



Competition between [2 + 1]- and [4 + 1]-cycloaddition mechanisms in reactions of conjugated nitroalkenes with dichlorocarbene in the light of a DFT computational study

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Abstract

The competition between [2 + 1] and [4 + 1] channels regarding reactions of conjugated nitroalkenes with dichlorocarbene was explored based on B3LYP/6-31G(d) calculations. It was found that, in the case of cycloadditions involving parent nitroethene and its 1-substituted analogs, the [2 + 1] scheme should be treated as possible only from the kinetic process point of view. On the other hand, in similar reactions involving 2-substituted nitroethenes, both channels considered may compete. Additionally, mechanistic aspects of all cycloadditions were analyzed. It was found that the considered [2 + 1]-cycloadditions proceed via a non-polar mechanism with a biradicaloidal transition state (TS), whereas [4 + 1]-cycloadditions proceed via a polar mechanism with a zwitterionic TS.

Keywords Nitroalkenes · Cycloaddition · Molecular mechanism · DFT study · Molecular electron density theory

Introduction

Nitro-functionalized carbo- and heterocycles play an important role in modern organic chemistry. This is a consequence of a wide range of further functionalization that may be realized via transformation of nitrocompounds into nitrile N-oxides [1, 2], oximes [3, 4], hydroxylamines [5, 6], nitronates [2, 4], carbonyl compounds [4, 7], aminoalcohols [8, 9] and others [4, 10]; this makes the effective synthesis of many valuable compounds possible.

The most universal methodology for preparing nitro-functionalized cyclic compounds is cycloaddition reactions involving respective conjugated nitroalkenes (CNA) [4, 11]. In this way, several four- [12, 13], five -[14–17], and

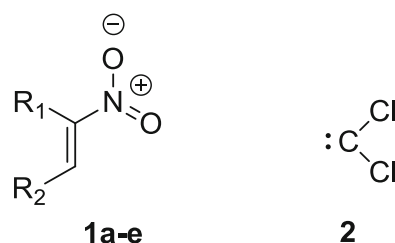
six-membered [18–21] nitro-cycles have been prepared. This is possible via [2 + 2], [3 + 2], and [4 + 2] cycloadditions, respectively. All these processes have been realized under relatively mild conditions and with full atomic economy. A detailed literature survey shows, unfortunately, [11], that any examples of [2 + 1]-cycloaddition involving conjugated nitroalkenes (which gave the possibility of the synthesis of nitro-functionalized cyclopropanes) are not known. The work presented here initiates a comprehensive study in this area. In particular, we decided to shed light on the molecular mechanism of model transformations involving a representative series of conjugated nitroalkenes (**1a–e**) and dichlorocarbene (**2**) (Scheme 1). Carbene **2** is well known and may be easily generated in the reaction environment [22–25]. On the other hand, five nitroalkenes (**1a–e**) characterized by a different type of substitution were selected. All these nitrocompounds may be prepared with good yields [26], can exist as relatively stable compounds, and have been recently tested as components of other type cycloadditions (nitroethene **1a** [14, 16, 27], 2-nitroprop-1-ene **1b** [28], 1-chloro-1-nitroethene **1c** [14, 18, 29], E-1-nitroprop-1-ene **1d** [28, 30, 31], E-2-chloro-1-nitroethene [31]). We hope that this study will help to further understand the nature of the title reactions and will be useful in organic synthesis.

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$\text{R}_1=\text{R}_2=\text{H}$ (**a**), $\text{R}_1=\text{Me}$, $\text{R}_2=\text{H}$ (**b**), $\text{R}_1=\text{Cl}$, $\text{R}_2=\text{H}$ (**c**), $\text{R}_1=\text{H}$, $\text{R}_2=\text{Me}$ (**d**), $\text{R}_1=\text{H}$, $\text{R}_2=\text{Cl}$ (**e**)

