Theoretical Studies on the Synthetic Pathways of Monoallene

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Abstract

All the intermediates of the formation of 3-(3-hydroxyprop-1-ynyl)-5,5-dimethyl-2-(3-(phenylsulfonyl)penta-3,4-dienyl)cyclohex-2-enone were studied by DFT method. All the possible intermediates were optimized to the minimum potential energy using Gaussian 09 software package at the theoretical level of density functional theory (DFT) using B3LYP/6-31G(d,p). The total electronic energy, effective squared charges (χ^2), and dipole moment (μ), were used to propose the best synthetic pathway of the reaction. The analyses reveal that 5,5-dimethyl-2-(3-(phenylsulfinyl)penta-3,4-dienyl)-3-(1-(phenylsulfinyl)propa-1,2-dienyl)cyclohex-2-enone is hardly formed because of the high energy requirement (+91.12 kJmol^{-1}) and also its dipole moment (μ = 8.2218D) is higher compared to the 3-(3-hydroxyprop-1-ynyl)-5,5-dimethyl-2-(3-(phenylsulfonyl)penta-3,4-dienyl)cyclohex-2-enone (41.87 kJmol^{-1}, μ = 5.4380D). The calculation of the effective squared charges (χ^2), followed by -Ln χ^2 showed the supportive result for the path 1. Unexpectedly, this calculation also indicated that the mono propargyl sulfoxide group derivative is unstable which easily transformed to propargyl alcohol group derivative.

Keywords: Monoallene, Total electronic energy, Dipole moment, Density-functional theory

INTRODUCTION

Allene chemistry has become one of the most important and exciting fields in organic synthesis. Allene also has an accumulated diene structure that containing a sp-hydridized central carbon which creates not only a higher reactivity, but also a wide variety of possible reaction modes and their tedious methods of preparation would prove to be relatively unstable (Figure 1)[1-3]. The reactivity of allenes is very different from those of alkenes and alkynes.
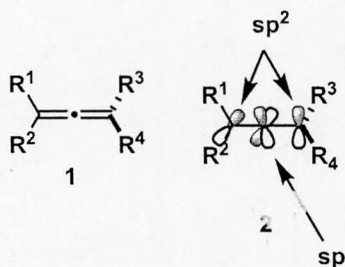

Figure 1. Structure of allenes

However, many natural products and pharmaceuticals contain the allene moiety. In fact, the chemistry of allenes has been shown to have significant potential in organic synthesis[4-6].The chemical transformation of the sulfonyl group **6** into other functionalities can be easily achieved. Benzenesulfenyl chloride and subsequent oxidation of the resulting sulfoxide **5** can be form through a [2,3]-sigmatropic rearrangement (Scheme 1)[7-8].
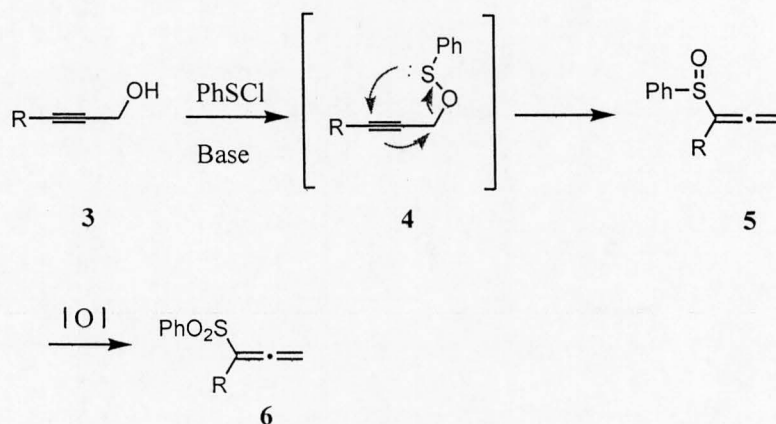
Scheme 1. Synthesis of sulfonylallenes **6** from propargyl alcohol **3**

In the previous study, we have successfully developed a synthetic method for the construction of the 6-8-5 tricyclic ring systems by the Rh(I)-catalyzed intramolecular Pauson-Khand-type reaction (PKTR)[9]. However, a common issue of the synthesis of these compound is the formation of the phenylsulfonylallene that significantly very low yield. Scheme 2[9] show that the propargyl alcohol (**7**) was converted into the phenylsulfonylallene (**8**) in 18% overall yield via the successive phenylsulfenyl ester formation, [2,3]-sigmatropic rearrangement and oxidation instead of the desired bis(allene) **9**.
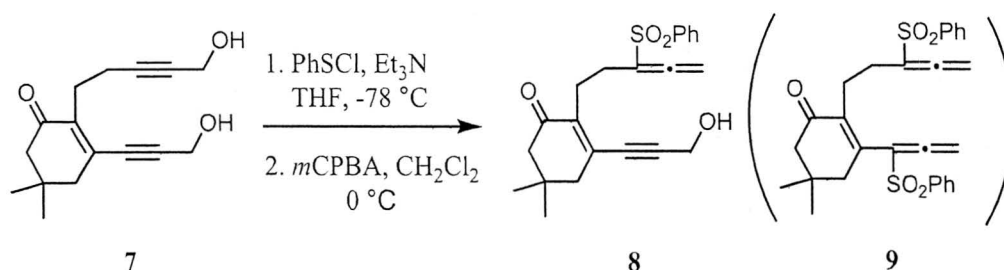
Scheme 2. Preparation of allenes

