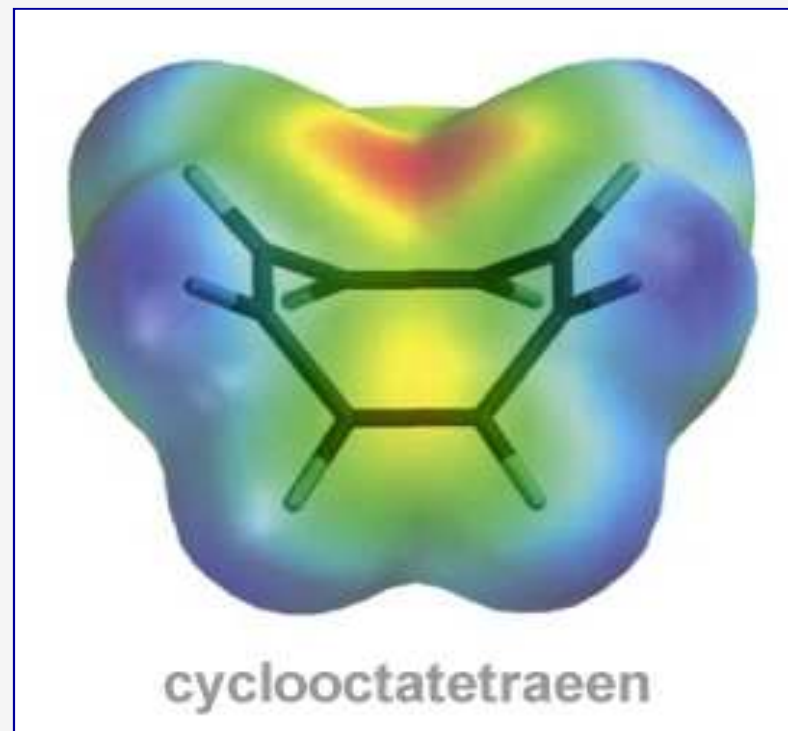


Scheikunde II



hoorcollege5

Prof. Dr. I. De Vynck

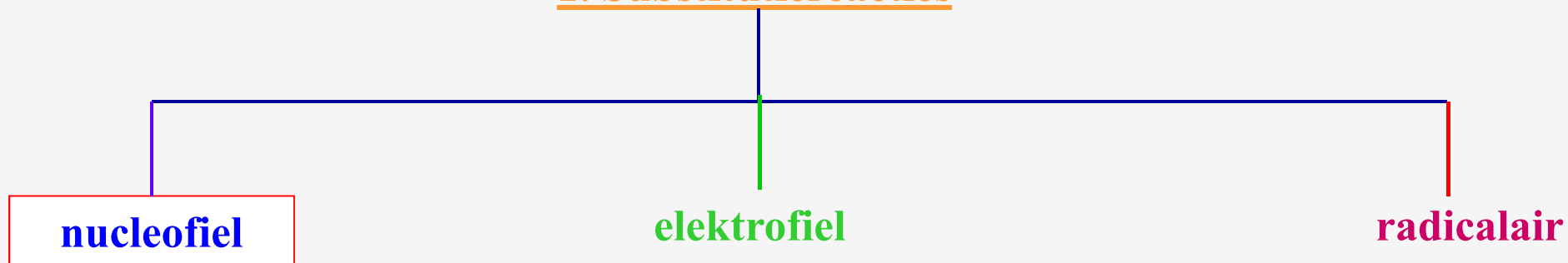
Prof. Dr. M.-F. Reyniers

2^{ste} semester 2002 - 2003

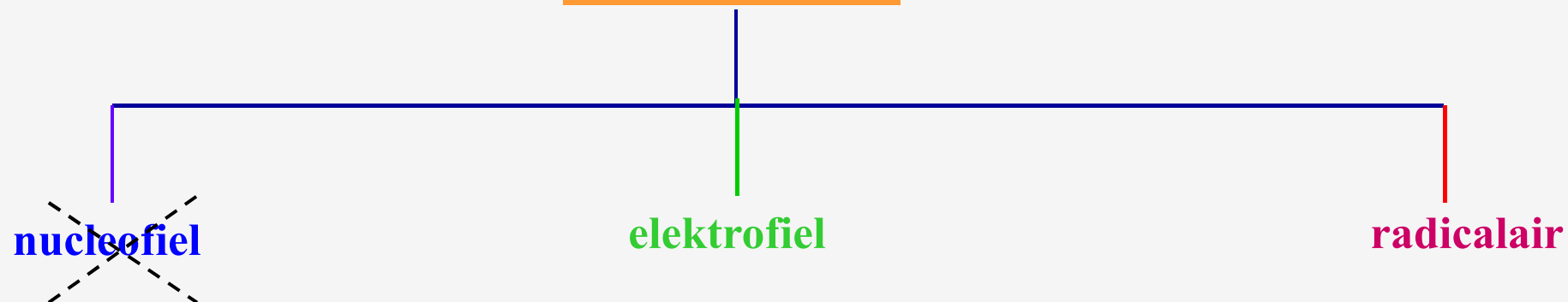
Scheikunde II

Belangrijke types chemische reacties

1. Substitutiereacties



2. Additiereacties



3. Eliminatiereacties

4. Omleggingsreacties

1,2 hydridesift

1,2 methylsift

Alifaten = niet-aromatische verbindingen vb.: alkanen, alkenen, alkynen, cyclo-alkanen...



– alifatische nucleofiele substitutie

1 σ -binding $sp^3C-X \rightarrow 1 \sigma$ -binding sp^3C-Y



Y = nucleofiel, intredende groep

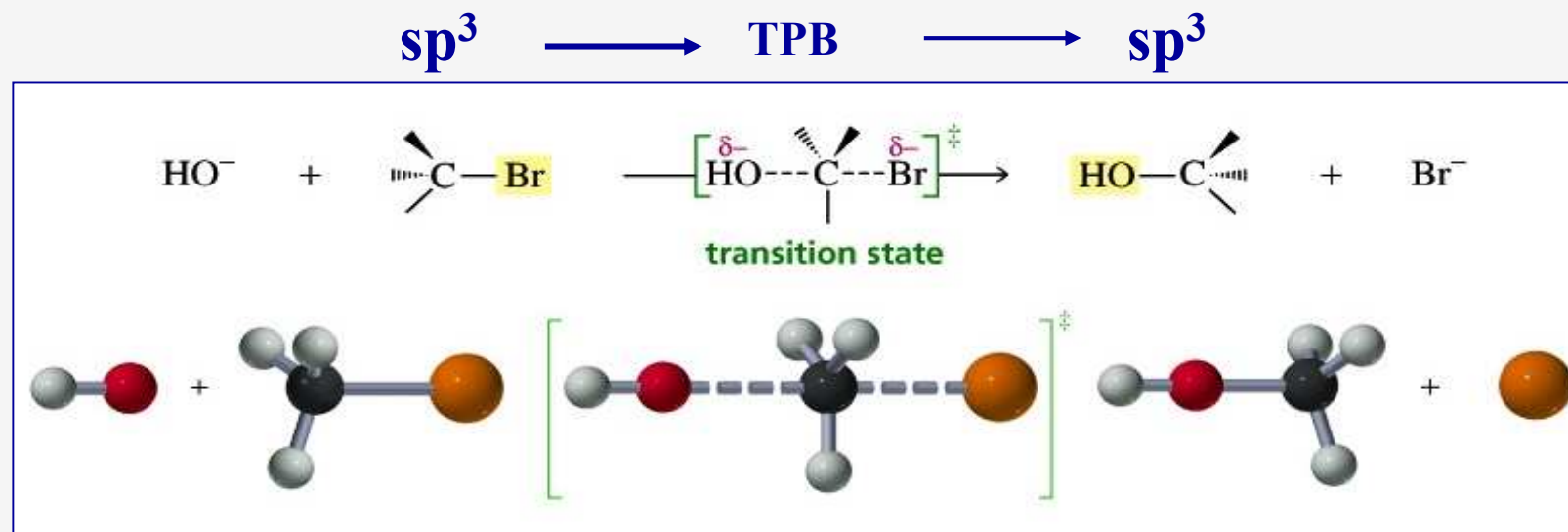
X = uitredende groep of “leaving” groep

Timing: twee extremen

1. **Twee-stapsreactie**: eerst breking C-X dan vorming C-Y, **SN1**

2. **Eén-stapsreactie**: simultaan breken C-X en vorming C-Y, **SN2**

♣ SN2-type: nucleofiele substitutie 2^{de} orde



- één-stapsmechanisme
- inversie van configuratie
- reactiviteit R-X: methyl > primair > secundair > tertiair
- reactiviteit R-X: I > Br > Cl > F (zwakste base = beste uittredende groep)

2. Nucleofiele substitutiereacties

♣ SN2-type: nucleofiele substitutie 2^{de} orde

- ✓ mechanisme
- ✓ stereochemie
- ✓ sterische effecten
- ✓ “leaving” capaciteit
- ✓ nucleofielen & nucleofiliciteit

♣ SN1-type: nucleofiele substitutie 1^{ste} orde

♣ SN1 versus SN2

✓ nucleofiliciteit

meten r voor CH_3I + nucleofiel in methanol

t.o.v.

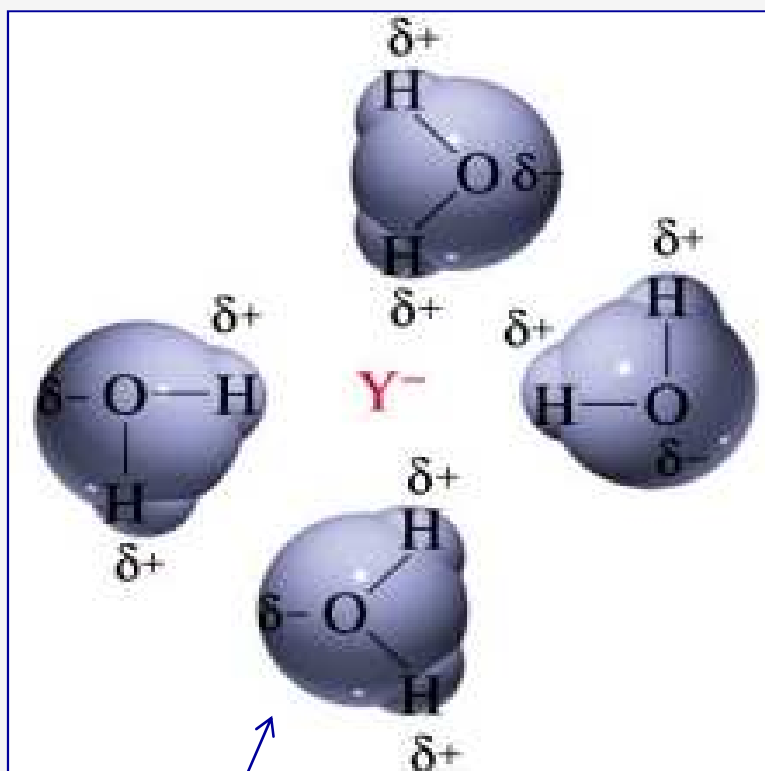
Reactiviteitsklasse	Nucleofiel	Relatieve reactiviteit
Zeer goed nucleofiel	I^- , HS^- , RS^-	$> 10^5$
Goed nucleofiel	Br^- , HO^- , RO^- , CN^- , N_3^-	10^4
Nucleofiel	NH_3 , Cl^- , F^- , RCOO^-	10^3
Zwak nucleofiel	H_2O , ROH	1
Zeer zwak nucleofiel	RCOOH	10^{-2}

neutrale moleculen zijn zwakke nucleofielen

vuistregel: basesterkte $\uparrow \Leftrightarrow$ nucleofiliciteit \uparrow

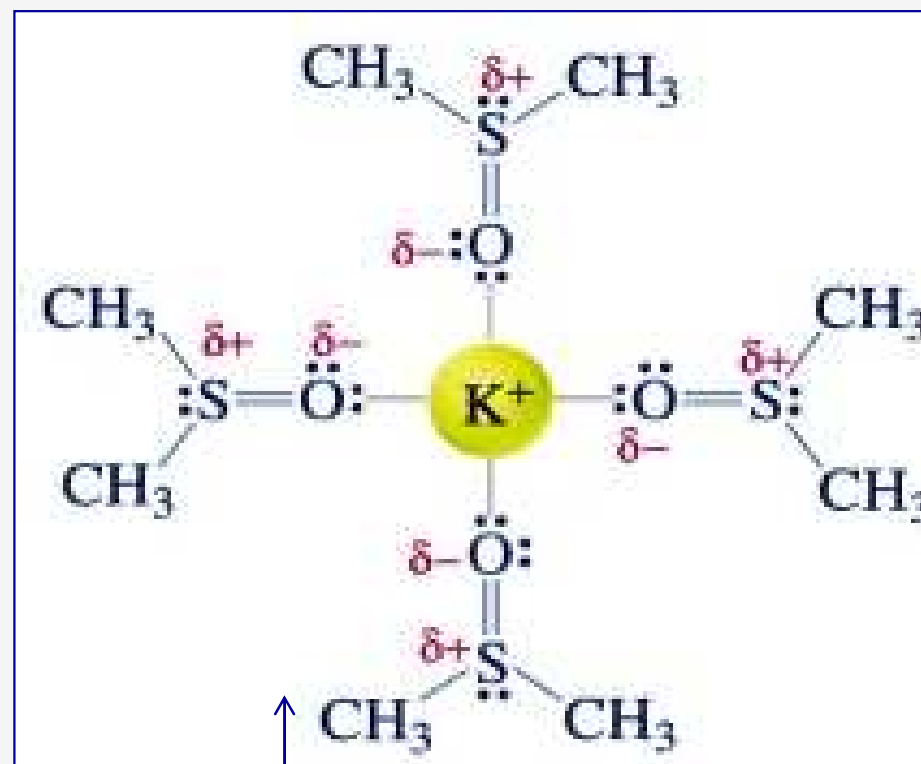
→ **LET OP: SOLVENT!!!**

polair protisch solvent



Vb.: water, methanol, ethanol,
azijnzuur, mierenzuur...

