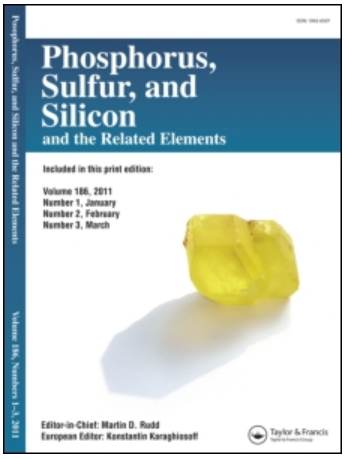

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

A DFT Study of NBO and NICS Analysis of the Allylic Rearrangements (the Claisen and Thio-Claisen Rearrangements) of 3-(Vinyloxy)prop-1-ene and Allyl Vinyl Sulfide

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Online publication date: 13 January 2011

To cite this Article Zahedi, Ehsan , Shiroudi, Abolfazl , Ali-Asgari, Safa and Keley, Vahid(2011) 'A DFT Study of NBO and NICS Analysis of the Allylic Rearrangements (the Claisen and Thio-Claisen Rearrangements) of 3-(Vinyloxy)prop-1-ene and Allyl Vinyl Sulfide', Phosphorus, Sulfur, and Silicon and the Related Elements, 186: 1, 159 — 170
To link to this Article: DOI: 10.1080/10426507.2010.492364
URL: http://dx.doi.org/10.1080/10426507.2010.492364

Phosphorus, Sulfur, and Silicon, 186:159–170, 2011

ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426507.2010.492364

A DFT STUDY OF NBO AND NICS ANALYSIS OF THE ALLYLIC REARRANGEMENTS (THE CLAISEN AND THIO-CLAISEN REARRANGEMENTS) OF 3-(VINYLOXY)PROP-1-ENE AND ALLYL VINYL SULFIDE

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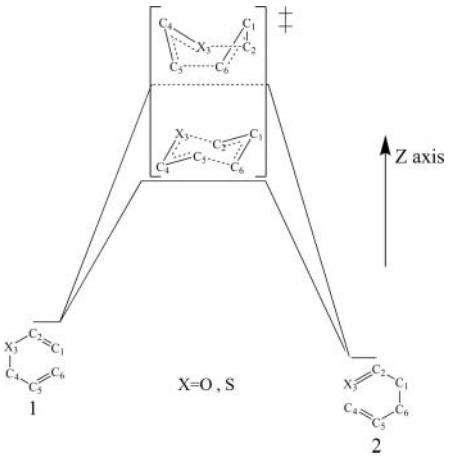
GRAPHICAL ABSTRACT



Abstract *Ab initio density functional theory (DFT) calculations have been performed on the 3,3-sigmatropic rearrangements of 3-(vinyloxy)prop-1-ene (Claisen) and allyl vinyl sulfide (thio-Claisen) in the gas phase. The barrier height of the Claisen rearrangement calculated at the B3LYP/6-311G** level of theory was in good agreement with the corresponding experimental value. Optimized transition states at the B3LYP/6-311G** level were used for calculating of nucleus independent chemical shift (NICS) and also natural bond orbital (NBO) analysis at the same level. Our results indicate that aromaticities of the transition states are controlled by the out-of-plane component and that the strongest aromatic character is for the chair-like transition state of the thio-Claisen rearrangement. Analysis of donor-acceptor (bonding and antibonding) interactions suggests that the aromatic character of TS structure in the allyl vinyl sulfide reaction (the thio-Claisen rearrangement) is more than the 3-(vinyloxy)prop-1-ene reaction (the Claisen rearrangement). The NBO results show that in these rearrangements, activation energies are controlled by resonance energies.*

Keywords Claisen rearrangement; DFT; NBO; NICS; thio-Claisen rearrangement

Received 6 April 2010; accepted 7 May 2010.

