

Pericyclic versus Pseudopericyclic 1,5-Electrocyclization of Iminodiazomethanes. An ab Initio and Density Functional Theory Study

Walter M. F. Fabian,[‡] Vasilij A. Bakulev,[†] and C. Oliver Kappe*[‡]

Institute of Organic Chemistry, Karl-Franzens-University Graz, Heinrichstrasse 28, A-8010 Graz, Austria, and Department of Technology of Organic Synthesis, Ural State Technical University, Mira 19, 620002 Ekaterinburg, Russia

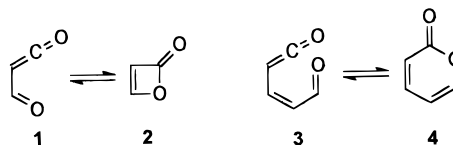
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Density functional (B3LYP/6-311+G**) and ab initio (MP2/6-311+G** and MP4(SDTQ)/6-311+G**//MP2/6-311+G**) calculations on the ring closure reactions of (*E*)- and (*Z*)-iminodiazomethane ((*E*)-**5**, (*Z*)-**5**), vinyldiazomethane **7**, and formyldiazomethane **9** to 1*H*-1,2,3-triazole **6**, 3*H*-pyrazole **8**, and 1,2,3-oxadiazole **10**, respectively, are reported. (*E*)-**5** cyclizes via a low barrier (ca. 10 kcal mol⁻¹) pseudopericyclic nonrotatory transition state. Ring closure of (*Z*)-**5** and **7** proceeds by a monorotatory movement of the imino or vinyl group with a substantially higher barrier (ca. 25 kcal mol⁻¹). Despite being endothermic, for the reaction **9** → **10** also a rather low activation energy (ca. 10 kcal mol⁻¹) is computed. The NBO analysis is used to interpret the electronic structures of the respective transition states in terms of their pericyclic monorotatory (TS ((*Z*)-**5** → **6**), (TS (**7** → **8**)) or pseudopericyclic nonrotatory ((TS ((*E*)-**5** → **6**), (TS (**9** → **10**)) nature.

Introduction

The subset of pericyclic reactions for which there is no cyclic orbital overlap was originally described by Lemal as pseudopericyclic reactions.¹ In a recent series of publications, Birney et al.² have reported a number of examples for thermal pseudopericyclic reactions that include cycloadditions,^{2a–e,g} sigmatropic rearrangements,^{2e,f,3} and electrocyclizations.^{2b,f} Such pseudopericyclic reactions are typically characterized by planar (or almost planar) transition states and low activation barriers.² Furthermore, since there is no closed loop of interacting orbitals, a pseudopericyclic reaction is orbital symmetry allowed regardless of the number of participating electrons.² In the case of electrocyclic reactions both the 1,4-cyclization of formylketene (**1** → **2**)^{2b,4} and the 1,6-cyclization of 5-oxo-2,4-pentadienal (**3** → **4**)^{2f} were found to proceed in a pseudopericyclic manner, by in-plane attack of the lone-pair of electrons on the carbonyl oxygen to the electrophilic ketene carbon. In contrast to classical electrocyclizations,⁵ for ring closure reactions of this general type, no distinction between a conrotatory

or disrotatory pathway based on the number of π electrons can therefore be made.



Given the large number of known electrocyclizations involving heterosubstituted π -conjugated systems,⁶ it is likely that apart from the two cases involving oxoketenes reported by Birney^{2b,f} there are other examples of such pseudopericyclic ring closure reactions that have not yet been recognized as such. In this context, we now report the results of ab initio and density functional theory calculations on the 1,5-electrocyclization of iminodiazomethanes of type **5**, for which both a pericyclic and a pseudopericyclic cyclization mode seems feasible (see below).^{6,7,8a} For comparison purposes, we have also carried out analogous calculations for vinyldiazomethane (**7** → **8**) and formyldiazomethane (**9** → **10**) cyclizations. In this context it should be noted that for the related iminoazide–tetrazole equilibrium an apparent pseudopericyclic reaction pathway was already proposed in 1976

* To whom correspondence should be addressed. Fax: (43)-(316)-3809840. E-mail: kappeco@balu.kfunigraz.ac.at.

[‡] Karl-Franzens-University, Austria.

[†] Ural State Technical University, Russia.