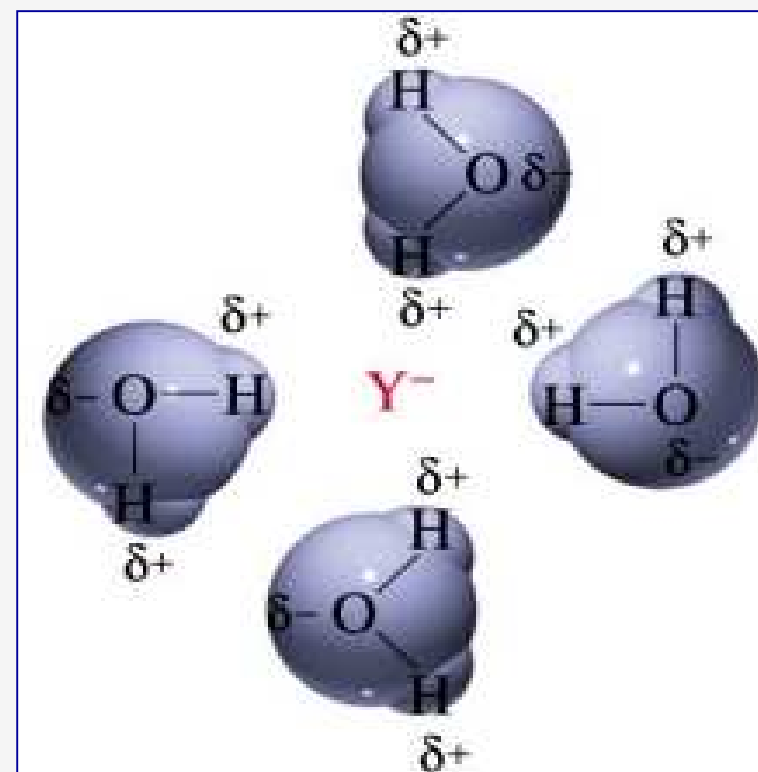
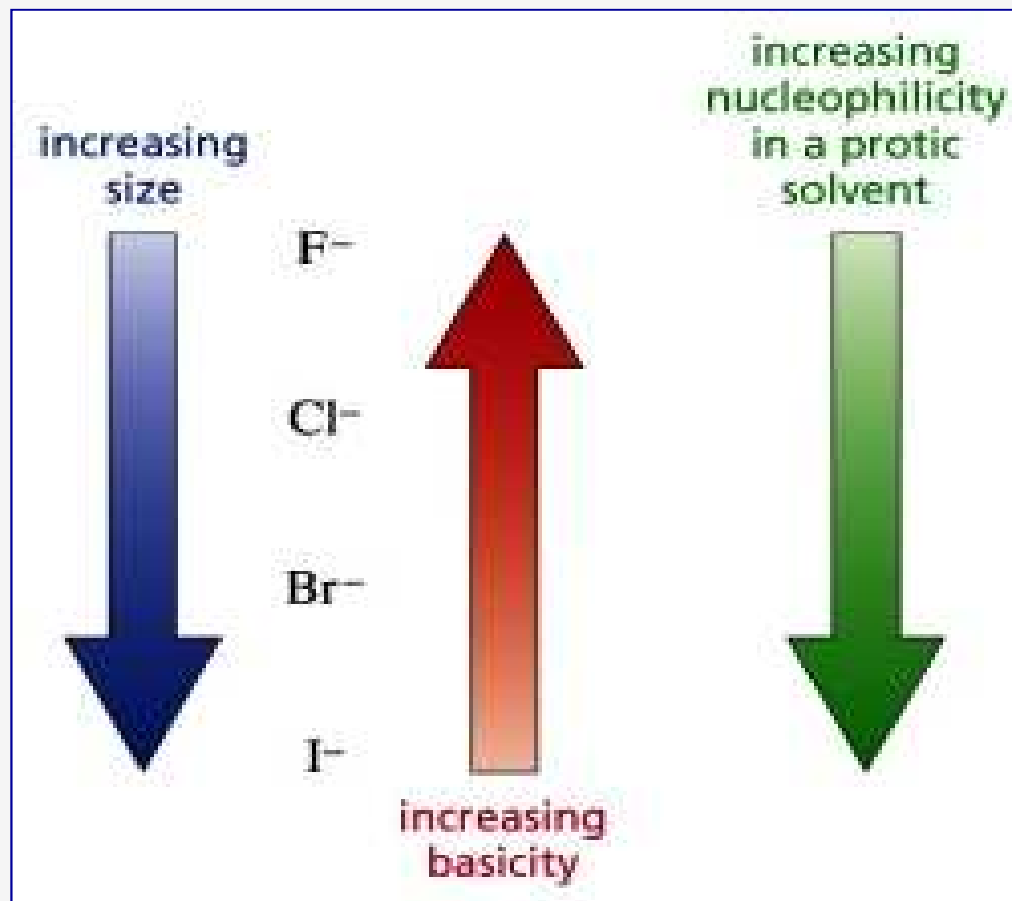
dipolair aprotisch solvent



Vb.: DMSO, aceton, DMF

polair protisch solvent

basesterkte \uparrow ~~nucleofiliciteit~~ \uparrow

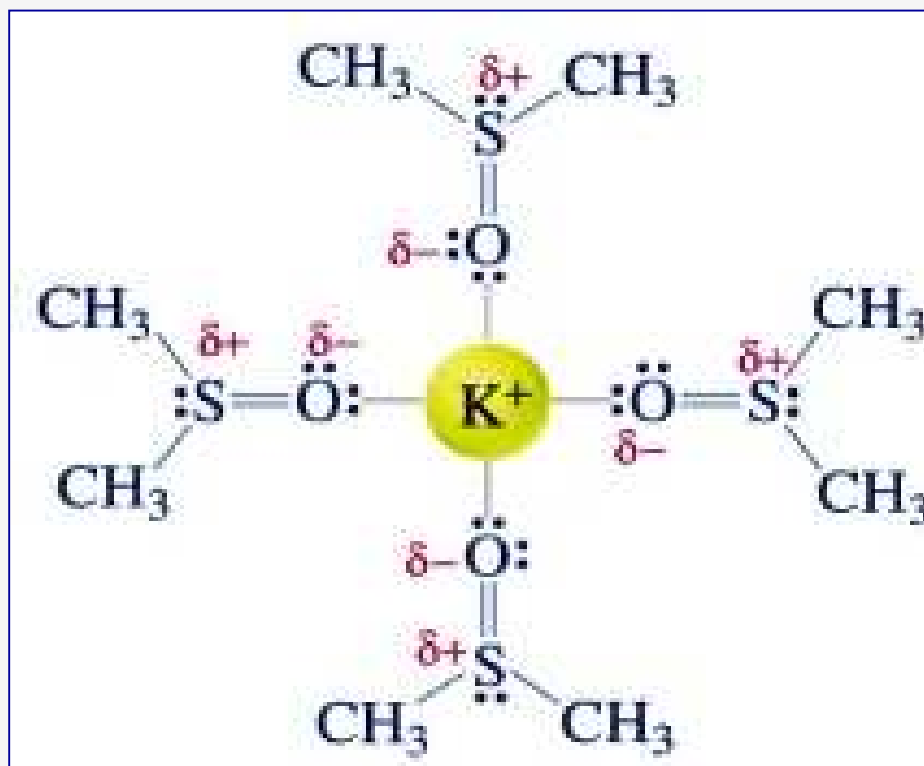


F^- : best gesolvateerd

kleine ionen worden beter gesolvateerd dan grotere ionen

dipolair aprotisch solvent

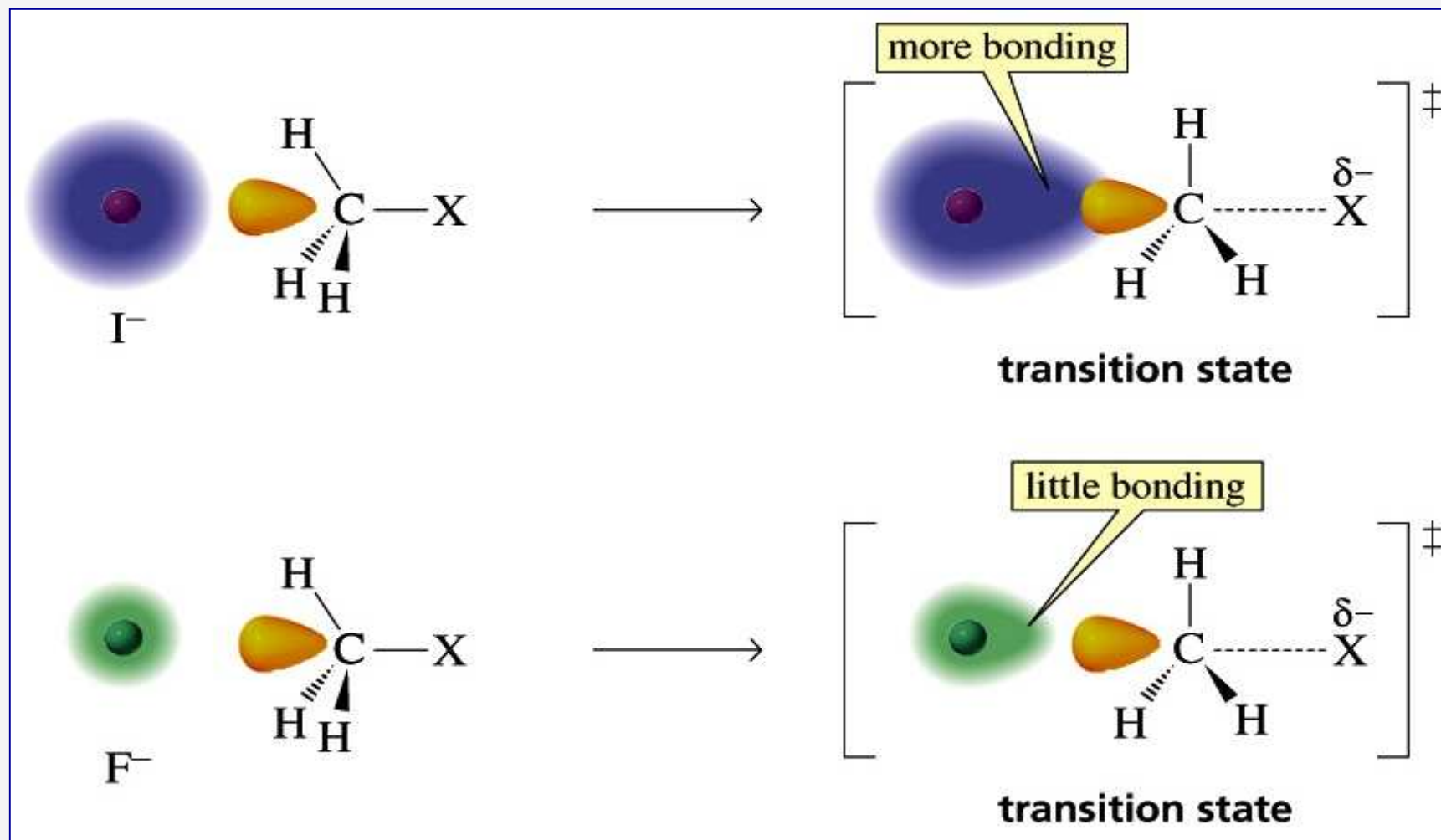
basesterkte $\uparrow \Leftrightarrow$ nucleofiliciteit \uparrow



anionen worden niet gesolvateerd \Rightarrow anionen zeer reactief

polarizeerbaarheid $\uparrow \Leftrightarrow$ nucleofiliciteit \uparrow

Afmeting atoom \uparrow



	SN2
Mechanisme	Eén-stapsmechanisme
Kinetisch gedrag	SBS = bimoleculair R = [R-X] [nucleofiel]
Stereochemie	Inversie configuratie
R-X	Methyl > prim > sec > tert Sterisch ongehinderd
Nucleofiel	Sterk nucleofiel R ≈ [nucleofiel]
Solvent	Polair aprotisch DMF, DMSO, aceton...
Uittredende groep	I > Br > Cl > F zwakste base, beste uittredende groep

