CICLOALCANI – HIDROCARBURI SATURATE CICLICE

CURS

http://www.chim.upt.ro/ro/cb-profile/94-mihai-medeleanu-upt-ro

→ Documente

Definiţie

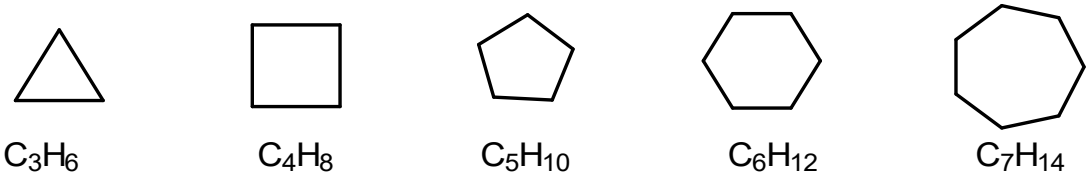
- sunt hidrocarburi saturate (numai cu legături simple C –C) cu catenă ciclică avand atomii de C hibridizaţi sp^3 (cifra de nesaturare =1 datorită pierderii a doi at. de hidrogen prin închiderea ciclului)

Formula generală : **C_nH_{2n}**

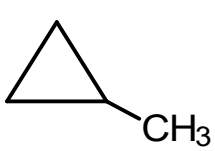
în funcţie de numărul ciclurilor din moleculă şi de poziţia reciprocă a acestora formule sunt: **C_nH_{2n-2}; C_nH_{2n-4}; C_nH_{2n-6};** etc.

Clasificare:

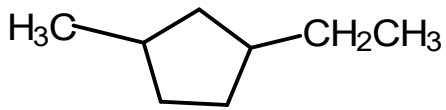
- cu un ciclu, cu sau fara ramificaţii (catene laterale):



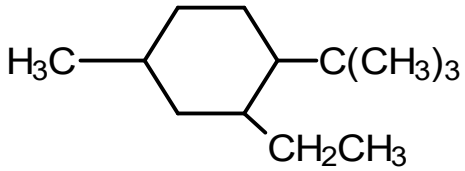
C_3H_6 C_4H_8 C_5H_{10} C_6H_{12} C_7H_{14}



1 C_4H_8



2 C_8H_{16}

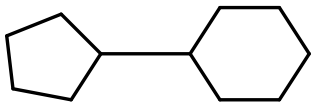


3 $C_{13}H_{26}$

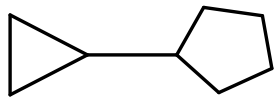
Clasificare:

- cu două sau mai multe cicluri, bi-, tri- …policiclici;

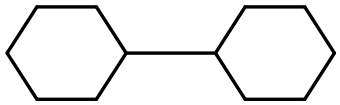
1) Sisteme policiclice izolate



4 $C_{11}H_{20}$

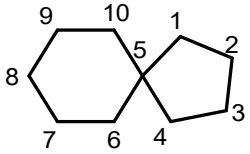


5 C_8H_{14}

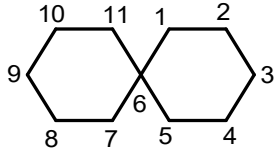


6 $C_{12}H_{22}$

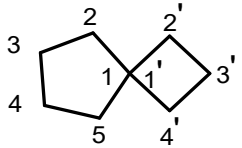
2) Sisteme ciclice cu un atom de carbon comun – ***spiranice***:



7 $C_{10}H_{18}$

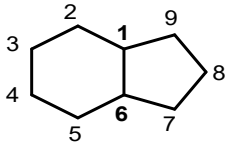


8 $C_{11}H_{20}$



9 C_8H_{14}

3) Sisteme ciclice cu mai mulţi atomi de carbon comuni – ***bi-, tri-, …, poli-cicluri:***



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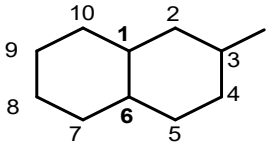

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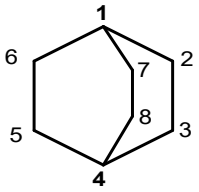

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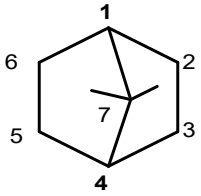

