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Transition Structure for the Retroene-Type Elimination Reaction of Propene from Allylamines

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ABSTRACT

The transition-state geometries of retroene elimination reactions of propene from allylamines have been calculated by using the semiempirical AM1 method. The most favored geometry resembles a half chair or a flattened boat. It is also found that the transition states are of polar character and that the negative charge on the N atom decreases in the transition state; thus, the reaction is favored by electron donor substituents on the nitrogen atom, as observed experimentally. © 1997 John Wiley & Sons, Inc.

INTRODUCTION

Retroene fragmentation reactions constitute an increasingly useful tool in organic chemistry for the generation of novel double-bonded species, whose scope and broad applicability have been reviewed [1–3]. The application of this reaction to heteroatomic molecules has not yet been extensively studied [1–3]; nevertheless, it has been used for the generation of some carbon-heteroatom double bonds; among these can be cited C=O [4–6], C=S [7,8], C=N [9–12], C=Si [13,14], and recently, C=P [15,16].

Kinetic studies of the thermal elimination of propene from allylic molecules (Figure 1) showed that the elimination proceeds via a six-center transition-state retroene **1–5** H-shift mechanism. These studies have permitted also to make suggestions about the nature and the likely geometry of the transition state. The temperature dependence of the kinetic deuterium isotope effect and a lack of substituent effects on the reaction rate for allyl ethers [4–6] were used as evidence to propose a nonplanar transition state and a highly concerted mechanism. The allyl sulfides [7,8], on the other hand, showed a temperature-independent kinetic isotope effect [8] and an important substituent effect [7] on the rate

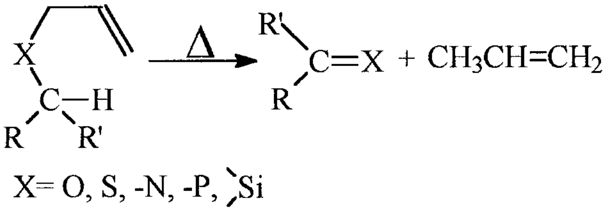

FIGURE 1

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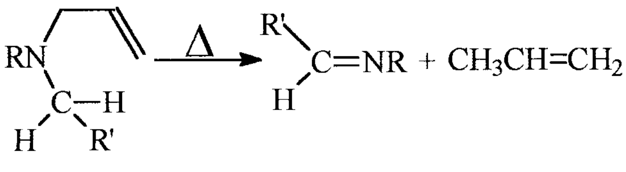
of the pyrolysis, suggesting a polar transition state in which the higher reactivity was due to an enhanced acidic character of the α-H atom to be transferred in a nonlinear **1–5** shift path. For the thermal generation of silenes from allylsilanes [3,13,14], a concerted retroene elimination of propene was proposed. Thermal decomposition of allylamines [9–12] has shown that the rate of pyrolysis is dependent on the substituent on the N atom and on the acidity of the H atom likely to be transferred, suggesting a polar transition state with a, perhaps, less concerted mechanism than for the allyl ethers.

To our knowledge, no calculations have been reported on the transition state of the thermal elimination of propene from allylic heteroatomic molecules, as has been done for hydrocarbon ones [17–20]. In this work, we report on the transition structure calculations for propene elimination from allylamines, using the semiempirical AM1 method [21]. The results are discussed on the basis of the available experimental data, with the aim of providing a better insight into this potentially useful reaction.

RESULTS AND DISCUSSION

Calculations were made for the following allylamines: Allylmethylamine **1**, diallylamine **2**, allylcyanomethylamine **3**, and cyanomethyldiallylamine, in which case two ways, **4** and **5**, for the elimination are possible (Figure 2). The computed transition structures were confirmed by the presence of only one negative eigenvalue in the hessian matrix.

In Table 1 are reported the calculated total energies (kJ/mol) for the reactants and the transition states, the computed activation energies for the chosen allylamines, and the experimental observed values. It can be seen that the calculations overestimate the activation energies by a factor of about 2.16. Using this as a scaling factor, one can consider that the corrected activation energies obtained by these calculations reproduce the experimental values with the accuracy expected for this method [21] (±25 kJ/mol).



