Alkenes and Alkynes
(aka Olefins and Acetylenes)

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Resources

‘Organic Chemistry’ by Clayden, Greeves, Warren and Wothers.

‘Classics in Total Synthesis’ by Nicolaou and Sorensen

http://www.york.ac.uk/res/pac/teaching/alkenes.html

Scope of the Course

We will look at the structure, synthesis and reactivity of alkenes and alkynes. In particular we will discuss the stereochemical, regiochemical and mechanistic aspects of their synthesis and reactivity.

Alkenes: including Wittig, cross coupling, epoxidation, dihydroxylation, ozonolysis and Diels-Alder reactions.

Alkynes: including acidity of, couplings, reductions.

Learning Objectives

1) To be familiar with the nomenclature, structure and reactivity of alkenes and alkynes.

2) To appreciate and understand regiochemical, stereochemical and mechanistic aspects of reactions involving alkenes and alkynes as starting materials or products.

3) To understand important reactions involving alkenes and alkynes and to know the reagents employed.

4) To be able to design synthetic routes for the preparation of target alkenes and alkynes.

Course Outline

Alkynes
Structure, bonding and nomenclature.
Acidity of alkynes.
Methods for the preparation of alkynes.
Reactivity of alkynes.

Alkenes
Structure, bonding and nomenclature.
Methods for the preparation of alkenes.
Reactions 1: Electrophilic additions, radical additions, hydroboration.
Reactions 2: epoxidation, dihydroxylation, ozonolysis, Diels-Alder, cross coupling.

Alkynes

Nomenclature

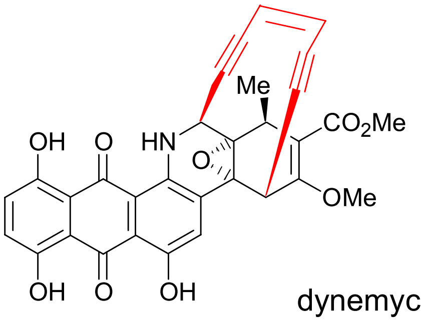
1) Select the longest continuous chain containing the alkyne.

2) Use the suffix “yne”.

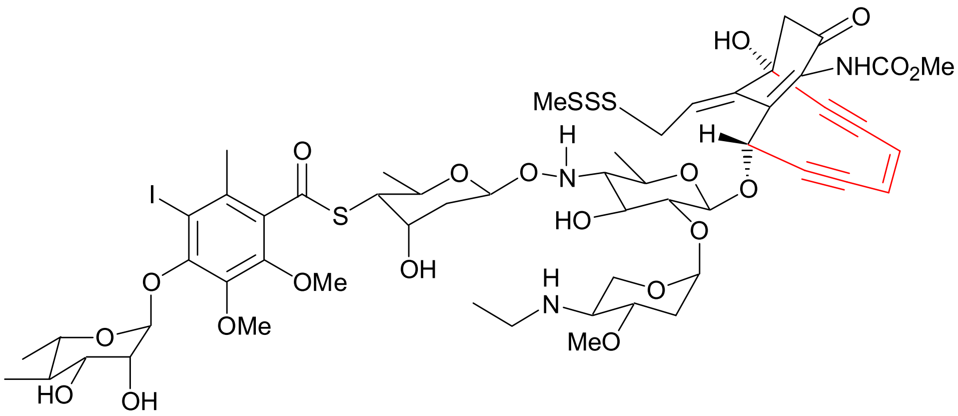
3) Number the chain to include both atoms of the triple bond with the lowest number for the first carbon of the alkyne.

