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Review Article

Theoretical investigation on carbene-catalyzed [3 + 3] annulation of vi-nyl sulfoxonium ylide with enal for synthesis of 2-sulfenylidene-3-cyclohexen-1-one

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Abstract:

The first theoretical investigation was provided by our DFT calculation on trazolum carbene-catalyzed [3 + 3] annulation of vinyl sulfoxonium ylide with enal. Free carbene NHC is formed via deprotonation by BF4 with enhanced nucleophilicity. NHC attacks positive carbonyl of enal with its negative carbon followed by proton transfer leading to Breslow intermediate, which is easily transformed to α, β-unsaturated acylazolium inter-mediate through dehydrogenation. Spontaneous electron delocalization in vinyl sulfoxonium ylide makes car-banion available at α-position of ester. Michael addition undergoes linking two substrates. Followed by pro-ton shift, the carbanion attacks positive carbonyl in crucial ring closure yielding six-membered carbocycle. The second proton shift generates isomer of desired 2-sulfenylidene-3-cyclohexen-1-one after release of proto-nated NHC.

Key words: carbene; [3 + 3] annulation; sulfoxonium ylide; cyclohexanone; enal

1.Introduction

As privileged structural components, cyclohexanones are ubiquitous in nature and can be found in various organisms including terpenoids and steroids [1,2]. In this field, the cyclohexanone backbone has attracted significant interest due to bioactivity and structural diversity as fungi and higher plants in biology [3,4]. For instance, Joshi et al. researched regioselective synthesis of substituted cyclohexa-1,3-dienes via base-mediated cyclisation of α,β-unsaturated carbonyl compounds and γ-phosphonylcrotonates [5]. Li et al. discovered effective [3+1+1+1] cycloaddition to six-membered carbocycle based on dmso as dual carbon synthon [6]. Fujii et al. obtained stereoselective cyclohexadienylamine synthesis through Rh-catalysed [2+2+2] cyclotrimerization [7]. There are also processes such as radical reaction in xanthate route [8], specific asymmetric inverse-electron-demand Diels-Alder reaction of 2-pyrones with indenes leading to cephanolides and the stereoselective synthesis of five- and six-membered carbocycles via matteson homologation/ring closing metathesis [9,10].

However, transition metal or high temperature cannot be avoided making organocatalytic strategy desirable under mild conditions. N-Heterocyclic carbenes (NHC) are valuable in synthesizing intricate molecular structures with significant medical and biological implications [11]. They exhibit versatile reactivity to facilitate umpolung and convert carbonyl carbon to acyl nucleophilic reagent. Daelemans et al. reported advances in NHC-catalyzed fluorination and fluoroal-kylation encompassing benzoin condensation [12]. Mondal et al. explored covalent immobilization of NHC on pristine carbon substrates from nano-scale characterization to bulk catalysis [13]. Wang et al. prepared enantioselective construction of dihydropyranone-fused indoles by [3 + 3] annulation of in situ-derived indolin-3-ones and unsaturated carboxylic esters [14]. Yetra et al. realized generation of α,β-unsaturated acylazoliums for heterocycles and carbocycles [15]. Yao et al. developed catalytic [4 + 2] cyclization of 3-alkylenyloxindoles with enals via γ-carbon activation for assembly of spirocarbocyclic oxindoles [16]. Zhu et al. and Gao et al. utilized formal [3 + 3] cyclo-addition in construction of benzene [17,18]. Furthermore, the mechanism underlying formation of six-membered carbocycles via intramolecular cyclization was elucidated by Lupton and Liang group [19,20].

