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**Photolysis of azoalkanes. Reactions and kinetics of the
1-cyclopropyl-1,3-cyclopentanedyl biradical and 1-cyclopropylcyclopentyl
radical**

Culotta, Anne Marie, Ph.D.

Rice University, 1991

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RICE UNIVERSITY

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CYCLOPROPYL-1,3-CYCLOPENTANEDIYL BIRADICAL AND 1-
CYCLOPROPYLCYCLOPENTYL RADICAL.

by

ANNE MARIE CULOTTA

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DOCTOR OF PHILOSOPHY

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Abstract

PHOTOLYSIS OF AZOALKANES. REACTIONS AND KINETICS OF THE 1-CYCLOPROPYL-1,3-CYCLOPENTANEDIYL BIRADICAL AND 1- CYCLOPROPYLCYCLOPENTYL RADICAL.

by

Anne Marie Culotta

The 1-cyclopropylcyclopentyl radical (**114a**) and 1-cyclopropylcyclohexyl radical (**114b**) were generated in the presence of PhSH via 366 nm photolysis of azo-1-cyclopropylcyclopentane and azo-1-cyclopropylcyclohexane respectively. These radicals undergo cyclopropylcarbinyl (CPC) rearrangement to primary homoallylic radicals **115a** and **115b**, respectively, at rates of $1.45 \times 10^7 \text{ s}^{-1}$ and $1.1 \times 10^7 \text{ s}^{-1}$ based on competitive trapping with PhSH. These rates are 6 - 9 times slower than the parent CPC radical. E_a for **114a**→**115a** was found to be 7.0 kcal/mol and $\log A = 12.3$. Deuterium labeling studies show that homoallylic radical **115a** recloses to **114a** with $k_{rr} = 5.5 \times 10^4 \text{ s}^{-1}$.

Unsymmetrical triplet biradical 1-cyclopropyl-1,3-cyclopentanedyl (**104T**) is produced from the triplet sensitized photolysis of 1-cyclopropyl-2,3-diazabicyclo[2.2.1]hept-2-ene (**123**). Biradical **104T** undergoes CPC rearrangement to a pair of 1,6-biradicals **105E** and **105Z** the latter of which undergoes rapid intramolecular disproportionation to Z-3-propylidenecyclopentene (**108Z**). On account of its geometry, **105E** cannot lead directly to a stable product; hence, it recloses to **104T** ($k_{ra} = 1.2 \times 10^5 \text{ s}^{-1}$).

but interestingly, not to **104S**. If the CPC rearrangement rate of **104T** is taken as that of **114a**, we calculate from the product distribution that the lifetime ($\tau = 1/k_{ISC}$) of **104T** is 59 ns. This figure is only one half the lifetime of the parent 1,3-cyclopentanedyl and is close to $\tau = 42$ ns for 1,3-dimethyl-1,3-cyclopentanedyl, showing that the effect of the cyclopropyl group is similar to that of methyl.

ISC of **104T** displays linear Arrhenius behavior over 3.4 - 61.0 °C. Activation parameters for ISC of **104T** were determined via competition with the CPC rearrangement and were found to be E_a (ISC) = 1.6 kcal/mol and $\log A = 8.4$. Thus **104T** is shown to be a ground state triplet and the low value of $\log A$ is characteristic of spin-forbidden ISC.

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I would like to thank Dr. Paul S. Engel for his work as my graduate advisor in the Rice University Department of Chemistry. The time that he spent in the lab showing me new or better techniques *himself* is most appreciated. I feel very fortunate to have an advisor who is so willing to discuss chemistry in a challenging and informative manner. I would also like to thank the members of Dr. Engel's research group, both past and present, for contributing to my learning experiences at Rice University.

To Mom and Dad, whose kind advice and inspiration have always helped me to pursue my goals. Everybody needs a good support network and I could not have had a better one than my parents.

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Introduction, Part I

The cyclopropylcarbinyl (CPC) rearrangement

The cyclopropyl group adjacent to a carbon radical can be thought of as "spring-loaded" because opening of the strained ring is favored both by enthalpy and entropy.¹ Therefore, CPC rearrangements are generally rapid (10^6 - 10^8 s⁻¹) and the potential exists to tailor these rates through structural modification.² Such rapid unimolecular rearrangements are well suited for use as "free radical clocks" as will be described in the second part of this introduction.

The CPC radical has been generated from a variety of precursors, as illustrated below.³⁻⁵

The first study of the parent CPC rearrangement (**1**→**2**) was carried out at low temperature using ESR.³ Since then, the parent CPC rearrangement has been studied with a variety of radical traps such as 2,2-dimethylpropane thiol (t-butyl thiol),^{4a} PhSH,⁵ Bu₃SnH,^{4b} 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO),⁶ and 1,1,3,3-tetramethylisoindolin-2-yloxy.^{4c} Scheme I illustrates how trapping is used to determine the rate of CPC rearrangement, k_{rf} .

Scheme I. Formation of trapping products from CPC radicals.

Determination of the ratio of trapped (T) to rearranged (R) products, coupled with a knowledge of trapping rates (k_t), allows calculation of k_{rf} from eq 1.

$$k_{rf} = k_t[T] \times (R/T) \quad (1)$$

Newcomb and coworkers⁵ combined their data from trapping of **1** with PhSH (-37 to +50 °C) with the low temperature (-21 to +3 °C) ESR data of Maillard et al,³ and the spin trapping data (80-120 °C) of Beckwith et al⁶ in

order to calculate the activation parameters for the parent CPC rearrangement over a 160 °C temperature range. Values of $E_a=7.05$ kcal/mol and $\log A=13.15$ were determined, leading to the currently accepted rearrangement rate for the parent CPC radical, $k_{rf}=9.4 \times 10^7$ s⁻¹ at 25 °C.⁵

Numerous CPC rearrangements in other systems have been studied (more qualitative than quantitative) employing "tin hydride method".^{7,8} The examples shown below illustrate how stereoelectronic

effects can outweigh thermodynamics in the CPC rearrangement. Although thermodynamics favors secondary radicals over primary, steroidal radical **10** rearranged to give primary radical **11**⁷, but its epimer **8** rearranged to secondary radical **9**. Radical **12** rearranged to the less favored **13**⁷ roughly 30 times faster than to **14** at 3 °C. Conformational preferences of the molecule affect cyclopropane bond/radical p-orbital overlap which can lead to the less thermodynamically favored product.

Figure 1. Steric effects on the CPC rearrangement.

Figure 1 supplements the above explanation. Conformations A and C, in which overlap of the radical p-orbital and a cyclopropane bond occurs, favor ring opening whereas the bisected nature of conformer B precludes CPC rearrangement. One can easily see how interactions between R or R' and R''' could influence the equilibrium between conformers. A splendid example of such stereoelectronic control of the CPC rearrangement in a freely rotating CPC radical is shown below.⁹

Unfavorable eclipsing interactions between the two cyclopropyl groups in radical **15** (corresponding to conformer **A** in figure 2 where $R = \text{CH}_2\text{S}(t\text{-Bu})$, $R' = \text{cyclopropyl}$, $R'' = \text{H}$, and $R''' = \text{H}$) lead to exclusive formation of **17**.

The technique of kinetic absorption spectroscopy (KAS) was used to study the CPC rearrangement of a series of phenyl-substituted CPC radicals.^{2b} A sampling of rate constants is given below.

The radicals, generated by pulse radiolysis of 1-aryl-1-cyclopropyl methylbenzoates, were found to rearrange with rates of $2.1 \times 10^5 \text{ s}^{-1}$ to $3.6 \times 10^5 \text{ s}^{-1}$ at 25°C , depending on the nature of **X**.

A line broadening analysis of the muon spin rotation (μSR) spectrum of a series of methyl substituted CPC radicals was used to determine activation parameters (E_a in kcal/mol, A in s^{-1} , rate at 25°C) for the CPC rearrangements

in eqs. 7-9.¹⁰ These radicals were derived from addition of muonium to the required substituted vinylcyclopropane.

The μ SR study on the parent CPC rearrangement is in good agreement with the earlier ESR work,³ but it gives k_{rr} about 40% higher than the currently accepted value ($9.4 \times 10^7 \text{ s}^{-1}$) determined by Newcomb et al.⁵ The limited availability of activation parameters for the CPC rearrangement makes this study especially noteworthy. The stability of the CPC radical affects the rate of rearrangement in that less stable primary radicals rearrange 20 times faster than more stable tertiary CPC radicals, and 10 times faster than secondary CPC radicals.

CPC radicals have been implicated as discrete intermediates in 1,3-vinyl migrations,¹¹ the mechanism of which is shown below.

Scheme II. Mechanism of vinyl group migration.

Ring closure of 3-alkenyl radicals is known to be several orders of magnitude slower than ring opening of the CPC radical.¹² These rate differences make detection of the CPC radical by spectroscopic methods difficult, and trapping almost impossible. The rate of closure of the 3-butenyl radical to the CPC radical, k_{rr} , was determined to be $4 \times 10^3 \text{ s}^{-1}$ (at 25 °C) by ESR and by ^2H scrambling in the presence of radical scavengers.¹³ Thus the equilibrium constant for the CPC radical is calculated to be 2.4×10^4 (at 25 °C), showing the large degree to which ring opening is favored.

Vinyl group migration of **27** was studied by Newcomb and coworkers.¹⁴

The closure of **27**, which benefits greatly from the Thorpe-Ingold effect, was found to occur with $k_{rr} = 5 \times 10^6 \text{ s}^{-1}$ (at 25 °C). To our knowledge, no other rate

constants for ring closure of 3-alkenyl radicals to CPC radicals have been determined.

Introduction, Part II

Biradicals

Biradicals (BRs) have become a recent focus of mechanistic investigation¹⁵ because they are postulated as intermediates or transition states in photochemical¹⁶ and thermal reactions.¹⁷ In thermolysis reactions, BR mechanisms compete thermodynamically with concerted pathways, and offer a simpler alternative to ionic pathways.¹⁸ In many cases, evidence supporting BRs in thermal reactions is permissive rather than conclusive.^{19,20} Spin selection rules allow the formation of covalent bonds from singlet biradicals (SBRs), and the rapid collapse to products (eg. **40S**→**41**) usually precludes

direct observation or bimolecular trapping of simple SBRs (BRs lacking a heteroatom or delocalizing substituent adjacent to a radical center). An example of a long-lived SBR is **42S**,²¹ whose lifetime (ca. 20 ps at ambient temperature) is enhanced greatly by radical stabilizing phenyl groups.

Sources of biradicals

It is commonly assumed that BRs from thermal sources are produced in the singlet state and that intersystem crossing (ISC) to triplets is negligible.²¹⁻²⁴ BRs can be produced photochemically in singlet or triplet states, depending on the spin state of the excited precursor. Since triplet biradicals (TBRs) cannot form covalent bonds (eg. **40T**→**41**) prior to ISC (eg. **40T**→**40S**), the potential for direct observation and bimolecular trapping of TBRs is much higher.²⁵ Some of the more common photochemical sources of biradicals are shown below.

Thermolysis or photolysis of azoalkanes gives monoradicals (MRs) cleanly and often efficiently.²⁶ Cyclic azoalkanes are a useful source of BRs of known multiplicity since slow ISC of excited bicyclic azoalkanes relative to deazotation allows the production of SBRs from direct irradiation,²⁷ and TBRs from triplet sensitized decomposition. Norrish type I and II cleavages of ketones afford BRs,²⁸ and when ISC of the excited ketone is rapid, the result is formation of TBRs.^{29a} Irradiation of the acetophenone moiety in **46** leads to TBR **47**.³⁰ Some photochemical [2+2] cycloadditions are thought to proceed through biradical pathways, for instance, the Paterno-Buchi^{31,32} reaction or the cycloaddition of olefins.³³

Mechanisms of ISC in TBRs.

TBRs must undergo ISC before products can be formed; therefore, ISC influences both the rate of product formation and the product ratio from TBRs.³⁴ There are two mechanisms by which BRs can undergo the spin forbidden process of ISC. In electron nuclear-hyperfine coupling (HFC), magnetic communication of the radical free electrons with neighboring nuclear spins facilitates ISC.^{29,35} HFC is responsible for ESR,³⁶ CIDNP^{29,35} and magnetic field effects³⁶ in geminate radical pairs and BRs. Spin-orbit (SOC) coupling, in which torque on an electron spin is created by orbital angular momentum, is the dominant mechanism of ISC in constrained BRs.³²⁻³⁶ The dependence of ISC on chain dynamics³⁷ shows that in long chain BRs, where the free electrons are far apart, HFC is responsible for ISC, but when the free electrons are brought into close spatial proximity through chain dynamics, SOC is responsible for ISC.

Four factors have been found to determine the magnitude or effectiveness of SOC in BRs.^{34,36-39}

1. The energy gap, E_{S-T} , between the BR spin states. As the energy gap increases, the magnitude of SOC decreases.
2. The distance between the free electrons. It has been suggested that $SOC \propto e^{-br} \sin \phi$, where r is the average distance between electrons and ϕ is the angle between the half occupied orbitals, and $b=3.07 \text{ \AA}^{-1}$.
3. The orthogonality of the orbitals bearing the free electrons (related to ϕ in rule 2 above). SOC is most favored when the radical p-orbitals are mutually orthogonal because in this orientation, maximum torque on electron spins is generated.

4. The ionic character of the singlet state. As the ionic character of the singlet state increases, for example in BRs with oxygen atoms adjacent to a radical center, the magnitude of SOC is increased.

The effect of "r" on τ is evident from the series of BRs (**54T-57T**) studied by LFP⁴⁰ (cf. Figure 2).

Figure 2. Effects of electron-electron distance "r" on τ .

As alkyl chain length increases, SOC decreases and τ gets longer.

Acyclic BRs have a large number of possible orbital orientations, but this number is restricted in cyclic biradicals. The study of BRs such as **58T**⁴¹ and **40T**^{42,43} gives a better understanding of the effects of orbital orientation on τ (cf. Figure 3).

Figure 3. Effects of orbital orientation on τ .

BR **58T** is locked in a twist boat conformation where the radical p-orbitals are parallel, thereby disfavoring SOC and increasing τ relative to **70T**. ESR observation of BR **40T** showed that all α protons (α to the radical centers) were equivalent to each other, as were all β protons,⁴⁴ indicating a time-averaged planar biradical (**40B**). It has been argued that conformations **40A** and **40C**

Figure 4. Conformations of **40T**.

occur in regions where the singlet and triplet energy surfaces of the BR intersect, and and that the small thermal barrier to attainment of these conformations increases τ relative to **70T**. This theory gives the same qualitative result as the Salem-Roland rules of SOC which predict that conformations **40A** and **40C** should favor ISC because of the non-parallel orientation of the free electron orbitals (and also because a lowering of E_{S-T} will favor SOC).

Comparison of $\tau=190 \text{ ns}$ for **55T**⁴⁰ with $\tau=365 \text{ ns}$ for **60T**^{45,46} supports the Salem-Roland theory of orbital orientation as well. Unconstrained **55T** can adopt a variety of conformations conducive to SOC, but constrained **60T** is thought to have essentially parallel orbitals disfavoring SOC and hence the longer lifetime. BR **59T**, which possesses a geometry favoring SOC³⁹ is more than 100 ns shorter-lived than **60T**,⁴⁷ yet it is longer lived than **55T**.

Techniques of BR detection.

Methods commonly employed in the study of TBRs (not an exhaustive list) are laser flash photolysis (LFP),⁴⁸ electron spin resonance (ESR),²⁵ CIDNP^{29,35} photoacoustic calorimetry (PAC),^{49,50} oxygen trapping (OT),⁴⁷ and the free radical clock (FRC) method.⁵¹⁻⁵³ LFP, PAC, and ESR are methods of direct observation because one monitors an electronic signal assignable to a BR. The OT and FRC techniques are indirect because biradical behavior is inferred from reaction mechanisms and product distributions.

Direct observation of BRs.

In LFP, a high, localized concentration of BRs is produced by a flash of laser light. The absorbance of the BR is monitored over time to deduce the rate of BR decay. Lifetimes of 10 ns-100 μs can be studied using LFP; however, the

presence of a chromophore conjugated with the radical center is usually required to shift the absorption spectrum of the BR into an experimentally observable region of the UV-visible spectrum (350-600 nm). BRs lacking such chromophores are termed "transparent" and cannot be observed directly by LFP. In such instances, the buildup of a cation radical from oxidation of an electron donor (such as paraquat) can be monitored instead.⁴⁸

Study of BRs by LFP has provided a tremendous amount of data on BR lifetimes, and has contributed significantly to theories of ISC. In order to probe yet more subtle features of ISC, study of BRs lacking heteroatoms or delocalizing substituents is required.^{47,25} Lacking a chromophore, these BRs must be studied by other methods described below.

Buchwalter and Closs' direct observation of a pure hydrocarbon BR, 1,3-cyclopentanediyI (**40T**), by ESR⁴⁴ was a turning point in the study of simple BRs. Measurement of the variation of signal intensity with temperature leads to activation parameters for k_{isc} , and ultimately to τ . While this approach was successful for **40T**, which was shown to have a triplet ground state through CIDNP studies,⁴⁴ it failed for alkyl substituted analogs.⁴⁴ It has been suggested that a triplet ground state may be required for observation of an ESR signal from simple biradicals^{54,55} since SBRs possess a built-in mechanism of self-destruction through ring closure. A reordering of the energy levels of 1,3-cyclopentanediyIs upon alkyl substitution could be responsible for the failure to observe ESR signals.^{15a}

Dougherty and coworkers have observed many 1,3-cyclobutanediyls by ESR,^{15a,25, 55} and have found that alkyl substitution does not lower the singlet state below the triplet. The zero field splitting (ZFS) values, D/hc and E/hc , provide information on BR structure and electronic interactions. Since D/hc

varies with $1/r^3$, where r is the distance between electrons, large values of D/hc indicate close proximity of electrons. E/hc provides a measure of the symmetry of the BR. Shown below are values of D/hc (cm^{-1}) and E/hc (cm^{-1}) for various cyclobutane- and cyclopentane-diyls.^{25,55}

61T	62T	63T
D/hc 0.112	D/hc 0.082	D/hc 0.060
E/hc 0.005	E/hc 0.003	E/hc 0.002

40T	64T	65T
D/hc 0.084	D/hc 0.047	D/hc 0.049
E/hc 0.002	E/hc 0.001	E/hc 0.001

Figure 5. ZFS values of 1,3-cyclobutane- and -cyclopentane-diyls determined by ESR.

A comparison of **40T** and **61T** is worthy of mention. D/hc was found to be 0.084 for **40T**^{25,44} and 0.112 for **61T**,^{25,55} indicating that the radical centers in **40T** are farther apart than in the case of **61T**. In accord with the ESR results, ab initio calculations gave $r=2.37 \text{ \AA}$ ^{51,56} and $2.10 \text{ \AA}$ ^{25,55} for **40T** and **61T**, respectively.

Figure 6. Distance between electrons, "r", in cyclobutane- and cyclopentanedilyls.

For **64T** and **65T**, D/hc was found to be 0.047^{46} and 0.049^{46} respectively, indicating that the free electrons are similar distances apart these molecules. Comparison with **40T** shows, as expected, that the "r" is greater in the delocalized phenyl cases.

Herman and Goodman used the sensitive technique of PAC to determine $\tau = 316$ ns for **40T**.⁴⁹ PAC allows simultaneous probing of dynamics and energetics of photoinitiated reactions by measurement of heat deposition over time. According to this work, ΔH_f of **40T** = 71.5 ± 2.3 kcal/mol, which is significantly greater than the 67 kcal/mol⁵⁷ predicted on the basis of group additivity. The experimental ΔH_f of **40T** provides impetus for the upward revision of radical heats of formation^{58,59} (used in group additivity calculations).

Methods of indirect observation of BRs.

The oxygen trapping method.

The most common method of studying triplet lifetimes of simple BRs, developed by Adam, Wilson and coworkers, has been oxygen trapping (OT)⁴⁷ wherein a bimolecular reaction with oxygen competes with ISC. In order for OT to be successful, competitive formation of peroxide (**P**) and hydrocarbon (**H**) products is required, as well as knowledge of trapping rate constants of O_2 with

BRs. The case of **40T**^{42, 43} provides an example of the OT method of determining τ .

Scheme III. Oxygen trapping of triplet 1,3-cyclopentanediyI (**40T**)

Decomposition of **DBH** in the presence of sensitizer gives **40T** which either reacts with O_2 giving **P**, or undergoes ISC to give **H**. Measurement of the mole fractions **H** (X_h) and **P** (X_p) produced at various concentrations of O_2 leads to τ by use of equation (10). T_f , the trapping factor, is defined as $k_{to}/(k_{to} + k_{co})$, and is a measure of the efficiency of trapping with O_2 as opposed to ISC catalyzed by O_2 . A plot of $1/(1-X_h)$ versus $[O_2]^{-1}$ allows one to evaluate τ from the slope, and T_f from the y-intercept of eq 10. When T_f is unity, O_2 does not cause catalyzed ISC, but as the y-intercept of equation (10) increases beyond unity,

O₂ catalyzed ISC is indicated. The absence of either **P** or **H** from an OT experiment precludes determination of T_f , and one is left to wonder whether the absence of **P** indicates a short τ , or is merely the result of O₂ catalyzed ISC.⁶⁰

$$1/X_p = 1/(1-X_h) = 1/(\tau k_{tO}[O_2]) + 1/T_f \quad (10)$$

The OT method gave $T_f=1.02$ for **40T**⁴³, indicating no catalyzed ISC, and $\tau=92$ ns, which is 3.5 times smaller than the value determined by Goodman.⁴⁹

A study of other 1,3-cyclopentanediyIs, however, was much less fruitful.

None of the BRs shown above gave any peroxide product, and an upper limit of 0.1 ns was assigned to τ in all cases.⁶¹ The short τ 's, relative to **40T**, were rationalized by a reduction in E_{S-T} due to diminished through bond coupling of the radical centers upon dialkyl substitution.^{54,61} The buttressing effect of gem-dimethyl groups (which would decrease "r") seems unlikely because of the similarity in ZFS parameters observed for **64T** and **65T** (cf. Figure 2).

Alternative explanations are: 1) The gem-dialkyl substituents in **66T-69T** slow k_{tO} due to steric hindrance, and 2) O₂ catalyzes ISC (although this seems less likely since $T_f=1$ for **40T**).

In the case of **70T**, an amount of peroxide too small to quantify reliably was found using 10 atmospheres of O₂.⁶²

Scheme IV. Oxygen trapping of triplet 1,4-cyclohexanediyl (**70T**).

This negative result was also interpreted as a case of rapid k_{ISC} , and an upper limit of 0.1 ns was postulated for τ of **70T**. As in **66T** - **69T**,⁶¹ it is possible that the short lifetime of **70T** is the result of efficient O_2 catalyzed ISC.⁶⁰

Much of the uncertainty of TBR lifetimes determined by the OT method comes from difficulty in determining k_{tO} ,⁴³ which is diffusion controlled. Calculation of k_{tO} requires a knowledge of the diffusion rate of O_2 in the solvent employed^{47, 43} and the fraction of collisions between triplet oxygen and TBR that actually lead to trapping products.⁴⁷ The statistical factor should be 4/9; however, this theory has never been tested rigorously. The lifetime of **40T** has varied over the years from 900 ns⁴² to 720 ns⁴² to 320 ns⁴³ to 100 ns⁴³ because of the difficulty in estimating the diffusion behavior of oxygen in various solvents. The uncertainty in k_{tO} , the difficulty in quantifying unstable endoperoxide and

hydroperoxide products, and the potential for O₂ catalyzed ISC lead to a large error in τ .

The case of **76T**,^{45,63} whose lifetime was determined to be 243 ns and 280 ns by LFP and OT respectively, was touted as an example of the accuracy of the OT method.

76T

$\tau = 240\text{-}280$ ns

The two lifetimes agreed only because k_{t0} was determined by LFP and its value was used in eq. 10, eliminating a major source of uncertainty in τ .

FRC techniques.

Wagner used the well characterized 5-hexenyl cyclization⁶⁴ (**77** $\rightarrow$ **78**) to study the triplet lifetime of a Norrish type II BR by the FRC technique.⁵²

Scheme V. Use of the 5-hexenyl cyclization as a FRC.

The CPC rearrangement was employed by Wagner as the free radical clock in another study of a Norrish type II BR.⁵³

Scheme VI. Use of the CPC rearrangement as a FRC to evaluate τ of a Norrish type II biradical (**86**).

The ratio of appearance quantum yields of **90**:**89** was $0.26/0.03=8.6$ in benzene. Although the mechanism of product formation was not investigated, the authors estimated $\tau=35\text{-}50$ ns for **86** (assuming that the CPC rearrangement occurs at a rate of $2 \times 10^7 \text{ s}^{-1}$ and that 38% of **86** undergoes this rearrangement.).

The work of Becker et al³³ used the CPC rearrangement to obtain evidence for the intermediacy of BRs in a photochemical [2+2] cycloaddition (cf. scheme VII).

Scheme VII. Interception of a 1,4-BR by the CPC rearrangement.

Our work employs the CPC rearrangement as a FRC in the study of simple TBR lifetimes. Over a considerable range of lifetimes,⁶⁴ the FRC method provides an opportunity to determine τ of transparent BRs where orbital orientation and electronic interaction may be related to structure without the influence of heteroatoms and delocalizing groups.

