

The Stereochemistry of the Thermal Cheletropic Decarbonylation of 3-Cyclopentenone As Determined by Multiphoton Infrared Photolysis/Thermolysis

Gregory R. Unruh¹ and David M. Birney*

Contribution from the Department of Chemistry and Biochemistry, Texas Tech University, Lubbock, Texas 79409-1061

Received March 28, 2003; E-mail: david.birney@ttu.edu

Abstract: There are two allowed pathways for the thermal cheletropic decarbonylation of 3-cyclopentenone. The stereochemistry of decarbonylation of an unconstrained derivative (*trans,trans*-2,5-dimethyl-3-cyclopentenone, **4**) has been determined for the first time. Under conventional pyrolysis conditions, thermal rearrangements of the initial product (*trans,trans*-2,4-hexadiene, **5**) occur at the high temperatures required for the decarbonylation. However, by using multiphoton infrared photolysis/thermolysis to initiate decarbonylation, it was shown that the initial products from thermal decarbonylation of **4** are solely carbon monoxide and stereospecifically **5**. The stereochemistry of decarbonylation is thus disrotatory, in accord with prior theoretical studies. A survey of crystal structures reveals ground-state distortions along this reaction coordinate as well.

Introduction

In 1966, Lemal and McGregor applied the newly developed theory of the conservation of orbital symmetry to the thermal, cheletropic decarbonylation of 3-cyclopentenones.² Although the ground state of **1** is planar (C_{2v} symmetry),³ they predicted that the allowed pathway was disrotatory on the diene, while the carbon monoxide departed along the so-called linear pathway, remaining in the vertical plane of symmetry, as in Figure 1.⁴ Subsequently, Woodward and Hoffmann proposed that this reaction could also occur via another orbital symmetry allowed pathway, the so-called nonlinear and conrotatory path.⁶ Cheletropic fragmentations are one of the few pericyclic reactions with two orbital symmetry allowed reaction pathways. We now present the first direct experimental evidence that disrotatory diene formation is exclusively observed in unconstrained decarbonylations of 3-cyclopentenones. This relies on multiphoton infrared photolysis/thermolysis to initiate thermal decomposition, while avoiding subsequent thermal rearrangements of the diene products. X-ray crystal structures are also shown to support the linear, disrotatory pathway.

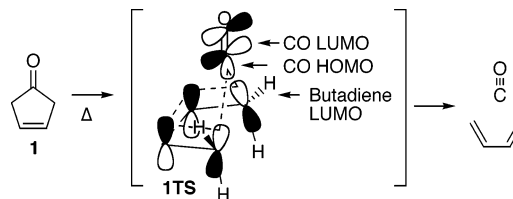


Figure 1. Disrotatory transition state for the thermal decarbonylation of **1**. The geometry of **1TS** is based on the ab initio calculated geometries.^{7–9}

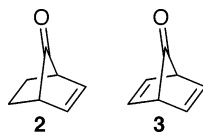
Background

In the years since the first theoretical descriptions, there have been numerous studies on cheletropic reactions in a variety of systems.^{7–23} The stereochemistry of thermal cheletropic extrusion of SO_2 from sulfolenes has been shown to be disrotatory.¹³ The facile thermal decarbonylations of bicyclo[2.2.1]hept-2-en-

- (1) Taken in part from the Ph.D. dissertation of GRU. Unruh, G. R. *Stereochemical and ab Initio Studies of the Multiple Photon Infrared Initiated Decarbonylation of cis-2,5-Dimethyl-3-cyclopentenone*; Texas Tech University, 1995.
- (2) Lemal, D. M.; McGregor, S. D. *J. Am. Chem. Soc.* **1966**, *88*, 1335.
- (3) Bevan, J. W.; Legon, A. C. *J. Chem. Soc., Faraday Trans. 2* **1973**, *69*, 902–925.
- (4) An orbital symmetry correlation diagram is found in the Ph.D. thesis of D. M. Birney. Birney, D. M. *Synthesis and Characterization of Bicyclo[2.2.1]hepta-2,5-dien-7-one. A Search for Ethylenedione*; Yale University: New Haven, CT, 1987. The C_s pathway is also predicted by an OCAMS analysis.⁵
- (5) Halevi, E. A. *Orbital Symmetry and Reaction Mechanism. The OCAMS View*, 1st ed.; Springer-Verlag: New York, 1992.
- (6) Woodward, R. B.; Hoffmann, R. *The Conservation of Orbital Symmetry*; Verlag Chemie, GmbH: Weinheim, 1970.

