

# Bridged rings, Caged molecules and Adamantane

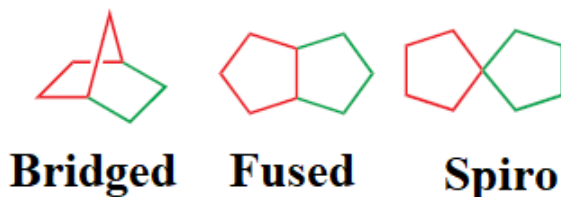
***Paper 4201 B***

***Organic Chemistry  
(Special-II)***

# BRIDGED BICYCLIC RINGS

## Mainly three kinds of bicyclic compounds

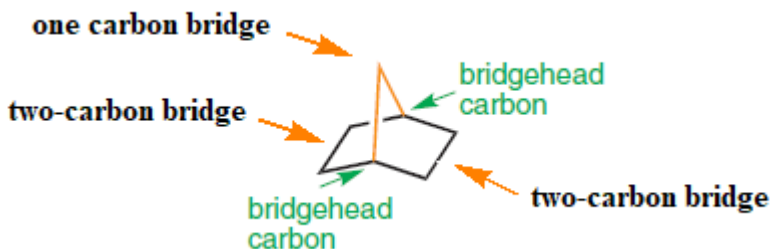
- **Bridged** bicyclic compounds-a bridge of atom(s) is thrown across from one side of the ring to the other.
- **Fused** bicyclic compounds- one *bond* common to both rings
- **Spiro** compounds - one *atom* common to both rings



## Naming bicyclic compounds:

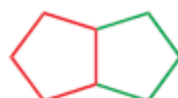
e.g., Norbornane: The total number of carbons is 7 carbons so the **parent name is heptane**.

The total number of carbons between bridgeheads are 2, 2, and 1, they are placed in descending order between brackets separated by dots.



Norbornane

**bicyclo[2.2.1]heptane**



**bicyclo[3.3.0]octane**



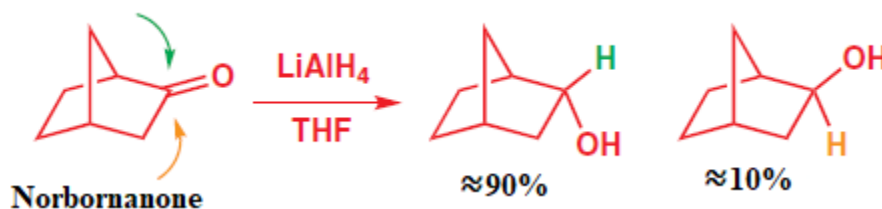
**spiro[4.4]nonane**

**Fused and bridged bicyclic compounds get the prefix *bicyclo*, whereas spirocyclic compounds get the prefix *spiro*.**

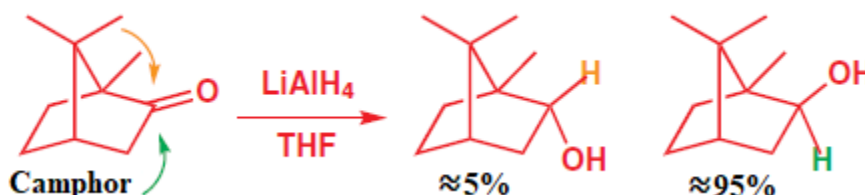
## Reactions:

Bridged structures (**also referred to as cage structures**) are generally very rigid and generally adopt a single conformation

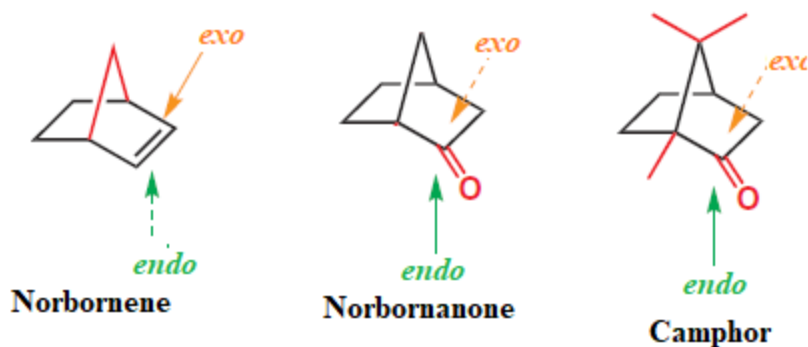
*Attack on unsubstituted bridged ketone (norbornanone) occurs predominantly from the side of the one-atom bridge rather than the two-atom bridge*



