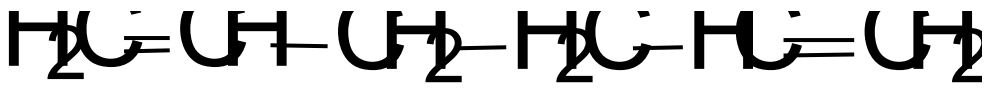
Dienes

Dienes

Types of dienes: isololated

cumulated

conjugated



hexa-1,5-diene

Double bonds are not in conjugation and do not influence each other and therefore react in reactions characteristic for alkenes ⟶ addition reactions

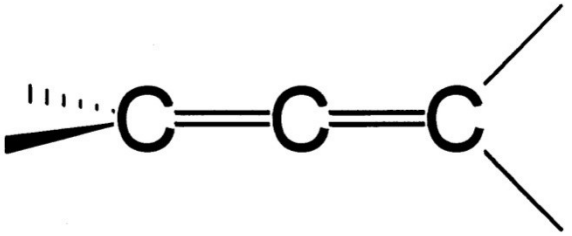
Hydrogen atoms in allylic position are reactive in substitution reactions ⟶ in radical reactions

Dienes

Types of dienes: isololated

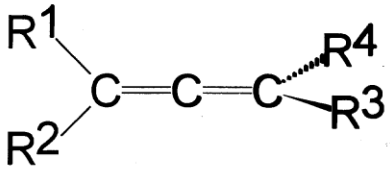
cumulated

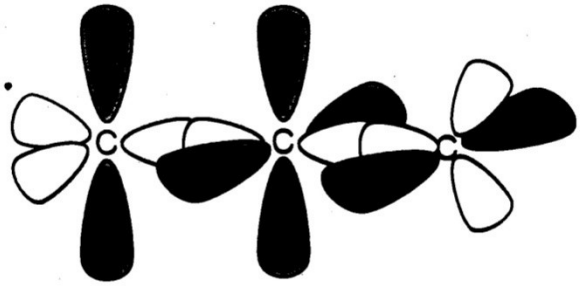
conjugated



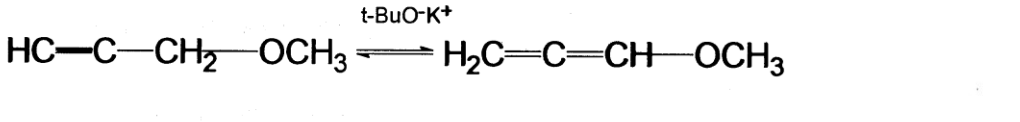
$H_2C{=}C{=}CH_2$ **allene (propa-1,2-dien)**

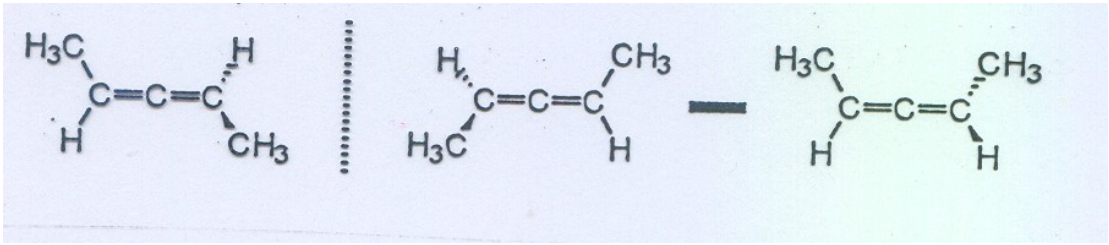
1.Compounds are able of isomeration to alkynes
2.They undergo a nucleophilic attack of a nucleophile to the central carbon atom

