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Synthesis and Properties of Azoles and Their Derivatives. Part LV*. Mechanism of C,C,N-Triphenylnitrone [2+3]-Cycloaddition with (*E*)-3,3,3-Trichloro-1-nitropropene-1 in the Light of AM1 and AM1/COSMO Calculations

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AM1 calculations suggest that the [2+3]-cycloaddition of C,C,N-triphenylnitrone **(1)** to (*E*)-3,3,3-trichloro-1-nitropropene-1 **(2)** in gas phase occurs in concerted manner. Kinetic factors favour the formation of cycloadduct with nitrogen group in position C4 of the isoxazolidine ring (path **A**). Introduction of toluene as a dielectric medium does not alter this preferable. However, the character of the energy profile for path **A** undergoes a critical change. In this case, two transition states and intermediate with zwitterionic character were localized by means of AM1/COSMO method.

Key words: [2+3]-cycloaddition, AM1 calculation, nitrone, nitroalkene, isoxazolidine

Recent literature accounts put in question the common views on the mechanism of concerted [2+3]-cycloaddition as the only possible one, no matter what is the structure of the addends [2–10]. Synchronous formation of new σ bonds can be evidenced for alkenes, in which the substituent at the double bond of the dipolarophile is of donor or weak acceptor character. There is, however, another two-step mechanism with a zwitterionic intermediate, that in the case of strong acceptor substituents, can compete with the mechanism of the concerted [2+3]-cycloaddition [4–12]. Recently, Huisgen and Mlostoń have provided an evidence for the presence of the ionic intermediate in the reaction of [2+3]-cycloaddition of sterically crowded thiocarbonyl *S*-methylylides to tetracyanethene [10] and some other π-deficient alkenes [4–9]. On the other hand, there is no enough convincing data on the mechanism of the reaction between nitrones and strongly π-deficient alkenes. Therefore, quantum mechanical studies have been performed within this work to elucidate the nature of [2+3]-cycloaddition of C,C,N-triphenylnitrone (**1**) to *(E)*-3,3,3-trichloro-1-nitropropene-1 (**2**), which π-IP is equal 10.8 eV (data from PE spectrum). The main objective of the studies was the analysis of critical structures on the potential energy hypersurface of the reaction (PES). To this purpose the AM1 method [13] from MOPAC 93 package was used. As

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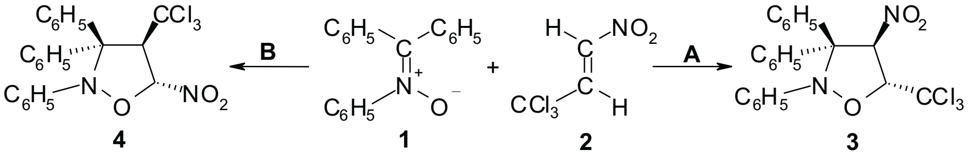
* Part LIV see [1].

**Corresponding author. Fax: +48 (12) 628-20-37, E-mail: pcbarans@usk.pk.edu.pl it was proven on many examples this method provides relatively the most satisfactory results in the case of [2+3]-cycloaddition of nitrones to nitroolefines [1,2,14–16]. The computational procedure was described in detail in previous works [2,3]. The calculations were carried out for the reaction in the gas phase and simulated presence of toluene as a solvent.

RESULTS AND DISCUSSION

Cycloaddition of C,C,N-triphenylnitrone (**1**) to *(E)*-3,3,3-trichloro-1-nitropropene-1 (**2**) could lead theoretically to *4,5-trans*-2,3,3-triphenyl-4-nitro-5-trichloromethylisoxazolidine (**3**) and *4,5-trans*-2,3,3-triphenyl-4-trichloromethyl-5-nitroisoxazolidine (**4**) (Figure 1, paths **A** and **B**). The character of the energy profiles of both reaction paths in the gas phase is similar. A single transition state (**TS**) is localized between the minima of the substrates and products, preceded by a shallow local minimum (**LM**).



