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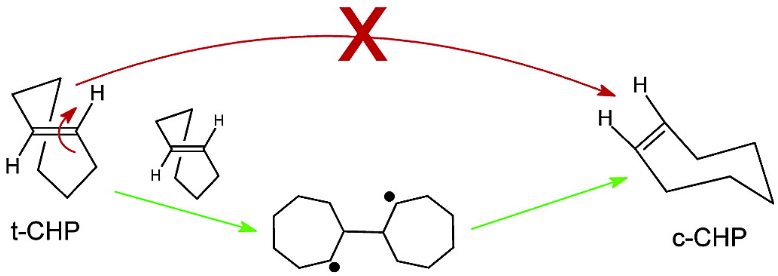

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How Stable Is *trans*-Cycloheptene?

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Abstract: There is a discrepancy between the observed and calculated stability of *trans*-cycloheptene (t-CHP). Generation of t-CHP has always led to its low-temperature (−40 °C) isomerization to *cis*-cycloheptene (c-CHP). However, force field and semiempirical calculations on the energy difference between the two isomers have suggested that t-CHP should be stable at room temperature. We performed a series of ab initio calculations, which predicted that the simple process of double bond rotation leading from t-CHP to c-CHP would have an activation barrier too high to permit isomerization below 100 °C (35 kcal/mol). The validity of our calculation method on this very strained system was supported by the agreement between the calculation and the dynamics of the ring flip of the unsymmetrical t-CHP ring and the observed NMR shifts and coupling constants for the system. This incompatibility between the experimental behavior of t-CHP and our calculations led to our reexamining the decay kinetics of t-CHP. We find that this decay is second order and represents an “interrupted” dimerization, where an initially formed 1,4-biradical rapidly changes its geometry and cleaves back to produce two c-CHP molecules. This mechanism was supported by calculations of the 1,4-biradical potential energy surface.

Introduction

The existence of geometric isomers about double bonds has been known since the beginnings of organic chemistry. However, when the double bond is part of a medium-sized ring system, ring strain destabilizes the trans isomers and only the cis isomers are known. *trans*-Cyclooctene, which is stable at room temperature, is currently the smallest *trans*-cycloalkene that has been fully characterized. *trans*-Cycloheptene (t-CHP) is much more strained than *trans*-cyclooctene and has been shown to be unstable at room temperature. The strain in t-CHP is caused by a twisting force rather than the more usual bending force on the double bond present in other very strained double bonds,[1] so the structural response to this strain is of considerable interest.

t-CHP was first generated via elimination of a thiocarbamate and revealed as an intermediate when trapped with 2,5-diphenylisobenzofuran.[2] Inoue has generated it photochemically from *cis*-cycloheptene (c-CHP) first by short wavelength irradiation[3] and later by singlet sensitization using methylbenzoate (Figure 1).[4] In both instances, he utilized Kropp's acidic methanol trapping technique[5] to prove the existence of the t-CHP, which he found to be stable only at low temperatures. Michl and co-workers generated t-CHP by photolyzing a copper complex of the cis isomer and releasing t-CHP oxidatively.[6] These workers were the first to obtain spectroscopic evidence of t-CHP by cleaving the t-CHP copper complex at low temperatures in an NMR spectrometer. We later used Inoue's method to generate t-CHP and were able to obtain its complete carbon and proton NMR spectra as well as its UV, again all at low temperature.[7] We also showed that t-CHP, like its copper complex, has an unsymmetrical ring structure and shows dynamic NMR due to a ring flip process at temperatures below −40 °C.

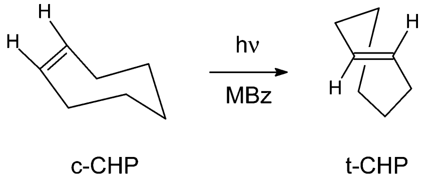

Figure 1. Production of t-CHP via singlet sensitization.