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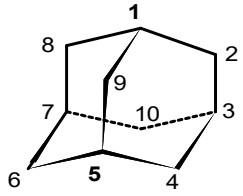

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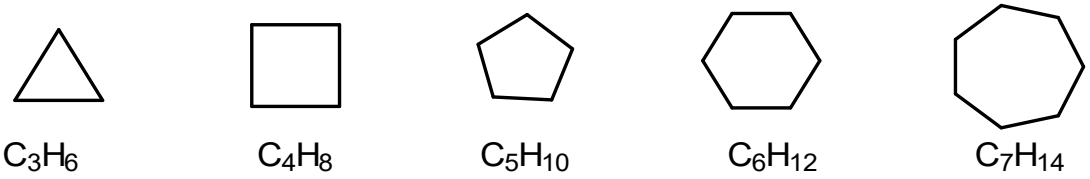
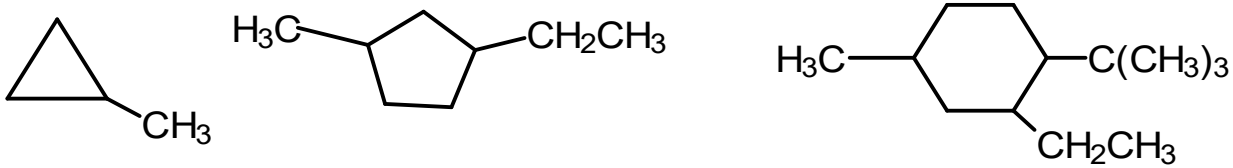
Denumirea cicloalcanilor - conform regulilor **IUPAC**



C_3H_6 C_4H_8 C_5H_{10} C_6H_{12} C_7H_{14}

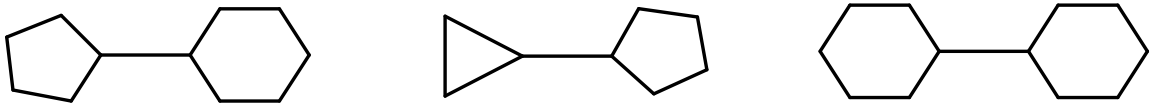
ciclopropan; ciclobutan; ciclopentan; ciclohexan; cicloheptan;



1 C_4H_8 **2** C_8H_{16} **3** $C_{13}H_{26}$

1: Metilciclopropan **2**: 1-Etil-3-metilciclopentan; **3**: 1-*terţ*-Butil-2-etil-4-metilciclohexan

Numerotarea!

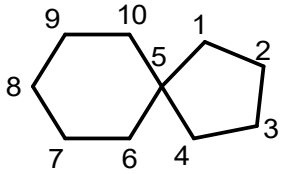


4 $C_{11}H_{20}$ **5** C_8H_{14} **6** $C_{12}H_{22}$

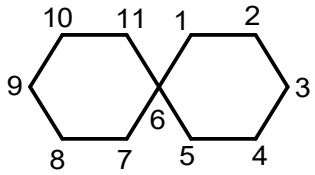
4: ciclopentilciclohexan **5**: ciclopropilciclopentan **6**: ciclohexilcilohexan

Se denumește prima dată ciclul mai mic – ca radical

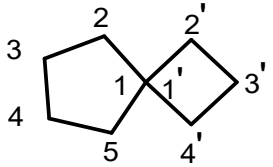
Denumirea cicloalcanilor



7 $C_{10}H_{18}$

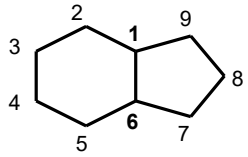


8 $C_{11}H_{20}$



9 C_8H_{14}

7 Spiro[4.5]decan; **8** Spiro[5.5]undecan **9** Ciclopentan-1-spiro-1'-ciclobutan



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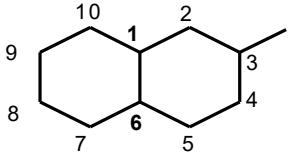

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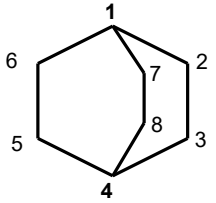

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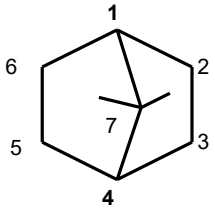

