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Experimental Support for Planar Pseudopericyclic Transition States in Thermal Cheletropic Decarbonylations

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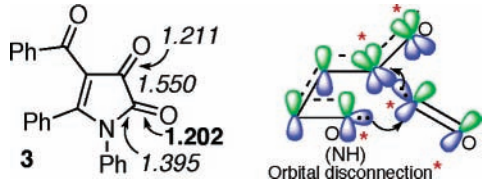
ABSTRACT



Low-temperature crystal structures of three pyrroledíones (3–5) and a furandione (9) were obtained and compared to structurally related compounds that cannot undergo decarbonylation. Systematic trends in bond lengths and angles are consistent with distortions along the reaction coordinate, in accord with the structure correlation principle of Dunitz. Since the pyrroledione and furandione rings in 3–5 and 9 are planar, these ground-state geometries prefigure the calculated planar, pseudopericyclic transition states.

Many pseudopericyclic reactions are calculated to have planar transition states,[1] in contrast to pericyclic reactions, which have nonplanar ones.[2] How can this prediction be explored experimentally? In this work, we do so by examining ground-state geometries that prefigure the transition state.

The structure correlation principle, as elaborated by Dunitz, suggests that structures of molecules can show distortions along a reaction coordinate, but only when the same electronic factors that stabilize the transition state are present in an appropriate ground-state geometry.[3] This is indeed a corollary of the well-known Hammond postulate and the older, but less cited, Bell−Evans−Polanyi principle.[4] Such distortions are indeed observed in pericyclic reactions.[5] We have shown that cyclohexenes are distorted toward retro-Diels−Alder reactions, only when constrained to a boat conformation, as in the transition state.[5a,b] Thermal cheletropic decarbonylation of 3-cyclopentenone (eq 1) has only recently been shown by one of us[5c] to follow the linear, disrotatory stereochemistry predicted by Woodward and Hoffman and by ab initio calculations.[6] Examination of crystal structures of nonplanar 3-cyclopentenone derivatives shows that they are similarly distorted along the reaction coordinate for cheletropic decarbonylation.[5c] In contrast to the nonplanar distortions toward nonplanar, pericyclic transi-

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(1) (a) Birney, D. M.; Wagenseller, P. E., *J. Am. Chem. Soc.* **1994**, *116*, 6262−6270. (b) Birney, D. M.; Xu, X.; Ham, S., *Angew. Chem., Int. Ed.* **1999**, 38, 189−193.

(2) Houk, K. H.; Gonzalez, J.; Li, Y. *Acc. Chem. Res.* **1995**, *28*, 81.

(3) (a) Burgi, H. B.; Dunitz, J. D.; Shefter, E. *J. Am. Chem. Soc.* **1973**, *95*, 5065−5067. (b) Jones, P. G.; Kirby, A. J. *J. Chem. Soc., Chem. Commun.* **1979**, 288−289. (c) Bürgi, H. B.; Dunitz, J. D. *Acc. Chem. Res.* **1983**, *16*, 153−161.

(4) (a) Hammond, G. S. J., *J. Am. Chem. Soc.* **1955**, *77*, 334−338. (b) Bell, R. P. *Proc. R. Soc. London, Ser. A* **1936**, *154*, 414. (c) Evans, M. G.; Polanyi, M. *Trans. Faraday Soc.* **1938**, *34*, 11−29. (d) For a recent illustration of this, see Figure 4 in ref 5a. For a broader perspective on these and related ideas, see: Jenks, W. P. *Chem. Rev.* **1985**, *86* (6), 511−527.

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(6) (a) Woodward, R. B.; Hoffmann, R. *The Conservation of Orbital Symmetry*.; Verlag Chemie, GmbH: Weinheim, 1970. (b) Birney, D. M.; Wiberg, K. B.; Berson, J. A. *J. Am. Chem. Soc.* **1988**, *110*, 6631−6642.