Engel and Keys estimated τ of **97T**⁵¹ and **102T**^{51b} using the FRC method. The bimolecular trapping reaction of TBRs with O_2 is replaced by the unimolecular CPC rearrangement. Thus the potential for O_2 catalyzed ISC is eliminated, but the CPC rearrangement rate must be estimated from similar

rearrangements in the literature.^{3,4,64} Scheme VIII demonstrates how τ is evaluated by the FRC method.

Scheme VIII. Determination of τ for **97T** using the FRC method.

Triplet sensitized decomposition of azoalkane **96** affords **97T** which partitions itself between k_{isc} and k_{rf} . ISC to **97S** gives closure product **99** or scission product **100**, both of which contain an intact cyclopropane ring and hence are referred to as unrearranged products. CPC rearrangement of **97T** affords the 1,7-BR **98** which disproportionates intramolecularly to products lacking a cyclopropyl group, hence referred to as rearranged products. By inspection of scheme VIII, we derive eq 11, which relates the

$$k_{isc} = k_{rf}(99 + 100)/101 \quad (11)$$

experimentally determined ratio of unrearranged to rearranged products to k_{r} and k_{isc} . By the FRC method, Engel and Keys determined TBR lifetimes (including CPC rearrangement) of 28 ns and 33 ns for **97T** and **102T** respectively;^{51b} however, these values have been revised to 138 and 188 ns.⁶⁵

The merits of the FRC method are listed below.

1. Elimination of O_2 and the possibility of catalyzed ISC.
2. Production of easily quantifiable hydrocarbon products.
3. The reaction competing with ISC is unimolecular CPC rearrangement, whose rate can be deduced from similar literature reactions and is unaffected by diffusion or spin statistics.

The drawback to the FRC technique is that bridgehead cyclopropyl substituted bicyclic azoalkanes, precursors to the required BRs, are very difficult to prepare (cf. synthesis of bicyclic azoalkanes).

One can rationalize the much shorter τ of **70T** relative to **97T** and **102T** determined by the OT and FRC methods in the following ways:

1. The lifetime difference by the two methods is real and there is some undiscovered effect of structure on k_{ISC} . For example, the cyclopropyl group in **97T** may add an unusual degree of stabilization,⁶⁶⁻⁶⁸ or may induce rapid conformational changes which disfavor SOC relative to **70T**⁴².
2. The lifetime of **70T** is really much longer than determined by OT, and O_2 catalyzed ISC is responsible for the small observed τ .

Adam et al. estimated $\tau=0.3\text{-}3.0$ ns (including CPC rearrangement)⁶⁹ for BR **103T** using the FRC method with the rearrangement of a spiro-CPC biradical.

The upper limit of the CPC rearrangement rate was taken as that of the parent ($2.1 \times 10^8 \text{ s}^{-1}$)⁶⁴ and the lower limit ($2.2 \times 10^7 \text{ s}^{-1}$)^{51b} from the estimate by Engel and Keys used to obtain τ of **97T**. The short lifetime of **103T** was rationalized by the flexibility of the seven-membered ring which possesses a variety of conformations favorable for SOC.

While the OT method of studying 1,4-cyclohexanediyls appears limited, it is also evident that the FRC method requires improvement. From a synthetic perspective, better methods for preparation of bridgehead cyclopropyl substituted bicyclic azoalkanes are required as existing routes are often complicated by undesired isomers and low yields.⁵¹ Such azoalkanes are important tools for mechanistic study, not only in the investigation of BR

lifetimes, but as probes into the photochemistry of azoalkane decomposition.⁷⁰ Limited availability of these important compounds has prevented growth of an interesting area of research.

An experimental determination of the rate of CPC rearrangement would eliminate a potential source of error in τ . Assuming that MRs and BRs rearrange at the same rate,⁵³ the study of MRs analogous to **97T** and **102T** would provide a better value of k_{rf} . As discussed above, the possibility exists that the cyclopropyl group somehow dramatically alters k_{isc} in the case of **97T** and **102T**. The matter remains unresolved, however, because interpretable OT data for other simple 1,4-cyclohexanediyls do not exist.

Purpose of this work.

We chose to study **104T** to evaluate the effect of a cyclopropyl group on the lifetime of a well characterized TBR. The lifetime of **40T** has been

determined by the OT method⁴⁷ and PAC⁴⁹ with somewhat similar results (τ of **40T** is 40% lower by the OT method). Furthermore, **40T** has also been observed directly by ESR and CIDNP,⁴⁴ techniques that provide additional information about E_{S-T} and orbital orientation.

We undertook a study of **104T** and MRs **114a,b** with the following goals in mind:

1. Determine the CPC rearrangement rate (k_{H}) of **114a,b** and explore the chemistry of these MRs.
2. Use the CPC rearrangements from above to determine τ of **104T** for comparison with **40T**, and reevaluate τ of six-membered biradicals **97T** and **102T**.
3. Design better synthetic routes to α -cyclopropyl substituted azoalkanes in which the the cyclopropyl group rotates freely.

We were interested to see whether conformational differences between five and six-membered rings would affect the relative rearrangement rates of MR's **114a** and **114b**. In addition to the previously mentioned interest in **104T**, the intriguing possibility of producing a pair of constrained 1,6-BR isomers (**105E** and **105Z**) from CPC rearrangement of **104T** was further impetus for the work.

We were curious to see how **105Z** and **105E** would differ in reactivity. Shown below are some interesting examples which demonstrate how other BRs born in awkward geometries form covalent bonds.^{51b}

Synthesis of compounds

Overview of routes to 2,3-diazabicyclo[2.2.1]hept-2-enes (DBHs).

The synthesis of 1-alkyl substituted 2,3-diazabicyclo[2.2.1]hept-2-enes (DBHs) is particularly challenging relative to other bicyclic azoalkanes.

Outlined below are three general approaches.

In our laboratory, Keys attempted the synthesis of related 2,3-diazabicyclo[2.2.2]oct-2-enes (DBOs) via Diels-Alder reaction of olefins with azines (analogous to eq 18); however, the approach was unsuccessful.⁷¹

The Diels-Alder route in eq 19 suffers from the use of 1-substituted cyclopentadienes which, in most cases, undergo rapid, thermally allowed 1,5-hydrogen shifts.⁷² The end result is formation of undesired 5-substituted azoalkanes in addition to the desired 1-isomer (123).

Furthermore, N-alkyl-substituted triazolinediones (in eq 19), which serve as superior dienophiles in Diels-Alder reactions,⁷³ are not commercially available and both fragments in the convergent synthesis (eq 19) require several steps for preparation.

Eq 20 represents a dramatically different approach to the synthesis of **DBHs**. The problem of undesired isomers from eq 19 is eliminated, and tosylhydrazide is a more convenient source of nitrogen than triazolinediones. The available evidence suggests that Lewis acid catalyzed ring closure in eq 20 involves a carbocation α to R.^{74a,b} When R = cyclopropyl, ring opening becomes a potential side reaction.

We were interested in **123**, a **DBH** derivative whose synthesis is further complicated by the presence of the cyclopropyl group at the 1-position. The tendency of cyclopropyl cations to undergo ring opening⁷⁵ dictates that cyclopropyl be used in the form of cyclopropyllithium, or any reagent where cyclopropyl is introduced as the anion.

Synthesis of 1-cyclopropyl-2,3-diazabicyclo[2.2.1]hept-2-ene (**123**): The Diels-Alder route.

Despite anticipated complications of the Diels-Alder approach, we concentrated our efforts on the synthesis of diene **121**. The planned approach to **121** involved 1,2-addition of cyclopropyllithium to 2-cyclopentene-1-one.

Scheme IX. Idealized synthesis of diene **121**.

Dehydration of **124** with 2,4-dinitrophenylsulfenyl chloride⁷⁶ would give **121** barring any 1,5-hydrogen shifts. In reality, the 1,2-addition of cyclopropyllithium to 2-cyclopentene-1-one was plagued with competing enolization and polymerization which caused a low yield. Use of organocerium chemistry⁷⁷ to minimize the enolization was unsuccessful. Several attempts to prepare an organocerium reagent from anhydrous CeCl_3 and cyclopropyllithium failed. The enone failed to disappear, indicating that either the organocerium reagent was unreactive, or was never formed.

Dehydration of **124** to **121** (in scheme IX) was sluggish giving a 1:1 mixture of dienes **121** and **122** in low yield. Use of other reagents such as POCl₃/pyridine,⁷¹ FeCl₃/SiO₂,⁷⁸ p-toluenesulfonic acid⁷⁹, and pyrolysis met with varying degrees of failure due to the sensitivity of the tertiary allylic alcohol.

An alternate route to **121** was based on pyrolysis of **125** over alumina.⁸⁰ Though the overall yield was higher than from **124**, a 1:1 mixture of dienes was again obtained. Conjugate addition of higher order cuprates to unsaturated epoxides is gaining popularity in synthetic chemistry.⁸¹ Allylic alcohol **125** was obtained from conjugate addition of Li₂(c-C₃H₅)₂CuCN to cyclopentadiene monoepoxide. The reaction proceeded in relatively high yield, but suffered from the waste of one equivalent of cyclopropyl bromide, used to prepare the cuprate.

Scheme X. Synthesis of **121** and **122**.

Attempts to conserve cyclopropyl bromide by using lower order cuprates,^{82a} or thienyl^{82b} dummy ligands met with varying degrees of failure. The lower order cuprate, $\text{Li}(\text{c-C}_3\text{H}_5)\text{CuCN}$ was not reactive enough to carry out the desired transformation. Use of the thiophene ligand gave **125**, but only at the expense of purity.

The 1:1 mixture of **121** and **122**, prepared in Scheme X, was reacted with N-methyltriazolinedione (MTAD), giving a similar ratio of tricyclic urazole adducts, and catalytic (Pd/C) hydrogenation was employed to saturate the double bond.

Scheme XI. Diels-Alder route to azoalkane 123.

The hydrogenation was complicated by the presence of the vinylcyclopropane moiety in the undesired isomer **127**, and resulted in formation of saturated tricyclic urazoles with n-propyl groups.⁸³ The mixture of **128-130** was converted to the azoalkane copper chloride salt by refluxing with KOH/*i*-PrOH and treatment with aqueous CuCl₂.^{73b} The free azoalkanes were liberated from the rust-colored copper chloride salt using aqueous NaOH and continuous

extraction with pentane. The desired azoalkane **123** was obtained by preparative GC.

Attempts to reduce the unsaturated urazole mixture using diimide⁸⁴ were unsuccessful (cf. scheme XII).

Scheme XII. Hypothetical diimide reduction of **126** and **127**.

Since diimide preferentially reduces disubstituted over trisubstituted double bonds,^{84d} the advantage of hydrogenation in this fashion would have been preferential reaction of the desired unsaturated tricyclic urazole **126**.

Conversion of the resulting mixture of **127** and **128** urazoles to azoalkanes, in theory, would have led only to **123** since **129** would have undergone a reverse Diels-Alder reaction to **122** and nitrogen.

Synthesis of **123**: The tosylhydrazone route.

The second route to **123** was developed in response to the need for a more efficient, higher yield procedure than the Diels-Alder route. The final step in the sequence relied on the elegant acid-catalyzed tosylhydrazone cyclization developed by Marshall Wilson (eq 20).^{74a} A synthesis based on the Wilson

chemistry was first attempted by Dr. Akihide Kitamura,⁸⁵ and it employed the oxy-Cope rearrangement to obtain aldehyde **133** from vinyl ether **132**.

Scheme XIII. Hypothetical oxy-Cope route to **133**.

The vinyl anion **130**, generated from the trisylhydrazone^{86a} of cyclopropyl methyl ketone (CMK) **134d** (scheme XIV),⁸⁷ was reacted with monomeric formaldehyde. The desired alcohol, however, was obtained in low yield and conversion to the terminal vinyl ether **132** would have been tedious.

Scheme XIV. Mechanism of vinyl anion (**130**) formation.⁸⁷

c, X = p-tolyl
d, X = 2,4,6-triisopropylphenyl

Our first attempts to prepare aldehyde **133** were based on the work of Dr. Kitamura. Since tosylhydrazide was commercially available, we began by

attempting to generate **130** from tosylhydrazone **134c** and 4-5 equivalents of n-butyllithium. A side reaction of aryl proton exchange with butyllithium required the large excess of base. Quenching with bromide **137** from eq 37 gave no reaction, and the bromide was recovered. Quenching with potent electrophiles such as CO₂, or DMF also met with failure.

We attempted to generate **130** from trisylhydrazone **134d** and 2.2 equivalents of n-butyllithium. The isopropyl groups prevented the unwanted aryl hydrogen-butyllithium exchange, and only 2.2 equivalents of alkyl lithium were required.

Quenching the reaction with **137** in eq 37 led only to elimination, but use of the TBDMS (t-butyldimethylsilyl) ether of 1-bromopropanol⁸⁸ gave the desired **139** in good yield.

Oxetane is known to undergo ring opening reactions with alkyl and aryl Grignard and lithium reagents,⁸⁹ but the analogous reaction with vinyl organometallic reagents has not been studied. Since deprotection of **139** was more tedious than expected, we experimented with oxetane as the electrophile and obtained **140** in good yield.

PDC⁹⁰ oxidation of **140** afforded **133** which was converted to unstable tosylhydrazone **141** by reaction with tosylhydrazide in methanol.

Scheme XV. Tosylhydrazone Synthesis of **123**.

Azoalkane **123** was obtained upon reaction of **141** with $\text{BF}_3 \cdot \text{OEt}_2$ at -20°C .

The success of the tosylhydrazone cyclization in the synthesis of **123** can be accounted for by the stability of the tertiary cation **143**,^{74c} and our results support the reaction mechanism proposed by Wilson (scheme XVI).^{74a}

Scheme XVI. Mechanism of **141** $\rightarrow$ **123**.

The advantages of this new synthesis of **123** over the Diels-Alder route are listed below.

1. The new synthesis is more cost effective because **CMK** is cheaper than cyclopropyl bromide, and only one equivalent of the ketone was required.
2. The Wilson chemistry eliminates the formation of undesired azoalkane isomers, facilitating isolation of **123** by preparative GC.
3. The number of steps in the sequence is reduced, and the overall yield of the reaction is an order of magnitude better (20% versus 2%).

Attempted synthesis of rearranged azoalkanes **146**.

In the hope of studying biradicals from azoalkanes **146E** and **146Z**, we attempted to prepare these compounds by heating the reaction used to convert **141** to **123**.

When the reaction was carried out in refluxing benzene, only azoalkane **123** was isolated. Attempts to encourage ring opening⁹¹ of **143** by decreasing the nucleophilicity of the nitrogen atoms (using the 2,4-dinitrobenzenesulfonyl hydrazone of aldehyde **133**) met with failure. At room temperature, the reaction gave only **123**, and at higher temperature, no product was isolated at all.

The following synthetic sequence is an alternative route to the desired azoalkanes; however, no experimental work has been carried out along these lines.

Scheme XVII. Proposed synthesis of **146**.

The synthesis of **148** has been described in the literature.⁹² N-alkylazodicarboxylates are known to undergo the ene reaction with olefins,⁹³ and **149** should be obtained without difficulty. Reduction of **149** over platinum should give **150**, which can be converted to **151** by three carbon homologation, deprotection and oxidation. The key step in formation of the bicyclic azoalkane **146** will be an intramolecular titanium induced carbonyl coupling reaction followed by Dougherty's⁵⁵ mild hydrolysis/oxidation sequence.

Attempted synthesis of photoproducts from azoalkane **123**.

Initial NMR and GC studies on the triplet sensitized photolysis of **123** showed several hydrocarbons possessing olefinic and cyclopropyl moieties. The presence of rearrangement and closure products indicated competition between k_{isc} and k_{rf} . We undertook the identification of these compounds by authentic synthesis since the azoalkane precursor was available in limited quantity.

It was fairly certain that **107** was the major photoproduct under triplet sensitized conditions of azoalkane decomposition. No problems were anticipated in the identification of this photoproduct because the spin correlation effect predicts that **107** can be obtained pure by direct irradiation of **123**.²⁷

Of more concern was the identification of the olefins that accounted for about 33% of the product mixture. Because the expected dienes were surprisingly difficult to synthesize, their identification was eventually accomplished by preparative GC isolation of the triplet sensitized photolysis products. Several attempts to prepare these deceptively simple dienes were carried out prior to GC isolation.

The most straightforward approach was the Wittig reaction of 2-cyclopentenone and *n*-propylenetriphenylphosphorane.

Despite attempts to effect this reaction under various conditions, and observed disappearance of starting ketone, the desired dienes were not obtained.

We considered a modification of the Julia method⁹⁵ to prepare the homoallylic diene-bromide **153** from **124**, a compound that was already in hand. Reduction of **153** with $\text{Li}(\text{Et})_3\text{BH}$ would give **108**.

Under the conditions in eq 24, we observed complete disappearance **124**, but a complex product mixture that did not contain **108** resulted. It is likely that the failure was due to the instability of either the starting alcohol or **153**. Control

experiments on model compound **154** gave homoallylic bromide **155** in good yield and reduction to **156** was accomplished easily with $\text{LiB}(\text{Et})_3\text{H}$.

In another attempt to prepare **108E** and **108Z**, we tried the Barton-Crich⁹⁶ method of generating radicals from alcohols, a method that could also lead to a study of an allylic radical. We again started with **124** and reacted it with DMAP and oxalyl chloride followed by the sodium salt of N-hydroxythiopyridone, in hopes of obtaining the mixed ester **157**. Scheme XVIII shows the anticipated products from decomposition of **157** in the presence of thiophenol.

Scheme XVIII. Anticipated products from mixed ester **157**.

The reaction gave an intractable mixture of products, and **108E&Z** were not among them. Hydrocarbon **162** was obtained without difficulty when the same reaction was run on alcohol **161**.

The final route attempted to prepare the deceptively simple dienes involved catalytic hydrogenation of one of the internal double bonds of fulvene **164**.

Scheme XIX. Attempted synthesis of **108** from cyclopentadiene.

The required fulvene could be prepared in two steps from trimethylsilylcyclopentadiene and propionaldehyde.⁹⁷ Elimination of TMSOH from the alcohol would give the desired fulvene. This route was never carried beyond the alcohol step.

The work of Huntsman⁹⁸ offered an appealing alternative synthesis of **108E** and **108Z**, though we never tried this approach.

Scheme XX. Proposed route to **108** and **168** based on allene thermolysis.

Conversion of alcohol **165** to its acetate,⁹⁹ followed by conjugate addition^{99,100} of allylcuprate would give **167**, whose pyrolysis⁹⁸ should give the desired **108E&Z** as well as the nonconjugated isomer (**168**).

Isolation of photoproducts from triplet sensitized decomposition of azoalkane **123**.

Since all attempts to synthesize **108E&Z** were without success, we isolated the triplet sensitized photoproducts of **123** in the following manner. A 100 mg sample of pure **123** (from the Diels-Alder route) in pentane was subjected to room temperature xanthone¹⁰¹ sensitized photolysis. The resultant photoproducts were separated and isolated by preparative GC. The isolated compounds were analyzed by GC/MS, proton, and carbon NMR. The isomeric dienes, **108E&Z**, were distinguished by high field NOE. The spectral data can be found in the experimental section.

Each photoproduct collected also contained some impurity, most likely from thermal rearrangement of the photoproducts on the GC injector or column. Other samples of **123** photolyzed in the same way and analyzed directly by

NMR and GC did not give these impurities. Compounds **169**, **170** and **120** were

prepared independently and were identified by comparison of their NMR spectra and GC retention times with the samples obtained by preparative GC from **123**. Compounds **169** and **170** were obtained from reaction of sodium cyclopentadienide with n-propylbromide, and compound **120** was prepared from pyrolysis of alcohol **178a** over alumina (cf. Scheme XXVI. "Authentic synthesis of photoproducts from **113a,b**").

A small amount of **107** may have thermolyzed on the hot metal GC injector to produce biradical **104**, which could have undergone a 1,2-hydrogen shift to **120**. Likewise, **169** and **170** could have originated from rearrangement of **108** on the GC injector or column. GC columns made with Chromosorb P solid support, such as the one used in the isolation of **108E&Z**, have been reported to cause such isomerizations.⁹⁸

The "mystery product" from photolysis of azoalkane **123**.

Because there remained one last unidentified GC peak that accounted for 2-8% of the photoproducts of **123**, we undertook the independent synthesis of hydrocarbons suspected to be the "mystery product". The following compounds were deemed likely candidates.

Figure 7. Possible structures of the "mystery product" from **123**.

Compound **160** could be the result of a 1,2-H shift from **104**.

Olefin **171** would be the result of a 1,4-hydrogen shift involving the cyclopropyl methine of **104**.

Hydrocarbon **172** would result if cyclopentane ring scission of **104** were to occur.

This reaction, while very common for conformationally flexible 1,4-cyclohexanediyls,^{45,51,62} is not known in the more rigid 1,3-cyclopentanediyli series.²⁰

The required sigma bond-p/orbital overlap for such a reaction is easily achieved by unconstrained 1,4-cyclohexanediyls through a chair conformation. The more rigid cyclopentanediyli, in a sense still 1,4-biradicals, cannot achieve the required chair conformation and do not usually undergo scission.²⁰

GC retention times of the compounds in figure 7 differed from that of the mystery peak showing that none of the authentically prepared materials was the mystery product. We later discovered that the mystery product came from an impurity in **123** prepared by the Diels-Alder route. These synthetic efforts were not wasted; however, because we learned that none of compounds in figure 7 had the same GC retention time as **107** or **108**, and that the synthesized

compounds comprised less than 0.5% of photoproducts from **123**. Described below are syntheses of the suspected C₈ hydrocarbons.

Synthesis of candidates for the "mystery product" in figure 7.

Scheme XXI. Synthesis of **160** and **175**

Ketone **173** was prepared by the conjugate addition¹⁰² of $\text{Li}_2(\text{c-C}_3\text{H}_5)_2\text{CuCN}$ to 2-cyclopentenone. Conversion of **173** to the tosylhydrazone followed by Shapiro^{86,103} reaction gave olefins **160** and **175**. Authentic **171**¹⁰⁴ was prepared by the Wittig reaction of cyclopentanone and cyclopropyltriphenylphosphonium bromide.

Synthesis of **172** began with the coupling of cyclopropyl cyanide and allyl bromide to give ketone **176**.¹⁰⁵

Scheme XXII. Synthesis of hydrocarbon 172.

Conversion to 172 was accomplished in two steps using an organocerium modification of the Petersen olefination.¹⁰⁶ Elimination of TMSOH with HF caused a certain amount of olefin isomerization so that the desired diene had to be isolated by preparative GC.

Synthesis of azoalkanes 113a and 113b

No cyclopropylcarbinyl cation rearrangement was observed in the synthesis of the acyclic azoalkanes 113a and 113b.

Scheme XXIII. Synthesis of azoalkanes 113a,b.

Treatment of **178a,b** with CF_3COOH and NaN_3 ¹⁰⁷ gave a single azide with the cyclopropyl ring intact. The azides were reduced with excess LAH ¹⁰⁸ and the amines coupled with IF_5 ,¹⁰⁹ giving the desired azoalkanes after column chromatography.

Synthesis of allylic radical dimers **181**

Hydrocarbon **181** and its various isomers were required to verify their absence among the photolysis products of **113a**.

There are twelve possible regio- and stereo-isomers resulting from the various recombinations of allylic radical **116a**; these were obtained by sonication¹¹⁰ of chloride **184** and Li sand (2% Na) in THF.

Scheme XXIV. Synthesis of authentic dimers of allylic radical **181a**.

Chloride **184** was obtained in two steps from trisylhydrazone **182** by treatment with 2.2 equivalents of n -butyllithium and propionaldehyde.⁸⁶ The resulting

alcohol, **183**, was converted to the chloride using triphenylphosphine and CCl_4 .¹¹¹

Synthesis of (1-bromopropylidene)-3-cyclopentane (**185**)

Homoallylic bromide **185** was required to study the cyclization of radical **115a** $\rightarrow$ **114a**.

This synthesis was carried out in one step from **178a**, which was already in hand.

Reaction with 2 equivalents CF_3COOH and NaBr produced the desired bromide in 80% yield after column chromatography. Rearrangement during synthesis of **185** contrasts with the preparation of azides **179a,b** (Scheme XXIV). Diffusion controlled reaction of azide¹¹² must allow attack on the cyclopropylcarbinyll carbonium ion faster than ring opening. Reaction of bromide is apparently considerably slower, and the cyclopropylcarbinyll cation has time to open prior to nucleophilic attack.

Synthesis of (1-bromo-1,1-²H-propylidene)-3-cyclopentane (190)

The dideuterated homoallylic bromide **190** was required for further study of the cyclization **115a**→**114a**. The compound was prepared in four steps starting from conjugated ester **186**.

Scheme XXV. Synthesis of ²H labeled bromide **190**.

Photochemical deconjugation¹¹³ was accomplished by irradiation with 254 nm light. The reaction goes to completion because product **187** does not absorb 254 nm light. The required deuterium labels were introduced by reduction of **187** with excess LiAlD_4 . Conversion to **190** was carried out in two steps¹¹⁴ via $\text{S}_{\text{N}}2$ displacement¹¹⁵ on tosylate **189**.

Authentic synthesis of photoproducts from decomposition of azoalkanes **113a** and **113b**.

Irradiation of degassed solutions of **113a** or **113b**, thiophenol and decane (internal standard) in fluorobenzene gave four new GC peaks. These peaks were identified by GC/MS as C_8 - or C_9 hydrocarbons, respectively. All products, except **118a**, were synthesized independently and were identified by coinjection on a capillary GC column.

