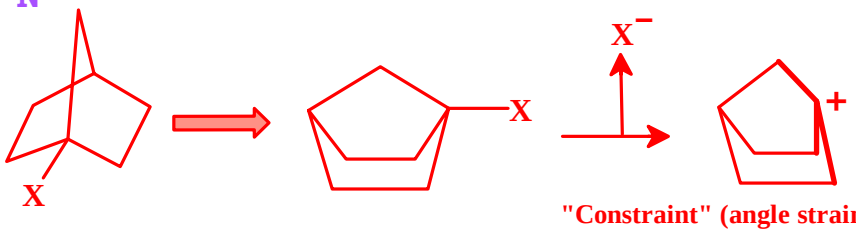
Syllabus Supplement #1

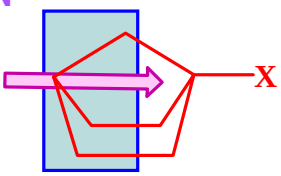
Nucleophilic Substitution At a Bridgehead

S_N1

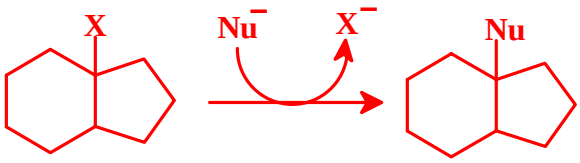


"Constraint" (angle strain) as the inflexible bicyclic system is distorted as it tries to form a planar carbocation

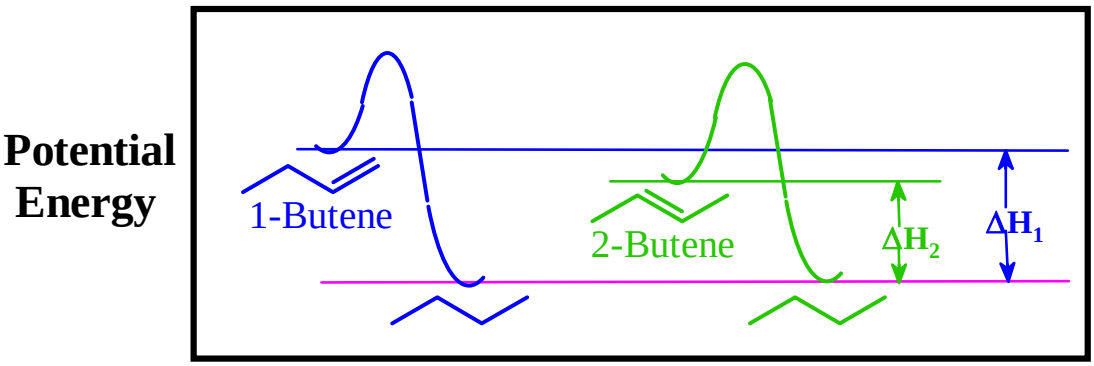
S_N2



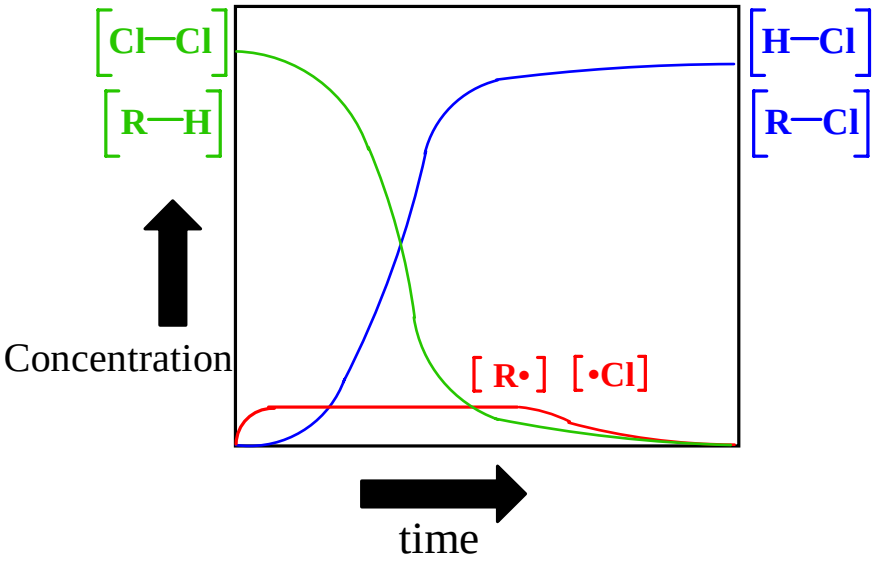
The "backside attack" by the nucleophile is blocked by the "cage" of carbon atoms surrounding the reaction site. Also, the constraints of the bicyclic system would prevent the necessary inversion of configuration.



