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Heteroelectrocyclic reactions of 3-acyl-4-azido heterocycles: ab initio and density functional calculations on 3-azido-propenal as a model system

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Abstract. Concerted as well as stepwise reaction pathways for cyclization of 3-azido-propenal to isoxazole have been investigated by density functional (B3LYP) and ab initio methods up to CCSD(T)/cc-pVQZ methods. These calculations clearly establish the pathway with concerted albeit asynchronous nitrogen extrusion and ring closure as the most feasible mechanism. Barriers for cyclization increase in the order Hartree–Fock < B3LYP < ACPF < CCSD(T). According to the geometrical parameters and the electronic structure of the TS as evidenced by natural bond order analysis this cyclization can be interpreted as a pseudopericyclic (heteroelectrocyclic) reaction.

Keywords: 3-Azido-propenal – Heteroelectrocyclization – Pseudopericyclic reaction – Coupled-cluster single–double and perturbative triple excitation – Density functional theory

Introduction

Azides are useful starting materials for a variety of synthetic transformations in organic chemistry [1]. Specifically, (hetero)aryl azides bearing in ortho-positions unsaturated groups, for example, carbonyl, azomethine, azo, or nitro, readily cyclize to a variety of bicyclic and polycyclic heteroaromatics [1] with a concomitant loss of nitrogen. For instance, isoxazoloquinolones and pyrazoloquinolones with potential biological activity are obtained by reaction of 4-azido-quinolines with a 3-acyl or 3-hydrazonoalkyl group [2]. In a series of papers, Dyall and coworkers [3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15] have investigated the mechanism and kinetics of the pyrolysis of substituted aryl azides. The large rate enhancement exerted by ortho substituents having lone pairs was attributed to a neighboring group participation in an electrocyclic ring closure reaction. Thus, although in a few cases products indicative of free radical [11] or nitrene [13] intermediates were found, a concerted mechanism was proposed. Alternatively, an intramolecular 1,3-dipolar cycloaddition giving a bicyclic intermediate followed by nitrogen extrusion has also been suggested [16]. Since nitrenes might also be formed by thermolysis and/or photolysis of aryl azides [17, 18], a stepwise mechanism with nitrogen loss preceding ring closure of the resulting (hetero)aryl nitrene has been postulated to account for the kinetic evidence obtained in the case of *ortho*-iminoalkyl aryl azide pyrolysis reactions [19]. Finally, in analogy to the formation of arenefurazan-1-oxides [20], ring closure in advance of elimination of N_2 is also a possibility.

As a model system for the cyclization of, for example, 3-acyl-4-azido-quinoline derivatives [2] ab initio [Hartree–Fock, HF, averaged coupled pair functional, ACPF, and coupled-cluster single–double and perturbative triple excitation, CCSD(T)] and density functional theory (Becke's three-parameter hybrid method with the Lee, Yang and Parr correlation functional, B3LYP) calculations on 3-azido-propenal **1** are presented. The various mechanistic possibilities, as already outlined, for cyclization of **1** to isoxazole **5** are depicted in Scheme 1. Only recently a computational study on the mechanism and kinetics of the pyrolysis of 2-nitrophenyl azide has been published [21]. In contrast to the nitro group in that compound, in **1** (as in the putative nitrene **2** derived therefrom) the formyl group can adopt either an *s-trans* (**1a**,**2a**) or the *s-cis* conformation (**1b**,**2b**). Only the latter orientation of the carbonyl group can lead to

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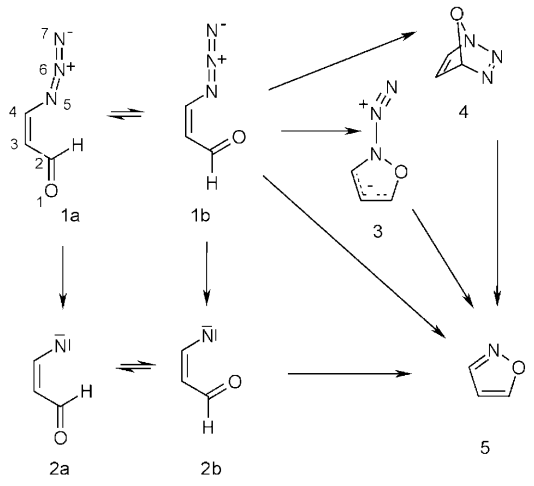
the cyclized product **5**. Locking this orientation by incorporation into a cyclic system, for example, in 8-azido-5-methoxy-1-tetralone or 1-azido-anthracen-9,10-dione, has been shown experimentally to result in large enhancements of the rates of pyrolysis [7, 10].