Amine	R	R′
1	H	H
2	H	CH=CH$_2$
3	H	CN
4	CH$_2$CN	CH=CH$_2$
5	CH$_2$CH=CH$_2$	CN

FIGURE 2

In Tables 2 and 3 are listed, respectively, selected bond lengths and bond angles of the computed transition structures, for atoms directly involved in the transition state, as represented in Figure 3. No remarkable geometrical differences are observed among the amines. One can observe analogies with reported values for bond lengths and bond angles obtained by ab initio calculations for the ene reactions of ethylene with formaldehyde and propene [17,18]. The C–C bond lengths for the propene moiety show almost the same value, 1.41 Å, intermediate between a single and a double bond (average values are 1.34 and 1.54 Å for these types of bonds). The C3–N4 and C5–H6 bonds to be broken are considerably stretched, 1.73 Å and more than 1.55 Å, respectively, instead of the normal values of 1.47 and 1.10 Å. In this way, the N4–C5 bond about to become double presents an average value of 1.37 Å, intermediate between 1.47 and 1.28 Å, for single and double bonds, respectively.

A large difference, however, is observed between the C1H6C5 angle of the migrating hydrogen, around 116° by our calculations, and the reported 156° for the ene reaction [17–20].

The transition structure resembles somewhat a half chair or a flattened boat, Figure 3. C3, N4, C5, H6, and C1 atoms are nearly in a plane, with the C5 carbon atom slightly out of the plane, and C1, C2, and C3 being located in another plane. C1 and C3 atoms of the propene moiety, to be eliminated during the reaction, show a geometry intermediate between the characteristic sp^2 and sp^3 hybridization geometries, pointing out the changes in the hybridization of these atoms during the reaction. In this way, the hydrogen atom to be transferred from C5 to C1 is located at almost the same distance (2.0 and 2.28 Å) from the other two hydrogen atoms on the C1 atom, in order to improve the orbital overlap between the *s*-H6 and the *p*-C1 orbitals. The same behavior is observed in the nitrogen atom, which, in order to maintain optimum orbital overlap in the transition state, is located nearly opposite the C3 carbon atom. Both C3 and N4 atoms, changing their hybridization states from sp^3 to sp^2, show a geometry intermediate between these two states. These facts explain the geometry of the transition state. It seemed possible to have a more marked "chairlike" transition state; nevertheless, we were unable to locate such a minimum

TABLE 1 Computed Activation Energies for Propene Elimination in kJ/mol[a]

R	*R′*	*E(gs)*[b]	*E(ts)*[c]	*Ea*[d]	*Ea(corr)*[e]	*Eexp*[f]
H	H	−80964.88	−80571.98	392.9	182	182
H	$CH=CH_2$	−108155.75	−107764.96	390.8	181.0	155 + 1
H	CN	−111758.73	−111356.15	402.6	186.5	189 + 5
CH_2CN	$CH=CH_2$	−153874.10	−153420.70	453.4	209.8	183 + 3
$CH_2CH=CH_2$	CN	−153874.10	−153417.06	457.0	211.7	—

[a] Reaction stoichiometry as in Figure 2.
[b] Total energy in the ground state.
[c] Total energy in the transition state.
[d] Calculated activation energy.
[e] Corrected activation energy = *Ea*/2.16.
[f] Experimental activation energy.

TABLE 2 Selected Bond Lengths in the Transition State (Å)[a]

R	*R′*	*C1–C2*	*C2–C3*	*C3–N4*	*N4–C5*	*C5–H6*	*H6–C1*
H	H	1.40	1.41	1.73	1.36	1.53	1.78
H	$CH=CH_2$	1.40	1.42	1.73	1.37	1.63	1.62
H	CN	1.43	1.42	1.73	1.37	1.54	1.78
CH_2CN	$CH=CH_2$	1.41	1.42	1.73	1.37	1.65	1.63
$CH_2CH=CH_2$	CN	1.41	1.42	1.73	1.35	1.65	1.63

[a] Reaction stoichiometry as in Figure 2. Atom number as in Figure 3.

