with improved time resolution, we hope to determine the bond energies for very weak ligands such as Kr.

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Note Added in Proof. The author would like to point out that Turner and co-workers[32] have previously used CO substitution kinetics in liquid Kr to determine the N_2-Ni bond energy in $Ni(CO)_3(N_2)$. In this system, the kinetics are complicated by the existence of parallel associative and dissociative pathways. Nevertheless, the authors were able to extract a bond energy and the reader is referred to their paper for a thorough discussion of the kinetics.

Picosecond Radical Kinetics. Ring Openings of Phenyl Substituted Cyclopropylcarbinyl Radicals

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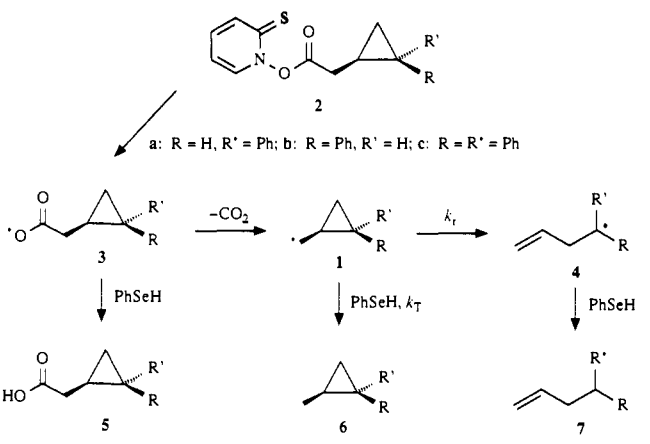
Abstract: Rate constants for ring openings of the *trans*-(2-phenylcyclopropyl)carbinyl radical (**1a**), the *cis*-(2-phenylcyclopropyl)carbinyl radical (**1b**), and the (2,2-diphenylcyclopropyl)carbinyl radical (**1c**) were studied by competition kinetics using PTOC esters as radical precursors and hydrogen atom transfer trapping from benzeneselenol as the basis reaction. Radical **1a** was studied in two solvents, toluene and THF; the experimental Arrhenius function for ring opening of **1a** was log (k_r·s) = 13.9 - 3.3/2.3RT (R in kcal/mol). It is possible that the immediate precursor to **1a**, acyloxy radical **3a**, suffers a concomitant decarboxylation-ring opening process that competes with simple decarboxylation leading to **1a**. The experimental rate constant for ring opening of **1a** at 25 °C is 3×10^{11} s^{-1}. Preliminary kinetic studies of radicals **1b** and **1c** gave Arrhenius functions of log (k_r·s) = 13.9 - 3.1/2.3RT and log (k_r·s) = 13.1 - 2.0/2.3RT, respectively, and the respective rate constants for ring openings at 25 °C are 4 and 5×10^{11} s^{-1}. Rate constants for ring openings of substituted cyclopropylcarbinyl radicals were estimated by Marcus theory using the known rate constants and equilibrium constant for the parent system and expected $\Delta G°$ values for the substituted systems. From these results, the estimated rate constants at 25 °C for ring opening of **1a** and **1b** were 1×10^{11} s^{-1} and that for **1c** was 4×10^{11} s^{-1}. Precursors to radicals **1**, such as the corresponding hydrocarbons, represent hypersensitive radical probes that, in principle, can provide unequivocal conclusions regarding the intermediacy of a radical in a reaction.

Radical rearrangements are useful both for mechanistic probe studies in which one attempts to determine whether or not a radical intermediate is formed during a particular reaction and for radical clock[1] applications wherein one wishes to measure the kinetics of competing radical reactions. The archetypal radical rearrangements are cyclization of the 5-hexenyl radical ($k = 2 \times 10^5$ s^{-1} at 25 °C)[2] and ring opening of the cyclopropylcarbinyl radical ($k = 1.0 \times 10^8$ s^{-1} at 25 °C),[3] the most precisely calibrated radical reaction. Despite the relatively large rate constant of the cyclopropylcarbinyl ring opening, this reaction is considerably slower than the fastest possible unimolecular reactions, and the failure to detect rearranged products in a mechanistic study employing this ring opening as a probe reaction does not provide unequivocal evidence that radical intermediates were not formed. Radical rearrangements faster than that of cyclopropylcarbinyl are desired for this reason and for radical clock applications involving very fast first-order or pseudo-first-order competitions.

Over the past few years, the kinetics of several fast radical rearrangements have been characterized. These include ring openings of a series of (poly)methyl-substituted cyclopropylcarbinyl radicals ($k = 1 \times 10^8$–4×10^9 s^{-1} at 25 °C),[3,4] the bicyclo[2.1.0]pent-2-yl radical ($k = 2 \times 10^9$ s^{-1} at 25 °C),[4b,5] spirocyclic cyclopropylcarbinyl radicals ($k = 2$–9×10^9 s^{-1} at 75 °C),[6] and the cubylcarbinyl radical ($k = 3 \times 10^{10}$ s^{-1} at 25 °C).[7] In developing radical probes for enzyme mechanistic studies, Castellino and Bruice estimated a lower limit for ring opening of *trans,trans*-(2,3-diphenylcyclopropyl)carbinyl radical at 25 °C of $k = 2 \times 10^{10}$ s^{-1};[8] this result prompted us to investigate ring openings of phenyl-substituted cyclopropylcarbinyl radicals. In

Scheme I



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0002-7863/92/1514-10915$03.00/0

this paper, we report a detailed kinetic study of the ring opening of the *trans*-(2-phenylcyclopropyl)carbinyl radical (**1a**) and preliminary studies of ring openings of the *cis*-(2-phenylcyclopropyl)carbinyl radical (**1b**) and the (2,2-diphenylcyclopropyl)carbinyl radical (**1c**).[9] Radicals **1** rearrange thousands of times faster than the cyclopropylcarbinyl radical and have lifetimes at room temperature of only a few picoseconds. When used in a mechanistic probe study, rearrangements with such large rate constants can, in principle, permit one to reach an unequivocal conclusion about the presence or absence of a radical intermediate.