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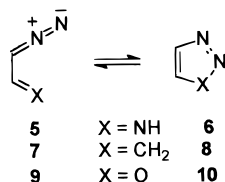
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Table 1. Relative Energies (kcal mol⁻¹) for Cyclizations 5 → 6, 7 → 8, 9 → 10, and *E/Z*-Isomerization (*Z*)-5 → (*E*)-5 Obtained at Various Levels of Theory^a

compound	I ^b	II ^c	III ^d
(<i>E</i>)-5	0.00	0.00	0.00
TS ((<i>E</i>)-5 → 6)	8.97	12.13	8.84
6	-14.88	-20.04	-16.86
7	0.00	0.00	0.00
TS (7 → 8)	25.30	23.08	22.15
8	-4.91	-9.25	-9.67
9	0.00	0.00	0.00
TS (9 → 10)	12.55	15.37	9.11
10	12.05	9.61	9.01
TS ((<i>Z</i>)-5 → 6)	25.14	25.98	21.90
(<i>Z</i>)-5	2.03	2.75	2.19
TS ((<i>E</i>)-5 → (<i>Z</i>)-5)	23.52	27.34	27.66

^aTotal energies and ZPE's are given in Table S1 of the Supporting Information. ^bB3LYP/6-311+G**/B3LYP/6-311+G** + 0.98*ZPE(B3LYP/6-311+G**). ^cMP2/6-311+G**/MP2/6-311+G** + 0.9646*ZPE(MP2/6-311+G**). ^dMP4(SDTQ)/6-311+G**/MP2/6-311+G** + 0.9646*ZPE(MP2/6-311+G**).

by Burke et al.^{8b} before the introduction of the term pseudopericyclic by Lemal.¹



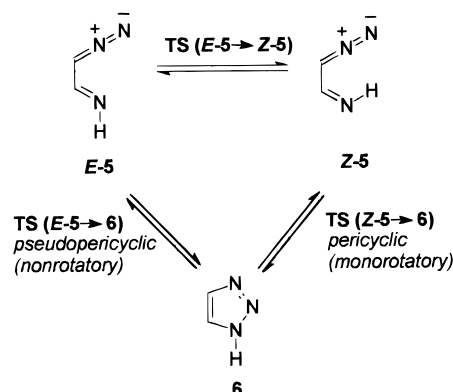
Computational Methods

All computations were done by the Gaussian 94 program suite.⁹ The 6-311+G** basis was used throughout. Geometries were completely optimized at both Becke's three-parameter¹⁰ hybrid density functional-HF method with Lee-Yang-Parr correlation function¹¹ (B3LYP/6-311+G**) as well as by *ab initio* second-order Møller-Plesset perturbation theory¹² (MP2/6-311+G**). All stationary points were characterized as minima or transition states by frequency calculations. For transition states in addition, intrinsic reaction coordinate calculations at the B3LYP/6-311+G** level of theory were performed. Zero point energies (ZPE) were scaled by 0.98 (B3LYP/6-311+G**) and 0.9646 (MP2/6-311+G**).¹⁴ Single point calculations were done at the MP4(SDTQ)/6-311+G**/MP2/6-311+G** level of theory. Electronic structures were analyzed with the aid of the natural bond orbital (NBO)¹⁵ method (program G94NBO¹⁶) using the HF/6-311+G** density.

Results and Discussion

Energetic aspects (relative energies in kcal mol⁻¹ with respect to the open chain isomers) obtained at the various levels of theory for the four cyclizations (*E*)-5 → 6, (*Z*)-5 → 6, 7 → 8, and 9 → 10 are collected in Table 1 (total energies and ZPE's are provided in Table S1 of the

Supporting Information). Relevant structural data of the respective transition states are depicted in Figure 1. Results for the NBO analysis of the electronic structures of reactants, transition states, and products are given in Table S2 of the Supporting Information.



Iminodiazomethane → 1,2,3-Triazole Cyclization

(5 → 6). Iminodiazomethanes of type 5 are with very few exceptions highly reactive substances that are in equilibrium with, or undergo spontaneous 1,5-cyclization to 1*H*-1,2,3-triazoles 6.^{6,7,8a,17} Only iminodiazomethanes bearing strong electron-withdrawing substituents on the imine nitrogen (i.e. *N*-cyano) have been isolated in pure form.¹⁷ In line with this experimental finding is the rather large calculated exothermicity (≥15 kcal mol⁻¹) of this ring closure reaction as well as its rather low barrier (ca. 10 kcal mol⁻¹, Table 1). Iminodiazomethanes of type 5 may exist as geometrical isomers which in some cases have been observed spectroscopically in solution.¹⁷ We have therefore considered both isomers, (*E*)-5 and (*Z*)-5, in our calculations.

