# An *Ab Initio* Study of the Mechanism of the α-Alkynone Cyclization

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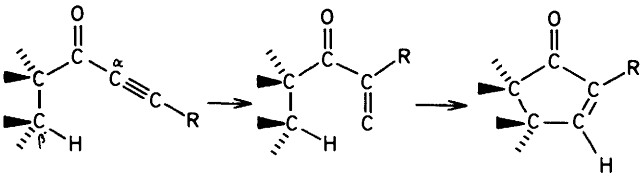
*Ab initio* calculations at different levels of accuracy (MP4SDQ/6-31G and HF/6-31G*) on two model isomerizations but-2-ynone→cyclobut-2-enone and pent-2-ynone→cyclopent-2-enone, suggest that the vinylidene can be regarded as a plausible intermediate during the α-alkynone cyclization. Its conversion into the cyclic product (rather than its formation) constitutes the rate-determining step for the overall reaction.

On gas-phase pyrolysis, ethyl ethynyl ketones (**1**) isomerize to cyclopent-2-enones (**2**). This elegant transformation is called the 'α-alkynone cyclization'[1] in which two intramolecular processes occur: the 1,2-shift of one of the substituents at the C≡C triple bond and the formation of a new C–C single bond. This conversion offers a useful route for the preparation of a number of cyclic compounds containing a cyclopent-2-enone moiety. In their pioneer work, Karpf and Dreiding[1] postulated that the vinylidene (**3**) is a reaction intermediate which subsequently undergoes an insertion into the $C_{\beta}$–H bond. An obvious question arising from such a mechanism is the identity of the rate-determining step. In a subsequent paper, Kaneti *et al.*[2] attempted to provide an answer to this question on the basis of *ab initio* calculations (at the HF/DZP and SCEP/DZ levels). Arguing that the carbene insertion into a C–H bond [(**3**)→(**2**)] occurs almost without activation energy, they have considered the 1,2-migration (**1**)→(**3**) as the most likely slow step of the cyclization. These authors only studied the acetylene–vinylidene interconversion pathways of three model α-alkynones (propynal, but-2-ynal, and butynone). Accordingly, the 1,2-hydrogen or alkyl migration competes favourably with the acyl shift during the rearrangement (**1**)→(**3**).

Nevertheless, recent theoretical work on unsaturated carbenes (>C=C:)[3] and their close chemical parents such as carbon monoxide (O=C:) and isocyanides (R–N≡C:)[4] indicate that the addition or insertion reactions of these species require much higher activation energies than those involving ordinary carbenes (>C:). In other words, the mechanism of the α-alkynone cyclization remains to be determined. Hence we now report the results of *ab initio* calculations on the cyclization of the but-2-ynone ($CH_3$–CO–C≡C–H) and pent-2-ynone ($C_2H_5$–CO–C≡C–H) molecules to cyclobut-2-enone and cyclopent-2-enone, respectively. The former pathway provides us with a comparison with earlier results[1] whereas the latter constitutes a proper model for the transformation being studied. For each molecule, both the hydrogen and formyl migration connecting it to the vinylidene intermediate and the concerted conversion of the latter into the cyclic product are considered.

## Calculations

The molecular geometries of stationary points on the reaction pathways have been optimized by the force method with analytical gradient and numerical second derivatives (by gradient finite difference) as implemented in the MONSTERGUASS HF program[5] by using the split-valence 3-21G basis set.[6] In order to estimate the relative energies between stationary points, we have recalculated single-point energies at the Hartree–Fock (with the polarized 6-31G* and 6-31G** basis[7]) and the Møller–Plesset perturbation theory to second, third, and fourth order[8] levels (with the 6-31G basis) making use of their 3-21G-optimized geometries. The latter were calculated employing the Gaussian-82 program.[9] Finally, the molecular electrostatic potentials were computed by means of a modified version of the DENPOT program.[10]



(**1**) (**3**) (**2**)

## Results and Discussion

(A) *The But-2-ynal–Cyclobut-2-enone Cyclization.*—The geometries of the six relevant stationary points determined with the 3-21G basis set are displayed in Figure 1. They include three minima, the reactant (**4**), the intermediate (**7**) (acetylvinylidene) and the cyclic product (**9**), and three transition states, the hydrogen-shift (**5**), the acetyl-shift (**6**) [both connecting (**4**) to (**7**)], and the hydrogen-shift (**8**) [converting (**7**) into (**9**)]. Their total and relative energies calculated at different levels of accuracy are recorded in Table 1.

