Reactivity of Three-membered Heterocyclic Rings with respect to Sodium Methoxide

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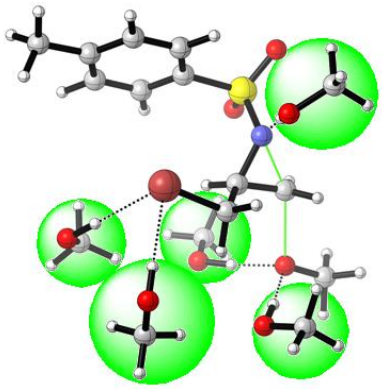
Aziridines can be 'activated' or 'non-activated', depending on whether their *N*-substituent is an electron-withdrawing group or an electron-donating group, respectively. Activated aziridines are much more susceptible to ring opening than non-activated aziridines and epoxides are even more reactive. The difference in reactivity between activated 2-(bromomethyl)-1-tosylaziridines, non-activated 1-benzyl-2-(bromomethyl)aziridines and epibromohydrins with respect to sodium methoxide was comparatively analysed by means of DFT calculations, such as BMK, MPW1K and MPWB95 [1].

Nucleophilic substitution reactions are known to be influenced by the solvent environment. Therefore, the gas-phase results were extended towards a discrete solvent approach. The solvent effect was taken into account by inspecting the convergence behaviour of the energy of solvation in terms of a systematically increasing number of solvent molecules. To model each of the reactive profiles of the various substrates, a supermolecule model was used with five explicit methanol molecules. Solvation has significantly changed the landscape of the energy profiles, which nicely shows the necessity of taking into account explicit solvation molecules to obtain the correct reaction profiles.

The barriers for direct displacement of bromide by methoxide in methanol are comparable for all three heterocyclic species under study. However, ring opening is only feasible for the epoxide and the activated aziridine and not for the non-activated aziridine.



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