Module 3, Lecture 6

Structure and Reactions of Organic Molecules

Introduction to Reaction Mechanisms
Organic Reactions

James Crowley

jcrowley@chemistry.otago.ac.nz

Dr. Bill Hawkins

bhawkins@chemistry.otago.ac.nz

References to Brown *et al* text shown in BLUE

1

Learning Objectives:

- **to have an understanding of "curved" arrow notation**
- **to have an understanding homolytic and heterolytic bond cleavage**
- **to begin have an understanding of nucleophilic substitution reactions**
- **to be able to identify S_N2 reaction mechanism**

Textbook: **Chapters 26 and 27, sections 26.3, 27.4-27.5, Brown**

2

Organic Chemical Reactions

As most biological molecules are organic (carbon-based) it is important to understand the principles of organic chemical reactions to fully appreciate the changes undergone by biological systems.

The detailed process of an organic chemical reaction (i.e. the process of transforming molecules by making and breaking bonds) can be explained and manipulated by using the concepts of ***reaction mechanisms*.**

3

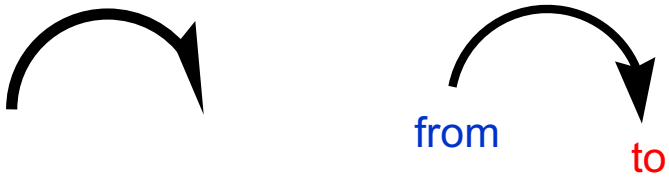
Organic Chemical Reactions…

Reaction Mechanisms: The "curved" arrow notation in bond making and breaking. (24.3)

4

Organic Chemical Reactions…

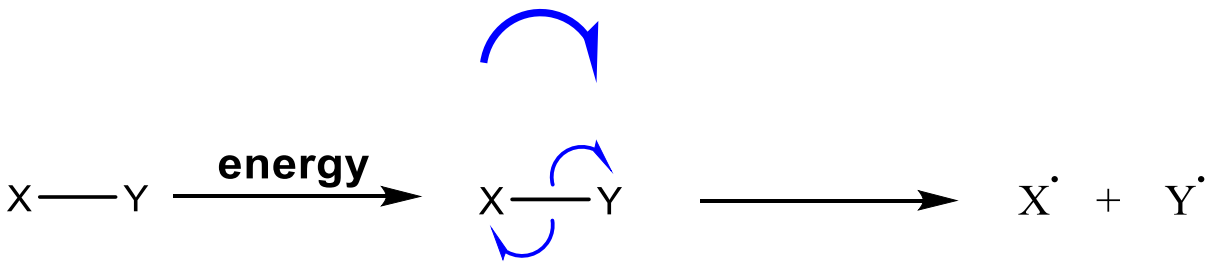
Reaction Mechanisms: The "curved" arrow notation in bond making and breaking. (15.4, 17.1, 16.5, 18.1)



5

Organic Chemical Reactions…

One electron transferred - represented by a 'half-headed' arrow (fish hook)



Homolytic bond cleavage

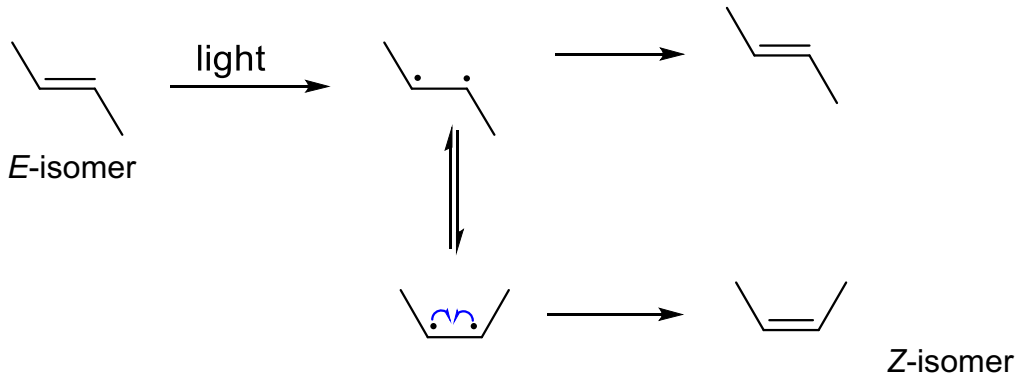
One electron is transferred to each of the two atoms

The species generated (X• and Y•) are radicals.

