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Diaziridines thermal cleavage possibilities: Disrotatory or conrotatory?

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Abstract

Ab initio calculations are carried out at UB3LYP/6-311++G (3df, 2p) levels of theory, on electrocyclic thermal cleavage of four (*S*) derivatives of diaziridines, $\mathbf{1}_{\mathbf{X}\text{-}\boldsymbol{R}}$, to their corresponding (*Z*) and (*E*) azomethine imides ($\mathbf{2}_{\mathbf{X}\text{-}\boldsymbol{Z}}$, $\mathbf{2}_{\mathbf{X}\text{-}\boldsymbol{E}}$, $\mathbf{3}_{\mathbf{X}\text{-}\boldsymbol{Z}}$ and $\mathbf{3}_{\mathbf{X}\text{-}\boldsymbol{E}}$), where X=–H, –Me, *t*-Bu and Ph. Cleavage of $\mathbf{1}_{\mathbf{X}\text{-}\boldsymbol{R}}$ Series to $\mathbf{2}_{\mathbf{X}\text{-}\boldsymbol{Z}}$ (Path 1) emerged as the more favored, for producing the most stable products, $\mathbf{2}_{\mathbf{X}\text{-}\boldsymbol{Z}}$. In IRC calculations that were shown in Paths 1 and 2, C_6–N_1 bond was cleavage, before reaching reaction rate determinating step (transition state).

Keywords: Diaziridines; Azomethine imides; Electrocyclic; Thermal cleavage; Conrotatory; IRC

1. Introduction

Two recent papers absorb our attention [1,2]. In first paper, was reported that bicyclic allyl anion obtained at room temperature by rearrangement of tri-cyclic anion, in a forbidden disrotatory process (Scheme 1). Later paper supposed an initial conrotatory motion is therefore proposed to operate in the ring opening of the cyclopropyl anion. When the change in the sense of this rotation comes to pass; the system has already crossed the transition state. In contrast to bicyclic allyl anion that has only one possible product, we select diaziridines that has two possible products via four paths. Our results confirm that in both reaction paths (Paths 1 and 2), before reaching transition state (detrminating reaction rate), C–N_1 bond cleavage.

The opportunity of pericyclic reactions commonly can be established, consistent with the Woodward–Hoffmann rules. For thermally electrocyclic reactions wherein a ring is opened (or formed), systems having odd- and even-numbered electron are predicted to endure disrotatory or conrotatory movements, respectively [1].

Azomethine imides are the product of cleavage of diaziridines and in 1,3-dipolar cycloadditions with dipolarophiles produce five memberd rings [3,4]. Diaziridines react with alkenes to give *N*-unprotected aziridines directly [5]. Halogenated diazirines are applied as: photolabel mimics of the inhaled haloalkane anesthetics, potential one-heteroatom transfer agents to olefins, and precursor of carbene synthesis [6–8].

In an electrocyclic ring opening process, heating cleavages diaziridines: (6*R*)-X-1,5-diazabicyclo [3.1.0]hexan-2-one ($\mathbf{1}_{\mathbf{X}\text{-}\boldsymbol{R}}$ and/or $\mathbf{1}_{\mathbf{X}\text{-}\boldsymbol{S}}$; where X=H, methyl, *t*-butyl and phenyl), to their corresponding azomethine imides: (*Z*) and (*E*) isomers of 1-(Y)-pyrazolidin-3-one: $\mathbf{2}_{\mathbf{X}\text{-}\boldsymbol{Z}}$, $\mathbf{2}_{\mathbf{X}\text{-}\boldsymbol{E}}$ (where, Y=methylene; ethylidene; 2,2-dimethylproplidene and benzylidene). Although formation of $\mathbf{3}_{\mathbf{X}\text{-}\boldsymbol{Z}}$ and $\mathbf{3}_{\mathbf{X}\text{-}\boldsymbol{E}}$ are possible, here we will show their formation is not favored thermodynamically.