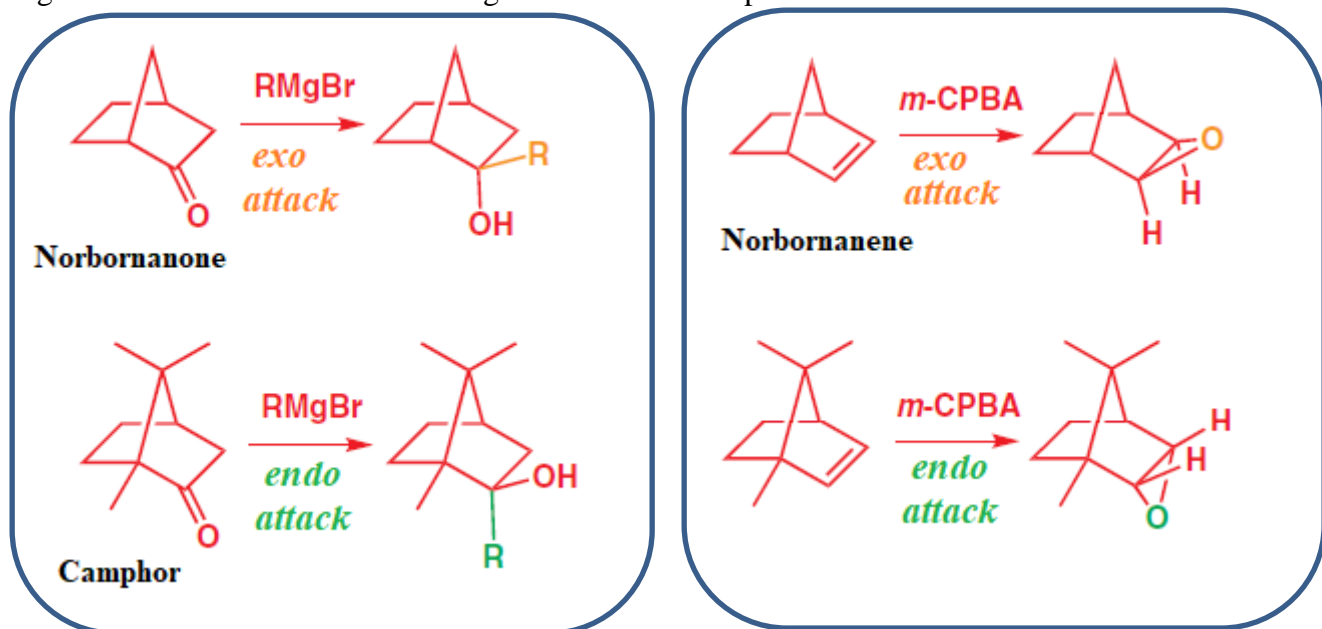
- A complete reversal of selectivity is seen in camphor due to steric hinderance from the side of one-atom bridge



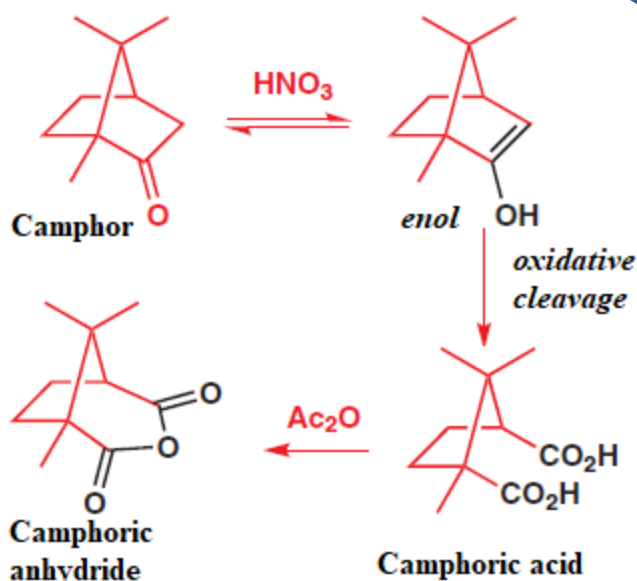
- The two faces of the ketonic group or the C=C double bond in bridged bicyclic compounds are called *endo* (inside) and *exo* (outside) of the boat-shaped six-membered ring.



