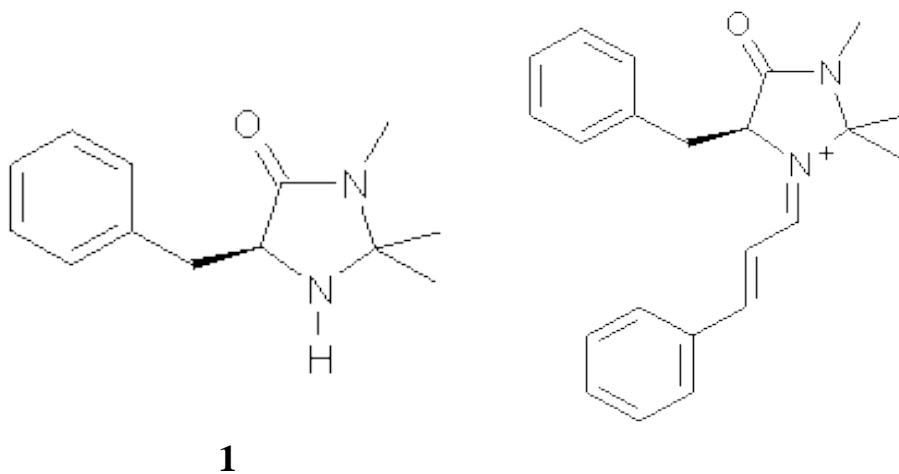


# MACMILLAN'S IMIDAZOLIDINONE: ORIGINS OF STEREOSELECTION

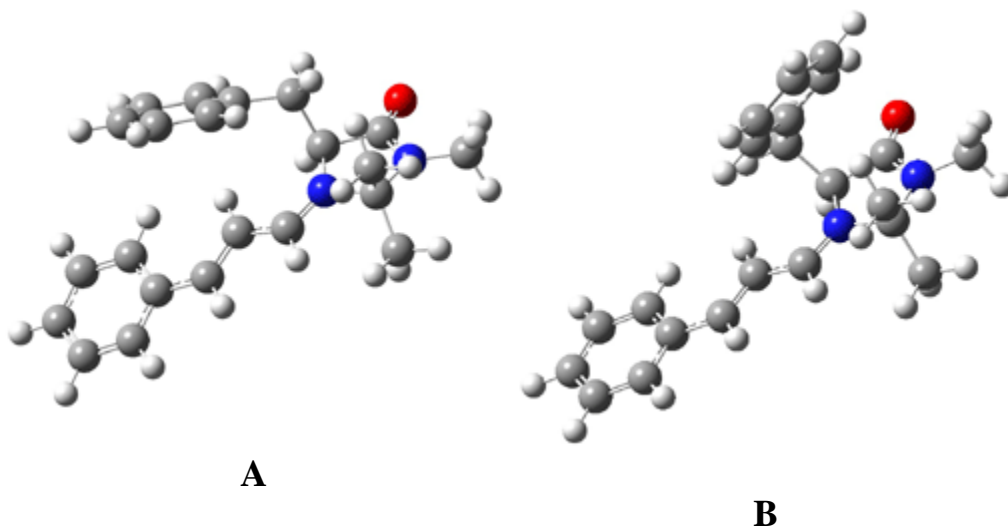
Organic catalysis is a major topic of Chapter 5 of my book. The use of iminium ions as a catalyst and to provide stereoselection, pioneered by MacMillan,<sup>1</sup> was not discussed in the book.

Macmillan had proposed that the iminium **2** formed of imidazolinone **1** and (E)-3-phenylprop-2-enal has conformation **A**. This conformation blocks access to one face of the alkene and directs, for example, dienophiles to the opposite face. Houk found that conformer **B** is lower in energy at B3LYP/6-31G(d).<sup>2</sup>



Now Tomkinson<sup>3</sup> has produced a study that convincingly shows that **2** exists as conformer **B**. An x-ray structure shows this conformation in the solid state. Proton NMR shows that the methyl group signals are interpretable only as coming from **B**. Finally, SCS-MP2/aug-cc-pVTZ//BHandH/6-31+G(d,p) (see Figure 1) computations show that **B** is 1.2 kcal mol<sup>-1</sup> more stable than **A** in the gas phase, and PCM computations indicate that this gap is reduced by less than 0.5 kcal mol<sup>-1</sup> in methanol or acetonitrile.

Conformation **B** provides little steric hindrance at the  $\beta$ -carbon of the iminium ion, explaining its poor stereoselectivity in conjugate additions.



**Figure 1.** BHandH/6-31+G(d,p) optimized structures of conformers **A** and **B** of **2**.

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