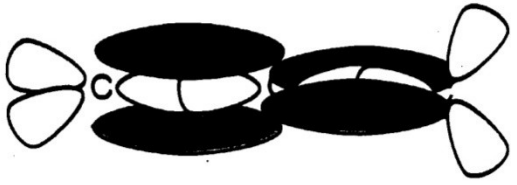




sp^2 sp sp^2

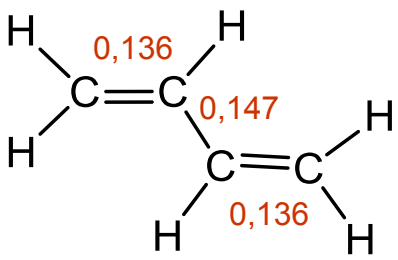




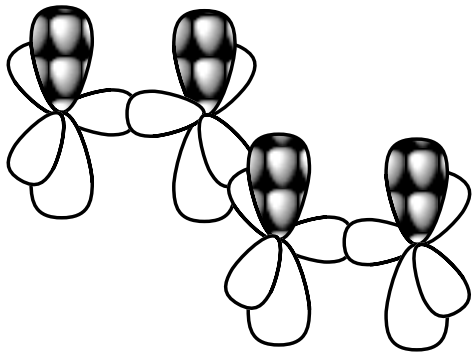


Dienes

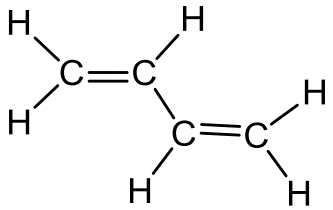
Conjugated dienes



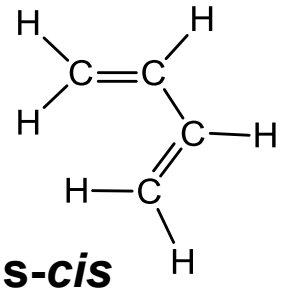
C-C 0,154 nm
C=C 0,134 nm



ISOMERISATION of conjugated dienes



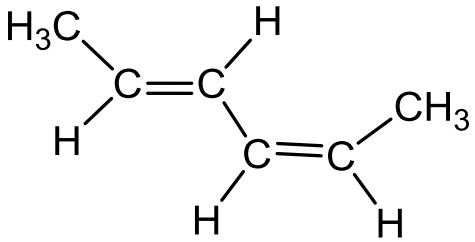
s-*trans*



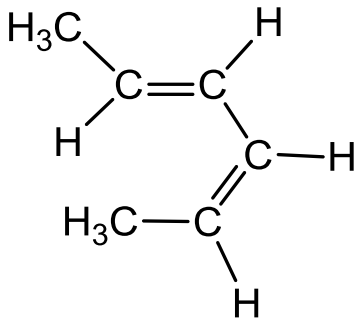
s-*cis*

Geometric isomerism

Conformation (conformation isomerie) – rotation is restricted

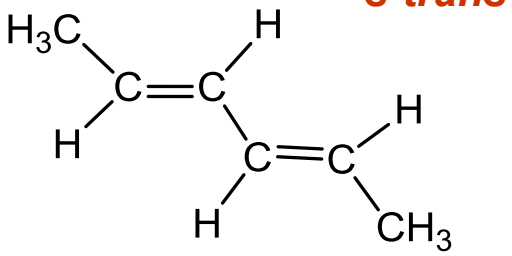


***trans, cis*- hexa-2,4-diene**

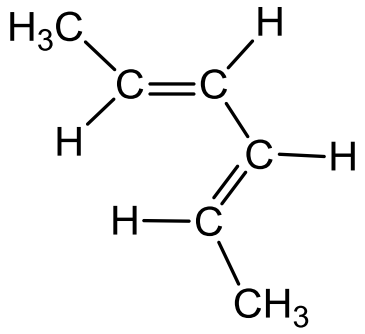


s-*cis*

s-*trans*

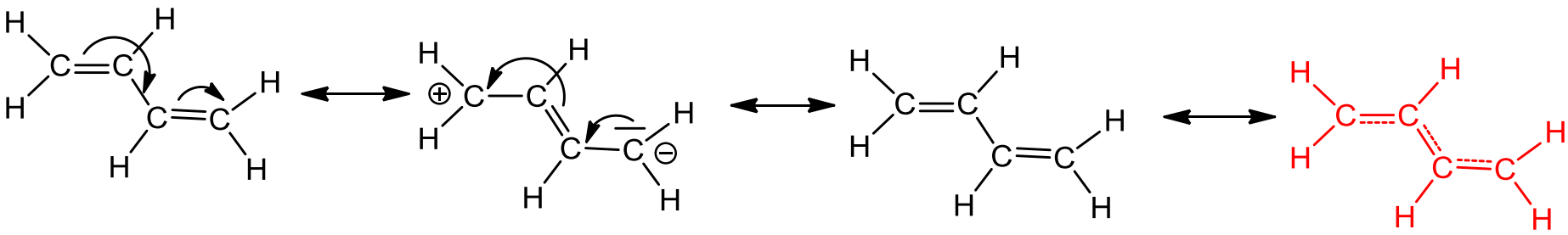


***trans, trans*- hexa-2,4-diene**



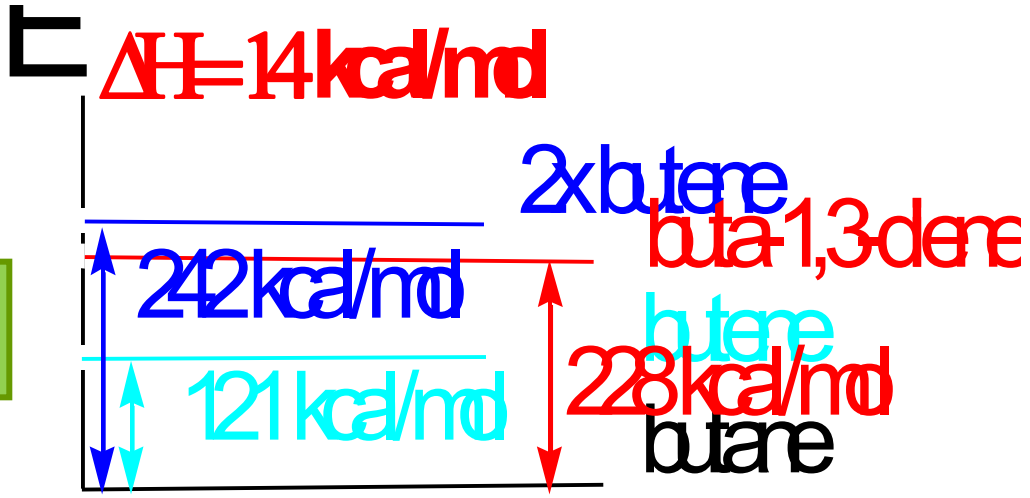