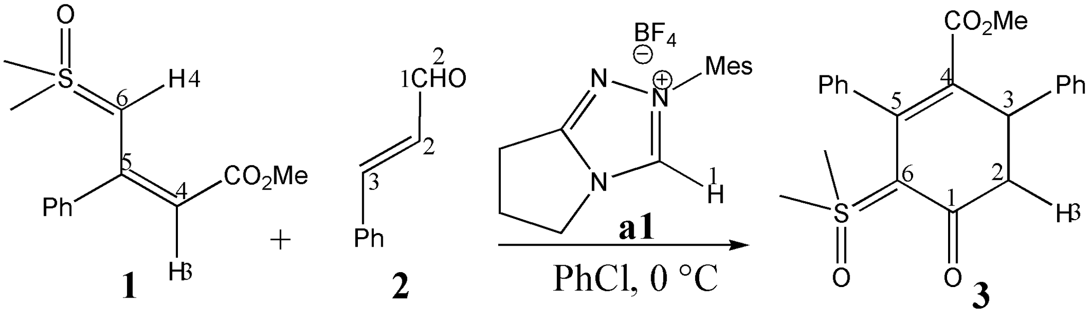
Recently, sulfur ylides gained attention compared to diazonium compounds due to their enhanced stability [21]. Bhardwaj et al. also found its high nucleophilicity in gem-difunctionalization of diazo compounds with vinyl sulfoxonium ylides and thiols via metalloradical catalysis [22]. Aspired by this, Fu et al. developed carbene-catalyzed [3 + 3] annulation of enals and vinyl sulfoxonium ylides [23]. Similar with Deshwal's catalyst-controlled divergent synthesis of 2H-chromenes with quinones [24], how the product was formed during competition between direct attack on β-position of acyl azolium or double bond transfer to γ-position from α-position carbanion in sulfoxonium ylide? As described by Chen, the steric hindrance of sulfoxide group may hinder the attack of carbo-negative ions at α-position [25]. So what's the difference between divergent synthesis of tetrasubstituted phenols and this generation of six-membered carbocycle?

2 Computational details

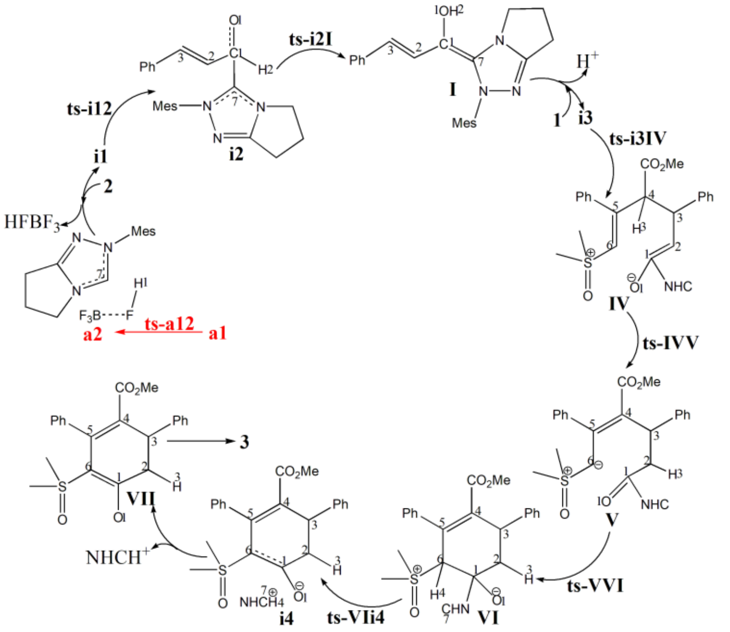
Structures were optimized at M06-2X/6-31G(d) level with GAUSSIAN09 [26]. Among various DFT methods [27], M06-2X functional has smaller deviation between experimental and calculated value than B3LYP hybrid functional [28,29]. With 6-31G(d) basis set, it can provide best compromise between time consumption and energy accuracy. It was also found to give accurate results for stepwise (2 + 2) cycloaddition, enantioselective (4 + 3) and Diels−Alder reaction [30,31]. Together with good performance on noncovalent interaction, it is suitable for this system [32-34]. To obtain zero-point vibrational energy (ZPVE), harmonic frequency calculations were carried out at M06-2X/6-31G(d) level gaining thermodynamic corrections at 303 K and 1 atm in chlorobenzene. At M06-2X/6-311++G(d,p) level, the solvation-corrected free energies were obtained using integral equation formalism polarizable continuum model (IEFPCM) [35-39] on M06-2X/6-31G(d)-optimized geometries. NBO procedure was performed with Natural bond orbital (NBO3.1) obtaining lone pair and bond to characterize bonding orbital interaction and electronic properties [40-42]. Using Multiwfn_3.7_dev package [43], wave function analysis was explored on Mayer bond order (MBO) and frontier molecular orbital (FMO). Detailed are listed in Table S3 and Figure S2.

