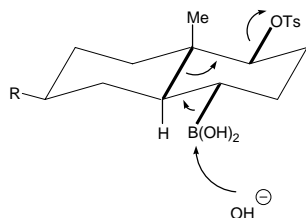


2ND YEAR ORGANIC Tutorial Answers 2003/2004
Dr Alan Spivey – Introduction to Stereoelectronics

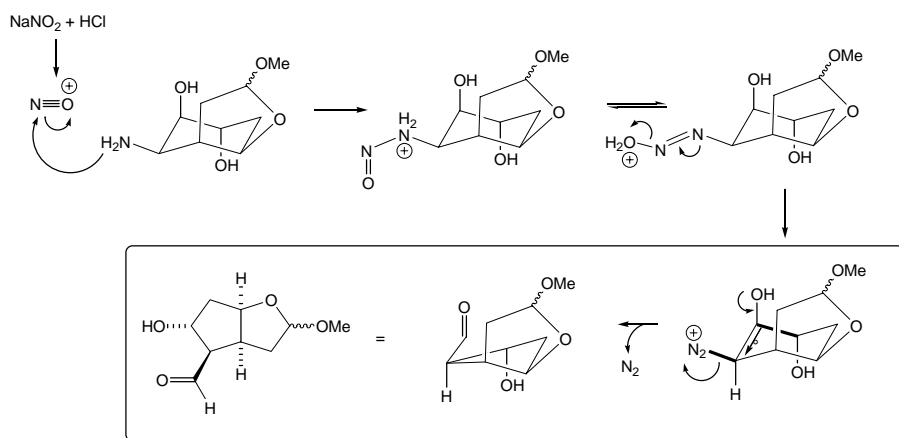
1. (a) The mechanism and key orbital interactions are indicated below. Any acceptable diagrams showing the shapes of the interacting sigma and sigma star orbitals are OK.



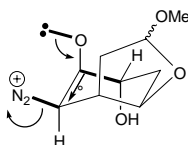
NB. bold bonds are all anti-periplanar with respect to each other

- 1) $n_{\text{O}} \rightarrow \sigma^*_{\text{C-B}}$ (OH- attacks boronic acid)
- 2) $\sigma_{\text{C-B}} \rightarrow \sigma^*_{\text{C-C}}$ (C-B bond cleavage, C=C bond formation, & C-C bond cleavage)
- 3) $\sigma_{\text{C-C}} \rightarrow \sigma^*_{\text{C-O}}$ (C=C bond formation and C-O bond cleavage)

- (b) (i) The mechanism shown includes the method of formation of the diazonium salt 'starting material' given in the question. The expected mechanism is given in the boxed area:



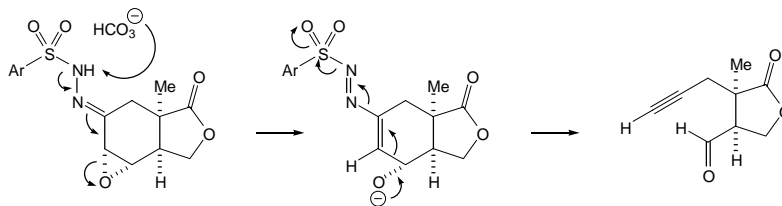
- (ii) See below. Any acceptable diagram(s) showing the shapes of the interacting sigma and sigma star orbitals is OK.



NB. bold bonds are all anti-periplanar with respect to each other

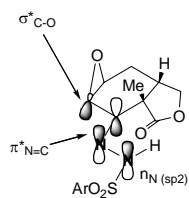
- 1) $n_{\text{O}} \rightarrow \sigma^*_{\text{C-C}}$ (oxygen lone pair interacts with C-C anti-bond forming C=O bond)
- 2) $\sigma_{\text{C-C}} \rightarrow \sigma^*_{\text{C-N}}$ (suprafacial C-C bond migration, & C-N bond cleavage)

- (c) (i) Mechanism:

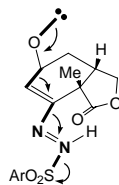


- (ii) For the formation of the alkoxide 'intermediate' all the p-orbitals of the hydrazone must be perpendicular to the 'plane' of the ring and therefore overlap

well with the epoxide sigma star orbital...which they do. For the fragmentation the (*E*)-stereochemistry about the N=N double bond is important to ensure anti-periplanar overlap in 'step 5' below. Again, any acceptable diagram(s) showing the shapes of the interacting sigma and sigma star orbitals is OK.



then



NB. bold bonds are all anti-periplanar with respect to each other

- 1) $n_N \rightarrow \pi^*_{N=C}$
- 2) $\pi_{C=N} \rightarrow \sigma^*_{C-O}$
- 3) $n_O \rightarrow \sigma^*_{C-C}$
- 4) $\sigma_{C-C} \rightarrow \sigma^*_{C-N}$
- 5) $\sigma_{C-N} \rightarrow \sigma^*_{N-S}$