Dienes

Conjugation



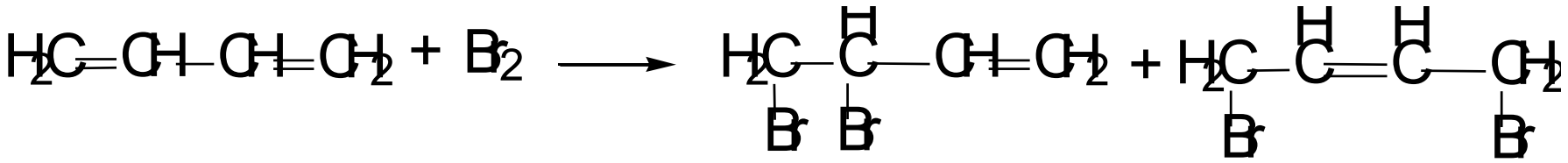
RESONANCE ENERGIE

Heat of hydrogenation reflects situation in bonding



Dienes

REACTIVITY of conjugated dienes - conjugated additions



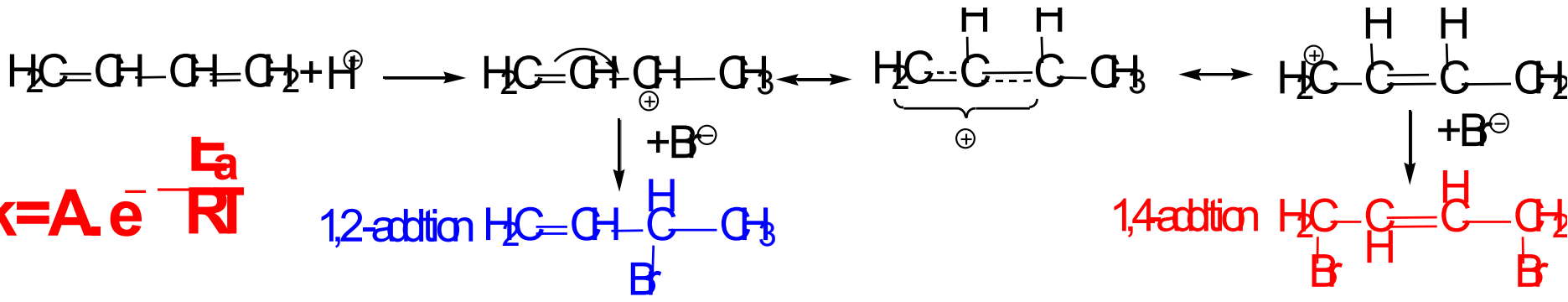
1,2- aduct 1,4- aduct

The result of reaction depends upon the temperature of reaction

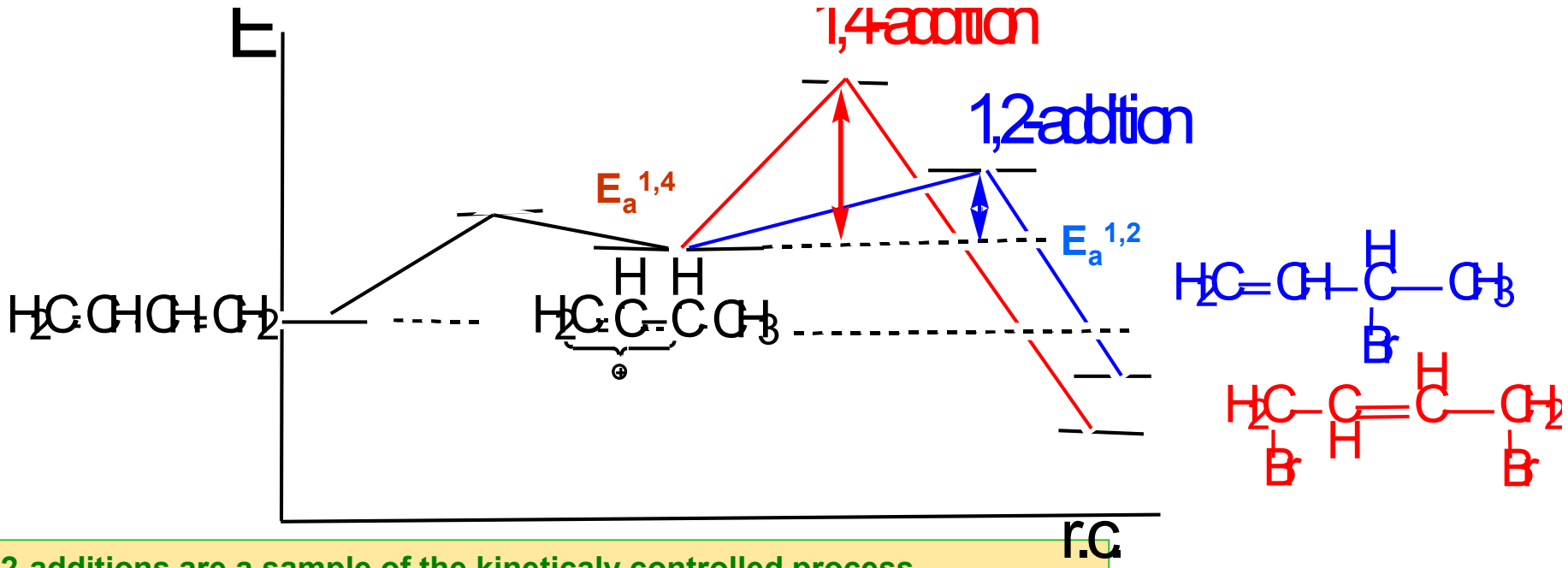
Buta-1,3-diene	reagent	temperature °C	1,2-aduct %	1,4-aduct %
	Cl_2	25	100	0
	Cl_2	100	0	100
	HBr	-80	90	10
	HBr	40	0	100

Dienes

MECHANISM



$k = A \cdot e^{-\frac{E_a}{RT}}$



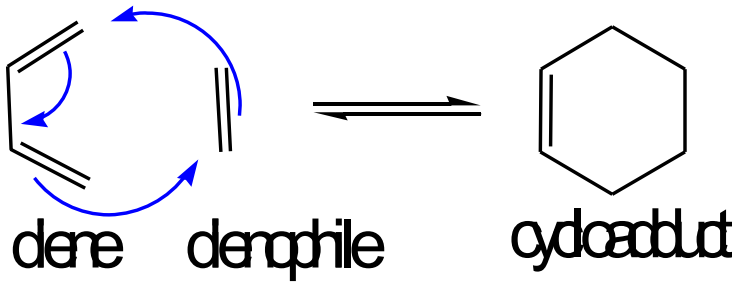
1,2-additions are a sample of the kineticaly controlled process,
1,4-additions are a sample of the thermodynamically controlled process