- Steric hinderance in the bridged bicyclic compounds governs the selectivity of the product by directing the attack from the *exo*- or *endo*- side.
- e.g. this effect can be seen in the Grignard reaction and epoxidation reaction as shown below:



- C–C bonds can be cleaved by powerful oxidizing agents such as  $\text{HNO}_3$ . e.g. Oxidation of camphor with Conc.  $\text{HNO}_3$  cleaves a C–C bond adjacent to the C=O group and gives diacid.
- Since the molecule has a fixed conformation due to the bridge, the cleaved diacid has *cis*-COOH groups.
- This was confirmed by forming bridged bicyclic anhydride from camphoric acid.



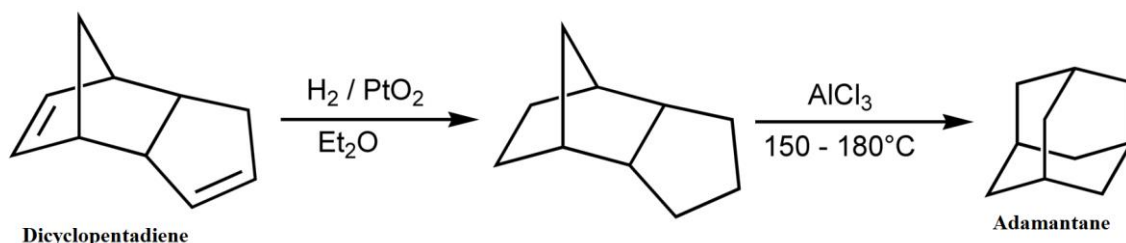
# Adamantane (C<sub>10</sub>H<sub>16</sub>)

- Adamantane molecules consists of three connected cyclohexane rings arranged in the "armchair" configuration.
- It both rigid and strain-free.

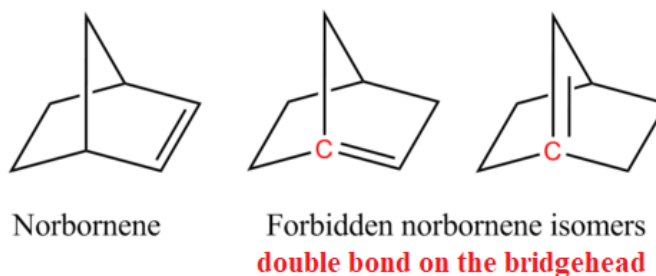


## Synthesis

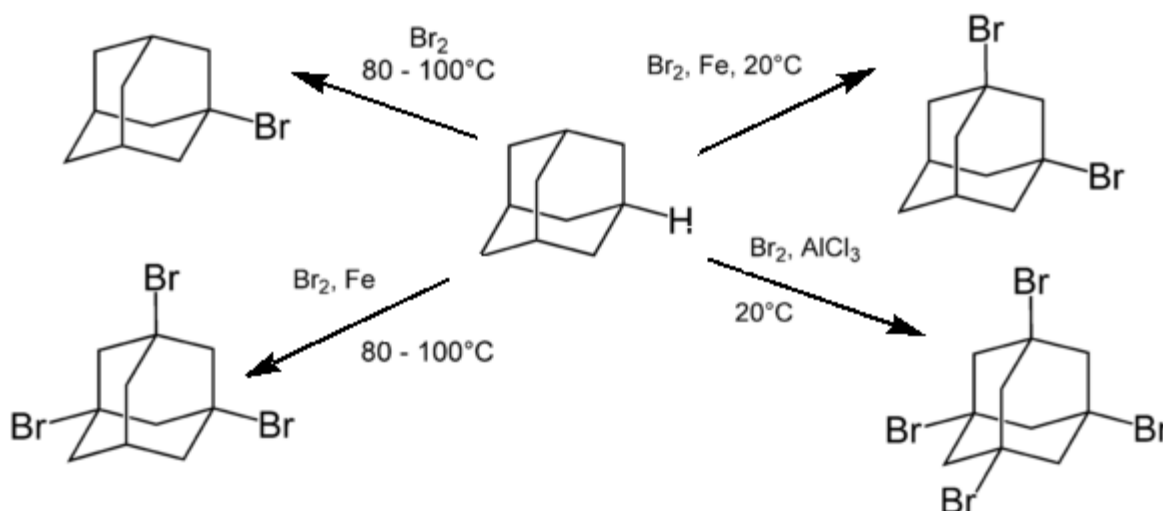
Hydrogenation of dicyclopentadiene in the presence of PtO<sub>2</sub> as catalyst followed by its transformation into adamantane using AlCl<sub>3</sub> (Lewis acid catalyst).



