

- 1) Descriptions of C^{\oplus} , C^{\cdot} , C^{\ominus}
- 2) Reactivity of C^{\oplus} , C^{\cdot} , C^{\ominus}
- 3) Reactions of C^{\oplus} , C^{\cdot} , C^{\ominus}



carbocation ions

C(AMW) ~ 408-415

six valence e^-
electron deficientseven $v.e^-$
electron deficienteight $v.e^-$

unstable due to negative charge

} all three-coordinate C
only difference is
electronic structure

} all unstable
at carbon

Carbocations

3 filled bonding orbitals
1 empty orbital



$\Rightarrow sp^2$ hybridised
 \Rightarrow planar



- stabilised by e^- donors
- destabilised by e^- withdrawing groups

radical

3 filled bonding orbitals
(6 e^- in bonding orbitals)
1 e^- in non-bonding



\Rightarrow tends towards
 sp^3 hybridised
 \Rightarrow tetrahedral



- stabilised by e^- donors
- destabilised by EWGs

Carbanions

3 filled bonding orbitals
1 filled non-bonding orbital



$\Rightarrow sp^3$ hybridised
 \Rightarrow tetrahedral

full octet at C^{\ominus} , negative charge \Rightarrow

- stabilised by EWG
- destabilised by EDG



Substituent effects

N is electron donating
 N is electronegative \therefore electron withdrawing } both are true ... two competing effects

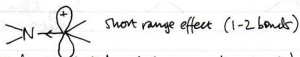
Inductive effect (σ -donating/withdrawing)

- Depends on the relative electronegativity
- Inductive effect

SHORT RANGE

electronegativities

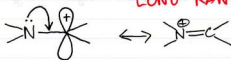
H	2.20
C	2.55
N	3.04
O	3.44
F	3.98
Cl	3.16
Br	2.96



π -donation/withdrawal (resonance/mesomeric)

- but also N has a lone pair

LONG RANGE if conjugated



(I, Si) 2.66, 1.90) — all a bit weird

I⁻ can diffuse e⁻ around a larger volume \therefore more stable than Br⁻, Cl⁻, F⁻

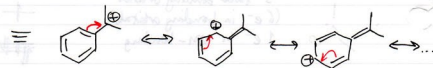
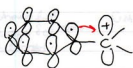
e.g.



allylic cation



oxocarbenium ion



- effectively "spreads" (delocalises) the positive charge over two (or more) centres — effectively halving (or more) the charge on each centre.

- much stronger than inductive effect
- BUT the donor must be conjugated with the accepting orbital i.e. depends on conformation of carbocation. (so if conformation prevents conjugation, only inductive effects present)



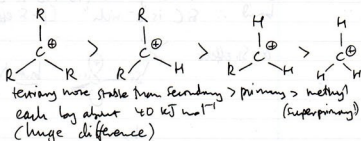
- π -donation depends on the ability of the atom to donate a lone pair
- therefore also depends on electronegativity so N > O > F

more inductively withdrawing than mesomeric donor.

\uparrow mesomeric effects always win over inductive effects except with fluorine

So what about :

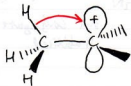
relative stability of C^{\oplus}



R_3C^{\oplus} 100 million times more stable than R_2CH^{\oplus}

Hyperconjugation

Donation of a pair of bonding electrons into an unfilled or partially filled orbital.



can only occur when C-H (or C-X) bond aligns with the carbocation p orbital



because donating bonding electrons, effect is weaker than π -donation of lone pairs:

weak inductive effects < medium hyperconjugation < strong mesomeric (π) effects

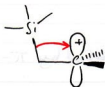
↳

Hyperconjugation: Corollary 1.

The donor bond in hyperconjugation must be able to overlap with the acceptor orbital i.e. rigid structures that hold donor orbital out of alignment are less stable.

Corollary 2

Silicon is fantastic at stabilising β -Carbocations

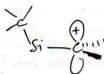


β -silyl carbocation is very stable



Because Si is electropositive (relative to C), it is able to donate e^- into $\sigma-C$ bond \therefore $\sigma-C$ is e^- rich" (β -Si effect).