Results and Discussion

Kinetics of the ring openings of radicals **1** were determined by the PTOC-thiol method (Scheme I).[3d,11] In this indirect technique, acyloxy radicals **3** are produced mainly in chain reactions of the PTOC ester precursors **2**.[12] Decarboxylations of the acyloxy radicals provide radicals **1** that ring open to radicals **4** in competition with a hydrogen atom transfer trapping reaction. The highly reactive hydrogen atom donor benzeneselenol was employed as the trapping agent in this study.[10,13] Reaction of radicals **1** with PhSeH gave cyclic products **6**, and reaction of the ring opened radicals with PhSeH gave products **7**. The PhSe• radical formed in the trapping reactions adds to the PTOC precursor in a chain propagation step.

A competing radical reaction in the PTOC-thiol method is hydrogen atom transfer trapping of the acyloxy radicals to give acids **5**.[3d,7b,10,13] In addition, polar reactions of the PTOC esters (actually mixed anhydrides of a carboxylic acid and the thiohydroxamic acid) with nucleophilic species such as PhSH and PhSeH can occur.[14] These side reactions are not of kinetic significance, but they can limit the precision of the kinetic method by reducing the total amount of radicals **1** produced.

Cyclopropylacetic acids **5a** and **5b** were prepared by homologation of the corresponding cyclopropanecarboxylic acids, and the methyl ester of **5c** was prepared by cyclopropanation of methyl 3,3-diphenyl-2-propenoate. Acids **5** were converted to PTOC ester precursors **2** by a standard method.[12] Attempted purification of precursors **2** by column chromatography on silica gel, the standard procedure employed for PTOC esters used in kinetic studies,[3d] resulted in substantial decomposition as evidenced by low recoveries. PTOC esters **2b** and **2c** appeared to decompose more extensively than **2a**. Filtration through a pad of silica gel gave less decomposition but also less pure PTOC esters. The decomposition on silica gel was atypical; in our experience, simple PTOC esters are generally recovered from silica gel chromatography in yields of 70% or more. We presume that the instability of compounds **2** on silica gel reflects strain that led to enhanced reactivity of the activated acyl compounds with adventitious water. An apparent high polar reactivity of the PTOC esters also was manifested in the kinetic studies.

Kinetics of Ring Opening of 1a. Competition kinetic studies of radical **1a** were conducted over the temperature range −48 to 26 °C. Table I lists the results. Yields of hydrocarbon products were determined against an internal standard, and ratios of products **7a** to **6a** are reported. From the ratios of hydrocarbon products and the average concentration of PhSeH in each reaction, the ratios of rate constants (k_r/k_T) were calculated from eq 1 where $[PhSeH]_m$ is the average concentration of selenol during the reaction.

$$k_r/k_T = ([7]/[6])\,[PhSeH]_m \qquad (1)$$

An obvious problem in the kinetic studies of **1a** was the low and variable total yields of hydrocarbons **6a** and **7a**. Even lower yields of hydrocarbon products were obtained in reactions of **1b** and **1c** (see below). As noted, low yields of hydrocarbons can result either from acyloxy radical trapping or from polar reaction of the PTOC precursors with the nucleophilic trapping agent PhSeH. On the basis of the results in chromatographic purifications, hydrolysis of **2** by traces of water in the solvents also was possible. Acyloxy radical trapping by PhSeH should give a concentration dependent ratio of hydrocarbons **6** and **7** (from radical **1**) to acid **5**. However, polar reactions of the PTOC esters are expected to result in capricious ratios of hydrocarbons to acid derivatives because the induction period required to deplete radical inhibitors (presumed to be mainly oxygen) in the reaction mixtures will vary in an unpredictable manner. Therefore, we conclude that the low yields of hydrocarbons reflect intrusion of the polar reactions, consistent with the lability of the PTOC esters seen in column chromatography.[15]

A second problem apparent in the data in Table I is the high ratios of rearranged to unrearranged products. Obviously, we were

Table I. Results from Reactions of PTOC Ester **2a**

series[a]	temp[b]	$[PhSeH]_m$[c]	(**6a** + **7a**)[d]	(**7a**/**6a**)[e]	(k_r/k_T)[f]
A	20	1.6	63	64	103
	20	2.4	58	48	114
	0	1.4	38	67	94
	0	2.1	41	44	93
	−45	0.9	38	76	68
	−45	0.9	35	72	65
	−45	1.6	28	40	63
B	25	1.04	49	129	134
	25	1.04	50	116	121
	25	1.56	67	83	129
	25	2.39	64	48	115
	0	1.04	45	102	106
	0	1.06	45	101	107
	0	1.74	43	55	96
	0	2.62	42	43	112
	−22	1.36	54	63	85
	−22	1.36	54	64	86
	−48	1.36	49	55	75
	−48	1.36	48	51	70
C	26	1.31	39	140	184
	26	1.39	5	136	189
	25	1.14	25	137	156
	25	0.88	29	166	146
	23	0.86	7	222	194
	0	1.14	32	113	129
	0	0.88	38	165	145
	0	0.86	7	187	162
	0	1.31	61	95	124
	0	1.39	42	98	136
	−26	0.88	33	142	125
	−26	0.88	28	134	118
	−45	0.88	32	138	121
	−45	0.88	47	119	105

[a] Series A and B in toluene, series C in THF. The concentrations of PTOC **2a** were 0.02 to 0.1 M. [b] ±1 °C. [c] Average molar concentration of PhSeH. [d] % yield. [e] Ratio of products. [f] Ratio of rate constants in units of M.

(9) A preliminary report of the kinetics of ring opening of radical **1a** has appeared.[10]

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(15) One might consider further the possibility that other radical reaction channels diverted radicals **1** or **4**. Among the fastest alternative radical reactions to hydrogen transfer from PhSeH are group transfer from PhSeSePh, a minor contaminant in the PhSeH (to give alkyl phenyl selenides), and addition to the PTOC ester precursors (to give, ultimately, alkyl pyridyl sulfides). For simple alkyl radicals, the rate constants for these reactions at 25 °C are only ca. 1×10^7 and 2×10^6 M^{-1} s^{-1}, respectively.[16] Both reactions are slower than hydrogen atom transfer from PhSeH, and the concentrations of each of these species were considerably less than that of PhSeH. In some of the studies of radical **1a**, attempts were made to identify alkyl phenyl selenides or alkyl pyridyl sulfides from radicals **1a** and **4a**. Small amounts of high weight products were observed by GC in some cases, but the yields of these products were <1%. Another reaction that might compete with PhSeH trapping is reaction of a radical with another radical. Simple radical–radical reactions are generally thought to occur at the diffusion limit with a spin statistical correction factor (k ca. 5×10^9 M^{-1} s^{-1} in nonviscous organic solvents),[17] but relatively high concentrations of radicals must be attained before radical–radical reactions can become effective. In the design of our studies, this would require that radical **4** was persistent, i.e., that it did not react rapidly with any of the possible trapping agents.