Using molecular mechanics (MOLBD III) and semiempirical quantum mechanical calculations (MNDO), Michl et. al. found energy differences between *trans*- and *cis*-cycloheptene of 29.3 and 23.3 kcal/mol, respectively. The barrier for rotation of the double bond in ethene is 65 kcal/mol,[8] and, as seen by Gano,[9] unrelieved strain in the transition states of the rotational event in sterically hindered alkenes can raise the energy of the transition state further. By this approach, using the t-CHP strain

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Table 1. Calculated Difference in Strain Energy at Various Levels

methods	$\Delta H_{c\leftarrow t}$ (kcal/mol)
PCMODEL (MMX)	33.2
AM1	30.9
HF/6-31G(d)	35.4
B3LYP/6-31G(d)	29.8
CASSCF(2,2)/6-31(G)d	30.9
CASSCF(2,2)/6-31G(d) MP2	30.0

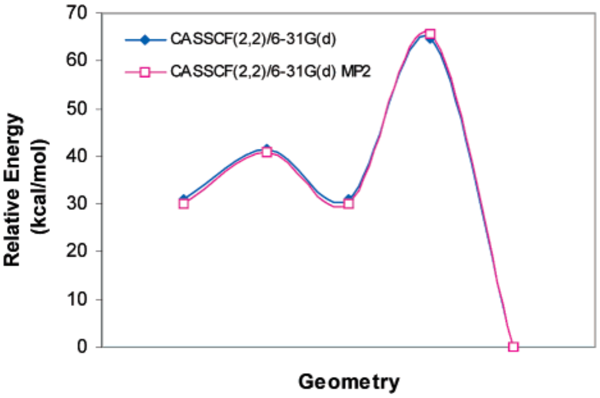

Figure 2. Calculated potential energy profile for double bond rotation of cycloheptene.

energies found by Michl, the trans to cis rotational barrier of t-CHP should be at least 35 kcal/mol. In other words, t-CHP should be stable at temperatures well above room temperature! However, Inoue[4] found this barrier to be only about 17 kcal/mol, which is in accordance with Michl's[6] and our[7] observations of −30 °C as the upper temperature limit of t-CHP stability. Given this discrepancy, we felt further calculations and a reexamination of the decay of t-CHP were in order.

Results and Discussion

We calculated the energy difference of the trans and cis isomers of cycloheptene at various computational levels (Table 1). As seen, there is a consistent confirmation of Michl's computations,[6] in that t-CHP showed roughly 30 kcal/mol additional strain as compared to c-CHP. We were also able to locate the transition state for the double bond rotation. The result is pictured in Figure 2. At the CASSCF (2,2)/6-31G(d)-MP2//CASSCF (2,2)/6-31G(d) level, we found a trans to cis rotational barrier of 33.8 kcal/mol. So these calculations do not relieve the mystery surrounding the stability of t-CHP. They, in fact, confirm the prediction that this molecule should be stable at room temperature given the calculated trans to cis rotational barrier.

The reliability of this result can be determined by examining other aspects of the calculation. The calculated geometry of t-CHP shows the expected deformations caused by the ring strain and agrees with our experimental result, which showed 12 different protons in the ^{1}H NMR spectrum of t-CHP.[7]

The geometry of *trans*-CHP calculated using the CASSCF(2,2)/6-31G(d) method shows the unsymmetrical ring structure and has a very small "trans" C−C═C−C torsional angle of 113.8°. The two allylic C−C═C angles (116.8° and 118.1°) also adapt to the ring strain by "closing down" as compared to the 126° allylic angle of the cis isomer. The calculated length of the C═C double bond (1.352 Å) is increased by about 0.01 Å as compared to that of c-CHP. The geometry calculated at the B3LYP/6-31G(d) level is almost identical to the CASSCF(2,2)/6-31G(d) geometry, differing at most by 2° in the ring torsional angles.

Table 2. Distortion Angles (deg) of Some *trans*-Cycloalkenes

	t-CHP	1	2	3
τ	30.0	18.0	19.6	23.1
χ_{av}	36.2	24.0	13.2	26.1
ξ	66.2	42.3	32.8	49.2
η	−6.2	−6.0	6.4	−3.0

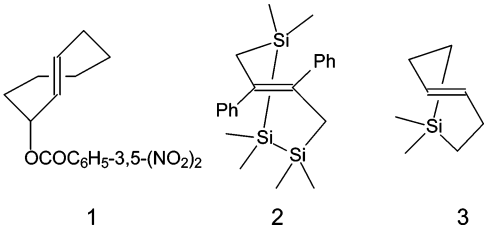

Figure 3. *trans*-Cycloalkenes.