6

Organic Chemical Reactions…

eg. Isomerisation of alkenes

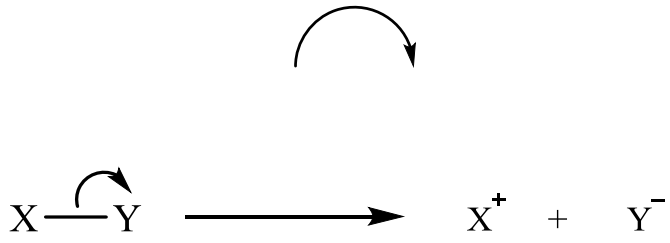


Is there preference for *E* or *Z*?

7

Organic Chemical Reactions…

Two electrons transferred - represented by a 'full-headed' arrow



Heterolytic bond cleavage

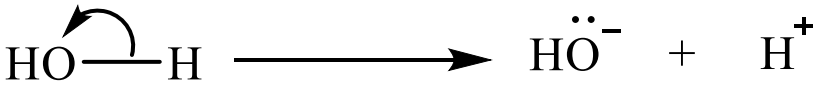
Two electrons are transferred from the bond to one atom (Y)

Obtain charged intermediates

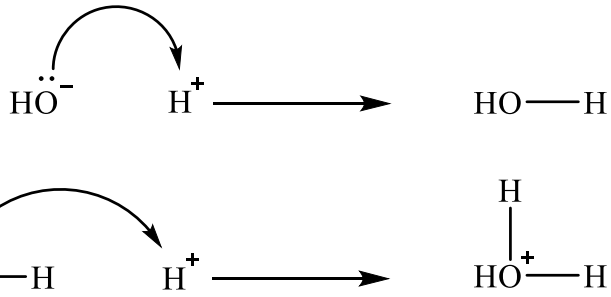
8

Chemical Reactions…

eg. Ionization of water

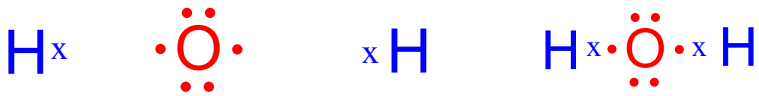


Bond forming, two electrons transferred to form a bond.
eg. protonation

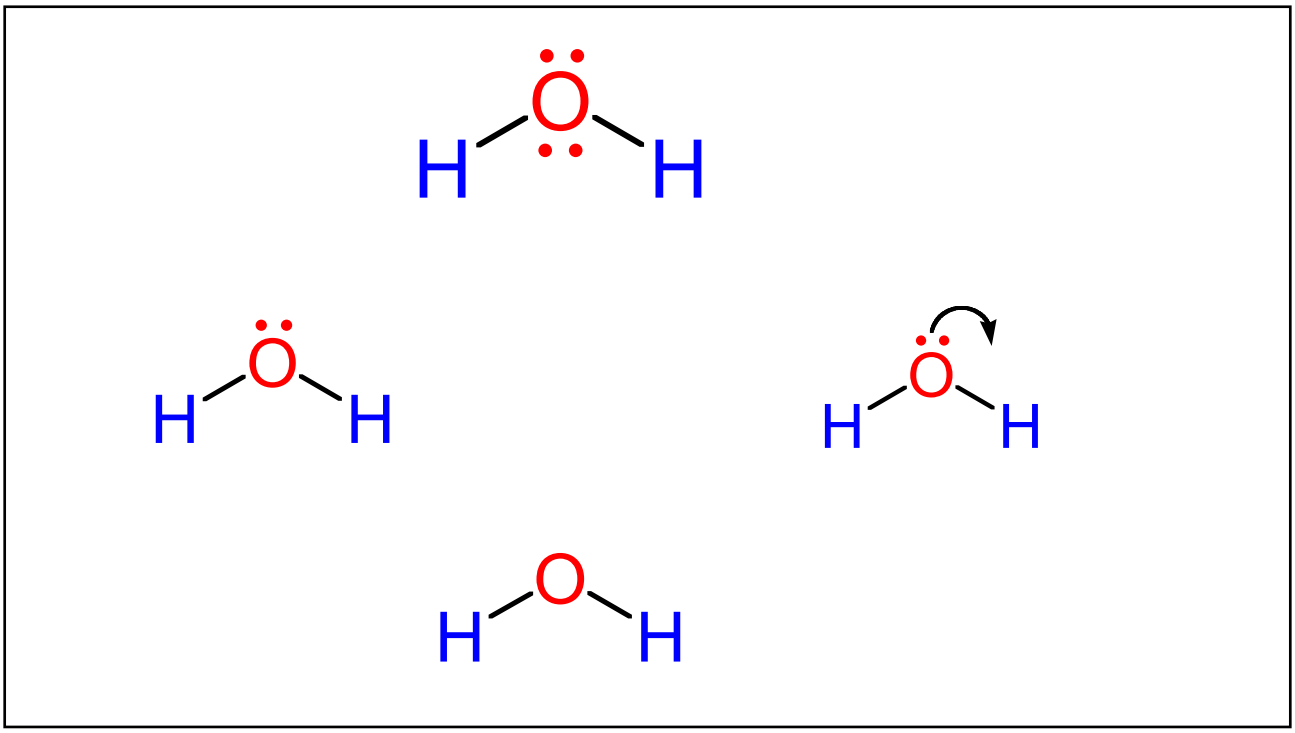


9

H: 1 electron **x**
O: 6 electrons ●