2. Nucleofiele substitutiereacties

♣ **SN2-type: nucleofiele substitutie 2^{de} orde**

♣ **SN1-type: nucleofiele substitutie 1^{ste} orde**

✓ **mechanisme**

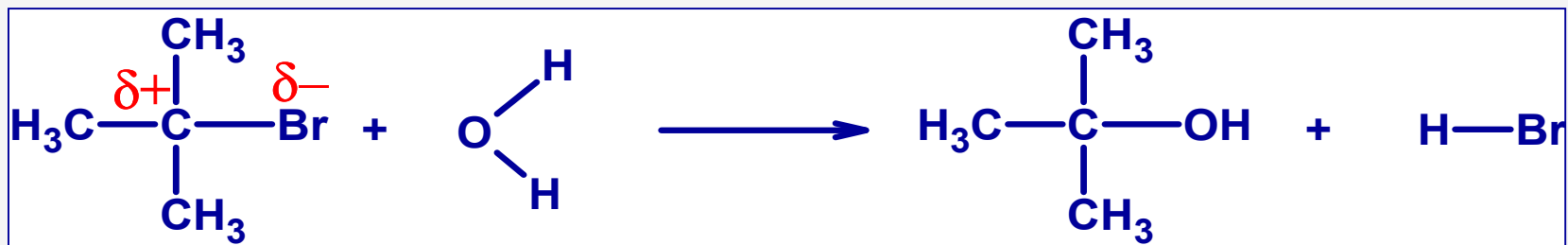
✓ **stereochemie**

✓ **sterische effecten**

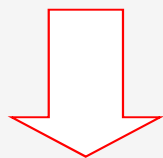
✓ **solventeffecten**

♣ **SN1 versus SN2**

✓ mechanisme

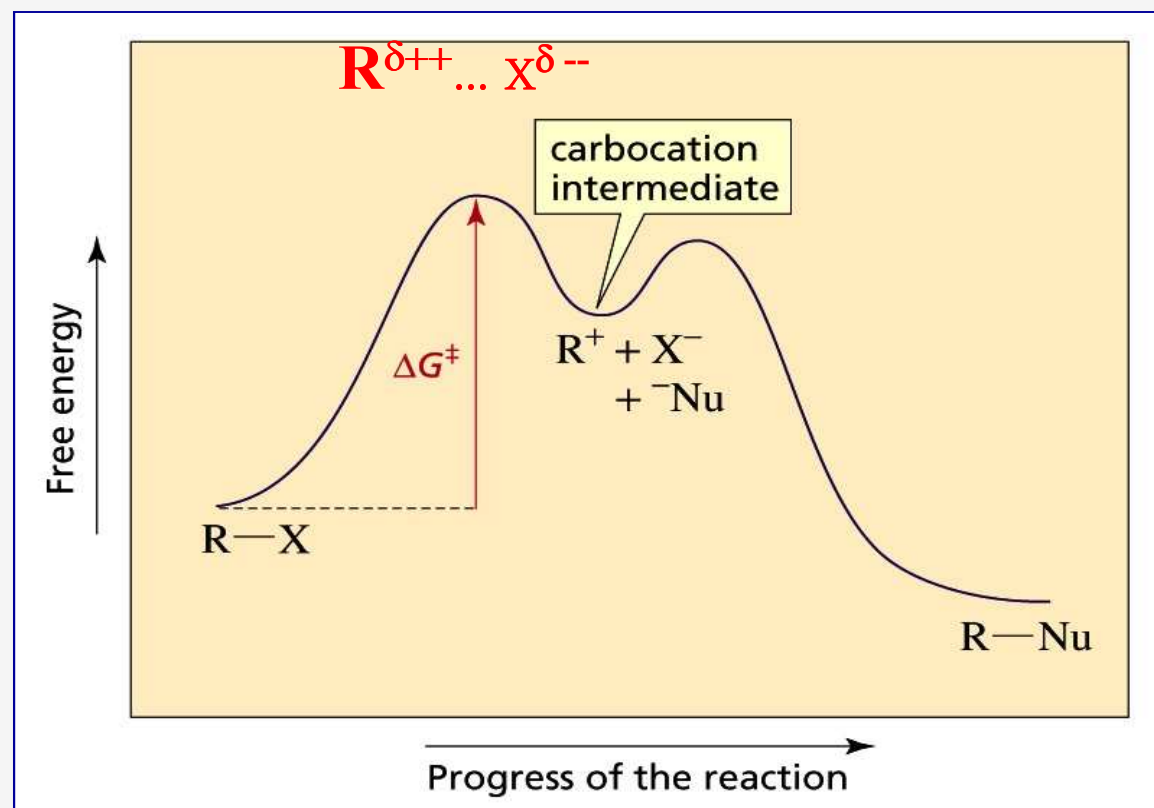


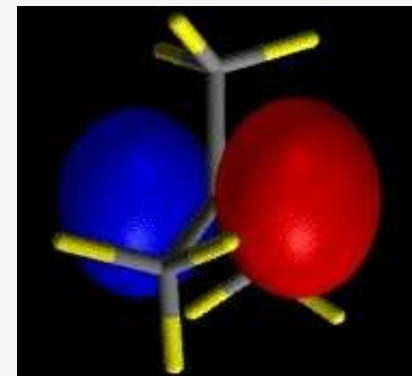
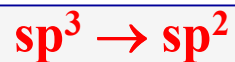
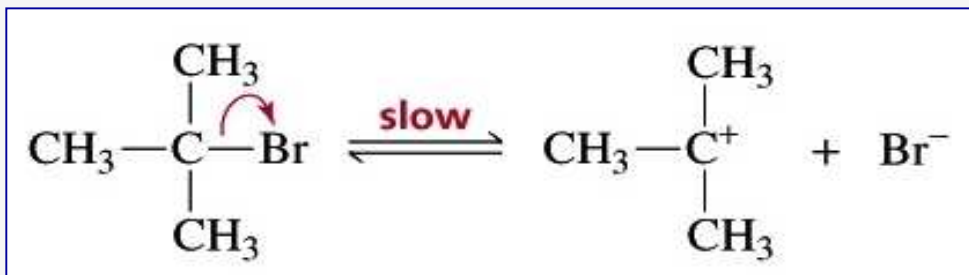
$$r = k [(\text{CH}_3)_3\text{C}-\text{Br}]$$



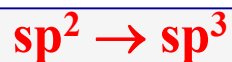
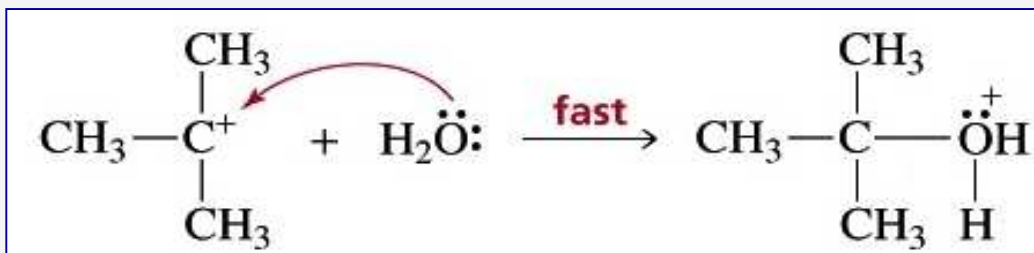
SBS = unimoleculair

↓
enkel R-X betrokken in vorming TTS

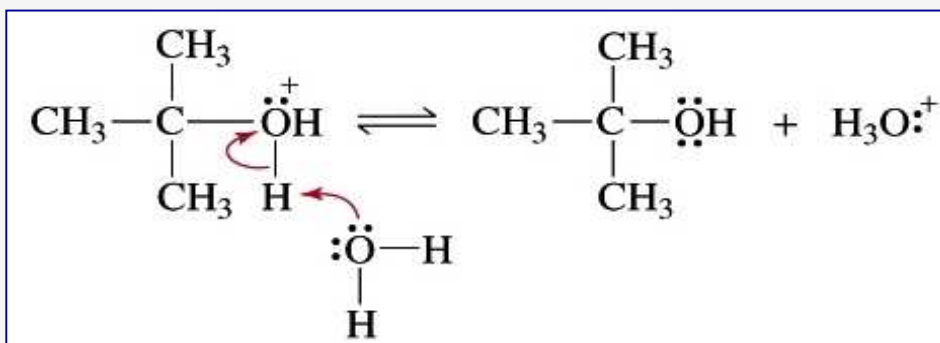


Stap 1: vorming carbenium ion = SBS; traag

C^+ : planair

Stap 2: nucleofiele aanval op C^+ ; snel

alkyloxonium ion

Stap 3: snelle zuur-base reactie

2. Nucleofiele substitutiereacties

♣ **SN2-type: nucleofiele substitutie 2^{de} orde**

♣ **SN1-type: nucleofiele substitutie 1^{ste} orde**

✓ **mechanisme**

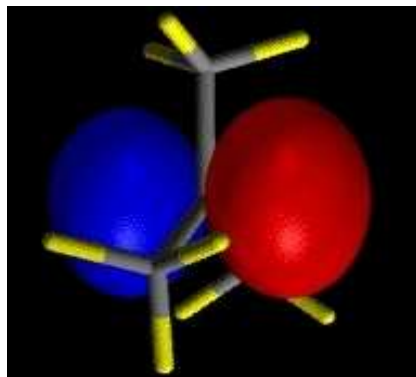
✓ **stereochemie**

✓ **sterische effecten**

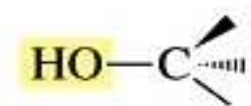
✓ **solventeffecten**

♣ **SN1 versus SN2**

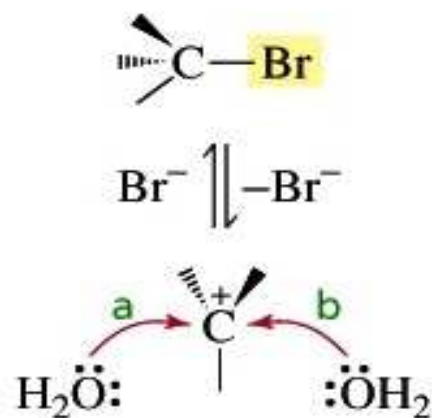
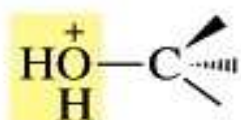
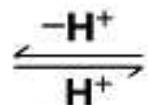
✓ stereochemie