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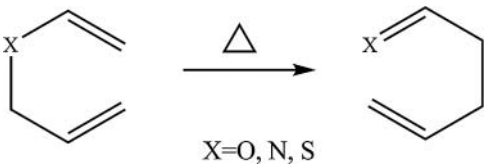

Figure 1 The thermal isomerization of allyl vinyl ether and its nitrogen- or sulfur-containing analogues.

INTRODUCTION

The heating of an allyl vinyl ether allows the preparation of γ,δ-unsaturated carbonyl compounds via a [3,3] sigmatropic rearrangement. This type of reaction, first discovered in 1912 by Rainer Ludwig Claisen, was originally described as the thermal $\sigma^2s + \pi^2s + \pi^2s$ isomerization of an allyl vinyl ether or its sulfur or nitrogen containing analogue (Figure 1) derivatives to produce a bifunctionalized molecule.

This reaction is irreversible in the direction of the formation of the carbonyl compound and takes place under thermodynamic control. The Claisen rearrangement term was, in principle, used for rearrangements of allyl aryl ethers to produce *ortho*- and occasionally *para*-substituted phenols, then this term was extended to rearrangements of allyl vinyl ethers.[1,2] The aromatic transition state (boat-like and chair-like) for this rearrangement is allowed by the Woodward–Hoffmann rules, and it is formed by a combination of σ and π overlap of $2p$ atomic orbitals of the atoms of both allylic fragments,[3–5] but investigations for obtaining the precise quality and geometry of the transition states are continuing, and a large number of experimental studies and theoretical computations are focused on determining the structure of the transition state.[6–12] Most of them assent a concerted rearrangement via chair-like channel, but there is no general agreement about chair-like geometry, and the difficulty of describing it still persists.[2]

Thermolysis of allyl phenyl sulfides requires a higher temperature to afford the corresponding thiols, but on the contrary, the aliphatic version of the thio-Claisen rearrangement easily leads to a [3,3] sigmatropic rearrangement. The applicability of this methodology is low because of the instability of the product (thioaldehyde).[13,14] This subject prompted the development of qualifications to snaring and transforming the unstable product into a more stable compound, for example, the hydrolysis of the thioaldehyde into the corresponding aldehyde.[15]

In this study, we calculated and compared kinetic and thermodynamic quantities for the Claisen rearrangement of 3-(vinyloxy)prop-1-ene and the thio-Claisen rearrangement of allyl vinyl sulfide in the gas phase. Finally, we justify these results using natural bond orbital (NBO) analysis and nucleus independent chemical shift (NICS) techniques.

COMPUTATIONAL ASPECTS

Geometry optimizations for the reactant, transition state, and product of all the studied reactions were performed with the Gaussian 03 software package.[16] Full optimization of geometries has been carried out at the B3LYP/6-311G** level of theory. This corresponds to the approximation method that makes use of Becke-style three-parameter density functional theory with the Lee–Yang–Parr correlation functional. The triple-ζ basis set adds three sizes of s and p functions to the atoms and adds a d function to heavy atoms and a p function to hydrogen atoms. To confirming the nature of the stationary species and evaluate the

activation energy barriers, frequency calculations are carried out at the same level of theory. For the structures of minimum states, only real frequency values are accepted, and for the transition states, only a single imaginary frequency value is selected. The synchronous transit-guided quasi-Newton (STQN) method[17] was used to locate the TSs. The activation energies, E_a, were computed using Eq. (1), which was derived from the transition state theory[18,19]:

$$E_a = \Delta H^{\neq}(T) + RT \quad (1)$$

Thermodynamic functions were calculated at 298.15 K and 1.0 atm.

Based on the optimized ground states geometries, the NBO and nuclear magnetic resonance (NMR) calculations have been accomplished with the B3LYP method and 6-311G** basis set.

RESULTS AND DISCUSSION

Kinetic and Thermodynamic Study

Two possible pathways have been suggested for the [3,3] sigmatropic rearrangement of 3-(vinyloxy)prop-1-ene (the Claisen rearrangement) and allyl vinyl sulfide (the thio-Claisen rearrangement) in the gas phase: (1) a pathway with chair-like aromatic transition state and (2) another pathway with a boat-like aromatic transition state. The thermochemical parameters for the reactions (ΔH, ΔS, and ΔG) were obtained from the thermochemistry calculations and are reported in Table 1. Before discussing the results from all the systems in detail, a comparison with other calculations using the B3LYP/6-311G** level of theory for the reactions has been made in Tables 1 and 2.