- (7) Birney, D. M.; Wiberg, K. B.; Berson, J. A. *J. Am. Chem. Soc.* **1988**, *110*, 6631–6642.
- (8) Birney, D. M.; Ham, S.; Unruh, G. R. *J. Am. Chem. Soc.* **1997**, *119*, 4509–4517.
- (9) Bencivenni, L.; Ramondo, F.; Quirante, J. J. *J. Mol. Struct. (THEOCHEM)* **1995**, *330*, 389–393.
- (10) Clarke, S. C.; Johnson, B. L. *Tetrahedron* **1971**, *25*, 3555–3561.
- (11) Dolbier, W. R., Jr.; Frey, H. M. *J. Chem. Soc., Perkin Trans. 2* **1974**, 1674.
- (12) Ott, W. *Synthesis* **1976**, 478–479.
- (13) Mock, W. L. In *Cheletropic Reactions*; Marchand, A. P., Lehr, R. E., Eds.; Academic Press: New York, 1977; Vol. 35, Pt. 2 (Pericyclic Reactions), pp 141–197.
- (14) Battiste, M. A.; Visnick, M. *Tetrahedron Lett.* **1978**, 4771–4774.
- (15) Nakamura, K.; Koda, S.; Akita, K. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 1665.
- (16) Buxton, J. P.; Simpson, C. J. S. M. *Chem. Phys.* **1986**, *105*, 307–316.
- (17) Rzepa, H. S. *J. Chem. Res., Synop.* **1988**, 224–225.
- (18) LeBlanc, B. F.; Sheridan, R. S. *J. Am. Chem. Soc.* **1985**, *107*, 4554–4555.
- (19) Birney, D. M.; Berson, J. A. *J. Am. Chem. Soc.* **1985**, *107*, 4553–4554.
- (20) Birney, D. M.; Berson, J. A. *Tetrahedron* **1986**, *42*, 1561–1570.
- (21) Simpson, C. J. S. M.; Price, J.; Holmes, G.; Adam, W.; Martin, H.-D.; Bish, S. *J. Am. Chem. Soc.* **1990**, *112*, 5089–5094.
- (22) Prather, K. A.; Rosenfeld, R. N. *J. Phys. Chem.* **1991**, *95*, 6544–6548.
- (23) Jimenez, R.; Kable, S. H.; Loison, J.-C.; Simpson, C. J. S. M.; Adam, W.; Houston, P. L. *J. Phys. Chem.* **1992**, *96*, 4188–4195.

7-one (**2**, $\Delta G^\ddagger = 31.9 \pm 0.5$ kcal/mol)^{10,14} and of bicyclo[2.2.1]-hepta-2,5-dien-7-one (**3**, $\Delta G^\ddagger = 15$ kcal/mol)^{18–20} are both constrained to disrotatory pathways. These remarkably low barriers certainly reflect the significant exothermicities of these reactions, but have also been interpreted as evidence that the disrotatory pathway is allowed.²⁰ On the other hand, the experimental activation energy for the thermal decarbonylation of **1** is quite high. It has been measured as 51.3 ± 0.2 kcal/mol¹¹ or 46.4 ± 2.4 kcal/mol.¹⁶

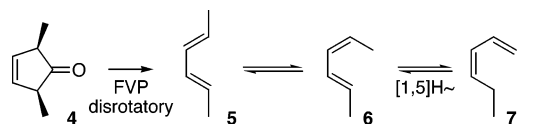


Information on the mode of departure of the carbon monoxide is quickly lost after a decarbonylation; however, there have been a number of studies designed to examine the fate of the CO. Elegant pump–probe studies have determined the vibrational, rotational, and translational energy distributions in the CO immediately following gas-phase photodissociation of **1**.^{22,23} Their results were interpreted in terms of a concerted fragmentation,²³ with both C–C bonds breaking simultaneously as the CO bends out of the molecular plane. In contrast to more familiar pericyclic reactions, both thermal and photochemical decarbonylations are allowed via the linear, disrotatory pathway.⁴ However, the decarbonylation of **1** has been shown to occur from the triplet state.¹⁵ In any case, the details of the photochemical reaction are not necessarily transferable to the thermal reaction. In shock-tube experiments by Simpson et al., fragmentation occurs from the ground state.²¹ These authors suggest that the observed energy partitioning indicates that, at the transition state, the CO bond length is closer to that of the product CO than to that of the carbonyl in **1**. This qualitative prediction is borne out in the calculated transition state geometries^{7–9} and is consistent with the disrotatory pathway in Figure 1.

