Direct Measurements of the Kinetics of 3-*exo* Radical Cyclizations Using Radical Reporter Groups

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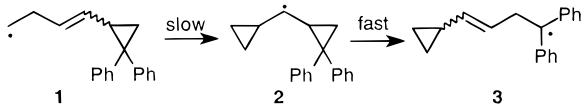
The *E* and *Z* isomers of the 4-(2,2-diphenylcyclopropyl)-3-butenyl radical (**1**), produced by laser flash photolysis of the corresponding PTOC esters in THF, cyclized to the (2,2-diphenylcyclopropyl)-(cyclopropyl)methyl radical (**2**) that rapidly opened to 1,1-diphenyl-4-cyclopropyl-3-butenyl radicals (**3**). Radicals **3** were monitored by UV spectroscopy, but the observed rate constants were for the initial, relatively slow cyclizations of radicals **1** to radical **2**. The Arrhenius functions determined in the temperature range of 20−58 °C were $\log(k/s^{-1}) = (11.46 \pm 0.38) - (9.10 \pm 0.54)/\theta$ for (*E*)-**1** and $\log(k/s^{-1}) = (12.34 \pm 0.32) - (10.10 \pm 0.45)/\theta$ for (*Z*)-**1** where $\theta = 2.3RT$ in kcal/mol and errors are at 2σ. Radical (*Z*)-**1** cyclizes somewhat faster than radical (*E*)-**1** as a result of a more favorable entropy of activation and despite the fact that the activation energy for cyclization of (*Z*)-**1** through the requisite *syn*-transition state is *greater* than that for cyclization of (*E*)-**1** through an *anti*-transition state.

The kinetics of a wide range of alkyl radical reactions have been determined by indirect methods over the past few decades.[1] Most of these studies ultimately provide rate constants that are based on the rate constants for bimolecular reactions of Bu_3SnH with alkyl radicals determined by Ingold's group by direct laser flash photolysis (LFP) methods in the early 1980s.[2,3] Others relate to primary kinetic data for reactions of thiols and nitroxyls.[1] The popularity of the indirect method results from the ability to perform the experiments without special (and usually expensive) instrumentation and the absence of useful chromophores in the reactant and product radicals, which precludes UV detection in the simplest "special" technique, LFP with UV detection. The precision of an indirect kinetic determination can be quite good, but the absolute values of the rate constants thus determined contain the known uncertainty of the initial kinetic measurements of the trapping reactions and an unknown error due to the common requisite assumption that one radical is an appropriate model for another, closely related radical.[1]

Our group has developed the use of internal "reporter groups" for direct LFP kinetic measurements of reactions of radicals that do not otherwise contain useful chromophores.[4−6] The reporter groups are 2-aryl-cyclopropanes positioned such that the initial radical reactions produce 2-aryl-substituted cyclopropylcarbinyl radical intermediates. The aryl-substituted intermediate radicals ring open with rate constants exceeding 1×10^{11} s^{-1} at ambient temperature[7−9] to give benzylic or diphenylalkyl radicals that are readily detected by UV spectroscopy,[10] and because the follow-up reaction is so fast, only the kinetics of the initial slow reaction are measured. One attractive feature of the reporter group approach is that the fast reporter reaction can divert an inherently reversible reaction such that the kinetics for a thermodynamically unfavored step can be measured directly.[6] In this work, we have employed the reporter group approach for direct measurements of rate constants for 3-*exo* cyclizations of 3-butenyl radicals to a cyclopropylcarbinyl radical, a reaction that is inherently unfavorable by more than 5 kcal/mol. Radicals **1**, produced photochemically by LFP, cyclized to radical **2** that rapidly opened to the UV-detectable radicals **3** (Scheme 1).

