PERKIN 2

# 1,3-Dipolar additions involving allenes: A density functional study of concerted and stepwise mechanisms†

**Kaliaperumal Kavitha and Ponnambalam Venuvanalingam** *

*Department of Chemistry, Bharathidasan University, Tiruchirappalli, 620 024, India.*
*E-mail: venuvanalingam@yahoo.com*

***Received (in Cambridge, UK) 5th July 2002, Accepted 26th September 2002***
***First published as an Advance Article on the web 25th October 2002***

Structures and energetics of reactants, transition structures, diradical intermediates and products of the 1,3-dipolar cycloadditions of allene with diazomethane, nitrile oxide and nitrone, have been investigated using DFT calculations at B3LYP/6-31G(d) level and the entire reaction surface has been explored. Two pathways are open for these reactions leading to two regiochemical products and in each way, the reaction can proceed in concerted or stepwise manner. In the stepwise process, there are two modes of attack, one leading to an allylic intermediate and the other an anti intermediate. A thorough search and analysis of these reaction paths show that stepwise modes are preferred over concerted modes, and regio 1 reaction prefers a stepwise path that involves a *gauche* intermediate whereas regio 2 reaction follows a stepwise path where an allylic intermediate is formed. Mainly the heteroatomic influence on the stability of diradical intermediates and other species in the reaction path and the cumulenic strain on allene determine the mechanism. Above factors also explain greater stability of allylic TS of regio 2 reaction compared to anti TS of regio 1 reaction, and this in turn explains the observed regioselectivity of the allene–diazomethane reaction. Computed deformation energies and bond orders establish that the favoured transition states are reactant-like and hence involve lower activation energies.

## Introduction

The femtosecond experiments of Zewail and co-workers have proved the existance of both concerted and stepwise pathways for the Diels–Alder reaction and have also settled the mechanism of this reaction once and for all.[1] They have followed the dynamics of the retro Diels–Alder reaction of norbornene[1] and confirmed that the concerted transition state is stabilized by 4.1 kcal mol$^{-1}$ over the diradical intermediate. The issue of concerted *vs.* stepwise mechanism for Diels–Alder reaction has been the topic of numerous studies, both theoretical and experimental[2–6] and mostly the concerted mechanism has been found to be favoured. The issue of concertedness is a pertinent question in allene reactions in view of the cumulenic strain in the system. Allene as a dienophile or dipolarophile presents a different case. Though a lot of experimental work has been done on the Diels–Alder chemistry of allenes, the mechanism of these reactions have been explored only recently.[3,7,8] We have employed allenes as dienophiles and dienes[7] and showed computationally that the concerted transition structures in the reaction path are highly asynchronous. Rastelli and co-workers have also reported,[8] similar observations using an *ab initio* theory at Hartree–Fock level. Recently Houk and co-workers[9] have, in an experimental and computational study, showed that allenes and strained allenes reacted with furan and 1,3-butadiene in a stepwise pathway and concerted transition structures were extremely asynchronous. Comparing the reactions of 1,3-butadiene with ethylene and allene, they have showed that allene reaction was more exothermic than ethylene reaction but the activation energy for the concerted process was higher by 5 kcal mol$^{-1}$ for the allene reaction than the one for ethylene. This has led to the mechanistic crossover in allene reaction. They have further observed that, in the stepwise path, there were two attacking modes and the one leading to a diallylic intermediate was lying well below the concerted transition state. They have further reported that the transition states leading to the diallylic intermediate have not been traced and investigations at CASSCF level may be necessary to track them accurately. These interesting observations have stimulated our interest to look at the mechanism of 1,3-dipolar reaction of allene in a detailed way. In this paper we investigate computationally at the DFT level, the mechanism of 1,3-dipolar reaction of simple allene with three dipoles, namely nitrone, diazomethane and nitrile oxide. More importantly, the area in the potential energy surface that is close to the diradical intermediate will be scanned to locate the transition states preceeding and succeeding the intermediate. This may reveal the role of cumulenic strain of allene as well as the influence of the hetero atom of the dipoles on the kinetic and thermodynamic control of the reaction.

The above dipoles are known to undergo 1,3-dipolar reactions with ethylene and are widely investigated.[10–13] Much similar to 1,3-butadiene–ethylene reaction, they follow the concerted mechanism. Their reactions with allene have rarely been investigated and earlier studies report[8,14,15] only concerted transition states. We therefore investigate thoroughly the reaction surface of the above for all possible pathways with a view to establish the mechanism.

## Computational details

Density functional theory calculations have been performed using Gaussian 94W Rev.B.3. and Gaussian 98W Rev.A.9.[16] In DFT calculations 6-31G(d) basis set has been used throughout and B3LYP functional—Becke's three parameter non-local exchange functional with the non-local correlation functional of Lee, Yang and Parr—has been used for closed shell species and concerted transition structures. For open shell systems, *i.e.* transition structures and reaction intermediates in the stepwise pathways, UB3LYP has been used. These models have been reported to give very reliable energies and structures in general

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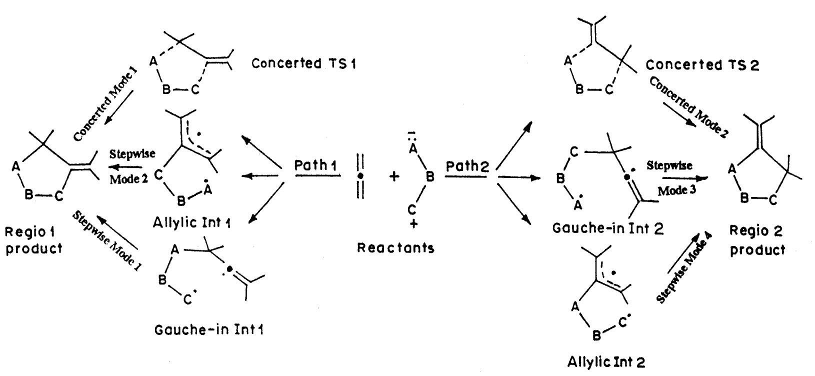
† Electronic supplementary information (ESI) available: Cartesian co-ordinates of all the structures with their computed total energies. See http://www.rsc.org/suppdata/p2/b2/b206470g

DOI: 10.1039/b206470g



**Scheme 1** Possible reaction pathways for the 1,3-dipolar cycloadditions of allene with dipoles, diazomethane, nitrile oxide and nitrone.