Scheme 1 Structures of selected cycloaddition components

Computational methods

All quantum-chemical calculations were performed using ‘Prometheus’ infrastructure shared by the ACK ‘Cyfronet’ in Krakow, Poland. The B3LYP method is formed through a combination of Becke’s three-parameter hybrid functional [32] and the LYP semi-local correlation function [33] with 6-31G(d) basis set, and was implemented in the Gaussian 09 [34] program. We recently applied an identical level of theory successfully to resolving several different aspects of cycloaddition reactions involving CNAs, such as regioselectivity [14, 17, 21, 30], stereoselectivity [21, 31], molecular mechanism [14, 16, 17, 21, 31, 35], solvent effects [21], substituent effects [14, 21, 35], etc. So, it may be assumed that this approach is adequate for analysis of the issues described above. Subsequently, we also examined higher levels of theory for resolving of the title problem. In these calculations, different types of functionals and basis sets were applied. It was found that all these approaches suggest the same kinetic preferences of reaction channels and similar nature of asynchronicity of transition states (TS). This confirms that the B3LYP/6-31G(d) theory level is adequate for our needs.

All critical structures were optimized using the Berny algorithm [36] and were characterized by frequency calculations. It was found that all addends, molecular complexes (MC), and products (P) had positive Hessian matrices, whereas all TS had one negative eigenvalue in their Hessian matrices. For all TS, intrinsic reaction coordinate (IRC) calculations were performed. The solvent effect was implemented using the polarizable continuum model (PCM) [37]. Global electron density transfer between substructures of the transition state (GEDT) [38] was calculated according to the equation:

$$\text{GEDT} = \sum q_A$$

where q_A is the net charge, and the sum is taken over all the atoms of nitroalkene.

Results of quantum chemical calculations are collected in Tables 1, 2, 3, 4, and 5.

Results and discussion

The [2 + 1]-cycloaddition (21CA) process involving CNAs **1a–e** and dichlorocarbene **2** (Scheme 1) formally should be resulted in nitrofunctionalized, cyclopropane derivatives (**3a–e** respectively). A few, recent theoretical works [39–41] suggest a one-step mechanism for some [2 + 1]-cycloadditions involving dichlorocarbene. On the other hand, earlier reports [42] suggest a stepwise mechanism, with zwitterionic intermediate. It should be additionally underlined that stepwise mechanisms have been recently documented based on comprehensive experimental and quantum-chemical studies regarding a group of different type cycloadditions involving conjugated nitroalkenes [35, 43, 44]. Therefore, neither one-step nor stepwise mechanisms can be excluded a priori for the reactions studied (Scheme 2).

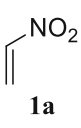
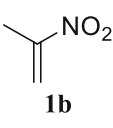
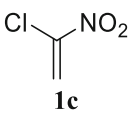
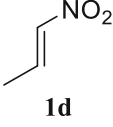
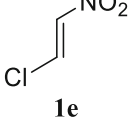
Next, recent reports confirm that, in some cases, CNAs can be accessed in the addition reactions as hetero-analogs of the 1,3-diene under non-catalytic conditions [45–47]. Therefore, the [4 + 1]-cycloaddition (41CA) scheme should also be considered in the analyzed processes (Scheme 3). Finally, we considered six theoretically possible reaction channels (A–E) for reactions **1a–e**+**2** (Schemes 2 and 3).

Firstly, we decided to analyze the nature of intermolecular interactions during title reactions in the framework of molecular electron density theory (MEDT) [48]. For this purpose, global electrophilicity (ω) for all considered addends were calculated using equations recommended by Parr [49] and Domingo [50, 51]:

Table 1 Key electronic properties of CNAs **1a–e** and carbene **2**

Cycloaddition components	μ [eV]	η [eV]	ω [eV]
1a	−5.33	5.45	2.61
1b	−5.16	5.48	2.43
1c	−5.47	5.11	2.93
1d	−5.08	5.48	2.35
1e	−5.59	5.40	2.89
2	−5.45	3.80	3.91

Table 2 Kinetic and thermodynamic parameters for 21CA and 41CA of selected conjugated nitroalkenes (**1a–e**) with dichlorocarbene **2** in different solvents in the light of B3LYP/6-31G(d) calculations (ΔH and ΔG are in kcal mol⁻¹; ΔS is in cal mol⁻¹ K⁻¹)