Scheme XXVI. Authentic synthesis of photoproducts from 113a,b.

Compound **118a** was isolated by preparative GC from the photolysis of **113a** with PhSH at -78 °C. Compound **118b** was synthesized from vinylcyclohexane (**191b**) using a modification of the Simmons-Smith reaction.¹¹⁶ Propylidenecycloalkanes **119a** and **119b** were prepared via the Wittig reaction^{104b,117} starting with the appropriate cycloalkanone and n-propyltriphenylphosphonium bromide. Cyclopropyl alkenes **120a** and **120b** were synthesized by pyrolysis of alcohols **178a** and **178b**, respectively, while

alkenes **117a** and **117b** were obtained by pyrolysis of **192a** and **192b**, respectively.

Partial synthesis of azoalkane **200**.

Azoalkane **200**, the dimethylated analog of **123**, was required to probe the effects of the gem-dimethyl group on the lifetime of cyclopentanediyls using the FRC method.

Scheme XXVII. Synthesis of azoalkane **200**.

Scheme XXVII, cont.

The synthesis of **196**, as shown in Scheme XXVII, has been described briefly in the literature.¹¹⁸ This hindered ketone was unreactive to cyclopropyllithium in ether between -78 °C and room temperature. When the alkyllithium reagent was prepared with ultrasound¹¹⁹ (from Li sand and cyclopropyl bromide) in the presence of **196**, alcohol **197** was obtained pure and in 92% yield.

Preliminary experiments on the pyrolysis of **197** over alumina suggest that diene **198** can be obtained easily by this method. It would be most convenient if diethylazodicarboxylate (DEAD) could be used in the Diels-Alder reaction with **198**. Conversion of DEAD to its cis isomer by irradiation with visible UV light may speed up the reaction. If use of DEAD should fail, however, surely reaction with **MTAD** will afford a tricyclic urazole (analogous to **126** in Scheme XI) which can be transformed to azoalkane **200** by the standard methods.^{73b}

Monoradicals

Studies of monoradicals 114a&b.

Monoradicals **114a** and **114b** were required to study the CPC rearrangement rate of the analogous biradicals (**104T**, **97T**, **102T**). By providing some reaction pathway of known rate which competes with the CPC rearrangement, one can use product ratios to determine k_{rf} . In this instance, the competing reaction is scavenging of radicals **114a** and **114b** with a thiol. Scheme XXVIII shows the products expected from decomposition of azoalkanes **113a** and **113b** in the presence of a radical scavenger, and the relationship between product ratios and the various rate constants.

Scheme XXVIII. Products expected from azoalkanes **113a,b**.

$$(118/119) = k_{ta}[\text{PhSH}] / k_{rf}$$

(33)

The CPC rearrangement of monoradicals **114a&b** was initially studied using 2,2-dimethyl propanethiol (t-butylthiol) as the radical scavenger,¹²⁰ but the overall hydrocarbon product balance was low, and several unidentified products complicated the kinetic analysis. Reactions of carbon radicals with PhSH have been studied in greater detail than reactions with t-butyl thiol.¹²⁰ Since our kinetic analysis was already complicated by the presence of unknown products, we began experimentation with PhSH in the photolysis of azoalkanes **113a,b**.

The use of PhSH as the radical scavenger offers several advantages over t-butylthiol. Trapping rate constants, k_{ta} , were determined by Franz¹²¹ using KAS, and were found to be insensitive to the nature of the carbon radical. Furthermore, the phenylthiyl radical is much less reactive than the t-butylthiyl radical¹²² and reaction mixtures obtained from decomposition of azoalkanes **113a&b** in the presence of PhSH did not suffer from low yields of hydrocarbon products or the presence of unidentified compounds. These features simplified the kinetic analysis.

The solvent chosen to study the desired CPC rearrangements was fluorobenzene because it possess a low freezing point ($-41.2\text{ }^{\circ}\text{C}$)^{123a} relative to benzene ($-5\text{ }^{\circ}\text{C}$) and this property facilitated the degassing of samples for photolysis. Radical additions to fluorobenzene are known;^{123b} however, trapping by thiophenol was efficient enough to suppress such reactions in our systems.

All azoalkane decompositions, unless otherwise noted, were carried out on degassed, sealed samples in pyrex vessels. The hydrocarbon products

were analyzed using decane as an internal standard, and at least three GC injections on each sample in order to ensure reproducibility of results.

Identification of photoproducts from decomposition of 113a and 113b.

Irradiation of degassed solutions of **113a** or **113b**, thiophenol and decane (internal standard) in fluorobenzene gave four new GC peaks. These peaks were identified by GC/MS as C₈ or C₉ hydrocarbon products, respectively. All products except **118a** were synthesized independently and were identified by coinjection on a capillary DB-5 column (*vide infra*).

Results from the photochemical decomposition of 113a and 113b.

The absolute yield of hydrocarbons at various PhSH concentrations and temperatures was determined by GC. The results are summarized in Tables I-III.

Table I. Product Yields (%)^a from Photolysis of **113a** (0.0187 M) at 24.7 °C.

[PhSH] _i ^{b,c}	[PhSH] _{ef} ^{b,d}	120a ^e	118a ^f	119a ^g	117a ^h	T/R ⁱ	Bal. ^j
0.032	0.018	39.14	23.15	37.09	0.62	0.42	87.8
0.040	0.025	40.50	19.61	39.21	0.69	0.52	89.2
0.059	0.045	46.18	22.91	30.35	0.56	0.75	89.1
0.130	0.115	55.80	19.93	23.90	0.38	1.48	89.3
0.234	0.219	62.36	19.88	17.43	0.33	2.39	88.4
0.294	0.279	65.05	20.98	13.81	0.16	3.16	89.9

^a. Errors in GC peak area measurements were propagated to obtain the standard deviation in the yields, which are given in footnotes as the average for each product at all six thiophenol concentrations. ^b. concentration in mol/L. ^c. initial. ^d. effective; see text. ^e. ± 0.19 . ^f. ± 0.04 . ^g. ± 0.09 . ^h. ± 0.02 . ⁱ. trapped **114a**/rearranged **114a**; see text. The first entry is ± 0.02 ; all others are ± 0.01 . ^j. total yield of hydrocarbons.

Table II. Product Yields (%)^a from Photolysis of **113a** (0.0103 M) at 58.5 °C.

[PhSH] _i ^a	[PhSH] _{ef} ^a	120a ^b	118a ^c	119a ^d	117a ^e	T/R ^a	Bal. ^{a,f}
0.039	0.030	26.75	12.03	57.74	3.48	0.24 ± .03	78.0
0.045	0.036	29.62	14.01	52.76	3.60	0.28 ± .01	82.3
0.068	0.059	32.30	14.84	49.33	3.54	0.33 ± .04	85.4
0.144	0.135	41.94	14.35	40.94	2.78	0.63 ± .07	77.9
0.227	0.218	49.20	14.86	34.17	1.77	0.96 ± .10	82.5
0.325	0.316	55.46	12.88	29.67	1.99	1.35 ± .12	81.4

a. See footnotes to Table I. b. ± 0.76. c. ± 0.32. d. ± 0.94. e. ± 0.26. f. ± 0.88.

Table III. Product Yields (%)^a from Photolysis of **113b** (0.0142 M) at 25.0 °C.

[PhSH] _i ^a	[PhSH] _{ef} ^a	118b ^b	120b ^c	119b ^d	117b ^e	T/R ^a	Bal. ^f
0.039	0.027	36.68	17.08	45.98	0.26	0.42 ± .01	85.7
0.045	0.032	41.21	17.08	41.48	0.23	0.58 ± .02	83.3
0.068	0.056	47.71	17.61	34.53	0.15	0.87 ± .02	79.2
0.118	0.106	56.76	17.73	25.41	0.09	1.53 ± .03	81.5
0.202	0.190	64.94	17.60	17.37	0.10	2.71 ± .10	83.6
0.313	0.301	69.28	17.84	12.82	0.07	3.99 ± .17	81.7

a. See footnotes to Table I. b. ± 0.42. c. ± 0.11. d. ± 0.28. e. ± 0.01. f. Total yield of hydrocarbons; ± 0.88.

The quantity (T/R), which represents the ratio of trapped to rearranged products of **113a,b**, increases at higher [PhSH] and at lower temperature, in accord with expectation. The method used to calculate (T/R) and [PhSH]_{ef} will be described after the photolysis mechanism of **113a** is considered (cf. Scheme XXIX).

Scheme XXIX. Formation of products from azoalkanes **113a&b**.

As usual for acyclic azoalkanes, deazotation produces a pair of caged radicals which either disproportionates (k_{dis}) to give **120a** and **118a**, or escapes (k_e) from the solvent cage¹²⁴ to produce free **114a**. Radicals **114a** may be trapped by thiophenol to afford **118a** or they may rearrange to **115a**, which are also trapped by the thiol. CPC rearrangement within the solvent cage ($k \sim 10^7 \text{ s}^{-1}$) is much slower than escape ($k \sim 10^{10} \text{ s}^{-1}$), so cage disproportionation between **114a** and **115a** is negligible. Recombination of **114a** is also neglected because 1) tertiary radicals disproportionate much more than they recombine,¹²⁵ 2) recombination dimer constituted only 2% of

the product in the case of tricyclopropylmethyl radicals,⁶⁶ 3) recombination and disproportionation outside the solvent cage should be completely inhibited by thiophenol, 4) the cage effect should be less than 60%, judging by comparison with azo-*tert*-butane.¹²⁶

Although **117a** forms in low yield, its presence in the photolysate of **113a** was surprising. Two mechanisms of formation were considered plausible: 1) 1,5-hydrogen shift of homoallylic radical **115a** to allylic radical **116a**, which was trapped by thiophenol (eq 34). 2) isomerization of **119a** through allylic hydrogen transfer to phenylthiyl radical (eq 35).

The 1,5-hydrogen shift is important because it could also occur in BRs **105E&Z**. This reaction would go through a favorable cyclic, six-membered transition state and would form the thermodynamically stable allylic radical **116a**.

A rate constant of $8 \times 10^4 \text{ s}^{-1}$ at 25°C was reported for the similar rearrangement of **201** to **202** (eq 36),⁹ but the value has been revised upward to $2.8 \times 10^6 \text{ s}^{-1}$.¹²⁸ It is known that in order for 1,5-hydrogen shifts to be favorable, coplanarity of the abstracted H atom, the pi orbital of the double bond, and the abstracting carbon radical is required.¹³⁰ Models show that only a small amount strain is introduced into the transition state for the hydrogen shift in **201** which benefits from stabilization of **202** by the adjacent sulfur atom. Although radical **203** lacks the substituent advantage in **201**, there are no geometric constraints for reaction and **203** rearranges to **204** (eq 37) with a rate of 500 s^{-1} .¹²⁹ In radical **115a** however, the abstractable hydrogens are tied back away from the reactive radical center through incorporation into the 5-membered ring. The lack of a substituent or geometric advantage in **115a** should slow the 1,5 hydrogen shift considerably. Based on these analogies, and on a value of $k_{1a} = 1.47 \times 10^8 \text{ M}^{-1}\text{s}^{-1}$, we estimate that between 0.4% and 14% of **115a** will undergo the 1,5-hydrogen shift (k_{15}) if eq 34 is correct.

We devised an experiment to test the 1,5-hydrogen shift of **115a** by photolysing **113a** without added thiophenol. In the absence of scavenger, $k_{1,5}$ should become more important since **114a** would go largely to **115a** and on to **116a**. Allylic radical recombination products (from **116a**) should be produced

in the absence of scavenger because the activation energy for recombination of allylic radicals is very low ($E_a=2.76$ kcal/mol, $\log A=11.2$),¹³¹ and because they recombine rather than disproportionate.¹²⁵ Almost no GC peaks attributable to dimers of **116a** were detected, and their absence was demonstrated conclusively by authentic synthesis (scheme XXIV).

Another critical test of the 1,5-hydrogen shift was carried out by thermolyzing a sample of **113a** in dodecane at 151 °C without added thiophenol. In the absence of scavenger, and at the higher temperature, the CPC rearrangement and 1,5-hydrogen shift should be favored and should produce allylic radical recombination products of **116a**. No GC peaks were found in the C₁₆ dimer region again, by comparison with the authentic compounds. Since these products were absent under conditions that favored their formation, surely they were not formed from photolysis of **113a** in the presence of thiophenol.

With the demise of eq 34, our attention turned to the second hypothesis: allylic hydrogen abstraction from **119a** (eq 35). Although methylthiyl radicals abstract hydrogen from cyclopentene,¹³² phenylthiyl radicals exhibit a rate constant less than 50 M⁻¹s⁻¹ for hydrogen abstraction from cumene.¹³³ Synthetic chemists, who use phenylthiyl radicals for geometric isomerization of olefins through an addition-elimination mechanism, have not concerned themselves with allylic hydrogen abstraction.¹³⁴ Even though these facts argue against the allylic hydrogen abstraction mechanism, we designed experiments to test eq 35 because we had already ruled out the 1,5-hydrogen shift (eq 34).

A pure sample of **119a**, isolated by preparative GC, was exposed to phenylthiyl radicals generated by irradiation of diphenyldisulfide in benzene at 366 nm. The formation of 1% **117a** and 99% **119a** (absolute yields)

suggested that phenylthiyl radicals are capable of abstracting allylic hydrogen from **119**. Such a positional isomerization,¹³⁵ though not very efficient, is favored thermodynamically by the 3 kcal/mol lower heat of formation of an endocyclic than an exocyclic double bond in a five membered ring.

With a reasonably secure mechanism in hand for all photolysis products, we may proceed to the calculation of T/R. It is first necessary to realize that trapping of **114a** is not the only pathway to **118a** since disproportionation creates one molecule of **118a** for every molecule of **120a**. The amount of **118a** formed by trapping of **114a** with thiophenol must be corrected by subtracting the yield of **120a**. Since **117a** is a secondary product from **115a**, these two compounds must be taken together in calculating T/R. We therefore obtain the ratio of trapped to rearranged products as $T/R = [(118a) - (120a)]/[(119a) + (117a)]$.

The effective thiol concentration, $[PhSH]_{ef}$, is lower than that used initially because some of it is consumed by the radicals generated. However, only a fraction of the decomposed azoalkane produces the expected free radicals on account of the cage effect (CE). The numerical value of CE is given by $k_{dis}/(k_{dis} + k_e)$ where k_{dis} and k_e are as shown in Scheme XXIX; moreover, the value of CE can be calculated from our experimental data (Tables I - III) by $CE = 2(120a)/[(120a) + (119a) + (118a) + (117a)]$. The cage effects (42%, 28%, and 35% respectively) are not only in a reasonable range but they show the expected decrease at higher temperature for **113a**.^{124,126} We define the effective thiol concentration as the average of its initial and final concentrations, so that $[PhSH]_{ef} = [PhSH]_i - \{[113a](1 - CE)\}$. Our estimate of $[PhSH]_{ef}$ is subject to some uncertainty because thiophenol is depleted to a greater extent at lower ratios of thiol/azoalkane than at higher ones. The use of low

thiol/azoalkane ratios was required in order to obtain sufficient quantities of rearrangement product to quantify accurately.

One could overcome the difficulty of estimating $[\text{PhSH}]_{\text{ef}}$ by quantifying the products at low conversions of **113**. If azoalkane were depleted by no more than 10%, $[\text{PhSH}]$ would remain essentially constant and the reaction could be treated as pseudo-first order. Unfortunately, analysis of the hydrocarbons obtained by this method would be subject to large error since unreacted azoalkane would also decompose to the same products upon GC injection. Furthermore, the large molecular weight of **113a&b** makes their quantitation by GC difficult because the azoalkane GC peaks are broad and hard to integrate accurately. For these reasons, all product quantitation runs on azoalkanes **113a&b** were carried out to complete conversion.

In hopes of avoiding the difficulty of estimating $[\text{PhSH}]_{\text{ef}}$, we attempted to derive an integrated rate expression for the relationship between T/R and $[\text{PhSH}]$. The complexity of the kinetics ultimately led us to computer simulation of Scheme XXIX where concentration versus time profiles of all reagents, intermediates, and products could be obtained based on a set of input differential equations, initial concentrations and rate constants. The details of the computer program, "Simula2" can be found in appendix 1. All rate constants except k_{rf} were known and held constant, while k_{rf} was varied until the simulated (T/R) matched our experimentally observed value (see the next section on CPC rearrangement of **114a,b** for experimental values of k_{rf}). The results of this simulation are given in Table IV.

Table IV. Computer simulation of Scheme XXIX used to compare observed and calculated values of (T/R) and k_{rf} (compare to data in Table I).

Rate constants as defined in Scheme XXIX and used in simulation.

$$k_i = 1 \text{ s}^{-1}$$

$$k_e = 1 \times 10^{10} \text{ s}^{-1}$$

$$k_{rr} = 5.5 \times 10^4 \text{ s}^{-1}$$

$$k_{ta} = 1.5 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$$

$$k_{dis} = 7.2 \times 10^9 \text{ s}^{-1}$$

[PhSH] _i ^a	10 ⁻⁶ k_{rf} , s ⁻¹	(T/R) ^{b,c}
0.032	7.0	0.45
0.032	8.0	0.39
0.032	7.5	0.42
0.040	7.5	0.58
0.040	8.5	0.51
0.059	10.0	0.72
0.059	9.7	0.74
0.130	10.0	1.79
0.130	12.0	1.49
0.234	15.0	2.23
0.234	14.0	2.39
0.294	14.0	3.04
0.294	14.5	3.15

^a M. ^b as defined in text. ^c Boldface indicates value of k_{rf} (for CPC rearrangement of **114a**) which best reproduces the experimentally observed (T/R) in Table I.

This computer simulation suggests that our estimate of [PhSH]_{ef} is in error only for the kinetic runs with low PhSH/azoalkane ratios. The result is a value of T/R which is too high because of the [PhSH] at the beginning of the reaction leads to more trapped than rearranged products. We feel, however, that the good agreement of the k_{rf} from the three runs at higher PhSH/azoalkane with our $k_{rf}=1.45 \times 10^7 \text{ s}^{-1}$ that is based on [PhSH]_{ef} (refer to CPC rearrangement of **114a,b** below) justifies the use of [PhSH]_{ef}.

CPC rearrangement rate of 114a,b

In our earlier use of the FRC technique to determine τ of biradicals **97T** and **102T**, their CPC rearrangement rate (k_{rr}) was estimated⁵¹ to be

$2.2 \times 10^7 \text{ s}^{-1}$ at 25°C based on the $2.0 \times 10^8 \text{ s}^{-1}$ value for unsubstituted CPC radical (the parent system)³ and the 8.9 fold decrease in the rate of cyclobutylcarbinyl rearrangement caused by α -dimethylation.¹³⁶ Since k_{rr} of the parent system has been revised to $9.4 \times 10^7 \text{ s}^{-1}$,⁵ this approach now predicts k_{rr} for **97T** to be $1.1 \times 10^7 \text{ s}^{-1}$. The present study allows us to evaluate k_{rr} more directly, thus lending greater credibility to the lifetime determination of **97T** and **102T**.

By inspection of Scheme XXIX, it is apparent that k_{rr} is related to T/R as shown in eq 38.

$$T/R = k_{ta}[\text{PhSH}]_{\text{ef}}/k_{rr} + k_{rr}/k_{rr} \quad (38)$$

A plot of (T/R) versus $[\text{PhSH}]_{\text{ef}}$ from Tables I and II turned out to be linear ($r = 0.9986$ and 0.9995) with a slope of 10.15 and 3.867 respectively. From the thiophenol trapping rate constant of $1.47 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$,¹²¹ the value of k_{rr} for **114a** at 24.7°C was calculated to be $1.45 \times 10^7 \text{ s}^{-1}$. Similar treatment of the

data for **114b** (Table III) also gave a linear plot ($r = 0.9991$) with a slope of 13.03, corresponding to $k_{rf} = 1.13 \times 10^7 \text{ s}^{-1}$.

Figure 8. Graph of T/R versus $[\text{PhSH}]_{\text{ef}}$ according to eq 38. A.) From data in Table II. B.) From data in Table I. C.) From data in Table III.

Thus k_{rf} of **114b** is close to our original estimate⁵¹ of $1.1 \times 10^7 \text{ s}^{-1}$ and to the value of $7.4 \times 10^6 \text{ s}^{-1}$ measured for α,α -dimethylcyclopropylcarbonyl (eq 9).¹³⁶ The CPC rearrangement of the five membered system **114a** is 1.4 times faster than its six-membered homolog, suggesting that conformational factors come into play.^{137,138}

Reversibility of the CPC rearrangement in monoradical **114a**

The non-zero y-intercepts in Figure 8 are worthy of mention. According to eq 38, the y-intercepts represent the inverse of the equilibrium constant ($K_{\text{eq}} = k_{rf}/k_{rr}$) for **114a,b**→**115a,b**. Our data (from Table I) suggest that $K_{\text{eq}} = 4.30$, and $k_{rr} = 3 \times 10^6 \text{ s}^{-1}$, an unusually large value for ring closure to a

CPC radical at ambient temperature. Small variations in the slope of eq 38 can lead to large changes in the y-intercept, and since our y-intercept data are subject not only to random errors, but also to the error in estimation of $[\text{PhSH}]_{\text{ef}}$, we chose a better method to evaluate k_{rr} . The value of k_{rr} is important for our biradical studies to be described later; moreover, the ring closure rates of only two homoallylic radicals are known: 3-butenyl¹³ and 2,2-dimethyl-3-butenyl (27).^{14,137} Attempts were made to estimate k_{rr} by trapping **114a** in the free radical chain decomposition of bromide **185** according to Scheme XXX.

Scheme XXX. Expected products from free radical decomposition of **185**.

The following product distribution was obtained: 97.5% **119a**, 1.7% **117a**, 0.70% **120a**, and 0.07% **118a** with an overall product balance of 90%. The low yield of **118a** and the presence of unusual products such as **117a**, and **120a** prompted us to abandon this approach and to study reclosure of **115a** to **114a** with the same technique as for the parent system, namely, reaction of dideuterio homoallylic bromide **190** with tributyltin hydride. Products **208** and

209, which were monitored by ^2H NMR, were formed as shown in Scheme XXXI.

Scheme XXXI. Formation of ^2H scrambled products from radical **205**.

Since isotope effects are neglected, there are only four rate constants to be considered: k_i , k_{tC1} , k_{rr} , and k_{rf} . The value of k_{rr} can be determined by computer simulation with only one adjustable parameter because k_{tC1} ($2.4 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$)¹³⁹ and k_{rf} ($1.45 \times 10^7 \text{ s}^{-1}$) are known and because the product ratio **208**:**209** is independent of k_i . Using 0.0533 M Bu_3SnH and 0.0404 M **190** in benzene, we observed **208**:**209** = 3.62. This figure could be reproduced with $k_{rr} = 5.5 \times 10^4 \text{ s}^{-1}$, but a 20% uncertainty in the product ratio translates into a 50% error in

k_{rr} . Our value of k_{rr} is 7 times faster than closure of the parent homoallyl radical but 100 times slower than the 2,2-dimethyl-3-butenyl radical, which benefits greatly from the Thorpe-Ingold effect.¹⁴ Alkyl substitution on the vinyl terminus of the homoallyl radical accelerates closure by a larger factor than in the 5-hexenyl to cyclopentylcarbonyl radical case. Rate constants (s^{-1} , 25 °C) for these cyclizations are summarized immediately below.¹⁴⁰

Figure 9. Rate constants of various radical ring closure reactions at 25 °C.

The equilibrium constant (K_e) at 25 °C for opening of **114a** to **115a** can be calculated from our data to be $1.45 \times 10^7 s^{-1} / 5.5 \times 10^4 s^{-1} = 260$. This value is 46 times smaller than that of the parent CPC radical ($K_e = 9.4 \times 10^7 s^{-1} / 8.0 \times 10^3 s^{-1} = 1.2 \times 10^4$), most likely because the tertiary radical center in **114a** is of lower energy than the primary center in 3-butenyl. We are aware of only one other CPC rearrangement whose equilibrium constant is known.¹⁴

Biradical Studies

Photolysis of 123

Armed with experimental values of k_{rf} and k_{rr} for **114a**, we may now examine the more complex case of biradicals arising from bicyclic azoalkane **123**. This compound is an ideal photochemical source of triplet biradicals because its UV spectrum ($\lambda_{max} = 346$ nm) exhibits a sharp cutoff that allows selective irradiation of triplet sensitizers, because its large excited state singlet-triplet energy gap ensures that those sensitizers will populate the azoalkane triplet state, and because the latter decomposes with high efficiency.¹⁴¹ Direct irradiation of **123** at 313 nm in

Figure 10. Product distributions from direct and sensitized decomposition of **123**.

pentane afforded 99.6% **107** and 0.4% **108Z** while triplet sensitized decomposition (Michler's ketone, 366 nm in fluorobenzene) gave 70% **107** and 30% **108E,Z**. The azoalkane excited singlet state decomposes to nitrogen and **104S** before it undergoes intersystem crossing (ISC) to triplet **123**.

Direct irradiation of **123** Triplet sensitized decomposition of **123** Figure 11. Photochemical steps in decomposition of **123**.