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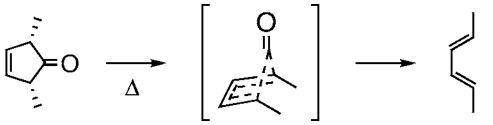
tion states found for pericyclic reactions, the crystal structure of the [4 + 2] dimer of camphorketene shows in-plane ground-state distortions toward the calculated planar and, therefore, pseudopericyclic transition state.[7]



(1)

Calculations at the MP2(FC)/6-31G* level[8] predict planar transition states for the known cheletropic decarbonylations of 2,3-pyrroledione (**1**)[9] and 2,3-furandione (**2**)[10] (Figure 1). They may be understood as pseudopericyclic reactions, with orbital disconnections as shown. Recently, Chamorro[11] analyzed the bonding in these transition states using the electron localization function, and Rodriguez-Otero et al.[12] calculated that the transition states are nonaromatic; both concur that the pathways are pseudopericyclic.

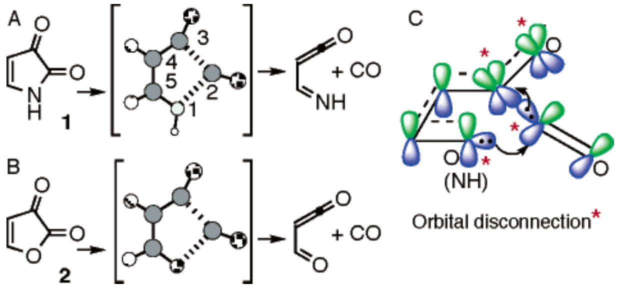


Figure 1. Decarbonylation of **1** (A) and **2** (B) at the MP2/6-31G-(d) level; from ref 8. (C) Pseudopericyclic orbital overlap in the transition state.

Given the dramatic difference between nonplanar transition states for pericyclic decarbonylations (supported by experiment and calculation) and the prediction of planar transition states for the pseudopericyclic ones, we sought to confirm this experimentally. The stereochemical outcome, commonly used to infer transition-state geometry of pericyclic reactions, is not an option for **1** or **2**, as none of the breaking bonds have stereochemical markers. However, the structure-correlation principle is ideally suited for this task. The prediction is that the ground-state geometries of **1** and **2** will show geometric distortions toward the loss of carbon monoxide if, and only if, the rings are in the proper conformation for this reaction. Specifically, if the rings are planar and distorted, then this provides strong experimental support for the calculated planar, pseudopericyclic transition states.

Therefore, structures of three pyrrolediones were determined and comparisons were made with related structures that lack one or more of the features necessary for the decarbonylations. Compounds **3**−**8** were prepared, and the crystal structures were determined at 130 K to reduce thermal errors.[13] The uncertainties in the distances and angles are available in the CIF files, but are uniformly <0.002 Å and < 0.2°. As expected, the pyrroledione rings in **3** − **5** are all planar. Selected bond distances and angles are shown in Figure 2. Compounds **3** and **4** can readily undergo thermal cheletropic fragmentation;[8,9a] compound **5** is more stable because decarbonylation disrupts the aromatic ring.[9b] Thus, it would be expected that **5** will therefore show smaller distortions along the reaction coordinate.[4] Compounds **6**−**8** are reference compounds; they have the same hybridization at C3 as the pyrrolediones but cannot readily lose CO.