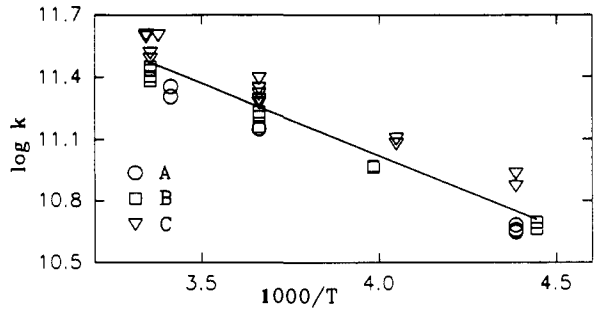

Figure 1. Rate constants for ring opening of radical **1a** calculated from the data in Table I and eq 3. The legend indicates the corresponding data set in Table I. The line is eq 4.

working at the fringe of the indirect method with trapping reactions at the 2% level at best and ratios of **7a**:**6a** ranging up to 200. Clearly either a small contaminant of unrearranged product **6a** in the starting material or a minor side reaction that produced **6a** would have comprised the study. However, by using the PTOC ester as a radical precursor, both of these problems were avoided. No pathway for production of hydrocarbons **6** in the synthesis of carboxylic acids **5** was available, and the only entry to **6** from the carboxylic acid derivatives was an acyloxy radical decarboxylation.

Three independent data sets, collected in groups, comprise the results in Table I. At a given temperature, differences in the k_r/k_T values between the data sets were found. These differences, which are nearly as great as a factor of 2 at low temperatures, apparently reflect systematic errors because the trends between different data sets are consistent and plots of log (k_r/k_T) against $1/T$ for each data set had approximately equal slopes. One likely source of systematic errors in these studies is the use of two solvents, toluene and THF. The two data sets for reactions run in toluene are in much better agreement with one another than is either with the THF data set. Although the rates of most simple radical reactions are relatively solvent insensitive, that of PhSeH trapping is partially diffusion controlled in organic solvents and will vary with viscosity.[10,13] The rate dependence on viscosity is complex because the E_a term in an Arrhenius plot of diffusional rate constants (ca. 2–2.5 kcal/mol) is substantially greater than the E_a term for the actual hydrogen atom transfer from PhSeH (estimated to be ca. 1 kcal/mol).[13] The result is that PhSeH trapping is described by a slightly nonlinear Arrhenius plot because the reaction becomes increasingly diffusion controlled as the temperature is lowered.[18]

Given our current lack of knowledge concerning the detailed behavior of PhSeH at the high concentrations employed in this study, there seemed to be little advantage in attempting to consider the data sets in Table I separately. Therefore, we have combined all of the results and treated them as a single set. This gives the relative Arrhenius function in eq 2 which contains somewhat large errors (given as 2σ for the last figure).

$$\log((k_r/k_T)\cdot M^{-1}) = 3.07(35) - 1.24(42)/2.3RT \quad (2)$$

We take the rate constants for cyclopropylcarbinyl radical ring openings[3d] to be a primary standard and assume that trappings of radical **1a** and the cyclopropylcarbinyl radical occur with the same rate constants. These values of k_T are described by eq 3, the average Arrhenius function for cyclopropylcarbinyl radical trapping by PhSeH in THF and toluene,[13] where the error limits in parentheses are 2σ for the last figure.

$$\log(k_T\cdot Ms) = 10.87(14) - 2.10(17)/2.3RT \quad (3)$$

From the k_r/k_T values in Table I and the k_T values described by eq 3, the rate constants for ring opening of **1a** can be calculated (Figure 1). From these values of k_r or by addition of eqs 2 and 3, one obtains the temperature dependent function for the ring opening reaction shown in eq 4. The error limits in eq 4 are 2σ for the last figure; they include the relative errors in the trapping kinetics and reflect the uncertainty in the ring opening kinetics of **1a** relative to cyclopropylcarbinyl ring opening kinetics.[19] The uncertainty in k_r must be evaluated at a specific temperature; at 25 °C, the uncertainty in log $(k_r\cdot s)$ is 0.24 at 1σ or a factor of 1.7 in the value of k_r.

$$\log(k_r\cdot s) = 13.94(36) - 3.34(44)/2.3RT \quad (4)$$

From eq 4, the calculated rate constant for ring opening of radical **1a** at 25 °C is 3×10^{11} s^{-1}. This ring opening reaction is faster than any previously reported radical rearrangement involving bond breaking.

For the relatively rigid radical **1a**, the log A value in eq 4 can serve as an indicator of possible accumulated or systematic errors in the indirect kinetic method. In the case of the cyclopropylcarbinyl radical ring opening, the transition state requires the isolation of one degree of rotational freedom which results in a theoretical[21] log A value quite close to the experimental value of 12.85 per bond.[3] The presence of two equivalent bonds in cyclopropylcarbinyl that can cleave raises the log A value by log 2 to 13.15. For ring opening of radical **1a**, one would expect[21] a maximum log A term of 13.1 at 25 °C, and this would occur only if no rotations were isolated in achieving the transition states, i.e., if both the methylene group and the phenyl group were locked in the ground state in the proper orientation for the transition state. The experimental log A value in eq 4 suggests that the calibration of the PhSeH trapping rate constants might be in error, but we believe that that is not likely.[22]

As an alternative explanation of the large log A value in eq 4, we speculate that the ring opening of the highly reactive system could involve two distinct processes, a pathway involving formation of radical **1a** followed by ring opening (Scheme I) and a second pathway involving ring opening *concomitant* with decarboxylation of the acyloxy radical. As a fragmentation reaction, the latter pathway should have a larger log A value, in the range of 16,[21] due to entropic release. The apparent kinetic values in this work might reflect a combination of the two processes.