The most prominent structural feature (see Figure 1) of TS ((*E*)-5 → 6) is its complete planarity ($\tau(\text{C}3-\text{C}4-\text{N}5-\text{N}1) = 0.0^\circ$, $\tau(\text{C}3-\text{C}4-\text{N}5-\text{H}5a) = 180.0^\circ$ with both B3LYP and MP2), confirming the pseudopericyclic^{1,2} nature of this ring closure reaction. This in-plane iminodiazomethane → 1,2,3-triazole cyclization requires an *E*-configuration of the imine group as in (*E*)-5 so that the lone pair of electrons on the imine nitrogen is oriented toward the diazo functionality. Note that for this cyclization mode *no rotation* of the imine group is required which therefore can be designated as a "nonrotatory" cyclization. In sharp contrast, the present calculations on the cyclization of the isomeric (*Z*)-5 lead to a nonplanar ($\tau(\text{C}3-\text{C}4-\text{N}5-\text{N}1) = -2.5^\circ$ (B3LYP), -3.5° (MP2); $\tau(\text{C}3-\text{C}4-\text{N}5-\text{H}5a) = -61.5^\circ$ (B3LYP), -48.9° (MP2), see Figure 1) transition state TS ((*Z*)-5 → 6) resembling those obtained for "conventional" electrocyclic processes, e.g. the vinyldiazomethane → 3*H*-pyrazole cyclization described below. For this type of cyclization *one rotation* (of the imine group) is required which therefore can be described as "monorotatory" cyclization process (the determination of a possible rotation of the N=N-terminus is, of course, prohibited by the geometrical arrangement of the diazo group).^{6b} In agreement with the general features of pseudopericyclic reactions² the activation

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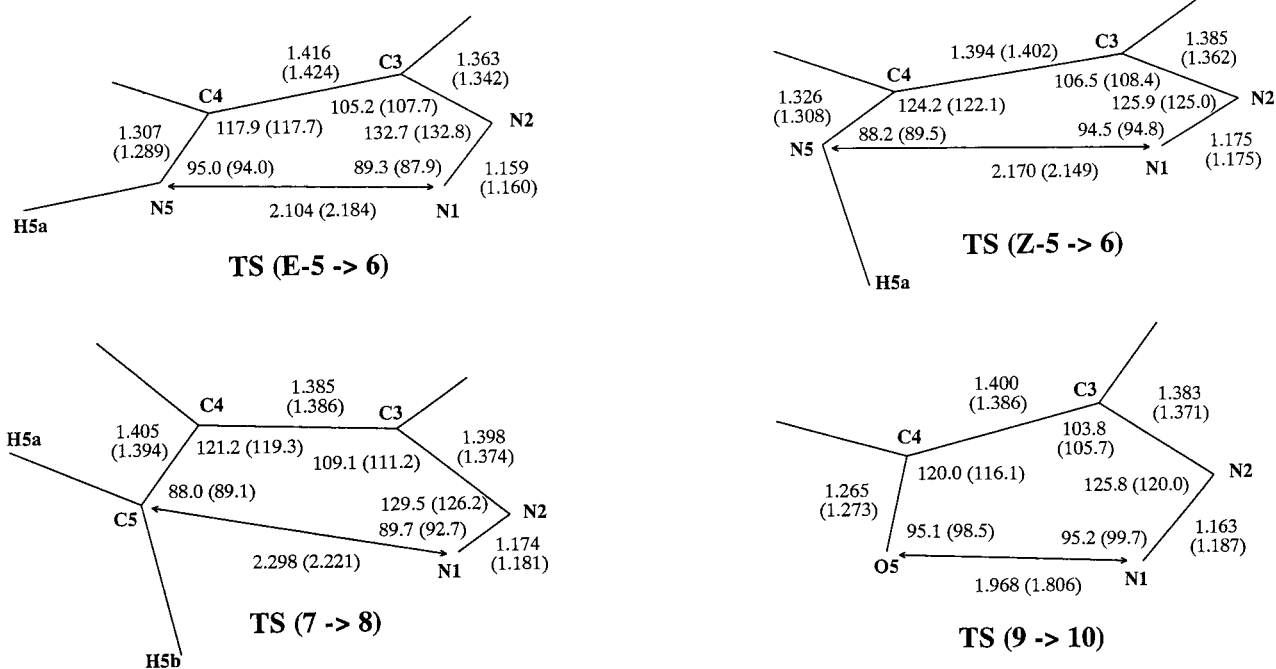


Figure 1. MP2/6-311+G**⁻-calculated structures of transition states TS ((*E*)-5 → 6), TS ((*Z*)-5 → 6), TS (7 → 8), and TS (9 → 10). Distances are in angstroms, angles in degrees (B3LYP/6-311+G** values are given in parentheses).

energy for the pericyclic ring closure (*Z*)-5 → 6 is at least twice that for the pseudopericyclic process (*E*)-5 → 6 (see Table 1).