The 3-21G-geometries of structures (**4**)—(**7**) are found to be similar to the previously reported results with a double-zeta basis set and have been discussed in detail.[2] We note that the hydrogen-shift occurs in the molecular plane whereas the acetyl-shift involves a carbon-bridged structure with two nearly perpendicular planes. As expected, cyclobut-2-enone is calculated to have a planar ring. As far as we know, there are no experimental data on its molecular structure. By comparing the geometric parameters between (**7**) and the transition state (**8**), it may be noted that the deformation within the four-membered ring is substantial. Both the C(4)C(1)C(2) and C(1)C(2)C(3) bond angles become *ca.* 20° smaller in the transition state, implying a significant shortening (0.9 Å) of the C(3)C(4) distance. Of particular interest is the position of the migrating hydrogen H(1). The bond distances C(4)H(1) = 1.574 Å and C(3)H(1) = 1.146 Å clearly indicate that H(1) is already transferred to the mono-co-ordinated C(3) in the transition state (**8**). The ring closure can be expected to occur just *after this transition state* implying that both the 1,4-hydrogen transfer and cyclization are quite asynchronous.

Table 1 shows that at all levels of theory, the overall reaction (**4**)→(**9**) is mildly exothermic. Although the polarization *d*-functions slightly stabilize the cyclic product, inclusion of *p*-functions on hydrogen atoms appears to be not crucial. On the other hand, electron correlation energies only slightly alter the energy difference between (**4**) and (**9**). In contrast, the latter appreciably increases the relative energy between (**4**) and the

**Table 1.** Total (a.u.) and relative (kcal mol$^{-1}$, in parentheses) energies for six stationary points of the but-2-ynone–cyclobut-2-enone cyclization

| Method[a] | (4) | (5) | (6) | (7) | (8) | (9) |
|---|---|---|---|---|---|---|
| HF/3-21G | −227.311 65<br>(0.0) | −227.214 15<br>(61.2) | −227.201 85<br>(68.9) | −227.249 20<br>(39.2) | −227.166 10<br>(91.3) | −227.312 78<br>(−0.7) |
| HF/6-31G | −228.491 72<br>(0.0) | −228.397 20<br>(59.3) | −228.376 48<br>(72.3) | −228.431 86<br>(37.6) | −228.345 09<br>(92.0) | −228.493 57<br>(−1.2) |
| HF/6-31G* | −228.587 89<br>(0.0) | −228.511 92<br>(47.6) | −228.491 60<br>(60.4) | −228.533 02<br>(34.4) | −228.456 17<br>(82.6) | −228.602 35<br>(−9.1) |
| HF/6-31G** | −228.594 85<br>(0.0) | −228.521 58<br>(45.9) | −228.498 64<br>(60.4) | −228.539 91<br>(34.5) | −228.466 49<br>(80.5) | −228.609 41<br>(−9.1) |
| MP2/6-31G | −228.970 36<br>(0.0) | −228.869 24<br>(63.4) | −228.865 86<br>(65.6) | −228.883 67<br>(54.4) | −228.841 43<br>(80.8) | −228.964 41<br>(−3.7) |
| MP3/6-31G | −228.974 63<br>(0.0) | −228.875 58<br>(62.1) | −228.867 69<br>(64.4) | −228.898 80<br>(44.9) | −228.847 70<br>(77.0) | −228.975 48<br>(−3.2) |
| MP4SDQ/6-31G | −228.994 55<br>(0.0) | −228.896 80<br>(61.3) | −228.889 56<br>(65.9) | −228.918 80<br>(47.5) | −228.868 41<br>(79.1) | −228.993 14<br>(0.9) |
| Estimated[b] | (0.0) | (49.6) | (54.0) | (44.3) | (69.7) | (−7.0) |

[a] Using 3-21G geometries given in Figure 1. [b] Estimated values employing the additivity relationship, see text.