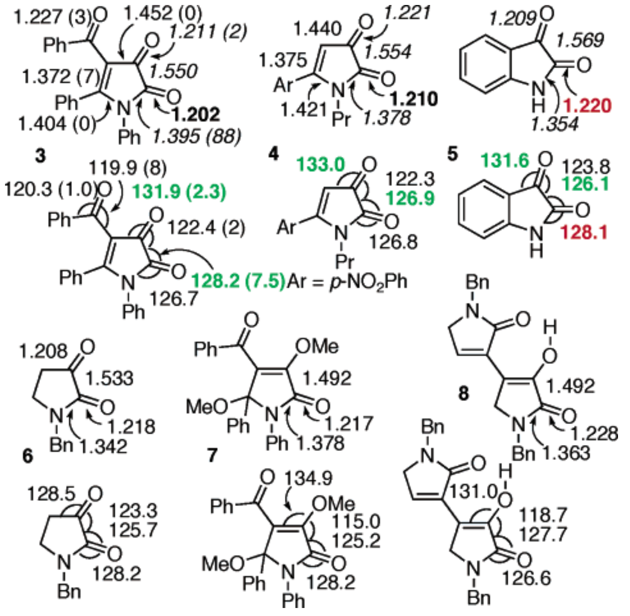


Figure 2. Selected bond lengths (Å) and angles (deg) from low-temperature X-ray crystal structures. There are two independent molecules of **3** in the asymmetric cell; replacing the rightmost digits with the values in parentheses gives the lengths and angles in the second molecule. The structure/reactivity principle predicts distances in bold to be shorter and in italics to be longer than in model systems. Angles in green are predicted to be more open. Values in red do not follow the predicted trends. Atom numbering is as in Figure 1.

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[7] Shumway, W. W.; Dalley, N. K.; Birney, D. M. *J. Org. Chem.* **2001**, *64*, 5832−5839.

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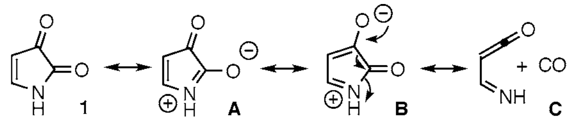
[10] (a) Murai, S.; Hasegawa, K.; Sonoda, N., *Angew. Chem* **1975**, *87* (18), 668−669. (b) Wentrup, C.; Heilmayer, W.; Kollenz, G. *Synthesis* **1994**, 1219−1248.

[11] Chamorro, E. *J. Chem. Phys.* **2003**, *118*, 8687−8698.

[12] Rodriguez-Otero, J.; Cabaleiro-Lago, E. M.; Hermida-Ramon, J. M.; Pena-Gallego, A. *J. Org. Chem.* **2003**, *68*, 8823−8830.

[13] Compounds were synthesized as described in the literature or by analogy to related systems. See the Supporting Information for details of the synthesis and X-ray structure determination, CIF data have been deposited with CCSD, 252543−252549. (a) Roberts, E.; Turner, E. E. *J. Chem. Soc. London* **1927**, 1832−1857. (b) Kollenz, G.; Igel, H.; Ziegler, E. *Monatsh. Chem.* **1972**, *103*, 450−459. (c) Kappe, C. O.; Terpetschnig, E.; Penn, G.; Kollenz, G.; Peters, K.; Peters, E.-M.; von Schnering, H. G. *Liebigs Ann.* **1995**, 537−543. (c) Baldwin, J. E.; Chan, M. F.; Gallacher, G.; Otsuka, M.; Monk, P.; Prout, K. *Tetrahedron* **1984**, *40*, 4513−4525.

What distortions of a pyrroledione would be expected for a planar transition state? A pseudopericyclic reaction can often be recognized if the π-electrons can be rearranged independently of the σ-electrons, as in resonance structures **B** and **C** (eq 2). Thus, in **3**−**5**, the N1−C2, C2−C3, and C3=O bonds (in *italics* in Figure 2) as well as the C4−C5 bonds should be lengthened relative to model systems, while the C2=O bonds (**bold**) as well as the C3−C4 and N1−C5 bonds should be shorter. In the calculated transition states (Figure 1A,B), the departing CO bends toward N1. Thus, the N1−C2=O angle should be reduced and the O=C2−C3 angle should be opened. The C4−C3=O angle should also be opened, toward the linear ketene. The angles predicted to be more open are shown in green. With only two exceptions (shown in red, both for **5** which should show the least distortion) all of the distances and angles in **3**−**5** follow these trends, as discussed below. The fact that the rings are planar and the geometries are distorted toward fragmentation strongly suggests that the transition states are also planar and therefore pseudopericyclic. These distortions can also be found in previous MP2/6-31G* calculations of **1** and **2**.[8] These data are reproduced in the Supporting Information.



