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A B3LYP/6-31G(d) study of Diels-Alder reactions between cyclopentadiene and (*E*)-2-arylnitroethenes†

Research Article

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Abstract: The B3LYP/6-31G(d) simulations of competing CDA and HDA reactions between cyclopentadiene and (E)-2-arylnitroethenes prove that regardless of the medium polarity, the processes leading to respective 5-nitro-6-aryl-bicyclo-[2,2,0]-hept-2-enes **3**,**4** (paths **A** and **B**) should be most favoured, and the more electrophilic (E)-2-(p-nitrophenyl)-nitroethene should be more reactive than the less electrophilic (E)-2-(p-methoxyphenyl)-nitroethene. Asymmetry of the transition complexes on the favoured pathways increases with increase of medium polarity, but not sufficiently to enforce the zwitterionic mechanism. Analysis of competing pathways leading to HDA adducts proves that not all these compounds can be formed directly from the adducts. In particular, on the path **C**, the initially formed 5-nitro-6-aryl-bicyclo-[2,2,0]-hept-2-enes **3** is converted to 2-phenyl-4-aza-5-oxy-bicyclo-[3,4,0]-nona-3,7-diene N-oxides **5** as a result of a [3.3]-sigmatropic shift. On the paths **D-F** leading to 2-phenyl-4-aza-5-oxy-bicyclo-[3,4,0]-nonadienes N-oxides **6-8**, the reaction proceeds according to a one-step mechanism.

Keywords: *Diels-Alder reaction • Nitroalkene • Cyclopentadiene • B3LYP/6-31G(d) • Mechanism*

1. Introduction

This work is intended as a continuation of our study related to reactivity of conjugated nitroalkenes in Diels-Alder (DA) reactions [2-7]. It is well known [3,4,7-13] that conjugated nitroalkenes can function both as dienophiles and heterodienes in DA reactions. Therefore, in the products of the reaction between cyclopentadiene **1** and (*E*)-2-arylnitroethenes **2a-g,** tested by us recently [2], we expected both *carbo*-Diels-Alder (CDA) and *hetero*-Diels-Alder (HDA) cycloadducts (Scheme 1). Detailed analysis of the post-reaction mixtures [2] confirmed that regardless of the nature of the substituent (R) in the phenyl ring of nitroalkene, this reaction proceeded exclusively according to the CDA scheme (paths **A** and **B**), resulting in a mixture of the respective 5-*endo*-nitro-6-*exo*-aryl-bicyclo-[2,2,0]-hept-2-enes **3a-g** and 5-*exo*-nitro-6-*endo*-aryl-bicyclo-[2,2,0]-hept-2-enes **4a-g,** in a ratio of 2.5-5.3:1. Additionally, by means of kinetic measurements [2] it was established that reactivity of nitroalkenes in the reactions studied increased with increase of their electrophilicity, which according to *Domingo* terminology [14] quantified index ω.

The aim of this work was a quantum-chemical analysis intended to understand the role and reactivity of the nitroalkenes **2a-g** in DA reactions with the diene **1**. The reaction paths **A-F** (shown in Scheme 1) for pairs of substrates with the largest (**1**+**2a,** Δω=2.87eV) and smallest (**1**+**2g**, Δω=1.59eV) difference in electrophilicity [2] were simulated. To shed light on the role of the dielectric medium on the reaction course the simulations were performed for three solvents with different polarity. Recently [7], we have adopted a similar approach to explain the role and reactivity of E-2-phenyl-1-cyanonitroethene in the DA reaction with cyclopentadiene. These experiments showed a good correlation between theoretical and experimental data [5,7].

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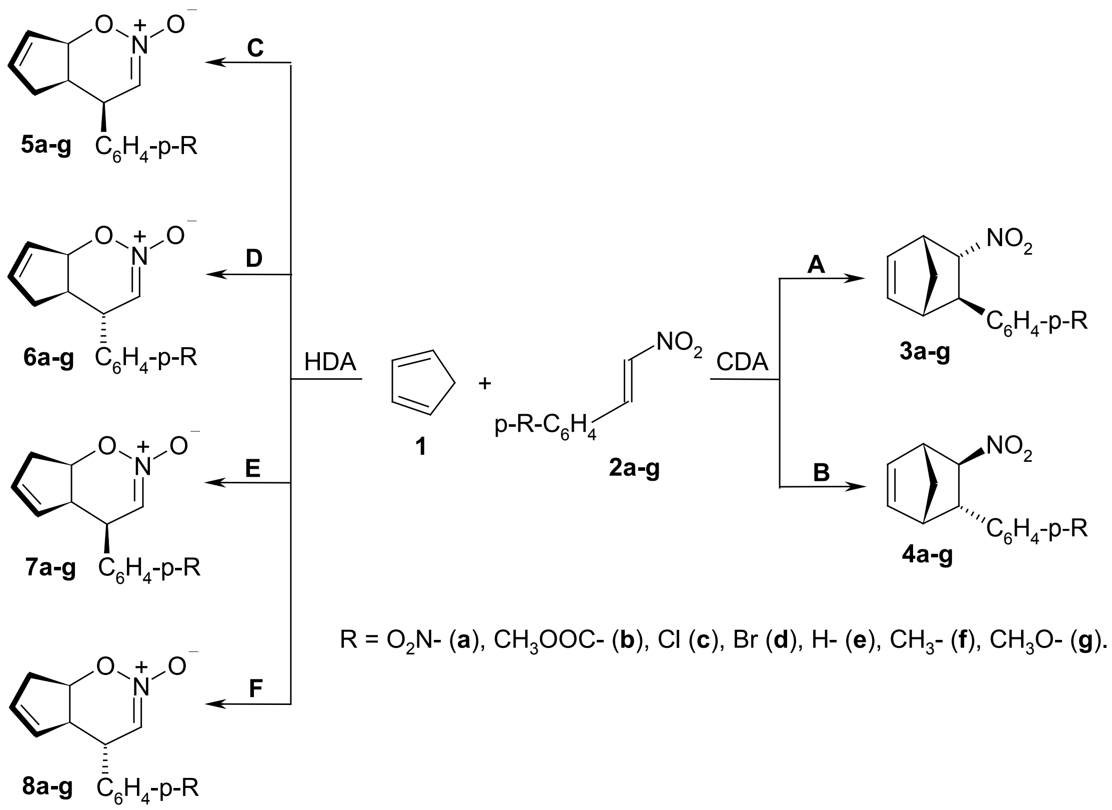
† *Part 8 of the series 'Conjugated Nitroalkenes in Cycloaddition Reactions'; Part 7 see Ref. [1].*



Scheme 1. Theoretically possible reaction paths of cyclopentadiene with (E)-2-arylnitroethenes.