Nitroalkene	Solvent	Transition	[2+1] cycloaddition (21CA)			[4+1] cycloaddition (41CA)		
			ΔH	ΔG	ΔS	ΔH	ΔG	ΔS
 1a	Toluene	1a+2→MC				-1.11	6.55	-25.71
		1a+2→TS	1.49	12.77	-37.84	6.46	18.32	-39.75
		1a+2→P	-56.65	-43.10	-45.43	-68.72	-54.72	-46.96
	Nitromethane	1a+2→MC				-0.28	6.98	-24.37
		1a+2→TS	1.75	12.93	-37.51	6.33	18.40	-40.48
		1a+2→P	-56.12	-42.57	-45.45	-68.91	-55.00	-46.64
 1b	Toluene	1a+2→MC				-0.89	6.21	-23.79
		1a+2→TS	0.52	11.68	-37.40	5.92	17.79	-39.80
		1a+2→P	-54.28	-40.62	-45.80	-70.47	-57.06	-44.99
	Nitromethane	1a+2→MC				-2.51	4.48	-23.47
		1a+2→TS	0.87	11.99	-37.30	5.67	17.55	-39.84
		1a+2→P	-53.72	-40.06	-45.81	-70.93	-57.57	-44.83
 1c	Toluene	1a+2→MC				-1.09	6.22	-24.54
		1a+2→TS	0.29	11.47	-37.50	7.40	19.25	-39.74
		1a+2→P	-52.32	-38.64	-45.90	-68.74	-54.71	-47.06
	Nitromethane	1a+2→MC				-0.30	6.70	-23.49
		1a+2→TS	0.71	11.82	-37.28	7.98	19.41	-38.35
		1a+2→P	-51.70	-37.97	-46.04	-68.59	-54.68	-46.66
 1d	Toluene	1a+2→MC	-1.22	4.53	-19.31	-2.50	4.39	-23.11
		1a+2→TS	1.58	12.53	-36.74	3.41	14.86	-38.39
		1a+2→P	-54.85	-41.82	-43.71	-64.94	-51.10	-46.42
	Nitromethane	1a+2→MC	-0.72	4.91	-18.87	-1.62	4.93	-21.95
		1a+2→TS	2.03	12.89	-36.45	2.92	14.32	-38.23
		1a+2→P	-54.04	-41.02	-43.67	-64.68	-50.90	-46.20
 1e	Toluene	1a+2→MC	-1.72	5.99	-25.88	-1.72	5.90	-25.56
		1a+2→TS	4.79	16.60	-39.61	5.62	17.56	-40.06
		1a+2→P	-51.98	-38.33	-45.80	-62.26	-47.99	-47.84
	Nitromethane	1a+2→MC	-0.81	6.63	-24.95	-0.83	6.79	-25.57
		1a+2→TS	5.05	16.81	-39.46	5.77	17.76	-40.21
		1a+2→P	-51.33	-37.64	-45.90	-62.19	-48.03	-47.50

$$\omega = \mu^2/2\eta$$

$$\mu \approx (E_{\text{HOMO}} + E_{\text{LUMO}})/2$$

$$\eta \approx E_{\text{LUMO}} - E_{\text{HOMO}}$$

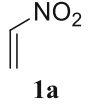
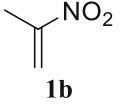
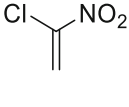
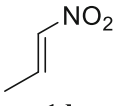
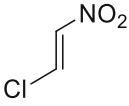
As is evident in the light of the data presented in Table 1, in the Domingo scale [50], all considered CNAs should be treated as strongly electrophilic agents. Dichlorocarbene **2** should be localized in the same group. However, its global electrophilicity ω is higher. In particular, the difference between ω values in the reactions involving nitroethene **1a** and their alkyl-substituted analogs is equally more than 1.3 eV. Next, for the similar processes involving chloro-substituted CNAs (**1c,e**), the analogous different is equal about 1 eV. So, in the case of all considered reactions, the polar mechanism can be treatment as allowed.