pKa Values of Hydrocarbons

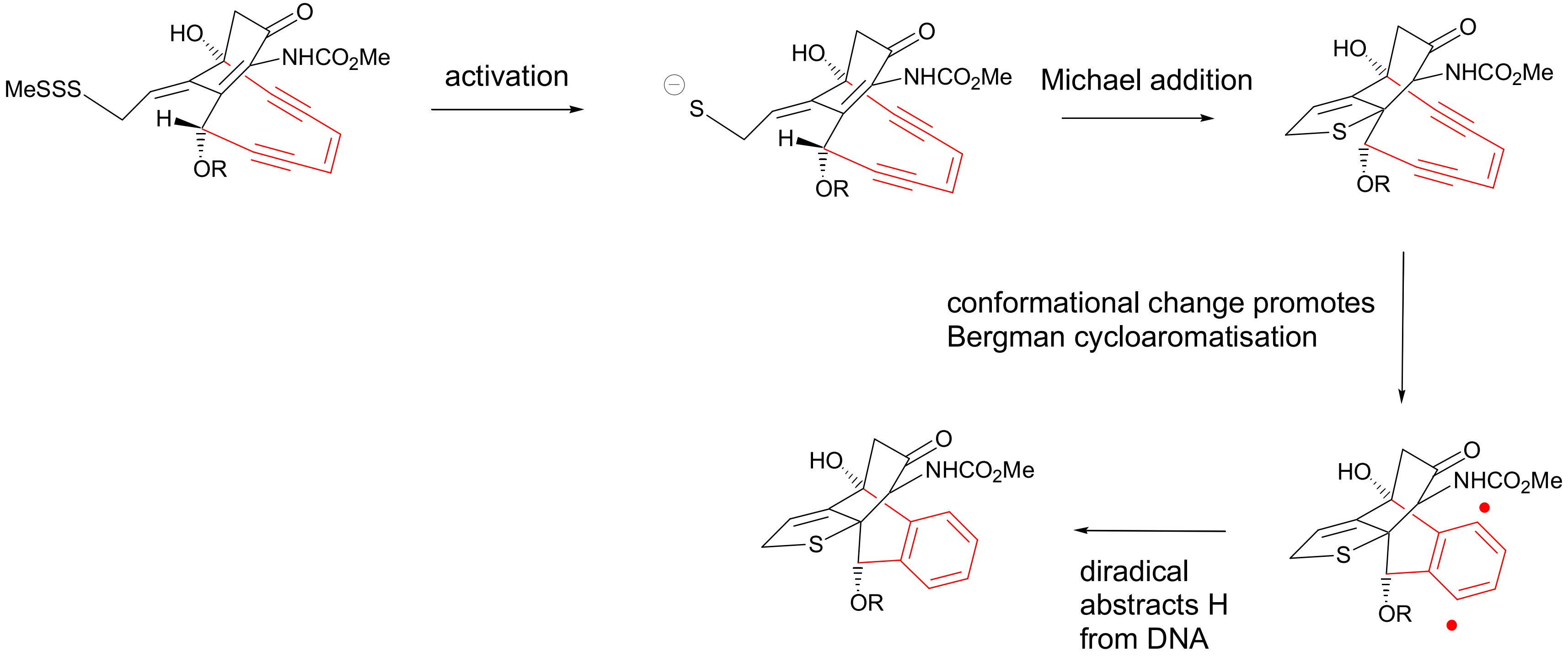
CH_3CH_3	~50	Weak acid
$CH_2{=}CH_2$	~44	
NH_3	~30	
$HC{\equiv}CH$	~26	
H_2O	14	
CH_3CO_2H	5	
H_2SO_4	-9	Strong acid



dynemycin



calicheamicin $\gamma_1{}^1$



Alkenes

Nomenclature

1) Select the longest continuous chain containing the alkyne.

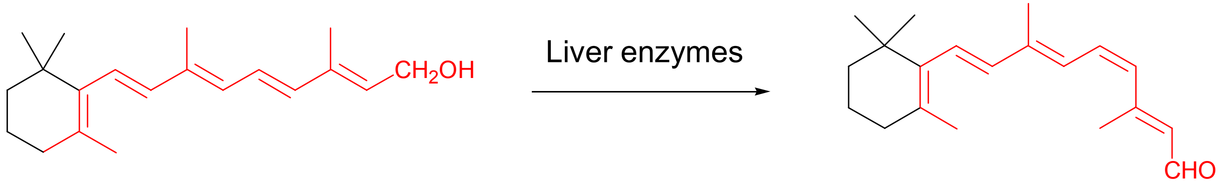
2) Use the suffix “ene”.

3) Number the chain to include both atoms of the double bond and begin numbering at the end of the chain closest to the double bond. The position of the double bond is specified by the number of the first alkene carbon.

4) Designate the geometry of the double bond. If the two highest priority substituents are on the same side (*Z*) if on opposite sides (*E*). Priority determined by the Cahn-Ingold-Prelog convention.

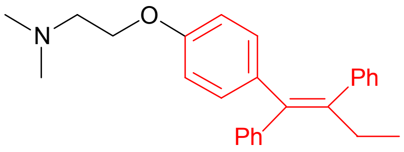
5) Number cycloalkenes in the way that gives the carbons of the double bond the 1 and 2 positions and that also gives the substituent groups the lowest numbers at the first point of difference.