and for pericyclic reactions[17–22] in particular. Stationary points located have been characterized by computing the vibrational frequencies; reactants, products and intermediates had all real frequencies and the transition states had a single imaginary frequency. Transition states have been further confirmed by examining their transition vectors and by animating the imaginary frequency in MOLDEN. Recently Rastelli and co-workers[8] have demonstrated that B3LYP also gives reliable results for 1,3-dipolar reactions. Schlegel[23] observed that B3LYP potential energy surfaces had the correct shape compared to full CI surfaces for bond dissociation. Further Schlegel[24a] and Cremer[24b] have concluded that the use of spin projection procedure to remove spin contamination from UB3LYP wave function of open shell species is not satisfactory and therefore we have not performed any spin projected calculations. Rastelli and co-workers[14] have recently confirmed that uncorrected UB3LYP values adequately describe the stepwise process. Bond orders were calculated as the Wiberg indices[25] derived from the natural atomic orbital analysis and from them bond formation index $\mathrm{BF}_i$or bond cleavage index $\mathrm{BC}_j$ have been calculated as described below:

$$\mathrm{BF}_i \text{ or } \mathrm{BC}_j = \frac{\mathrm{BO}_i^{\mathrm{TS}} - \mathrm{BO}_i^{\mathrm{R}}}{\mathrm{BO}_i^{\mathrm{P}} - \mathrm{BO}_i^{\mathrm{R}}} \times 100$$

forming bonds

$$\mathrm{BF}_{\mathrm{Ave}} = 1/n_i \sum_i \mathrm{BF}_i$$

cleaving bonds

$$\mathrm{BC}_{\mathrm{Ave}} = 1/n_j \sum_j \mathrm{BC}_j$$

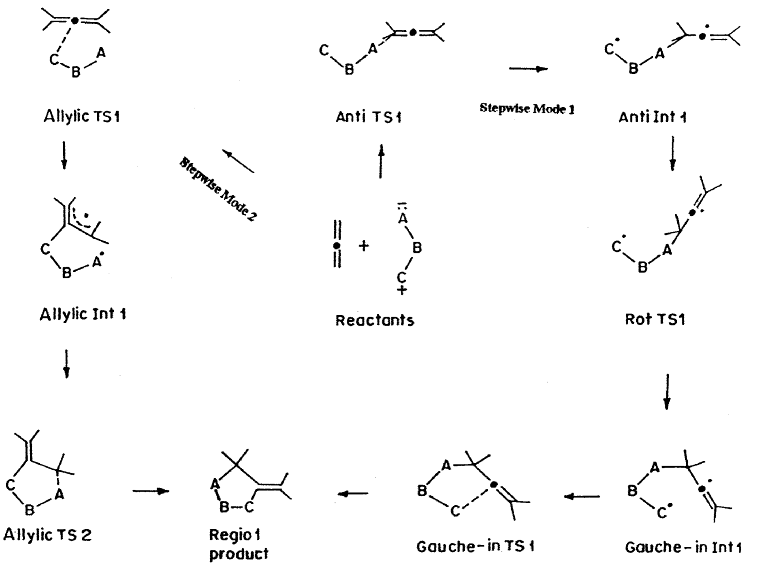
Bond formation–cleavage average ($\mathrm{BFC}_{\mathrm{Ave}}$) values have been calculated as:

$$\mathrm{BFC}_{\mathrm{Ave}} = \tfrac{1}{2}\,(\mathrm{BF}_{\mathrm{Ave}} + \mathrm{BC}_{\mathrm{Ave}}).$$

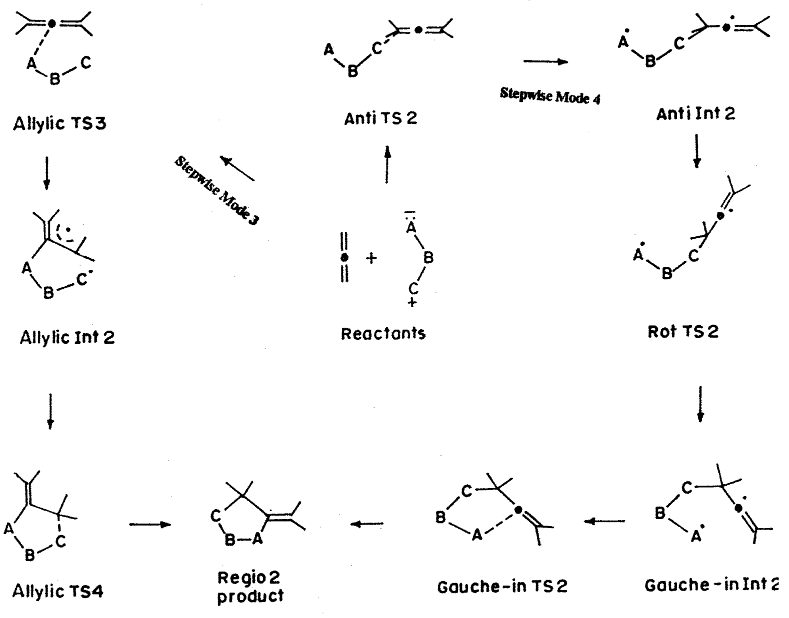
Deformation energy of a reactant has been calculated as the difference between the energy of the reactant in the transition state calculated as the single point energy of the reactant at the geometry of that fragment in the transition state and the energy of that system in its equilibrium state.[7]