Scheme 1



Results and Discussion

The radical precursors employed were Barton PTOC esters[11] **5** prepared from the corresponding carboxylic acids **4**. The diastereomeric acids (*E*)-**4** and (*Z*)-**4** were obtained by reduction of a mixture of the acids, chromatographic separation of the diastereomeric alcohols, and oxidation of the purified alcohols back to acids **4**. The (*E*) and (*Z*) stereochemical assignments were based on the consistent vinyl coupling constants for the intermedi-

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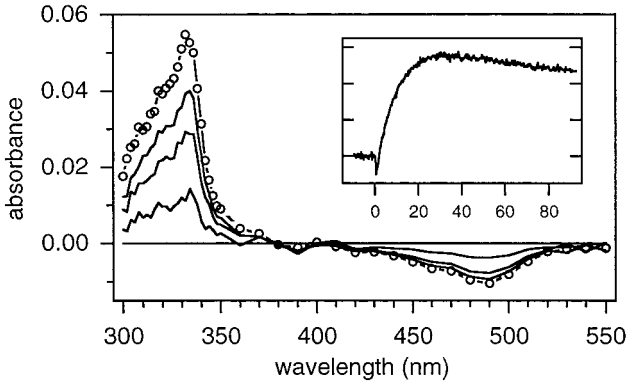
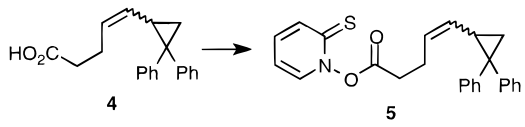


Figure 1. Time-resolved spectra from reaction of radical (*E*)-**1** at ambient temperature. The traces are at 4.2, 8.2, 12.2, and 30.2 μs after laser irradiation with data at 2.2 μs subtracted to give a baseline. Radicals **3** are growing in with λ_{max} at 332 nm, and the 2-pyridinethiyl radical with λ_{max} at 490 nm is decaying. Symbols on the 30.2 μs spectrum show the wavelengths monitored. The inset is the trace observed at 332 nm where the *X*-axis is time in μs.

ates and PTOC esters **4**; J = 10.4−10.9 Hz for all (*Z*) compounds, and J = 15.2−15.4 Hz for all (*E*) compounds. As determined by NMR spectroscopy, the sample of (*E*)-**4** used in preparation of the PTOC ester contained about 5% of the (*Z*) isomer, and the sample of (*Z*)-**4** contained <1% of the other isomer.



Carboxylic acids **4** and the intermediate alcohols from their reduction were characterized by NMR spectroscopy and HRMS. Because PTOC esters are thermally unstable and sensitive to visible light, radical precursors **5** were characterized only by NMR spectroscopy. The samples of PTOC esters used in the LFP kinetic studies were judged to be >95% pure on the basis of the ^{1}H NMR spectra. Impurities in the PTOC ester samples did not affect the kinetic measurements because the concentrations of precursors used in the LFP studies were only about 2 × 10^{-5} M.

PTOC esters are efficiently cleaved by 355 nm light from a Nd:YAG laser and have been used in a number of kinetic studies.[12] The initial photochemical reactions of **5** gave acyloxyl radicals that decarboxylated "instantly" on the nanosecond time scale to produce radicals **1**. The byproduct of the photolysis, the 2-pyridinethiyl radical, has a long wavelength absorbance with λ_{max} = 490 nm[13] but does not absorb appreciably at 330−335 nm, which was the expected λ_{max} of product radicals **3**.[10] Figure 1 shows time-resolved spectra obtained following photolysis of (*E*)-**5**. The ultimate product radicals **3** are growing in with λ_{max} at 332 nm, and decay of the signal from the 2-pyridinethiyl radical is observed (490 nm).