2. Computational procedure

All calculations were carried out on a SGI-Altix 3700 computer in the regional computational centre CYFRONET in Cracow. The B3LYP functional with 6-31G(d) basis set included in the GAUSSIAN 03 program package [15] was applied.

The critical points on the potential energy surface (PES) were localized in an analogous manner as in the case of the previously analyzed DA reaction of cyclopentadiene with (*E*)-2-phenyl-1-cyanonitroethene [7]. In particular, for the simulation of the solvent effect on the reaction paths, the polarisable continuum model (PCM) of *Tomasi's* group [16] with full geometry optimizations was applied. The reaction path simulations were performed taking into account toluene (ε=2.38), acetone (ε=20.70), and water (ε=78.39) as the dielectric medium. For structure optimization of the reactants and the reaction products the *Berny* algorithm [17] was applied. First-order saddle points were localized using the QST2 procedure. The transition states were verified by diagonalization of the Hessian matrix and by analysis of the internal reaction coordinates (IRC). For optimized structures the thermochemical data for the temperature T=298 K and pressure p=1atm were computed using vibrational analysis data. The kinetic parameters as well as essential properties of critical structures are displayed in Tables 1 and 2.

Consistently with the previous [2-4,7] conventions, in this paper the pre-reaction complexes are denoted as **LM** and the transition complexes as **TS**. They are distinguished by appending the letters **A-F**, depending on the reaction pathway.

3. Results and discussion

Recently performed thermodynamic calculations [18] were focused on the substrates and products of the reaction tested. However, these calculations cannot be used as a source of information about the rate the reaction proceeds, or about different events that occur when the reaction progresses from initial to final products. In other words, the reaction mechanism cannot be deduced from the determination of thermodynamic quantities (ΔG, ΔH, ΔS) for starting and ending states of the reacting system. It is necessary to know all the critical structures formed in each of the theoretically possible reaction paths. Hence, the B3LYP/6-31G(d) simulations of the reaction paths **A-F** (Scheme 1) were carried out and the results are presented below.

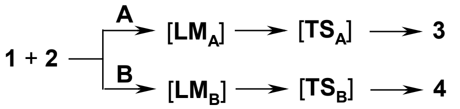
3.1. Reaction profiles

B3LYP/6-31G(d) calculations indicate that the energy profiles of CDA reactions (pathways **A** and **B**) in the presence of toluene as a dielectric medium are very similar to those obtained in the gas phase [2]. Irrespective of the electrophilicity of the nitroalkene on each competing pathway (Scheme 2, Fig. 1), there is always one transition state **TS** preceded by a shallow local minimum of the pre-reaction complex **LM**, between the energy minimum of the substrates (**1+2a** and **1**+**2g**) and the minimum of the respective cycloadduct (**3,4a** and **3,4g**).

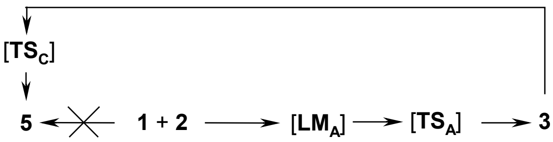
Formation of the **LM** complex is associoated with a slight reduction of enthalpy of the reaction system ($\Delta H < 1$ kcal mol^{-1}) and it does not require any activation barrier to overcome. At 298 K all the localised **LM**s are exclusively enthalpic in character. The entropic factor (TΔS) forces $\Delta G > 0$, which excludes possibility of their existence as stable intermediates (Table 1).

The transition of the reacting system from the valley corresponding to **LM** towards the product valley requires overcoming the activation barrier. For the reaction **1+2a**, the increase in the system free enthalpy related to the transition state ($\Delta G^{\neq}$) is 31.7 kcal mol^{-1} on pathway **A** and 32.0 kcal mol^{-1} on pathway **B**. In the case of the reaction **1+2g**, the free activation enthalpies on the pathways **A** and **B** are 35.6 kcal mol^{-1} and 36.4 kcal mol^{-1}, respectively. This means that the CDA reactions leading to 5-*endo*-nitro-6-*exo*-aryl-bicyclo-[2,2,0]-hept-2-enes are kinetically favoured irrespective of the nitroalkene electrophilicity. However, the reactions leading to 5-*exo*-nitro-6-*endo*-aryl-bicyclo-[2,2,0]-hept-2-enes are only slightly less favoured ($\Delta\Delta G^{\neq} = 0.3$–$0.8$ kcal mol^{-1}).

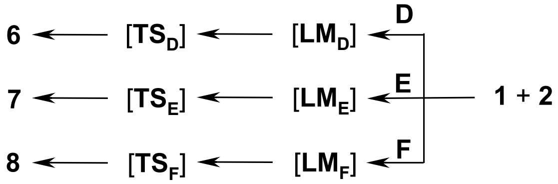
Similar to the CDA reactions, the HDA pathways also involve enthalpy minima ($-0.6 < \Delta H < -0.1$) for the **LM** complexes whose formation does not require overcoming the activation barrier. However, further transition of the reacting system from the **LM**s towards respective products does not follow the same mechanism. The conversion of substrates to 2-aryl-4-aza-5-oxy-bicyclo-[3,4,0]-nona-3,7-diene N-oxides **5a** and **5g** (pathway **C**) is a two-step process (Scheme 3). Initial products include bicyclo-[2,2,0]-hept-2-enes **3a** and **3g** (pathway **A**), which subsequently rearrange to the HDA adducts **5a** or **5g**. Free activation enthalpies for the reactions **3a**→**5a** and **3g**→**5g** are more than 4 kcal mol^{-1} higher than those for the reactions **1+2a**→**3a** and **1+2g**→**3g**



Scheme 2. Conversion of substrates into CDA adducts.



Scheme 3. Conversion of substrates into HDA adduct 5.



