

Subject: Alkyl halides

↑ سال١

↑ سال٢

دیکس ۱۰

مذكرة

۲۰۲۱ / ۱ / ۲۰

* The general formula: $R-X$ halogen
alkyl halide

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الـ بـ عـ اـ فـ ضـ اـ لـ اـ

صـ يـ بـ عـ اـ فـ ضـ اـ لـ اـ

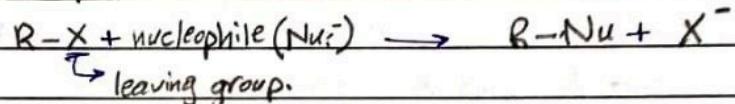
1) Primary: $R-CH_3-X$

2) Secondary: $R-CH_2-X$

3) Tertiary $R-C(X)_3$

Reactions of alkyl halides:-

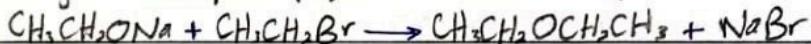
I nucleophilic substitution reaction



Types of nucleophiles:-

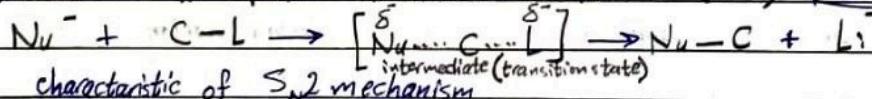
1) Oxygen nucleophiles 2) nitrogen nucleophiles 3) sulfur nucleophiles

4) halogen nucleophile (I^-) 5) carbon nucleophiles



Mechanism

1) Bimolecular nucleophilic substitution mechanism. (S_N2) S_N2 is one step mechanism



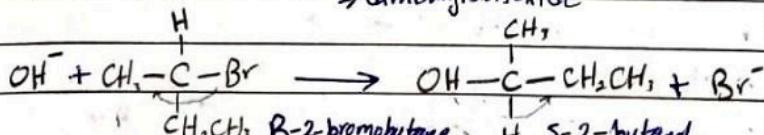
characteristic of S_N2 mechanism

1- rate of reaction = constant [alkyl halide][nucleophile].

2- inversion in stereochemistry of the product compared to the reactant.

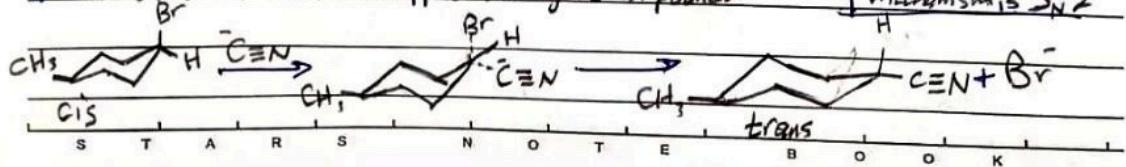
3- rate of reaction with primary halide > secondary > tertiary.

* It needs ^{Polar} aprotic solvent:- 1) acetone 2) dimethylsulfoxide



If we notice an inversion orientation of the chiral centers we know that the mechanism is S_N2

* The same mechanism is applied on cyclic compounds.



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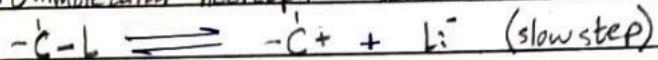
Arrange the following compounds in order of decreasing S_N2 reactivity toward sodium ethoxide: secondary CH_3 primary CH_3 primary
 $\text{CH}_3\text{CH}_2\text{CH}_2\text{Br} < \text{CH}_3\text{CHCH}_2\text{Br} < \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Br}$

كلوريد الإيثيل (الثاني) < كلوريد الإيسي (الأول)

$\text{S}_{\text{N}}2$ is one

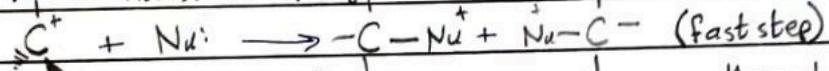
$S_{\text{N}}1$ is one
step mechanism

(2) Unimolecular nucleophilic substitution mechanism ($S_{\text{N}}1$)



* The bond between carbon atom and the halogen is broken heteronitically.

* The slowest step of any reaction determines the overall rate of the reaction.



* $S_{\text{N}}1$ mechanism form a racemic mixture, as the carbon atom is sp^3 hybridized.