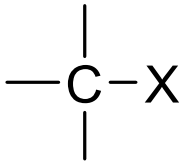


10



11

Singly Bonded Functional Groups (26, 27)



X = halogen, OH, OR, NH_2, etc.

The C–X bond is polar; i.e. $C^{\delta+} – X^{\delta-}$ (because X is more electronegative than C)

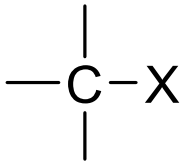
slightly positive

Electronegativity

C	2.5
O	3.5
Cl	2.8
Br	2.7
N	3.1

12

Singly Bonded Functional Groups



X = halogen, OH, OR, NH_2, etc.

The C–X bond is polar; i.e. $C^{\delta+} - X^{\delta-}$ (because X is more electronegative than C)

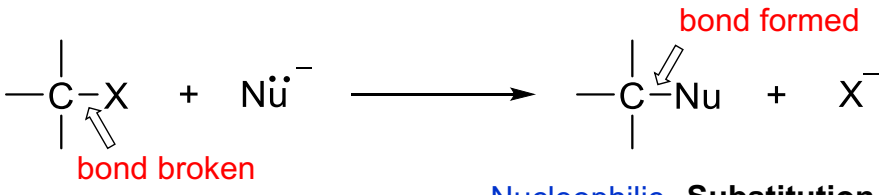
$C^{\delta+}$ atom is electrophilic (seeking electrons)

Nucleophiles are species that can donate a pair of electrons to $C^{\delta+}$ to form a bond.

