

Building models in RMG – PART 3

Shamel Merchant

Reaction Libraries – usage and pitfalls

- Reaction Library

Usage:



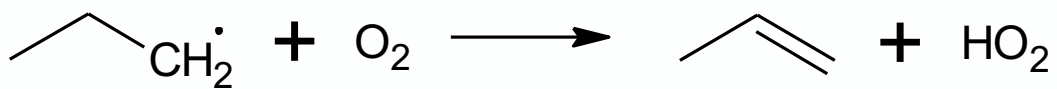
1. If the reaction rate is measured experimentally

Pitfall:

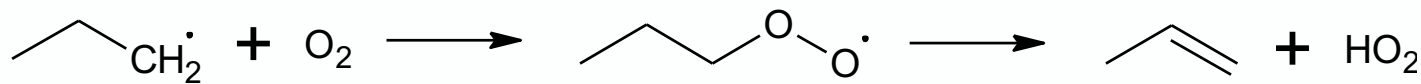
Once reaction libraries has mixed high-P and Pdep rates, you cannot run Pdep module of RMG. This leads to double accounting for the rates.

Reaction Libraries – usage and pitfalls

- Literature rates are reporting the overall rate for this reaction not the disproportionation rate which is being represented above

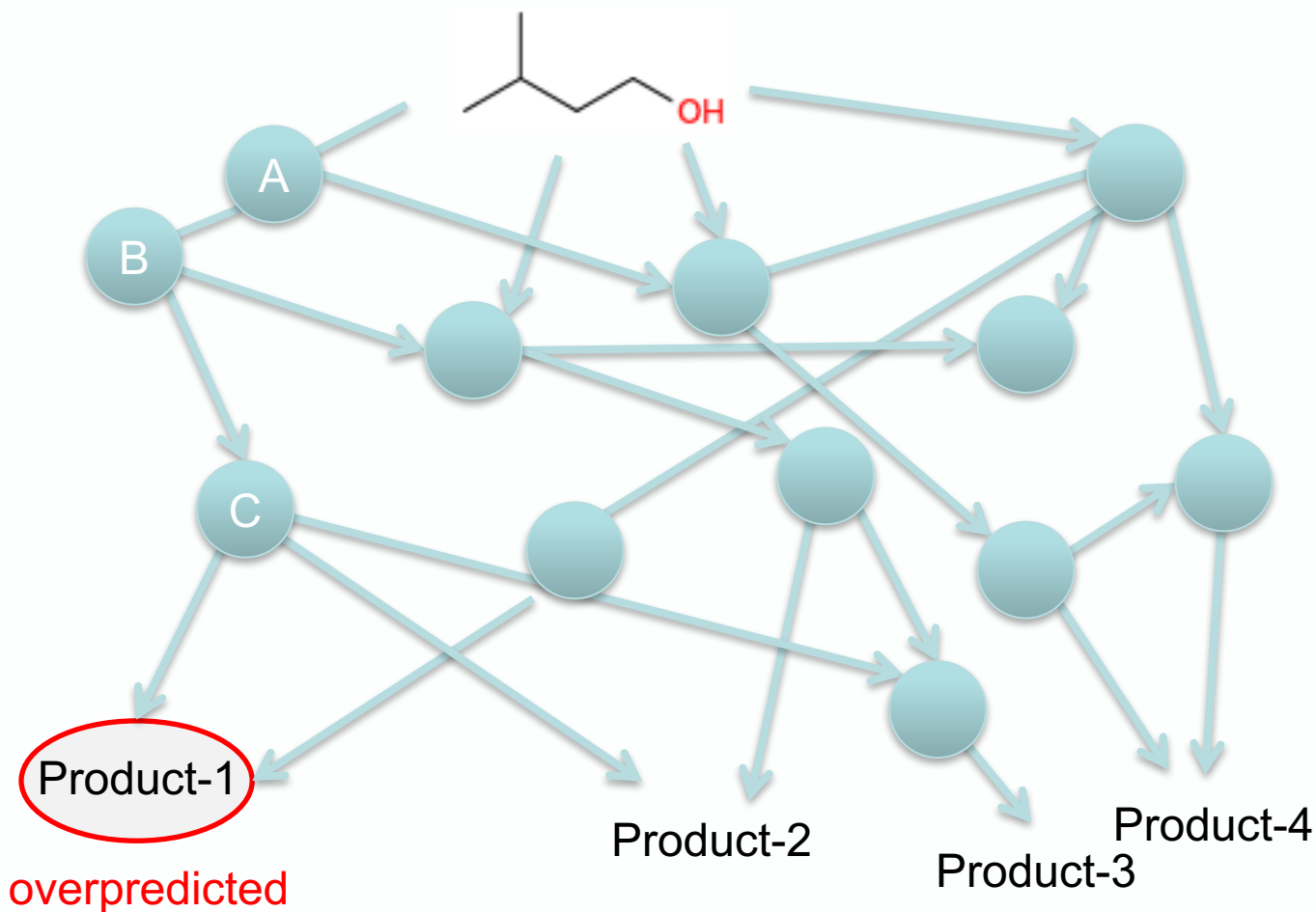


- If we now run RMG with pressure dependence and use the reaction rate in Reaction Libraries then RMG uses it as a high P for disproportionation rate.



