

[2 + 3] Cycloaddition of *C,C,N*-triphenylnitronone to *trans*-substituted nitroethylenes in the light of an AM1 and AM1/COSMO computational study[†]

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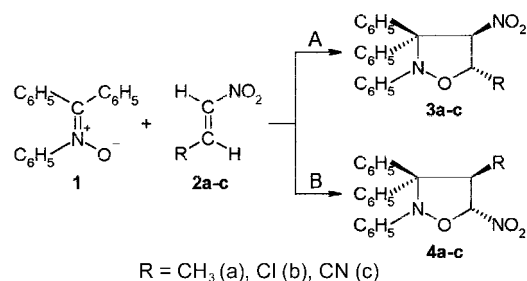
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ABSTRACT: AM1 calculations suggest that the [2 + 3] cycloaddition of triphenylnitronone **1** to nitroalkenes **2a–c** in the gas phase takes place in a concerted manner. However, the azolidine ring bonds C3—C4 and O1—C5 are not formed fully synchronously. Kinetic factors favor the formation of cycloadducts with nitro group in position C-4 of the azolidine ring (path **A**). Introduction of toluene, acetone or acetonitrile as a reaction medium increases the activation barriers for both regioisomeric paths. Simultaneously, the energy profiles for path **A** undergo qualitative change. In this case, two transition states and an intermediate with zwitterionic character were localized by means of the AM1/COSMO method. Copyright © 2003 John Wiley & Sons, Ltd.

KEYWORDS: [2 + 3] cycloaddition; nitrones; nitroalkenes; regioselectivity; solvent effect; AM1

INTRODUCTION

This work is a continuation of our systematic studies concerning the mechanistic aspects of thermally allowed cycloadditions with participation of nitroalkenes as 2π -components.^{1–7} In previous paper in this series⁶ we reported AM1/COSMO calculations for [2 + 3] cycloaddition of (*Z*)-*C,N*-diphenylnitronone to *trans*- β -nitrostyrenes. We concluded there that in toluene solution the reaction with *p*-dimethylamino- β -nitrostyrene takes place in a concerted manner. However, when very electron-deficient *p*, β -dinitrostyrene was used as a dipolarophile, a change in mechanism to one involving a zwitterionic intermediate was found. This suggests that the reaction course can be profoundly influenced by variations in the electronic features of alkenes. In order to provide a better understanding of this phenomenon, we are now extending our investigations to the study of substituent and solvent effects on the reaction. For this purpose *C,C,N*-triphenylnitronone (**1**) and *trans*-*R*-substituted nitroethylenes (**2a–c**) with different electron distributions on the reaction sites were chosen as model compounds (Scheme 1). Theoretically, the reaction



R = CH₃ (a), Cl (b), CN (c)

Scheme 1

should lead to regioisomeric (4*SR*,5*RS*)-2,3,3-triphenyl-4-nitro-5-*R*-isoxazolidines (**3a–c**) and (4*RS*,5*SR*) 2,3,3-triphenyl-4-*R*-5-nitroisoxazolidines (**4a–c**). In practice, however, at 298 K in toluene solution a high degree of regiochemical control was observed and only 4-nitroisoxazolidines **3a–c** were obtained (in addition to a small quantity of benzophenone).⁷

[2 + 3] Cycloaddition of nitrones to conjugated nitroalkenes provides an important synthetic route for the regio- and stereoselective synthesis of nitroisoxazolidines, which in a number of cases are difficult, or even impossible, to obtain in another way. Therefore, a detailed understanding of the reaction mechanism is essential. It is necessary to note that for nitronone [2 + 3] cycloadditions to some electron-deficient dipolarophiles, Black *et al.*⁸ and Abou-Gharbia and Joullie⁹ suggested the possibility of a zwitterionic mechanism. Some years ago such a mechanism was unequivocally confirmed by

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Huisgen *et al.*^{10,11} for cycloaddition of 2,2,4,4-tetraethyl-1-oxocyclobutane-3-thione *S*-methylide and of adamantanethione *S*-methylide to dimethyl 2,3-dicyanofumarate.

COMPUTATIONAL PROCEDURE

All calculations on the reactions in the gas phase were carried out using the AM1 method in the MOPAC 93 (Fujitsu) package of programs,¹² implemented on a Pentium III (733 MHz) computer. Although the AM1 method is unsuitable for the calculation of absolute activation energies because the electron correlation is neglected,^{13,14} the relative activation energies of reactions with different substituents or stereochemically different transition states can be estimated fairly accurately, since these species involve similar bonding and thus similar correlation energy changes from reactants to transition states.¹⁵ Moreover, calculations by this method are much faster than those by any *ab initio* methods¹⁴ and, as we showed recently, for nitroalkenes and nitrones give reliable values.⁶ Analogously to the [2 + 3] cycloaddition of nitropropene with methylazide,⁵ for calculation purposes the reactants were envisaged as placed on two parallel planes with the carbon-carbon double bond of nitroalkenes **2a-c** situated symmetrically over the >C=N(O)- moiety of nitrone **1**. The distance of 10 Å between the oxygen atom of the nitrone and the β (path **A**) or α (path **B**) carbon atom of nitroalkene was chosen arbitrarily. Optimizations of the stable structures were performed with the EF routine, whereas the transition states were calculated using the SADDLE procedure followed by the NLLSQ and/or TS method. The keyword PRECISE was used. The requested convergence for the gradients of energy was always less than $0.2 \text{ kcal mol}^{-1} \text{ \AA}^{-1} \text{ rad}^{-1}$ ($1 \text{ kcal} = 4.184 \text{ kJ}$). Stationary points were characterized by frequency calculations. All reactants, products and local minima had positive Hessian matrices. All transition states showed only one negative eigenvalue in their diagonalized Hessian matrices, and their associated eigenvectors were confirmed to correspond to the motion along the reaction coordinate under consideration. For several reactions, IRC calculations were performed to connect previously computed transition structures with local minima and products.