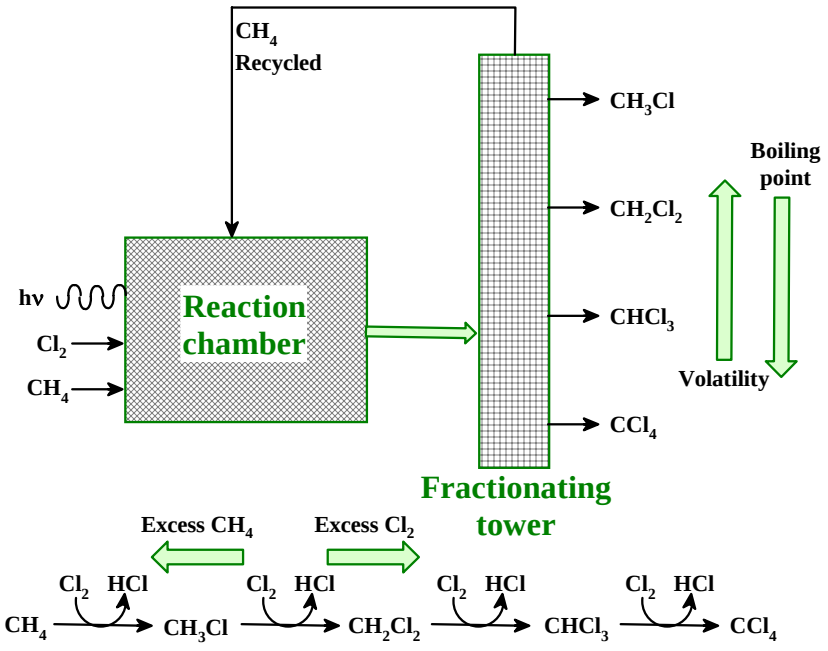
Fused bicyclic systems, such as the 1-halobicyclo[4.3.0]nonyl system to the left do not suffer these constraints. They undergo S_N1 or S_N2 reactions with little or no difficulty.



Electronic Reorganization



INDUSTRIAL PREPARATION OF POLYCHLOROMETHANES



EXAMPLE PROBLEMS—BOND DISSOCIATION ENERGY

1. Given the following bond dissociation energies, ΔH°, in kcal/mole:

   CH_3—OH 91 H—F 136 CH_3—F 109 H—OH 119

   Calculate the heat of reaction ΔH°_r, for the following reaction:

$$\underset{91}{CH_3OH} + \underset{136}{HF} \longrightarrow \underset{109}{CH_3F} + \underset{119}{H_2O} \qquad 91 + 136 - 109 - 119 = -1 \text{ kcal}$$

$$CH_3\text{—}OH \longrightarrow \bullet CH_3 + \bullet OH \qquad \Delta H^\circ = +91 \text{ kcal}$$

$$H\text{—}F \longrightarrow \bullet H + \bullet F \qquad \Delta H^\circ = +136 \text{ kcal}$$

$$\bullet CH_3 + \bullet F \longrightarrow CH_3\text{—}F \qquad \Delta H^\circ = -109 \text{ kcal}$$

$$\bullet H + \bullet OH \longrightarrow H\text{—}OH \qquad \Delta H^\circ = -119 \text{ kcal}$$

$$CH_3OH + HF \longrightarrow CH_3F + H_2O \qquad \Delta H^\circ = -1 \text{ kcal}$$

2. For the following reaction, ΔH° = –66.8 kcal:

   $CH_3OOCH_3 + H_2 \longrightarrow 2\ CH_3OH$

   Given the following bond dissociation energies, ΔH°, in kcal/mole:

   CH_3O—OCH_3 38 H—H 104.2

   Calculate the bond dissociation energy for CH_3O—H .

$$\underset{38}{CH_3O\text{—}OCH_3} + \underset{104.2}{H\text{—}H} \longrightarrow 2\ \underset{x}{CH_3O\text{—}H}$$

$$38 + 104.2 - 2x = -66.8$$

$$2x = 38 + 104.2 + 66.8 = 209$$

$$x = +\overline{104}.5 \Longrightarrow +105 \text{ kcal/mole}$$

IMPORTANT!