The kinetics of cyclization of radicals (*E*)-**1** and (*Z*)-**1** were measured over the temperature ranges 20−58 °C and 20−48 °C, respectively, and the results are in Table 1. These cyclization reactions are relatively slow, which

Table 1. Rate Constants for Cyclizations of Radicals 1 in THF

radical	temp (°C)[a]	$10^{-5} \times k_{obs}$ (s^{-1})[b]	
(*E*)-**1**	19.5	0.38 ± 0.04	0.41 ± 0.03
	19.7	0.45 ± 0.03	0.55 ± 0.07
	29.8	0.84 ± 0.05	0.75 ± 0.06
	30.3	0.84 ± 0.03	0.78 ± 0.06
	39.2	1.18 ± 0.07	1.21 ± 0.04
	40.0	1.30 ± 0.09	1.29 ± 0.13
	48.7	1.91 ± 0.07	1.90 ± 0.10
	58.2	2.73 ± 0.10	2.76 ± 0.24
	58.2	2.76 ± 0.12	
(*Z*)-**1**	20.3	0.65 ± 0.06	0.62 ± 0.04
	29.6	1.15 ± 0.06	1.04 ± 0.06
	38.9	1.77 ± 0.03	1.78 ± 0.09
	48.5	2.84 ± 0.21	2.99 ± 0.05

[a] ±0.2 °C. [b] Errors are 1σ. Rate constants in the two columns are from independent experiments.

results in a problem in the LFP kinetic measurements. Specifically, radical−radical and radical−oxygen reactions have pseudo-first-order rate constants that can approach 1 × 10^4 s^{-1} and will contribute to the observed rate constants for reactions of radicals **1**.[14] To minimize the kinetic contribution from radical−radical reactions, the solutions of precursors employed for kinetic measurements were more dilute than those used for obtaining time-resolved spectra; the resulting kinetic traces displayed significantly less decay than is seen in the inset in Figure 1. In addition, rate constants for the lower temperature runs were determined by solving the data with double exponential functions, for growth and decay; at higher temperatures, no decay was apparent. These procedures do not avoid a kinetic contribution from reactions of radicals **1** with residual oxygen, however, and kinetic measurements at temperatures below 20 °C would be increasingly in error. The upper temperature limit is due to the thermal instability of the PTOC ester precursors.

The Arrhenius parameters from the kinetic data (Figure 2) are given in eqs 1 and 2 where $\theta = 2.3RT$ in kcal/mol and errors are at 2σ. The errors in these parameters are somewhat larger than those often found in LFP studies of first-order reactions[6] as a result of the relatively narrow temperature ranges studied. The calculated rate constants at 20 °C are 4.6 × 10^4 s^{-1} and 6.2 × 10^4 s^{-1} for (*E*)-**1** and (*Z*)-**1**, respectively.

$$(E)\text{-}\mathbf{1}\text{: } \log(k/s^{-1}) = (11.46 \pm 0.38) - (9.10 \pm 0.54)/\theta \quad (1)$$

$$(Z)\text{-}\mathbf{1}\text{: } \log(k/s^{-1}) = (12.34 \pm 0.32) - (10.10 \pm 0.45)/\theta \quad (2)$$

The Arrhenius parameters might seem unusual, but they are readily rationalized. The larger activation energy for cyclization of radical (*Z*)-**1** results from the facts that the transition states for the cyclizations of the two isomers are different and strain energy in the ground state of the (*Z*) radical is not necessarily relieved in the requisite transition state for cyclization.[15] The larger log *A* term for cyclization of (*Z*)-**1** is due to the loss of one

(12) See refs 4−6 and references therein.
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(14) In our experimental design, radical−radical reactions and reactions of radicals with residual oxygen have pseudo-first-order rate constants summing to about 5 × 10^3 s^{-1}. See: Musa, O. M.; Horner, J. H.; Shahin, H.; Newcomb, M. *J. Am. Chem. Soc.* **1996**, *118*, 3862−3868.