C^+ : planair

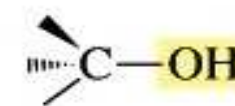
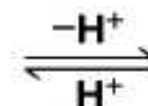
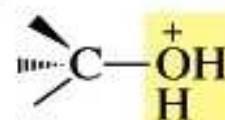


inversie



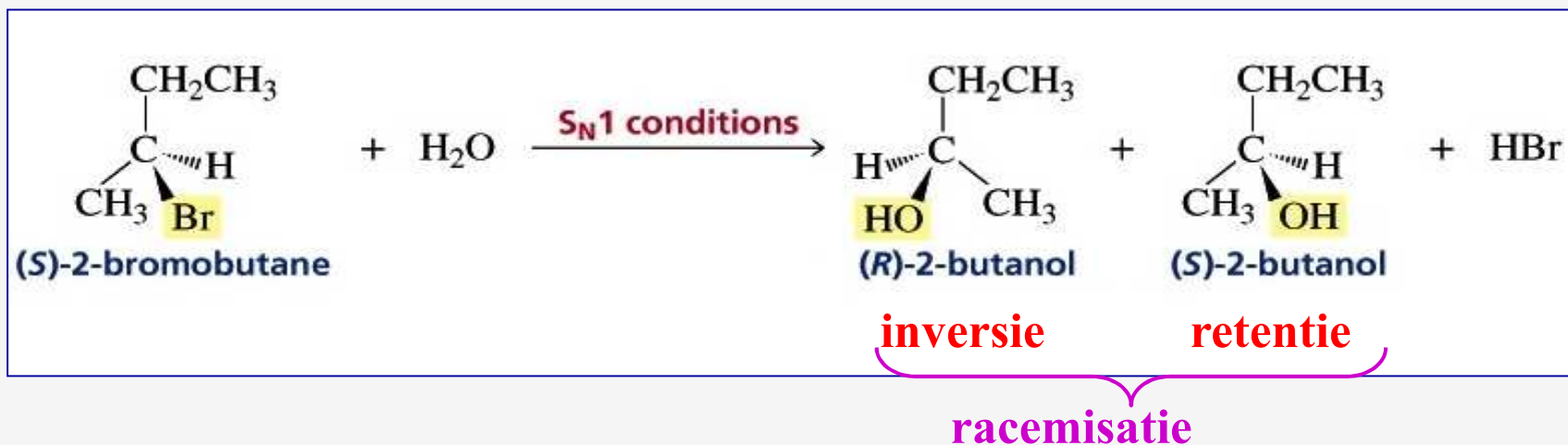
a

b

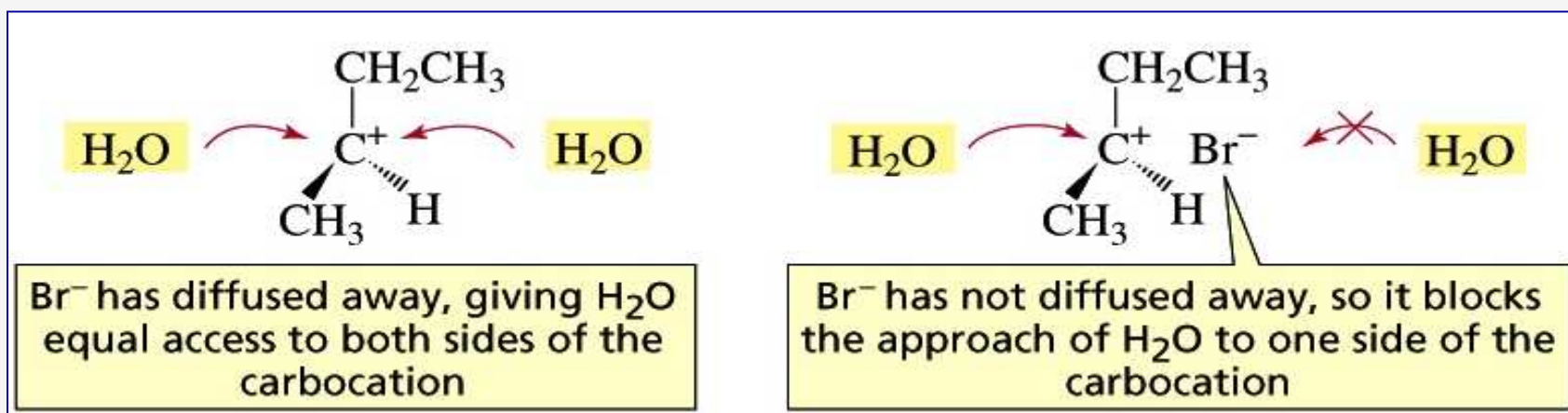


retentie

SN1 \Rightarrow racemisatie



Experimenteel: geen volledige racemisatie wegens afscherming van C^+ door X^-
 \Rightarrow meer inversie



2. Nucleofiele substitutiereacties

♣ **SN2-type: nucleofiele substitutie 2^{de} orde**

♣ **SN1-type: nucleofiele substitutie 1^{ste} orde**

✓ **mechanisme**

✓ **stereochemie**

✓ **sterische effecten**

✓ **solventeffecten**

♣ **SN1 versus SN2**

✓ Sterische effecten

meten r van \neq R-X voor hydrolyse in SN1 condities



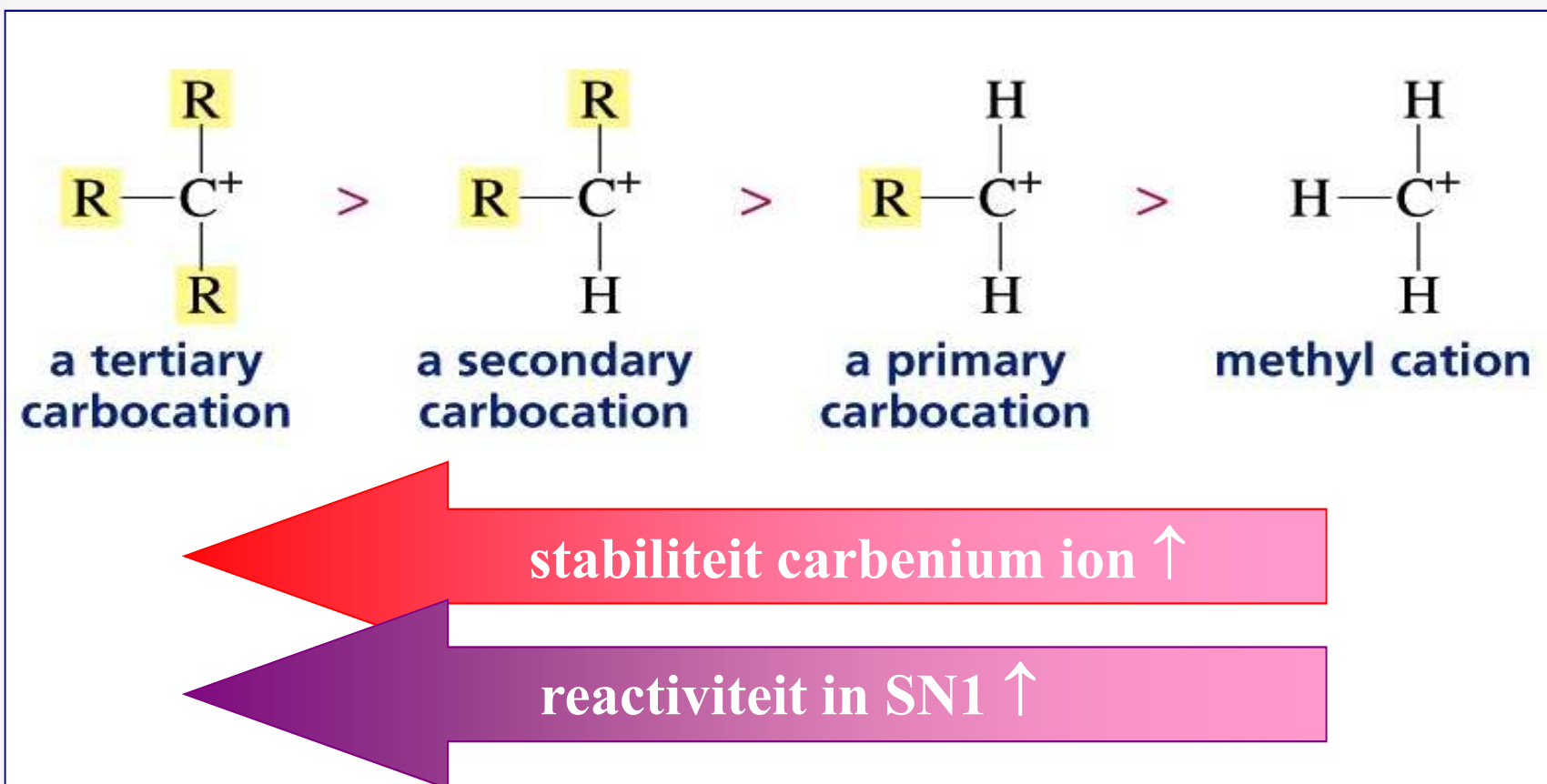
in HCOOH

Alkyl bromide	Class	Relative rate
$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3\text{C}-\text{Br} \\ \\ \text{CH}_3 \end{array}$	tertiary	1,200,000
$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3\text{CH}-\text{Br} \\ \\ \text{CH}_3 \end{array}$	secondary	11.6
$\text{CH}_3\text{CH}_2-\text{Br}$	primary	1.00*
CH_3-Br	methyl	1.05*

↑
Reactiviteit ↑

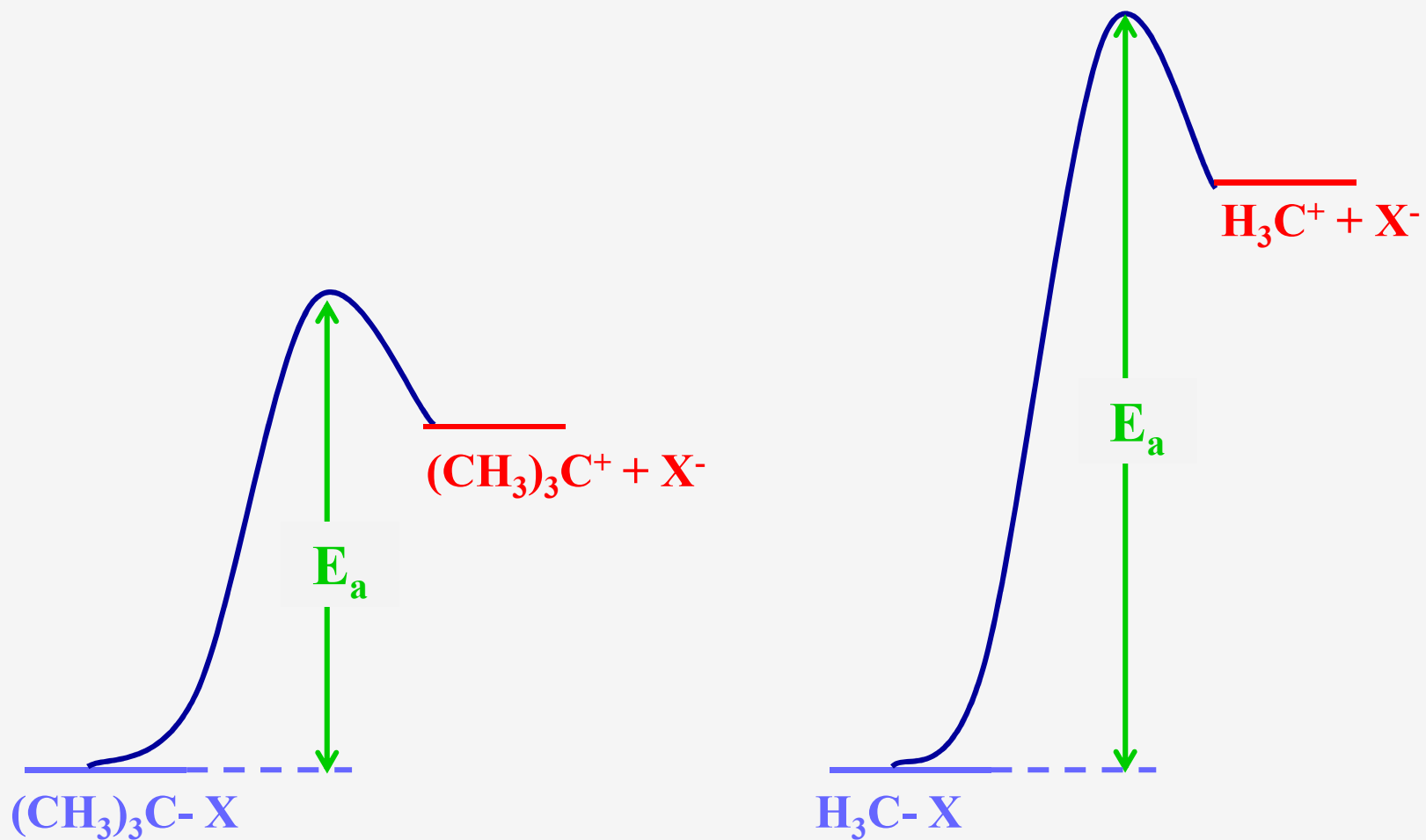
*Although the rate of the S_N1 reaction of this compound with water is 0, a small rate is observed as a result of an S_N2 reaction.

