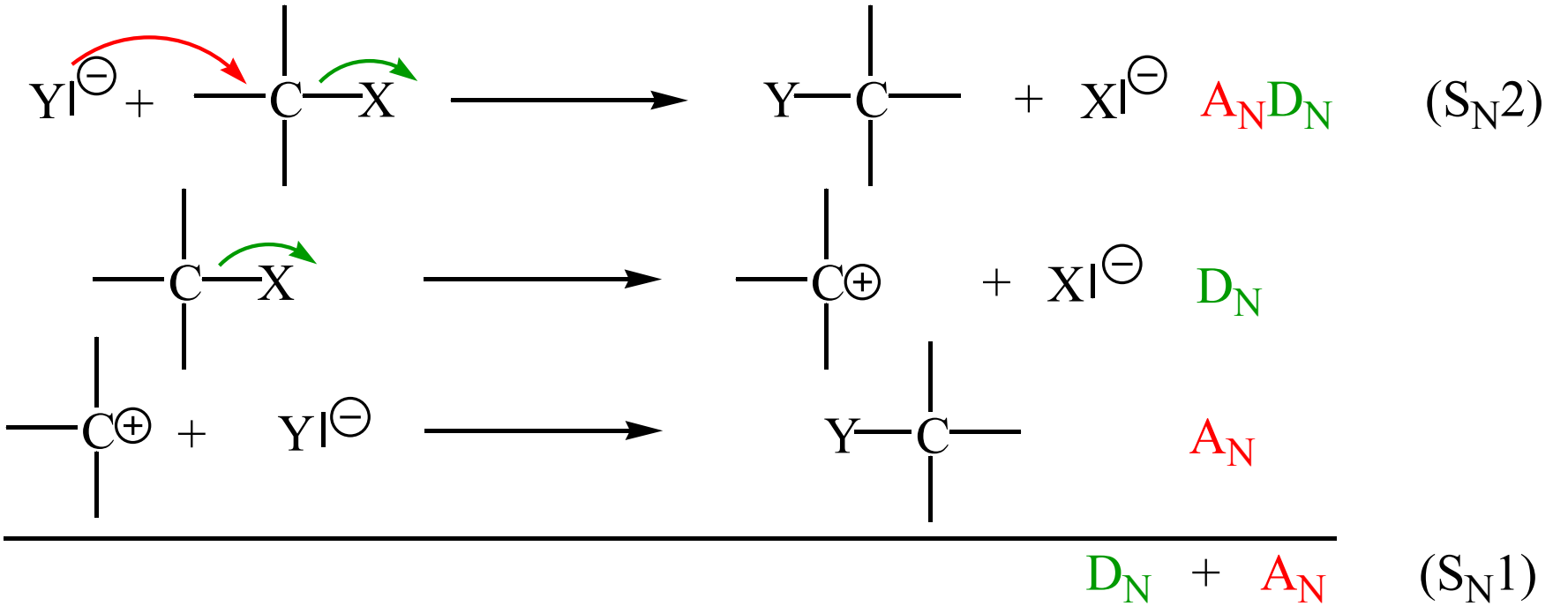


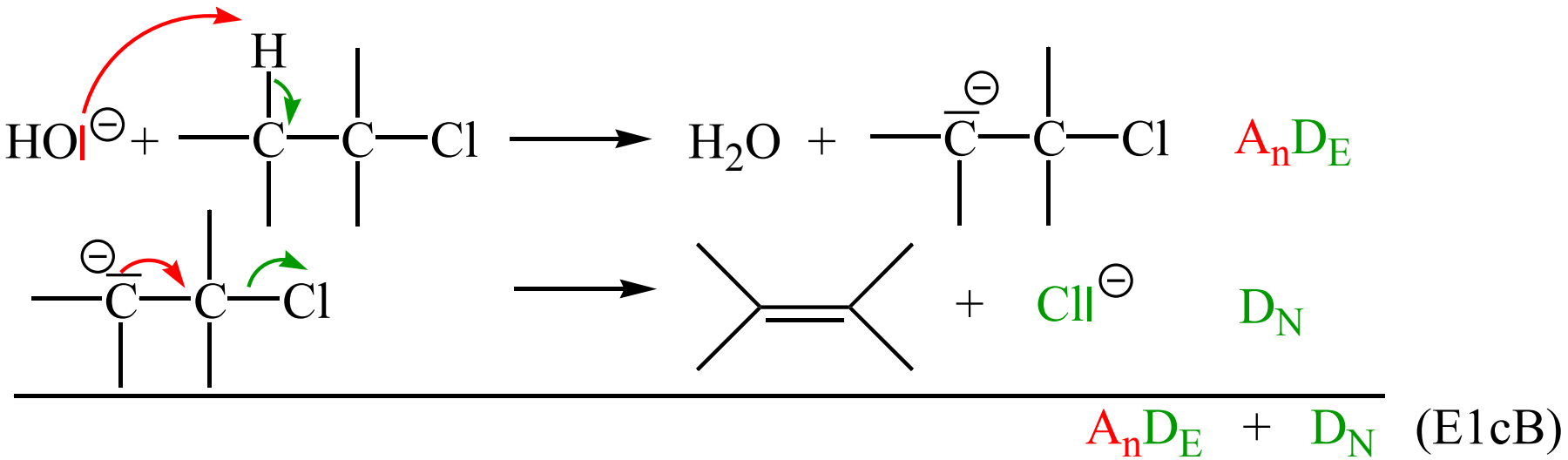




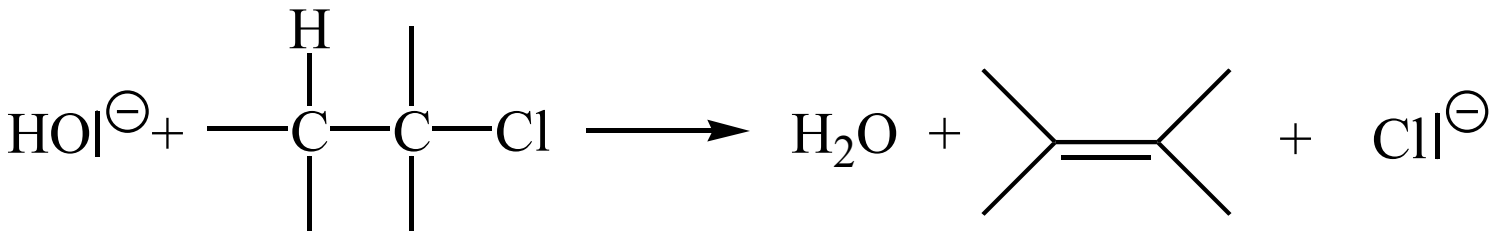
3. Reaktionsmechanismen

3.1 IUPAC-System für die symbolische Darstellung von Mechanismen



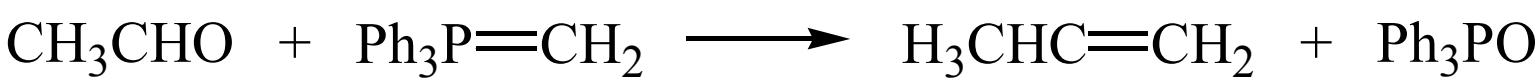


IUPAC-Nomenklatur für Transformationen



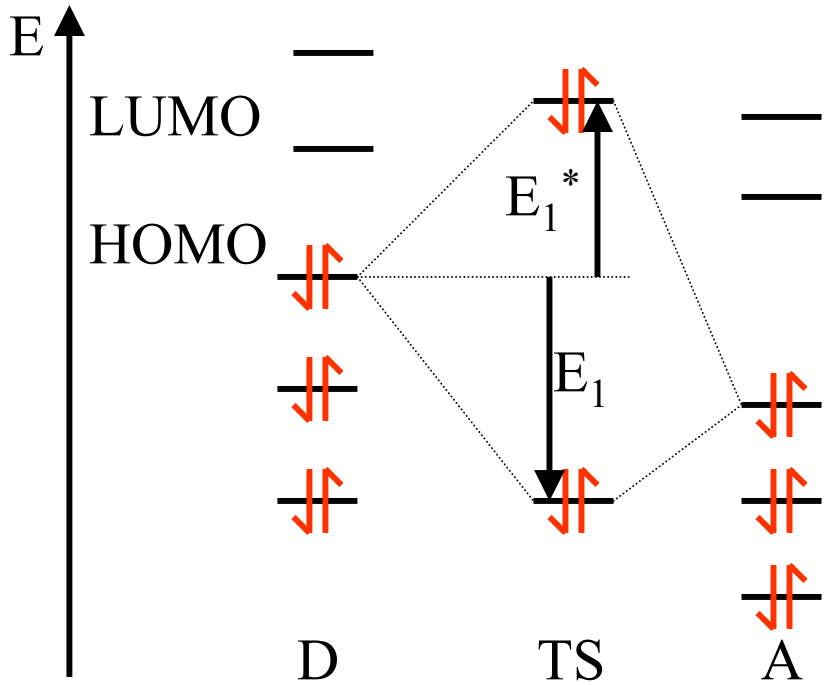
Hydro-chlor-eliminierung

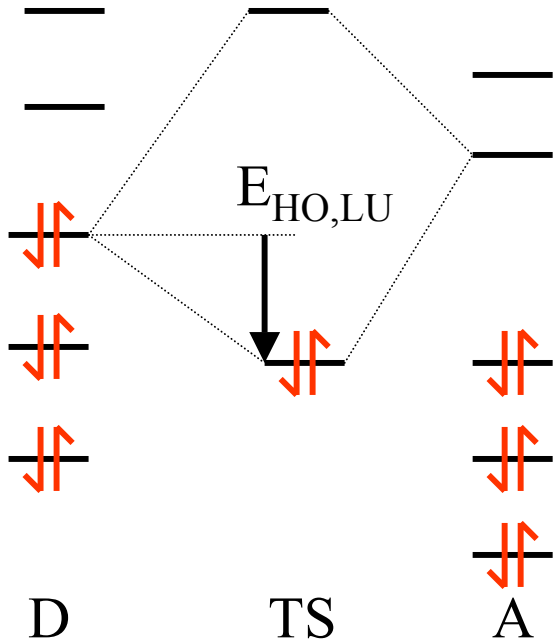
Methoxy-de-bromierung



Methylen-de-oxo-bisubstitution

3.2 Grenzorbitaltheorie





$$E_1 + E_1^* = \Delta E_1 > 0$$

$$\Delta E_{HO,LU} < 0$$

$$\sum \Delta E_n >> 0$$

$$\Delta E_{Coulomb} = \frac{Q_d \cdot Q_a}{\sum R}$$

$$\Delta E_{A,D} = \sum \Delta E_n + \Delta E_{HO,LU} + \Delta E_{Coulomb}$$

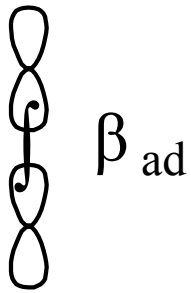
Grenzorbitaltheorie

$$\Delta E_{HO,LU} = \frac{2\left(c_{d,HO} \cdot c_{a,LU} \cdot \beta_{ad}\right)^2}{E_{HO,D} - E_{LU,A}}$$

β = Resonanzintegral

LUMO A: a

HOMO D: d



β_{ad}

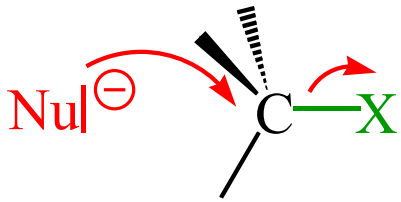
$c < 1$ = Koeffizient des AO von d im HOMO von D

bzw. von a im LUMO von A

Lit.: I. Fleming: Grenzorbitale und Reaktionen organischer Verbindungen, VCH

Grenzorbitaltheorie

S_N2 $(A_N D_N)$

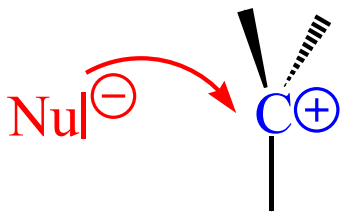


D HOMO

A LUMO

Grenzorbitalwechselwirkung dominiert!

S_N1 $(D_N + A_N)$



Coulomb-Term dominiert!

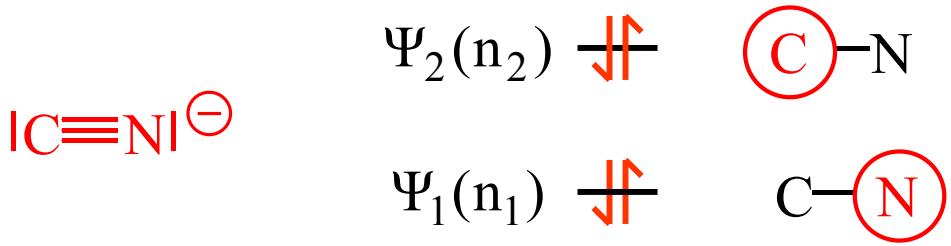
Nucleophile mit energiereichem HOMO - weich

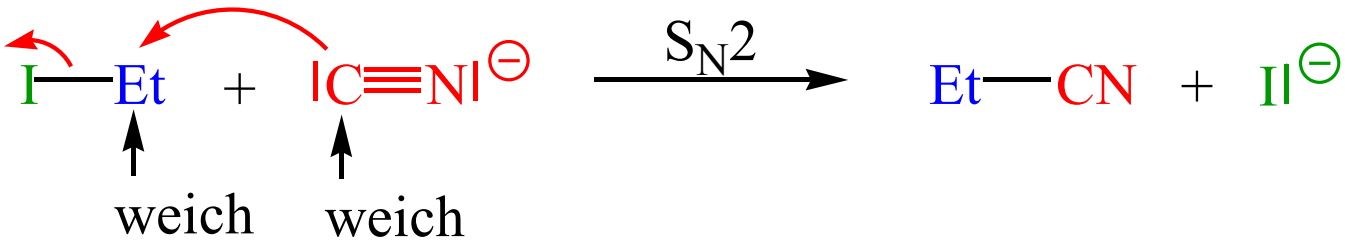
mit energiearmem HOMO - hart

Elektrophile mit energiearmem LUMO - weich

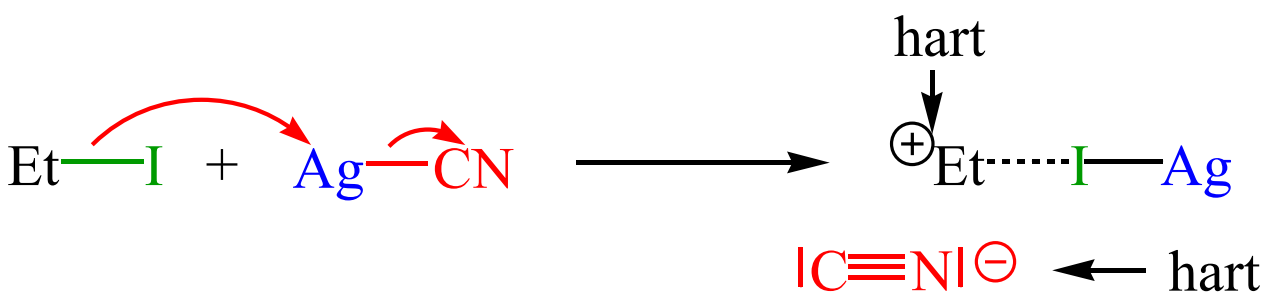
mit energiereichem LUMO - hart

Ambidente Nucleophile



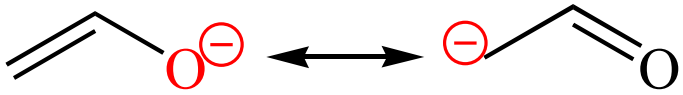


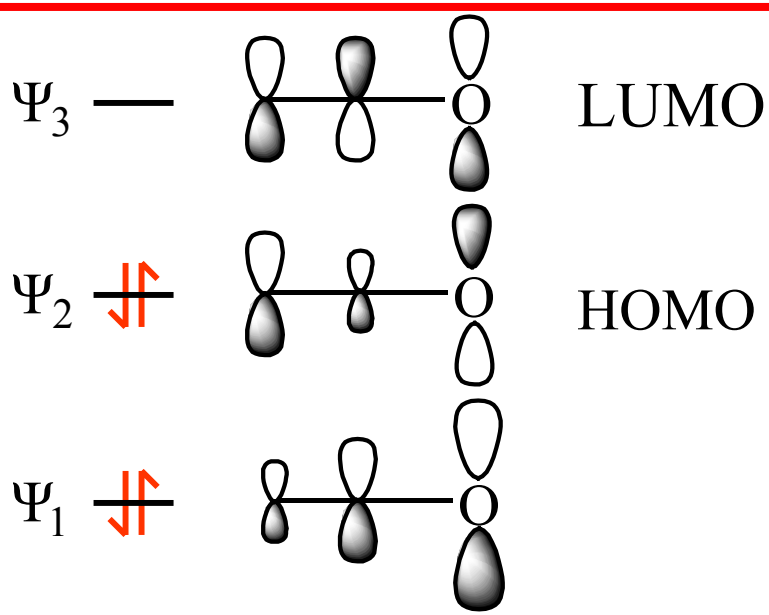
Grenzorbitalterm dominiert!

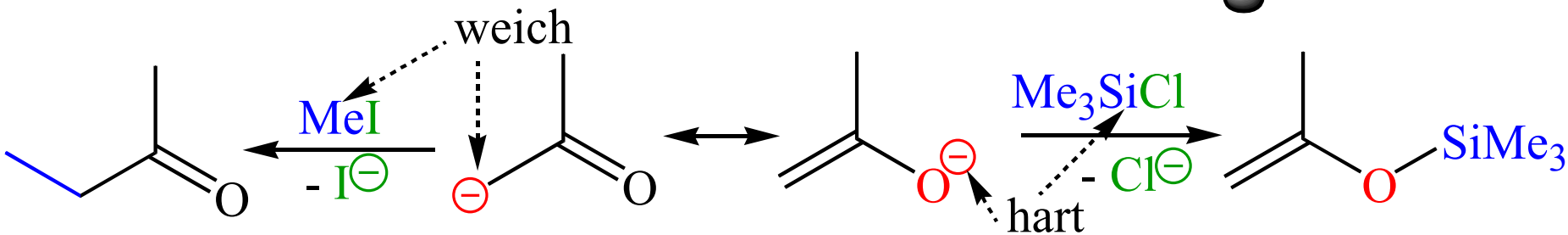


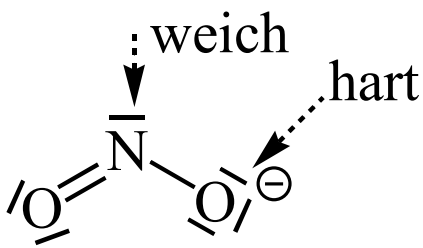
Coulomb-Term dominiert!

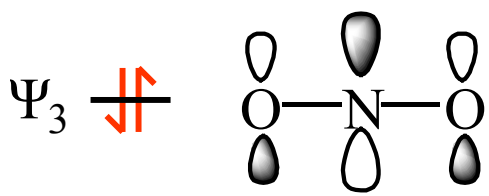
Ambidente Nucleophile



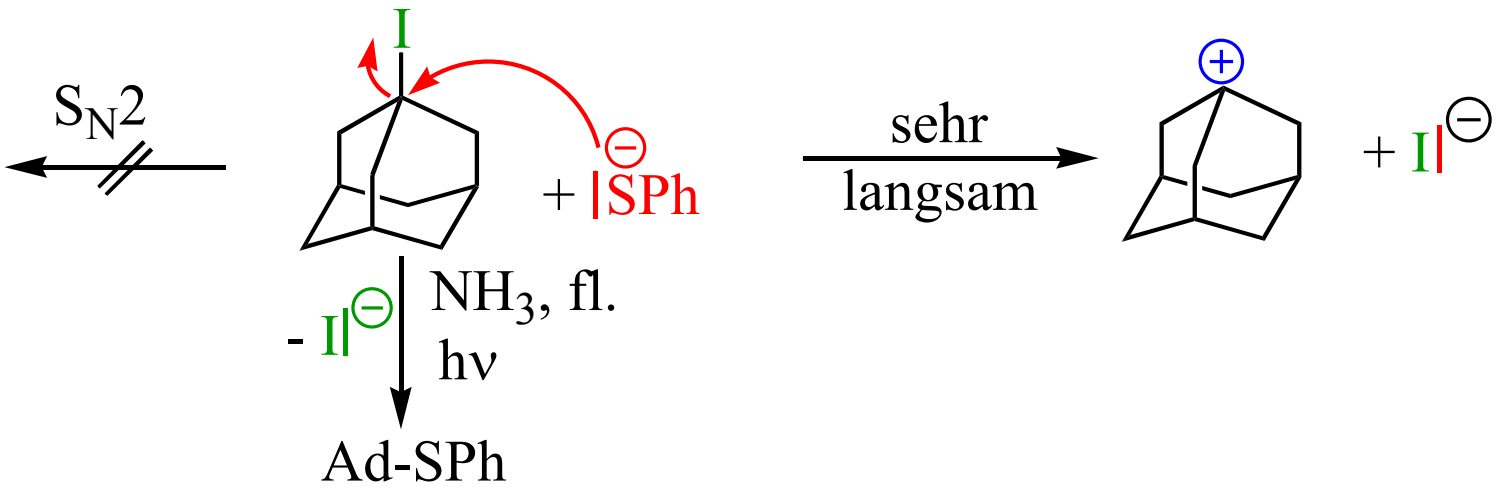


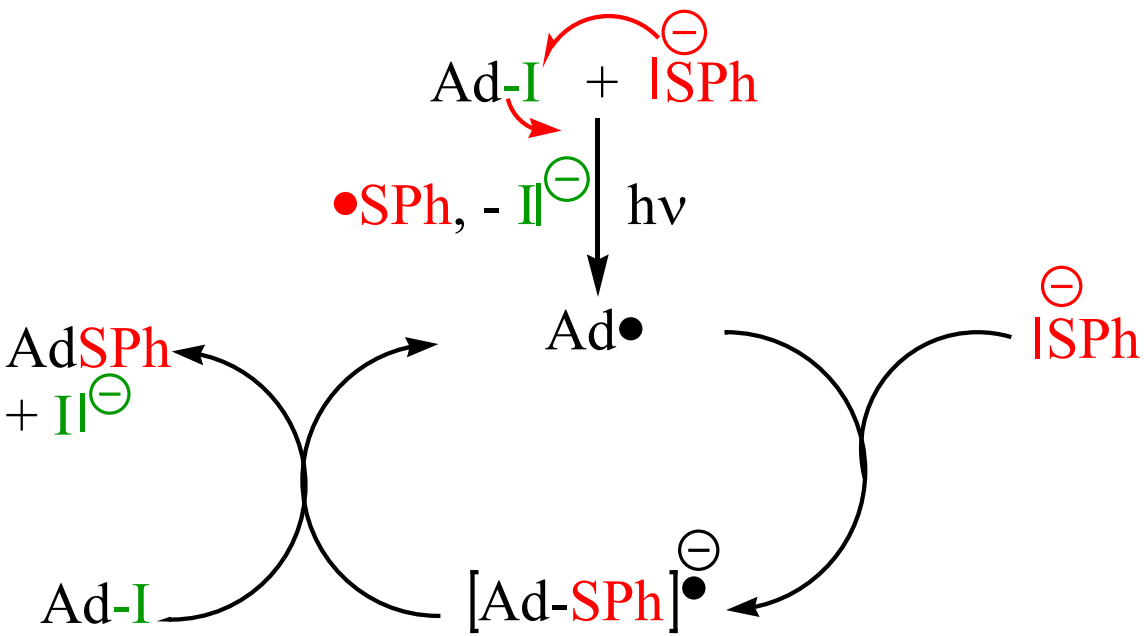






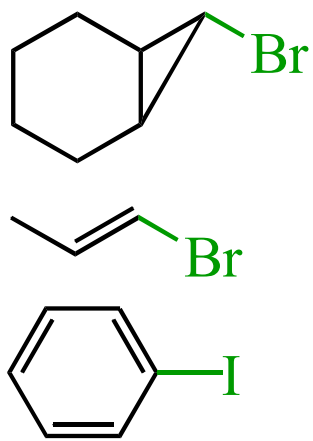
Nucleophile Substitution



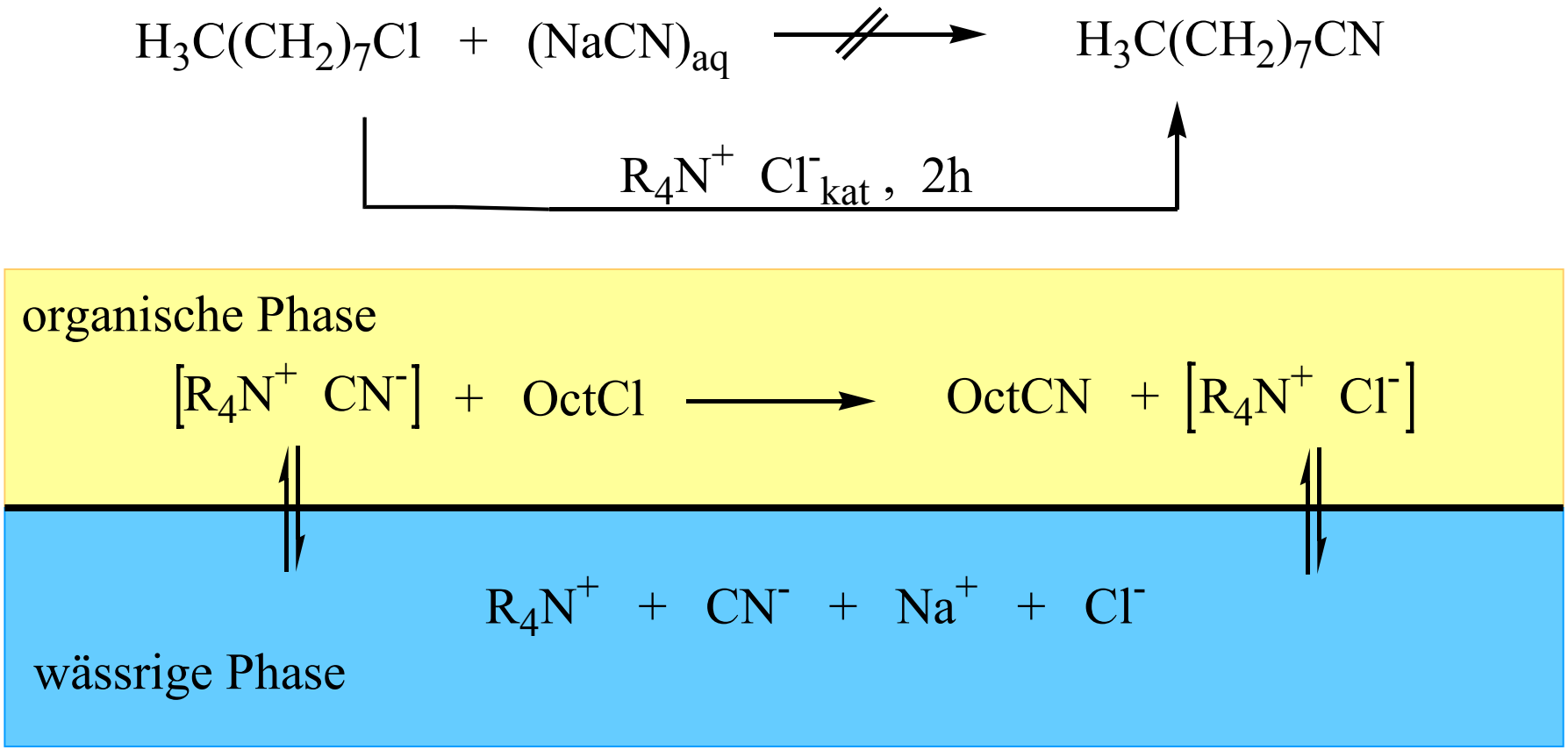


$S_{RN}1$-Reaktion
(IUPAC: T + D_N + A_N)

Analog:



Phasentransfer-Katalyse

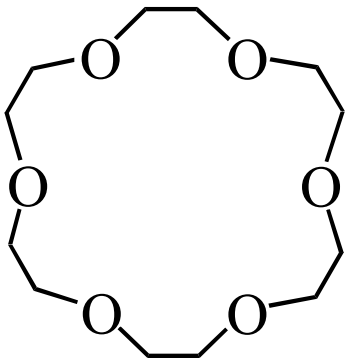


$MeN(Oct)_3^+Cl^-$ Aliquat 336

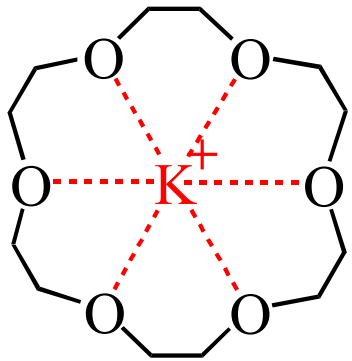
$PhCH_2NEt_3^+Cl^-$ TEBA

Fest-flüssig Phasentransfer-Katalyse

Kronenether



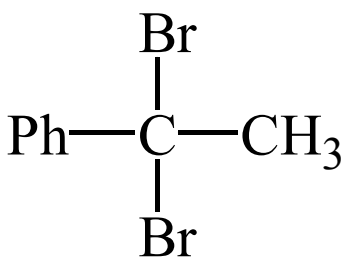
+ $KMnO_4$ $\xrightarrow{C_6H_6}$



+ MnO_4^-

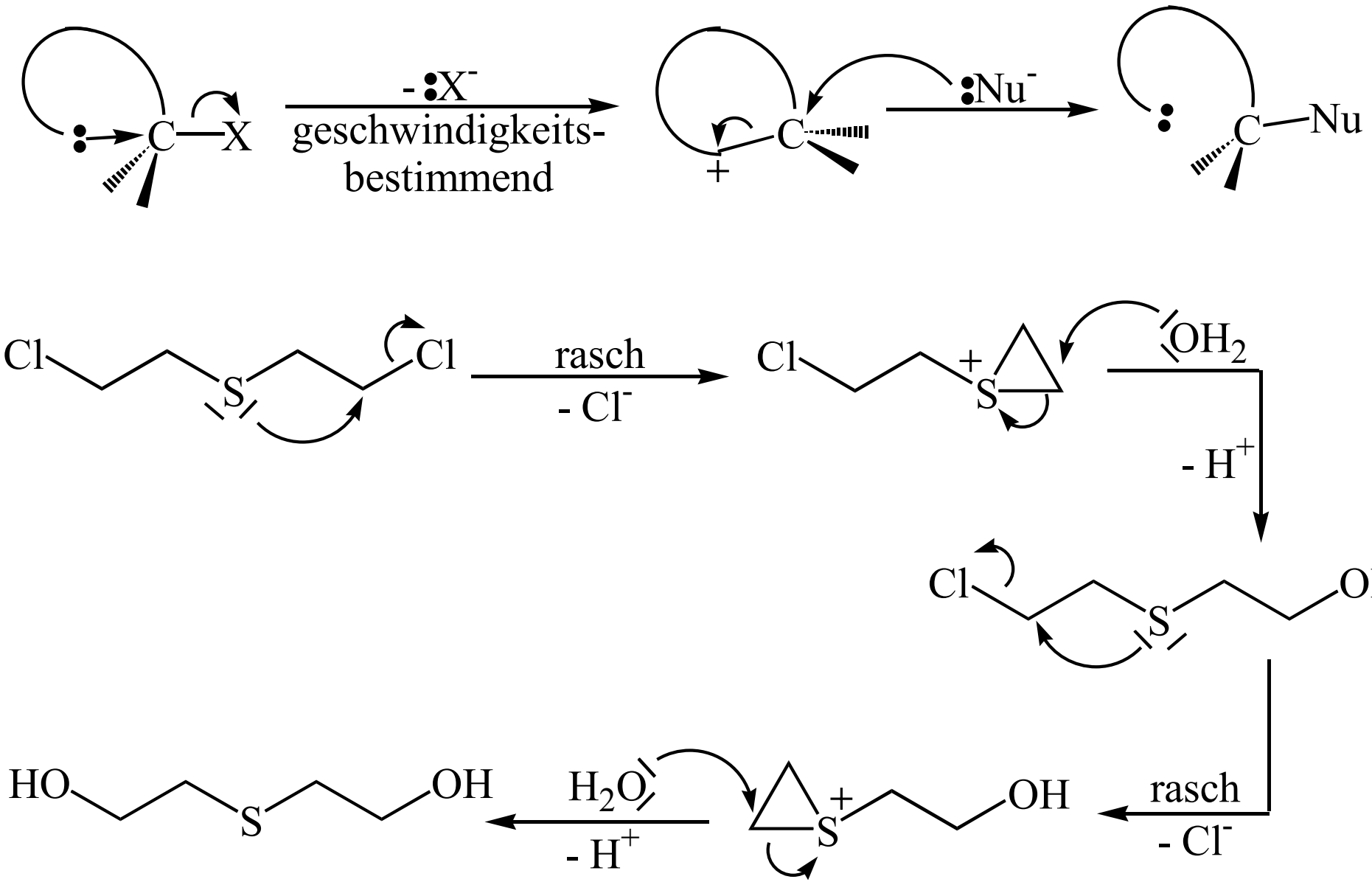
violette Lösung in Benzol

$$OctCl + KCN_{fest} \xrightarrow[\text{org. Solvens}]{\text{18-Krone-6}_{kat}} OctCN + KCl$$

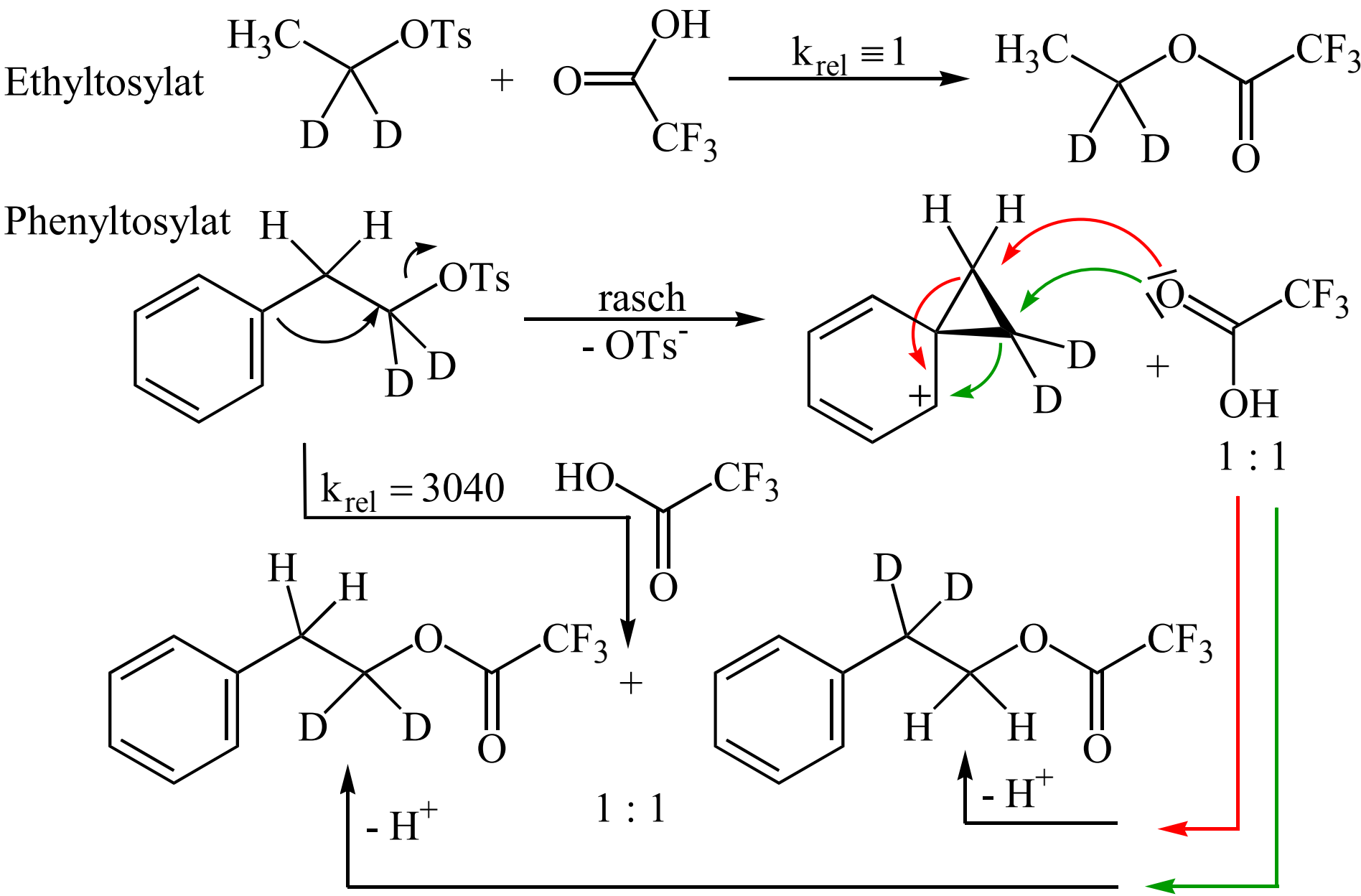


$\xrightarrow[\text{18-Krone-6}]{KOH}$ $PhC{\equiv}CH + 2\ KBr$

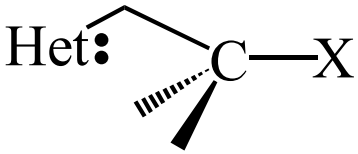
Nachbargruppeneffekte

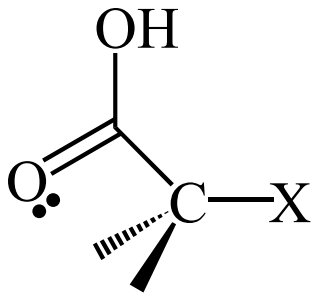


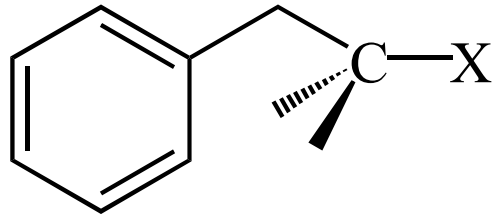
Nachbargruppeneffekte



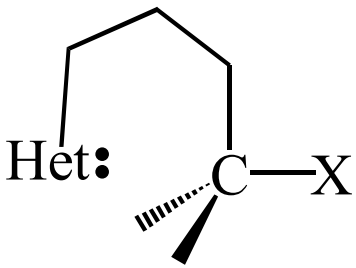
Nachbargruppeneffekte



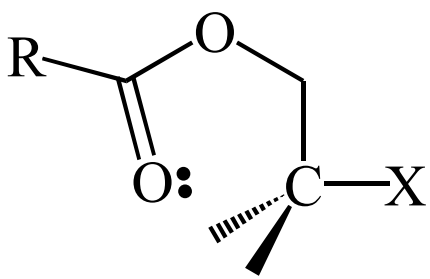




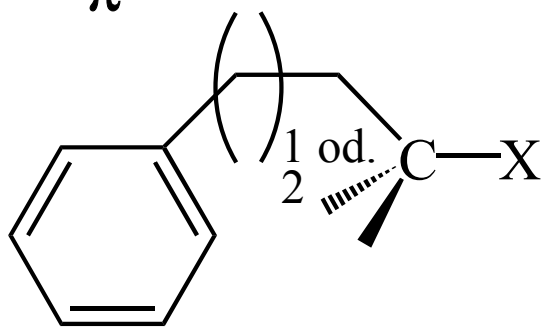
n_{sp^3}

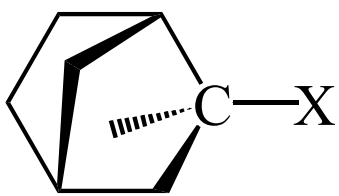


n_{sp^2}



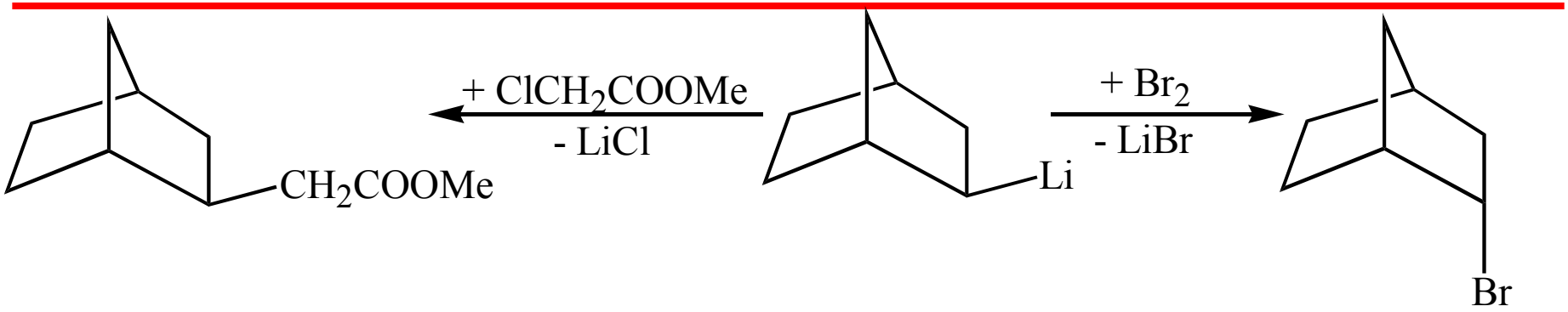
π



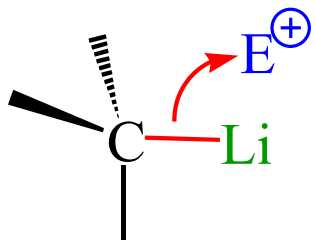


σ

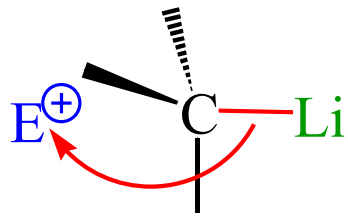
Aliphatische elektrophile Substitution



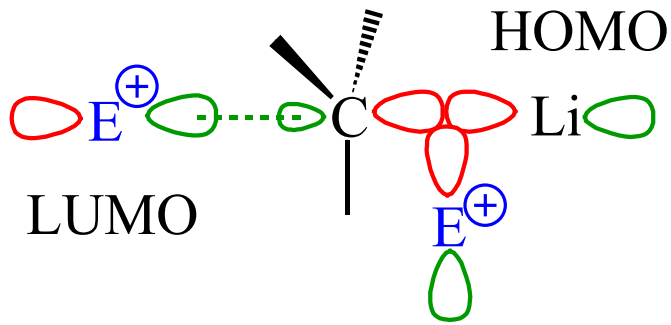
S_E2 (D_EA_E)



