A vinylsilane-ketiminium ion cyclization involving iminium species derived from amines 6 and 7 was investigated experimentally as a possible approach to some biologically interesting 1-azaspirocycles. However, even under conditions of microwave irradiation at high temperatures no such cyclization was observed whereas (in line with previous results) the corresponding vinylsilane-aldiminium ion cyclizations were more successful. Aldiminium species substituted a to nitrogen displayed no diastereoselectivity in the cyclization of precursors derived from 6 while high trans diastereoselectivity could be obtained for iminium species derived from 7. Quantum-mechanical investigations of the general reaction mechanism underlined the lack of reactivity of ketiminium species and also convincingly explained the observed diastereoselectivities of aldiminium species. The calculations further revealed that (Z)-vinylsilanes cyclize via a silicon-stabilized b-carbocation, and that any formal aza-Cope rearrangement of the starting material to an allylsilane-iminium species does not take place in a concerted fashion. However, the calculations show that the aza-Cope rearrangement precedes cyclization for the corresponding (E)-vinylsilanes, the overall reaction being energetically slightly less favoured than cyclization of the (Z)-isomers.