There have been numerous theoretical studies of the ground state of **1** and of transition states for its cheletropic decarbonylation using both semiempirical^{17,24} and ab initio methods.^{7–9,17} Recently, Quirante et al. have reported that a synchronous transition state for this reaction is found at the MP2(FU)/6-31G* level,⁹ and we have reported single point energies at the MP4(SDQ)/D95**//MP2(FC)/6-31G* level.⁸ The geometry of the transition state (as in Figure 1) and the displacements of the imaginary frequency correspond to a disrotatory motion on the butadiene fragment.⁹ The barrier to thermal decarbonylation of **1** is calculated to be 49.0 kcal/mol,⁸ which is in good agreement with the experimental activation energy (vide supra). The overall reaction is calculated to be 18.9 kcal/mol endothermic.⁸

In view of the intense and long-standing interest in the decarbonylation of 3-cyclopentenone, it may be surprising that, over the past 30 years, the stereochemistry of the thermal decarbonylation of unconstrained 3-cyclopentenones has not previously been studied. There are presumably two reasons for the lack of progress in this regard. The first is that the synthesis of a stereochemically labeled 3-cyclopentenone, for example, **4**, has appeared to be difficult. The second reason was more

critical; upon consideration of the high barrier for decarbonylation (vide supra), it was apparent that the pyrolysis temperatures required to effect the decarbonylations of stereochemically labeled 3-cyclopentenones would be sufficiently high to isomerize the product diene(s) as in eq 1.²⁵

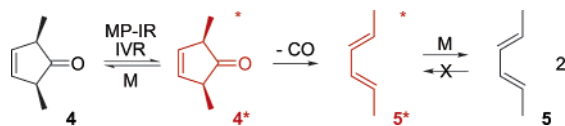


In the work reported here, multiphoton infrared (MP-IR) irradiation was used to carry out the thermal pyrolysis of *cis*-2,5-dimethyl-3-cyclopentenone (**4**) while avoiding subsequent thermal isomerization of the product hexatriene(s). We refer to this as MP-IR photolysis/thermolysis; it is a photolysis because of the absorption of IR photons, but it is a thermolysis because the chemistry occurs via thermally excited ground-state molecules. MP-IR photolysis/thermolysis is initiated by the sequential absorption of IR photons from a pulsed IR laser.²⁶ Absorption is accompanied by intramolecular vibrational energy redistribution (IVR), which in large organic molecules is very rapid.^{26,27} Thus, MP-IR produces highly vibrationally excited molecules in the ground electronic state with an effectively randomized energy distribution, similar to that obtained in conventional pyrolysis. There is, however, a significant difference. By tuning the IR laser and by judicious choice of reactants, only one component of a gas mixture may absorb the light and is heated. The overall rate of a reaction will depend on the rate of IR absorption as well as the competition between collisional cooling of the hot molecule and the rate of the unimolecular reaction. The important point for this work is that collisions can cool hot product molecules before they can react further. This amounts to a pyrolysis in a room-temperature environment. MP-IR decompositions of a number of systems have been reported.^{28–38} Of the most relevance to the current work, MP-IR thermolysis of cyclobutyl acetate yields cyclobutene, while pyrolysis gives only butadiene as the product of secondary thermolysis of cyclobutene.³⁹ Thus, we anticipated that the reaction scheme for the MP-IR photolysis/thermolysis of **4** would be as in eq 2. MP-IR would sufficiently heat **4** to give **4*** and induce decarbonylation. This would generate **5**, possibly