Scheme 4. Conversion of substrates into HDA adducts 6-8.

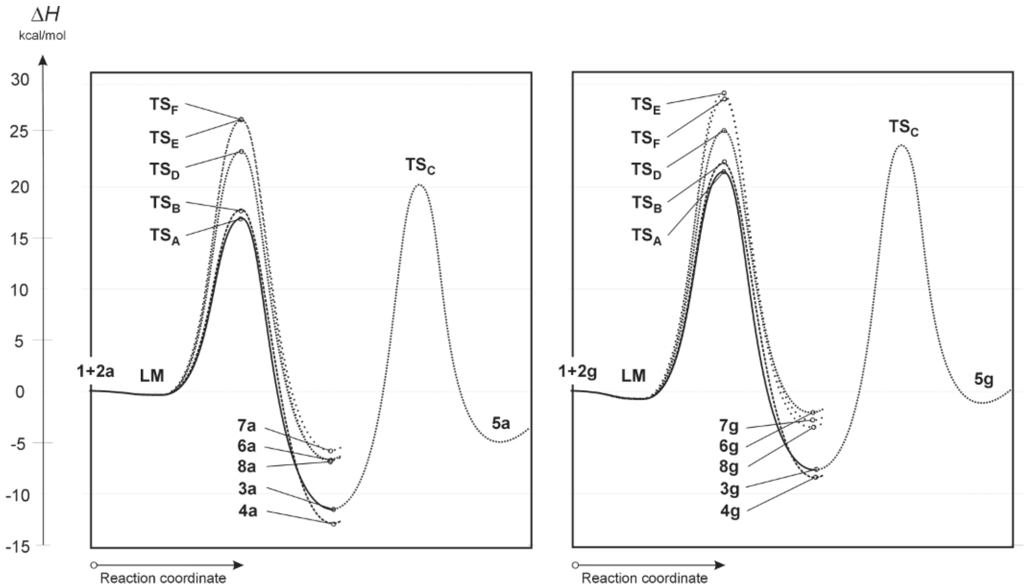


Figure 1. The profiles of DA reaction of cyclopentadiene **1** with (*E*)-2-arylnitroethenes **2a,g** in the toluene solution.

Table 1. Kinetic and thermodynamic parameters of DA reaction of cyclopentadiene 1 with (E)-2-arylnitroethenes 2a,g (T=298 K; ΔH and ΔG values are in kcal mol^{-1}; ΔS values are in cal mol^{-1} K^{-1}).

Solvent	**Transition**		**1+2a**			**1+2g**	
		ΔH	**ΔS**	**ΔG**	**ΔH**	**ΔS**	**ΔG**
Toluene	**$1+2\rightarrow \mathrm{LM}_{A}$**	-0.3	-30.8	8.9	-0.6	-21.3	5.7
	$1+2\rightarrow \mathrm{TS}_{A}$	17.1	-49.0	31.7	21.3	-48.1	35.6
	$1+2\rightarrow 3$	-11.7	-51.0	3.5	-7.4	-49.9	7.5
	$1+2\rightarrow \mathrm{LM}_{B}$	-0.3	-27.4	7.9	-0.6	-19.9	5.3
	$1+2\rightarrow \mathrm{TS}_{B}$	17.6	-48.2	32.0	22.2	-47.7	36.4
	$1+2\rightarrow 4$	-12.9	-50.9	2.3	-8.6	-49.4	6.1
	$1+2\rightarrow \mathrm{LM}_{A}$	-0.3	-30.8	8.9	-0.6	-21.3	5.7
	$1+2\rightarrow \mathrm{TS}_{A}$	17.1	-49.0	31.7	21.3	-48.1	35.6
	$1+2\rightarrow 3$	-11.7	-51.0	3.5	-7.4	-49.9	7.5
	$1+2\rightarrow \mathrm{TS}_{C}$	19.9	-53.5	35.8	23.8	-57.6	41.0
	$1+2\rightarrow 5$	-4.9	-51.9	10.6	-0.9	-51.2	14.4
	$1+2\rightarrow \mathrm{LM}_{D}$	-0.2	-25.8	7.5	-0.1	-21.9	6.4
	$1+2\rightarrow \mathrm{TS}_{D}$	22.8	-48.3	37.2	25.4	-47.9	39.7
	$1+2\rightarrow 6$	-7.2	-50.3	7.8	2.1	-49.0	16.7
	$1+2\rightarrow \mathrm{LM}_{E}$	-0.6	-34.4	9.7	-0.6	-18.4	4.9
	$1+2\rightarrow \mathrm{TS}_{E}$	26.3	-48.5	40.8	29.2	-48.2	43.6
	$1+2\rightarrow 7$	-6.2	-51.8	9.2	3.0	-51.1	18.2
	$1+2\rightarrow \mathrm{LM}_{F}$	-0.1	-22.8	6.7	-0.5	-30.1	8.5
	$1+2\rightarrow \mathrm{TS}_{F}$	26.2	-48.0	40.5	28.9	-48.8	43.4
	$1+2\rightarrow 8$	-7.4	-49.9	7.5	-3.6	-49.4	11.1
Acetone	**$1+2\rightarrow \mathrm{TS}_{A}$**	16.8	-48.1	31.1	21.0	-47.1	35.0
	$1+2\rightarrow 3$	-10.5	-51.3	4.8	-5.7	-49.2	9.0
	$1+2\rightarrow \mathrm{TS}_{B}$	17.6	-47.6	31.8	22.1	-47.1	36.1
	$1+2\rightarrow 4$	-11.5	-50.8	3.6	-6.6	-48.6	7.9
	$1+2\rightarrow \mathrm{TS}_{A}$	16.8	-48.1	31.1	21.0	-47.1	35.0
	$1+2\rightarrow 3$	-10.5	-51.3	4.8	-5.7	-49.2	9.0
	$1+2\rightarrow \mathrm{TS}_{C}$	17.7	-53.1	33.5	22.2	-51.4	37.5
	$1+2\rightarrow 5$	-4.9	-52.2	10.7	-0.5	-50.4	14.5
	$1+2\rightarrow \mathrm{TS}_{D}$	21.1	-47.6	35.3	23.8	-46.6	37.7
	$1+2\rightarrow 6$	-7.3	-50.3	7.7	-3.1	-48.4	11.3
	$1+2\rightarrow \mathrm{TS}_{E}$	25.9	-48.5	40.4	29.1	-47.0	43.1
	$1+2\rightarrow 7$	-5.8	-51.4	9.5	-1.5	-50.2	13.5
	$1+2\rightarrow \mathrm{TS}_{F}$	26.0	-48.1	40.3	28.9	-47.0	42.9
	$1+2\rightarrow 8$	-7.1	-49.9	7.8	-2.9	-48.7	11.6
Water	**$1+2\rightarrow \mathrm{TS}_{A}$**	16.8	-48.0	31.1	20.8	-46.2	34.6
	$1+2\rightarrow 3$	-10.5	-51.3	4.8	-5.6	-49.4	9.1
	$1+2\rightarrow \mathrm{TS}_{B}$	17.3	-48.0	31.6	22.0	-47.1	36.0
	$1+2\rightarrow 4$	-11.5	-51.0	3.7	-6.9	-51.8	8.5
	$1+2\rightarrow \mathrm{TS}_{A}$	16.8	-48.0	31.1	20.8	-46.2	34.6
	$1+2\rightarrow 3$	-10.5	-51.3	4.8	-5.6	-49.4	9.1
	$1+2\rightarrow \mathrm{TS}_{C}$	17.6	-53.1	33.4	22.0	-51.4	37.3
	$1+2\rightarrow 5$	-4.9	-52.2	10.7	23.3	-46.8	37.2
	$1+2\rightarrow \mathrm{TS}_{D}$	20.5	-47.5	34.7	23.3	-46.8	37.2
	$1+2\rightarrow 6$	-7.2	-50.3	7.8	-3.0	-48.7	11.5
	$1+2\rightarrow \mathrm{TS}_{E}$	25.9	-48.5	40.4	29.0	-47.3	43.1
	$1+2\rightarrow 7$	-5.9	-51.2	9.4	-1.5	-50.3	13.5
	$1+2\rightarrow \mathrm{TS}_{F}$	25.8	-48.3	40.2	28.6	-47.4	42.7
	$1+2\rightarrow 8$	-7.0	-49.7	7.8	-2.8	-48.8	11.7

