## Picosecond Radical Kinetics. Benzeneselenol as a Fast **Radical Trapping Agent and Rate Constants for Ring** Opening of the trans-(2-Phenylcyclopropyl)carbinyl Radical

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The measurement of radical reaction rate constants by indirect methods involving competition reactions with known rate constants is a well-established technique. The most popular method for studying relatively fast radical reactions is the tin hydride method, which usually employs Bu<sub>3</sub>SnH as the trapping agent and an alkyl halide or pseudohalide as the radical precursor; with a reaction rate constant of  $2 \times 10^6$  M<sup>-1</sup> s<sup>-1</sup> at 25 °C,<sup>1</sup> Bu<sub>3</sub>SnH can compete against a first-order reaction somewhat faster than  $1 \times 10^8$  s<sup>-1</sup> at 25 °C. We recently reported<sup>2</sup> a method using a Barton PTOC ester<sup>3</sup> (e.g., 1) as a radical precursor and PhSH trapping  $(k_{25^{\circ}C})$ =  $1.1 \times 10^8 \text{ M}^{-1} \text{ s}^{-1})^4$  (the PTOC-thiol method) that can be applied in competition with first-order reactions with rate constants greater than  $1 \times 10^{10} \text{ s}^{-1}$  at 25 °C. Alkyl radical trapping by nitroxyl radicals such as 2,2,6,6-tetramethylpiperidine-N-oxyl (TEMPO)  $(k_{20^{\circ}C} \sim 1 \times 10^{9} \text{ M}^{-1} \text{ s}^{-1})^{5}$  could, in principle, be employed in competition with a first-order reaction at  $1\times10^{11}$  $s^{-1}$ . We now report an extension of the PTOC-thiol method<sup>2</sup> in which benzeneselenol is used as the trapping agent, and we demonstrate its application in the trapping of a radical with a lifetime of only several picoseconds.

The PTOC esters are excellent radical precursors for indirect kinetic studies for several reasons.<sup>6</sup> Because the PhSe<sup>•</sup> radical propagates chain reactions with PTOC esters efficiently,7ª PhSeH is a viable trapping agent for kinetic studies.<sup>7b</sup> Rate constants for PhSeH trapping were determined by using the cyclopropylcarbinyl radical ring opening<sup>8</sup> as a radical clock<sup>10</sup> (Scheme I).

Radical chain reactions with the PTOC precursor 1<sup>2</sup> were conducted in THF and in toluene in the presence of 0.04-0.13 M PhSeH over the temperature range -45 to 53 °C.<sup>11</sup> Acyloxy radical 2 was partially trapped (0-50%) by PhSeH in competition with decarboxylation that gave the cyclopropylcarbinyl radical (4).<sup>12</sup> From the distribution of products 6 and 7 and the concentrations of PhSeH, the relative rate constants for rearrangement

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(6) The virtues of PTOC esters as precursors in kinetic studies are discussed in ref 2. They include access to highly strained systems, propagation reactions with a variety of radicals, visible light initiation, and a wide practical temperature range.

(7) (a) Barton, D. H. R.; Bridon, D.; Zard, S. Z. Tetrahedron Lett. 1984, 25, 5777. (b) Newcomb, M.; Manek, M. B.; Glenn, A. G. J. Am. Chem. Soc., in press.

(8) The cyclopropylcarbinyl ring opening is currently the best calibrated fast radical rearrangement. Kinetic studies by four groups<sup>2,9</sup> using three different methods were combined<sup>94</sup> to give an Eyring equation of  $\ln (k, T^{-1}s)$ = 23.9-6.68/RT (R in kcal/mol).

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(10) Griller, D.; Ingold, K. U. Acc. Chem. Res. 1980, 13, 317.

(11) The method was the same as that used in the PTOC-thiol kinetic studies.2

(12) We believe that the acyloxy trapping reaction, which is increasingly important at lower reaction temperatures,<sup>76,13</sup> will permit determinations of rate constants for decarboxylations of alkylacyloxy radicals. We also caution that PhSeH trapping of acyloxy radical precursors to quite unstable radicals will be problematic

(13) Newcomb, M.; Varick, T. R., unpublished results.