- (25) Hess, B. A., Jr.; Baldwin, J. E. *J. Org. Chem.* **2002**, *67*, 6025–6033.
 (26) Bagratashvili, V. N.; Letokhov, V. S.; Makarov, A. A.; Ryabov, E. A. *Multiple Photon Infrared Laser Photophysics and Photochemistry*; Harwood Academic Publishers: Chur, Switzerland, 1985.
 (27) Seder, T. A.; Weitz, E. *Chem. Phys. Lett.* **1984**, *104*, 545–551.
 (28) Hints, E. J.; Wodtke, A. M.; Lee, Y. T. *J. Phys. Chem.* **1988**, *92*, 5379–5387.
 (29) Farneth, W. E.; Thomsen, M. W.; Beck, T. L. *J. Phys. Org. Chem.* **1990**, *3*, 567–574.
 (30) Goodale, J. W.; Evans, D. K.; Ivanco, M. *Can. J. Chem.* **1990**, *68*, 1437.
 (31) Kumar, A.; Chowdhury, P. K.; Rama, K. V. Z. *Chem. Phys. Lett.* **1991**, *182*, 165.
 (32) Yamamoto, S.; Suzuki, M.; Sueishi, Y. *Bull. Chem. Soc. Jpn.* **1992**, *65*, 3112.
 (33) Coronado, E. A.; Ferrero, J. C. *J. Photochem. Photobiol., A: Chem.* **1998**, *114*, 89–94.
 (34) Meco, D.; Lasorella, A.; Riccardi, A.; Servidei, T.; Mastrangelo, R.; Riccardi, R.; Samoudi, B.; Daz, L.; Oujja, M.; Santos, M. *J. Photochem. Photobiol., A: Chem.* **1999**, *125*, 1–11.
 (35) Pola, J.; Urbanova, M.; Daz, L.; Santos, M.; Bastl, Z.; Subrt, J. *J. Organomet. Chem.* **2000**, *605*, 202–208.
 (36) Rubio, L.; Santos, M.; Torresano, J. A. *J. Photochem. Photobiol., A: Chem.* **2001**, *146*, 1–8.
 (37) Santos, M.; Daz, L.; Pola, J. *J. Photochem. Photobiol., A: Chem.* **2002**, *152*, 17–24.
 (38) Chowdhury, P. K. *J. Photochem. Photobiol., A: Chem.* **2003**, *154*, 259–265.
 (39) Nguyen, H. H.; Danen, W. C. *J. Am. Chem. Soc.* **1981**, *103*, 6253–6255.

(24) Quirante, J. J.; Enriquez, F. *Theor. Chim. Acta* **1994**, *89*, 251–259.

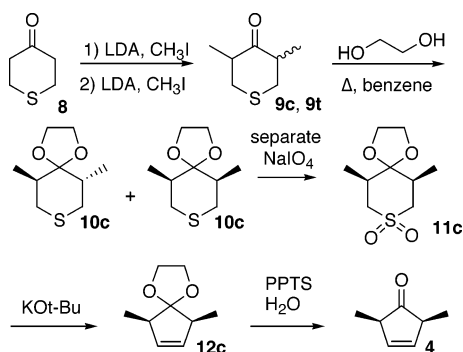
in a vibrationally excited state. Collisional cooling of **5***, along with the lack of heating of **5** by absorption (or by collision, because the ambient pressure is low), would ensure that no further thermal chemistry of **5** would be observed.



Results and Discussion

The planning of the synthesis of 2,5-dimethyl-3-cyclopentenones is complicated by the expectation that the Δ -2 isomer would be the more stable one, both because it is more highly substituted and because it is conjugated.⁴⁰ Of the several approaches to **4** which were investigated,¹ the most successful one in our hands was based on the Ramburg–Backlund reaction⁴¹ and is outlined in Scheme 1. Dimethylation of

Scheme 1



commercially available tetrahydrothiopyran-4-one (**8**) with LDA and MeI gave a mixture of the *cis*- and *trans*-3,5-dimethyltetrahydrothiopyran-4-ones (**9**). The diastereomers were separated after ketalization. At this stage, it was possible to unambiguously assign the stereochemistry of both isomers, **10t** and **10c**. The two carbons of the ethylene ketal are equivalent in the ¹³C NMR spectrum for the *trans* isomer **10t**, but are different in the *cis* isomer **10c**. Conversely, the ketal CH₂ hydrogens are diastereotopic in **10t**, and a multiplet is observed, while a singlet is observed for the enantiotopic ketal CH₂ hydrogens in **10c**. The individual isomers were oxidized to the sulfone (**11c** or **11t**) and subjected to the Ramburg–Backlund conditions, giving the cyclopentenone ketals **12c** or **12t**. Mild deprotection of **12c** using pyridinium *p*-toluenesulfonate (PPTS) gave *cis*-2,5-dimethyl-3-cyclopentenone (**4**) without double bond migration.