Alternative experimental confirmations of the rate constants for ring opening of **1a** and a test of the hypothesis that a direct pathway from acyloxy radical **3a** to ring opened radical **2a** exists will be difficult. In principle, a determination of the ratios **7a**:**6a** at varying PhSeH concentrations should reveal a direct process, but, in practice, this is not possible because the large ratios **7a**:**6a** require a precision of better than 1% in the ratio for a meaningful extrapolation. Direct kinetic studies of **1a** ring opening also are not possible; the reaction is too fast for a picosecond resolution spectrometer, and the decarboxylation reaction of acyloxy radical **3a** is almost certainly slower than the ring opening reaction of **1a**;[23] therefore, a direct study can only provide the rate constant for decarboxylation. Production of radical **1a** by an alternative pathway (hydrogen atom abstraction) followed by nitroxyl radical

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(18) Further complicating the situation, we do not know the effect of PhSeH on solvent viscosity in the two solvents nor do we know if PhSeH aggregation occurs. At low concentrations employed in the original determination of the hydrogen atom transfer trapping rate constants for PhSeH (0.05–0.4 M),[10,13] these two potential problems were likely to be minimal. At the high concentrations of PhSeH required to trap radical **1a** (1–2 M), however, they may be substantial.

(19) Error propagation involved conventional methods with the standard assumption that the covariance is negligible.[20]

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(22) Although a cyclic argument, calculation of log A for cyclopropylcarbinyl radical ring opening against PhSeH trapping will give the correct value of 12.85 per bond. In addition, in a recent study[7b] of the rearrangement of the highly rigid cubylcarbinyl radical, PhSeH competition trapping kinetics gave a log A value that matched the theoretical value closely, and PhSeH trapping of the 6-cyano-5-hexenyl radical gave kinetic values that were the same as those found with PhSH trapping.[13]

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Table II. Results from Reactions of PTOC Esters **2b** and **2c**[a]

radical	temp[b]	$[PhSeH]_m$[c]	(6 + 7)[d]	(7/6)[e]	(k_r/k_T)[f]
1b	23	1.70	30	96	164
	23	1.81	50	97	174
	0	1.70	60	85	144
	0	1.81	60	82	148
	−27	0.78	5	149	117
	−45	0.78	5	142	111
	−45	0.74	5	145	107
	−73	0.74	5	117	87
1c	28	1.84	9	108	199
	0	1.90	10	111	210
	0	1.96	4	96	187
	0	1.73	8	139	240
	−45	1.08	44	210	227
	−73	0.88	47	299	262
	−78	0.68	34	390	265

[a] Reactions run in THF. The concentrations of PTOC **2** were ca. 0.05 M. [b-f] See notes to Table I.

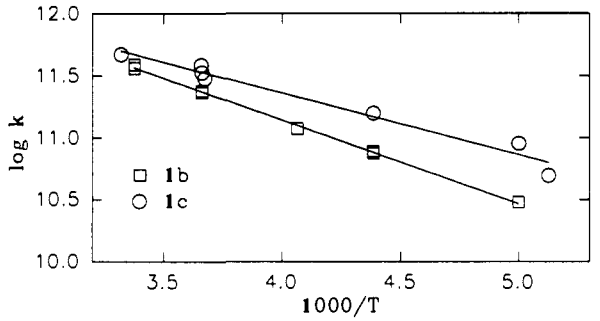

Figure 2. Rate constants for ring openings of radicals **1b** and **1c** from Table II and eq 5. The lines are eqs 6 and 7.

trapping[24] is a possible method for confirming the PhSeH rate constants, but trapping of **1a** by nitroxyl radicals will again give product ratios exceeding 100:1. A semiquantitative analysis of cyclopropylcarbinyl ring openings by Marcus theory (see below) supports the order of magnitude of the ring opening reaction but cannot exclude a competing synchronous decarboxylation–ring opening pathway.

The order of magnitude of the rate constant for ring opening of **1a** was confirmed experimentally by employing thiophenol as the radical trap. PhSH reacts with primary alkyl radicals about 0.05 times as fast as does PhSeH.[25] Experiments at 0, −12, and −14 °C gave values of k_r of 4, 0.8, and 0.7 × 10^{11} s^{-1}, respectively. These results were quite imprecise due to high product ratios (up to 2000:1). However, they are in general agreement with the PhSeH trapping results and confirm that radical **1a** opens very rapidly.

Ring Openings of 1b and 1c. As discussed in the next section, a Marcus theory analysis of the kinetics of phenyl-substituted cyclopropylcarbinyl radical ring openings suggested that PhSeH should trap small amounts of radicals **1b** and **1c** in competition with ring opening. Competition kinetic studies in THF were conducted for both of these species. The results are in Table II.

The PTOC esters **2b** and **2c** appeared to be more reactive in polar reactions than PTOC ester **2a**, and the yields of hydrocarbon products were quite low in some runs. It is noteworthy that the total yields of hydrocarbon products were batch dependent which confirms our conclusion regarding high polar reactivity. Despite the variable total yields of hydrocarbons, plots of log (k_r/k_T) versus $1/T$ were linear for both **1b** and **1c**, and the **7/6** ratios were reproducible between batches. We believe that the data is reliable for preliminary kinetic values.

We again assume that the rate constants for PhSeH trappings of **1b** and **1c** are equal to those of cyclopropylcarbinyl trapping.

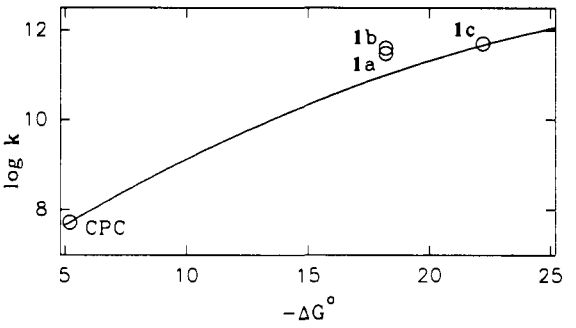

Figure 3. Estimated rate constants for ring opening of cyclopropylcarbinyl radicals via Marcus theory. The line shows the estimated rate constants at 25 °C. The symbols are the experimental rate constants for ring opening of the cyclopropylcarbinyl radical (CPC) and radicals **1** at 25 °C.

