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AM1 study of the two ways of retro-ene reaction for the cyanomethildiallylamine

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Abstract

The transition state (TS) geometries of propene elimination from cyanomethildiallylamine (**1**) to obtain N-cyanomethilvinylimine (**2**) and N-propenilcyanoimine (**3**) were calculated with the semiempirical AM1 method. For the two cases, our calculations led to TS's that consist of non planar six center cyclic structures with distorted chair-like geometries. These results show that the TS geometries have a marked "reactant-like" character and the TS geometries for the two reactions are remarkably similar. It is also found that the TS are of polar character and that a negative charge is developed on the carbon atom from which the hydrogen atom is transfered, thus, the activaction energy increases when strong electron-attractor substituents are coordinated to this carbon atom. The calculated activation energies indicate that the reaction with formation of **2** is favored over the reaction with formation of **3**, in agreement with experimental evidence.

Key words: AM1, transition state, retro-ene, allylamines.

Estudio AM1 de las dos vías de reacción retro-ene para la cianometildialilamina

Resumen

Las geometrías de estados de transición (TS) para la eliminación de propeno a partir de cianometildialilamina (**1**) para obtener N-cianometilvinilimina (**2**) y N-propenilcianoimina (**3**) fueron calculadas con el método semi-empírico AM1. En los dos casos, nuestros cálculos conducen a TS's que consisten de una estructura cíclica de seis miembros no plana con una geometría tipo silla distorsionada. Estos resultados muestran que las geometrías de los TS tienen un marcado carácter tipo reactante y las geometrías de los TS para las dos reacciones son notablemente similares. También se encontró que los TS son de carácter polar y que sobre el átomo de carbono desde el cual se transfiere el átomo de hidrógeno se desarrolla una carga negativa; así, la energía de activación aumenta cuando este átomo de carbono está coordinado a sustituyentes atractores de electrones fuertes. La energía de activación indica que la reacción con formación de **2** está favorecida sobre la reacción con formación de **3**, en concordancia con la evidencia experimental.

Palabras clave: AM1, estados de transición, retro-ene, alilaminas.

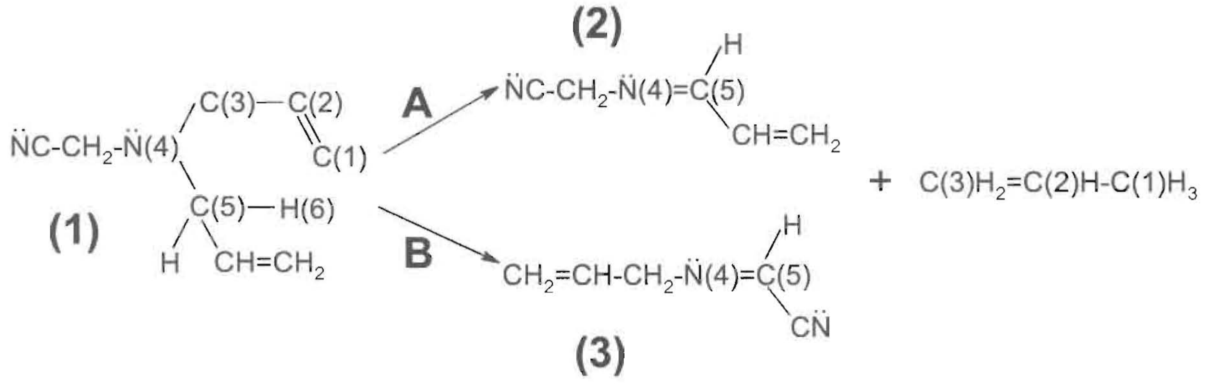
Introduction

The complete characterization of an organic chemical reaction requires the full determination of the potential energy surface for the reaction system as a function of the nuclear coordinates [1]. In the classical transition state theory this requirement is reduced to a determination of the surface around the reactant(s) (R), the product(s) (P), the transition state (TS), and the lowest energy pathway conneting them. Therefore, the precise localization and identification of the TS geometry is of great importance in the sophisticated stereoselective mechanism of the pericyclic reactions [2]. Pericyclic reactions are characterized by the formation and breaking of several bonds simultaneously, therefore, they are concerted reactions. For this reason, there has been considerable attention in recent years to develop methods of geometry optimization, i.e., the location of stationary points corresponding to minima and TS (saddle point) on the potential energy surface. The high dimensionality of these hyper-surfaces makes very difficult its construction and analysis. Thus, many efforts have been devoted for improving the methodology for TS search [3-11].