General tip for model construction

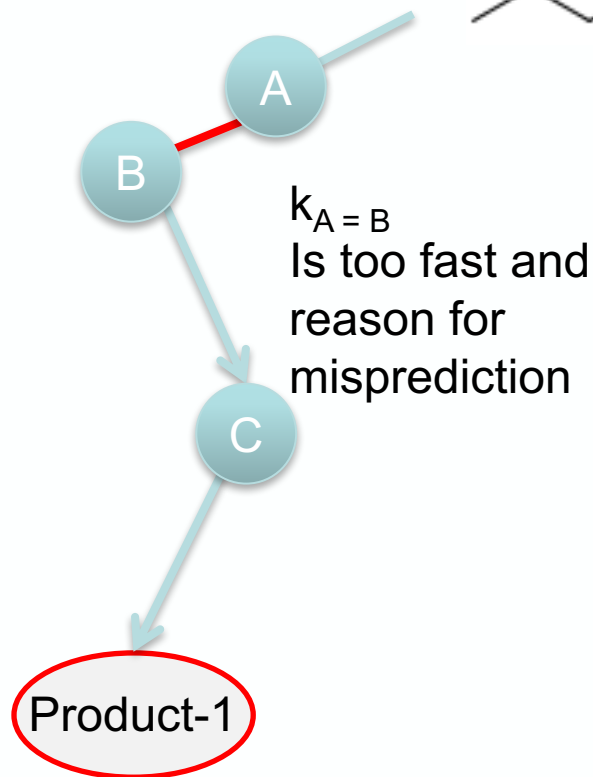
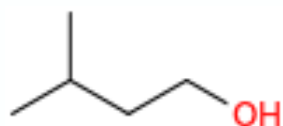
1. Start making your models initial at high pressure limit – the model is more transparent and easy to track



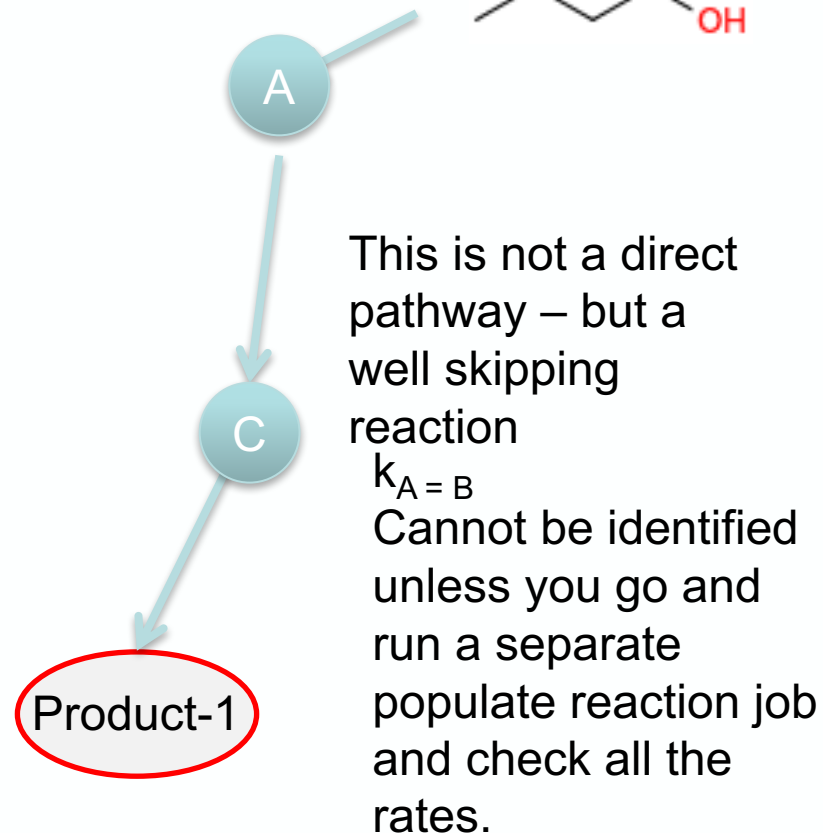
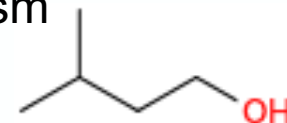
General tip for model construction