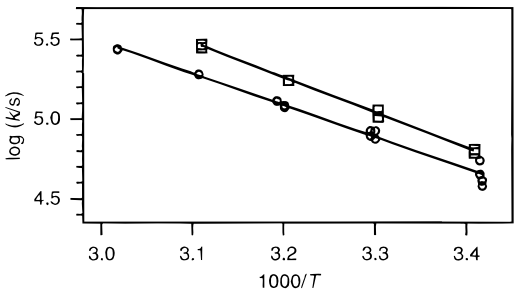

Figure 2. Arrhenius plots for radical (*E*)-**1** (circles) and (*Z*)-**1** (squares).

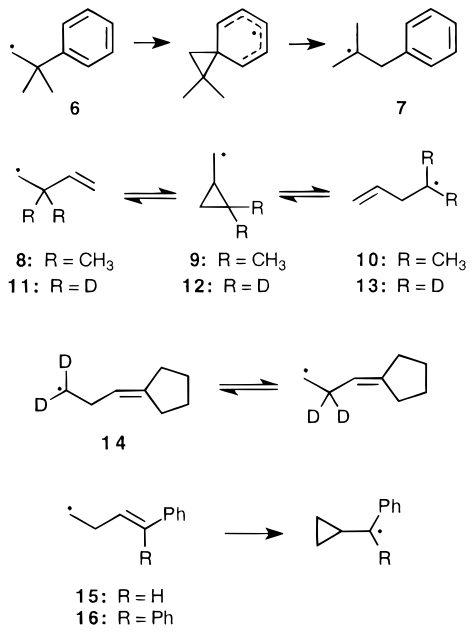

Figure 3. Radical reactions involving 3-*exo* cyclizations.

free internal rotation in this isomer in comparison to (*E*)-**1** and the corresponding reduced entropy demand for achieving the transition state.[16,17]

Although 3-*exo* cyclizations of simple 3-butenyl radicals to give cyclopropylcarbinyl radicals are thermodynamically unfavorable, they occur in vinyl migration reactions or the equivalent (Figure 3).[18] Perhaps the most well-known example is the neophyl radical (**6**) rearrangement to the 1,1-dimethyl-2-phenylethyl radical (**7**).[18] Isomerization of the 2,2-dimethyl-3-butenyl radical (**8**) to the 1,1-dimethyl-3-butenyl radical (**10**)[19,20] was demonstrated to proceed through the intermediate (2,2-dimethylcyclopropyl)methyl radical (**9**) by the kinetic competency of the ring opening of **9** and the fact that cyclic radical **9** was trapped in low yields in reactions of **8**.[20] The cyclization of **8** to **9** is accelerated by a Thorpe−Ingold effect of the two methyl groups, but the cyclizations that ultimately result in deuterium label scrambling in the homoallyl radicals **13**[21] and **14**[22] are quite similar to the reactions of radicals **1** studied here.

The deuterium label scrambling in radical **13** was studied over a wide temperature range by ESR and competition kinetic studies involving trapping by Bu_3SnH.[21] The rate constants for rearrangements determined from the tin hydride trapping experiments must be corrected with the now-accepted rate constants for reactions of alkyl radicals with Bu_3SnH.[2] When this is done, the Arrhenius function in eq 3 is obtained for the cyclization of **13** to **12**, where it is assumed that the isotopic substitution has negligible kinetic effects in the cyclization of **13** and ring opening of **12**. The rate constant for cyclization of **13** at 20 °C from eq 3 is 6500 s^{-1}, or only about 10−15% as large as those for cyclizations of radicals **1**. This difference in cyclization rate constants reflects the steric and electronic effects of the reporter group substituent in radicals **1**. The rate constant for cyclization of radical **14** at 25 °C ($k = 5.5 \times 10^4$ s^{-1})[22] is quite similar to those of radicals **1**.