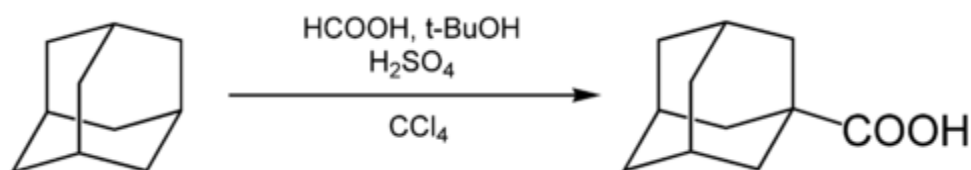
**Bredt's rule** (empirical rule) states that a double bond cannot be placed at the bridgehead of a bridged ring system, unless the rings are large enough. Therefore, the two isomers of norbornene (shown below) violate Bredt's rule, which makes them too unstable to prepare.



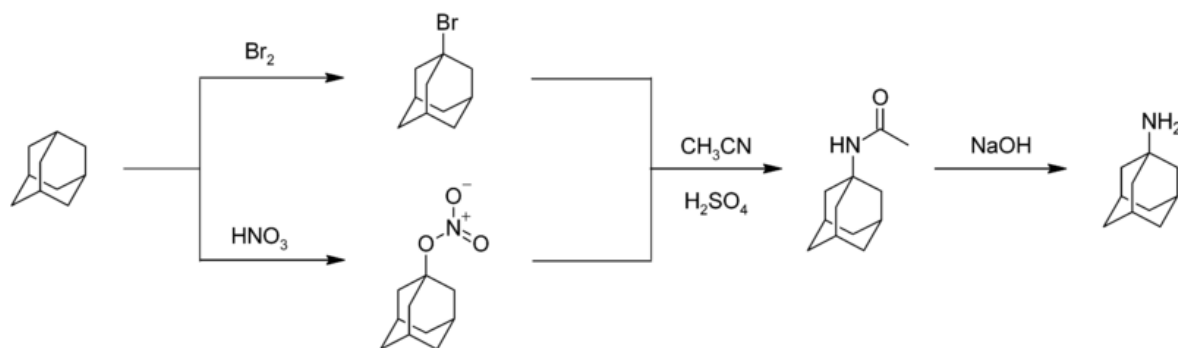
- **For the same reason, introduction of double bond in the ring system of adamantane is sterically impossible.**
- **Adamantane undergoes bromination readily.** The composition and the ratio of the reaction products depend on the reaction conditions and the type of catalyst used.



**Carboxylation of adamantane:** using formic acid as a carboxylating agent in  $\text{CCl}_4$ . *t*-BuOH and sulfuric acid are added to generate adamantane cation which is then carboxylated by carbon monoxide generated *in situ* in the interaction between the  $\text{HCOOH}$  and  $\text{H}_2\text{SO}_4$ .



### Some other reactions:



### Rearrangements involving the Peripheral Shift of Substituents

Substituted adamantanes undergo acid-catalyzed peripheral shifts easily.



Exposure of 1-adamantanol to 96%  $\text{H}_2\text{SO}_4$  at  $70^\circ\text{C}$  gives adamantanone in good yields. Experiments revealed that in 96 %  $\text{H}_2\text{SO}_4$ , 1-adamantanol exists at equilibrium with 2-adamantanol ( $\approx 2\%$ ) of the mixture at  $25^\circ\text{C}$ . Thus, it was suggested that the ketone is formed by disproportionation and/or direct oxidation of the secondary alcohol.