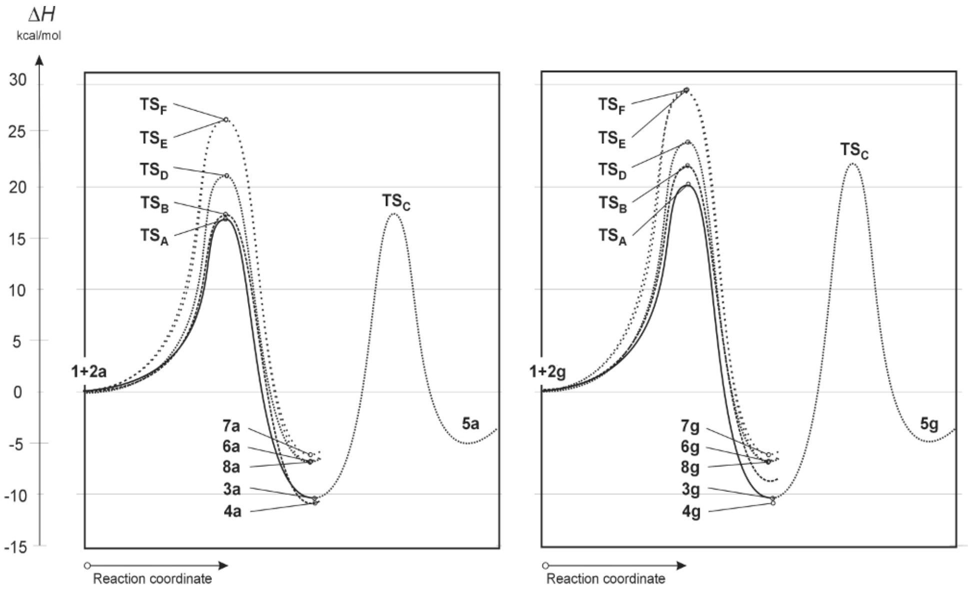


Figure 2. The profiles of DA reaction of cyclopentadiene **1** with (*E*)-2-arylnitroethenes **2a,g** in the acetone solution.

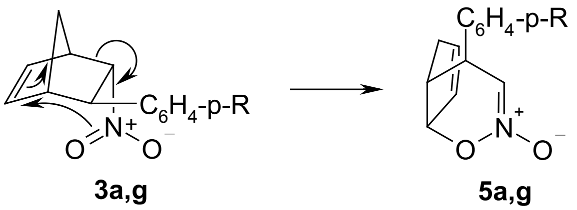
(Table 1), therefore, the second reaction step is quite improbable. Attempts to find a direct pathway from the substrates to HDA adducts were not successful.

The other reactions leading to HDA adducts (pathways **D–F)** are one-step processes (Scheme 4). Similar to the CDA reactions, irrespective of the electrophilicity of the nitroalkene only one transition state occurs in the energy profiles between the **LM** valleys and the product valleys. This is conclusively confirmed by IRC calculations.

The transition between the **LM** valley and the valley of the adducts **6a** and **6g** (pathway **D**) requires overcoming of the activation barrier of 37.2 kcal mol^{-1} and 39.7 kcal mol^{-1}, respectively. From the kinetic perspective, the formation of the adducts **6a** and **6g** in the reactions **1+2a** and **1+2g** is quite unlikely. The activation barriers for the reactions, which lead to the adducts **7a** and **7g** (pathway **E**) and **8a** and **8g** (pathway **F**), are so high ($\Delta G^{\neq} > 40$ kcal mol^{-1}) that they are considered kinetically forbidden in the analysed system of competitive reactions.

When toluene is replaced by more polar acetone, the **LM** complex valleys in the energy profiles disappear (Fig. 2). Higher polarity of the dielectric medium also leads to activation barriers being lowered by 0.2–0.6 kcal mol^{-1} for the reactions leading to the adducts **3, 4, 7, 8** (pathways **A, B, E, F**) and by 2–3.5 kcal mol^{-1} for those leading to the adducts **5** and **6** (pathways **C** and **D**). The pathways **A** and **B** are still the most favoured.