* Aprotic

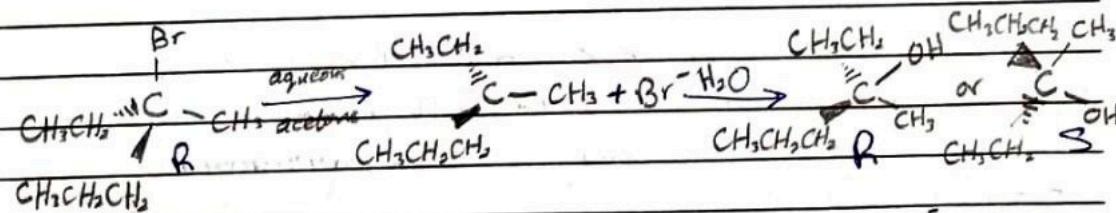
characteristic of $S_{\text{N}}1$ mechanism

1- rate of reaction = constant [alkyl halide]

2- Inversion and retention is stereochemistry of the product

compared to the reactant. Forming racemic mixture.

3- rate of tertiary halide > secondary > primary halide

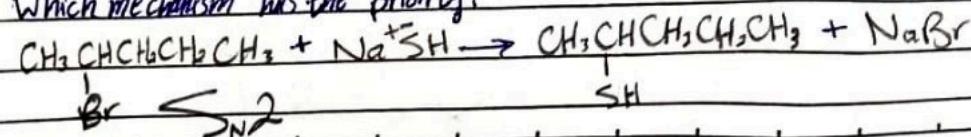


* Negative ions are more nucleophilic than neutral molecules: $\text{OH}^- > \text{H}-\text{OH}$

* Elements in lower periods/rows are more nucleophilic: $\text{HS}^- > \text{OH}^-$

* Elements in greater column are less nucleophilic: $\text{F}^- > \text{N}^- > \text{R}-\text{O}^- > \text{S}^-$

Which mechanism has the priority?



$\text{Br} \leftarrow S_{\text{N}}2$

S T A R S N O T E B O O K

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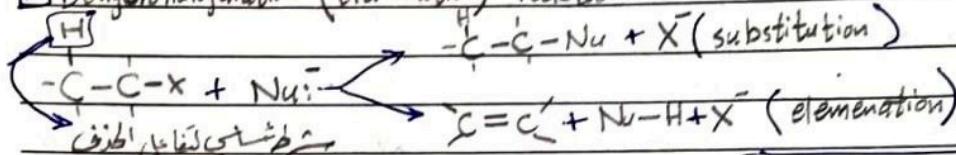
الموارد

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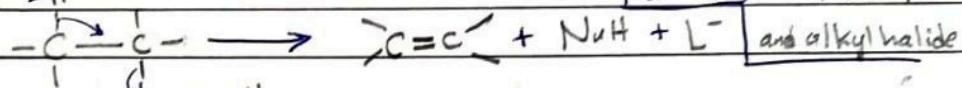
$\text{PCl}_3 \approx 10$

2) Dehydrohalogenation (elimination) reaction.

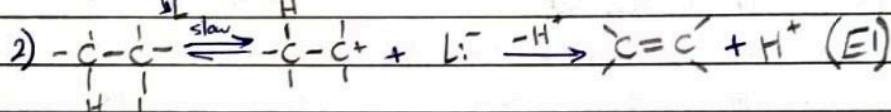


Mechanisms

1) Bimolecular elimination mechanism (E_2)

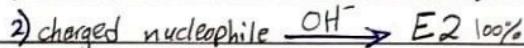
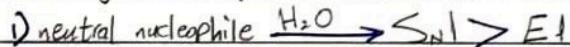


The rate of reaction is
depends on the
concentration of nucleophile
and alkyl halide

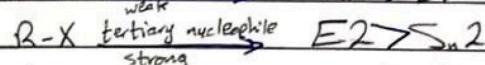


* The mechanism of E_1 share the first step with $S_{N}1$, so both products are possible.

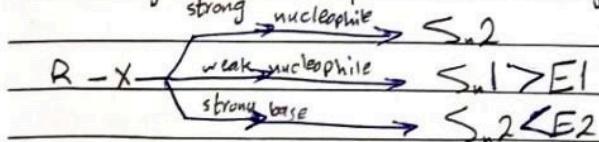
* Tertiary halides prefer E_1 and $S_{N}1$ more than E_2 and $S_{N}2$. However,



* Primary halides prefer E_2 and $S_{N}2$ more than E_1 and $S_{N}1$.



* Secondary halides can pass a reaction through all mechanisms.



Notes - In alkenes, when
the double bond is
located between more
alkyl groups, eventually
the compound is more
stable