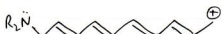
α -Si effect



but this is actually destabilising relative to β -Si effect



when $x=Si$, formation of 5th bond is not unreasonable



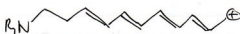
more stable than because nitrogen lone pair is conjugated to C^+



NO_2
 π -withdrawing
activates $C=O$

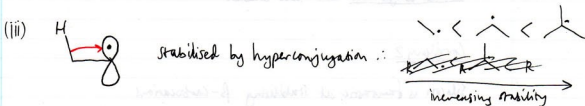
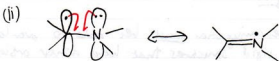
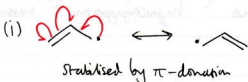


F
 σ -withdrawing (short range)
cannot activate $C=O$



not conjugate to N lp \therefore not stabilized.

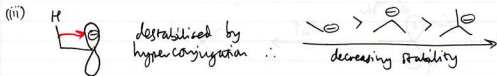
Radicals



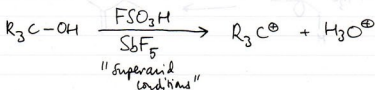
Carbanions



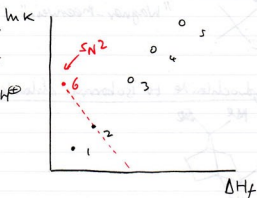
(ii) S_N1 - same argument as before - adjacent e^- donate destabilizing.









Measure stability of R_3C^+ from ΔH_f of



for solvolysis of RBr eg in $EtOH/H^+$

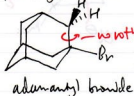


- ①  
- ② 
- ③ 
- ④ 
- ⑤ 

$\therefore R_3C^+$ is being formed in this Nu^- substitution rxn

\therefore the mechanism is S_N1

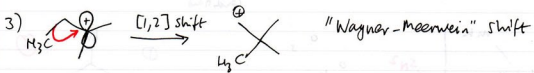
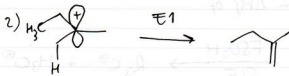
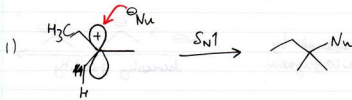
Also relative rates of solvolysis ($EtOH/H^+$)



10^{-4}

\leftarrow - worth about this bond \therefore C-H bonds cannot effectively hyperconjugate with C^+

Reactions of Carbocations

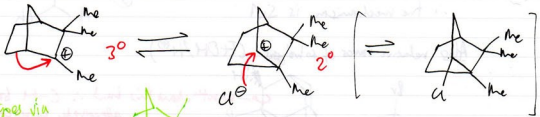
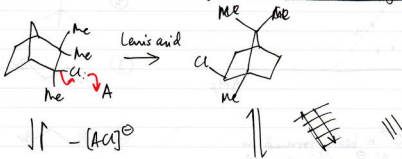


Rearrangement of camphene hydrochloride to isobornyl chloride.

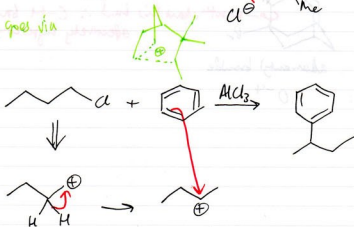
Chengde
Camphene, p. 1449

Non-classical
Carbocations
p. 973

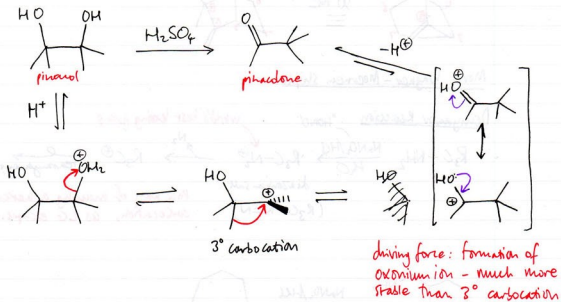
Camphene
- isobornyl
p. 981-982



actually goes via

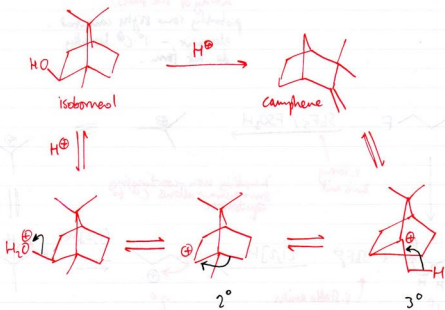
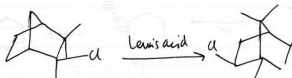


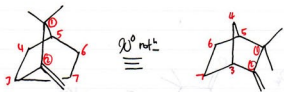
Pinacol rearrangement



The driving force is the formation of a more stable carbocation.