As revealed by the NBO analysis, the two transition states TS ((*E*)-5 → 6) and TS ((*Z*)-5 → 6) differ also substantially in their electronic structure: in TS ((*E*)-5 → 6) the C4=N5 π -bond is still largely intact whereas in TS ((*Z*)-5 → 6) this bond is already broken due to rotation. This in turn leads to formation of the C3=C4 π -bond—which in contrast is not yet present in TS ((*E*)-5 → 6)—and a σ -type interaction between $p_x(N1)$ and a p_x-p_z hybrid (stemming from the p_z -orbital of the original π -(C4–N5) bond) at N5 with a quite substantial bond order of ca. 0.6. In contrast, bonding between N1 and N5 in TS ((*E*)-5 → 6) is mediated by the sp^2 -type lone pair at N5. This involvement of a lone pair in the development of the new σ -bond has been shown to be one of the characteristic features of pseudopericyclic reactions.^{2,18} In striking contrast to TS ((*Z*)-5 → 6), there is no N1–N5 NBO in TS ((*E*)-5 → 6). Consequently, bonding between these two centers is rather weak (bond order ca. 0.2). Bending in TS ((*Z*)-5 → 6) at N2 leads to a complete breaking of the original in-plane N1–N2 π -bond with a concomitant development of a sp^2 -type lone pair at N2. On the other hand, in TS ((*E*)-5 → 6) this bond is, albeit more localized at N2 than in (*E*)-5, still present. Both TS ((*E*)-5 → 6) and TS ((*Z*)-5 → 6) still contain a

$\pi_z(N1-N2)$ NBO, thus justifying the description of these two cyclizations as nonrotatory and monorotatory, respectively.

E/Z-isomerization of imines preferentially occurs via inversion rather than rotation of the C=NR group.¹⁹ The B3LYP/6-311+G** calculations predict inversion of (*Z*)-5 → (*E*)-5 to be slightly more feasible than direct cyclization (*Z*)-5 → 6. In contrast, at the MP2/6-311+G** and, especially, the MP4(SDTQ)/6-311+G** level of theory, a higher activation energy for *E/Z*-isomerization by inversion than for monorotatory electrocyclization (Table 1) is obtained.

Vinyldiazomethane → 3*H*-Pyrazole Cyclization (7 → 8). In contrast to their imino analogues (i.e. 5) vinyldiazomethanes 7 are somewhat more stable and many examples of this type of cyclization are known.⁶ The experimentally determined activation energy for the 1,5-cyclization of vinyldiazomethane 7 to 3*H*-pyrazole 8 is 22.6 kcal mol⁻¹.²⁰ Apparently, substituents have little effect on the rate of cyclization as one would expect for an electrocyclic reaction.²¹ The considerably lower computed reaction energy for the cyclization 7 → 8 as compared to 5 → 6 is understandable in terms of the dienic nature of the primary product, i.e., 3*H*-pyrazole 8 which generally is stabilized by subsequent tautomerization to the aromatic 1*H*-pyrazole.⁶ Note that the calculated activation energies for the process 7 → 8 (ca. 22–25 kcal mol⁻¹, Table 1) are in close agreement with the experimental value of 22.6 kcal mol⁻¹.²⁰ Importantly, the barrier for ring closure 7 → 8 is at least twice that for the pseudopericyclic, nonrotatory process (*E*)-5 → 6 and quite similar to the monorotatory cyclization (*Z*)-5 → 6. Formally, the cyclization 7 → 8 requires one 90° rotation of the vinyl double bond (monorotatory electrocyclization).