Replacing acetone with water does not change the nature of the energy profiles or kinetic preferences of the reactions. The activation barriers for particular reactions are reduced by 0.1 to 0.6 kcal mol^{-1} compared to those in acetone.



Scheme 5. Conversion of 5-endo-nitro-6-exo-aryl-bicyclo-[2,2,1]-hept-2-enes 3 into 2-aryl-4-aza-5-oxy-bicyclo- [3,4,0]-nona-3,7-diene N-oxides 5

B3LYP/6-31G(d) calculations provide a good description of the course of the reactions studied. It follows from our experiments [2] that irrespective of solvent polarity and nitroalkene electrophilicity, the reactions proceed as CDA processes and lead to mixtures of respective 5-*endo*-nitro-6-*exo*-aryl-bicyclo-[2,2,0]-hept-2-enes and 5-*exo*-nitro-6-*endo*-aryl-bicyclo-[2,2,0]-hept-2-enes with the first stereoisomer always being dominant.

3.2. Geometries and electronic properties of critical structures

3.2.1. Pre-reaction complexes

In toluene, the distances between reaction centres in the **LM** complexes are above 3.4 Å. They are much higher than the range typical for the bonds in **TS** complexes. For the reactions **1+2a→3a** and **1+2a→4a**, the **LM** complexes have properties of an orientation complex (OC). In the other cases, the reaction centres in the **LM**s do not show the spatial orientations observed in the **TS**'s. None of the **LM**'s exhibits the properties of a CT complex. However, in many cases the presence of CT complexes on the paths of DA reactions was confirmed

Table 2. Essential molecular properties from the B3LYP/6-31G(d) calculations of critical structures for reaction of cyclopentadiene **1** with (*E*)-2-arylnitroethenes **2a,g**.

Reaction	Solvent	Structure	C4-C5 r [Å]	C4-C5 l	C1-C6 r [Å]	C1-C6 l	C2-O7 r [Å]	C2-O7 l	C2-C6 r [Å]	C2-C6 l	C1-O7 r [Å]	C1-O7 l	Δl	μ [D]	t [e]
1+2a	Toluene	1												0.49	
		2a												0.69	
		LM$_A$	3.759		3.705									0.77	0.01
		TS$_A$	2.220	0.592	2.230	0.605							0.01	5.40	0.24
		3a	1.577		1.598									5.69	0.15
		LM$_B$	3.665		3.794									0.56	0.01
		TS$_B$	2.232	0.586	2.232	0.594							0.01	5.57	0.25
		4a	1.579		1.588									5.88	0.15
		TS$_C$	2.679		1.625		2.278	0.447						6.98	0.39
		5a			1.552		1.467							4.60	0.36
		LM$_D$			4.420		3.641							5.08	0.01
		TS$_D$			1.955	0.746	2.338	0.383					0.36	7.22	0.33
		6a			1.559		1.446							4.62	0.38
		LM$_E$							4.043		3.943			0.57	0.00
		TS$_E$							2.272	0.556	1.886	0.698	0.14	4.08	0.29
		7a							1.573		1.449			4.22	0.37
		LM$_F$							4.253		3.498			0.71	0.02
		TS$_F$							2.230	0.578	1.913	0.682	0.10	4.31	0.29
		8a							1.568		1.451			4.50	0.37
	Acetone	1												0.56	
		2a												0.72	
		TS$_A$	2.357	0.507	2.114	0.677							0.17	6.38	0.30
		3a	1.579		1.598									6.38	0.17
		TS$_B$	2.391	0.487	2.104	0.676							0.19	6.83	0.31
		4a	1.581		1.589									6.61	0.17
		TS$_C$	2.714		1.626		2.458	0.334						8.78	0.47
		5a			1.552		1.476							5.32	0.38
		TS$_D$			1.971	0.736	2.467	0.322					0.41	9.09	0.38
		6a			1.559		1.470							5.26	0.41
		TS$_E$							2.231	0.582	1.929	0.674	0.09	4.84	0.33
		7a							1.573		1.455			4.85	0.39
		TS$_F$							2.192	0.602	1.965	0.653	0.05	5.17	0.32
		8a							1.568		1.458			5.06	0.39
	Water	1												0.56	
		2a												0.75	
		TS$_A$	2.406	0.495	2.082	0.682							0.19	6.65	0.32
		3a	1.599		1.579									6.55	0.16
		TS$_B$	2.437	0.467	2.075	0.687							0.22	7.13	0.33
		4a	1.589		1.581									6.70	0.18
		TS$_C$	2.723		1.626		2.484	0.318						9.07	0.48
		5a			1.552		1.477							5.39	0.39
		TS$_D$			1.972	0.735	2.489	0.308					0.43	9.31	0.39
		6a			1.559		1.471							5.37	0.41
		TS$_E$							2.221	0.588	1.940	0.668	0.08	5.01	0.33
		7a							1.573		1.457			4.93	0.39
		TS$_F$							2.189	0.604	1.969	0.650	0.05	5.29	0.33
		8a							1.568		1.458			5.12	0.40

Continued **Table 2.** Essential molecular properties from the B3LYP/6-31G(d) calculations of critical structures for reaction of cyclopentadiene **1** with (*E*)-2-arylnitroethenes **2a,g**.

