

REGULAR ARTICLE

THEORETICAL STUDY OF 1, 3-DIPOLAR CYCLOADDITIONS REGIOSELECTIVITY OF BENZYL AZIDE WITH GLYCOSYL-O-ACETYLENE USING DENSITY FUNCTIONAL THEORY (DFT)

Adib GHALEB^{1*}, Adnane AOUIDATE¹, Abdelouahid SBAI¹, Tahar LAKHLIFI¹,
Hamid MAGHAT², Mohammed BOUACHRINE³

¹*Molecular Chemistry and Natural Substances Laboratory, school of Science, Moulay Ismail University, Meknes, Morocco.*

²*Laboratory of chemistry and biology applied to the environment, school of Science, Moulay Ismail University, Meknes, Morocco.*

³*EST, Moulay Ismail University, Meknes, Morocco.*

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Abstract: A theoretical study of 1, 3 cycloaddition has been carried out using density functional theory (DFT) methods at the B3LYP/6-31G* level. The regioselectivity of the reaction have been clarified through different theoretical approaches: Case of a Two-Center Process (domingo approach), HSAB principle (Gazquez and Mendez approach), and the activation energy calculations. The analysis of results shows that the reaction takes place along concerted asynchronous mechanism and the isomer meta is favored, in agreement with the experiment results.

Keyword: 1, 3-dipolar cycloadditions; 1,2,3-Triazole; regioselectivity; DFT calculations; Parr Functions.

* Corresponding Author: E-mail: adib.ghaleb@gmail.com

1. Introduction

Cycloaddition reactions are one of the most important synthetic processes, with both synthetic and mechanistic interest in organic chemistry. Among them, 1,3-dipolar cycloadditions (1,3DCs) [1], that have a tremendously successful history of building five-membered heterocycles. Now they are utilized in almost every area of chemistry, including, materials chemistry [2], drug discovery [3], and chemical biology [4]. The general concept of 1,3-dipolar cycloadditions was introduced by Huisgen and co-workers in the early 1960s[5]. Huisgen's work stated the basis for the understanding of the mechanism of concerted cycloaddition reactions. The formation of triazoline from Azides and olefins was first reported by Wolff [6]. Subsequently, many theoretical studies have been devoted to study the regioselectivity of the reaction between triazole and alkyls [7-8]. In this context molecular orbitals frontier (FMO) seemed to be able to explain the regioselectivity and reactivity differences [9], over the last decades, reactivity descriptors, as Parr function indices, local electrophilicity and local softness, derived from density functional theory were widely used for the interpretation of the regioselectivity [10].

Our work is aimed to study the regio-selectivity of 1,3DC between benzyl azide and glycosyl-o-acetylene (Figure1) by using three different approaches: Case of a Two-Center Process (domingo approach), HSAB principle (Gazquez and Mendez approach), and the activation energy calculations, these approaches are successfully allowed us predict the favored stereoisomer, and it is according to the experimental results [11].

2. Theory and computational details

All energies and geometries of the reactants, transition states (TSs) and cycloaddition

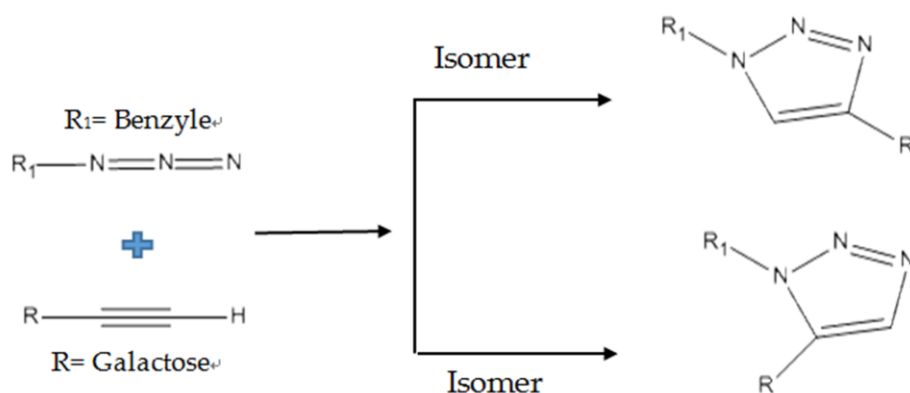


Figure 1: 1,3-Dipolar cycloaddition reaction.