Having obtained **4** stereochemically pure, we then investigated the original expectation that flash vacuum pyrolysis (FVP) of **4** would give rise to rearranged products. FVP was carried out at 540, 560, and 580 °C. The products were collected in a liquid nitrogen trap and analyzed by GC. Products were identified by comparison to authentic standards. Product ratios are reported in Table 1 and are corrected for response factors. In each case, there was significant rearrangement to *cis*-1,3-hexadiene (**7**). Both *trans,trans*- and *cis,trans*-2,4-hexadiene (**5** and **6**, respectively, eq 1) were also observed.

(40) Hess, H. M.; Brown, H. C. *J. Org. Chem.* **1967**, *32*, 4138–4139.

(41) Matsuyama, H.; Miyazawa, Y.; Takei, Y. *J. Org. Chem.* **1987**, *52*, 1703.

Table 1. Percent of Hexadienes Produced from Pyrolysis of **4**

hexadiene product	flash vacuum pyrolysis			MP-IR
	540 °C	560 °C	580 °C	
5	23.5	63.1	88.0	100
6	trace	11.9	1.7	0
7	70.0	25.0	10.3	0

We then subjected *cis*-2,5-dimethyl-3-cyclopentenone (**4**) to gas-phase multiphoton infrared photolysis/thermolysis. A sample of **4** was introduced into a vacuum manifold, freeze–pump–thawed, and allowed to volatilize into a gas cell with NaCl windows. The output from a Lumonics 840 pulsed TEA grating tuned CO₂ laser at 1041 cm⁻¹ was focused with a ZnSe lens into the cell. The laser line was selected because **4** absorbed at this wavelength, while the hexadiene products **5**, **6**, and **7** did not. The sample was irradiated with 1000 laser pulses. Each pulse was approximately 200 ns long, with a pulse energy somewhat less than 50 J. Figure 2 shows the difference IR spectra before and after MP-IR photolysis/thermolysis; carbon monoxide and *trans,trans*-2,4-hexadiene (**5**) are formed. No other diene products which could be formed either by rearrangement (eq 1) or via the nonlinear conrotatory pathway proposed by Woodward and Hoffmann were detected by GC. Thus, we have demonstrated, for the first time, that unconstrained thermal decarbonylation of **4** (and therefore of **1**) proceeds via the disrotatory pathway for cheletropic fragmentation as predicted.

Crystallographic Evidence for the Disrotatory Pathway.

The structure correlation principle predicts that the ground states of molecules can show distortions along a reaction coordinate.^{42,43} Perhaps the best-known examples of this are the Bürgi–Dunitz trajectory for the addition of nucleophiles to carbonyls⁴⁴ and bond lengthening as a consequence of the anomeric effect.⁴⁵ White and Birney have recently shown that similar distortions can be observed in the retro-Diels–Alder reaction^{46,47} and in pseudopericyclic [4+2] retrocycloadditions as well.⁴⁸

Having demonstrated that the decarbonylation of **4** is disrotatory, we surveyed 3-cyclopentenone derivatives including ones along the disrotatory pathway in the Cambridge Structural Database⁴⁹ to see if there is crystallographic evidence for the linear, disrotatory pathway for decarbonylation as well. The results are summarized in Figure 3; atom numbering is based on **13**, and details are provided in the Supporting Information. Seven unconstrained cyclopentenones were located, all of which adopt essentially a planar geometry (C1–C2–C5–C4 dihedral > 163°) consistent with the planar microwave structure of the parent **1**.³ Structure **13** shows the average bond distances and

(42) Bürgi, H. B.; Dunitz, J. D. *Acc. Chem. Res.* **1983**, *16*, 153–161.

(43) Ferretti, V.; Dubler-Steudle, K. C.; Bürgi, H.-B. In *Structure Correlations, Reaction Pathways and Energy Surfaces for Chemical Reactions*; Domenicano, A., Hargittai, I., Eds.; International Union of Crystallography; Oxford University Press: Oxford, 1992.

(44) Bürgi, H. B.; Dunitz, J. D.; Shefter, E. *J. Am. Chem. Soc.* **1973**, *95*, 5065–5067.

(45) Jones, P. G.; Kirby, A. J. *J. Chem. Soc., Chem. Commun.* **1979**, 288–289.

(46) Pool, B. R.; White, J. M. *Org. Lett.* **2000**, *2*, 3505–3507.