## Results and discussion

Allene undergoes 1,3-dipolar cycloaddition with dipoles diazomethane, nitrile oxide and nitrone to form two regioselective products and there are several attacking modes possible for the reaction. The reaction can be normal or reverse with reference to the adduct, concerted or stepwise with reference to the mechanism and can involve either allylic or anti diradical intermediate in the stepwise reaction depending on the site of attack. In regio 1 reaction, the stepwise mode that involves terminal carbon C-1 attack on allene and leading to anti intermediate will be referred to as stepwise mode 1 and the one involving central carbon (C-2) attack on allene and leading to allylic intermediate as stepwise mode 2. Similarly, in the regio 2 reaction the stepwise mode that involves anti intermediate-(terminal carbon (C-1) attack) is referred to as stepwise mode 3, and that involving allylic intermediate (central carbon (C-2) attack)—as stepwise mode 4. Therefore, altogether there are six reacting modes, as shown in Scheme 1. Path 1 leads to normal or regio 1 adduct and path 2 leads to reverse or regio 2 adduct. In both paths, the reaction can proceed through either a concerted process or through one of the two stepwise modes. Concerted transition states of both paths are found to be highly asynchronous and this is in view of the asymmetry in the structures of the dipole and allene. Stepwise modes involve several intermediates and transition states and they are shown in Schemes 2 and 3. Schemes 2 and 3 describe various stages in the stepwise modes along path 1 and path 2, respectively. Both in path 1 and path 2, the stepwise modes involve similar stage sequences and therefore, as a representative case, those involved in path 1 are explained as follows. In the stepwise mode, there are two ways in which regio 1 adduct can be formed: (1) the positive centre, atom a, (Scheme 2) in the dipole reacts with the terminal carbon atom C-1 of allene and forms *anti int 1*; (2) the negative centre, atom c (Scheme 2), forms a bond with the cumulenic carbon atom C-2 of allene and forms *allylic int 1*. The former is denoted as stepwise mode 1 and the latter as stepwise mode 2. In stepwise mode 1, *anti TS 1* is first formed which then transforms into *anti int 1*. This intermediate rotates around the newly formed bond through a rotational TS, (*rot TS 1*), to form *gauche int 1* and this brings the two remaining reacting centres into close proximity. This *gauche int 1* then passes through *gauche TS 1* to form regio 1 adduct. In mode 2, *allylic TS 1* is first formed and followed by *allylic int 1* is formed. Further, this intermediate forms *allylic TS 2* and this leads to regio 1 adduct. Totally 60 species, 20 in each of the 1,3-dipolar cycloaddition reaction mentioned above have been located and characterized and their structures are presented in Fig.1–3. Numbering and the type of atoms in the optimized structures are indicated in the first structure of each figure. Computed deformation energies of the reactants during the initial phase of the reaction are listed in Table 1 and $\mathrm{BF}_i$ and $\mathrm{BC}_j$ values of various bonds and $\mathrm{BFC}_{\mathrm{Ave}}$ values of all transition states and intermediates are compiled in Tables 2–4. To check the reliability of B3LYP results a set of calculations—concerted TS1, allylic TS1 and anti TS1 of regio 1 reaction of allene with nitrile oxide have been performed at MP2 level with higher basis set 6-311G(d,p). Computed activation energies B3LYP (MP2) for concerted TS1, allylic TS1 and anti TS1 are found to be, respectively, 15.56 (9.09), 13.76 (5.33) and 13.45 (6.23) kcal $\mathrm{mol}^{-1}$ and this reveals that calculations performed at higher level show the same trend. This confirms the reliability and suitability of B3LYP/6-31G(d) basis set for this work.



Scheme 2 Two stepwise reacting modes of 1,3-dipolar addition of allene leading to regio 1 adduct.



Scheme 3 Two stepwise reacting modes of 1,3-dipolar addition of allene leading to regio2 adduct.

**Table 1** Deformation energies[a] (kcal mol$^{-1}$) of the dipoles and allene in the 1,3-dipolar reactions of allene with diazomethane, nitrile oxide and nitrone:

| | Allene– | | Allene–nitrile oxide | | Allene–nitrone | |
|---|---|---|---|---|---|---|
| Species: | DE1[b] | DE2[c] | DE1 | DE2 | DE1 | DE2 |
| Concerted TS1 | 19.2 | 11.2 | 21.2 | 7.2 | 15.4 | 8.3 |
| Anti TS1 | 7.4 | 5.3 | 8.9 | 2.7 | 7.3 | 2.9 |
| Allylic TS1 | 15.3 | 9.3 | 8.0 | 4.2 | 5.3 | 3.2 |
| Concerted TS2 | 19.2 | 11.3 | 20.2 | 7.5 | 14.3 | 7.2 |
| Anti TS2 | 20.7 | 10.8 | 19.3 | 11.4 | 21.2 | 15.3 |
| Allylic TS3 | 6.3 | 3.0 | 7.9 | 3.2 | 6.5 | 2.8 |

[a] These values have been calculated only for first TS in each reacting mode. [b] DE1 is the deformation energy of dipole. [c] DE2 is the deformation energy of allene.

## 1,3-Dipolar addition between allene and diazomethane

Energy profiles for various modes of this reaction are presented in Scheme 4. The concerted transition states along both concerted TS1 and TS2 are high-lying and therefore the concerted mechanism is ruled out. There are four stepwise modes, and in stepwise mode 1 the carbon atom of diazomethane first forms a bond to C-1 of allene and this is referred to as the anti-intermediate because the diazomethane moiety is anti to allene in this conformation. The *anti int 1* formed through *anti TS 1* rotates around the newly formed C–C bond through a barrier of 26.5 kcal mol$^{-1}$ forming *gauche int 1*. This intermediate leads to regio 1 product through *gauche TS 1*. In stepwise mode 2, the terminal nitrogen atom of diazomethane first forms a bond to C-2 of allene through an *allylic TS 1*. This TS lies 11.5 kcal mol$^{-1}$ above the *anti TS 1* and this reveals that stepwise mode 1 is much more favourable kinetically than stepwise mode 2. Computed deformation energies listed in Table 1 show that both the dipole and allene deformed to a lesser extent in forming *anti TS1* than *allylic TS1* and this explains the relative stability of anti TS1 than *allylic TS1*. It should also be noted that the deformation energies of both reactants in forming concerted transition states are much higher than those for stepwise modes and this explains why concerted paths are high lying. It is also found that *anti int 1* and *gauche int 1* are more stable than the *allylic int 1* by 11 kcal mol$^{-1}$. Rotation around the central