In the next step, we decided to fully explore of reaction channels leading finally to competitive cycloadducts **3** and **4**. It was found that the energetic profile of model 21CA **1a + 2** → **3a** suggests a one-step mechanism of addents

transformation in toluene solution (Fig. 1, Table 1). In particular, between valleys of individual reagents and product, only one critical point was detected, which is associated with the existence of TS. Reaching this point in the reaction system required rather a small amount of enthalpy ($\Delta H = 1.5$ kcal mol⁻¹). Subsequently, due to the reduction of the entropy of the reaction system, the Gibbs free energy of the activation is higher than ΔH and is equal to 12.8 kcal mol⁻¹. Generally, it is a rather low value, which allowed the reaction to proceed at room temperature.

Within the localized TS, two new sigma-bonds are formed: C3–C1 and C2–C1 (Fig. 2, Table 2). The key distances between reaction centers within the TS are, however, distinctly different. In particular, the bond formed with the participation of β carbon atom derived from nitrovinyl moiety (2.271 Å) is more advanced. The second new bond (C3–C1) is more than 0.5 Å longer. This suggests that the considered TS may exhibit a polar, zwitterionic nature. However, this hypothesis can be excluded due to the value of GEDT, which is nearly equal to

Table 3 Key parameters of critical structures for 21CA and 41CA of selected conjugated nitroalkenes (**1a–e**) with dichlorocarbene **2** in different solvents in the light of B3LYP/6-31G(d) calculations

Nitro-alkene	Solvent	Structure	[2+1] cycloaddition (21CA)			[4+1] cycloaddition (41CA)		
			r_{C3-C1} [Å]	r_{C2-C1} [Å]	GEDT [e]	r_{O5-C1} [Å]	r_{C2-C1} [Å]	GEDT [e]
 1a	Toluene	MC				2.931	3.537	0.00
		TS	2.861	2.271	-0.01	1.790	2.641	0.15
		P	1.520	1.491		1.367	1.546	
	Nitromethane	MC				2.976	3.580	0.00
		TS	2.879	2.292	-0.02	1.691	2.765	0.25
		P	1.521	1.490		1.363	1.545	
 1b	Toluene	MC				2.934	3.583	0.00
		TS	2.901	2.331	0.04	1.769	2.670	0.16
		P	1.530	1.494		1.364	1.542	
	Nitromethane	MC				2.984	3.651	0.00
		TS	2.911	2.350	0.04	1.700	2.763	0.24
		P	1.532	1.493		1.360	1.540	
 1c	Toluene	MC				2.981	3.523	0.00
		TS	2.969	2.377	0.01	1.999	2.479	0.03
		P	1.504	1.501		1.379	1.542	
	Nitromethane	MC				3.029	3.544	0.00
		TS	2.980	2.390	0.00	2.001	2.489	0.03
		P	1.505	1.498		1.380	1.542	
 1d	Toluene	MC	3.764	3.287	0.00	2.904	3.552	0.00
		TS	2.743	2.239	0.01	1.732	2.715	0.21
		P	1.520	1.499		1.369	1.555	
	Nitromethane	MC	3.778	3.795	0.00	2.954	3.603	0.00
		TS	2.752	2.254	0.01	1.697	2.834	0.29
		P	1.521	1.498		1.365	1.554	
 1e	Toluene	MC	4.139	3.408	0.00	2.938	3.408	0.00
		TS	2.773	2.199	-0.05	1.827	2.626	0.12
		P	1.526	1.503		1.377	1.566	
	Nitromethane	MC	4.170	3.427	0.00	2.986	3.430	0.00
		TS	2.789	2.211	-0.07	1.743	2.742	0.22
		P	1.527	1.502		1.372	1.566	

zero. Therefore, the analyzed TS probably has a biradicaloidal character. The IRC calculations connect the energetic maximum of the transition state, directly with the valleys of individual addends and expected product **3a**. Due to Jaque and Murray observation [52, 53], the shape of IRC profiles can be connected with the degree of TS asynchronicity. The formation of **3a** is full exothermic, which excludes the reversible nature of considered transformation. It should be mentioned that all attempts to optimize the critical structures that can be associated with hypothetical mechanisms **B** and **C** were unsuccessful. Thus, transformation **1a** + **2** → **3a** is realized via a non-polar one-step mechanism with a highly asynchronous, biradicaloidal TS.