tertiair > secundair > primair > methyl



reactiviteitsvolgorde SN1 \gg reactiviteitsvolgorde SN2

E_a vorming tertiair $C^+ \lll E_a$ vorming primair C^+



2. Nucleofiele substitutiereacties

♣ **SN2-type: nucleofiele substitutie 2^{de} orde**

♣ **SN1-type: nucleofiele substitutie 1^{ste} orde**

✓ **mechanisme**

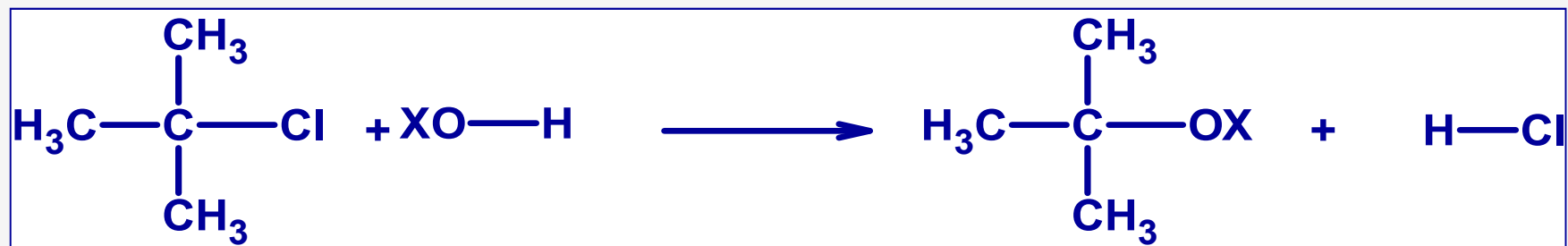
✓ **stereochemie**

✓ **sterische effecten**

✓ **solventeffecten**

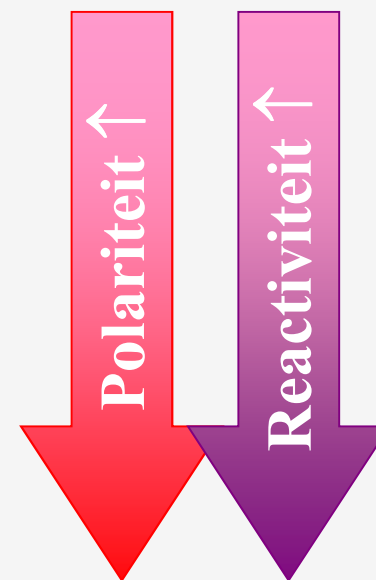
♣ **SN1 versus SN2**

✓ solventeffecten

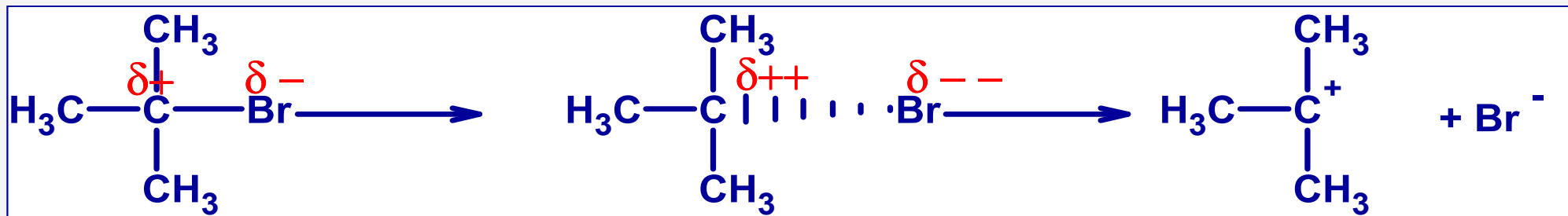


Solvent = nucleofiel	Diëlektrische constante ϵ	Relatieve snelheid
Azijnzuur	6	1
Methanol	33	4
Mierenzuur	58	5 000
Water	78	150 000

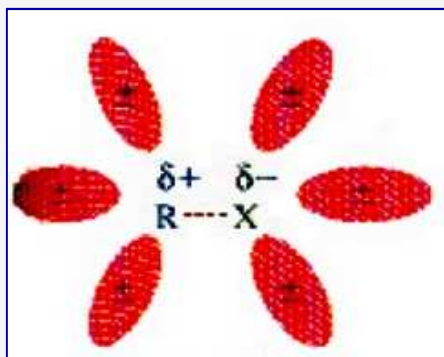
ϵ = maat voor polariteit solvent



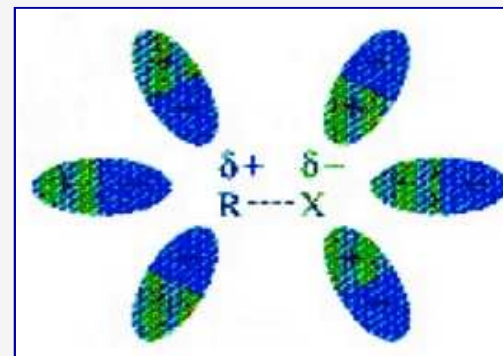
TTS



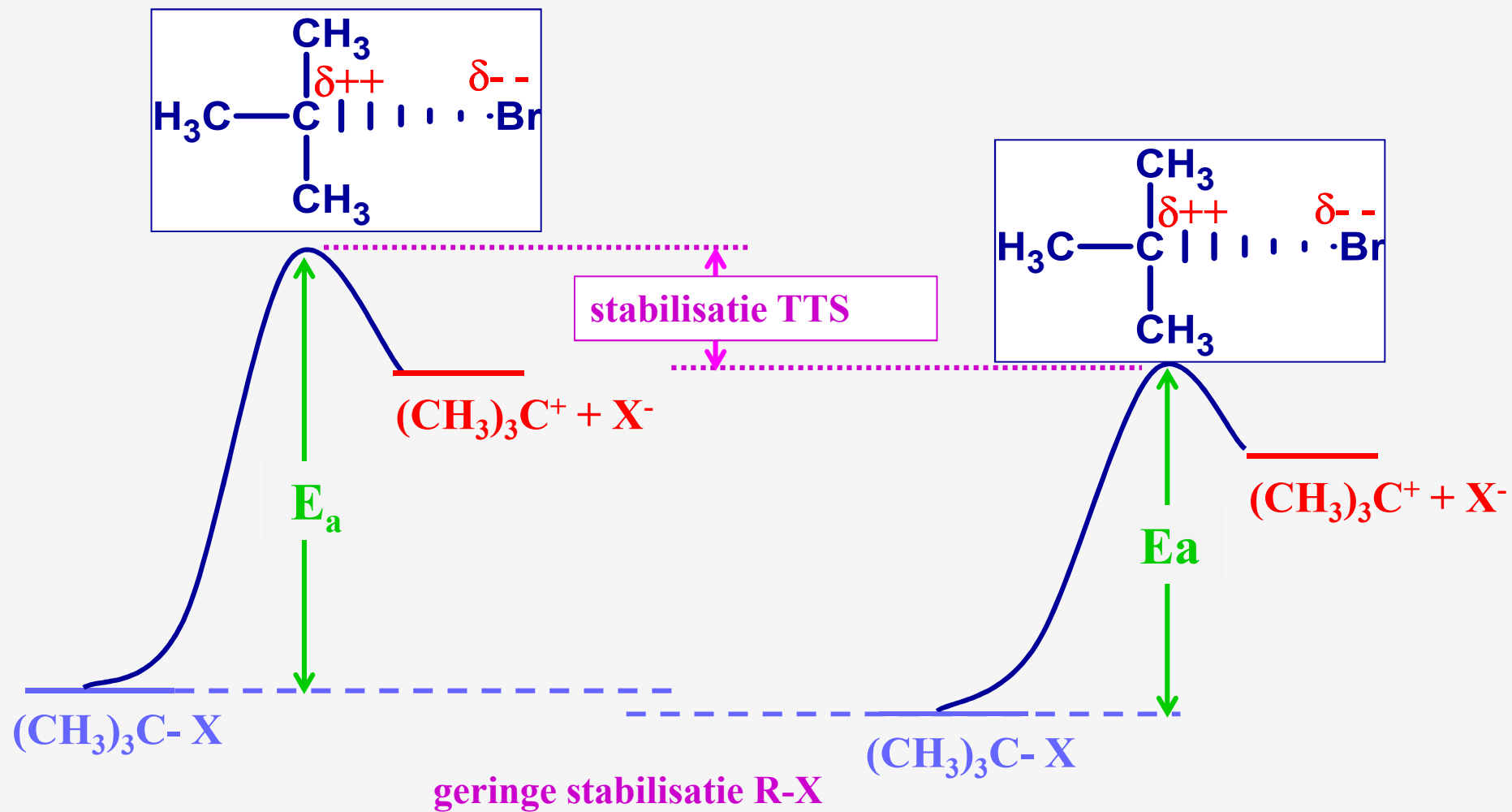
apolair solvent



polair solvent



stabiliseert TTS

apolair solventpolair solvent

	SN1
Mechanisme	Twee-stapsmechanisme
Kinetisch gedrag	SBS = unimoleculair R = [R-X]
Stereochemie	Inversie & retentie configuratie (racemisatie)
R-X	Tert > sec > prim > methyl Stabiel C⁺
Nucleofiel	Nucleofiel neemt pas deel na SBS
Solvent	Polair protisch Alkoholen, water....
Uittredende groep	I > Br > Cl > F zwakste base, beste uittredende groep

2. Nucleofiele substitutiereacties

♣ **SN2-type: nucleofiele substitutie 2^{de} orde**

♣ **SN1-type: nucleofiele substitutie 1^{ste} orde**

♣ **SN1 versus SN2**

SN2	SN1
Eén-stapsmechanisme	Twee-stapsmechanisme
SBS = bimoleculair	SBS = unimoleculair
R = [R-X] [nucleofiel]	R = [R-X]
Inversie configuratie	Inversie & retentie configuratie
Methyl > prim > sec > tert	Tert > sec > prim > methyl
I > Br > Cl > F	
zwakste base, beste uittredende groep	

Factor	SN2	SN1
R-X	Methyl > prim > sec > tert Sterisch ongehinderd	Tert > sec > prim > methyl Stabiel C ⁺
Nucleofiel	Sterk nucleofiel R ≈ [nucleofiel]	Nucleofiel neemt pas deel na SBS;
Solvent	Polair aprotisch DMF, DMSO, aceton..	Polair protisch alcoholen, water...
Uittredende groep	I > Br > Cl > F zwakste base, beste uittredende groep	

♣ Examenstof

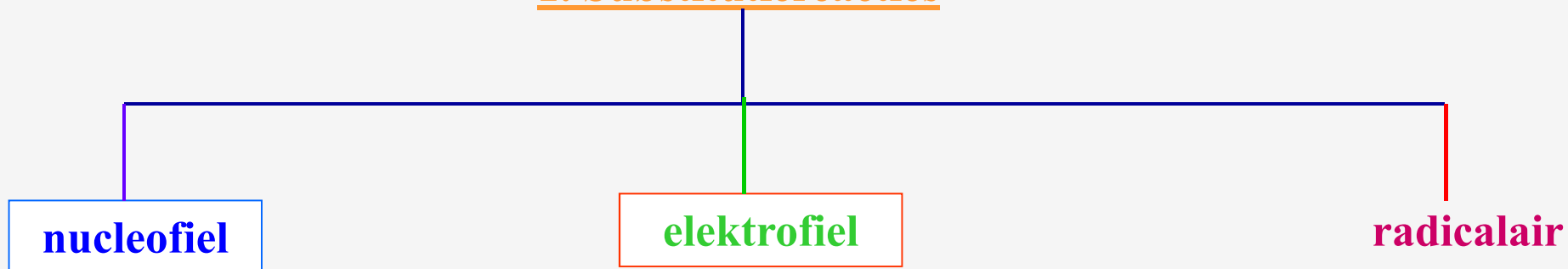
♠ **theoretische kennis** (collegenota's + hoorcollege)