Geometry optimizations of the stationary structures in the presence of solvent were carried out using the AM1/COSMO method implemented in the MOPAC 93 package. In this method, the solvent is assimilated to a continuous medium, which surrounds a molecule-shaped cavity in which the solute is placed. The solvent is characterized by its relative permittivity (EPS), effective solvation radius (RSOLV) and the number of segments per atom (NSPA), which defines the solvent-accessible surface area based on the van der Waals radii. Analogously as in previous papers,^{5,6} we used EPS of

2.3, 20.0 and 35.9 corresponding to toluene, acetone and acetonitrile, respectively,¹⁶ RSOLV of 1 Å and NSPA of 40. The same calculation methodology was applied to the solutions as to the gas phase. All structures were optimized to an energy gradient less than $0.5 \text{ kcal mol}^{-1} \text{ \AA}^{-1} \text{ rad}^{-1}$. Because a problem was detected in IRC calculations when the COSMO routine was included, the transition structures were verified by increasing and decreasing newly formed C—C and C—O bonds by 0.1 Å and optimizing the so-obtained geometry with the EF procedure. All calculations were performed for 298 K. The absolute entropies of stationary structures were estimated from the complete vibrational analysis. Enthalpies were corrected to Gibbs free energies using the calculated entropies.

In this paper the letters **R**, **LM**, **TS** and **P** design starting supermolecules (**1 + 2**), local minimas, transition states and products, respectively. Their molecular properties are given in Table 1.

RESULTS AND DISCUSSION

In the gas phase, the energy profiles of all of the reactions studied are similar (Fig. 1). In the first step, interactions of 1,3-dipole molecules with the molecules of a dipolarophile lead to formation of **LM** supermolecules, which correspond to local minima on the potential energy hypersurface (PES). This process occurs without an activation barrier. In **LM**, the reagent geometries remain practically unchanged. The reagents rearrange in space so as to maximize electrostatic interactions between the reaction centers (Fig. 2). The magnitude of the charge on the reaction centers changes slightly, but the charge distribution remains unaffected. No charge transfer between the **LM** components was detected. The existence of **LM** on the PES decreases the enthalpy (ΔH^\ddagger) of the reaction system by 5.93–6.50 kcal mol^{-1} relative to the substrates (Table 2). However, the Gibbs free energy (ΔG^\ddagger) values exclude the existence of stable **LM** structures at 298 K, because of large negative entropy changes. It is interesting that similar species have recently been found in the reaction of ozone with ethylene in the gas phase and were confirmed by *ab initio* calculations.^{17,18}

The next critical point on the PES was found to be a saddle point. In this area, the transition state structures (**TS**) exhibit a large degree of rehybridization at the reaction centers. The bonds between the O1 and N2 atoms and between the C4 and C5 atoms undergo noticeable elongation. These changes are greater for path **A** than for path **B**. The new σ -bonds form simultaneously, although to different extents for different reaction paths. The transition states leading to adducts **4a-c** are more symmetrical (Table 1 and Fig. 2). In particular, the newly formed bonds C3—C4 and C5—O1 have lengths of 3.00–2.80 Å and 1.64–1.58 Å in the adducts **3a-c** and,