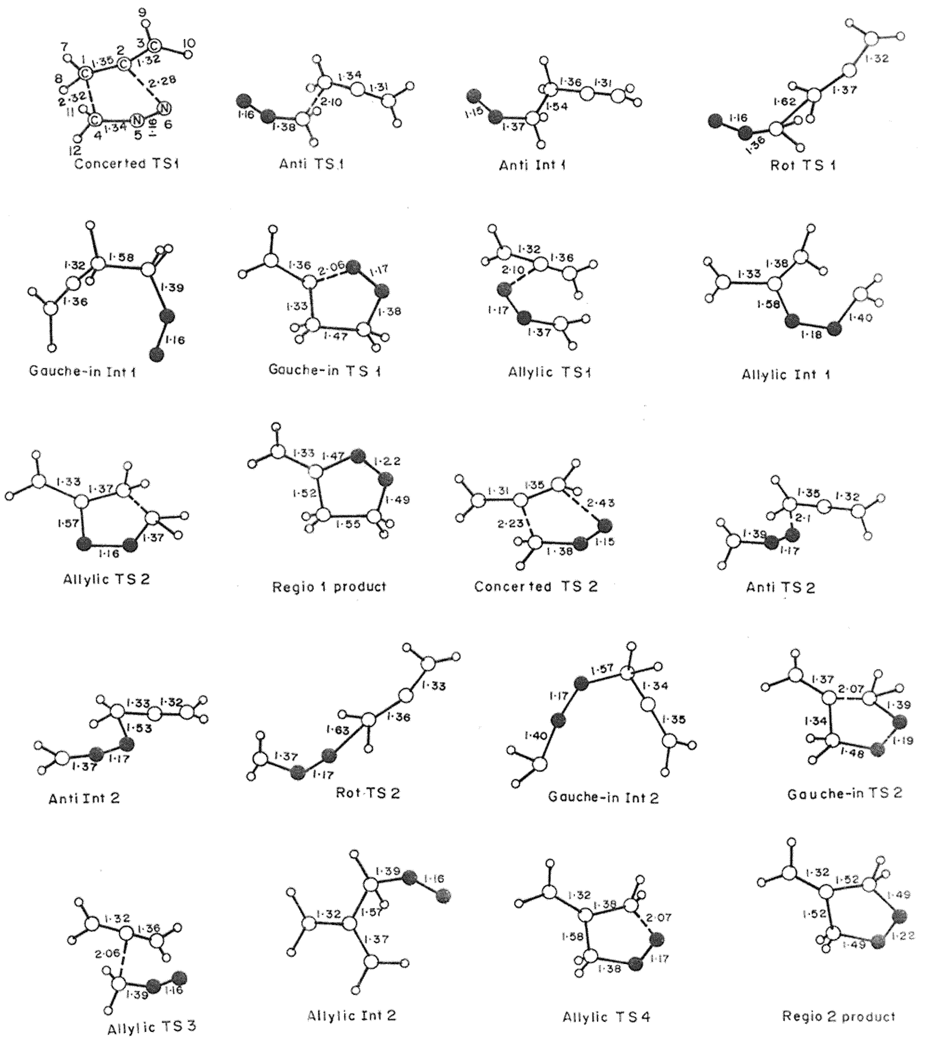


**Fig. 1** Structures of the intermediates, transition state species and the adducts of the reaction between allene and diazomethane.

carbon–carbon single bond of the diradical intermediate *anti int 1* requires an activation energy of *ca.* 27 kcal mol$^{-1}$. In the stepwise mode 1, one unpaired electron is localized on the terminal nitrogen atom of diazomethane and this dramatically stabilizes the diradical (anti int 1). On the other hand, in the stepwise mode 2, the unpaired electron in the diazomethane fragment resides on the carbon atom and this has a destabilizing influence. This even offsets the stability gained by the allylic fragment. Between stepwise mode 3 and stepwise mode 4, the latter is found to be kinetically more favourable than the former. The *allylic TS 3* lies 19.5 kcal mol$^{-1}$ lower than the *anti TS 2*. Such a large difference in the stabilities of the transition states can be understood from the extent of deformation (Table 1) allene and diazomethane undergo in forming the respective transition states. In contrast to the earlier case, *allylic int 2* is much stabler than both *anti int 2* and *gauche int 2* and is lying 43 kcal mol$^{-1}$ lower from *anti int 2* and this again is due to stability differences arising from localization of one unpaired electron on the nitrogen atom in the former and on the carbon atom in the latter. Higher stability of *allylic int 2* has again led to a very high barrier (42.51 kcal mol$^{-1}$) for the formation of regio 2 adduct. The barrier for the rotation of *anti int 2* through the newly formed C–N bond is around 9.3 kcal mol$^{-1}$ and is much lower compared to the rotation that *anti int 1* undergoes. The exothermicities of both regio 1 and regio 2 reactions are the same and both products are lying 50 kcal mol$^{-1}$ lower from the reactants. Overall, stepwise mode 1 and stepwise mode 4 are found to be kinetically favoured over other two stepwise modes and the concerted paths. Further, the *allylic TS 3* is lying lower by 3.4 kcal mol$^{-1}$ from *anti TS 1* and this difference in barriers predicts a relative dominance of regio 2 reaction over regio 1 reaction. The computed $BFC_{Ave}$ values listed in Table 2 reveal that the concerted transition states are late transition states and *anti TS 1* and *allylic TS 3* are found to be early transition states. Therefore, it is natural that stepwise mode 1 and stepwise mode 4 have lower activation energies and are kinetically favoured. Bond forming and cleaving indices listed in Table 2 show clearly how gradually C1–C4, C2–N6 and C1–C2 bonds are formed and C4–N5 and N5–N6 bonds are cleaved. The data also reveal that C2–C3 bond first cleaves till the intermediate—*anti* or *allylic*—is formed and then re-establishes gradually. In the product C4–N5 and N5–N6 bonds become single and double bonds, respectively.

The reaction of allene with diazomethane was first studied experimentally by Crawford and co-workers[26] and they have reported only one regioisomer, 4-methylene-1-pyrazoline, referred to as regio 2 product in this work. Recently, Rastelli and co-workers[15] have investigated this reaction experimentally and theoretically and reported that the 7% of the alternative regioisomer, referred to here as regio 1 product, was formed. They have also performed calculations at various levels of theory and have explained the regiochemistry of the reaction based on the transition states located on the concerted pathway. As seen above, when the entire potential energy surface of this reaction is explored, it becomes quite clear that the stepwise paths are lying lower than concerted paths and the difference in activation energies for the regio 2 to regio 1 reaction works out to be 3.2 kcal mol$^{-1}$, *i.e.* the *allylic ts 3* is lying 3.2 kcal mol$^{-1}$ below than the *anti TS 1*. Rastelli and co-workers[15] have found that an estimate of the activation energy difference for these