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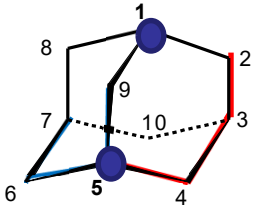

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10 Biciclo[4.3.0]nonan **11** 3-Metil-biciclo[4.4.0]decan **12** Biciclo[2.2.2]octan

13 7,7-Dimetilbiciclo[2.2.1]heptan **14** Triciclo[3.3.1.$1^{3,7}$]decan (adamantan)

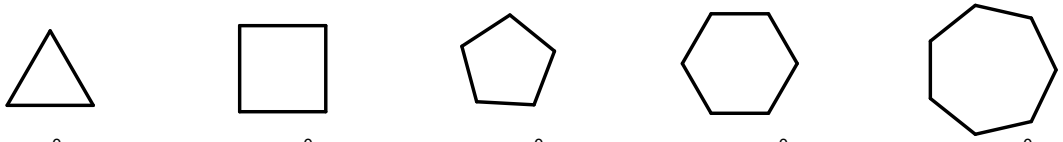
Structura electronică şi geometria cicloalcanilor

- toti atomii de carbon sunt hibridizaţi sp^3

-au geometrie tetraedrică,

-legăturile C – C şi C – H sunt de tip σ şi practic nepolare.

-deformare unghiurilor de valenţă pentru legăturile C – C din ciclu (daca ar fi plane)



<u>"teoria tensiunii în cicluri"</u>- Bayer

Stabilitatea ciclurilor (bazata pe reactivitate):

- ***ciclurile mici*** (de 3 şi 4 atomi de carbon) - stabilitate mica (mai reactive);
- ***ciclurile normale*** (cu 5 – 7 atomi de C) - cele mai stabile
- ***ciclurile medii*** (cu 8 – 12 atomi de C) - mai puţin stabile (tensiuni inverse);
- ***ciclurile mari*** (cu peste 12 atomi de C) - stabile

Tabel: Căldurile de ardere, stabilitatea şi clasificarea cicloalcanilor: $(CH_2)_n$

n	ΔH_{CH_2} (Kcal/mol)	$\Delta H_{CH_2} - 157,4$ (Kcal/mol)	Clasificare, stabilitate (calitativ)
3	166,6	9,2	***Cicluri mici**;* stabilitate mică;
4	164,4	6,6	
5	158,7	1,3	***Cicluri normale**;* stabilitate mare;
6	157,4	0	
7	158,3	0,9	
8	158,6	1,2	***Cicluri medii**;* stabilitate medie;
9	158,8	1,4	
12	157,6	0,2	***Cicluri mari**;* stabilitate mare;
15	157,5	0,1	
16	157,2	- 0,2	

$$C_nH_{2n} + 3n/2O_2 \longrightarrow nCO_2 + nH_2O \quad \Delta Hr \qquad \Delta H_{CH2} = \frac{\Delta Hr}{n}$$

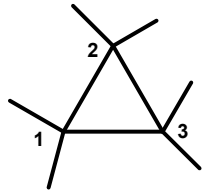
$$CH_3 - (CH_2)_n - CH_3 + (3n+7)/2\ O_2 \longrightarrow (n+2)CO_2 + (n+3)H_2O \quad \Delta Hr_{alc}$$

$$\Delta H_{CH2} = \frac{\Delta Hr_{alc} - \Delta H_{(CH3)2}}{n} = 157,4 \text{ Kcal/mol}$$

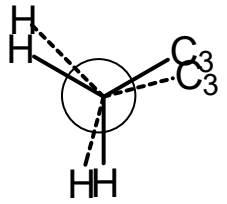
<u>Ciclopropanul</u> – singurul ciclu plan, - stabilitatea cea mai mică datorita:

- ***tensiunii angulare (Bayer) mari***

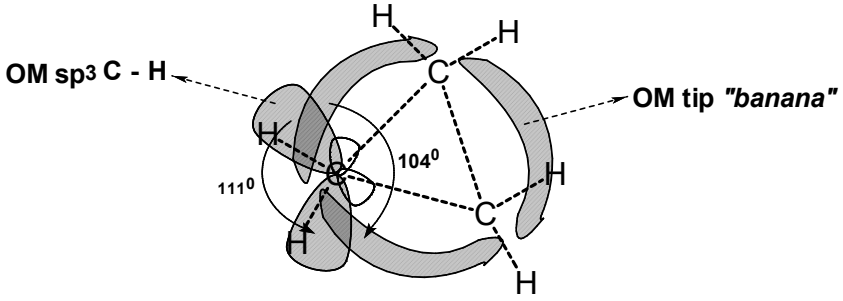
- conformaţie eclipsata - ***"tensiunea Pitzer"***:



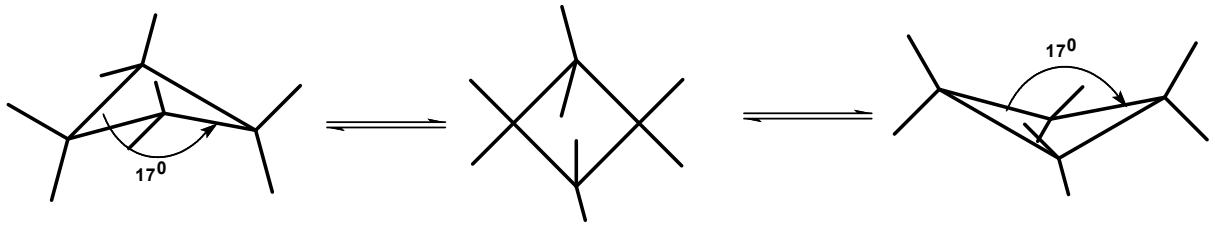
Ciclopropanul plan



Proiectia *Newman* prin legatura C_1- C_2

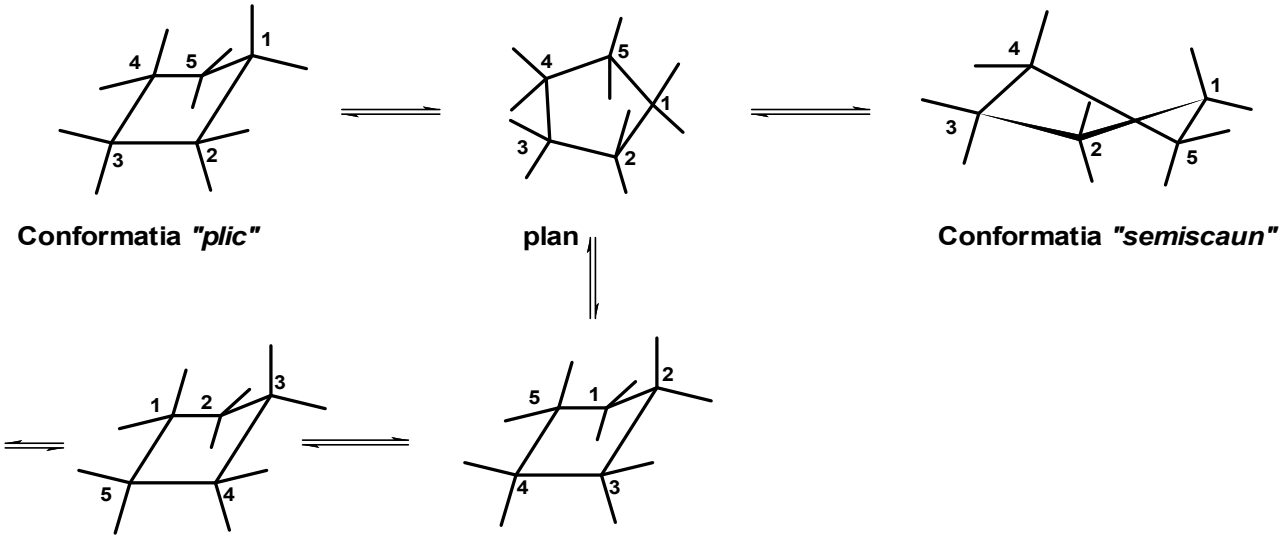


Ciclobutanul – **conformatie** neplană ***"pliată"*** mai stabila



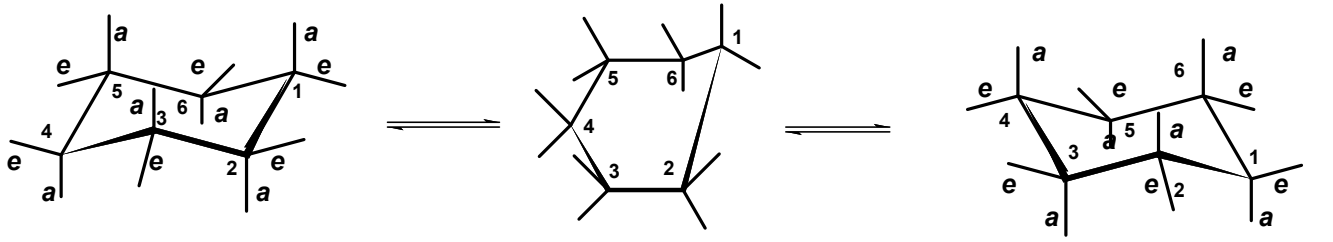
Ciclobutanul *"flexibil"*

Ciclopentanul – 2 conformatii neplane flexibile (semiscaun si plic)

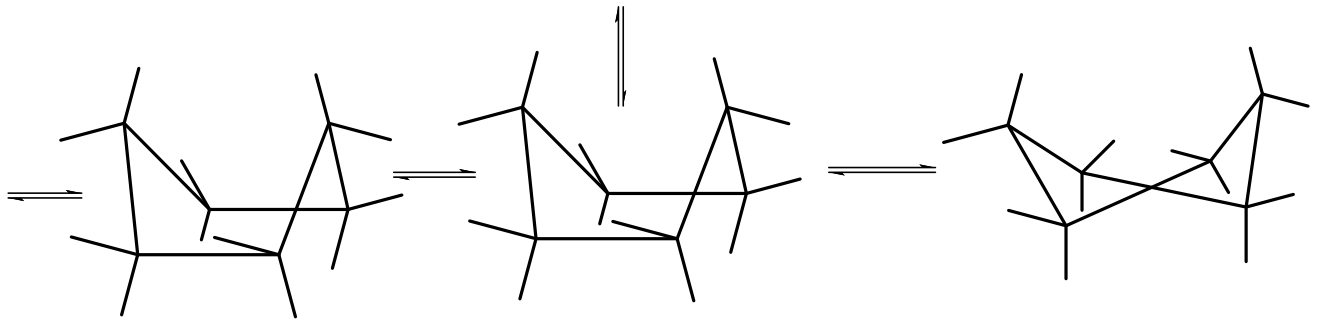