Table 1. continued

Solvent [ϵ]	Reactants Path	Structure	Bond length (\AA)										Angle [$^\circ$] O1—N2—C3	ΔH_{298} (kcal mol $^{-1}$)	ΔS_{298} (cal mol $^{-1}$ K $^{-1}$)	f^a (e)	Charge on the reaction sites (e)				
			O1—N2	N2—C3	C3—C4	C4—C5	C5—O1	O1	C3	C4	C5										
Acetone [20.0]	B	LM	1.230	1.345	5.005	1.344	3.158	124.05	149.06	123.9	0.00	-0.497	-0.096	0.007	-0.118						
		TS	1.257	1.395	2.331	1.406	1.863	117.21	180.17	128.0	0.20	-0.296	0.125	-0.201	-0.006						
	A	P	1.352	1.518	1.582	1.545	1.431	109.26	137.84	125.3	—	-0.153	0.111	-0.050	0.026						
		I + 2c	1.242	1.339	—	1.346	—	—	131.44	183.0	—	-0.596	-0.021	-0.118	0.031						
	Acetonitrile [35.9]	B	TS1	1.278	1.338	3.587	1.400	1.836	122.31	153.09	127.0	0.34	-0.413	0.163	-0.455	0.255					
			I	1.331	1.339	3.464	1.472	1.478	119.84	144.68	121.0	0.73	-0.171	0.307	-0.511	0.196					
A		TS2	1.322	1.385	2.390	1.477	1.496	115.76	156.04	123.9	0.18	-0.169	0.330	-0.490	0.141						
		P	1.349	1.517	1.591	1.547	1.445	107.65	132.10	125.6	—	-0.196	0.115	-0.131	0.075						
B		TS	1.290	1.338	3.456	1.393	1.704	121.65	163.00	118.9	0.44	-0.360	0.209	-0.478	0.194						
		P	1.353	1.518	1.582	1.544	1.430	109.33	127.10	125.7	—	-0.172	0.113	-0.057	0.035						
Acetonitrile [35.9]	A	I + 2c	1.243	1.339	—	1.346	—	—	129.91	184.8	—	-0.604	-0.014	-0.116	0.033						
		TS1	1.277	1.338	3.598	1.400	1.844	122.33	152.20	128.1	0.34	-0.418	0.161	-0.449	0.256						
	B	I	1.332	1.339	3.473	1.473	1.476	119.74	142.59	124.4	0.74	-0.167	0.310	-0.500	0.193						
		TS2	1.322	1.387	2.376	1.478	1.495	115.60	154.89	120.7	0.17	-0.169	0.330	-0.483	0.138						
	A	P	1.349	1.517	1.591	1.547	1.456	107.65	131.29	129.1	—	-0.198	0.115	-0.130	0.075						
		TS	1.290	1.338	3.460	1.392	1.711	121.69	161.79	118.9	0.43	-0.364	0.209	-0.475	0.194						
B	P	1.354	1.518	1.582	1.544	1.429	109.35	126.27	125.8	—	-0.174	0.113	-0.058	0.036							

^a Charge transfer was calculated according to expansion given by Leroy *et al.*²²

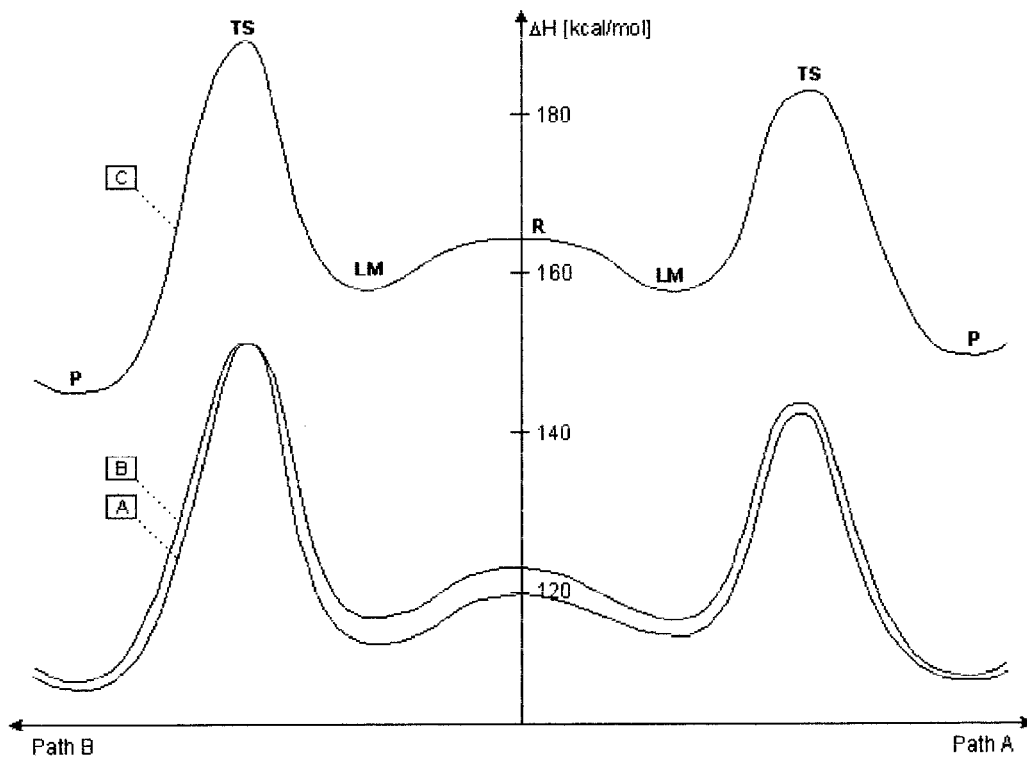


Figure 1. The reaction profiles for the [2 + 3] cycloaddition of triphenylnitronone **1** to nitropropene **2a** (A), chloronitroethylene **2b** (B) and cyanonitroethylene **2c** (C) in the gas phase. Structures at the marked points for the reaction with **2c** are depicted in Fig. 2