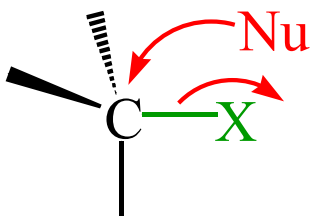
front
Retention

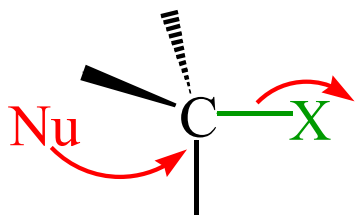


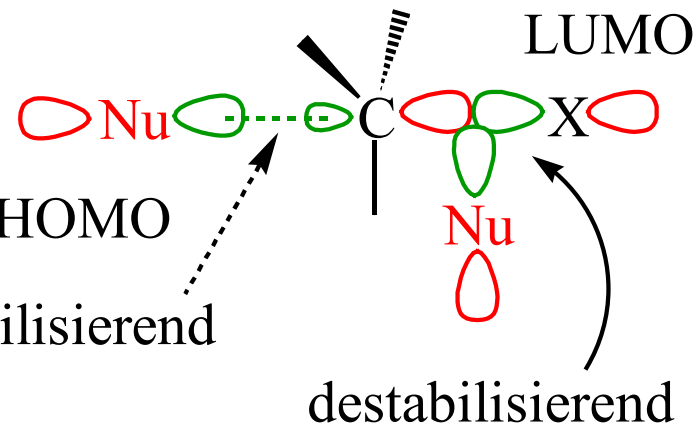
back
Inversion



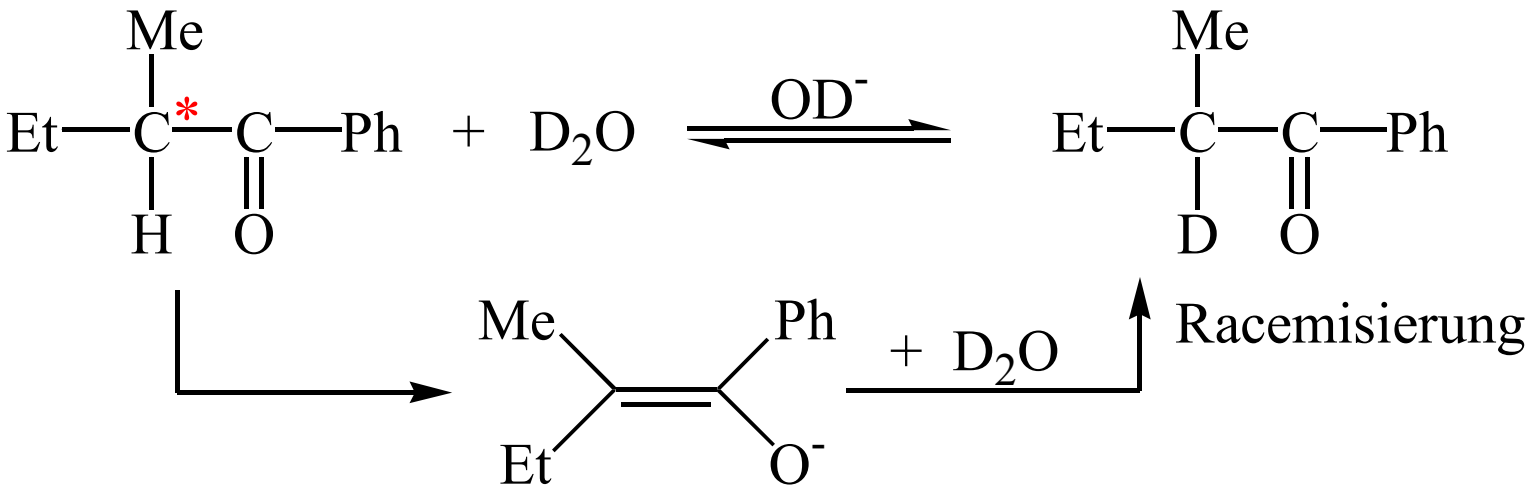
S_N2



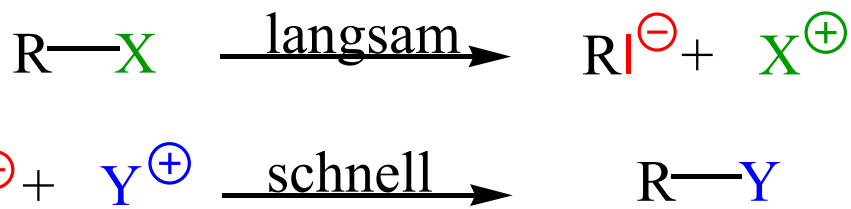




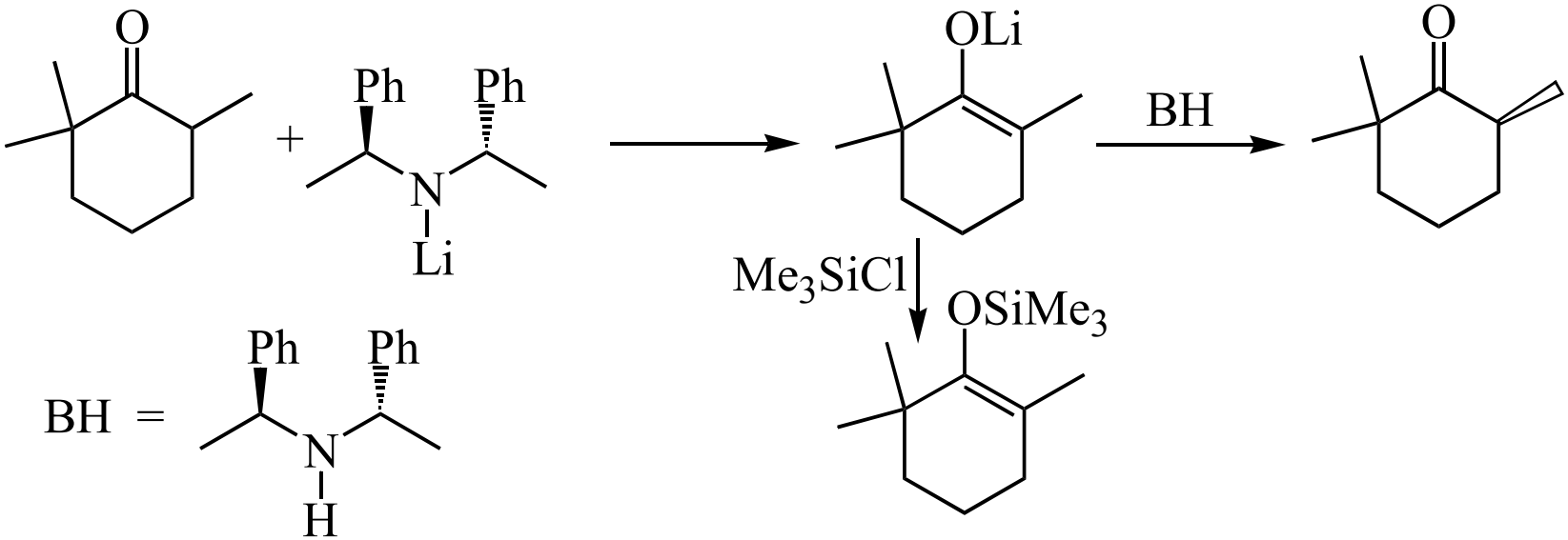
Aliphatische elektrophile Substitution

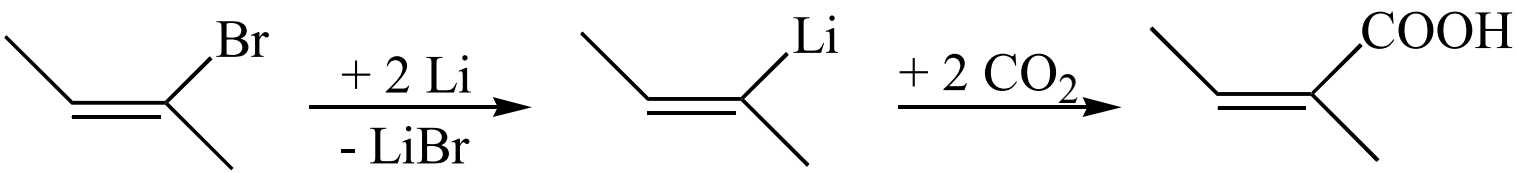


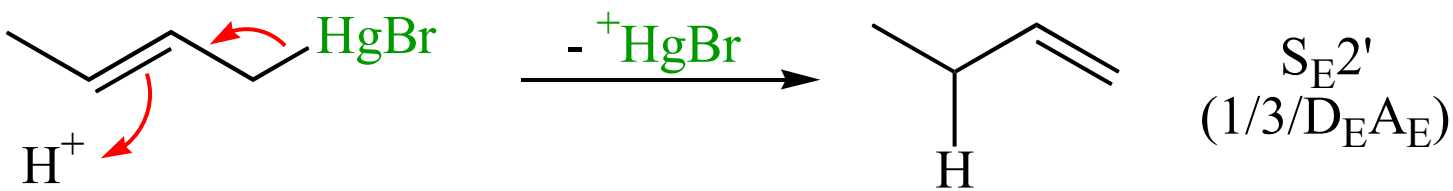
S_E1 ($D_E + A_E$)



Aliphatische elektrophile Substitution

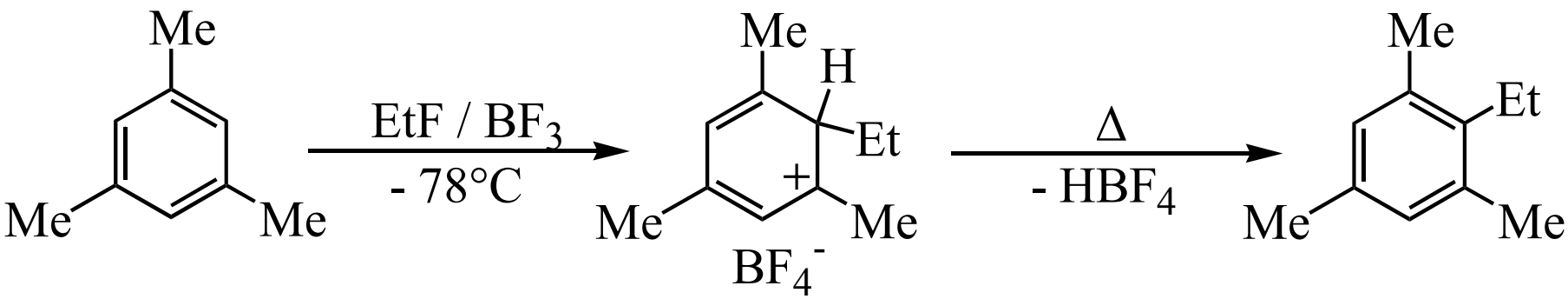






nBuHgBr reagiert 10^7mal langsamer.

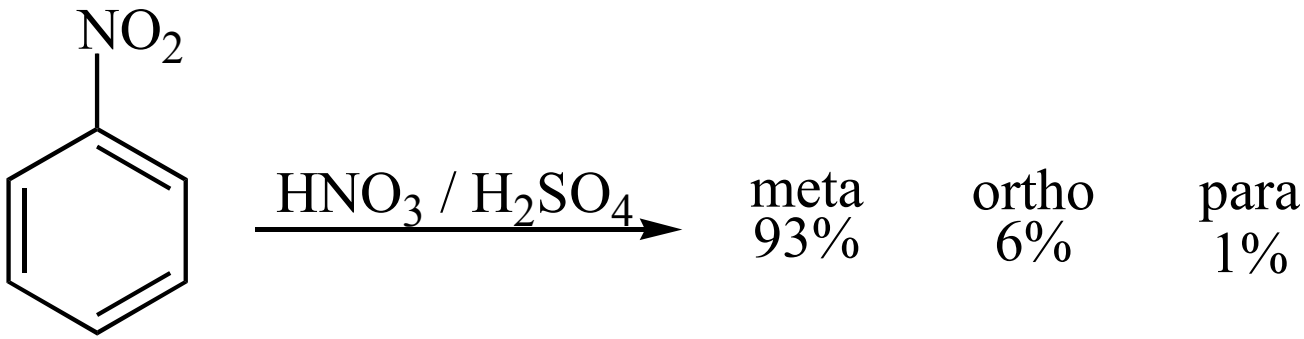
Aromatische elektrophile Substitution



Kinetischer Isotopeneffekt $k_H/k_D \approx 1$

π-Komplex i.A. nicht auf der Reaktionskoordinate

Regel der Zweitsubstitution



Anwendung des Hammond-Postulats:

- Stabilität des Areniumions

Mechanismus: $A_E + D_E$

Röntgenstrukturanalyse eines Chlorareniumkations

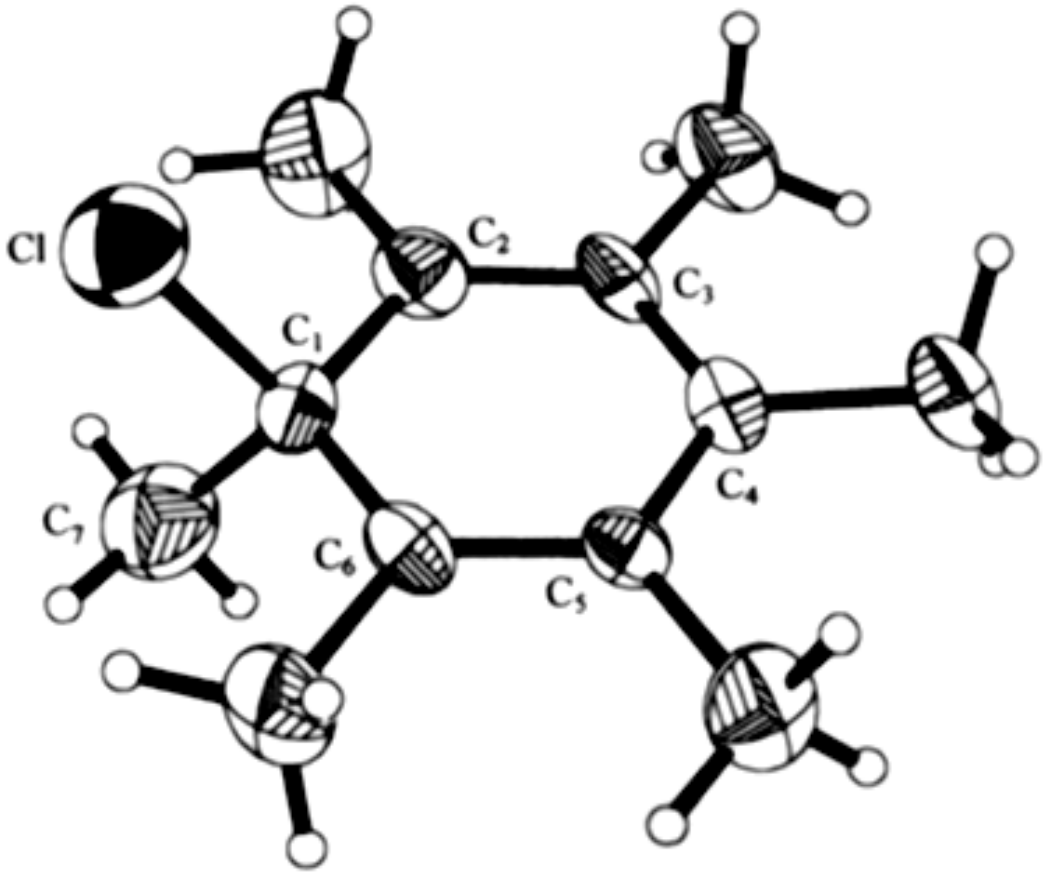


Figure 1. ORTEP diagram showing chlorine attechment to a single carbon center in the chloroarenium cation 1-Cl^+ from hexamethylbenzene

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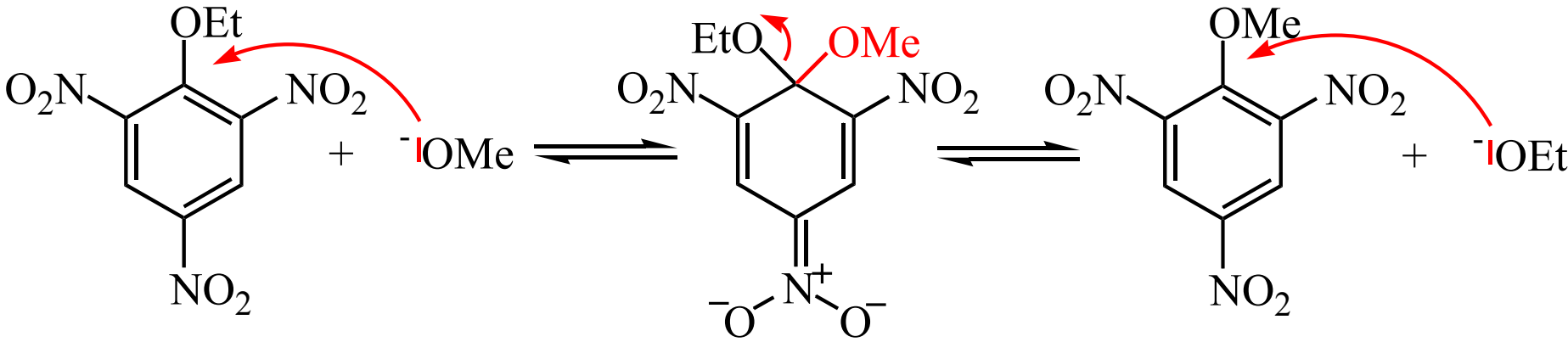
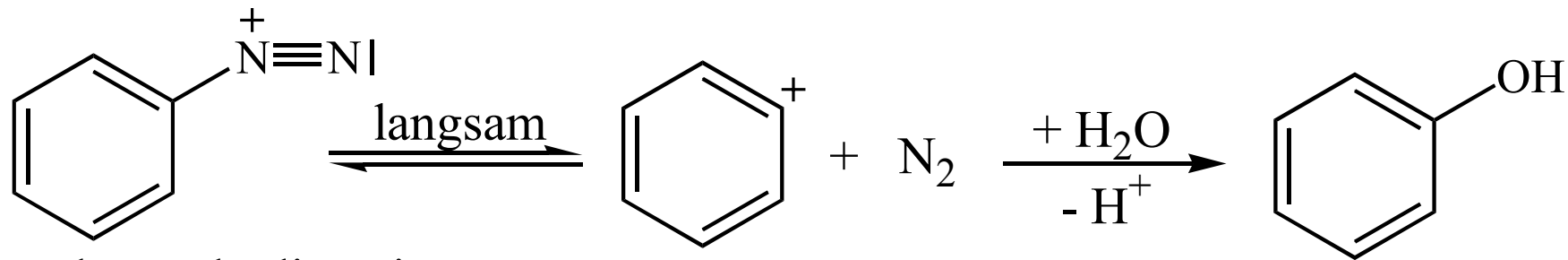
Aromatische nucleophile Substitution

S_NAr-Mechanismus ($A_N + D_N$)

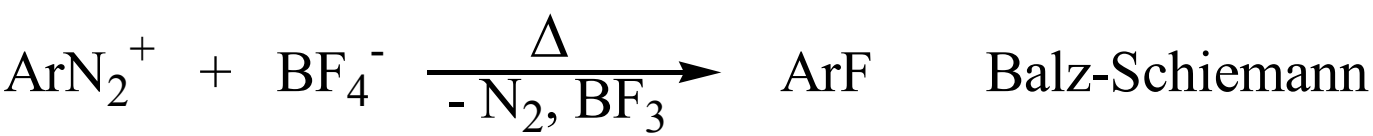


Meisenheimer Salze

S_N1-Mechanismus ($D_N + A_N$)



Hydroxy-de-diazotierung

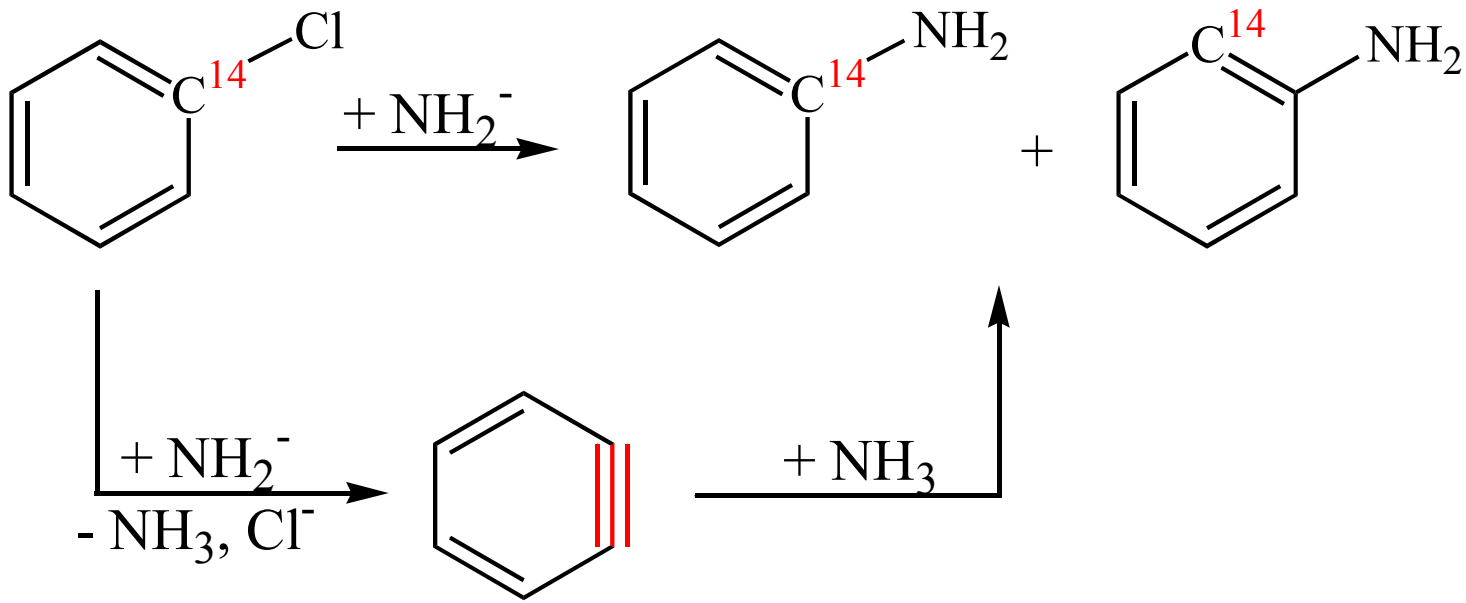


Balz-Schiemann

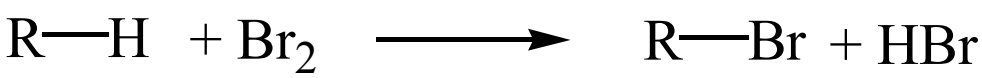
Aromatische nucleophile Substitution

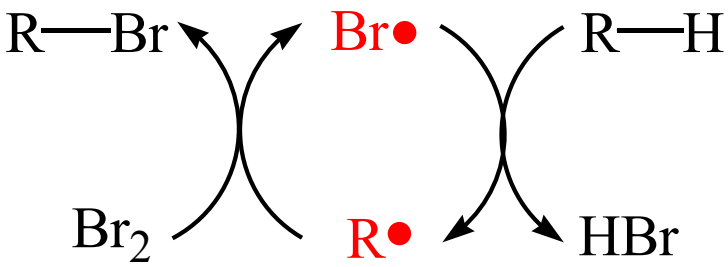
Benzin-Mechanismus: Eliminierungs-Additions-Mechanismus

$A_N D_E D_N + A_E + A_N$

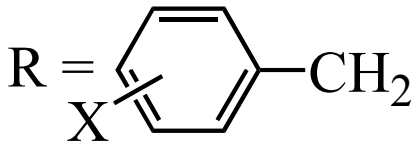


Radikalische Substitution S_H (A_rD_R + A_RD_r)

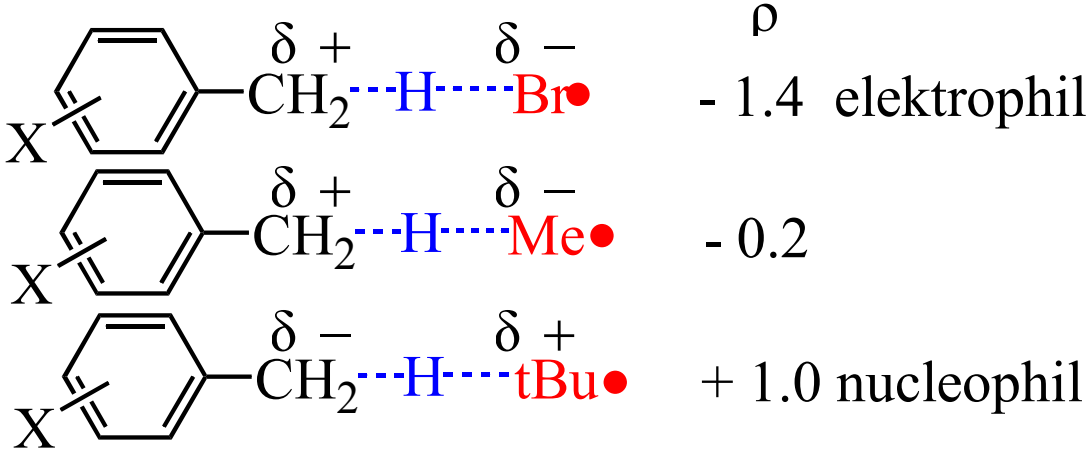




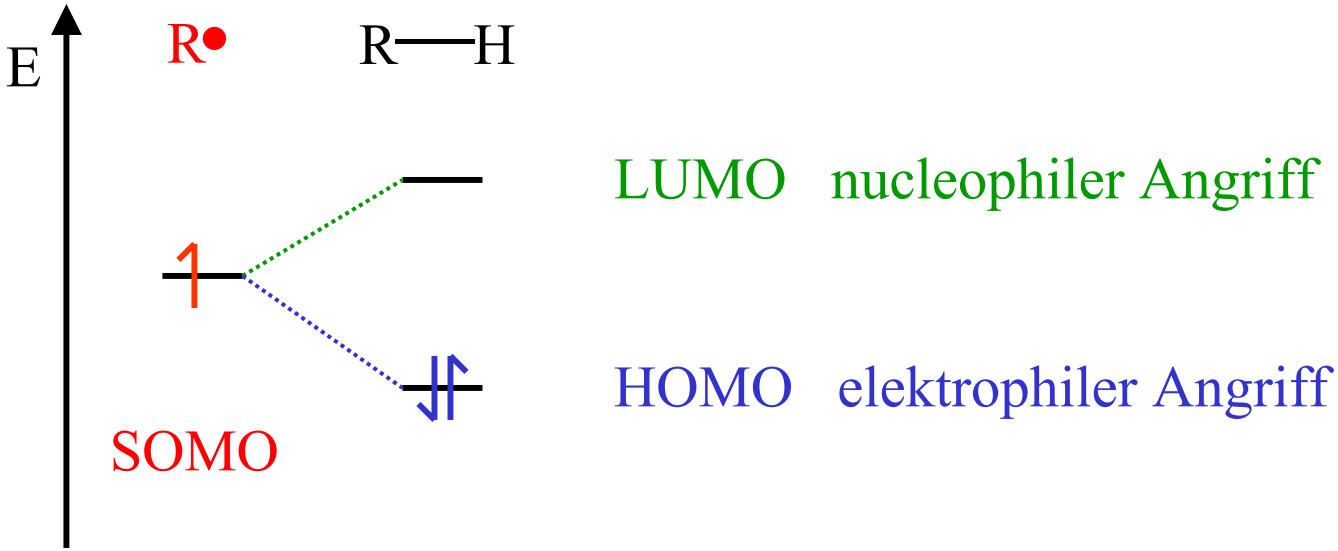
Kettenfortpflanzung



ρ = −1.4



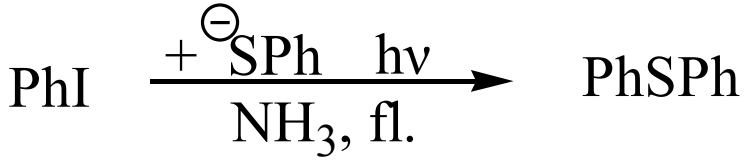
Radikalische Substitution

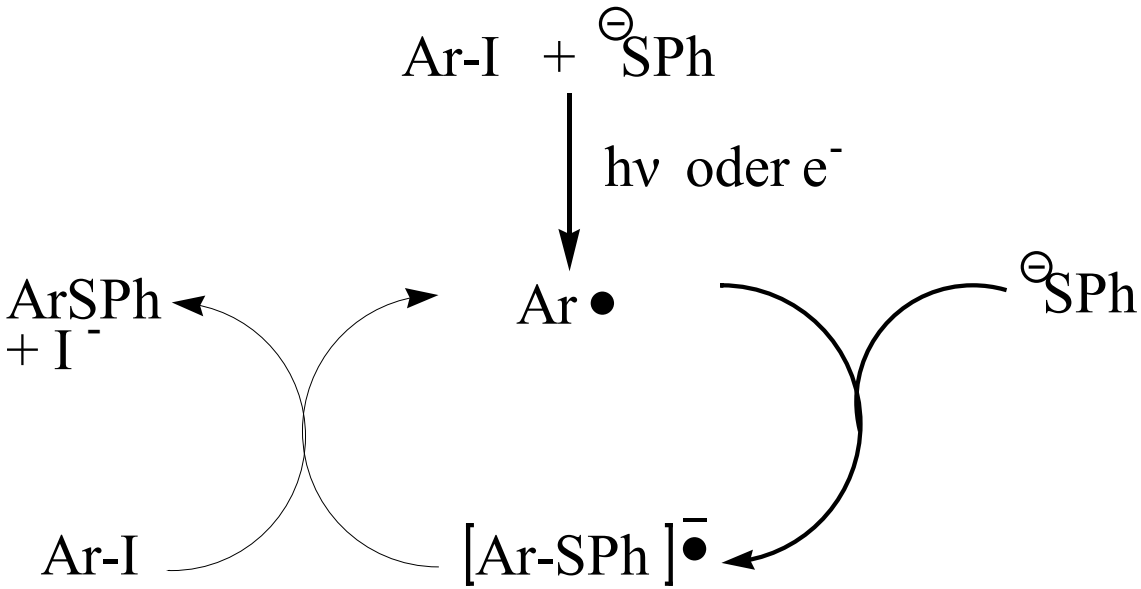


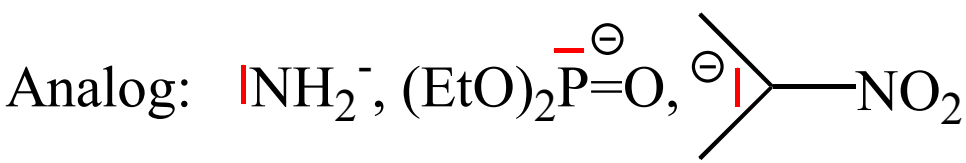
Nucleophile Rad•: tBu•, $ROCH_2$• , R_2NCH_2•, u.a.
Elektrophile Rad•: Br•, Cl•, •CH_2CN, •CH_2COOMe, u.a.

	H_3C-CH_2-COOH	
Me•	1	7.8
Cl•	1	0.03

Radikalische Substitution

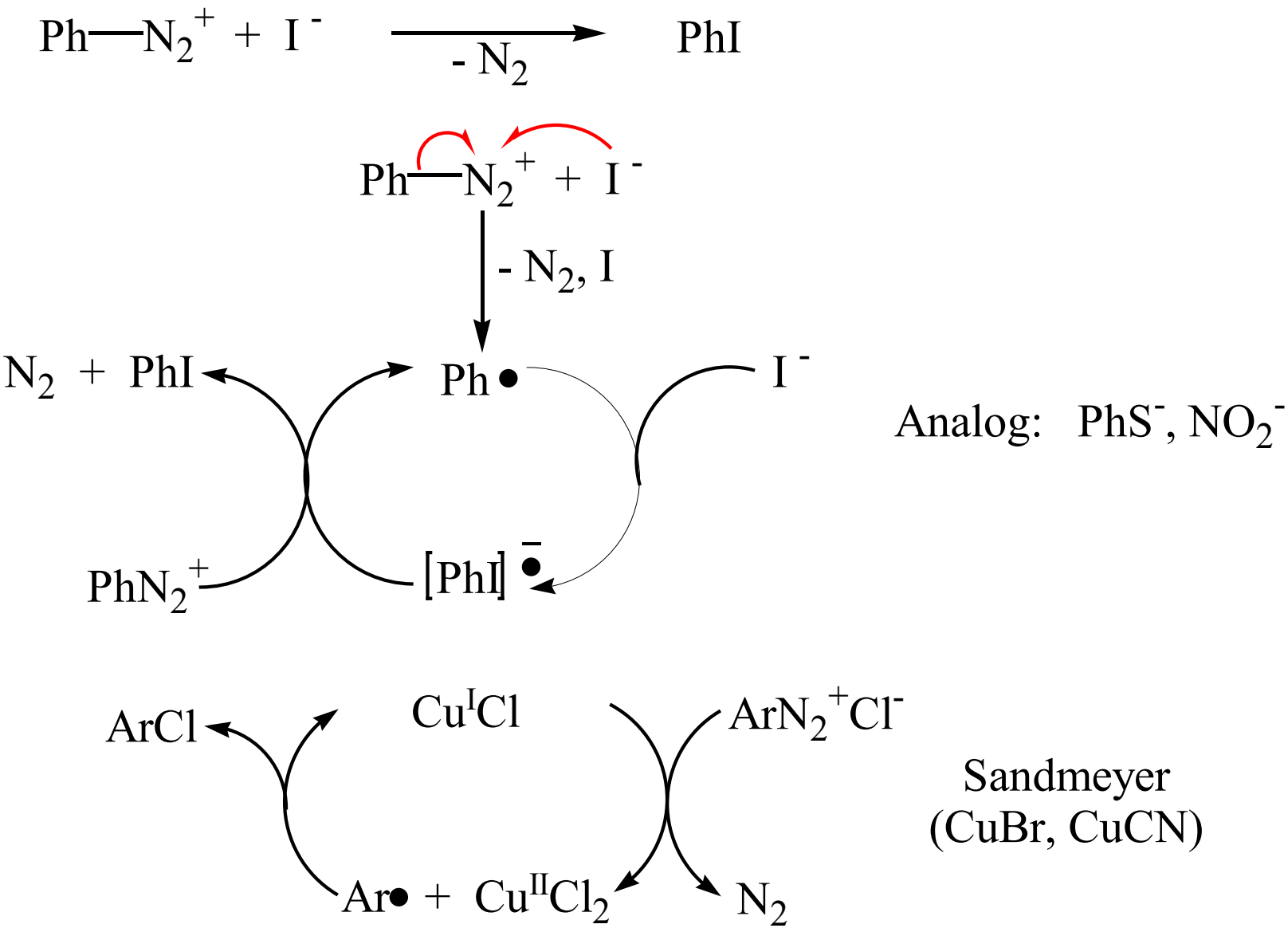




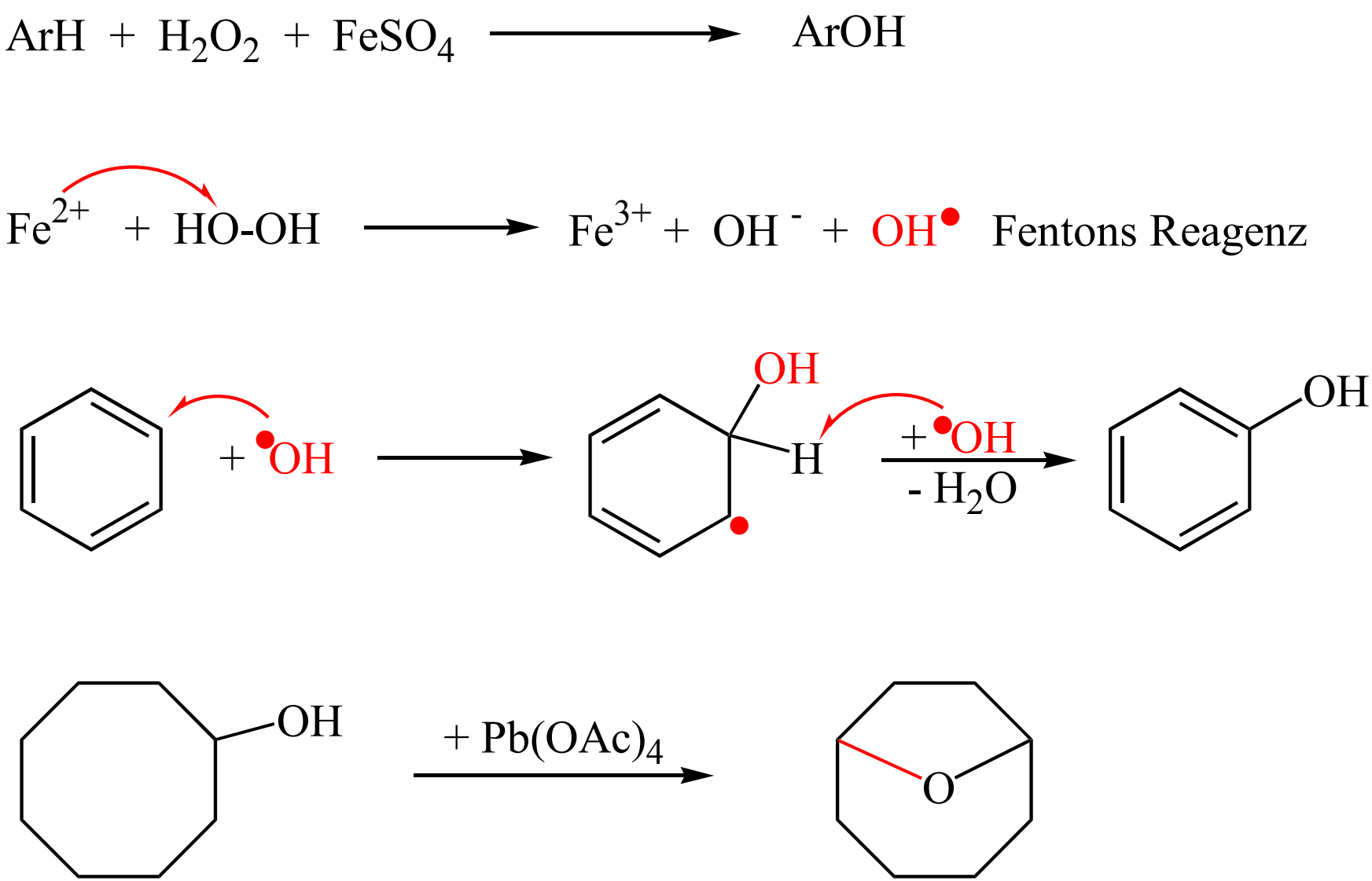


$S_{RN}1$ (T + D_N + A_N)