The ene reaction and its reverse, the retro-ene reaction, are common paths of many organic reactions and an efficient tool in synthesis as well [12]. In general, the ene reactions are related both to cycloadditions and to sigmatropic hydrogen shifts, where one π bond is converted to a σ bond, and at the same time, a hydrogen atom is transferred. In the context of Woodward and Hoffmann theory, this retro-ene reaction may be classified as a thermally allowed 1-5 hydrogen shift [13-15]. Moreover, the retro-ene fragmentation reactions constitute an increasingly useful tool in organic chemistry for the generation of novel double-bonded species, when a heteroatom is present. The application of this reaction to heteroatomic molecules has not yet been extensively studied [16]; nevertheless, it can be used for the generation of some carbon-heteroatom double bonds, as in the case of C=O [17-18], C=S [19-21], C=N [22-24], C=P [25-26].

In this work, we report TS structure calculations of propene elimination from diallylcyanomethilamine **1**, using the semiempirical AM1 method [27]. The focus of this work is on the analysis of the geometrical and electronic properties of the TS structure. The variations in the geometries from reactant to products are analyzed in terms of distances and angles between the atom that experiences larger modifications in the reactions. The bond orders and atomic charges are also presented in order to further support the proposed mechanism. We also evaluate the activation energy of the reactions and compare our calculated results with experimental data.

Scheme 1 depicts the two possible retro-ene reaction for **1**. As can be observed, reactant **1** has two transferable hydrogen atoms in the alpha position with respect to nitrogen; therefore, two retro-ene reactions are possible. In one case, the transferable hydrogen atom comes from the allyl group and this reaction (called reaction **A**, hereafter) gives N-cyanomethylvinylimine **2** and propene. For the other case, the transferable hydrogen atom comes from the cyanomethyl group and here, (called reaction **B**, hereafter) the products are N-propenilcyanoimine **3** and propene. It is im-



Scheme 1

portant to emphasize that the products for the reactions **A** and **B** are not the same; however, the reactant and the reaction are identical. The underlying difference here depends on which group substituent on the nitrogen atom supplies the transferable hydrogen for the retro-ene reaction.

Computational procedure

The reactions were modelled by means of calculations for R, TS and P structures; where the structure of R and P are completely optimized and the computed TS is confirmed by the presence of only one negative eigenvalue in the hessian matrix. In a potential energy surface, the TS is characterized as a stationary point having one, and only one, negative hessian eigenvalue (the hessian being the matrix of second energy derivatives with respect to the geometrical parameters being varied). Minima have all positive hessian eigenvalues and n negative eigenvalues represent an n^{th} order saddle point. Thus, ordinary transition state are first order saddle points.

All calculations were performed with the AMPAC [28] program package from the Quantum Chemistry Programs Exchange bank (QCPE). In all cases considered here, the energy minimization was carried out using internal coordinates as variables. The geometries of the stable species (R and P) were fully optimized using the keyword PRECISE and their total energies and thermodynamic parameters were calculated. It is important to mention that an identical format of atomic definition or sequence connection in internal coordinates was used for both R and P. This is a requirement of the routine SADDLE for searching TS structures. Moreover, this allowed us to have a quick identification of the atoms and facilitates the reading of the tables. The numbered atoms in the scheme 1 form the ring of the TS structures and they undergo the larger changes in the course of the reactions. The TS structures were obtained from the optimized R and P structures using the keyword SADDLE and were characterized by vibrational analysis (with the keyword=FORCE) to ensure the presence of a single negative eigenvalue in the force constant matrix. Additionally, the thermodynamic calculations were carried out with the keyword THERMO, where the temperature range of the calculations was indicated. The activation energies were calculated at 723 K to make a comparison with experimental results.