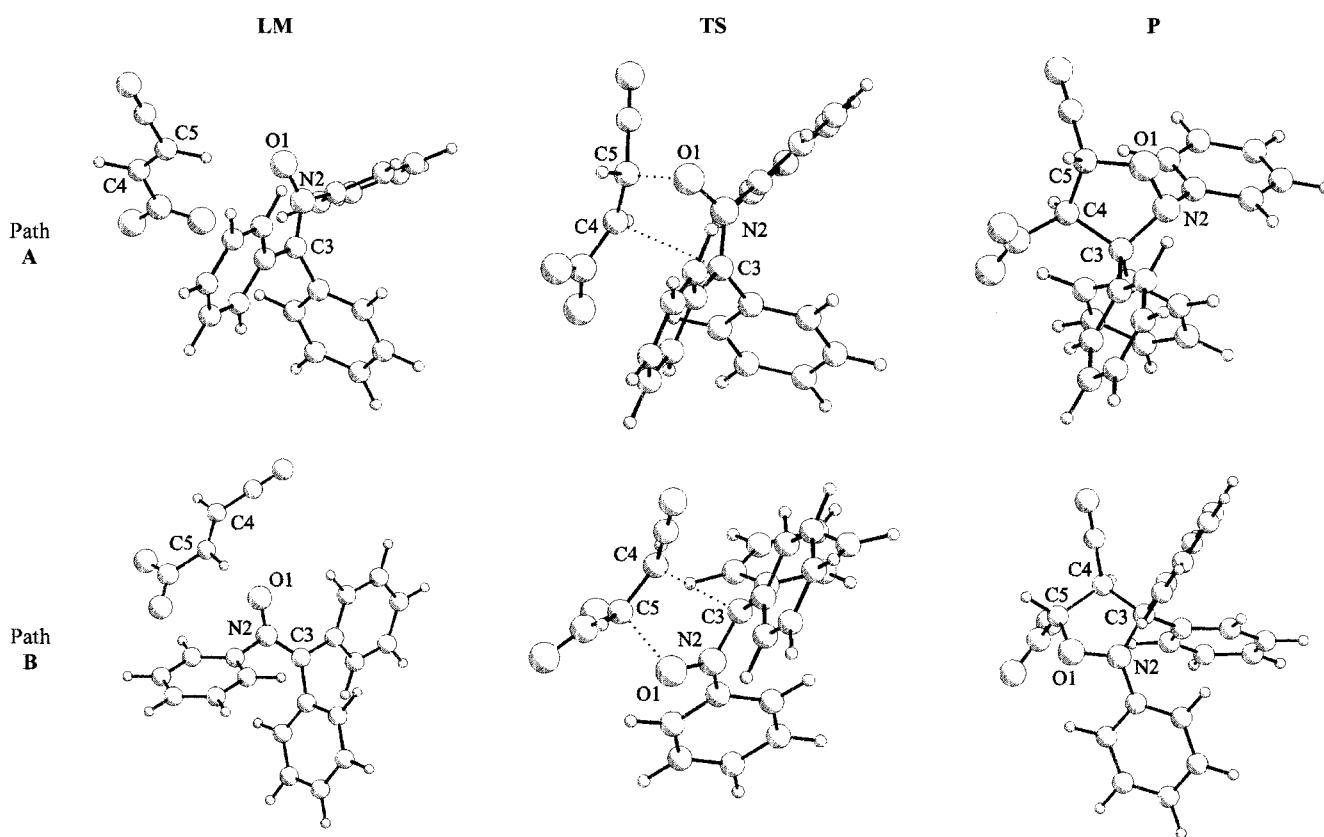


Figure 2. PLUTO views of stationary structures for [2 + 3] cycloaddition of triphenylnitronone **1** to cyanonitroethylene **2c** in the gas phase

Table 2. Eyring parameters for the [2 + 3] cycloaddition of triphenylnitron **1** to nitroalkenes **2a–c**

Solvent [ϵ]	Reactants	Path A				Path B			
		Structure	ΔH^\ddagger (kcal mol ⁻¹)	ΔS^\ddagger (cal mol ⁻¹ K ⁻¹)	ΔG^\ddagger (kcal mol ⁻¹)	Structure	ΔH^\ddagger (kcal mol ⁻¹)	ΔS^\ddagger (cal mol ⁻¹ K ⁻¹)	ΔG^\ddagger (kcal mol ⁻¹)
Gas phase [1.0]	1 + 2a	LM	-6.50	-81.97	17.93	LM	-4.55	-77.50	18.55
		TS	23.36	-79.38	47.02	TS	31.08	-75.57	53.60
	1 + 2b	LM	-5.93	-84.57	19.27	LM	-5.28	-78.33	18.06
		TS	21.41	-88.14	47.68	TS	28.34	-77.46	51.42
	1 + 2c	LM	-6.17	-78.21	17.14	LM	-6.50	-74.81	15.80
		TS	20.42	-75.68	42.97	TS	24.96	-76.20	47.67
Toluene [2.3]	1 + 2a	LM	-1.80	-54.71	14.50	LM	-2.73	-57.36	14.36
		TS1	20.23	-54.18	36.38	TS	35.18	-54.06	51.28
		I	19.42	-50.93	34.60				
		TS2	24.09	-53.96	40.17				
	1 + 2b	LM	-2.25	-63.81	16.77	LM	-0.64	-54.80	15.69
		TS1	21.00	-59.78	38.81	TS	33.76	-56.89	50.71
		I	18.44	-59.93	36.29				
		TS2	21.60	-59.98	39.48				
	1 + 2c	LM	-2.41	-63.44	16.50	LM	-0.91	-59.86	16.93
		TS1	19.96	-56.65	36.84	TS	30.21	-55.82	46.84
		I	18.49	-59.39	36.18				
		TS2	21.25	-56.55	38.10				
Acetone [20.0]	1 + 2c	TS1	21.66	-56.00	38.34	TS	31.57	-64.09	50.67
		I	13.24	-61.92	31.69				
		TS2	24.60	-59.06	42.20				
		TS1	22.29	-56.70	39.19	TS	31.88	-65.91	51.53
Acetonitrile [35.9]	1 + 2c	I	12.68	-60.40	30.67				
		TS2	24.98	-64.06	44.07				