Its easier to inspect the pathway

High Pressure
Mechanism



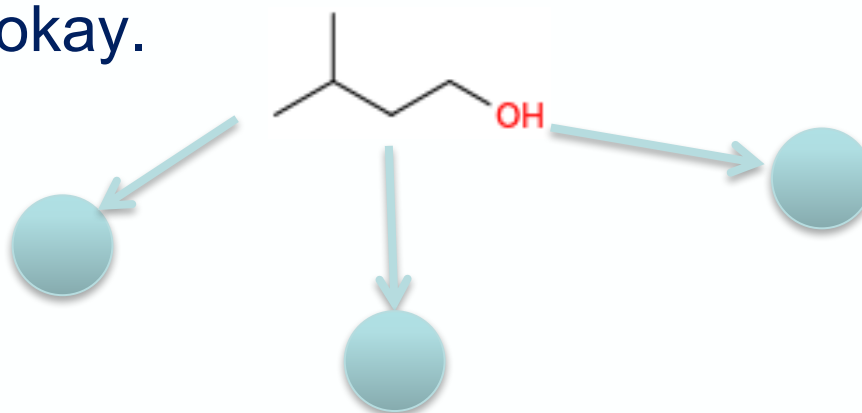
Pressure – Dep
Mechanism



General tip for model construction

2. Control the tolerance to get model which are adequate for your purpose

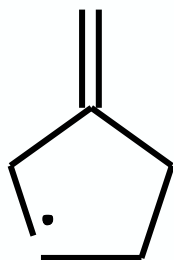
My general strategy is to start with as loose tolerance I can and check if my initial branching and major product distribution is okay.



In this particular case, I found out RMG had a too slow dehydration rate and underpredicted my H₂O speciation data. This is usually the first reaction and you do not need a very tight tolerance to get it in the model.

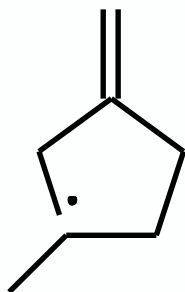
General tip for model construction

3. RMG cannot estimate thermochemistry for unsaturated cyclic molecules even with QM on. This error is enough to cause RMG to start exploring completely different pathways



H_{298}

CBS-QB3 (kcal/mol)	QM PM-7 (kcal/mol)
50.95	40.75



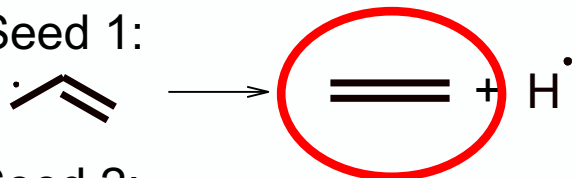
H_{298}

CBS-QB3 (kcal/mol)	QM PM-7 (kcal/mol)
42.25	34.5

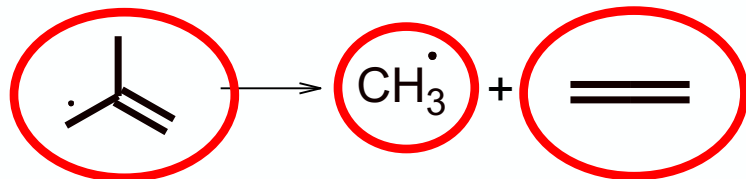
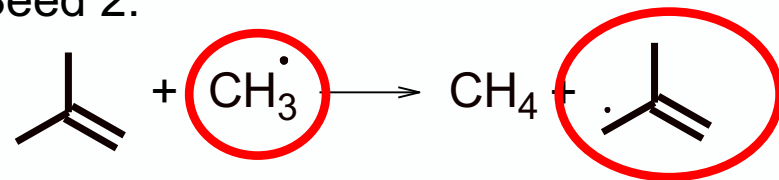
The problem with Seed libraries

- In some cases reactions might be missing out because of the interconnectivity between different seed libraries
- Example:

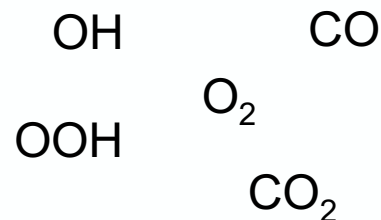
Seed 1:



Seed 2:



Seed 3: Combustion core

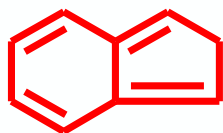


All species are occurring in the seed, so this reaction will be missed out!