The ring strain is accommodated by a combination of pyramidalization and twisting of the carbons of the double bond.[10] The CASSCF(2,2)/6-31G(d) geometry shows similar pyramidalization angles (χ) of 37.0° and 35.4° for the two vinyl carbons and a p-orbital twist angle (τ) of 30.1°. The sum of the twist angle and the average of the pyramidalization angles (ξ) has been used as a measure of the strain in double bonds, while the difference of these two angles (η) was looked on as a measure of the relative importance of twisting and pyramidalization. Table 2 reports these values for t-CHP as well as those of a *trans*-cyclooctene[11] (**1**) and a tri-[12] (**2**) and a monosila[13] (**3**) *trans*-cycloheptene (Figure 3) for comparison. As can be seen from the table, the ξ value for t-CHP is much larger than those of the other cyclic trans alkenes implying considerably more strain in this compound. Except for the highly substituted **2**,[10] the η values are all negative, suggesting that pyramidalization is more important than twisting for relieving the strain in these cyclic trans alkenes.

The unsymmetrical structure of t-CHP allows for a ring flip through a C_2-symmetric transition state as was evidenced by the dynamic NMR we saw for the system.[7] We were able to calculate the transition state for this process and found it to be 10.8 kcal/mol higher in energy than t-CHP itself. Again, the calculation compares very well to our experimental value of 10.0 kcal/mol.[7]

The ^{13}C chemical shifts of both the cis and the trans isomers of cycloheptene were calculated and are compared to the experimental data in Table 3. We were initially surprised that the vinyl shifts of t-CHP were only slightly downfield from that of the cis isomer and perhaps even more surprised when the calculated shifts for this very strained double bond matched the experimental. Carbon chemical shifts are determined primarily by the paramagnetic shielding term, which in turn depends on the mixing of excited state with the ground-state

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Table 3. Experimental and Calculated ^{13}C Chemical Shifts of Both c- and t-CHP

	c-CHP		t-CHP	
carbon	exp[a]	calc[b]	exp[a]	calc[b]
1	130.2	130.6	135.5	134.8
2	130.2	130.6	131.8	130.6
3	29.4	28.5	36.2	35.2
4	29.4	28.5	25.3	23.8
5	27.9	27.0	31.7	30.6
6	27.9	27.0	33.9	32.6
7	33.4	32.8	26.2	24.8

[a] Observed ^{13}C chemical shifts in acetone-d_6. [b] Method used was MP2/6-311+G(2d,p)//B3LYP/6-31G(d).

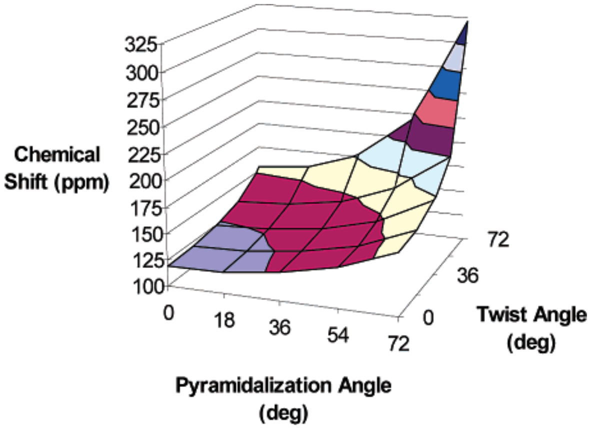

Figure 4. Dependence of ^{13}C NMR chemical shift of ethylene on twist and pyramidalization angles.

wave function.[14] Pyramidalized alkenes, as a consequence of the rehybridization, show a decrease of the LUMO and a small increase of the HOMO energies on increasing pyramidalization,[15] and indeed highly pyramidalized double bonds show ^{13}C chemical shifts with values of 150 ppm and higher.[14] Our smaller downfield shift raised the question of whether twisting had an inherently smaller effect on vinyl carbon shifts than pyramidalization.

To examine this further, we performed a series of chemical shift calculations at the MPW1PW91/6-31G(d)//B3LYP/6-31G(d) level for twisted and pyramidalized ethene. A matrix of chemical shifts was calculated for combinations of twist and pyramidalization angles both in 9° increments, and the results are pictured in Figure 4. As seen, twisting and pyramidalization appear to have approximately the same effect on vinyl carbon shifts, and further this effect is relatively small for any combination of twist and pyramidalization angles where both angles are below 36° as is the case for t-CHP. Finally, it is also interesting to point out that, because of the combined twist and pyramidalization of the vinyl carbons, the vinyl hydrogens of t-CHP are predicted to have a near normal trans dihedral angle of 173.8°. Experimentally, this is confirmed by the 18 Hz coupling between these two hydrogens.