Reac-tion	Solvent	Struc-ture	C4-C5		C1-C6		C2-O7		C2-C6		C1-O7		ΔI	μ	t
			r [Å]	I	r [Å]	I	r [Å]	I	r [Å]	I	r [Å]	I		[D]	[e]
1+2g	Toluene	1												0.49	
		2g												8.57	
		LM$_A$	7.518		7.333									9.17	0.03
		TS$_A$	2.302	0.540	2.119	0.671							0.13	7.10	0.21
		3g	1.576		1.595									4.63	0.11
		LM$_B$	7.228		5.724									9.88	0.03
		TS$_B$	2.328	0.525	2.122	0.661							0.14	6.90	0.21
		4g	1.578		1.585									4.48	0.12
		TS$_C$	2.709		1.633		2.359	0.392						6.39	0.36
		5g			1.552		1.467							5.08	0.34
		LM$_D$			3.810		4.236							8.53	0.02
		TS$_D$			1.946	0.750	2.291	0.425					0.33	9.41	0.30
		6g			1.557		1.455							5.78	0.33
		LM$_E$							8.139		4.525			9.88	0.03
		TS$_E$							2.222	0.586	1.891	0.696	0.11	7.40	0.22
		7g							1.571		1.450			5.34	0.34
		LM$_F$							4.696		4.816			8.01	0.02
		TS$_F$							2.195	0.598	1.908	0.685	0.09	7.75	0.24
		8g							1.566		1.451			6.19	0.35
	Acetone	1												0.56	
		2g												10.03	
		TS$_A$	2.528	0.399	1.976	0.761							0.36	8.98	0.30
		3g	1.579		1.595									5.10	0.13
		TS$_B$	2.502	0.416	2.014	0.729							0.31	8.80	0.29
		4g	1.579		1.585									4.92	0.14
		TS$_C$	2.712		1.634		2.476	0.323						7.88	0.43
		5g			1.552		1.476							5.90	0.37
		TS$_D$			1.949	0.749	2.413	0.359					0.39	11.46	0.36
		6g			1.558		1.471							7.65	0.38
		TS$_E$							2.173	0.616	1.942	0.666	0.05	8.87	0.28
		7g							1.571		1.456			7.16	0.37
		TS$_F$							2.159	0.622	1.956	0.658	0.04	9.16	0.28
		8g							1.566		1.458			7.04	0.37
	Water	1												0.56	
		2g												10.21	
		TS$_A$	2.603	0.351	1.943	0.782							0.43	9.48	0.33
		3g	1.579		1.595									5.12	0.13
		TS$_B$	2.541	0.391	1.997	0.749							0.36	9.24	0.31
		4g	1.579		1.595									4.97	0.14
		TS$_C$	2.716		1.633		2.498	0.309						8.12	0.45
		5g			1.552		1.477							11.79	0.38
		TS$_D$			1.951	0.748	2.432	0.348					0.40	11.79	0.37
		6g			1.558		1.472							7.78	0.39
		TS$_E$							2.163	0.623	1.952	0.661	0.04	9.12	0.29
		7g							1.571		1.458			7.32	0.37
		TS$_F$							2.142	0.633	2.000	0.629	0.00	9.36	0.32
		8g							1.567		1.459			7.18	0.38

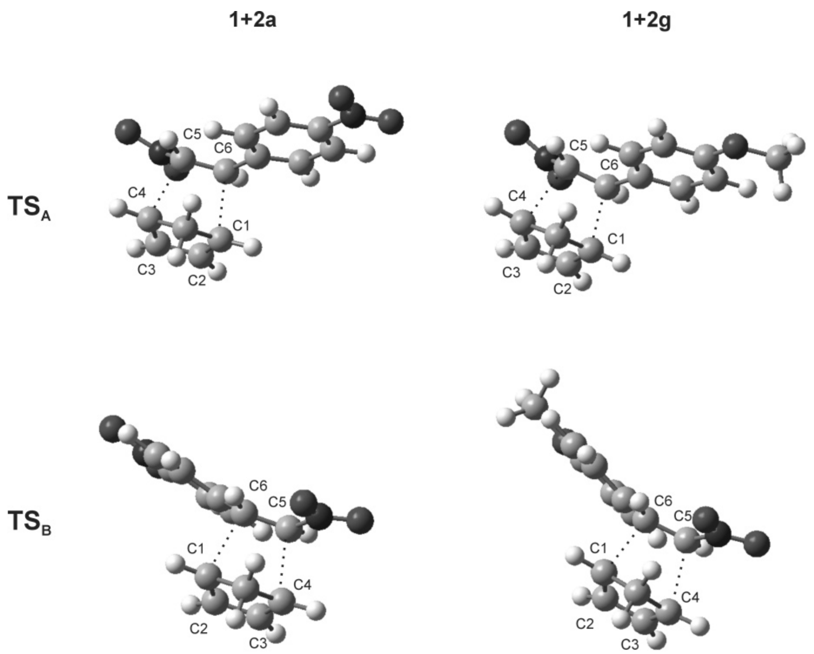


Figure 3. Views of the **TS** structures of the CDA reaction between cyclopentadiene **1** and (*E*)-2-arylnitroethenes **2a,g** in toluene solution.

experimentally [19,20]. This was confirmed by the lack of charge transfer between the substructures (Table 2), whose magnitude was calculated by *Leroy* relationship [21]:

$$t=-\sum q_A$$

where q_A is the charge on atom A, and the summation is over all of the dienophile substructure atoms.

As noted earlier, in more polar solvents the reactions proceed without formation of **LM** complex.

3.2.2. Transition complexes of the CDA reactions

In the presence of toluene as the reaction medium, the **TS** complexes in CDA reactions have a sandwich structure, which is typical for low asynchronous polar DA reactions [22]. σ-Bonds between the reaction centres C4 and C5 as well as C1 and C6 (Fig. 3) form simultaneously, even though their degree of advancement vary. In particular, the bond between atoms C1 and C6 is always more advanced than the other one. This is proven by the distances between key atoms (r_{C4-C5} and r_{C1-C6}) and the values of indices l_{C4-C5} and l_{C1-C6} (Table 2), calculated according to the relationship suggested earlier [7]:

$$l_{X-Y}=1-(r^{TS}_{X-Y}-r^{P}_{X-Y})/r^{P}_{X-Y}$$

where r^{TS}_{X-Y} is the distance between the reaction centres X and Y in the transition complex and r^{P}_{X-Y} is the corresponding distance in the product.

The degree of asymmetry of the transition complexes (Δl) is determined by the nature of the substituent in the nitroalkene phenyl ring. For **TS$_A$** and **TS$_B$** complexes and the reactions involving the more electrophilic nitroalkene **2a**, Δl does not exceed 0.01, whereas for the corresponding complexes and reactions involving the less electrophilic nitroalkene **2g**, Δl is 0.13 and 0.14 respectively. All the transition complexes for CDA reactions are polar, as confirmed by the values of dipole moment (μ > 4.5 D) and the degree of charge transfer between substructures (t = 0.16–0.21e).