The Claisen rearrangement of 3-(vinyloxy)prop-1-ene and the thio-Claisen rearrangement of allyl vinyl sulfide are exothermic ($\Delta H < 0$) and spontaneous ($\Delta G < 0$) processes. The exothermicity of the Claisen rearrangement is essentially due to the thermodynamic stability of carbonyl moiety formed in the product. The homolytic dissociation energies of bonds[20,21] that undergo a net change in the reaction are given in Table 3. The greater stability of the C—O bond in the enol ether structure compared to the C—C bond in the carbonyl product tips the equilibrium toward the left (6 kcal/mol). The comparative weakness of the C=C bond versus the C=O bond is compensated by 24 kcal/mol. Therefore, the enthalpy of the Claisen rearrangement is about −18 kcal/mol, and similar calculation for the thio-Claisen rearrangement shows that the enthalpy of this reaction is about −0.5 kcal/mol. The entropy changes during the Claisen rearrangement are positive and for the

Table 1 Calculated thermodynamic parameters at 298.15 K and 1.0 atm for the Claisen and thio-Claisen rearrangements in the gas phase

Thermodynamic functions	Method					
	B3LYP/6-31G*		BHandHLYP/6-31G*		B3LYP/6-311G**	
	Claisen	Thio-Claisen	Claisen	Thio-Claisen	Claisen	Thio-Claisen
ΔG (kcal/mol)	–18.79	–3.83	–19.65	–4.22	–18.38	–2.76
ΔH (kcal/mol)	–18.14	–3.89	–18.99	–4.23	–17.64	–2.88
ΔS (cal/mol.K)	2.16	–0.19	2.22	–0.03	2.44	–0.40

Table 2 Calculated kinetic and activation parameters at 298.15 K and 1.0 atm for the Claisen and thio-Claisen rearrangements in the gas phase

	Method								
	B3LYP/6-31G*			BHandHLYP/6-31G*			B3LYP/6-311G**		
Reaction and pathway	$\Delta S^{\neq}$ (cal/mol.K)	$\Delta G^{\neq}$ (kcal/mol)	E_a (kcal/mol)	$\Delta S^{\neq}$ (cal/mol.K)	$\Delta G^{\neq}$ (kcal/mol)	E_a (kcal/mol)	$\Delta S^{\neq}$ (cal/mol.K)	$\Delta G^{\neq}$ (kcal/mol)	E_a (kcal/mol)
Claisen (chair-like ts)	–5.01	28.72	27.81	–5.38	36.40	35.39	–4.54(–7.7[a,b])	28.75	27.99(30.6, [a]30.39[b])
Claisen (boat-like ts)	–3.72	32.32	31.80	–4.08	40.80	40.17	–3.33	31.86	31.46(33.39[c])
Thio-Claisen (chair-like ts)	–7.99	23.06	21.27	–8.17	29.18	27.34	–7.88	24.20	21.94
Thio-Claisen (boat-like ts)	–6.62	27.55	26.17	–6.80	34.60	33.16	–6.49	27.88	26.53

[a]Ref. [22].
[b]Ref. [23].
[c]Ref. [24].