TABLE 3 Selected Angles in the Transition State (deg)[a]

R	*R′*	*C1C2C3*	*C2C3N4*	*C3N4C5*	*N4C5H6*	*C5H6C1*	*H6C1C2*
H	H	123.9	103.3	103.9	127.8	115.1	91.8
H	$CH=CH_2$	123.4	102.7	104.2	130.5	116.8	92.4
H	CN	123.8	103.3	103.9	127.9	114.9	91.8
CH_2CN	$CH=CH_2$	123.4	103.0	104.2	130.2	116.9	92.4
$CH_2CH=CH_2$	CN	123.1	102.6	104.2	129.1	115.9	92.4

[a] Reaction stoichiometry as in Figure 2. Atom number as in Figure 3.

energy transition state on the potential energy surface considered.

Some results of studies of the substituent effects on the kinetics of these reactions are summarized in Table 4. It can be observed that the activation energies and log A are within the ranges 165 ± 30 $kJ \cdot mol^{-1}$ and 11.5 ± 1, respectively; the latter is in the usual range for reactions having a six center transition state. Important differences are observed in the rate coefficients of the reactions. In columns 5 and 6 of Table 4 are shown the rate coefficients relative to diallylamine, at 420°C and 470°C, respectively. The substituent effects can be summarized as (a) donor substituents on the nitrogen atom (entries 6, 9, 13, and 14) accelerate the reaction, (b) electron deficient substituents on the nitrogen atom (entries 2, 7, 8, 10, and 11) decelerate the reaction, and (c)

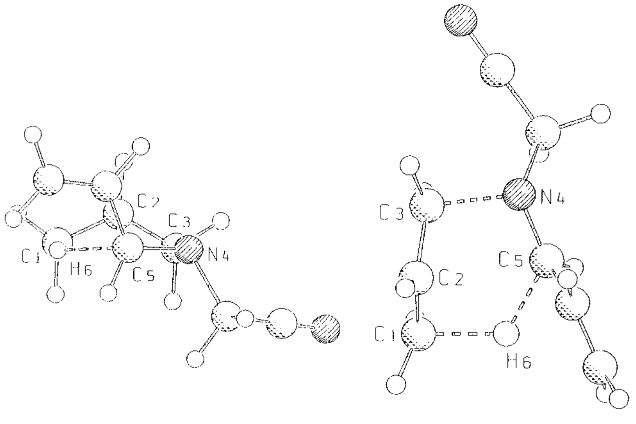


FIGURE 3 Views of computed transition-state geometry for propene elimination from cyanomethyldiallylamine *4*.