The values of k_r for ring openings of **1b** and **1c** were determined from the k_r/k_T values in Table II and the k_T values from eq 5 which is the temperature dependent function for PhSeH trapping in THF.[13] These gave the Arrhenius functions in eqs 6 and 7 which are shown graphically in Figure 2. The calculated rate constants for ring opening of **1b** and **1c** at 25 °C are 4 × 10^{11} and 5 × 10^{11} s^{-1}, respectively.

$$\log(k_T \cdot Ms) = 11.03 - 2.27/2.3RT \quad (5)$$

$$\log(k_r \cdot s) = 13.9 - 3.1/2.3RT \quad \text{(for 1b)} \quad (6)$$

$$\log(k_r \cdot s) = 13.1 - 2.0/2.3RT \quad \text{(for 1c)} \quad (7)$$

The apparent precision in eqs 6 and 7 was high with the maximum errors at 2σ of 0.2 for both the log A and E_a terms, but, given the limited number of data points and low yields of hydrocarbon products, we are cautious about accepting this level of precision. As was the case with radical **1a**, the log A value for rearrangement of radical **1b** suggests a positive entropy of activation term that would be consistent with a direct decarboxylation–ring opening process for acyloxy radical **3b** in competition with simple decarboxylation. The log A value for radical **1c** is consistent with no competing direct process.

Estimation of Cyclopropylcarbinyl Ring Opening Rate Constants by Marcus Theory. Experimental confirmation of the very large constants for ring openings of radicals **1** might require the development of new approaches, but a semiquantitative method for checking the kinetic values for ring openings of radicals **1** exists. If one assumes a linear free energy relationship in the ring openings of a series of cyclopropylcarbinyl radicals,[26] then the rate constants for ring openings of radicals **1** can be calculated by Marcus theory.[27]

The rate constants at 25 °C for ring opening of the cyclopropylcarbinyl radical (**8**) to the 3-butenyl radical (**9**) and for cyclization of **9** to **8** are known.[28] Using these values in the Marcus equation (eq 8) gives a value for the intrinsic activation term ($\Delta G^{\ddagger}_i$) of 9.3 kcal/mol; this is the expected activation energy for a thermoneutral cyclopropylcarbinyl ring opening. With this value for $\Delta G^{\ddagger}_i$, we calculate expected values of $\Delta G^{\ddagger}$ for increasingly exergonic cyclopropylcarbinyl ring openings. The results are shown graphically in Figure 3.

$$\Delta G^{\ddagger} = \Delta G^{\ddagger}_i + \Delta G^{\circ}/2 + (\Delta G^{\circ})^2/16\Delta G^{\ddagger}_i \quad (8)$$

In order to estimate the rate constants for ring opening of radicals **1** by the Marcus approach, we assume that complete delocalization of the phenyl rings will be available in the transition states for ring openings. The total exergonicity of the reactions

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(26) Such an assumption appears to be justified based on the rigidity of the cyclopropylcarbinyl system. This assumption also was made in a study of the ring opening of the bicyclo[2.1.0]pent-2-yl radical[5b] and a recent extensive study of ring openings of substituted cyclopropylcarbinyl radicals;[4b] in both cases, the results appeared to be consistent with the assumption.

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is then approximated by adding the expected increase in resonance stabilization energy (RSE) of product radicals **4** in comparison to that for the 3-butenyl radical to the observed $\Delta G°$ for cyclopropylcarbinyl ring opening (i.e., −5.2 kcal/mol). The RSE in radicals **4a** and **4c** are expected to be, respectively, 13 and 17 kcal/mol greater than that in **9** on the basis of the bond dissociation energies[31] of a primary C–H, ethylbenzene, and 1,1-diphenylethane. The result is that the rate constants for ring openings of radicals **1a** and **1b** are predicted to be 1×10^{11} s^{-1} at 25 °C, and that for **1c** is predicted to be 4×10^{11} s^{-1} (Fig 3).[32]

When one considers that the Marcus approach assumes a linear free energy relationship and involves an extrapolation in rate constants over several orders of magnitude, the agreement between the predicted and observed rate constants for ring opening of radicals **1** is seen to be very good. We note that our simple analysis ignores a likely strain energy contribution in radicals **1b** and **1c** (due to the syn disposition of a phenyl ring and the methylene group) that should slightly increase the exergonicity of these ring openings. It is also interesting to note that the predicted rate constants from Marcus theory for reactions of **1a** and **1b** differ from the experimental values more than does that for reaction of **1c**. This is qualitative agreement with the observed trends in the log A values. The Marcus approach assumed a constant ΔS^* for the series of cyclopropylcarbinyl ring opening reactions, but this would not be the case if there is a competing direct ring opening pathway. A positive entropy of activation value as suggested by the experimental log A terms for **1a** and **1b** would give an observed rate constant greater than that predicted by Marcus theory.

The Marcus theory analysis leads to another important point regarding the rates of ring openings of radicals **1**. We assumed that full delocalization of the developing radical character in the transition states for ring openings was possible. However, in a case where complete overlap of the aryl π-systems with the breaking cyclopropyl bond was not possible, the effective delocalization should be a $\cos^2$ function of the dihedral angle of the phenyl π-system and the cyclopropyl plane. In a case where the aromatic ring was held such that the optimal angle for delocalization was not achieved, one could calculate an expected rate constant for ring opening if this dihedral angle was known. Conversely, if the aryl group can be constrained with an unknown dihedral angle with respect to the cyclopropyl plane, then the rate constants for ring opening of radicals **1** cannot be estimated with confidence. In the extreme case where no delocalization of developing radical character in the transition state could occur due to orthogonality of the aromatic π-system and the cyclopropyl ring, the effect of the phenyl ring should be reduced to a purely inductive effect which might be approximated as about the same effect as that of an alkyl group. The predicted rate constant for ring opening of radical **1a** at 25 °C in this extreme case is only about 4×10^8 s^{-1}.[33]

Finally, we note that the activation energies for rotation of the methylene group in cyclopropylcarbinyl radical[35] and for rotation about the phenyl–cyclopropyl bond in cyclopropylbenzene[36] are of the same order of magnitude as the experimental activation energies for the ring openings of radicals **1**. Thus, it is possible that the ring opening processes are linked to rotational processes. One manifestation of this possible phenomenon would be that different rate constants for ring openings of radicals **1** might be found when the radicals are produced by methods other than acyloxy decarboxylations. That is, the conformational populations at the instant of radical formation could affect the rate of ring opening.

