

2. Relative configuration continued

A. Through chemical interconversion

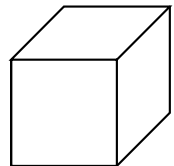
B. Through chiroptical methods

"C". Sign of the CE and the octant rule

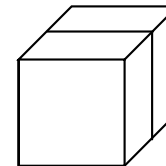
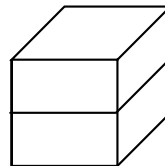
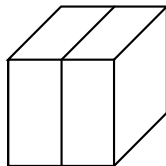
- for **cyclohexanones** only (sector rules are available for many more systems)

- based on general observations of the sign of α with substitution

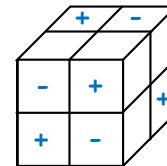
- **principle:** - space around the cyclohexanone is divided into octants



space



space halved



octants

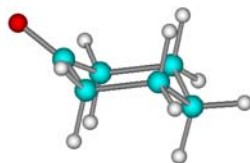
- octants receive signs (+ or -)

- atom in an octant makes a contribution to the CE
according to the sign of the octant

- contributions are additive

2. Relative configuration continued

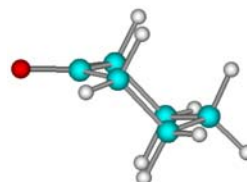
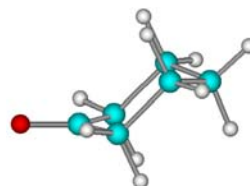
I. Viewing the cyclohexanone



or

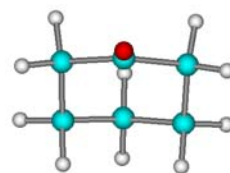
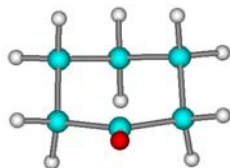


- upward position of the ring



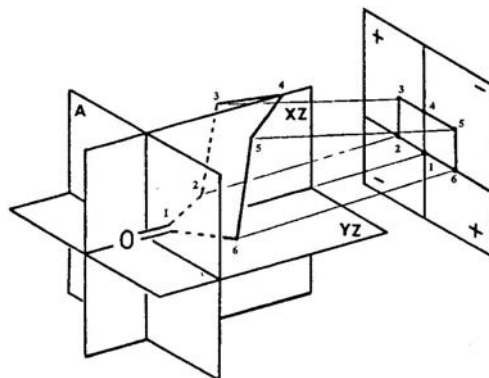
not like this:
downward position!

- along the O=C bond towards the ring

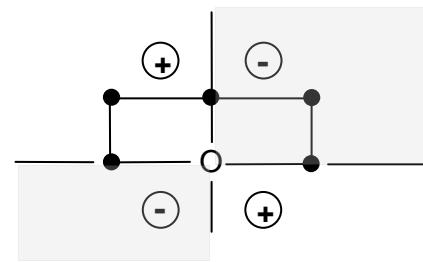


would give a wrong
analysis!

placed in the octants
(Djerassi, 1960):



viewed
projection:
back octants
matter!



"octant system"

2. Relative configuration continued

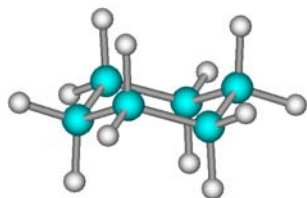
II. Placing substituents

Simplified for our purposes:

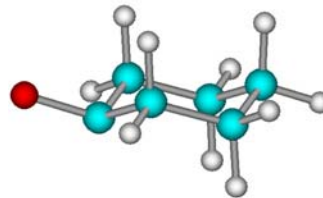
- substituent in a **positive** sector in general makes a **positive** contribution
- substituents on or near **nodes** make **no** or small contributions

But first:

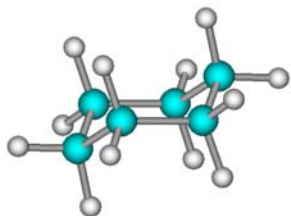
Common mistakes when drawing cyclohexan(on)es, to avoid!!