2.59–2.32 Å and 1.88–1.90 Å in the adducts **4a–c**, respectively.

In all of the **TS** structures, charge transfer (t) between the substructures was observed. This effect is stronger for the transition states leading to the regioisomers **3a–c** (0.39–0.50e) than in the case of alternative transition states leading to **4a–c** (0.09–0.18e). The extent of charge transfer increases with increase in electron-acceptor character of the substituent in the alkene molecule.

The calculated activation Gibbs free energies (Table 2) indicate that in the reactions of nitron **1** with alkenes **2a–c**, adducts containing a nitro group in position 4 (path **A**) will be kinetically preferred. The preference, defined as $\Delta\Delta G^\ddagger = \Delta G_B^\ddagger - \Delta G_A^\ddagger$, is very clear. In the case of the reaction with alkenes **2a**, **2b** and **2c**, $\Delta\Delta G^\ddagger = 6.58$, 3.74 and 4.70 kcal mol⁻¹, respectively. On the other hand, when activation barriers for path **A** and path **B** are considered, it is noticeable that the electron-withdrawing cyano group in the *trans*-position to the nitrovinyl moiety lowers the barrier more than the electron-donating methyl group. However, evaluation of these quantities is not easy, since Eyring parameters for the reaction under study have not been experimentally determined in the gas phase.

Passing over the **TS** barrier leads the reacting system to the energy minimum **P**, which corresponds to the fully formed cycloadduct. Gibbs free energies of the product formation from the alkenes **2a**, **2b** and **2c** are 10.91, 8.64 and 9.07 kcal mol⁻¹ for path **A** and 8.00, 7.40 and 6.21 kcal mol⁻¹ for path **B**, respectively. Hence nitro-

soxazolidines **4a–c** should be more thermodynamically stable than the regioisomeric nitroisoxazolidines **3a–c**. As expected, the azolidine rings formed are not flat.

When the presence of toluene as a solvent is simulated, the energy profiles for path **A** of the reaction undergo significant change. Then, not two, but the following four critical points are localized on the PES between substrates (**R**) and products (**P**): local minimum (**LM**), two transition states (**TS1** and **TS2**) and an intermediate (**I**). However, no qualitative change is observed for path **B** (Fig. 3 and Table 1).

For both regioisomeric reaction paths, the reactant structure undergoes only slight change within **LM**. As in the gas phase, no charge transfer between reactants is observed in toluene. However, ΔG of the system at **LM** is substantially smaller by 0.64–2.73 kcal mol⁻¹.

As in the gas phase, in the dielectric medium path **A** is kinetically preferred ($\Delta\Delta G^\ddagger = 10.0$ – 14.9 kcal mol⁻¹). Hence the predicted regioselectivity is in full agreement with the experimental data⁷ and with PMO predictions.¹ Within the first transition state (**TS1**), only one of the newly formed σ -bonds is in an advanced state of completion. This is the bond between the C5 and O1 atoms (Fig. 4). The length of the C3–C4 bond is much greater than the bond lengths typical for transition states. Passing over the activation barrier corresponding to **TS1** to the intermediate **I** requires a considerable amount of energy ($\Delta G^\ddagger = 36.38$ – 38.82 kcal mol⁻¹). The intermediate **I** has zwitterionic character, as indicated by the charge