Scheme 1

Computational details

HF and density functional theory calculations (B3LYP [22, 23]) were performed using the Gaussian 98 program suite [24] with Dunning's correlation-consistent basis sets (cc-pVDZ, cc-pVTZ and, partly, cc-pVQZ) [25]. The geometries obtained thereby were characterized by frequency calculations as minima and transition states (TSs). TSs were further characterized by intrinsic reaction coordinate calculations along both directions of the normal mode corresponding to the imaginary frequency. Zero-point-energy (ZPE) corrections are unscaled. Electron correlation was taken into account by single-point ACPF [26] and CCSD(T) [27] calculations, employing the MOLPRO suite of programs [28]. Barriers and reaction energies obtained in this way were extrapolated by a rational function approach according to the scheme proposed by Martin [29].

Results and discussion

The energies of the various minima and TSs obtained by HF and B3LYP calculations relative to *s-cis*-3-azido-propenal **1b** are summarized in Table 1. First of all, basis set effects are quite small, especially in going from TZ to QZ. This gives us confidence that the basis sets used will be of sufficient reliability (for a discussion of these aspects in closely related systems, see, e.g., Ref [21]). The *s-trans* conformer **1a** is predicted to be slightly more stable (about 3 kcal mol^{-1}) than *s-cis*-3-azido-propenal **1b**. The barrier for interconversion between these two structures is quite low (9 kcal mol^{-1}, B3LYP/cc-pVTZ). Thus, unless severe steric hindrance prevents rotation to adopt the *s-cis* conformation, this reactive structure can easily be attained.

Concerted mechanism

Formation of isoxazole **5** is calculated to be strongly exothermic, although at the HF level ΔE_{react} appears to be rather exaggerated (Table 1). In line with these rather negative reaction energies, HF calculations also result in consistently lower values for the barrier of concerted elimination of nitrogen and ring closure to isoxazole [TS**(1b–5)**] than are obtained by the B3LYP procedure. However, while geometries for these systems generally are reproduced reasonably well by density functional theory methods, energies might not [21]. The values for the barriers of the concerted reaction **1b** –**5** as well as the elimination of N_2 from **1a** to give the assumed *s-trans*-nitrene **2a** obtained with the aid of the ACPF and CCSD(T) methods are listed in Table 2. Interestingly, with both methods a significant increase (about 8 kcal mol^{-1}, Table 2) in the barrier for concerted elimination ring closure [TS**(1b–5)**] is found in going from a DZ to a TZ basis set. Further enlargement of the basis set (TZ versus QZ) has essentially no effect on the calculated barrier height. Except for results obtained by using the cc-pVDZ basis, the activation energy for concerted formation of **5** increases in the order HF < B3LYP < ACPF < CCSD(T). Extrapolation according to the schemes of Martin [29] to the basis set limit yields barriers of 24.8 kcal mol^{-1} (B3LYP), 26.2 kcal mol^{-1} (ACPF), and 28.6 kcal mol^{-1} [CCSD(T)], respectively, as can be recognized from the values in Table 2. Inclusion of B3LYP/cc-pVTZ ZPE-corrections reduces these barriers by 1.8 kcal mol^{-1}. Experimentally, the activation energy, E_{act}, for thermolysis of 2-acetyl phenylazide was determined to be 25.8 kcal mol^{-1} in decaline [3].