TABLE 4 Kinetic Parameters for Propene Elimination in Allyamines

Entry	*Reactant*	*Ea*[a]	*log A*	$k_{420}{}^{b}$	$k_{470}{}^{b}$	*Ref.*
1	$CH_3NHCH_2CH{=}CH_2$	182	11.4	0.03	0.04	9
2	$(CH_2{=}CH–CH_2)_2NCH_2CN$	183 ± 3	13.00 ± 0.20	0.72	0.97	11
3	$CH_2{=}CH–CH_2NHCH_2CN$	189 ± 5	13.29 ± 0.35	0.98	1.46	11
4	$(CH_2{=}CH–CH_2)_2NH$	155 ± 1	11.04 ± 0.13	1	1	9
5	$CH_2{=}CHCH_2NHCH_2C{=}CH$	134 ± 5	9.36 ± 0.37	1.61	1.26	12
6	$CH_2{=}CH–CH_2N(CH_2SCH_3)CH_2C{=}CH$	180 ± 4	12.92 ± 0.34	1.93	2.66	12
7	$CH_2{=}CH–CH_2N(SO_2CH_3)–CH_{2\,-}C\equiv CH$	182 ± 5	12.11 ± 0.32	0.13	0.22	12
8	$CH_2{=}CHCH_2N(SO_2C_6H_{4-p}–CH3)CH_2C\equiv CH$	197 ± 5	12.66 ± 0.37	0.03	0.07	22
9	$CH_2{=}CH–CH_2N(t\text{-}C_4H_9)–CH_2C\equiv CH$	131 ± 3	9.72 ± 0.23	3.8	3.7	22
10	$CH_2{=}CH–CH_2N[C_6–H_5]–CH_{2\,-}C\equiv CH$	149 ± 8	10.44 ± 0.65	0.80	0.95	22
11	$CH_2{=}CH–CH_2N(CH_2–CN)–CH_{2\,-}C\equiv CH$	145 ± 4	9.77 ± 0.34	0.38	0.43	12
12	$(CH_2{=}CH–CH_2)_3N$	160 ± 1	11.74 ± 0.07	1.4	1.5	10
13	$t\text{-}C_4H_9N(CH_2–CH{=}CH_2)_2$	139 ± 2	10.32 ± 0.12	3.2	2.5	22
14	$(CH_3)_3CCH_2N(CH_2–CH{=}CH_2)_2$	168 ± 3	12.87 ± 0.26	7.2	8.2	22
15	$c\text{-}C_6H_{11}–NH–CH_2–CH{=}CH_2$	181 ± 2	11.44 ± 0.21	0.11	0.15	23

[a] $kJ \cdot mol^{-1}$.

[b] Rate coefficients, per α-H atom, relative to diallylamine, calculated at 420°C and 470°C.

TABLE 5 Atomic Charge Variation in the Transition State

	1[a]		*2*[a]		*3*[a]		*4*[a]		*5*[a]	
Atom	*q(ts)*[b]	δ[c]	*q(ts)*[b]	δ[c]	*q(ts)*[b]	δ[c]	*q(ts)*[b]	δ[c]	*q(ts)*[b]	δ[c]
C1	−0.212	0.016	−0.207	0.020	−0.231	−0.013	−0.200	0.020	−0.210	0.009
C2	−0.183	−0.025	−0.187	−0.028	−0.159	0.011	−0.190	−0.026	−0.173	−0.003
C3	−0.124	−0.076	−0.130	−0.082	−0.123	−0.076	−0.119	−0.071	−0.123	−0.077
N4	−0.207	0.096	−0.199	0.100	−0.196	0.100	−0.106	0.145	−0.116	0.134
C5	−0.248	−0.121	−0.194	−0.140	−0.148	−0.160	−0.221	−0.175	−0.166	−0.184
H6	0.056	−0.032	0.110	0.008	0.122	−0.005	0.111	−0.002	0.123	−0.006

[a] Reactant number as in Figure 2.

[b] Atom charge in transition state.

[c] Transition state–ground state charge difference.

the more acidic the migrating hydrogen is, the faster the reaction proceeds.

In Table 5 are listed the atomic charges, $q(ts)$, developed on atoms that participate directly in the transition state, and the respective differences, δ, with atomic charges in the ground state. It can be seen that the calculations are consistent with the above experimental observations; i.e., (a) the N4 nitrogen atom is less negative in the transition state than in the ground state; thus the reaction is favored by electron-donor substituents on the N4 atom, and less favored when the substituents are not electron donors; (b) as a minor effect, the acidic character of the migrating H6 hydrogen atom in the ground state is slightly compensated in the transition state by the orbital overlap with the C1 carbon atom, which become less negative. Inexplainably, for allyl(cyanomethyl)amine **3**, an increase of the atomic charge of the C1 atom is observed. In this case, the electron deficiency created on the C1 carbon atom by the orbital overlap with the H6 hydrogen atom is compensated by an electron density transfer from the C2 atom to the C1 carbon atom.

These changes in the atomic charges, when going from ground state to transition state, suggest a polar character for the transition state of these retroene reactions of allylamines.

Further calculations on other heteroatomic allyl systems, as phosphines and sulfides, are currently being carried out in order to provide more information on the factors influencing the outcome and kinetics of these reactions.

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