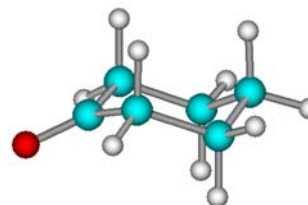
axial substituent:
straight up or down



wrong angle on C=O group,
looks like upright position



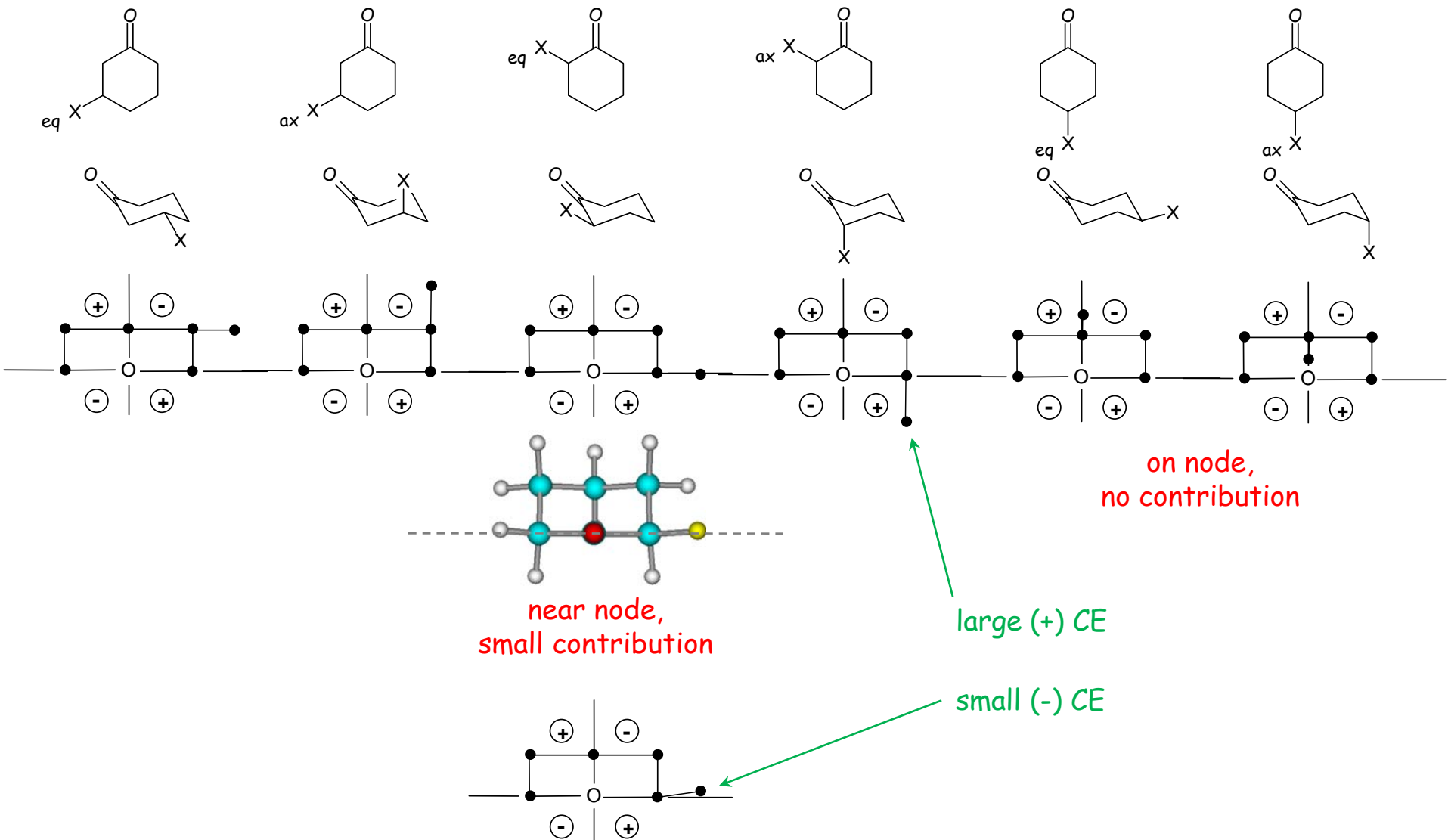
not, though, when
ring bonds are horizontal!



... but is in fact
upside down!

2. Relative configuration continued

II. Placing substituents

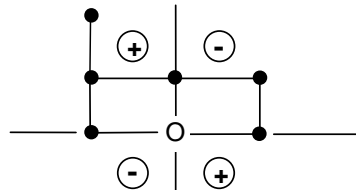
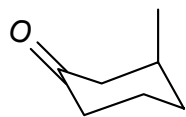
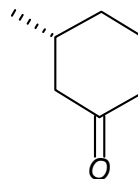
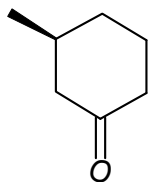


2. Relative configuration continued

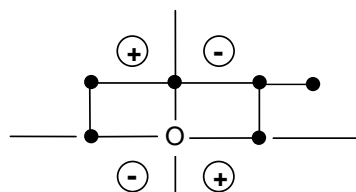
III. Determining the absolute configuration (!!!)

example

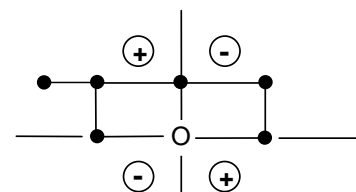
Is (+)-3-methylcyclohexanone R or S configured?



would be
(+) CE
but axial



(-) CE



(+) CE

Requirement for ORD/CD as an absolute method:

Knowledge of the conformation!

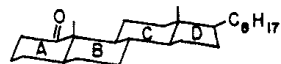
⇒ configuration is R

from the drawing on top

2. Relative configuration continued

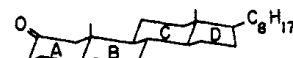
IV. Size of the CE and front octants

cholestanones



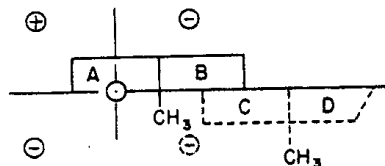
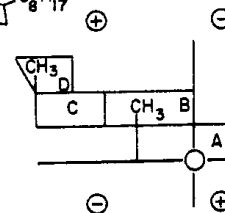
$\alpha = \text{small}$

3



$\alpha = +121$

4



front octants
occupied



$\alpha = +55$

5