Scheme I



versus trapping were determined.<sup>14</sup> The resulting values of  $k_r/k_T$ were then combined with the values<sup>8</sup> of  $k_r$  for radical 4 to give values of  $k_{\rm T}$ . PhSeH trapping of 4 is so fast that the reactions are partially diffusion controlled and, therefore, solvent dependent. Operational Arrhenius functions for PhSeH trapping in the two solvents are given in eqs 1 and 2, where the error limits for the last significant figure are  $2\sigma$ .<sup>15</sup> With values for  $k_{diff}$  in each solvent, one could factor out the hydrogen-transfer rate constants for PhSeH,<sup>16</sup> but for practical applications, the  $k_{T}$  values are useful.<sup>17</sup> At 20 °C, PhSeH trappings have rate constants of 2.0  $\times$  10<sup>9</sup> M<sup>-1</sup> s<sup>-1</sup> and 1.7  $\times$  10<sup>9</sup> M<sup>-1</sup> s<sup>-1</sup> in THF and toluene, respectively; the trapping reactions are faster than coupling of the nitroxyl radical TEMPO with a primary alkyl radical.

for THF:  $\log (k_{\rm T} \cdot {\rm M} \cdot {\rm s}) = 11.13 \ (6) - 2.44 \ (8) / 2.3 RT \ (1)$ 

 $\log(k_{T} \cdot M \cdot s) =$ for toluene:

10.84(11) - 2.17(13)/2.3RT(2)

Ring openings of phenyl-substituted cyclopropylcarbinyl radicals are expected to be very fast on the basis of the results of Castellino and Bruice.<sup>18,19</sup> The PTOC ester precursor 8 for the trans-(2-

(14) Complete results (13 runs in THF, 15 runs in toluene) are reported in the supplementary material. Representative results in toluene follow: temperature, [1], [PhSeH]<sub>0</sub>, yield (6 + 7), 7/6; 53 °C, 0.020 M, 0.060 M, 98%, 2.230; 38 °C, 0.033 M, 0.130 M, 92%, 0.698; 20 °C, 0.038 M, 0.060 M, 73%, 1.080; 0 °C, 0.023 M, 0.082 M, 61%, 0.320; -22 °C, 0.023 M, 0.060 M, 60%, 0.214; -45 °C, 0.020 M, 0.060 M, 57%, 0.078.

(15) The errors are for the deviations of the function and do not include estimates of the errors in the ring-opening kinetics. The Arrhenius plots were slightly curved because partial diffusion control becomes increasingly important at the lower temperatures. The curvature was so slight, however, that quadratic functions for describing  $k_T$  were not necessary; the coefficients for the quadratic terms were within  $1\sigma$  of 0.

(16) Determination of the  $k_{chem}$  values for PhSeH is currently under study; ultimately, this should result in more precise kinetic measurements. Partially diffusion controlled reactions are described by eq i, where  $k_{diff}$  is the diffusion rate constant and  $k_{chem}$  is the chemical rate constant. Approximate values of  $k_{diff}$  from simple diffusion theory are 2.1 × 10<sup>10</sup> M<sup>-1</sup> s<sup>-1</sup> and 1.1 × 10<sup>10</sup> M<sup>-1</sup> s<sup>-1</sup> and 1.1 × 10<sup>10</sup> M<sup>-1</sup> s<sup>-1</sup> for THF and toluene, respectively, at 20 °C. These values and the  $k_{\rm T}$  values at 20 °C give  $k_{chem}$  for PhSeH at 2.3 × 10<sup>9</sup> M<sup>-1</sup> s<sup>-1</sup> and 2.1 × 10<sup>9</sup> M<sup>-1</sup> s<sup>-1</sup> for THF and toluene studies, respectively.

$$k_{\rm obsd} = k_{\rm chem} k_{\rm diff} (k_{\rm chem} + k_{\rm diff})^{-1}$$
(i)

(17) On the basis of PhSH trapping results,<sup>2</sup> these Arrhenius functions should be accurate for any primary alkyl radical. They should also provide reasonable estimates for trappings of secondary and tertiary radicals; such behavior is typical for highly reactive hydrogen atom donors such as Bu<sub>3</sub>SnH and PhSH.<sup>1,4</sup>

(18) Castellino and Bruice<sup>19</sup> used a (2,3-diphenylcyclopropyl)carbinyl radical ring opening reaction as a probe for radical intermediates in epoxidations by cytochrome P-450 models. They estimated a rate constant for ring opening at 30 °C of  $k_r > 2 \times 10^{10} \text{ s}^{-1}$ .