The concerted electrocyclic mechanism proposed by Dyall and Kemp [3, 15] with neighboring group assis-

Table 1. Calculated energies (kcal mol^{-1}) relative to *s-cis*-3-azido-propenal **1b** (zero-point-energy, *ZPE*, corrections included). The values in *parentheses* are given relative to **1a**

Compound	Hartree–Fock			B3LYP		
	cc-pVDZ	cc-pVTZ	cc-pVQZ	cc-pVDZ	cc-pVTZ	cc-pVQZ
1a	− 3.7	− 4.1	− 4.1	− 2.4	− 2.7	− 2.8
TS**(1b–5)**	14.8	15.4	15.5	21.6	22.6	22.9
5	− 57.4	− 58.0	− 57.9	− 38.1	− 39.4	− 39.4
4	59.6					
TS**(1a–2a)**	15.1 (18.9)	15.4 (19.5)	15.5 (19.6)	27.9 (30.3)	27.4 (30.1)	–
6	− 67.9	− 69.3		− 41.8		
7	− 70.2	− 70.9		− 43.5		

Table 2. Calculated barriers (kcal mol^{-1}) for TS**(1b–5)** and TS**(1a–2a)**. Inclusion of B3LYP/cc-pVTZ ZPEs reduces the barriers by 1.8 kcal mol^{-1} [TS**(1b–5)**] and 2.8 kcal mol^{-1} [TS**(1a–2a)**]

Method	Basis	TS**(1b–5)**	TS**(1a–2a)**
ACPF	cc-pVDZ	18.1	24.9
	cc-pVTZ	25.7	25.5
	cc-pVQZ	26.1	–
	Extrapolated[a]	26.2	25.8
CCSD(T)	cc-pVDZ	20.0	30.5
	cc-pVTZ	28.1	32.0
	cc-pVQZ	28.5	–
	Extrapolated[a]	28.6	32.6
Experimental[b]		25.8	

[a]Extrapolation according to the scheme of Martin [29]
[b]Experimental value for thermolysis of 2-acetyl-phenylazide in decaline [3]

tance requires coplanarity of the reorganizing π bonds. However, in classical pericyclic reactions, overlap between the *p* atomic orbtals in the newly formed σ bond requires rotation (conrotatory or disrotatory motion) of the terminal unsaturated centers. Replacing one or both of these terminal carbons by heteroatoms bearing a lone pair makes possible the formation of the σ bond from this lone pair rather than the π orbital. Thus, no such rotation will be necessary for bonding interactions to occur. Reactions of this type have been dubbed pseudopericyclic [30] or heteroelectrocyclic [31] reactions. As amply described by Birney and coworkers [32, 33, 34, 35, 36, 37, 38] among the distinguishing and rather unexpected features of these reactions are a low or almost vanishing barrier, a planar or nearly planar transition structure, and symmetry rules do not apply, i.e., pseudopericyclic reactions will always be allowed irrespective of the number of electrons involved. Some pertinent structural features (B3LYP/cc-pVTZ, for atom numbering, see Scheme 1) of starting azides **1a** and**1b**, the respective TSs TS**(1a–2a)** and TS**(1b–5)** as well as the ring-closed product **5** are summarized in Table 3. First of all, both azide conformers are perfectly planar and *r* (N_5–N_6) is considerably longer (by about 0.1 Å) than *r* (N_6–N_7) which is close to the distance found in the nitrogen molecule. As expected for a heteroelectrocyclic (pseudopericyclic) reaction [34, 35, 36, 37] the heavy atom skeleton for the TS**(1b–5)** is also planar. In contrast, for TS**(1a–2a),** which lacks the neighboring group participation of C=O, substantial deviations from planarity are found. Although in TS**(1b–5)** the interaction O_1...N_5 seems to be an important feature, the distance *r* (O_1–N_5) is still quite long, whereas *r* (N_5–N_6) has already become rather elongated, i.e., from structural features one can conclude that ring closure significantly lags behind extrusion of nitrogen. From kinetic data, an early TS with N–O bond formation being less advanced than other changes in bonds has been inferred [10].