(47) Birney, D.; Lim, T. K.; Koh, J. H. P.; Pool, B. R.; White, J. M. *J. Am. Chem. Soc.* **2002**, *124*, 5091–5099.

(48) Shumway, W. W.; Dalley, N. K.; Birney, D. M. *J. Org. Chem.* **2001**, *66*, 5832–5839.

(49) Allen, F. H.; Davies, J. E.; Galloy, J. J.; Johnson, O.; Kennard, O.; Macrae, C. F.; Mitchell, E. M.; Mitchell, G. F.; Smith, J. M.; Watson, D. G. *J. Chem. Inf. Comput. Sci.* **1991**, *31*, 187–204.

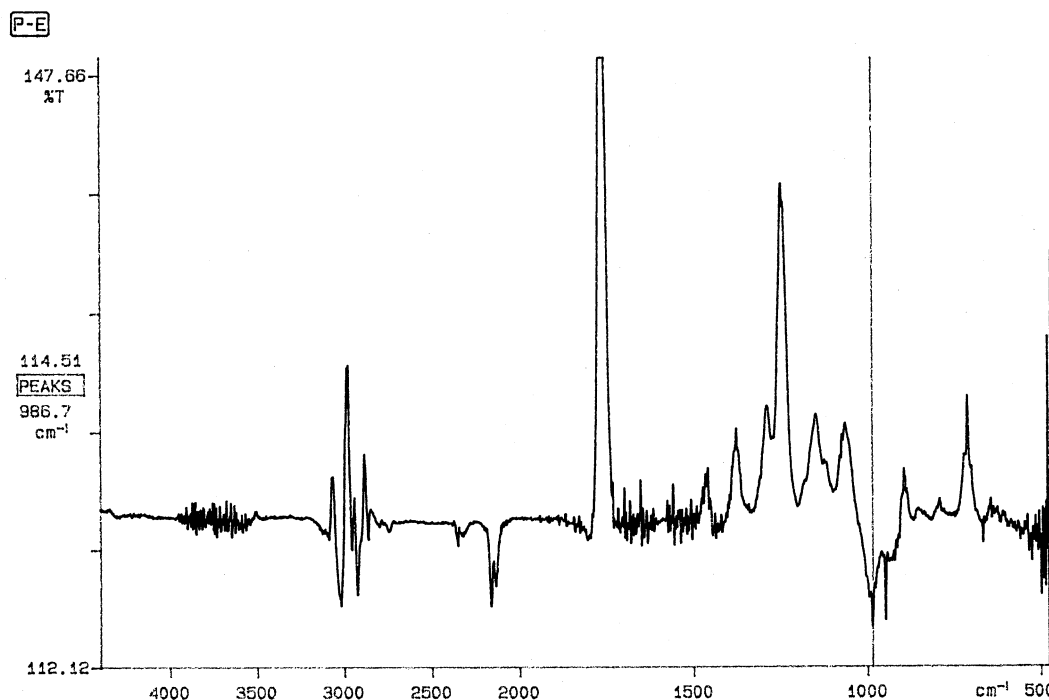


Figure 2. Difference IR spectrum of MP-IR photolysis/thermolysis of **4**. Upward (negative) peaks show the disappearance of **4**; downward (positive) peaks show the formation of carbon monoxide and **5**.

