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Allyloxy Radicals are Formed Reversibly from Oxiranylcarbinyl Radicals: A Kinetic Study

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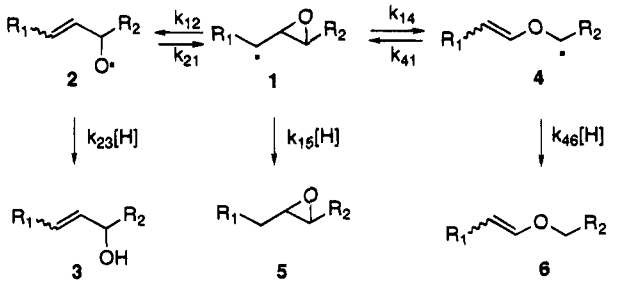
Oxiranylcarbinyl radicals **1** undergo rapid C–O bond cleavage to afford allyloxy radicals **2** (Scheme 1). Spectroscopic studies[1] have placed a lower limit of 10^8 s^{-1} for the forward reaction (k_{12}) while a competitive fragmentation against a cyclopropylcarbinyl radical clock has provided a lower limit estimate of 10^{10} s^{-1}.[2] Evidence for the back reaction (**2** → **1**) exists. Allyloxy radicals generated from allyl hypoiodites have been trapped on carbon as iodo epoxides[3-5] and an allyl nitrite has afforded an oxime epoxide.[6] In these instances, the carbon substituted product is more stable than the starting material under the reaction conditions.[7] On the contrary, epoxides are not formed from oxiranylcarbinyl radicals in the presence of stannane donors because the bimolecular rate constant k_{23} (10^8 M^{-1} s^{-1})[8,9] is approximately 10^2 times greater than k_{15}.[10] If k_{21} is significantly less than k_{12}, the reaction is additionally biased in favor of allylic alcohol **3** at the expense of epoxide **5**.[11]

Products of carbon-carbon bond fragmentation (**1** → **4**) are observed when the resultant carbon-centered radical is stabilized (R_2 = Ph, vinyl, or acyl).[12-15] Murphy has examined the fragmentation of a series of oxiranylcarbinyl radicals **1** (R_1 = Me, R_2 = Ph; R_1, R_2 = Ph; R_1 = H, R_2 = α-naphthyl) that were generated from the chlorides and bromides in the presence of *n*-Bu$_3$SnH. In these cases, only carbon–carbon bond cleavage occurred to give a mixture of vinyl ethers **6**. Only in the fragmentation of *trans*-cinnamyl bromide epoxide **7** (Scheme 2) was a mixture of C–O and C–C bond cleavage products obtained (allylic alcohol **11** and vinyl ether **12**, respectively).

In spite of the different conditions employed to generate primary oxiranylcarbinyl radical **9** compared with the three examples cited earlier, we suspected that allyloxy radical **8** was being formed reversibly from the oxiranylcarbinyl radical in these experiments. Herein we provide evidence for this equilibrium as described in Scheme 2. Furthermore, a rate constant for k_{-1} has been obtained.

Scheme 1



Scheme 2

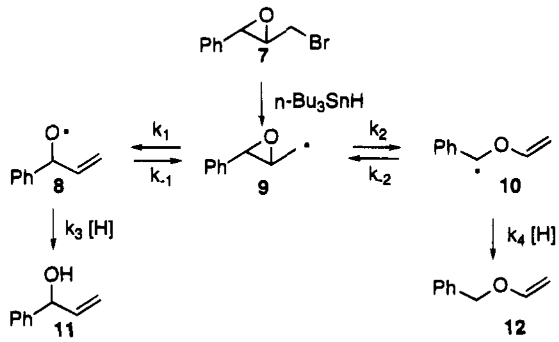
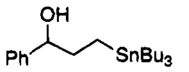


Table 1

entry	[H]	R_o
1	0.058	0.050
3	0.116	0.080
5	0.175	0.130
7	0.233	0.180
9	0.465	0.370
11	0.930	0.750
13	1.240	0.870
15	1.860	1.220
17	3.100	1.820
19	3.720	1.940

The ratio (R_o) of allylic alcohol **11** to vinyl ether **12** was measured as a function of *n*-Bu$_3$SnH concentration ([H]) under pseudo-first order conditions [0.02 M in substrate; 0.05 to 3.7 M (neat) in stannane; 0.5 h reaction time] at 70 °C in benzene (19 data points; Table 1).[16] At high concentrations of stannane, addition of tri-*n*-butylstannyl radical to the alcohol **11** and vinyl ether **12** occurred to produce adducts **13** and **14**, respectively.[17] These adducts were included in the mass balance and in the refined value of R_o. Ratios at high stannane concentration were obtained by thermal gas chromatography after chromatographic removal of excess stannane; at low stannane concentration ratios were measured by direct injection. The products were synthesized independently and their response factors were determined. In one run, R_o was shown to be invariant with time. Mass recovery was greater than 95% as monitored by gas chromatography using an internal standard (3-phenylpropanol).