Dienes

Diels – Alder cycloaddition reactions

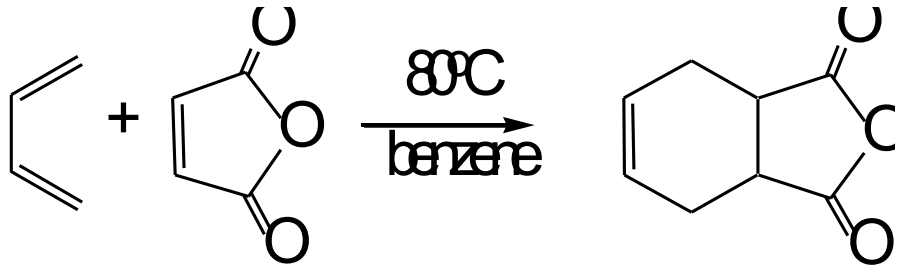
found 1928, Nobel Prize 1950

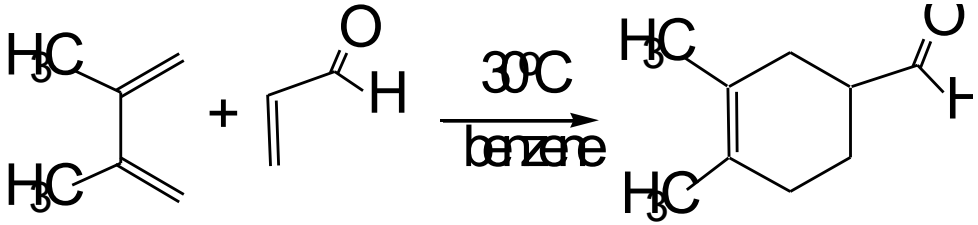
2 components: diene + dienophile



[4 + 2] cykloadditions

Reactions are easy when one of the components contains EWG and the other EDG

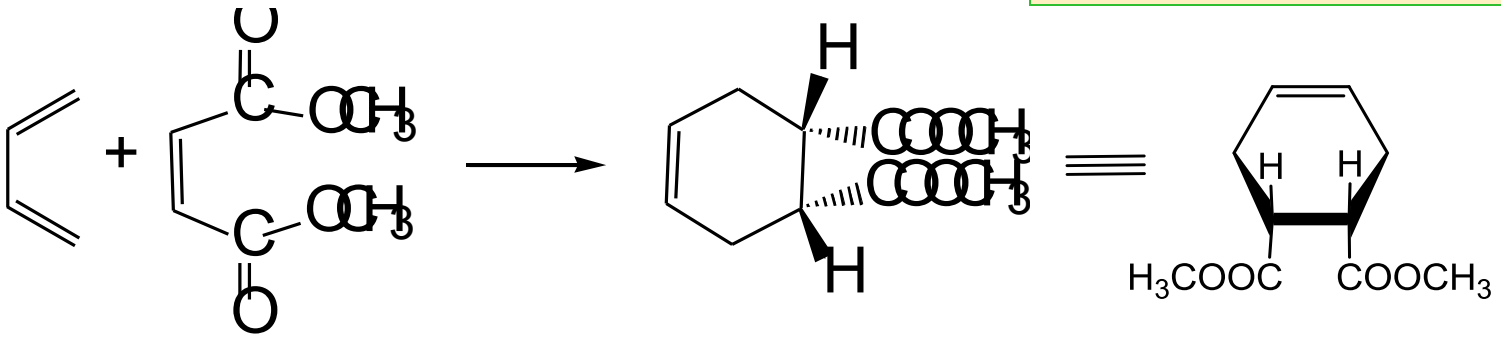


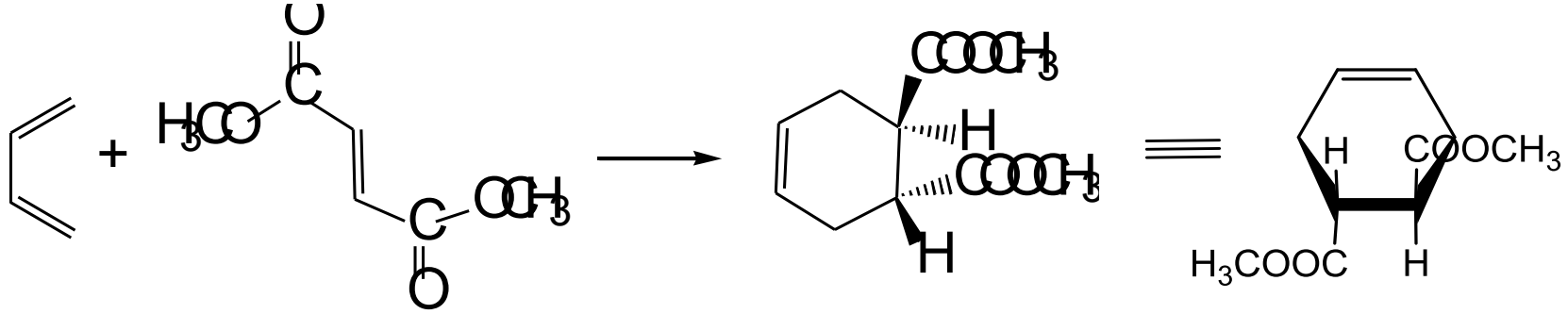


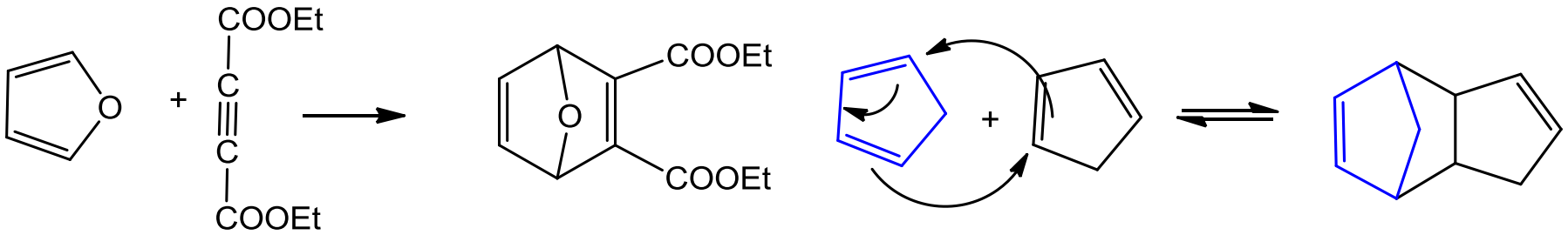
Dienes

Diels – Alder cycloaddition reaction

Reactions are stereospecific