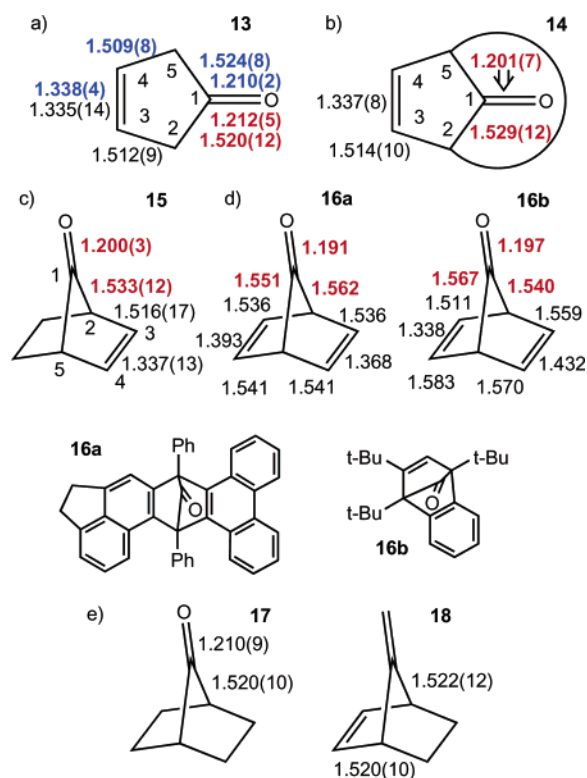


Figure 3. Bond distances in angstroms from the Cambridge Structural Database⁴⁹ of 3-cyclopentenone derivatives. Distances in red are relevant to the cheletropic decarbonylation pathway. (a) Average geometries (standard deviations) of seven planar 3-cyclopentenone derivatives **13**. Distances (experimental error) in blue are from the microwave structure of the parent molecule **1**.³ (b) Average geometries of eight nonplanar 3-cyclopentenone derivatives **14**. (c) Average geometries of 12 bicyclo[2.2.1]hept-2-en-7-one derivatives **15**. (d) Geometries of **16a** (± 0.004 Å) and **16b** (± 0.002 Å). (e) Average geometry of six derivatives of **17** and **18**.

angles. Eight compounds were constrained by larger rings to dihedral angles between 133.99° and 154.26° (**14**). Twelve derivatives of bicyclo[2.2.1]hept-2-ene-7-one (**2**) were found. Remarkably, crystal structures of two derivatives of bicyclo[2.2.1]hepta-2,5-diene-7-one (**3**) have been obtained,^{50,51} despite the extremely low barrier for the decarbonylation of the parent molecule.^{18–20,52} Structures **13–16a** can be viewed as moving the carbonyl from an in-plane geometry (**13**) to an out-of-plane one; the carbonyl remains along the approximate plane of symmetry. These correspond to the disrotatory and linear motions, respectively, predicted for the allowed cheletropic decarbonylation.

The structure correlation principle then suggests that distortions along the bond breaking coordinates should be correlated with the out-of-plane distortion of the carbonyl. On the basis of ab initio calculations, we have previously made similar arguments.^{7,53} The X-ray structures indeed show this predicted correlation. The casual reader may wish to skip the detailed analysis below that verifies these distortions are outside experimental error, are indeed along the reaction coordinate, and are not simply due to strain effects.

The average of the C1–C2 and C1–C5 bond lengths in **13** is 1.520 ± 0.012 Å. These bonds are lengthened to an average of 1.529 ± 0.012 Å in **14** and 1.533 ± 0.012 Å in **15**. And in **16a**, the bonds are 1.551 and 1.562 Å, while in **16b** they are 1.540 and 1.567 Å. The structure correlation principle also predicts that the C1=O bond would be shortened, as this becomes more like carbon monoxide. This trend is observed;

(50) Plummer, B. F.; Currey, J. A.; Russell, S. J.; Steffen, L. K.; Watson, W. H.; Bourne, S. A. *Struct. Chem.* **1995**, *6*, 167.

(51) Zhang, J.; Ho, D. M.; Pascal, R. A., Jr. *J. Am. Chem. Soc.* **2001**, *123*, 10919–10926.

(52) Birney, D. M. *Synthesis and Characterization of Bicyclo[2.2.1]hepta-2,5-dien-7-one. A Search for Ethylenedione*; Yale University: New Haven, CT, 1987.

(53) Birney, D. M. *J. Org. Chem.* **1996**, *61*, 243–251.

the average C1=O bond distance in **13** is 1.214 ± 0.005 Å and becomes steadily shorter in **14** and **15** (1.201 ± 0.007 Å and 1.200 ± 0.003 Å, respectively). In **16b**, it is 1.197 Å, and in **16a** it is the shortest of all, 1.191 Å.

In making these comparisons, the hybridization of each atom has been kept the same. However, there is more strain in the bicyclo[2.2.1]hept-2-en-7-one systems than in the 3-cyclopentenone systems. Strain is expected to lengthen endocyclic bonds and shorten exocyclic bonds;^{54,55} this is the same trend as was observed above. To estimate the contributions of strain to these changes in bond distances, five derivatives of **17** were examined. The average C1=O bond distance in **17** is 1.210 ± 0.009 Å. This is essentially the same as in **13**, where the C1=O bond length is an average of 1.212 ± 0.005 Å. In contrast, the C1=O bonds in **15**, **16a**, and **16b** are all significantly shorter than that in **17**; there must be another factor shortening the CO bond in the former compounds. The C1–C2 and C1–C5 bonds are no longer in **17** than in **13** (1.520 ± 0.010 Å and 1.520 ± 0.012 Å, respectively). Therefore, ring strain is insufficient to explain the progressive lengthening of the C1–C2 and C1–C5 bonds in **14**, **15**, **16a**, and **16b**. We suggest these longer bonds, as well as the shorter C1=O bonds in these latter compounds, are indeed a manifestation of the structure correlation principle; there are increasing ground-state distortions toward the transition state for linear, disrotatory decarbonylation along the series **14**, **15**, **16**.⁵⁶