3 Results and Discussion

The mechanism of carbene **a1**-catalyzed [3 + 3] annulation was explored for vinyl sulfoxonium ylide **1** with enal **2** leading to 2-sulfenylidene-3-cyclohexen-1-one **3** (Scheme 1). The best trazolum carbene **a1** was selected here as catalyst precursor according to experiment. Illustrated by red arrow of Scheme 2, an active free carbene NHC is initially formed via deprotonation by base BF_4 with enhanced nucleophilicity. Then, NHC attacks positive carbonyl of unsaturated aldehyde **2** with its negative carbon followed by proton transfer resulting in Breslow intermediate **I**, which is transformed to α, β-unsaturated acylazolium intermediate **II** via dehydrogenation. The electron delocalization spontaneously occurs in vinyl sulfoxonium ylide **1** leading to carbanion, which transfers electron to α-position of ester group through double bond. Subsequently, this active structure of **1** and **II** undergo Michael addition to form **IV**. A further proton shift leads to intermediate **V**, from which the carbanion attacks carbonyl carbon yielding **VI**. Finally, **VI** undergoes proton shift generating intermediate **VII** as isomer of desired product **3a** after the release of protonated positive carbene. Figure 1 listed schematic structures of optimized TSs in Scheme 2. Table 1 gave activation energy for all steps.



Scheme 1 Carbene **a1**-catalyzed [3 + 3] annulation of vinyl sulfoxonium ylide **1** with enal **2** leading to 2-sulfenylidene-3- cyclohexen-1-one 3. Mes denotes 2,4,6-trimethylphenyl.

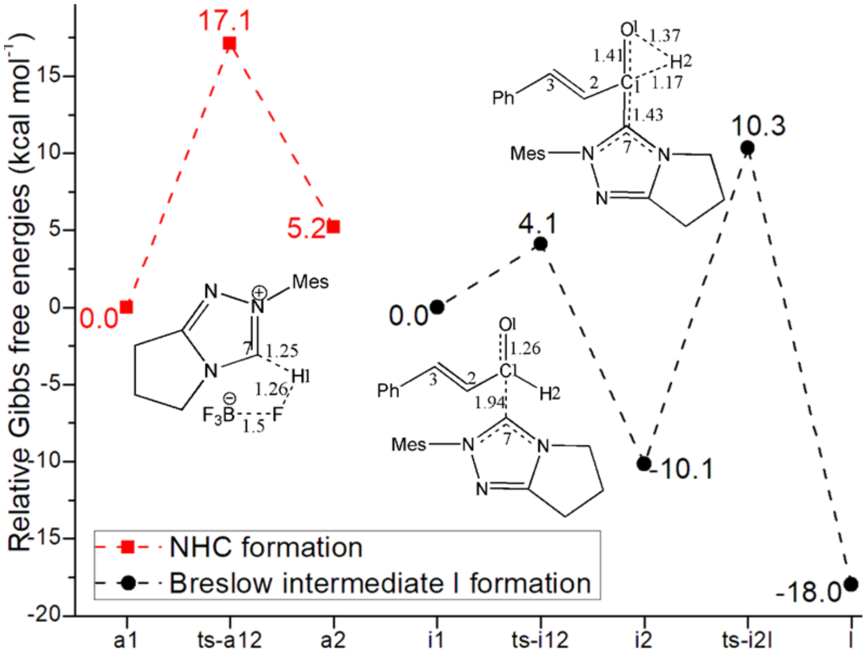


Scheme 2: Reaction mechanism of carbene a1-catalyzed [3 + 3] annulation of vinyl sulfoxonium ylide 1 with enal 2 leading to 2-sulfenylidene-3-cyclohexen-1-one 3.

TS	$\Delta G^{\neq}_{gas}$	$\Delta G^{\neq}_{sol}$
ts-a12	20.9	17.1
ts-i12	6.8	4.1
ts-i2I	23.0	20.4
ts-i3IV	13.6	12.0
ts-IVV	31.2	22.8
ts-VVI	32.4	26.3
ts-VIi4	18.6	18.3

(a)

Table 1: The activation energy (in kcal mol^{-1}) of all reactions in gas and solvent



(b)