Subsequently, in the similar way, we analyzed the competitive reaction channel of the transformation **1a** + **2** → **4a**. It was found that four critical points exist on the energetic profile of model 41CA (**1a** + **2** → **4a**). These points can be associated with: individual reagents, pre-reaction MC, TS and reaction product **4a** (Fig. 1, Table 2). The interactions between starting molecules lead, in the first step, to the formation of the pre-reaction complex MC. This does not require an activation barrier, and is associated with a reduction in enthalpy of about 1 kcal mol⁻¹. It should be underlined that, due to the entropy factor, the ΔG value of MC formation is greater than zero. Therefore, MC cannot exist at room temperature as a stable intermediate. Within the MC, the distances between reactions centers are evidently longer than the

Table 4 Selected parameters of transition states for 21CA and 41CA nitroethene **1a** with dichlorocarbene **2** in toluene in the light of DFT calculations at different theory levels

Level of theory	[2 + 1] cycloaddition (21CA)		[2 + 1] cycloaddition (41CA)	
	r_{C3-C1} [Å]	r_{C2-C1} [Å]	r_{O5-C1} [Å]	r_{C2-C1} [Å]
B3LYP/6-31G(d)	2.861	2.271	1.790	2.641
B3LYP/6-31G(d,p)	2.856	2.264	1.790	2.640
B3LYP/6-31 + G(d)	2.855	2.253	1.980	2.484
B3LYP/6-311G(d)	2.816	2.230	1.837	2.556
B3LYP/6-311++G(3d2f,3p2d)	2.827	2.247	1.777	2.679
B97XD-6-311++G(3d2f,3p2d)	2.690	2.170	1.729	2.615
M062x/6-31 + G(d)	2.750	2.223	1.755	2.596

typical C–C bonds formed in the TS (Fig. 3). Additionally, MC does not exhibit a CT-complex nature. This was confirmed by the GEDT value (0.00e).

Further transformation of the reaction system along the reaction coordinate lead to an energetic maximum. This maximum is associated with the existence of the TS. The transition into TS required an increase in enthalpy of about 6.5 kcal mol⁻¹. In the parallel, due to the reduction of the entropy of the reaction system, the Gibbs free energy of the activation is higher than ΔH , and is equal to >18 kcal mol⁻¹. Within localized TS, two new sigma-bonds are formed: O5–C1 and C2–C1 (Fig. 3, Table 2).

Interestingly, the asynchronicity of this TS is clearly higher than in the case of the TS of transformation **1a** + **2** → **3a**. In particular, the interatomic distance O5–C1 is 1.8 Å, whereas the C2–C1 distance is 0.85 Å longer. The high asynchronicity is accompanied by transfer between TS substructures. This effect is illustrated by GEDT value, which is 0.15e. So, in contrast to the TS of transformation **1a** + **2** → **3a**, the