We also examined 10 derivatives of **18**. In these compounds, the hybridizations are the same as in **15**, but loss of vinylidene is a high-energy reaction as compared to carbon monoxide, and distortions along this reaction coordinate are not expected. Indeed, the C1–C2 and C1–C5 distances in **18** average 1.522 ± 0.012 Å, again much shorter than in **15**. It is also possible to compare the C2–C3 and C4–C5 bond distances in **18** (1.520 ± 0.010 Å, average) with those in **15** (1.516 ± 0.017 Å, average). Although there is not a dramatic difference in these bond lengths, they are perhaps shorter in **15**, as expected for incipient double bonds. A similar trend is not observed in **16a** and **16b**; this is not entirely unexpected, as both are stabilized to some degree by aromaticity and by additional strain outside the bicyclo[2.2.1] ring system (vide infra).

(54) Wiberg, K. B.; Bader, R. F. W.; Lau, C. D. H. *J. Am. Chem. Soc.* **1987**, *109*, 1001–1012.

(55) Stanger, A. *J. Am. Chem. Soc.* **1998**, *120*, 12034–12040.

(56) Plummer made no comment on the lengths of the bonds in **16a**.⁵⁰ Pascal noted that several of the C–C bonds in **16b** were “unusually long”.⁵¹ We emphasize that the C1–C2 and C1–C5 bonds are more distorted than in **15** and that the 1.567 Å bond in **16b** is longer than any of the other comparable bonds.

Clearly then, in molecules where the carbonyl is out-of-plane, the orbital overlap required for loss of CO becomes possible, and the C1–C2 bonds lengthen. This effect is of greater magnitude than can be accounted for by strain. It is arguably a manifestation of the structure correlation principle, consistent with decarbonylation of derivatives of **1** through the linear, disrotatory pathway.

Why are **16a** and **16b** stable at room temperature? We would suggest that loss of CO from **16a** cannot be as exothermic as in the parent system (**3**); the incremental increase in the aromatic stabilization of the product must be small. We further suggest that the stability of **16b** is due in part to the nonplanarity of the incipient aromatic ring, due to steric crowding of the *tert*-butyl groups. The C2–C1–C4–C5 and related dihedrals in **16b** are 128.24° , 127.37° , 118.77° , and 117.36° , while the incipient aromatic ring is more planar in **16a** (124.63° , 122.40° , 113.21° , and 111.83°).

Conclusion

Flash vacuum pyrolysis of *cis*-2,5-dimethyl-3-cyclopentenone (**4**) gives a mixture of hexadienes via cheletropic decarbonylations followed by isomerization of the product hexadiene(s). However, through the use of multiphoton infrared photolysis/thermolysis, it has been possible to determine, for the first time, the stereochemistry of the thermal decarbonylation of an unconstrained 3-cyclopentenone derivative, specifically **4**. The demonstration of stereospecific formation of **5** as the sole primary product from thermal decarbonylation indicates that the disrotatory fragmentation pathway is followed. This is as was originally predicted by the qualitative molecular orbital theory and more recently by *ab initio* calculations. It is also consistent with observed distortions in the ground-state geometries of derivatives of 3-cyclopentenone.

Acknowledgment. Financial support from Tech Spray, Inc. and the Robert A. Welch Foundation is gratefully acknowledged. Discussions with Dr. Jonathan A. White on the structure correlation principle were most helpful. Synthetic efforts by Melissa R. Fortner and Thomas Hampton are also appreciated.

Supporting Information Available: Experimental procedures for the synthesis and ¹H and ¹³C MR spectra of *cis*- and *trans*-**9**, **-10**, **-11**, and **-12**, and *cis*-**4**. HETCOR spectra of **9c** and **12c**. A description of the MP-IR apparatus and experiment. Details of CSD searches (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

JA0353661