2. Computational methods

Using GAUSSIAN 98 system of programs [9] with basis set of McGrath, Curtiss included the diffuse functions (6-311++G (3df, 2p)) through density functional theory (UB3LYP) was selected, with the Becke three-parameter exchange functional [10,11] and the nonlocal correlation functional of Lee, Yang, and Parr for obtaining more accurate values of structures and energies [12]. DFT are selected among all methods, because it is less common to find any significant spin contamination in DFT calculations, even when unrestricted Kohn-Sham orbitals are used. In our DFT calculations, all of the $\langle S^2\rangle$[1] values, before

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[1] Spin contamination negligible if the value of $<S^2>$ differ from $(s+1)$ by less than 10%. Molecules studied in this manuscript have singlet multiplicity thus their $s(s+1)=0(0+1)=0$

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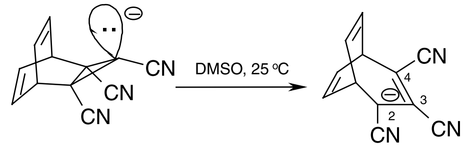

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Scheme 1. Rearrangement of cyclopropyl anions fused to bicyclic structures [2].

and after annihilation step are equal to 0.00 and 0.00, respectively.

In order to find transition states, Keyword 'QST3' are used. Also reaction path are followed by IRC to confirm transition states related to corresponding minimums [13,14]. Frequency calculations are carried out for determination of thermodynamic properties of stationary species. For minimum state structures, only real frequency values and for transition state structures one imaginary frequency values are accepted [15].

3. Result and discussion

Thermodynamic data are calculated at UB3LYP/6-311++G (3df, 2p) levels of theory for $\mathbf{1}_{\mathbf{X}\text{-}\boldsymbol{R}}$, $\mathbf{1}_{\mathbf{X}\text{-}\boldsymbol{S}}$, $\mathbf{2}_{\mathbf{X}\text{-}\boldsymbol{E}}$, $\mathbf{2}_{\mathbf{X}\text{-}\boldsymbol{Z}}$, $\mathbf{3}_{\mathbf{X}\text{-}\boldsymbol{E}}$, and $\mathbf{3}_{\mathbf{X}\text{-}\boldsymbol{Z}}$ (Table 1, Fig. 1). These data include: sum of electronic and thermal energies (E), sum of electronic and thermal enthalpies (H), sum of electronic and thermal Gibbs free energies (G) for all of the ground state as well as their corresponding transition states (TS) which are obtained by the FREQUENCY option of the GAUSSIAN 98 program.

Using the above data changes of activation electronic energies ($\Delta E^{\#}$); enthalpies of activation ($\Delta H^{\#}$) and Gibbs activation free energies ($\Delta G^{\#}$) are calculated for Paths 1 and 2 (Table 2).

Relative energies (E_{r}), enthalpies (H_{r}) and free energies (G_{r}) for all substituents (X) are presented in Table 3. This Table facilitates comparisons between ground states within Series. It is subdivided into boxes. Each box represents relative E_{r}, H_{r} and G_{r} values corresponding to a specific substituent (X).

Table 1
Calculated UB3LYP/6-311++G (3df, 2p) data, showing: sum of electronic and thermal energies (E), sum of electronic and thermal enthalpies (H), sum of electronic and thermal Gibbs free energies (G) along with zero-point vibrational energies (ZPVE) for $\mathbf{1}_{\mathbf{X}\text{-}\boldsymbol{R}}$, $\mathbf{1}_{\mathbf{X}\text{-}\boldsymbol{S}}$, $\mathbf{2}_{\mathbf{X}\text{-}\boldsymbol{Z}}$, $\mathbf{2}_{\mathbf{X}\text{-}\boldsymbol{E}}$, $\mathbf{3}_{\mathbf{X}\text{-}\boldsymbol{Z}}$ and $\mathbf{3}_{\mathbf{X}\text{-}\boldsymbol{E}}$ (where X = H, methyl, *t*-butyl and phenyl) together with transition states (Ts) of Paths 1 and 2