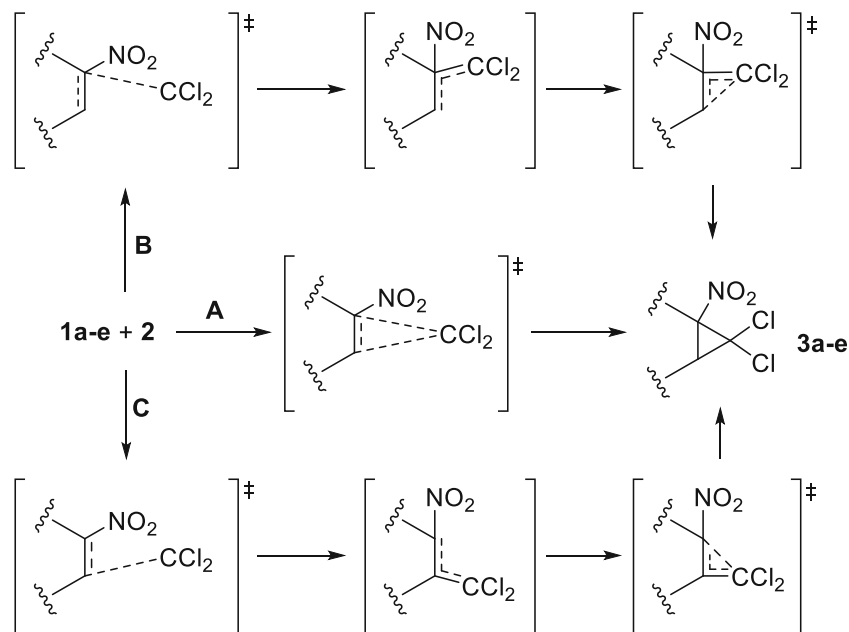
considered TS should be treated as a polar, zwitterionic structure. IRC calculations connect the energetic maximum of the TS directly with the valleys of individual addends and expected product **4a**. All attempts to optimize critical structures associated with the hypothetical mechanisms **E** and **F** were unsuccessful. Thus, the transformation **1a** + **2** → **4a** was realized via a polar one-step mechanism with a highly asynchronous, zwitterionic TS. Finally, it can be noted that, in the conditions of competition between 21CA and 41CA schemes, the second direct addend transformation should be treated as forbidden from a kinetic point of view ($\Delta\Delta G > 5$ kcal mol⁻¹).

The introduction of a more polar solvent (nitromethane) to the reaction environment does not change the nature of energetic profiles of competitive reaction paths. The quantitative description of critical points is, however, quite different. In particular, the activation barriers are slightly higher; this, however, did not change the kinetic preferences of possible channels of addends transformation. Within the TS of **1a** + **2** → **3a** transformation, the advancement of both new sigma bonds

Table 5 Selected parameters of transition states for 21CA and 41CA of selected conjugated nitroalkenes (**1f–m**) with dichlorocarbene **2** in toluene in the light of B3LYP/6-31G(d) calculations

Nitroalkene	[2 + 1] cycloaddition (21CA)		[2 + 1] cycloaddition (41CA)	
	r_{C3-C1} (Å)	r_{C2-C1} (Å)	r_{O5-C1} (Å)	r_{C2-C1} (Å)
1f	2.516	2.046	1.876	2.591
1g	2.876	2.324	1.755	2.642
1h	2.983	2.425	1.916	2.538
1i	2.951	2.331	2.187	2.527
1j	2.639	2.158	1.737	2.832
1k	2.776	2.219	1.875	2.597
1l	2.778	2.204	1.997	2.484
1m	2.783	2.168	1.840	2.613

Scheme 2 Possible mechanism of [2 + 1] cycloadditions involving **1** and **2a–e**



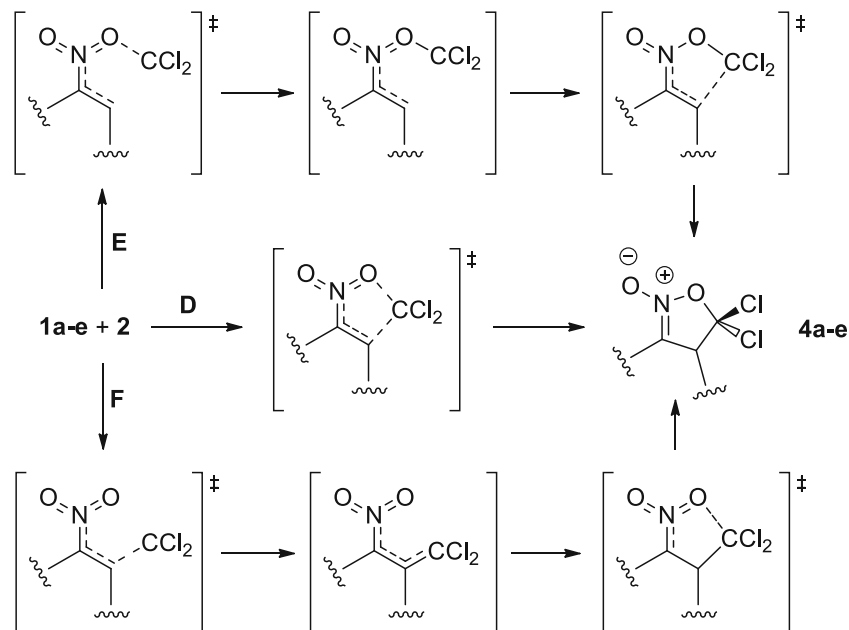
increased similarly. In consequence, the asynchronicity of TS is rather similar as in the case of similar reaction in toluene environment; this is understandable for non-polar reactions and confirms the nature of **1a + 2** → **3a** transformation proposed above.