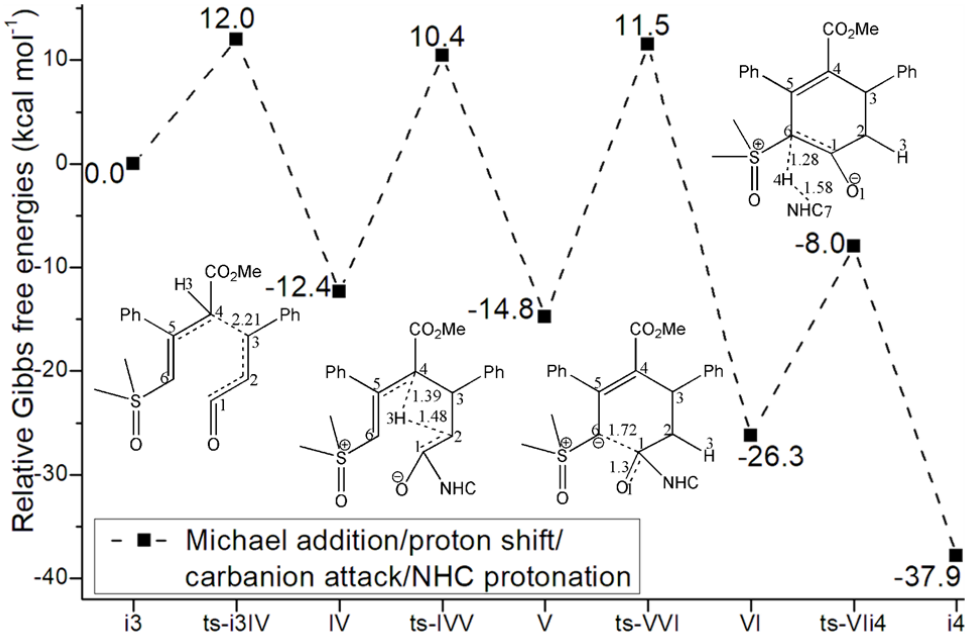


Figure 1: Relative Gibbs free energy profile in solvent phase starting from complex (a) **a1**, **i1** (b) **i3** (Bond lengths of optimized TSs in Å).

3.1 NHC/Breslow intermediate formation

As catalyst precursor, the trazolum carbene **a1** is taken as starting point, which is deprotonated by base BF_4 via **ts-a12** in step 1 with the activation energy of 17.1 kcal mol^{-1} endothermic by 5.2 kcal mol^{-1} producing reactive complex **a2** binding $HFBF_3$ and active free carbene NHC (red dash line of Figure 1a). The transition vector includes proton H1 transfer from C7 to F and simultaneous cleavage of F⋯B single bond (1.25, 1.26, 1.5 Å). In resultant **a2**, both HF and BF_3 exist as independent molecule. After deprotonation, the nucleophilicity of C7 in NHC is greatly enhanced ready to initiate the following process.

The initial complex is located as **i1** between NHC and substrate unsaturated aldehyde **2** taken as new starting point of next two steps (black dash line of Figure 1a). Via **ts-i12**, NHC attacks positive carbonyl C1 of **2** with its negative C7 in step 2 with low activation energy of 4.1 kcal mol^{-1} exothermic by -10.1 kcal mol^{-1} generating stable **i2**. The transition vector suggests nucleophilic attack of C7 to C1 and resulting elongation of C1-O1 double bond (1.94, 1.26 Å) (Figure S1a). Once typical C1-C7 single bond is formed, C1 turns to be sp3 hybrid.

The Breslow intermediate **I** predicted in experiment is obtained in the following step 3. That is proton transfer taking place via **ts-i2I** with activation energy of 20.4 kcal mol^{-1} affording **I** exothermic by -18.0 kcal mol^{-1}. The transition vector is complicated contains a series of atomic motion. On one hand, proton H2 moves from C1 to O1. On the other, C1-O1 is continuously stretching to single bond along with the contraction of C1-C7 single bond (1.17, 1.37, 1.41, 1.43 Å) (Figure S1b). Ultimately, the interaction between NHC and **2** is strengthened to be C1=C7 double bond via two steps in **I** involving newly formed hydroxyl O1H2, which is easily transformed to α, β-unsaturated acylazolium intermediate **II** through dehydrogenation. The removal of H2 makes O1 negatively charged and C1-C7 recovering to single bond.

3.2 Michael addition/proton shift/ring closure /protonated NHC release

Owing to spontaneous electron delocalization in vinyl sulfoxonium ylide **1**, carbanion is available at C4 when electron transfers to α-position of ester through double bond. Thus this active structure of **1** and **II** forms **i3** as starting point of next four steps (black dash line of Figure 1b). Subsequently, Michael addition readily occurs via **ts-i3IV** in step 4 with activation energy of 12.0 kcal mol^{-1} exothermic by -12.4 kcal mol^{-1} delivering **IV**. The transition vector corresponds to the approaching of carbanion C4 to terminal alkene positive C3 (2.21 Å) (Figure S1c). Once single C4-C3 is bonded, C1-C2, C5-C6 becomes double one with negative charge remaining on O1 and positive charge focus on sulfoxonium ylide S in **IV**.