Results and Discussion

Table 1 shows the bond lengths of the selected distances for R, TS and P in the reactions **A** and **B**. No remarkable geometrical differences are observed between the structures for both reactions. This table gives a clear indication of the course of the reactions. For example, the C1-C2 distance variations, show how they are transformed from double to single bonds. An inverse change occurs for C2-C3 bonds. It is important to mention that the average of TS's C1-C2 and C2-C3 bond lengths (1.416 Å) is almost an intermediate value between single (1.488 Å) and double bonds (1.331 Å). The bond lengths C3-N4 in R for the reactions **A** and **B** increase from 1.460 Å and 1.459 Å, (a typical distance for single C-N bond) to 3.000 Å in P. At this bond length the interac-

Table 1
Selected bond distances for R, TS and P (in Å).
(Reaction **A** / Reaction **B**)

Bond	R	TS	P
C1-C2	1.330 / 1.331	1.404 / 1.414	1.479 / 1.478
C2-C3	1.497 / 1.497	1.422 / 1.422	1.332 / 1.332
C3-N4	1.460 / 1.459	1.733 / 1.731	3.000 / 3.000
N4-C5	1.459 / 1.458	1.373 / 1.350	1.288 / 1.285
C5-H6	1.131 / 1.132	1.652 / 1.649	2.499 / 2.501
C1-H6	3.200 / 3.152	1.630 / 1.630	1.118 / 1.119

tion C-N decreases significantly and the bond practically disappears. For the N4-C5 bonds, we observe how single bonds in R (1.459 and 1.458 for **A** and **B** reactions, respectively) are converted to double bonds, in P (1.288 Å and 1.285 Å for **A** and **B** reactions, respectively) as expected. These results are also in good agreement with the calculated value of 1.25 Å for C=N bond obtained from high level ab-initio calculations of CH_2NH [29]. The last two distances in this table are very important due to the fact that the transferable hydrogen atom (H6) is involved. Here, we can observe that H6, initially coordinated to C5, is transfered to C1. An analysis of the C5-H6 and C1-H6 bond distances for reaction **A**, indicates that H6 in the TS is closer to C1 than to C5, although the displacement of H6 from its initial position is 0.521 Å, and its distance to P is now 0.847. Thus, in the TS the transferable hydrogen atom is at less than half way its distance to P. This might be taken as evidence that the C1-H6 bond formation is a very difficult step for the reaction. However, a conclusive answer to this matter requires further kinetic studies. For reaction **B** the same behavior is observed. All observations indicate that the TS structure have more resemblance with the R than with the P, which is similar to ab-initio results for the ene reaction between methyl acrylate and propene using split-valence 3-21G and 6-31G basis sets [30].

The reaction studied in the present work is a sigmatropic reaction, one which occurs in just one step. Hence, we are dealing with a concerted mechanism where all bonds are modified at the same time, if not with the same extension. Again, for a definitive conclusion on this issue further kinetic studies are needed. The latter, however, lies beyond the scope of this work. However, we can said that the mechanism studied here is concerted but non-synchronous and involves a non-simultaneous bond-breaking bond-making process. This point will be discussed in more detail below together with the electronic properties: bond orders and atomic charges.

Table 2 shows the selected bond angles for R, TS and P in the reactions **A** and **B**. The C1C2C3 angles practically do not present major changes due to the fact that there is no change in the hybridization of C2 during the reactions. The C2C3N4 and C3N4C5 variation angles are not much conclusive since the bonds between C3 and N4 are broken in the reaction. The N4C5H6 and C5H6C1 angles show the change from sp^3 to sp^2 hybridizations for C5. Finally, the H6C1C2 angles for the P indicate that H6 is coordinated to C1 in an approximately tetrahedral angle. It is important to mention that the angles in this table are in very good agreement with the values reported by Loncharich and Houk for the ene reaction of ethylene and formaldehyde with propene [31]. The TS geometries obtained in this work for reactions **A** and **B** are shown in Figure 1.

The TS structures in both reactions present a high similarity in distances and angle values, i.e., the TS structures of the two reactions are remarkably similar and provide evidence of a small effect of the substituents on the TS geometries. The geometrical properties of the TS's depend almost exclusively on the type of atoms that integrate the six center ring, and do not depend on the nature of the substituents. Nevertheless, the electronic properties for these TS's show significant differences, as discussed below.