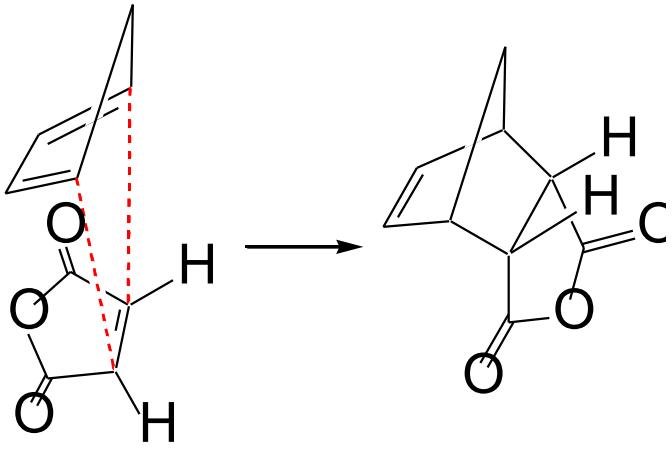


Dienes

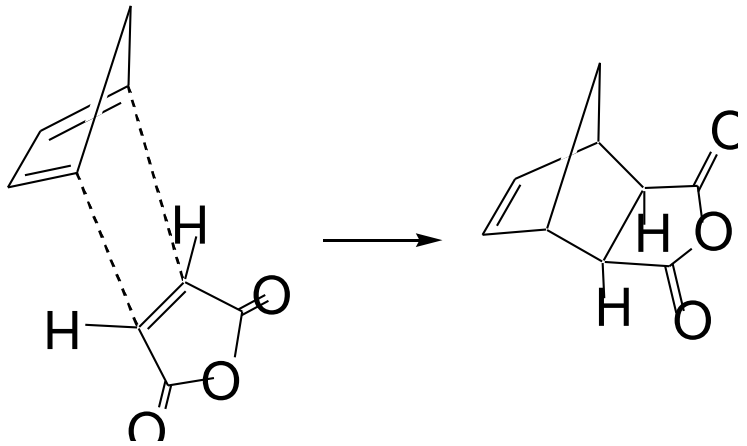
Diels – Alder cycloaddition reaction

Reactions are stereospecific

The two components - diene and dienophile react that way, they orient one to the other in the intermediate state affording **mainly *endo*-product** (*exo*- product is a minor product).



endo - product

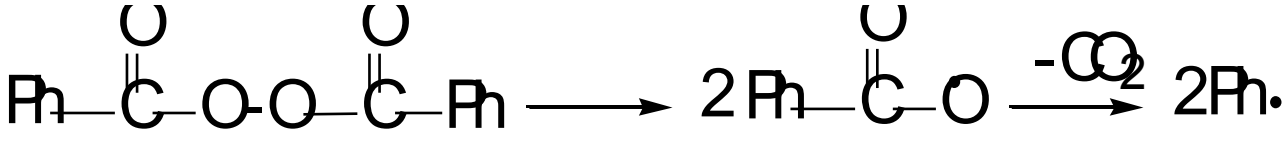


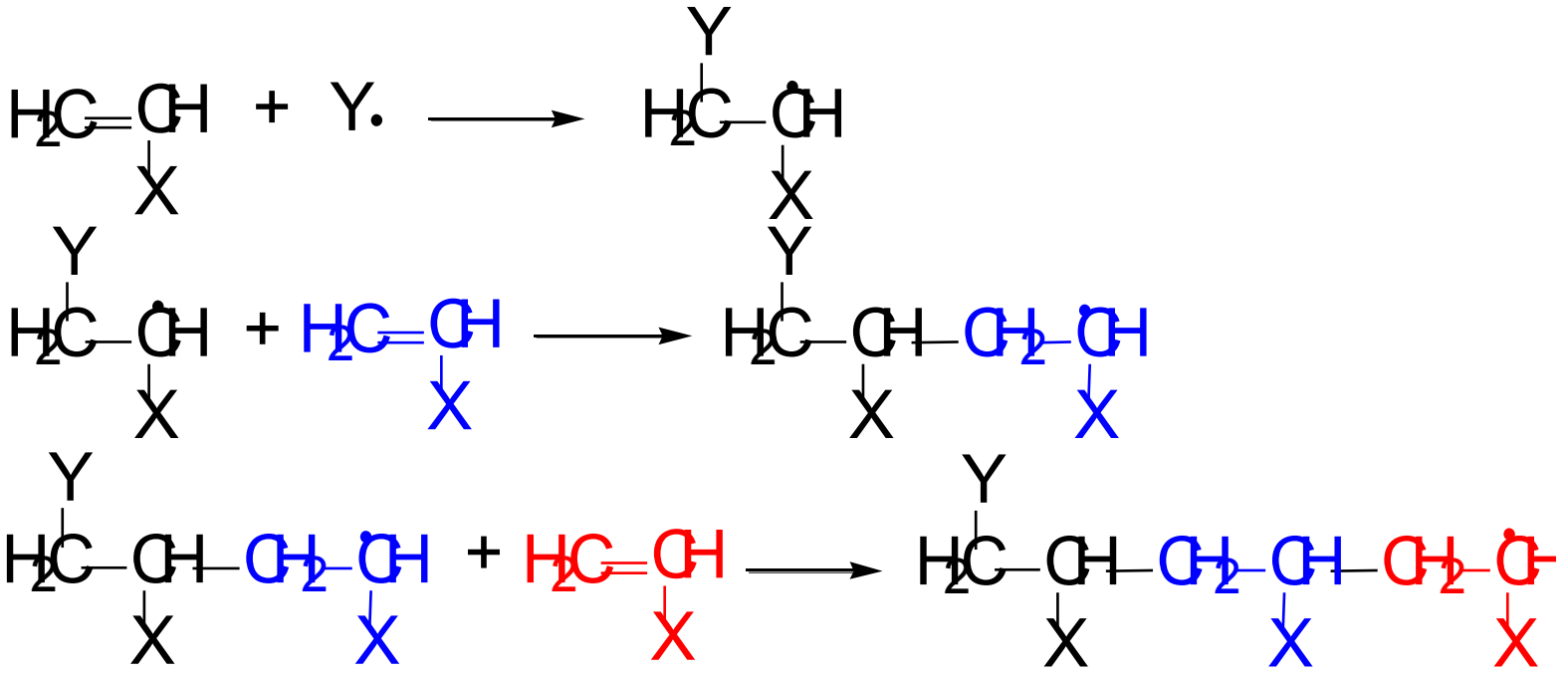
exo – product (minor)

The two largest rings are oriented out of their connection (trans-)