Then, a further proton shift happens via **ts-IVV** in step 5 with activation energy of 22.8 kcal mol^{-1} exothermic by -14.8 kcal mol^{-1} generating intermediate **V**. The transition vector reveals detailed atomic motion about proton H3 transfer from C4 to C2 (1.39, 1.48 Å) (Figure S1d). This causes a series of changes not only including exchange of hybrid form between C4 and C2 but the movement of double bond from C1=C2, C5=C6 to C1=O1, C4=C5 as well as negative charge shifting to C6 preparing for the next crucial ring closure.

Subsequently, the carbanion C6 attacks positive carbonyl C1 via **ts-VVI** in step 6 with activation energy of 26.3 kcal mol^{-1} yielding six-membered carbocycle intermediate **VI** exothermic by -26.3 kcal mol^{-1}. This process is illustrated according to the transition vector composed of nucleophilic addition of C6 to C1 and concerted stretching of carbonyl C1-O1 from double to single (1.72, 1.30 Å). In resultant **VI** involving C6-C1 single bond, both C6 and C1 are sp3 hybrid with negative charge returning to O1.

Finally, **VI** undergoes a second proton shift giving H4 from C6 to C7 of NHC via **ts-VIi4** in step 7 with a barrier of 18.3 kcal mol^{-1} exothermic by -37.9 kcal mol^{-1} affording **i4**. Demonstrated by the transition vector, this process is accomplished via noticable C6⋯H4⋯C7 proton transfer and shortened C1-C6 single bond (1.28, 1.58 Å) (Figure S1e). After the release of protonated positive carbene $NHCH^+$, the last intermediate **VII** is yielded as precursor of desired product 2-sulfenylidene-3-cyclohexen-1-one **3**. Since the relative energy of **3** is lower by -41.1 kcal mol^{-1} than **VII**, this isomerization is favored by thermodynamics. Comparatively, the ring closure in step 6 forming six-membered carbocycle is determined to be rate-limiting for NHC-facilitated [3 + 3] annulation. Although the barrier is somewhat high, it is capable to overcome under the reaction temperature 30°C in experiment.

4 Conclusions

The first theoretical investigation was provided by our DFT calculation on trazolum carbene-catalyzed [3 + 3] annulation of vinyl sulfoxonium ylide with enal. An active free carbene NHC is formed via deprotonation by base BF_4 with enhanced nucleophilicity. Then, NHC attacks positive carbonyl of unsaturated aldehyde with its negative carbon followed by proton transfer leading to Breslow intermediate **I**, which is easily transformed to α, β-unsaturated acylazolium intermediate **II** through dehydrogenation. Owing to spontaneous electron delocalization in vinyl sulfoxonium ylide, carbanion is available at α-position of ester when electron transfers through double bond. Subsequently, this active structure **III** and **II** undergo Michael addition forming **IV** linking two substrates. A further proton shift leads to intermediate **V**, from which the carbanion attacks positive carbonyl in next crucial ring closure yielding six-membered carbocycle intermediate **VI**. Finally, **VI** undergoes second proton shift generating intermediate **VII** as isomer of desired product 2-sulfenylidene-3-cyclohexen-1-one after the release of protonated positive NHC. The ring closure in step 6 forming six-membered carbocycle is determined to be rate-limiting for NHC-facilitated [3 + 3] annulation.

Electronic Supplementary Material

Supplementary data available: [Computation information and cartesian coordinates of stationary points; Calculated relative energies for the ZPE-corrected Gibbs free energies (ΔG_{gas}), and Gibbs free energies (ΔG_{sol}) for all species in solution phase at 303 K.]

Author contributions: Conceptualization, Nan Lu; Methodology, Nan Lu; Software, Nan Lu; Validation, Nan Lu; Formal Analysis, Nan Lu; Investigation, Nan Lu; Resources, Nan Lu; Data Curation, Nan Lu; Writing-Original Draft Preparation, Nan Lu; Writing-Review & Editing, Nan Lu; Visualization, Nan Lu; Supervision, Chengxia Miao; Project Administration, Chengxia Miao; Funding Acquisition, Chengxia Miao. All authors have read and agreed to the published version of the manuscript.

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Conflict of interest: The authors declare no conflict of interest.

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