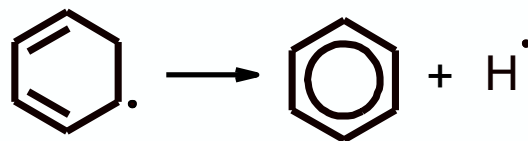
Detection of aromaticity

Before...

- Some species were wrongly recognized as being aromatic



- Benzene bonds were sort of unreactive (not included in R_Addition_Multiplebond)
 - Consequently all pathways that could form aromatic products, such as benzene, toluene... needed to be provided in libraries because RMG would not find them



New algorithm to detect aromaticity in PAH

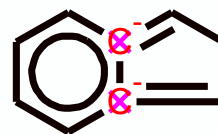
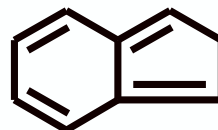
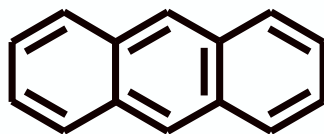
- Based on the initial algorithm that was there but recursive
- Smart checks: no saturated C atoms (forbid sp^3)
- Hückel rule: AROMATIC if $n_{\text{elec}} = 4n + 2$
- Code:

Old code:

For each ring

$$n_{\text{elec}} = \text{EndoPiElectrons} + \text{ExoPiElectrons}$$

6 / 6 / 6



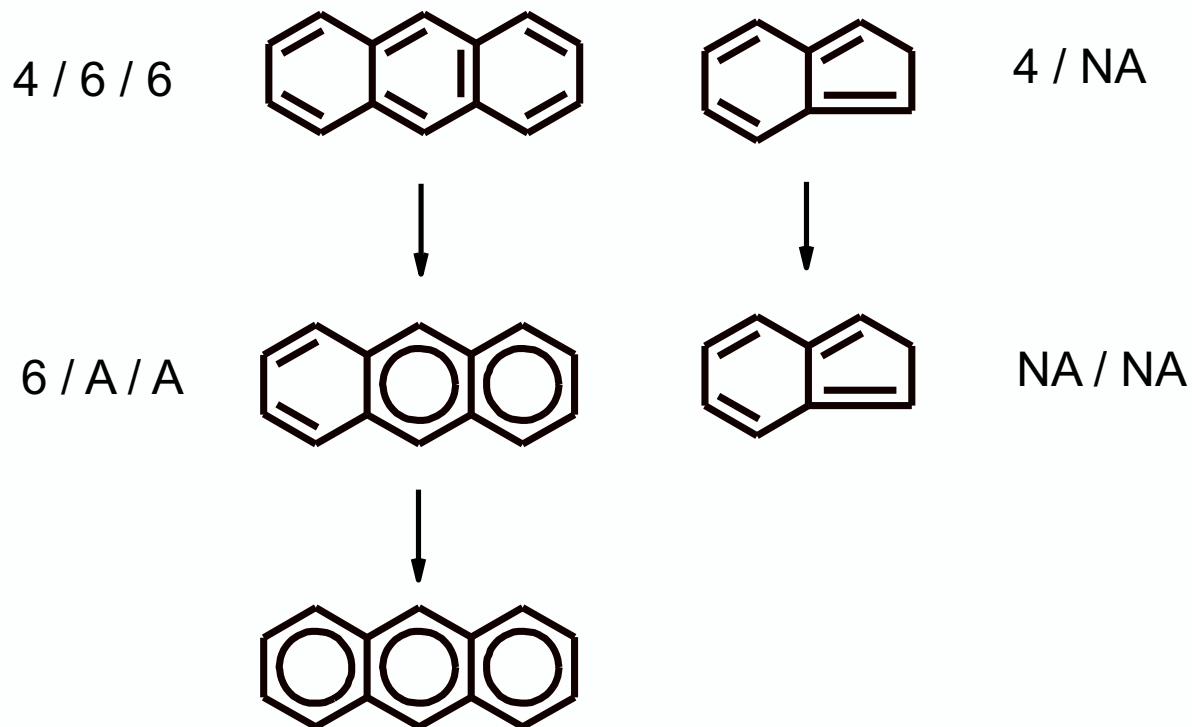
6 / 4

New algorithm to detect aromaticity in PAH

New code:

For each unrecognized ring

$$n_{\text{elec}} = \text{EndoPiElectrons} + (\text{ExoPiElectrons})_{\text{arom}}$$

