



CHAPTER II

[SUPPL Chapter II # 3]

Arabic compound numbers in TAPSOC,
Roman numerals in Supplementary material

Intramolecular π - π interactions in reaction mechanism

Frequently found in carbon scaffolds possessing two or more unsaturations, these reactions are prompted by heat, microwave radiation, and high energy photons in the UV. Heavy metal catalysts like in metathesis reactions can induce these couplings as well [1]. The gamut of mechanistic possibilities is thus large although they can be considerably simplified by application of the Woodward-Hoffmann rules and a measure of common sense.

The reaction of Scheme II.4 that you were asked to provide a mechanism for [2] can be tackled without much hesitation, but this attitude may not guarantee any success. I'd prefer to apply stepwise problem analysis, starting with a few basic questions to get to the roots and then building from there to extract ripe facts:

Preliminary problem analysis:

1. Which is the *visible* process? Ring enlargement of cyclobutenone and further cyclization by non obvious means.
2. What do we have at hand to work with? Multiple carbon to carbon bonds. Ketone, also a reactive site after boron trifluoride activation, is a likely reaction trigger.
3. Are carbon atoms lost or gained? No. Compounds **16** and **17** have as many carbon atoms as **15**. Thus, both products are deep-seated isomerizations.

4. Is the ketone a good marker for labeling atoms? Probably not. It might as well participate, be modified and then regenerated at a different site.

These questions lead to the following first round conclusions:

- a.- All operations are self contained within **15**, with the aid of $\text{BF}_3 \cdot \text{Et}_2\text{O}$.
- b.- The ketone is a good docking place for $\text{BF}_3 \cdot \text{Et}_2\text{O}$, (C=C and C≡C bonds are not ruled out as anchoring sites). Polarization of the α, β unsaturated ketone increases chances of pericyclic interaction with C=C-C≡C if architectural constraints permit.
- c.- The aromatic ring in **16** strongly suggests a [4+2] cycloaddition at some point, in consonance with issue (b).
- d.- As eight-membered rings can be built from ring expansion of [5.1.0]-, [4.2.0]- or [3.3.0] bicyclic scaffolds, a cycloaddition derivative of cyclobutenone in **15** would suggest the intermediacy of a [4.2.0] fused ring.

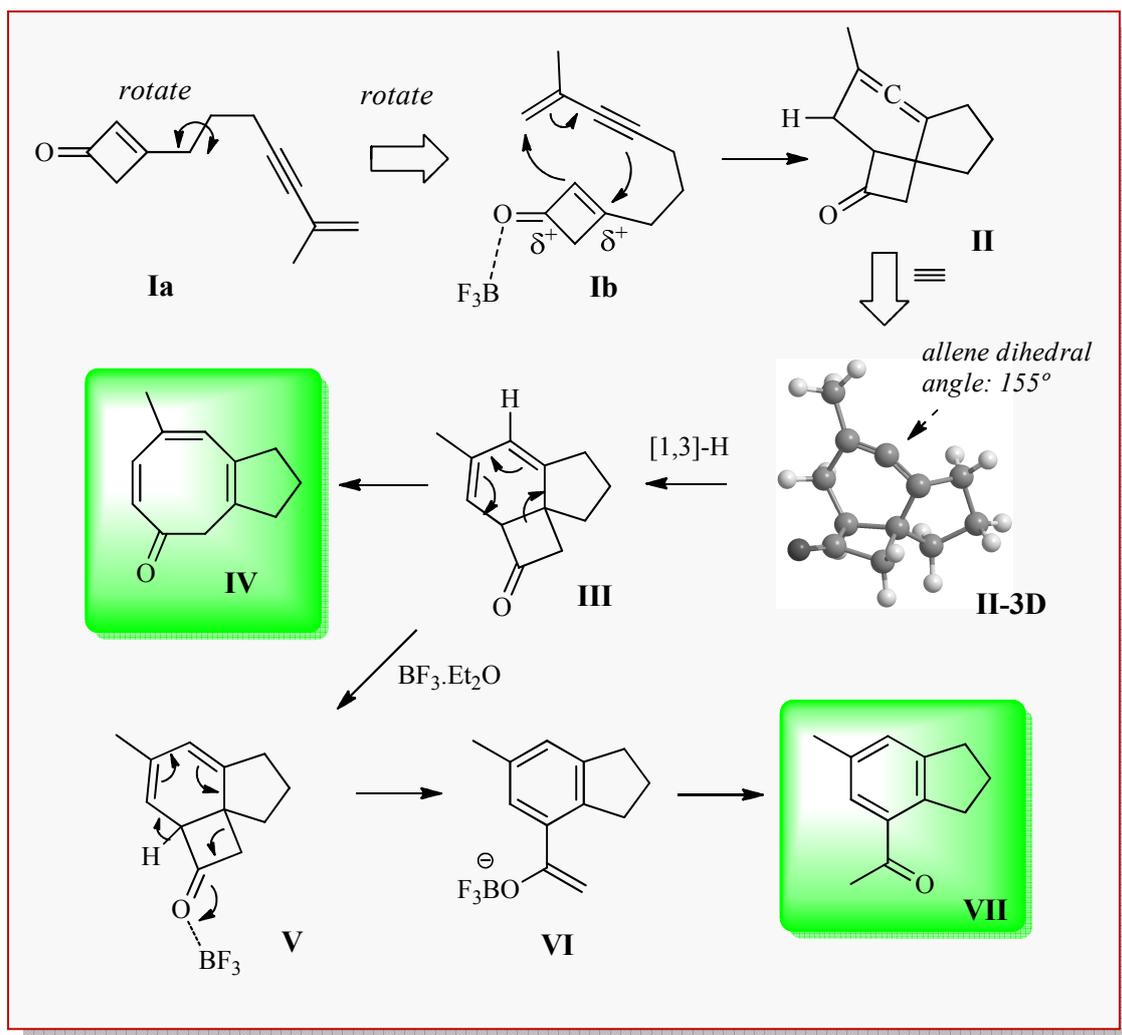
With these ideas in the pipeline one can draw the beginning of a mechanism [Scheme S(II)3.1] whereby the predicted pericyclic reaction seems in order.

Please keep in mind that we use roman numerals in supplementary materials. The equivalence with APSOC scheme II.4 is: **15 = I**; **16 = IV**, **17 = VII**.

One can redraw the starting material to move these functions closer, as in **Ib**. The desired electrocyclization is readied in accordance with the $\text{C}=\text{O} \cdots \text{BF}_3$ association, thereby furnishing a first cyclohexyl unit, a likely precursor of the benzene ring in **VII**.

However, and this is a big one, the resulting intermediate **II** is a *cyclic allene*, quite an oddity if part of a six-membered ring, although not unique. A MM2 calculated structure shows a bent C=C=C bond (bond angle: 155° instead of 180°) (3D model inset) while the ring strain energy went up about 12 kcal in the **I** → **II** transition.

One can get around this roadblock by assuming a transitory quality to this intermediate with simultaneous [1,3]-H transfer to a more comfortable conjugated diene **III**. The strain energy goes down some 10.4 kcal/mol in addition to the energy reduction earned from the diene conjugation. From this key intermediate, products **IV** and **VII** emerge via electrocyclic ring opening and deprotonation – ring breakage, respectively.



SCHEME S(II) 3.1

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REFERENCES

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