Dienes

POLYMERIZATION

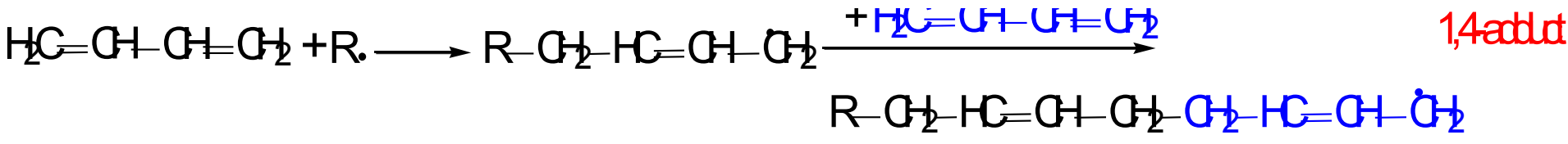




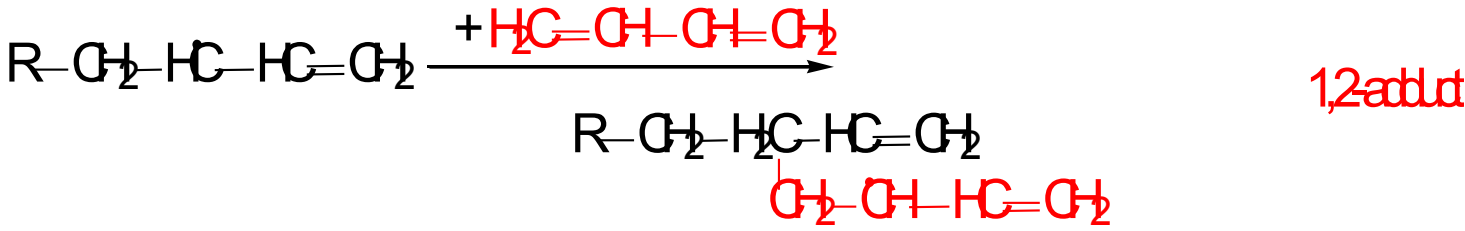
Dienes

POLYMERIZATION

radical



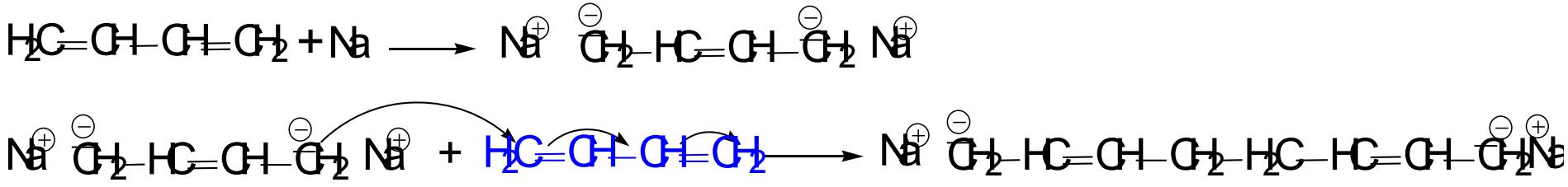
1,4-adduct



1,2-adduct

Ratio of *1,4 : 1,2* aducts in synthetic polymer is 3 : 1

anionic

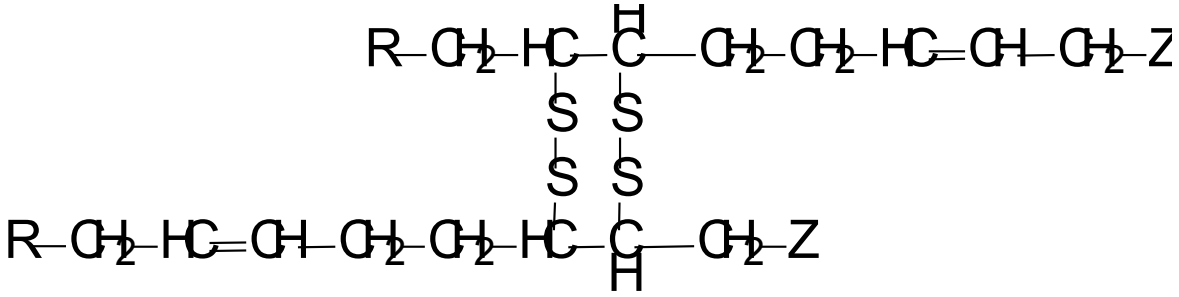


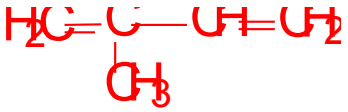
Dienes

POLYMERIZATION

In polymeric chain of synthetic rubber they are free double bonds – the polymer is very flexible and sticky and the shape of the products is not stable

For the improvement of the physical properties a **vulcanization** is carried out. Vulcanization is a process connected with a formation of covalent bonds when the polymer is heated with powder sulfur. Cross-linking via existing double bond forming new –S-S- bond proceeds.

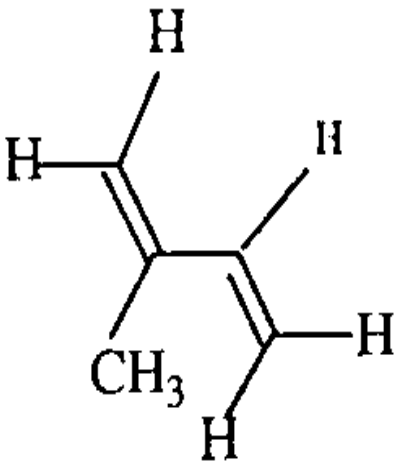




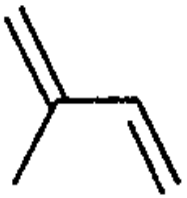
Natural ruber is formed by isoprene units and the configuration is (*Z*)

2-methylbuta-1,3-diene = isoprene

Isoprenoides – terpenes and terpenoides

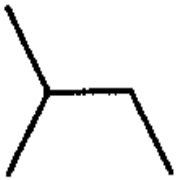


hlava



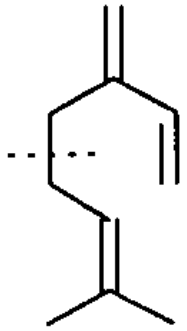
ocas

hlava

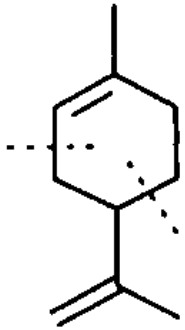


ocas

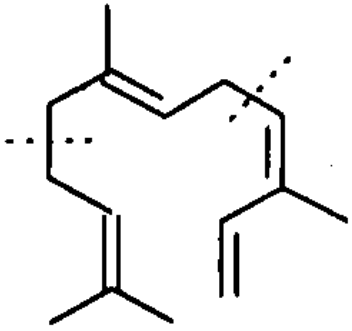
5.1.1.



myrcen



limonen



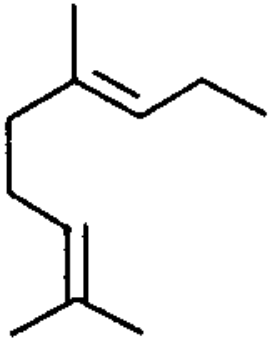
farnesen

6.1.2.