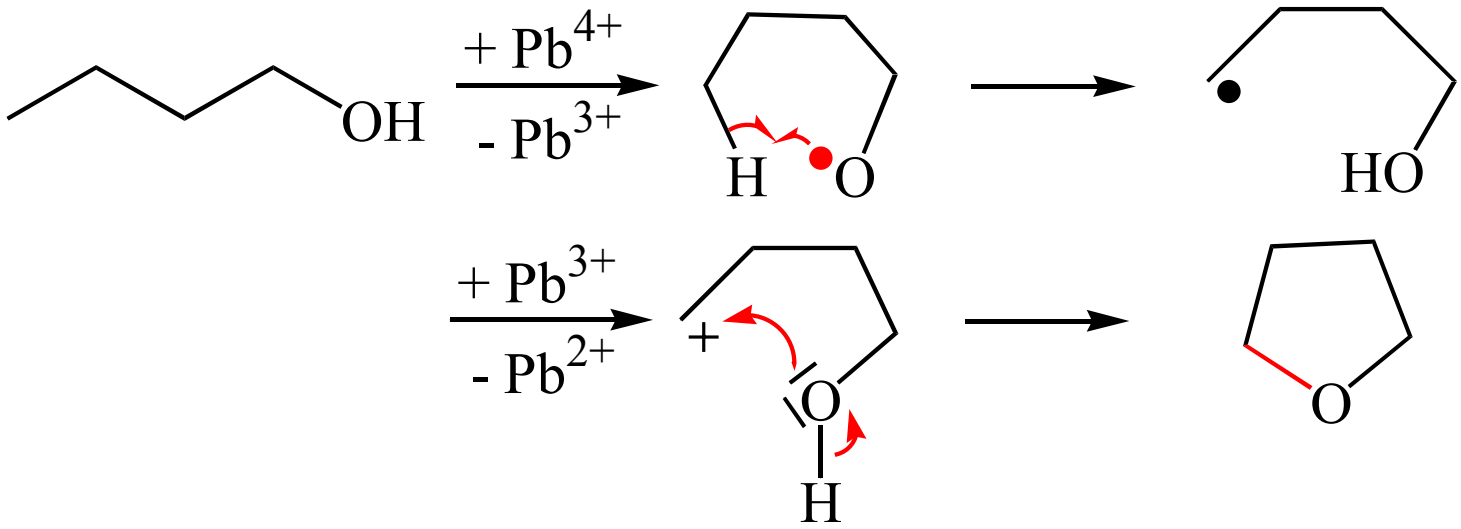
Radikalische Substitution



Radikalische Substitution

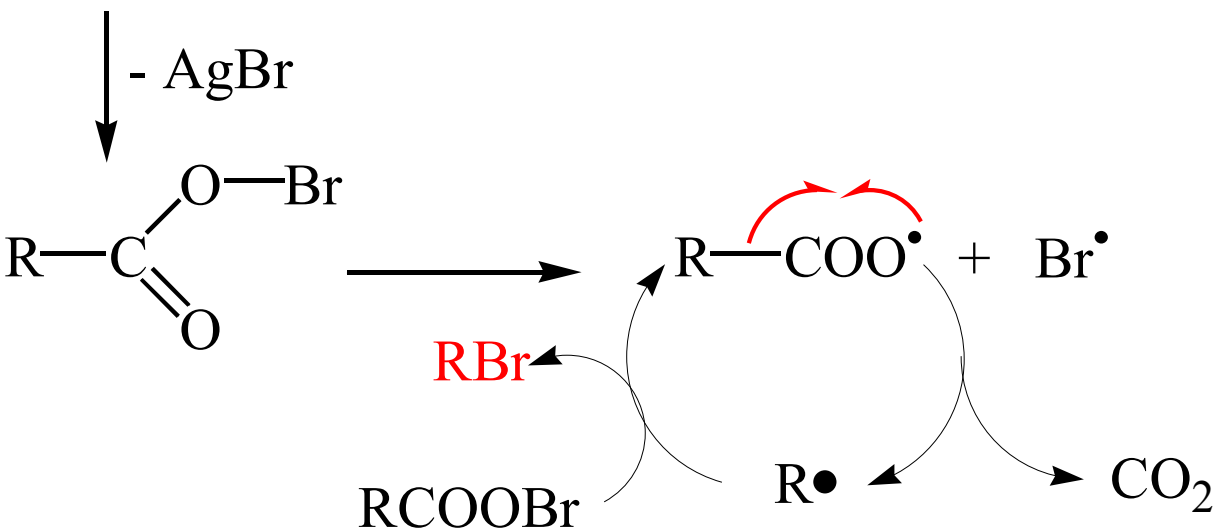


Hydroxylierung von Aromaten

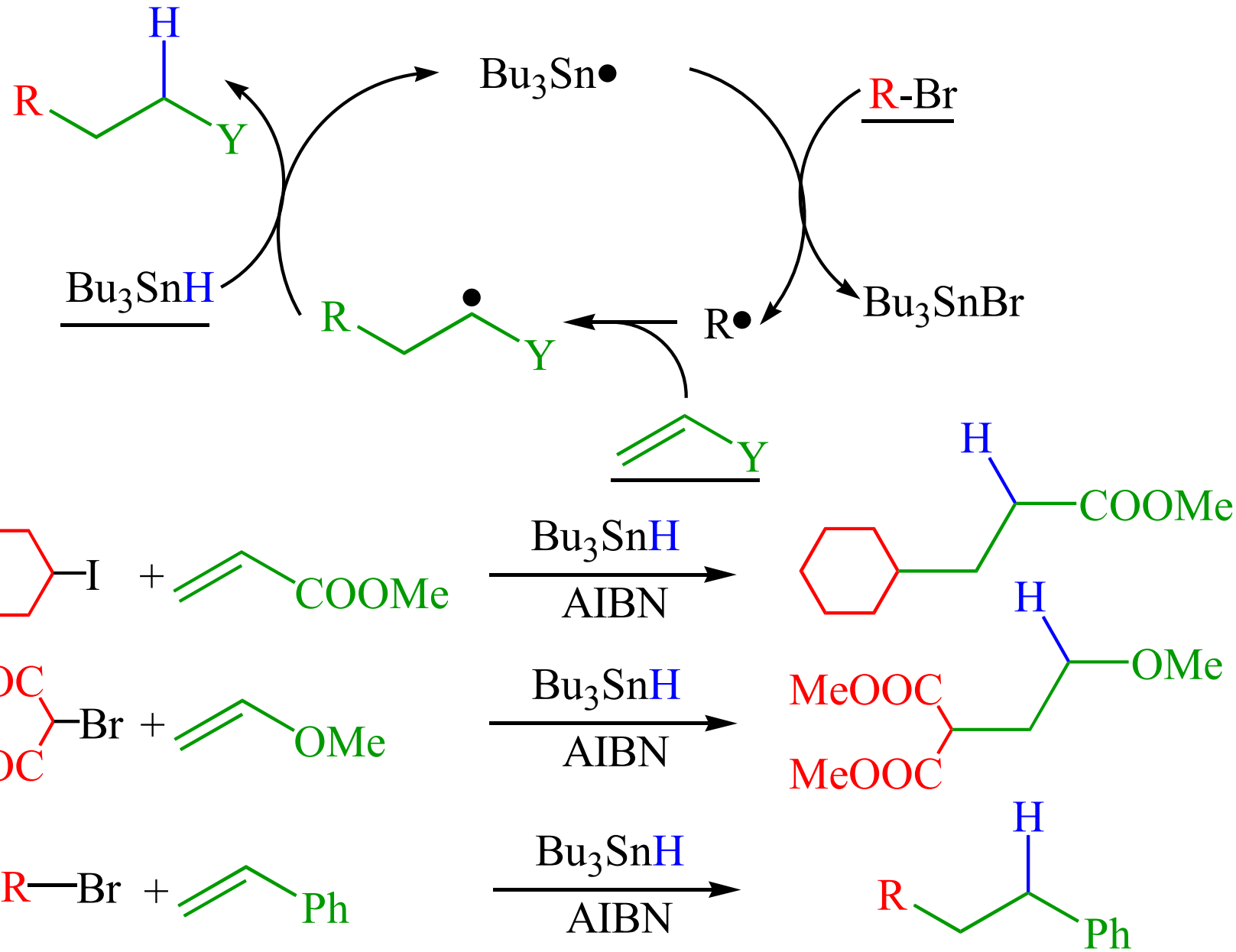


$RCOOAg + Br_2 \longrightarrow RBr + CO_2 + AgBr$

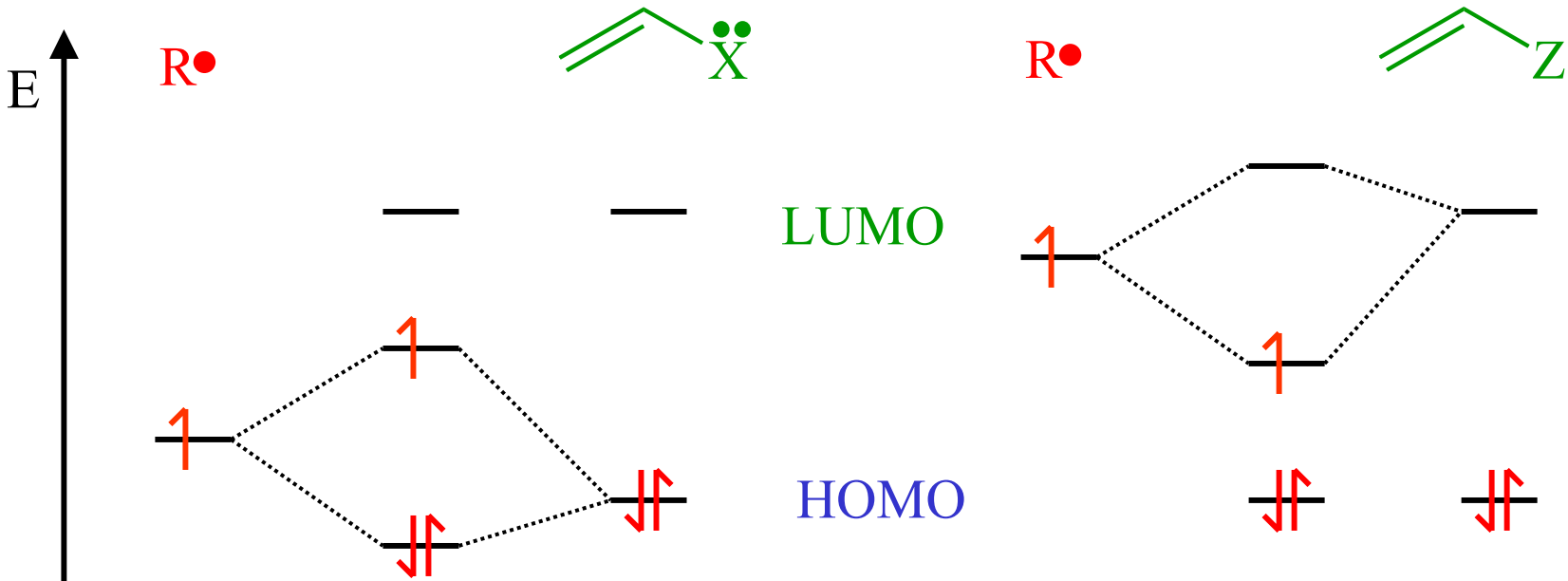
Hunsdiecker Reaktion



Radikalische Additionen ($A_R + A_RD_T$)

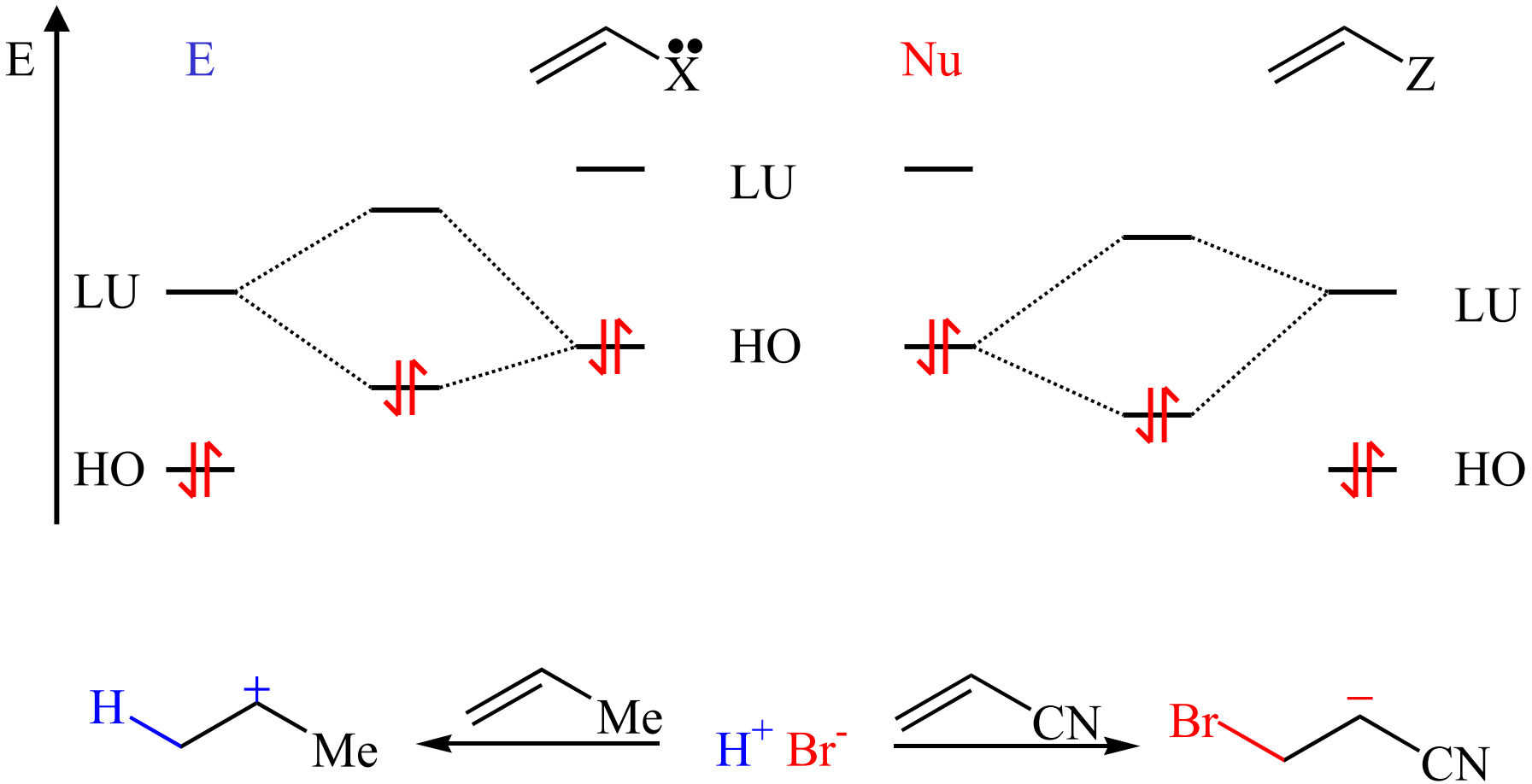


Radikalische Additionen



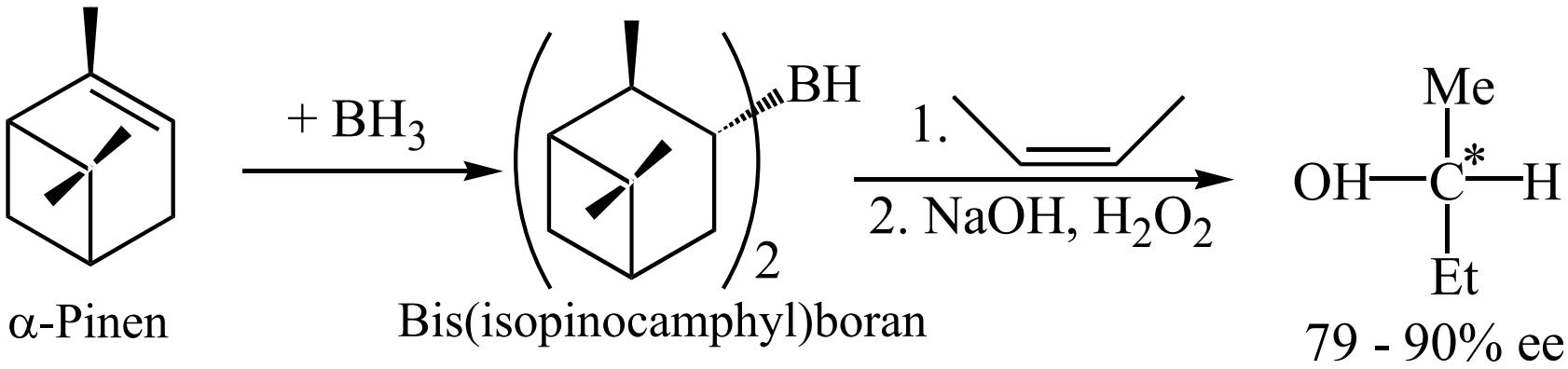
Elektrophile R• addieren schneller an elektronenreiche, nucleophile R• schneller an elektronenarme Doppelbindungen und umgekehrt.

Elektrophile (A_E + A_N) und nucleophile (A_N +A_E) Additionen



Elektrophile Additionen

Hydroborierung (H.C. Brown, 1979 Nobelpreis)

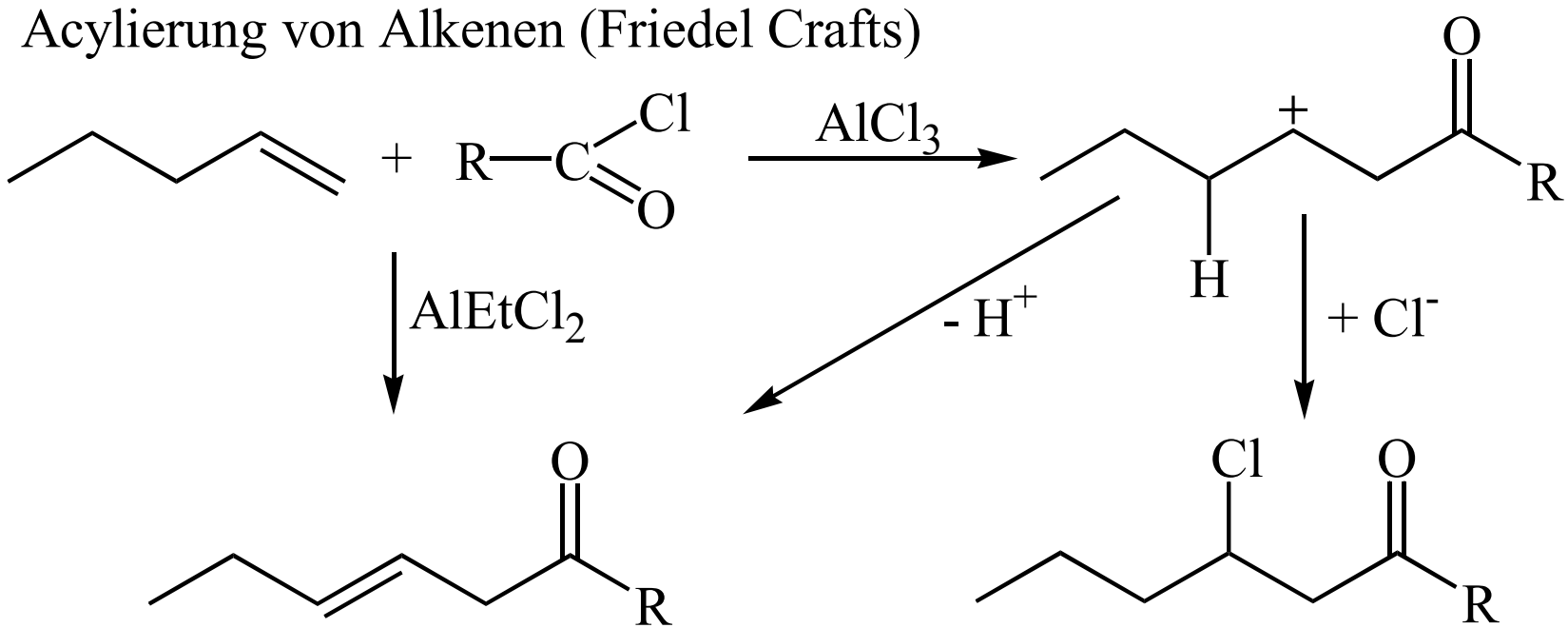


α-Pinen

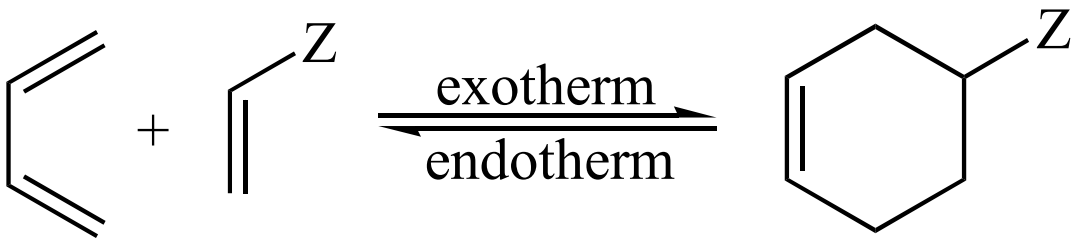
Bis(isopinocamphyl)boran

79 - 90% ee

Acylierung von Alkenen (Friedel Crafts)



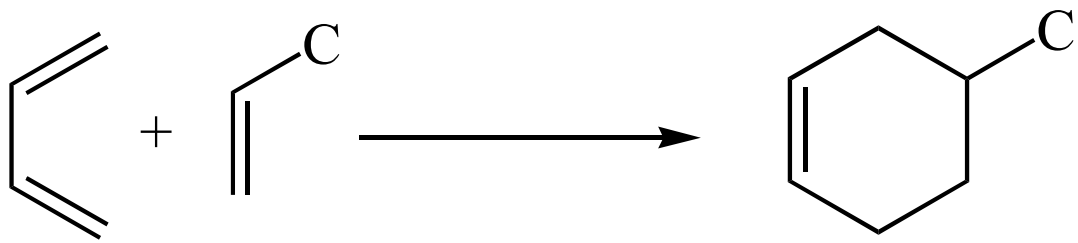
Cycloaddition - Cycloreversion



Z = CHO, $COCH_3$, COOR
CN, NO_2, SO_2Ph, u.a.

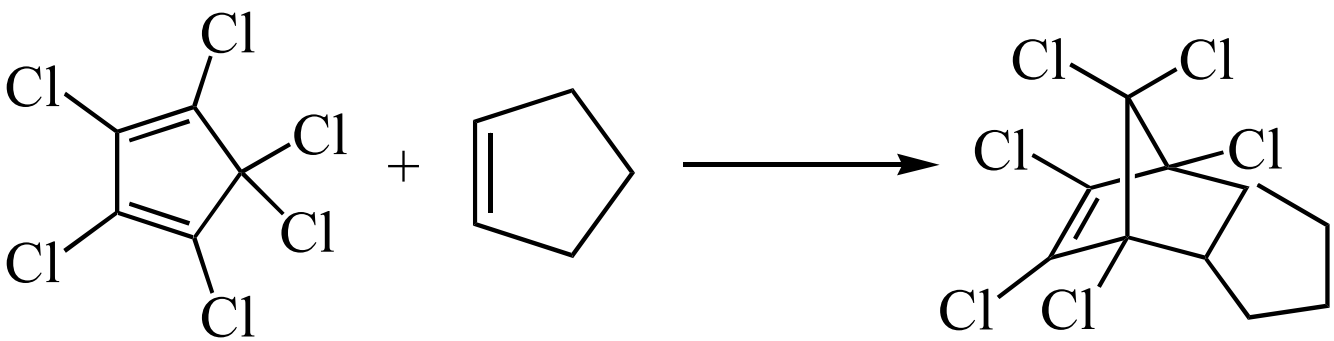
Dien Dienophil

Diels-Alder-Reaktion ⇌ Retro-Diels-Alder (Nobelpreis 1950)



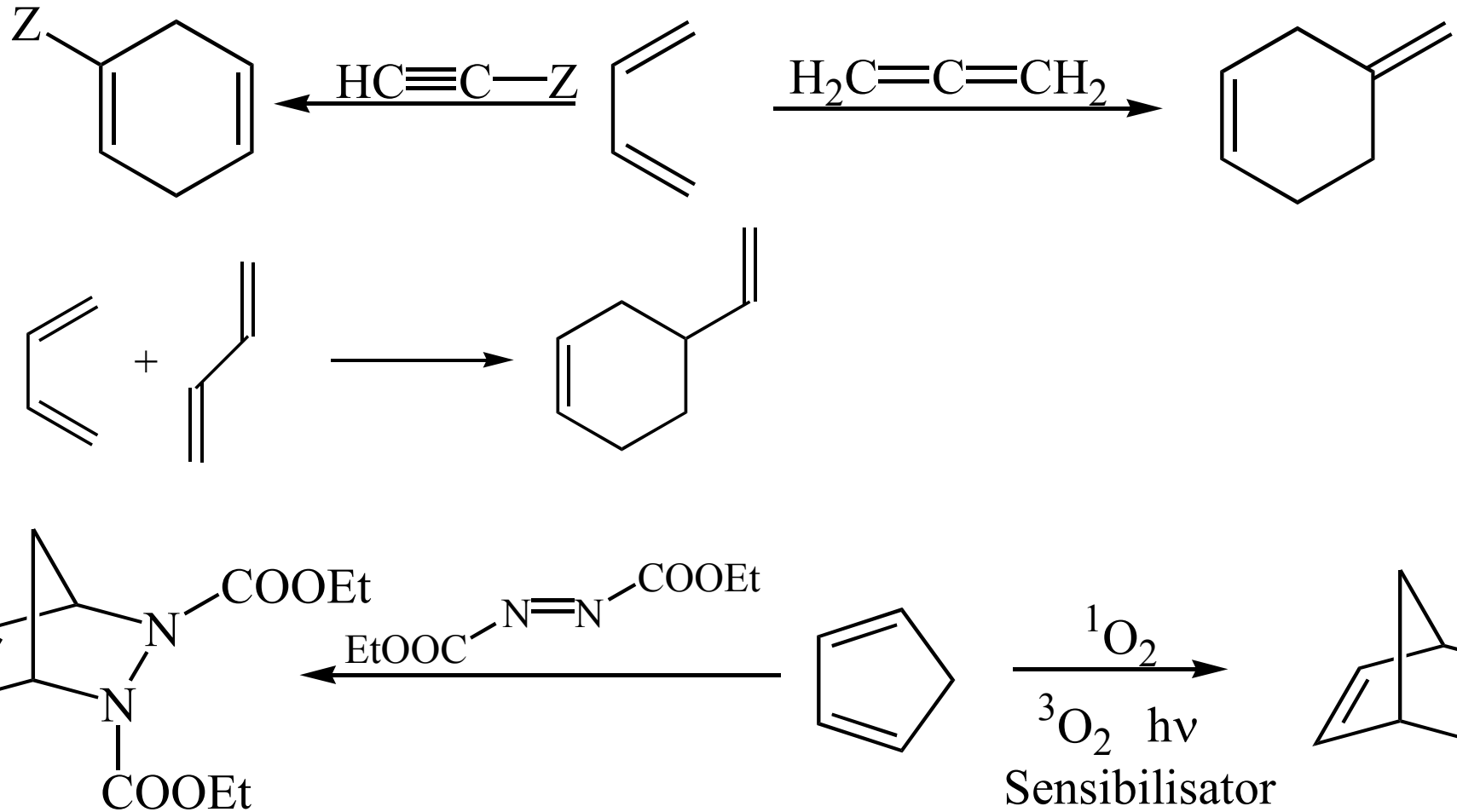
C = Ph, $CH{=}CH_2$, u.a.

Diels-Alder mit <u>normalem Elektronenbedarf</u>



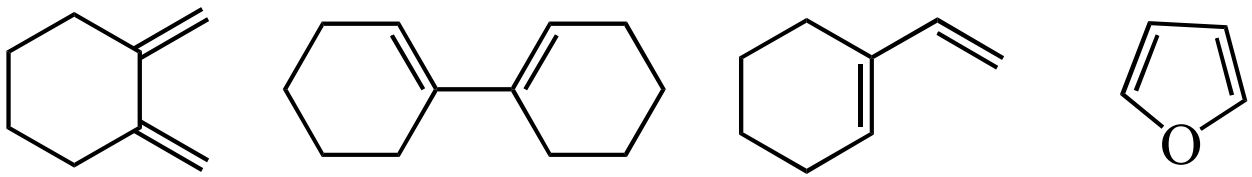
Elektrophil Nucleophil D-A mit <u>inversem Elektronenbedarf</u>

Dienophile

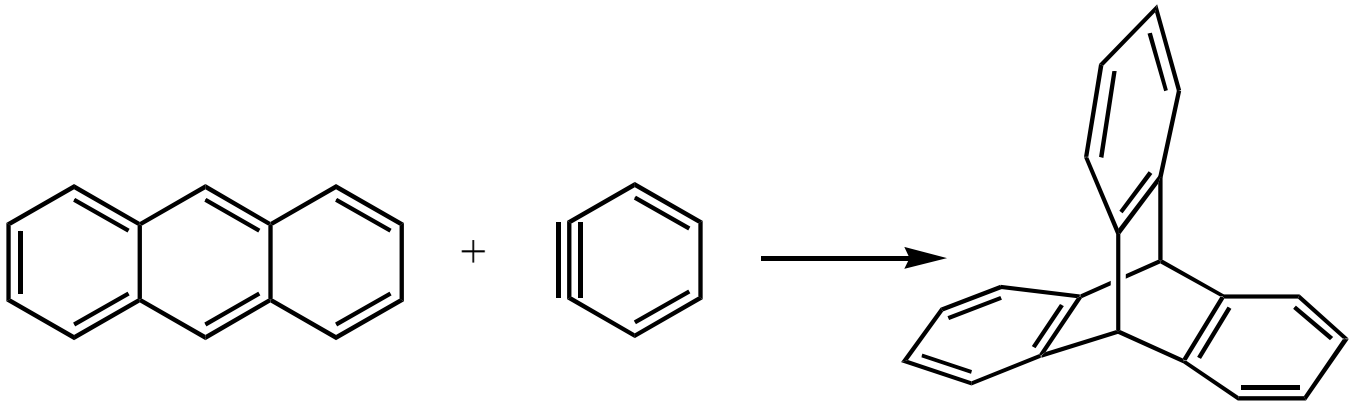


Heterodienophile: $-C\equiv N$ $-C=N-$ $-N=O$ $-C=O$ u.a.

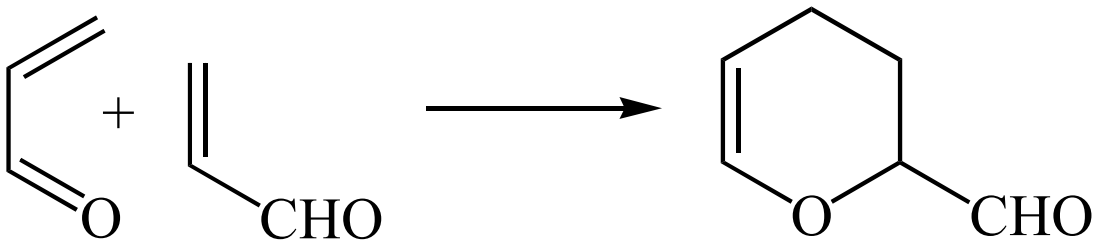
1,3-Diene



cisoide Konformation

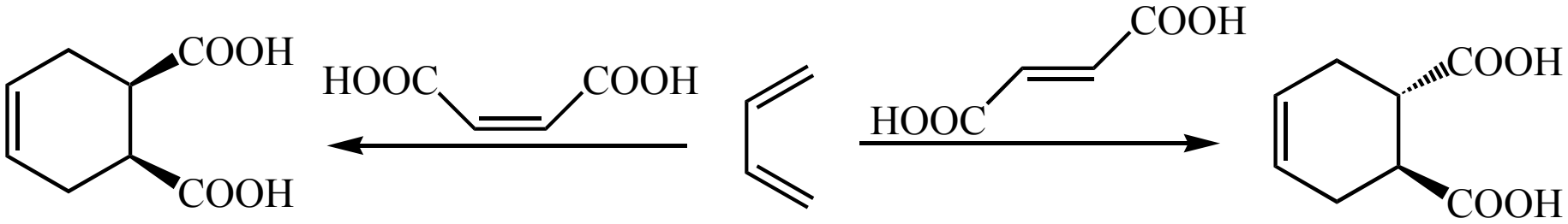


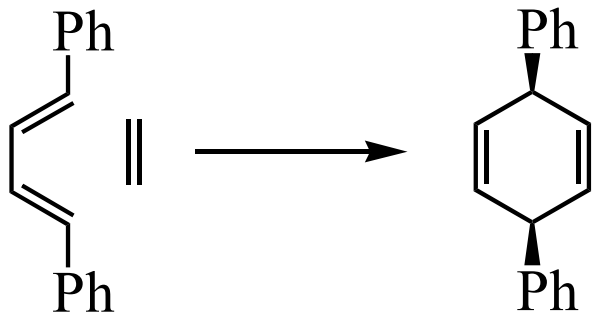
Triptycen



Regioselektiv

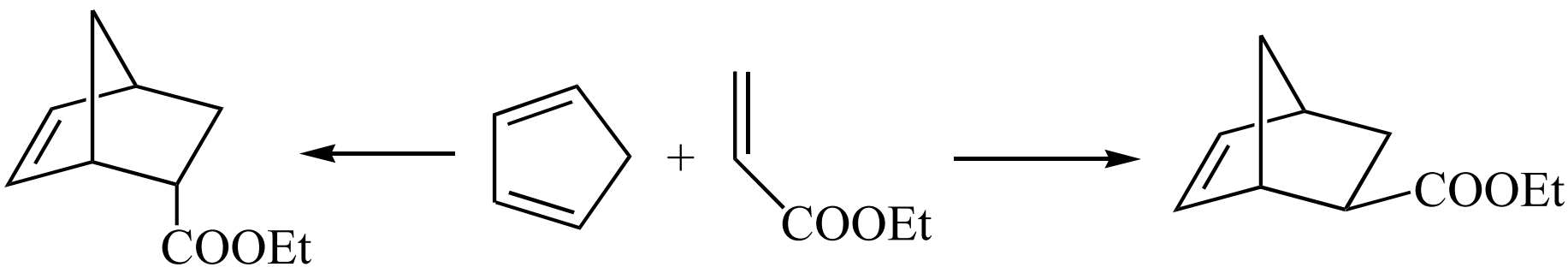
Stereochemie





stereospezifische syn-Addition,
suprafacial

Diels-Alder Reaktion ist $\pi^4s + \pi^2s$ (4 + 2)-Cycloaddition

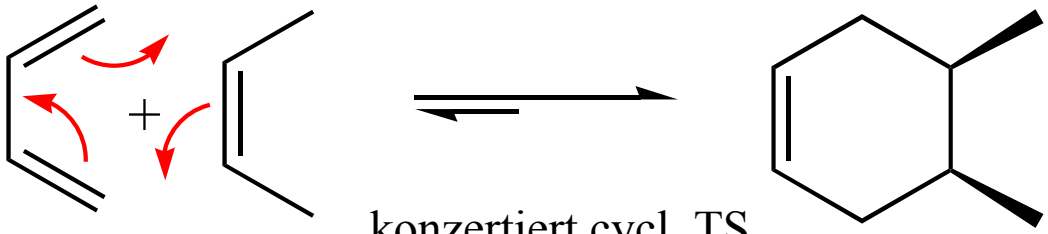


endo: kinetische Kontrolle

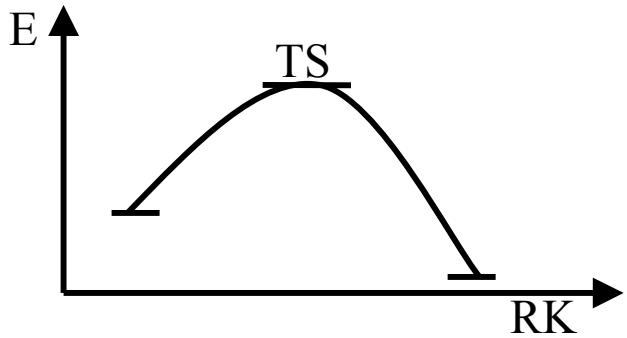
exo: thermodyn. Kontrolle

D-A wird durch Lewis-Säuren beschleunigt, endo-Selektivität wird erhöht.

