Molecular mechanism of Diels–Alder reaction between (E)-3,3,3-trichloro-1-nitropropene and cyclopentadiene: B3LYP/6-31G(d) computational study

Radomir JASIŃSKI,[*] **Andrzej BARAŃSKI**
Institute of Organic Chemistry and Technology, Krakow University of Technology, Krakow, Poland

Abstract: Analysis of reactivity indexes supports the polar character of the reaction between (E)-3,3,3-trichloro-1-nitropropene and cyclopentadiene. This is confirmed by the analysis of electronic properties of transition complexes involved in the reaction paths using the B3LYP/6-31G(d) algorithm. The transition state's asymmetry is large, but it is insufficient to provoke a zwitterionic reaction mechanism. Attempts to find a heterocyclic intermediate **7** in the reaction path ultimately leading to 5-*endo*-nitro-6-*exo*-trichloromethylnorbornene **3** have been unsuccessful.

Key words: Polar Diels–Alder reaction, mechanism, cyclopentadiene, nitroalkene, electrophilicity, nucleophilicity

1. Introduction

Some years ago[2] it was found that the Diels–Alder (DA) reaction between (E)-3,3,3-trichloro-1-nitropropene (global electrophilicity,[3] $\omega = 3.27$ eV[4]) and cyclopentadiene yields a mixture of stereoisomeric 5-*endo*-nitro-6-*exo*-trichloromethyl (**3**) and 5-*exo*-nitro-6-*endo*-trichloro-methylnorbornenes (**4**) with a total yield of 87% (Scheme 1).
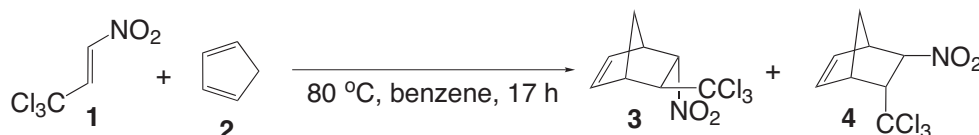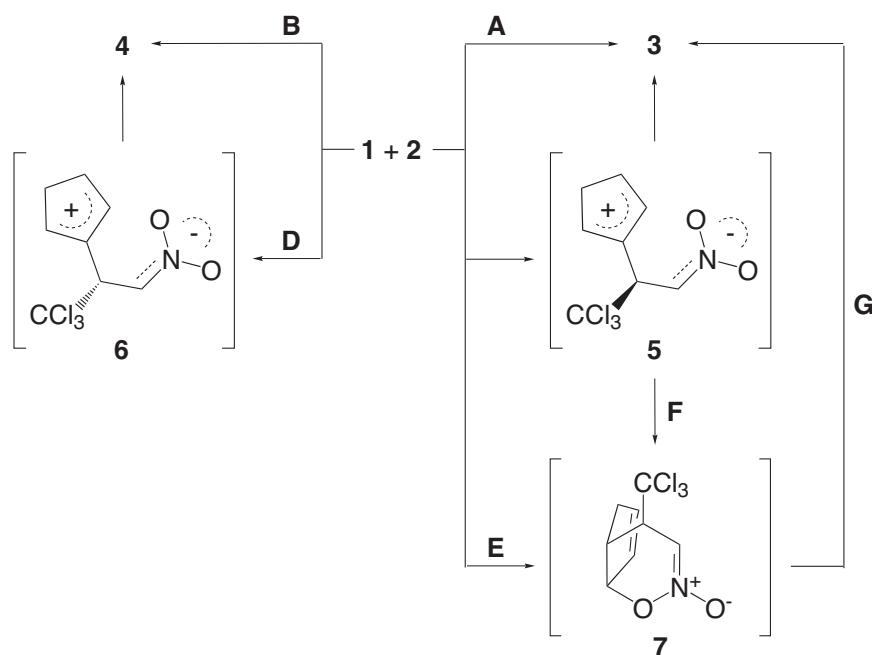

Scheme 1.

The authors assumed a priori a classic, 1-stage mechanism[5] (Scheme 2, paths A and B). However, a 2-stage zwitterionic mechanism[6−8] may compete with the 1-stage mechanism in the DA reactions (Scheme 2, paths C and D) when strongly electrophilic alkenes ($\omega > 1.5$ eV) participate in the reaction.[4,9] Furthermore, it cannot be ruled out that in the conversion of addents into nitronorbornene **3** the original reaction product is 2-trichloromethyl-4-aza-5-oxy-bicyclo-[3.4.0]-nona-3,7-diene N-oxide (**7**). In the second step, **7** undergoes [3,3]-sigmatropic rearrangement to nitronorbornene **3** (Scheme 2, paths E and G). Such a mechanism has been suggested recently on the basis of B3LYP/6-31G(d) simulations of the reaction paths for cycloaddition of (E)-2-aryl-1-cyano-1-nitroethenes ($\omega = 2.82$–3.80 eV)[10] and nitrobenzodifuroxane ($\omega = 4.80$ eV)[11] with

cyclopentadiene. Therefore, in this contribution, we report details of our theoretical studies aimed at a better understanding of the nature of these reactions. In this study, we determined the nature of the addends' interactions with respect to the widely promoted theory of reactivity indexes,[12,13] and we performed B3LYP/6-31G(d) simulations of actual reaction paths. It should be noted that in the case of DA reactions between dienes and nitroalkenes, calculations at the B3LYP/6-31G(d) theoretical level correlate perfectly with experimental data. In other work[14,15] the values of α-deuterium secondary kinetic isotope effects were determined for the DA reaction of the same cyclopentadiene with (E)-2-phenylnitroethene[15] and excellent correlations were obtained with experimental data.