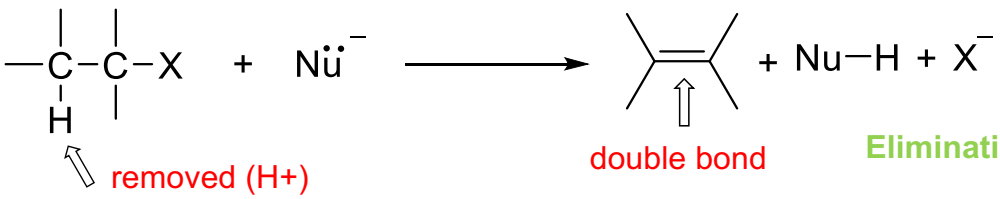
13

Singly Bonded Functional Groups

If X is a good *leaving group* (C-X bond weak, X can readily accept a pair of electrons from the breaking bond), two types of reactions with nucleophiles are possible:



Nucleophilic **Substitution**



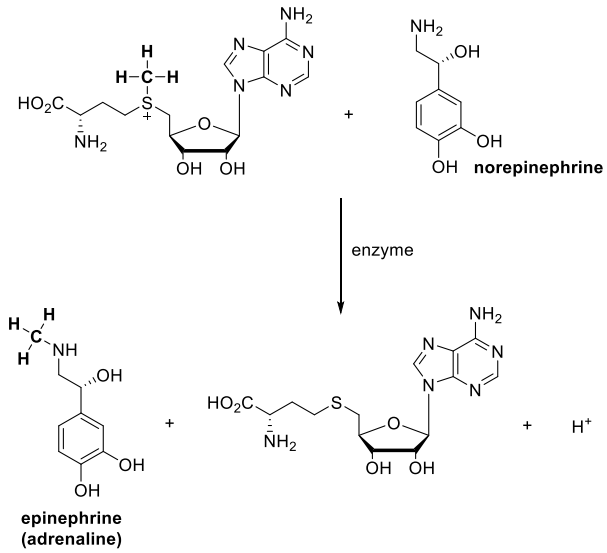
Elimination

14

Nucleophilic Substitution

Example in biological systems: production of adrenaline.

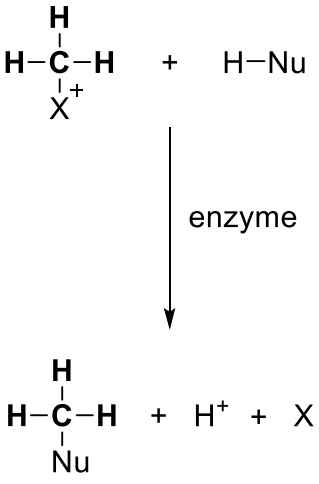
(The reaction centre, CH_3–X, is in bold). Methyl-group transfer.

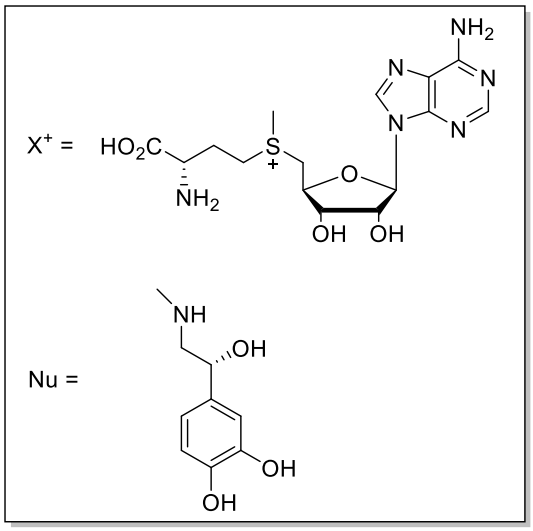


15

Nucleophilic Substitution

Looks complicated but can be simplified to:

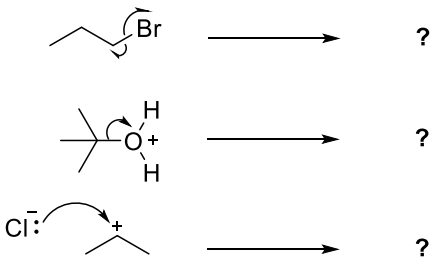




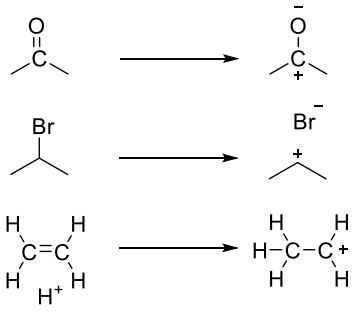
16

Questions

1. Draw the product(s) from the following steps in reaction mechanisms:

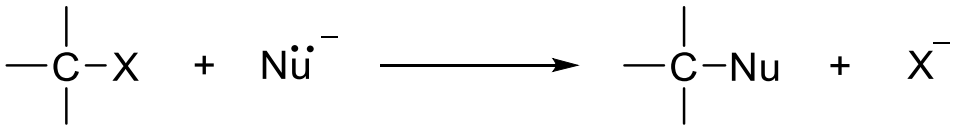


2. Draw in the arrow(s) for the following steps in reaction mechanisms:



17

Nucleophilic Substitution



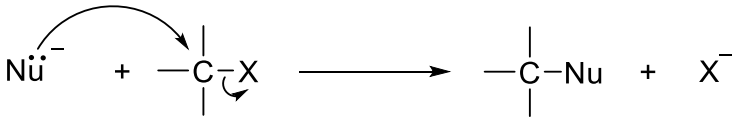
Nucleophilic Substitution

18

Nucleophilic Substitution

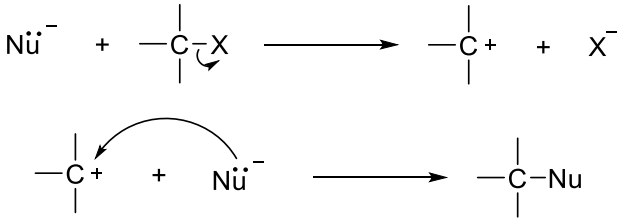
Possible Reaction Sequences for nucleophilic substitution:

- X leaves as Nu:⁻ attaches: **OPTION 1**



rate = *k* [C-X] [Nu:⁻]

- X leaves and then Nu:⁻ attaches: **OPTION2**



If 1st step is rate determining: rate = *k* [C-X]

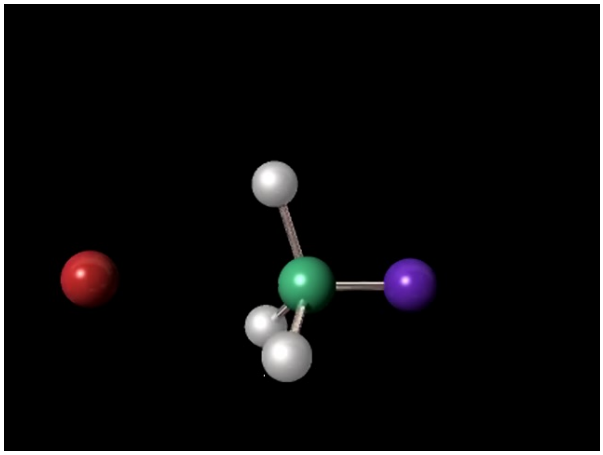
19

Nucleophilic Substitution - OPTION 1

rate = *k* [C-X] [Nu:⁻]

