2. Relative configuration continued

A. Through chemical interconversion

B. Through chirooptical 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 $\alpha$ with substitution

- principle: space around the cyclohexanone is divided into 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

- upward position of the ring
- along the O=C bond towards the ring

placed in the octants (Djerassi, 1960):

viewed projection: back octants matter!

not like this: downward position!

would give a wrong analysis!

Lightner, Gurst, Stereochemistry from circular dichroism spectroscopy, Wiley, NY, 2000

“octant system”
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

- near node, small contribution
- on node, no contribution
- large (+) CE
- small (-) CE
2. Relative configuration continued

III. Determining the absolute configuration (!!!!)

Example

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

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

Eliel, Wilen, Stereochemistry of organic compounds, Wiley, NY, 1994