Table 3 Energy contribution (kcal/mol) to the enthalpy of the Claisen and thio-Claisen rearrangements in terms of transposed bonds

Bond	Energy (left side)	Energy (right side)
=C−O−	84[a]	–
−C−O−	84[a]	–
C=C	148[a]	–
=C−C−	–	81[a]
−C−C−	–	81[a]
C=O	–	172[a]
=C−S−	69.2[b]	–
−C−S−	69.2[b]	–
C=S	–	124.9[b]

[a]Ref. [20].
[b]Ref. [21].

thio-Claisen rearrangement are negative and can be neglected in the calculations because the calculated entropy values are generally small (the absolute values of ΔS° are less than 2.5 cal/mol.K for the Claisen rearrangement and 0.4 cal/mol.K for the thio-Claisen rearrangement). The B3LYP/6-31G*, BHandHLYP/6-31G*, and B3LYP/6-311G** results show that the activation energies for the Claisen rearrangement in the chair-like transition state pathway are 27.812, 35.389, and 27.987 kcal/mol, respectively, and in the boat-like transition state pathway are 31.801, 40.172, and 31.456 kcal/mol, respectively. For the thio-Claisen rearrangement, the activation energies in the chair-like transition state pathway are 21.270, 27.336, and 21.935 kcal/mol, and in the boat-like transition state pathway are 26.170, 33.164, and 26.534 kcal/mol, as calculated by B3LYP/6-31G*, BHandHLYP/6-31G*, and B3LYP/6-311G** levels of theory, respectively.

These results reveal that the activation energies of the Claisen rearrangement of 3-(vinyloxy)prop-1-ene in the chair-like and boat-like transition states are higher than the thio-Claisen rearrangement of allyl vinyl sulfide. For both rearrangements, the activation energies in the boat-like transition state pathway are higher than the chair-like transition state pathway. It is interesting to note that the obtained results using the B3LYP/6-311G** level of theory are in good agreement with the available experimental data (Table 2). This agreement justifies use of the B3LYP/6-311G** level of theory for investigation of these types of reactions (energetic calculations, NICS study, and NBO analysis). In both rearrangements, entropies of activation are negative. Negative values for activation entropies confirm concerted mechanism and formation of cyclic transition state for the studied rearrangements.

Hammond's postulate can be interpreted in terms of the position of the transition state structure along the reaction coordinate, n_T [Eq. (2)], as defined by Agmon and Levine[25]:

$$n_T = \frac{1}{2 - (\Delta G^o / \Delta G^{\neq})} \tag{2}$$

According to this equation, the position of the transition state along the reaction coordinate is determined solely by ΔG° (a thermodynamic quantity) and $\Delta G^{\neq}$ (a kinetic quantity). In the Claisen rearrangement of 3-(vinyloxy)prop-1-ene and the thio-Claisen rearrangement of allyl vinyl sulfide, the transition state structures for both pathways resemble the reactant form more than its product. The values of n_T for the chair-like and boat-like pathways

of the Claisen rearrangement are 0.379 and 0.388, respectively, and for the chair-like and boat-like pathways of the thio-Claisen rearrangement are 0.473 and 0.476, respectively. The magnitudes of n_T indicate the degree of similarity between the structure of the transition state and the product.

The Nucleus-Independent Chemical Shift (NICS) Study

In the NICS study, the gauge-invariant atomic orbitals (GIAO) method was applied to estimate the diamagnetic ring current intensity on the optimized geometries in the gas phase. Magnetic properties of organic molecules arise from the diamagnetic ring current of aromatic systems.[26] The NICS is defined as the negative value of the absolute magnetic shielding in centers of rings or 1 Å above or below the molecular plane.[27] NICS at an empty point in space equals zero and in principle does not require reference molecules and calibrating (homodesmotic) equations for evaluation of aromaticity. Negative values of NICS indicate a shielding effect resulting from the induced diatropic ring current understood as aromaticity at a specific point. On the contrary, its positive values are interpreted as the deshielded-paratropic ring current and thus antiaromaticity. Schleyer et al., after studies on an extensive set of heterocyclic compounds, proved that there are very good linear correlations among the geometric, energetic, and magnetic properties providing straightforward interpretation of the electronic structures and properties of organic molecules.[28]

For all the studied transition state structures, the sets of points lying below and above the rings' geometric centers were used. Their locations correspond to distances from -1 to 1 Å with 1 Å steps (Figure 2). The NICS 0 Å values calculated at the center of the ring were influenced by σ bonds, whereas the NICS 1 and -1 Å values calculated at the