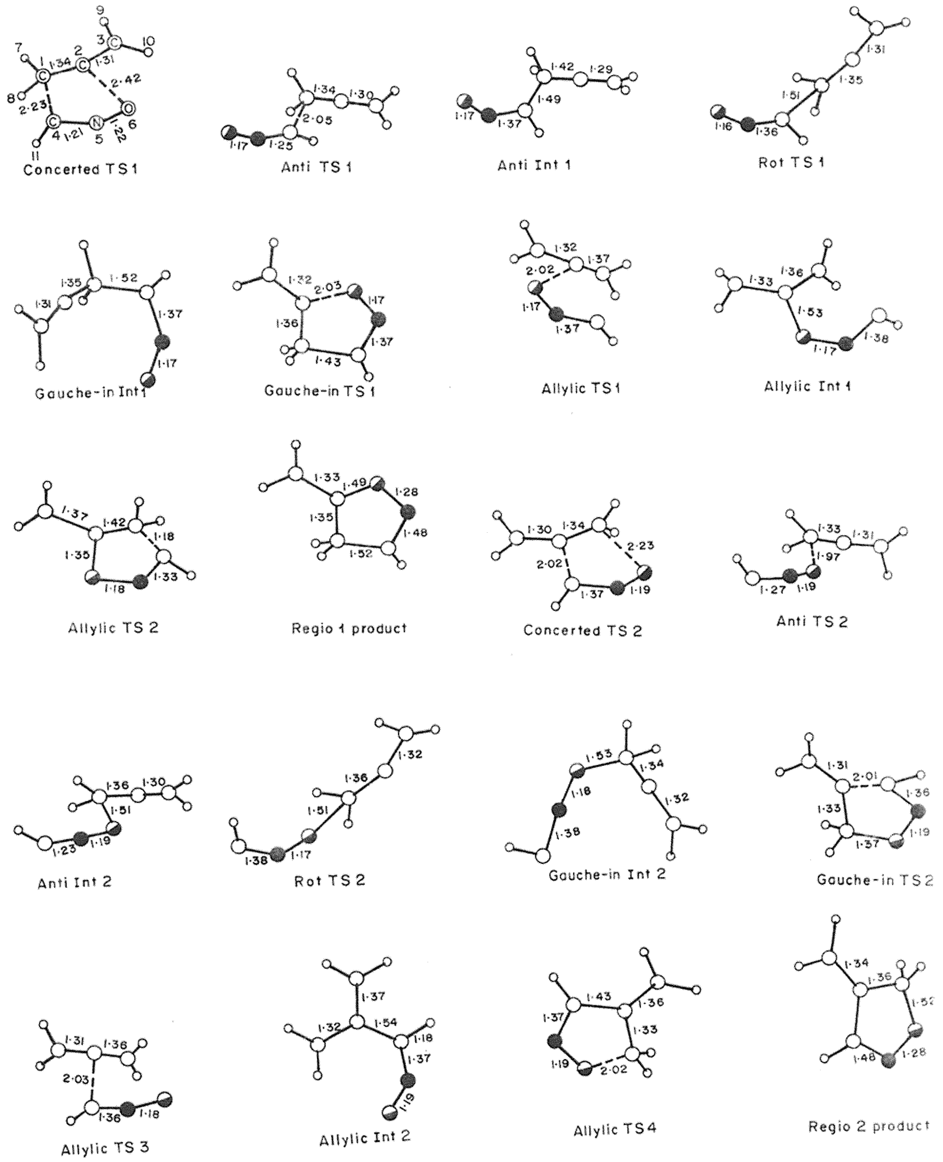


**Fig. 2** Structures of the intermediates, transition state species and the adducts of the reaction between allene and nitrile oxide.

two processes is 1.53 kcal mol$^{-1}$ from the experimental yields for the regio isomers. The above values indicate that the theoretical selectivity based on our calculations clearly explains the experimental regiochemistry. The preference of stepwise path over the concerted path is characteristic of the cumulenic system as reported by Houk and co-workers recently.[3]

## 1,3-Dipolar addition between allene and nitrile oxide

The concerted mechanism is not found to be favourable in this case, also similar to allene–diazomethane reaction seen above. It can be observed from Scheme 5, that the activation energies for the concerted processes are higher compared to stepwise processes, the difference is around 2 and 4 kcal mol$^{-1}$, respectively, for regio 1 and regio 2 reactions. The deformation energies listed in Table 1 indicate clearly that concerted processes require substantial deformation of reactants and explain the higher activation energies involved in these processes. It should be noted that the deformations of the dipole in these processes are much higher than those of allene. BFC$_{\mathrm{Ave}}$ values listed in Table 2 also show that concerted TS1 and TS2 are late transition states and justify higher activation energies. In regio 1 reaction, stepwise mode 1 and stepwise mode 2 are in close competition. In stepwise mode 1, the carbon atom of the nitrile oxide first forms a bond with the C-1 carbon of the allene resulting in a diradical intermediate, *anti int 1*. This diradical rotates through a barrier of 26 kcal mol$^{-1}$ and then cyclizes to form regio 1 product. In stepwise mode 2, the oxygen atom of the nitrone attacks the C-2 carbon of the allene and forms a diradical *allylic int 1*. The *allylic int 1* is formed through *allylic TS 1*. The activation energies of the formation of *anti int 1* and *allylic int 1* show that both modes are equally favourable. The energy profiles presented in Scheme 5 show that stepwise mode 3 is high lying and therefore it is not favourable. It is the stepwise mode 4, where the carbon atom of the nitrile oxide first forms a bond with C-2 of allene, is low-lying and is highly favoured. This is in view of the fact that the unpaired electron is localized on the oxygen atom of nitrile oxide and this strongly stabilizes *allylic TS 3* and other species in the reaction path. In comparison, the species on the stepwise mode 3 and stepwise mode 2 are less stabilized in view of the fact that the unpaired electrons in these species are localized on the carbon atom of nitrile oxide. The activation energy for the formation of *allylic int 2* is around 11.3 kcal mol$^{-1}$ and is the most stable intermediate. The very high stability of *allylic int 2* compared to *allylic int 1* shows that the oxygen atom of nitrile oxide attacking the C-2 of allene is the most favourable nucleophillic addition compared to the carbon atom of nitrile oxide attacking C-2 of allene. For the same reason, the *allylic TS 3* is more stabilized than *anti TS 2* and *anti int 1* is more stabilized than *allylic int 1*. For regio 1 reaction, though both mode 1 and 2 appear to be equally favourable, mode 1 has two high barriers