Scheme 2.

2. Computational details

The reactivity indexes μ and ω for reactants **1** and **2** were estimated according to the equations recommended by Parr et al.[3] and Domingo et al.[12] In particular, the electronic chemical potentials (μ) and chemical hardness (η) of the reactants under study were evaluated in terms of the one-electron energies of frontier molecular orbitals using the following equations:

$$\mu \approx (E_{HOMO} + E_{LUMO})/2; \qquad \eta \approx E_{LUMO} - E_{HOMO}.$$

The values of μ and η were then used for calculation of the global electrophilicity (ω) in accordance with the following formula:

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

The global nucleophilicity (N) of cyclopentadiene can be expressed as:

$$E_{HOMO(Nu)} - E_{HOMO(TCE)},$$

where $E_{HOMO(TCE)}$ is the HOMO energy of tetracyanoethene taken as a reference.

The critical points on the potential energy surface (PES) were located in an analogous manner as in the case of the previously analyzed reaction of (E)-2-arylnitroethenes with cyclopentadiene,[14] using the B3LYP/6-31G(d) theoretical level and the Gaussian 2003 software suite.[16] In particular, for structure optimization of the substrates (**1** and **2**) and the cycloaddition products, the FOPT procedure was applied. Saddle points were localized using STQ2 and FOPT procedures. For the purpose of the reaction path simulation, the substrates were envisaged as placed symmetrically on 2 parallel planes. Optimizations of the stable structures were performed with the Berny algorithm, whereas the transition states were calculated using the QST2 procedure followed by the TS method. Stationary points were checked by vibrational frequency analyses to see whether they constituted minima or maxima on the PES. All transition structures showed a single imaginary frequency (ν_i), whereas reactants, products, and prereaction complexes had none. The intrinsic reaction coordinate path was traced in order to check the energy profiles connecting each transition structure to the 2 associated minima of the proposed mechanism. The calculations were carried out for the reaction in the simulated presence of benzene as a solvent. For this purpose, the polarizable continuum model with full geometry optimizations was applied. All calculations were performed for T = 353 K and p = 1 atm. Consistently with the previously used convention,[14] in this paper the letters **LM** and **TS** denote prereaction complexes and transition states, respectively.

3. Results and discussion

Comparison of the electron chemical potential μ of the addents suggests that charge transfer in the cycloadditions studied occurs from cyclopentadiene (–0.111 a.u.) to 3,3,3-trichloro-1-nitropropene (–0.215 a.u.). The global electrophilicity ω of nitroalkene **1** is 3.27 eV, and so according to the classification of Domingo et al.,[9] it may be considered a strong electrophile. However, cyclopentadiene **2**, being a strong nucleophile (N = 3.36 eV), has moderately electrophilic properties (ω = 0.83 eV). The electrophilicity difference ($\Delta\omega$) for the reagent pair **1**+**2** is 2.44 eV. Therefore, the cycloaddition in question can be classified as a polar DA (P-DA) reaction.[12]

Table. Selected parameters for critical structures and activation parameters for DA reaction between (E)-3,3,3-trichloro-1-nitropropene **1** and cyclopentadiene **2** in benzene according to B3LYP/6-31G(d) calculations (T = 353 K; ΔH and ΔG values are in kcal/mol; ΔS values are in cal/mol K).

	r_{C4-C5} (Å)	r_{C6-C1} (Å)	μ (D)	Electron transfer, t (e)	ΔH	ΔG	ΔS
1			0.49				
2			2.50				
LM$_A$	3.723	4.261	2.70	0.01	–0.2	11.0	–31.7
TS$_A$	2.412	2.204	5.60	0.30	16.0	33.3	–49.1
3	1.575	1.585	4.34	0.18	–19.8	–1.2	–52.7
LM$_B$	3.726	4.437	1.96	0.00	–0.2	8.2	–23.8
TS$_B$	2.476	2.143	5.85	0.30	14.9	32.4	–49.5
4	1.580	1.578	4.53	0.19	–19.8	–1.1	–53.1