On the other hand, within the TS of **1a + 2** → **4a** transformation, the sigma bond O5–C1 is formed faster than in the case of reaction in toluene, whereas the sigma bond C2–C1 is formed more slowly than in the case of the reaction in toluene. As a consequence, the asynchronicity of TS is higher than in the case of the analogous reaction in a toluene environment, but not enough to enforce a stepwise mechanism. The

observed influence of solvent polarity on the synchronicity of the TS structure, however, confirms the polar nature of the **1a + 2** → **4a** transformation.

Analogously, the competitive 2ICA and 4ICA processes involving substituted nitroethenes **1b–e** were also explored. It was found that, in all considered cases, the molecular mechanism of addend transformation was very similar to the case of the **1a + 2** reaction. Interestingly, the kinetic preference of possible cycloaddition channels is notably changed to some degree. In particular, reactions involving 2-substituted nitroethenes **2d,e**, the 4ICA scheme may really compete with the 2ICA process. As a

Scheme 3 Possible mechanism of [4 + 1] cycloadditions involving **1** and **2a–e**



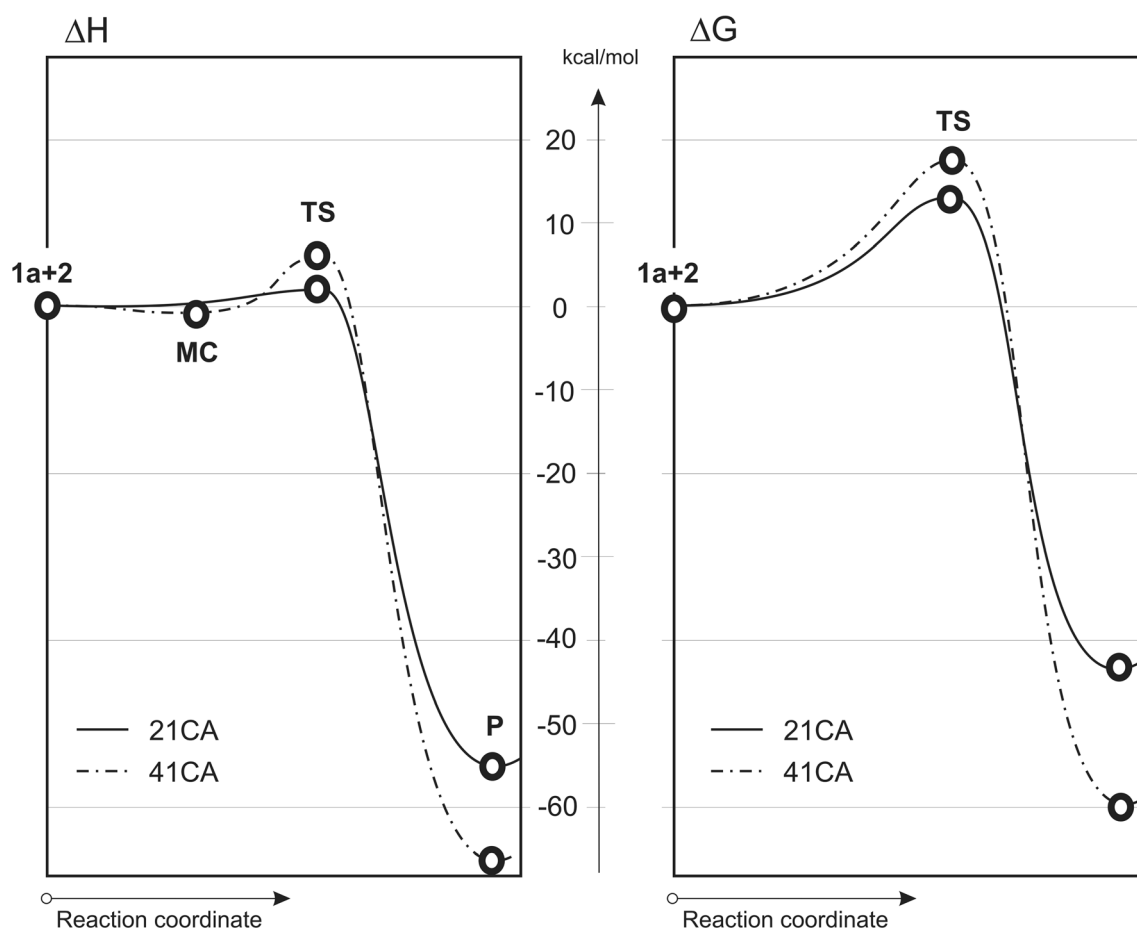


Fig. 1 Reaction profiles for 21CA and 41CA of nitroethene (**1a**) with dichlorocarbene **2** in toluene solution in the light of B3LYP/6-31G(d) calculations

consequence, within these reactions, two different cycloaddition products (respective [2 + 1] and [4 + 1] cycloadducts) may form, with some preference for the [2 + 1] pathway. So, the process analyzed may be considered as an exciting alternative to known, generally complicated, protocols [54–56] for synthesis of five-membered internal nitronates.