The agreement between the calculation and the overall ring symmetry, the dynamics of the ring flip, and the NMR shifts and coupling constants points to the trustworthiness of this level of ab initio calculation and suggests that the discrepancy between the experimental and predicted barriers for this process must be due to a problem with the experimental values. Two possible explanations for an error in the experimental decay values are: (a) the experimental values are due to an impurity-catalyzed process, although the fact that three different groups all see low-temperature decay of t-CHP speaks against this, or (b) the process is not first order as assumed.

Table 4. ^{1}H NMR Integrations for t-CHP and c-CHP for Decay Study in Untreated, Base-Washed, and Silanized NMR Tubes

NMR tube preparation	untreated	base-washed	silanized
$T_{1/2}$ (s)	643	668	722

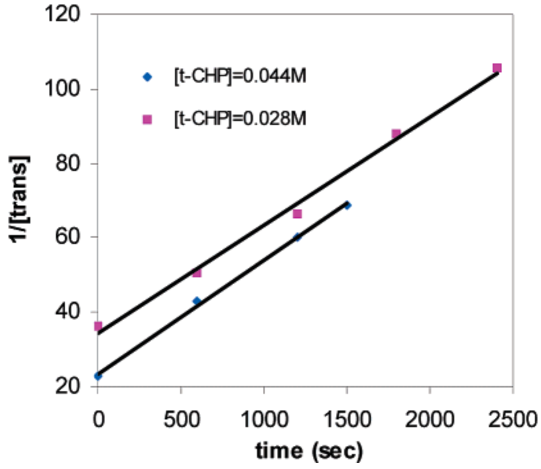

Figure 5. Second-order decay plots of t-CHP at different concentrations.

To check for the presence of impurities that might catalyze the decay process, we rigorously purified the reagents and glassware and used plastic ware whenever possible. Of special concern was the presence of any acidic impurities because, upon addition of a trace of *p*-toluenesulfonic acid, t-CHP isomerized immediately even at low temperatures. We used Inoue's method[4] to produce t-CHP under rigorously acid-free conditions and used base-washed or silanized NMR tubes to remove any active sites on the glass surface. From the decay data collected by warming the sample of t-CHP to −50 °C and recooling to −90°, it is evident that, while some wall-based acid-catalyzed decay occurred, there was no significant change in t-CHP lifetime with these treatments (Table 4). Thus, we concluded that the low-temperature decay is not due to an adventitious impurity.

This leaves the possibility that this isomerization was not a first-order process. A reexamination of our decay data showed a slightly better fit to second-order rather than first-order kinetics. Unfortunately, due to the detection limits of NMR, even the best data could be collected only to 2.5 half-lives, which is insufficient to unambiguously determine the order of the reaction. Therefore, rate studies at −60 °C of the decay of t-CHP at different concentrations were undertaken (Figure 5). The ratio of the half-lives depended inversely on the initial concentrations in these experiments and so represents a second-order process. A fit of the data gave a rate constant of 0.030 M^{-1} s^{-1}, which corresponds to a free energy of activation of 13.8 kcal/mol at −60 °C for the isomerization of t-CHP to c-CHP.

Isomerizations of strained *trans*-cyclcoalkenes have been discovered to occur by a variety of mechanisms. In the gas-phase thermolysis of *cis*,*trans*-1,5-cyclooctadiene, dimers are produced via 1,4-biradical intermediates, while, concurrently, double bond isomerization is thought to proceed through