Conformatia *"plic"* **plan** **Conformatia *"semiscaun"***

Ciclohexanul – 2 conformatii neplane (scaun si baie)

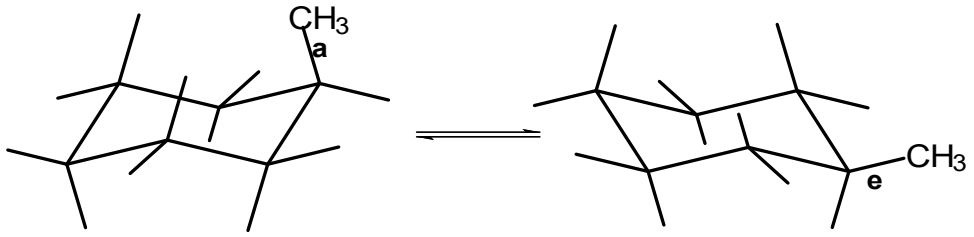


"scaun" *"semiscaun"* *"scaun" inversata*



Conformatii *baie (vana, barca)* (flexibile) **Conformatie *"baie rasucita"***

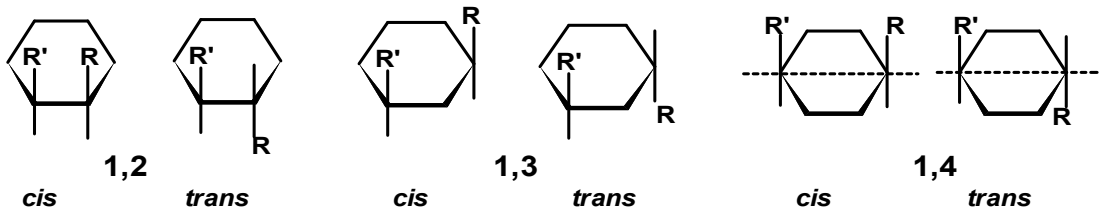
a: pozitii *"axiale"*
e: pozitii *"ecuatoriale"*