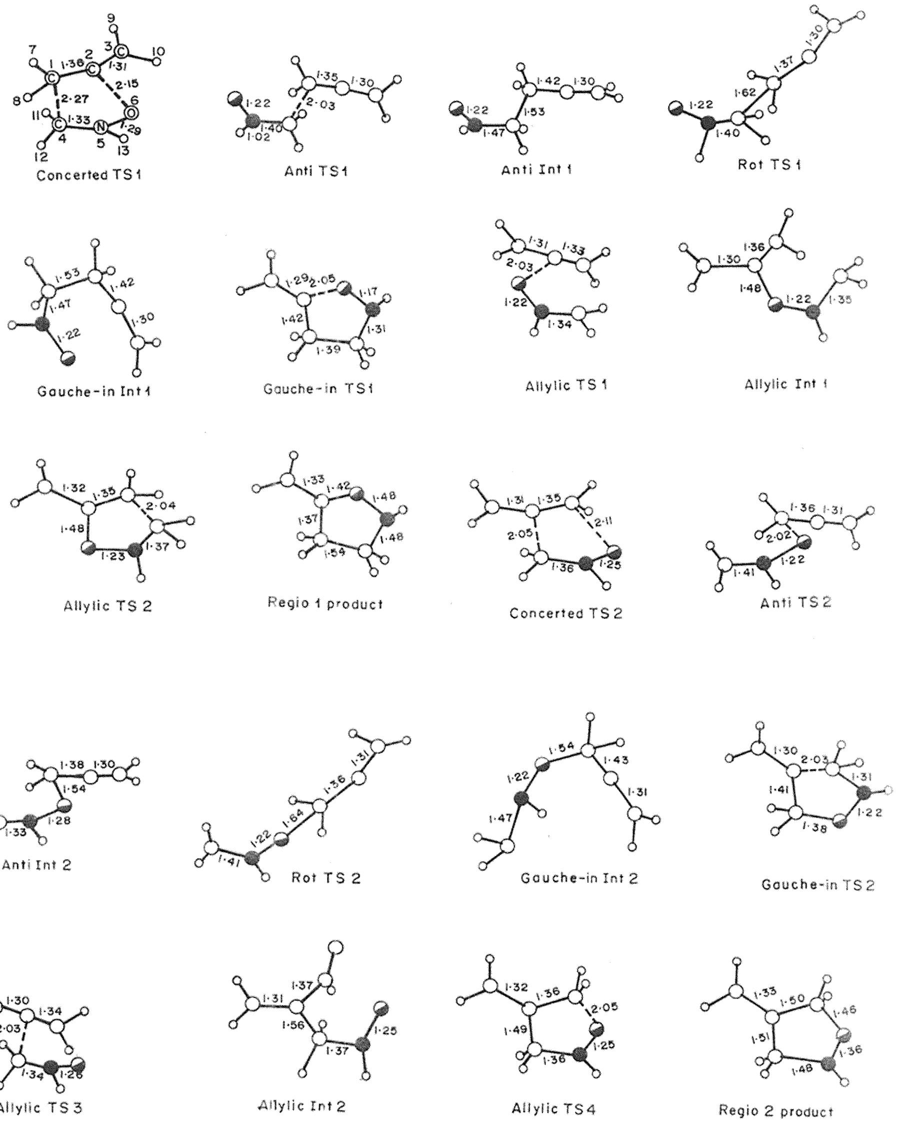
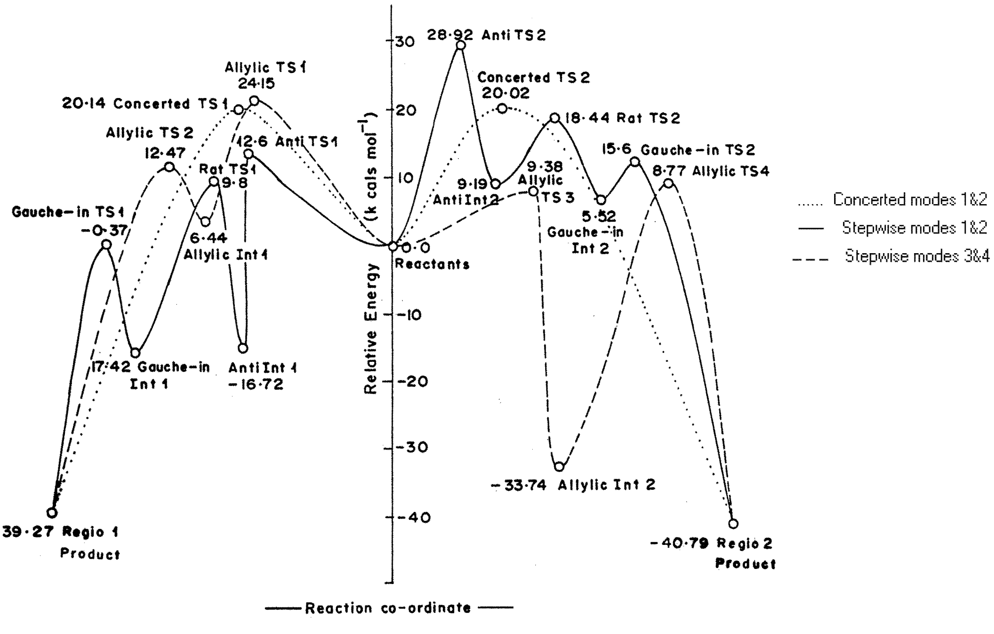


**Fig. 3** Structures of the intermediates, transition state species and the adducts of the reaction between allene and nitrone.



**Scheme 4** Schematic energy diagram of the reaction between allene and diazomethane.

after the formation of the diradical intermediate whereas mode 2 has one small barrier after the formation of the diradical intermediate. This makes stepwise mode 1 favourable. For regio 2 reaction, mode 4 is the only favourable pathway in view of the low lying *allylic TS 3*. This stepwise process has a second barrier of 19 kcal mol$^{-1}$. The deformation energies presented in

**Table 2** Computed bond indices[a] for various species in the reaction path of allene –diazomethane

| | | $BF_i$ | | | $BC_j$ | | $BFC_{Ave}$ |
|---|---|---|---|---|---|---|---|
| | | Regio 1 reaction | | | | | |
| Mode | Species | C1–C4 | C2–N6 | C1–C2 | C4–N5 | N5–N6 | |
| Concerted Mode 1 | Concerted TS1 | 43 | 28 | 76 | 44 | 47 | 46 |
| | Anti TS 1 | 37 | 0 | 46 | 43 | 53 | 33 |
| Stepwise Mode 1 | Anti Int 1 | 94 | 1 | 75 | 41 | 23 | 47 |
| | Rot TS 1 | 95 | 1 | 74 | 41 | 23 | 47 |
| | Gauche Int 1 | 95 | 1 | 73 | 41 | 23 | 47 |
| | Gauche TS 1 | 98 | 36 | 84 | 30 | 84 | 66 |
| Stepwise Mode 2 | Allylic TS 1 | 4 | 36 | 16 | 68 | 26 | 28 |
| | Allylic Int 1 | 8 | 94 | 15 | 74 | 42 | 47 |
| | Allylic TS 2 | 40 | 98 | 27 | 76 | 83 | 65 |
| | | $BF_i$ | | | $BC_j$ | | $BFC_{Ave}$ |
| | | Regio 2 reaction | | | | | |
| | | C2–C4 | C1–N6 | C1–C2 | C4–N5 | N5–N6 | |
| Concerted Mode 2 | Concerted TS 2 | 40 | 27 | 76 | 42 | 48 | 44 |
| | Anti TS 2 | 2 | 36 | 44 | 68 | 51 | 37 |
| Stepwise Mode 3 | Anti Int 2 | 3 | 99 | 43 | 89 | 21 | 51 |
| | Rot TS 2 | 3 | 99 | 43 | 90 | 23 | 51 |
| | Gauche Int 2 | 3 | 99 | 43 | 90 | 23 | 52 |
| | Gauche TS 2 | 35 | 99 | 23 | 98 | 86 | 60 |
| Stepwise Mode 4 | Allylic TS 3 | 28 | 5 | 22 | 8 | 24 | 18 |
| | Allylic Int 2 | 95 | 6 | 96 | 10 | 45 | 51 |
| | Allylic TS 4 | 97 | 33 | 98 | 38 | 84 | 69 |

[a] By definition, bond indices $BF_i$ and $BC_j$ for various bonds listed above are 0 and 100, respectively, for reactants and products.