Important Alkenes

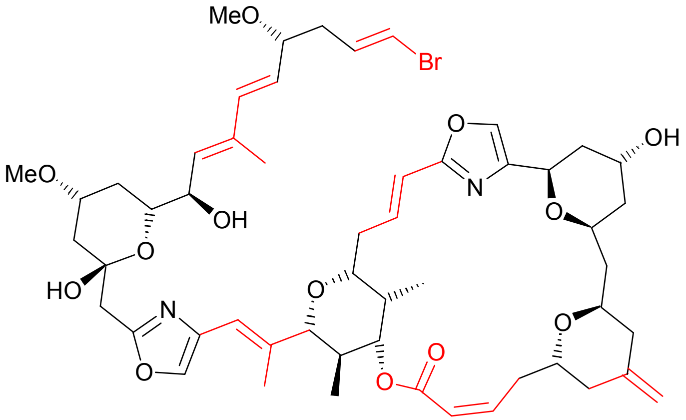


vitamin A

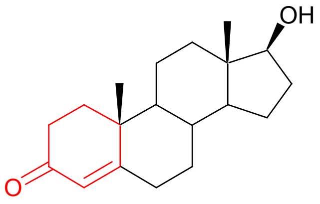
retinal



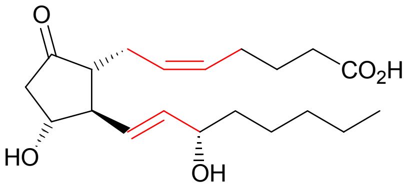
tamoxifen: breast cancer



phorboxazole A: anti-cancer



testosterone: male hormone



prostaglandin E2: fertility and anti-ulcer

Saytzev and Hofmann Elimination

Saytzev:

When the leaving group is a halide, etc., the more stable alkene (more highly substituted alkene) is formed as the major product.

Hofmann:

When positively charged leaving groups are used (ammonium, sulfonium, etc.,) then the less substituted alkene product predominates.

[See substitution and elimination lecture notes for full details]

Notes on Radical addition of HBr

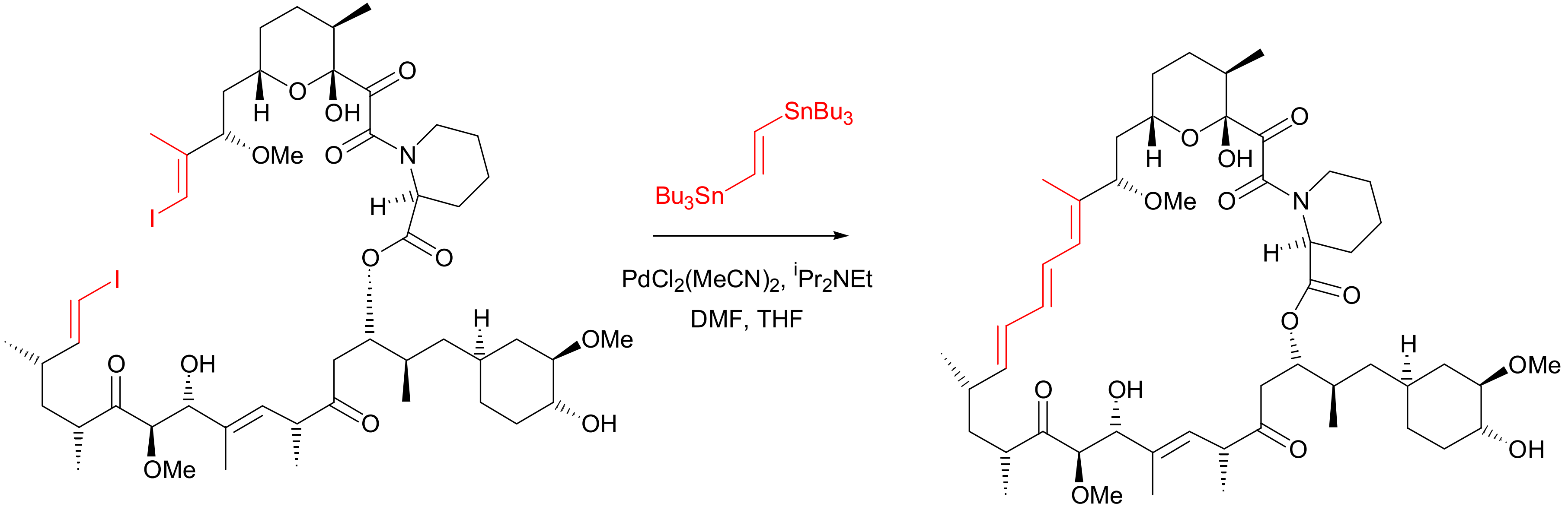
1) Chain reaction mechanism (Br radical continues the process).

2) Use of single headed *'fishhook'* arrows denotes the movement of 1 electron.

3) Goes *via* a carbon centred radical.

4) Radicals are electron deficient so they are stabilised by the same things which stabilise carbocations.

Stille Reaction in Natural Product Synthesis



$PdCl_2(MeCN)_2$, $^iPr_2NEt$

DMF, THF

rapamycin: immunosuppresant

End of the Course

During these lectures we have looked at the structure, bonding, synthesis and reactivity of alkenes and alkynes. You should appreciate and understand the regiochemical, stereochemical and mechanistic aspects of reactions involving alkenes and alkynes as starting materials or products and be able to provide curly arrow mechanisms for the transformations discussed. You should also be able to design synthetic routes for the preparation of target alkenes and alkynes.