Triplet sensitization of **123** populates the azoalkane triplet state which also loses nitrogen but gives only **104T**. Since closure of **104T** to **107** is spin forbidden, CPC rearrangement diverts a fraction of **104T** to homoallyl radical **105Z** which undergoes ISC and intramolecular disproportionation to yield **108Z**. This change in product distribution is a classic example of the spin correlation effect.^{27,51}

Because singlet biradicals can proceed directly to product without the need for spin inversion, it is no surprise that closure of **104S** to **107** dominates over CPC rearrangement. However, the presence of 0.4% **108Z** from direct irradiation of **123** suggests either that a) **104S** was intercepted by the CPC rearrangement, b) a small fraction of **104S** underwent ISC to **104T**, or c) a

small fraction of singlet **123** underwent ISC to triplet azoalkane before loss of nitrogen. The last possibility was favored by Buchwalter and Closs, who observed **40T** by ESR upon direct irradiation of **DBH** at low temperatures.⁴⁴

The unexpected formation of **108E** in the sensitized photolysis of **123** was shown to be a secondary process, namely, sensitized isomerization of **108Z**. At conversions of **123** up to 50%, NMR analysis revealed only **108Z**. Since dienes are known to be good triplet quenchers, **108Z** is better able to compete with **123** for sensitizer triplets later in the reaction. The ratio of the products was found to be constant at conversions from 20 to 100% when **108Z** and **108E** were considered together. Finally, the product balance was at least 94%, leaving little room for other reactions.

Benzene sensitized decomposition of 123.

Fluorescence quenching studies show that energy transfer from the singlet state of excited hydrocarbons leads to azoalkane decomposition.¹⁴³ The energy transfer properties of excited benzene were studied using **123** as a mechanistic probe. The UV spectrum of **123** has a window at 254 nm, allowing selective irradiation of benzene ($E_T=84.3$ kcal/mol, $E_S=113$ kcal/mol).¹⁴² Because **123** absorbs no light at 254 nm, any azoalkane decomposition must be the result of energy transfer from excited benzene molecules. We have already demonstrated that **108E&Z** arise from the azoalkane triplet excited state, while **107** is derived from the singlet excited state. Thus, the product distribution from photolysis of benzene in the presence of **123** should reveal the degree to which benzene acts as a triplet sensitizer.

A degassed pentane solution 1.05×10^{-3} M in **123** and 5.80×10^{-2} M in benzene was irradiated at 254 nm (ambient temperature). The products

consisted of 43% **107**, 12% **108**, and 31% unidentified hydrocarbons. (Based on the similarity in GC retention times of **107** or **108** and the unidentified peaks, we assume that the unidentified products are also C₈.) A similar experiment using 3.50×10^{-3} M **123** and 6.13×10^{-2} M benzene gave 59% **107**, 22% **108**, and 20% of the same unidentified hydrocarbons as in the previous experiment. In both cases, the unidentified products had to be included to obtain a material balance over 90%. Since unreacted azoalkane makes up the remainder of the product balance, we may conclude that high molecular weight products are negligible. The ratio of **107:108** in these experiments was 3.59 and 2.76, respectively; while the ratio under conditions of triplet sensitized (Michler's ketone) decomposition of **123** was 2.34. The presence of **108** in the benzene sensitized experiments indicates that triplet energy transfer from benzene to **123** contributes to azoalkane decomposition, but the larger ratios of **107:108** compared to triplet sensitized decomposition suggest that the singlet excited state of benzene also transfers energy to **123**.

It is unclear why there is less **108** present at the lower initial [**123**], since one may imagine that at lower concentrations of quencher (**123**), benzene singlets would undergo more singlet-triplet ISC before collision with azoalkane. Since not all of the photoproducts from the benzene sensitized experiments are identified, it is impossible to advance a satisfactory explanation for this trend. A control experiment is needed to check the stability of the hydrocarbons under the reaction conditions.

The quantum yield (Φ) for azoalkane disappearance in the benzene experiment with 3.50×10^{-3} M **123** was determined to be 0.40 using potassium ferrioxalate actinometry. Pertinent data can be found in the experimental section. The benzene sensitized quantum yield for decomposition of **123** is

considerably lower than $\Phi=0.77^{143c}$ for triplet sensitized decomposition of **DBH** with Michler's ketone, and $\Phi=0.73$ for singlet sensitized decomposition with triphenylene ($E_S=83.5$ kcal/mol, $E_T=66.6$ kcal/mol).^{143c}

Thermolysis of **123**

When identical solutions of **123** and **DBH** were thermolyzed in the same oil bath at 161.6 °C, the substituted azoalkane decomposed 2.97 times faster. This figure is somewhat smaller than the 4.27 fold rate enhancement found in the diazabicyclooctyl (**DBO**) system at 230 °C.¹⁴⁴ GC analysis of **123** thermolyzed at 143 °C in 1:1 C_6D_6 -toluene- d_8 showed 98% **107**, 0.06% **108**, and a few minor, unidentified peaks. Since the yield of **108** was about 7 times lower than in direct photolysis (vide supra), it is unlikely that **104S** is intercepted by the CPC rearrangement because the perceptible activation energy for this process predicts *more* **108** at higher temperature. We are assuming that **104S** has the same geometry whether produced thermally or photochemically.

Mechanism of product formation from **104T**

Since **104T** is unsymmetrical, there are two different 1,6-biradicals that might form: **105E** and **105Z**.

The latter possesses a favorable geometry for intramolecular 1,5-hydrogen shift, a reaction that should be exothermic by 63 kcal/mol. The fact that **105Z** can give a conjugated diene through a six membered transition state should accelerate this hydrogen shift considerably relative to the analogous reaction of six-membered homolog **98**, which proceeds with a rate constant of $2.8 \times 10^6 \text{ s}^{-1}$.^{51,145}

Biradical **105E** presents a much greater problem since none of its readily imagined reaction pathways (Scheme XXXII) affords a stable product in one step. Moreover, we observe no product for which **105E** is clearly the

Scheme XXXII. Hypothetical reaction pathways of **105E**.

only precursor. It follows that either **105E** is not formed from **104T** or that one or more of the pathways in Scheme XXXII converts **105E** to **107** or **108Z**.

Path c, the 1,5-hydrogen transfer, is ruled out because it did not occur in monoradical **114a** even under optimum conditions (*vide supra*). We have probed the other pathways by adding a radical scavenger, 1,4-cyclohexadiene (CHD), to the triplet sensitized decomposition of **123**. CHD was chosen because it does not interfere with triplet energy transfer from Michler's ketone to **123** and because the trapping rate constants of carbon centered radicals with this scavenger are known.^{146,147} Table V shows the product yields and ratios obtained from **123** with increasing CHD concentration.

Table V. Product Yields (%) from Triplet Sensitized Photolysis of **123** at 24.7 °C with added CHD.

[CHD] ^a	1/[CHD] ^b	119a ^c	107 ^d	108 ^e	107/108	108/119 ^f	Bal. ^g
0.208	4.80	3.70	67.42	28.88	2.33 ± .02	7.82	98.2
0.411	2.43	5.66	66.06	28.28	2.34 ± .01	5.00	100
0.614	1.63	7.60	64.82	27.58	2.35 ± .06	3.63	100
0.815	1.23	8.86	63.99	27.15	2.36 ± .02	3.07	98.3
1.64	0.610	12.94	61.65	25.41	2.43 ± .01	1.96	91.8
2.81	0.356	16.22	59.24	24.54	2.41 ± .02	1.51	92.5

a. Concentration in mol/L. b. (mol/L)⁻¹ c. ± 0.14. d. ± 0.83. e. ± 0.33. f. ± 0.003.

g. total yield of **119a**, **107**, **108**; ± 1.0.

Because CHD is not a rapid hydrogen atom donor (*vide infra*), the new product **119a** must arise from trapping of a long-lived biradical. If this biradical were **105Z**, the ratio of **107:108** would increase at higher CHD concentration since **105Z** would lie on the pathway to **108** but not **107** (cf. Scheme XXXIII). Not only is the ratio essentially constant (cf. Table V and the discussion before "Lifetime of **104T** and **97T**"), but intramolecular disproportionation (k_{id}) of

105Z should proceed considerably faster than in **98** ($2.8 \times 10^6 \text{ s}^{-1}$, vide supra), so that trapping is most unlikely. Instead we propose that CHD selectively traps **105E**, which is in pseudoequilibrium with **104T**. This mechanism accounts for the increase in **119a** at the expense of *both* **107** and **108** at higher CHD concentrations.

The lifetime of **105E** can be obtained from eq 39, which is readily derived from Scheme XXXIII.

$$(\mathbf{108})/(\mathbf{119a}) = \{(k_{ra} + k_{rb})/k_{td}[\text{CHD}]\} + 1 \quad (39)$$

A plot of **108/119a** versus $1/[\text{CHD}]$ gave a straight line ($r = 0.9955$) with a slope of 1.42 and an intercept of 1.23. This non-zero intercept argues further against

Figure 12. Graph of eq 39 and 107/108 using data in Table V.

105Z as the precursor of both **108** and **119a** since the yield of **108** would then have to approach zero at infinite CHD concentration. Although k_{td} has been determined as $5.8 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ for ethyl radicals with CHD, this value is only accurate within a factor of three.¹⁴⁷ We shall instead estimate k_{td} as $1 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ by extrapolating the trapping rate constant of 5-hexenyl radicals in benzene at 50 °C ($2.3 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$)¹⁴⁶ to 25 °C, assuming that E_a is the same as for methyl radicals (5.5 kcal/mol).¹⁴⁷ Although a value of $(k_{ra} + k_{rb})$ equal to $1.4 \times 10^5 \text{ s}^{-1}$ can now be calculated from eq 39, one more correction remains to be made.

The intercept of our plot according to eq 39 was higher than the expected 1.0, indicating that more **108** than **119a** is produced at infinite CHD concentration. Apparently **104T** exhibits a slight preference for CPC rearrangement to **105Z** over **105E**. If Scheme XXXIII is modified to use different values of k_{rf} for the two pathways, we find that the slope in eq 39 equals the intercept times $(k_{ra} + k_{rb})/k_{td}$. It follows that $(k_{ra} + k_{rb}) = 1.15 \times 10^5 \text{ s}^{-1}$, corresponding to a lifetime of 9 μs for **105E**.

Scheme XXXIII. Mechanism of product formation from triplet sensitized decomposition of 123 in the presence of CHD.

The much longer lifetime of **105E** than **98** ($\tau = 0.36 \mu\text{s}$) is of interest.

Biradical **98** undergoes intramolecular disproportionation to **101** despite its relatively strained transition state because this reaction is faster than homoallylic ring closure, which should proceed at similar rates in **105E**, **98**, and **115** ($k_{\text{rr}} \sim 10^4\text{-}10^5 \text{ s}^{-1}$). On the other hand, intramolecular disproportionation of **105E** to give **168** is unfavorable. Since we observed no GC peak that could be assigned to **168**, its formation from **105E** must be at least ten times slower than ring closure ($k_{\text{rr}} = 5.5 \times 10^4 \text{ s}^{-1}$) and therefore 500 times slower than intramolecular 1,5-hydrogen shift of **98** ($2.9 \times 10^6 \text{ s}^{-1}$), no doubt because of the highly strained transition state required for **105E** $\rightarrow$ **168**.

Having established the trapping of **105E** but not **105Z**, we may now use the product distributions in the presence of CHD to evaluate paths a, b, and d in Scheme XXXII. Paths b and d represent cyclization modes of **105E** to **104S** and **211** respectively. Since both of these 1,3-biradicals should close rapidly to

107, k_{rb} is kinetically equivalent to k_d . Either path preceded by CPC rearrangement of **104T** provides an alternative to the usual ISC mechanism for conversion of **104T** to **107**. Because $(k_{ra} + k_{rb})$ of **105E** and k_{rr} of **114a** represent the same reaction, they ought to have the same value. These two rate constants differ by a factor of two but the discrepancy can be attributed to experimental error and especially to uncertainty in k_{td} .¹⁴⁷ In order to evaluate k_{rb} individually, we must scrutinize the kinetics of CHD trapping more closely. Eq 40, which is derived from Scheme XXXIII, predicts that **107/108** should

$$\mathbf{107/108} = 2k_{isc}/k_{rf} + k_{rb}/(k_{ra} + k_{rb} + k_{td}[\text{CHD}]) \quad (40)$$

decrease as [CHD] increases, providing that neither k_{ra} nor k_{rb} greatly exceed $k_{td}[\text{CHD}]$. From $(k_{ra} + k_{rb}) = 1.15 \times 10^5 \text{ s}^{-1}$, $k_{td} = 1 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ and the concentrations of CHD used in our trapping experiments (cf. Table V), we conclude that $(k_{ra} + k_{rb})$ cannot overwhelm $k_{td}[\text{CHD}]$ in eq 40. The only way left for eq 40 to accommodate the observed constant ratio **107:108** is for k_{rb} and hence k_d to be negligibly small. It should be noted that eq 40 contains a statistical factor of two needed to compare **114a** with **104T**.

Although the above argument excludes paths b and d (in Scheme XXXII), we note that the latter was unappealing in the first place. Not only does path d involve cyclization to a housane with twice the ring strain of **104S**, but it affords a 1°, 2° biradical as opposed to the 2°, 3° biradical arising from paths a or b. Together, these factors make path d about 24.7 kcal/mol more endothermic than paths a and b, whose reaction free energy is calculated from the equilibrium constant for **114a**→**115a** ($k_{rf}/k_{rr} = 260$) to be + 2.9 kcal/mol.

The free energy change of path d is therefore 27.6 kcal/mol, corresponding to an equilibrium constant of 5.8×10^{-21} . If the rate constant for CPC rearrangement of **211** is taken to equal that for **212** ($k_r = 2.4 \times 10^9 \text{ s}^{-1}$),¹⁴⁸ we calculate that k_d is $1.4 \times 10^{-11} \text{ s}^{-1}$. This value is very much smaller than the $1.15 \times 10^5 \text{ s}^{-1}$ we find for k_{ra} , thus rendering path d most unlikely.

There remains one pathway from **105E** to **104S** that could evade our

kinetic scrutiny. A critical look at Table V reveals that the ratio **107:108** rather than being absolutely constant, actually *increases* slightly at high CHD concentration. This observation suggests that a small amount of **105Z** might be intercepted by CHD. In fact, a substantial amount of **105Z** might be trapped and yet increase in the **107:108** ratio only slightly if there were some other mechanism working to decrease the ratio. A kinetic leak from **105E** to **104S** is such a mechanism. Although we cannot rule out this possibility, it calls for a

coincidence of rate constants, it is unnecessarily complicated, and it requires that k_{Id} be unexpectedly slow.

Having ruled out paths b, c, and d in Scheme XXXII, we suggest that Scheme XXXIII best describes the mechanism of product formation from the sensitized photolysis of **123**. The fact that **105E** arises from a triplet biradical **104T** and then recloses to **104T** but not to **104S** immediately suggests that **105E** is a triplet biradical. However, it is unlikely that **105E** would survive for 9 μs before undergoing ISC, based on the shorter lifetime of analogous biradicals.⁴⁰ If **105E** is an equilibrium mixture of singlet and triplet, one must say that ring closure of the triplet is greatly favored. Perhaps the fact that **104T** lies 1.6 kcal/mol below **104S** (vide infra) leads to a preference for closure of **105E** to the lower energy spin state.

Lifetime of **104T** and **97T**

If k_{rb} is neglected, eq 40 simplifies to eq 41, which relates k_{isc} of **104T** to the product ratio (2.34 at 24.7 °C). We assume that k_{rf} equals the rearrangement rate of **114a** ($1.45 \times 10^7 \text{ s}^{-1}$), and conclude that the ISC rate

$$k_{\text{isc}} = k_{\text{rf}}[\mathbf{107}/\mathbf{108}]/2 \quad (41)$$

of **104T** is $1.7 \times 10^7 \text{ s}^{-1}$, corresponding to a lifetime of 59 ns. This value is one half that of **40T** but is not far from the 42 ns determined for 1,3-dimethyl-1,3-cyclopentanediyli (**213T**) by oxygen trapping.⁴⁷

104T

$\tau = 59 \text{ ns}$

213T

$\tau = 42 \text{ ns}$

40T

$\tau = 92 \text{ ns}$

Since the reaction mechanism of **104T** is reasonably well represented by Scheme XXXIII, we must inquire whether reversibility of the CPC rearrangement affects the lifetime of the six-membered biradical **97T**. Scheme XXXIV illustrates how the reaction **98**→**97S** can serve as an alternative mechanism of ISC in CPC biradicals.

Scheme XXXIV. Consideration of **98**→**97S**; an alternative to ISC.

Previously, we estimated that ring opening of **97T** was faster than reclosure of **98** ($k_1 = 1.3 \times 10^4 k_{-1}$) and intramolecular disproportionation of **98** was much faster than ring closure ($k_2 = 1.6 \times 10^3 k_{-1}$).^{51b} The ratio of products derived from (**99** + **100**):**101** is given by $(k_{isc'}/k_1)(1 + [k_{-1} + k_3]/k_2) + k_3/k_2$ where $k_{isc'}$ is the desired ISC rate of **97T**, and k_3 is the rate of **98** → **97S** (analogous to k_{rb} in Scheme XXXIII). If k_3/k_2 were larger than about 0.05, corresponding to $k_3 > 1.4 \times 10^5 \text{ s}^{-1}$, our value of $k_{isc'}$ would decrease perceptibly. However, k_3 is surely

less than 1.15×10^5 as we have already shown, so k_3 can be neglected. With k_3 out of the picture, all of the other quantities are known and a corrected value of k_{isc}' can be calculated from $(18\% + 21\%)/(61\%) = k_{isc}'/1.13 \times 10^7(1 + [5.5 \times 10^4/2.8 \times 10^6])$. It follows that $k_{isc}' = 7.09 \times 10^6 \text{ s}^{-1}$ and τ (**97T**) = 141 ns, which is close to the 138 ns given in the introduction. Whereas our original lifetime of **97T** was in error, the problem was the value of k_1 , not reversibility of the CPC rearrangement.⁶⁵

Activation Parameters for CPC Rearrangement of **114a** and for ISC of **104T**

Because the CPC rearrangement rate constant of **114a** is slower than that of the parent system, our activation parameters should differ from the $E_a = 7.05 \text{ kcal/mol}$ ($\log A = 13.15$) found for the CPC radical itself.⁵ Precise rate constants for CPC rearrangement of **114a** at two widely spaced temperatures can be calculated from the data in Tables I and II and the known values of k_{1a} .¹²¹ These values of k_{rf} ($1.45 \times 10^7 \text{ s}^{-1}$ at 24.7°C and $4.84 \times 10^7 \text{ s}^{-1}$ at 58.5°C) lead to $E_a = 7.0 \text{ kcal/mol}$ ($\log A = 12.3$) for rearrangement of **114a** to **115a**.

The activation parameters for ISC of **104T** were determined by competition with the CPC rearrangement. As shown in Table VI, a higher temperature during the sensitized decomposition of **123** enhances the formation of rearranged product **108**. Since $107/108 = 2k_{isc}/k_{rf}$, an Arrhenius plot of $\ln(107/108)$ versus $1/T$ should be linear, with a slope equal to the $[E_{a(rf)} - E_{a(isc)}]/R = \Delta E_a/R$. The plot of the data in Table VI was indeed linear ($r = 0.9980$) with a slope corresponding to $\Delta E_a = 5.4 \text{ kcal/mol}$. Subtracting this value from E_a for the CPC rearrangement of **114a** (7.0 kcal/mol) gave $E_a = 1.6 \text{ kcal/mol}$ for ISC

of **104T**. The y-intercept of the Arrhenius plot, -8.30, was corrected for $\ln 2$ and $\log A$ of the CPC rearrangement, giving $\log A = 8.4$ for ISC of **104T**.

Figure 13. Arrhenius plot of **107/108** versus $1/T$.

Table VI. Product Yields from Triplet Sensitized Photolysis of **123** at Various Temperatures.

T, °C	$10^3/T$	107 ^a	108 ^b	$\ln(107/108)$	Bal. ^c
3.40	3.62	83.96	16.04	$1.66 \pm .03$	93.1
13.70	3.49	77.88	22.12	$1.26 \pm .05$	93.7
24.80	3.36	70.12	29.88	$0.85 \pm .07$	92.2
41.10	3.18	59.45	40.55	$0.38 \pm .07$	93.2
61.00	2.99	48.40	51.60	$-0.064 \pm .02$	94.4

a. ± 0.87 . b. ± 0.27 . c. total yield of **107** and **108**; ± 0.65 .

The activation energy determined for ISC of **104T** is very similar to that recently reported for **40T** (2.1 kcal/mol),⁴⁴ 1,3-diphenyl-1,3-cyclopentenediyl

(**64T**) (2.6 kcal/mol), and its 2,2-dimethyl substituted analog (**65T**) (1.2 kcal/mol),⁴⁶ while the low A value for ISC of **104T** is characteristic of the spin forbidden nature of intersystem crossing.

Conclusions

In our determination of reaction rates for both MRs and BRs, we have minimized uncertainty by demonstrating good material balances in all radical clock experiments, and by multiple analytical measurements. Furthermore, all kinetic data used in the determination of rate constants fit linear equations with $r \geq 0.996$. We have carried out a detailed study of monoradicals **114a,b** analogous to BRs **104T** and **97T**, respectively, so that we could better understand both the reactions and rearrangement rates of **114a,b** and **115a**. The rates of reaction and activation parameters determined for **114a,b** are shown below.

The rearrangement rates of radicals **114a** & **114b** are 2.1 times and 1.6 times faster, respectively, than $k_{\text{H}}=7.0 \times 10^6 \text{ s}^{-1}$ determined by Burkhard et al¹⁰ for CPC radical **22**.

It is noteworthy that radical **115a** and analogous BR **105E** do not undergo the 1,5-hydrogen shift. The 1,5-hydrogen shift in BR **105Z** occurs in spite of geometric constraints because stable, conjugated diene **108Z** results. The

lifetimes of BRs **105E** ($\tau=9 \mu\text{s}$) and **98** ($\tau=0.36 \mu\text{s}$) are novel in that they are governed by the rates of intramolecular reaction of these BRs rather than by rates of ISC.

Based on the CPC rearrangement rate of **114a** ($k_{\text{H}}=1.45 \times 10^7 \text{ s}^{-1}$),^{15d} the lifetime of **104T** is found from its product distribution to be $59 \pm 2 \text{ ns}$ assuming that only random errors contribute to uncertainty in τ . The good agreement between this τ for **104T** with $\tau=92 \pm 28 \text{ ns}$ and $\tau=42 \pm 7 \text{ ns}$ for **40T**⁴⁷ and **213T**⁴⁷ respectively, (both determined by the OT method), shows that the cyclopropyl group does not alter τ via radical

stabilization or conformational effects. Thus the FRC method is validated for BRs in the 1,3-cyclopentanedyl family, but not necessarily for the 1,4-cyclohexanedyl family. Aside from the obvious potential for ISC catalyzed by O_2 , it is still possible that substituent induced conformational changes may cause the difference in τ for **70T**⁴⁷ (0.1 ns), **97T** (141 ns),^{51a} and **102T** (188 ns).^{51b}

An appealing experiment to test ISC catalyzed by O_2 would be to determine T_f for **97T**, or to determine τ of 1-methyl-1,4-cyclohexanedyl using the OT method.

The lifetime of **104T** displays linear Arrhenius behavior in fluid solution over the temperature range 3.4 °C - 61.0 °C. The activation parameters for ISC of **104T**, E_a (ISC)=1.6 kcal/mol and $\log A=8.4$, were determined by competition with the CPC rearrangement of monoradical **114a**. We are aware of no published examples of activation parameters for ISC of *simple* TBRs at ambient temperature in fluid solution. Our values are in good agreement with

$E_a(\text{ISC})=2.1$ kcal/mol (assumes $\log A=8$) for **40T**⁴⁴ (determined by low temperature ESR), and $E_a(\text{ISC})=2.6$ kcal/mol and 1.3 kcal/mol and $\log A=6.7$ and 6.9 for **64T**⁴⁶ and **65T**⁴⁶ (determined by LFP), respectively.

Thus **104T** is a ground state TBR, and the low value of $\log A$ is characteristic of spin forbidden ISC. Our findings support recent studies by Dougherty and coworkers^{15a} who suggest that 1,3-cyclopentadienyls are more robust than was once believed.^{15e}

There was not sufficient time to examine **104T** by ESR, but this would certainly be a worthwhile venture. Dougherty et al have suggested that a triplet ground state is necessary for observation of matrix isolated TBRs by ESR.⁵⁵ This TBR should be observable by ESR under conditions of low temperature matrix isolation since we have already demonstrated that **104T** possess a triplet ground state. If **104T** can be observed by ESR, then perhaps the importance of matrix isolation effects on tunneling in ISC of TBRs at low temperature can be investigated.

Finally, one of the objectives of this work was to develop better methods for synthesizing α -cyclopropyl substituted azoalkanes in which the cyclopropyl group rotates freely. In accord with this goal, the yield of azoalkane **123** obtained by the Lewis acid catalyzed cyclization of tosylhydrazone **141** was an

order of magnitude better than that obtained by the Diels-Alder route. In the synthesis of azoalkanes **113a,b**, the carbocation stabilizing capability of the

113
a, $n=1$
b, $n=2$

cyclopropyl group coupled with the good nucleophilic character of azide allowed transformation of alcohols **178a,b** to azides **179a,b**.