(19) Castellino, A. J.; Bruice, T. C. J. Am. Chem. Soc. 1988, 110, 7512.

phenylcyclopropyl)carbinyl radical (11) was prepared by standard methods from acid 10.2.3 Reaction of 8 (Scheme I) in the presence of thiophenol gave only 4-phenyl-1-butene (14). However, reactions of 8 in toluene in the presence of PhSeH gave acid 10 and small amounts of trans-2-methyl-1-phenylcyclopropane (13) in addition to 14.20 3-Phenyl-1-butene, the ultimate product from cleavage of the C1-C3 bond in radical 11, was not detected to the limit of our precision (<0.1%). Accurately calibrated GC measurements of the 13:14 ratio permitted determinations of the ratio of rate constants for ring opening and trapping of 11.20 With the assumption that the rate constants for trapping 11 are the same as those for trapping 4 (eq 2), the rate constants for ring opening of 11 were  $3.7 \times 10^{10} \text{ s}^{-1}$  (-45 °C),  $1.2 \times 10^{11} \text{ s}^{-1}$  (0 °C), and  $1.8 \times 10^{11} \text{ s}^{-1}$  (20 °C).<sup>21</sup> The lifetime of radical 11 at 20 °C is 5-6 ps.<sup>23</sup>

In advance of this study, one might have questioned whether or not radical 11 would exist as a discrete intermediate. Further, it is likely that 11 cannot be detected by conventional direct methods. Production of 11 would typically require photolysis of a peroxy precursor to give an acyloxy radical followed by decarboxylation. Alkylacyloxy radical decarboxylations, while not especially well studied, apparently are at least an order of magnitude slower than the ring opening of 11.24 This means that attempts to study the kinetics of ring opening of 11 by direct observation of the formation of 12 probably would instead measure a rate-limiting decarboxylation step.<sup>26</sup> The "slow" decarboxylation step does not hinder the indirect method, however, as long as the acyloxy radical does not react completely with the trapping agent.

Benzeneselenol has been shown to be an especially fast trapping agent in this work with an ultimate kinetic resolution of about 1 ps at room temperature. We can envision its application, along with PTOC radical precursors, for the study of several fast first-order radical reactions including rearrangements and inversion processes.

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Supplementary Material Available: Tables of product yields and  $k_r/k_T$  values for reactions of PhSeH in THF and in toluene (2 pages). Ordering information is given on any current masthead page.

20 °C, a reduction in  $k_{\text{diff}}$  by a factor of 1.4 can be estimated.<sup>22</sup> This would reduce  $k_{\text{T}}$ , and thus  $k_{\text{r}}$ , by about 6%.<sup>16</sup>

(22) This estimate is based on results obtained in pulse gradient spin echo NMR measurements of diffusional coefficients for solutions containing PhSH.  $^{7b}$ 

(23) The rate constant for ring opening of 11 is more than 3 orders of magnitude faster than that of the cyclopropylcarbinyl radical.<sup>8</sup> The phenyl-substituted cyclopropylcarbinyl radical clocks<sup>19</sup> thus represent a new generation of "timing" reactions with exciting potential applications. Radical 11 will be an excellent probe because ring opening will predominate even when trapping reactions are diffusion limited. In principle, the ring opening can also compete in measurable amounts against the fastest unimolecular radical process because the decay of a transition state at 20 °C is only about 30 times faster.