In conclusion, the rate constants for ring openings of phenyl-substituted cyclopropylcarbinyl radicals **1** are very fast with rate constants at room temperature of $3–5 \times 10^{11}$ s^{-1}. These radicals have lifetimes of only a few picoseconds at 25 °C, and the rearrangement reactions are much faster than diffusional processes and can compete in measurable amounts with even the fastest possible first-order process. Potential precursors to radicals **1** (such as cyclopropanes **6**) thus represent a new class of hypersensitive radical probes. If one were to apply such a precursor in a reaction that might involve a radical intermediate, a deduction concerning the intermediacy of radicals would result from either the presence or absence of radical derived products provided that one is assured that conformational constraints on rotations of the phenyl rings are not present. Mechanistic studies of hydrocarbon oxidations by iron-containing enzymes and their models are obvious applications of these probes; some such studies have already been performed.[8,34,37,38]

Experimental Section

Unless otherwise stated all reactions were performed in flame-dried glassware under an atmosphere of nitrogen. ^{1}H NMR spectra were obtained at 300 MHz on a General Electric QE-300 or GN-300 spectrometer or at 200 MHz on a Varian XL 200E spectrometer. Analytical GC was accomplished on Varian 3400 chromatographs equipped with flame ionization detectors; wide bore capillary SE-30 and Carbowax columns (15 m, Alltech) were used. THF was distilled from potassium benzophenone under nitrogen immediately before use. Benzeneselenol was prepared and handled as previously described;[10,13] typically, samples were contaminated with Ph_2Se_2 (5–15%). Commercially available reagents were purchased from Aldrich Chemical Co.

***trans*-(2-Phenylcyclopropyl)acetic Acid (5a).** To 5 g (31 mmol) of commercial *trans*-2-phenylcyclopropanecarboxylic acid in 50 mL of benzene was added 3.4 mL (46 mmol) of thionyl chloride and two drops of DMF. The mixture was heated at reflux for 3 h and then stirred at room temperature for 12 h. A 50-mL portion of benzene was added, and the solvent and excess $SOCl_2$ were removed by distillation under N_2. Vacuum distillation yielded 4.5 g (80%) of *trans*-2-phenylcyclopropanecarbonyl chloride: $bp_{0.85}$ 100–102 °C (lit.[39] bp_{24} 126–128 °C).

The above acid chloride (1.16 g, 6.4 mmol) in 5 mL of ether was added dropwise under N_2 to a solution of diazomethane (from Diazald, prepared as described)[40] in ether. The solution was stirred for 12 h, and the remaining diazomethane was removed by distillation. The solvent was distilled at reduced pressure to yield 1.1 g (92%) of 1-diazo-3-(*trans*-2-phenylcyclopropyl)acetone: ^{1}H NMR ($CDCl_3$) δ 1.30–1.45 (m, 1 H), 1.70–1.80 (m, 1 H), 1.85–2.00 (m, 1 H), 2.55–2.70 (m, 1 H), 5.35 (br s, 1 H), 7.05–7.15 (m, 2 H), 7.20–7.35 (m, 3 H).

To a stirred mixture of AgO (1.92 g) and sodium thiosulfate (2.56 g) in 80 mL of water at 75 °C was added in 2-mL portions the above diazoketone (1.1 g, 5.9 mmol) in 30 mL of dioxane. The mixture was heated at 75 °C for 1.5 h, and the resulting mixture was filtered to remove the black precipitate. The filtrate was basified and washed with ether. The aqueous layer was acidified and extracted with ether. The ethereal solution was dried ($MgSO_4$), and solvent was removed at reduced pressure to yield 0.90 g (85%) of acid **5a**: mp 38–40 °C (lit.[41] mp

(28) The rate constant at 25 °C for ring opening[3] of one cyclopropyl bond in **8** is 5×10^7 s^{-1}, and that for cyclization[29] of **9** is 8000 s^{-1}.

(29) The reported[30] rate constant for cyclization of **9** has been corrected with a more recent determination of the rate constant for reaction of a primary radical with Bu_3SnH.[2]

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45–47 °C); ^{1}H NMR ($CDCl_3$) δ 0.80–0.95 (m, 1 H), 0.95–1.05 (m, 1 H), 1.30–1.50 (m, 1 H), 1.75–1.85 (m, 1 H), 2.3–2.55 (m, 2 H), 7.05–7.30 (m, 5 H), 10.6 (br s, 1 H); mass spectrum (*m/e*, rel abundance), 176 (M^+, 57), 130 (22), 117 (100), 115 (46), 91 (33).

***cis*-(2-Phenylcyclopropyl)acetic acid (5b)** was prepared from the ethyl ester of *cis*-2-phenylcyclopropanecarboxylic acid[42] by modification of a reported homologation procedure.[43] A solution of BuLi in hexanes (81 mmol) was added dropwise to a stirred solution of 2,2,6,6-tetramethylpiperdine (1.49 mL, 8.8 mmol) in 10 mL of THF that was maintained in a 0 °C bath. The mixture was stirred for 10 min. The resulting solution was transferred by cannula into an addition funnel fitted on a 250-mL, three-necked flask which contained dibromomethane (0.57 mL, 8.1 mmol) and 10 mL of THF at −90 °C (methanol–N_2 bath). The former solution was added dropwise, and the resulting mixture was stirred for 10 min. A solution of ethyl *cis*-2-phenylcyclopropanecarboxylate (0.70 g, 3.7 mmol) in 10 mL of THF was added dropwise followed by 2,2,6,6-tetramethylpiperidine (0.62 mL, 3.7 mmol) which was added in one portion via syringe. The resulting mixture was stirred for 10 min. A solution of BuLi in hexanes (22.1 mmol) was added dropwise. The −90 °C bath was replaced with a warm water bath (30 °C), and stirring was continued for an additional 15 min. The mixture was added via cannula to a rapidly stirring solution of acidified ethanol (10 mL of acetyl chloride in 50 mL of absolute ethanol) maintained in a 0 °C bath. The mixture was concentrated, and the residue was dissolved in ether. The resulting solution was washed with 10% sulfuric acid, 5% aqueous $NaHCO_3$, and brine. After drying ($MgSO_4$), the ethereal solution was concentrated, and the residue was purified by silica gel chromatography (1:9, ether/pentane) to give 0.35 g (47%) of homologated ester which was saponified with excess KOH in 95% ethanol to give acid **3b** that was used without further purification: ^{1}H NMR (300 MHz, CDCl3) δ 0.80 (q, J = 6 Hz, 1 H), 1.05–1.15 (m, 1 H), 1.40–1.50 (m, 1 H), 1.96 (d of d, J_{ab} = 17 Hz, J_{ax} = 8 Hz, 1 H), 2.12 (d of d, J_{ba} = 17 Hz, J_{bx}, = 7 Hz, 1 H), 2.25–2.30 (m, 1 H), 7.15–7.35 (m, 5 H), 10.80 (br s, 1 H); high resolution mass spectrum, calcd for $C_{11}H_{12}O_2$: 176.0837, found: 176.0837.