$$\log(k/s^{-1}) = 12.1-11.1/\theta \qquad (3)$$

The 3-*exo* cyclizations of radicals **15** and **16** give thermodynamically favored products as a result of the radical stabilization of the aryl groups, and these cyclization reactions are relatively fast. The kinetics of cyclization of radical **15** were studied by indirect methods involving tin hydride trapping[23] and nitroxyl radical trapping[24] reactions. More recently, the 3-*exo* cyclizations of both radicals **15** and **16** were measured directly by LFP methods that gave highly precise rate constants and Arrhenius parameters with good precision.[25] The rate constants for cyclization at 20 °C are 5.3×10^6 s^{-1} for **15** and 1.8×10^7 s^{-1} for **16**, and the Arrhenius log *A* terms are (11.41 ± 0.19) and (10.7 ± 0.4) for **15** and **16**, respectively, where the errors are at 2σ.[25]

The Arrhenius log *A* parameters are the entropic terms, and these should be similar for 3-*exo* cyclizations of various homoallyl radicals because few conformational options are available in formation of the small cyclopropyl ring. In general, this expectation is fulfilled. The values for the log *A* terms for radicals **1** are similar to those of radicals **13** and **15**, despite the large differences in rate constants. Because of the unusual steric demands of the two phenyl groups in radical **16**, it is perhaps not unexpected that the log *A* term for cyclization of this radical is not consistent with those for the other 3-*exo* radical cyclizations. It is noteworthy that the log *A* terms for the *trans*-substituted radicals (*E*)-**1** and **15**, both of which were determined with quite good precision, are

(15) A similar situation exists in the analogous 3-pentenyl radicals where computations at the B3LYP/6-31G* level indicated that the *anti* transition state for cyclization of the (*E*)-radical is 0.9 kcal/mol more stable than the *syn* transition state for cyclization of the (*Z*)-radical.[6]

(16) In radical (*Z*)-**1**, steric interactions between the substituents on the double bond will limit conformational mobility about the C4−C5 bond (between the vinyl and cyclopropyl groups), leading to a higher log *A* value. The difference in log *A* values for cyclizations of the two isomers of **1** (0.9) corresponds to a difference in $\Delta S^{\ddagger}$ of 4 eu, which is in the range of values expected for torsional entropy of rotation of a C−C single bond.[17]

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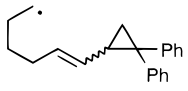
statistically indistinguishable; this reinforces the conclusion that an unusual entropic effect is at play in the cyclization of the *cis*-substituted radical (*Z*)-**1**.[16]

The similarities of the log *A* terms for 3-*exo* cyclizations of radicals **1** that contain the reporter groups and other radicals that do not and the similarities in the rate constants for cyclization of radicals **1**, **13**, and **14** suggest that the reporter groups are relatively benign in a mechanistic sense. The same conclusion was reached previously in studies of 5-*exo* cyclizations of radical **17**[4] and of ring openings of several cyclopropylcarbinyl radicals **18**[6] containing the same reporter group as in radicals **1**. For example, the log *A* term for the initial ring opening reactions of radical **18** (R = R′ = H) was nearly equal to that for the parent radical, the cyclopropylcarbinyl radical (**12** with R = H), and the E_a term for **18** was slightly reduced such that at 20 °C radical **18** fragmented five times faster than the cyclopropylcarbinyl radical.[6]



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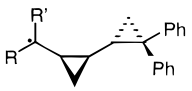

18

Experimental Section

General Methods. ^{1}H NMR spectra were obtained in $CDCl_3$ at 300 or 400 MHz. ^{13}C NMR spectra were obtained at 75 or 100 MHz. High resolution mass spectral analyses were performed by the Central Instrumentation Facility at Wayne State University. Commercially available reagents were purchased from either Aldrich Chemical Co. or Arcos Chemical Co. and were used as received. Ethyl ether and tetrahydrofuran (THF) were distilled under a nitrogen atmosphere from sodium−benzophenone ketyl. Benzene was distilled from CaH_2. The sodium salt of *N*-hydroxypyridine-2-thione was purified as described previously.[26]