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As expected for a possibly genuine pericyclic reaction,^{22,23} TS (**7** → **8**) strongly deviates from planarity originating from both rotation around the C4–C5 bond ($\tau(\text{C3–C4–C5–H5a}) = 152.9^\circ$ (B3LYP), 155.5° (MP2); $\tau(\text{C3–C4–C5–H5b}) = -54.0^\circ$ (B3LYP), -50.8° (MP2)) as well as pyramidalization of C5 (height of C5 above C4–H5a–H5b plane is 0.154 \AA (B3LYP) and 0.155 \AA (MP2)). The key electronic feature of TS (**7** → **8**) is a three-center-bond formed from the p_z -orbitals at C3 and C4 and a p_x – p_z hybrid at C5. The nonbonding combination of these three AO's (node at C4) is significantly delocalized to N1 and N2 (20% and 17%, respectively, Table S2 of the Supporting Information). This is responsible for the substantial N1–C5 bonding interaction (bond order ca. 0.4). In contrast to TS ((*Z*)-**5** → **6**), where the $\pi_x(\text{N1–N2})$ NBO is still present, here a significant rehybridization is discernible with a p_x – p_z mixing which would be compatible with a ca. 30° disrotatory motion of the diazo functionality. Furthermore, N1–C5 bonding in TS (**7** → **8**) is largely due to electron donation from the second C3–C4–C5 three-center-bond into the antibonding " π_z "(N1–N2) NBO (occupancy = 0.7e) rather than into the in-plane N1–N2 π -NBO as is the case in TS ((*Z*)-**5** → **6**).

Formyldiazomethane → 1,2,3-Oxadiazole Cyclization (9** → **10**).** Although formyldiazomethanes (α -diazoketones) have been known for a long time the existence of their 1,2,3-oxadiazole valence isomers has not been confirmed until recently. Benzo[1,2,3]oxadiazole was observed in equilibrium with its more stable diazoketone isomer in both the gas phase as well as low-temperature matrixes.²⁴ Naphtho[2,3-*d*][1,2,3]oxadiazole is an isolable substance and has been reported to be stable at -20°C for several days.²⁵ On the basis of ab initio calculations using HF/3-21G geometries, Nguyen et al.²⁶ concluded that the parent 1,2,3-oxadiazole **10** should not be isolable but rather undergo spontaneous ring-opening to **9**, even under low-temperature matrix conditions. To be consistent we have reoptimized this system at our considerably higher level of theory. Except for the MP2/6-311+G** result, the computations indicate a nearly barrierless ring opening of **10**, which is in essential agreement with the previous calculations by Nguyen et al.²⁶ Cyclization of formyldiazomethane **9** is special in two respects: first, it is endothermic and hence might not show the rather low barriers characteristic for pseudopericyclic reactions.^{2a} Second, there is no structural probe in **9** for a distinction between a pericyclic (here monorotatory) or a pseudopericyclic (nonrotatory) mode of reaction. Therefore, one has to rely solely on energetic criteria or the electronic structure of TS (**9** → **10**) rather than its geometry—which is completely planar. As shown by the data in Table 1—

despite being endothermic—the activation energy for ring closure **9** → **10** is comparable to the pseudopericyclic reaction (*E*)-**5** → **6** and about half that for the pericyclic **7** → **8** transformation. According to the NBO analysis, the surprisingly advanced bonding (N1–O5 bond order ca. 0.5 as compared to a N1–C5 bond order of ca. 0.4 in TS (**7** → **8**) and a N1–N5 bond order of ca. 0.2 in TS ((*E*)-**5** → **6**)) between N1 and O5 is accomplished by a $p_x(\text{N1})$ – $p_x(\text{O5})$ NBO derived from the N1–N2 in-plane π -bond and $lp(\text{O5})$ in **9**. Involvement of $lp(\text{O5})$ in the bonding appears to be characteristic for a pseudopericyclic process. On the other hand, development of the sp^2 -type lone pair at N2 as well as transformation of the C4–O5 π -bond present in **9** into a p_z -type lone pair at O5 and a significantly populated (1.76e) C3–C4 π -bond are electronic features more closely resembling TS ((*Z*)-**5** → **6**) rather than TS ((*E*)-**5** → **6**). Based on the present computational study, a definitive conclusion on the cyclization mode **9** → **10** is therefore not possible, although a pseudopericyclic nonrotatory pathway is most probable.