178
a, $n=1$
b, $n=2$

179
a, $n=1$
b, $n=2$

Experimental Section

General Information. NMR spectra were recorded on an IBM AF-300, Bruker AC-250, or JEOL FX-90Q spectrometer in CDCl_3 or C_6D_6 solvent. Chemical shifts (δ , ppm) are referenced against CHCl_3 (7.25) or C_6H_6 (7.15). Analytical GC was carried out on an HP5890A gas chromatograph equipped with a DB-5 capillary column (0.25 mm x 30 m) and flame ionization detector. Analytical GC data were collected and manipulated on an IBM PC compatible computer. Conditions for quantitative analysis of hydrocarbon mixtures were as follows: Inj. = 180 °C, det. = 250 °C, oven = 35 °C, initial time = 5 min., rate = 10 °C/min. Preparative GC was performed on an Antek 300 using the GC columns shown in Table VII. Melting points were determined with a Mel-Temp apparatus and are uncorrected. GC/MS was performed on a Finnigan 3300 spectrometer while high resolution mass spectra were obtained on a CEC DuPont 21-110B spectrometer. UV spectra were obtained on a Cary-17 or HP8452A diode array spectrometer interfaced to a PC. IR spectra were obtained on a Perkin-Elmer 1310 spectrometer.

Table VII. Preparative GC Columns^a

Designation	Length, Ft	Materials ^b
A	2	20% UCON 250-X HB(P)
B	18	20% UCON 250-X HB(P)
C	2	10% FFAP(W)
D	6	10% FFAP(W)
E	18	10% FFAP(W)
F	6	25% SE-30(P)

a. All columns were 0.25 in O.D. and contained 60/80 mesh chromosorb.

b. Percent liquid phase. Type of chromosorb is indicated in parentheses.

Materials. Ether and THF were distilled from Na/benzophenone while hexane and oxetane were distilled from sodium. TMEDA was distilled from butyric anhydride, then redistilled from sodium. Diisopropyl amine was distilled from KOH. Trifluoroacetic acid, carbon tetrachloride, methylene chloride, chloroform, benzene and fluorobenzene were distilled from P_2O_5 . 1,4-Cyclohexadiene was passed over neutral, Brockman activity grade 1 alumina just prior to use. Decane (as internal GC standard) was distilled. Thiophenol was distilled immediately before use. Without further purification, tributyltin hydride was degassed and sealed into ampules that were stored in the dark at $-5\text{ }^{\circ}\text{C}$. Pyridine was distilled from KOH while DMF was distilled from CaH_2 . Alkyl lithium reagents were titrated by the method of Watson and Eastham.¹⁵⁰ Analytical TLC plates were visualized with a solution of 15 ml anisaldehyde, 10 ml conc. H_2SO_4 , 10 ml HOAc and 350 ml absolute EtOH.

Solutions for Photolysis. All solutions of azoalkane, internal standard, radical scavenger, and sensitizer (when appropriate) were prepared such that no less than 0.0100 g of material was weighed on a Mettler H35AR analytical balance. Thus the error in concentration of components in photolysis solutions is negligible relative to the random errors associated with quantitative GC analysis of products.

Photolyses. Unless otherwise noted, all samples for photolysis were degassed and sealed in 5 mm standard wall pyrex tubes and then completely immersed in a thermostatted bath at the specified temperature. Irradiations were carried out with a 500 W Oriel high pressure mercury lamp employing either a K_2CrO_4 (313 nm) or a 2,7-dimethyl-3,6-diazacyclohepta-1,6-diene perchlorate (366 nm) filter solution.

Capillary GC analysis. GC injections for quantitative analysis employed a 1.00 μ l plunger in needle syringe possessing a needle guard. Sweep solvent (0.2 μ l of the analyte solvent), 0.2 μ l air, 0.2-0.4 μ l analyte solution, and 0.2 μ l more air were drawn into the GC syringe in the order given. The septum of the GC injector (which was changed every other day or so) was pierced with the syringe needle until further penetration was prevented by the needle guard. The plunger was depressed completely, injecting the entire contents of the syringe, then the needle was quickly and immediately removed from the injector. Consistent use of this method of sample introduction helped to minimize errors in quantitative analysis of products.

Syntheses

Diels-Alder route to 123.

1-cyclopropylcyclopent-2-ene-1-ol (124). A solution of 1.6 ml (20 mmol) cyclopropyl bromide and 40 ml dry ether was delivered to a round bottom flask equipped with a nitrogen inlet, addition funnel and serum stopper. The solution was cooled to -78 °C under an atmosphere of dry nitrogen. A solution of 1.5 M *tert*-butyllithium in hexane (11 ml, 16.5 mmol) was added dropwise to the cooled cyclopropyl bromide solution, after which the solution was stirred at -78 °C for 0.5 hr. A solution of 1.5 ml (18 mmol) 2-cyclopentenone in 35 ml ether was then added dropwise. The reaction was stirred for 3 hours without further addition of dry ice to the cooling bath, then quenched with 15 ml distilled water. The resulting mixture was filtered through celite to remove solids, and the aqueous layer was extracted three times with 15 ml ether. The combined ether layers were dried over K₂CO₃, filtered and concentrated on a rotovap. The resulting liquid was distilled in a molecular still at 16 mm Hg and 70-129 °C

oil bath. Tertiary alcohol **124** was obtained in this way in 16% yield. 90 MHz ^1H NMR (CDCl_3) δ 0.20 - 0.60 (m, 4H), 1.0 - 1.40 (m, 1H), 1.60 (s, 1H), 1.70 - 2.20 (m, 2H), 2.20 - 2.60 (m, 2H), 5.40 - 5.60 (m, 1H), 5.80 - 6.0 (m, 1H).

6-oxa-bicyclo[3.1.0]hex-3-ene (cyclopentadiene monoepoxide)¹⁵¹ **Warning.** Although the references cited give no warning concerning the health hazards of cyclopentadiene monoepoxide, butadiene monoepoxide is known to be a potent carcinogen. This reaction should be carried out in a well ventilated hood. **Caution!** Explosions have been known to occur in reactions involving peracetic acid. This reaction should be carried out behind a shield. A reaction vessel equipped with a mechanical stirrer, variable immersion thermometer and Claisen adapter equipped with a reflux condenser and addition funnel was assembled. Methylene chloride (500 ml), Na_2CO_3 (160 g, 1 mol) and cyclopentadiene (56 g, 0.85 mol) were delivered to the reaction vessel. A mixture of 76 g (0.48 mmol) of a 40% peracetic acid solution and 2g (0.02 mol) NaOAc was added in a dropwise fashion with vigorous stirring while the reaction temperature was maintained at 20 °C. Progress of the reaction was followed by mixing a 0.2 ml aliquot of the reaction mixture with an equal volume of cold water. Ceric sulfate solution (0.1 M) was then added dropwise until its orange color barely persisted. Excess (ca. 1 g) KI was added and the solution turned dark brown. The solution was then titrated with standardized (0.103 M) aqueous $\text{Na}_2\text{S}_2\text{O}_3$ until a color change to light brown/yellow was observed. At this point, 2.5-5.0 ml starch indicator was added and the solution turned purple. Titration was continued until the purple color went away. Volume $\text{Na}_2\text{S}_2\text{O}_3$ used $\times 0.103 \text{ M} \times 1 \text{ mmol } \text{I}_2/2 \text{ mmol } \text{Na}_2\text{S}_2\text{O}_3 =$ mmol peracid in the aliquot titrated. Alternatively, the reaction could be stirred

until a negative test to moist starch iodide paper was observed. The reaction was worked up by addition of a small spatula full of activated charcoal to destroy any residual peroxides. The reaction was filtered by suction and the solids were rinsed with several copious portions of methylene chloride. To remove the solvents, the filtrates were distilled carefully through a 20 cm column filled with glass helices until the pot temperature reached 50 °C. **Caution! Heating above 50 °C can lead to a violent exothermic reaction according to the references cited.** The residue was flash distilled and the desired epoxide redistilled, bp 39-41 °C (46 mm). 90 MHz ¹H NMR (CDCl₃) δ 2.50 (dm, 2H), 3.85 (m, 2H), 6.08 (dm, 2H). 75 MHz ¹³C (CDCl₃) δ 36.63, 56.88, 59.26, 128.68, 131.30.

4-cyclopropyl-2-cyclopentene-1-ol (125). A solution of cyclopropyllithium was prepared, in the usual fashion, by addition of 5 ml *tert*-butyllithium/hexane (1.7M, 8.5 mmol) to a solution of 0.67 ml cyclopropyl bromide in 10 ml ether at -78 °C, then the solution was diluted with another 15 ml ether. In a separate 3-neck round bottom flask fitted with two rubber serum stoppers and a vacuum adapter, CuCN (0.338 g, 3.8 mmol) and a stir bar were heated with a hot air gun under vacuum at 0.4 mm. The flask was brought up to atmospheric pressure with dry nitrogen, and the procedure was repeated two more times, after which the flask contents were left under a positive pressure of nitrogen. The cream-colored CuCN was slurried in 2 ml ether and cooled to -78 °C. The cyclopropyllithium solution was transferred to the CuCN slurry via cannula. In order to ensure complete transfer of the cyclopropyl lithium, the flask was rinsed with ether, and the washings were also added to the CuCN flask. A milky solution resulted and the mixture was allowed to warm to 0 °C for several minutes in an unsuccessful attempt to effect homogenization. The

cloudy reaction was recooled to -78 °C, and a solution of cyclopentadiene monoepoxide (0.330 g, 4.0 mmol) in 1 ml ether was added all at once. An immediate color change to bright yellow was observed, and the reaction was stirred for 3.5 hours at -78 °C. Workup was effected by quenching with 15 ml of a solution comprised of 10 ml NH₄OH (conc.) and 90 ml saturated aqueous NH₄Cl, followed by filtration through a celite pad. The filtrate was extracted three times with 20 ml portions of ether, and the combined extracts were dried over K₂CO₃.^{81,82} Rotary evaporation yielded the desired crude product which was distilled in a molecular still at 13 mm (oil bath temperature was 100 °C). Yield: 0.21 g (60%). A sample of the alcohol was isolated by preparative GC; and capillary GC analysis showed the presence of two isomers. 300 MHz ¹H NMR (CDCl₃) δ 0.20-0.28 (m, 4H), 0.30-0.50 (m, 4H), 0.50-0.75 (m, 2H), 1.32-1.50 (m, 1H), 1.60 - 1.80 (br s, 2H + H₂O), 1.80-2.20 (m, 3H), 2.20-2.41 (m, 1H), 2.42-2.60 (m, 1H), 4.75 (t, 1H), 4.87 (m, 1H), 5.72-5.95 (m, 4H). 75 MHz ¹³C NMR (CDCl₃) δ 2.87, 3.16, 3.29, 3.41, 15.86, 16.53, 40.18, 40.46, 48.61, 48.86, 76.50, 133.10, 133.48, 137.47, 139.00. MS (30eV), m/e (%) 124(4), 123(4), 109(22), 106(12), 96(55), 95(100), 91(26), 83(32), 81(31).

1&2-cyclopropylcyclopentadiene (121&122).⁷⁹ The mixture of cyclopentadienes was obtained by pyrolysis of alcohol **125** in the same manner used to prepare 1-cyclopropylcyclopentene (**120**). ¹H NMR (90 MHz, CDCl₃) δ 0.40-1.00 (m, 8H), 1.50-2.00 (m, 2H), 2.80 (s, 2H, belongs to **121**), 2.95 (s, 2H, belongs to **122**), 5.90-6.50 (m, 6H).

1-cyclopropyl-4-methyl-2,4,6-triazatricyclo[5.2.1.0^{2,6}]dec-8-ene-3,5-dione (126) and 8-cyclopropyl-4-methyl-2,4,6-triazatricyclo[5.2.1.0^{2,6}]dec-8-ene-3,5-dione (127). To the liquid nitrogen trapped cyclopentadienes was added a chloroform solution of

sublimed *n*-methyl-triazolinedione (**MTAD**)¹⁵² with stirring, until the red color of the dienophile barely persisted. Adventitious water from the pyrolysis step was removed with MgSO₄. The solution was concentrated by rotary evaporation, leaving a viscous orange oil. **MTAD** decomposition products were removed by dilution with ether and filtration through celite. A roughly 1:1 mixture of isomers was obtained from this reaction. ¹H NMR (90 MHz, CDCl₃) δ 0.40-1.00 (m, 8H), 1.20-2.30 (m, 6H), 2.95 (br s, 6H), 4.80 (br s, 1H), 4.93 (br s, 2H), 5.75 (br s, 1H), 6.15 & 6.20 (AB pattern, 2H). A 300 MHz ¹H NMR spectrum was obtained on a similar urazole mixture obtained by addition of excess **MTAD** to a CDCl₃ solution of **121** and **122** isolated by preparative GC. Because interpretation of the aliphatic region is not clear, only chemical shifts (δ) are given and ¹H assignments are made when possible. 0.30 - 0.45 (m), 0.50 - 0.65 (m), 0.80 - 0.95 (m), 1.45 - 1.55 (m), 1.60 (H₂O), 2.10 (m), 2.97 (s, *n*-Me of **126**), 3.00 (*N*-Me of **127**), 3.29 (br s, excess **MTAD**), 4.82 (s, bridgehead H of **126**), 4.98 (s, bridgehead H's on **127**), 5.81 (s, vinyl H of **127**), 6.15 (part of AB pattern, one of two vinyl H's in **126**), 6.20 (part of AB pattern, one of two vinyl H's in **126**).

1-cyclopropyl-4-methyl-2,4,6-triazatricyclo[5.2.1.0^{2,6}]decane-3,5-dione (128**) and other urazoles.** An ethyl acetate solution of 4.77 g (21.8 mmol) of urazoles **126** and **127** was swirled with a spatula full of charcoal and filtered through a celite pad. Pd/C catalyst (~0.4 g) was added to the filtrate and the solution was hydrogenated at ambient temperature under 1 atm of H₂. When hydrogen uptake had ceased, the solution was filtered through the same celite pad as before and concentrated on a rotovap, yielding a viscous orange oil. NMR experiments with Eu(fod)₃ indicated the presence several isomers, judging from the three singlets observed near 3.5 ppm (*N*-Me)

upon addition of the shift reagent. A partial separation was achieved under forcing conditions of preparative GC: Column F, inj.= 293 °C, oven = 240 °C, det.= 263 °C, flow = 37.5 ml/min. Two GC peaks were observed and collected. A representative GC trace can be found at the end of the experimental section, see Figure 14. GC peak 1 (T_r = 48.8 min.) appeared to contain more than one urazole; however, absence of the cyclopropyl ring was evident from NMR and GC/MS. The NMR spectrum is given at the end of the experimental section. Only GC peak 2 (T_r = 57.8 min.) contained a urazole with an intact cyclopropyl ring but the presence of two bridgehead hydrogens indicated that the cyclopropyl group was not at the desired bridgehead position. Failure to isolate **128** by preparative GC was distressing since NMR and GC/MS analysis of the urazole mixture before isolation suggested its presence. Sheridan et al¹⁵³ demonstrated that a methoxy group on the carbon adjacent to a urazole nitrogen can be replaced with other nucleophiles under conditions of Lewis acid catalysis. Our isolation of azoalkane **123** and Sheridan's observations suggest that cleavage of the (c-C₃H₅)-C-N bond in **128** is possible. Therefore, under the forcing conditions used in this separation, it is likely that **128** decomposed. GC peak 2 spectral data: 90 MHz ¹ H NMR (CDCl₃) δ 0.13 (d, 2H), 0.45-0.55 (m, 2H), 0.85-1.00 (m, 2H), 1.25-1.49 (m, 2H), 1.90-2.10 (m, 2H), 3.15 (s, 3H), 4.47 (s, 1H), 4.51 (s, 1H). GC/MS of mixture before preparative GC (30 eV), m/e (%) (hydrogenated adducts) 221(5), 192(4), 152(36), 116(21), 107(100), 106(100), 96(72), 79(90); (over-hydrogenated adducts) 223(25), 194(28), 152(100), 116(71), 109(100), 108(100), 95(43), 93(38), 81(59), 80(61), 79(61), 69(58), 67(100).

1-cyclopropyl-2,3-diazabicyclo[2.2.1]hept-2-ene (123) and isomers as copper (I) chloride salts. To a solution of the isomeric urazole mixture from reduction of **126&127** (0.82 g, 3.7 mmol) and 25 ml isopropanol was added a stir bar and 2.6 g (46 mmol) KOH. The mixture was refluxed with stirring for 24 hours. After this period of time, most of the isopropanol was distilled, concentrating the reaction to about 5 ml. The resulting brown residue was diluted with 5 ml distilled water, and this solution was acidified with 8N HCl until pH paper indicated pH = 5-6. The solution was filtered and the filtrate was treated with aqueous CuCl₂. Formation of a dark red precipitate was observed, as well as a lowering of the pH of the solution. The pH was readjusted to 5-6 by addition of 5N NH₄OH, and more aqueous CuCl₂ was added. This process was repeated several more times until no further pH change was observed upon addition of aqueous CuCl₂. The red solid (0.1129 g, 13 %) was collected by suction.

1-cyclopropyl-2,3-diazabicyclo[2.2.1]hept-2-ene (123) and other azoalkane isomers. The free azoalkanes were liberated from the red copper (I) chloride complex by treatment of 0.47 g of the red powder from above with 0.19 g (4.8 mmol) NaOH in 40 ml H₂O, followed by continuous extraction with pentane for 2 days. Careful removal of the pentane by distillation through a short Vigreux column gave the mixture of azoalkanes, from which the desired **123** was isolated by preparative GC on column B. Conditions: Inj.= 130 °C, oven = 178 °C, det.= 171 °C, flow = 30 ml/min. See Figure 15 at the end of the experimental section for a representative GC trace. Three GC peaks were collected, and analysis by NMR revealed that only two of the peaks (labeled 2 and 3) were bicyclic azoalkanes with an intact cyclopropyl ring. The remaining

GC peak (labeled 1) appeared to be a mixture of azoalkanes containing n-propyl and cyclopropyl groups with the n-propyl group dominating the product mixture. GC peak 1 spectral data (no assignment made, integral given in cm since sample appears to contain more than one azoalkane.) 300 MHz ^1H NMR (CDCl_3) δ 0.52 (dm, 1.1 cm), 0.85 - 0.98 (t with multiplet buried underneath, 6.0 cm), 1.13 - 1.50 (2 overlapping complex multiplets, 9.4 cm), 1.75 (7 line pattern, 1.8 cm), 1.90 - 2.05 (m, 1.8 cm), 5.08 (s, 1.5 cm), 5.16 (s, 1.5 cm). 75 MHz ^{13}C (CDCl_3) δ 13.97, 21.55, 27.28, 33.69, 37.42, 41.86, 77.52, 78.60. GC peak 2 spectral data (assigned to 123): 300 MHz ^1H NMR (C_6D_6) δ 0.33 (d, 1H), 0.40-0.56 (m, 4H), 0.58-0.83 (m, 3H), 0.83-1.0 (m, 2H), 1.23-1.35 (m, 1H), 4.63 (br s, 1H). 75 MHz ^{13}C NMR (CDCl_3) 2.34 (CH_2), 11.25 (CH), 22.44 (CH_2), 24.64 (CH_2), 42.81 (CH_2), 76.58 (CH). MS (30 eV), m/e (%) 107(20), 93(50), 91(35), 80(80), 79(100), 77(52), 67(100). UV (hexane) λ_{max} 346 nm. GC peak 3: 300 MHz ^1H NMR (C_6D_6) δ -0.33 to -0.15 (m, 1H), -0.10 to +0.02 (m, 1H), 0.05-0.35 (m, 3H), 0.40 (d, 1H), 0.50-0.68 (m, 2H), 0.69-0.85 (m, 1H), 1.20 (m, 1H), 4.70 (s, 1H), 4.79 (s, 1H). 75 MHz ^1H NMR (C_6D_6) δ 5.08 (CH_2), 12.50 (CH), 27.71 (CH_2), 40.21 (CH_2), 43.00 (CH), 77.58 (CH), 83.35 (CH). MS (30 eV), m/e (%) 107(2), 105(2), 93(28), 91(24), 80(48), 79(100), 77(31), 67(52), 66(33), 54(4), 53(3). Peak 3 in CDCl_3 , 300 MHz ^1H NMR (CDCl_3) δ -0.10 to 0.00 (m, 1H), 0.00 - 0.42 (m, 3H), 0.42 - 0.55 (m, 1H), 0.75 (dm, 1H), 1.15 (2 lines of unequal intensity, 1H), 1.30 (dm, 2H), (1.80, 7 line pattern, 1H), 5.15 (s, 1H), 5.18 (s, 1H). The spectral data suggest that GC peak 3 is 5-cyclopropyl-2,3-diazabicyclo[2.2.1]hept-2-ene, however, a conclusive exo or endo assignment of the cyclopropyl group has not been made.

Tosylhydrazone route to 123.

Cyclopropyl methyl ketone-2,4,6-triisopropylbenzenesulfonylhydrazone (134d). Cyclopropyl methyl ketone (1.15 g, 13 mmol) was added to a stirred solution of 2,4,6-triisopropylbenzenesulfonylhydrazide in 40 ml THF. The mixture was stirred for 30 min. under N₂ and the THF was removed in vacuo, giving a white, amorphous solid. The solid was dissolved in 25 ml hot MeOH and was reprecipitated by cooling and adding water.⁸⁶ After filtration and vacuum drying over P₂O₅, 3.3 g (66%) **134d** was obtained. mp 121 - 122 °C. 90 MHz ¹H NMR (CDCl₃) δ 0.66 (m, 5H), 1.26 (d, 18H), 1.66 (m, 3H), 1.86 (septet, 1H), 4.23 (m, 2H), 7.16 (s, 3H). 75 MHz ¹³C NMR (CDCl₃) δ 5.29, 6.32, 13.62, 17.91, 23.62, 24.44, 24.87, 29.87, 29.98, 30.07, 34.22, 123.75, 123.82, 124.10, 151.34, 153.18. MS (30 eV), m/e (%) 145(65), 98(100), 97(100), 84(100), 67(100).

4-Cyclopropyl-4-penten-1-ol (140). Trisylhydrazone **134d** (6.4 g, 18 mmol) was dissolved in 64 ml 50% TMEDA/hexane and cooled to -78 °C under N₂. Dropwise addition of n-butyllithium (18 ml, 40 mmol) led to an intense orange color. Stirring was continued for an additional 15 min.; then the mixture was warmed to 0 °C, resulting in gas evolution. After 15 min., no further gas was evolved and the solution turned clear yellow. Oxetane¹⁷⁰ (0.94 g, 16 mmol) in 25 ml hexane was added to the ice cooled solution. After stirring for several hours, workup was effected by dilution with 225 ml H₂O and extraction with 3 x 75 ml ether. The combined ether layers were washed with 0.5 N HCl, H₂O, 0.75 M NaOH, and brine. The ether solution was dried over MgSO₄, filtered and concentrated giving 1.97 g (99%) product **140**. 300 MHz ¹H NMR (CDCl₃) δ 0.39 - 0.46 (m, 2H), 0.59 - 0.66 (m, 2H), 1.25 - 1.30 (m, 1H), 1.77 (quintet, 2H, J

= 6.5 Hz), 2.12 (t, 2H, J = 7 Hz), 3.66 (t, 2H, J = 7 Hz), 4.62 (s, 1H), 4.64 (s, 1H). 75 MHz ^{13}C NMR (CDCl_3) δ 6.24, 16.01, 31.16, 32.44, 62.85, 106.33, 150.70.

4-Cyclopropyl-4-pentenal (133). Alcohol **140** (0.63 g, 5 mmol), was added to a slurry of 4.7 g pyridinium dichromate (PDC)⁹⁰ in 35 ml CH_2Cl_2 and the mixture was stirred overnight. Workup was effected by dilution with ether and filtration through a celite pad. The ether solution was concentrated to a few mls and passed through a plug of silica gel to remove any traces of chromium species. The aldehyde was purified by distillation. Yield 43%, bp 74 - 77 °C (3.4 mm). 300 MHz ^1H NMR (CDCl_3) δ 0.42 - 0.47 (m, 2H), 0.61 - 0.68 (m, 2H), 1.23 - 1.27 (m, 1H), 2.34 (t, 2H, J = 7.5 Hz), 2.65 (t, has extra fine splitting, 2H, J = 7.8 Hz, J = 1.6 Hz), 4.63 (s, 1H), 4.66 (s, 1H), 9.78 (t, 1H, J = 1.6 Hz). 75 MHz ^{13}C NMR (CDCl_3) δ 6.11, 16.6, 28.40, 42.30, 107.14, 149.03, 202.39. MS (30 eV), m/e (%) 124(5), 109(28), 95(30), 82(60), 67(100).

4-Cyclopropyl-4-pentenal tosylhydrazone (141). Aldehyde **133** (0.13 g, 1.0 mmol) was stirred with tosylhydrazide (0.196 g, 1.06 mmol) in MeOH for several hours under nitrogen. The solvent was removed in vacuo, giving a yellow oil. The oil could be purified by chromatography on silica gel (EtOAc/Hexane) but was generally used without further purification due to instability and sensitivity to air.⁷⁴ 300 MHz ^1H NMR (CDCl_3) δ 0.28-0.62 (m, 4H), 1.09-1.27 (m, 2H), 1.91-2.04 (m, 3H), 2.32 (m, 4H), 4.61 (m, 2H), 7.18 (m, 2H), 7.53 (t, 1H, J = 9.4 Hz), 7.68 (d, 1H, J = 9.8 Hz), 7.79 (d, 1H, J = 9.9 Hz).