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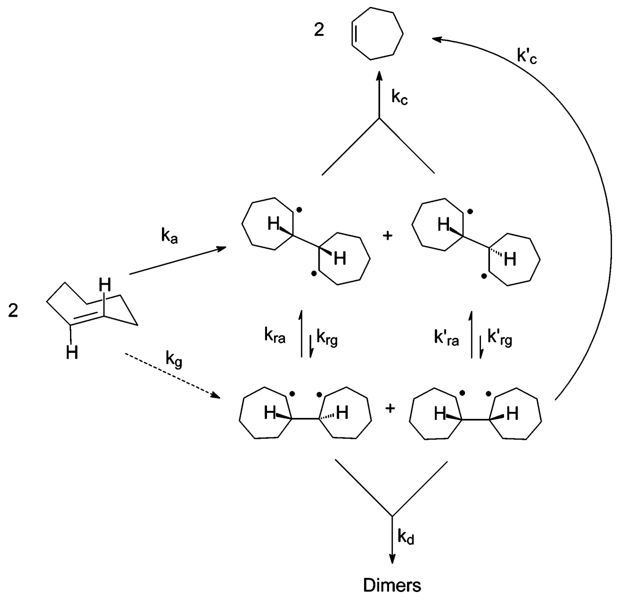
Scheme 1. Bimolecular Mechanism for Trans to Cis Isomerization of CHP ($k_a \gg k_g$ and $k_c \gg k_{rg}$)



successive cope reactions. The first Cope produces *cis*-1,2-divinylcylcobutane, which quickly rearranges to *cis,cis*-1,5-cyclooctadiene.[16] It is not clear if this mechanism also pertains in solution. The situation with *cis,trans*-1,3-cyclooctadiene is a bit more confused. Upon heating *cis,trans*-1,3-cyclooctadiene, an equilibrium is established via electrocyclic closure with bicyclo[4.2.0]oct-7-ene.[17] *cis,cis*-1,3-Cyclooctadiene is also produced along with three dimers, which again have been shown to be derived from 1,4-biradical intermediates.[18] The source of the cis,cis isomer was initially postulated to be produced from the cis,trans by a 1,5 hydrogen shift.[17c] This has been disproved with labeling studies[19] and kinetic isotope effect experiments,[20] so the ultimate source of the cis,cis isomer is still unresolved. Finally, at 290 °C in the gas phase a "simple twist" about the double bond isomerizes *trans*-cyclooctene to its cis isomer,[21] while in solution at 150 °C dimerization predominates, but isomerization also occurs by an undetermined mechanism.[22]

The presence of dimers and the proven existence of 1,4-biradical intermediates in these strained cyclic double bond isomerizations suggests a bimolecular mechanism that explains our observed second-order isomerization of t-CHP and might also explain the solution-phase isomerizations occurring for the above-mentioned eight-membered ring trans alkenes. As shown in Scheme 1, two t-CHP molecules can combine to form a 1,4-biradical, which can have a gauche or transoid form.[23] The rings of this biradical will untwist as it forms to give stable twist-chair or chair conformations for the two seven-membered cyclic radicals. The biradical then quickly cleaves to become two c-CHP molecules.

The problem with this mechanism is that there is no dimer formation observed in the NMR spectrum. However, small amounts of dimer were apparent in a GC/MS of a warmed solution that had contained a 1:13 ratio of *trans*- to *cis*-cycloheptene. Integration of the GC peaks indicated that ~1% of the trans isomer does indeed dimerize. This is still much less dimer than is formed upon heating *trans*-cyclooctene,[22] *cis,trans*-1,5-cyclooctadiene,[16] or *cis,trans*-1,3-cyclooctadiene,[18] but the amount of dimer formed will be dependent on the relative rates of the steps indicated in Scheme 1. In particular, because the dimer forms from the gauche biradical, the relative rates of formation of the transoid and gauche forms (k_t vs k_g) as well as the ratio of cleavage and rotation rates of the biradicals will determine the relative amount of dimer formation.

The complexity of this system mirrors that found for 1,3-cyclooctadiene.[18b] There are two possible transoid biradicals (Scheme 1) that differ by the relationship between the hydrogens of the bridging bond (syn or anti). These transoid biradicals can twist about their central bonds to form two different gauche biradicals (Scheme 1), and both rotomeric pairs of biradicals have multi conformations. A conformational search of the four biradicals using the GMMX subroutine of the PCMODEL[24] force-field program results in 22 distinct geometries for the anti gauche dimer within 3 kcal/mol of each other and 13 conformations of its rotational partner, the syn transoid biradical, again within the same 3 kcal/mol range. The energy difference between the lowest energy conformations of this rotomeric pair of biradicals was only 0.84 kcal/mol. Similarly, the GMMX program gave four syn gauche biradical conformations within 3 kcal/mol of each other and 24 geometries for anti transoid biradical.