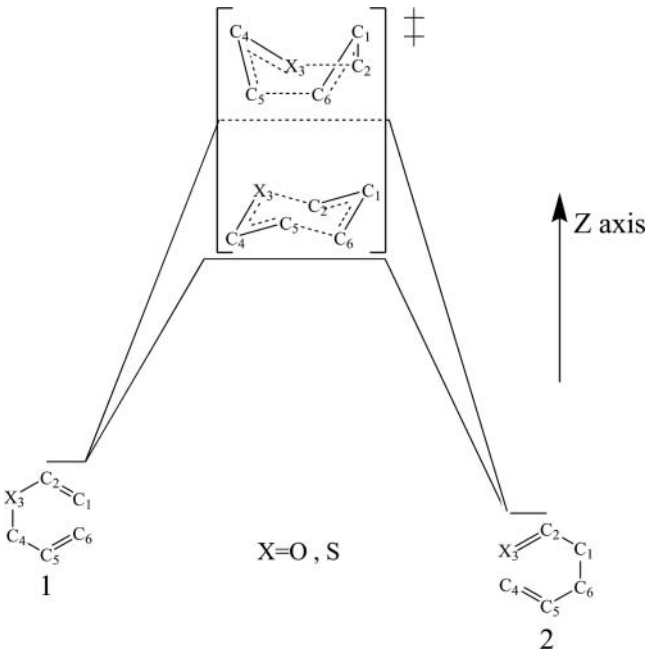

Figure 2 The Claisen and thio-Claisen rearrangements via two pathways (chair-like and boat-like).

1 Å above and 1 Å below the plane were more affected by the π-system.[29] From Table 4, one may conclude that all the transition states are aromatic. The transition states exhibit characteristic decreasing of the NICS values from the point located in the geometric center of the ring to the 1 Å above or below of it. The NICS values are the isotropic chemical shifts of the respective bq's, and the eigenvalues of the chemical shift tensors were used to separate the isotropic NICS values into their in-plane and out-of-plane components. Since the NICS values are distance-dependent, the N@r symbol will be used in this article to denote the NICS value (ppm) at distance r(Å) from the molecular plane. Table 4 shows the NICS values for the transition states. The transition states are not planar; therefore, the 1 Å distance from the ring center perpendicular to the C_1-C_3-C_4-C_6 plane is considered (Figure 2). The magnitudes of the isotropic chemical shifts, however, are very different; the minimal values are −20.6244@0, −16.7760@0, −22.9211@0, and −18.1694@0 in the chair-like Claisen, the boat-like Claisen, the chair-like thio-Claisen, and the boat-like thio-Claisen transition states, respectively. The separation of the isotropic values into in-plane and out-of plane contributions indicates that the in-plane components in all the transition states behave similarly, that is, diatropic shifts at short distances and the out-of-plane component of the chemical shifts are very large. Consequently, aromaticities of the transition states are controlled by the out-of-plane component.

The strongest aromatic character was found for the chair-like transition state of the thio-Claisen rearrangement. The chair-like transition state of the Claisen rearrangement was also characterized by a significant relative aromaticity, but less compared to the chair-like transition state of the thio-Claisen rearrangement. The boat-like transition states of the Claisen and the thio-Claisen rearrangements have the least aromaticity. As a result, the activation energies decrease with increase of the diatropic current of the transition states (aromaticity).

The NBO Analysis

Delocalization of electron density between the filled (bonding or lone pair) Lewis-type NBOs and the empty (antibonding and Rydberg) non-Lewis NBOs (Figures 3–6) leads to transfer of occupancy from the localized NBOs of the idealized Lewis structure into the empty non-Lewis orbitals (and thus, departure from the idealized Lewis structure description). It is referred to as "delocalization" correction to the zero-order natural Lewis structure to a stabilizing donor–acceptor interaction. The energies of these interactions can be estimated by the second-order perturbation theory.[30] For each donor NBO (i) and acceptor NBO (j), the stabilization energy (E_2) associated with i → j delocalization, is explicitly estimated by the following equation[31]:

$$E_2 = \Delta E_{ij} = q_i\left[F^2_{(i,j)}/(\varepsilon_i - \varepsilon_j)\right] \tag{3}$$

where q_i is the donor orbital occupancy, ε_i and ε_j, are diagonal elements (orbital energies), and $F_{(i,j)}$ is the off-diagonal NBO Fock matrix elements.