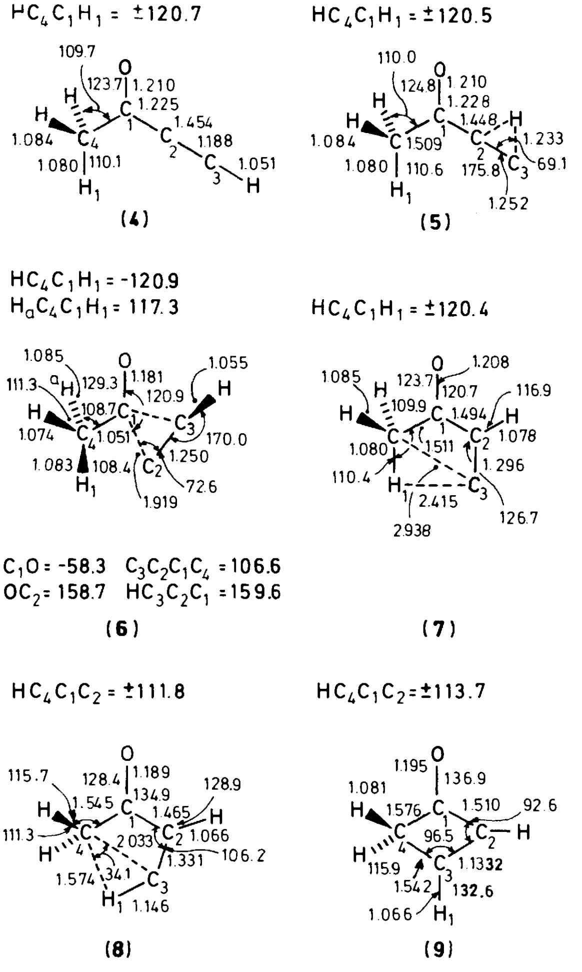


**Figure 1.** Optimized geometries (HF/3-21G) of six stationary points relevant to the but-2-ynone→cyclobut-2-enone cyclization. Bond lengths in Å and bond angles in degrees

intermediate (**7**) (≥ 10 kcal mol$^{-1}$). With regard to the transition states, the situation is also different in going from one to another: (a) in (**5**), the polarization functions decrease the energy barrier (~ 12 kcal mol$^{-1}$) while the correlation energies slightly increase it (2 kcal mol$^{-1}$); (b) in (**6**), both corrections lower the barrier but the former reduces it considerably; and finally (c) in (**8**), both effects lower it by a similar amount of energy.