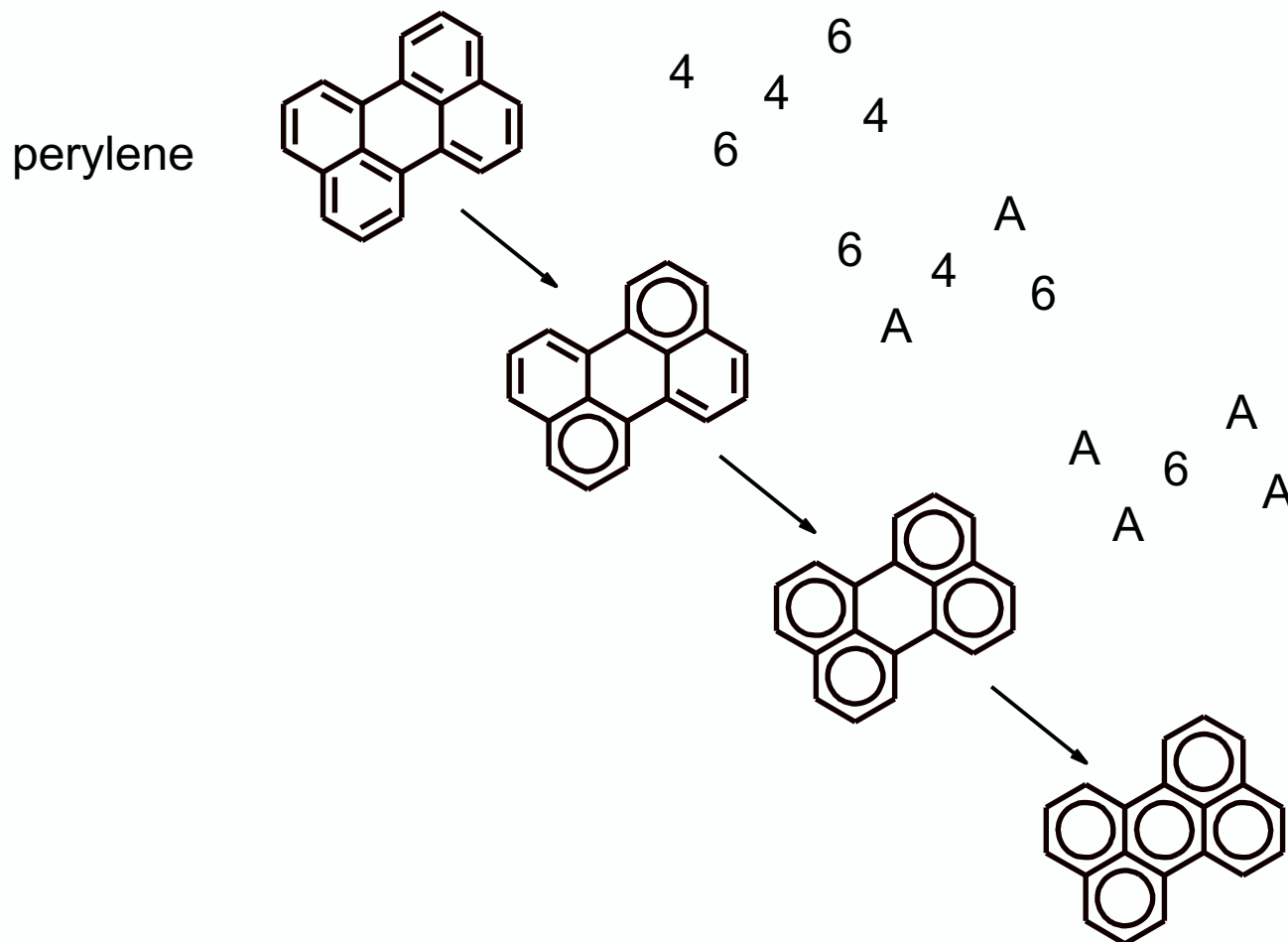


New algorithm to detect aromaticity in PAH

New code:

For each unrecognized ring

$$n_{\text{elec}} = \text{EndoPiElectrons} + (\text{ExoPiElectrons})_{\text{arom}}$$



How to make B bonds active?

- Do not convert to B bonds (keep the original structure with the S/D bonds)
- For each ChemGraph representing a compound:

```
thermo_graph = ChemGraph.copy(this)
```

```
thermo_graph.determineAromaticityAndWriteBBonds()
```

```
thermoData = gen.generateThermo(this);
```

```
    if(!this.fromprimarythermolibrary && this.isAromatic) {
```

```
        thermoData = gen.generateThermo(thermo_graph);
```

```
    }
```