(2,2-Diphenylcyclopropyl)acetic acid (5c) was synthesized by cyclopropanation of methyl 3,3-diphenyl-2-propenoate[44] using a reported Simmons–Smith cyclopropanation procedure.[45] The zinc–copper couple was prepared in an Erlenmeyer flask by refluxing a mixture of cupric acetate monohydrate (0.10 g, 0.5 mmol) in 10 mL of glacial acetic acid as zinc dust (1.65 g, 16.8 mmol) was added. The mixture was heated for 1 min following the addition. The couple was allowed to settle for 1 min. Acetic acid was decanted, and the couple was quickly washed with a 10-mL portion of acetic acid and four 10-mL portions of dry ether. The couple was then covered with 10 mL of ether, and the flask was fitted with a Claisen head, a reflux condenser, and an addition funnel. The system was flushed with N_2, and 1.5 g of diiodomethane was added. The solution was heated at reflux, and an additional 3.0 g of diiodomethane (11.8 mmol total) and 2.0 g (7.8 mmol) of methyl 3,3-diphenyl-2-propenoate in 10 mL of ether was added dropwise over 30 min. The dark maroon mixture was heated at reflux for 48 h. The ether was decanted, and the residue was washed with a 0 °C 1 M HCl solution, water, and brine. The dried ($MgSO_4$), concentrated material showed a 30% conversion of the olefin by ^{1}H NMR spectroscopy. The reaction sequence was repeated on the product mixture to give a mixture with ca. 50% conversion of the olefin. The crude product mixture was treated with excess *m*-chloroperoxybenzoic acid in CH_2Cl_2 to epoxidize the remaining olefin. The desired ester was isolated in ca. 35% yield by silica gel chromatography (hexanes–ethyl acetate or benzene elution) as a slightly yellow oily product: high resolution mass spectrum (of the ethyl ester), calcd for $C_{19}H_{20}O_2$: 280.1463; found: 280.1462.

Saponification of the ester with excess KOH in aqueous alcohol followed by a conventional workup gave **5c** as a viscous oil: ^{1}H NMR[46] ($CDCl_3$) δ 1.3 (d, J = 7 Hz, 2 H), 1.95–2.0 (m, 1 H), 2.2 (d, J = 7 Hz, 2 H), 7.1–7.5 (m, 10 H).

1-[[[(*trans*-2-Phenylcyclopropyl)methyl]carbonyl]oxy]-2(1*H*)-pyridinethione (2a) was prepared by the general method described below for **2c** from 3.2 mmol of (*trans*-2-phenylcyclopropyl)acetic acid. Chromatography of the crude oily product on silica gel (ethyl acetate–hexanes, 2:3, v:v) in a column shielded from light gave 0.51 g (57%) of compound **2a** as a yellow oil: ^{1}H NMR ($CDCl_3$) δ 0.95–1.05 (m, 1 H), 1.10–1.20 (m, 1 H), 1.45–1.60 (m, 1 H), 1.90–2.00 (m, 1 H), 2.84 (d, J = 7 Hz, 2 H), 6.63 (d of t, J = 2, 7 Hz, 1 H), 7.10–7.30 (m, 5 H), 7.57 (d of d, J = 2, 8 Hz, 1 H), 7.70 (d of d, J = 2, 9 Hz, 1 H). The purity of **2a** in various batches was >90% and often >95% on the basis of NMR spectra.

1-[[[(*cis*-2-Phenylcyclopropyl)methyl]carbonyl]oxy]-2(1*H*)-pyridinethione (2b) was prepared by the procedure described below for **2c** from 0.17 g of acid **5b**. Crude PTOC ester **2b** was obtained in 37% after filtration chromatography through silica gel with hexanes–ethyl acetate elution. The product solidified upon concentration of the solvents from chromatography to give **2b** as a yellow semisolid that melted upon handling and which was >95% pure by NMR spectroscopy: ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.90–1.00 (m, 1 H), 1.15–1.30 (m, 1 H), 2.30–2.60 (m, 3 H), 6.58 (t, J = 7 Hz, 1 H), 7.10–7.35 (m, 7 H), 7.65 (d, J = 8 Hz, 1 H).

1-[[[(2,2-Diphenylcyclopropyl)methyl]carbonyl]oxy]-2(1*H*)-pyridinethione (2c) was prepared by a general method described by Barton.[12] A mixture of (2,2-diphenylcyclopropyl)acetic acid (0.14 g, 0.56 mmol) and oxalyl chloride (0.1 mL, 1.1 mmol) in 5 mL of dry benzene was stirred for 12 h. Excess oxalyl chloride and benzene were removed under high vacuum, and the residue was dissolved in 10 mL of benzene. A suspension of 2-mercaptopyridine-*N*-oxide sodium salt (Olin, 0.10 g, 0.63 mmol), and *p*-(dimethylamino)pyridine (DMAP, 0.007 g, 0.056 mmol) in 10 mL of benzene in a flask shielded from light was cooled in a 0 °C bath. To the latter solution was added via cannula the acid chloride solution. The ice bath was removed, and the mixture was stirred for 4 h. The reaction mixtures were protected from light in all subsequent steps. The solution was successively washed with 10% $KHSO_4$, 10% $NaHCO_3$, and brine solutions and dried ($MgSO_4$). The product mixture was concentrated, and the crude product was passed rapidly through a pad of silica gel to give 0.12 g (60%) of **2c** as a yellow-orange oil which was 80–85% pure as determined by NMR spectroscopy: ^{1}H NMR ($CDCl_3$) δ 1.3–1.4 (m, 2 H), 2.1–2.25 (m, 1 H), 2.5 (d of d, J = 8, 18 Hz, 1 H), 2.65 (d of d, J = 8, 18 Hz, 1 H), 6.6 (t, J = 7 Hz, 1 H), 7.0–7.4 (m, 12 H), 7.7 (d, J = 8 Hz, 1 H). Attempted purification by conventional chromatography resulted in substantial decomposition of **3c**.

