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KINETIC STUDY OF A HOMODIENYL-[1,5]-HYDROGEN SHIFT IN A VINYLZAZIRIDINE

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The thermal rearrangement of an *N*-substituted vinylaziridine to the corresponding (*Z*)-allylic imine, i.e. a homodienyl-[1,5]-hydrogen shift, was studied at different temperatures in the range 40–90 °C. ^{1}H NMR spectroscopy was used to follow the reaction. Rate constants and activation parameters were determined in solvents that differ in polarity, namely 1,4-dimethylbenzene, 1,2-dichlorobenzene and dimethylformamide (DMF). The activation enthalpies and entropies obtained clearly indicate that the solvent polarity has little influence on the rearrangement, since these values are almost the same in the three solvents used. The low $\Delta H^{\ddagger}$ values (89, 84 and 91 kJ mol^{-1}, respectively) are consistent with a concerted mechanism, while the activation entropies are all small and negative, which is also supportive of a cyclic transition state. The rate constant is slightly higher in the most polar of the solvents used, DMF.

Since its discovery by Radlick and Winstein,[1] the retro-ene reaction in vinycyclopropanes, also known as the homodienyl-[1,5]-hydrogen shift, to yield the corresponding (*Z*)-hexa-1,4-dienes has received interest from both synthetic and theoretical perspectives.[2] In an early review of this process, a transition structure was proposed in which the vinyl moiety adopts an *endo* conformation, projecting over the three-membered ring, thus accounting for the stereochemical outcome.[3] Later, it was suggested that the conformational preference of the alkenyl group was due to orbital overlap factors[4] and this was recently supported by *ab initio* quantum mechanical calculations on the rearrangement.[5] In contrast, the corresponding rearrangement in vinylaziridines has received considerably less attention, with only a few examples being documented previously.[2a,6] In connection with an ongoing study of the aza-[2,3]-Wittig rearrangement of these substrates, we recently showed that properly functionalized vinylaziridines **1** are excellent substrates for the homodienyl-[1,5]-hydrogen shift, yielding the corresponding (*Z*)-allylic imines **2** in quantitative yield (Scheme 1). The stereochemical outcome of these reactions was rationalized by invoking transition structure **3** (which is analogous to that discussed in the vinylcyclopropane series) and, based solely on steric interactions in **3**, the imine moiety in product **2** was assigned to have *E* stereochemistry.[7] In a subsequent study of this rearrangement, we also demonstrated that substituents on both the rearrangement origin and terminus have, for steric or electronic reasons, a marked influence on the reaction rate and the stereochemistry of the imine moiety in **2**.[8]

In order to gain a more thorough understanding of the homodienyl-[1,5]-hydrogen shift in vinylaziridines, we have undertaken the first kinetic investigation of the process and present the results in this paper. The substrate used in this study, aziridine **1a**, was judged to be ideal since it is easily prepared and exists as a single nitrogen invertomer, thus simplifying the kinetic interpretations.[9] The activation enthalpy and entropy for the rearrangement were measured in three solvents in order to study the influence of the solvent and to provide information about the process.

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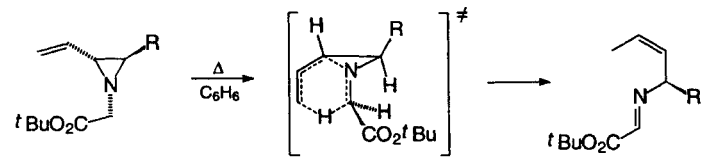


1a R = *t*Bu **3** **2**

Scheme 1

The synthesis of vinylaziridine **1a** has been described.[9,10] The thermal rearrangement of **1a** to the product imine **2** was followed by ^{1}H NMR spectroscopy at 400 MHz. According to the ^{1}H NMR spectra of the equilibrated kinetic solutions, the only product formed was the imine **2**, and no remaining reactant was detected. The kinetic experiments were performed in three solvents, namely 1,4-dimethylbenzene (*p*-xylene), 1,2-dichlorobenzene (*o*-DCB) and dimethylformamide (DMF). The solvents were mainly chosen for having different polarites ($\varepsilon = 2{\cdot}27$, 9·93 and 36·7, respectively)[11], for being commercially available in their deuterated forms and for having high boiling points, making it possible to perform the kinetics using relatively wide temperature ranges.

The reaction follows first order kinetics, which were monitored by measuring the integrals of the *tert*-butyl group on the ester, which appeared at different shifts in the substrate and in the product. The integrals from the disappearing CH_2 group in the substrate and from the forming CH_3 group in the product were also used. The results of the kinetic experiments are given in Tables 1 and 2. The observed rate constants in Table 1 are averages from two or three kinetic runs, and were calculated by least-squares fitting of the experimental data. The activation energy and the logarithm of the pre-exponential factor (ln *A*) were obtained by least-squares fitting of ln *k* versus $1/T$. The correlation coefficient was > 0·999 in all cases.

Table 1. First-order rate constants for the thermal rearrangement of vinylaziridine[a] **1a** in the deuterated solvents *p*-xylene, *o*-DCB and DMF

Temperature (°C)	k^b (10^{-6} s^{-1})		
	p-Xylene	*o*-DCB	DMF
40	6·30 (8)	7·59 (3)	11·30 (2)
50	16·8 (1)	18·5 (1)	30·57 (4)
60	54·1 (5)	52·8 (5)	86·0 (2)
70	132 (1)	140 (1)	270 (1)
80	310 (4)	287 (5)	663 (5)
90	818 (14)	770 (9)	1456 (18)

[a] The substrate concentration was 0·03–0·06 M.
[b] Error limits, given in parentheses, are estimates of the maximum error and are based on the standard deviations.