The conformations calculated are chair and twist-chair conformations of the seven-membered rings. Dihedral angle driving using the MMX force-field can obtain the sterically derived rotational barriers between the gauche and transoid biradical pairs, but these barriers are highly dependent on the particular ring geometries of the biradicals, as might be expected. The lowest barrier from the syn-transoid to the anti-gauche biradical calculated by dihedral angle driving was found to be 4.09 kcal/mol, while the lowest rotational barrier found in this manner for the anti-transoid to syn-gauche biradical was 3.97 kcal/mol.

Ab initio calculations on these biradicals were more problematic with cleavage often occurring spontaneously depending on the ring conformation of the biradical. For instance, at the UB3LYP/6-31G(d) level (the highest practical level available to us for molecules of this size), no minimum for the syn-gauche biradical could be found with closure occurring spontaneously. We calculated [UB3LYP/6-31G(d)] the anti-transoid, the syn-transoid, and the anti-gauche biradicals to be 8.62, 9.76, and 12.74 kcal/mol, respectively, higher in energy that two t-CHP molecules with cleavage barriers of only 1.86, 1.54, and 2.66 kcal/mol, respectively.

In the parent 1,4-biradical, tetramethylene, rotation, cleavage, and closure are calculated to be nearly barrierless[25] in agreement

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(24) PCMODEL v6.00 Serena Software: Bloomington, IN.

with the minuscule observed lifetime.[26] In this case, however, rotation about the central bond of our biradicals will induce a substantial steric interaction between the seven-membered rings as shown by the steric barriers calculated with MMX, and in neither the transoid nor the gauche biradical will rotation compete with cleavage.

To compare our experimental value for the decay of t-CHP to the cis isomer, we calculated the pathway of two t-CHPs approaching each other in an anti and syn transoid geometry. An enthalpic barrier of 11.3 kcal/mol at the UB3LYP/6-31G(d) level was found for the pathway leading to the syn transoid biradical, while the pathway that would form the anti transoid biradical was calculated to have a 9.5 kcal/mol barrier. These values compare well with the free energy of activation of 13.8 kcal/mol we found for the t-CHP decay considering there will be a substantial entropic contribution to the free energy barrier for this bimolecular reaction. When calculated without constraints, approaches of two t-CHP in a syn gauche or an anti gauche initial geometry both rotated to a transoid approach geometry, showing that, due to steric interactions, two t-CHPs will come together to form a transoid biradical to a much greater extent than a gauche biradical as has been seen during the dimerization of 1,3-cyclooctadiene.[18b] In fact, in our case, the anti-gauche biradical was calculated to have an energy above the cleavage transition states of the transoid biradicals, so $k_a \gg k_g$ (Scheme 1).

The bisallylic biradical produced during the dimerization of *cis*,*trans*-1,3-cyclooctadiene has been trapped with nitroxyls.[18b] In our case, however, no trapping products were observed with either 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO) or SeH_2.[27] The lack of any trapping is not in fact surprising, as the biradical produced in this case is not stabilized by the delocalization present in the bisallylic 1,4-biradical of the *cis*,*trans*-1,3-cyclooctadiene dimerization. The lifetimes of the biradicals present in our system will therefore be considerably shorter and trapping would be unlikely.

Conclusion

The seeming discrepancy between the observed and calculated stability of t-CHP has been resolved by showing that the observed decay of t-CHP to c-CHP is not represented by a direct twisting of the double bond. Rather, it is a second-order process, an "interrupted" dimerization, where an initially formed 1,4-biradical rapidly changes its geometry and cleaves back to produce two c-CHP molecules. Blocking this bimolecular process may allow for the synthesis of thermally stable *trans*-cycloheptenes.

Experimental Section

Methods. *cis*-Cycloheptene (*c*-CHP) was GC purified on a 32 ft, 30% SE-30 on chromsorb P column operating at 140 °C. Toluene-d_8 99.8%D was purified by distillation from $LiAlH_4$.