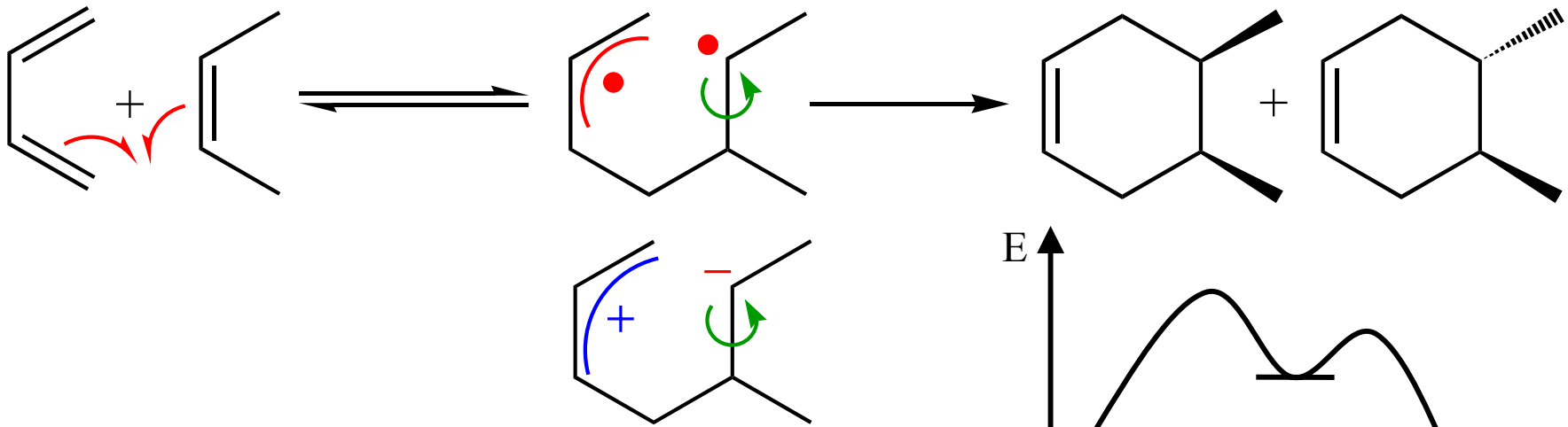
Mechanismus



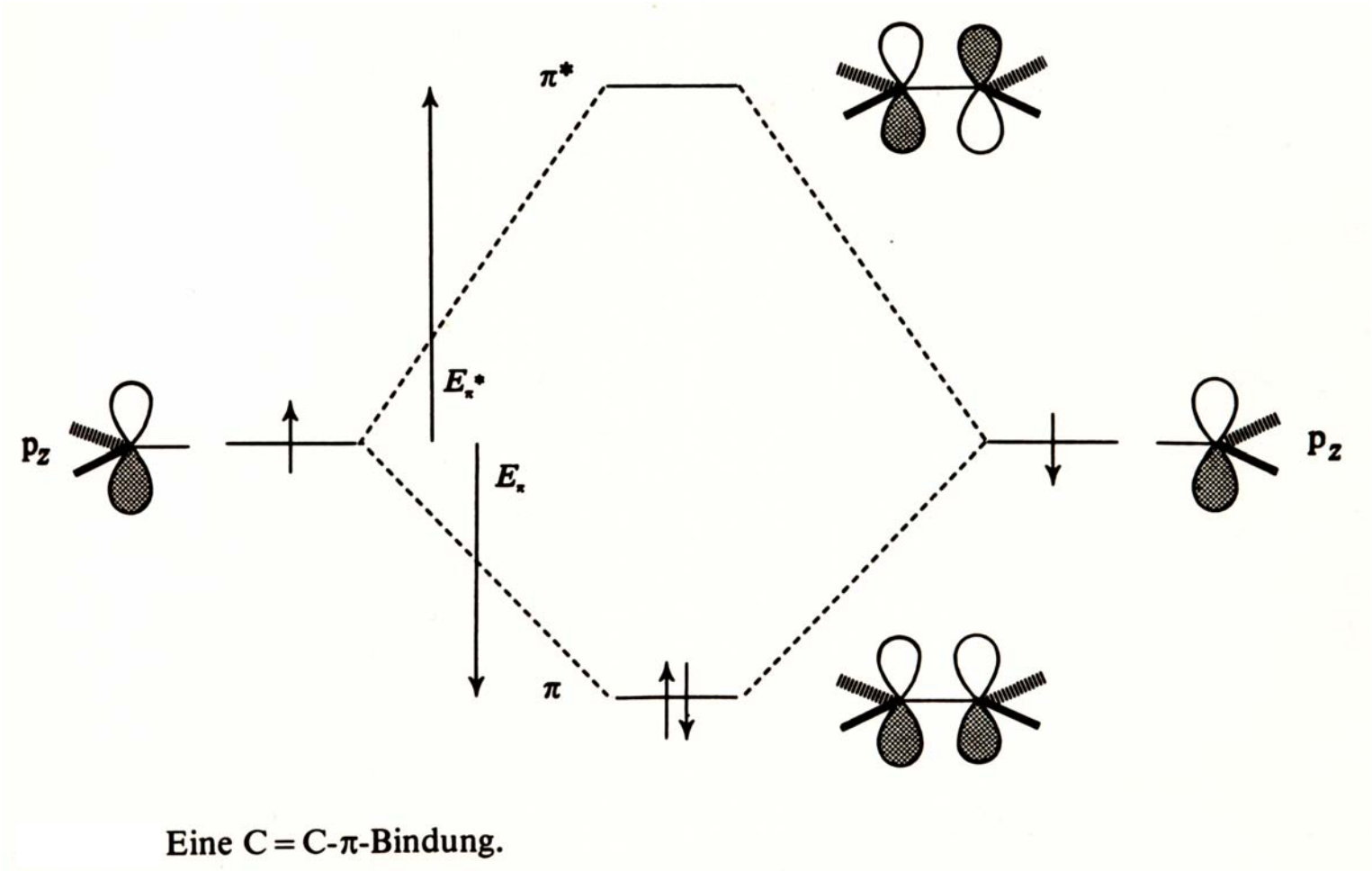
konzertiert cycl. TS



Woodward (Nobelpreis 1965), R.Hoffmann (1985): Pericyclische Reaktionen



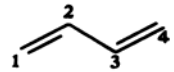
Orbitale der C=C-Bindung



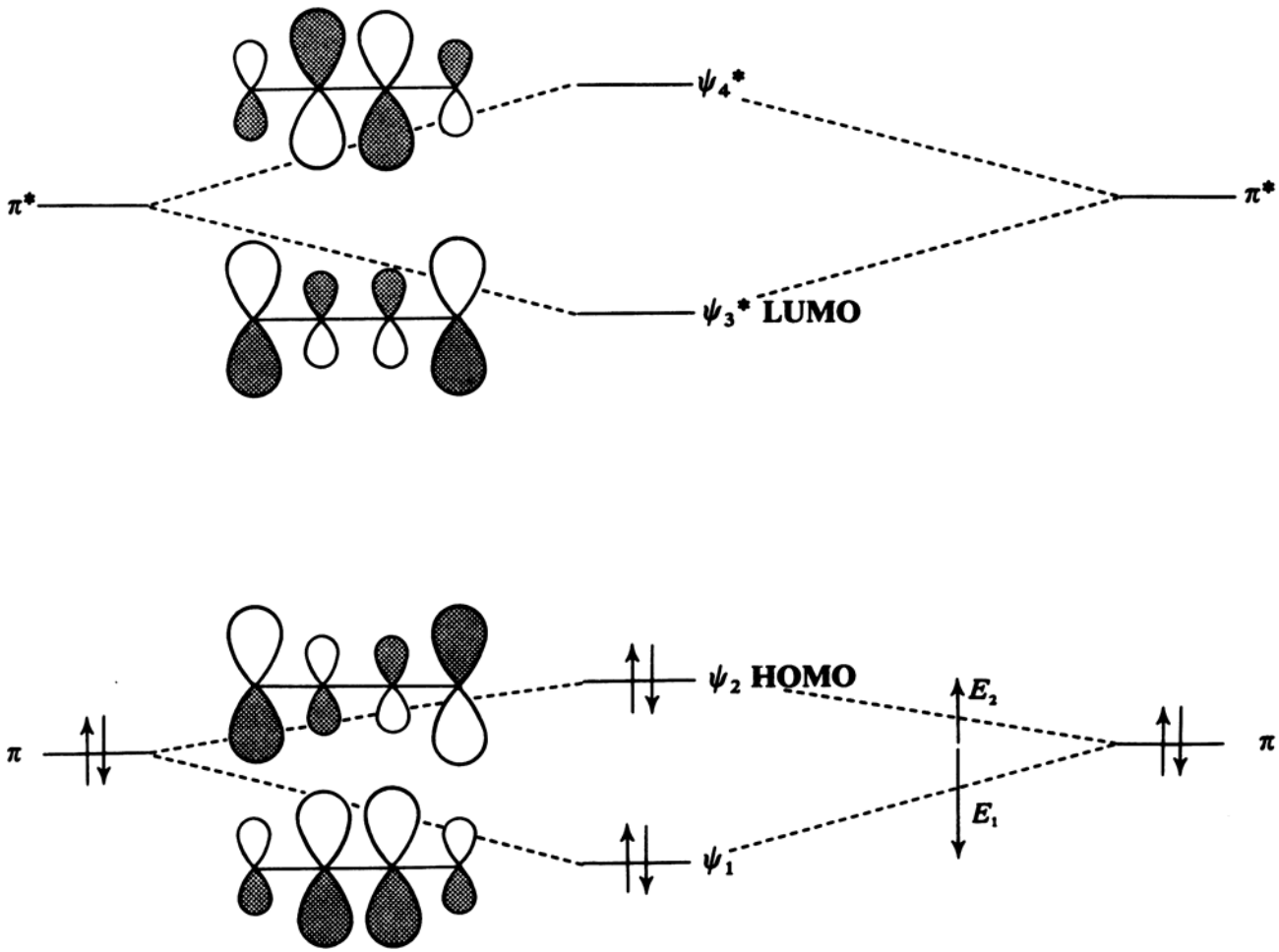
Eine C = C-π-Bindung.

Lit.: Ian Fleming, Grenzorbitale und Reaktionen organischer Verbindungen, VerlagChemie, 1979

Orbitale der C=C-Bindung

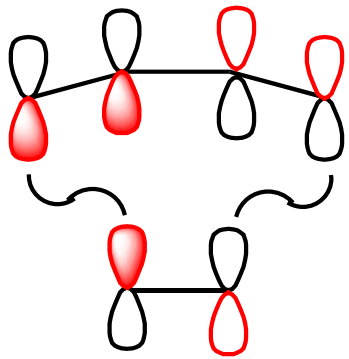


(23)



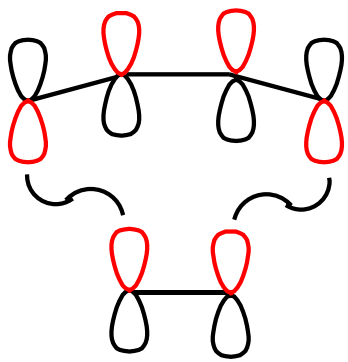
Die Energien der π-MOs von Ethylen und 1,3-Butadien.

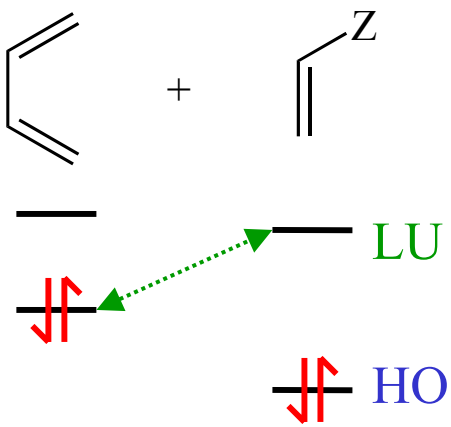
Grenzorbitalwechselwirkungen

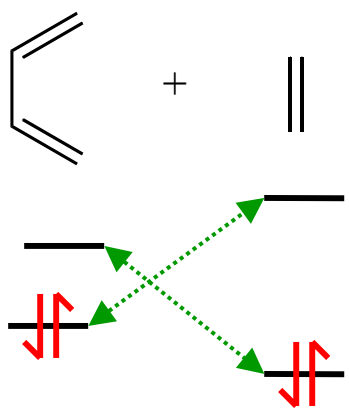


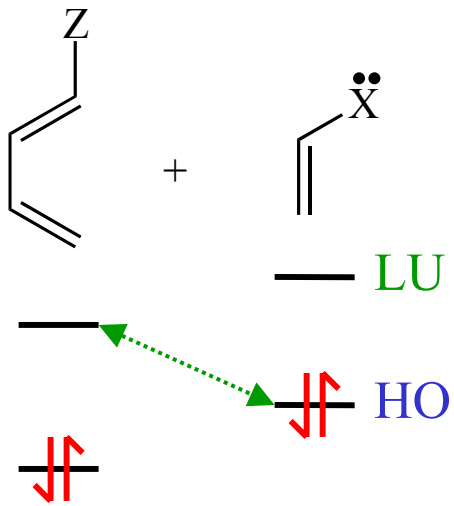
HOMO Dien LUMO

LUMO Dienophil HOMO







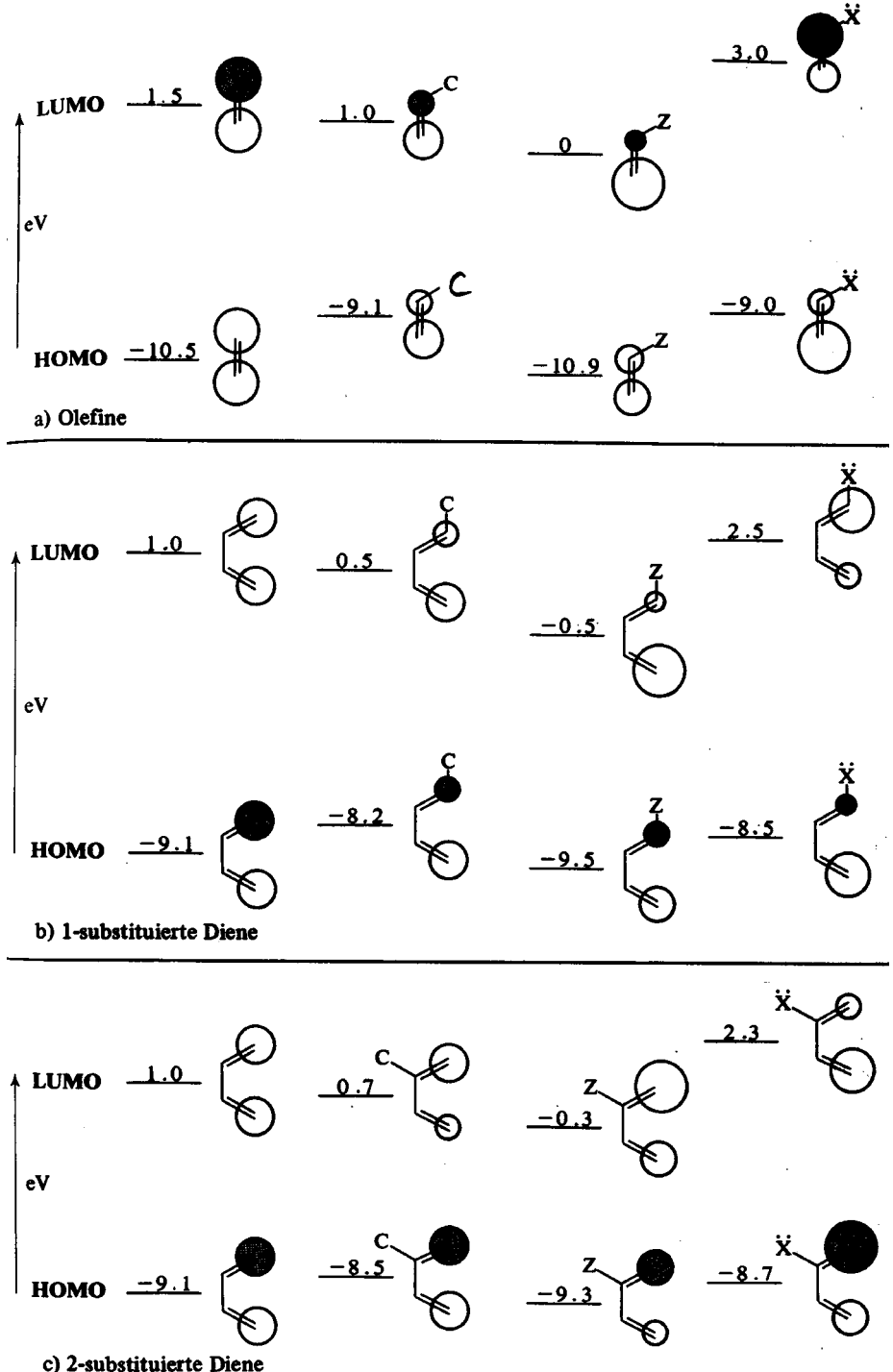


$HOMO_{Dien}$ - $LUMO_{Dienophil}$
dominierend
D-A mit normalem
Elektronenbedarf

$HOMO_{Dienophil}$ - $LUMO_{Dien}$
dominierend
D-A mit inversem
Elektronenbedarf

Grenzorbitalenergien

Grenzorbitalenergien und –koeffizienten für Olefine und Diene. Die Energiemittelwerte sind für die verschiedenen Klassen von Olefinen und Dienen typisch.
(1 eV = 96.5 kJ = 23 kcal)



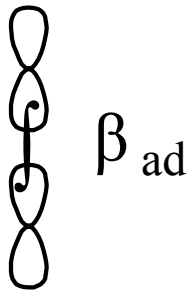
Grenzorbitaltheorie

$$\Delta E_{HO,LU} = \frac{2\left(c_{d,HO} \cdot c_{a,LU} \cdot \beta_{ad}\right)^2}{E_{HO,D} - E_{LU,A}}$$

β = Resonanzintegral

LUMO A: a

HOMO D: d



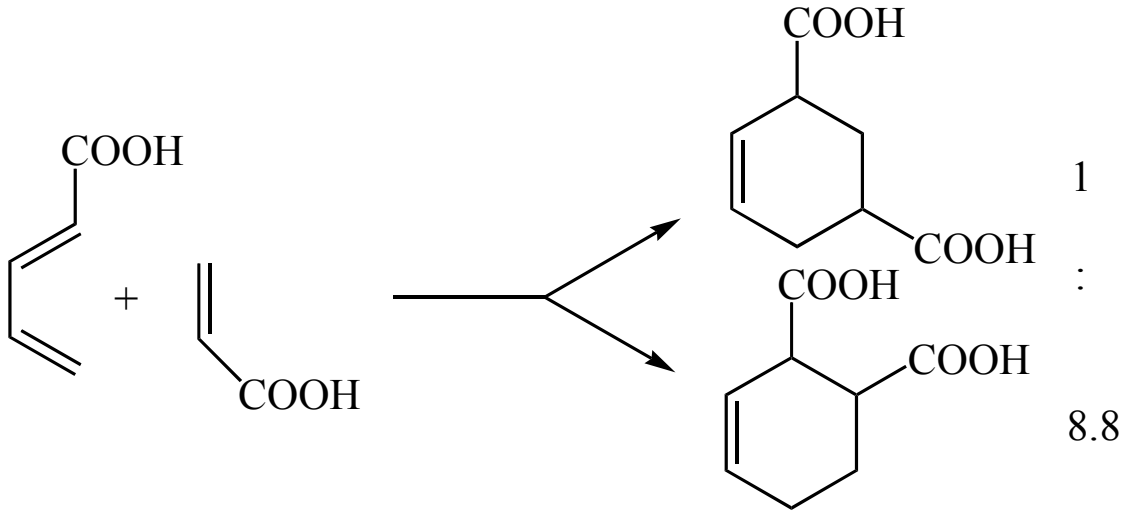
β_{ad}

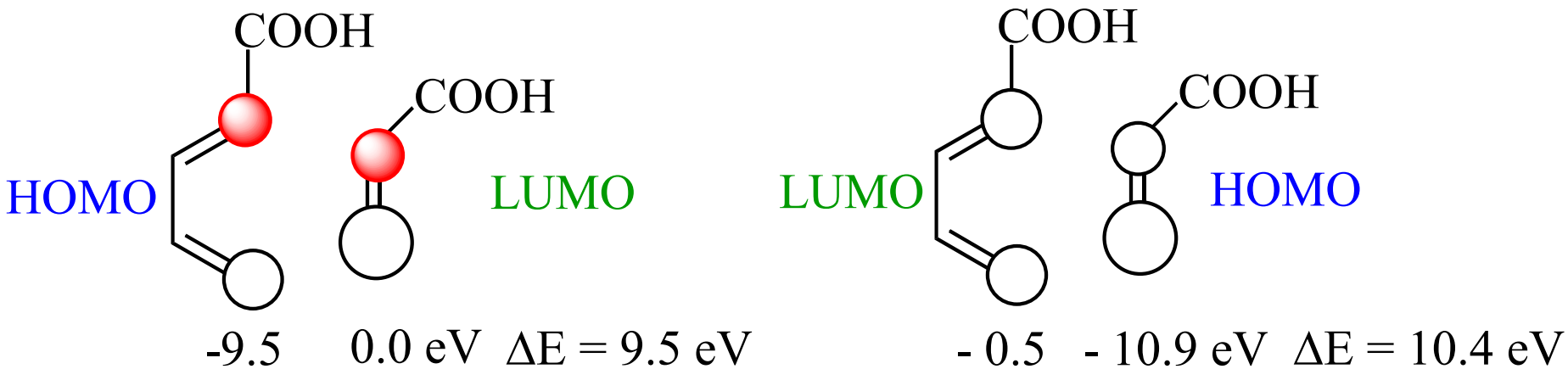
$c < 1$ = Koeffizient des AO von d im HOMO von D

bzw. von a im LUMO von A

Lit.: I. Fleming: Grenzorbitale und Reaktionen organischer Verbindungen, VCH

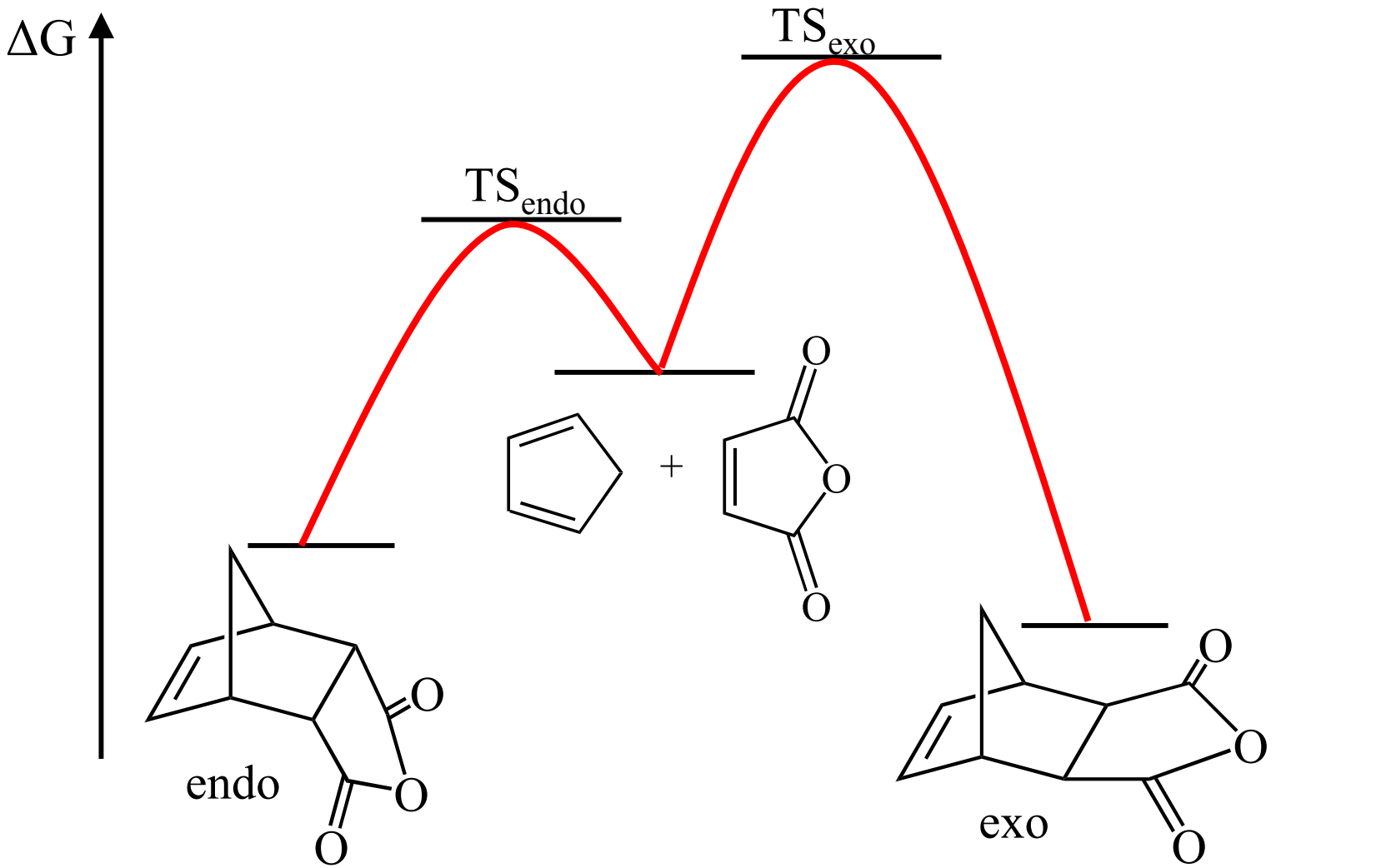
Regioselektivität





1. Bestimmung der dominierenden Wechselwirkung
2. Größe der Koeffizienten in HOMO und LUMO

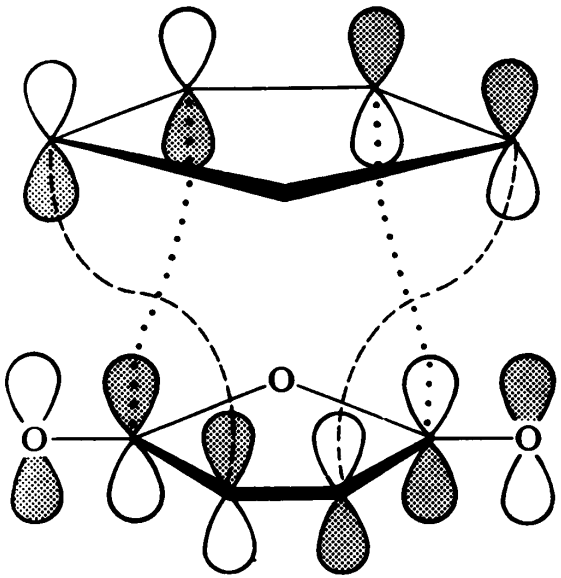
Endo-Selektivität



kinetisch kontrolliertes Produkt

thermodyn. kontrolliertes Produkt

Sekundärüberlappung

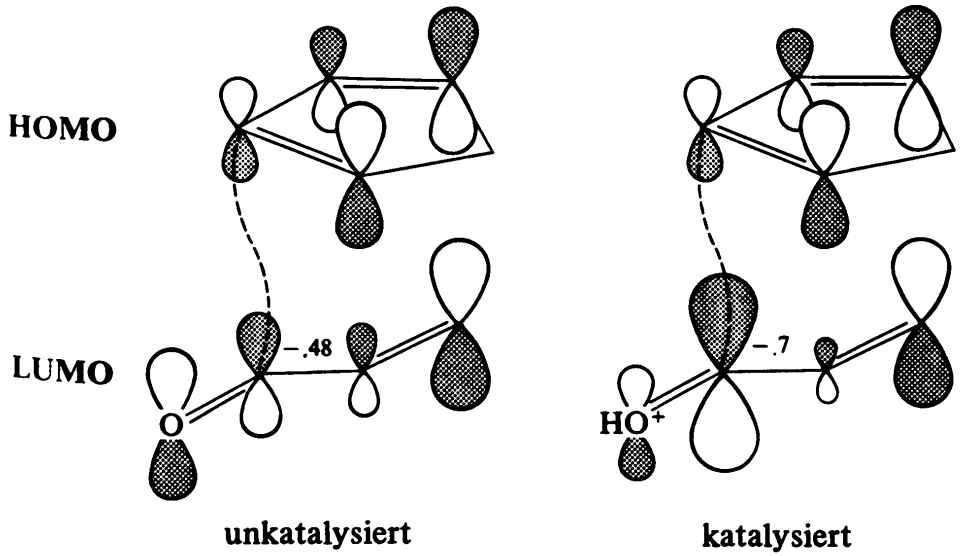


HOMO

LUMO

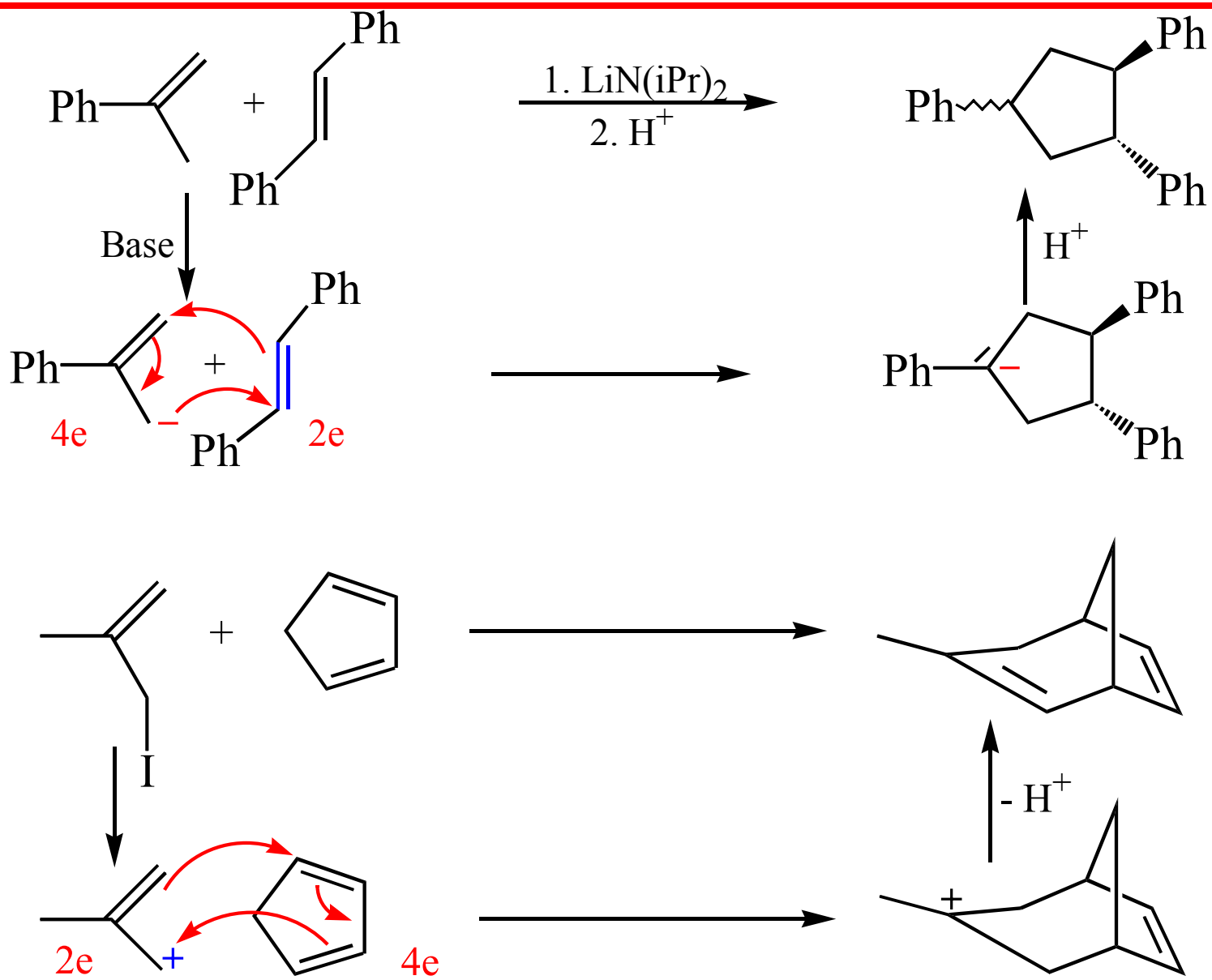
Sekundärüberlappung der Grenzorbitale in Diels-Alder-Additionen. Die gepunkteten Linien repräsentieren die bindende Überlappung, die den *endo*-Übergangszustand stabilisiert.

Katalysierte Diels-Alder-Reaktion

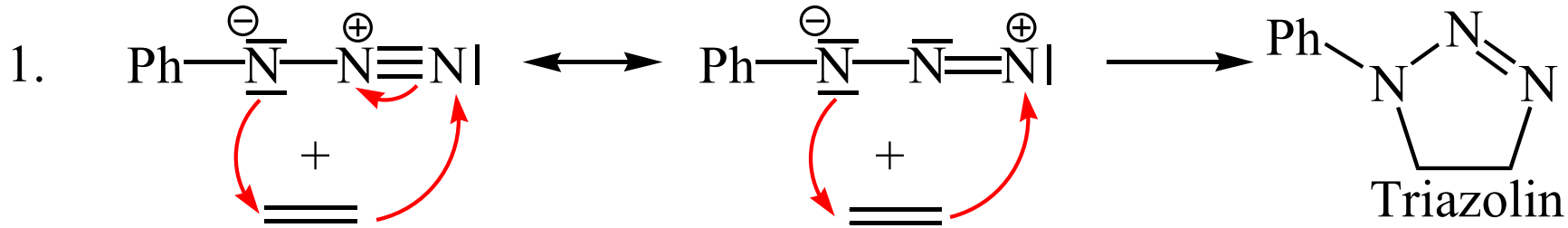


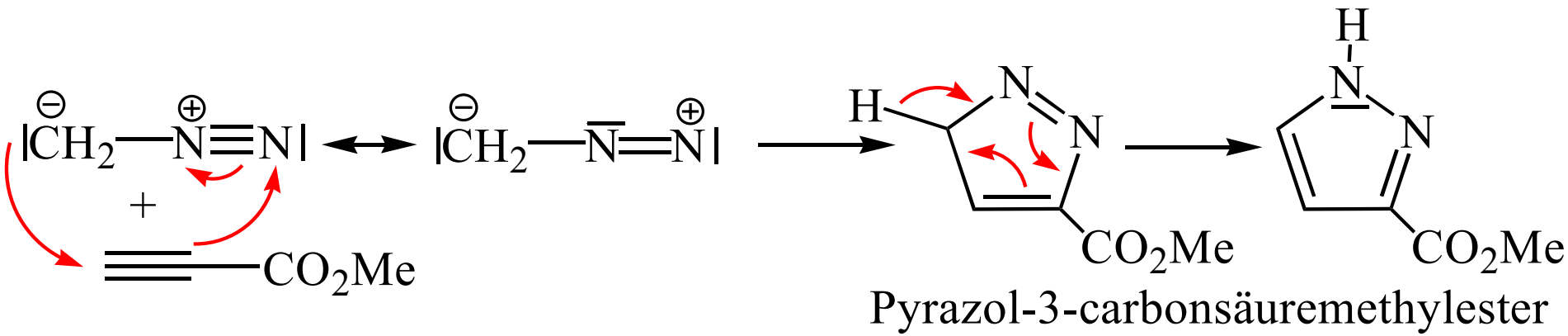
Grenzorbitale und gesteigerte *endo*-Selektivität einer Säure-katalysierten Diels-Alder-Reaktion

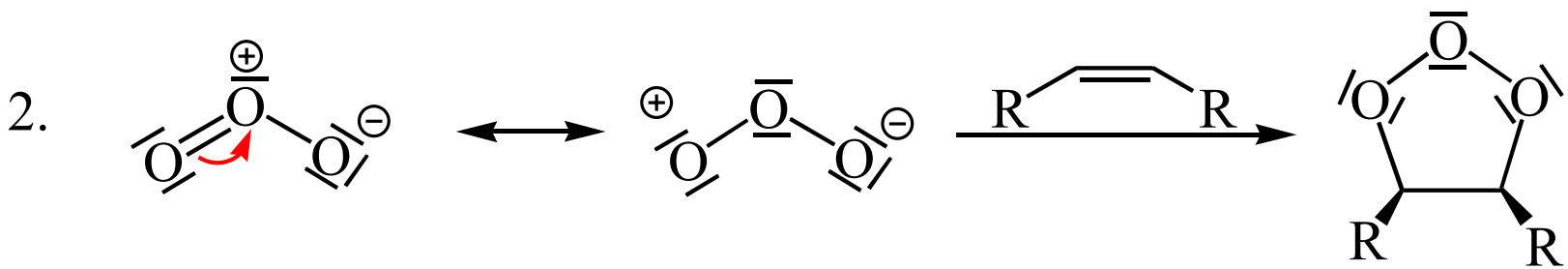
Cycloadditionen



1,3-Dipolare Cycloadditionen

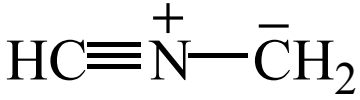




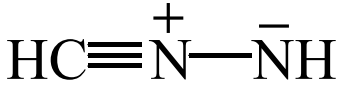


1. 1,3 Dipole vom Propargyl-/Allenyl-Anion-Typ(C,N,O): 6
2. 1,3 Dipol vom Allyl-Anion-Typ:8

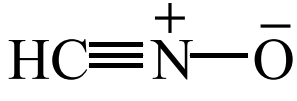
Die wichtigsten 1,3-Dipole



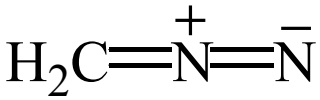
Nitrilylide



Nitrilimine

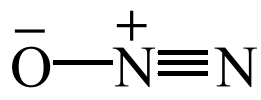


Nitriloxide

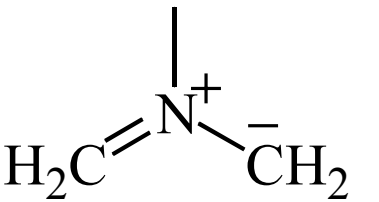


Diazoalkane

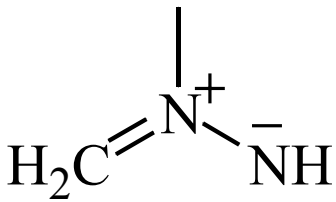
Azide



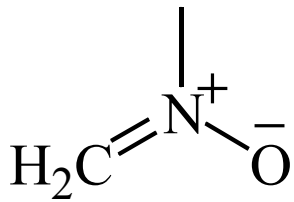
Distickstoffoxide



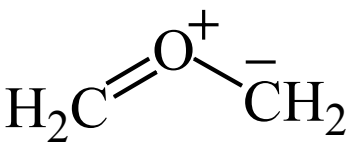
Azomethinylide



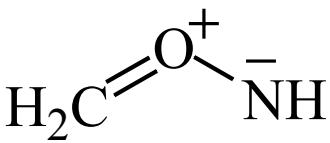
Azomethinimine



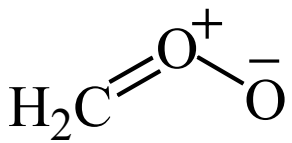
Nitrone



Carbonylide

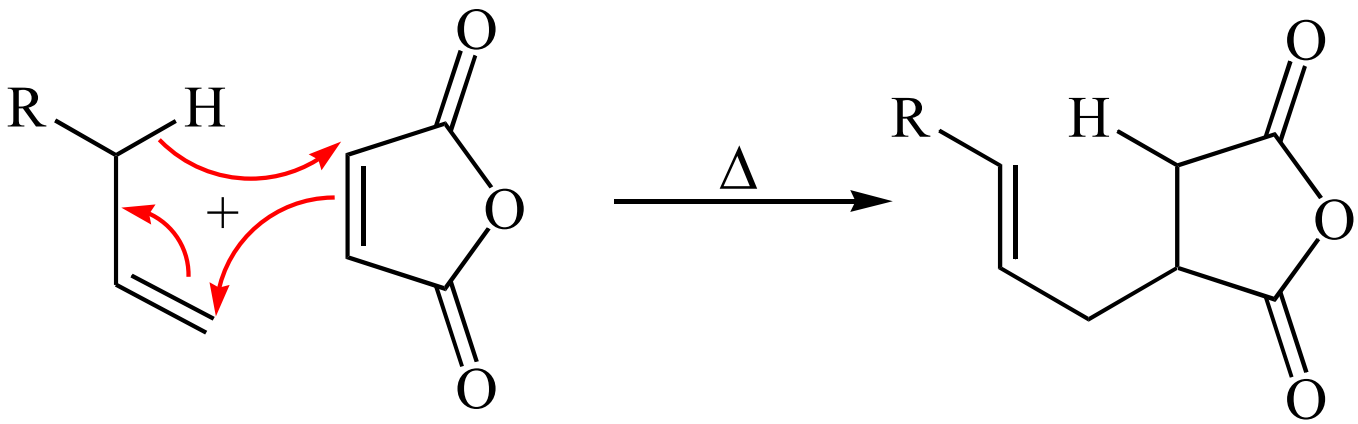


Carbonimine



Carbonyloxide

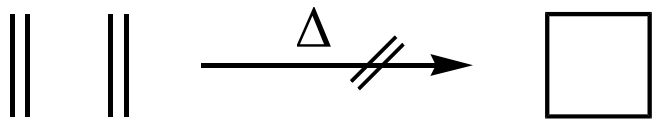
En-Reaktion

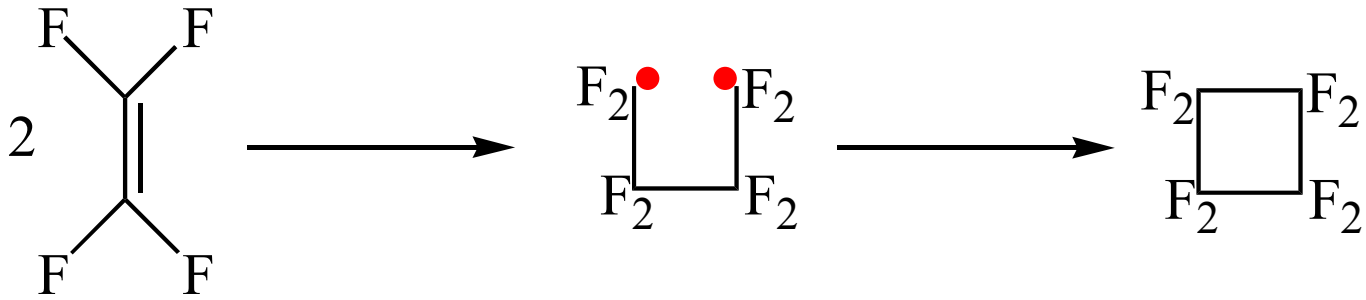


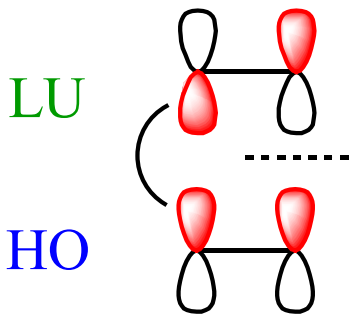
$[(\pi^2 + \sigma^2)s + \pi^2 s]$

En-Reaktion (Alder)

2 + 2 Cycloadditionen

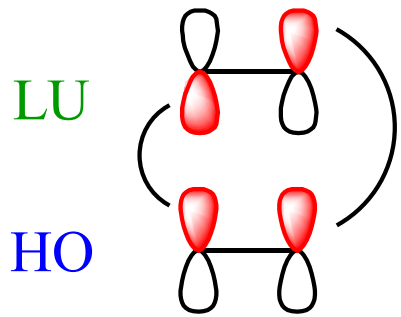






$\pi^2s + \pi^2s$

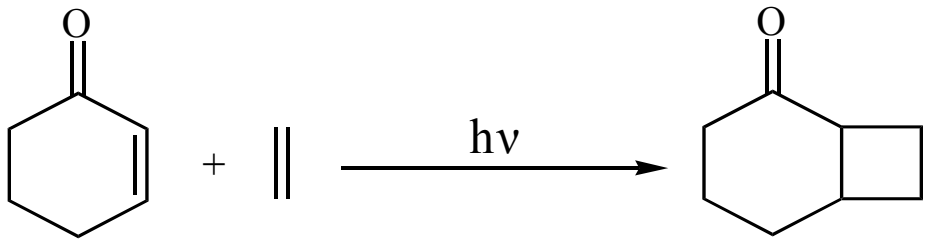
„verboten“

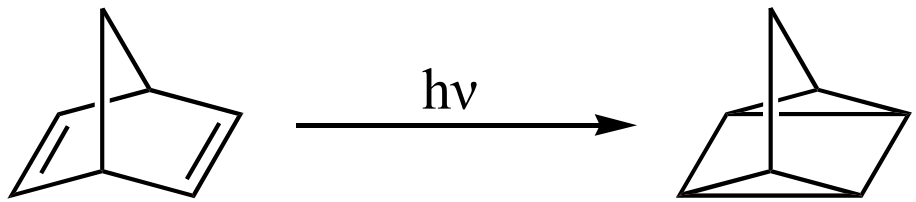


$\pi^2s + \pi^2a$

„erlaubt“, aber
geometrisch nicht möglich!