As an estimation taking both corrections into account, the estimated values given in Table 1 were determined from the additivity relationship[11,12a] $\Delta E$(estimated) = $\Delta E$(MP4SDQ/6-31G) + $\Delta E$(HF/6-31G*) − $\Delta E$(HF/6-31G). Accordingly, the best estimate predicts that within the three local minima considered, the cyclobut-2-enone (**9**) is the most stable and lies at 7 kcal mol$^{-1}$ below the but-2-ynone (**4**). The vinylidene (**7**) is at 44.3 kcal mol$^{-1}$ higher in energy than (**4**). The latter is somewhat smaller than the value of 50 kcal mol$^{-1}$ obtained by Kaneti *et al.*[2] from a similar estimation employing the SCEP/DZ and HF/DZP wavefunctions. These authors also reported that the 1,2-hydrogen shift *via* (**5**) requires less activation energy (54.9 kcal mol$^{-1}$) than the acetyl-shift *via* (**6**) (57.9 kcal mol$^{-1}$). Although the present values of 49.6 and 54.0 kcal mol$^{-1}$ are again found to be smaller, they concur with this. In addition, the transition structure (**8**), allowing an asynchronous movement of the 1,4-hydrogen shift and ring closure, is calculated to be at 69.7 kcal mol$^{-1}$ above (**4**) (Table 1). Accordingly, the cyclization of (**7**) to the cyclic product (**9**) requires a larger energy barrier (25.4 kcal mol$^{-1}$) than the back-conversion (**7**)→(**5**)→(**4**) (5.3 kcal mol$^{-1}$). In other words, the present calculations suggest that the second step (**7**)→(**8**)→(**9**) is the likely rate-determining one of the entire formation (**4**)→(**9**). The reaction is in a formal sense Woodward–Hofmann forbidden and multireference description may be necessary to define more precisely the energetics and geometry.[12b]

(B) *The Pent-2-ynone→Cyclopent-2-enone Cyclization.*—The 3-21G-optimized geometries of six relevant stationary points, namely: pent-2-ynone (**10**), hydrogen-shift transition state (**11**), propanoyl-shift transition state (**12**), propanoyl-vinylidene (**13**), hydrogen-shift transition state (**14**), and cyclopent-2-enone (**15**) are shown in Figure 2. The energy data are summarized in Table 2. Except for the $CH_2$ group, geometric parameters of the structures (**10**)—(**13**) are close to those of (**4**)—(**7**), respectively (see Figure 1). For instance, the transition state (**11**) possesses a hydrogen-bridged structure in the molecular plane whereas (**12**) exhibits a carbon-bridged structure with two almost perpendicular planes. In particular, both the C(1)C(3) (2.897 Å) and C(3)H(1) (2.005 Å) distances in the vinylidene (**13**) are shorter than the corresponding C(3)C(4) (2.938 Å) and C(3)H(1) (2.415 Å) in (**7**).

A previous microwave study[13] of cyclopent-2-enone (**15**)