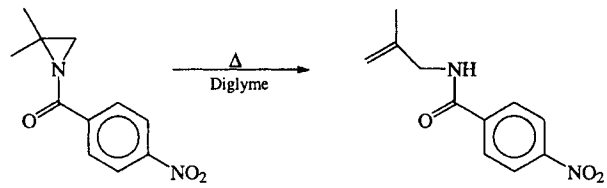
Thermal ring fission of a vinylcyclopropane unit is believed to occur by any of three mechanisms: a [1,5] sigmatropic hydrogen shift, a $[2\sigma_s + 2\pi_s]$ concerted reorganization to cyclopentene or a diradical fission followed by further reactions of the diradicals. Under certain conditions, the [1,5] sigmatropic shift of hydrogen, from an alkyl group oriented *cis* to the vinyl group, is the lowest energy pathway available for a vinylcyclopropane. This rearrangement usually proceeds with an activation energy of 125–146 kJ mol^{-1} (30–35 kcal mol^{-1}).[2a,12]

Vinylaziridines are subject to a number of rearrangements that parallel the pathways available to vinylcyclopropanes. Much of the thermal and photochemical behaviour of vinylaziridines has been rationalized by invoking either diradical or zwitterionic (azomethine ylid) intermediates.[2a,6ad,13] The examples found in the literature of the concerted homodienyl-[1,5]-hydrogen shift upon thermolysis of *N*-substituted vinylaziridines have in most cases been characterized by stereospecificity.[6d,7,8,13] In an early study, the kinetics of an analogous thermal isomerization of 1-*p*-nitrobenzoyl-2,2-dimethylaziridine, in the solvent diglyme, was

Table 2. Activation parameters for the thermal rearrangement of vinylaziridine **1a**

Solvent	ε	ln A^a	E_a^a (kJ mol^{-1})	$\Delta H^{\ddagger b}$		$\Delta S^{\ddagger b}$	
				kJ mol^{-1}	kcal mol^{-1}	J mol^{-1} K^{-1}	cal mol^{-1} K^{-1}
p-Xylene	2·27	23·2 (6)	92 (2)	89	21	−53	−13
o-DCB	9·93	21·6 (7)	87 (2)	84	20	−66	−16
DMF	36·7	24·5 (6)	94 (2)	91	22	−42	−10

[a] Error limits, given in parantheses, are standard deviations.
[b] The activation enthalpy and entropy were calculated from the relations $\Delta H^{\ddagger} = E_a - RT$ and $\ln A = \Delta S^{\ddagger}/R + \ln(kT/h)$, respectively, at the median temperature (338 K) in the temperature interval used.



E_a= 105 kJ·mol^{-1} (25.2 kcal·mol^{-1}) and ΔS^{*}= -43.5 J·mol^{-1}·K^{-1} (-10.4 cal·mol^{-1}·K^{-1})

Scheme 2.

reported (see Scheme 2).[14] To the best of our knowledge, no determinations of activation parameters have been reported since then for this type of rearrangement.

The activation enthalpies and entropies, shown in Table 2, are of the same magnitude as those obtained for the benzoylaziridine transformation. The values clearly indicate that the solvent polarity has little influence on the thermal rearrangement of vinylaziridine **1a**, since they are almost the same in the three solvents used. The low ΔH^{*} values are consistent with a concerted mechanism, where bond formation compensates for bond breaking when passing from the reactant molecule to the activated complex.

The size of ΔS^{*} depends mainly on the change in translational and rotational freedom when the reactants change to the activated complex. If the reaction passes through a cyclic transition state, as in a [1,5] sigmatropic hydrogen shift, there will be a hindrance to certain internal rotations (torsions) and such reactions usually show a small negative ΔS^{*} value. For the isomerization of vinlyaziridine **1a**, the observed activation entropies are small and negative (see Table 2), and they are of the same size as those reported for comparable reactions of vinylcyclopropanes.

The observed rate constants (see Table 1) are almost the same in *p*-xylene and *o*-DCB, but about twice as high in DMF, the most polar of the solvents used. In view of the activation parameters determined, this seems to be an effect of the activation entropy rather than the enthalpy, although the values are similar in the different solvents. If the reaction is concerted but not synchronous, then bond changes occur within a single elementary step but do not keep in time with each other. As a result, the activated complex will be more polar than the reactant molecule and will have a higher demand for solvation. The value of ΔS^{*} in a polar solvent is usually a smaller negative number than in an apolar solvent. In the latter case, the formation of a solvation shell represents an appreciable increase in ordering, whereas a polar solvent is already well ordered and no marked change will take place for solvation. For this reason, to reach the transition state in apolar solvents, the entropy must decrease more than it does in polar solvents.

To summarize, the kinetic results presented here are consistent and support a concerted homodienyl-[1,5]-hydrogen shift mechanism, as earlier proposed for stereochemical reasons. The slightly higher reaction rate observed in the most polar of the solvents used, DMF, may indicate a transition state possessing some charge separation owing to a time lag between the bond-forming and bond-breaking processes.

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