[2 + 2] - Cycloadditionen und -reversionen

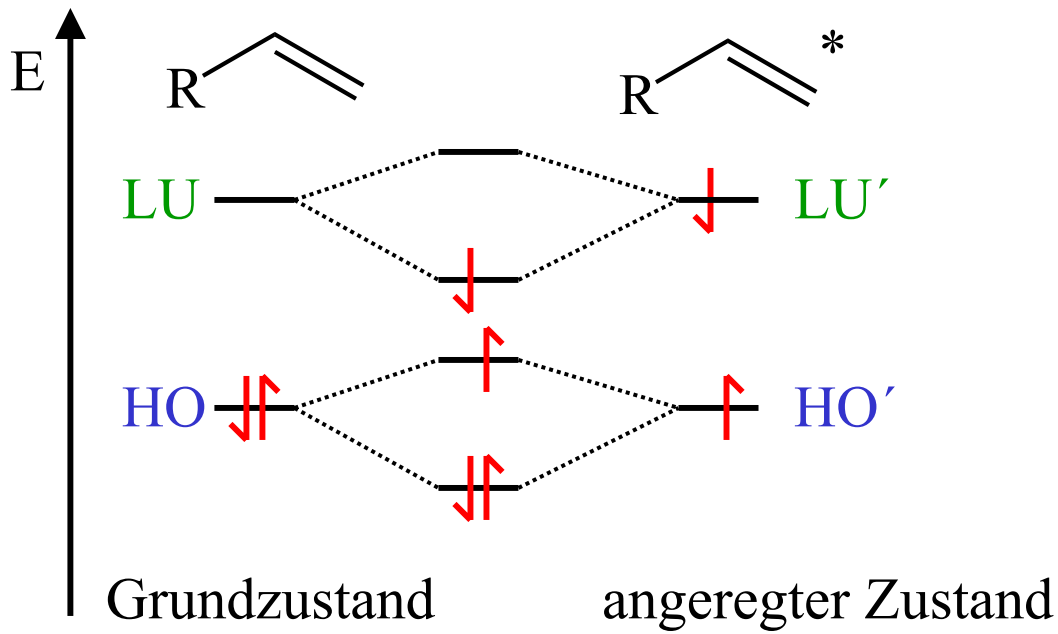




Quadricyclan

<u>Cycloreversion</u>

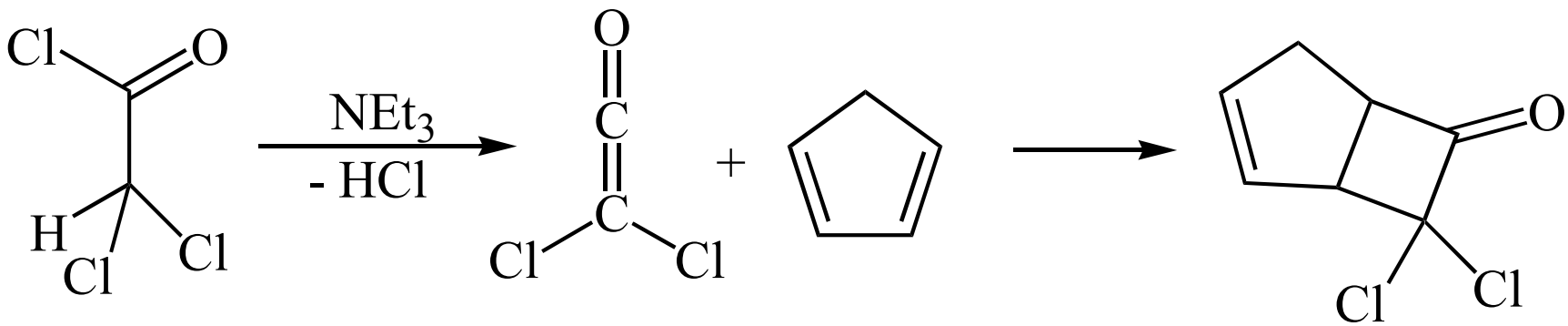
thermische „verboten“

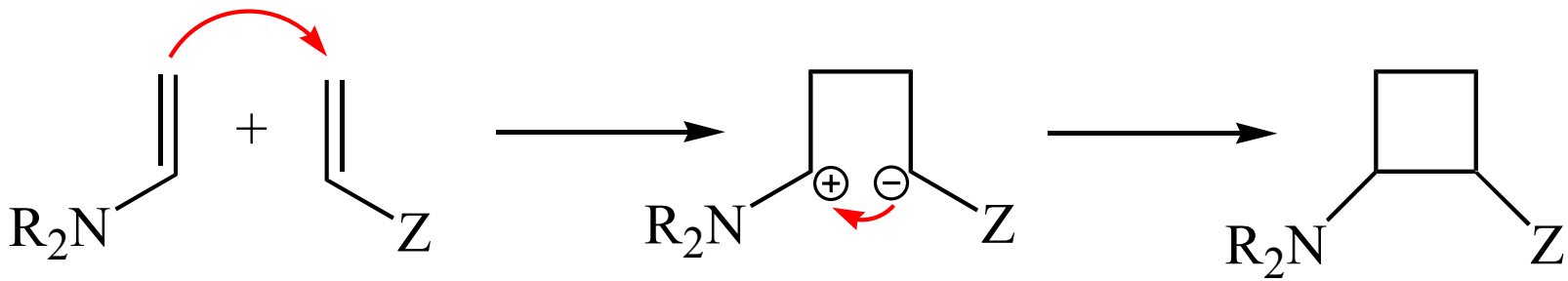


[π^2s + π^2s] - Cycloadditionen

photochemisch „erlaubt“

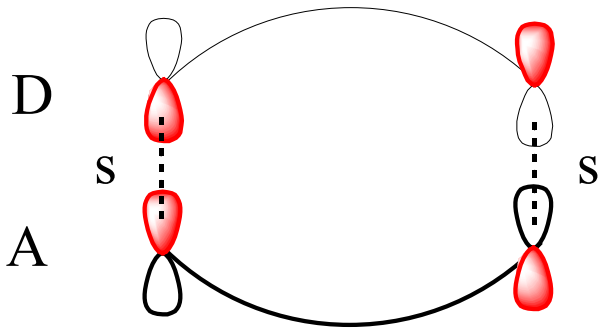
Thermische [2 + 2] - Cycloadditionen





Cycloadditionen - Verallgemeinerung

Thermische Grundzustandsreaktionen



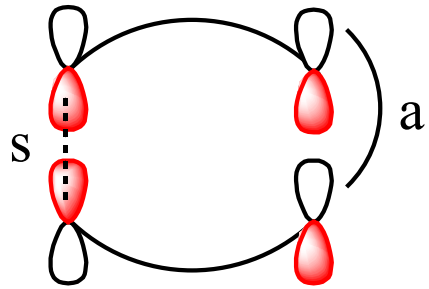
HOMO

LUMO

Zahl der e^-

m

n



$m_s + n_s = 4q + 2$
(Hückel-aromatischer TS)

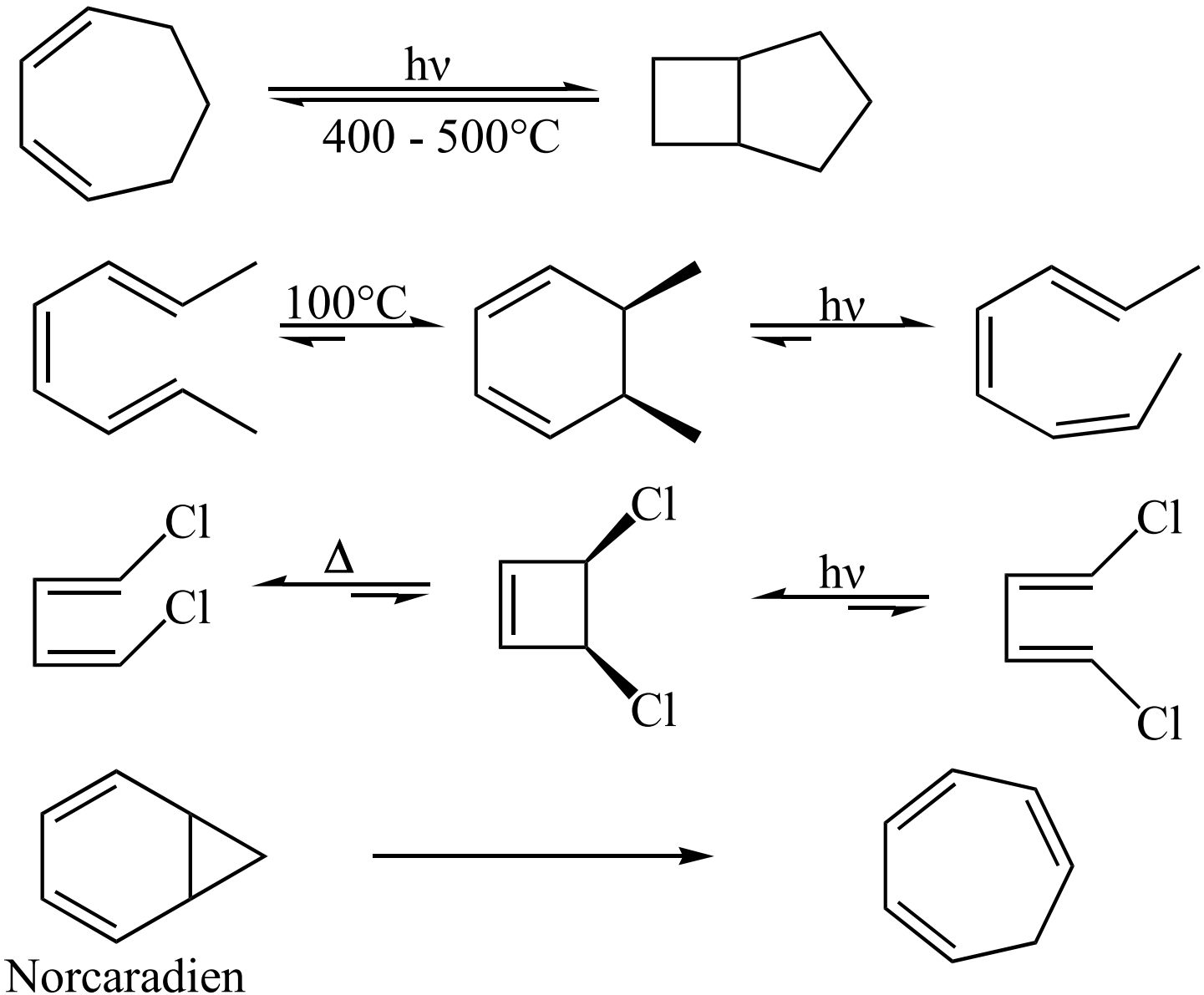
$m_a + n_s = 4q$
(Möbius-aromatischer TS)

Woodward - Hoffmann - Regeln

[m + n] - Cycloadditionen

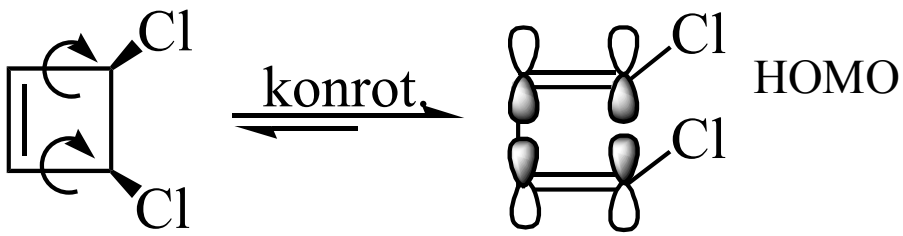
Zahl der e^-	thermische Reaktion	photochemische Reaktion
4q + 2	$m_s + n_s$	$m_s + n_a$
4q	$m_s + n_a$	$m_s + n_s$

Beispiele für elektrocyclische Umlagerungen



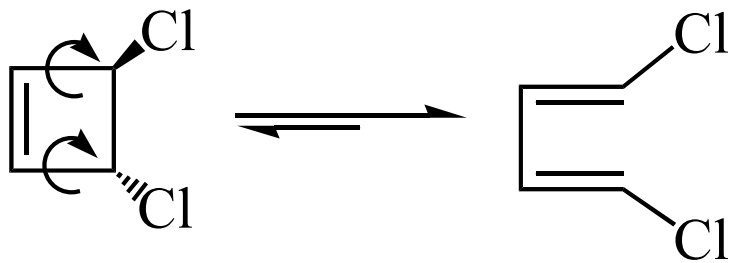
Regeln für elektrocyclische Reaktionen

Thermische Reaktionen



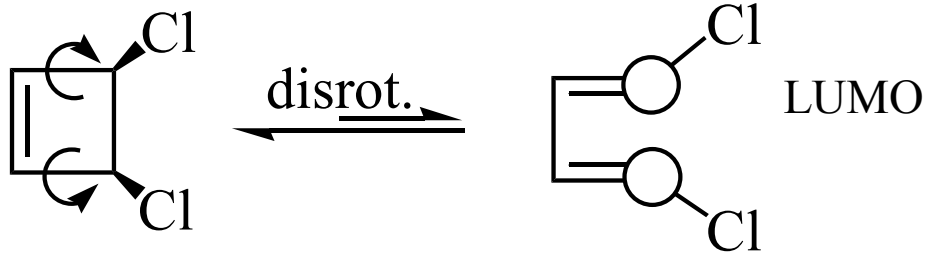
4q (q = 1)
antarafacial
Möbius

cis-trans-

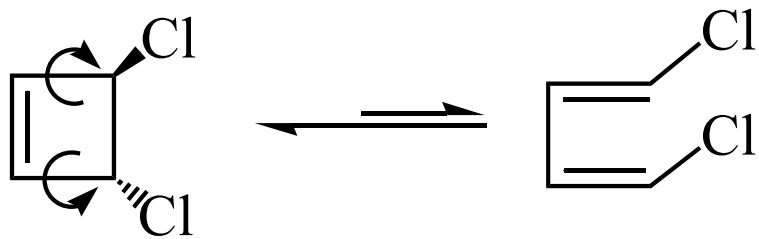


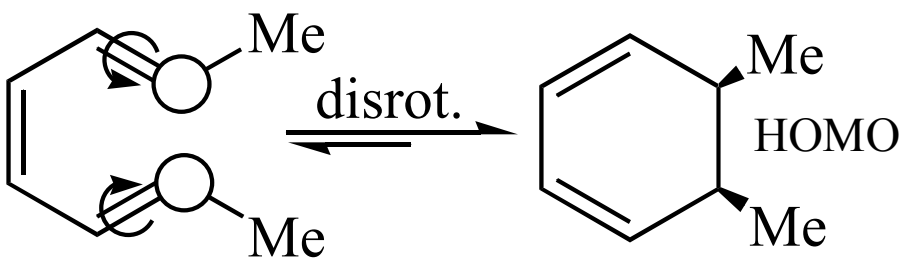
trans-trans-

Photochemische Reaktionen

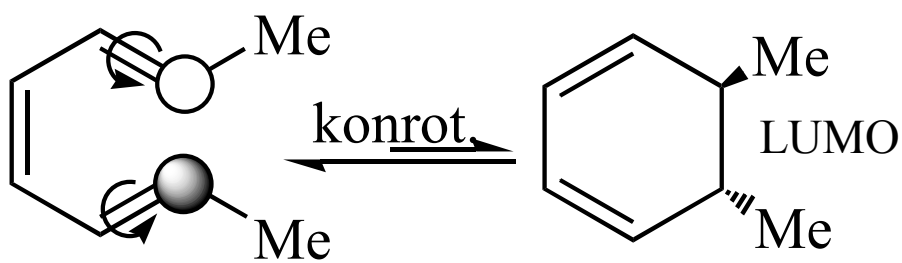


suprafacial



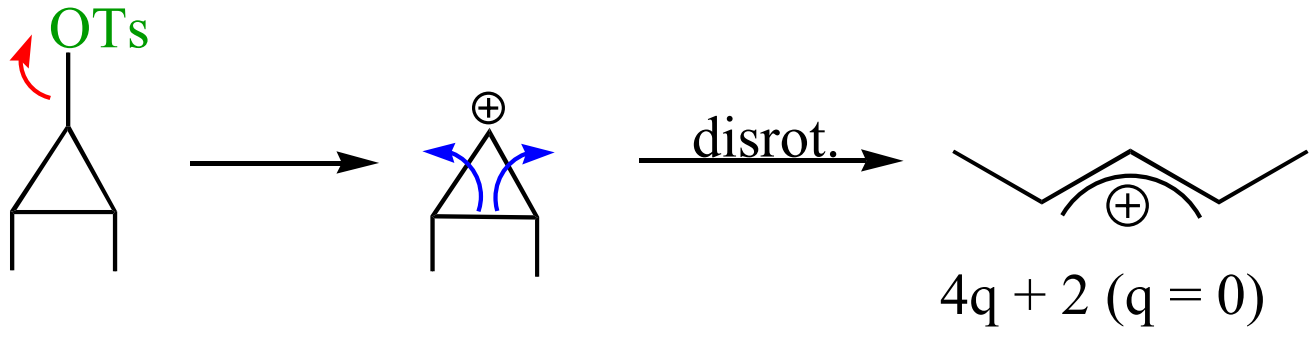


4q + 2 (q = 1)
suprafacial; Hückel

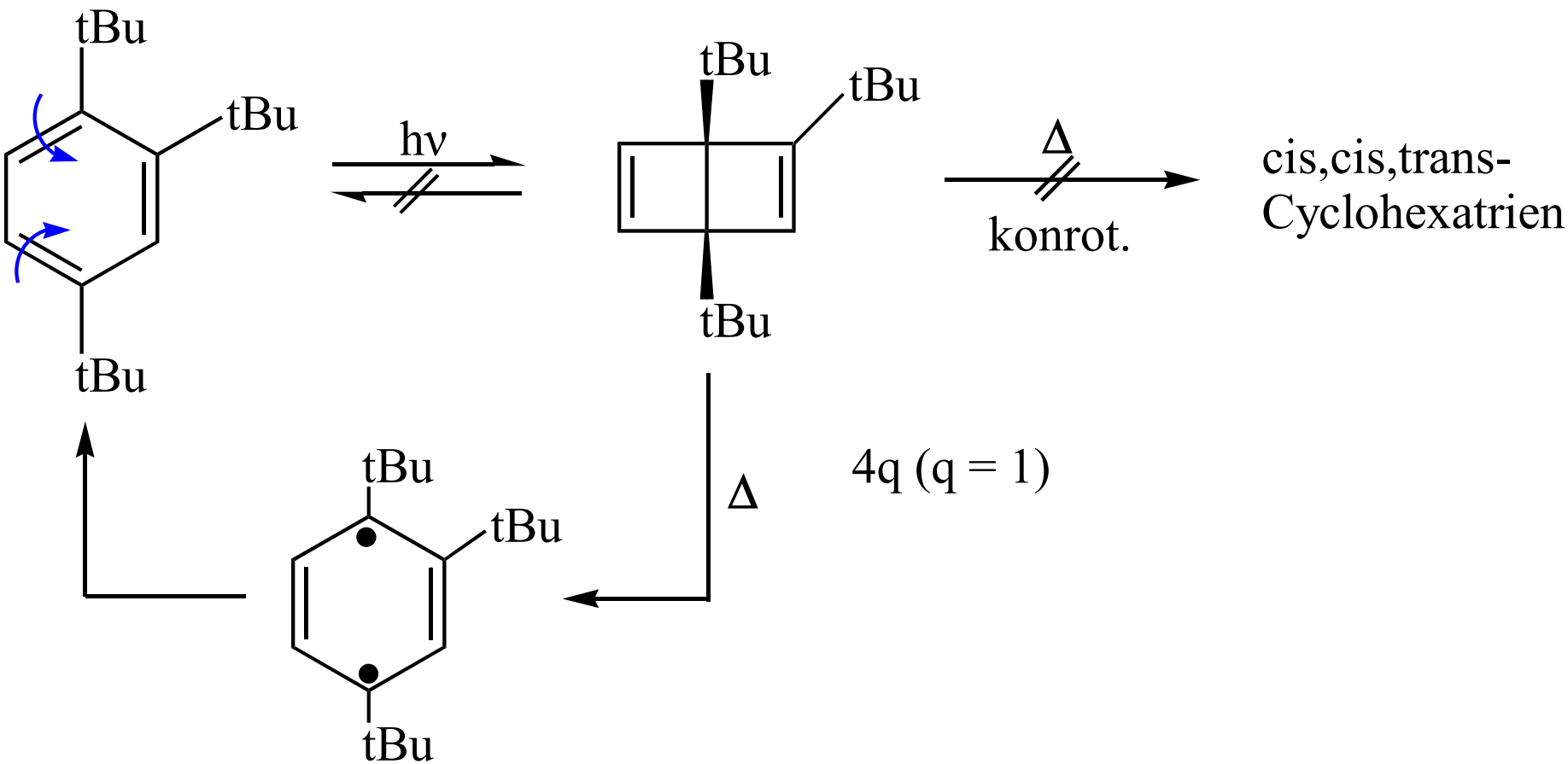


antarafacial

Elektrocyclische Reaktionen



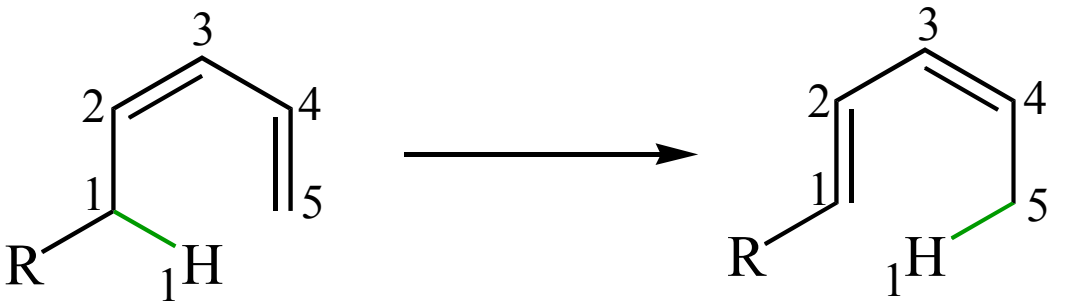
4q + 2 (q = 0)



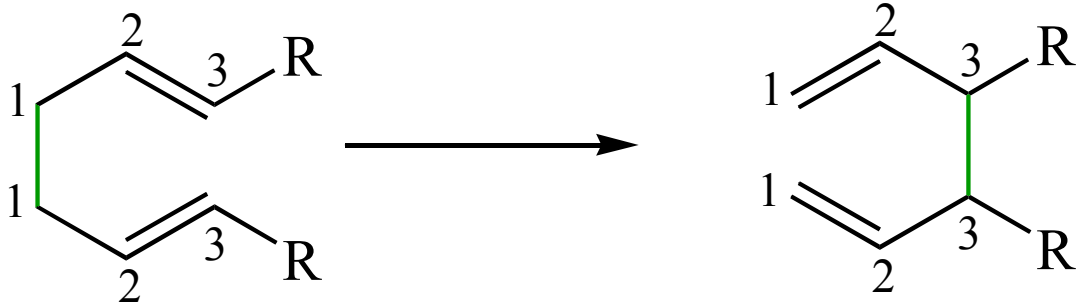
4q (q = 1)

[i , j] - Sigmatrope Umlagerungen

- intramolekular
- unkatalysiert
- neue Position der σ-Bindung
- Umorganisation der π-Bindungen

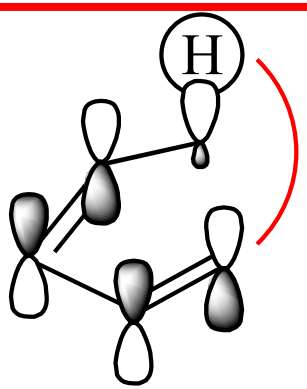


[1.5]-Sigmatrope Umlagerung



[3.3]- ~

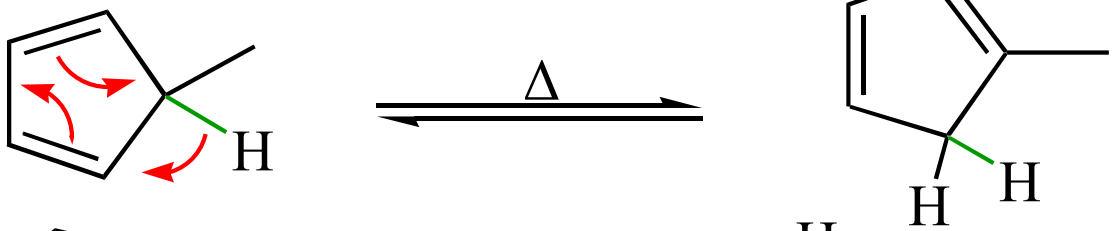
Sigmatrope H-Wanderungen



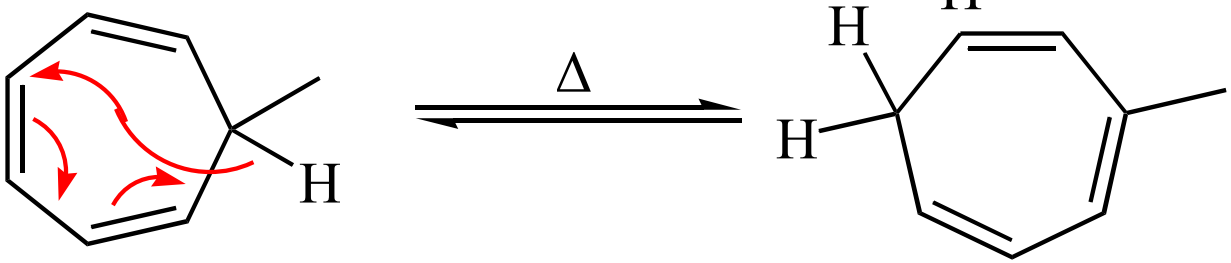
HOMO

LUMO

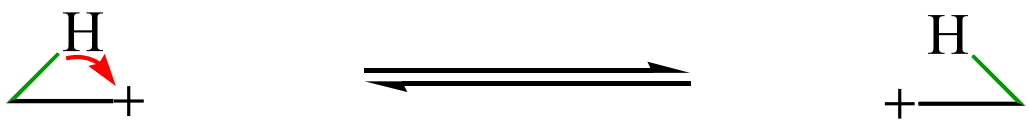
4q + 2 (q = 1)
suprafacial
(k_H/k_D = 5 bei 200°C)



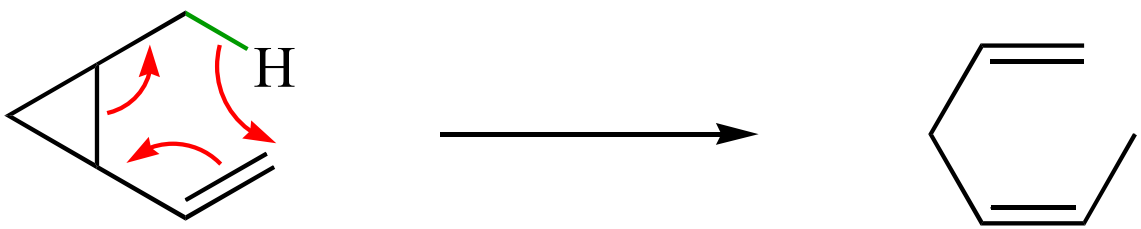
analog Indene



[1.5]- ~

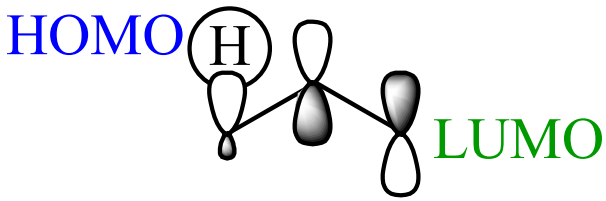


[1.2]- H-Shift (q=0)

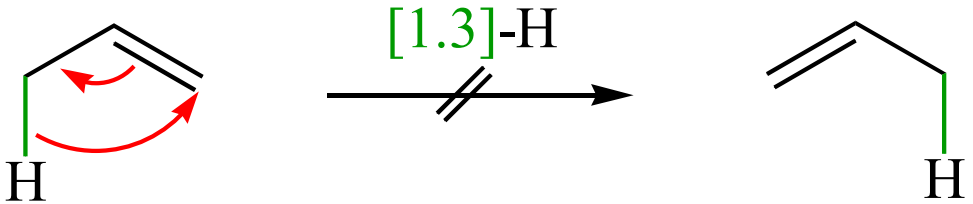


Homodienyl-[1.5]-H-Shift

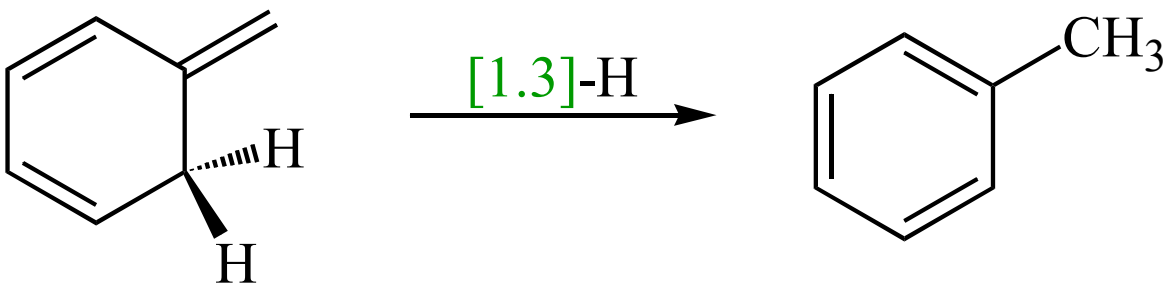
Sigmatrope H-Wanderungen



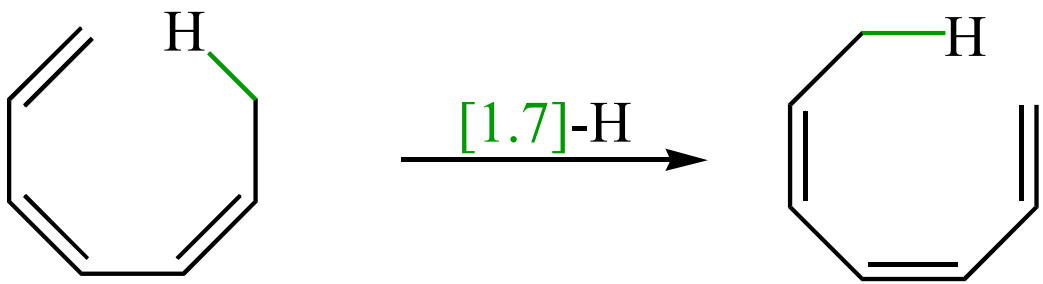
4q (Möbius)



q = 1, antarafacial

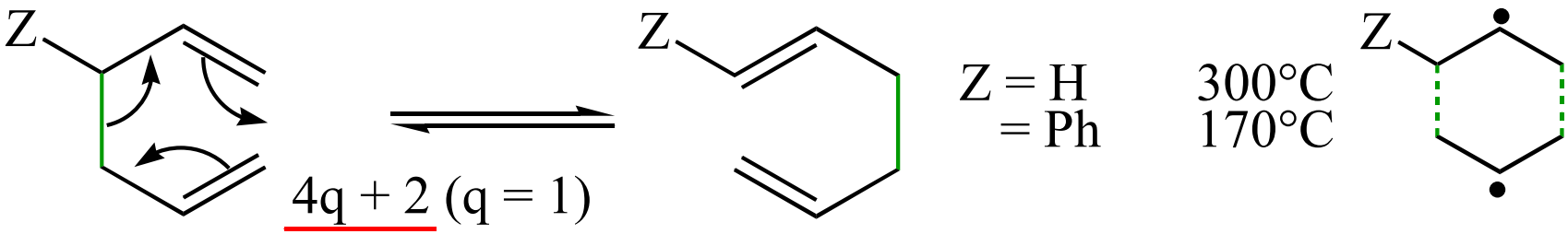


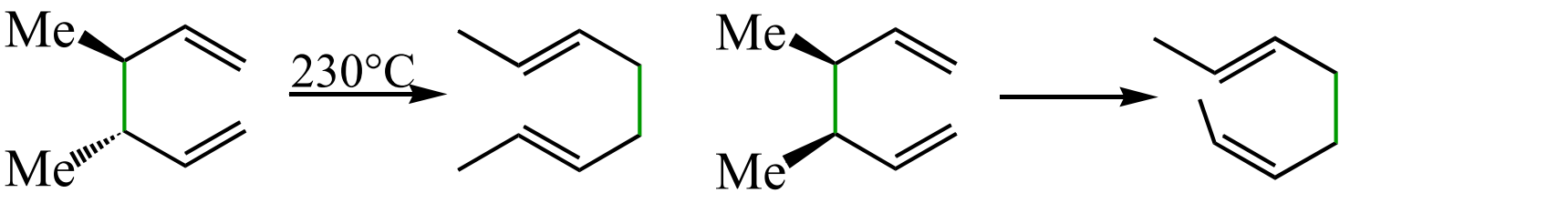
Isotoluol,
stabil < -30°C



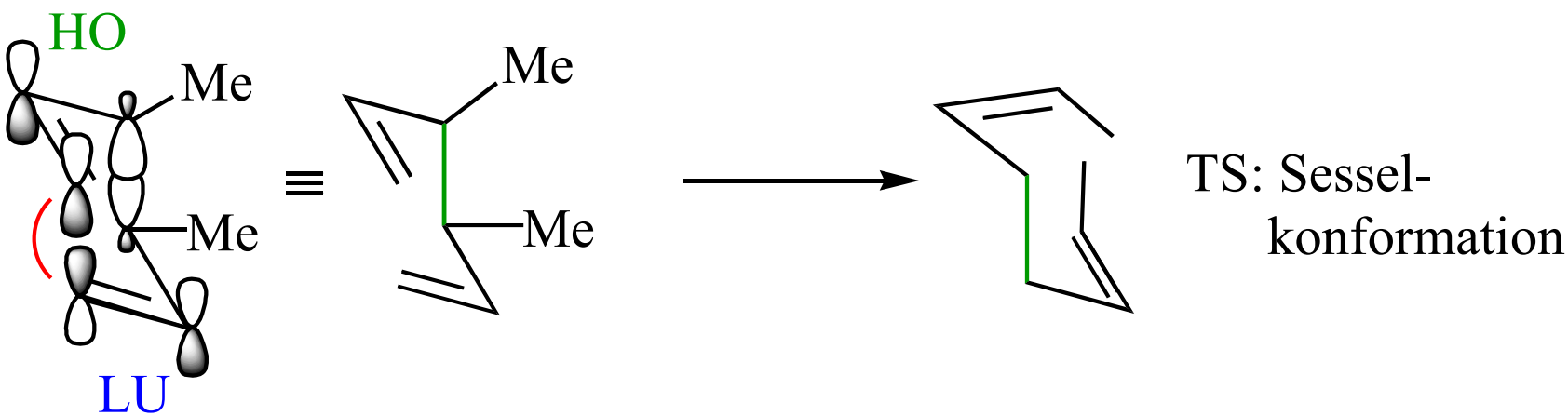
q = 2, antarafacial

[3.3]-Sigmatrope Umlagerungen (Cope-Umlagerung)