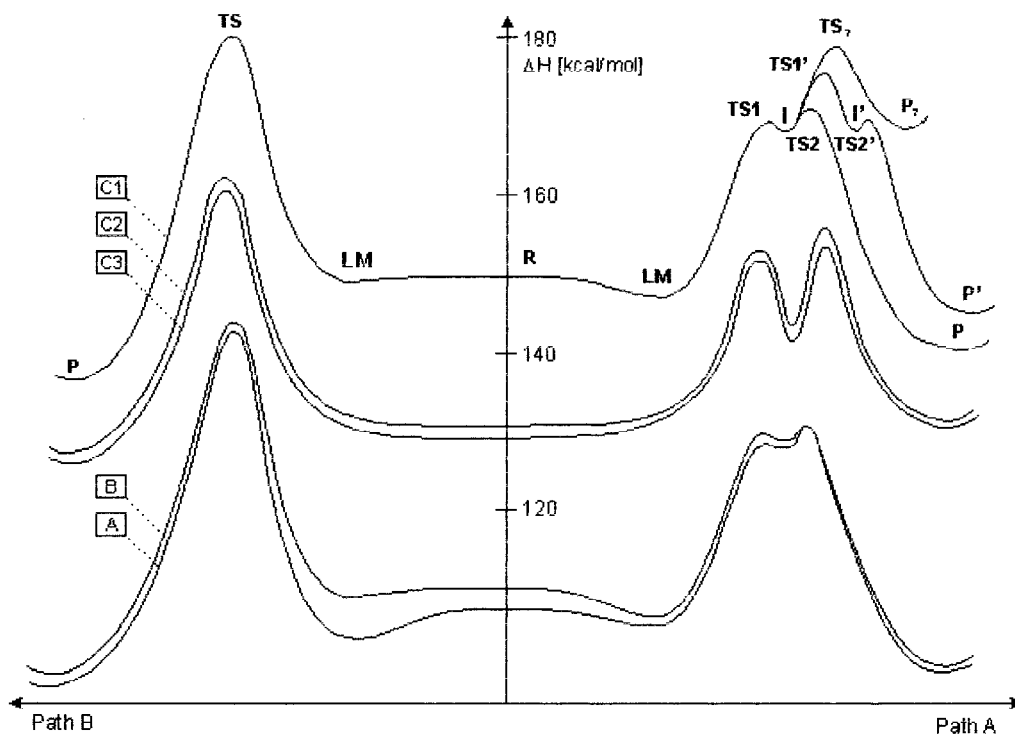


Figure 3. The reaction profiles for [2 + 3] cycloaddition of triphenylnitronone **1** to nitropropene **2a** (A), chloronitroethylene **2b** (B), cyanonitroethylene **2c** (C1) in toluene solution and cyanonitroethylene **2c** in acetone (C2) and acetonitrile (C3). Selected structures of the marked points for the reaction with **2c** in toluene solution along path A are depicted in Fig. 4

distribution within **I** and the amount of charge transferred between its substructures.

Formation of the five-membered heterocyclic ring of the product **P** from the zwitterion **I** occurs via the transition state **TS2** (Fig. 3). In comparison with **I**, the formation of the C3—C4 bond is clearly advanced within the transition state **TS2** (Fig. 4). The transition **I**→**P** requires a relatively small activation energy ($\Delta G^\ddagger = 1.92$ – 5.57 kcal mol⁻¹). In each case in toluene solution the activation Gibbs free energy for the process **R**→**P** is lower than those calculated for the gas phase. Moreover, the data in Table 2 indicate that the reactivity of nitroalkenes **2** decreases with increase in electron-donating character of the substituent in a *trans* position to the nitrovinyl moiety (**1a** < **1b** < **1c**). This phenomenon is in excellent agreement with kinetic data obtained for these reactions in our laboratory (A. Baranski, unpublished results). It should be noted, however, that the solvent effect calculated with the COSMO procedure does not account for specific effects, which may be important with the activated systems of solutes and solvents.^{19,20} An increase in polarity of the reaction medium ($\epsilon = 20.0$ and 35.9) slightly changes the energy profiles, as shown for the reaction with nitroalkene **2c** (Fig. 3). Namely, no local minima (**LM**) are observed along the reaction coordinate between the substrates and the first transition state on the reaction path leading to the adduct **3c**. The Gibbs free energy (ΔG^\ddagger) required to cross

the first activation barrier increases by 1.50 and 2.35 kcal mol⁻¹ in acetone and acetonitrile, respectively, in comparison with toluene. However, in those solvents the Gibbs free energy of the intermediate **I** is lower than that in toluene (Table 1). The enthalpy required to pass the second activation barrier also increases upon solvent change from toluene to more polar solvents. In acetone, the second activation barrier increases by 8.59 kcal mol⁻¹ and in acetonitrile by 11.48 kcal mol⁻¹ relative to toluene.

Theoretically, there is also a possibility of rotation around the C4—C5 bond within the structure **I**. Consequently, the substituent configuration on the C4 atom can change to yield the isomeric structure **I'** (Fig. 4). The relationship between the rotamers **I** and **I'** and their reactivity is illustrated in Scheme 2, which is the basic Curtis–Hammett kinetic system.²¹ In the case of the cycloaddition of alkene **2c** to nitronone **1** in toluene, the activation barrier of 6.84 kcal mol⁻¹ corresponding to the transition state **TS1'** has to be overcome (Fig. 3). The transition **I'**→**P'** is similar to the transition **I**→**P**, although the former requires less energy. The ΔG^\ddagger difference for the reaction with alkene **2c** is 1.13 kcal mol⁻¹. However, the rotation around the C4—C5 bond (**I**→**I'**) is energetically disfavored, because the energy required for ring closure to the product **P** with preserved original substituent configuration is lower than that for **P'**. The difference is 4.92 kcal mol⁻¹.