Kinetic Measurements and Data Analysis. Kinetic measurements were carried out with an Applied Photophysics LK-50 laser kinetic spectrometer using the third harmonic (355 nm) of a Nd:YAG laser (7 ns pulse duration, 40 mJ/pulse). Dilute solutions of the PTOC esters were placed in a jacketed addition funnel attached to a UV cuvette via a short length of Teflon tubing. The solutions were deoxygenated with helium sparging. The temperature of the sample in the funnel was adjusted to the desired temperature by circulating fluid from a constant temperature circulating bath. Sample temperatures were measured by means of a copper−constantan thermocouple wire inserted into the interior of the cuvette through the sample outflow opening. Data were digitized using a Hewlett-Packard 54522 oscilloscope. Each kinetic trace contained 500 points. Two sets of data, each containing 14 kinetic traces, typically were collected at one temperature. Each set was summed to improve the signal/noise ratio.

5-(2,2-Diphenylcyclopropyl)-4-pentenoic Acid (4). *n*-Butyllithium (20 mL, 2.5 M in hexanes, 0.05 mol) was added to a solution of hexamethyldisilazane (10.5 mL, 0.05 mol) in THF (40 mL). After 10 min of stirring (3-carboxypropyl)-triphenylphosphonium bromide (8.58 g, 0.02 mol) was added slowly via a solids addition funnel. The dark red solution was stirred at 0 °C for 1.5 h. A solution of 2,2-diphenylcyclopropanecarboxaldehyde[27] (4.45 g, 0.02 mol) in THF (10 mL) was added via syringe, and the mixture was stirred at 0 °C for 3 h. The solution was washed with 10% aqueous HCl solution, which was back-extracted with ether (200 mL). After drying over $MgSO_4$, the solvents were removed under reduced pressure. The crude product (6.7 g, 0.023 mol) was purified by chromatography on silica gel (2:1, hexanes/EtOAc) to give 4.2 g (72%) of a mixture of the isomeric acids as an oil. The product was a 75:25 (*Z*/*E*) mixture that was not separable by chromatography on silica gel.

(*Z*)- and (*E*)-5-(2,2-Diphenylcyclopropyl)-4-penten-1-ol. The above mixture of acids (2.6 g, 0.009 mol) in ether (20 mL) was added to a mixture of LAH (0.71 g, 0.019 mol) in ether (100 mL). The mixture was stirred for 2 h. Water was then added carefully to quench the excess LAH. The resulting precipitate was removed by filtration and washed thoroughly with ether. The filtrate was dried ($MgSO_4$), and the solvent was removed under reduced pressure to give the desired alcohols (2.2 g, 90%) as a 3:1 (*Z*/*E*) mixture. Repeated chromatography on silica gel (3/1 pentane/ethyl ether) gave the purified isomers. The ^{1}H NMR spectra indicated that the (*E*) isomer was 95% pure and the (*Z*) isomer was >99% pure.

(*Z*)-Alcohol. ^{1}H NMR (500 MHz): δ 1.35 (s, 1 H), 1.45 (dd, J = 5.7, 4.7 Hz, 1H), 1.62 (dd, J = 8.7, 4.8 Hz, 1 H), 1.75 (quintet, J = 6.6 Hz, 2H), 2.35 (qd, J = 7.4, 1.5 Hz, 2H), 2.50 (dddd, J = 9.9, 8.6, 5.8, 1.0 Hz, 1H), 3.73 (t, J = 6.6 Hz, 2H), 4.64 (ddt, J = 11.1, 9.9, 1.6 Hz, 1H), 5.40 (dtd, J = 10.9, 7.3, 1.1 Hz, 1H), 7.2−7.4 (m, 10H). ^{13}C NMR (75 MHz): δ 22.7, 24.0, 25.2, 32.6, 37.1, 62.6, 125.9, 126.4, 127.5, 128.2, 128.3, 128.7, 130.7, 133.1, 141.6, 146.8. MS (EI): *m*/*z* (rel int), 278 (M^+, 25), 205 (93), 165 (50), 91 (100). HRMS: calcd for $C_{20}H_{22}O$, 278.1671; found, 278.1668.