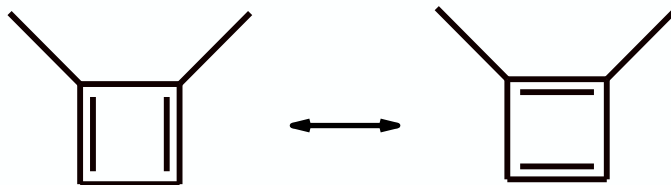
- No changing the original ChemGraph

New resonance isomers: kekulized forms

- At a certain point we found out we had two indene structures



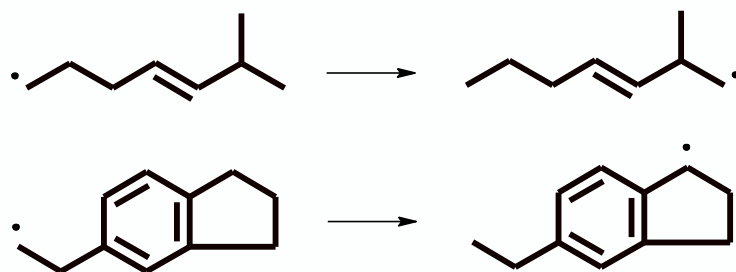
- `generateResonanceIsomersFromConjugatedRings()`
 - Check for each ring
 - Do I have alternating single and double bonds?
 - If YES then make corresponding resonance isomer



Initial attempt to
get some 3D in

Problem

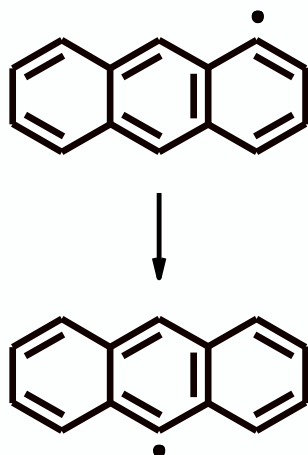
- Intramolecular rate rules were mainly obtained from linear molecules



- Rates are not suited for polycyclics, moreover most of them are simply impossible
- Hard-coded check for feasibility

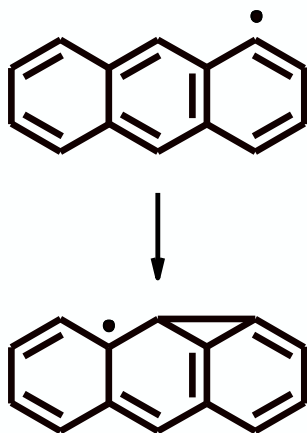
Two checks

- The unreachable H atom



- Check the distance: n (**3**)
- How many atoms along minimum path are in the same ring as site 1? n_1 (**3**)
- How many atoms along minimum path are in same ring as site 2? n_2 (**3**)
- If $(n+1)/2 \leq n_x - 1$ then this reaction won't occur

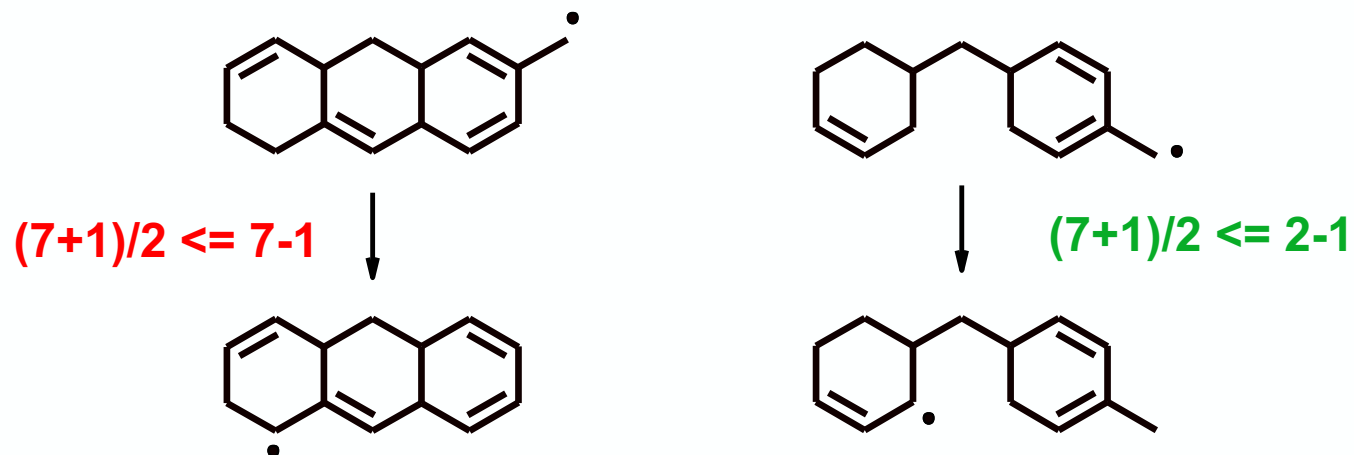
- Sterically hindered reactions



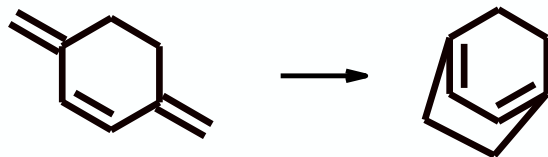
- Determine minimum path from site 1 to site 2
- Number of atoms that are part of two rings in product? n_{biring}
- If $n_{\text{biring}} > 1$ then reaction hampered

