Are vinylidenes possible intermediates in thermal rearrangements of substituted cyclopropenes? A theoretical study†

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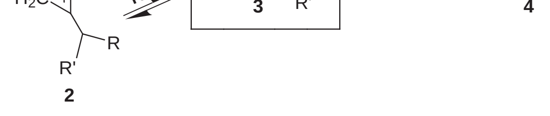
The thermally induced ring-opening reactions of substituted cyclopropenes to the corresponding vinylidenes have been investigated computationally; the alkyl-substituted singlet vinylidenes have been found to lie in potential wells of 7–11 kcal mol^{-1} (DFT calculations; 1 kcal = 4.184 kJ).

Vinylidenes, unsaturated carbenes of the type $R_2C{=}C{:}$, have received a great deal of attention during recent years. They have been postulated as reactive intermediates in organic reactions[1] and the simplest member of this family of compounds, $H_2C{=}C{:}$, was characterised by mass spectrometry[2] and negative ion photoelectron spectroscopy[3] of the corresponding vinylidene anion, $H_2C{=}C^{-\cdot}$. These experimental as well as several theoretical studies[4] demonstrate that the singlet vinylidene, $H_2C{=}C{:}$, lies in a very shallow potential energy well and readily rearranges to acetylene on the picosecond time scale.[3b] Thus, the observation of a vinylidene species in the mass spectrometric studies was attributed to a long-lived, excited triplet species.

Another experimental entry into the chemistry of vinylidenes was predicted by Yoshimine and co-workers[4b] in a theoretical study on the thermal ring opening of cyclopropene. Based upon their calculations, the authors proposed that cyclopropene may not only rearrange to propyne *via* a homolytic bond cleavage to vinyl carbene and subsequent hydrogen migration (as previously assumed[5]), but that methylvinylidene also constitutes an energetically viable intermediate. Recent experimental studies on the pyrolysis of substituted cyclopropenes[6] have furnished the first experimental evidence for the involvement of vinylidene carbenes as intermediates in the thermal rearrangements of highly strained cyclopropenes. Hopf *et al.*[6d] found that isomeric cyclopropenes can be thermally interconverted and proposed that the common intermediates in these reactions are vinylidenes. However, to the best of our knowledge the only singlet vinylidene that has been successfully trapped and characterized is difluorovinylidene, $F_2C{=}C{:}$, which was recently observed by matrix isolation and theoretical studies.[7]

These interesting experimental results have prompted us to investigate the possible intermediates in the thermal isomerizations (Scheme 1) of a number of substituted cyclopropenes [Structures **1**, **3** and **4**, where R = R′ = H (**1a**, **3a**, **4a**), R = H, R′ = CH_3 (**1b**–**4b**) and R = R′ = CH_3 (**1c**–**4c**)] by means of hybrid density-functional (B3LYP) and *ab initio* (CCSD(T)) methods.[8]



Scheme 1 Thermally induced formation of vinylidenes (**3**) from cyclopropenes (**1** and **2**) and alkyne formation (**4**) *via* alkyl migration.

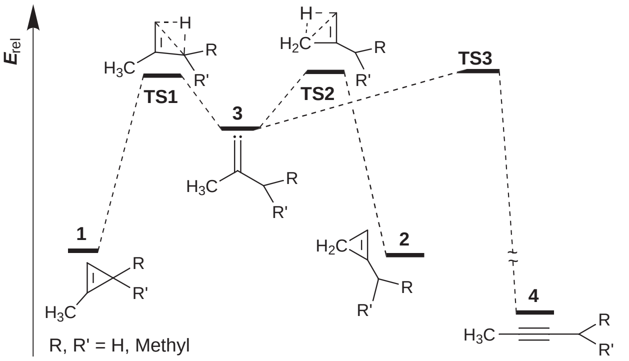


Fig. 1 Schematic singlet potential energy surface of alkyl-substituted cyclopropenes (**1**, **2**), vinylidenes (**3**), alkynes (**4**) and transition states (**TS1**,**TS2** and **TS3**).