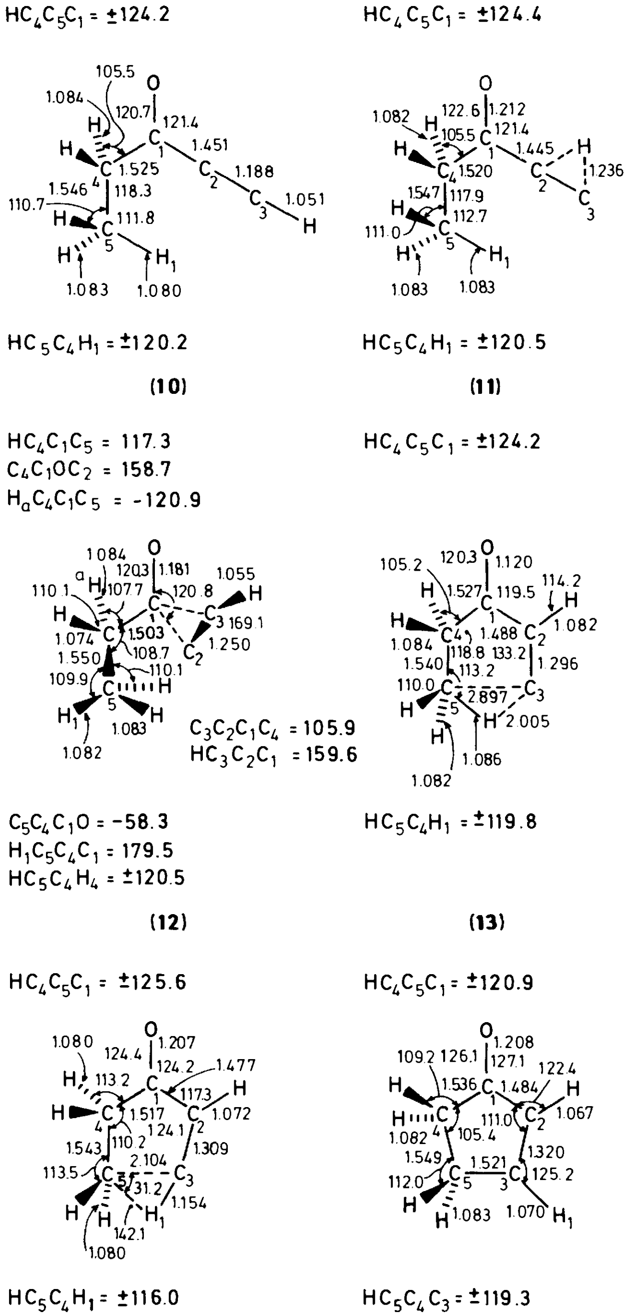


**Figure 2.** Optimized geometries (HF/3-21G) of six stationary points relevant to the pent-2-ynone→cyclopent-2-enone cyclization. Bond lengths in Å and bond angles in degrees

indicated that the heavy-atom skeleton of the molecule is planar. The present calculations support this analysis. Table 3 lists the calculated rotational constants and dipole moments of (**15**) along with those of cyclobut-2-enone (**9**). The experimental values of (**15**) are also given for comparison.

With respect to the corresponding angles in (**13**), the three bond angles C(5)C(4)C(1), C(4)C(1)C(2), and C(1)C(2)C(3) in (**14**) are reduced by 8—9°. Except for a shorter C(5)H(1) distance (1.421 Å) the hydrogen-bridged C(3)H(1)C(5) moiety in (**14**) is quite similar to that in the above transition structure (**8**). Like the latter, H(1) is also shifted to the terminal C(3).

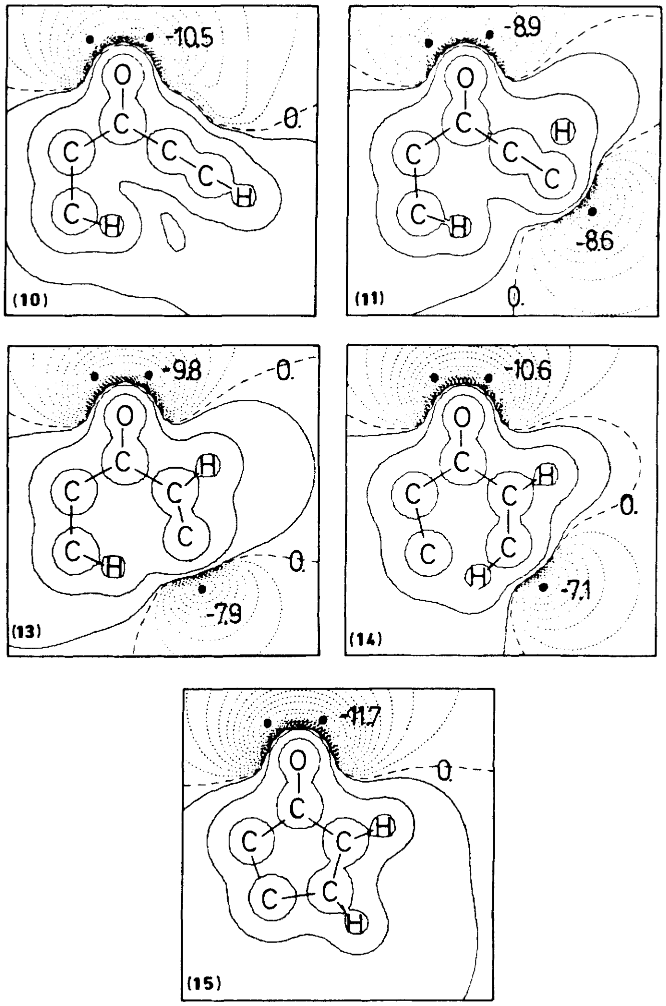


**Figure 3.** Molecular electrostatic potential maps (HF/6-31G) of (**10**), (**11**), (**13**)—(**15**). Potentials given in $10^{-2}$ a.u. Isocontour values are: 100, 50, 10, 0, −1, −2, −3, −4, −5, −6, −7, −8, −9, and −10

With regard to the energy difference between the species considered, the trend of corrections made by both the polarization and correlation effects is similar to that observed in the previous case. In the following discussion we employ the values estimated from the additivity relationship given in Table 2.