**Table 3** Computed bond indices[a] for various species in the reaction path of allene–nitrile oxide

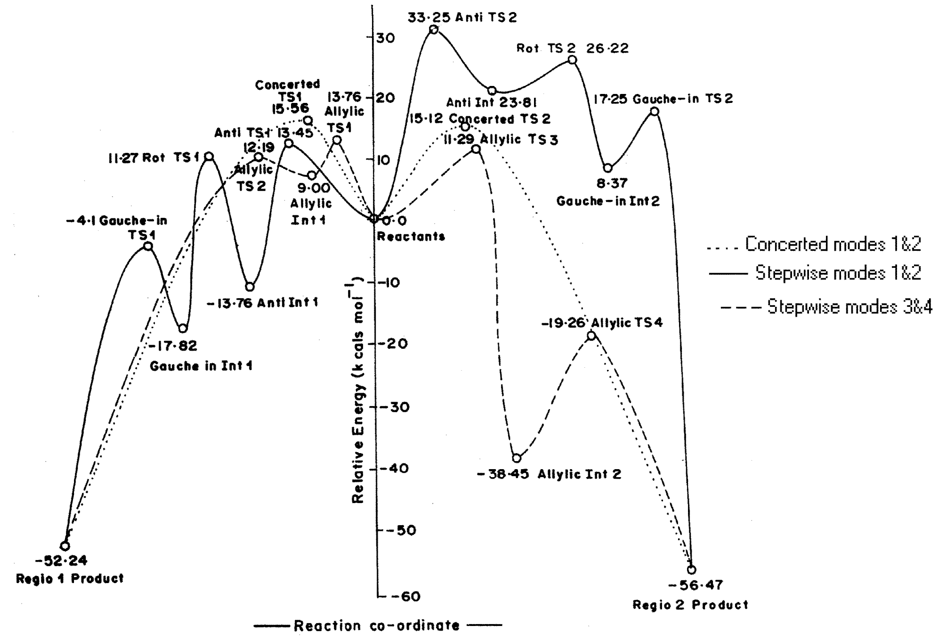
| | | $BF_i$ | | | $BC_j$ | | $BFC_{Ave}$ |
|---|---|---|---|---|---|---|---|
| | | Regio 1 reaction | | | | | |
| Mode | Species | C1–C4 | C2–O6 | C1–C2 | C4–N5 | N5–O6 | |
| Concerted Mode 1 | Concerted TS1 | 36 | 16 | 36 | 35 | 44 | 32 |
| | Anti TS 1 | 43 | 2 | 46 | 82 | 57 | 42 |
| Stepwise Mode 1 | Anti Int 1 | 95 | 3 | 76 | 97 | 90 | 68 |
| | Rot TS 1 | 96 | 3 | 79 | 44 | 27 | 69 |
| | Gauche Int 1 | 97 | 6 | 78 | 43 | 27 | 70 |
| | Gauche TS 1 | 100 | 46 | 86 | 27 | 83 | 69 |
| Stepwise Mode 2 | Allylic TS 1 | 5 | 47 | 35 | 100 | 28 | 40 |
| | Allylic Int 1 | 11 | 95 | 21 | 83 | 53 | 53 |
| | Allylic TS 2 | 45 | 100 | 26 | 75 | 85 | 67 |
| | | $BF_i$ | | | $BC_j$ | | $BFC_{Ave}$ |
| | | Regio 2 reaction | | | | | |
| | | C2–C4 | C1–O6 | C1–C2 | C4–N5 | N5–O6 | |
| Concerted Mode 2 | Concerted TS 2 | 32 | 17 | 33 | 34 | 39 | 30 |
| | Anti TS 2 | 2 | 48 | 46 | 25 | 51 | 33 |
| Stepwise Mode 3 | Anti Int 2 | 2 | 98 | 49 | 28 | 25 | 61 |
| | Rot TS 2 | 2 | 98 | 93 | 94 | 24 | 60 |
| | Gauche Int 2 | 8 | 98 | 95 | 95 | 24 | 62 |
| | Gauche TS 2 | 48 | 100 | 24 | 98 | 84 | 71 |
| Stepwise Mode 4 | Allylic TS 3 | 26 | 5 | 64 | 98 | 27 | 39 |
| | Allylic Int 2 | 96 | 10 | 98 | 55 | 47 | 60 |
| | Allylic TS 4 | 98 | 57 | 99 | 38 | 86 | 76 |

[a] By definition, bond indices $BF_i$ and $BC_j$ for various bonds listed above are 0 and 100 respectively for reactants and products.

**Table 4** Computed bond indices[a] for various species in the reaction path of allene–nitrone

| Mode | Species | $BF_i$ | | | $BC_j$ | | $BFC_{Ave}$ |
|---|---|---|---|---|---|---|---|
| | | Regio 1 reaction | | | | | |
| | | C1–C4 | C2–O6 | C1–C2 | C4–N5 | N5–O6 | |
| Concerted Mode 1 | Concerted TS1 | 39 | 32 | 48 | 45 | 45 | 41 |
| Stepwise Mode 1 | Anti TS 1 | 44 | 2 | 51 | 80 | 53 | 42 |
| | Anti Int 1 | 94 | 3 | 74 | 40 | 24 | 47 |
| | Rot TS 1 | 97 | 3 | 77 | 40 | 24 | 49 |
| | Gauche Int 1 | 98 | 6 | 77 | 41 | 24 | 50 |
| | Gauche TS 1 | 99 | 47 | 86 | 29 | 83 | 69 |
| Stepwise Mode 2 | Allylic TS 1 | 7 | 48 | 20 | 65 | 25 | 32 |
| | Allylic Int 1 | 11 | 95 | 18 | 80 | 51 | 52 |
| | Allylic TS 2 | 45 | 99 | 25 | 77 | 84 | 67 |
| | | $BF_i$ | | | $BC_j$ | | $BFC_{Ave}$ |
| | | Regio 2 reaction | | | | | |
| | | C2–C4 | C1–N6 | C1–C2 | C4–N5 | N5–O6 | |
| Concerted Mode 2 | Concerted TS 2 | 40 | 28 | 74 | 45 | 49 | 45 |
| Stepwise Mode 3 | Anti TS 2 | 2 | 39 | 60 | 87 | 50 | 43 |
| | Anti Int 2 | 3 | 98 | 92 | 92 | 23 | 60 |
| | Rot TS 2 | 4 | 98 | 92 | 93 | 23 | 60 |
| | Gauche Int 2 | 4 | 99 | 94 | 94 | 23 | 61 |
| | Gauche TS 2 | 37 | 97 | 23 | 96 | 84 | 67 |
| Stepwise Mode 4 | Allylic TS 3 | 26 | 6 | 62 | 98 | 26 | 39 |
| | Allylic Int 2 | 95 | 7 | 97 | 53 | 47 | 59 |
| | Allylic TS 4 | 97 | 36 | 99 | 40 | 86 | 71 |