(2)

Many factors can influence bond lengths and angles, including hybridization, resonance, and strain. To accurately assess the importance (or not) of the structure correlation principle in this context requires consideration of these effects. In the discussion below, the comparisons are between systems in which these are as similar as possible; situations where the comparisons are more complicated are noted.

The trends in the bond lengths are the most straightforward and these predictions are uniformly followed in compounds **3** and **4**. Although decarbonylation of **5** is more endothermic and thus would be expected to show less distortion, these predictions are generally followed in **5** as well. In the absence of other effects, amide resonance (as in **A**) is stronger than in a vinylogous amide (**B**, see **S7** in the Supporting Information). And this is clearly the case for **6**, in which the C3=O bond is significantly shorter than the C2=O bond. Yet, the C2=O carbonyl is shorter than C3=O (1.202 Å vs 1.211 Å in **3** and 1.210 Å vs 1.221 Å in **4**). This is consistent with a contribution from resonance structure **C**. The C3=O bonds in **3** and **6** are the same within experimental error, arguably because the vinylogous ester resonance in **3** is mitigated by resonance with the exocyclic carbonyl.

The C2−C3 bonds in **3**−**5** are long by any standard (1.550, 1.554, and 1.569 Å respectively). They are much longer than those in the comparison structures **6**−**8** (1.533, 1.492, 1.492 Å) even though these bonds are all between sp^2 carbons with an oxygen attached. Others have discussed the lengthening of this bond in **5** as due to lone-pair repulsion between the carbonyls[14] or a negative hyperconjugative interaction between the oxygen lone pairs and the adjacent C−C σ^* orbital.[15] These cannot be full explanations, as this bond in **6** is significantly shorter at 1.533 Å. The benzannulation in **5** increases the strain in the five-membered ring, contributing to longer endocyclic bonds N1−C2 and C2−C3. The aromatic ring would interrupt resonance as in **B** and since decarbonylation of **5** is more endothermic,[9b] resonance structure **C** would also contribute less and **A** more.

In **3** and **4**, the N1−C2 bonds are longer (1.395 and 1.378 Å) and the C2=O bonds are shorter (1.202 and 1.210 Å) than in the model systems **6** and **8**. This is consistent with a reduction in the amide resonance (**A**), attributable to resonance structures **B** or **C**. Comparing **3** with **4**, N1−C5 and C2=O are shorter in **3**, while N1−C2 is longer, consistent with less amide resonance **A** in **3**. This likely reflects the conjugation of two carbonyls in **3**. The N1−C2 bonds in **4** and **7** are equal (1.378 Å). This is not an appropriate comparison, however, because the nitrogen substituents are different, Pr in **4** and Ph in **7**. The phenyl conjugation in **7** would be expected to compete with amide resonance, lengthening the N1−C2 bond. The appropriate comparisons for the N1−C2 bonds are between **3** and **7** (1.395 and 1.378 Å) and between **4** and **6** or **8** (1.378 and 1.342 or 1.363 Å). In each of these comparisons, the molecule that can decarbonylate has the longer N1−C2 bond.[16]

The trends in the bond angles of **3** and **4** also reflect distortions toward the calculated, pseudopericyclic transition states. Most significantly, the C3−C2=O angles in **3** and **4** (128.2° [127.5°] and 126.9°) are wider than the N1−C2=O angles (126.7° and 126.8°). This is consistent with the angle of the departing CO in the calculated transition state (Figure 1). In contrast, in **5**−**8**, the N1−C2=O angles are the larger ones. Formation of the ketene also requires the O=C3−C4 angle to become more linear and indeed, in **3** and **4** these angles (131.9° [132.3°] and 133.0°) are larger than the O=C3−C2 angles (122.4° [122.2°] and 122.3°). However, this trend is the same in **5**−**8**, so it is not unambiguous. It is noteworthy that in **5**, O=C3−C4 (131.6°) is more linear than N1−C2=O (128.1°) while the angles are almost identical in **6**. This suggests that resonance structure **C** contributes even to **5**.