When toluene is replaced by a more polar solvent the degree of formation of new σ-bonds in the **TS$_A$** and **TS$_B$** complexes changes. In acetone, the distance between the reaction centres C1 and C6 is reduced, while the C4-C5 distance increases (Table 2). Consequently, the degree of asymmetry of both complexes increases. However, the **TS**'s of the reactions that involve the less electrophilic nitroalkene **2g** remain more asymmetrical. In particular, Δl values for the **TS$_A$** and **TS$_B$** complexes in the reaction **1**+**2a**, are 0.17 and 0.19, respectively, whereas those for the reaction **1+2g** are 0.36 and 0.31, respectively. Increased complex asymmetry is accompanied by its higher polarity (cf. the μ and t values in Table 2). When water is used as a dielectric medium, the asymmetry and polarity of the **TS$_A$** and **TS$_B$** complexes further increase. For **TS$_A$** and **TS$_B$** complexes involved in the reaction **1**+**2a**, Δl is 0.19 and 0.22, respectively, whereas the corresponding data for the reaction **1+2g** are as high as 0.43 and 0.36. In conclusion, an increase

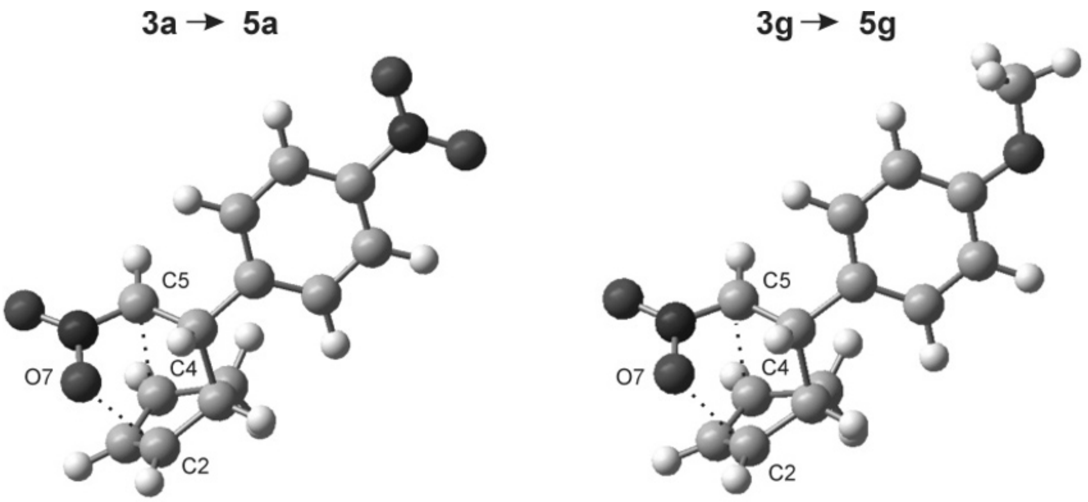


Figure 4. Views of the **TS** structures of the 5-endo-nitro-6-exo-aryl-bicyclo-[2,2,1]-hept-2-enes **3a,g** conversion into 2-aryl-4-aza-5-oxy-bicyclo-[3,4,0]-nona-3,7-diene N-oxides **5a,g** in toluene solution.

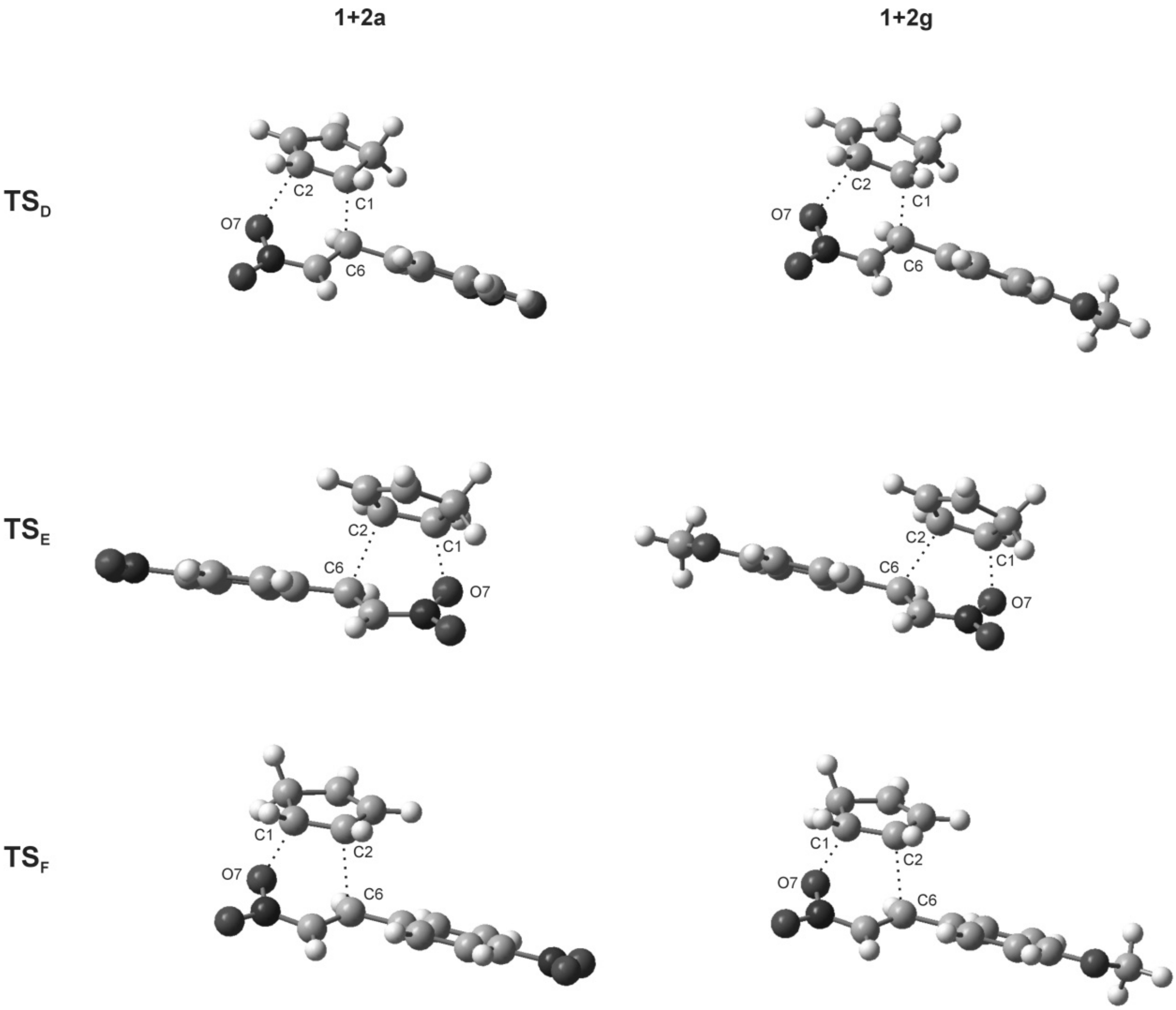


Figure 5. Views of the **TS** structures of the HDA reaction between cyclopentadiene **1** and (E)-2-arylnitroethenes **2a,g** in toluene solution.