Finally, we also explored in similar way some other reaction systems, including different type substituents at the C1 or C2 position of nitroalkene (Table 5). It was found that the molecular mechanism of all of the explored reactions is very similar. So, the proposed reaction scheme can

be assumed as the general mechanism for the vast range of cycloaddition reactions between conjugated nitroalkenes and dichlorocarbene.

Conclusions

DFT investigations at the B3LYP/6-31G(d) level show that molecular mechanisms of competitive [2 + 1] and [4 + 1] cycloadditions of conjugated nitroalkenes with dichlorocarbene are substantially different. In particular, all considered [2 + 1]-cycloadditions proceed via a non-polar mechanism with a

Fig. 2 View of key structures for 21CA of nitroethene (**1a**) with dichlorocarbene **2** in toluene solution in the light of B3LYP/6-31G(d) calculations



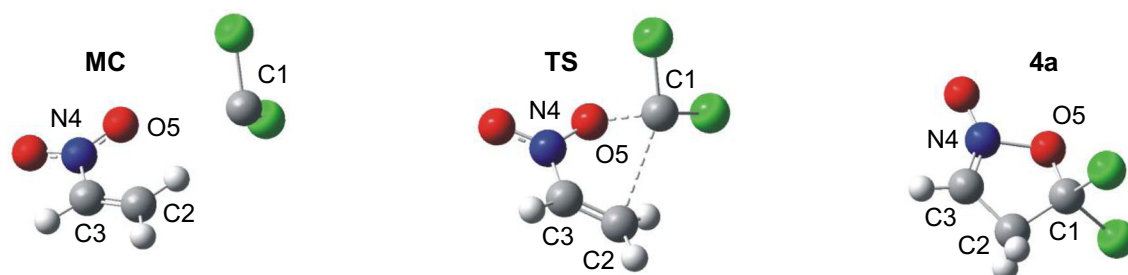


Fig. 3 View of key structures for 4ICA of nitroethene (**1a**) with dichlorocarbene **2** in toluene solution in the light of B3LYP/6-31G(d) calculations

biradicaloidal TS, whereas [4 + 1]-cycloadditions proceed via a polar mechanism with a zwitterionic TS. Subsequently, we established that the competition between mentioned cycloaddition schemes is possible only in the case of reactions involving 2-substituted nitroethene analogs. In the case of reactions involving a parent nitroethene as well as its 1-substituted analogs, the [4 + 1] cycloaddition scheme should be treated as forbidden from a kinetic point of view. From a practical point of view, our study suggests that the analyzed processes can be realized under mild conditions, and are a convenient way to prepare nitro-substituted cyclopropane derivatives and (in some cases) five-membered nitronates, which are difficult to realize using other preparation methods.

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