Additional information about the pericyclic versus pseudopericyclic nature of ring-closure TSs [39, 40] can be provided by the natural bond order (NBO) analysis [41, 42]. Relevant details are provided in the Electronic Supplementary Material. In line with the structural features just described, the azido group in both **1a** and **1b** can be interpreted in terms of an N_5–N_6 formal single bond and an N_6–N_7 triple bond. The π-type lone pair at N_5 is significantly delocalized into the C_3–C_4 and, even more so, the N_6–N_7 π bonds, thus providing some double-bond character to the C_4–N_5 and, especially, the N_5–N_6 bonds. Similarly the σ-type lone pair at N_5 shows some delocalization into the in-plane N_6–N_7 π bond. In both TS**(1a–2a)** as well as TS**(1b–5)** the N_5–N_6 σ bond is still present although strongly polarized towards N_6, indicating substantial weakening of this bond. Also, the NBO analysis does not point towards any bonding interaction yet present in TS**(1b–5)** between O_1 and N_5. Thus, in line with structural data as well as the experimental interpretation of kinetic data, formation of isoxazole **5** from 3-azido-propenal **1b** should occur in a concerted manner albeit with nitrogen extrusion considerably more advanced than ring closure. Furthermore, according to the notation of a pseudopericyclic (hetero-

Table 3. Selected structural parameters obtained by B3LYP/cc-pVTZ calculations. For atom numbering, see Scheme 1

	1a	**1b**	TS**(1a–2a)**	TS**(1b–5)**	**5**
r (O_1–C_2)	1.213	1.211	1.216	1.239	1.341
r (C_2–C_3)	1.463	1.466	1.453	1.411	1.354
r (C_3–C_4)	1.342	1.345	1.384	1.377	1.420
r (C_4–N_5)	1.396	1.386	1.312	1.346	1.305
r (N_5–N_6)	1.235	1.236	1.707	1.597	
r (N_6–N_7)	1.126	1.126	1.102	1.108	1.091[a]
r (O_1–N_5)	4.137	2.881	3.926	2.194	1.397
∠(H–C_2–C_3)	115.9	113.7	115.3	120.7	133.4
∠(O_1–C_2–C_3)	123.2	126.0	123.5	119.6	110.5
∠(C_2–C_3–C_4)	124.7	126.7	123.2	113.4	103.1
∠(C_3–C_4–N_5)	122.5	123.6	112.0	120.8	112.4
∠(C_4–N_5–N_6)	117.8	117.8	110.3	107.9	
∠(N_5–N_6–N_7)	172.7	171.8	143.9	143.6	
τ(C_4–C_3–C_2–O_1)	180.0	0.0	174.0	0.0	0.0
τ(C_3–C_4–N_5–N_6)	180.0	180.0	160.3	180.0	
τ(C_3–C_4–N_5–O_1)		0.0		0.0	0.0
τ(C_2–C_3–C_4–N_5)	0.0	0.0	−32.4	0.0	0.1

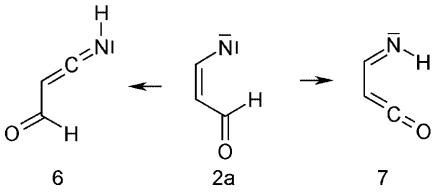
[a]Value for N_2

electrocyclic) ring closure, the newly formed $\sigma(O_1–N_5)$ bond stems from the *p*-type lone pair on O_1 in **1b** rather than the $C_2=O_1$ π orbital as is normally the case in classical pericyclic reactions. Alternatively, formation of isoxazole can be regarded as an intramolecular nucleophilic substitution with molecular nitrogen as a leaving group and the lone pair on the carbonyl oxygen acting as a nucleophile. In this view, the stability of the ejected N_2 leads to the strong asynchronicity in the TS.

Stepwise mechanisms

Three stepwise mechanisms have been considered (Scheme 1). The calculated (HF/cc-pVDZ) relative energy of the proposed product **4** of a 1,3-dipolar cycloaddition pathway [16] is substantially higher than the barrier for the concerted reaction and, despite extensive potential-energy surface (PES) scans, no TS for its formation could be located. Furthermore, optimization with B3LYP/cc-pVTZ leads to immediate extrusion of nitrogen from **4**. For 2-nitrophenyl azide the concerted cyclization–elimination appears to be generally accepted [15], whereas for 2-benzoylphenyl azide bicyclic intermediates of type **4** were proposed [16]. Given these results, at least for the 3-azido-propenal model system no such stepwise mechanism proceeding via 1,3-dipolar cycloaddition is operative in the formation of **5**. Similarly, all attempts to locate an intermediate of type **3** were unsuccessful. PES scans using either *r* ($O_1–N_5$) or *r* ($N_5–N_6$) as scan parameters in **1b** invariably resulted in identical transition structures, i.e., TS**(1b–5)**, describing concerted loss of N_2 and ring closure to isoxazole **5**. In addition, optimization of the nitrene **2b** immediately led to **5**.