A schematic potential energy surface for the important pathways leading to vinylidenes and the subsequent formation of alkynes upon alkyl migration is shown in Fig. 1. Formation of the corresponding vinylidenes occurs *via* a transition state involving the simultaneous breaking of a bond and a hydrogen shift, which for the reverse reaction is best described as an intramolecular insertion of the vinylidene carbene into the C–H bond (Fig. 2). Both types of substituted cyclopropenes, **1** and **2**, thus give rise to identical vinylidenes.

Our theoretical results (Table 1) indicate that the alkyl-substituted vinylidenes **3a**–**c** are all intermediates in the ring-opening reactions of alkylcyclopropenes (**1a**–**c** and **2a**–**c**). In the case of dimethylvinylidene **3a**, the symmetry-allowed 1,2-migration of a methyl group (**TS3a**) (with retention of its configuration), lies 11.1 kcal mol^{-1} above the vinylidene, while the transition state for the cyclization reaction (**TS1a**) giving

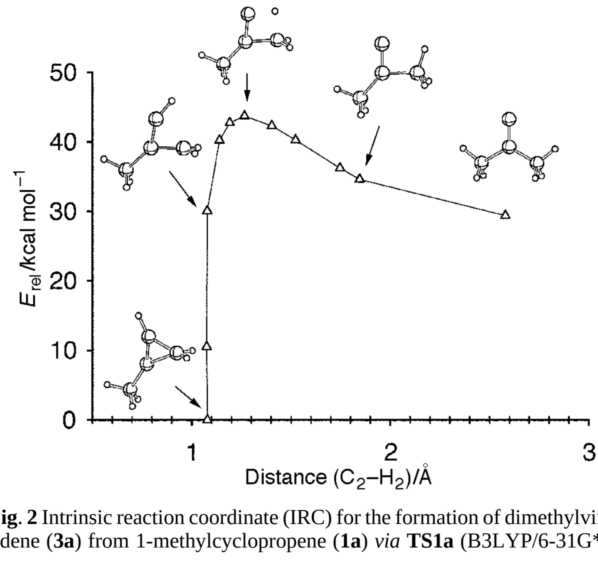


Fig. 2 Intrinsic reaction coordinate (IRC) for the formation of dimethylvinylidene (**3a**) from 1-methylcyclopropene (**1a**) *via* **TS1a** (B3LYP/6-31G*).

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† Details of the theoretical study are available from the RSC web page, see http://www.rsc.org/suppdata/cc/1998/2761

Table 1 Relative energies [in kcal mol^{-1}; B3LYP/6-311+G(2d,p) and CCSD(T)/6-31G(d) level of theory] of alkylvinylidenes (**3a**–**c**) with respect to their cyclopropene precursors (**1a**–**c** and **2b**,**c**), their connecting transition states (**TS1a**–**c** and **TS2b**,**c**) and the transition states for the alkyl migrations leading to alkynes (**TS3a**–**c**)

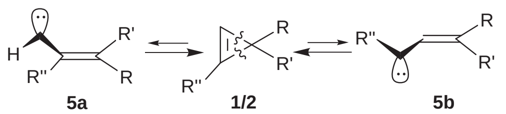
	1a		**3a**	**TS1a**		**TS3a**	
B3LYP	−25.9		0.0	12.5		11.1	
CCSD(T)	−29.2		0.0	15.0		13.0	
	1b	**2b**	**3b**	**TS1b**	**TS2b**	**TS3b-Me**	**TS3b-Et**
B3LYP	−28.4	−26.0	0.0	9.4	12.5	11.3	9.6
CCSD(T)	−29.1	−26.6	0.0	12.3	15.4	13.8	12.0
	1c	**2c**	**3c**	**TS1c**	**TS2c**	**TS3c-Me**	**TS3c-Pr^i**
B3LYP	−30.4	−26.3	0.0	7.3	12.5	10.9	9.7
CCSD(T)	−31.3	−27.1	0.0	9.8	15.1	13.1	11.1

rise to the 1-methylcyclopropene is 12.5 kcal mol^{-1} higher in energy (all B3LYP results). The lowest exit channel for ethylmethylvinylidene **3b** lies 9.4 kcal mol^{-1} above the vinylidene and the lowest isomerization pathway of methylisopropylvinylidene **3c** requires 7.3 kcal mol^{-1}. Thus all three investigated vinylidenes correspond to minima on their energy surfaces, substantiating the proposal that these reactive species are indeed common intermediates in the isomerization of cyclopropenes.[6d]