Based on the B3LYP/6-311G** optimized ground state geometries, the NBO analysis of donor–acceptor interactions shows that the resonance energies for $\sigma_{3\text{-}4} \rightarrow \pi^*_{1\text{-}2}$ delocalization (Figures 3 and 4)[32] in 3-(vinyloxy)prop-1-ene and allyl vinyl sulfide are < 0.5 and 1.82 kcal/mol, respectively, and for $\sigma_{3\text{-}4} \rightarrow \sigma^*_{1\text{-}2}$ delocalization (Figures 5 and 6)[32] are < 0.5 and 1.31 kcal/mol, respectively. Likewise, the resonance energies for $\sigma_{3\text{-}4} \rightarrow \pi^*_{5\text{-}6}$ delocalization (Figures 3 and 4) in 3-(vinyloxy)prop-1-ene and allyl vinyl

Table 4 NICS values as a function of distance (Angström) for the transition states of the Claisen and thio-Claisen rearrangements: isotropic chemical shift, in-plane component, and out-of-plane component

	NICS (−1) (ppm)			NICS (0) (ppm)			NICS (+1) (ppm)		
Transition state	Isotropic	Out-of-plane	In-plane	Isotropic	Out-of-plane	In-plane	Isotropic	Out-of-plane	In-plane
Chair-like Claisen	–11.0333	–26.5985	–6.5015	–20.6244	–43.1532	–18.7199	–11.9008	–28.7069	–6.9955
Boat-like Claisen	–6.5863	–18.7727	–0.9862	–16.7760	–37.4352	–12.8926	–14.9758	–32.9718	–11.9555
Chair-like thio-Claisen	–14.0661	–33.2585	–8.9397	–22.9211	–48.8777	–19.8857	–13.6634	–32.4638	–8.5264
Boat-like thio-Claisen	–8.0194	–22.3533	–1.7048	–18.1694	–41.3311	–13.1769	–17.3789	–37.9980	–14.1387

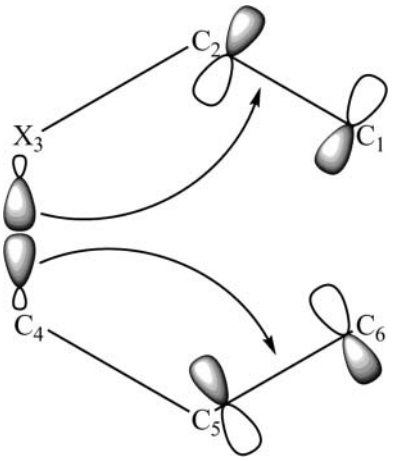

Figure 3 Schematic representation of hyperconjugation between bonding ($\sigma_{3\text{-}4}$) and antibonding ($\pi^*_{1\text{-}2}$ or $\pi^*_{5\text{-}6}$) orbitals.

sulfide are < 0.5 and 4.33 kcal/mol, respectively, and for $\sigma_{3\text{-}4} \rightarrow \sigma^*_{5\text{-}6}$ delocalization (Figures 5 and 6) are < 0.5 and 0.84 kcal/mol, respectively (Table 5). This fact could explain that the aromatic character of TS structure in the allyl vinyl sulfide reaction (the thio-Claisen rearrangement) is more than the 3-(vinyloxy)prop-1-ene reaction (the Claisen rearrangement), and also this is in agreement with the NICS data. Likewise, based on this argument, the activation energy of the thio-Claisen rearrangement of allyl vinyl sulfide should be lower than the Claisen rearrangement of 3-(vinyloxy)prop-1-ene (Table 2). Also, we can expect that by increasing of the $\sigma_{3\text{-}4} \rightarrow \pi^*_{1\text{-}2}$ and $\sigma_{3\text{-}4} \rightarrow \sigma^*_{1\text{-}2}$ delocalizations, the $\sigma_{3\text{-}4}$ bonding orbital occupancy should be decreased. The NBO results show that the $\sigma_{3\text{-}4}$ bonding orbital occupancies in 3-(vinyloxy)prop-1-ene and allyl vinyl sulfide are