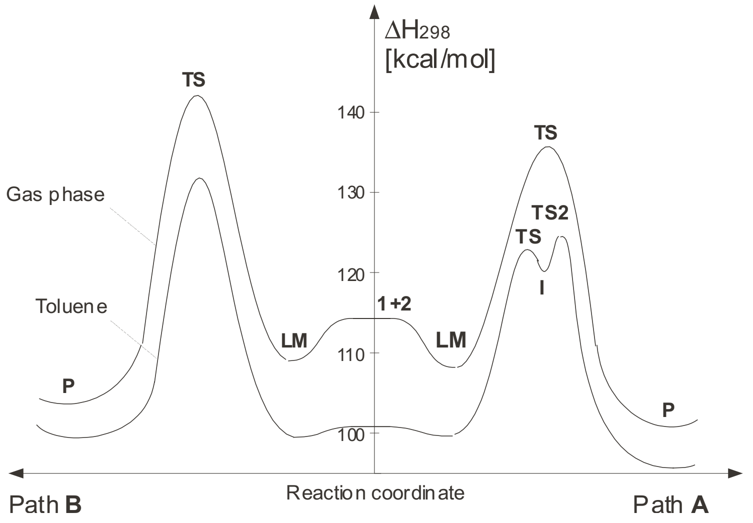
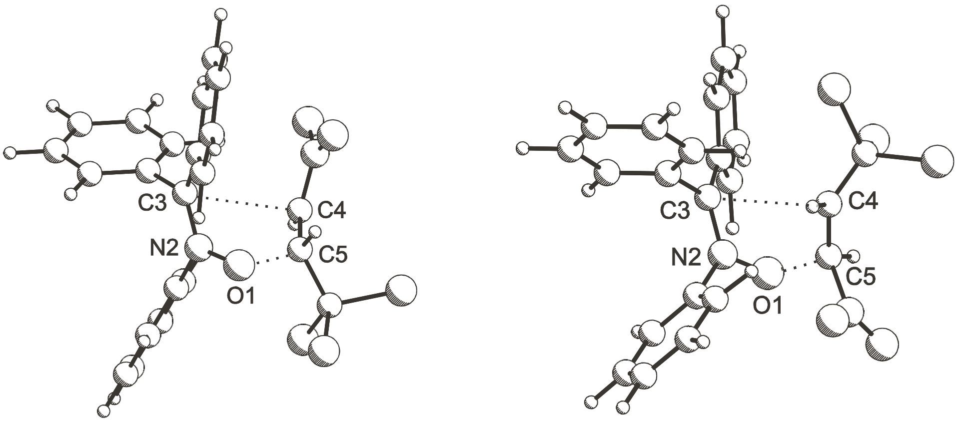
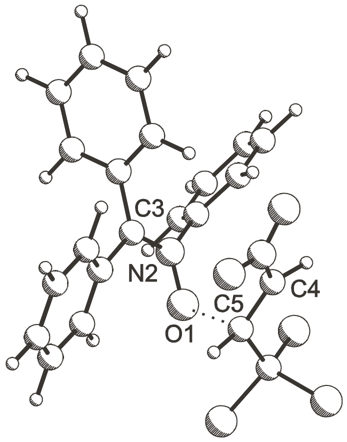


Figure 1. The reaction profiles for the [2+3]-cycloaddition of C,C,N-triphenylnitrone (**1**) with (*E*)-3,3,3-trichloro-1-nitropropene-1 (**2**) in gas phase and toluene solution.

Within **LM** the structures of the addends remain virtually unchanged. The molecules of nitrone and nitroalkene are approaching each other at the distance of few Å. The presence of **LM** on the PES is related to the decrease of the enthalpy of the system by 5.51 and 4.68 kcal/mol on the **A** and **B** paths, respectively. Significant changes in the structure and energetics of the reacting system appear, however, within the vicini-


TS (Path **A**, gas phase)
TS (Path **B**, gas phase)


TS (Path **A**, toluene)

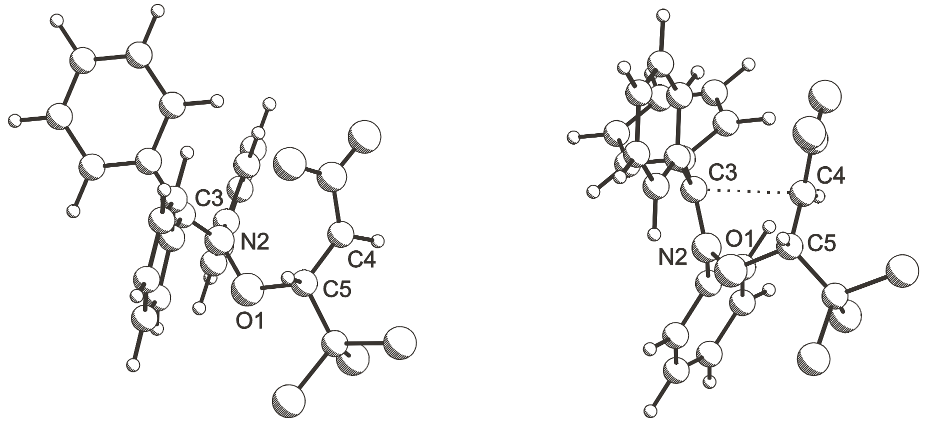

I (Path **A**, toluene)
TS2 (Path **A**, toluene)

Figure 2. PLUTO views of selected critical structures of [2+3]-cycloaddition of C,C,N-triphenylnitrone **(1)** with (*E*)-3,3,3-trichloro-1-nitropropene-1 **(2)**.

ty of the transition states. In the case of the **TS** structures the newly arising σ bonds are formed simultaneously, though the degree of advancing of this process is different (Table 1, Figure 2). The C5–O1 bond, having the length of 1.553 Å on the path **A** and the length of 1.533 Å on the path **B**, is formed apparently faster. The C3–C4 bond has a length of 2.659 Å in the case of the **A** path, and 2.529 Å in the case of the **B** path. Within both **TS** structures a large charge transfer between the substructures (0.55 and 0.52 e) has been observed. The free enthalpy of activation $\Delta G^{\neq}$ on the path **A** is 46.32 kcal/mol, while on the path **B** it is equal 53.46 kcal/mol.

