Course Chem 343 11 AM Lecturer Sam Gellman

Day Monday Date 11/14/11

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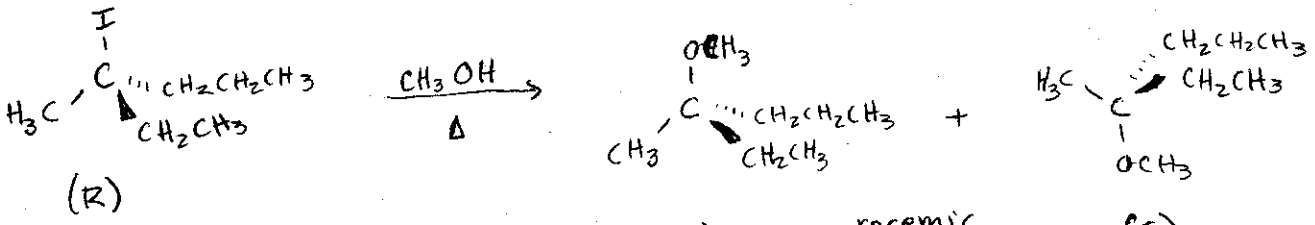
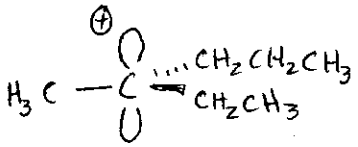
Recall: stereochemical consequences of S_N1 Mechanism



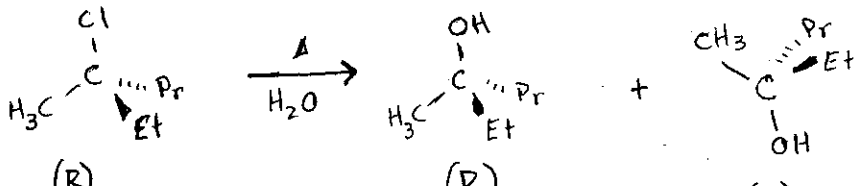
(R) (R) racemic (S)

Carbocation intermediate



Planar!

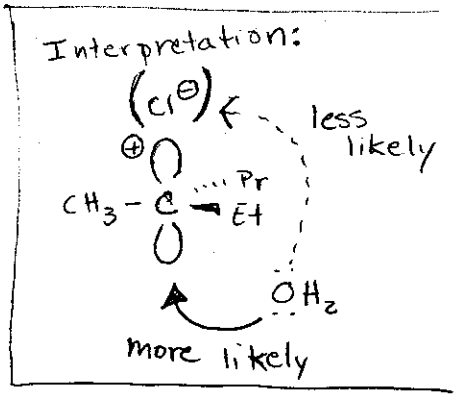
Sometimes in such cases, loss of configurational information is incomplete:



(R) (R) 30% (S) 70%

not exacty racemic

Interpretation:



* For this course, assume complete racemization if not otherwise indicated but be prepared to account for this issue if indicated.

Overview of $S_N1/S_N2/E1/E2$ rxn manifold:

⇒ Summary Table 9.7

In terms of predicting rxn outcomes:

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some situations easy to predict...

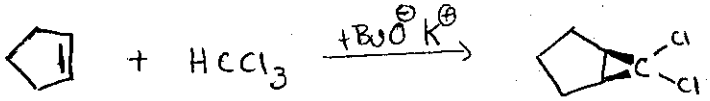
① 1° alkyl halides ⇒ NO $S_N1/E1$ pathways
∴ usually S_N2, or E2 with strong base

② 3° alkyl halide ⇒ No S_N2
Strong base ⇒ E2
Polar protic solvent (H_2O, CH_3OH, EtOH) ⇒ $S_N1/E1$ pathway

③ 2° alkyl halides
All pathways must be considered...
- Need polar protic solvent for S_N1, E1, etc

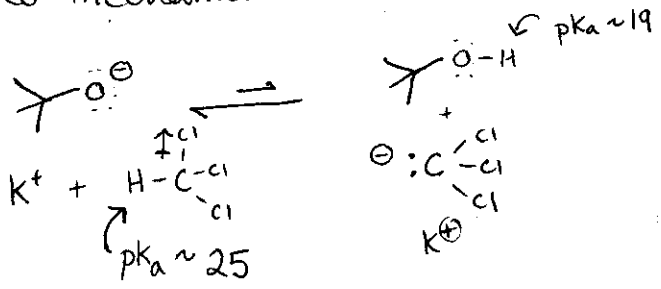
Carbenes - highly electron-deficient carbon atom

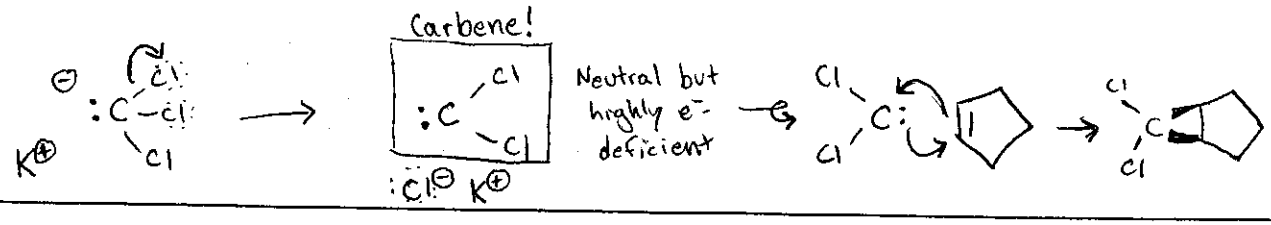
Consider:



(+ KCl + tBuOH)

Accepted mechanism:





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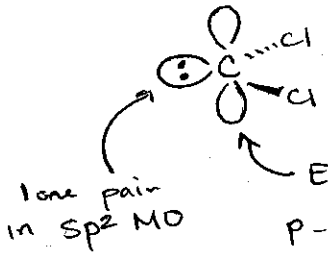
A closer look at the Carbene:



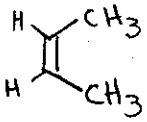
6 e⁻ around Carbon
↳ very electron deficient

Behaves like:

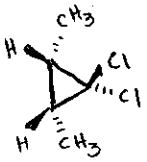
"  " Both nucleophilic and electrophilic at the same time!

Insight from stereochemistry leads us to conclude that cyclopropane ring formation is concerted.

Ex:

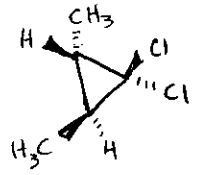


$\xrightarrow[CHCl_3]{t\text{BuOK}}$



Methyl groups cis on ring

(**NOT** observed:



trans)

2 new C-C bonds form at once ("concerted")

Carbenes are very reactive. "Hard to tame" synthetically

Ex: ":CH_2" ("methylene") very hard to control

Zinc useful for taming carberes

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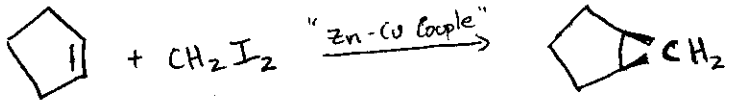
Simmons-Smith Reagent

⇒ "carbenoid" - metal atom taming a carbene

Ex:



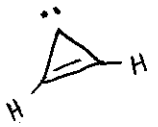
(alloy of Zn^0 and Cu^0 metals)

Organo-Zinc intermediate ("Simmons-Smith Reagent")

$$CH_2I_2 + Zn^0 \longrightarrow I-CH_2-Zn-I$$

(reacts as if "$:CH_2$")
less voracious

Carbenes - vast quantities in interstellar space



$H_2C=C=C:$