- ◆ terminologie: p I-1 t.e.m. p I-7
- ◆ SN2: p I-7 t.e.m. p I-14
- ◆ SN1: p I-15 t.e.m. p I-20
- ◆ SN1 versus SN2: p I-20

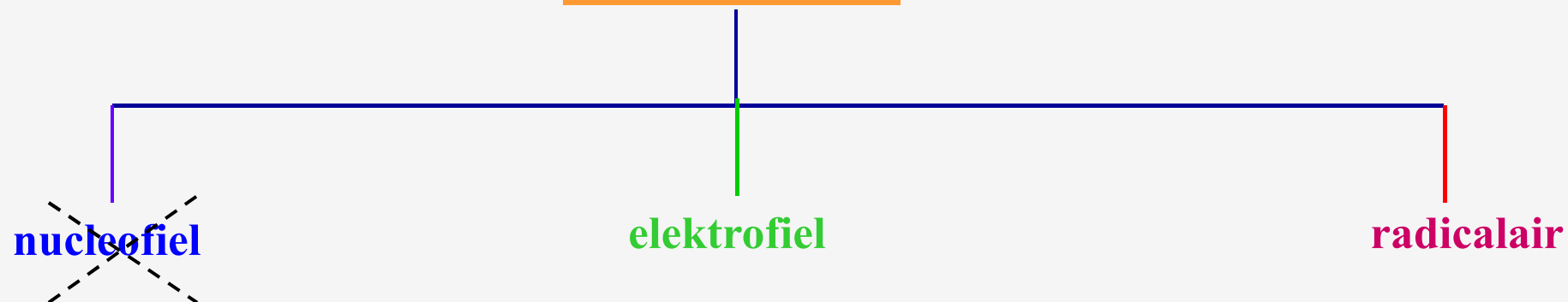
♠ **belangrijke vaardigheden**

- ◆ herkennen reactietype
- ◆ bepalen relatieve stabiliteit radicalen/carbeniumionen/carbanionen
- ◆ uitschrijven reactiemechanisme SN1/SN2
- ◆ bepalen relatieve nucleofiliciteit/leaving capaciteit
- ◆ bepalen van structureffect van R-X op SN1/SN2
- ◆ herkennen polair protisch solvent/dipolair aprotisch solvent
- ◆ bepalen solventinvloed op SN1/SN2

1. Substitutiereacties



2. Additiereacties



3. Eliminatiereacties

4. Omleggingsreacties

1,2 hydrideshift

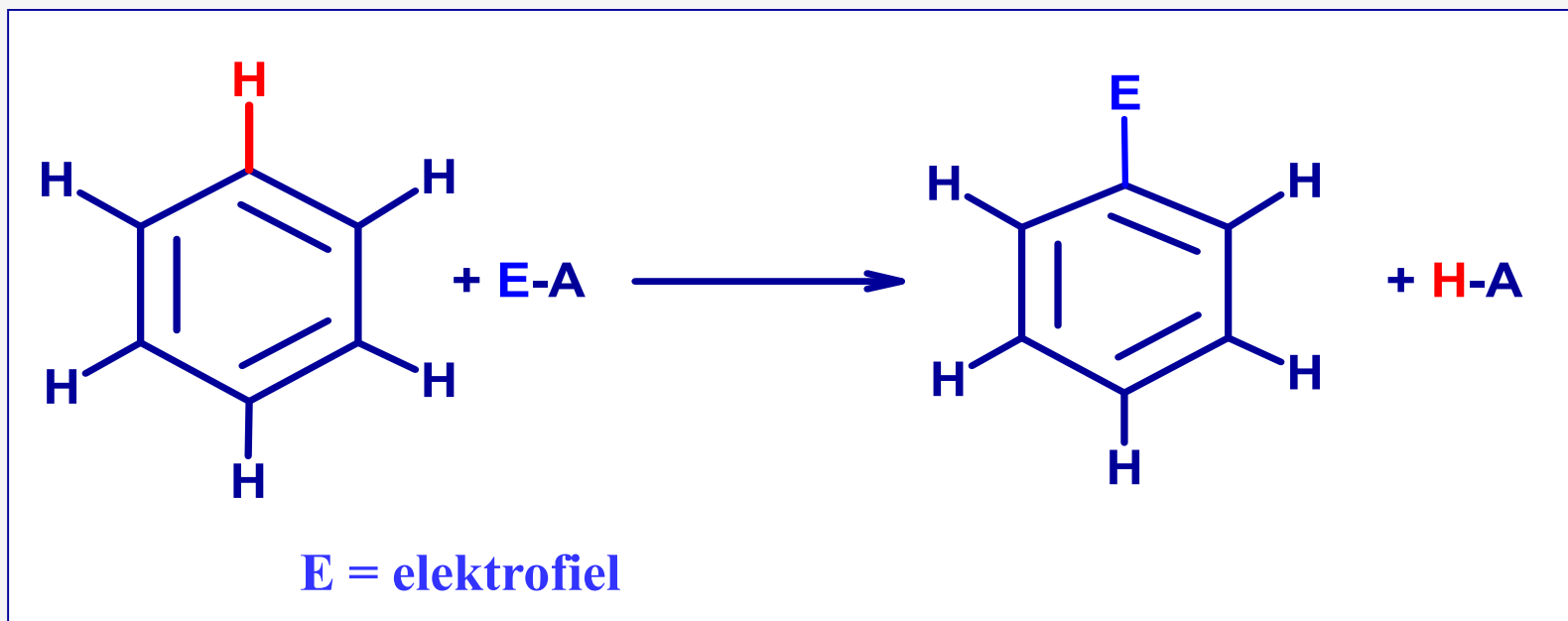
1,2 methylshift

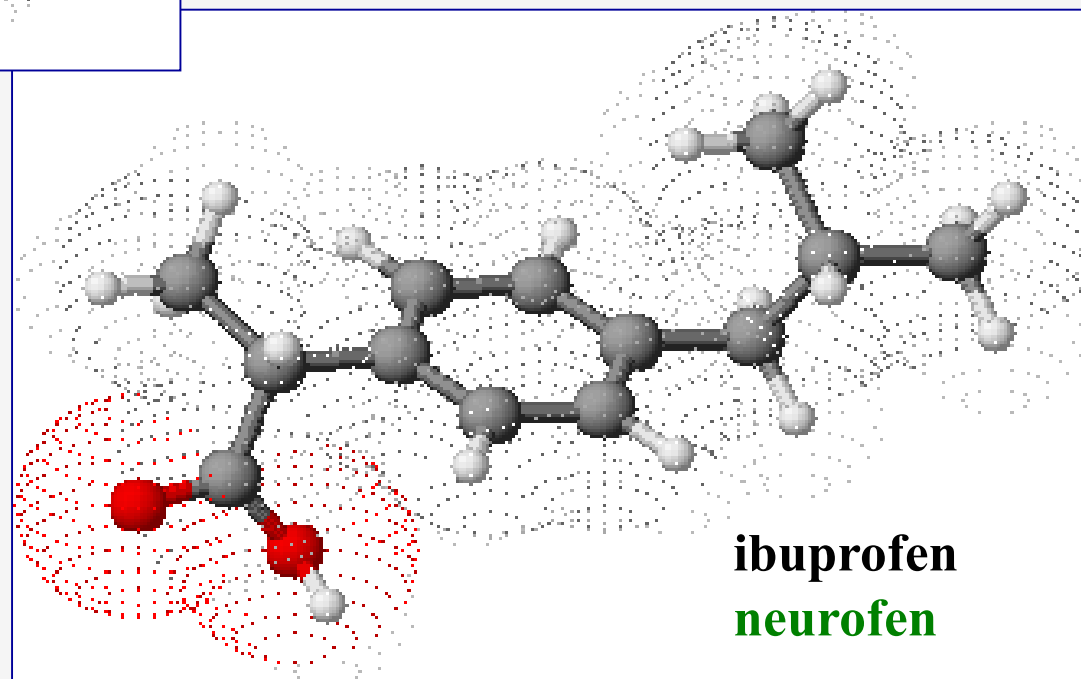
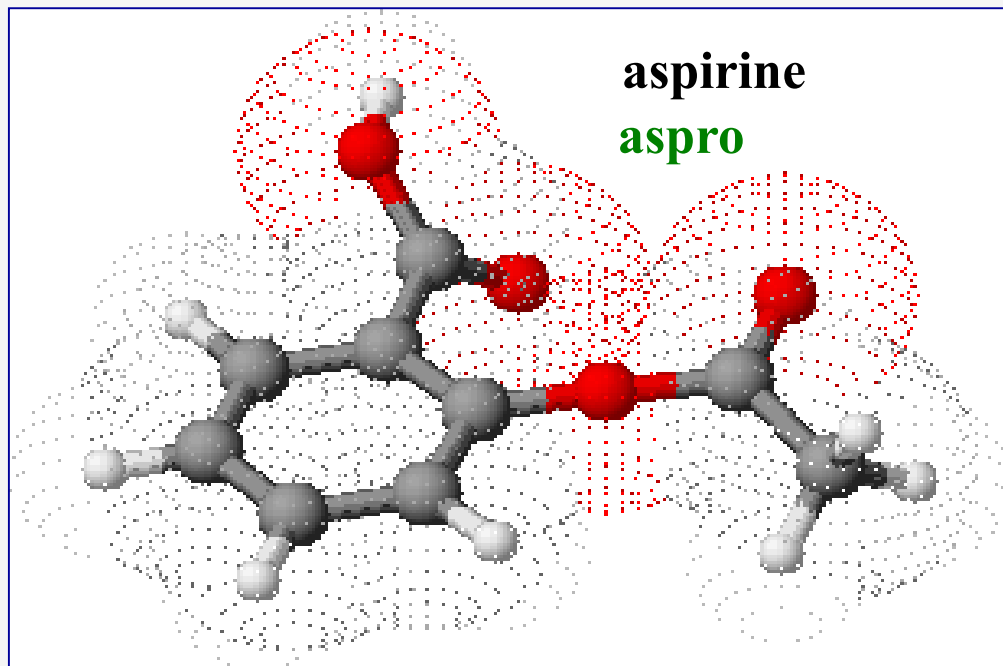
Belangrijke types chemische reacties

- 1. Terminologie**
- 2. Nucleofiele substitutiereacties**
- 3. Elektrofiele substitutiereacties**
- 4. Elektrofiele additiereacties**
- 5. Eliminatiereacties**
- 6. Radicaalreacties**