in the polarity of the solvent increases the synchronicity of the bond formation because the DA reaction becomes more polar in character. However, these changes are not sufficiently high for the formation of a bipolar ion [23].

3.2.3. Transition complexes involved in conversion of 5-endo-nitro-6-exo-aryl-bicyclo-[2,2,1]-hept-2-enes into 2-aryl-4-aza-5-oxy-bicyclo-[3,4,0]-nona-3,7-diene N-oxides

The conversion of 5-*endo*-nitro-6-*exo*-aryl-bicyclo-[2,2,1]-hept-2-enes **3a** and **3g** to 2-aryl-4-aza-5-oxy-bicyclo-[3,4,0]-nona-3,7-dieneN-oxides **5a** and **5g** is a [3.3]-sigmatropic rearrangement [24,25]. It consists of the movement of σ–bonds within the six-membered $\mathbf{TS_C}$ transition complex (Fig. 4). During that process, the C4-C5 bond is broken while the C2-O7 bond is formed simultaneously (Scheme 5). The possibility of such type conversions have been proven experimentally [8-10, 26-29]. It should be noted at this point that a similar conversion of 5-*exo*-nitro-6-*endo*-aryl-bicyclo-[2,2,1]-hept-2-enes **4a** and **4g** is impossible due to geometrical restrictions (*i.e.*, NO_2 group in the *exo* position).

In toluene, $\mathbf{TS_C}$ complexes have similar structures, irrespective of the type of R substituent in the phenyl ring. Within the $\mathbf{TS_C}$, the C2 and O7 reaction centres approach the distance of approximately 2.3 Å. The degree of loosening of the C4-C5 bond, whose length is more than 2.6 Å, is significant.

When toluene is replaced by a more polar dielectric medium, the distances between the reaction centres C2 and O7 as well as C4 and C5 increase only slightly (Table 2). This is accompanied by increased dipole moments, but the nature of the $\mathbf{TS_C}$ complexes does not undergo any qualitative change.

3.2.4. Transition complexes of the HDA reactions

The transition complexes of HDA reactions (pathways **D–F)** have biplanar structures (Fig. 5) in which new σ-bonds form simultaneously. These are the bonds C2-O7 and C1-C6 for $\mathbf{TS_D}$ structures and the bonds C2-C6 and C1-O7 for $\mathbf{TS_E}$ and $\mathbf{TS_F}$ structures.

In the presence of toluene, the bond formed at the C1 site in HDA complexes is more advanced ($l_{C1\text{-}C6}$≈0.75; $l_{C1\text{-}O7}$≈0.69). The degree of advancement of the other bond, which is necessary to form the heterocyclic ring, is within the range 0.38–0.60 (Table 2). $\mathbf{TS_D}$ complexes are most asymmetrical ($\Delta l > 0.30$), while $\mathbf{TS_E}$ and $\mathbf{TS_F}$ complexes are least asymmetrical ($\Delta l < 0.15$). The degree of the complex asymmetry depends on the nitroalkene electrophilicity. The **TS**'s of the reactions that involve less electrophilic nitroalkenes are more asymmetrical. All the **TS**'s tested are polar ($\mu > 4D$; $t = 0.22$–$0.33e$).

The presence of a more polar solvent affects symmetry of the transition complexes. $\mathbf{TS_D}$ structures in water become slightly more asymmetrical than in toluene ($\Delta l = 0.39$–0.43)., In turn the $\mathbf{TS_E}$ and $\mathbf{TS_F}$ structures, are less asymmetrical ($\Delta l < 0.1$). However, all **TS's** are more polar in water than in toluene (Table 2).

4. Conclusions

The B3LYP/6-31G(d) simulations of competing CDA and HDA reactions between cyclopentadiene and (*E*)-2-arylnitroethenes prove that irrespective of medium polarity, the processes leading to respective 5-nitro-6-aryl-bicyclo-[2,2,0]-hept-2-enes should be most favoured, and the more electrophilic (*E*)-2-(p-nitrophenyl)-nitroethene (ω=3.70 eV) should be more reactive than the less electrophilic (*E*)-2-(p-methoxyphenyl)-nitroethene (ω=2.42 eV). Asymmetry of the transition complex on the favoured pathways increases with increase of the medium polarity, but not sufficiently enough to enforce the zwitterionic mechanism. In terms of *Domingo* terminology [30-32], these reactions in polar solvents can be interpreted as polar DA reactions with zwitterionic character. These predictions are consistent with experimental results [2].

The detailed analysis of competing pathways leading to HDA adducts proves that not all these compounds can be formed directly from the adducts. In particular, attempts to find one-step pathways leading to 2-aryl-4-aza-5-oxy-bicyclo-[3,4,0]-nona-3,7-diene N-oxides with *endo* conformations of condensed rings were not successful. Formation of such compounds is possible by [3,3]-sigmatropic rearrangement of respective 5-*endo*-nitro-6-*exo*-aryl-bicyclo-[2,2,0]-hept-2-enes. The other 2-aryl-4-aza-5-oxy-bicyclo-[3,4,0]-nonadiene N-oxides are formed according to the one-step mechanism. It is noted that kinetic factors do not favour the formation of 2-aryl-4-aza-5-oxy-bicyclo-[3,4,0]-nonadiene N-oxides. The reaction pathways leading to 2-aryl-4-aza-5-oxy-bicyclo-[3,4,0]-nona-3,8-diene N-oxides are considered kinetically forbidden.

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