Density functional theory (DFT) approaches using hybrid functional have become an efficient tool in the prediction of the various structural characteristics, vibrational and electronic properties, interactions among different orbitals and gave the consistent results. B3LYP functional has provide an excellent calculation for the small and the large molecule[10-12]. Ku Bulat has reported about the invariant known as the square of the effective charge (χ^2) on the αth atom and its relationship to the intensity sum that allow the definition of the atomic contribution to all vibrational and rotational infrared intensities[13-14].

In order to understand the synthetic reaction pathway (Scheme 3) of monoallene instead of the desired bisallene in detail, the bis(propargyl alcohol) and all the intermediate of the substrates were studied in the present work. Therefore, the present study has been undertaken to study the molecule characteristics such as total electronic energy, effective squared charges (χ^2), and dipole moment (μ) to determine the best reaction pathways of the monoallene.
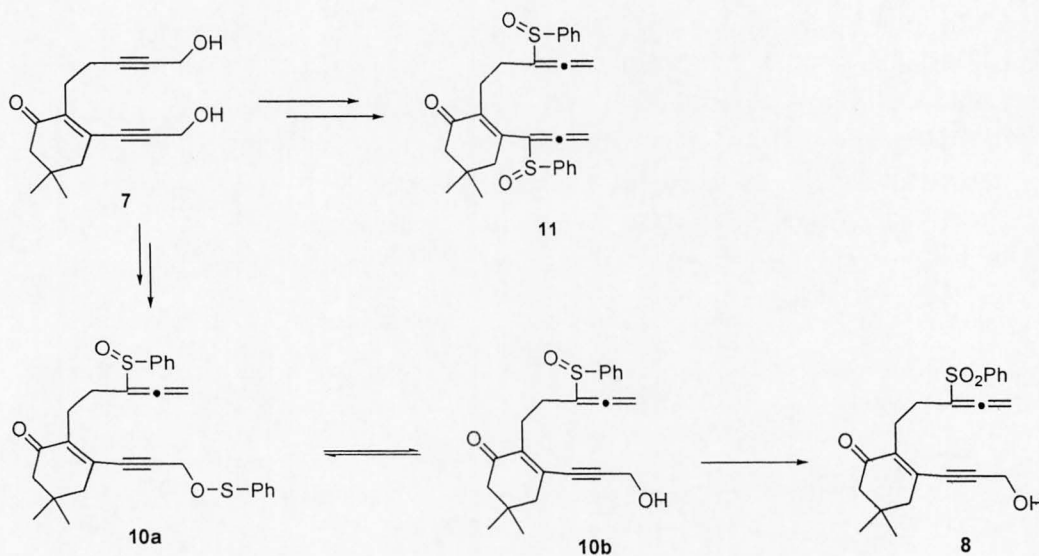
Scheme 3. Pathway reaction for the formation of 5-dimethyl-2-(3-(phenylsulfinyl)penta-   3,4-dienyl)-3-(1-(phenylsulfinyl)propa-1,2-dienyl)cyclohex-2-enone **(8)** and 5-dimethyl-2-(3-(phenylsulfinyl)penta-3,4-dienyl)-3-(1-(phenylsulfinyl)propa-1,2 dienyl)cyclohex-2-enone **(11)**

EXPERIMENTAL DETAILS

The monoallene **8** has been successfully developed instead of the bis(allene) **9** through the experimental. The bis(propargyl alcohol) **7** was synthesized from dimedone as a common precursor of bis(allene) **9**. The treatment of the bis(propargyl alcohol) **7** with PhSCl and triethylamine as a base in THF at -78 °C and followed by the oxidation afforded the monoallene **8** in a low yield . For further details, please refer to the reference no.9.

COMPUTATIONAL DETAILS

Density functional theoretical computation of all the substrates intermediate were performed by using GAUSSIAN 09 software package[15] with 6-31G(d,p) basis set to derive the complete geometry optimization. Furthermore, effective squared charges (χ^2), total electronic energy and dipole moment calculations were analyzed for all the intermediates of the substrate with the Gaussian 09 software and DFT/B3LYP functionality combined with the standard 6-31G(d,p) basis set.