1-Cyclopropyl-2,3-diazabicyclo[2.2.1]-hept-2-ene (123). The crude tosylhydrazone **141** was taken up in CH_2Cl_2 and was stirred over molecular sieves for 1 h under nitrogen. This CH_2Cl_2 solution was added dropwise to a flask containing $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (0.31 g, 2.6 mmol) cooled in an ice/salt bath. Stirring was continued for 30 min. and the reaction was warmed to room

temperature. The reaction was worked up immediately by addition of 20 ml 1 M K_2CO_3 and extraction with CH_2Cl_2 .^{74a} The combined CH_2Cl_2 phases were dried over $MgSO_4$, filtered, and concentrated by careful distillation through a short vigreux column. The crude azoalkane was purified by GC on column C. Inj = 150 °C, oven = 150 °C, det = 160 °C, flow = 30 ml/min. The yield before GC was 20%. A representative GC trace is given at the end of the experimental section. See Figure 16. 90 MHz 1H NMR (C_6D_6) δ 0.20 - 1.50 (m, 11H), 4.62 (br s, 1H). 300 MHz 1H NMR (C_6D_6) δ 0.33 (d, 1H), 0.40-0.56 (m, 4H), 0.58-0.83 (m, 3H), 0.83-1.0 (m, 2H), 1.23-1.35 (m, 1H), 4.63 (br s, 1H). 75 MHz ^{13}C NMR ($CDCl_3$) 2.34, 11.25, 22.44, 24.64, 42.81, 76.58. MS (30 eV), m/e (%) 107(20), 93(50), 91(35), 80(80), 79(100), 77(52), 67(100). UV (hexane) λ_{max} 346 nm, ϵ 182. HRGC/MS¹⁷¹ (Molecular ion was not visible so analysis was carried out for the M-N₂ fragment.) Calcd for C_8H_{12} : 108.0939 Found: 108.0933.

1-Cyclopropylcyclopentanol (178a)¹⁵⁴. A 500 ml, 3 neck, round bottom flask equipped with a stirring bar, nitrogen inlet, and a 100 ml pressure equalized addition funnel was charged with a solution of 7.67 g (63 mmol) cyclopropyl bromide in 100 ml ether. A serum stopper was inserted in the top of the addition funnel and was secured by a wire. The cyclopropyl bromide solution was cooled to -78 °C under nitrogen; then 38 ml (62 mmol) *tert*-butyllithium (1.6M in pentane), which had been delivered to the addition funnel via cannula, was added dropwise to the cyclopropyl bromide solution, followed by 80 ml ether. After the mixture had stirred for 1 hour at -78 °C, cyclopentanone, 84 g (62 mmol), in 80 ml ether was added dropwise at -78 °C. The solution was kept at -78 °C for four hours and was then allowed to warm to room temperature over the course of 2-3 hours. The reaction was quenched with 80 ml H_2O and the water layer was extracted once with ether. The

combined ether layers were dried over MgSO_4 , filtered, and rotary evaporated. Yield 7.8 g (94%). 90 MHz ^1H NMR (CDCl_3) δ 0.25-0.50 (m, 4H), 0.80-1.30 (m, 1H), 1.4-2.0 (m, 9H). 75 MHz ^{13}C NMR (CDCl_3) δ 1.32, 19.95, 23.72, 38.35, 82.12. MS (30 eV). m/e (%) 126(3), 109(5), 98(87), 97(100), 84(37), 83(36), 70(25), 69(38), 55(29).

1-Cyclopropylcyclopentylazide (179a). A 3.5 g (54 mmol) portion of NaN_3 , 4 ml (53 mmol) CF_3COOH , and 26 ml CHCl_3 were placed in a 50 ml 3 neck round bottom flask equipped with a mechanical stirrer and a 50 ml addition funnel. To the mixture, which was cooled in an ice/salt bath, was added a solution of 3.32 g (27 mmol) 1-cyclopropylcyclopentanol (**178a**) in CHCl_3 with stirring under nitrogen. Stirring was continued for 4 hours as the solution rose to ambient temperature. A 25 ml portion of conc. NH_4OH was added and the CHCl_3 layer was separated and washed twice with 20 ml H_2O .¹⁰⁷ The organic layer was dried over MgSO_4 , filtered, and rotary evaporated to yield 3.6 g (91%) of the desired azide. 90 MHz ^1H NMR (CDCl_3) δ 0.20-0.40 (m, 4H), 1.00-1.40 (m, 1H), 1.40-1.90 (m, 8H). 75 MHz ^{13}C NMR (CDCl_3) δ 1.32, 17.91, 23.58, 35.28, 4°C not visible. IR (CCl_4 , cm^{-1}): 2090.

1-Cyclopropylcyclopentylamine (180a). The azide obtained above was dissolved in 25 ml ether and added dropwise to a slurry of 1.8 g (47 mmol) LAH in 30 ml ether under nitrogen.¹⁵⁵ The reaction was stirred for about 12 hours, then refluxed for one hour. Workup consisted of careful addition of H_2O to the room temperature solution until gas evolution ceased. The ether layer was decanted and the remaining solids were washed with 75 ml ether. The combined organic layers were dried over MgSO_4 , filtered, and concentrated by rotary evaporation, giving 2.5 g (82%) of the desired amine. 300 MHz ^1H NMR (CDCl_3) δ 0.178-0.194 (d, 2H), 0.328-0.354 (d, 2H), 0.866-0.958 (m, 1H), 1.18-

1.91 (m, 10H). 75 MHz ^{13}C NMR (CDCl_3) δ 1.04, 21.57, 24.03, 38.91, 60.10.

MS (30 eV), m/e (%) 125(28), 110(13), 96(100), 82(100), 69(41).

Azo-1-cyclopropylcyclopentane (113a). A 50 ml 3 neck round bottom flask equipped with a 10 ml addition funnel and a stir bar was charged with 3.0 ml (8.5 mmol) of a 2.8 M $\text{IF}_5/\text{CH}_2\text{Cl}_2$ solution.¹⁰⁹ A 1.7 g (22.1 mmol) portion of pyridine was added and the flask was cooled in a dry ice/ CCl_4 bath under nitrogen. A solution of 1.3 g (10.2 mmol) 1-cyclopropylcyclopentylamine (**180a**) in CH_2Cl_2 was added dropwise to the cooled IF_5 solution. The reaction was stirred at -20 to -10 $^\circ\text{C}$ for one hour, then at -10 to 0 $^\circ\text{C}$ for another hour. After addition of 23 ml H_2O , the organic layer was washed successively with 20 ml 1N HCl, 2 x 12 ml 0.1 M $\text{Na}_2\text{S}_2\text{O}_3$, and 20 ml H_2O . The organic phase was dried over MgSO_4 , filtered and concentrated on a rotovap. The crude product was column chromatographed on 10 g neutral alumina with hexane elution. The product was liquid, yield 24%. 300 MHz ^1H NMR (C_6D_6) δ 0.22-0.40 (m, 8H), 1.00-1.15 (m, 2H), 1.30-1.50 (m, 12H), 2.15-2.25 (m, 4H). 75 MHz ^{13}C NMR (CDCl_3) δ 0.818, 18.26, 24.18, 33.57, 80.28. HRMS Calcd for $\text{C}_{16}\text{H}_{26}\text{N}_2$: 246.20959. Found: 246.21002. UV (hexane) λ_{max} 374 nm, ϵ 20.

1-Cyclopropylcyclohexanol (178b)¹⁵⁴ was prepared in the same manner as **178a** starting with 1.79 g (14.8 mmol) cyclopropyl bromide, 8 ml (13.6 mmol) 1.7 M *tert*-butyllithium/pentane, and 1.30 g (13.3 mmol) cyclohexanone. 1.09 g (59%) of the desired alcohol was obtained. 300 MHz ^1H NMR (CDCl_3) δ 0.30-0.33 (m, 4H), 0.85-0.93 (m, 2H), 1.19-1.59 (m, 10H). 75 MHz ^{13}C NMR (CDCl_3) δ 0.38, 21.88, 22.05, 25.99, 37.32. MS (30 eV), m/e (%) 140(9), 123(5), 112(25), 97(100), 84(28), 55(35).

1-Cyclopropylcyclohexylazide (179b) was prepared in the same manner as **179a** from 0.33 g (2.3 mmol) **178b**, 0.38 g (5.8 mmol) NaN_3 , and

0.4 ml CF_3COOH . Yield 91%. 90 MHz ^1H NMR (CDCl_3) δ 0.38-0.53 (d, 4H), 0.70-2.60 (m, 11H). IR(CCl_4 , cm^{-1}): 2900, 2480, 2065.

1-Cyclopropylcyclohexylamine (180b) was prepared in the same manner as **180a** using 0.26 g (1.6 mmol) **179b** and 0.22 g (5.8 mmol) LAH.¹⁵⁵ 250 MHz ^1H NMR (CDCl_3) δ 0.24-0.28 (m, 4H), 0.79-0.90 (m, 3H), 1.19-1.54 (m, 10H); 65 MHz ^{13}C NMR (CDCl_3) δ -0.45, 21.92, 22.45, 26.07, 38.05, 48.90. MS (30 eV), m/e (%) 139(17), 124(12), 110(15), 95(100), 83(33), 68(12).

Azo-1-cyclopropylcyclohexane (113b) was prepared in the same manner as **113a** using 2.88 g (20.4 mmol) **180b**, 1 ml (16.9 mmol) IF_5 , and 3.51 g (44.4 mmol) pyridine.¹⁰⁹ The crude product was column chromatographed on 30 g neutral alumina with hexane elution to give 0.27 g solid product which was recrystallized from methanol. mp 46-48 °C. Yield = 11%. 300 MHz ^1H NMR (CDCl_3) δ 0.22-0.34 (m, 8H); 0.92-0.97 (m, 2H), 1.25-1.43 (m, 12H); 1.48-1.54 (m, 4H); 1.90-1.95 (m, 4H). 75 MHz ^{13}C NMR (CDCl_3) δ 0.039, 20.04, 22.25, 26.14, 33.23, 68.48. HRMS Calcd for $\text{C}_{18}\text{H}_{30}\text{N}_2$: 274.24089 Found: 274.24111. UV (hexane) λ_{max} 384 nm, ϵ 25.

(1-bromopropylidene)-3-cyclopentane (185). NaBr (2.20 g, 21.4 mmol) was slurried in 50 ml CHCl_3 and cooled to -5 °C in an ice/salt bath. Trifluoroacetic acid (1.6 ml, 1.7 mmol) was added, followed by dropwise addition of **178a** (1.20 g, 9.7 mmol) in 5 ml CHCl_3 . Stirring was continued for 2.5 hours and the reaction was worked up by dilution with 30 ml H_2O , extraction with CHCl_3 , then washing the CHCl_3 solution with saturated aqueous NaHCO_3 solution. The combined organic phases were dried over MgSO_4 , filtered, and concentrated on a rotovap to give 1.19 g (65%) of the desired bromide which was further purified on 30 g neutral alumina and hexane eluent. 300 MHz ^1H NMR (CDCl_3) δ 1.50-1.72 (m, 4H), 2.10-2.30 (m, 4H), 2.50-2.63 (q, 2H, $J = 8.7$

Hz), 3.30 (t, 2H, $J = 8.8$ Hz), 5.20-5.30 (m, 1H). 75 MHz ^{13}C NMR (CDCl_3) δ 26.35, 26.42, 28.93, 33.03, 33.41, 33.74, 116.49, 146.92. MS (30 eV), m/e (%) 190 (5), 188 (5), 109 (31), 95 (42), 81 (15), 79 (14), 67 (100).

Ethyl 3-cyclopentylidene propanoate (187).¹⁵⁶ The nonconjugated ester was prepared by 254 nm irradiation of ethyl 3-cyclopentylpropanoate (**186**),¹⁵⁷ (0.95 g, 5.7 mmol) in 47 ml dry pentane in a 2.3 cm diameter quartz tube under nitrogen. The reaction was followed by capillary GC under the conditions used for hydrocarbon analysis described in the "general information" section. Approximately 20 hours of irradiation time was required to complete the photoisomerization. Yield 99%. 250 MHz ^1H NMR (CDCl_3) δ 1.27 (t, 3H, $J = 6.8$ Hz), 1.56-1.68 (m, 4H), 2.17 (br t, 2H), 2.25 (br t, 2H), 2.98 (d, 2H, $J = 6.0$ Hz, $J = 1.0$ Hz), 4.11 (q, 2H, $J = 7.2$ Hz), 5.4 (br s, 1H). 63 MHz ^{13}C NMR (CDCl_3) δ 14.30, 26.30, 26.50, 29.0, 33.70, 35.30, 60.50, 111.5, 147.4, 172.6. MS (30 eV), m/e (%) 168(88), 140(68), 123(100), 122(51), 95(69), 94(100), 93(67).

(1,1- ^2H -1-hydroxypropylidene)-3-cyclopentane (188). The dideuterated alcohol was prepared by reduction of **187** (0.93 g, 5.5 mmol) with excess LiAlD_4 in ether. The product was isolated by careful dilution with H_2O , filtration, drying over MgSO_4 , and concentration. The alcohol was distilled at 1 mm in a molecular still giving 0.41 g (58%) of the desired product. 300 MHz ^1H NMR (C_6D_6) δ 1.44-1.65 (m, 5H), 2.08-2.21 (m, 6H), 5.09-5.15 (m, 1H). 46 MHz ^2H NMR (C_6D_6) δ 3.40 (br s). 75 MHz ^{13}C (C_6D_6) δ 26.36, 26.42, 28.93, 33.02, 33.78, 115.4, 147.2. MS (30 eV), m/e (%) 125(35), 95(100), 93(61), 67(40).

(1,1- ^2H -1-hydroxypropylidene)-3-cyclopentane, tosyl ester (189). A (0.42 g, 3.2 mmol) portion of alcohol **188** was added to an ice/salt cooled solution of tosyl chloride (0.84 g, 4.4 mmol) in 4 ml pyridine. A white precipitate formed after 30 min but stirring was continued until tlc showed the

reaction to be complete (~ 2 hours). Workup was effected by addition of 40 ml H₂O and extraction with CH₂Cl₂. The CH₂Cl₂ layers were combined and extracted with 2N HCl until the washings were acidic, then dried over K₂CO₃, filtered and concentrated on a rotovap to give 0.64 g (71%) of the desired tosylate. 300 MHz ¹H NMR (CDCl₃) δ 1.50-1.66 (m, 4H), 2.05-2.28 (m, 6H), 2.43 (s, 3H), 5.02-5.09 (m, 1H), 7.31 (d, 2H, J = 8.1 Hz), 7.83 (d, 2H, J = 8.2 Hz). 75 MHz ¹³C (CDCl₃) 21.71, 26.28, 26.37, 28.79, 29.23, 33.71, 113.2, 128.0, 129.83, 133.4, 144.7, 147.6. MS (30 eV), m/e (%) 173 (3), 155(23), 109(100), 95(49), 93(58), 91(84), 83(8), 82(13), 81(14), 80(15), 79(5), 78(8), 65(18), 66(5), 67(20), 68(5), 69 (10).

(1-bromo-1,1-²H-propylidene)-3-cyclopentane (190). Tosylate **189** (0.63 g, 2.2 mmol) was stirred with NaBr (0.33 g, 3.2 mmol) in 7 ml DMF for 2 days,¹¹⁵ at which time tlc (SiO₂, 20% EtOAc/hexane) showed complete reaction. The mixture was worked up by addition of 100 ml H₂O and extraction with ether. The ether solution was washed with H₂O, dried over MgSO₄, filtered, and concentrated on a rotovap. The crude bromide was chromatographed on 12 g silica gel with hexane eluent to afford 0.43 g (100%) of the bromide **190**. 300 MHz ¹H NMR (C₆D₆) 1.35-1.53 (m, 4H), 1.93 (br t, 2H, J = 6.7 Hz), 2.11 (br t, 2H, J = 5.5 Hz), 2.26 (d, 2H, J = 7Hz), 5.06-5.11 (m, 1H). 46 MHz ²H NMR (C₆H₆) 2.93 (br s). 75 MHz ¹³C (C₆D₆) δ 26.47, 26.55, 28.83, 33.27, 33.81, 116.97, 146.26. MS (30 eV), m/e (%) 192(100), 190(100), 111(38), 81(58), 67(38).

Cyclopentanone 2,4,6-triisopropylbenzenesulfonylhydrazone (182).¹⁵⁸ To a solution of 1.90 g (23 mmol) distilled cyclopentanone in 50 ml dry THF was added 6.9 g (23 mmol) solid 2,4,6-triisopropylbenzenesulfonyl hydrazide. The mixture was stirred at room temperature for 30 minutes. The

THF was removed under vacuum and the residual solid was recrystallized by dissolution in warm methanol, cooling in ice and addition of water. The pure product (5.8 g, 70%) was collected by suction and dried under vacuum. Mp 125-130 °C dec. (Lit. 133-134 °C dec.).¹⁵⁸ 90 MHz ¹H NMR (CDCl₃) δ 1.25 (d, 18H), 1.50 - 2.00 (br s, 4H), 2.00 - 2.50 (m, 4H), 2.95 (sept., 1H), 4.30 (sept., 2H), 7.10 (s, 3H, NH & arom. H's).

1-Cyclopentenyl-1-propanol (183).¹⁵⁹ A solution of 2.7 g (7.4 mmol) **182** in 27 ml of dry 50% TMEDA/hexane solution was cooled to -78 °C under nitrogen, and 6.5 ml of 2.2 M n-BuLi/hexane was added dropwise.^{86,87} The resulting dark orange solution was stirred for 15 minutes, and then the dry ice bath was replaced with an ice bath. As the solution warmed, gas was evolved and the solution became less cloudy. Gas evolution was complete after 15 minutes and the solution was recooled to -78 °C. Freshly distilled propionaldehyde (0.77 g, 13 mmol) was added in 6 ml dry hexane. The mixture was stirred for 30 minutes at -78 °C, warmed to 0 °C for 15 minutes, then to room temperature for 30 minutes. Workup was accomplished by addition of 75 ml water and extraction with ether. The combined ether layers were washed with 1N HCl and thrice with water. The organic layer was dried over MgSO₄, filtered, and rotary evaporated to afford **183** (0.72 g, 77%). A portion of the product was purified by preparative GC (Column C, inj = 185 °C, oven = 125 °C, det = 165 °C). For a representative GC trace, see Figure 18 at the end of the experimental section. 300 MHz ¹H NMR (CDCl₃) δ 0.89 (t, 3H, J = 7.4 Hz), 1.60 (m, 3H), 2.27 (quint, 2H, J = 7.4), 2.34 (br m, 4H), 4.18 (t, 1H, J = 6.3 Hz), 5.58 (br d, 1H, J = 1.1 Hz). 75 MHz ¹³C NMR (CDCl₃) δ 9.89, 23.46, 28.46, 31.09, 32.23, 72.83, 125.65, 146.96. MS (30 eV), m/e (%) 126 (58), 97 (100),

79 (61), 69 (56), 67 (62), 57 (17), 55 (18). HRMS Calcd for $C_8H_{14}O$: 126.10446. Found: 126.10475.

1-Cyclopentenyl-1-chloropropane (184). A solution of 1.17 g (4.5 mmol) triphenylphosphine, 0.44 g (3.5 mmol) **183**, and 0.25 ml nonane as an internal standard in 5 ml dry CCl_4 was heated under nitrogen in a 75 °C oil bath.¹¹¹ According to GC, the reaction required about 15 hours. The CCl_4 was removed under vacuum, the remaining solids were rinsed from the reaction flask with hexane, and the heterogenous mixture was filtered through a celite pad. The filtrate was extracted with water and the organic layer was dried over $MgSO_4$, filtered, and concentrated to give 0.31 g (62%) of **184**. A small sample was collected by preparative GC (Column C, inj = 185 °C, oven = 100 °C, det = 155 °C). Figure 17 at the end of the experimental section shows a representative GC trace. 300 MHz 1H NMR ($CDCl_3$) δ 0.94 (t, 3H, J = 7.3), 1.88 (m, 4H,), 2.35 (br m, 4H), 4.50 (t, 1H, J = 6.3), 5.69 (d, 1H, J = 1.9). 75 MHz ^{13}C NMR ($CDCl_3$) δ 11.65, 23.30, 30.34, 30.94, 32.35, 63.37, 128.67, (4° carbon not visible). MS (30 eV), m/e (%) 146 (3), 144 (10), 109 (59), 108 (65), 93 (100), 91 (57), 79 (70), 77 (65), 67 (72). HRMS Calcd for $C_8H_{13}Cl$: 144.07058. Found: 144.07024.

Synthesis of authentic allylic radical dimers (181 & other isomers). The reaction was executed in the special apparatus shown in Figure 33 at the end of the experimental section. A 94 mg portion of lithium dispersion with 1% Na (30% in mineral oil) under an argon atmosphere was washed twice with 5 ml portions of dry THF. A solution of 0.46 g (3.2 mmol) **184** in 5 ml dry THF was added to the lithium and the mixture was immersed up to the solvent line in a laboratory ultrasonic cleaner.¹¹⁰ After one hour of sonication and mechanical stirring under argon, the initially gray suspension

had become orange. Capillary GC analysis after two hours showed complete disappearance of the starting allylic chloride. The reaction was worked up by careful dilution with water and addition of a small amount of saturated aqueous NH_4Cl . The mixture was extracted thrice with hexane and dried over MgSO_4 . The resulting solution was concentrated to 5 ml by short path distillation. GC/MS analysis showed the presence of n-propylcyclopentene, propylidenecyclopentane, and numerous dimers of the resulting 1-cyclopentyl-1-propyl radical. A typical fragmentation pattern for these dimers was m/e (%) 218 (6), 189 (13), 109 (93), 108 (100), 93 (58), 67 (65). The products were analyzed by capillary GC under the standard conditions for hydrocarbon products given under "General Information". Representative GC traces can be found in Figures 31 and 32 at the end of the experimental section.

Authentic synthesis of decomposition products from azoalkanes 113a,b.

Cyclopropylcyclopentane (118a).¹⁶⁰ A 60.5 mg portion of azoalkane **113a** and 83 mg thiophenol in 0.5 ml pentane was transferred to an NMR tube fitted with a serum stopper and a drying tube. The solution was cooled to -78°C and irradiated at 366 nm for 6.5 hours. Cyclopropylcyclopentane was isolated from the photolysate by preparative GC. (See Figure 19 at the end of the experimental section for a representative GC trace). 300 MHz ^1H NMR (CDCl_3) δ 0.024-0.073 (m, 2H), 0.33-0.37 (m, 2H), 0.57-0.61 (m, 1H), 1.16-1.32 (m, 3H), 1.45-1.52 (m, 2H), 1.55-1.62 (m, 2H), 1.63-1.76 (m, 2H). 75 MHz ^{13}C NMR (CDCl_3) δ 3.54, 15.98, 25.20, 32.09, 45.13. MS (30 eV), m/e (%) 110(5), 95(14), 82(84), 81(76), 69(60), 67(100), 55(15).

Propylidenecyclopentane (119a).¹⁶¹ To a slurry of 5.9 g (15.4 mmol) of n-propyl-triphenylphosphonium bromide in 35 ml ether under nitrogen was added 7 ml (15.4 mmol) of 2.2 M n-butyllithium/hexane. The deep red solution was stirred for 5 hours. A solution of 1.2 g (14.3 mmol) cyclopentanone in 8 ml ether was added dropwise with stirring. The resulting thick mixture was stirred vigorously and refluxed overnight. After filtering the reaction mixture through a coarse frit, the solids were washed with ether and the combined ether phases were extracted with H₂O. The combined organic layers were dried over MgSO₄, filtered, and distilled through a short vigreux column.

Propylidenecyclopentane was isolated from the concentrated ether solution by preparative GC. (See Figure 27 at the end of the experimental section for a representative GC trace). 300 MHz ¹H NMR (CDCl₃) δ 0.87-0.96 (t, 3H), 1.52-1.66 (m, 4H), 1.91-1.98 (quintet, 2H), 2.13-2.22 (m, 4H), 5.20-5.23 (m, 1H). 75 MHz ¹³C NMR (CDCl₃) δ 14.31, 22.90, 22.46, 26.54, 28.49, 33.61, 122.02, 142.54. MS (30 eV), m/e (%) 110(28), 95(29), 81(37), 67(100), 55(5).

1-Cyclopropylcyclopentene (120a).¹⁶² A 10 cm x 13 mm pyrolysis tube was attached to a side arm adapter connected to a 5 ml round bottom flask. A plug of glass wool was inserted into the tube followed by 2.5 cm Brockmann activity grade 1, neutral alumina for chromatography (Baker). A serum stopper was wired to the top of the tube, which was wrapped once with electrical heating tape. A thermometer was inserted between the glass and the tape. The side arm was connected to a vacuum pump at 4 mm, the tube was heated to 210-220 °C, and the receiver flask was cooled in liquid nitrogen. Nitrogen was bled through the apparatus via a very small bore needle. A 90 µl portion of 1-cyclopropylcyclopentanol (**178a**) was delivered dropwise through the serum stopper from a 100 µl syringe. The nitrogen bleed was removed and the

pyrolysis tube was heated to 280 °C for 10 min. After the system had cooled, it was brought to atmospheric pressure with nitrogen. The receiver flask contained 1-cyclopropylcyclopentene plus water. 300 MHz ^1H NMR (CDCl_3) δ 0.43-0.49 (m, 2H), 0.57-0.63 (m, 2H), 1.47-1.50 (m, 1H), 1.79-1.86 (m, 2H), 2.08-2.16 (m, 2H), 2.10-2.30 (m, 2H), 5.36 (t, 1H). 75 MHz ^{13}C NMR (CDCl_3) δ 5.24, 12.12, 23.28, 32.26, 32.50, 122.14, 146.02. MS (30 eV), m/e (%) 108(65), 93(110), 79(72), 77(45), 67(27).