Substituent X	Structures	*E*	*H*	*G*	ZPVE
H	$\mathbf{3}_{\mathrm{H}}$	−340.67149	−340.67055	−340.7065	63.210
	$\mathbf{1}_{\mathrm{H}}$	−340.66746	−340.66652	−340.70282	64.359
	$\mathbf{2}_{\mathrm{H}}$	−340.69711	−340.69616	−340.73435	64.268
	TS path 1	−340.61267	−340.61173	−340.64805	62.702
	TS path 2	−340.61573	−340.61478	−340.65095	62.722
Me	$\mathbf{1}_{\mathrm{Me}\text{-}R}$	−379.97318	−379.97223	−380.01217	81.658
	$\mathbf{1}_{\mathrm{Me}\text{-}S}$	−379.96594	−379.96499	−380.00456	81.895
	$\mathbf{2}_{\mathrm{Me}\text{-}E}$	−379.99819	−379.99724	−380.03703	81.521
	$\mathbf{2}_{\mathrm{Me}\text{-}Z}$	−380.00239	−380.00145	−380.04447	81.729
	$\mathbf{3}_{\mathrm{Me}\text{-}E}$	−379.96453	−379.96358	−380.00456	80.995
	$\mathbf{3}_{\mathrm{Me}\text{-}Z}$	−379.97553	−379.97458	−380.01556	80.112
	TS($\mathbf{1}_{\mathrm{Me}\text{-}R}$ to $\mathbf{2}_{\mathrm{Me}\text{-}Z}$) path 1	−379.9247	−379.92376	−379.96339	80.086
	TS($\mathbf{1}_{\mathrm{Me}\text{-}R}$ to $\mathbf{2}_{\mathrm{Me}\text{-}E}$) path 2	−379.92365	−379.92271	−379.96248	80.001
t-Bu	$\mathbf{1}_{t\text{-}\mathrm{Bu}\text{-}R}$	−497.85938	−497.85843	−497.90773	134.206
	$\mathbf{1}_{t\text{-}\mathrm{Bu}\text{-}S}$	−497.84088	−497.85843	−497.88973	133.8
	$\mathbf{2}_{t\text{-}\mathrm{Bu}\text{-}E}$	−497.87477	−497.87382	−497.9236	134.715
	$\mathbf{2}_{t\text{-}\mathrm{Bu}\text{-}Z}$	−497.88464	−497.8837	−497.93471	134.629
	$\mathbf{3}_{t\text{-}\mathrm{Bu}\text{-}E}$	−497.84095	−497.84095	−497.88945	133.78
	$\mathbf{3}_{t\text{-}\mathrm{Bu}\text{-}Z}$	−497.85727	−497.85632	−497.90608	133.809
	TS($\mathbf{1}_{t\text{-}\mathrm{Bu}\text{-}R}$ to $\mathbf{2}_{t\text{-}\mathrm{Bu}\text{-}Z}$) path 1	−497.81036	−497.80942	−497.85831	132.811
	TS($\mathbf{1}_{t\text{-}\mathrm{Bu}\text{-}R}$ to $\mathbf{2}_{t\text{-}\mathrm{Bu}\text{-}E}$) path 2	−497.80916	−497.80822	−497.85758	132.811
Ph	$\mathbf{1}_{\mathrm{Ph}\text{-}\boldsymbol{R}}$	−571.69791	−571.69696	−571.74576	114.78
	$\mathbf{1}_{\mathrm{Ph}\text{-}\boldsymbol{S}}$	−571.68863	−571.68769	−571.7357	115
	$\mathbf{2}_{\mathrm{Ph}\text{-}\boldsymbol{E}}$	−571.72503	−571.72408	−571.77323	115.473
	$\mathbf{2}_{\mathrm{Ph}\text{-}\boldsymbol{Z}}$	−571.73355	−571.73261	−571.78293	115.342
	$\mathbf{3}_{\mathrm{Ph}\text{-}\boldsymbol{E}}$	−571.69203	−571.69109	−571.74028	114.252
	$\mathbf{3}_{\mathrm{Ph}\text{-}\boldsymbol{Z}}$	−571.70483	−571.70359	−571.75727	114.252
	TS($\mathbf{1}_{\mathrm{Ph}\text{-}R}$ to $\mathbf{2}_{\mathrm{Ph}\text{-}z}$) path 1	−571.65716	−571.65621	−571.70406	113.507
	TS($\mathbf{1}_{\mathrm{Ph}\text{-}R}$ to $\mathbf{2}_{\mathrm{Ph}\text{-}E}$) path 2	−571.66275	−571.6618	−571.70933	113.703