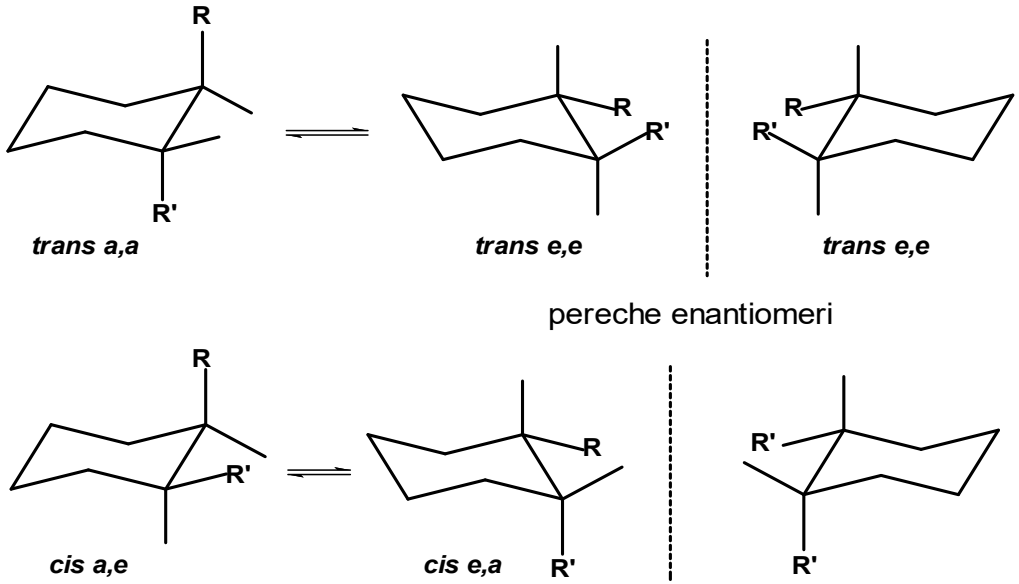
***"inversia"* ciclului**

Ciclohexanul disubstituit- tipuri de izomerie

Diastereoizomerie cis-trans

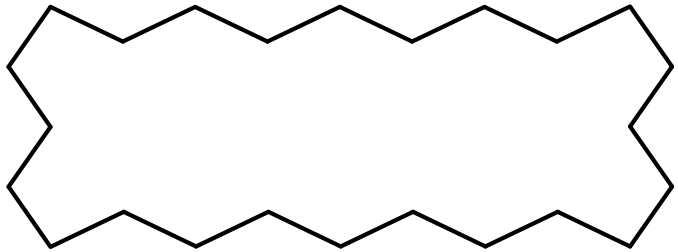


Diastereoizomerie optica



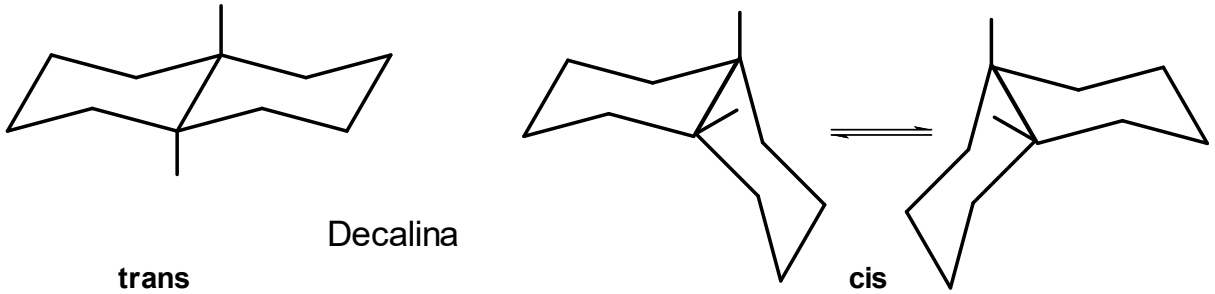
R = R' - pereche enantiomeri
R = R' - 1 izomer ***mezo***

