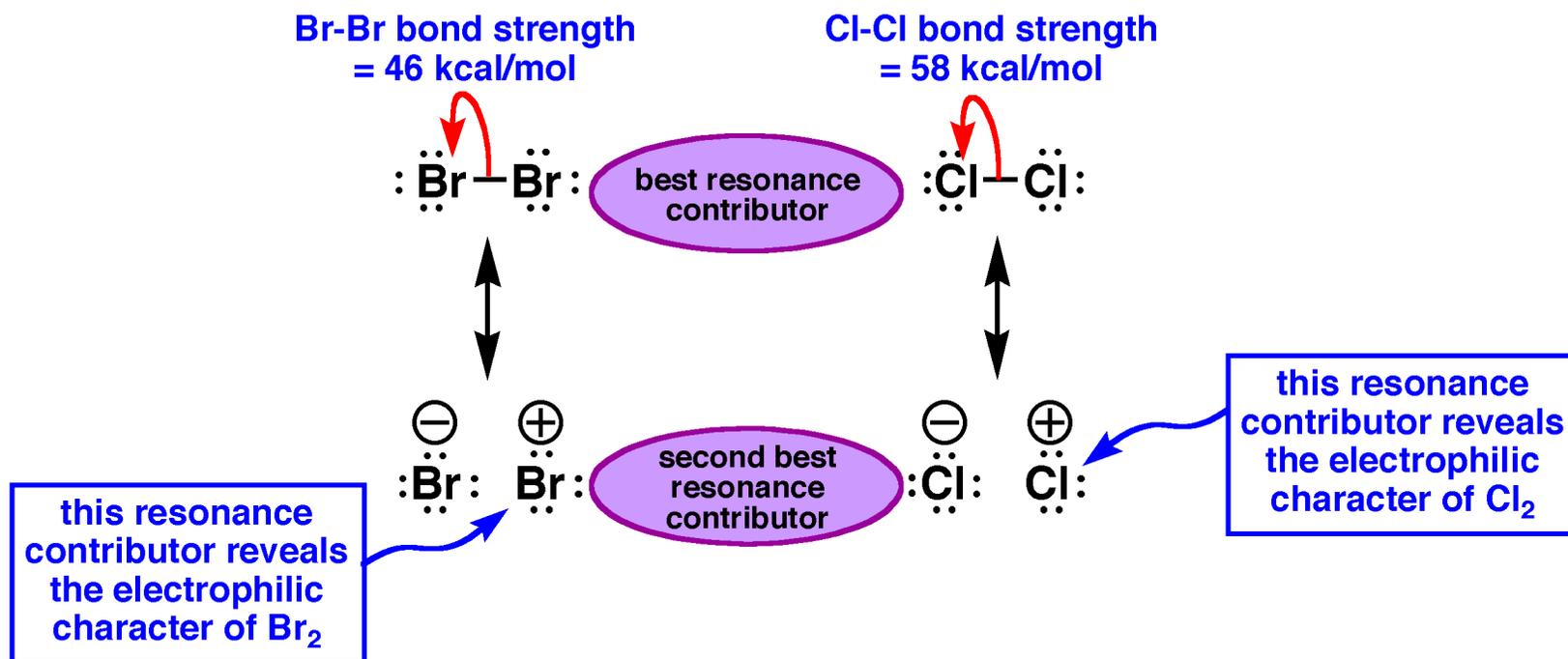


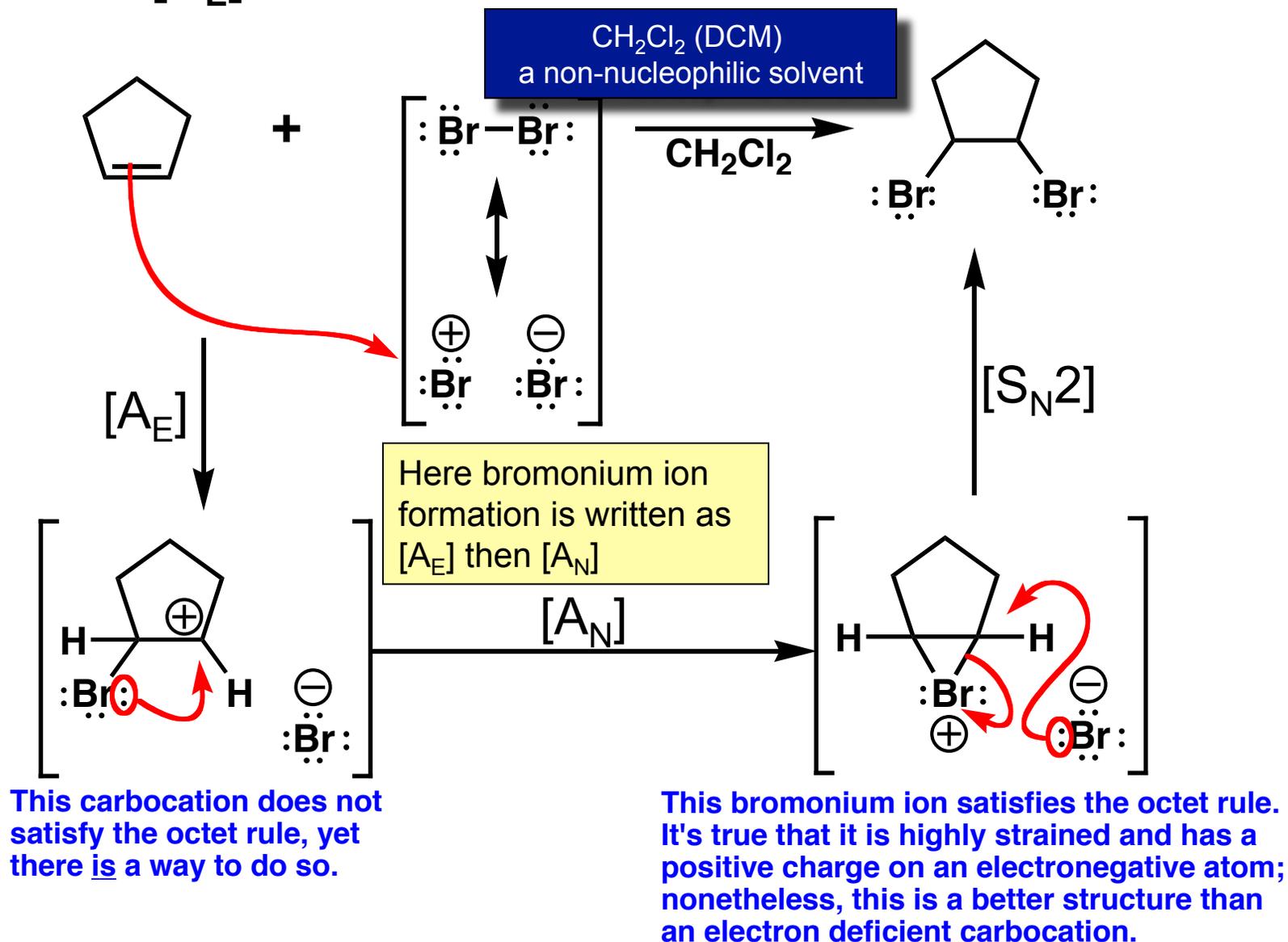
Rationalizing Br₂ and Cl₂ As Electrophiles

Reagents such as Cl₂, Br₂, I₂, and ICl are electrophiles that add to alkenes. We will see that these reactions follow the [Ad_E2] mechanism with a slight variation, as a consequence of the lone pair on these electrophiles. First, how can these reagents be rationalized as electrophiles? The answer is that they have weak bonds and low lying empty σ* orbitals. The resonance picture below may help build your intuition about structure and reactivity. Very often the second best resonance contributor provides insight about reactivity.



Addition of Br₂ to an Alkene