(*E*)-Alcohol. ^{1}H NMR (300 MHz): δ 1.55 (m, 5H), 2.01 (qd, J = 8.9, 5.8 Hz, 2H), 2.27 (td, J = 8.9, 5.8 Hz, 1H), 3.54 (t, J = 6.6 Hz, 2H), 4.80 (ddt, J = 15.4, 9.0, 1.3 Hz, 1H), 5.61 (dt, J = 15.3, 6.9 Hz, 1H), 7.12−7.39 (m, 10H). ^{13}C NMR (75 MHz): δ 22.0, 28.8, 30.0 32.2, 36.6, 61.2, 125.7, 126.4, 127.2, 128.18, 128.22, 129.5, 131.0, 131.2, 141.5, 146.7. MS (EI): *m*/*z* (rel int), 278 (M^+, 20), 205 (80), 91 (100). HRMS: calcd for $C_{20}H_{22}O$, 278.1671; found, 278.1675.

(*Z*)-5-(2,2-Diphenylcyclopropyl)-4-pentenoic Acid ((*Z*)-4). Jones reagent was added dropwise to a stirred solution of the above (*Z*)-alcohol (0.40 g, 1.4 mmol) in acetone (50 mL) at 0 °C until an orange color persisted. The mixture was stirred for 5 min and then added to water, and the mixture was extracted with ether. The ethereal solution was dried ($MgSO_4$), and the solvent was removed under reduced pressure. The crude product was purified by chromatography on silica gel (2:1, hexanes/ethyl acetate) to yield (*Z*)-**4** (0.18 g, 43%). ^{1}H NMR (300 MHz): δ 1.48 (t, J = 5.2, 1H), 1.63 (dd, J = 8.5, 4.7 Hz, 1H), 2.50 (m, 3 H), 2.62 (m, 2H), 4.70 (t, J = 10.7 Hz, 1H), 5.35 (dt, J = 11.0, 7.0 Hz, 1 H), 7.20−7.40 (m, 10 H). ^{13}C NMR (75 MHz): δ 22.7, 23.0, 25.1, 34.2, 37.3, 125.9, 126.5, 126.8, 127.5, 128.27, 128.34, 130.7, 132.1, 141.4, 146.6, 179.6. MS (EI): *m*/*z* (rel int), 292 (M^+, 25), 205 (100), 91 (77). HRMS: calcd for $C_{20}H_{20}O$, 292.1463; found, 292.1463.

(*E*)-5-(2,2-Diphenylcyclopropyl)-4-pentenoic acid ((*E*)-4) was prepared from the above (*E*)-alcohol by the same procedure as used for preparation of (*Z*)-**4**. (*E*)-Alcohol (0.38 g, 1.4 mmol) gave (*E*)-**4** (0.16 g, 40%). ^{1}H NMR (300 MHz): δ 1.50 (t, J = 5.8, 1H), 1.61 (dd, J = 8.5, 4.9 Hz, 1H), 2.32 (m, 5 H), 4.85 (dd, J = 15.3, 9.2 Hz, 1 H), 5.65 (dt, J = 15.3, 6.7 Hz, 1 H), 7.20−7.40 (m, 10 H). ^{13}C NMR (75 MHz): δ 22.1, 27.4, 29.8, 34.0, 36.6, 125.7, 126.4, 127.1, 127.5, 128.2, 130.9, 132.2, 141.2, 146.6, 179.2. MS (EI): *m*/*z* (rel int), 292 (M^+, 32), 205 (100), 183 (71), 91 (79). HRMS: calcd for $C_{20}H_{20}O$, 292.1463; found, 292.1457.