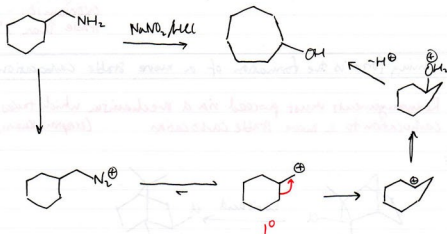
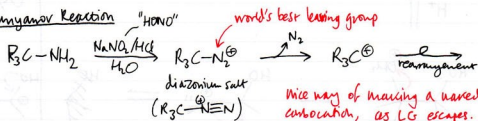
\Rightarrow Rearrangements must proceed via a mechanism which takes a less stable carbocation to a more stable carbocation (excepts Kramm, though).



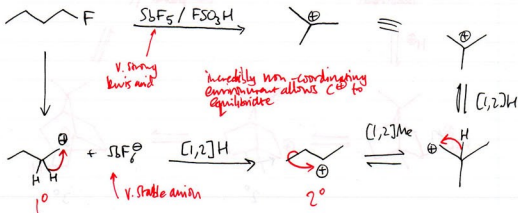


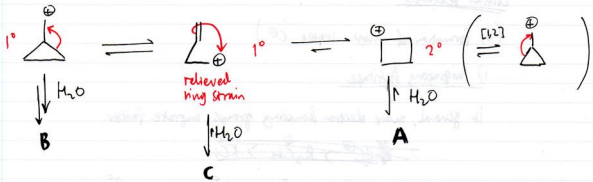
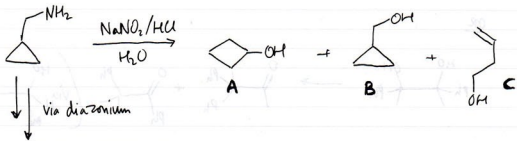
More Wagner-Meerwein shifts

Demjanov Reaction



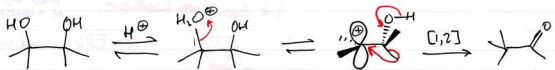
(technically wrong, a slight hiding of the facts)
probably some slight concerted element - $1^{\circ} C^{\oplus}$ basically do not form.



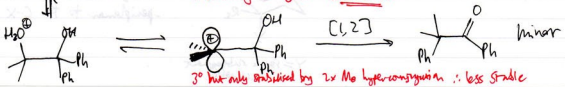
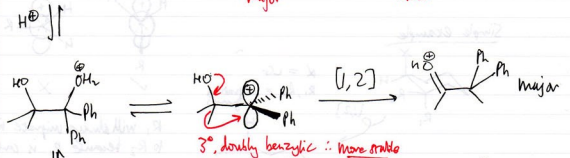
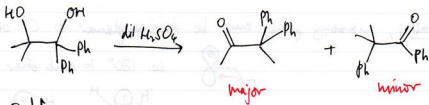


CPBL4

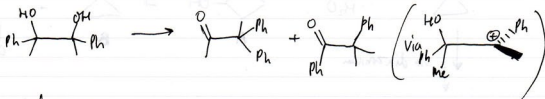
Pinacol / Pinacolone Rearrangement



What about asymmetric examples?



OR

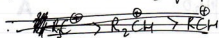


Control features

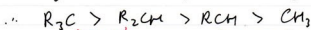
(0) formation of most stable C⁺)

1) Migratory Aptitude

In general, more electron donating groups migrate faster.



3° 2° 1° 0°



Ph relatively electron rich

any groups somewhat here but depends upon substituents.

hydride shifts around above here, depends on steric and electronic factors - proton small and solvent better at migration if sterically hindered.



X = EDG more migratory aptitude

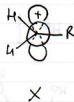
X = EWG less migratory aptitude

2) Stereoelectronic factors

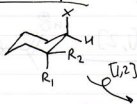
Generally, migrating group must be anti-periplanar to C⁺ orbital



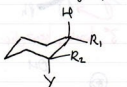
i.e. 180° to each other



Simple example



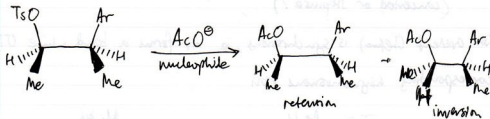
X = LG
R₁, R₂ = migrating groups



Y = some subsequent nucleophile

R₁ will always migrate in preference to R₂ because R₁ is anti-periplanar to the C-X bond

Complex example

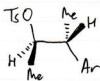


retention or inversion and rate of rxn depends on aryl group.