Passing through the activation barrier in the case of both paths allows for direct access to the valley of the products.

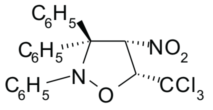
Table 1. Selected molecular properties of critical structures and Eyring parameters of [2+3]-cycloaddition of C,C,N-triphenylnitrone **(1)** with (*E*)-3,3,3-trichloro-1-nitropropene-1 **(2)** in gas phase and toluene solution.

Solvent	Path	Str.	r [Å]		ΔH_{298}	ΔS_{298}	t^{a}	$\Delta H^{\neq}$	$\Delta S^{\neq}$	$\Delta G^{\neq}$
[ε]			C3–C4	C5–O1	[kcal/mol]	[cal/mol·K]	[e]	[kcal/mol]	[cal/mol·K]	[kcal/mol]
Gas phase [1.0]	A	**1+2**			114.39	217.9				
		LM	5.153	3.003	108.88	132.6	0.00	–5.51	–85.25	19.90
		TS	2.659	1.553	136.61	137.0	0.55	22.22	–80.88	46.32
		P	1.587	1.449	102.72	138.1				
	B	**LM**	5.349	3.269	109.71	135.9	0.00	–4.68	–81.97	19.75
		TS	2.529	1.533	142.96	134.3	0.52	28.57	–83.53	53.46
		P	1.595	1.430	104.85	134.5				
Toluene [2.3]	A	**1+2**			101.14	194.7				
		LM	5.130	2.997	100.05	129.5	0.00	–1.08	–65.18	18.34
		TS	3.542	1.739	123.18	130.7	0.42	22.05	–64.02	41.13
		I	3.621	1.523	120.02	139.9	0.66	18.88	–54.85	35.23
		TS2	2.588	1.508	123.93	125.5	0.60	22.80	–69.25	43.43
		P	1.588	1.449	95.72	135.1				
	B	**LM**	5.338	1.340	100.35	133.0	0.00	–0.78	–61.73	17.61
		TS	2.652	1.433	132.69	133.9	0.57	31.55	–60.55	49.67
		P	1.580	1.545	97.61	134.9				

[a] – Charge transfer was calculated according to expension by Leroy *et al*. [17].

Upon introducing toluene as a dielectric medium the character of the energy profile on the **B** path remains essentially unaffected. On the other hand, a shallow valley of the intermediate appears in the case of the **A** path between the **TS** structure and the valley of the product **P**. This fact implies a two-step character of the process.

The **LM** structures in the case of the simulated presence of toluene look like those in the gas phase. At the same time, the decrease of the system enthalpy is slightly smaller. The structure of the transition state looks also likewise that in the gas phase, though the symmetry perturbation of the newly arising σ bonds is more visible. The effect of the charge transfer is a bit stronger as well. As opposed to this, the synchronism of the electron displacement in the case of the **TS** structure on the path **B** is perturbed to such a degree that only one of the two bonds, necessary to create an isoxazolidine ring, is formed. It is the C5–O1 bond (r = 1.739 Å). Closing of the heterocyclic ring requires passing through the second activation barrier existing on the PES related to the formation of the C3–C4 bond. Passing along the reaction coordinate in the direction of the transition state, **TS2**, leads initially to a shallow valley of the intermediate. A strong effect of the charge transfer seems to suggest a zwitterionic character of this structure. Within the intermediate **I** there is a possibility of rotation around the C4–C5 bond, which consequently could lead further on to formation of *4,5-cis*-2,3,3-triphenyl-4-nitro-5-trichloromethylisoxazolidine (**5**). However, the expense of the energy required to make such a turn is over 3 kcal/mol greater than in the case of closing the azolidine ring with preservation of the primary stereoconfiguration of the substituents.



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The values of $\Delta G^{\neq}$ obtained in the toluene environment prefer, by analogy to the gas phase, the path **A**.

CONCLUSIONS

The AM1 calculations suggest the mechanism of concerted [2+3]-cycloaddition of C,C,N-triphenylnitrone to *(E)*-3,3,3-trichloro-1-nitropropene-1 in the gas phase. In addition, the activation parameters favour the path leading to *4,5-trans*-2,3,3-triphenyl-4-nitro-5-trichloromethylisoxazolidine **3**. Introduction of toluene as a reaction medium to the reaction environment does not alter this preference. However, the character of the energy profile, within the kinetically favoured reaction path, undergoes a crucial change. In this case two transition states and one zwitterionic intermediate have been localized on the PES. We are carring out detailed kinetic experiments along this line. They will be published in the near future in separate publication.

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