1-n-Propylcyclopentanol (192a).¹⁶³ A Grignard reagent was prepared by addition of 3.8 g (30.9 mmol) n-propyl bromide in 10 ml ether to 0.87 g (0.036 g atom) magnesium turnings in 35 ml ether. After refluxing the cloudy solution for 1h, it was cooled in an ice/salt bath and a solution of 2.4 g (28.6 mmol) cyclopentanone in 5 ml ether was added. The solution was stirred for several hours at room temperature, then refluxed for 15 minutes. Workup was effected by diluting with 5% HCl and extracting twice with ether. The combined ether extracts were dried over MgSO_4 , filtered, and concentrated by rotary evaporation. Yield 2.74 g (75%). 250 MHz ^1H NMR (CDCl_3) δ 0.92 (t, 3H, J = 8.4 Hz), 1.38-1.80 (m, 12H). 65 MHz ^{13}C NMR (CDCl_3) δ 14.68, 17.91, 23.77, 39.63, 43.85, 82.58.

1-n-Propylcyclopentene (117a)¹⁶⁴ was prepared by pyrolysis of the above alcohol over alumina in the same manner used to prepare **120a**. Preparative GC (Column B, inj = 180 °C, oven = 160 °C, det = 190 °C, flow = 38 ml/min) was required to isolate a pure sample of **117a**, which eluted before **119a**. (See Figure 20 at the end of the experimental section for a representative GC trace). 300 MHz ^1H NMR (CDCl_3) δ 0.89 (t, 3H, J = 7 Hz), 1.41-1.49 (sextet, 2H, J = 7 Hz), 1.81-1.86 (q, 2H, 7 Hz), 2.00-2.05 (t, 2H, J = 7 Hz), 2.21-2.28 (br d, 4H), 5.31 (br s, 1H). 75 MHz ^{13}C NMR (CDCl_3) δ 14.13,

21.08, 23.53, 32.51, 33.44, 35.09, 123.21, 145.00. MS (30 eV), m/e (%) 110(18), 95(7), 81(22), 67(100).

Cyclopropylcyclohexane (118b).¹⁶⁵ Zinc dust (1.05 g 0.016 g atom) and CuCl (1.6 g, 16.1 mmol) were slurried in 22 ml ether and the mixture was refluxed with vigorous mechanical stirring for 30 min. Vinylcyclohexane (0.85 g, 7.7 mmol) was added followed by 2.17 g (8.1 mmol) CH₂I₂. The reaction was vigorously stirred and refluxed for 24 hours and was then filtered through a celite pad. The filtrate was washed twice with saturated NaCl solution, dried over MgSO₄, filtered, and concentrated by careful distillation through a short vigreux column. Cyclopropylcyclohexane was obtained by preparative GC. (See Figure 21 at the end of the experimental section for a representative GC trace). (Column A, inj = 160 °C, oven = 90 °C, det = 150 °C, flow = 30 ml/min.). 300 MHz ¹H NMR (CDCl₃) δ 0.14 (d, 2H, J = 4.7 Hz), 0.33 (d, 2H, J = 6.8 Hz), 0.40-0.52 (m, 1H), 0.95-1.23 (m, 6H), 1.65-1.85 (m, 5H). 75 MHz ¹³C NMR (CDCl₃) δ 3.15, 18.00, 26.49, 26.76, 33.17, 43.29. MS (30 eV), m/e (%) molecular ion was not visible, 96(37), 81(100), 67(38), 55(48).

Propylidenecyclohexane (119b)¹⁶⁶ was prepared in the same manner as **119a** from 5.93 g (15.4 mmol) n-propyltriphenylphosphonium bromide, 7 ml (15.4 mmol) 2.2 M n-butyllithium/ hexane, and 1.48 (15.1 mmol) cyclohexanone. The product was isolated by preparative GC (Column A, inj = 160 °C, oven = 100 °C, det = 160 °C, flow = 30 ml/min.) (See Figure 22 at the end of the experimental section for a representative GC trace). 300 MHz ¹H NMR (CDCl₃) δ 0.924 (t, 3H, J = 7 Hz), 1.44-1.51 (br s, 6H), 1.93-2.13 (m, 6H), 5.06 (t, 1H, J = 7 Hz). 75 MHz ¹³C NMR (CDCl₃) δ 14.95, 20.42, 27.09, 27.98, 28.66, 28.77, 37.20, 123.25, 139.02. MS (30 eV), m/e (%) 124 (100), 109 (27), 95(39), 81(70), 67(48), 55(15).

1-Cyclopropylcyclohexene (120b)¹⁵⁴ was prepared from 1-cyclopropylcyclohexanol by the same procedure used to prepare **120a**. A pure sample of **120b** was isolated by preparative GC (Column A inj = 160 °C, oven = 120 °C, det = 150 °C, flow = 30 ml/min.) 300 MHz ¹H NMR (CDCl₃) δ 0.38-0.46 (m, 2H), 0.47-0.54 (m, 2H), 1.27-1.29 (br t, 1H), 1.53-1.63 (m, 4H), 1.81 (br s, 2H), 1.97 (br s, 2H), 5.43 (s, 1H). 75 MHz ¹³C NMR (CDCl₃) δ 4.09, 17.50, 22.80, 119.72, 138.24. MS (30 eV), m/e (%) 122(51), 107(44), 93(34), 91(28), 79(100).

1-n-Propylcyclohexanol (192b) was prepared by the procedure used to make 1-n-propylcyclopentanol from 3.8 g (31 mmol) n-propyl bromide, 0.85 g (0.035 g atom) Mg turnings, and 2.8 g (28 mmol) cyclohexanone.

1-n-Propylcyclohexene (117b)¹⁵⁸ was prepared from 1-n-propylcyclohexanol by the procedure used for **117a**. A pure sample of **117b** was isolated by preparative GC (Column B, inj = 180 °C, oven = 160 °C, det = 190 °C, flow = 38 ml/min.) (See figure 23 at the end of the experimental section for a representative GC trace). ¹H NMR (300 MHz, CDCl₃) δ 0.86 (t, 3H), 1.35-1.43 (m, 2H), 1.51-1.61 (m, 4H), 1.86-1.91 (br t, 4H), 1.96 (br s, 2H), 5.37 (br s, 1H). ¹³C NMR (75 MHz, CDCl₃) δ 13.94, 20.66, 22.72, 23.14, 25.32, 28.30, 40.32, 120.76, 137.95; MS (30 eV), m/e (%) 124(19), 95(30), 82(57), 81(100), 67(38), 55(8).

Synthesis of C₈ hydrocarbons suspected of being the "mystery product" in figure 7.

3-cyclopropylcyclopentanone (173). To a cooled (-78 °C) solution of cyclopropyl bromide (0.89 g, 7.4 mmol) in 7 ml ether was added a 1.5 M pentane solution of *tert*-butyllithium (5.0 ml, 7.5 mmol). After 20 min., another 10 ml ether was added to dissolve the white precipitate which had formed. In a

separate flask, CuCN (0.37 g, 4.1 mmol) was heated under vacuum with a hot air gun, cooled, and purged with nitrogen several times to ensure dryness. The cream colored powder was slurried in 10 ml ether and cooled to -78 °C. The cyclopropyllithium prepared in the first flask was transferred to the CuCN flask via cannula, and rinsing with several portions of ether ensured complete transfer of the cyclopropyllithium. The reaction was stirred for 40 min. at -78 °C, then warmed to 0 °C briefly in an unsuccessful attempt to dissolve some solids which had formed. The heterogeneous mixture was recooled to -78 °C, and 2-cyclopentenone (0.33 g, 4.0 mmol) was added in 4 ml ether. An immediate color change from beige to yellow was observed. The reaction was stirred for 3 hours and then quenched with 40 ml of a 10% NH₄OH/saturated NH₄Cl solution.^{82,102} The aqueous layer was extracted twice with ether, dried over MgSO₄, filtered and concentrated on a rotovap. In this manner, 0.46 g product was obtained contaminated with a small amount of alcohol from 1,2-addition of cyclopropyllithium to 2-cyclopentenone. 90 MHz ¹H NMR (CDCl₃) δ 0.0-0.6 (m, 4H), 0.8-1.4 (m, 2H), 1.4-2.6 (m, 6H). 75 MHz ¹³C NMR (CDCl₃) δ 3.31, 3.43, 15.41, 29.08, 38.47, 41.83, 44.80, 220.12. MS (70 eV), m/e (%) 124(41), 109(9), 96(65), 83(50), 81(45), 67(100), 55(88), 41(26), 39(35), 28(22).

3-cyclopropylcyclopentanone tosylhydrazone (174). Ketone **173** (0.46 g, 3.7 mmol) was added to a solution of p-toluenesulfonylhydrazide (0.63 g, 3.4 mmol) and 1 ml of 60% MeOH/H₂O. Enough 60% MeOH/H₂O was added to give a homogenous mixture at 60 °C. After 5 min., a yellow oil separated from the reaction and heating was discontinued. After standing in the refrigerator for 1 hour, a solid had formed. The cold solution was filtered by suction, and the desired tosylhydrazone was dried under vacuum and used immediately in the next step.

3&4-cyclopropylcyclopentene (160 & 175). Tosylhydrazone **174** (0.71 g, 2.4 mmol) was slurried in 6 ml ether and cooled to 0 °C. A 1.4 M methyllithium solution in hexane (6.4 ml, 8.4 mmol) was added dropwise under nitrogen and formation of an orange color was observed along with gas evolution. After stirring overnight at ambient temperature, the brown reaction was worked up by cooling to 0 °C and carefully adding H₂O. Extraction with ether, drying over MgSO₄, filtration, concentration by careful distillation, and preparative GC on column B gave an inseparable mixture of **160** and **175**.

(See Figure 24 at the end of this section for a representative GC trace).

Capillary GC analysis of the preparative GC purified olefins showed two major peaks and impurity with a similar (but earlier) retention time. 300 MHz ¹H NMR (CDCl₃) δ 0.06-0.11 (m, 4H), 0.35-0.41 (m, 4H), 0.58-0.70 (m, 1H), 0.70-0.86 (m, 1H), 0.83 - 0.91 (m, impurity), 1.50-1.80 (m, 2H), 1.60 (H₂O), 2.00-2.55 (m, 8H), 5.60-5.80 (m, 4H), 7.10-7.31 (m, impurity). 75 MHz ¹³C (CDCl₃) δ 2.62, 2.94, 3.35, 15.82, 16.60, 29.47, 31.82, 38.23, 42.33, 49.84, 127.97, 128.78, 129.66, 130.58, 133.90 (contains olefinic impurity). MS (30 eV), m/e (%) 108(8), 93(24), 9(15), 79(75), 78(100), 67(60), 66(71).

Cyclopropyl allyl ketone (176). The synthesis of **176** required the use of acid-free Zn(Ag)¹⁰⁵ couple which was prepared as follows. A solution of glacial acetic acid (200 ml) and AgOAc (0.10 g) was heated to reflux and powdered Zn (100 g) was added all at once. The mixture was stirred vigorously with a mechanical stirrer for 0.5 min., then cooled in an ice bath and filtered by suction in a Buchner funnel. The solid was washed twice with 100 ml portions of anhydrous ether, and transferred to a large frit where it was washed four more times with 100 ml portions of anhydrous ether and dried under vacuum. A portion of the dried solid was slurried in water and the pH of the supernatant

liquid was determined to be 6 with pH paper. Because the presence of even trace amounts of acid is detrimental to the coupling reaction to follow, the solid was washed with 250 ml more anhydrous ether and dried under vacuum. To a mixture of cyclopropyl cyanide (0.61 g, 9.1 mmol), Zn(Ag) couple (0.81 g, 12.4 mmol) and 25 ml ether was added allyl bromide (1.47 g, 12.2 mmol) in 5 ml ether. The reaction was stirred vigorously with a mechanical stirrer and heated at reflux for 30 min., then cooled to room temperature and left to stir overnight during which time the color changed from grey to white. The reaction was poured into 30 ml saturated NH_4Cl and ice, followed by stirring for 10 minutes. The aqueous phase was extracted twice with ether, and the combined ether layers were dried over MgSO_4 , filtered, concentrated on a rotovap and the last traces of solvent were removed with a vacuum pump. In this manner, 0.56 g (65% yield) of the desired β,γ -unsaturated ketone was obtained. 300 MHz ^1H NMR (CDCl_3) δ 0.84-0.94 (m, 2H), 0.96-1.02 (m, 2H), 1.96-1.98 (m, 1H), 3.30 (d, 2H, $J = 6.8$ Hz), 5.11-5.19 (m, 2H), 5.89-5.95 (m, 1H). 75 MHz ^{13}C (CDCl_3) δ 11.12, 20.13, 40.39, 116.74, 130.80, 208.87.

2-cyclopropyl-1-trimethylsilyl-4-pentene-2-ol (177). A 3 neck, round bottom flask containing $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ (2.73 g, 7.33 mmol) was heated in a 140-145 $^\circ\text{C}$ oil bath at 5 mm pressure for 2 hours. During this period of dehydration, the initially white crystalline material turned to a powder which was cooled to ambient temperature and slurried in THF for 2 hours under nitrogen. The slurry was then cooled to -78 $^\circ\text{C}$ and a 1.05 M pentane solution of $\text{Me}_3\text{SiCH}_2\text{Li}$ (Aldrich, 6.5 ml, 6.9 mmol) was added dropwise. The resulting solution was stirred for 30 minutes. The reaction color changed from tan to black, then back to tan during the addition.¹⁰⁶ A solution of **176** (0.64 g, 5.8 mmol) in 5 ml THF was added dropwise and stirring was continued for 3.5

hours. Workup was effected by addition of TMEDA (0.85 g, 7.3 mmol) and warming to ambient temperature over 15 minutes. The mixture was poured into a separatory funnel containing 200 ml saturated aqueous NaHCO_3 and 150 ml CH_2Cl_2 . The aqueous phase was extracted twice with CH_2Cl_2 and the combined organic layers were washed with brine, dried over MgSO_4 , filtered and concentrated on a rotovap, and then with a vacuum pump. In this manner, 1.12 g (98% yield) of the desired alcohol was obtained. 90 MHz ^1H NMR (CDCl_3) δ 0.10 (br s, 9H), 0.20-0.60 (m, 4H), 0.70-1.20 (m, 4H), 2.10-2.50 (m, 2H), 4.90-5.25 (m, 2H), 5.40-6.20 (m, 1H).

2-cyclopropyl-1,4-pentadiene (172). A mixture of **177** (0.57 g), pyridine (1.45 ml, 1.9 mmol), 12 drops 48% aqueous HF, and 23 ml CH_3CN were stirred at ambient temperature for 2 hours. The reaction was worked up by pouring into 25 ml saturated aqueous NaHCO_3 and 100 ml pentane. The aqueous phase was extracted twice with pentane and the combined organic layers were washed with brine, dried over MgSO_4 , filtered, and concentrated by careful distillation. The desired olefin **172** was obtained by preparative GC on column B. (See Figure 25 at the end of this section for a sample GC trace). 300 MHz ^1H NMR (CDCl_3) δ 0.45 (m, 2H), 0.62 (m, 2H), 1.33 (m, 1H), 2.75 (d, 2H, $J = 9$ Hz), 4.64 (s, 1H), 4.66 (s, 1H), 5.05 (d, 1H, $J = 10$ Hz), 5.09 (br s, 1H), 5.80 (m, 1H). 75 MHz ^{13}C NMR (CDCl_3) δ 6.16, 16.22, 40.27, 107.27, 116.05, 136.69, 4°C not visible. MS (30 eV), m/e (%) 108(8), 93(100), 91(52), 81(83), 80(61), 79(75), 77(38), 67(45).

Cyclopropylidene-cyclopentane (171).¹⁰⁴

Cyclopropyltriphenylphosphonium bromide (1.72 g, 4.5 mmol) was slurried in 30 ml ether, and *n*-butyllithium (2.0 ml, 4.4 mmol) was added dropwise. Appearance of an intense orange color signaled formation of the required ylide,

and the reaction was stirred vigorously with a mechanical stirrer for 2 hours. Cyclopentanone (0.34 g, 4.0 mmol) in 10 ml ether was added and the reaction was brought to reflux and allowed to continue stirring overnight. Analytical GC showed complete disappearance of the starting ketone, and the reaction was worked up by vacuum filtration through a coarse frit. The filtrate was washed once with H₂O and the aqueous layer was extracted twice with ether. The combined organic layers were dried over MgSO₄, filtered, and concentrated to 8 ml by careful distillation at atmospheric pressure. The desired olefin was isolated by preparative GC on column B under the following conditions: Inj.= 150 °C, oven = 175 °C, det.= 150 °C, flow = 21.4 ml/min. (See Figure 26 at the end of this section for the GC trace.). 300 MHz ¹H NMR (CDCl₃) δ 0.95-0.97 (quint, 4H, J = 2 Hz), 1.66-1.71 (m, 4H), 2.29-2.35 (m, 4H). 75 MHz ¹³C NMR (CDCl₃) δ 2.27, 26.78, 32.15.

Synthetic steps leading to azoalkane 200.

3-Bromopropyl phenylsulfide. This compound was prepared according to the procedure of Bakuzis, et al.¹⁶⁷ 250 MHz ¹H NMR (CDCl₃) δ 2.18 (quint., 2H, J = 6.7 Hz), 3.10 (t, 2H, J = 6.9 Hz), 3.50 (t, 2H, J = 6.3 Hz), 7.25-7.35 (m, 5H). 75 MHz ¹³C NMR (CDCl₃) δ 31.76, 31.99, 32.07, 126.34, 129.06, 129.62, 135.60.

Methyl (2,2-dimethyl-5-thiophenoxy) pentanoate (193).¹¹⁵ A mixture of diisopropyl amine (7.20 g, 71 mmol) and 142 ml dry THF was cooled to -78 °C, and n-butyllithium (40.0 ml, 92 mmol) was added dropwise. Stirring was continued for 15 min. at -78 °C, then the reaction was warmed to 0 °C and stirred an additional 15 min. before introduction of methyl isobutrate (7.3 g, 71 mmol). Stirring was continued for 1 hour at 0 °C, after which time the reaction was recooled to -78 °C. HMPA (14 ml) was added, followed by 3-bromopropyl

phenyl sulfide (15.13 g, 66 mmol). The reaction was allowed to stir overnight with no further addition of dry ice to the cooling bath. The reaction was poured into 500 ml H₂O and extracted 4 times with 100 ml portions of CH₂Cl₂. The combined organic layers were washed once with 2M HCl and 5 times with 75 ml portions of H₂O. The organic phase was dried over MgSO₄, filtered, concentrated on a rotovap, and pumped to remove any residual THF. The crude product was distilled through a short Vigreux column, bp = 140-145 °C (0.6 mm). 90 MHz ¹H NMR (CDCl₃) δ 1.15 (s, 6H), 1.41-1.73 (m, 4H), 2.85 (t, 2H), 3.60 (s, 3H), 7.10-7.38 (m, 5H). MS (45 eV), m/e (%) 252 (44), 193 (9), 143 (100), 123 (42), 110 (88), 109 (47), 83 (85).

Methyl (2,2-dimethyl-5-phenylsulfoxy) pentanoate (194).¹¹⁸

Sulfide **193** (10 g, 40 mmol) was dissolved in 200 ml CH₂Cl₂ and cooled to -78 °C under nitrogen. A solution of MCPBA (Sigma, 85%, 8.04 g, 40 mmol) in 250 ml CH₂Cl₂ was added dropwise. Upon completion of the addition, TLC analysis (40% EtOAc, hexane) showed no remaining starting material. The reaction was poured into a mixture of 400 ml 10% Na₂SO₃ and 400 ml ether. The aqueous phase was extracted thrice with 250 ml portions of ether and the combined organic layers were washed 4 times with saturated NaHCO₃ solution, twice with H₂O, dried over MgSO₄, and filtered. The product was isolated by concentration on a rotovap. 90 MHz ¹H NMR (CDCl₃) δ 1.10 (s, 6H), 1.61 (br t, 4H), 2.60-2.90 (m, 2H), 3.60 (s, 3H), 7.40-7.70 (m, 5H).

2,2-dimethyl-5-phenylsulfoxy-cyclopentanone (195).¹¹⁸ LDA was prepared by addition of n-butyllithium (4.0 ml, 9.2 mmol) to a cooled (-78 °C) solution of diisopropyl amine (0.91 g, 9.0 mmol) in 37 ml THF. The reaction was stirred at -78 °C for 30 min., and addition of **194** gave a bright yellow solution. The reaction was stirred for 1 hour at -78 °C, then one hour at 0 °C.

TLC analysis (SiO₂, 40% EtOAc/hexane) showed complete disappearance of starting material. The reaction was quenched with a few ml of saturated NH₄Cl solution, then poured into a mixture of ether and H₂O. The organic layer was washed several times with H₂O, dried with MgSO₄, filtered, concentrated on a rotovap, and pumped to remove the last traces of ether. The product (0.92 g, 100%), obtained as a yellow solid, was used immediately in the next step.

2,2-dimethyl-4-cyclopentenone (196).¹¹⁸ The β -keto sulfoxide **195** was pyrolyzed by distillation at 0.6 mm, 110-150 °C. The product was collected in a dry ice/acetone cooled receiver, and was further purified by flash distillation at 0.4 mm. Yield = 32%. 90 MHz ¹H NMR (CDCl₃) δ 1.10 (s, 6H), 2.50 (t, 2H), 6.10 (dt, 1H), 7.60 (dd, 1H).

1-cyclopropyl-2,2-dimethyl-4-cyclopentenol (197). The preparation of this hindered, tertiary alcohol was carried out in the glassware shown in figure 33 located at the end of the experimental section. Li dispersion (Alfa, 30 % in mineral oil, 2 % Na, 0.20 g) was weighed into the bottom of the reaction vessel, and the rest of the apparatus was assembled. The mineral oil was removed from the metal by washing twice with 5 ml THF and twice with 5 ml pentane. THF (10 ml) was added to the free Li sand, and then cyclopropyl bromide (0.76 g, 6.3 mmol) was added. The reaction was immersed to the solvent line in a standard Branson laboratory ultrasonic cleaner. Stirring with sonication was begun, and ketone **196** (0.35 g, 3.2 mmol) in 4 ml THF was added almost immediately. Stirring and sonication were continued while the reaction was monitored by GC. After 35-40 min., **196** had disappeared and the reaction was quenched carefully with 100 ml H₂O. The aqueous phase was extracted with several portions of ether and the combined organic layers were washed with H₂O and dried over K₂CO₃. Filtration and rotary evaporation of

solvent gave **197** in 92% yield. 250 MHz ^1H NMR (CDCl_3) δ 0.20-0.60 (m, 4H), 0.90-1.10 (m, 1H), 1.15 (s, 6H), 2.20 (dd, 2H, $J = 14$ Hz), 5.38 (m, 1H), 5.90 (m, 1H). 75 MHz ^{13}C NMR (CDCl_3) δ 1.11, 2.07, 15.73, 23.56, 25.18, 47.42, 133.40, 133.74.

PhSH Trapping Studies of Radicals 113a,b

113a. Six solutions of 0.0187 M azoalkane, 0.0214 M decane (internal standard) and PhSH in $\text{C}_6\text{H}_5\text{F}$ were prepared for photolysis at 366 nm. The concentrations of PhSH were 0.0322, 0.0397, 0.0585, 0.1299, 0.2342, 0.2938 M. Irradiation was carried out for 35 min at 24.7 °C. Capillary GC analysis of the hydrocarbon product mixtures gave the results listed in Table I. A similar experiment at 58.5 °C employed azoalkane and decane concentrations of 0.0103 M and 2.61×10^{-3} M, respectively. The thiol concentrations were 0.0388, 0.0451, 0.0681, 0.1443, 0.2269, 0.3251 M. Results are given in Table II. A representative GC trace of the hydrocarbon products is shown below and the conditions are given under "General Information".

113b. An experiment similar to that with **113a** was carried out at 25.0 °C. The concentration of azoalkane and decane was 0.0142 M and 3.40×10^{-3} M, respectively, while the PhSH was 0.0388, 0.0451, 0.0681, 0.1181, 0.2017, 0.3126 M. Results are given in Table III. A representative GC trace is shown in Figure 35 and conditions are located under "General Information".

Figure 34. Representative GC trace of hydrocarbons 117a-120a obtained from photolysis of azoalkane 113a.

Figure 35. Representative GC trace of hydrocarbons 118b-120b obtained from photolysis of azoalkane 113b.

Attempt to trap cyclopropylcyclopentane from ring closure of homoallylic radical 115. A degassed, sealed NMR tube containing 0.53 M bromide **185**, 0.56 M Bu₃SnH, and 0.379 M decane (internal standard) was irradiated with a sun lamp at 25 °C. After 45 min. of irradiation, disappearance of the bromide was observed by 250 MHz ¹H NMR. The sample was worked up by dilution with 5 ml MeOH which had been treated with a small pebble of Na. After stirring 5-10 min., the solution was flash distilled with slight warming from an air gun to ensure complete transfer of C₈ products. The following products were obtained: 97.5% **119a**, 1.7% **117a**, 0.70% **120a**, and 0.07% **118a** in an overall yield of 90%.