Table 2
Selected angles for R, TS and P (in degrees)
(Reaction **A** / Reaction **B**)

Angle	R	TS	P
C1C2C3	122.77 / 122.81	123.40 / 123.10	123.40 / 124.03
C2C3N4	113.53 / 113.79	103.02 / 102.55	90.00 / 90.00
C3N4C5	112.57 / 112.11	104.20 / 104.20	90.00 / 90.00
N4C5H6	106.71 / 107.90	130.17 / 131.24	128.09 / 128.33
C5H6C1	106.46 / 108.82	116.86 / 116.09	121.43 / 121.50
H6C1C2	47.43 / 48.77	92.36 / 92.42	110.89 / 110.73

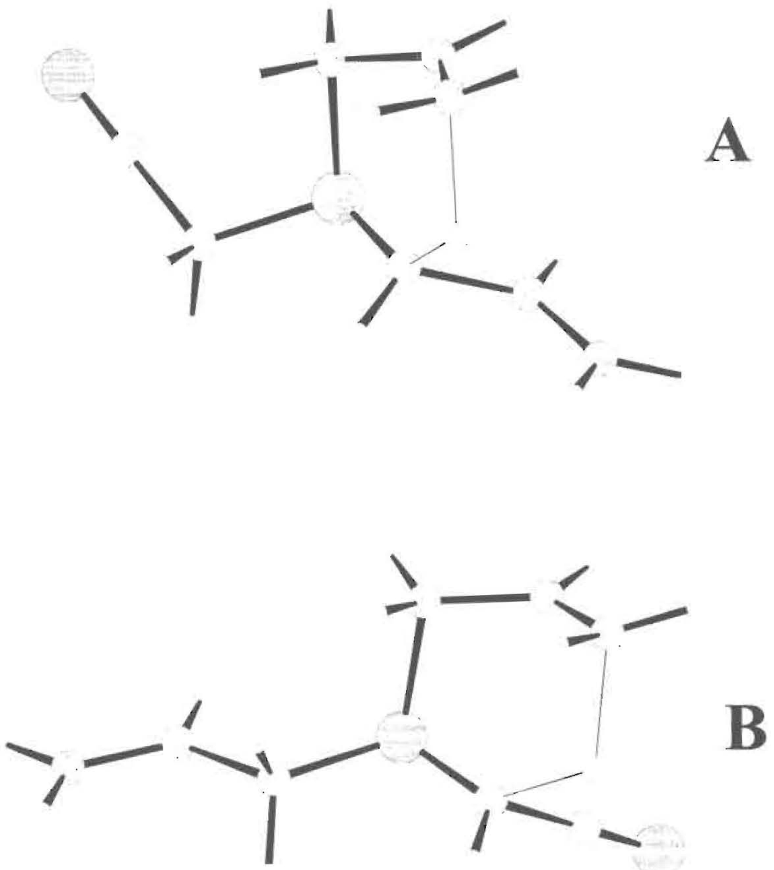


Figure 1. TS structures for reactions **A** and **B**.

The bond orders of R, TS and P for selected bonds are summarized in Table 3 for reactions **A** and **B**. In both cases, it can be observed that C1-C2 bonds are transformed from double to single, whereas C2-C3 and N4-C5 bonds undergo the opposite change. Moreover, the C3-N4 and C5-H6 bonds dissapear in the course of reactions, as reflected by the small values of their bond orders in P. Finally, the C1-H6 bonds in the P present typical values for single bonds. It can be observed that in the two reactions, the TS structures have higher orders for the C5-H6 bond than for C1-H6. This means that in the TS, H6 is bonded more strongly to C5 than C1; hence we can state that the TS have more resemblance with R than with P. This effect is also observed for reaction **B**, where the bond orders that involve H6 are almost identical. Furthermore, the bond orders for C3-N4 in the TS structure are both ≈ 0.68, which is closer to the value for the R than for the P. This is an indication that the scission of the C3-N4 bond is a very difficult reaction step. Usually, one can expect a value of 0.5 for this bond in synchronous reactions. These results indicate that the mechanism is concerted, but there are some rate-limiting steps such as the formation of C1-H6 bonds and the rupture of C3-N4 bonds. Again, to give a conclusive answer in this matter are indispensable particular kinetic studies. This last conclusion is in agreement with the results of Starflinger et. al. [32] of kinetic isotope studies for hetero enophiles in ene reactions. The concerted mechanism has been suported experimentally for the ene reaction of maleic anhydride with alkenes [33] and for the retro-ene reaction of allylic sulfinic acid [34, 35]. The results of this work are also in total agreement with the proposed mechanism for allylphosphines in gas phase thermolysis studies [23].