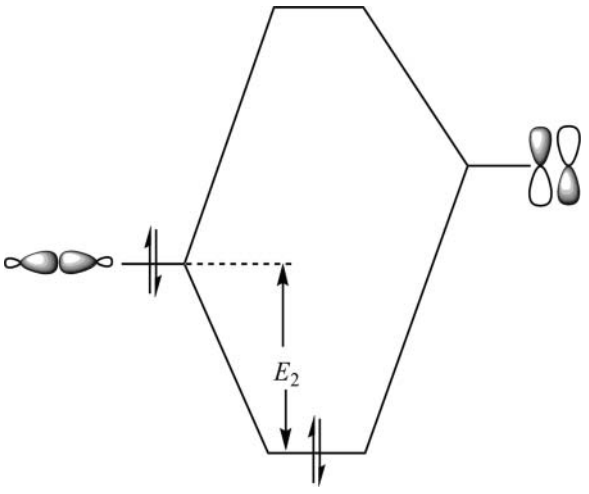

Figure 4 Stabilization resonance energy (E_2) from donor ($\sigma_{3\text{-}4}$) to acceptor ($\pi^*_{1\text{-}2}$ or $\pi^*_{5\text{-}6}$) for bonding and antibonding orbitals.

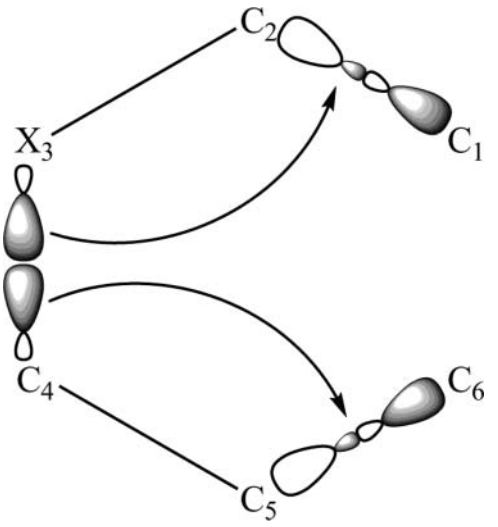

Figure 5 Schematic representation of hyperconjugation between bonding ($\sigma_{3\text{-}4}$) and antibonding ($\sigma^*_{1\text{-}2}$ or $\sigma^*_{5\text{-}6}$) orbitals.

1.99000 and 1.96411, respectively (Table 5). The greater $\sigma_{3\text{-}4} \rightarrow \pi^*_{1\text{-}2}$ and $\sigma_{3\text{-}4} \rightarrow \sigma^*_{1\text{-}2}$ stabilization energies and the lower $\sigma_{3\text{-}4}$ bonding orbital occupancy in allyl vinyl sulfide could facilitate the thio-Claisen rearrangement as compared with the Claisen rearrangement of 3-(vinyloxy)prop-1-ene (Table 2). Also, the B3LYP/6-311G** results showed that the HOMO-LUMO gap for 3-(vinyloxy)prop-1-ene and allyl vinyl sulfide are 6.705 and 5.625 eV, respectively (Table 5). That is, the HOMO-LUMO gap decreases in accordance with increase of the electronic delocalizations from $\sigma_{3\text{-}4}$ bonding orbital to $\pi^*_{1\text{-}2}$ and $\sigma^*_{1\text{-}2}$ antibonding orbitals .