Product Identifications. Authentic samples of *trans*-(2-phenylcyclopropyl)methane (**6a**), *cis*-(2-phenylcyclopropyl)methane (**6b**) and (2,2-diphenylcyclopropyl)methane (**6c**) were prepared from the appropriate cyclopropanecarboxylic acid or ethyl ester by reduction to the alcohol ($LiAlH_4$), mesylation at −5 °C, and reduction of the crude mesylate with $LiEt_3BH$ in THF at −5 °C. The identities of the known hydrocarbons **6** were established as follows: For **6a**: ^{1}H NMR[47] ($CDCl_3$) δ 0.65–0.75 (m, 1 H), 0.85–0.95 (m, 1 H), 1.00–1.15 (m, 1 H), 1.20 (d, J = 8 Hz, 3 H), 1.55–1.65 (m, 1 H), 6.95–7.35 (m, 5 H); high resolution mass spectrum, calcd for $C_{10}H_{12}$: 132.0939; found: 132.0941. For **6b**: ^{1}H NMR[48] ($CDCl_3$) δ 0.55 (q, J = 6 Hz, 1 H), 0.79 (d, J = 6 Hz, 3 H), 0.95–1.05 (m, 1 H), 1.10–1.20 (m, 1 H), 2.05–2.15 (m, 1 H), 7.25–7.65 (m, 5 H). For **6c**: bp 144 °C (20 Torr); ^{1}H NMR[49] ($CDCl_3$) δ 0.93 (d, J = 6 Hz, 3 H), 1.14 (t, J = 5 Hz, 1 H), 1.26 (q, J = 4 Hz, 1 H), 1.60–1.75 (m, 1 H), 7.05–7.35 (m, 10 H); high resolution mass spectrum, calcd for $C_{16}H_{16}$: 208.1252; found: 208.1250.

Authentic samples of acyclic hydrocarbons **7a**[50] and **7c**[51] were produced by reaction of allylmagnesium chloride with benzyl bromide and benzhydryl bromide, respectively. The ^{1}H NMR spectra were consistent with the structures.

The identities of hydrocarbons **6** and **7** produced by hydrogen atom transfer trapping of radicals **1** were confirmed by comparison to authentic samples by GC coelution and GC-mass spectral analysis on a Hewlett Packard (HP) 5890 GC interfaced to an HP 5971 mass selective detector.

Kinetic studies followed the general procedures previously reported[3d,10,13] with the exception that stock solutions of PhSeH were prepared immediately before use. The kinetic runs were performed in tubes sealed under vacuum that were equilibrated at the appropriate temperature for several minutes before radical chain reactions were initiated by irradiation with visible light. Following irradiation for 15 to 60 min, the tubes were cooled to −78 °C and opened, and the reaction mixtures were analyzed by GC. Yields were determined relative to an internal standard of dodecane (for reactions of **1a** and **1b**) or eicosane (for reactions of **1c**).

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GC response factors for products **6a**, **6c**, **7a**, and **7c** were determined with authentic samples; the GC response factor for **6b** was assumed to be equal to that of **6a**. The mean concentration of PhSeH was the average of the initial and final concentrations of PhSeH where the final concentration of PhSeH was calculated as the initial concentration of PhSeH minus the initial concentration of PTOC ester **5**.

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Ultrafast Studies of Photochromic Spiropyrans in Solution

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Abstract: The photochromic reaction dynamics of the spiropyran molecule 1′,3′,3′-trimethyl-6-hydroxyspiro[2*H*-1-benzopyran-2,2′-indoline] (HBPS) in solution have been studied with picosecond and femtosecond transient electronic absorption spectroscopy. Following excitation near 300 nm, the C–O bond of the molecule breaks in less than 100 fs to form a metastable species. A small fraction of this metastable species re-forms the broken C–O bond on the time scale of 200 fs. The major fraction of the metastable photoproduct vibrationally relaxes in a few picoseconds, and then undergoes isomerization to form a merocyanine product with a decay time constant of about 100 ps, depending on solvent viscosity. This isomerization decay is faster at shorter probe wavelengths and slower at longer wavelengths, indicating that this isomerization gives rise to a red-shifted absorption spectrum. The final merocyanine isomers are stable on the nanosecond time scale. All the results indicate that the initial steps of the photochromic reaction process of HBPS are extremely fast.

Introduction

Photochromism, first discovered in 1876,[1] is a phenomenon in which a compound changes color when exposed to light of one wavelength and reverts to its original color when irradiated with light of a different wavelength. Studies on photochromic substances were quite limited before 1930,[2-6] but the period from 1940 to 1960 saw an increase of interest in these substances.[7-10] A number of review articles[11-13] have been published outlining the development of thought regarding photochromism, and several books[14-16] have been devoted specifically to this subject. A variety of organic as well as inorganic compounds were found to exhibit photochromism both in the solid state and in solutions.[7-16] Recently there has been a renaissance in the study of photochromic materials[15-29] due to their potential applications in several important areas, including high-density optical storage, optical switching, image processing, and displays.[7,15,27]

One of the most important classes of photochromic materials is spiropyran compounds. These compounds have been studied extensively,[19-30] with the nitro derivatives of spirobenzopyran receiving the most attention.[19-22] Several models have been proposed to explain the properties and photochromic reaction mechanisms of these molecules based on both frequency domain[7-18] and time domain[19-28] spectroscopic studies. Time-resolved experiments have been carried out using techniques such as laser flash photolysis[19-23] and time-resolved resonance Raman scattering.[24,25] These studies found that the reaction dynamics for spiropyrans with a nitro group are significantly different from those for spiropyrans without a nitro group. A triplet state was found to play an important role in the photochemical reaction process of spiropyrans containing a nitro group, as indicated by the sensitivity of the dynamics to the presence of O_2.[19-22] For molecules containing no nitro group, the photoreaction was dominated by singlet states. These studies have improved the understanding of the reaction mechanisms of photochromic spiropyrans.

Previous studies have also found that the photochromic reaction of spiropyran molecules features the dissociation of a C–O bond, producing a distribution of isomers.[19-30] However, the rate and mechanism of the initial reaction steps for these molecules are yet to be determined. Furthermore, there is still no consistent model to explain all of the experimental observations due to the extremely fast C–O dissociation rate and to the complications caused by the presence of more than one merocyanine isomer produced in the reaction process.[27]

The advent of femtosecond lasers has made it possible to study extremely fast rate processes directly. The experiments carried

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