When the Electrophile Possesses a Lone Pair, [A_E] Gives a “Halonium Ion” Intermediate



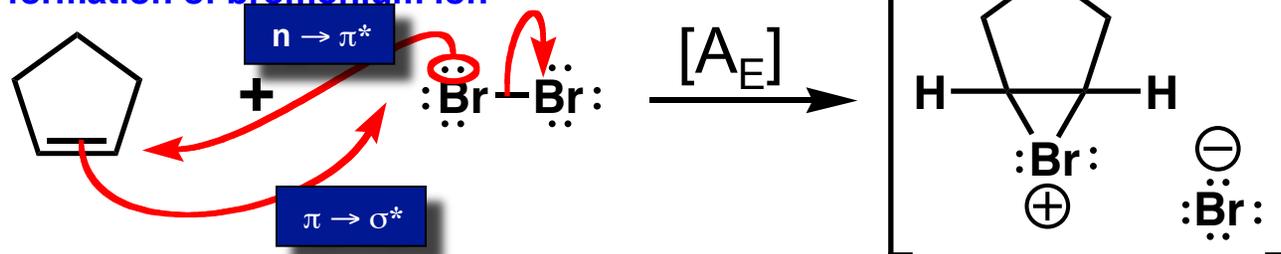
[A_E] of Br₂ to a Carbon-Carbon π-Bond

It is possible to proceed directly to the bromonium ion from Br₂ and alkene by combining [A_E] and [A_N] into one step. This reflects the fact that the carbocation may not be an intermediate on the MEP for this reaction. The curved arrow notation might seem complex, but shows all of the electron reconfiguration that accompanies this process. The overall process is [A_E], an association of the electrophile, Br₂, with C=C π-bond. The curved arrows imply a pair of filled-empty (frontier) orbitals for this step:

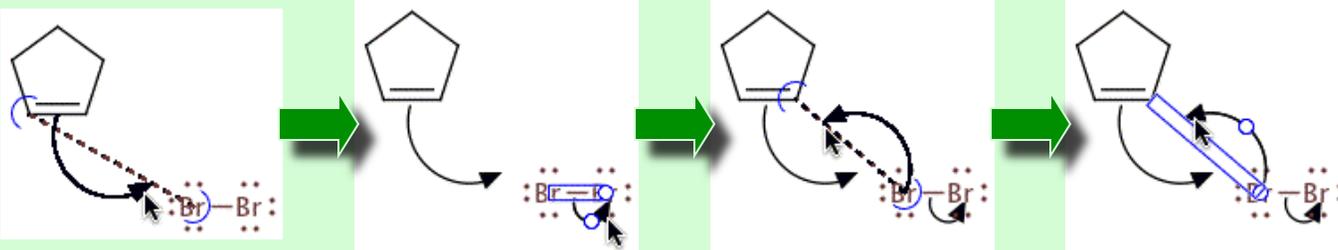
- $\pi \rightarrow \sigma^*$
- $n \rightarrow \pi^*$

Expressed in words, we've combined the alkene's HOMO with Br₂'s LUMO ($\pi \rightarrow \sigma^*$), and we've combined Br₂'s HOMO with the alkene's LUMO ($n \rightarrow \pi^*$).

curved arrow notation for direct formation of bromonium ion



What it looks like in ACE Organic...

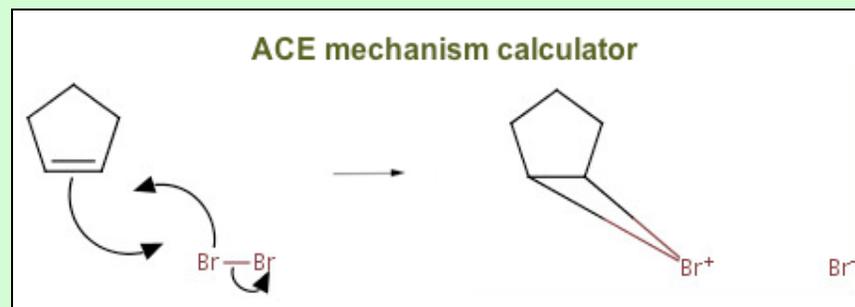


Draw the 1st arrow

After the 2nd arrow

Draw the 3rd arrow

After the 3rd arrow



Clean in 2D

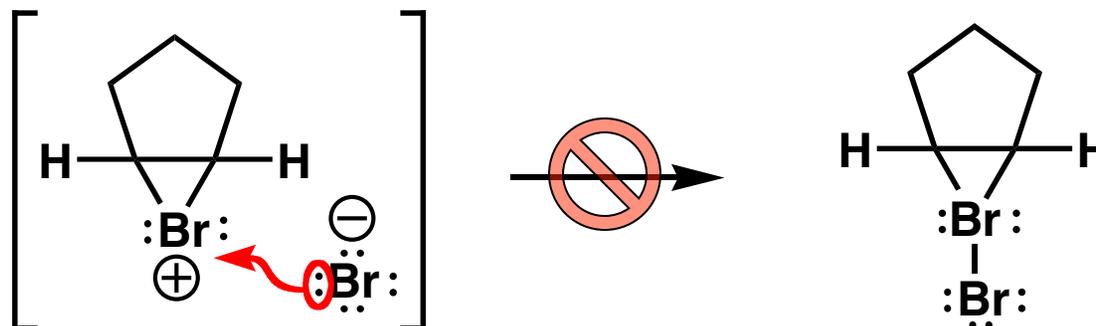
Electrophilic addition to alkenes	Stereospecific addition
Diels-Alder reactions	Epoxidation peracid
Nucleophilic substitution	Unsymmetrical alkenes HBr
Elimination	Regioselective addition
	Diene bromination

<http://www.chemtube3d.com/>

A Bromonium Ion Behaves Much Like a Protonated Epoxide

Reason by analogy

the bromide nucleophile does NOT attack the positively charged Br



[A_N] at Br⁺ is not reasonable because there's no low lying empty atom-centered orbital. [S_N2] at carbon (NOT Br⁺) is most reasonable.

the electrophilic sites of the bromonium ion are revealed by the second best resonance contributors