(*Z*)-5-(2,2-Diphenylcyclopropyl)-4-pentenoic Acid 2-Thioxo-2*H*-pyridin-1-yl Ester ((*Z*)-5). A mixture of (*Z*)-**4** (0.14 g, 0.46 mmol), one drop of DMF, and oxalyl chloride (0.16 mL, 1.8 mmol) in dry benzene (20 mL) was stirred for 30 min. Excess oxalyl chloride and benzene were removed under reduced pressure. The residue was dissolved in benzene (10 mL), and the solution was added to a suspension of *N*-hydroxypyridine-2-thione sodium salt (0.11 g, 0.72 mmol) and DMAP (0.007 g, 0.056 mmol) in benzene (10 mL) in a ice-cooled bath. The mixture was shielded from light during this reaction and all subsequent workup steps. The mixture was allowed to warm to room temperature. After 2 h, the reaction mixture was washed with $NaHCO_3$ (sat, aq), $KHSO_4$ (10%, aq), and

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brine. After drying over $MgSO_4$, the solvent was removed under reduced pressure. The crude product was chromatographed rapidly on silica gel (2:1, hexanes/ethyl acetate) to give (*Z*)-**5** (0.13 g, 68%) as a yellow oil. ^{1}H NMR (400 MHz): δ 1.52 (dd, J = 5.8, 4.8, 1H), 1.67 (dd, J = 8.7, 4.8 Hz, 1H), 2.48 (tdd, J = 9.3, 5.7, 0.8 Hz, 1H), 2.82 (m, 2H), 2.90 (m, 2H). 4.74 (tt, J = 10.4, 1.3 Hz, 1H), 5.41 (tdd, J = 10.8, 7.1, 0.8 Hz, 1H), 6.63 (td, J = 6.9, 1.8 Hz, 1H), 7.2−7.4 (m, 11H), 7.58 (dd, J = 6.7, 1.1 Hz, 1H), 7.74 (dd, J = 9.0, 1.2 Hz, 1H). ^{13}C NMR (100 MHz): δ 22.66, 22.74, 25.2, 31.8, 37.3, 112.5, 125.9, 126.0, 126.6, 127.5, 128.3, 128.3, 130.6, 132.8, 133.4, 137.4, 137.6, 141.2, 146.4, 168.5, 175.8.

(*E*)-5-(2,2-Diphenylcyclopropyl)-4-pentenoic Acid 2-Thioxo-2*H*-pyridin-1-yl Ester ((*E*)-5). The same procedure used for the preparation of (*Z*)-**5** was followed; (*E*)-**4** (0.16 g, 0.55 mmol) gave (*E*)-**5** (0.12 g, 55%) as a yellow oil. ^{1}H NMR (400 MHz): δ 1.51 (dd, J = 5.9, 5.1 Hz 1H), 1.62 (dd, J = 8.7, 4.9 Hz, 1H), 2.28 (td, J = 8.9, 6.0 Hz, 1H), 2.45 (m, 2H), 2.71 (t, J = 7.3, 2H). 4.8 (ddt, J = 15.4, 9.1, 1.4 Hz, 1H), 5.6 (dt, J = 15.2, 6.9 Hz, 1H), 6.64 (td, J = 6.9, 1.6 Hz, 1H) 7.14−7.38 (m, 11H), 7.51 (dd, J = 6.9, 1.4 Hz, 1 H), 7.74 (dd, J = 8.9, 1.8 Hz, 1 H). ^{13}C NMR (100 MHz): δ 22.1, 27.1, 29.8, 31.7, 36.8, 112.5, 125.8, 126.5, 126.7, 127.1, 128.22, 128.24, 130.9, 132.9, 133.5, 137.4, 137.6, 141.2, 146.5, 168.3, 175.8.

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Supporting Information Available: ^{1}H and ^{13}C NMR spectra for new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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