Deuterium scrambling experiments on (1-bromo-1,1-²H-propylidene)-3-cyclopentane (190). A solution of 0.0404 M bromide **190**, 0.0139 M C₆D₆, and 0.0533 M Bu₃SnH was prepared in C₆H₆, degassed and sealed in a 5 mm NMR tube. The solution was irradiated with a sun lamp at 26 °C and was followed by ²H NMR. The bromide signal at 2.9 ppm disappeared as two new signals at 0.93 and 1.9 ppm grew in. The new signals represent propylidenecyclopentane deuterated at either the homoallylic (**208**) or allylic (**209**) position respectively. The ratio of signals upon complete reaction of the bromide was 3.65:1, respectively.

Identification of products from the triplet sensitized photolysis of 1-cyclopropyl-2,3-diazabicyclo[2.2.1]-hept-2-ene (123).

Approximately 100 mg of **123** isolated by preparative GC (column E), and 5.4 mg xanthone in 0.5 ml pentane were photolyzed at 366 nm until complete disappearance of the azoalkane was observed by GC (column E, inj = 130 °C, oven = 177 °C, det = 173 °C). The photoproducts were separated and

collected by preparative GC (column B, inj = 191 °C, oven = 177 °C, det = 171 °C, flow = 46 ml/min). (See figure 28 at the end of this section.)

1-Cyclopropylbicyclo[2.1.0]pentane (107). 300 MHz ^1H NMR (CDCl_3) δ -0.17 to -0.14 (m, 1H), 0.11-0.16 (m, 1H), 0.27-0.50 (m, 3H), 0.51-0.53 (m, 1H), 0.99-1.05 (m, 1H), 1.22-1.35 (m, 1H), 1.35-1.45 (m, 1H), 1.45-1.58 (m, 1H), 1.93 (d, 2H, J = 1.7 Hz). 75 MHz ^{13}C (CDCl_3) δ 2.56, 3.24, 12.61, 16.64, 19.91, 21.41, 26.07, 4° carbon not visible. MS (30 eV), m/e (%) 93(45), 91(48), 80(46), 79(100), 77(42), 67(13).

Z-3-Propylidenecyclopentene (108Z). 300 MHz ^1H NMR (CDCl_3) δ 0.98 (t, 3H, J = 6.6 Hz), 2.05 - 2.25 (m, 2H), 2.50 (br s, 4H), 5.14 (t, 1H, J = 7.2 Hz), 6.08 (br s, 1H), 6.38 (d, 1H, J = 2.7 Hz). 75 MHz ^{13}C (CDCl_3) δ 14.61, 22.26, 28.90, 31.04, 119.6, 129.7, 137.5, 4°C not visible. MS (30 eV), m/e (%) 108(10), 93(100), 91(40).

E-3-Propylidenecyclopentene (108E). 300 MHz ^1H NMR (CDCl_3) δ 0.98 (t, 3H, J = 5.4 Hz), 2.05 (m, 2H), 2.50 (br s, 4H), 5.30 (t, 1H, J = 7.2 Hz), 5.98 (t, 1H, J = 2.5 Hz), 6.12 (d, 1H, J = 5.5 Hz). 75 MHz ^{13}C (CDCl_3) δ 14.10, 22.86, 25.68, 31.92, 121.2, 134.5, 135.88, 4°C was not visible. MS (30 eV), m/e (%) 108(10), 93(100), 91(40).

300 MHz ^1H NMR NOE difference experiment used to distinguish (108E) and (108Z). The sample of (108Z) was irradiated at the 2.15 ppm signal and Nuclear Overhauser enhancement of the triplet at 6.38 ppm was observed in a typical difference spectrum. In the same manner, the sample of (108E) was irradiated at the 2.05 ppm signal. No enhancement of the 6.12 ppm peak was observed, but instead, the signal at 2.50 ppm was enhanced.

Figure 36. ^1H chemical shifts of relevance to NOE difference experiments.

1 & 2-n-propyl cyclopentadiene (169&170). A 250 ml, 3 neck, round bottom flask was fitted with a pressure equalized addition funnel, a reflux condenser, and a nitrogen inlet. NaH, (1.07 g, 23.7 mmol) was added and washed three times with freshly distilled pentane. The NaH was overlaid with 50 ml THF and 1.6 ml freshly cracked cyclopentadiene was added dropwise with stirring. Upon warming to 40 °C, gas evolution was observed and monitored by water displacement. An additional 0.5 ml cyclopentadiene was added after insufficient gas evolution was observed. A total of 300 ml gas was evolved (0.0122 mol @ STP). The reaction was cooled to room temperature at which time the solution had turned deep purple. n-Propyl bromide (1.25 g, 10.2 mmol) in 9 ml THF was added dropwise to the room temperature solution. The reaction was stirred overnight and was worked up by quenching with 60 ml saturated NH_4Cl solution. The aqueous phase was extracted twice with 50 ml portions of pentane and the combined pentane phases were dried over MgSO_4 and filtered. A 50 ml portion of this pentane solution was concentrated to 10 ml by careful rotary evaporation. A sample of pure n-propylcyclopentadienes was obtained from the concentrated solution by preparative GC on column B. Inj.=200 °C, oven = 179 °C, det.= 183 °C, flow = 43 ml/min, and the exit port was heated by a nichrome wire connected to a variac. 300 MHz ^1H NMR

(CDCl₃) δ 0.92-0.97 (m, 6H, 2 superimposed methyl triplets), 1.52-1.62 (m, 4H), 2.32-2.41 (m, 4H), 2.68 (d, 2H, $J = 1.1$ Hz), 2.95 (d, 2H, $J = 1.3$ Hz), 6.01-6.46 (m, 6H).

Direct irradiation of 123. A sample of 0.0175 M **123** in pentane at 23 °C was irradiated at 313 nm for 20 min. Capillary GC analysis showed the products to be 99.6% 1-cyclopropyl-bicyclo[2.2.1]pentane **107** and 0.4% 3-propylidenecyclopentene (**108Z**).

Triplet sensitized photolysis of 123. A solution of 0.05515 M **123**, 0.0539 M decane (internal standard), and 2.325×10^{-3} M Michler's ketone (triplet sensitizer) in fluorobenzene was prepared. Seven aliquots of this solution were irradiated at 366 nm and 43.8-44.0 °C for varying periods of time to ensure that product ratios did not vary with the duration of photolysis. The results are given in Table VIII.

Table VIII. Product Ratios in the Triplet Sensitized Photolysis of **123**.

Time, min	% Conversion ^a	107/108 ^b	Balance ^c
1	20.3	1.38	95.1
2	33.3	1.36	93.5
5	74.0	1.36	96.1
16	80.0	1.36	95.5
30	98.0	1.35	93.6
55	100	1.36	93.9

^a. Percent azoalkane reacted. ^b. ± 0.02 . ^c. total yield of **107** and **108**.

The remaining samples were irradiated at 366 nm for a period of 1 hour at various temperatures. The product mixtures were analyzed by capillary GC and the results are given in Table VI (in the "Biradicals" chapter).

Thermolysis of 123. Degassed, sealed NMR samples of **DBH** and **123** in toluene-*d*₈ were thermolyzed simultaneously at 161.6 °C. The

disappearance of azoalkane bridgehead hydrogen(s) was followed by 90 MHz ^1H NMR through 10 half lives, using the solvent aromatic protons as a standard. Plots of $\log_e$ of the corrected peak area versus time were linear with slopes of $-1.59 \times 10^{-4} \text{ s}^{-1}$ ($r = -0.9982$) for **DBH**, and $-4.72 \times 10^{-4} \text{ s}^{-1}$ ($r = -0.9988$) for **123**.

A degassed, sealed NMR sample of **123** was thermolyzed in a 1:1 mixture of toluene- d_8 and benzene- d_6 at 143°C . Product analyses under the standard conditions showed 98% **107** and 0.06% **108**.

Benzene sensitized photochemical decomposition of 123. All volumetric measurements were carried out in volumetric glassware. Solutions were prepared in volumetric flasks, and were diluted to volume immediately prior to use. Deionized water was used to prepare all aqueous solutions. All work was carried out in the dark under a red safety light .

Potassium ferrioxalate actinometry.^{168,169}

Stock solutions.

(I) 1,10-phenanthroline (0.2000 g, 1.11 mmol) in 100.00 ml H_2O .

(II) $\text{NaOAc} \cdot 3\text{H}_2\text{O}$ (8.23 g, 60.5 mmol) and 100.00 ml H_2O .

(III) $\text{Fe}_2(\text{SO}_4)_3 \cdot x\text{H}_2\text{O}$ (10.0431 g) and 5.5 ml conc. H_2SO_4 in 100.00 ml H_2O

(The cloudy solution was filtered through a cotton plug into the volumetric flask prior to dilution to volume.)

(IV) $\text{K}_2\text{C}_2\text{O}_4$ (55 g, 0.30 mol) in 250.00 ml H_2O .

Preparation of the actinometer solution. The actinometer solution was prepared by mixing 5.00 ml of solution IV with 5.00 ml solution III in a 100.00 ml volumetric flask, and diluting to the mark with deionized H_2O . The solution was allowed to stand for 30 min. prior to use. The actinometer solution is extremely light sensitive, but may be stored for up to 1 month if protected from light.

Determination of light intensity. The actinometer solution (3.00 ml) was pipetted to a 1 cm quartz UV cell and irradiated at 254 nm in a stove pipe reactor equipped with 3 General Electric 15 W germicidal lamps. Following irradiation, 1.00 ml (V_1) of the irradiated solution was delivered to a 10.00 ml (V_3) volumetric flask, followed by 2.00 ml of the stock 1,10-phenanthroline solution (stock solution I), and 0.50 ml of the NaOAc solution (stock solution II). The mixture was diluted to the mark with deionized H_2O , and allowed to stand for 30 min.. A blank solution was prepared by treating 1.00 ml of non-irradiated actinometer solution in an identical fashion.

Absorbance (A) of the blank solution and of the worked up actinometer solution was measured at 510 nm. The light output, I (E/min.) of the stovepipe reactor (254 nm) was determined using the following equation.

$$I \text{ (E/min.)} = (A V_2 V_3) / (\epsilon \Phi t V_1)$$

A = absorbance of the actinometer solution at 510 nm - absorbance of the blank solution at 510 nm.

V_2 = Volume (in liters) of actinometer solution irradiated.

V_3 = Volume (ml) to which the actinometer solution was diluted during workup.

ϵ = Extinction coefficient of the $Fe(1,10\text{-phenanthroline})_3$ complex at 510 nm (1.11×10^4 L/mol cm).

Φ = Quantum yield for the reaction $Fe^{2+} \rightarrow Fe^{3+}$ at 254 nm (1.25).

V_1 = Volume (ml) of actinometer solution worked up (1.00 ml).

t = Minutes the actinometer solution was irradiated.

Table IX lists the results of several measurements.

Table IX. Measurement of light output for stovepipe reactor equipped with 3 15 W General Electric Germicidal Lamps.

Absorbance ^a	Time ^b	Light output ^c
0.9584	0.340	6.09×10^{-6}
0.9996	0.349	6.19×10^{-6}
0.8990	0.300	6.48×10^{-6}
0.9680	0.340	6.16×10^{-6}
1.16	0.320	7.84×10^{-6}

a. Corrected absorbance of worked up actinometer solution at 510 nm.

b. Irradiation time for the actinometer solution (min). c. E/min.

Quantum yield of sensitized decomposition of DBH and 123 at 254 nm. A pentane solution, 0.0610 M in benzene and 3.50×10^{-3} M in **123** was prepared and 3.00 ml was delivered to a 1 cm quartz UV cell equipped with a male 10/30 joint. The solution was degassed through three freeze-pump-thaw cycles, and sealed. After warming to room temperature, irradiation was carried out at 254 nm in the stovepipe reactor. The absorbance of **123** was monitored over 336-344 nm. A similar experiment using 0.0512 M **DBH** and 4.59×10^{-3} M benzene was also carried out; however, the absorbance of the initial solution was too large to measure over 336-344 nm. Therefore, absorbance measurements for actinometry could be taken only after the initial azoalkane concentration had been depleted to 0.0129 M through photoreaction at 254 nm. The results of these experiments are summarized below.

Table X. Quantum yields for benzene sensitized decomposition of **123**.

Time ^a	Absorbance ^b	Δ mmol ^c	Quantum yield ^d
0	0.578	-----	-----
21.95	0.524	9.8×10^{-4}	0.34
43.03	0.471	0.0019	0.34
63.77	0.432	0.0027	0.32
84.66	0.409	0.0031	0.28
106.75	0.375	0.0037	0.26
130.96	0.345	0.0042	0.25
151.92	0.327	0.0046	0.23

^a. Duration of irradiation at 254 nm (sec). ^b. Average of azoalkane absorbance at 2 nm intervals, 336-344 nm. ^c. Determined from $\{(A_0 - A_t)/A_0\}([123]_0 \times 3.00 \text{ ml})$ where A_0 is the average absorbance of the solution over 336-344 nm at time $t=0$, A_t is the average absorbance over 336-344 nm at time t , and $[123]_0$ is the initial azoalkane concentration ($3.50 \times 10^{-3} \text{ M}$). ^d. Based on light output of $7.84 \times 10^{-6} \text{ E/min}$ determined immediately before this experiment.

A graph of absorbance versus time from the data in Table X can be found in Figure 34 at the end of the experimental section. Figure 35, also located at the end of the experimental section, shows an analogous graph of the data in Table XI.

Table XI. Quantum yields for benzene sensitized decomposition of DBH.

Time ^a	Absorbance ^b	Δ mmol ^c	Quantum yield ^d
0	1.81	-----	-----
318	1.35	9.84×10^{-3}	0.30
447	1.19	0.0133	0.29
763	0.840	0.0207	0.27
1198	0.562	0.0267	0.22

^a. Duration of irradiation at 254 nm (sec) starting from $[DBH]_0 = 0.0129 \text{ M}$. ^b. Average of azoalkane absorbance at 2 nm intervals, 326-336 nm. ^c. See footnote c in Table X above, let $[DBH]_0 = 0.0129 \text{ M}$. ^d. Based on light output of $6.14 \times 10^{-6} \text{ E/min}$ determined immediately before this experiment.

The products from benzene sensitized decomposition of **123** were analyzed by GC in the usual manner and the following product ratios were obtained (remaining percentage is accounted for by unreacted **123**). A representative GC trace of the products can be found in Figure 30.

Table XII. Yields of products from benzene sensitized decomposition of **123**.

[PhH] ^a	[123] ^b	% 107	% 108	% unidentified ^c
0.058	1.05	43	12	31
0.061	3.05	59	22	20

a. M. b. Initial concentration of **123** $\times 10^3$ M. c. Based on GC retention time, the four unidentified GC peaks are thought to be C₈.

Biradical Trapping with CHD. Six solutions of 0.0542 M azoalkane **123**, 0.0392 M decane, 4.57×10^{-3} M Michler's ketone and 1,4-cyclohexadiene in C₆H₅F were prepared. The concentration of CHD was 0.2082, 0.4116, 0.6140, 0.8048, 1.604, 2.806 M. The solutions were irradiated at 366 nm and 24.7 °C for 1 hour. The products were analyzed by capillary GC, giving the results in Table V. A representative GC trace is shown below and the GC conditions can be found under "General Information".

Figure 37. Representative GC trace of hydrocarbons **107**, **108**, and **119a** from triplet sensitized photolysis of azoalkane **123** in the presence of CHD.

Figure 14. Partial separation of hydrogenated urazole mixture by preparative GC.

Figure 15. Isolation of 123 from the Diels-Alder route by preparative GC.

Figure 18. Isolation of 1-cyclopentenyl-1-chloropropane by preparative GC.

Figure 19. Isolation of cyclopropylcyclopentane by preparative GC.

Figure 20. Isolation of 1-n-propylcyclopentene and propylidenecyclopentane by preparative GC.

Figure 21. Isolation of cyclopropylcyclohexane by preparative GC.

Figure 22. Isolation of propylidenecyclohexane by preparative GC.

Figure 23. Isolation of propylidenecyclohexane and 1-n-propylcyclohexene by preparative GC.

Time (min.) 10.8

Figure 24. Isolation of 3,4-cyclopropylcyclopentene by preparative GC.

Time (min.) 15.0 19.8 25.8

Figure 25. Isolation of 2-cyclopropyl-1,4-pentadiene by preparative GC.

Time (min.) 4.5 17.4, 19.2

Figure 26. Isolation of cyclopropylidenecyclopentane by preparative GC.

Time (min.) 17.4

Figure 27. Isolation of propylidenecyclopentane by preparative GC.

#2 is a mixture of 1-cyclopropylcyclopentene, cyclopropylidene-cyclopentane, and minor unidentified components.

Figure 28. Isolation of photoproducts from triplet sensitized photolysis of 123.

Figure 29. Isolation of 1&2-n-propylcyclopentadiene by preparative GC.

Figure 30. Analytical GC of product mixture from the benzene sensitized photolysis of 123. Time values along X-axis are in min.

Figure 31. GC trace from analysis of sonication allylic chloride reaction

Figure 32. Expansion of the dimer region in the previous GC trace.

Figure 33. Glassware for ultrasonic reactions.

Figure 34. Graph of data in Table X.

Figure 35. Graph of data in Table XI.

^1H NMR of Peak #1a,f collected
by preparative GC in Fig. 14.

^1H NMR of Peak #2a,f collected
by preparative GC in Fig. 14.

Peak 1 from preparative GC of
isomers of 123 from the
Diels-Alder route.^{e,f}

Peak 3 from preparative GC
of isomers of 123c, from the
Diels-Alder route.

178b^{c,f} 178b^{c,f}

183

183^{c,f} 183^{g,f}

119b^{c,f}

CC=C1CCCCC1

¹H NMR spectrum (CDCl₃) showing peaks at 5.1-5.3 ppm (vinyl protons, integration 1.00), 1.9-2.1 ppm (allylic protons, integration 2.00), and 0.9-1.0 ppm (ethyl methyl protons, integration 3.00).

119b^{e,f}

Chemical structure of **119b^{e,f}** is shown above the spectrum.

¹³C NMR peaks (PPM):

- 139.832
- 123.242
- 77.531
- 76.478
- 37.192
- 28.768
- 28.523
- 27.892
- 27.868
- 14.953

120b^{c,f} 120b^{e,f}

117b^{c,f}

5.16974

9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0

PPM

117b^{e,f}

172^{o,f}

171^{c,f} 171^{g,f}

BrCCCCS1=CC=CC=C1
3-bromopropyl phenylsulfide^{b,f}

BrCCCCS1=CC=CC=C1
3-bromopropyl phenylsulfide^{a,f}

Hand-drawn ^1H NMR
of **108E**^{c,f} after having
authentically synthesized all
impurities in original sample
obtained from preparative GC.

Hand-drawn ^1H NMR
of **108Z**^{c,f} after having
authentically synthesized all
impurities in original sample
obtained from preparative GC.

~~BRUKER~~
TFH.001
DATE 1-7-88
SF 300.153
SY 210.0
D1 4761.963
SI 8192
TD 8192
SW 3205.128
HZ/PT .783

PW 5.6
RD 0.0
RQ 1.278
RG 4.0
NS 120
TE 297

FW 4100
O2 4021.433
DP 6L PD

LB 0.0
GB 0.01
CX 20.00
CY 10.00
F1 10.001P
F2 -4.009P
HZ/CM 112.501
PPM/CM -3.75
SR 3325.45

169 & 170 c,f

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- (171) This analysis was performed on a Kratos MS-80 instrument by Dr. Steve Colgrove of Exxon Research and Development Laboratories in Baton Rouge, LA. We gratefully acknowledge his help.

Appendix I. Computer simulation of kinetics.

Simulation of Scheme XXIX. Executable program is called "simula2".

```

C   EPFCN
C   MODIFIED BY A. M. C. ON 7/31/90
C   EDITED TO STUDY THE CYCLOPROPYLCARBINYL
C   ALLYLCARBINYL REARRANGEMENT USING PhSH
      SUBROUTINE DIFFUN (N, T, Y, YDOT)
      IMPLICIT DOUBLE PRECISION (A-H, O-Z)
      DIMENSION Y (10), YDOT (10)
      COMMON /PINK/NEQ, NRK, NPAR
      COMMON /RED/ RK (10), P(6)
      N=NEQ
C   THE DIFFERENTIAL EQUATIONS FOLLOW:
      YDOT (1) = -RK(1)*Y(1)
      YDOT (2) = RK(1)*Y(1) - RK(2)*Y(2) - RK(7)*Y(2)
      YDOT (3) = 2*RK(2)*Y(2) - RK(3)*Y(3) + RK(4)*Y(4)
      *+RK(5)*Y(7)*Y(3)
      YDOT (4) = RK(3)*Y(3) - RK(4)*Y(4) - RK(6)*Y(7)*Y(4)
      YDOT (5) = RK(5)*Y(7)*Y(3) + RK(7)*Y(2)
      YDOT (6) = RK(6)*Y(7)*Y(4)
      YDOT (7) = -RK(5)*Y(7)*Y(3) - RK(6)*Y(7)*Y(4)
      YDOT (8) = RK(7)*Y(2)
      RETURN
      END

C   SUBROUTINE PARAM (YCALCI, RKS, PAR)
      IMPLICIT DOUBLE PRECISION (A-H, O-Z)
      DIMENSION YCALCI (10), RKS (10), PAR (6)
      COMMON /PINK/ NEQ, NRK, NPAR
C   THE VALUES OF YCALCI ARE THE INITIAL CONCENTRATIONS
      YCALCI (1) = 0.0187
      YCALCI (2) = 1.E-10
      YCALCI (3) = 1.E-10
      YCALCI (4) = 1.E-10
      YCALCI (5) = 1.E-10
      YCALCI (6) = 1.E-10
      YCALCI (7) = 0.032
      YCALCI (8) = 1.E-10
C   NUMBER OF RATE CONSTANTS
      NRK=7
C   NUMBER OF DIFFERENTIAL EQUATIONS
      NEQ=8
C   MY GUESSES OF THE RATE CONSTANTS FOLLOW.
      RKS (1) = 1
      RKS (2) = 1.E10
      RKS (3) = 1.5E7
      RKS (4) = 5.5E4
      RKS (5) = 1.5E8
      RKS (6) = 1.5E8
      RKS (7) = 7.2E9

```

```
C   NUMBER OF FIXED PARAMETERS  
    NPAR=0  
    RETURN  
    END  
    SUBROUTINE PEDERV (NT, Y, PD, NO)  
    RETURN  
    END
```

Simulation allylcarbinyl-cyclopropylcarbinyl ring closure reaction. Program Is D3.

```

C   EPFCN
C   MODIFIED BY A. M. C. ON 7/31/90
C   EDITED TO STUDY THE ALLYL CARBINYL-
C   CYCLOPROPYL CARBINYL REARRANGEMENT USING
C   ALKYL HALIDES AND  $\text{Bu}_3\text{SnH}$ 
C   SUBROUTINE DIFFUN (N, T, Y, YDOT)
C   IMPLICIT DOUBLE PRECISION (A-H, O-Z)
C   DIMENSION Y (10), YDOT (10)
C   COMMON /PINK/NEQ, NRK, NPAR
C   COMMON /RED/ RK (10), P(6)
C   N=NEQ
C   THE DIFFERENTIAL EQUATIONS FOLLOW:
C   YDOT (1) = -RK(1)*Y(1) - RK(5)*Y(6)*Y(1) - RK(5)*Y(4)*Y(1)
C   YDOT (2) = RK(1)*Y(1) - RK(2)*Y(2)*Y(3) + RK(5)*Y(1)*Y(6)
C   *+RK(5)*Y(1)*Y(4) - 2RK(6)*(Y(2)**2)
C   YDOT (3) = -RK(2)*Y(3)*Y(2)
C   YDOT (4) = RK(2)*Y(2)*Y(3) - RK(3)*Y(4) + RK(4)*Y(5) -
C   *RK(5)*Y(1)*Y(4)
C   YDOT (5) = RK(3)*Y(4) - 2RK(4)*Y(5) + RK(3)*Y(6)
C   YDOT (6) = RK(4)*Y(5) - RK(3)*Y(6) - RK(5)*Y(1)*Y(6)
C   YDOT (7) = RK(5)*Y(1)*Y(6)
C   YDOT (8) = RK(5)*Y(1)*Y(4)
C   YDOT (9) = RK(6)*(Y(2)**2)
C   RETURN
C   END

C   SUBROUTINE PARAM (YCALCI, RKS, PAR)
C   IMPLICIT DOUBLE PRECISION (A-H, O-Z)
C   DIMENSION YCALCI (10), RKS (10), PAR (6)
C   COMMON /PINK/ NEQ, NRK, NPAR
C   THE VALUES OF YCALCI ARE THE INITIAL CONCENTRATIONS
C   YCALCI (1) = 0.0533
C   YCALCI (2) = 1.E-10
C   YCALCI (3) = 0.0404
C   YCALCI (4) = 1.E-10
C   YCALCI (5) = 1.E-10
C   YCALCI (6) = 1.E-10
C   YCALCI (7) = 1.E-10
C   YCALCI (8) = 1.E-10
C   NUMBER OF RATE CONSTANTS
C   NRK=6
C   NUMBER OF DIFFERENTIAL EQUATIONS
C   NEQ=9
C   MY GUESSES OF THE RATE CONSTANTS FOLLOW.
C   RKS (1) = 1E-4
C   RKS (2) = 2.6E7
C   RKS (3) = 5.50E4
C   RKS (4) = 1.5E7

```

```
RKS (5) = 2.4E6  
RKS (6) = 0.7E9  
C  NUMBER OF FIXED PARAMETERS  
   NPAR=0  
   RETURN  
   END  
   SUBROUTINE PEDERV (NT, Y, PD, NO)  
   RETURN  
   END
```