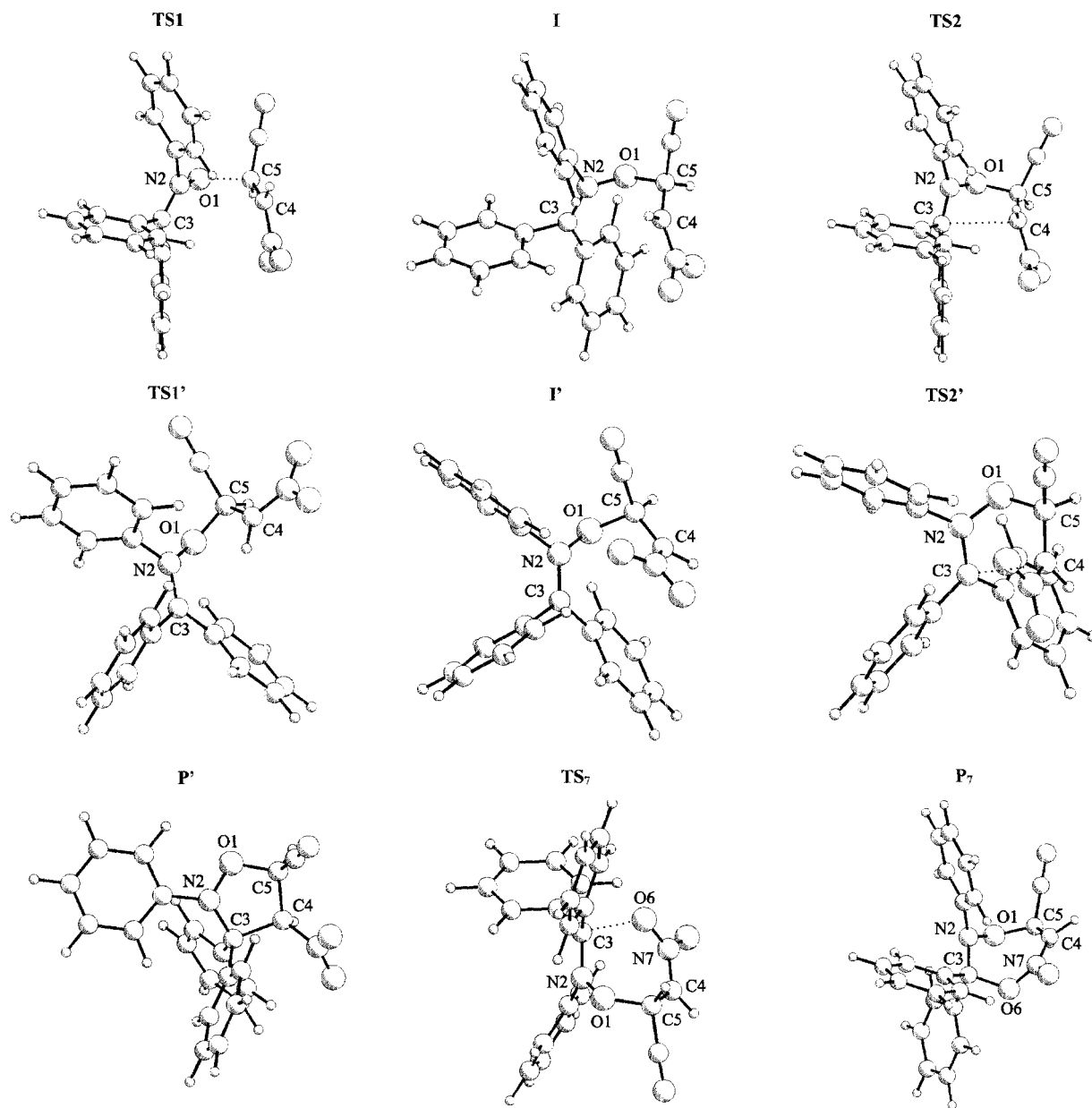
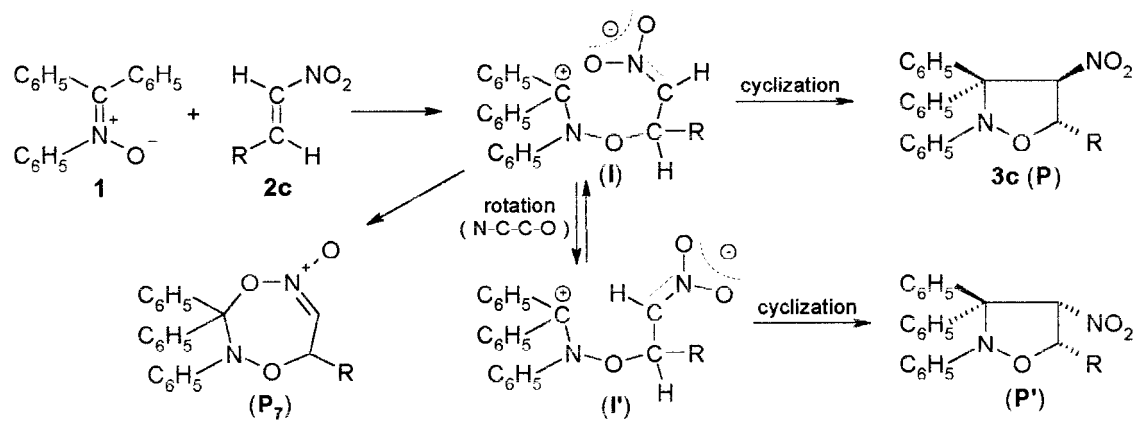