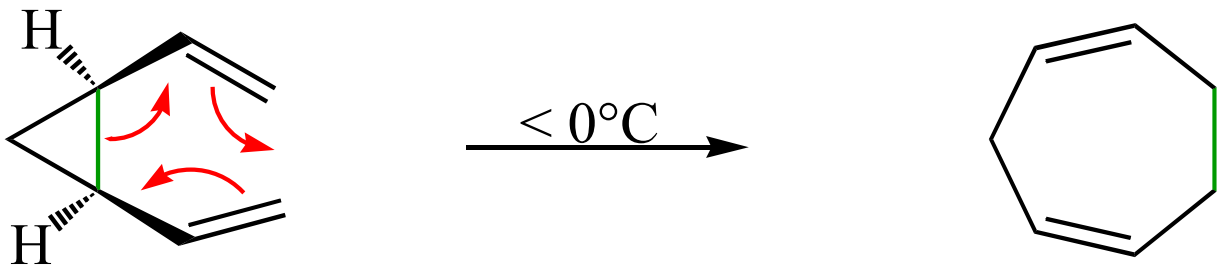


rac- trans,trans- meso- cis,trans-2,4-Octadien

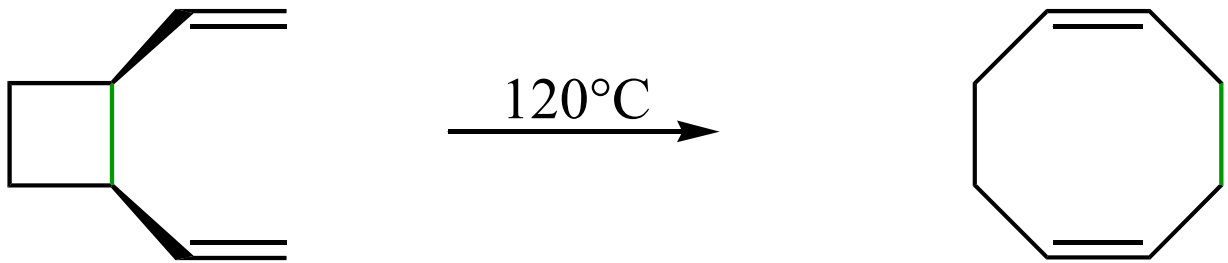


TS: Sessel-konformation

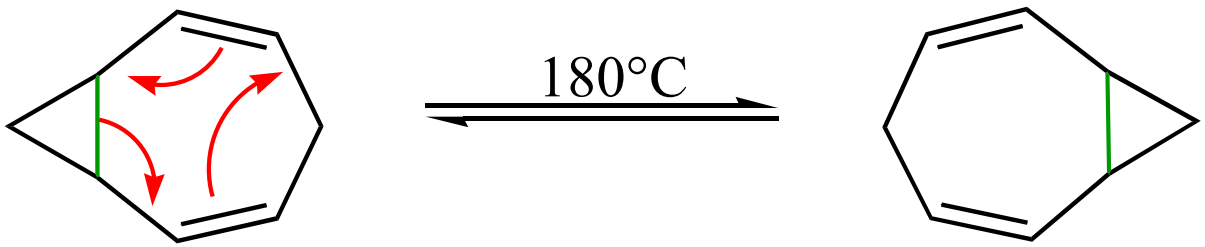
[3.3]-Sigmatrope Umlagerungen (Cope-, Claisen-)



cis-Divinylcyclopropan

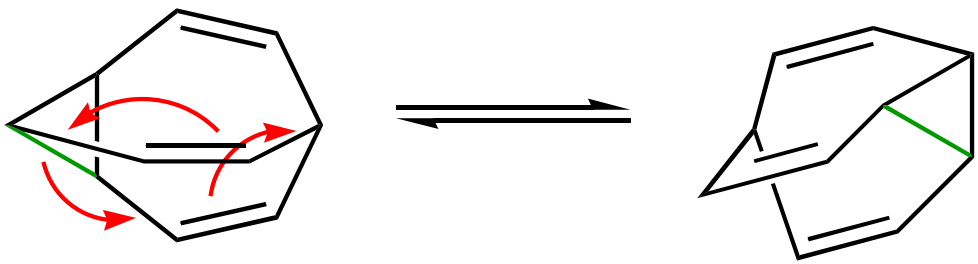


Valenztautomerie



Fluktuierende Bindungen

Bicyclo[5.1.0]octadien



$C_{10}H_{10}$ Bullvalen

1 209 600 Valenztautomere

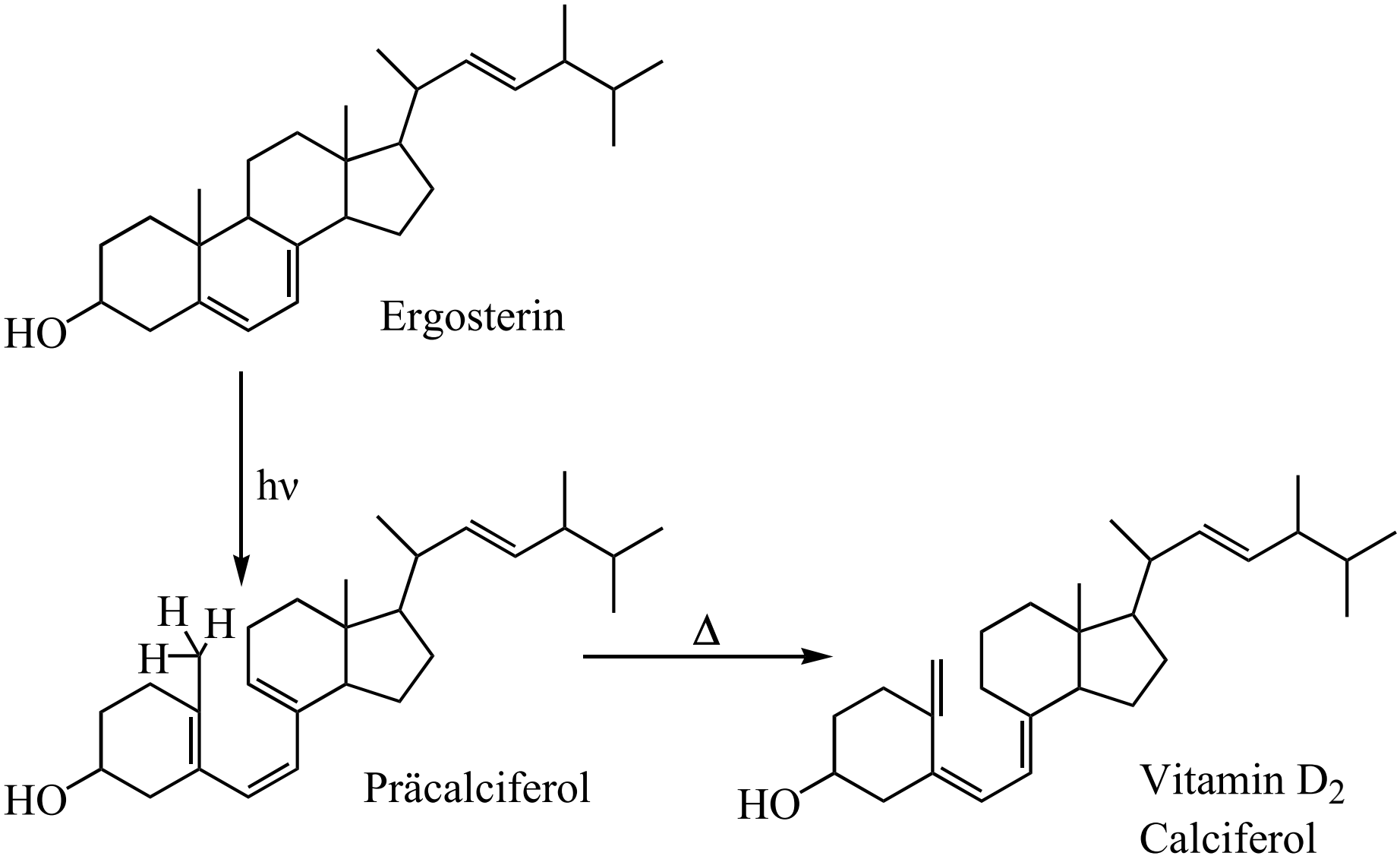
bei 100°C ein NMR-Signal

Woodward-Hoffmann-Regeln

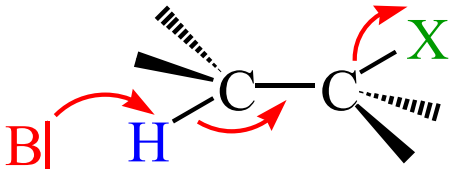
Zahl der Elektronen	thermisch	photochemisch
1. [m + n] – Cycloadditionen und –reversionen		
4q + 2	$m_s + n_s$ (Hückel)	$m_s + n_a$
4q	$m_s + n_a$ (Möbius)	$m_s + n_s$
2. Elektrocyclische Reaktionen		
4q + 2	suprafacial disrotatorisch	antarafacial konrotatorisch
4q	antarafacial konrotatorisch	suprafacial disrotatorisch
3. [i , j] – Sigmatrope Wanderungen		
4q + 2	suprafacial	-
4q	antarafacial	-

q = 0, 1, 2...

Vitamin D_2-Synthese

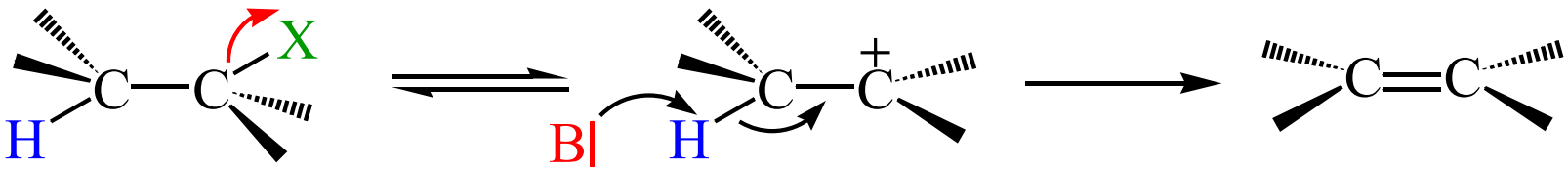


Eliminierungen: 1. β-Eliminierungen



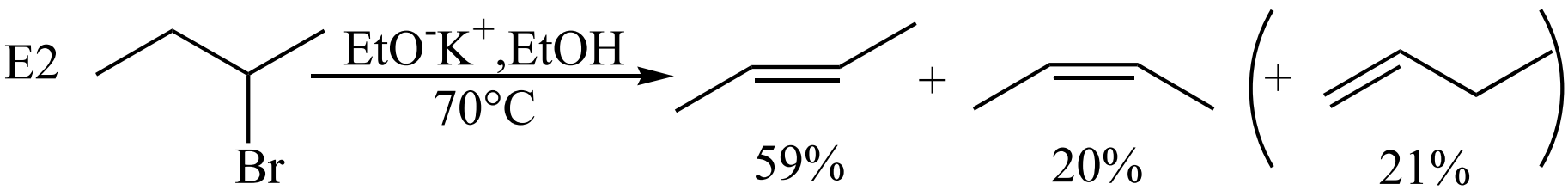
E2 ($A_nD_ED_N$)

Stereochemie: anti-Eliminierung
Stereochemie des Produkts: Curtin-Hammett-Prinzip

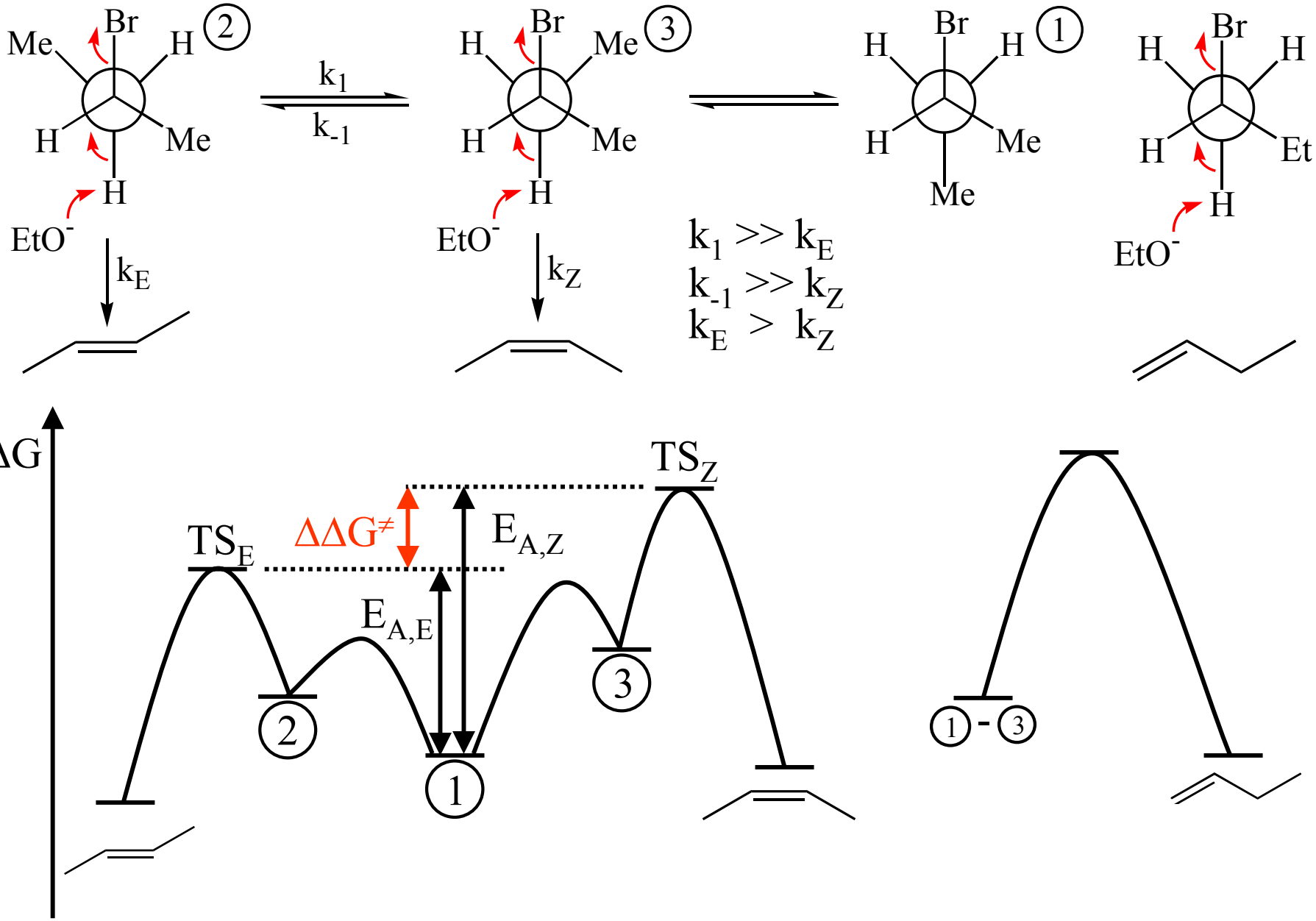


E1 ($D_N + D_E$)

Curtin-Hammett-Prinzip



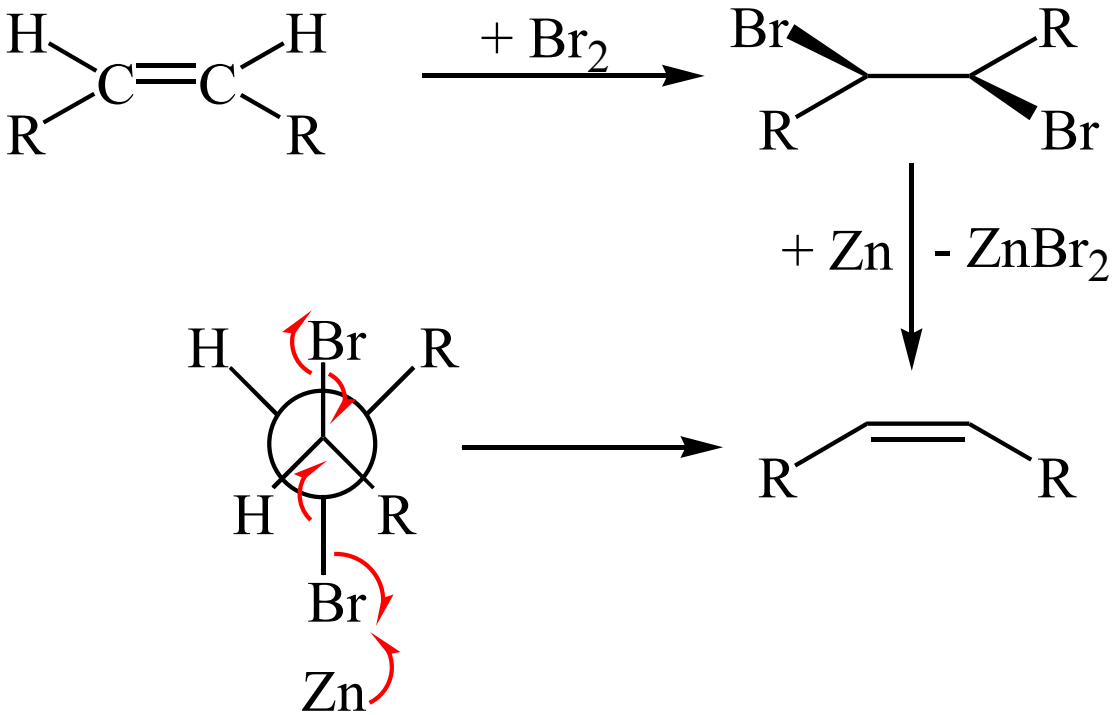
Curtin-Hammett-Prinzip

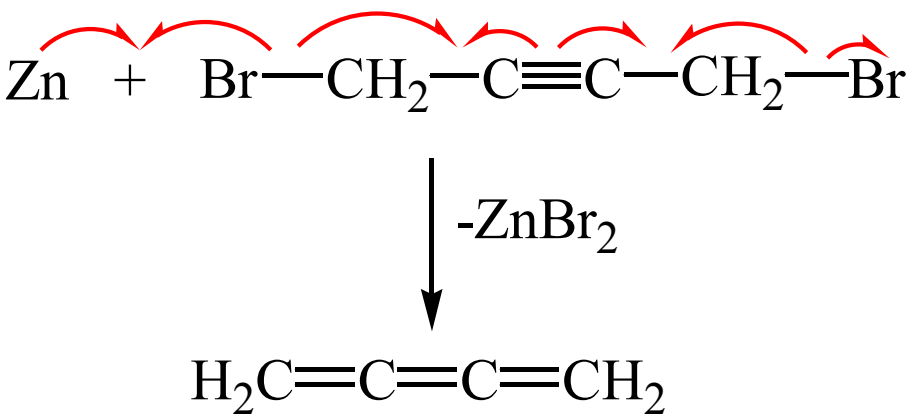


Curtin-Hammett-Prinzip

Bei einer kinetisch kontrollierten stereoselektiven Reaktion wird die Selektivität ausschließlich durch die Differenz der Freien Aktivierungsenthalpien der diastereomeren TS bestimmt und nicht durch $\Delta\Delta G^0$ der Konformationen des Grundzustands.

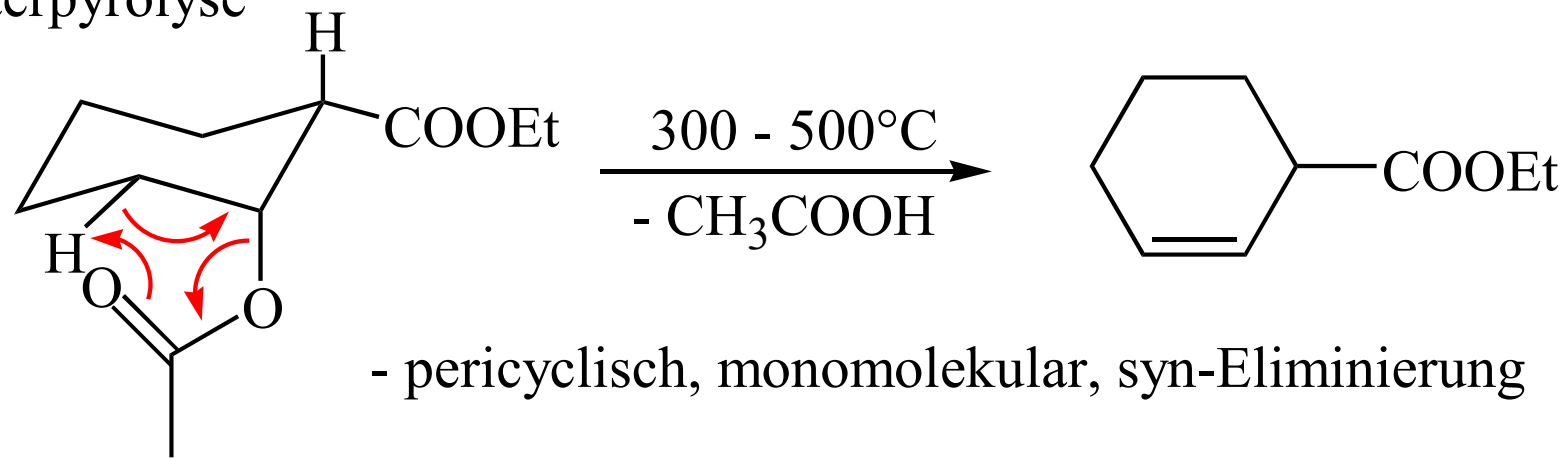
2. Dihalogeneliminierungen





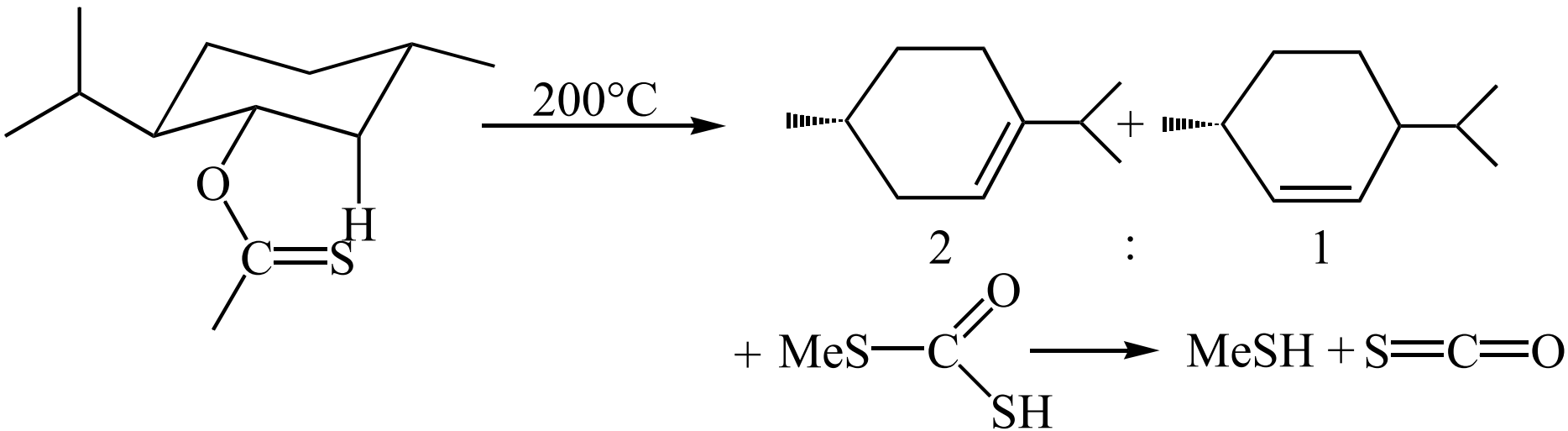
3. Thermische Eliminierungen

Esterpyrolyse



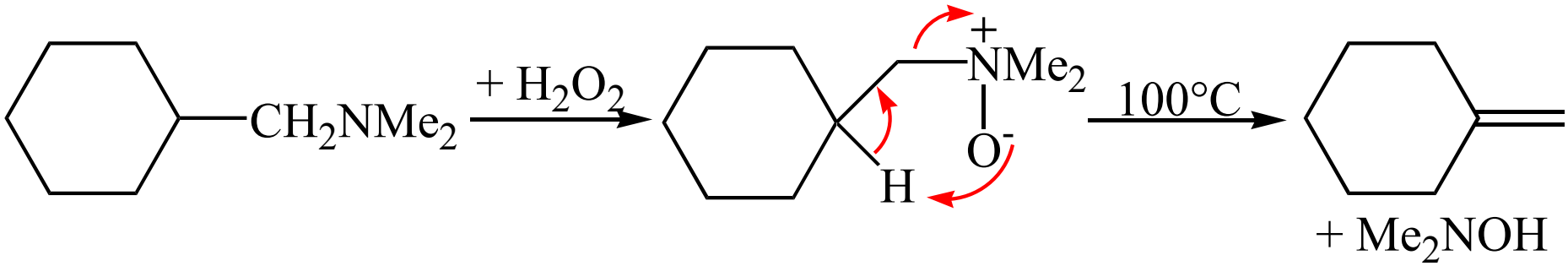
- pericyclisch, monomolekular, syn-Eliminierung

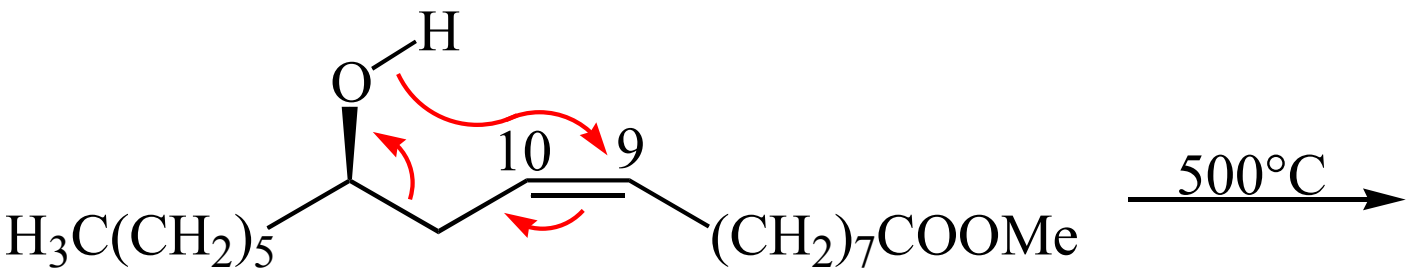
Chugaev-Reaktion



3. Thermische Eliminierungen

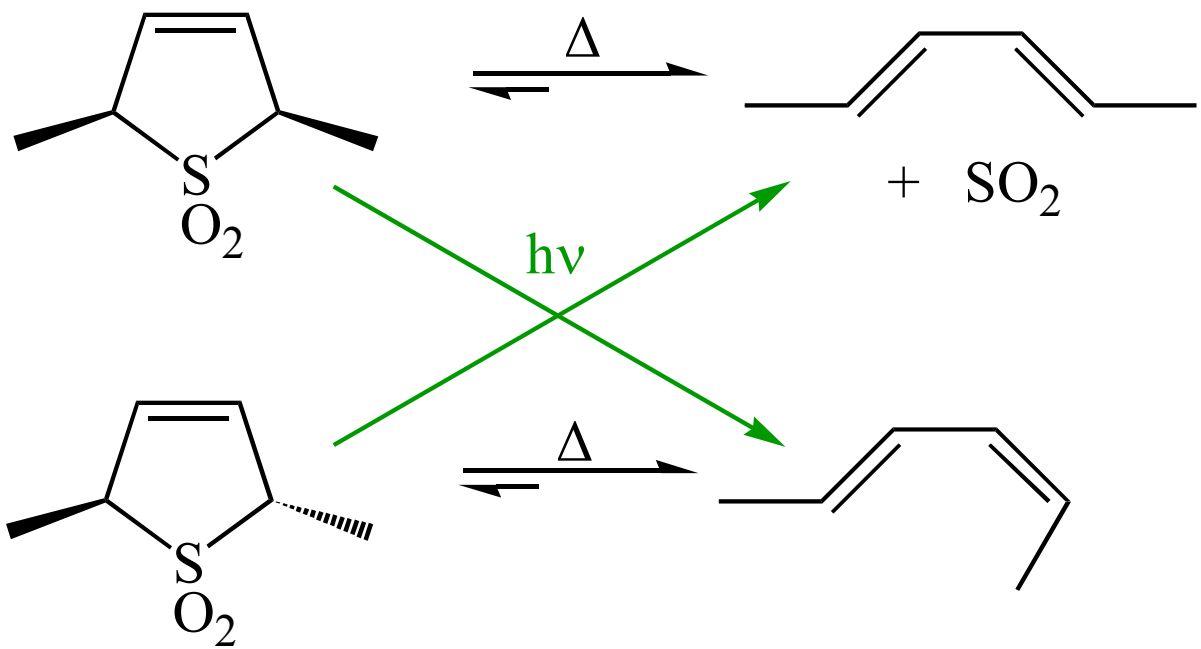
Cope-Eliminierung





$H_3C(CH_2)_5CHO + H_2C{=}CH(CH_2)_8COOMe$

4. Cheletrope Reaktionen

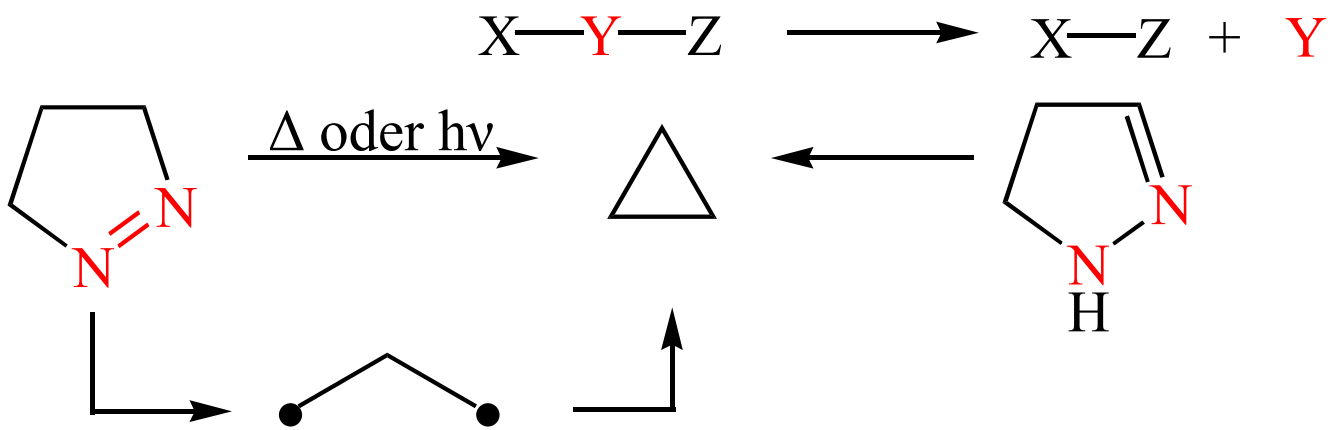


4q + 2 (q = 1)

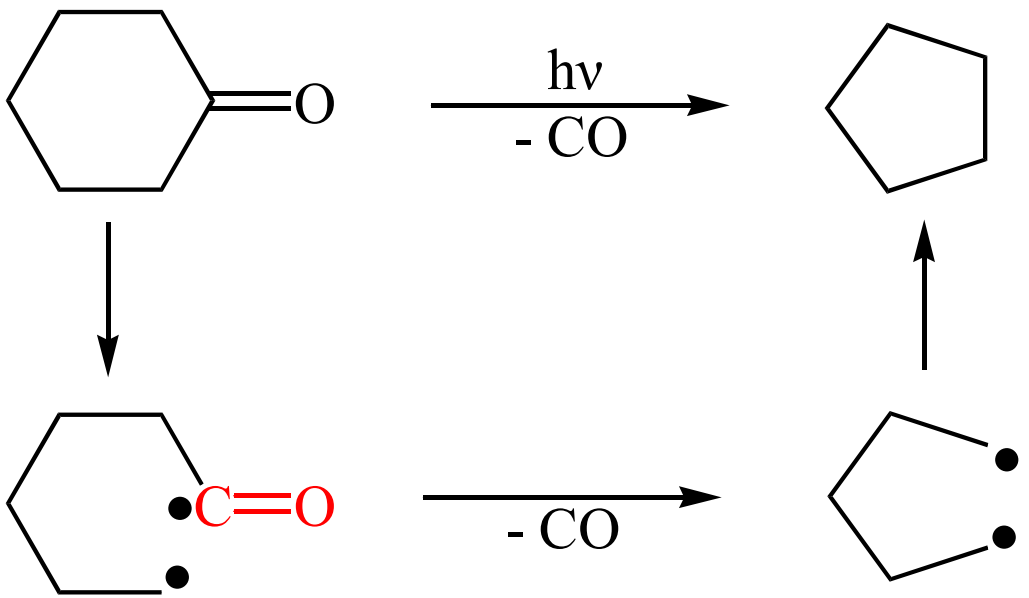
Δ: suprafacial

hν: antarafacial

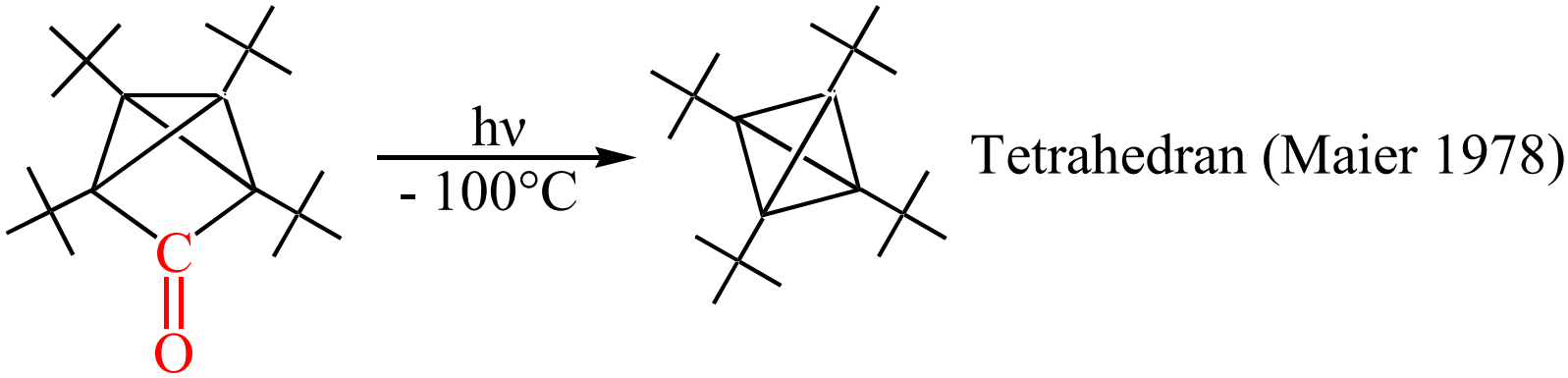
5. Extrusionen



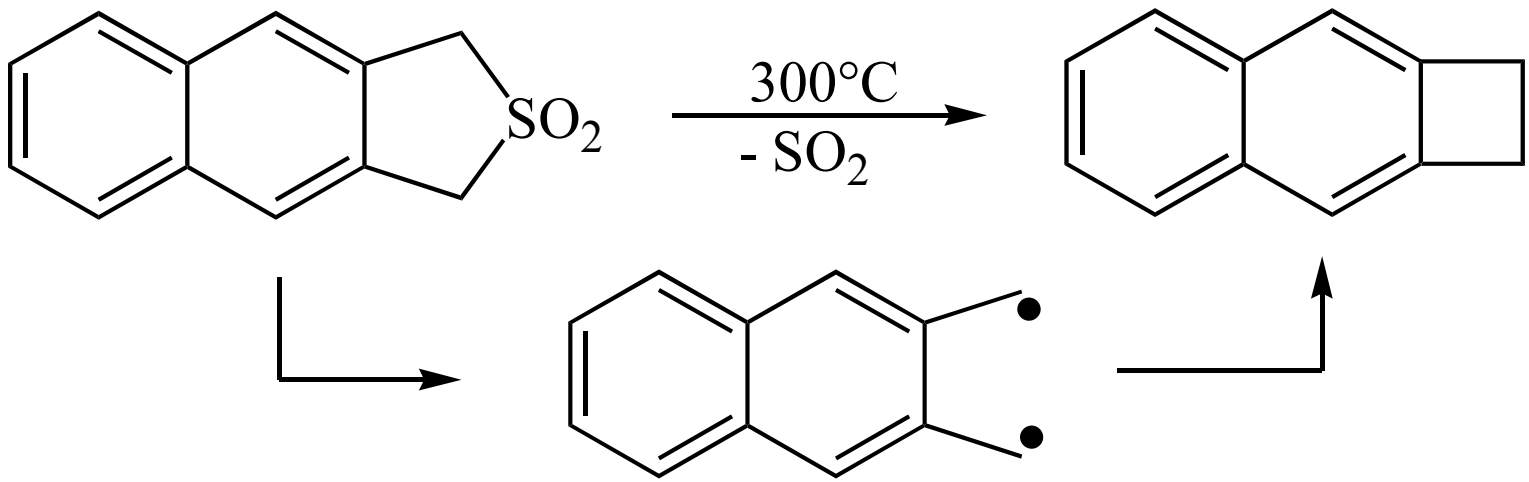
Norrish-TypI-Spaltung



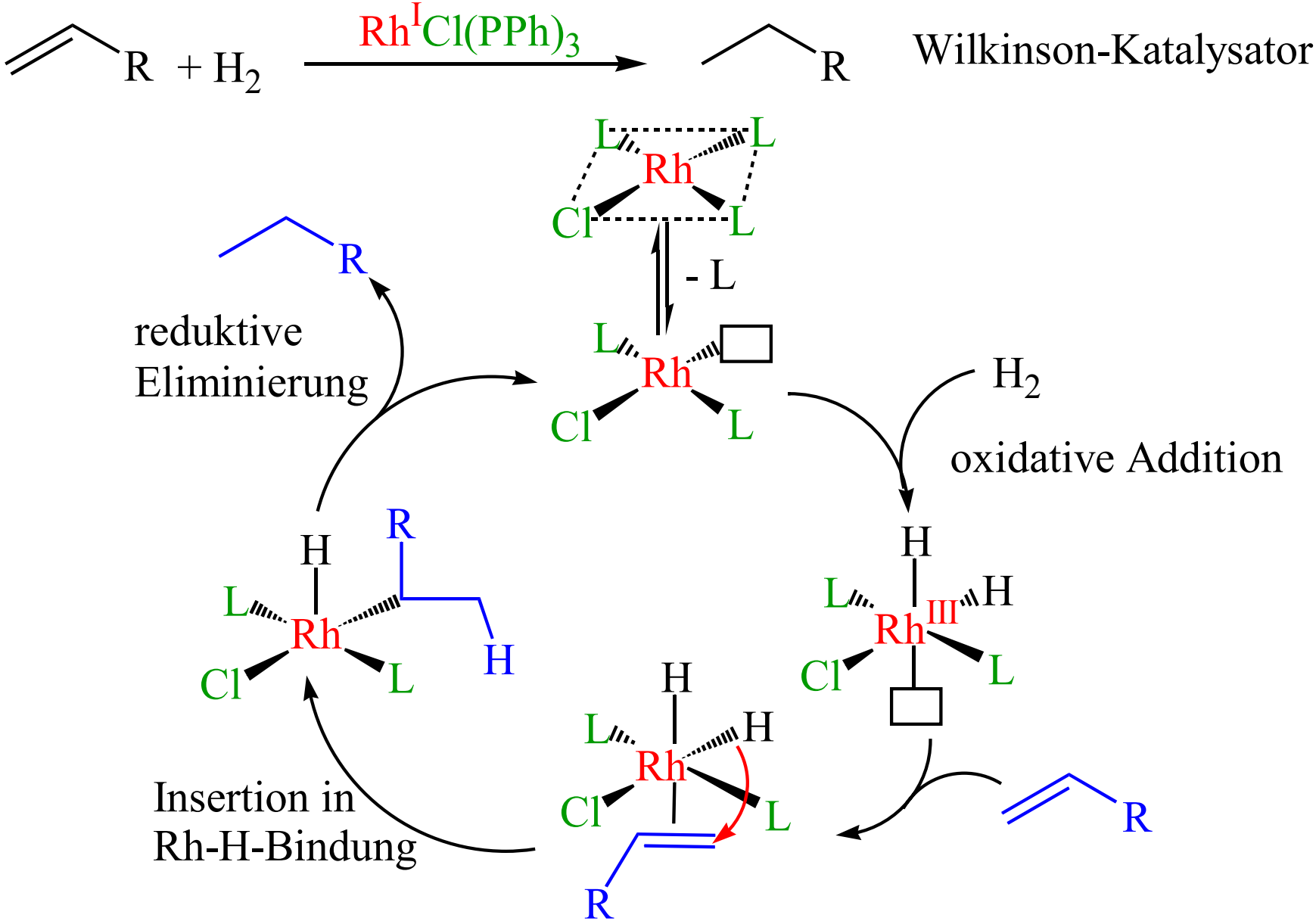
5. Extrusionen



Tetrahedran (Maier 1978)

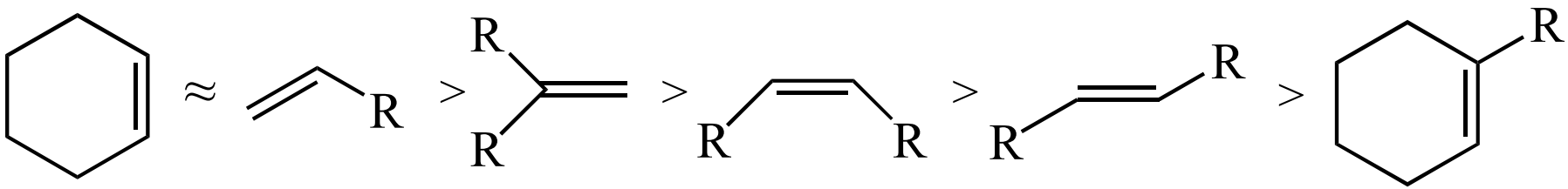


Hydrierung

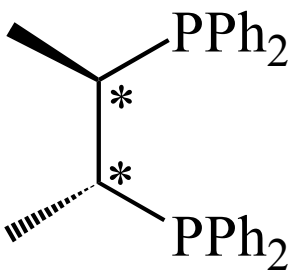

R + H2
RhICl(PPh3)3
R
Wilkinson-Katalysator
L
L
Rh
Cl
L
- L
L
Rh
Cl
L
H2
oxidative Addition
H
L
RhIII
H
Cl
L
H
L
Rh
H
Cl
L
R
Insertion in
Rh-H-Bindung
H
R
L
Rh
Cl
L
H
R
reduktive
Eliminierung
R