The atomic charges for R, TS and P for selected atoms are listed in Table 4 for the reactions **A**

Table 3
Selected bond orders for R, TS and P
(Reaction **A** / Reaction **B**)

Bonds	R	T S	P
C1-C2	1.964 / 1,964	1.576 / 1.582	1.006 / 1.006
C2-C3	0.984 / 0,984	1.207 / 1.204	1.960 / 1.960
C3-N4	0.962 / 0,961	0.682 / 0.683	0.000 / 0.000
N4-C5	0.962 / 0,972	1.233 / 1.240	1.899 / 1.922
C5-H6	0.945 / 0.942	0.547 / 0.537	0.001 / 0.001
C1-H6	0.000 / 0.000	0.321 / 0.318	0.960 / 0.960

Table 4
Selected atomic charges for R, TS and P
(Reaction **A** / Reaction **B**)

Atoms	R.	T S	P
C1	-0.220 / -0.219	-0.200 / -0.210	-0.193 / -0.191
C2	-0.164 / -0.170	-0.190 / -0.173	-0.169 / -0.168
C3	-0.048 / -0.046	-0.119 / -0.130	-0.219 / -0.224
N4	-0.251 / -0.250	-0.106 / -0.116	-0.173 / -0.129
C5	-0.046 / 0.018	-0.221 / -0.166	-0.023 / 0.006
H6	0.113 / 0.129	0.111 / 0.123	0.076 / 0.074

and **B**. For reaction **B**, the presence of a cyano group as substituent gives C5 a positive charge in R. As a result, the H6 coordinated to the C5 is more acidic for reaction **B**. However, this reaction requires a negative charge for shifting a hydrogen atom. Thus, the presence of the attractor electron substituents coordinated to C5 make less likely the reaction. For this reason, we expect that reaction **A** is energetically more favored than reaction **B**. Furthermore, the N4 atom is less negative in the TS than in the R, thus the reaction is also favored by electron donor substituents on the N4 atom.

The activation entropies were calculated at 723 K and the values are both less than zero. This confirms the hypothesis of loss of degrees of freedom in the TS with respect to R, due to the many restraints of its ring structure. The activation energy of reaction **B** is 0.86 Kcal/mol higher than the corresponding one for reaction **A**. Thus, reaction **A** is also energetically favored. This conclusion agrees with the experimental works of Martin et. al. [23], who only obtained the products of reaction **A** from pyrolisis of **1**.

Conclusions

The use of vibrational analysis to identify geometries of TS in organic reactions is a simple and useful way of predicting the stereochemistry of the products. This type of modelling is easily applicable to many organic reactions with a considerable number of atoms.

Althoug, the geometrical properties of the TS's depend almost exclusively on the type of the atoms that integrate the six center ring, and do not depend on the nature of the substituents, but, the electronic properties indicate that the reaction is favored by electron donor substituents on the N4 atom.

The presence of strong electron-attractor groups coordinated to carbon atom, from which the hydrogen atom is being transfered, increases the activaction energy.

All the results for the calculated geometrical and electronic properties agree with the proposal mechanism for propene elimination. Thus, the retro-ene reaction for 1 occurs through a concerted, but not synchronous, mechanism with a cyclic TS of six-center-chair-like geometry. Although the TS geometries are remarkably similar between then, they have a reactant-like character.

The calculated activaction energies indicate that the reaction with formation of **2** is favored over the reaction with formation of **3**, in agreement with the experimental data.

Future work in this line will involve phospines, sulphides and ethers in allylic systems and other qyauntum mechanical approach.

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