Figure 4. PLUTO views of essential stationary structures for **A** path of triphenylnitron **1** cycloaddition to cyanonitroethylene **2c** in toluene solution



Scheme 2

Table 3. Essential molecular properties from AM1/COSMO calculations of stationary structures **TS1'**, **I'**, **TS2'**, **P'**, **TS7** and **P7** in toluene solution

Structure	Bond length (Å)											Charge on the reaction sites (e)					
	O1—N2	N2—C3	C3—C4	C3—O6	O6—N7	N7—C4	C4—C5	C5—O1	ΔH_{298} (kcal mol ⁻¹)	ΔS_{298} (cal mol ⁻¹ K ⁻¹)	τ (e)	O1	C3	C4	C5	O6	
I	1.320	1.337	3.408	4.388	1.225	1.391	1.449	1.522	168.45	124.4	0.63	-0.225	0.271	-0.592	0.227	-0.532	
TS1'	1.334	1.339	3.435	—	1.229	1.376	1.472	1.472	176.22	127.5	0.73	-0.161	0.293	-0.619	0.239	-0.557	
I'	1.322	1.336	3.301	—	1.229	1.384	1.450	1.510	167.11	127.1	0.64	-0.219	0.278	-0.566	0.232	-0.529	
TS2'	1.312	1.363	2.507	—	1.221	1.409	1.458	1.523	169.09	129.9	0.54	-0.192	0.283	-0.524	0.178	-0.482	
P'	1.365	1.515	1.604	—	1.198	1.514	1.548	1.451	145.95	123.9	—	-0.196	0.115	-0.119	0.122	-0.378	
TS7	1.328	1.383	—	1.952	1.276	1.352	1.485	1.480	178.22	125.0	0.53	-0.154	0.405	-0.432	0.175	-0.500	
P7	1.326	1.484	—	1.497	1.346	1.332	1.492	1.461	168.09	124.4	—	-0.148	0.260	-0.276	0.127	-0.261	

Cyclization of the zwitterion **I** can also proceed according to a different scheme. There is a possibility of bond formation between the cationic center on the carbon atom of the >C=N(O)- fragment in nitrone and the anionic center on the oxygen atom of the NO_2 group in an alkene to yield the product **P**₇ (Scheme 2, Figs 3 and 4). Such cyclization is favored by electrostatic interactions between the reaction centers, as exemplified for the reaction with **2c** (Table 3). However, this process is not favored kinetically, because the seven-membered ring closure to form **P**₇ requires overcoming the activation barrier $\Delta G^\ddagger = 9.95 \text{ kcal mol}^{-1}$, while the Gibbs free energy barrier for the five-membered ring closure to form **P** does not exceed 2 kcal mol^{-1} .

In toluene solution, structures of the transition state for path **B** are similar to those in the gas phase (Table 1). The activation barriers follow similar trends. The ΔG^\ddagger values for the reaction with alkenes **2a**, **2b** and **2c** decrease by 2.33, 0.71 and $0.83 \text{ kcal mol}^{-1}$, respectively. An increase in solvent polarity leads to an increase in activation Gibbs free energy. For the reaction with nitroalkene **2c**, the value of ΔG^\ddagger increases by $1.36 \text{ kcal mol}^{-1}$ in acetone and by $1.67 \text{ kcal mol}^{-1}$ in acetonitrile.

In a dielectric medium, the structures corresponding to the minima **P** are similar to those in the gas phase. The Gibbs free energy of the product formation changes by 0.59 to $-1.83 \text{ kcal mol}^{-1}$ for path **A** and 0.04 to $1.45 \text{ kcal mol}^{-1}$ for path **B**.

CONCLUSIONS

From the AM1 calculations presented in this paper, it follows that the [2 + 3] cycloaddition of *C,C,N*-triphenylnitron (1) to nitroalkenes **2a–c** in gas phase occurs by a concerted mechanism, although the newly formed bonds, C3—C4 and O1—C5 (Fig. 2), are not formed synchronously. Kinetic factors favor the formation of cycloadducts with the nitro group in the C-4 position of the azolidine ring.

Introduction of toluene as a solvent increases the activation barriers for both regioisomeric reaction paths. It does not, however, affect the reaction regioselectivity although the energy profiles for path **A** undergo qualitative change. In this case, two transition states (**TS1** and **TS2**) and the intermediate (**I**) with zwitterionic character have been localized along the reaction coordinate between substrates and products. In more

polar solvents, such as acetone or acetonitrile, a two-step mechanism leading to 4-nitroisoxazolidines becomes more explicit. The energy difference between the transition state **TS2** and the intermediate **I** increases. Simultaneously, the local minimum (**LM**) between the substrates (**R**) and the first transition state (**TS1**) disappears. We are now finishing a kinetic study including secondary isotope and solvent effects. Some observations appear to confirm the possibility of a non-concerted mechanism of the reaction studied. These results will be published separately.

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