Abstract

The reaction of secondary amines namely, 1-methylpiperazine, pyrrolidine, morpholine, 2-methylpiperidine, diethylamine, 1-ethylpiperazine, piperazine and 1-amino-4-methylpiperazine with maleic anhydride have been investigated under kinetic and thermodynamic controls. Under kinetic control, addition of the amines occurs predominantly across the C=O group; the resulting products on heating in solution change into the corresponding maleamic acid derivatives to varied extents. The addition of amines across the carbonyl group only and non-occurrence of the Michael addition have been rationalized on the basis of the condensed Fukui functions calculated at the B3LYP/6- 311++G**//B3LYP/6- 31+G* level. The Fukui functions indicate that in contrast to an acyclic α,β-unsaturated carbonyl compound, such as acrolein, the difference between the hardness of the carbonyl carbon and the β--vinylic C atom in maleic anhydride is much greater due to which amine adds across the carbonyl group only.

The reaction of secondary amines with methyl propiolate occur with complete steroselectivity leading to the methyl *trans*- β-aminoacrylate exclusively. However, benzylamine reacts under similar conditions to afford a mixture of *trans* and *cis* isomers in 26:74 %, as determined by ^{1}H NMR spectrum. Theoretical calculations reveal that the reactions occur in two steps and is initiated by the attack of amine on a pre-formed amine-methyl propiolate complex. In the reaction with benzylamine, the mechanism of *trans*-*cis* isomerisation is established as taking place through an "enamine-imine-enamine" pathway.

The asymmetric aza-Michael addition of chiral α-methylbezylamines with α,β-unsaturated carbonyl compounds occurs with high diastereoselectivity ranging from 52 to 98%.

The maleamic acids obtained from the reaction of secondary amines with maleic anhydride form 1:1 complexes with dimethyltin dibromide. Theoretical calculations of a representative complex indicates that maleaic acid does not act as a

chelating ligand, instead the co-ordination occurs through the carbonyl O atom of the acidic group. All the complexes so obtained exhibit strong antibacterial activity against both Gram +ve and Gram -ve bacteria.