RESULTS AND DISCUSSION

Our analysis of the synthetic reaction pathways was illustrated in Scheme 4. All the possible intermediates were optimized to the minimum potential energy using Gaussian 09 software package at the theoretical level of DFT B3LYP/6-31G(d,p). The results indicated that the formation of bis(allene) **9** (Path 1) was more difficult in the process of forming the intermediate of **11**. The stabilization energy, (+91.12 kJmol^{-1}) and also its dipole moment (μ = 8.2218D) for the formation of the intermediate **11** were higher compared to the monoallene **10b** (+41.87 kJmol^{-1}, μ = 5.4380D). Furthermore, the calculation of the effective squared charges (χ^2) followed by $-Ln \chi^2$ showed the supportive result for the path 1 which the reaction pathway was difficult to occurred.
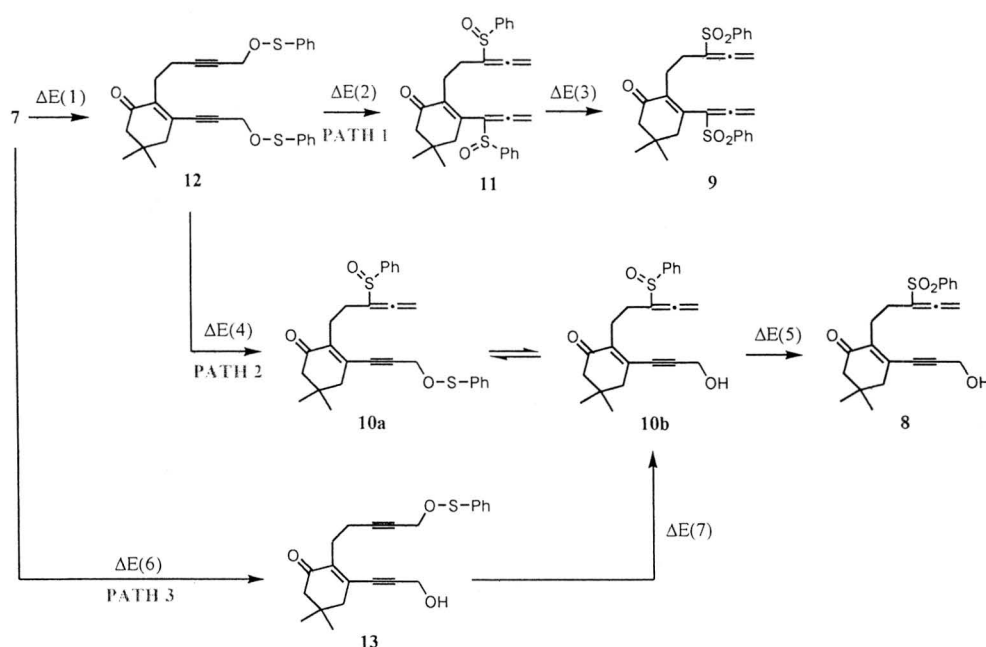
Scheme 4. Pathways reaction for the formation of monoallene **8** and bis(allene) **9**

The path 2 showed the pathway of the formation of **8**. This calculation indicated that the propargyl sulfoxide group of intermediate **10a** was unstable which easily transformed to alcohol functional group intermediate of **10b** (42. 68 kJmol-1, μ = 6.8499D). On the other hand, $-Ln\chi^2$ showed that this pathway can be occurred because the charges was lower and near with the ideal aromaticity charges (-31). Coincidently,

the path 3 also can be occurred based on the stabilization energy, dipole moments and square effective charges. Based on the factor of steric hindrance and Table 1, it was suggested that the path 3 approached from the less sterically hindered side of the rearrangement of **13** in the formation of **8** by the intermediate of **10b**. So, it showed that the path 3 was more favourable compare to the path 2 in the formation of the product **8**. In between, the solvent also play an important role in helping to increase the yield of the monoallene **8**.

Table 1. The squared effective charges (χ^2) of all carbon atoms on cyclohexene ring, total energy, dipole moment and formation energy of the carbonyl derivatives were evaluated at the theoretical level of B3LYP/6-31G(d,p).

Molecules	SCF Energy, au	Dipole Moment, μ	χ^2	$-Ln\chi^2$
7	-847.293144833	2.7537D	0.254760	29.4402
8	-1551.71345682	5.1639	0.256492	29.7866
9	-2256.12971971	5.6954D	0.258838	30.3848
12	-2105.74151116	1.8984D	0.256094	29.5759
11	-2105.70680448	8.2218D	0.265672	27.9503
10a	-2105.72556254	5.4380D	0.259739	29.5376
10b	-1476.50173027	6.8499D	0.258580	29.7226
13	-1476.51798569	2.7498D	0.255223	29.4316

Table 2. Stabilization energy were calculated at the theoretical level of B3LYP/6-31G (d, p).

Stabilization Energy (ΔE)	kJmol^{-1}
1	-3.304E6
2	+91.12
3	-3.949E5
4	+41.8731
5	-1.975E5
6	-1.652E6
7	+42.6775

CONCLUSION

The synthetic reaction pathways of the monoallene were explored computationally by using Gaussian 09 at the theoretical level of DFT B3LYP/6-31G(d,p). The calculated results indicated that the reaction at propargyl phenylsulfinylpropynyl **(13)** on upper side was the most favourable in the formation of monoallene than the lower side due to the steric hindrance factor. Base on the χ^2, the reaction pathway 3 was the most favourable among all of the reaction channels. This reaction also was solvent dependent. The reason of the low chemical yield might be due to the incompatibility of the solvent and the sterical hindrance with the substrate.

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