– aromatische elektrofile substitutie

1 σ -binding aromatisch sp^2C-H \rightarrow 1 σ -binding aromatisch sp^2C-E

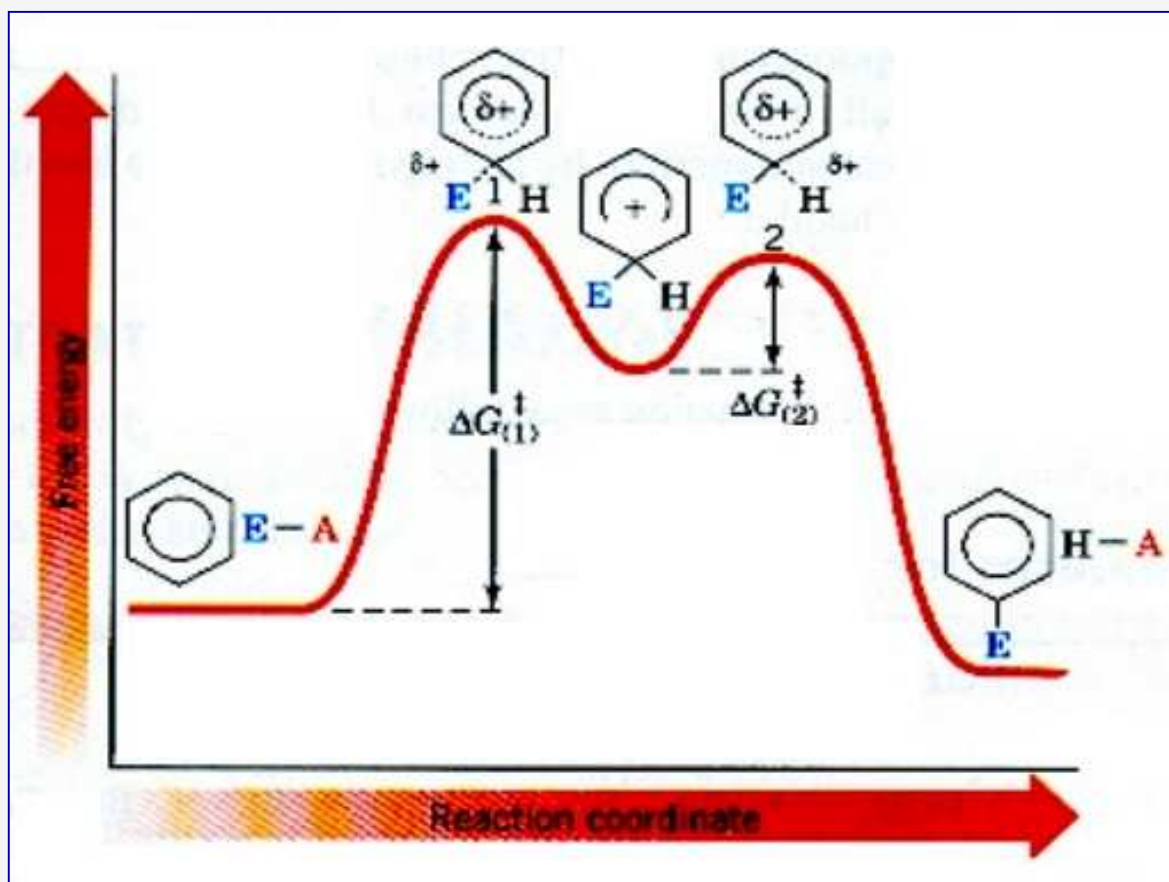
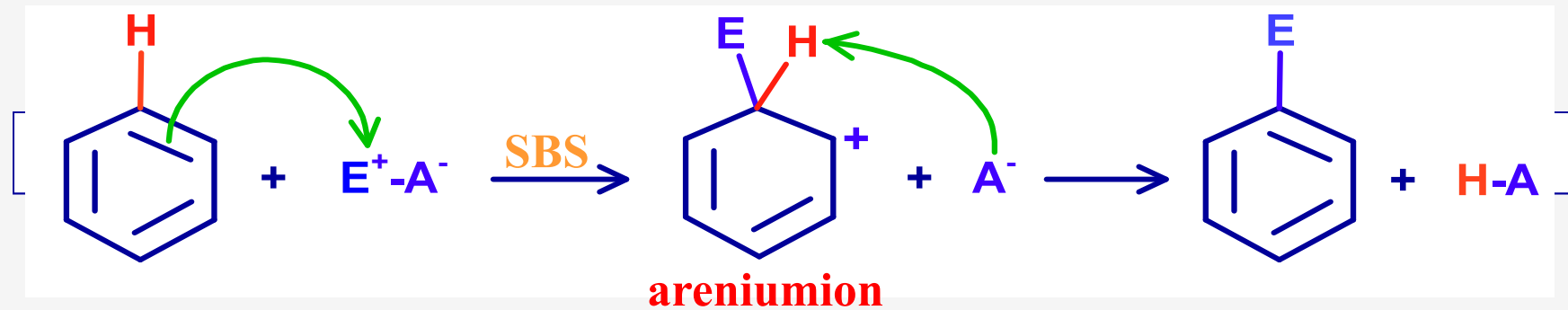


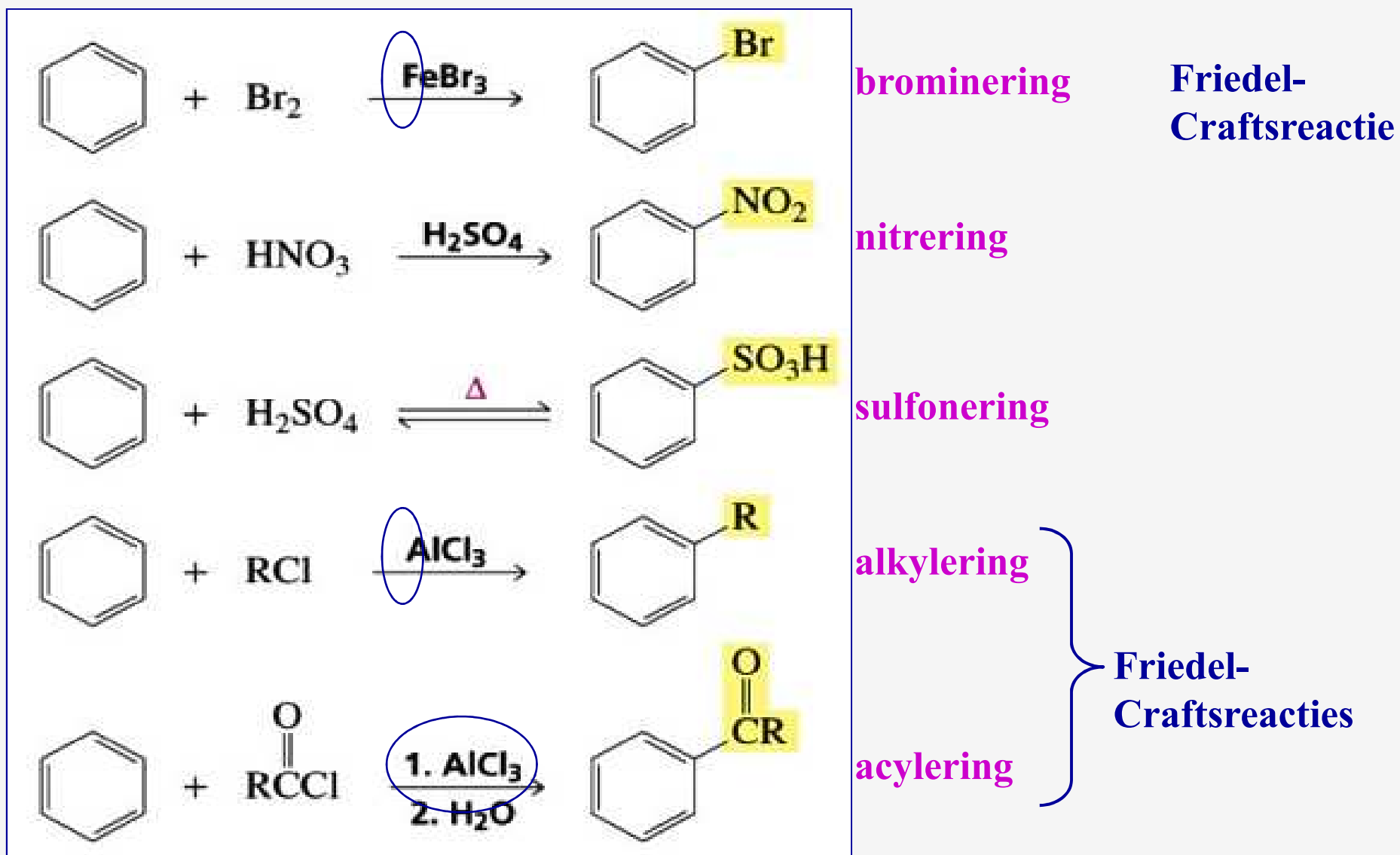


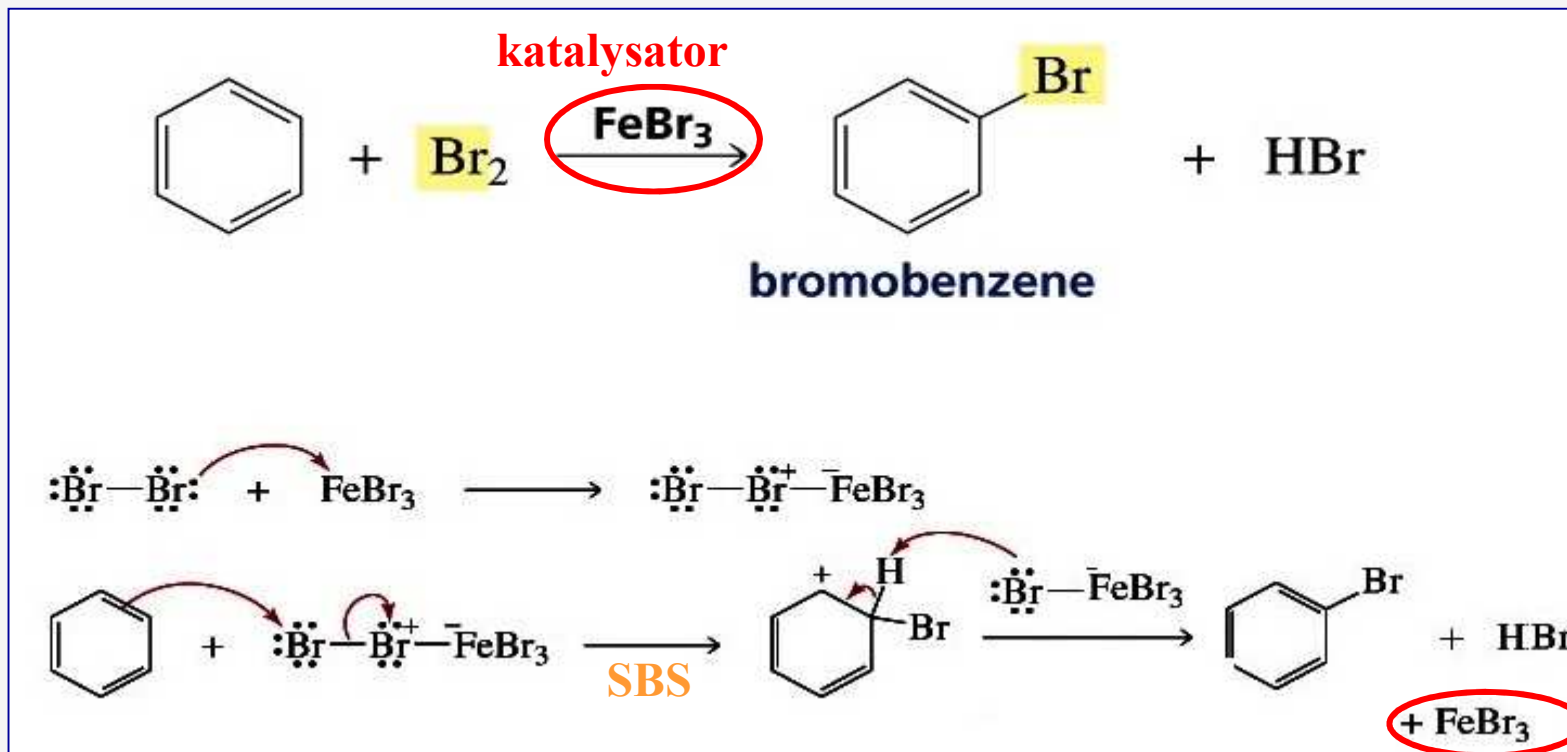
3. Electrofiële substitutiereacties

♣ **Mechanisme**

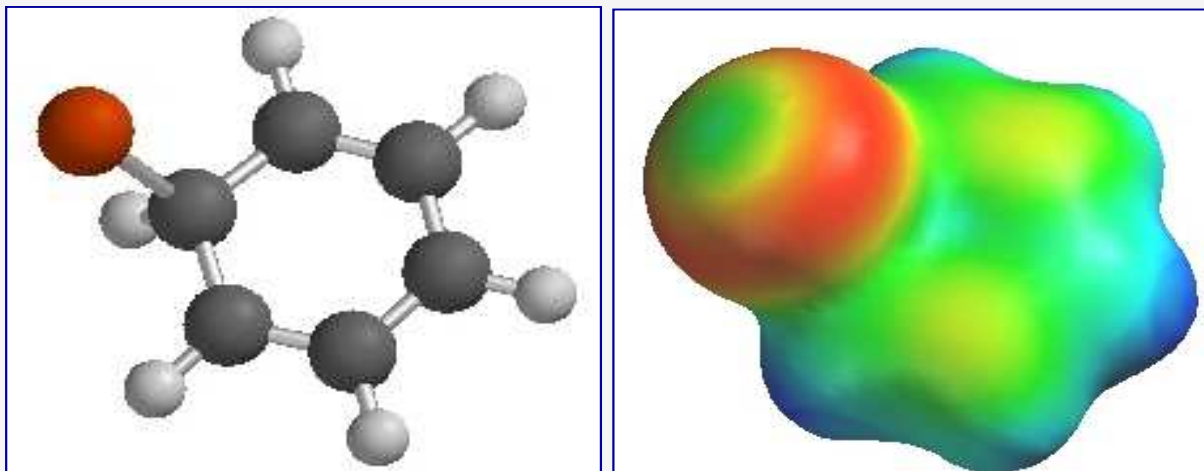
♣ **Effect van substituenten op reactiviteit & oriëntatie**