Analysis of the reactivity indexes suggests the nature of interactions between the addend molecules but provides no details about the reaction mechanism. Therefore, we performed B3LYP/6-31G(d) calculations of energy profiles to gain further insight into the reaction mechanism. The calculations were carried out in the simulated presence of benzene, which was used earlier as a solvent in experimental studies.[2]
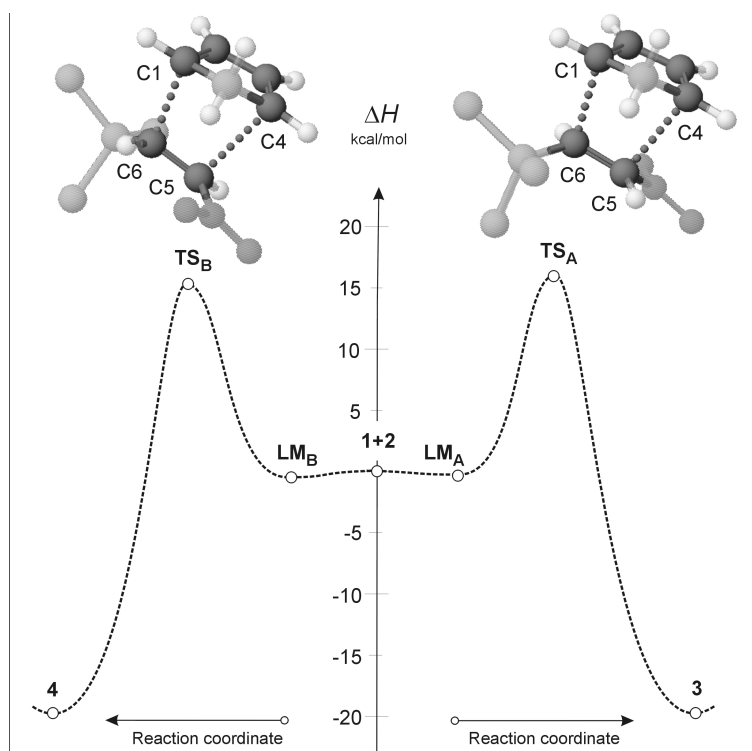
Figure. Reaction profiles for DA reaction between (E)-3,3,3-trichloro-1-nitropropene **1** and cyclopentadiene **2** in benzene according to B3LYP/6-31G(d) calculations.

The energy profiles of the reactions **1**+**2**→**3** and **1**+**2**→**4** appear to be quite similar (Figure). In both cases, only one transition state (**TS**), preceded by a shallow minimum of the prereaction complex (**LM**), occurs between the addends and the product minima. All attempts to find intermediates **5**–**7** on the reaction paths as well as optimization of zwitterions as stable structures have been unsuccessful. Only nitronic ester **7** exists as a stable structure, but beyond the reaction channel from addents into norbornene **3**.

When the addend molecules gradually approach each other, the prereaction complexes (**LM**) initially form. This involves a reduction in the enthalpy of the reaction system by 0.2 kcal/mol. Both of the **LM**s are purely enthalpic, because the entropic factor (TΔS) excludes the possibility of their existence at 353 K in the form of stable intermediates ($\Delta G > 0$). They are moderately polar (see the μ values in the Table), with no features of charge transfer complexes (CT).[17] This is demonstrated by the magnitude of charge transfer between substructures (t $\approx$ 0.00 e). At this stage, the reaction centers have already adopted the orientation, which is found later in the products. Therefore, they can be considered as orientation complexes.[5] However, the distances between the reaction sites are still far from the range typical for the transition states (see the r values in the Table).

Further movement of the reacting system along the reaction coordinates leads to the transition states (**TS$_A$** and **TS$_B$**, respectively). This involves an increase in enthalpy by 14.9 kcal/mol for path **B** and by 16.0 kcal/mol for path **A**. Both complexes (**TS$_A$** and **TS$_B$**) have strongly polar characters and may be considered as zwitterionic transition states. This is confirmed by the dipole moment values ($\mu > 0.5$ D) and the degree of charge transfer between substructures (t $\approx$ 0.30 e). In both of the **TS**s, 2 new σ bonds form, although their degree of advancement is different. In particular, the C1-C6 bond forms more rapidly (2.204 Å and 2.143 Å for **TS$_A$** and **TS$_B$**, respectively). At the same time, the other σ bond formed has a length greater than 2.4 Å. Therefore, the asymmetry of the **TS$_A$** and **TS$_B$** structures in the **1**+**2** cycloaddition is larger than that of

the transition complexes in the similar reaction involving (E)-2-arylnitroethenes,[14] but it is not large enough to force a zwitterionic reaction mechanism.

4. Conclusion

In conclusion, unlike (E)-2-aryl-1-cyano-1-nitroethenes, (E)-3,3,3-trichloro-1-nitropropene reacts with cyclopentadiene according to a one-step mechanism without the intervention of the heterocyclic intermediate. All attempts to find zwitterions in the reaction paths have been unsuccessful. It should be noted at this point that, according to the terminology of Domingo et al.,[12] the cycloaddition between (E)-3,3,3-trichloro-1-nitropropene and cyclopentadiene may be considered as a P-DA reaction. This is confirmed by analysis of reactivity indexes as well as the electronic properties of transition states.

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