



CHAPTER II

[SUPPL Chapter II # 1]

Arabic compound numbers in TAPSOC,
Roman numerals in Supplementary material

[1,3] and [1,5] H shifts and symmetry

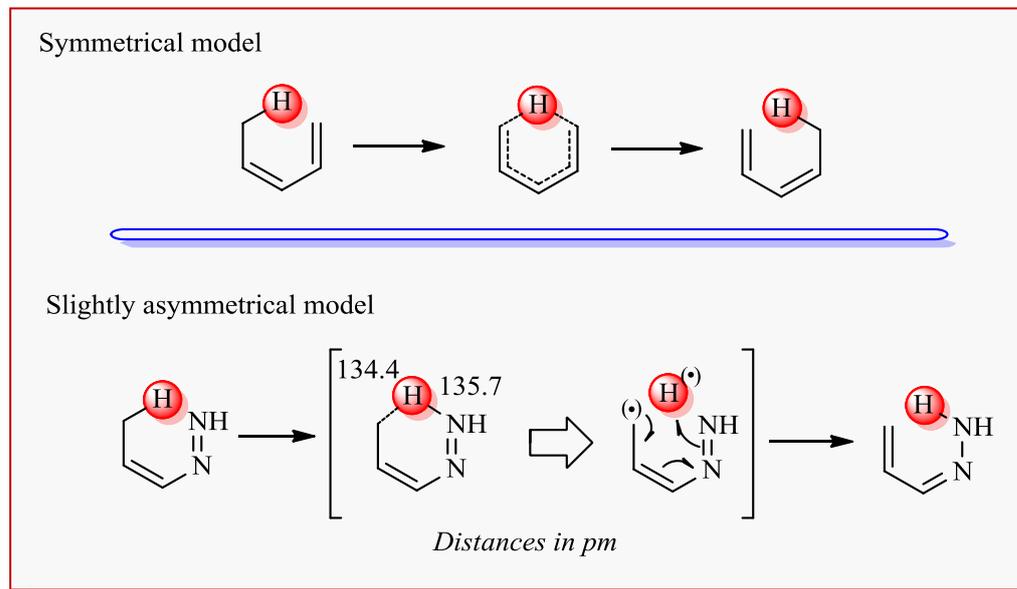
Hydrogen shifts in concerted reactions are generally thought to proceed through transition states where the H is placed midway between source and target atoms. While a certain degree of asymmetry (distances to participating atoms) is contingent upon the electronegativity of donor and acceptor atoms, it is usually accepted that *the transition state is symmetrical when only C and H are involved*. This is not always the case though.

Take for example the familiar [1,5]-H transfer depicted in Scheme S(II)1.1. This is commonly interpreted as a formal pericyclic transformation with simultaneous σ - π electron redeployment passing through an aromatic 6π e^- transition state. As such, we would simply draw three curled arrows to show how the electron reorganization proceeds.

However, recent theoretical studies in ene-imine models [1] have shown otherwise. Transition state geometries of several models where one would expect an equidistant H being transferred from C to the acceptor (N) is not symmetrical but slanted a bit towards C.

More importantly, authors conclude that in the transition state the C-H bond is broken while the N-H bond is not formed yet, leaving the H atom, shall we say, up in the air. This is equivalent to say that the C-H bond is broken homolytically furnishing a

pseudo-diradical. Meanwhile nothing happens in the vicinal π orbital of the N=N-C=C bond, having in the end that the sigmatropic rearrangement, at least in this system, is not fully concerted.



SCHEME S(II)1.1

[1] Brasil EM, Borges RS, Romero OAS, Alves CN, Sáez JA, Domingo LR. *Tetrahedron* 2012;68:6902-6907. DOI: 10.016/j.tet.2012.06.013.