faster.
(24) Acyloxy decarboxylations at ambient temperatures to give the stabilized radicals 9-methylfluorene-9-yl<sup>25a</sup> and benzyl<sup>25b</sup> have been reported to be 2 × 10<sup>10</sup> s<sup>-1</sup> and 5 × 10<sup>9</sup> s<sup>-1</sup>, respectively.
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(b) DeCosta, D. P.; Pincock, J. A. J. Am. Chem. Soc. 1989, 111, 8948.
(26) The direct approach is further complicated by the fact that photo-human enduction of the acultary radical might give a vibrationally excited

chemical production of the acyloxy radical might give a vibrationally excited intermediate that reacts before thermal equilibration is complete.<sup>25a</sup> In the indirect method used here, acyloxy radicals are almost entirely produced as ground-state species in radical chain reactions.

## On the Mechanism of a New Metallacycle Annelation **Reaction:** Evidence for an Intramolecular Methoxy **Group Transfer**

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The preparation and elaboration of metallacycle complexes is of central importance for the application of this compound class to organic synthesis<sup>1</sup> and materials science.<sup>2</sup> In an effort to develop fundamental new modes of metallacycle reactivity, we have been exploring the chemistry of metallacyclopentadiene complexes.<sup>3</sup> One of the most surprising and mechanistically ambiguous metallacycle transformations to date is the high-yield conversion of an iridiacyclopentadiene complex, 1, to a metallabicyclooctatrienone complex, 2, upon reaction with propiolic acid.<sup>4</sup> The propiolic acid substrate has undergone a decarboxylation, and the two sp alkyne carbons have been incorporated into the new ring of 2. In addition, a methyl or methoxy group has been transferred from the metallacycle  $\alpha$ -substituent in 1 to an  $\alpha$ -carbon of the newly formed ring in 2. Detailed spectroscopic and labeling studies have led us to propose a remarkable new annelation mechanism which includes an intramolecular methoxy group transfer between two ligands.<sup>5</sup>



Complex 3 (50.5 mg, 0.044 mmol) and ethyne (0.17 mmol) react in CDCl<sub>3</sub> at 23 °C over the course of days to give a 98%isolated yield of 4.6 In order to elucidate the mechanism of the 3 to 4 conversion, we required access to 3-O, selectively enriched with oxygen-18 at the carbonyl oxygen of the  $\alpha$ -methoxycarbonyl substituent adjacent to the aquo ligand (Scheme I). We took advantage of our earlier observation that bis(acetonitrile) complex 5 reacts with methyl propiolate in the presence of  $^{18}OH_2$  to give regioselectively labeled 6-O in 70% yield.<sup>6-8</sup> Removal of the CO

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(6) Complete spectroscopic and analytical data as well as X-ray crystal-lographic analysis data for 4 and spectroscopic data for 7 are provided as supplementary material.

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<sup>(20)</sup> Results with 0.05 M 8 in toluene: temperature, [PhSeH]<sub>0</sub>, yield (13 + 14), 14/13,  $k_r/k_T$ ; 20 °C, 1.6 M, 63%, 64.1, 102.6 M; 20 °C, 2.4 M, 58%, 47.5, 114.2 M; 0 °C, 1.4 M, 38%, 67.0, 93.8 M; 0 °C, 2.1 M, 41%, 44.5, 93.4 M; -45 °C, 0.9 M, 38%, 76.0, 68.4 M; -45 °C, 0.9 M, 35%, 72.0, 64.8 M; -45 °C, 1.6 M, 28%, 39.5, 63.2 M. This uncorrected, preliminary data<sup>21</sup> gave an Arrhenius function of log ( $k_r$ s) = 13.6 (1) - 3.2 (2)/2.3RT. It will be of interest to determine if the apparent slightly positive  $\Delta S^{\circ}$  value (2 eu) is real; radical 4 displays the expected  $\Delta S^{\circ} = 0.^{23.94}$  (21) The  $k_r$  values for 11 actually are upper limits because the viscosities of the toluene solutions should be somewhat greater than those of the solutions used in the calibration studies due to the increased PhSeH concentrations. At 20 °C, a reduction in  $k_{tirr}$  by a factor of 1.4 can be estimated.<sup>22</sup> This would