Benzeen-Br-areniumion

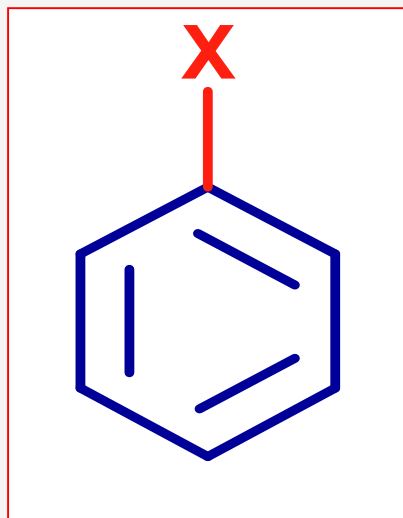


positieve lading in areniumion is gedelokaliseerd

3. Electrofiële substitutiereacties

♣ Mechanisme

♣ Effect van substituenten op reactiviteit & oriëntatie



$X \neq H$

reactiviteit

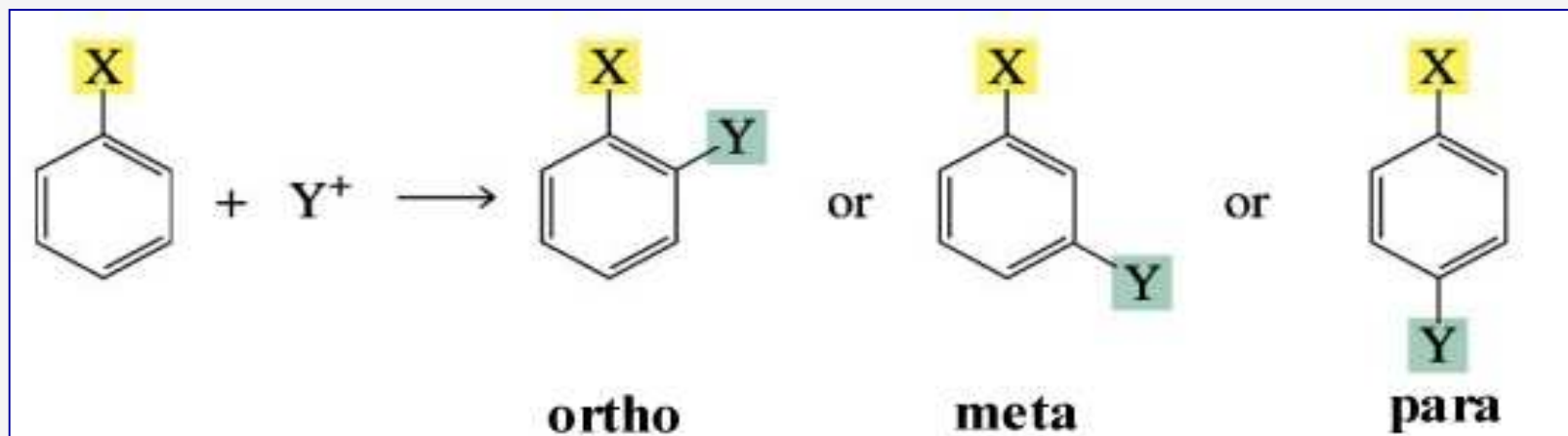


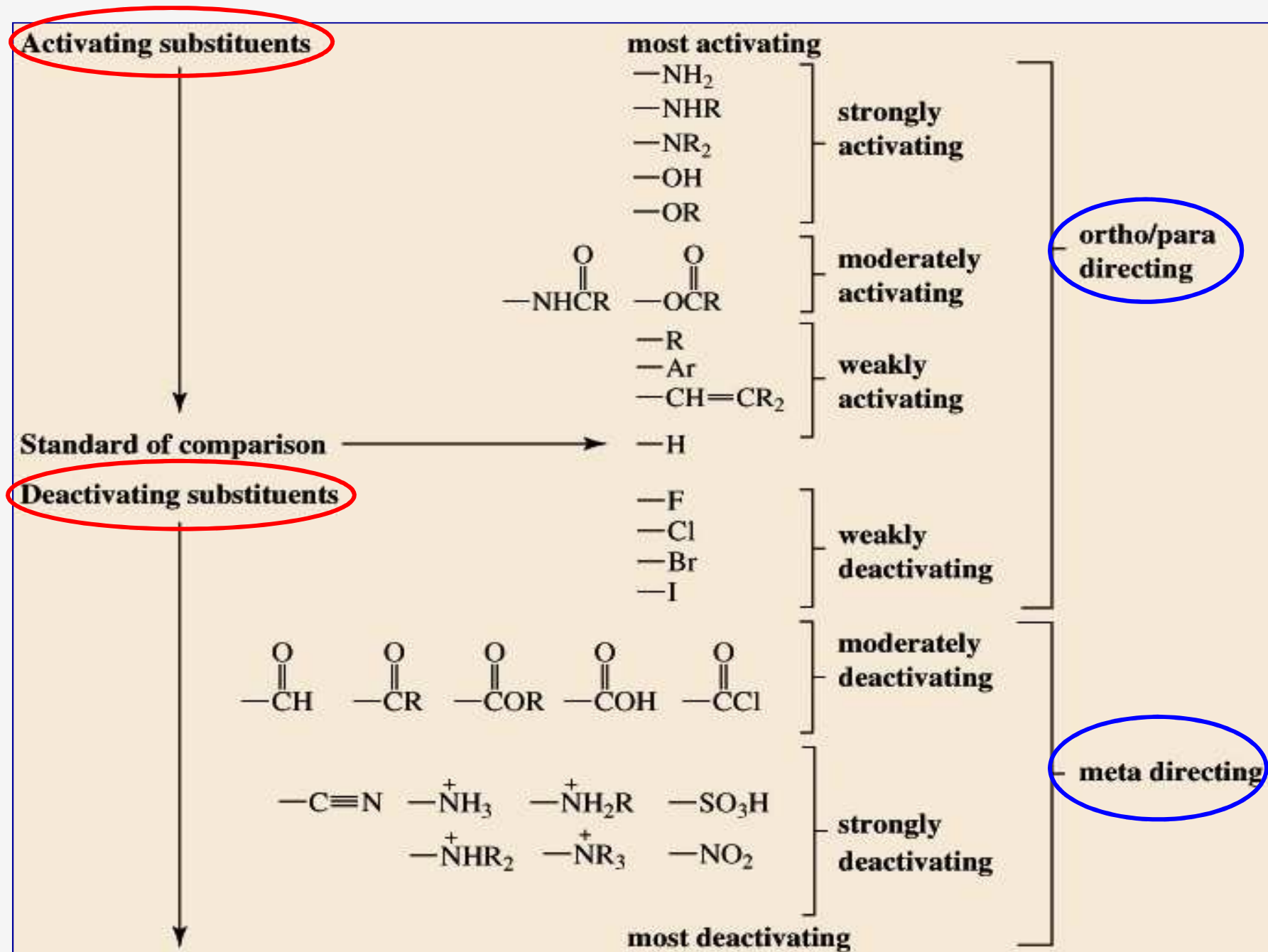
⇒ invloed op snelheid EAS

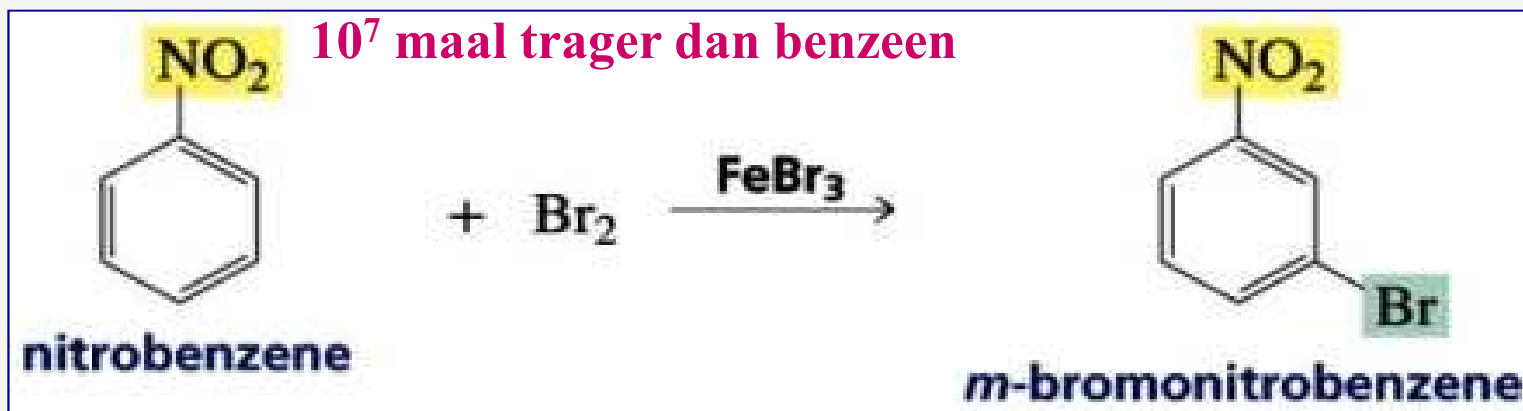
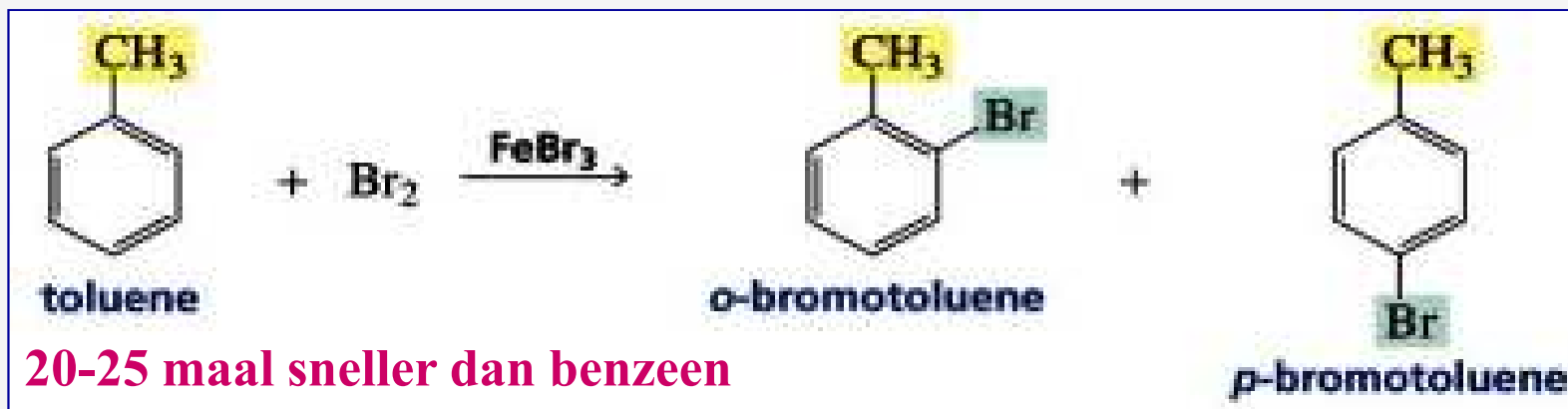
⇒ invloed op aanvalsplaats van E



oriëntatie; regioselectiviteit







Verklaring: inductieve & resonantie effecten

↓
zie oefeningenles

♣ Examenstof

♠ **theoretische kennis** (collegenota's + hoorcollege)

- ♦ **EAS mechanisme: p I-20 t.e.m. p I-22**
- ♦ **EAS substituentinvloeden: geen rechtstreekse theorievragen**

♠ **belangrijke vaardigheden**

- ♦ **uitschrijven reactiemechanisme EAS (+ vorming elektrofiel)**
- ♦ **herkennen/bepalen substituent \Leftrightarrow invloed reactiviteit/orientatie**