The overall cyclization (**10**)→(**15**) becomes more exothermic with a heat of reaction of −38.4 kcal mol$^{-1}$. It seems that the intermediate vinylidene (**13**) is slightly stabilized (1.4 kcal mol$^{-1}$) by replacing the methyl group by ethyl. Such a stabilization marginally lowers the energy barrier of the 1,2-hydrogen shift *via* (**11**) [49.1 against 49.6 kcal mol$^{-1}$ *via* (**5**)]. The latter remains the favoured process over the propanoyl-shift in converting (**10**) into (**13**). In contrast, the 1,5-hydrogen-shift involving the transition state (**14**) becomes a rather easier process (energy barrier being 56.5 kcal mol$^{-1}$).

Nevertheless, the transition state (**14**) is still higher in energy than (**11**). An energy difference of 7.4 kcal mol$^{-1}$ between them appears to be large enough so that the step (**13**)→(**14**)→(**15**) is also the rate-limiting one of the α-alkynone cyclization. Thus, the formation of the intermediate (**13**) can take place by either a hydrogen-shift or a propanoyl-shift.

Figure 3 displays the molecular electrostatic potential maps of five stationary points (**10**), (**11**), and (**13**)—(**15**) (calculated at the HF/6-31G level). The atomic net charges are summarized in

**Table 2.** Total (a.u.) and relative (kcal mol$^{-1}$, in parentheses) energies for six stationary points of the pentynone–cyclopentenone cyclization

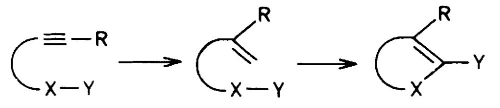
| Method[a] | **(10)** | **(11)** | **(12)** | **(13)** | **(14)** | **(15)** |
|---|---|---|---|---|---|---|
| HF/3-21G | −266.122 66<br>(0.0) | −266.026 57<br>(60.3) | −266.023 52<br>(62.2) | −266.060 93<br>(38.7) | −266.005 72<br>(73.4) | −266.187 19<br>(−40.5) |
| HF/6-31G | −267.502 50<br>(0.0) | −267.409 22<br>(58.5) | −267.295 95<br>(66.9) | −267.442 62<br>(37.6) | −267.391 60<br>(69.6) | −267.568 30<br>(−41.3) |
| HF/6-31G* | −267.614 28<br>(0.0) | −267.539 85<br>(46.7) | −267.523 27<br>(57.1) | −267.558 99<br>(34.7) | −267.509 90<br>(65.5) | −267.684 46<br>(−44.0) |
| MP2/6-31G | −268.072 68<br>(0.0) | −267.972 11<br>(63.1) | −267.976 20<br>(60.5) | −267.989 39<br>(52.3) | −267.973 86<br>(62.0) | −268.125 44<br>(−33.1) |
| MP3/6-31G | −268.085 05<br>(0.0) | −267.986 69<br>(61.7) | −267.986 05<br>(62.1) | −268.012 08<br>(45.8) | −267.988 93<br>(60.3) | −268.145 28<br>(−37.8) |
| MP4SDQ/6-31G | −268.107 60<br>(0.0) | −268.010 50<br>(60.9) | −268.010 37<br>(61.0) | −268.034 60<br>(45.8) | −268.011 01<br>(60.6) | −268.164 44<br>(−350.7) |
| Estimated[b] | (0.0) | (49.1) | (51.2) | (42.9) | (56.5) | (−38.4) |

[a] Using 3-21G geometries given in Figure 1. [b] Estimated values employing the additivity relationship, see text.