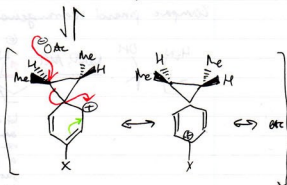
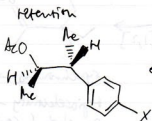
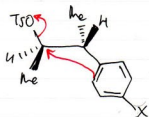
Ar	retention	inversion	rate
<chem>COC1=CC=CC=C1</chem>	100%	0%	fast
<chem>C1=CC=CC=C1</chem>	60%	40%	
<chem>O=[N+]([O-])C1=CC=CC=C1</chem>	1%	99%	slow

EDG v. good π donor \downarrow
 EWG v. poor π donor

Answer: The aryl group ^{can act} as a participating neighbour (neighbouring group participation).



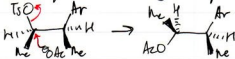
Ar is anti-periplanar to OTs.



Aryl group protects from inversion i.e. from nucleophile.

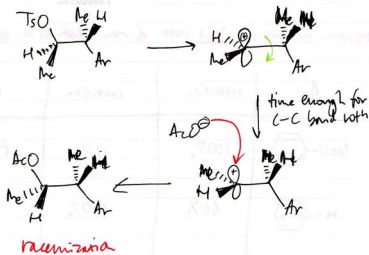
Arenium ion stabilized by X=EDG
destabilised by X=EWG

If Ar not v. good at stabilising C^+ , get S_N2 :



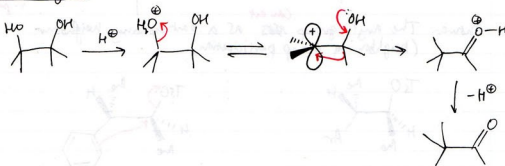
3) Timing / Synchronicity of a rearrangement
(concerted or stepwise?)

Rxn of acetate (below) is synchronous, i.e. Ar forms a bond while OTs leaves.
(Corresponding asynchronous rxn)

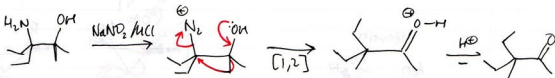


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Pinacol (again)



Compare pinacol rearrangement with Tiffeneau Demajov.

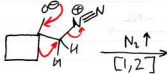
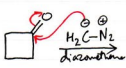


lot of argument over whether this rxn is synchronous or asynchronous - shown as synchronous here

synchronous \rightarrow stereochemical control
regioselectivity - only substituents on alcohol carbon can migrate

Superior alternative

diazohexane:



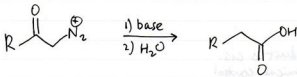
Homologation of a ketone

driving force is relief of ring strain in 4-ring.

Other common rearrangements (exam fodder)

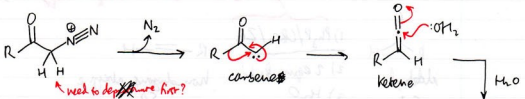
Migrations to electron-deficient carbon

Wolff rearrangement



- 2 possibilities:
- stepwise
 - concerted

Stepwise



Carbenes

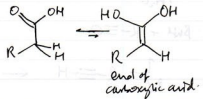


singlet carbene

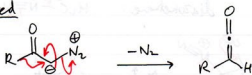


triplet carbene

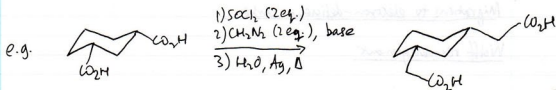
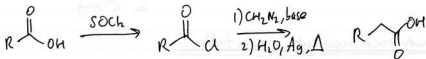
six-e⁻ neutral carbon
[electron deficient]



Concerted



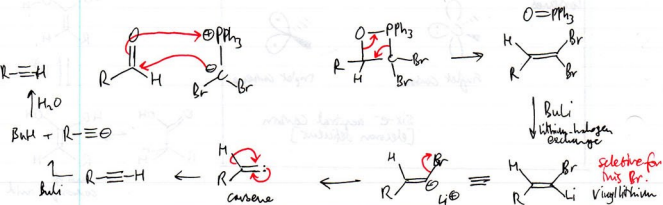
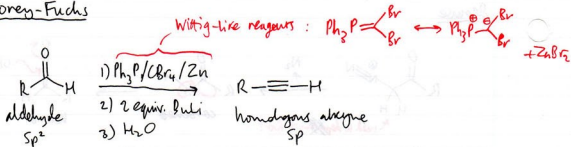
Arndt-Eistert Homologation

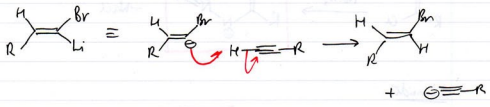
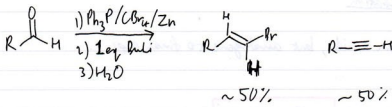


N.B. - S.M. is cis and product is cis.
 ∴ have stereochemical control

rearrangement proceeds with retention of stereochemistry.