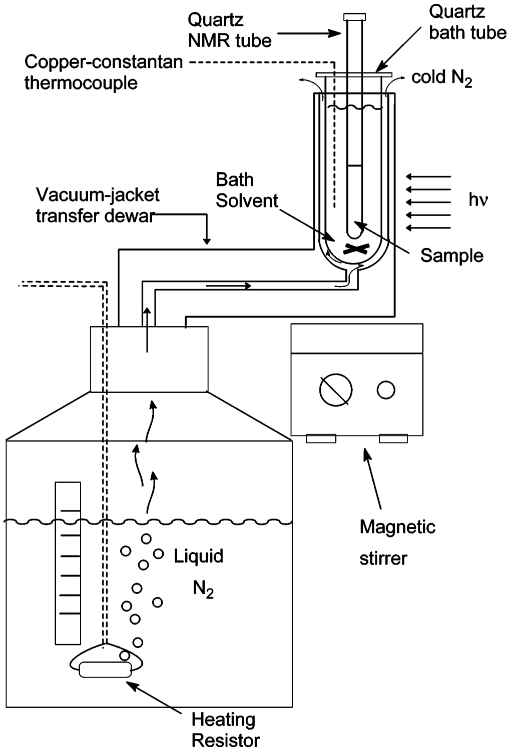

Figure 6. Low-temperature solution-phase photolysis apparatus.

Figure 6 shows the low-temperature photolysis apparatus. The quartz dewar has two 90° turns and two open ends. One end is fitted into a rubber stopper, which seals the top of a liquid nitrogen dewar. The other end holds a 25 mm ID quartz test tube. A 1 kΩ ceramic resistor was connected through the rubber stopper and placed into the liquid nitrogen dewar. A variac attached to the resistor controlled the boiling rate of the liquid nitrogen and thus the flow rate of the cold nitrogen gas through the apparatus. Pentane (HPLC grade) was used as the solvent in the test tube and served as the low-temperature bath for the reaction vessel, usually a 5 mm quartz NMR tube. The temperature was measured using a copper−constantan thermocouple (Omega sensor type T Chip) immersed in the bath, and the temperature gradient was held to less than 1 °C over the length of the sample by stirring using a magnetic stir bar.

Base-Washed Tube Samples. All NMR tubes, glass pipets, and disposable glass pipet tips used were soaked in ethanolic KOH for 4 h, rinsed with distilled deionized water, and vacuum-dried prior to use. The toluene-d_8 was measured out by using an auto-pipet with a disposable polypropylene tip. The c-CHP and methyl benzoate were measured out by adjustable auto-pipets with disposable glass tips.

Silanized Tube Samples. A base-washed NMR tube was soaked in 1,1,1,3,3,3-hexamethyldisilazene for 3 h. The silazene was distilled from the tube, and the tube was vacuum-dried prior to use.

***trans*-Cycloheptene.** In a standard experiment, c-CHP (17.5 μL, 0.15 mmol) and methyl benzoate (0.75 μL, 0.006 mmol) were dissolved in 600 μL of toluene-d_8 in a 5 mm quartz NMR. The sample was capped with a no-air septum and deoxygenated with a nitrogen gas flow for 10 m. The solution was photolyzed at −90 °C for 30 min. The sample was then placed into a precooled NMR probe to obtain initial ^{1}H NMR spectra. Rates of decay were measured by warming the NMR probe to −50 or −60 °C for a set amount of time, quickly recooling the sample to −90 °C, and integrating.

Other concentrations of t-CHP were obtained in an identical manner by changing the initial concentration of c-CHP with the ratio of c-CHP and methylbenzoate held constant. All photolyses were carried out at −90 °C with 254 nm irradiation in quartz NMR tubes.

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Determination of the Amount of Dimerization and Trapping with 2,2,6,6-Tetramethylpiperidin-1-oxyl Radical (TEMPO). A solution of GC purified c-CHP (17.5 μL, 0.15 mmol), methyl benzoate (0.75 μL, 0.006 mmol), and an internal standard decane (3.9 μL, 0.002 mmol) in 600 μL of acid-free toluene-d_8 (distilled from CaH_2) was irradiated with 254 nm at -90 °C for 30 min in an acid-free quartz NMR tube. The solution was divided into three equal portions in three acid-free NMR tubes at -90 °C by rapid cannulation through flexible Teflon tubing.