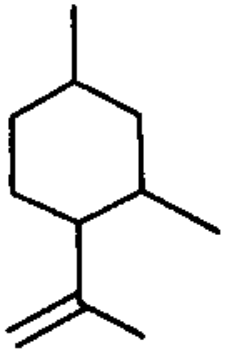
Isoprenoides – terpenes and terpenoides

MONOTERPENY

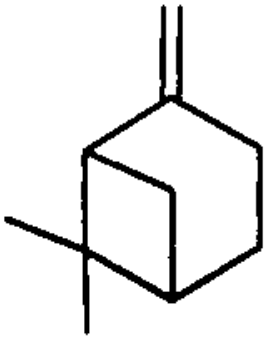
2 isoprenové jednotky = 10 C atomů



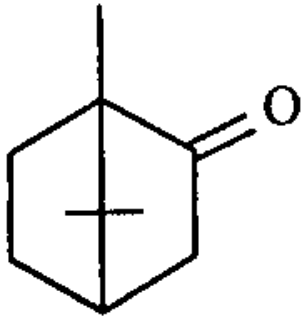
geraniol



menthol



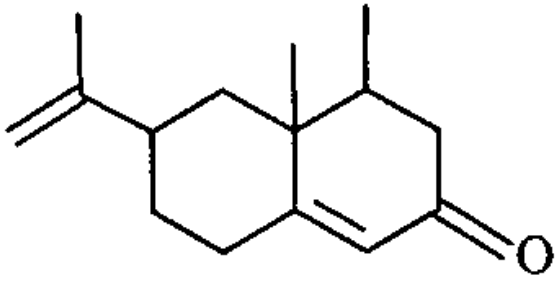
β – pinen



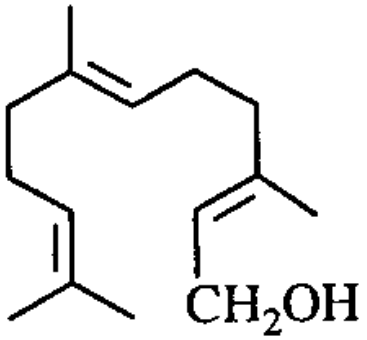
kafr

SESKVITERPENY

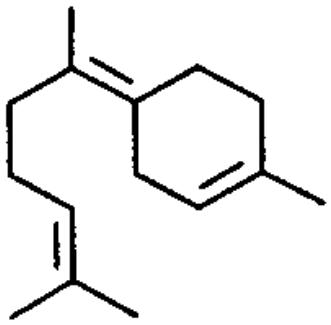
3 isoprenové jednotky = 15 C atomů



nootkaton



farnesol

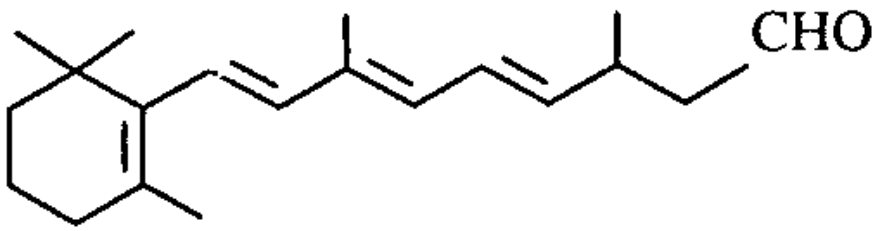


bisabolen

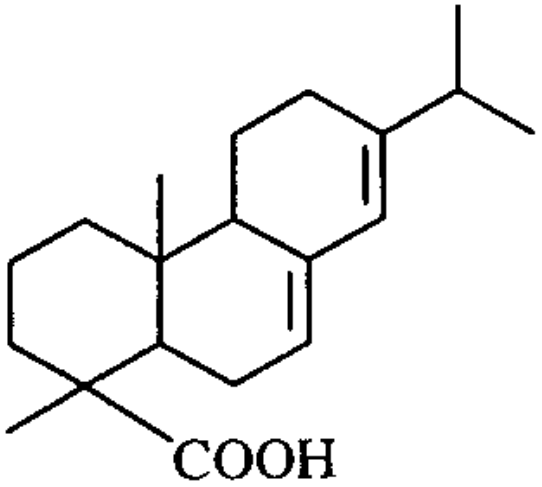
Isoprenoides – terpenes and terpenoides

DITERPENY

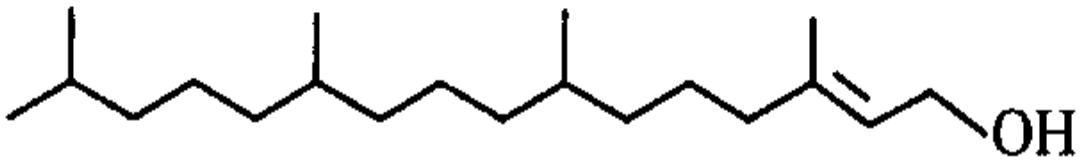