**Table 3.** Rotational constants and dipole moments of cyclobut-2-enone (**9**) and cyclopent-2-enone (**15**)

| Parameters[a] | Cyclopent-2-enone (**15**)[b] | Cyclobut-2-enone (**9**) |
|---|---|---|
| A (MHz) | 7 432.7 (7 410.0) | 12 651.5 |
| B( MHz) | 3 590.0 (3 586.4) | 5 248.8 |
| C (MHz) | 2 494.8 (2 492.6) | 3 798.8 |
| μ (D)[c] | 4.12 (3.64) | 3.79 |

[a] With the 3-21G-geometries given in Figures 1 and 2. [b] Experimental values given in parentheses are taken from ref. 13. [c] At the HF/6-31G* level.



**(16)** **(17)** **(18)**

**Table 4.** Net charges and dipole moments of five stationary points along the pent-2-ynone→cyclopent-2-enone cyclization pathway (HF/6-31G)

| | **(10)** | **(11)** | **(13)** | **(14)** | **(15)** |
|---|---|---|---|---|---|
| Net charges | | | | | |
| O | −0.49 | −0.51 | −0.53 | −0.54 | −0.55 |
| C(1) | 0.61 | 0.57 | 0.51 | 0.49 | 0.56 |
| C(2) | −0.10 | −0.28 | −0.53 | −0.39 | −0.20 |
| C(3) | −0.46 | −0.11 | 0.18 | −0.07 | −0.15 |
| C(4) | −0.40 | −0.40 | −0.39 | −0.39 | −0.40 |
| C(5) | −0.47 | −0.48 | −0.49 | −0.55 | −0.36 |
| H(1) | 0.18 | 0.20 | 0.15 | 0.32 | 0.21 |
| H[C(3)] | 0.37 | 0.23 | 0.29 | 0.25 | 0.23 |
| Dipole moments | | | | | |
| μ (D) | 3.70 | 2.50 | 2.01 | 4.14 | 4.40 |

Table 4. Some interesting features of the charge redistribution along the cyclization pathway can be noted. (a) Except for C(3) which becomes positively charged in the vinylidene (**13**), the signs of the atomic charges in all structures remains unchanged. The vinylidene (**13**) has the smallest dipole moment (Table 4). (b) The lone pair of the carbenic C(3) is virtually formed at the transition state (**11**). Like the vinylidene–acetylene rearrangement,[14] the HC(3) migrates as a proton in the earlier stage of the process. Table 4 indicates that there is however a small drop in its positive charge, probably due to a transfer from C(3). (c) As H(1) migrates, the negative potential region relevant to the C(3) lone pair in the transition state (**14**) is pushed slightly forward into the region of the forming C(3)H(1) bond without changing its minimum value. This suggests that when the transition state (**14**) is passed on the reaction co-ordinate, the C(3)-lone pair will capture the migrating hydrogen H(1), leading to the formation of the new $\sigma(C_3H_1)$ bond of the cyclic product (**15**). As a consequence, the $\sigma$[C(5)H(1)] electron pair will form the new $\sigma$[C(3)–C(5)] bond, thus achieving the cyclization process.

In summary, the present *ab initio* calculations on the two model isomerizations, but-2-ynone→cyclobut-2-enone and pent-2-ynone→cyclopent-2-enone, suggest that the vinylidene can be regarded as a plausible intermediate during the thermal α-alkynone cyclization, and its conversion into the cyclic product constitutes the rate-determining step of the overall transformation.

This mechanism could also be extended to a wide variety of gas-phase thermal unimolecular rearrangements of acetylenes (**16**) to cyclic compounds (**18**) *via* the vinylidene intermediates (**17**).[15,16]

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