Corey-Fuchs





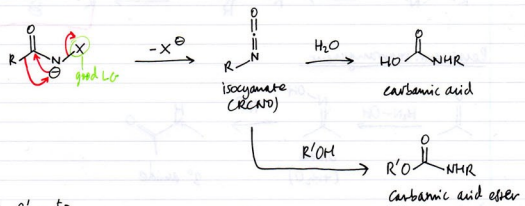
L6/6
 Fri 27 Feb. 2009.

Migrations to electron-deficient carbon...

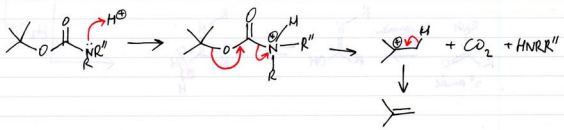
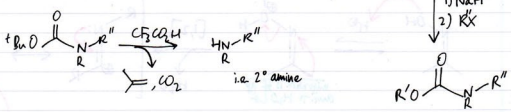
Wittig rearrangement (as before)

Migration to electron-deficient nitrogen

Common mechanism (Curtius, Lossen, Schmidt, Hofmann rearrangements).



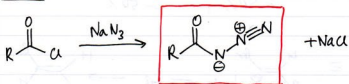
If $R' = \text{tBu}$



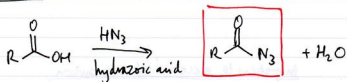
Hofmann degradation

Br_2/NaOH from amide, but analogous to final steps

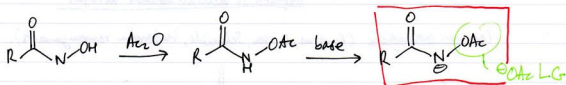
Curtius



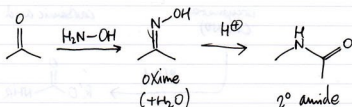
Schmidt



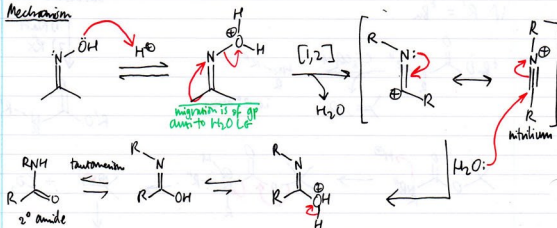
Lossen



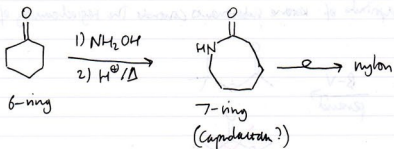
Beckmann rearrangement



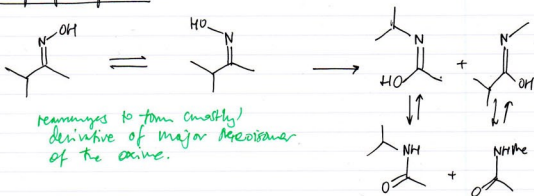
Mechanism



Application

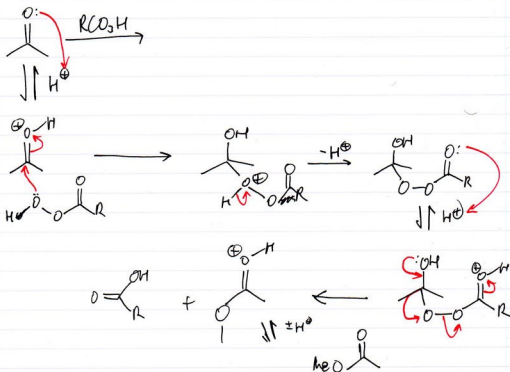


Which group migrates?



migration to e- deficient oxygen

Baeyer-Villiger Rearrangement



Migratory aptitude decides which groups migrate

Migratory aptitude of ketone substituents controls the regiochemistry of the product