A solution of 1,3-diphenylisobenzofuran (0.012 g, 0.044 mmol) in 100 μL of acid-free toluene-d_8 was precooled to -90 °C and quickly cannulated in the first NMR tube at -90 °C. After the solution was warmed to room temperature, NMR integration showed that 11.3% of the original c-CHP had been converted to the Diels−Alder adduct so that this was the amount of trans isomer produced in the photolysis.

The second portion of solution containing t-CHP was warmed to room temperature. Nothing but *c*-CHP and methylbenzoate were observed in the NMR spectrum. However, GC/MS using a HP-1 capillary column (conditions: carrier gas helium, injection temperature 200 °C, detector temperature 250 °C, with a temperature program of 5 min at 60 °C, 3 °C/min ramp up to 250 °C, and hold for 30 min) showed a peak with a retention time of 8.83 min for c-CHP, a peak with a retention time of 17.52 min for the internal standard decane, and a methylbenzoate peak with a retention time of 20.80 min. Two GC/MS peaks with retention times of 40.42 and 41.79 min show a mass peak of 192. These peaks represent cycloheptene dimers and integrate to 0.102% of the c-CHP peak. Thus, 1.2% of the t-CHP produced dimerized. Four small peaks with retention times of 47.85, 50.63, and 50.84 min showed parent ions of mass 232 corresponding to 1:1 cross-adducts of cycloheptene with MeBz and integrated to 0.04% of the c-CHP. An unphotolyzed solution of c-CHP and MeBz showed no peaks with m/z of 192 (CHP dimers) or 232 (cross-adducts of CHP and MeBz).

A solution of TEMPO (0.0025 g, 0.016 mmol) in 100 μL of acid-free toluene-d_8 was precooled at -90 °C and cannulated into one of the three NMR tubes. The mixture was maintained at -90 °C for 20 min, warmed to -60 °C, and maintained at that temperature for 2 h. The solution was then warmed to room temperature slowly, but the resulting GC/MS spectra showed no trapping products. Rather, it was identical to that of the untrapped photolyzed sample after it had been warmed and showed the same amount of cycloheptene dimers present.

Trapping with SeH_2. The extremely toxic hydrogen selenide was prepared[27a] by using a syringe pump to slowly add water to 0.15 mmol (43 mg) of powdered aluminum selenide under nitrogen. The H_2Se released was trapped in 200 μL of toluene-d_8 kept at -78 °C. This solution was cooled to -90 °C and quickly cannulated through flexible Teflon tubing into a previously prepared solution of a mixture of *cis*- and *trans*-cycloheptene also kept at -90 °C. A low-temperature NMR of the resulting solution showed a 5:1 ratio of H_2Se to t-CHP. Warming the solution resulted in isomerization of t-CHP to c-CHP with no other products observed.

Calculations. All quantum chemical calculations were carried out on the Cray SV1 supercomputer operated in Huntsville, AL, by the Alabama Supercomputer Authority. The Gaussian 03 quantum chemistry software package[28] was used for all ab initio calculations in this study. Force-field calculations used the MMX force-field implemented in the program PCMODEL version 6.0.[24]

The potential surface of the cycloheptene system was examined at four points, the cis minimum, the trans minimum, the transition state for trans $\rightleftharpoons$ trans ring-flip, and the trans → cis transition state. All geometries were optimized at the CASSCF(2,2)/6-31G(d) level, and MP2-CASSCF(2,2)/6-31G(d) energies were evaluated at these geometries.

^{13}C chemical shifts were calculated using the GIAO approach at the MP2/6-311+(2d,p) level with geometries optimized at the B3LYP/6-31G(d) level. These geometries were nearly identical to those calculated for the potential energy surface calculations. The chemical shifts predictions (δ_c) with respect to tetramethylsilane were determined using the calculated shielding of tetramethylsilane (σ_{TMS}) at the same level ($\delta_c = \sigma_{TMS} - \sigma_c$).

The dependence of the ^{13}C chemical shift of ethene with twist and pyramidalization angle was investigated by varying both angles by 9° increments while optimizing the other geometric parameters at the B3LYP/6-31G(d) level. The NMR shift was then determined for each geometry at the MPW1PW91/6-31G(d) level by comparing the isotropic shift to that calculated for tetramethylsilane at the same level.

Acknowledgment. Computer time was made available on the Alabama Supercomputer Network.

Supporting Information Available: Calculated geometries and energies and complete ref 28. This material is available free of charge via the Internet at http://pubs.acs.org.

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