Hydrierung

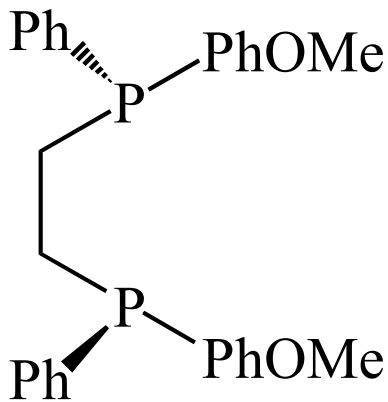
Wilkinson-Hydrierung:



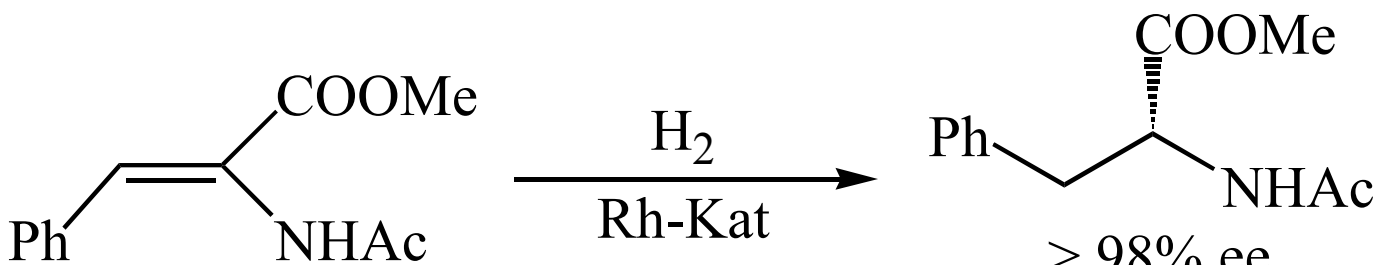
Enantioselektive Hydrierung



Chiraphos

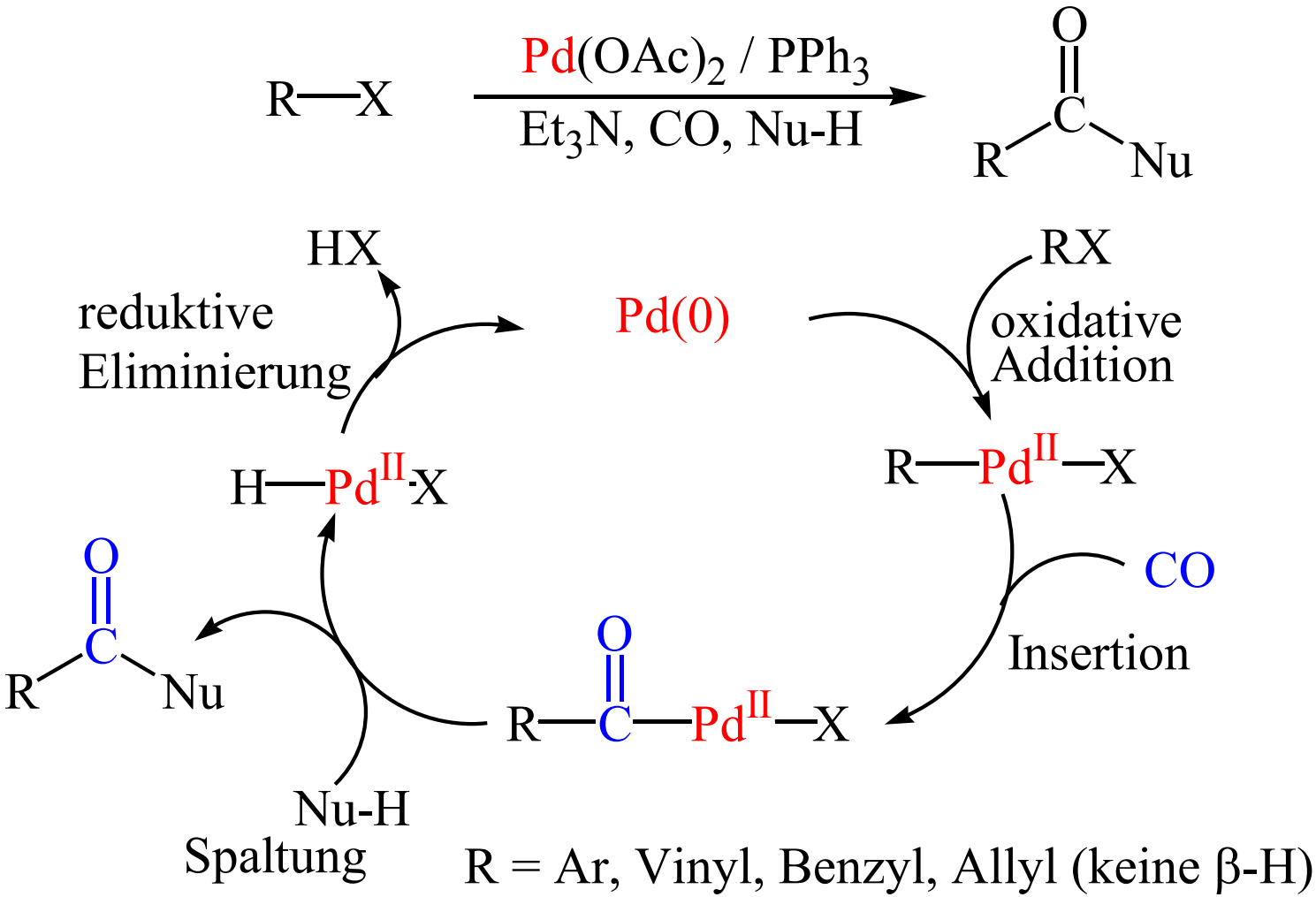


DIPAMP



> 98% ee

Carbonylierungen

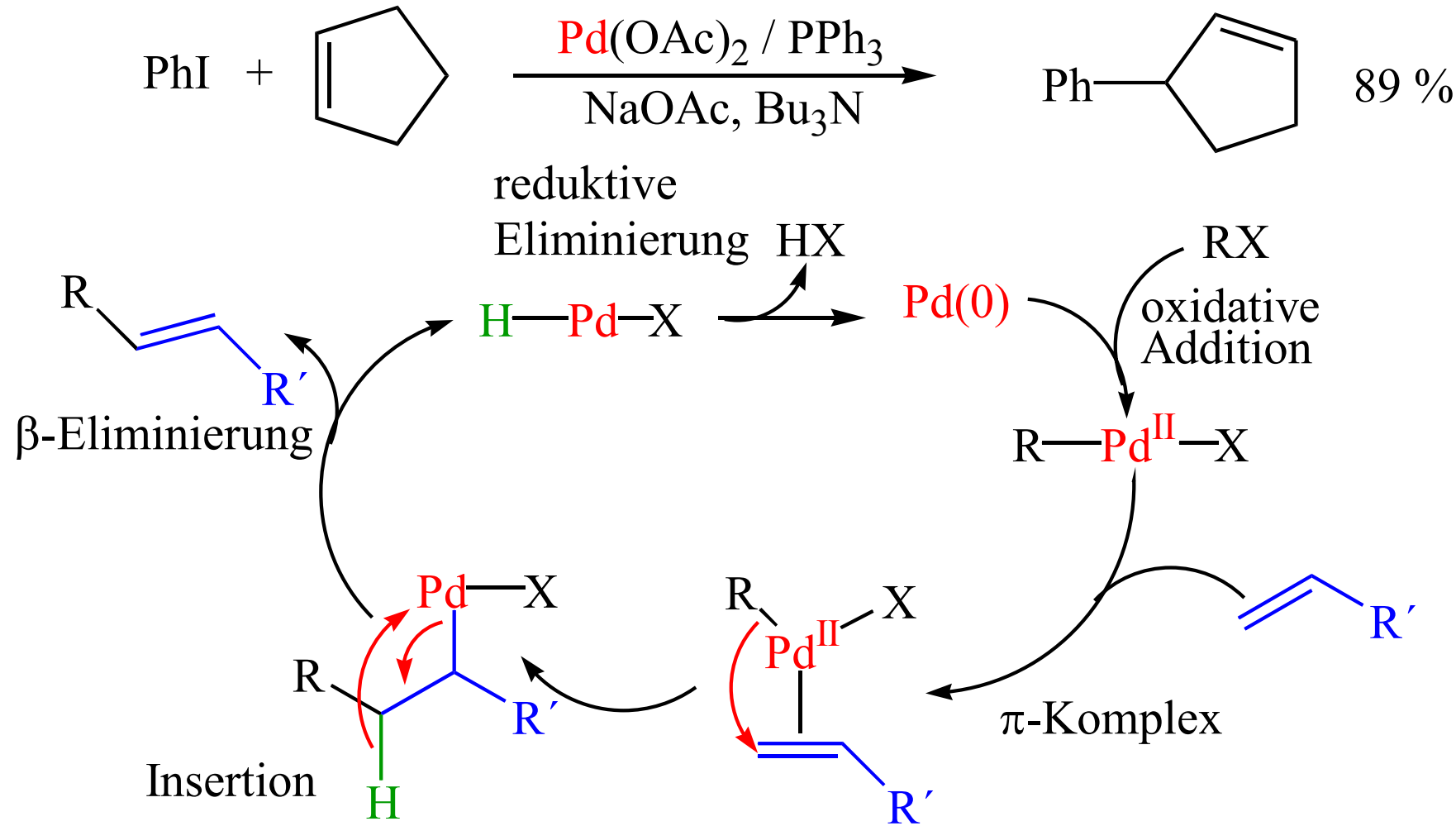


R = Ar, Vinyl, Benzyl, Allyl (keine β-H)

X = Br, I, CF_3CO_2, CF_3SO_3

Nu-H: R‘OH, R‘NH_2, u.a.

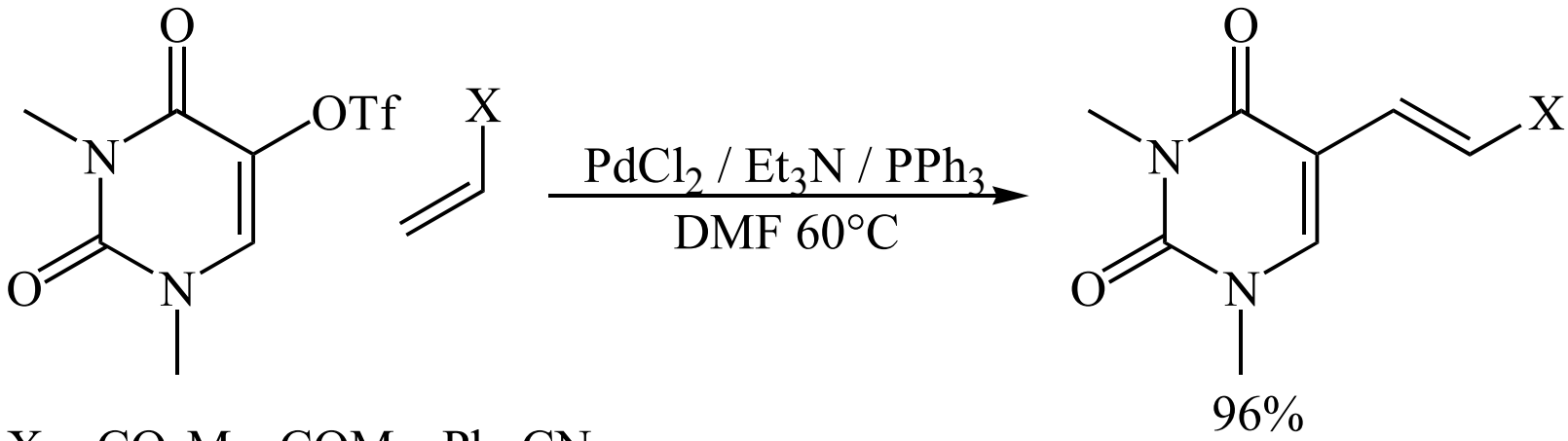
Heck-Reaktionen



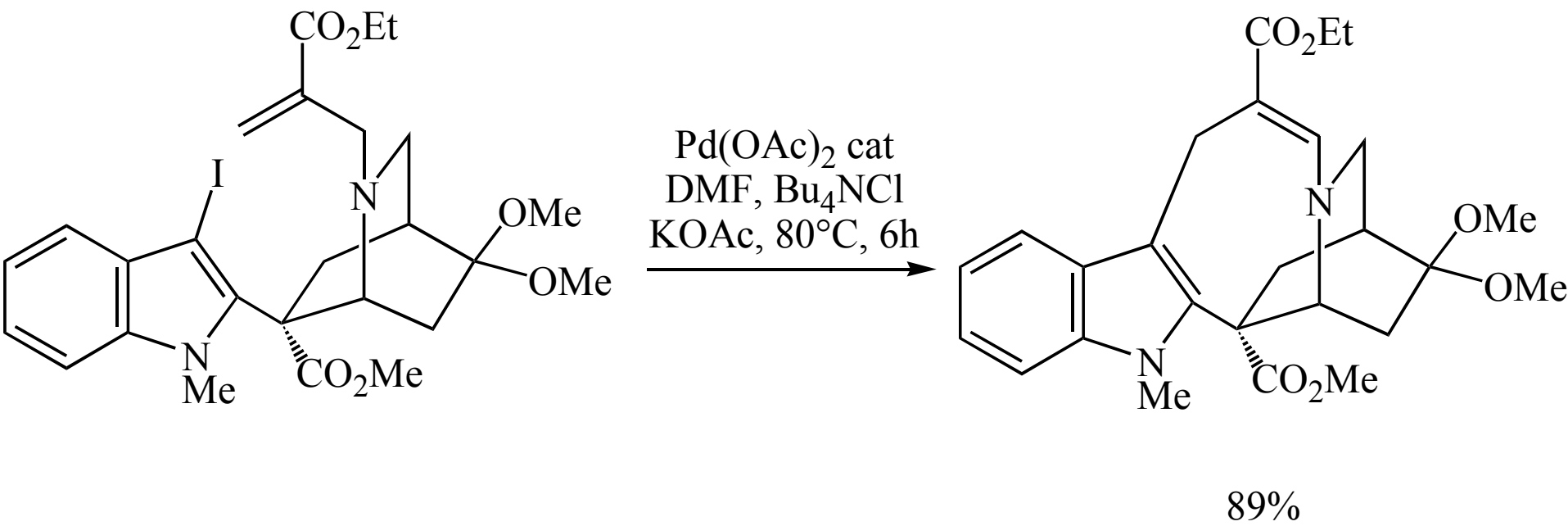
R = Ar, Alkenyl, Benzyl

X = Br, I, CF_3CO_2, u.a.

Heck-Reaktionen

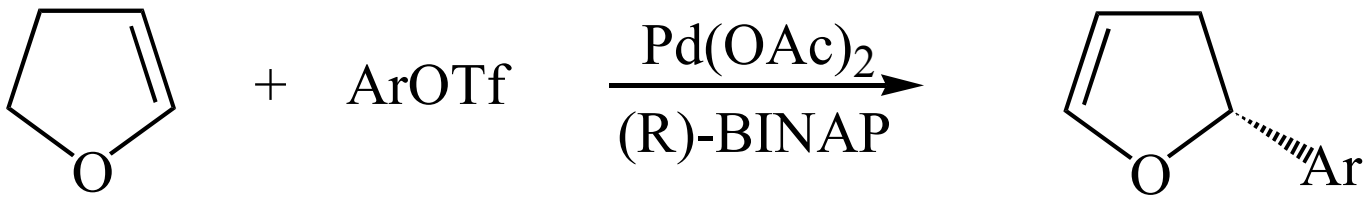


X = CO_2Me, COMe, Ph, CN

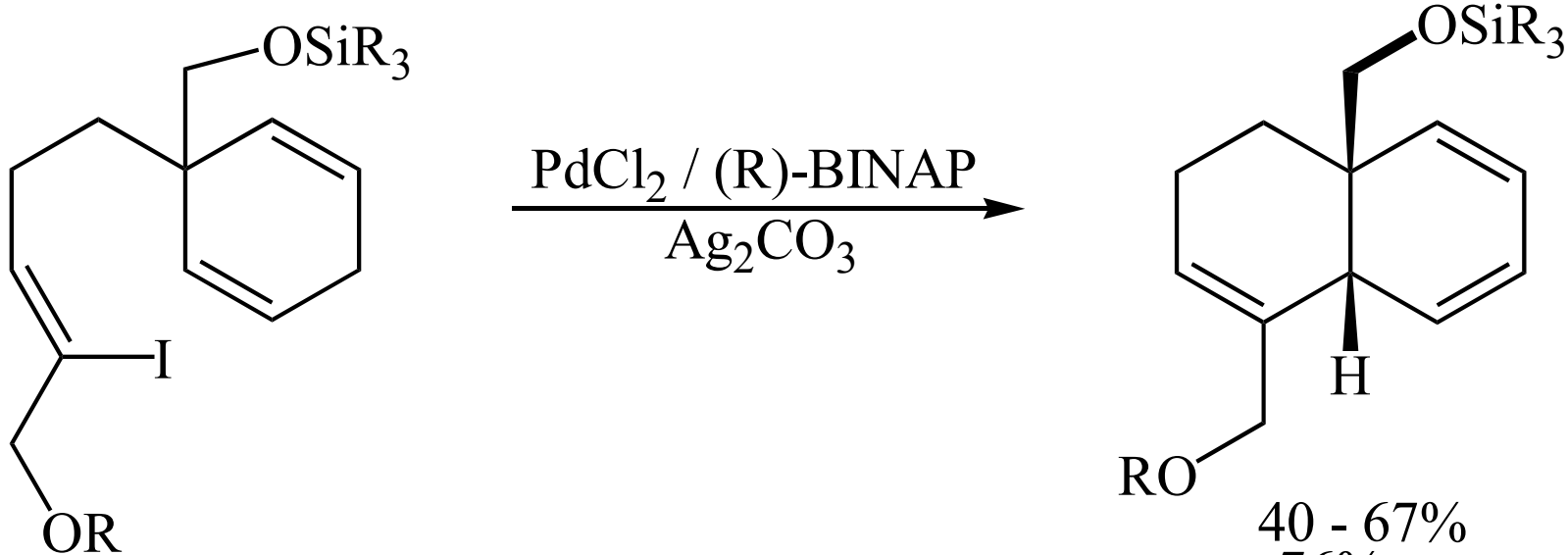


89%

Heck-Reaktionen

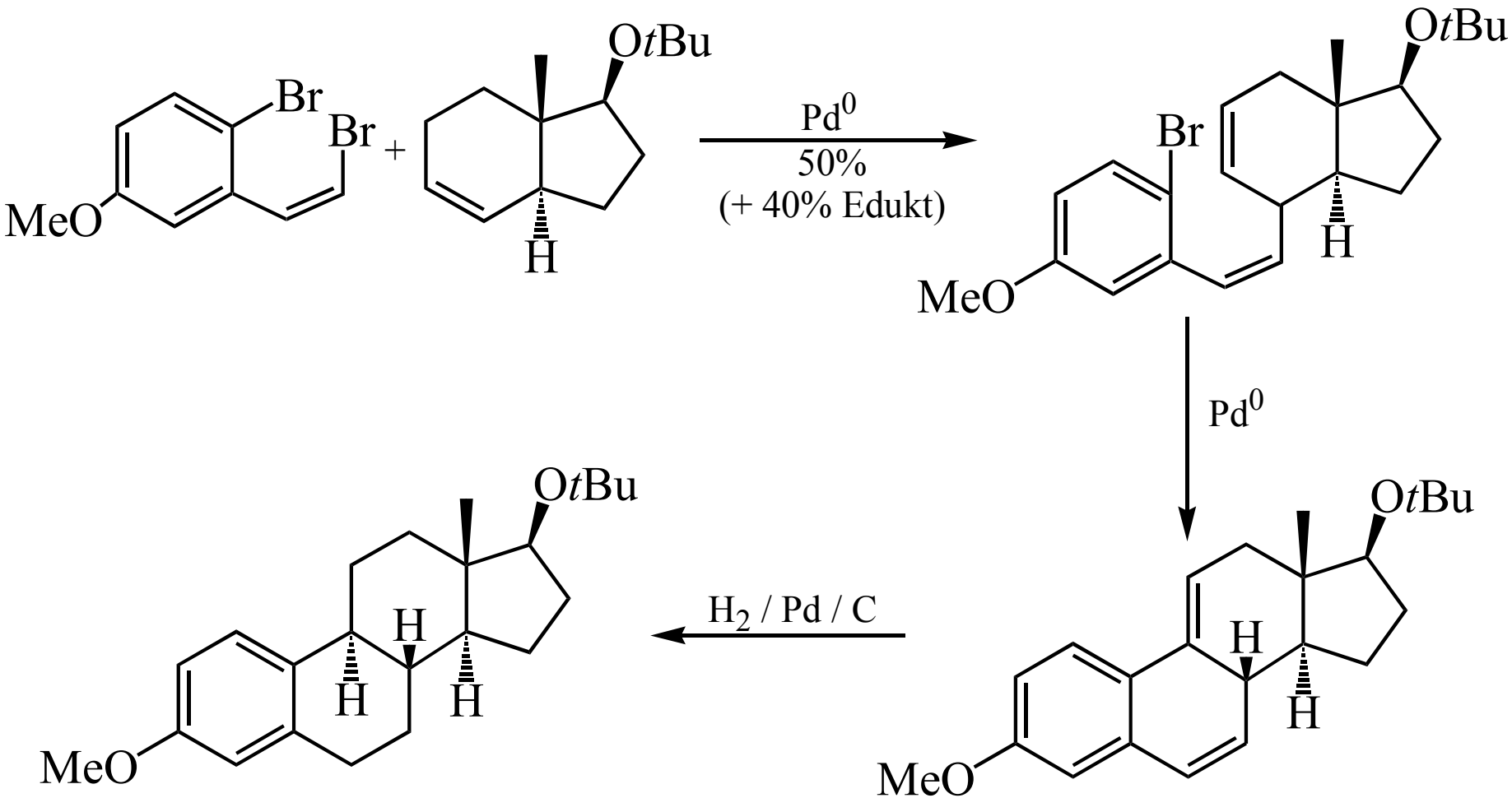


40 - 60%
>96% ee



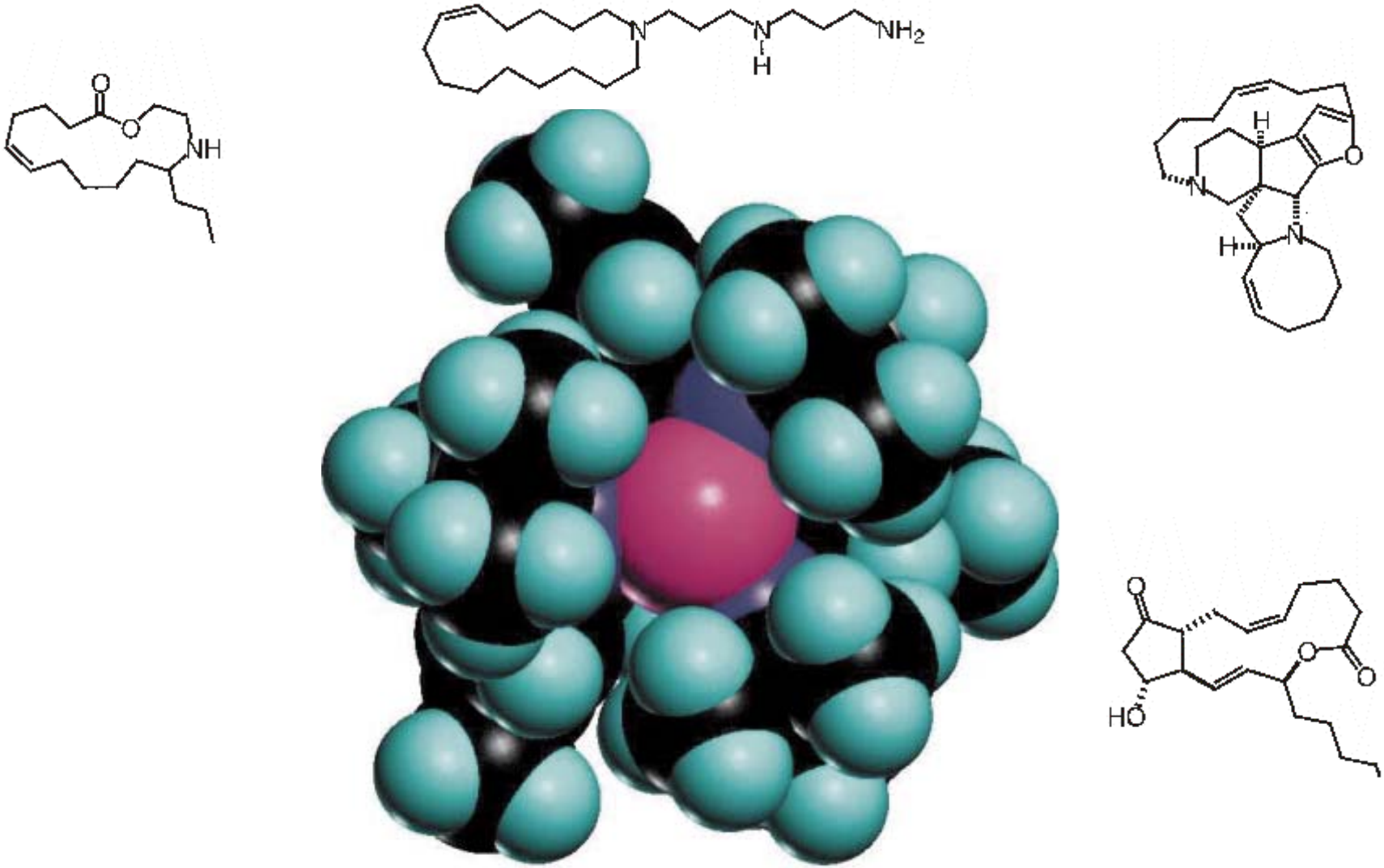
40 - 67%
76% ee

Totalsynthese von 17 β-Östradiol



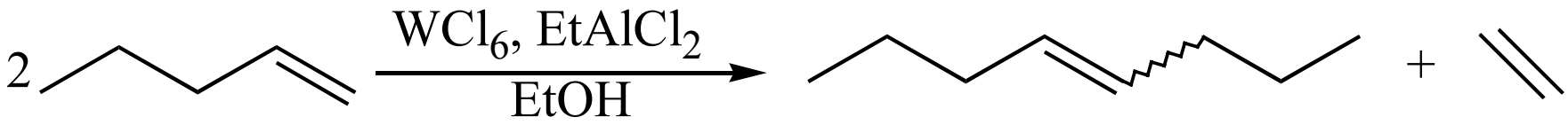
Totalsynthese von enantiomerenreinem 17 β-Östradiol durch zweifache Heck-Reaktion nach Tietze.

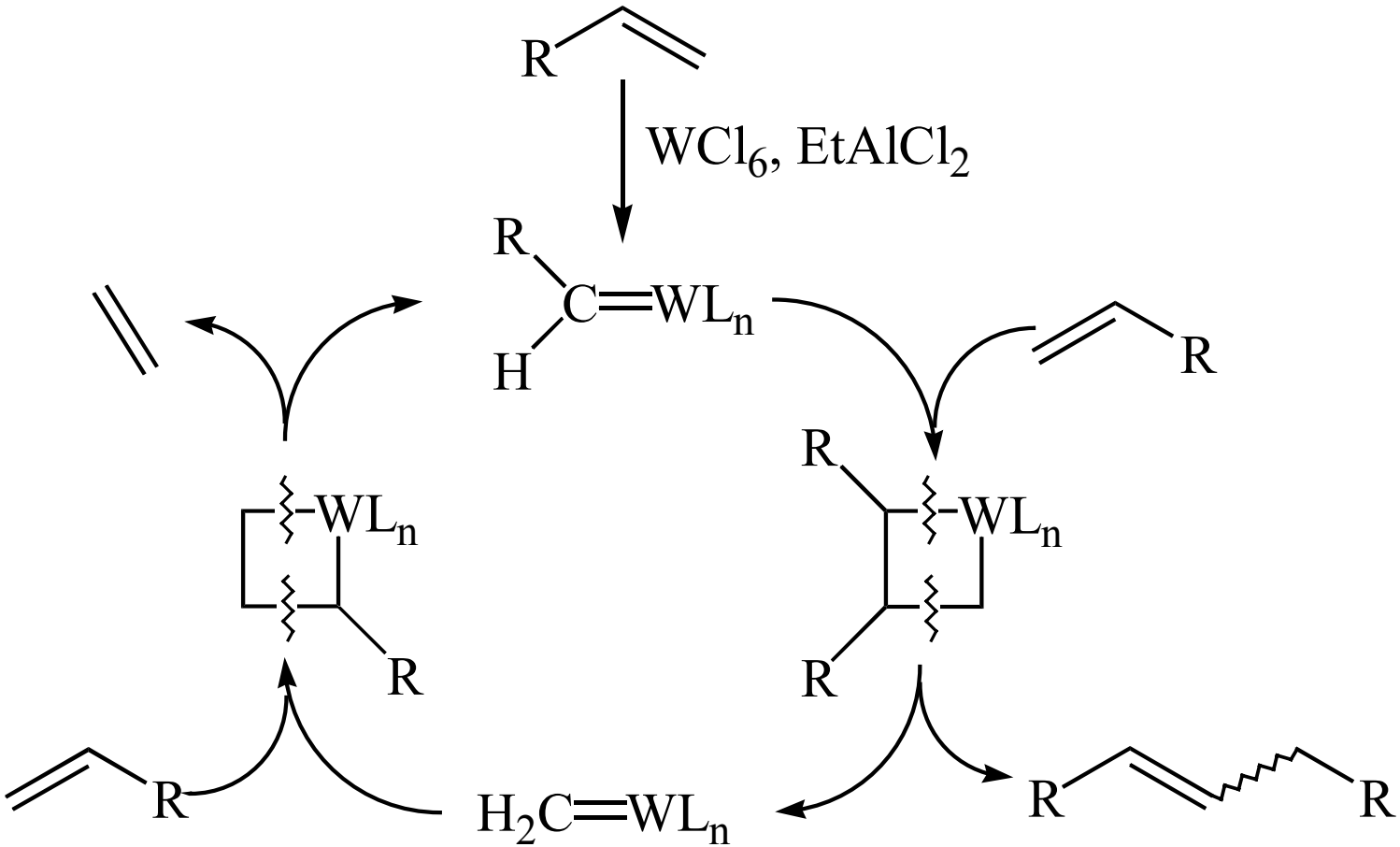
Kalottenmodell von [{(Ar)(tBu)N}$_3$MoCl]



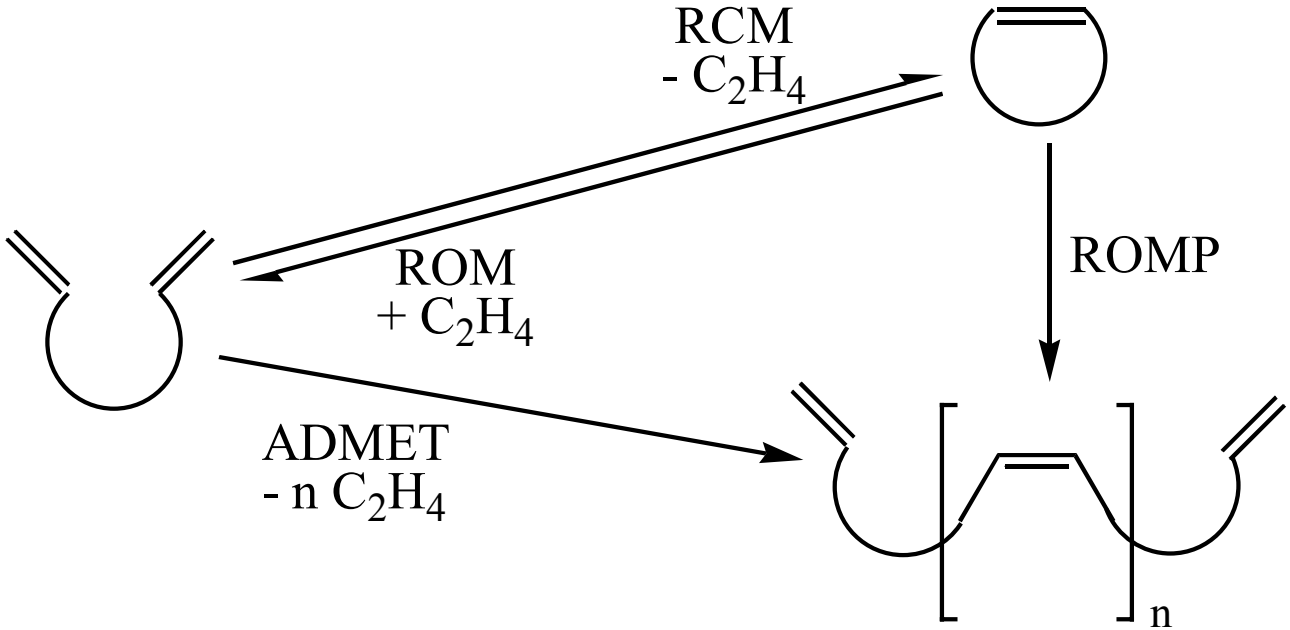
Das Kalottenmodell von [{(Ar)(tBu)N}$_3$MoCl], einem neuartigen Katalysator für die Ringschlussmetathese von Alkinen, ist umgeben von Strukturformeln einiger Naturstoffe, bei deren Synthese diese Methode eingesetzt wurde.

Olefin-Metathese





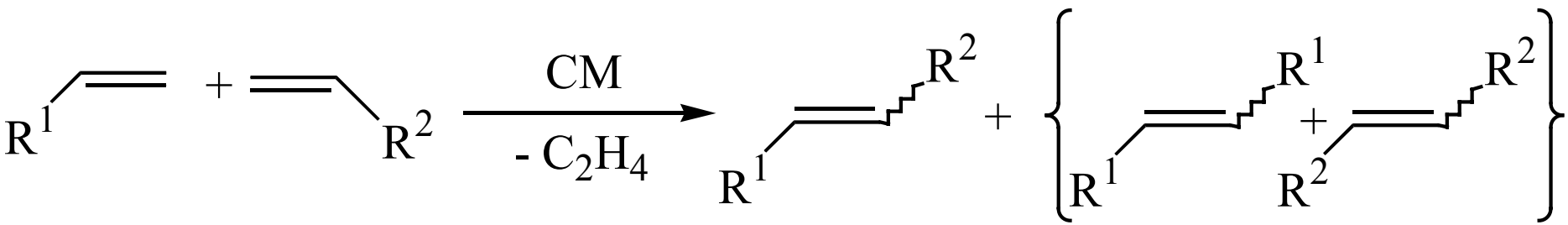
Wichtige Arten von Metathesereaktionen



RCM: Ringschlussmetathese (ring closing metathesis)

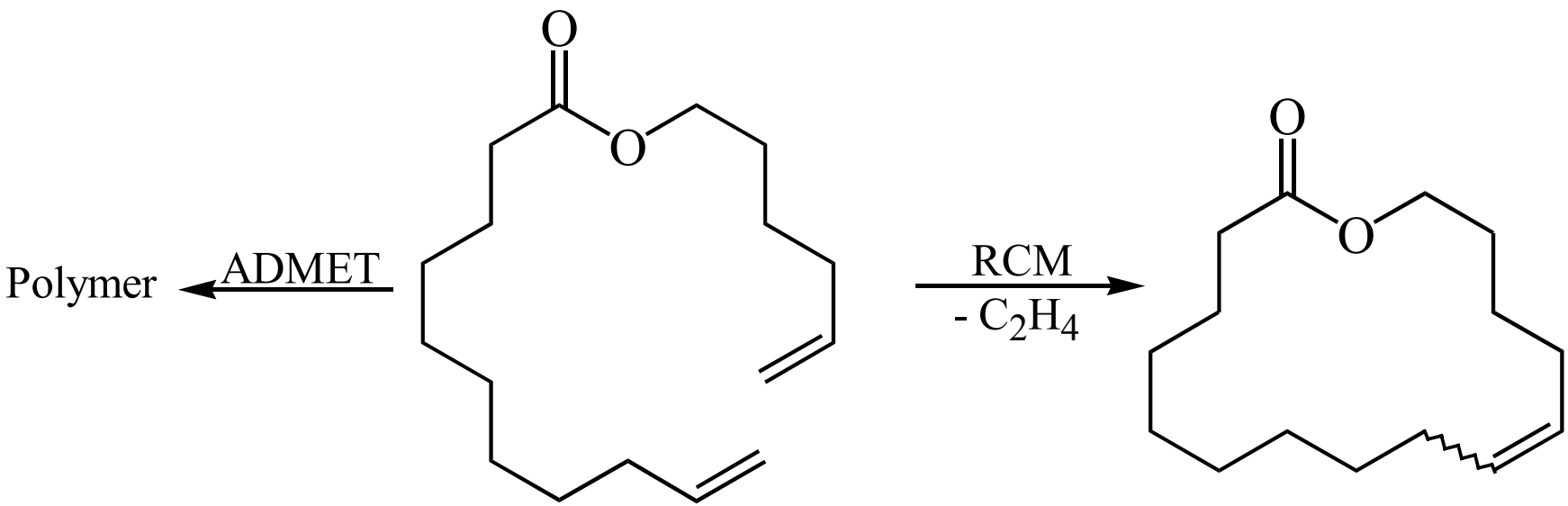
ADMET: acyclische Dienmetathese-Polymerisation (acyclic diene metathesis polymerization)

ROMP: Ringöffnungsmetathese-Polymerisation (ring opening metathesis polymerization)

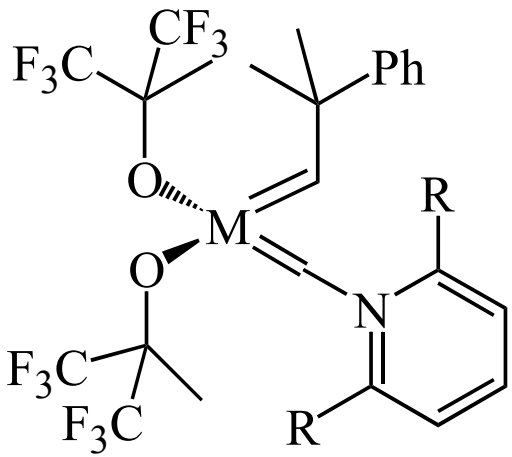


CM: Kreuzmetathese (cross metathesis)

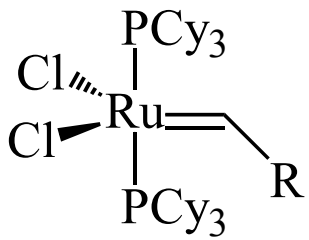
Metathesereaktionen



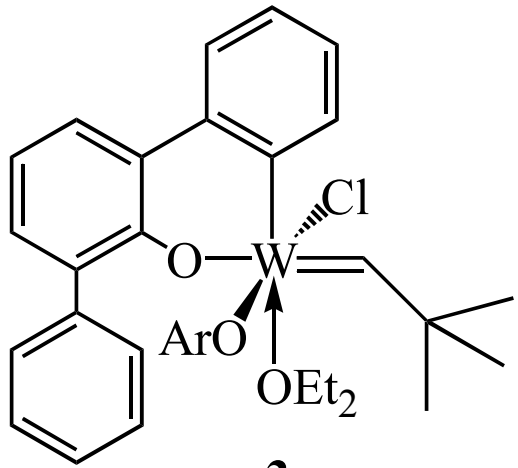
Metathesekatalysatoren und -katalysatorvorstufen



1 M = Mo, W



2 R = Ph, CH=CH$_2$, etc.



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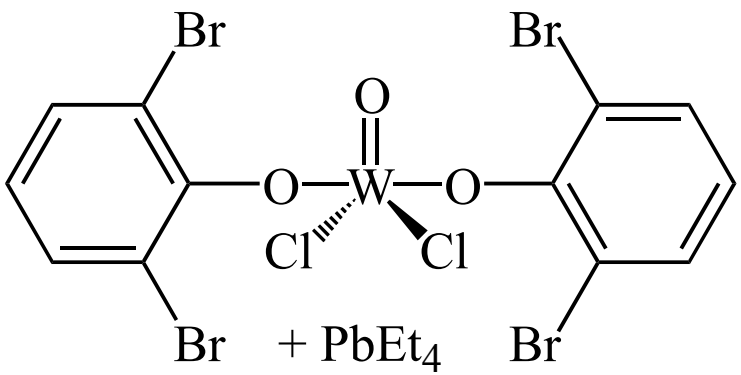