Ciclurile medii şi mari- geometrie neplana



$C_{24}H_{48}$

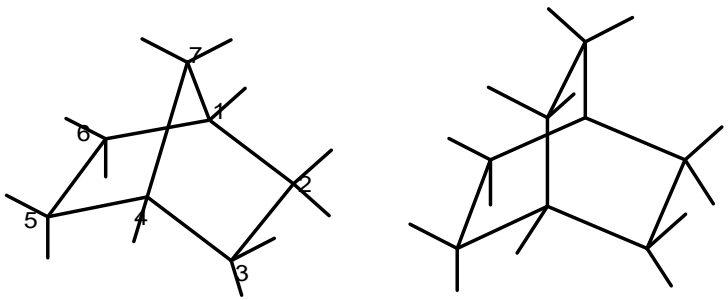
Sistemele biciclice condensate

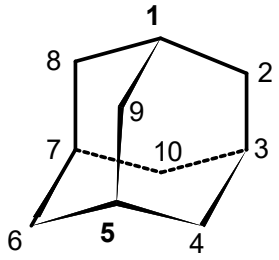


Decalina

trans **cis**

Sistemele biciclice cu mai mulţi atomi comuni





Reactivitatea generală - similară alcanilor.

- reacţii de substituţie radicalică

- descompuneri termice

- reacţii ionice în prezenţa unor acizi tari care generează carbocationi).

-pentru ciclurile mici, pentru care se poate considera că atomii de carbon au o hibridizare diferită de cea normală, legăturile C – C au caracter parţial de orbital p ceea ce face posibile şi eventuale reacţii de adiţie electrofilă sau radicalică.

Proprietăţi fizice

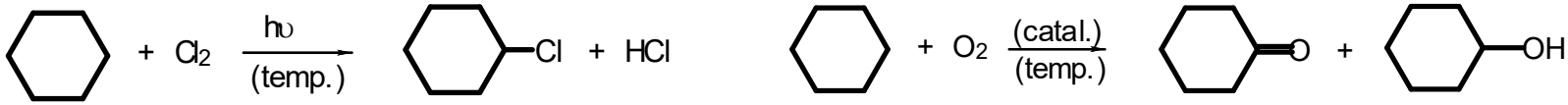
-substanţe nepolare, cu interacţiuni intermoleculare exclusiv de tip Van der Waals.

-punctele de topire şi de fierbere sunt scăzute, o influenţă remarcabilă asupra lor având însă şi simetria moleculei.

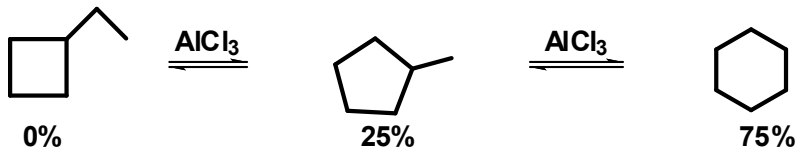
-solubilitatea în apă este foarte mică, cicloalcanii normali dizolvă însă substanţe organice nepolare sau puţin polare, fiind utilizaţi şi ca solvenţi nepolari.

Proprietăţi chimice

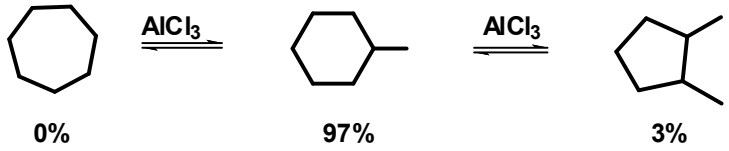
Reactii radicalice



Reactii ionice - izomerizarea



Concluzii ???



Proprietăţi chimice

Reactii de adiţie – la cicluri mici

- hidrogenarea catalitică cu H_2 si catalizatori Ni, Pt, Pd la presiune si temperatura

$$\textit{ciclo}\text{-}C_3H_6 + H_2 \longrightarrow CH_3 - CH_2 - CH_3$$
$$\textit{ciclo}\text{-}C_4H_8 + H_2 \longrightarrow CH_3 - CH_2 - CH_2 - CH_3$$

- **adiţia bromului**
- **adiţia acidului bromhidric,**
- **adiţia apei** (în prezenţă de acid sulfuric) la ciclopropan sau ciclobutan

$$+ Br_2 \xrightarrow{20^0} Br - CH_2 - CH_2 - CH_2 - Br + CH_3 - CH_2 - CH_2 - CHBr_2$$

$$+ HBr \longrightarrow CH_3 - CH_2 - CH_2 - Br$$

$$+ H_2O \xrightarrow{H_2SO_4} CH_3 - CH_2 - CH_2 - OH$$

Mecanismul acestor adiţii este asemănător cu cel al adiţiilor electrofile la alchene