Examples

- The unreachable H atom



- Sterically hindered reactions



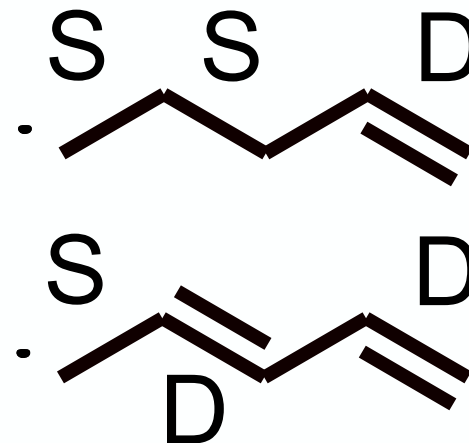
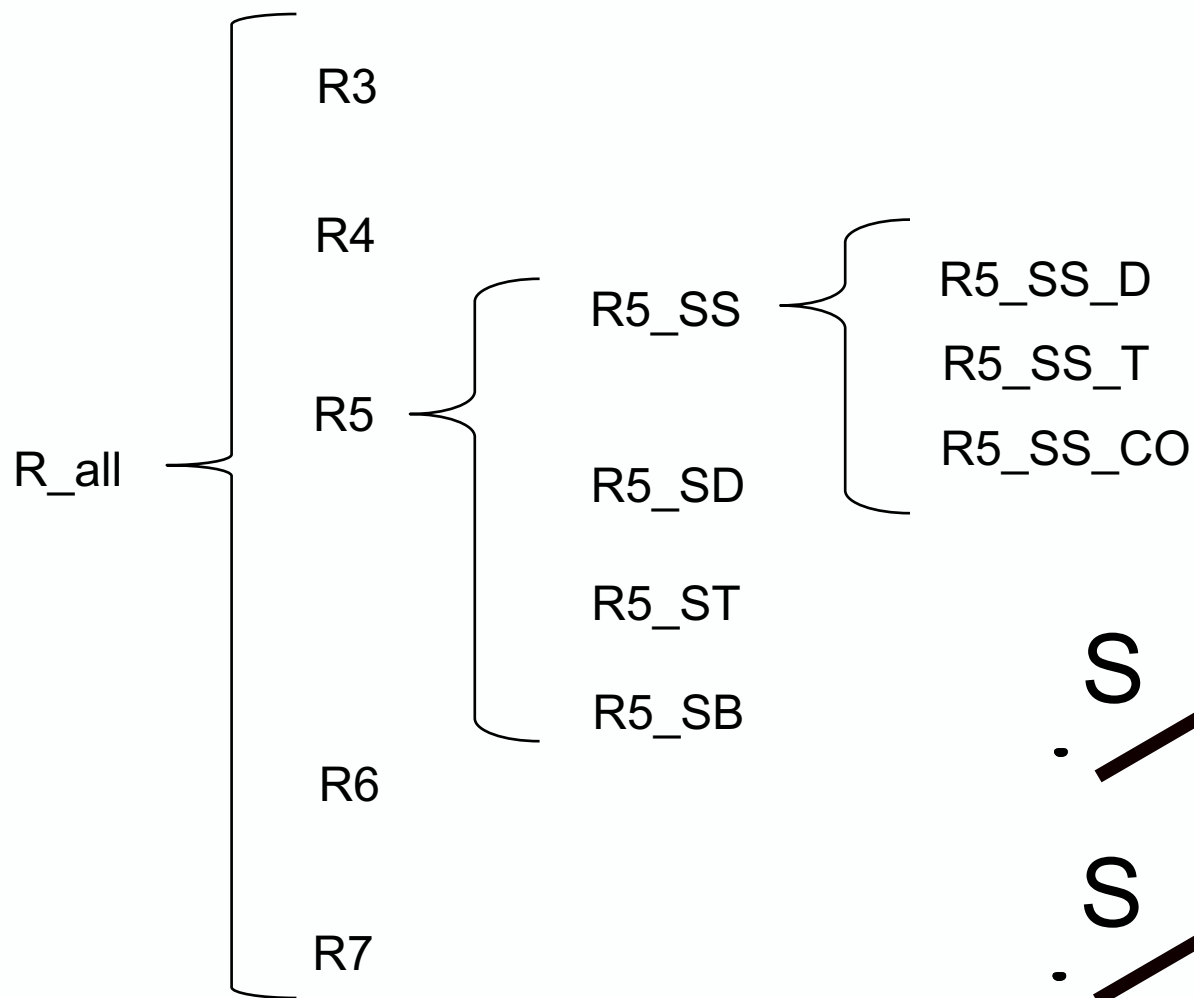
Branching the exo - endocyclic addition tree