Overall, the good correlation of *ab initio* and density-functional results lends confidence to the quality of our thermochemical predictions. Further support for the reliability of the B3LYP data comes from comparison of these results with experimentally determined activation energies. The average deviation of the calculated barrier heights from the experimentally obtained values for the cyclopropene-to-vinylidene transition states **TS1b**–**c** and **TS2b**–**c**[6d,9] is found to be 2.4 kcal mol^{-1} at the B3LYP/6-31G* level and 0.1 kcal mol^{-1} at the B3LYP/6-311+G(2d,p) level. The results of the B3LYP/6-311+G(2d,p) calculations lie within the experimental error bars. This means that, given an average experimental error of 0.4 kcal mol^{-1},[6d,9] the relative error in the B3LYP/6-311+G(2d,p) must be smaller than 0.5 kcal mol^{-1}. The deviation of the *ab initio* results [CCSD(T)/6-31G*] from the experimental values is about 3.5 kcal mol^{-1}. Similar excellent agreement between activation energies obtained with the B3LYP method and experimental values has recently been noted for [3,3]-sigmatropic rearrangements.[10]

The experimentally observed formation of alkynes from vinylidenes involves a rate-affecting alkyl migration. With unsymmetrically substituted vinylidenes (**3b**–**c**) either a methyl (**TS3b-Me** and **TS3c-Me**) or an alkyl (**TS3b-Et** and **TS3c-Pr^i**) migration can occur. The calculations show that alkyl migration **TS3b-Et** and **TS3c-Pr^i** is preferred over the methyl shift (**TS3b-Me** and **TS3c-Me**), although the differences in the activation energies for these processes are small [ΔE_a(B3LYP) = 1.7 and 1.2 kcal mol^{-1}, respectively]. This agrees with experimental results from the pyrolysis of ^{13}C-labelled cyclopropenes **1b** and **1c**,[6e] where the ratio of **TS3b-Et** and **TS3b-Me** is found to be 3:1 and of **TS3c-Pr^i** and **TS3c-Me** is 1.4:1. The reasons for these small energetic differences, although difficult to pinpoint, most likely result from a combination of hyperconjugation, which stabilizes the three-centre two-electron bonds in these transition states, and steric effects, leading to a destabilization of the TS for the migration of higher substituted alkyl groups.

We have also investigated the homolytic bond-cleavage that gives rise to vinyl carbenes (**5a** and **5b**) (Scheme 2). Although this reaction is in some cases energetically preferred over vinylidene formation, it leads to an energetic dead end.[11] Subsequent hydrogen shifts of these vinyl carbenes that would lead to the corresponding allenes or dienes are all found to lie higher in energy than the corresponding vinylidene pathways and the transition states for the direct formation of alkynes from these conjugated carbenes all lie approximately 20 kcal mol^{-1} above the transition states for the alkyne formation from the corresponding vinylidenes.



Scheme 2

These findings agree well with the experimentally observed product distributions in the pyrolysis of various cyclopropenes where the main decomposition channel was found to lead to alkynes.[6a–d,9]

The theoretical results support the proposed mechanistic pathway for the thermal ring-opening of highly strained cyclopropenes, and demonstrate that alkyl-substituted singlet vinylidenes correspond to intermediates that lie in potential energy wells deep enough to allow their characterization by spectroscopic methods. Experiments aimed at further characterisation of these interesting sub-valent carbon species thus seem promising. In contrast to previous assumptions, our theoretical investigations indicate that vinyl carbenes are not intermediates in the formation of alkynes from cyclopropenes.

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