**Reaction of Alkanes**

**Radical Halogenation:**

***NOTE:* Unlike carbocations, radicals do not rearrange/migrate**

The reaction between Cl2 or Br2 (NO I2 OR F2) and Alkanes

Can be summarized as 3 steps:

Mechanism:



Then… radical reacts with alkane:





More complicated one



However, if it was Cl2 , Cl2 is less selective than Br2 which will give 44% primary and 56% secondary

\*How to predict the percentage for this reaction?

|  |  |  |  |
| --- | --- | --- | --- |
|  | 3° > | 2° > | 1° |
| Br• | 1600 | 82 | 1 |
| Cl• | 5 | 3.8 | 1 |



3° = (0)(5) = 0

2° = (2)(3.8) = 7.6 % 2° = 7.6 / (13.6) x 100% = 56%

1° = (6)(1) = 6 % 1° = 6 / (13.6) x 100% = 44%

Total = 13.6

What if there is a resonance situation:



Recall Br2 or Cl2 will react with double bond if there is no radical, which means electrophilic addition competes with radical halogenation.

How to avoid competition? However, Br2 or Cl2 is usually easier to break and does not require initiator. HBr or HCl on the other hand will require initiator or it will go through the reaction as Note #1.

Using radical initiator: HOOH, ROOR OR NBS

For example:



**The most important reactions in second year:**

**SN2 : Nucleophile Substitution Reactions (one step) LG and Nu refers to page 6-7.**



**If it is a tertiary alkane, SN2 won’t happen.**

**Product is invert.**

**SN1: Nucleophile Substitution Reactions (two steps)**

 **If it is a primary alkane, SN1 won’t happen.**

**Product can be both configurations.**

**What is the different?**

**SN1 won’t happen at primary alkane, and SN2 won’t happen at tertiary alkane.**

**SN1 can be done by weak base (H2O), SN2 requires strong base.**

**SN1 and SN2 won’t happen, if the LG is on a double bond.**

**Ie.**



**Aprotic (non-polar, no OH, NH) solution promote SN2, Protic (OH, NH) solution promote SN1**

Protic *vs* Aprotic

- OH/NH: can H-bond - no OH/NH





**SN1 two steps which mean migration might happen. SN2 everything happen at one step, no migration.**

**For example:**



Intermolecular & Intramolecular Reactions

⮱ between 2 molecules ⮱ within one molecule

⇨ compare to intermural *vs* intramural sports

* If Nu- and LG are in the same molecule:



Intramolecular usually favored ⇨ doesn’t need to find 2nd molecule

(low conc. favors intra)

Ring size: 5-6 membered rings favor Intramolecular



3-4 membered rings ⇨ ring strain favor Intermolecular

7+ rings ⇨ ends far apart

What is LG (leaving group)?

Most common: Halides (I,Br,Cl)

General rule: weaker base=better LG

However, if OH (strong base) react with acid, it will become H2O.



Nu: Strong base, have a pair of electrons

General rule: Opposite of LG. Strong base=better Nu

Aprotic solvent = non-polar (No OH, NH)

Protic solvent = polar (have hydrogen bonding, OH, NH)

**However, beside Nucleophile Substitution Reaction, Elimination Reaction can also happen.**



**E2: Elimination Reaction (one step)**

Generally,

Trans and substituted is more stable

**However, three special situations need to consider:**



**E1: Elimination Reaction (two steps)**

E1 Might have migration.



In Summary:

**E2 with one step, E1 with two steps, as a result, E1 might have migration if there is an improvement.**

**E2 can do every degree of reaction, E1 can not do primary reaction.**

**E2 require strong base, E1 can be done with weak base.**

**Polar aprotic solvent promote E2, non-polar protic solvent promote E1.**



Cyclohexanes: H & LG must both be axial to be anti