Problem

- We only calculated the most likely reactions (fast)
- Doing so (and because of the averaging scheme going on in RMG) ALL less likely reactions were also fast
- Quick solution: give all rate rules priority 0 (= they are not used to average out the tree)
- But eventually people will want to have a working tree structure

Before

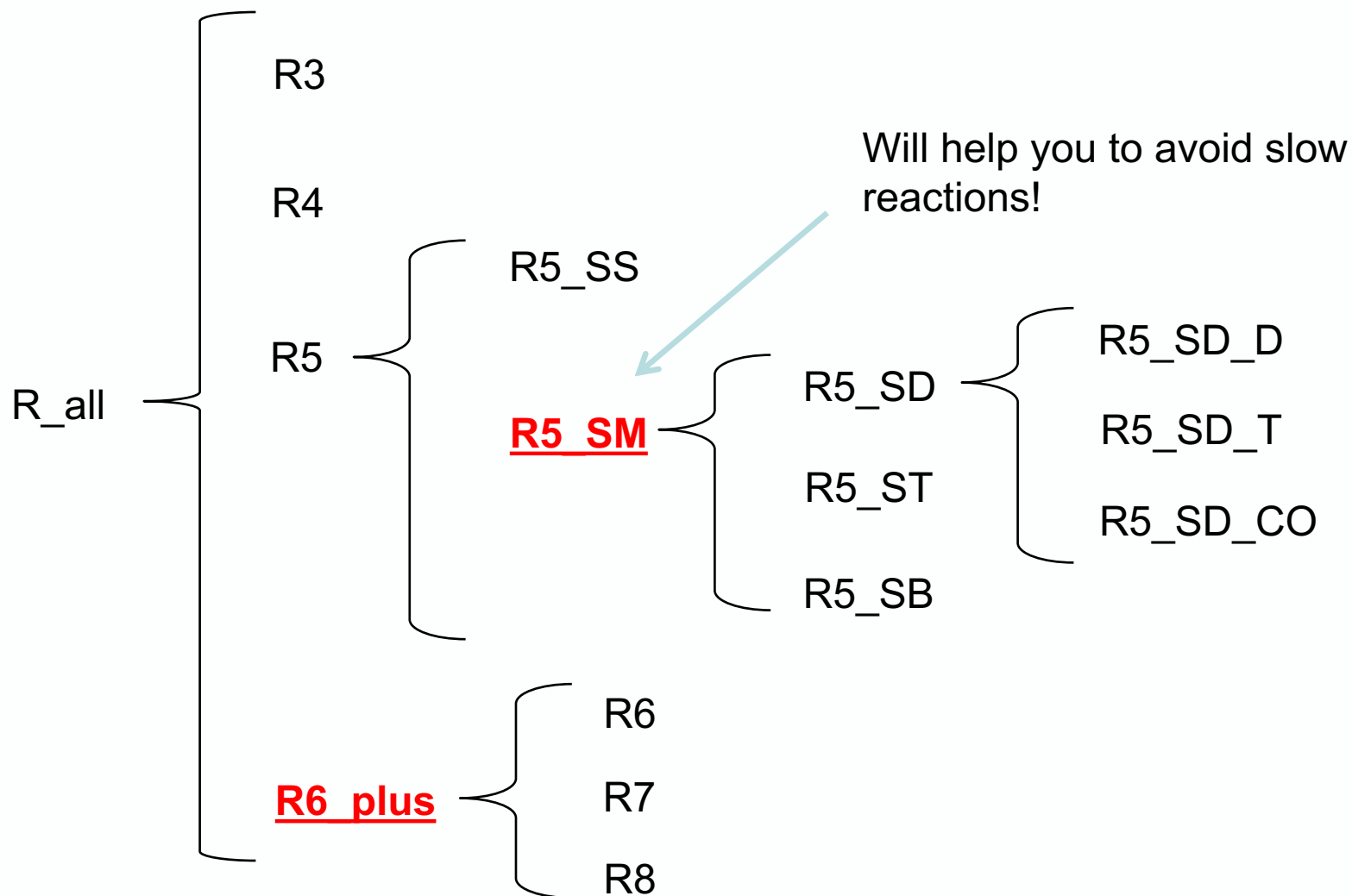
- Old tree



More



- New tree



Questions