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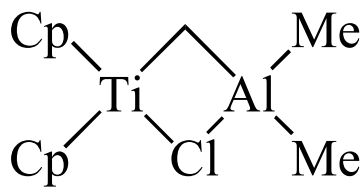

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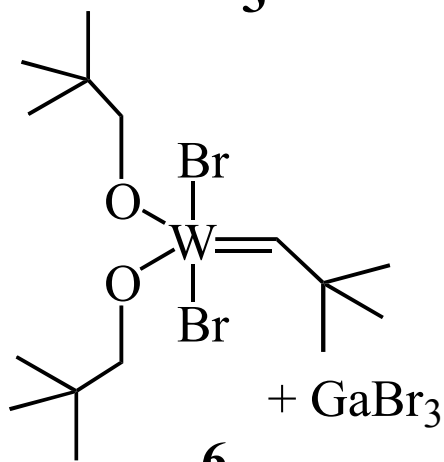
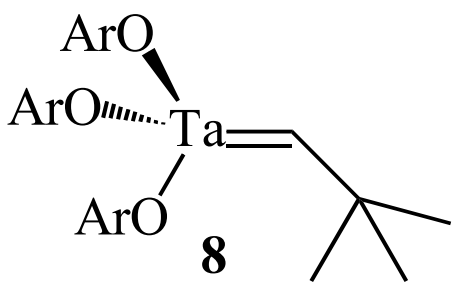


6

[MeReO$_3$] / Al$_2$O$_3$

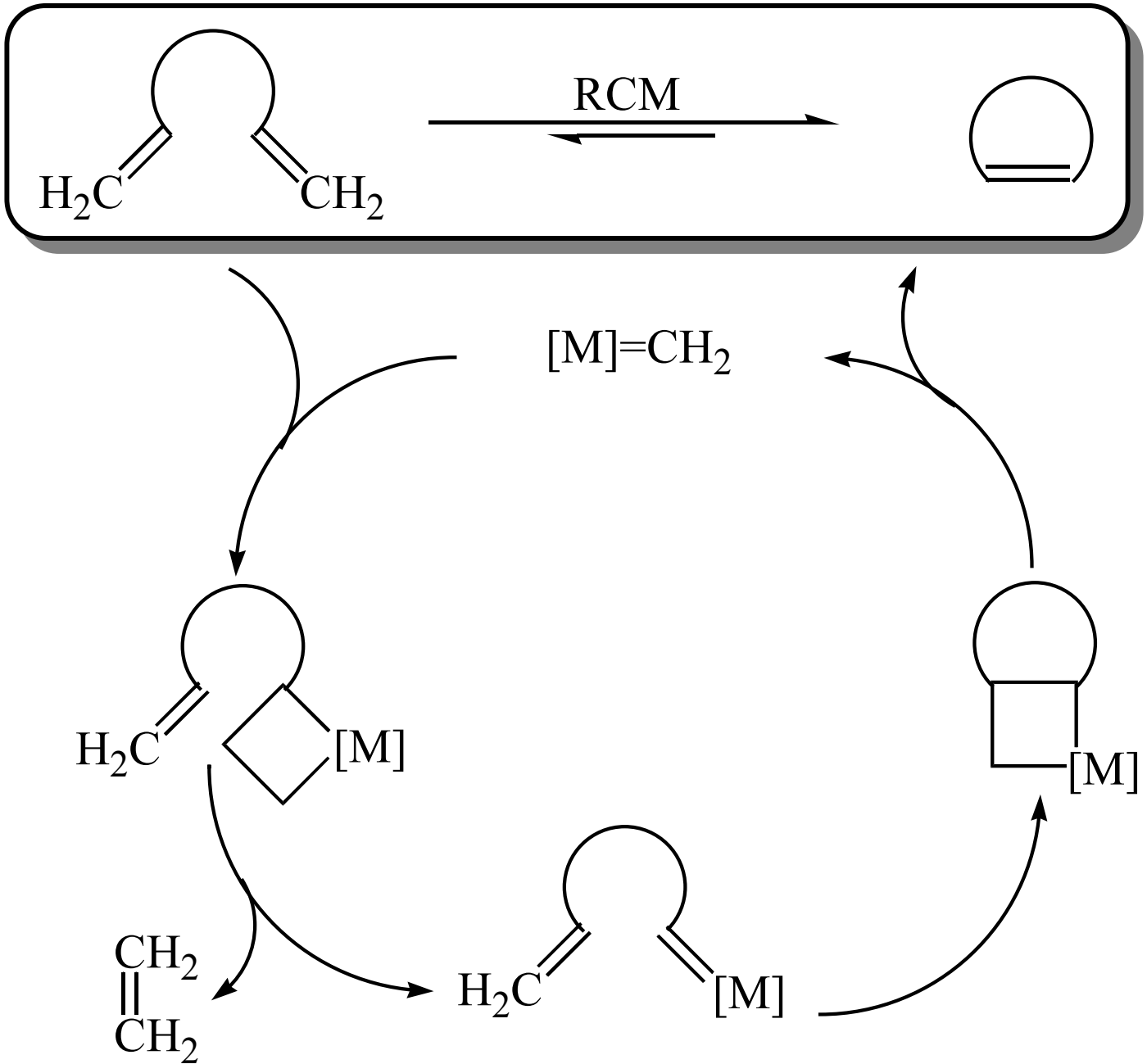
7



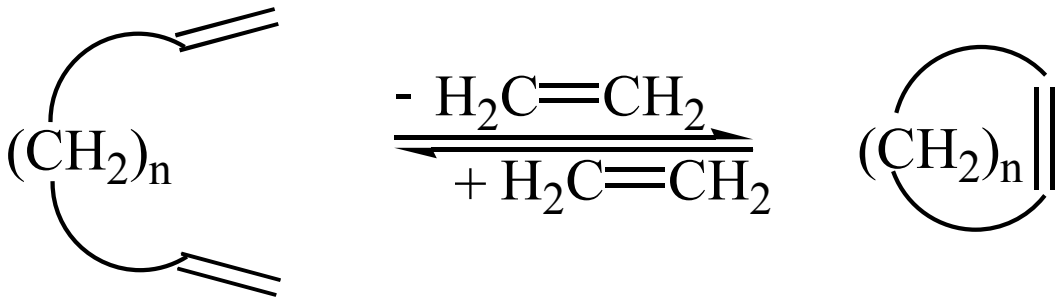
8

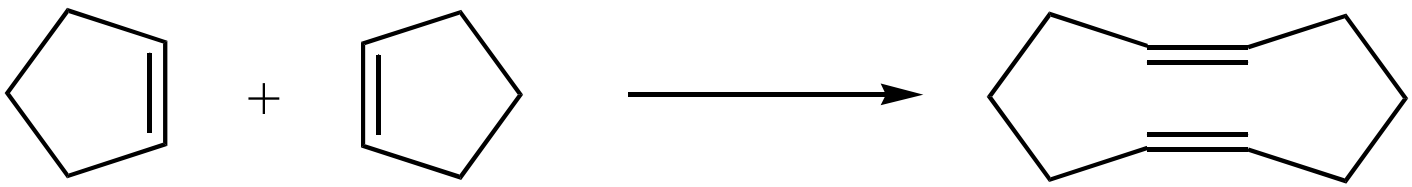
A. Fürstner:
Angew. Chem. **2000**, *112*, 3140

Katalysekreislauf der RCM

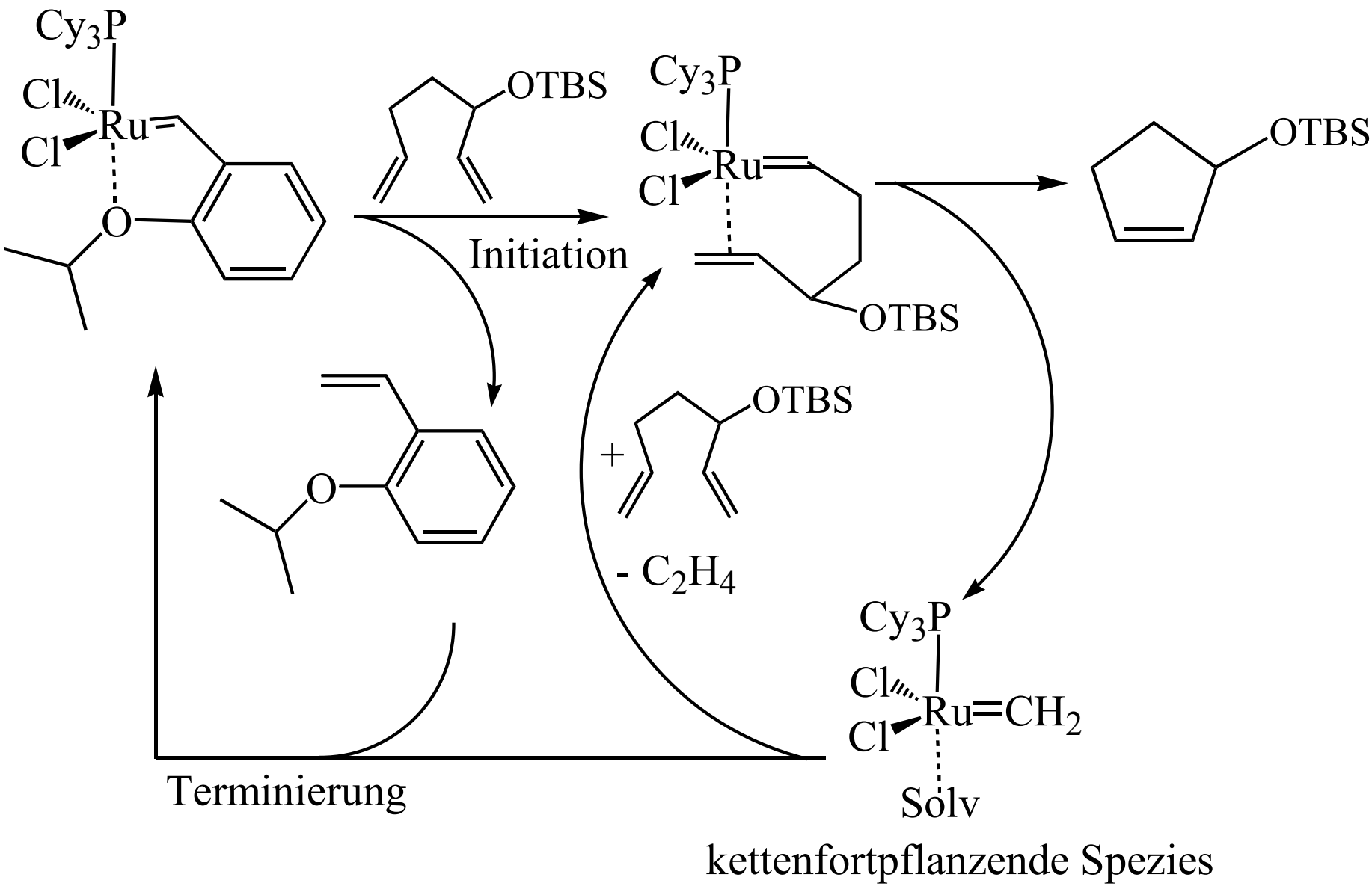


Olefin-Metathese

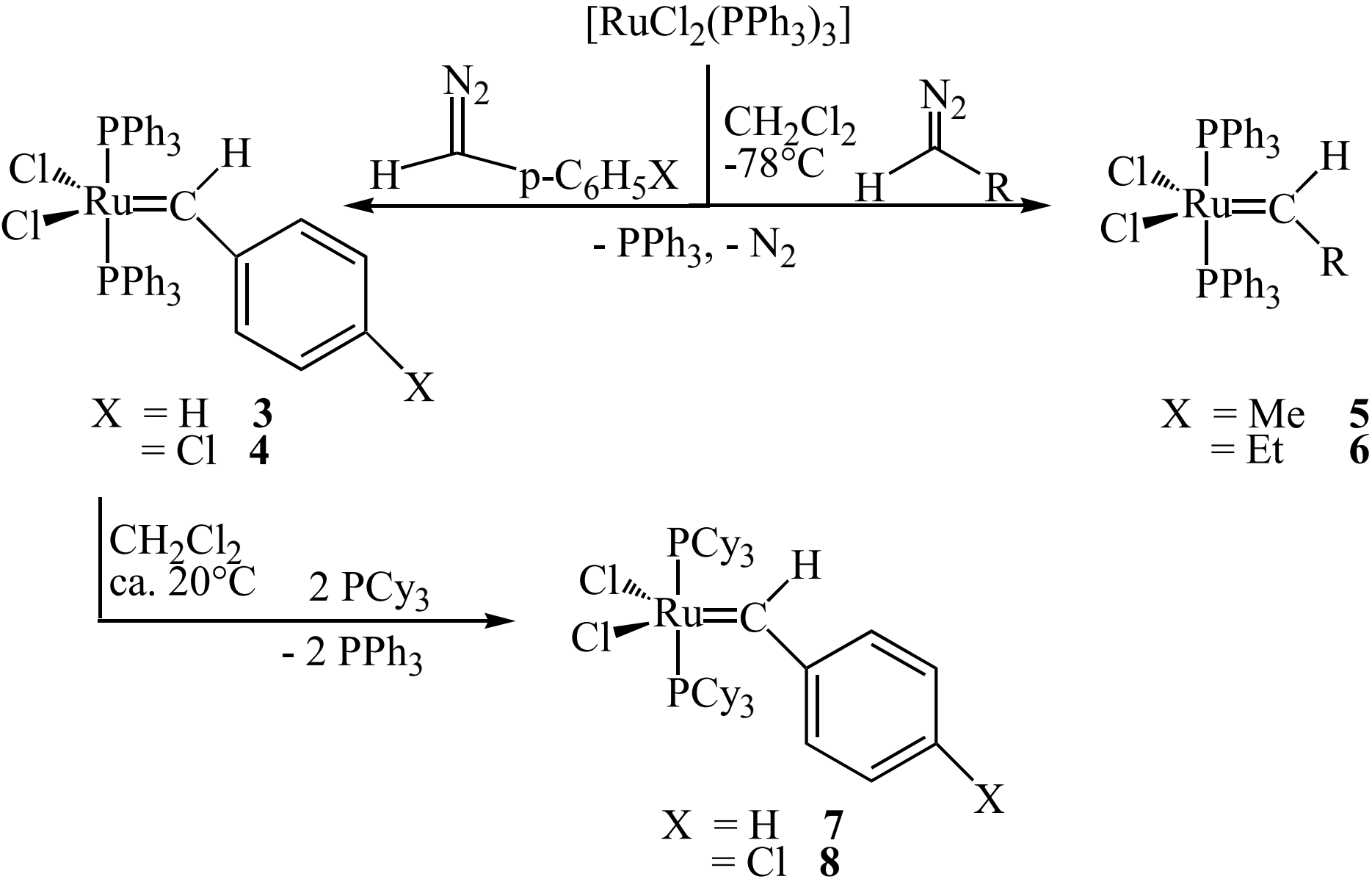




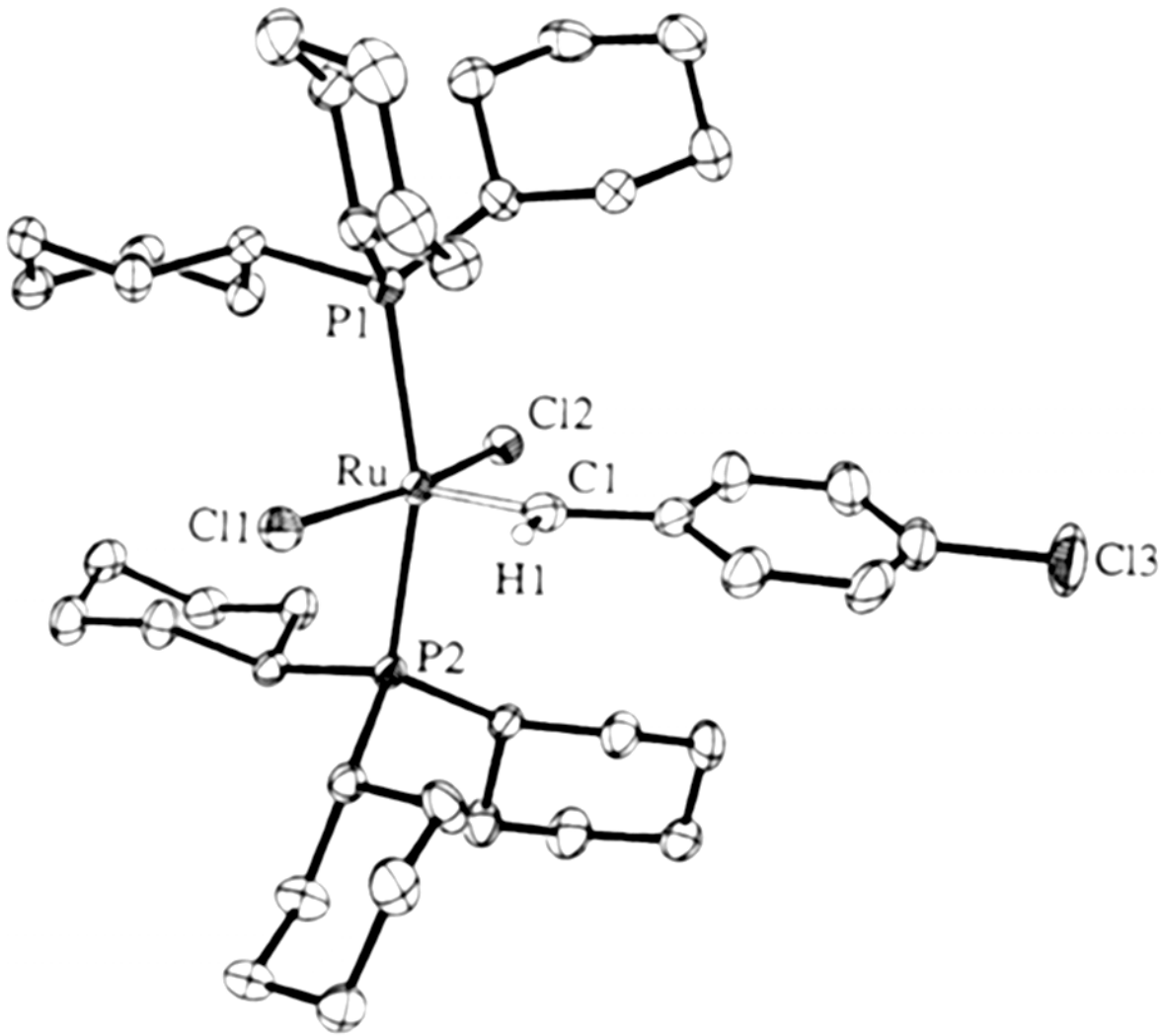
RCM mit einem Grubbs-Katalysator



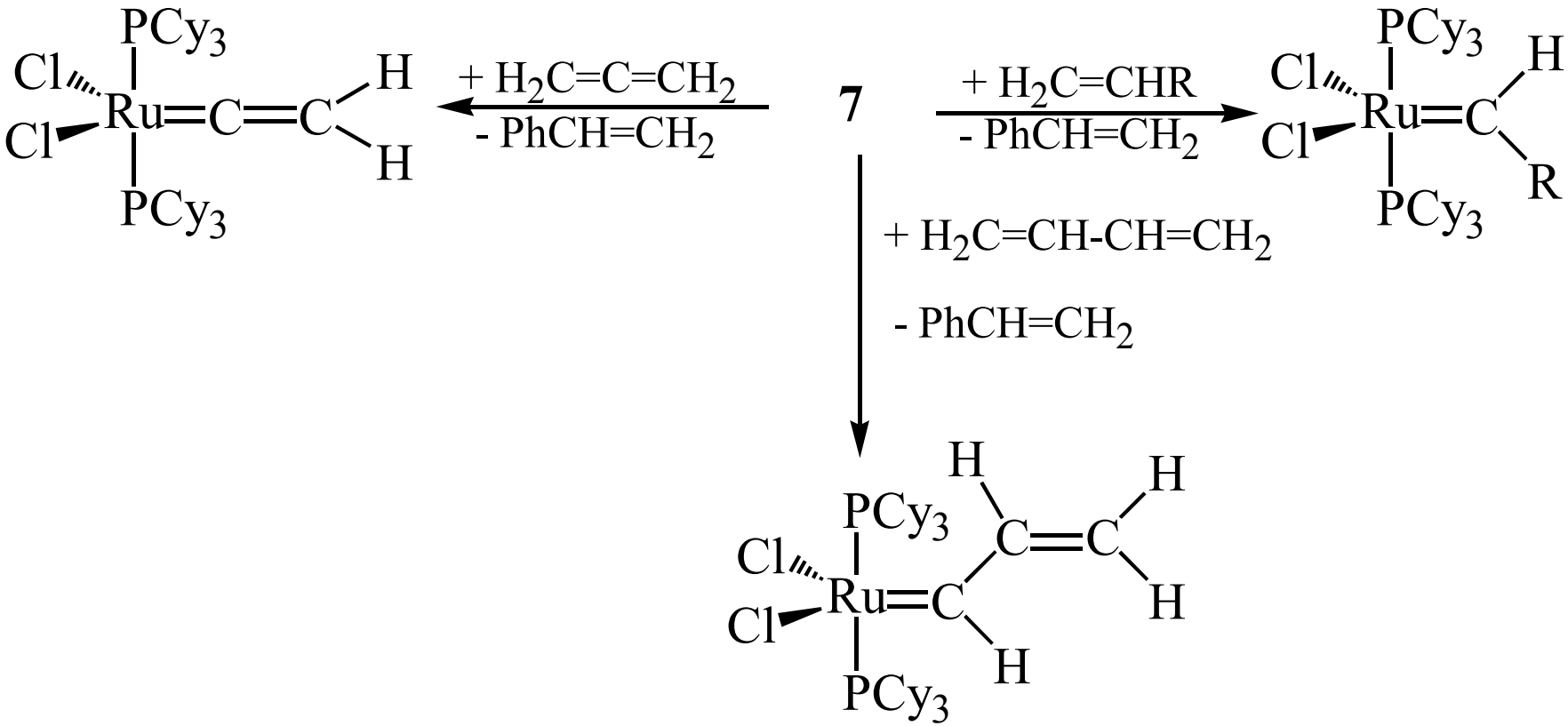
Synthese eines Metathesekatalysators



Struktur eines Grubbs-Metathesekatalysators

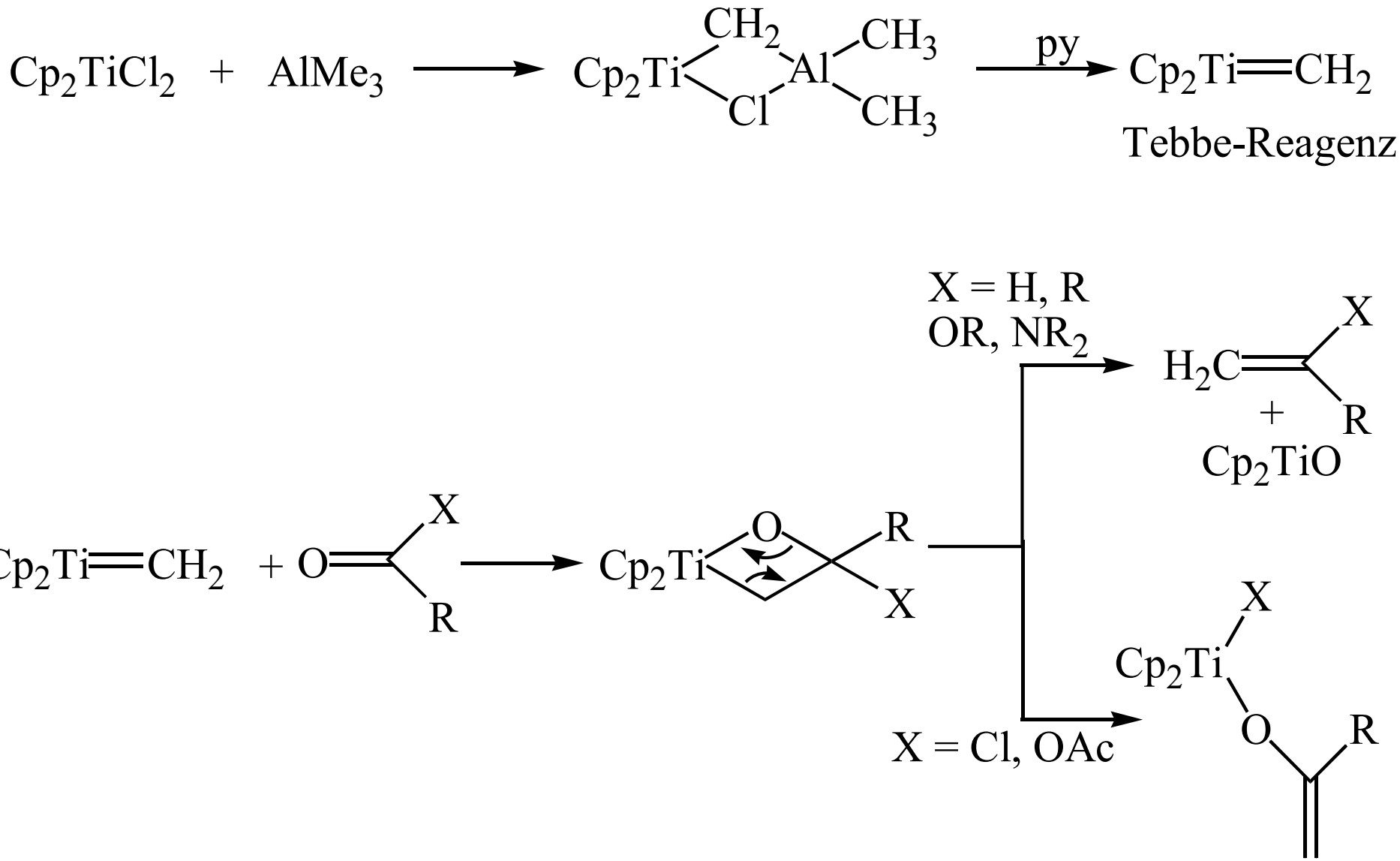


Metathese acyclischer Alkene mit Grubbs-Katalysator

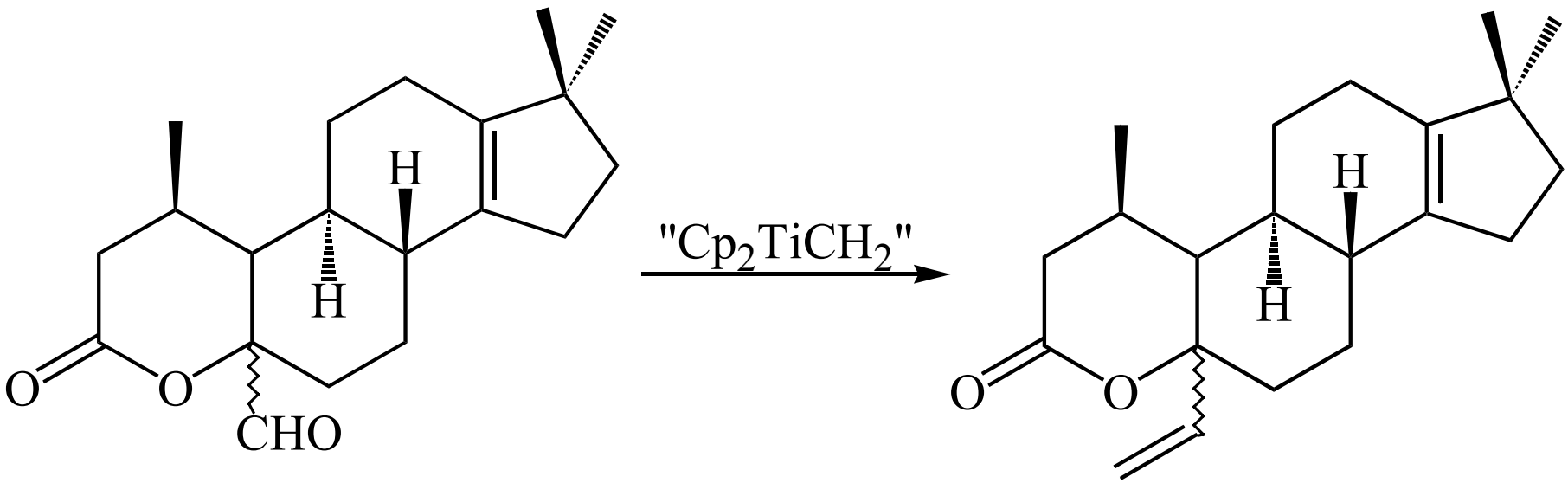


P. Schwab, M.B. France, J.W. Ziller, R.H. Grubbs,
Angew. Chem. **1995,** *107*, 2179-2181

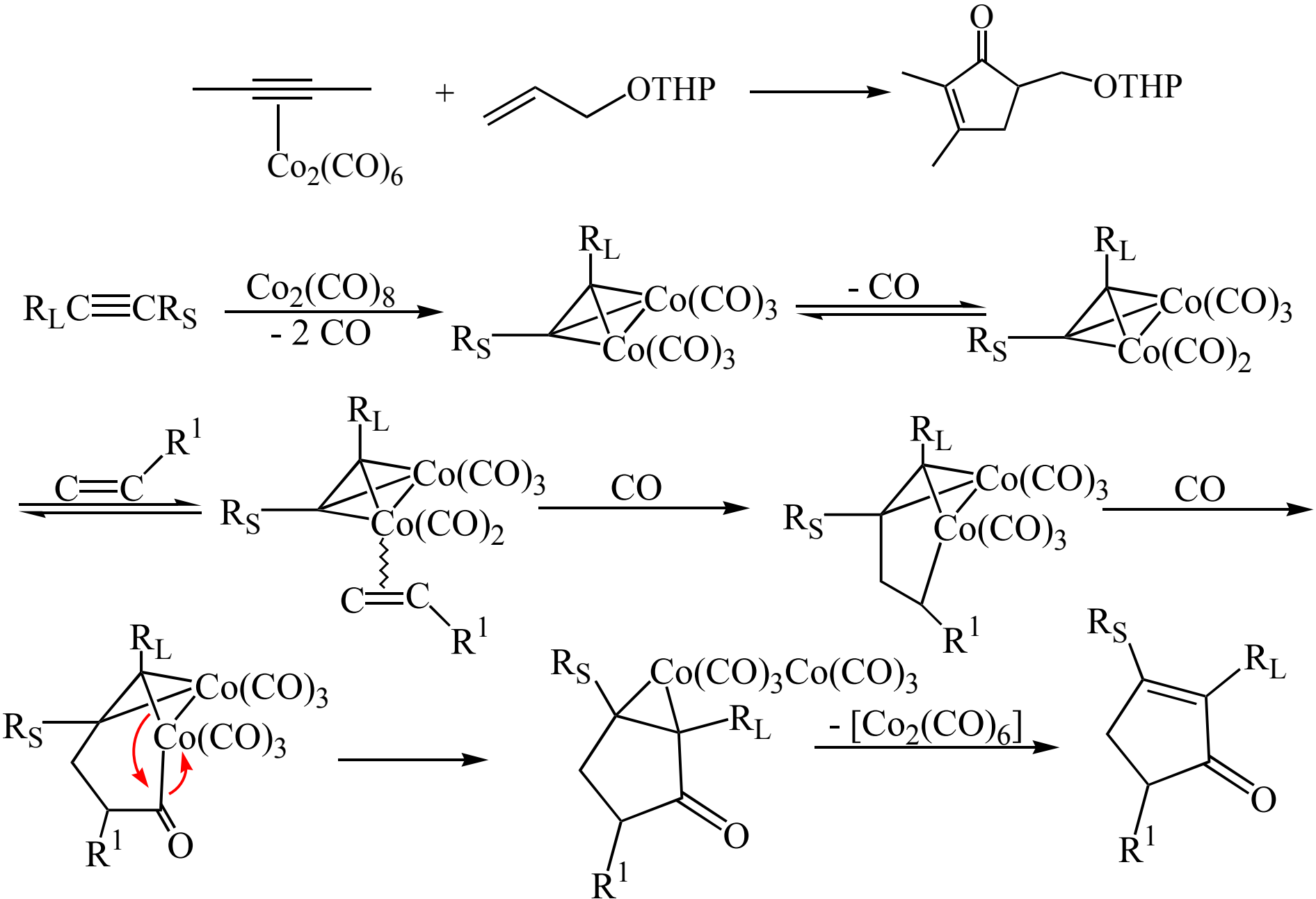
Tebbe-Reaktionen



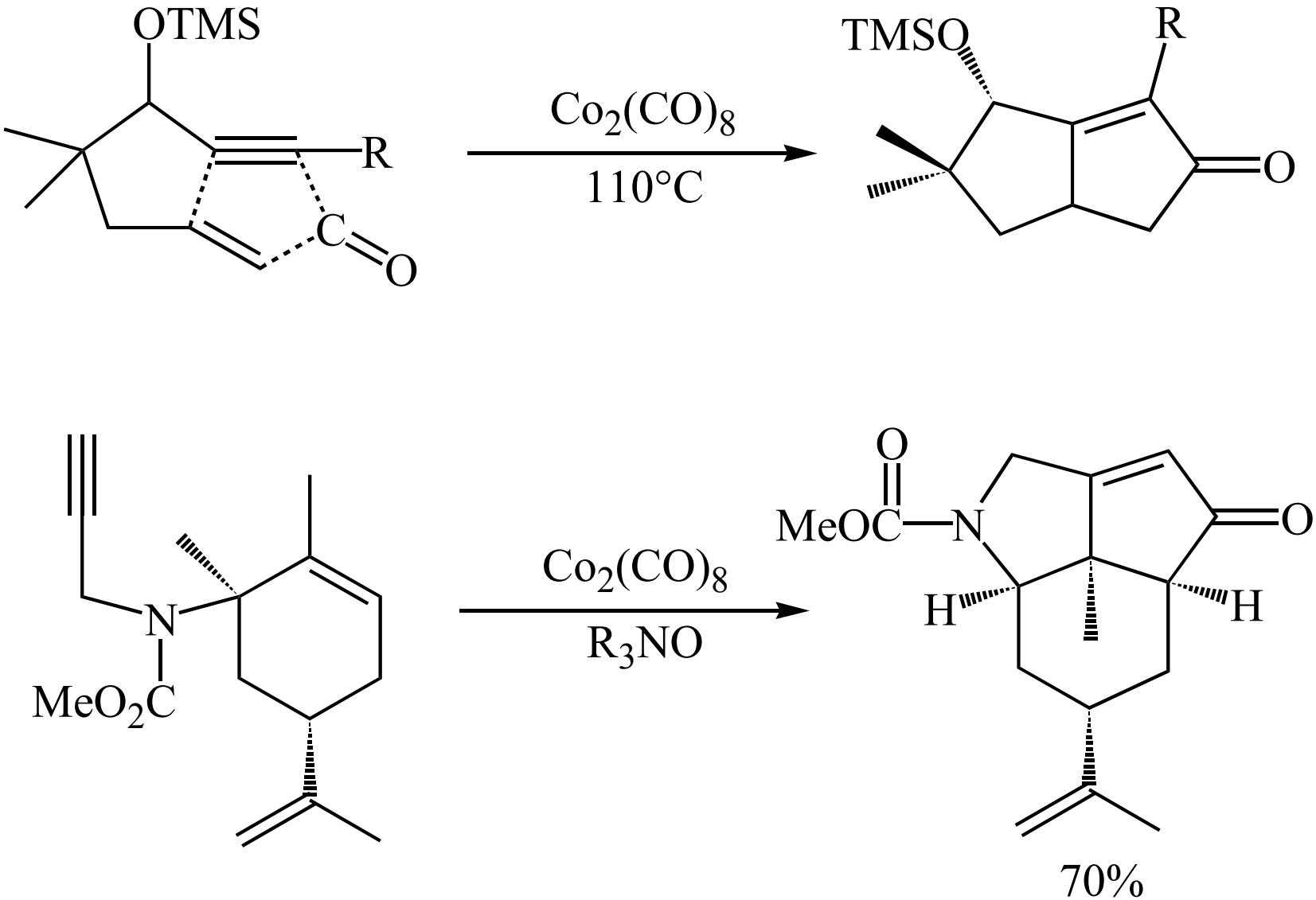
Tebbe-Reaktionen



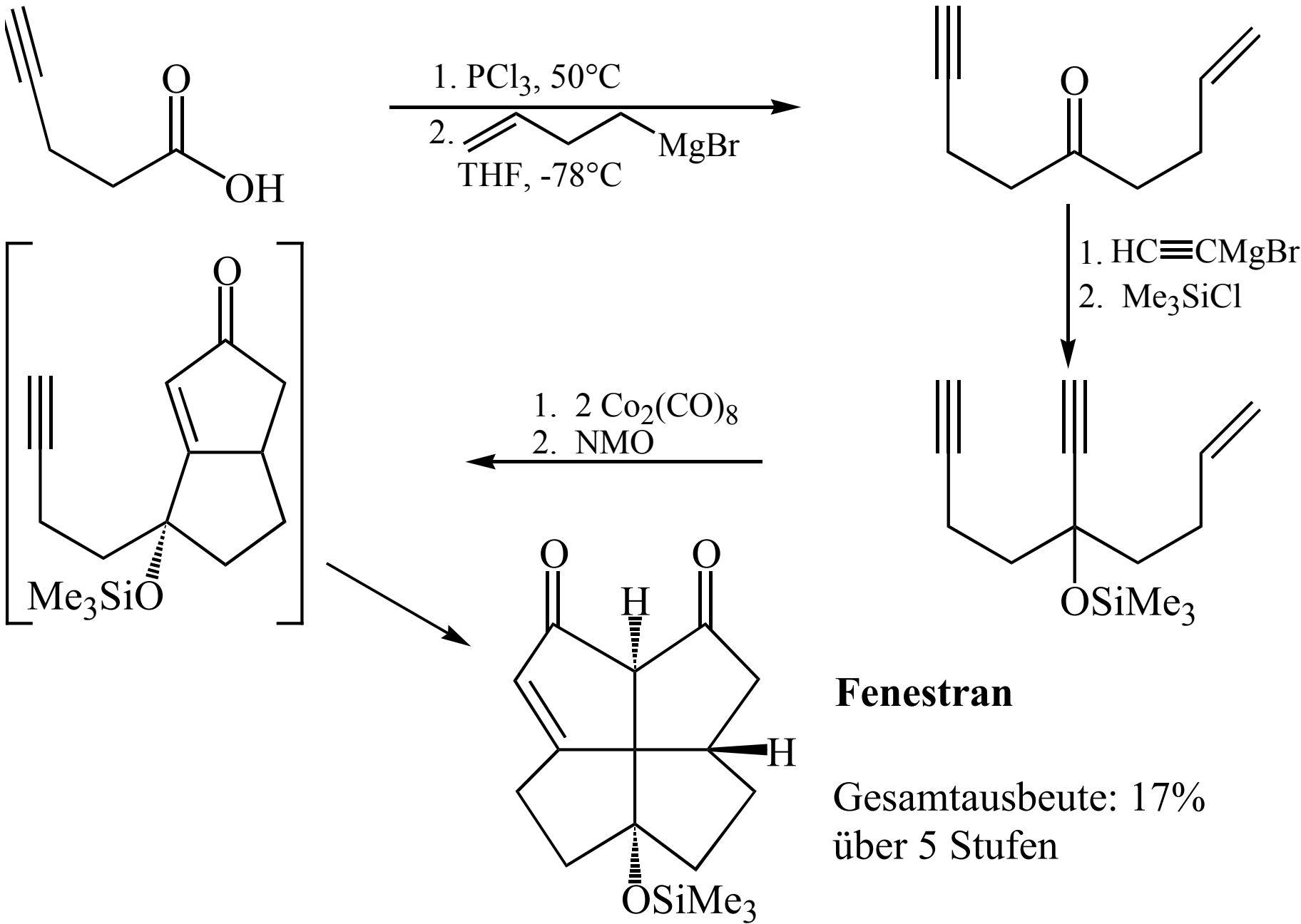
Pauson-Khand-Reaktion



Pauson-Khand-Reaktion



Synthese von Fenestran



Fenestran

Gesamtausbeute: 17%
über 5 Stufen