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Theoretical calculations on the mechanism of the elimination kinetics of allyl cyclohexyl-, -amine, -sulfide, -ether, and allyl ethyl ether in the gas phase

Solanged Espinoza^a, Jesus Lezama^a, José R. Mora^b, Tania Cordova^c, Gabriel Chuchani^{d*}

^a Departamento de Química, Escuela de Ciencias, Universidad de Oriente Núcleo Sucre, Cumana, Venezuela

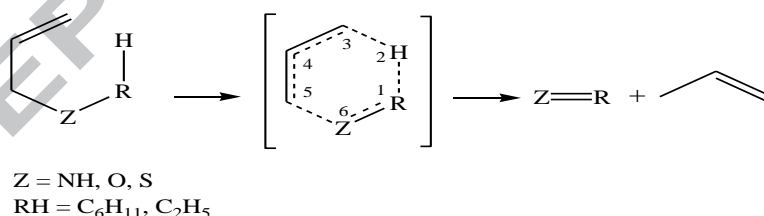
^b Departamento de Química, Universidad de San Francisco de Quito, Quito-Ecuador

^c HyperCube, Inc., Gainesville, Florida, 32610, U.S.A.

^d Centro de Química, Instituto Venezolano de Investigaciones Científicas (IVIC), Apartado 21827, Caracas1020A, Venezuela

ABSTRACT

The mechanism of the gas-phase elimination allyl cyclohexyl amine, allyl cyclohexyl sulfide, allyl cyclohexyl ether, and allyl ethyl ether has been studied by using *ab initio* combined methods CBS-QB3, and Density Functional Theory CAM-B3LYP, MPW1PW91, PBE1PBE, M06, and M062X. Products formation is described below:



Theoretical calculations of these reactions support the unimolecular process of these gas-phase eliminations. These thermal decompositions undergo a retro-ene type of mechanism and proceed through a non-planar concerted six-membered cyclic transition structure. The energy of activation follow the order allyl ethyl ether (187.0 kJ/mol) > N-allyl cyclohexyl amine (171.7 kJ/mol) > allyl cyclohexyl ether (170.5 kJ/mol) > allyl cyclohexyl sulfide (137.9kJ/mol). The polarization of C₅-Z₆ bond, and the electronegativity of the heteroatom (O, N) increases the reaction rate compared to allyl ethyl ether. Conversely, the S atom is positively charged and its electronic effect causes a high dissymmetry in the TS geometry,

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