4 isoprenové jednotky = 20 C atomů



retinal



kyselina abietová

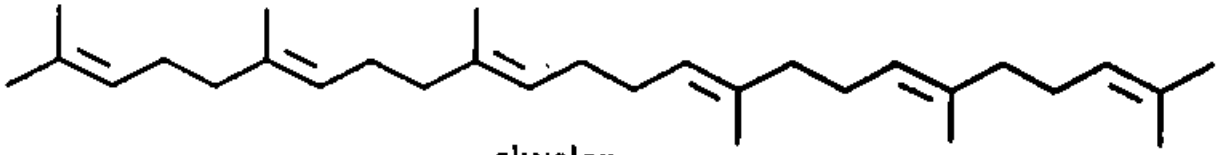


fytol

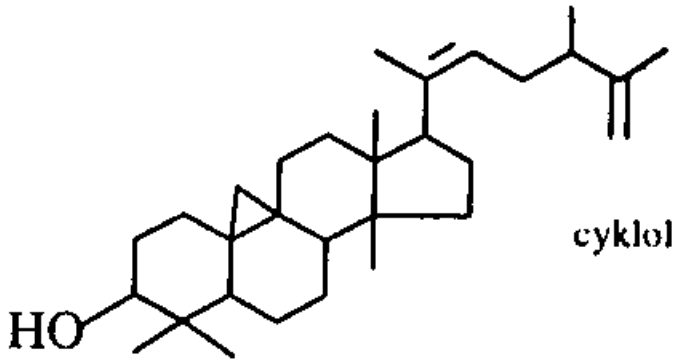
Isoprenoides – terpenes and terpenoides

6 isoprenové jednotky = 30 C atomů

TRITERPENY



skvalen

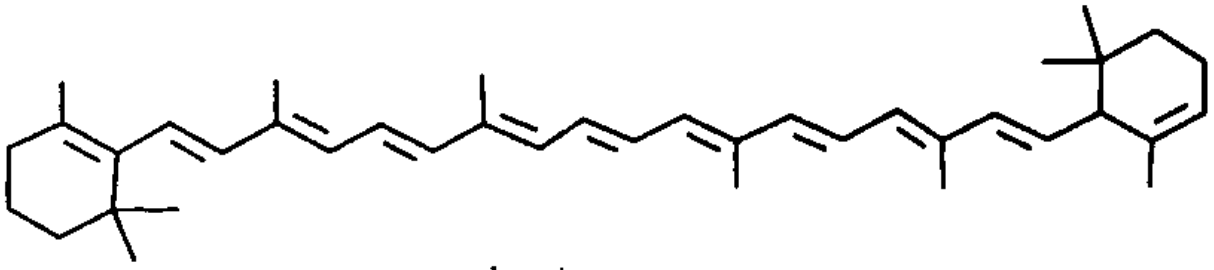


cyklolaudenol

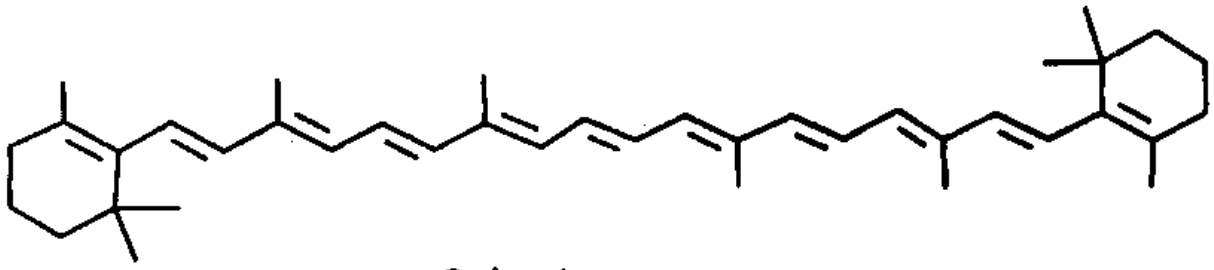
Isoprenoides – terpenes and terpenoides

TETRATERPENY

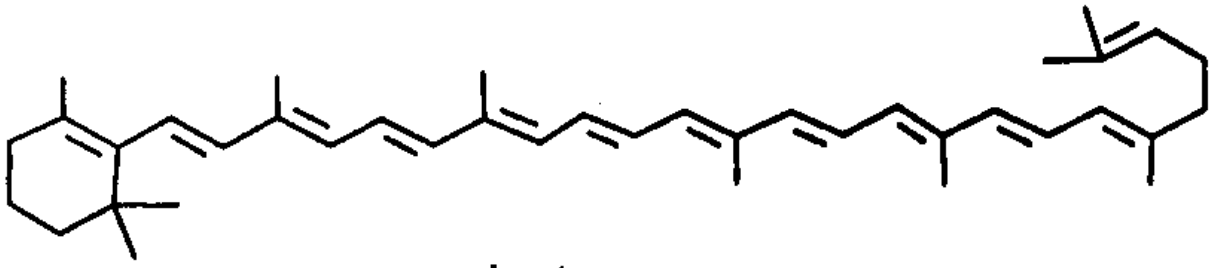
8 isoprenové jednotky = 40 C atomů



α – karoten



β – karoten

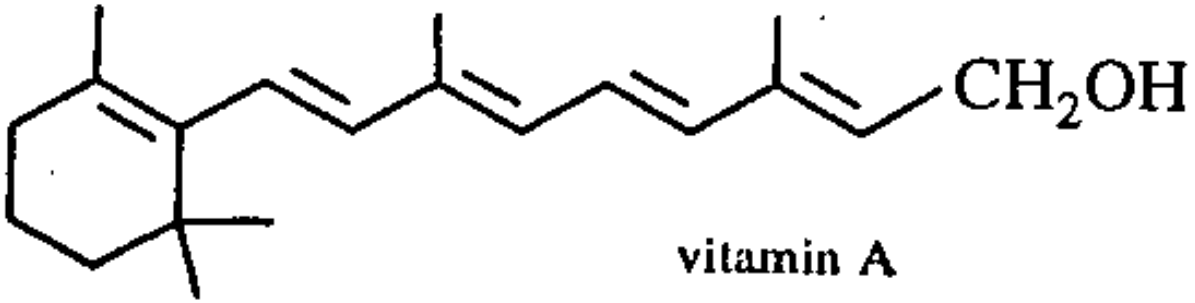


γ – karoten

Isoprenoides – terpenes and terpenoides

TETRATERPENY

8 isoprenové jednotky = 40 C atomů



vitamin A