



PROBLEM 16

[SUPPL Problem 16 # 2]

Arabic compound numbers in TAPSOC,
Roman numerals in Supplementary material

A concerted electrocyclization alternative

Product **2** (in your TAPSOC Scheme 16.1) can also result from a formally different mechanism although the molecular set up would run under similar lines of the diradical route. This is possible if we perform all *E/Z* isomerizations and σ bond turnings previously.

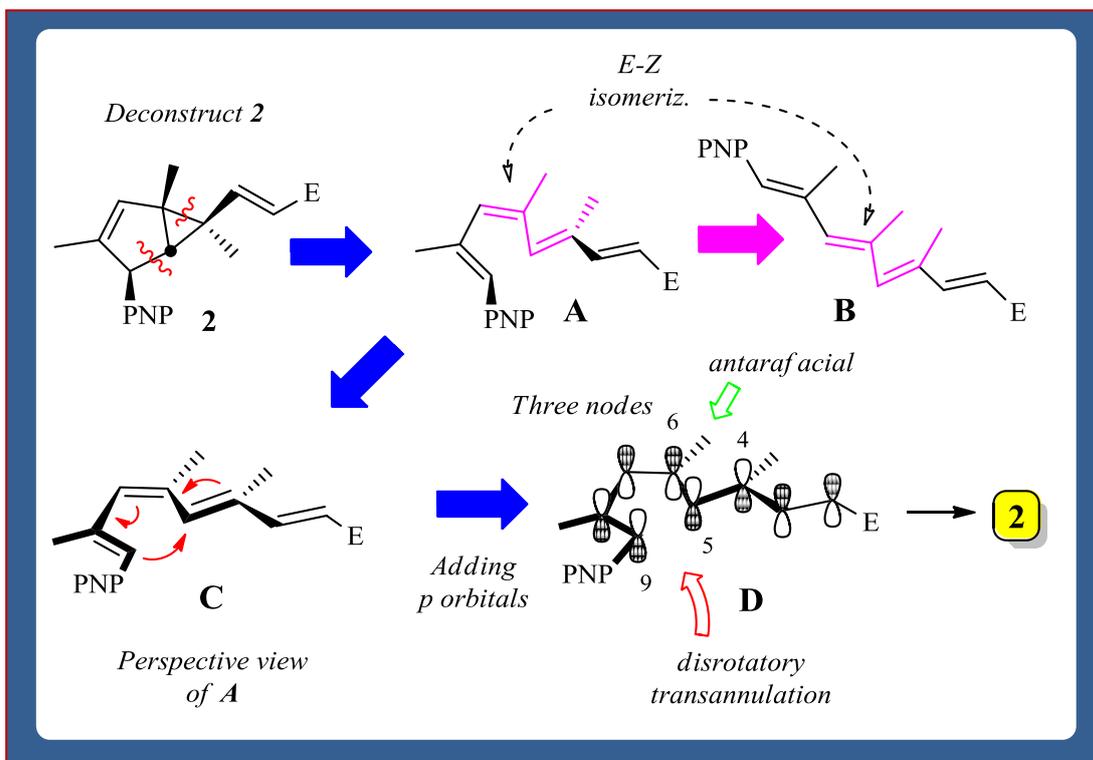
To be able to do this on paper, let us deconstruct compound **2** stepwise (Scheme SP16.2.1). We have depicted our first split structure **A**, a bit against established drawing codes to emphasize the back-twisting we need to end up with cyclopropane methyls in the *trans*-configuration. Progress toward perspective rendering **C** purports to show the sites where involved carbons should be for a feasible electrocyclic reaction.

Curly arrows in **C** do not give us a sufficiently satisfactory answer as one has to account for the participating p orbitals and explain their overlap in terms of the observed stereochemistry by an allowed process, following the Woodward and Hoffmann symmetry rules [1]. Structure **D** attempts to shed some light considering that:

1.- C^4 - C^6 bonding must occur *antarafacially* to yield the *trans*-dimethyl cyclopropane. You may convince yourself of this with hand-held Dreiding models, and that a suprafacial closing would furnish the *cis*-dimethyl isomer.

2.- For the *antarafacial* overlap to go, orbital phase needs to be as depicted in **D**, namely at a higher antibonding energy level (three nodes) of the 8 electron conjugation allowed by symmetry rules. It is the highest occupied molecular orbital HOMO which determines the stereochemistry of the product, in consonance with a fundamental tenet

of the frontier orbital theory of Fukui [2]. You may wish to play with lower energy levels, one node for instance and come to the conclusion that the incorrect stereochemistry would be obtained.



SCHEME SP16.2.1

3.- Having issue (2) as true, the C⁵-C⁹ closing would occur by *disrotatory* closure leading to the final product with the desired *cis* configuration between aryl and vinyl carboxylate groups. So, structure **D** explains the concerted mechanism whose correct nomenclature is $\pi 4s + \pi 2a$.

REFERENCES

- [1] Woodward RB, Hoffmann R. *The Conservation of Orbital Symmetry*. Verlag Chemie, Weinheim. 1970.
- [2] Fukui K Acc. Chem. Res. 1971;4:57-64; Fukui K Angew. Chem. Int. Ed.1982;21(11): 801-809.