These findings are in line with the theoretical investigations of Rauhut and Eckert [21] on the reaction of 2-nitrophenyl azide, which yielded no evidence for the existence of a nitrene intermediate either. In this case, however, formation of a nitrene could be possible by elimination of nitrogen from the *s-trans* conformation **1a** of the starting azide. However, the calculated barrier for nitrogen elimination [TS**(1a–2a)**, Tables 1, 2] is significantly higher than the rotational barrier for interconversion **1a**–**2a**. It also seems to be higher than the corresponding barrier TS**(1b–5)** calculated at the B3LYP and CCSD(T) levels of theory. As a result, unless steric hindrance prevents conformational interconversion of the starting azide, cyclization to **5** should occur via the *s-cis* conformation of 3-azido-propenal. In case this interconversion is not possible because of steric reasons, it will also be impossible for the resulting nitrene **2a**. Thus, no cyclization products can be expected for such compounds. Interestingly, nitrene **2a** also turned out to be unstable, since geometry optimizations lead either to 3-iminopropenal **6** or to 3-imino-propen-1-one **7** (Scheme 2). Neither of these rearrangements are possible in the actual systems investigated experimentally. Apparently then, both these reactions are artifacts of the model system used and, consequently, they were not pursued any further.



6 2a 7

Scheme 2

Conclusion

A detailed ab initio [HF, ACPF, CCSD(T)] and density functional (B3LYP) theory study on concerted and various stepwise mechanisms for the cyclization of 3-azido-propenal as a model system for (hetero)aromatic *ortho* -acyl azides has been presented. According to these calculations the following conclusions can be drawn:

1. The only feasible mechanism for the cyclization to isoxazole appears to be the concerted one. All putative intermediates for the various possible stepwise mechanisms turn out to be unstable.
2. On the basis of the geometric and electronic structure as revealed by NBO analysis, the corresponding transition structure TS**(1b–5)** is, however, highly asynchronous with ring closure significantly lagging behind nitrogen extrusion. Formation of **5** can be interpreted as pseudopericyclic heteroelectrocyclization with the *p*-type lone pair on O_1 providing the newly formed $O_1–N_5$ σ bond. The major difference between such pseudopericyclic (heteroelectrocyclic) reactions and an all-π mechanism, i.e., a pericyclic reaction, is an in-plane lone-pair nucleophilic attack. In the present reaction, this attack not only leads to cyclization but also to ejection of molecular nitrogen. Consequently, as an alternative interpretation, these ring closures can also be viewed as intramolecular nucleophilic substitution.
3. Barrier heights obtained by HF calculations are strongly underestimated and are considered to be unreliable. They increase in the order B3LYP < ACPF < CCSD(T).
4. Inclusion of ZPE corrections (at the B3LYP/cc-pVTZ level) reduces barrier heights by 1.8 kcal mol^{-1} [TS**(1b–5)**] and 2.8 kcal mol^{-1} [TS**(1a–2a)**], respectively.
5. The CCSD(T) barrier for the reaction **1b** $\rightarrow$ **5** + N_2 (28.6 kcal mol^{-1}, 26.8 kcal mol^{-1} with B3LYP/cc-pVTZ ZPE correction) is in close agreement with the experimental activation energy of 25.8 kcal mol^{-1} for cyclization of 2-acetylphenyl azide [3].

Finally, it should be mentioned that phenylnitrene [17] as well as vinylnitrene [43] have triplet ground states and intersystem crossing of the singlet nitrene might

compete with ring closure. However, formation of azobenzenes is considered to be one of the main reaction products resulting from triplet phenylnitrenes. In the actual reactions, i.e., cyclization of heterocyclic *ortho*-acyl substituted azides no such products indicative of triplet nitrenes were found.

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