1 step reaction

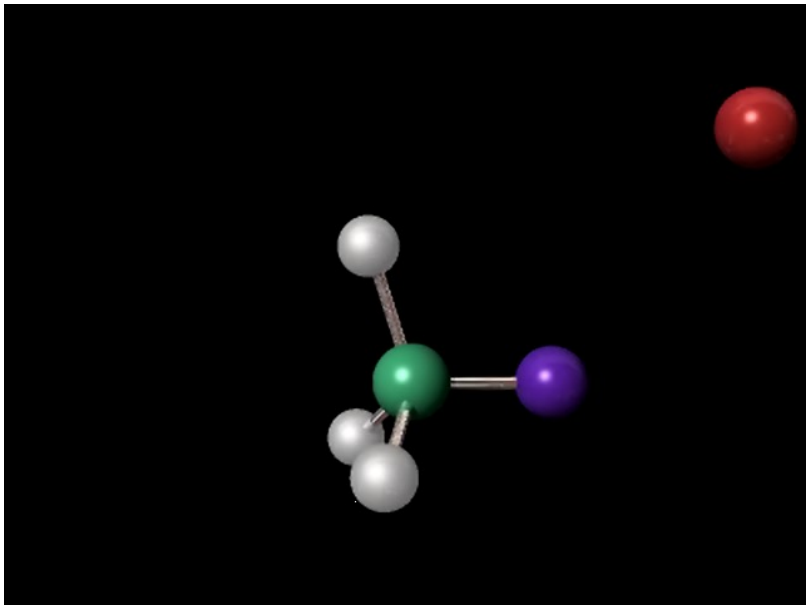
Nu:⁻ attaches as X departs



2nd order reaction - mechanism is called **S_N2** (27.5)

20

OPTION 1 S_N2



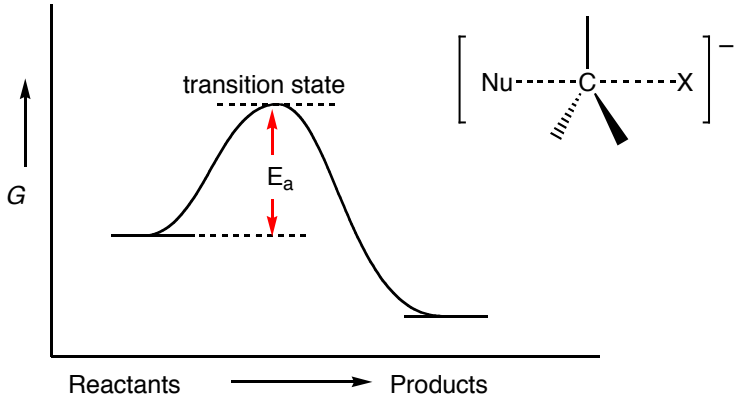
21

Nucleophilic Substitution - OPTION 1 S_N2

rate = *k* [C-X] [Nu:$^-$]

1 step reaction

Nu:$^-$ attaches as X departs

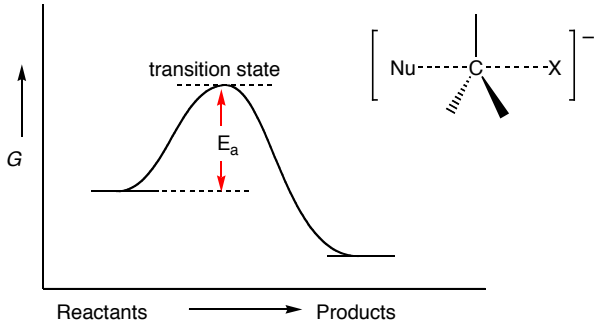


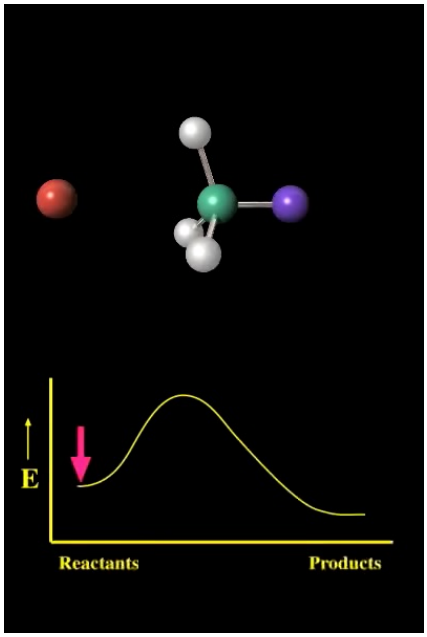
2nd order reaction - mechanism is called **S_N2** (25.5)