Conclusion and Outlook

The present calculations on the 1,5-cyclization of iminodiazomethanes to 1,2,3-*H*-triazoles ((*E*)-**5** → **6**) provide firm evidence for a pseudopericyclic molecular orbital topology² which involves an in-plane attack of the imine lone pair on the terminal nitrogen of the diazo functionality (Figure 1). Although the possibility of such a cyclization mode for iminodiazomethanes has been suggested previously by Huisgen,²⁷ Bakulev,⁷ and L'abbe,^{8a} the present ab initio and density functional calculations nicely confirm these earlier hypotheses. In agreement with the most recent proposals by Birney et al. on the characteristics of pseudopericyclic reactions^{2a} we find that the cyclization (*E*)-**5** → **6** has a planar transition state and a low activation barrier. In addition, we note that for electrocyclizations of this type no rotation of the terminal π -bonds takes place. This is in contrast to the cyclization (*Z*)-**5** → **6**, where not only the geometry but also the electronic structure of TS ((*Z*)-**5** → **6**)—as revealed by the NBO analysis—differs quite substantially. In this respect, the iminodiazomethane system (*E/Z*)-**5** is better suited for a distinction between a nonrotatory and a monorotatory pathway than the oxoketene cyclizations **1** → **2** or **3** → **4** (see above), since there is no structural probe in the latter systems to distinguish between the two cyclization modes. On the basis of the differentiation in the number of disconnections in the loop of interacting orbitals in (pseudo)pericyclic reactions,^{2a} the electrocyclization (*E*)-**5** → **6** may be classified as pseudopericyclic reaction with two orbital disconnections (the monorotatory electrocyclizations (*Z*)-**5** → **6**, and **7** → **8**) have one orbital disconnection). As speculated by Huisgen,²⁷ the electronic structure of TS ((*E*)-**5** → **6**), as given by the NBO analysis, is also compatible with a description of this ring closure as a nucleophilic addition of the imino nitrogen (i.e., the heteroatom e in **11**) to the diazo group (the electrophilic onium functionality $a \equiv b^+$ in **11**) with the sp^2 -type lone pair at N5 acting as donor and the in-plane N1–N2 π -orbital as electron acceptor. In contrast, unless one assumes a complete 90° rotation of the diazo group which would transform the original in-plane

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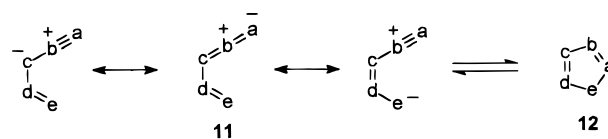
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π -orbital into the π_z -orbital of TS ((*Z*)-**5** \rightarrow **6**), ring closure of (*Z*)-**5** can be described as a monorotatory process. For the transformation **7** \rightarrow **8**, although there is no geometrical probe for such a discrimination, the NBO analysis points toward a disrotatory pericyclic reaction. The results for formyldiazomethane **9** are less clear-cut, but a nonrotatory pseudopericyclic mode of cyclization appears to be consistent with the computational results.

As a final point it seems appropriate to compare the present results and conclusions with very recent experimental and computational data obtained by Dolbier et al.²⁸ on the 6π -electrocyclization of *o*-vinyl isocyanates to 2-quinolinones. Despite the rather high activation energies (ca. 30 kcal mol⁻¹)—which may be caused by the endothermic nature of the primary cyclic product^{2a,28}—from the transition state structure a monorotatory pseudopericyclic 6π -electrocyclization has been proposed for these reactions. The key feature of the TS is an interaction of the terminal vinyl p-orbital with the in-plane C=O rather than the expected out-of-plane C=N π -bond. Thus, the electronic structure of this transition state more closely resembles our TS ((*Z*)-**5** \rightarrow **6**) rather than TS (**7** \rightarrow **8**).

The mechanistic concept of 1,5-electrocyclizations of conjugated 1,3-dipoles (i.e., **11** \rightarrow **12**) has been discussed



by Huisgen in his landmark review on 1,5-electrocyclizations in 1980.^{6b} The various issues associated with the peculiar molecular orbital topology in these cyclizations were recognized, and the question was posed: “are these numerous known ring closures (**11** \rightarrow **12**) still electrocyclic reactions of the pentadienyl anion type?”²⁷ Due to the recent redefinitions of pseudopericyclic reactions by Birney et al.² it becomes clear that many of these electrocyclizations involving heterosubstituted conjugated π -systems (including, but not restricted to, systems of type **11** where e is a heteroatom)⁶ may possess pseudopericyclic molecular orbital topology. For such cyclization reactions we have proposed²⁹ the term HeteroElectrocyclization Reactions (HER).³⁰ Further work will be devoted to identify the common features and structural requirements for cyclizations of this general type.

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Supporting Information Available: Total energies including ZPE's (Table S1), and results of NBO analysis (Table S2) of the electronic structures of reactants, transition states, and products (10 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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