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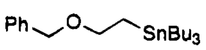

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A steady state analysis for the partitioning of oxiranylcarbinyl radical **9** between alcohol **11** and vinyl ether

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[11] To observe epoxide **5**, the ratio k_{12}/k_{21} would have to be sufficiently small to counteract k_{23}/k_{15}.

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[16] A complete list of data is available in the supplementary material.

[17] Alcohol **13** and ether **14** were formed in 8.5 and 14% yields, respectively, in neat n-Bu$_3$SnH.

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12 provides eq 1 for R_o as a function of stannane concentration. A lower limit value for k_{-1} can be extracted from this equation.

$$R_o = \frac{[\mathbf{11}]}{[\mathbf{12}]} = \frac{k_1 k_3 (k_{-2} + k_4[\mathrm{H}])}{k_2 k_4 (k_{-1} + k_3[\mathrm{H}])} \qquad (1)$$

Under kinetic conditions, where the stannane concentration is high, R_o approaches R_k (eq 2).

$$R_k = \frac{k_1}{k_2} \qquad (2)$$

At low hydrogen atom donor concentration, thermodynamic control will prevail wherein R_o approaches R_t (eq 3).

$$R_t = \frac{k_1 k_3 k_{-2}}{k_2 k_4 k_{-1}} \qquad (3)$$

Substituting eq 2 into eq 3, solving for k_{-2} and substituting the resulting value for k_{-2} into eq 1 gives eq 4 solved for k_{-1}.

$$k_{-1} = \frac{(R_k - R_o)k_3[\mathrm{H}]}{R_o - R_t} \qquad (4)$$

Assuming that R_t is small relative to the experimental values for R_o, then eq 4 can be expressed as a Lineweaver–Burk (double reciprocal) plot of $1/[R_o]$ vs $1/[\mathrm{H}]$ (eq 5). The linear plot satisfies the equation $1/[R_o] = 1.192\,(1/[\mathrm{H}]) + 0.2374$ ($R^2 = 0.986$). The value of R_k (4.2), which demonstrates that C–O cleavage is about four times faster than C–C cleavage, can be extracted from the *y*-intercept. The rate constant k_3 for the reaction **8** → **11** may be estimated from known values for the reaction of *tert*-butoxy radical with *n*-Bu_3SnH (2.2×10^8 $M^{-1}\,s^{-1}$ at 25 °C;[8] and 4×10^8 $M^{-1}\,s^{-1}$ at 80 °C[9]). A value of 2×10^9 s^{-1} for k_{-1} at 70 °C can be obtained from the slope.

$$\frac{1}{[R_o]} = \frac{k_{-1}}{k_3 R_k}\left(\frac{1}{[\mathrm{H}]}\right) + \frac{1}{R_k} \qquad (5)$$

Our results are in accord with recent high level calculations that demonstrate a kinetic preference for C–O ($\Delta H^\ddagger$= 4.8 kcal/mol) over C–C cleavage ($\Delta H^\ddagger = 11.5$ kcal/mol) in oxiranylcarbinyl radical itself. (Vinyloxy)methyl radical was shown to be 1.6 kcal/mol (ΔH°) and allyloxy radical 0.6 kcal/mol more stable than oxiranylcarbinyl radical.[18,19]

The results of these experiments suggest that the products of fragmentation of radicals **1** (R_1 = Me, R_2 = Ph; R_1, R_2 = Ph; R_1 = H, R_2 = α-naphthyl) may well be formed under thermodynamic conditions. The use of kinetic conditions in these experiments would be expected to afford products resulting from carbon–oxygen bond cleavage.

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Supplementary Material Available: Experimental details for the preparation of compounds **13** and **14**, copies of their ^1H and ^{13}C NMR spectra, and a complete table (19 entries) of [H] vs R_o are provided (7 pages).

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