A search of the Cambridge Structural Database[17] (CSD) revealed five other pyrolediones and numerous structures analogous to **6**−**8**. Several additional substructures were also examined, having most, but not all of the structural features of pyroledione and thus being unable to decarbonylate via a planar, pseudopericyclic transition state. These structures are discussed in detail in the Supporting Information. The trends in the bond distances and angles in these structures are uniformly consistent with the trends discussed above and

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(14) Palenik, G. S.; Koziol, A. E.; Katrizky, A. R.; Fan, W. Q. *J. Chem. Soc., Chem. Commun.* **1990**, 715.

(15) Rathna, A.; Chandrasekhar, J. *J. Chem. Soc., Perkin Trans. 2* **1991**, 1661−1666.

(16) This comparison is also validated by comparing **3** (N−Ph) with **4** (N−Pr); again, the N−Ph has the longer N1−C2 bond (1.395 vs 1.378 Å).

(17) CSD Version 5.24 (Oct 2003): (a) Allen, F. H. *Acta Crystallogr.* **2002**, *B58*, 380−388. (b) Allen, F. H.; Motherwell, W. D. S. *Acta Crystallogr.* **2002**, *B58*, 407−422.

thus consistent with the pseudopericyclic mechanism for decarbonylation of pyrolediones.

Furandiones also decarbonylate;[10] calculations again predict planar, pseudopericyclic transition states.[8] Furandione **9** was synthesized[10a] and its crystal structure determined (Figure 3). Structure **10** is the average of eight structures from the CSD. In **9**, the O1−C2 and C2−C3 bonds are long while the C2═O bond is short as compared to the model system **10**. The internal comparisons in **9** are also self-consistent; the C2═O bond (1.187 Å) is shorter than the C3═O bond (1.215 Å) and the C3−C2═O and C4−C3═O angles (130.7° and 131.8°) are wide as compared to the O1−C2═O and C2−C3═O angles (122.6° and 123.4°). However, these angles are quite similar to those found in **10**. Additional related structures from the CSD are also discussed in detail in the Supporting Information. As with the pyrrolediones, it is clear that the geometry of **9** is distorted toward the calculated, planar, pseudopericyclic transition state.

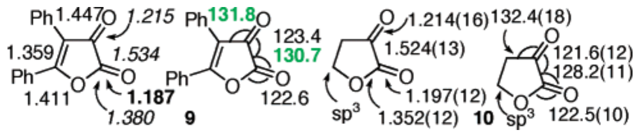

Figure 3. Geometry of **9**. Substructure **10** shows the average of **8** compounds from the CSD.[17] See Figure 1 for numbering, Figure 2 for key.

In summary, low-temperature crystal structures of pyrrolediones **3**, **4**, and **5** and of furandione **9** were obtained. When compared to related molecules that cannot decarbonylate, these structures show in-plane distortions well outside of experimental error. The most conservative interpretation is that the same stereoelectronic effects that are proposed for the calculated[8] pseudopericyclic transition states are manifest in the ground-state geometries, and thus, the pseudopericyclic pathways for decarbonylation are possible. The structure correlation principle[3] suggests a stronger conclusion, that the ground-state distortions prefigure, and provide experimental support for planar, and thus pseudopericyclic pathways for the loss of carbon monoxide from pyroledione and furandiones. By analogy, these results support planar transition states for pseudopericyclic reactions in general, in contrast to the familiar nonplanar transition states found for pericyclic reactions.

Acknowledgment. We thank the Robert A. Welch Foundation for generous support of this work and Bruce R. Whittlesey for the structure of **4**.

Supporting Information Available: Synthetic details and spectroscopic data for compounds **3**−**9**. Summaries of the substructure searches from CSD. Selected geometries of calculated structures from ref 8. This material is available free of charge via the Internet at http://pubs.acs.org.

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