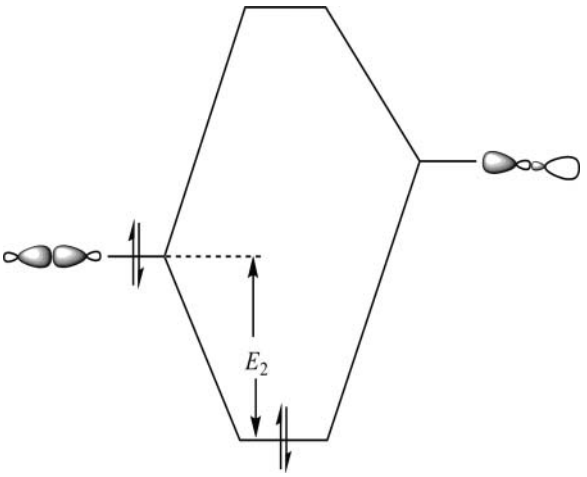

Figure 6 Stabilization resonance energy (E_2) from donor ($\sigma_{3\text{-}4}$) to acceptor ($\sigma^*_{1\text{-}2}$ or $\sigma^*_{5\text{-}6}$) for bonding and antibonding orbitals.

Table 5 NBO-calculated $\sigma_{3\text{-}4}$ bonding orbital occupancy, resonance energies, HOMO energies, LUMO energies, and HOMO-LUMO gaps in the ground states of 3-(vinyloxy)prop-1-ene and allyl vinyl sulfide

Compound	$\sigma_{3\text{-}4}$ (occupancy)	$\sigma_{3\text{-}4} \rightarrow \pi^*_{1\text{-}2}$ (kcal/mol)	$\sigma_{3\text{-}4} \rightarrow \sigma^*_{1\text{-}2}$ (kcal/mol)	$\sigma_{3\text{-}4} \rightarrow \pi^*_{5\text{-}6}$ (kcal/mol)	$\sigma_{3\text{-}4} \rightarrow \sigma^*_{5\text{-}6}$ (kcal/mol)	HOMO-LUMO (eV)
3-(Vinyloxy)prop-1-ene	1.99000	< 0.5	< 0.5	< 0.5	< 0.5	6.705
Allyl vinyl sulfide	1.96411	1.82	1.31	4.33	0.84	5.625

The thio-Claisen rearrangement of allyl vinyl sulfide has a calculated activation enthalpy of about 21.343 kcal/mol, which as compared with 27.395 kcal/mol related to the Claisen rearrangement of 3-(vinyloxy)prop-1-ene, is relatively small. The heterolytic bond cleavage energies of C—O and C—S bonds in the gas phase are 84 and 69.2 kcal/mol, respectively.[22,23] This is in agreement with higher activation energy of the Claisen rearrangement of 3-(vinyloxy)prop-1-ene than the thio-Claisen rearrangement of allyl vinyl sulfide. As a result, it can be concluded that in the 3-(vinyloxy)prop-1-ene and allyl vinyl sulfide rearrangements, activation energies are controlled by resonance effects.

CONCLUSION

The above reported DFT calculations, NICS study, and NBO analysis created a reasonable picture from structural, energetic, and bonding points of view for the Claisen rearrangement of 3-(vinyloxy)prop-1-ene and the thio-Claisen rearrangement of allyl vinyl sulfide. Based on the presented results, we can obtain the following conclusions:

- The chair-like transition state of the thio-Claisen rearrangement has higher diatropic current with respect to the Claisen rearrangement.
- Aromaticities of the transition states are controlled by the out-of-plane component of isotropic chemical shift.
- The resonance energies in allyl vinyl sulfide are higher than 3-(vinyloxy)prop-1-ene, and the $\sigma_{3\text{-}4}$ bonding orbital occupancy in allyl vinyl sulfide is less than 3-(vinyloxy)prop-1-ene.
- The HOMO-LUMO gap decreases in accordance with increase of the electronic delocalizations from $\sigma_{3\text{-}4}$ bonding orbital to antibonding orbitals.
- In the 3-(vinyloxy)prop-1-ene and allyl vinyl sulfide rearrangements, activation energies are controlled by resonance effects.

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