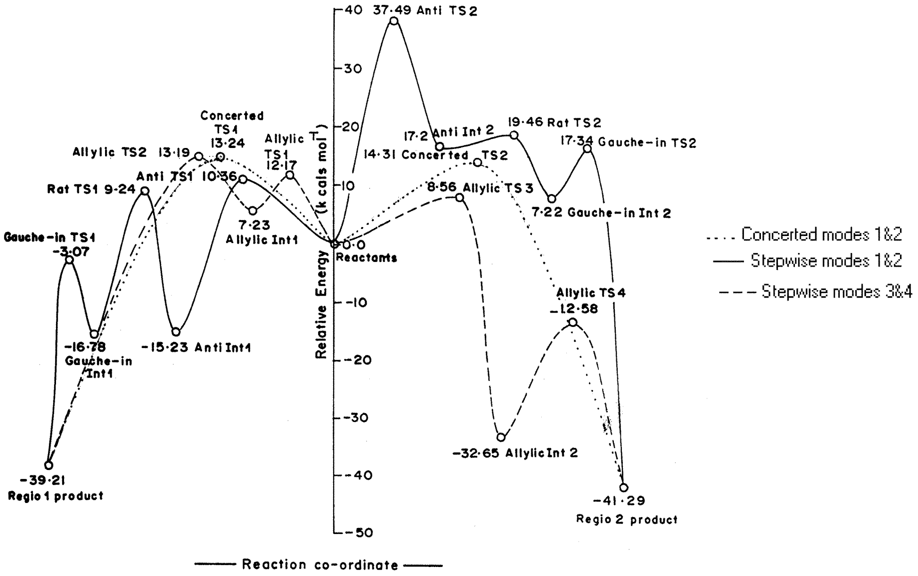
[a] By definition, bond indices $BF_i$ and $BC_j$ for various bonds listed above are 0 and 100 respectively for reactants and products.



**Scheme 5** Schematic energy diagram of the reaction between allene and nitrile oxide.

Table 1 show that only *allylic TS 3* and *anti TS 1* require lower extents of deformation and explain lower activation energies obtained in these cases. This observation is further supported by lowest BFC $_{Ave}$ values of the above species indicating reactant-like transition states.

The theoretical selectivity of cycloaddition of prototype nitrile oxide to allene could not be verified directly because no experimental reports of this reaction is available. Rastelli and co-workers[15] have investigated this reaction at various levels of theory and have compared their computed results with the experimental data obtained for the reactions of allene with benzonitrile oxide and mesitonitrile oxide. They have experimentally observed that regio 2 product was much favoured over regio 1 product for mesitonitrile oxide–allene reaction; for



**Scheme 6** Schematic energy diagram of the reaction between allene and nitrone.

benzonitrile oxide–allene reaction, regio 1 product was preferred. Therefore it is understandable that both regio isomers are formed in these reactions and the regiochemistry of these reactions is sensitive to substitution. Theoretically, they have investigated the concerted paths of formonitrile oxide–allene reaction and found that the transition state on the regio 2 reaction path is slightly lower lying than the other. Our calculations definitely indicate that the reaction prefers stepwise pathway and the regio 2 product is favoured over regio 1 product; the activation energies differing by 2.2 kcal mol$^{-1}$.

### 1,3-Dipolar addition between allene and nitrone

Similar to allene–diazomethane and allene–nitrile oxide reactions, the concerted mechanism is also ruled out in this case. The activation energy for the concerted process is higher by 3 kcal mol$^{-1}$ compared to one of the low lying stepwise modes for regio 1 reaction and 6 kcal mol$^{-1}$ compared to one of the low lying stepwise modes for regio 2 reaction (Scheme 6). The deformation energies given in Table 1 show that concerted processes involve greater deformation and therefore have higher activation energies. BFC$_{\text{Ave}}$ values also indicate that concerted transition states are late transition states. Energy profiles shown in Scheme 6 show that stepwise mode 1 is low lying compared to stepwise mode 2 and stepwise mode 4 is low lying compared to stepwise mode 3. This is clearly understandable from the heteroatomic influences on the stability of diradicals and other species in the reaction paths. In the allene–nitrone reaction, in the stepwise modes 1 and 4, the unpaired electron is localized on the oxygen atom and this stabilizes the path compared to stepwise modes 2 and 3, where the unpaired electron is localized on the carbon atom. For regio 1 reaction, mode 1 is preferred over mode 2 as *anti TS1* is lying 2 kcal mol$^{-1}$ lower than *allylic TS1*. For regio 2 reaction, the stepwise mode 4 is the most favourable pathway (Scheme 6). Computed deformation energies (Table 1) clearly show that *allylic TS 3* and *anti TS 1* involve lower extents of deformation and thus should be more favourable. BFC $_{\text{Ave}}$ values given in Table 2 also indicate that the above transition states are early transition states compared to the other four transition states and explain the preference of reaction modes.

Though the cycloaddition of nitrones with olefins is one of the most studied reactions, no reports are available on the nitrone–allene reaction. Dolbier and co-workers[4] investigated the regio and stereochemistry of nitrone cycloadditions with monofluoro and 1,1-difluoroallenes. They have also studied cycloadditions of fluoroallenes with a variety of nitrones. As nitrone cycloaddition with simple allene has not been studied so far, a straightforward comparison of our computed data could not be made.

## Conclusions

In this paper, we have investigated the potential energy surfaces for the gas phase 1,3-dipolar cycloaddition reactions of diazomethane, nitrile oxide and nitrone with simple allene using B3LYP approach with 6-31G(d) basis set. The computational results reveal that the above reactions have two concerted modes and four stepwise modes leading to two regio products. In all these reactions, stepwise modes are lower-lying than the concerted modes: effectively these reactions prefer a stepwise mechanism. Particularly, the regio 2 reaction passes through stepwise mode 4, and the regio 1 reaction prefers stepwise mode 1. Regio 1 and regio 2 reactions are equally exothermic, but there is a difference of *ca.* 2 kcal mol$^{-1}$ in the activation energy. Therefore, kinetically, regio 2 reactions are more facile than regio 1 reaction. Computed energy barriers indicate that mainly the heteroatomic influence on the stability of diradical intermediates and other species in the reaction path and the cumulenic strain determine the mechanism of these reactions. Computed deformation energies well explain the activation energy differences for various modes and BFC$_{\text{Ave}}$ values propose early transition states for favourably reacting modes. Bond order analyses show clearly the gradual formation of new bonds and cleavage of the reacting double bonds. It further reveals that the other double bond of allene undergoes partial cleavage during the first phase of the reaction and it re-establishes in the final phase. Computed energy barriers explain very well the experimental regiochemistry of the reactions.

## Acknowledgements

We are grateful to CSIR, India, for financial support to one of us (P.V.) through the major research grant (01)1649/00/EMR-II, and to Prof. Hiroshi Yamataka, Osaka University, Japan, for his critical comments.

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