Substitution Nucleophilic 2nd order

22

Nucleophilic Substitution - OPTION 1 S_N2





23

'Worrying' levels of toxic gas in Tauranga alleged - Bay of Plenty Times - Bay of Plenty Times News 5/2/17, 7:32 AM

The New Zealand Herald

Network
Fine 16° / 9° Auckland
Today's Paper
Register
Login
Subscribe
Help & Support

Bay of Plenty Times

Provided by NZX
POT4.06
$ 0.0000%
Open **4.06** High **0** Low **0** Bid Price **4.06**
Offer Price **4.12** Value **0** Volume **0**
Current as of 02/05/17 07:20AM NZST

'Worrying' levels of toxic gas in Tauranga alleged

Port of Tauranga. Photo/file

A company's bid to release a highly toxic gas into Tauranga's atmosphere has been quashed after environmental regulators found that its use has already reached "worrying" levels.

The Environment Court blocked an application by Envirofume Ltd to fumigate logs for export using methyl bromide at the Port of Tauranga.

Envirofume wanted to pump the gas into logs while they lay under tarpaulins, a method that lets some escape into the atmosphere and waft into surrounding areas. The company altered its application to allow gas to escape at a one to 14 ratio with air using a fan system, but the court still said no.

Use of the gas at Port Nelson was suspected to have caused the deaths of up to six people who contracted motor neurone disease between 2002 and 2005, although medical reports reached conflicting conclusions.

In its decision, the court rejected Envirofume's application but noted that another company, Genera, continued to use methyl bromide at the port.

Genera can release the gas so long as it does not exceed set limits at the port's boundary.

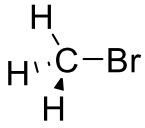
The court said measurements had found "worrying" quantities of the gas at the port's boundary of more than 10 times a limit set by the US Centre for Disease Control.

The court described the health effects of methyl bromide as "chilling" and said it had "no confidence" that its current use at the port was meeting standards set by New Zealand's Environmental Protection Authority.

Safer gases including phosphine are being used to fumigate logs in some New Zealand ports, but countries including India and China insist that imported logs be treated with methyl bromide.

A field worker for motor neurone disease charity MND, Graham Jones, said the disease was usually fatal within three to five years of being diagnosed as muscles wasted away and respiratory failure set in.

http://www.nzherald.co.nz/bay-of-plenty-times/news/article.cfm?c_id=1503343&objectid=11796882 Page 1 of 2



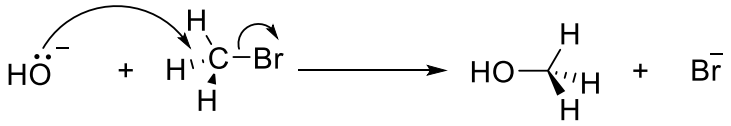
The court described the health effects of methyl bromide as "chilling" and said it had "no confidence" that its current use at the port was meeting standards set by New Zealand's Environmental Protection Authority.

24

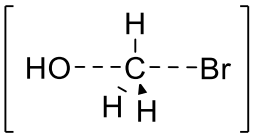
Nucleophilic Substitution - OPTION 1 S_N2

bromomethane + NaOH —> methanol + NaBr

rate = *k* [CH_3Br] [HO^-]



transition state



Nucleophile OH^- approaches and attaches opposite to the leaving group Br^-.

25

✱ Homework ✱

Chemistry – the central science 15th Ed

Brown et al.

Problems 26.47, 27.28

Answers on Blackboard

26